Supplementary Information for

Completing the Triad: Synthesis and full Characterization of Homoleptic and Heteroleptic Carbonyl and Nitrosyl Complexes of the Group VI Metals

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1. Supplementary Methods

General Conditions. All manipulations on substrates and products were undertaken in a MBraun glovebox filled with Ar or N_2 (O_2, H_2O < 1 ppm). All experiments were carried out in special double-Schlenk tubes[1] (Supplementary Figure 1) separated by a G3 or G4 frit with grease-free PTFE or glass valves in an inert atmosphere using vacuum and standard Schlenk techniques. Solvents were dried by standard methods using CaH_2 or P_4O_{10}, distilled prior to use and stored over activated molecular sieves. $Mo(CO)_6$, $W(CO)_6$ (both AlfaAesar) and I_2 (Acros) were purified by sublimation before use. $Ag[Al(OR^F)_4]$ {R^F = $C(CF_3)_3$} was synthesized according to literature[2] but in SO_2 instead of CH_2Cl_2. $NO[Al(OR^F)_4]$ {R^F = $C(CF_3)_3$} was synthesized according to literature.[3] $Ag[F\text{-}\{Al(OR^F)_3\}_2]$ {R^F = $C(CF_3)_3$} was prepared from $Ag[PF_6]$ (Acros) and $Me_3Si\text{-}F\text{-}Al(OR^F)_3$[4] according to literature.[5]

NMR Spectroscopy. NMR samples were prepared in 5 mm thick walled NMR tubes with J. Young valves. The ^1H, $^{13}C\{^1H\}$, ^{19}F and ^{27}Al spectra were recorded either on a Bruker Avance II+ 400 MHz, on a Bruker Avance III HD 300 MHz or on a Bruker Avance 200 MHz spectrometer either in 1,2-$F_2C_6H_4$ (*ortho*-difluorobenzene, *o*DFB) or CD_2Cl_2 (0.4-0.6 mL) at r.t. Measurements conducted in 1,2-$F_2C_6H_4$ were calibrated by using the ^{19}F signal of the

solvent 1,2-$F_2C_6H_4$ (δ = –139.0 ppm[6], rel. to CCl_3F). The field corrections of other nuclei were adjusted accordingly. Measurements conducted in 1,2,3,4-$F_4C_6H_2$ were calibrated to the residual solvent signal for ^1H (δ = 7.04 ppm[7], rel. to TMS). The field corrections of other nuclei were adjusted accordingly. The Bruker Topspin software package (version 3.2) was used for measuring and processing of the spectra. Typically, very tiny impurities were detected in the ^{19}F NMR at –74.8 ($HOC(CF_3)_3$) and –75.5 ppm. All graphical representations were performed using Topspin (version 3.5pl7).

Vibrational Spectroscopy. FTIR measurements were performed on a FTIR Bruker ALPHA with a QuickSnap Platinum ATR sampling module inside the glovebox. The data were processed with the Bruker OPUS 7.5 software package. Unless otherwise stated, the spectra were recorded in the range of 4000-550 cm^{-1} with a resolution of 2 cm^{-1} at r.t. and a base line correction with 3 iterations was applied. FT Raman spectra were recorded on a Bruker VERTEX 70 spectrometer equipped with a RAM II module (1064 nm exciting line of a NdYAG laser) by using a highly sensitive liquid N_2 cooled Ge detector. The samples were measured in flame sealed soda-lime glass Pasteur pipettes in the range of 4000-50 cm^{-1} with a resolution of 4 cm^{-1} at r.t. The data were processed with the Bruker OPUS 7.5 software package. Unless otherwise noted, the Raman spectra were cut off below 75 cm^{-1} and a baseline correction with 5 iterations was applied. All IR and Raman spectra were normalized to 1 and intensities are given as follows: vvw = very very weak (< 0.1), vw = very weak (< 0.2), w = weak (< 0.3), mw = medium weak (< 0.4), m = medium (< 0.5), ms = medium strong (< 0.6), s = strong (< 0.7), vs = very strong (< 0.8), vvs = very very strong (≥ 0.9). Extremely weak bands (< 0.025) are not reported. Typical artefacts in the spectra appear at about 2939 and 2757 cm^{-1}, especially for weakly scattering samples. Graphical representations have been done with OPUS 7.5 or with OriginPro (version 9.2).

Single-Crystal X-ray Diffraction. Single crystals were selected at r.t. under perfluoropolyalkylether oil (AB128330, ABCR GmbH & Co. KG) on 0.1, 0.2 or 0.3 mm micromounts (M1-L19-100/200/300). Structural data were collected from shock-cooled crystals on a Bruker SMART APEX II Quazar CCD area detector diffractometer using a D8 goniometer with an Incoatec Mo-Microfocus Source IμS with mirror-monochromated Mo-K_α radiation (λ = 0.71073 Å) at 100(2) K. The diffractometer was equipped with an Oxford Cryosystem 800 low temperature device. The data were processed with APEX v2013.6-2, integrated with SAINT[8] (V8.37A) and an empirical absorption correction using SADABS 2014/5[9] or SADABS 2016/2[9] was applied. The structures were solved by direct methods

using SHELXT[10,11]. Unless otherwise stated, all non-hydrogen atoms were refined anisotropically by full matrix least squares methods against weighted F^2 values based on all independent reflections by using SHELXL-2014/7[11,12] with ShelXle as GUI software[13]. Disordered fragments were modelled with the help of the DSR software[14]. The graphical presentation of crystal structures was prepared either with Mercury (version 3.9)[15] or with OLEX2 (version 1.2)[16]. CCDC codes 1952378-1952389 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via: https://summary.ccdc.cam.ac.uk/structure-summary-form.

Powder Diffraction. The powder diffractograms were recorded with the sample in a 0.5 mm thick capillary (Hilgenberg GmbH, wall thickness 0.01 mm) sealed with perfluoropolyalkylether oil (AB128330, ABCR GmbH & Co. KG), at RT and about 100(10) K in the 2-Θ range 2–44° with a STOE STADI P powder diffractometer with Mo-$K_{\alpha1}$ radiation (λ = 0.709300 Å) equipped with a Ge-(111) monochromator and a silicon microstripe detector (Mythen 1K). Data acquiring, processing and the calculation of powder diffractograms from single-crystal data were performed using STOE WinXPOW® package.

EPR Spectroscopy. EPR spectra at X-band (9.38 GHz) were carried out using a Bruker ELEXSYS E580 CW EPR spectrometer equipped with an Oxford Instruments helium cryostat (ESR900) and a MercuryiTC temperature controller. Samples were filled into fused silica glass tubes. Solvents were vacuum transferred to the samples and afterwards the sample tubes were sealed under vacuum. The spectral simulations were performed using MATLAB 9.6 (2019a) and the EasySpin 5.2.25 toolbox.[17]

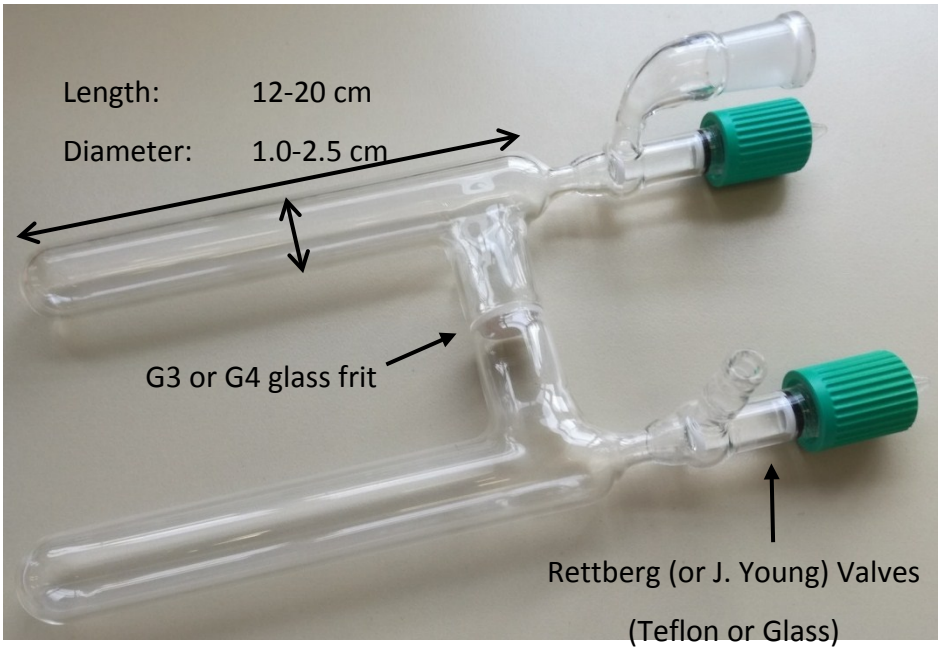
Computational Details. Quantum chemical calculations were performed with the TURBOMOLE[18] program package (version 7.0). All investigated molecular structures were optimized at the density functional theory (DFT) and were run in redundant internal coordinates using the BP86[19] and B3LYP[20] functional with the resolution-of-identity (RI) approximation[21] together with the basis set def2-TZVPP[22] and with dispersion correction (DFT-D3BJ)[23]. A fine integration grid (m4; 5 for NMR calculations) and the default SCF convergence criteria (10^{-6} a.u.) were used. All optimized structures were checked for minima (no imaginary frequencies) with the implemented module AOFORCE[24] and for proper spin occupancies using the implemented module EIGER. Entropic contributions to enthalpy and Gibbs free energy with inclusion of zero point energies (ZPE) were calculated at the BP86-D3BJ/def2-TZVPP level for standard conditions with the FREEH module. Solvation

effects were calculated using the COSMO[25] module combined with a geometry optimization in C1 symmetry. Default options and standard optimized COSMO radii included in the module were used. For the calculation of the reaction energies in solution, FREEH enthalpy/entropy of the gas phase calculation were used for the COSMO calculations.

Symmetry restricted structure optimizations of the $[Mo(CO)_6]^+$ and cation $[W(CO)_6]^+$ were performed with the TURBOMOLE 7.4 software package on the TPSSh[26]/def2-TZVPP level of theory with RI approximation and D3-BJ dispersion correction (integration grid m5, SCF convergence 10^{-9} a.u., density convergence $\leq 10^{-7}$, cartesian gradient $\leq 10^{-4}$). In a previous study we identified the TPSSh functional as suitable choice for minimum energy comparisons[27]. DLPNO-CCSD(T)/def2-TZVPP single point energy calculations were performed with the ORCA 4.2[28] program code without symmetry restriction. We have chosen tight thresholds for the domain-based local pair natural orbital method (DLPNO), i.e. pair correlation energy threshold TCutPairs=10^{-5} Eh, PNO occupation threshold TCutPNO=10^{-7} and domain size for PNO expansion TCutMKN=10^{-4}. We made use of the RIJCOSX procedure.[29]State Averaged (SA) Complete Active Shell Self Consistent Field (CAS-SCF)[30] calculations were done with ORCA 4.2. Scalar relativistic effects were taken into account by means of the second order DKH procedure[31]. A gaussian finite nucleus model was used.[32] The relativistically recontracted versions of the def2-TZVPP basis sets for carbon and oxygen as implemented by Dimitrios Pantazis into the ORCA program package, the def-TZVPP basis set for molybdenum[33] and the SARC-DKH-TZVPP basis set for tungsten were used.

The SA-CAS-SCF calculations were carried out in the basis of 9 doublet and 6 quartet roots arising from the 2I and 4G terms of the free Mo^+ and W^+ cations, respectively. The active space consists of 5 electrons in 5 orbitals of the second and third d-shell, respectively, and one additional d-orbital of the respective higher d-shell, i.e. CAS(5,6).

2. Experimental Glassware



Supplementary Figure 1. Double-Schlenk tube that was typically used for most reactions and crystallizations. Note that different varieties (sizes, Rettberg or J. Young valves) were used. Picture taken by Jan Bohnenberger.

3. Detailed Synthesis, Characterization and Spectra of Compounds 1 to 4

Synthesis of $[Mo(CO)_5(NO)][Al(OR^F)_4]$ (1)

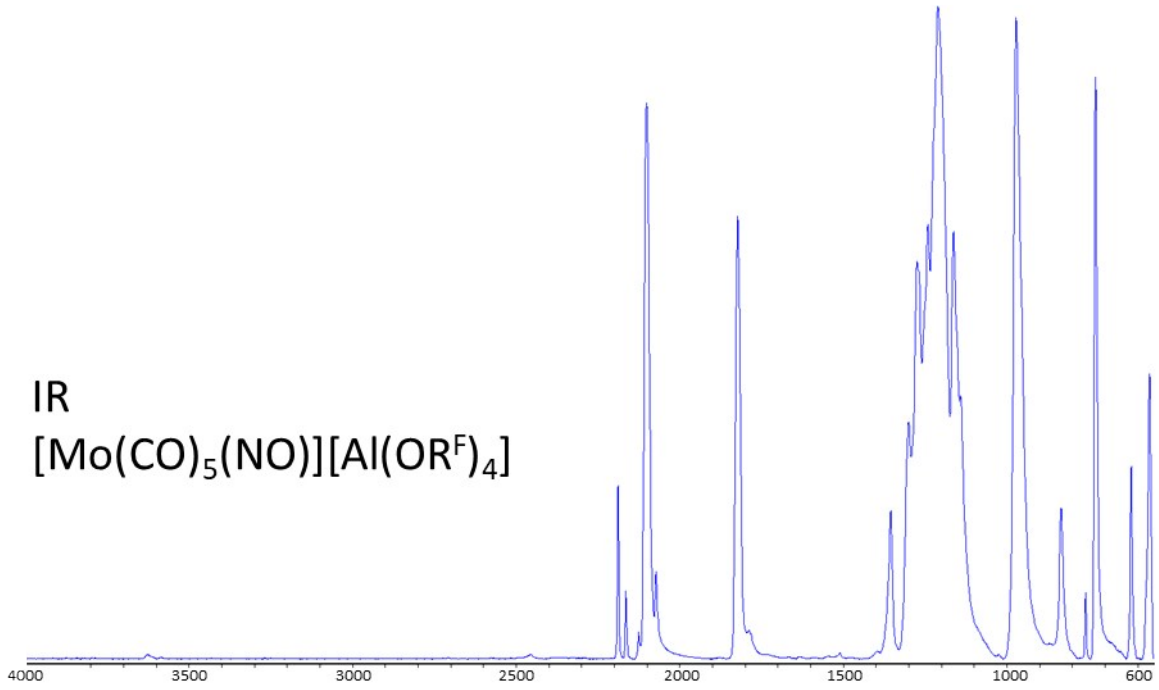
Inside the glovebox, $Mo(CO)_6$ (75 mg, 0.284 mmol) and $NO[Al(OR^F)_4]$ (283 mg, 0.285 mmol, 1 eq) were weighed into a double-Schlenk tube. Then, *o*DFB (~3 mL) was added and immediate gas evolution could be observed. After stirring at room temperature (r.t.) for a few minutes, the initially red-brown solution turned clear orange. The solution was stirred for a total of one hour to ensure a complete reaction and was then crystallized *via* slow vapour diffusion of *n*-pentane at r.t. into the *o*DFB solution. Bright red-orange block-shaped crystals of **1** were obtained after a few days. Crystalline yield: 302 mg, 86%.

FTIR (ZnSe, ATR): $\tilde{\nu}$/cm^{-1} (intensity) = 2186 (w), 2612 (vw), 2124 (vvw), 2099 (vvs), 2070 (vvw), 1820 (s), (1786 (vvw)), 1352 (w), 1297 (vvw), 1266 (vvw), 1239 (vvw), 1208 (vvs), 1160 (vvw), 1139 (vvw), 969 (vvs), 831 (w), 756 (vw), 726 (vvs), 617 (w), 560 (mw).

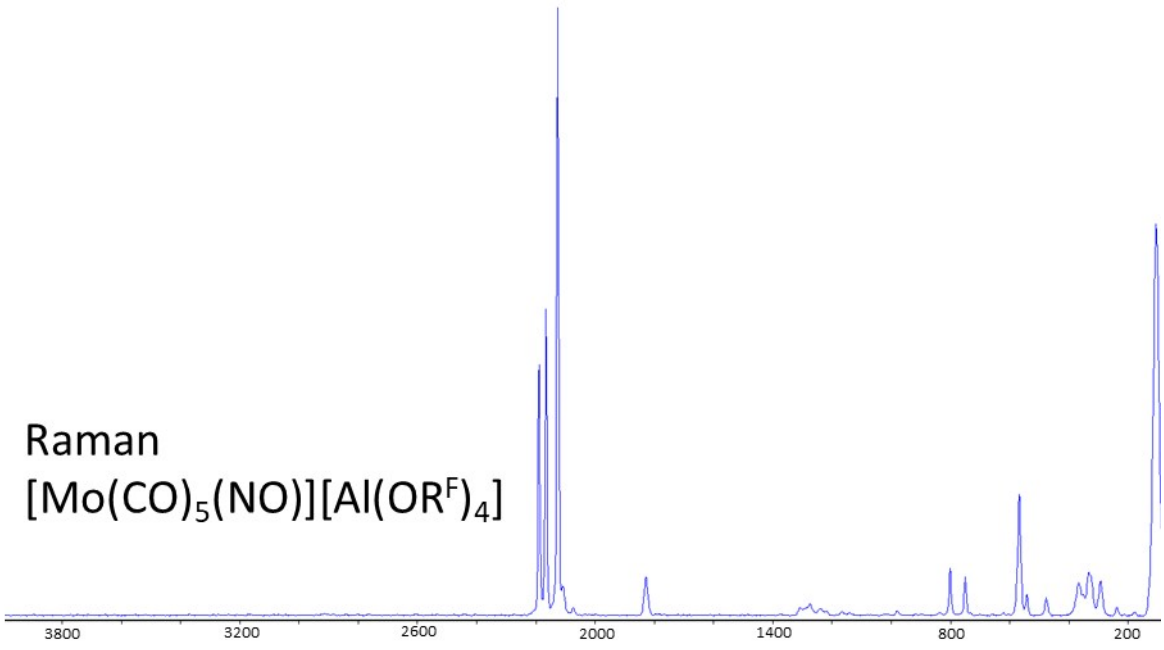
FT Raman (100 scans, 500 mW, 4 cm^{-1}): $\tilde{\nu}$/cm^{-1} (intensity) = 2187 (mw), 2163 (m), 2124 (vvs), 2106 (vvw) 2071 (vvw), 1825 (vvw), 1271 (vvw), 977 (vvw), 798 (vvw), 747 (vvw), 564 (vw), 538 (vvw), 473 (vvw), 363 (vvw), 329 (vvw), 289 (vvw), 234 (vvw), 101 (vs).

^{1}H NMR (400.17 MHz, *o*DFB, 298 K): *only solvent signals*; **^{13}C{^{1}H} NMR** (100.62 MHz, *o*DFB, 298 K): δ/ppm = 193.1 (s, 4C$_{eq}$, $[Mo(\mathbf{C}O)_5(NO)]^+$), 179.7 (s, 1C$_{ax}$, $[Mo(\mathbf{C}O)_5(NO)]^+$), 121.7 (q, ^1J(C,F) = 293 Hz, 12C, $\mathbf{C}F_3$, *in part overlapped by solvent signals*), 79.5 (m, 4C, $Al(O\mathbf{C}(CF_3)_3)_4$); **^{14}N NMR** (28.92 MHz, *o*DFB, 298 K): δ/ppm = –70.9 (s, N_2 from glovebox atmosphere), 3 (br. s, 1N, $[Mo(CO)_5(\mathbf{N}O)]^+$), ; **^{19}F NMR** (376.54 MHz, *o*DFB, 298 K): δ/ppm = –75.2 (s, 36F, 4 × $C(C\mathbf{F}_3)_3$); **^{27}Al NMR** (104.27 MHz, *o*DFB, 298 K): δ/ppm = 35.1 (s, 1Al, $\mathbf{Al}(OR^F)_4$).

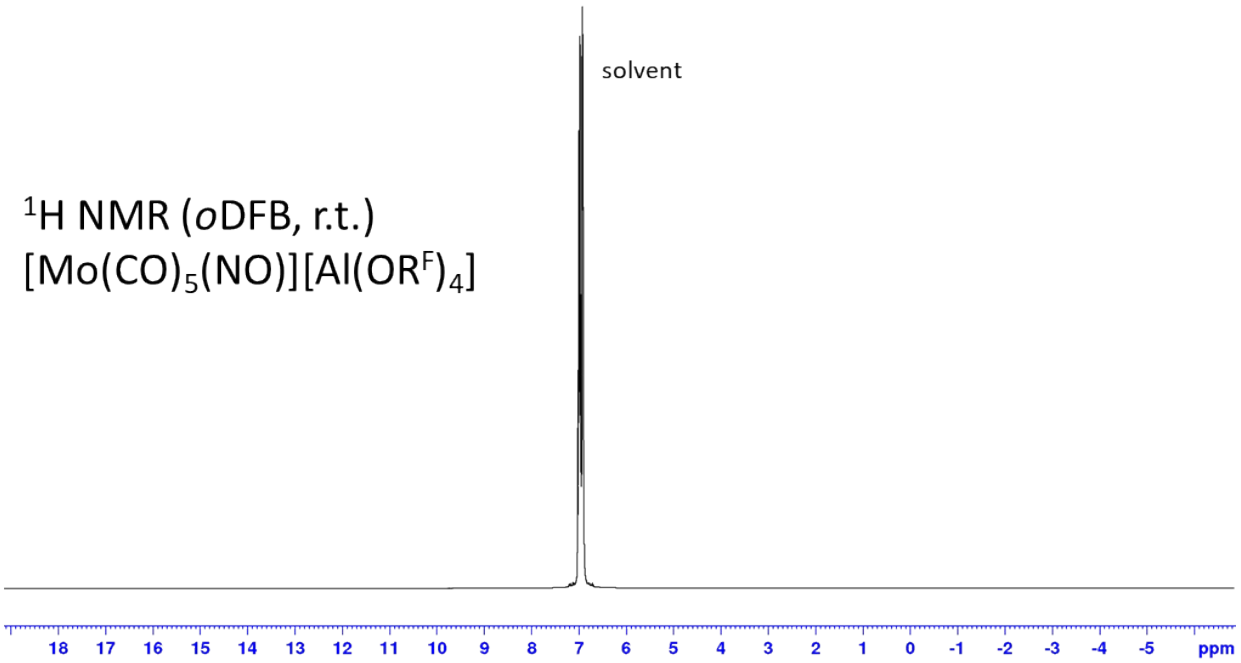
Note: This reaction also works in CH_2Cl_2 or SO_2. The solubility of the starting materials in CH_2Cl_2 is moderate, so longer reaction times are required. Especially **1** and **2** are poorly soluble in CH_2Cl_2 and the solvent needs to be changed to *o*DFB for crystallization.



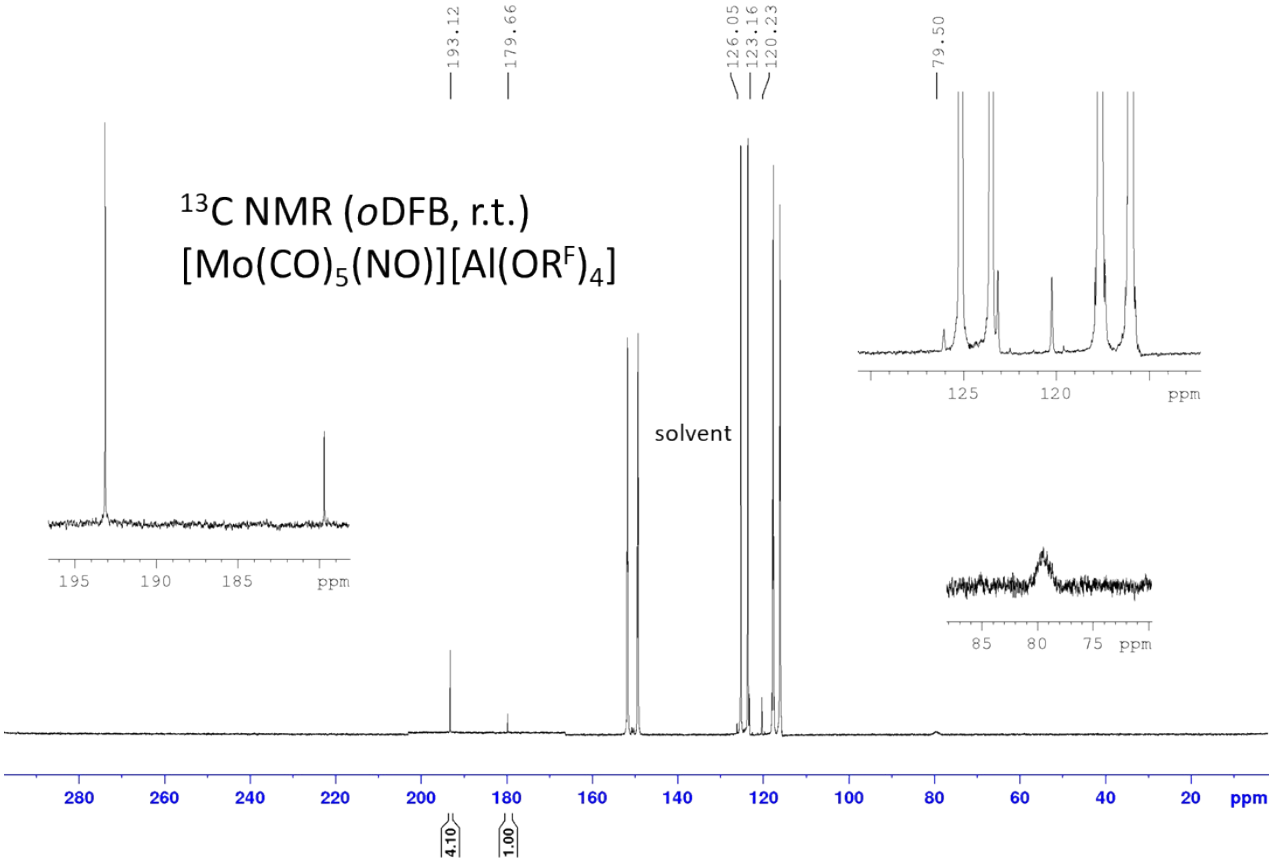
Supplementary Figure 2. Experimental IR spectrum of **1**.



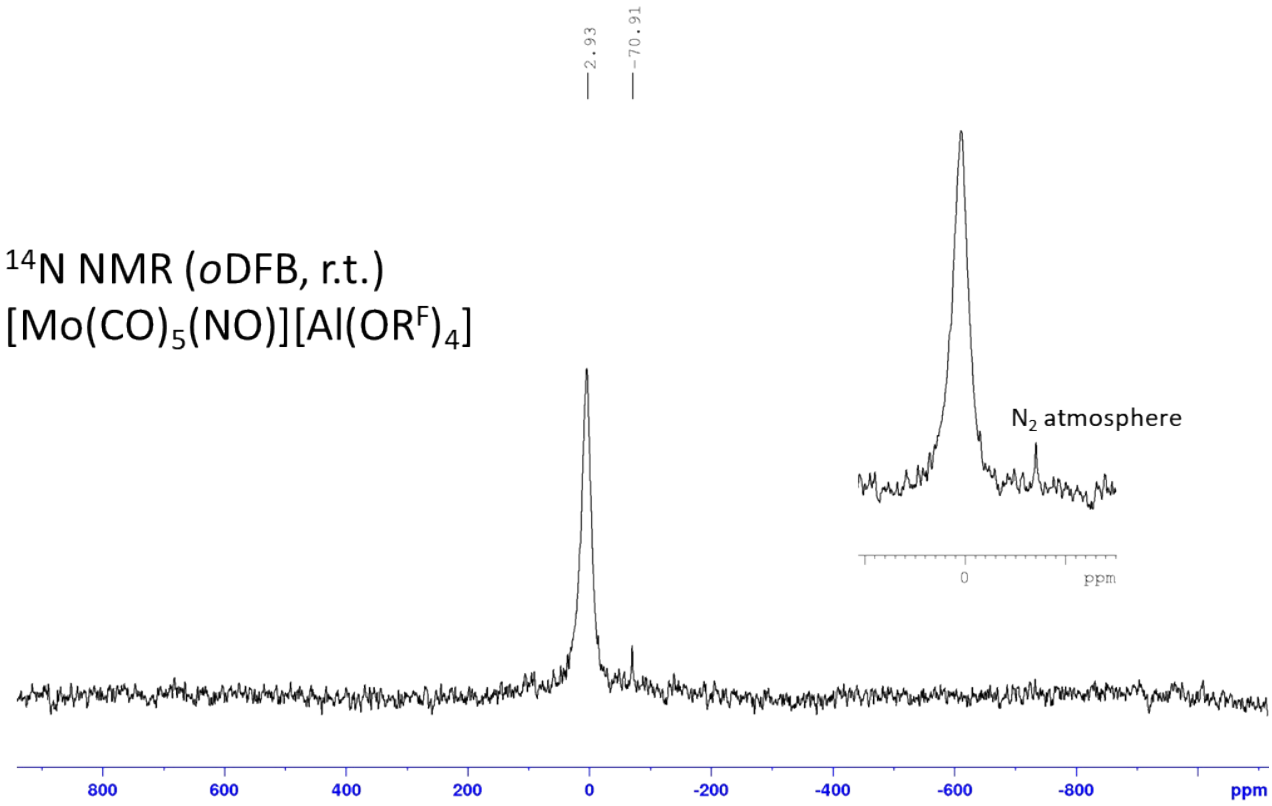
Supplementary Figure 3. Experimental Raman spectrum of **1**.



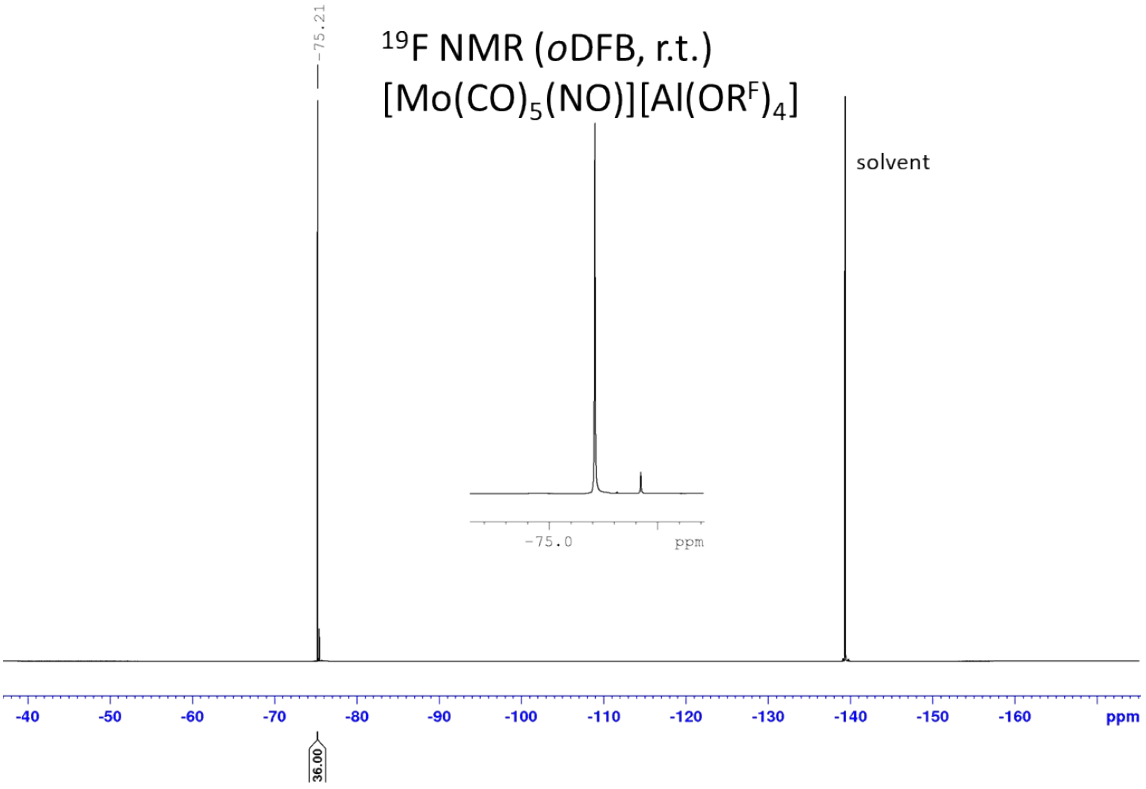
Supplementary Figure 4. ^{1}H NMR (400.17 MHz, *o*DFB, r.t.) spectrum of **1**.



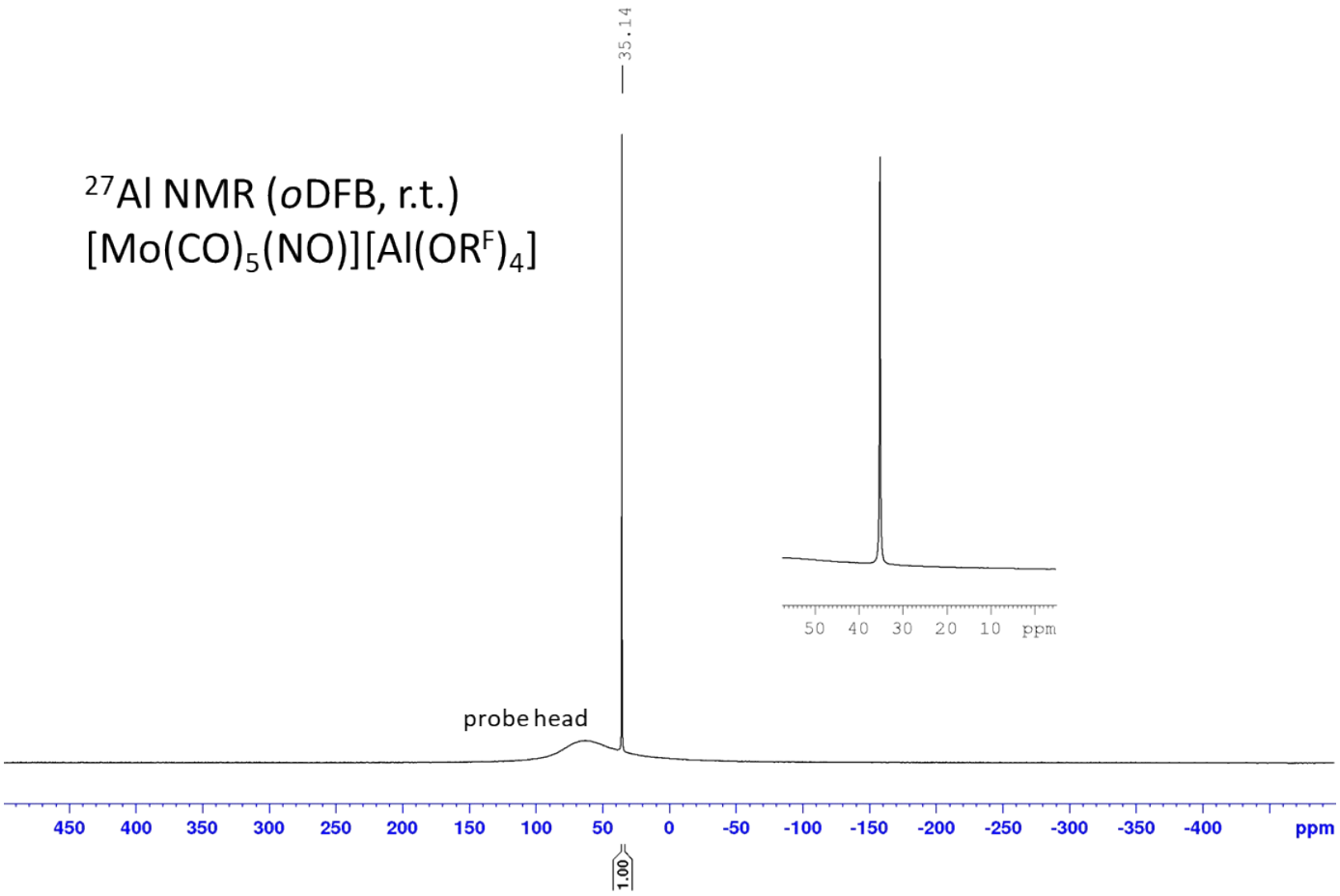
Supplementary Figure 5. ^{13}C NMR (100.62 MHz, *o*DFB, r.t.) spectrum of **1**.



Supplementary Figure 6. ^{14}N NMR (28.92 MHz, *o*DFB, r.t.) spectrum of **1**.



Supplementary Figure 7. ^{19}F NMR (376.54 MHz, *o*DFB, r.t.) of **1**.



Supplementary Figure 8. ^{27}Al NMR spectrum (104.27 MHz, *o*DFB, r.t.) of **1**.

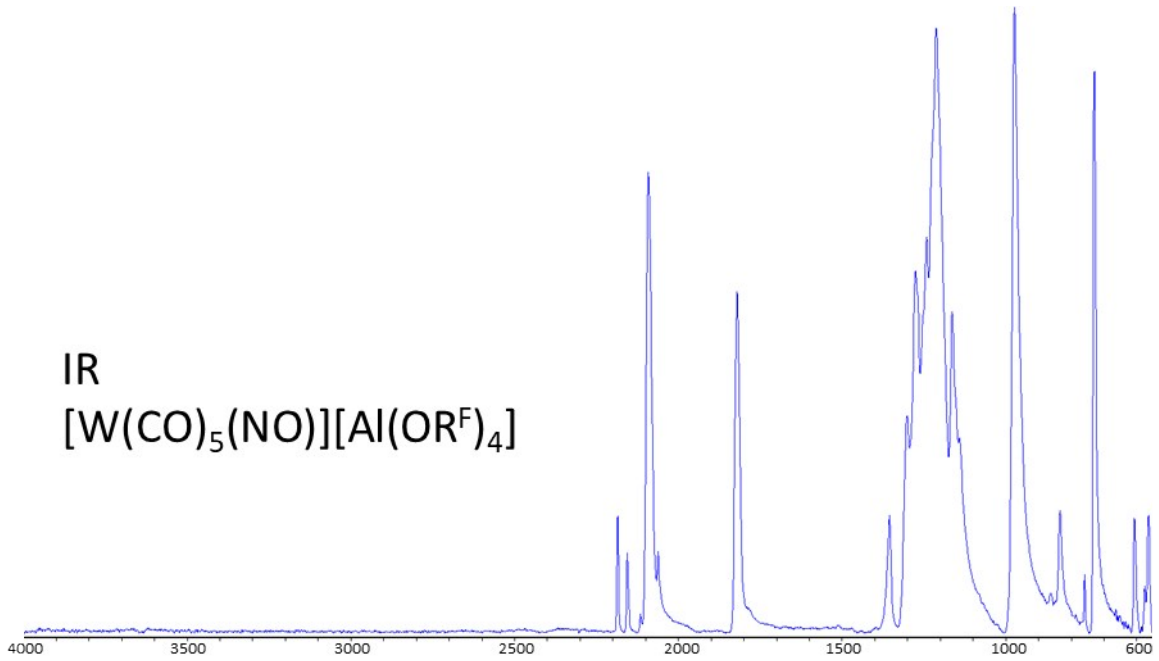
Synthesis of $[W(CO)_5(NO)][Al(OR^F)_4]$ (2)

Inside the glovebox, $W(CO)_6$ (75 mg, 0.213 mmol) and $NO[Al(OR^F)_4]$ (213 mg, 0.214 mmol, 1 eq) were weighed into a double-Schlenk tube. Then, *o*DFB (~3 mL) was added and immediate gas evolution could be observed. After stirring at room temperature (r.t.) for a few minutes, the initially red-brown solution turned clear orange. The solution was stirred for a total of one hour to ensure a complete reaction and was then crystallized *via* slow vapour diffusion of *n*-pentane at r.t. into the *o*DFB solution. Bright red-orange block-shaped crystals of **2** were obtained after a few days. Crystalline yield: 260 mg, 92%.

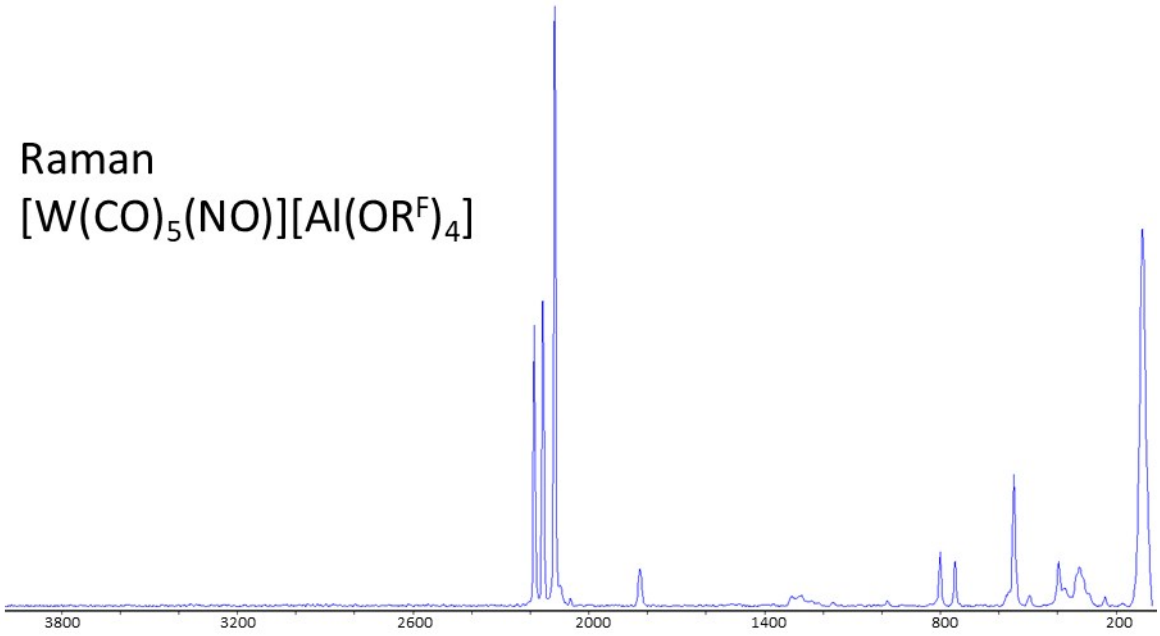
FTIR (ZnSe, ATR): $\tilde{\nu}$/cm^{-1} (intensity) = 2183 (vw), 2153 (vw), 2113 (vvw), 2090 (vs), 2059 (vvw), 1818 (ms), 1352 (vw), 1298 (vvw), 1273 (vw), 1239 (vvw), 1209 (vvs), 1161 (w), 1138 (vvw), 970 (vvs), (859 (vvw)), 831 (vw), 756 (vvw), 726 (vvs), 604 (vw), 572 (vvw), 561 (vw).

FT Raman (100 scans, 500 mW, 4 cm^{-1}): $\tilde{\nu}$/cm^{-1} (intensity) = 2184 (m), 2155 (m), 2114 (vvs), 2095 (vvw), 2061 (vvw), 1823 (vvw), 1271 (vvw), 978 (vvw), 797 (vvw), 747 (vvw), 546 (w), 492 (vvw), 393 (vvw), 374 (vvw), 321 (vvw), 234 (vvw), 106 (vs).

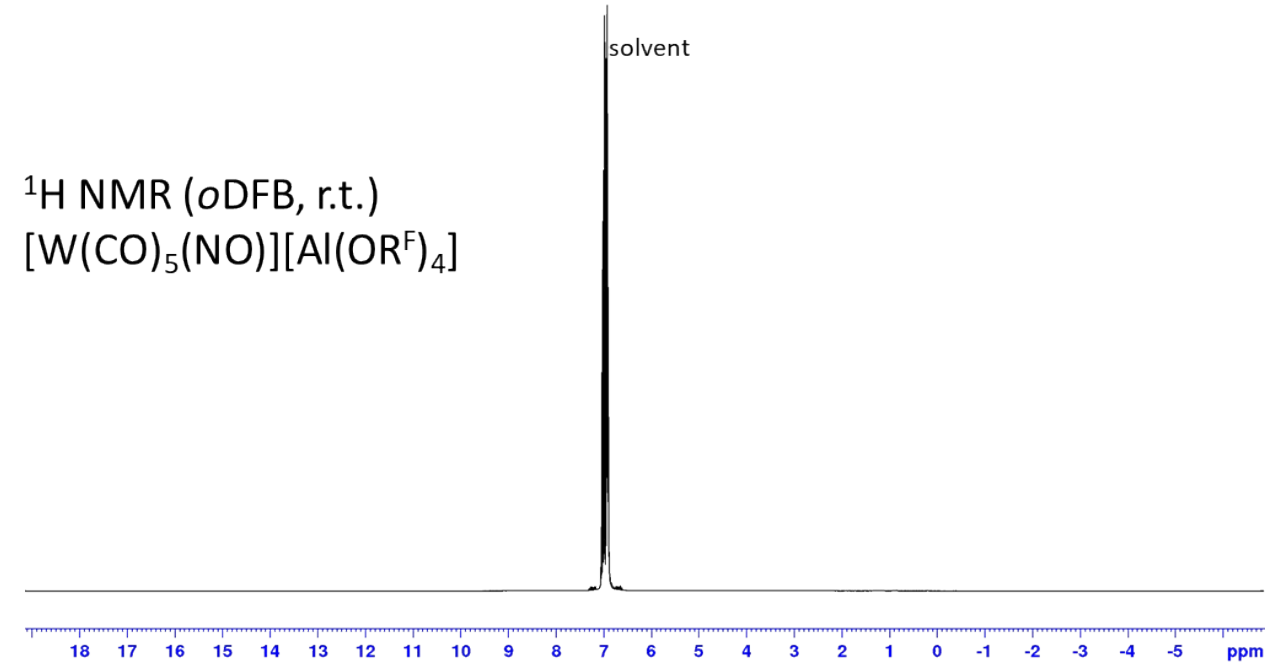
^{1}H NMR (300.18 MHz, *o*DFB, 298 K): *only solvent signals*; **^{13}C{^{1}H} NMR** (75.48 MHz, *o*DFB, 298 K): δ/ppm = 185.6 (s, 4C_{eq}, $[W(\mathbf{C}O)_5(NO)]^+$), 185.6 (d, ^1J(C,W) = 185 Hz, 4C_{eq}, 14% $[^{183}W(\mathbf{C}O)_5(NO)]^+$), 179.7 (s, 1$C_{ax}$, $[W(\mathbf{C}O)_5(NO)]^+$), 121.8 (q, ^1J(C,F) = 293 Hz, 12C, $\mathbf{C}F_3$, *in part overlapped by solvent signals*), 79.7 (m, 4C, $Al(O\mathbf{C}(CF_3)_3)_4$); **^{14}N NMR** (21.69 MHz, *o*DFB, 298 K): δ/ppm = –15 (br. s, 1N, $[W(CO)_5(\mathbf{N}O)]^+$), ; **^{19}F NMR** (282.45 MHz, *o*DFB, 298 K): δ/ppm = –75.2 (s, 36F, 4 × $C(C\mathbf{F}_3)_3$); **^{27}Al NMR** (78.22 MHz, *o*DFB, 298 K): δ/ppm = 35.1 (s, 1Al, $\mathbf{Al}(OR^F)_4$).



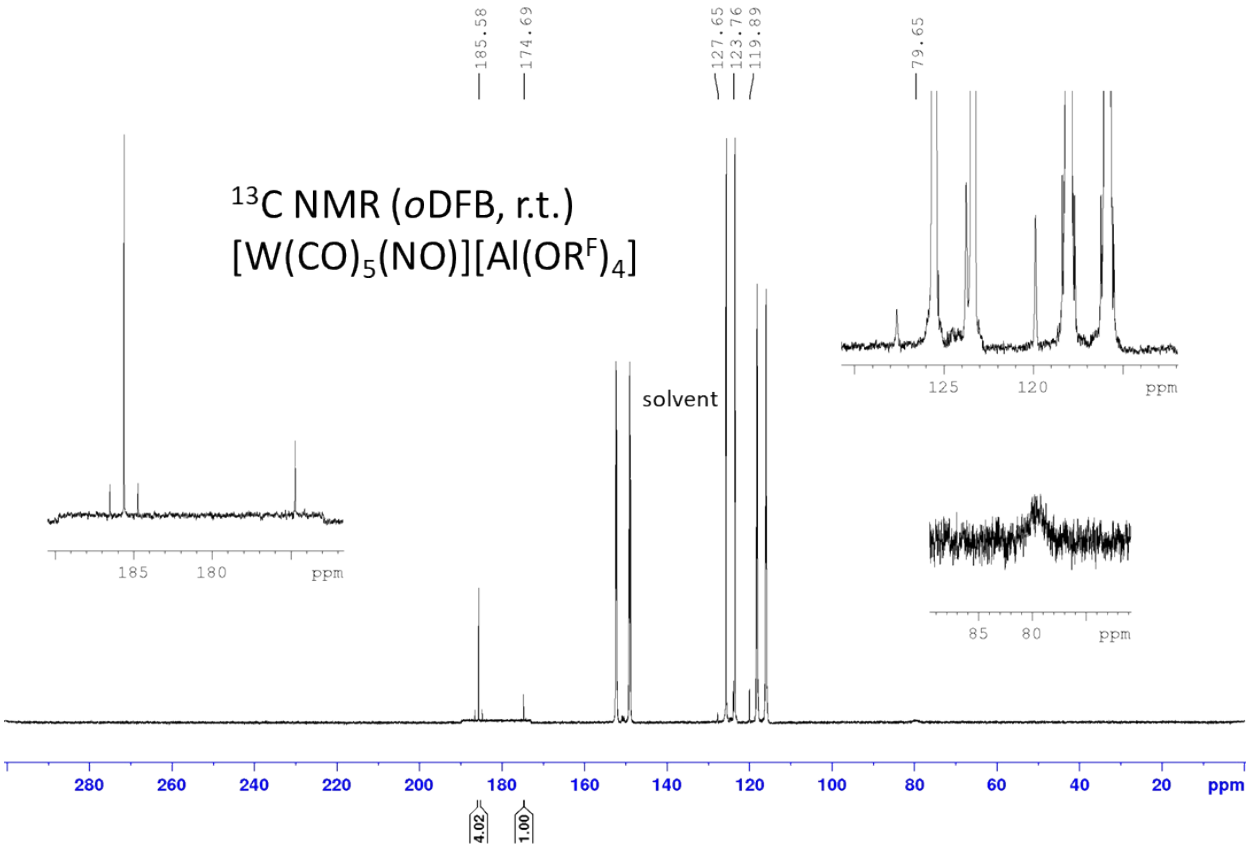
Supplementary Figure 9. Experimental IR spectrum of **2**.



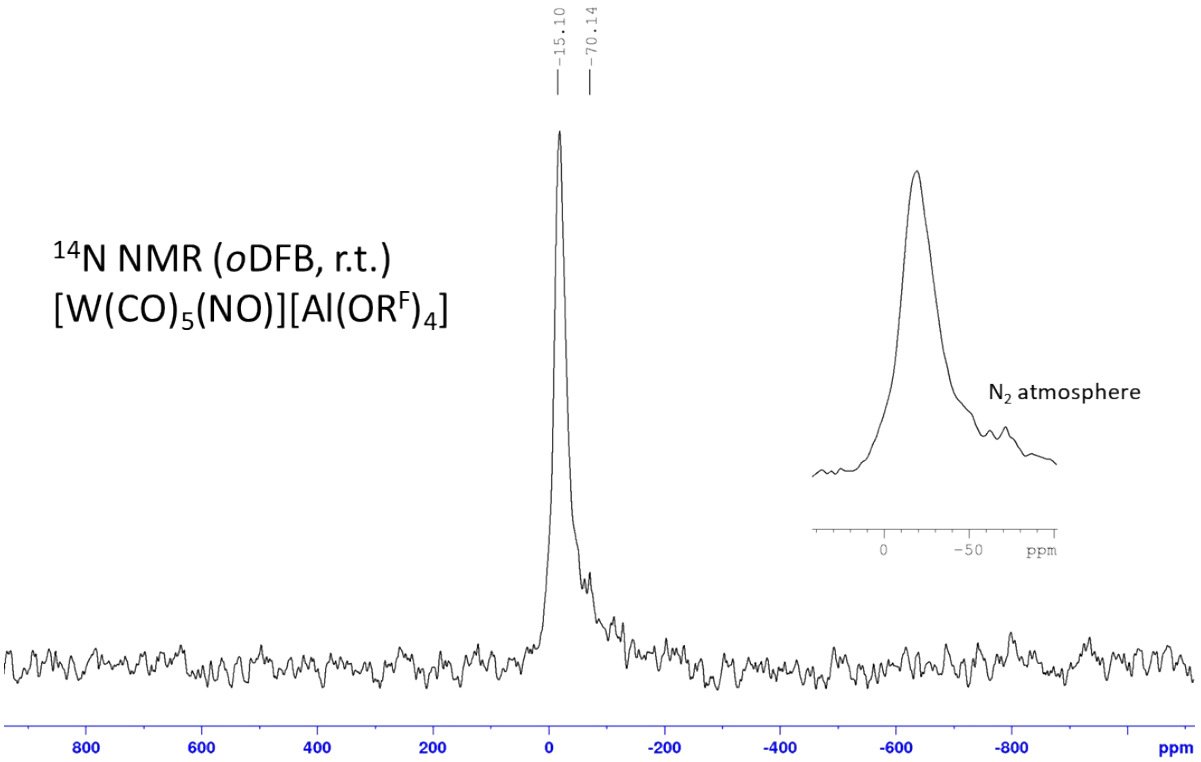
Supplementary Figure 10. Experimental Raman spectrum of **2**.



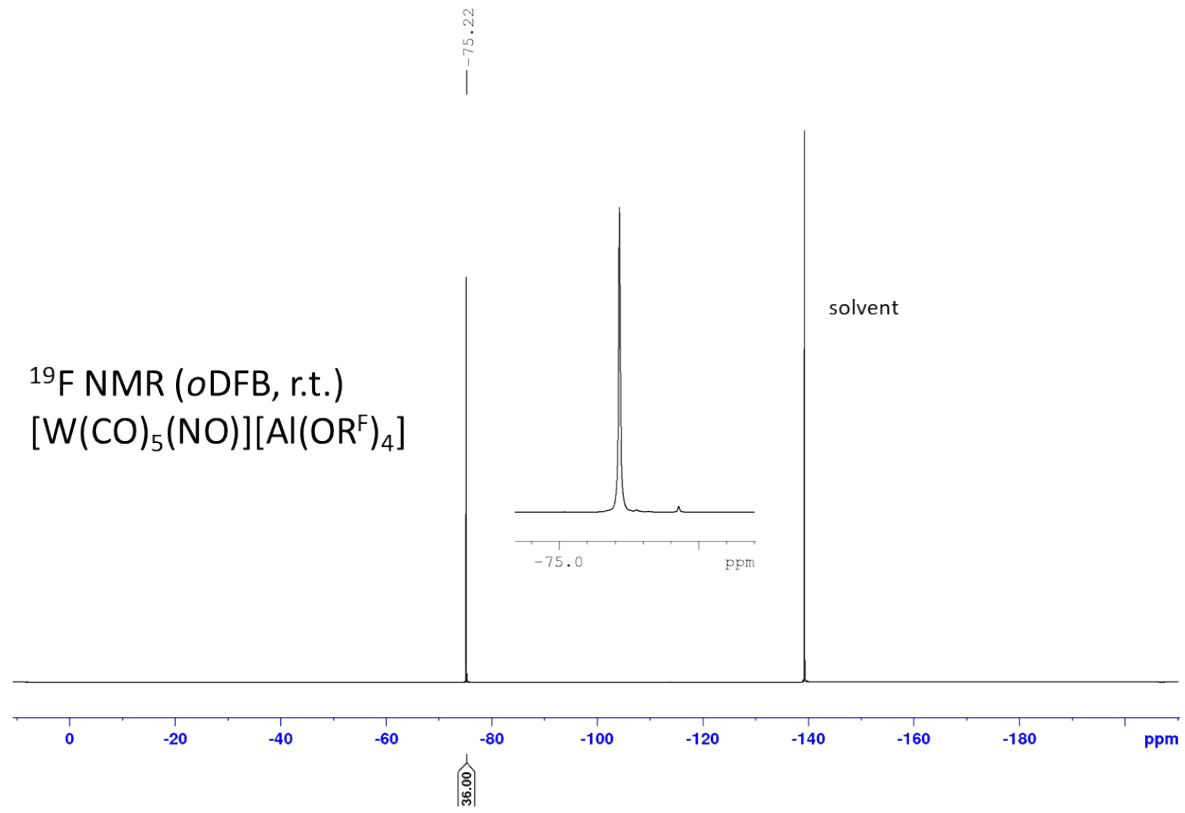
Supplementary Figure 11. ^{1}H NMR spectrum (300.18 MHz, *o*DFB, r.t.) of **2**.



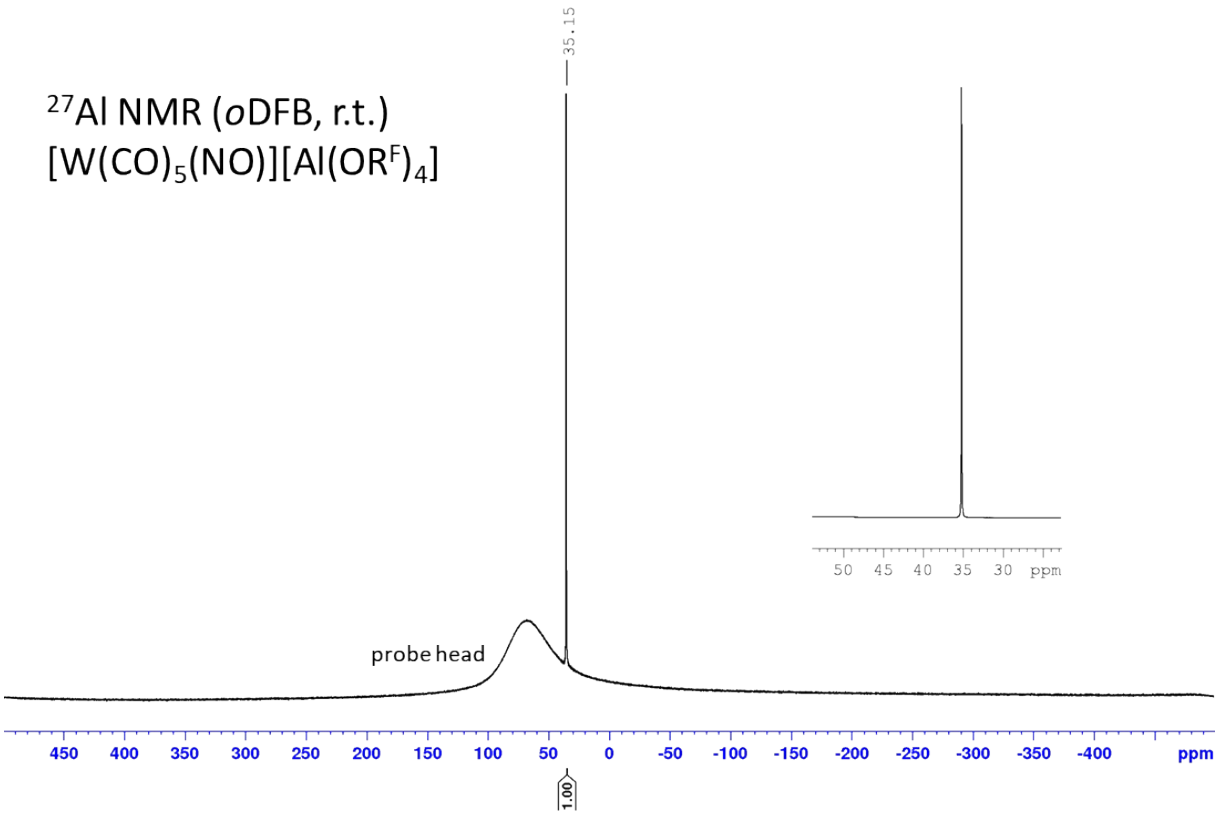
Supplementary Figure 12. ^{13}C NMR spectrum (75.48 MHz, *o*DFB, r.t.) of **2**.



Supplementary Figure 13. ^{14}N NMR spectrum (21.69 MHz, *o*DFB, r.t.) of **2**.



Supplementary Figure 14. ^{19}F NMR spectrum (282.45 MHz, *o*DFB, r.t.) of **2**.



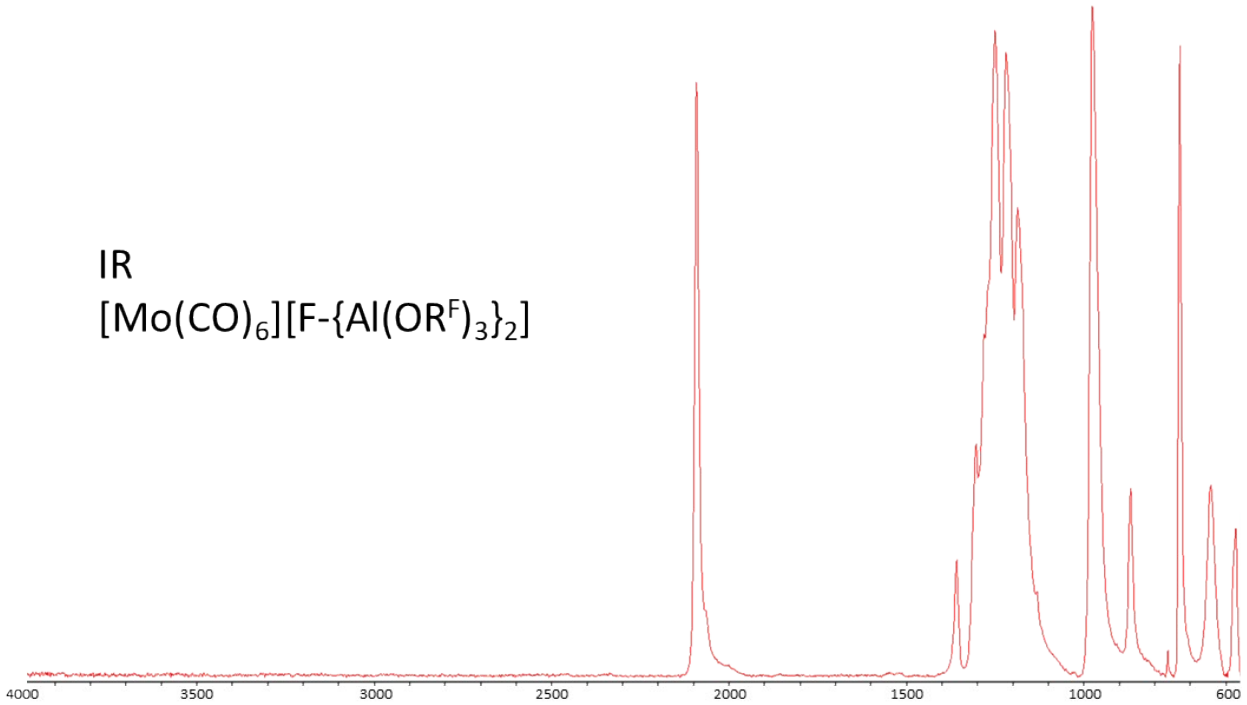
Supplementary Figure 15. ^{27}Al NMR spectrum (78.22 MHz, *o*DFB, r.t.) of **2**.

Synthesis of $[Mo(CO)_6][F\text{-}\{Al(OR^F)_3\}_2]$ (3)

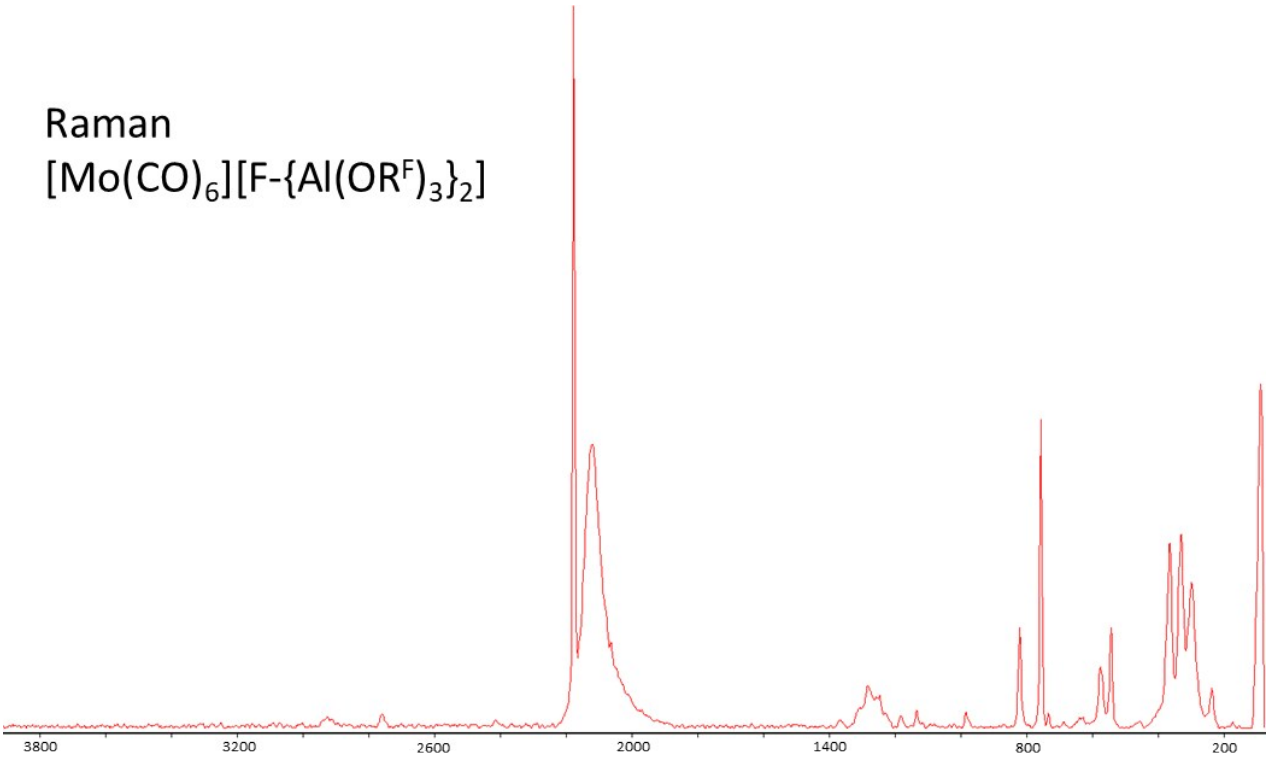
I_2 (53.9 mg, 0.212 mmol, 1 eq) was added to a double-Schlenk tube. Inside the glovebox, first $Ag[F\text{-}\{Al(OR^F)_3\}_2]$ (676 mg, 0.425 mmol, 2 eq) and afterwards $Mo(CO)_6$ (112 mg, 0.424 mmol, 2 eq) were added to the iodine. Upon contact of the solids, the formation of purple Ag/I_2 species was observed. Then, about 4 mL of 1,2,3,4-tetrafluorobenzene (TFB) were added at 0 °C and the initially purple solution turned to a brown suspension over the course of a few minutes of stirring. The reaction mixture was allowed to reach RT overnight and eventually a dark solution with yellow precipitate was obtained which was then filtered to remove the AgI. Subsequent crystallization by vapour-diffusion of *n*-pentane into the TFB solution over the course of five days led to the formation of near-colourless crystals of **3**. Yield: 580 mg, 78%.

FTIR (ZnSe, ATR): $\tilde{\nu}/cm^{-1}$ (intensity) = 2089 (vvs), 1355 (vw), 1300 (mw), 1278 (ms), 1247 (vvs), 1216 (vvs), 1184 (vs), 1129 (vw), 972 (vvs), 865 (w), 760 (vvw), 726 (vvs), 638 (w), 568 (w).

FT Raman (1000 scans, 250 mW, 4 cm^{-1}): $\tilde{\nu}/cm^{-1}$ (intensity) = 2175 (vvs), 2118 (mw), 1365 (vvw), 1280 (vvw), 1179 (vvw), 1131 (vvw), 981 (vvw), 818 (vw), 753 (m), 730 (vvw), 572 (vvw), 539 (vw), 361 (vw), 326 (w), 294 (vw), 233 (vvw), 84 (w).



Supplementary Figure 16. Experimental IR spectrum of **3**.



Supplementary Figure 17. Experimental Raman spectrum of **3**.

Synthesis of $[W(CO)_6][F\text{-}\{Al(OR^F)_3\}_2]$ (4)

Method A

I_2 (78.1 mg, 0.310 mmol, 1 eq) was added to a double-Schlenk tube. Inside the glovebox, first $Ag[Al(OR^F)_4]$ (667 mg, 0.620 mmol, 2 eq) and afterwards $W(CO)_6$ (218 mg, 0.619 mmol, 2 eq) were added to the iodine. Upon contact of the solids, the formation of purple Ag/I_2 species was observed. Then, about 4 mL of 1,2,3,4-tetrafluorobenzene (TFB) were added and the initially purple solution turned to a brown-green suspension over the course of a few minutes of stirring at room temperature. After 10 minutes, a brownish-green suspension was formed and yellow AgI precipitate was visible. The reaction mixture was stirred overnight and eventually a dark green solution was obtained which was filtered to remove the AgI. Subsequent crystallization by vapour-diffusion of *n*-pentane into the TFB solution over the course of five days led to the precipitation of grey amorphous solids as well was orange and yellow crystals. Those crystals were carefully transferred to a second double-Schlenk tube, dissolved again in TFB, and the clear-yellow solution was filtered and crystallized with *n*-pentane for a second time. After a few days, yellow block-shaped crystals of $[W(CO)_6][F\text{-}\{Al(OR^F)_3\}_2]$ (4) and orange needles of $[W(CO)_6(OC(CF_3)_3][F\text{-}\{Al(OR^F)_3\}_2]$ were obtained. Very careful manual separation of both species can be achieved inside the glovebox.

Method B

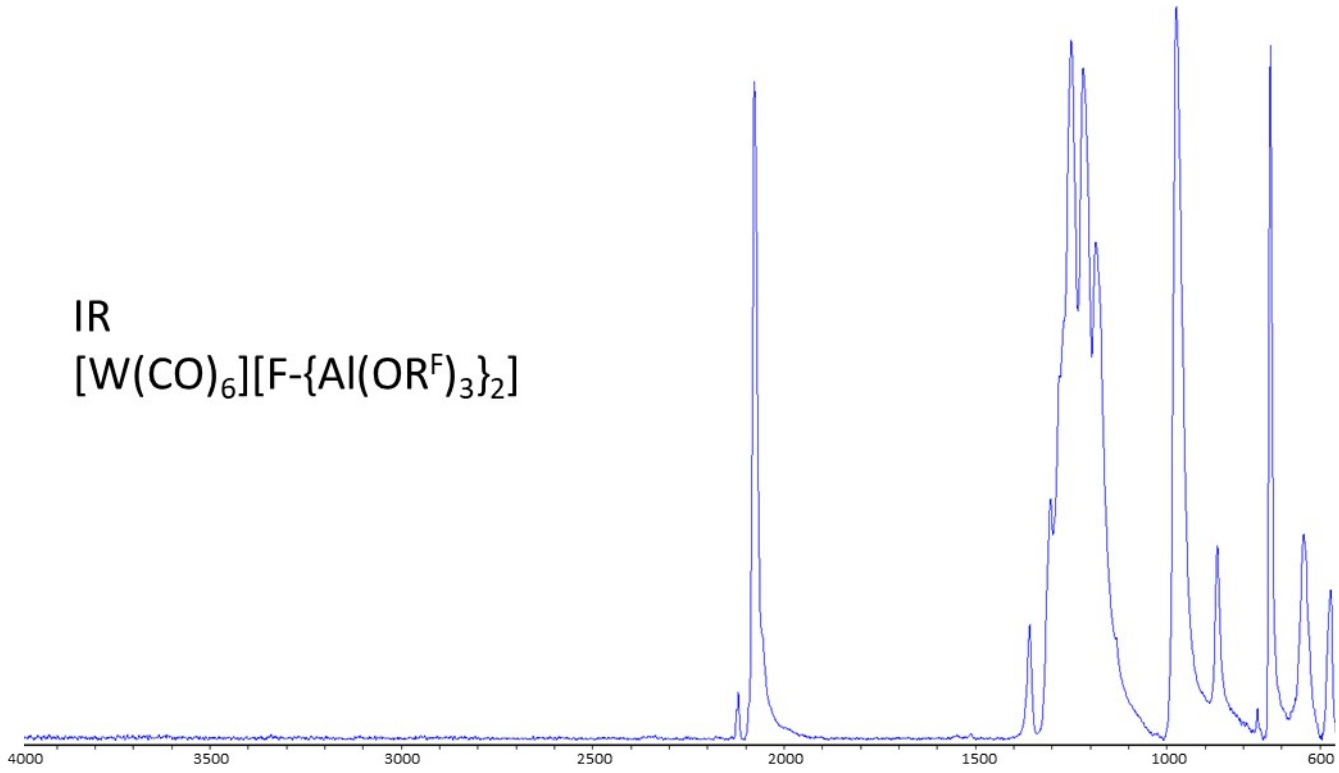
I_2 (49.5 mg, 0.195 mmol, 1 eq) was added to a double-Schlenk tube. Inside the glovebox, first $Ag[F\text{-}\{Al(OR^F)_3\}_2]$ (621 mg, 0.390 mmol, 2 eq) and afterwards $W(CO)_6$ (138 mg, 0.392 mmol, 2 eq) were added to the iodine. Upon contact of the solids, the formation of purple Ag/I_2 species was observed. Then, about 4 mL of 1,2,3,4-tetrafluorobenzene (TFB) were added at 0 °C and the initially purple solution turned to a yellow suspension over the course of a few minutes of stirring. After two hours at 0 °C, the dark-yellowish reaction mixture was allowed to reach RT overnight and eventually a dark green solution with yellow precipitate was obtained which then was filtered to remove the AgI. Subsequent crystallization by vapour-diffusion of *n*-pentane into the TFB solution over the course of five days led to the precipitation of grey amorphous solids as well was orange and yellow crystals. Those crystals were carefully and manually sorted inside the glovebox, wheres only the yellow block-shaped crystals were transferred to a second double-Schlenk tube, dissolved again in TFB, and the very dark to purple solution was

filtered and crystallized with *n*-pentane for a second time. After a few days, yellow block-shaped crystals of $[W(CO)_6][F\text{-}\{Al(OR^F)_3\}_2]$ (4) were obtained. Yield: 35%.

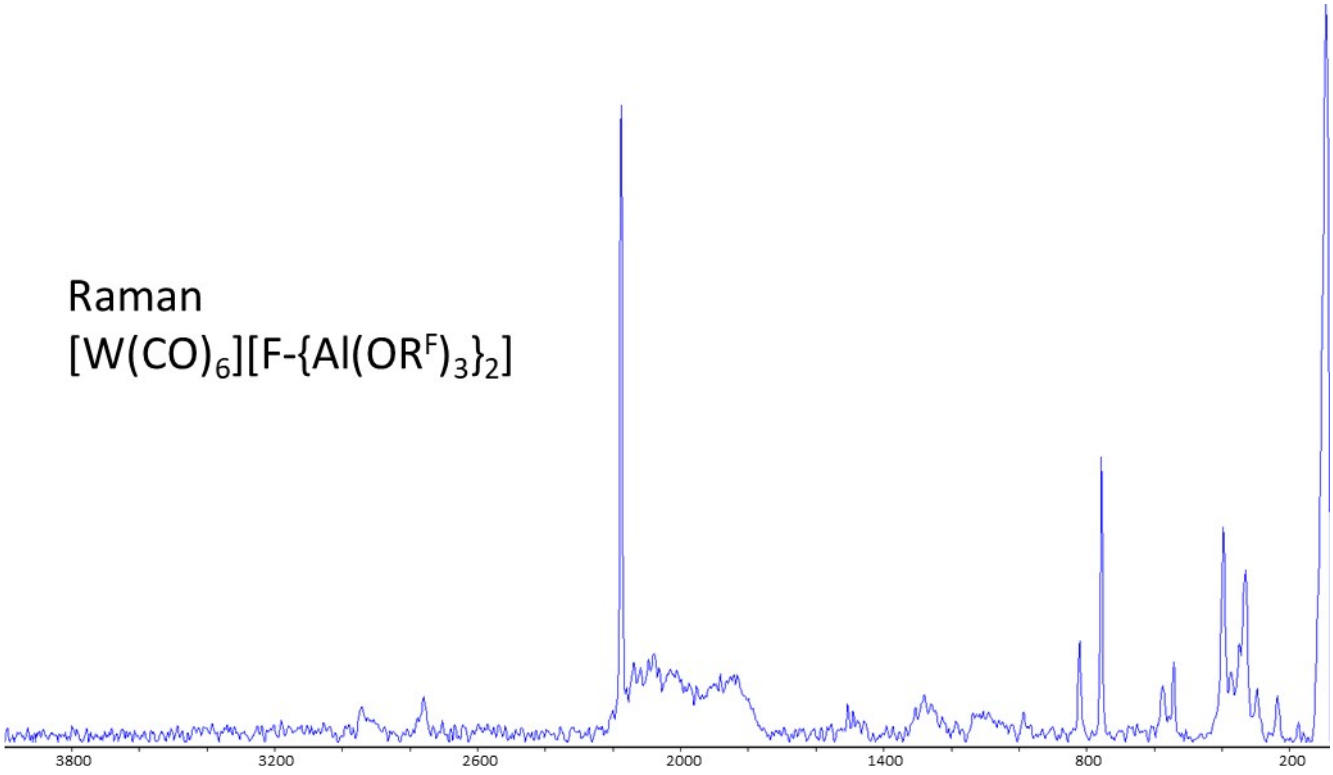
Note: The Ag[WCA] should be added first to the iodine in order to physically separate the $W(CO)_6$ from the I_2 before the solvent is added.

FTIR (ZnSe, ATR): $\tilde{\nu}$/cm^{-1} (intensity) = (2117 (vvw)), 2075 (vvs), 1355 (vw), 1301 (mw), 1277 (m), 1247 (vvs), 1215 (vvs), 1183 (s), 1129 (vw), 972 (vvs), 865 (w), 760 (vvw), 726 (vvs), 638 (w), 568 (w).

FT Raman (1000 scans, 100 mW, 4 cm^{-1}): $\tilde{\nu}$/cm^{-1} (intensity) = 2174 (vvs), 2075 (vvw), 1879 (vvw), 1276 (vvw), 1088 (vvw), 983 (vvw), 818 (vw), 753 (m), 572 (vvw), 539 (vw), 393 (mw), 370 (vvw), 345 (vvw), 327 (w), 293 (vvw), 233 (vvw), 170 (vvw), 88 (s).



Supplementary Figure 18. Experimental IR spectrum of **4**.



Supplementary Figure 19. Experimental Raman spectrum of ***4***.

4. Vibrational Analysis

Supplementary Table 1. Full assignment of all IR and Raman vibrations for complexes **1** and **2**.

$[Mo(CO)_5(NO)][Al(OR^F)_4]$ (1)		**$[W(CO)_5(NO)][Al(OR^F)_4]$ (2)**		**$[Mo(CO)_5(NO)]^+$ calcd.[a)]**		**$[W(CO)_5(NO)]^+$ calcd.[a)]**		**$[Al(OR^F)_4]^-$ [34]**		**Assignment [34,35] b)**
IR	Raman	IR	Raman	IR	Raman	IR	Raman	IR	Raman	
	101 (vs)		106 (vs)		78 (vvs)		84 (vvs)			δ(Mo–C) *E* δ(W–C) *E*
	234 (vvw)		234 (vvw)						233 (w)	- [Anion]
	289 (vvw)								291 (w)	C–C
				327 (vvw)						ν(Mo–C) A_1
						333 (vvw)				ν(W–C) A_1
	329 (vvw)		321 (vvw)						322 (s)	C–C, Al–O
						349 (vvw)				ν(W–C) *E*
				356 (vvw)						ν(Mo–C) *E*
	363 (vvw)		374 (vvw)						369 (w)	C–C, C–F, Al–O
					384 (vw)					ν(Mo–C) A_1
							389 (vvw)			ν(W–C) B_1
			393 (vvw)				404 (w)			ν(W–C) A_1
	473 (vvw)				485 (vw)					ν(Mo–N) A_1
			492 (vvw)				498 (vw)			ν(W–N) A_1
				521 (vvw)		524 (vvw)				δ(C–O) *E*
	538 (vvw)		546 (w)	570 (vvw)	570 (vw)	537 (vvw)	537 (vw)		538 (mw)	C–C, C–O, δ(C–O) A_1 ν(Mo–N) A_1 ν(W–N) A_1
560 (mw)	564 (vw)	561 (w)						559 (mw)	561 (w)	Al–O, C–C
		572 (vvw)						573 (w)	572 (w)	Al–O, C–C
617 (w)		604 (vw)		630 (vvw)		603 (vvw)				δ(N–O) *E*
726 (vvs)		726 (vvs)						726 (ms)		C–C, C–O
	747 (vvw)		*747 (vvw)*						*744 (ms)*	- [Anion]
756 (vw)		*756 (vvw)*						*755 (w)*		*C–C, C–O*
	798 (vvw)		*797 (vvw)*						*799 (ms)*	- [Anion]
831 (w)		*831 (vw)*						*830 (m)*		*Al–O, C–C*
		859 (vvw)[c)]								
969 (vvs)	977 (vvw)	970 (vvs)	978 (vvw)					975 (vs)	975 (mw)	C–C, C–F
1139 (vvw)		1138 (vvw)							1133 (mw)	C–C, C–F
1160 (mw)		1163 (w)						1176 (ms)	1173 (mw)	C–C, C–F
1208 (vvs)		1209 (vs)						1223 (vs)		C–C, C–F
1239 (vvw)		1239 (vvw)						1236 (vs)	1237 (mw)	C–C, C–F
1266 (vvw)	1271 (vvw)	1273 (vw)	1271 (vvw)					1274 (s)	1276 (mw)	C–C, C–F
1297 (vvw)		1298 (vvw)						1299 (s)	-	C–C, C–F
1352 (w)		1352 (vw)						1349 (ms)	1353 (w)	C–C, C–F
1786 (vvw)*										
1820 (s)	1825 (vvw)	1818 (ms)	1823 (vvw)	1877 (m)	1877 (vvw)	1868 (m)	1868 (vvw)			ν(N–O) A_1
2070 (vvw)	2071 (vvw)	2059 (vw)	2061 (vvw)							ν(^{13}C–O) *E***
2099 (vvs)	2106 (vvw)	2090 (vs)	2095 (vvw)	2078 (vvs)		2070 (vvs)				ν(C–O) *E*
2124 (vvw)	2124 (vvs)	2113 (vvw)	2114 (vvs)		2092 (vw)		2086 (w)			ν(C–O) B_1
2162 (vw)	2163 (m)	2153 (vw)	2155 (m)	2121 (vvw)	2121 (vw)	2114 (vvw)	2114 (vw)			ν(C–O) A_1
2186 (w)	2187 (mw)	2183 (vw)	2184 (m)	2162 (vvw)	2162 (vw)	2160 (vvw)	2160 (vw)			ν(C–O) A_1

[a)] BP86-D3BJ/def2-TZVPP, C_{4v} symmetry, **no scale factor was applied**. w: weak, m: medium, s: strong, v: very, sh: shoulder, br: broad.
[b)] The assignments of the respective anion bands and their intensities are based on $[N(Bu)_4][Al(OR^F)_4]$ (IR and Raman) in ref.[34] and $[CBr_3][F\text{-}\{Al(OR^F)_3\}_2]$ (IR only) in ref.[35]. The characteristic IR bands that are suited best for differentiation between $[Al(OR^F)_4]^-$ and $[F\text{-}\{Al(OR^F)_3\}_2]^-$ are given in italics; in Raman spectroscopy, the difference is subtle and shows best in the (roughly) 1:1 intensity of the bands at 747 and 795 cm^{-1} ($[Al(OR^F)_4]$) compared to a (roughly) 1:3 intensity for the bands at 753 and 817 cm^{-1} ($[F\text{-}\{Al(OR^F)_3\}_2]^-$).
[c)] Probably a small contamination with $[F\text{-}\{Al(OR^F)_3\}_2]^-$, although no impurities were visible in ^{19}F NMR.
* Shoulder of unknown impurity or ^{13}C-influenced N–O vibration. However, the difference between $[Mo/W(^{13}CO)_5(NO)]^+$ and $[Mo/W(^{12}CO)_5(NO)]^+$ is only a few cm^{-1} for the A_1 ν(N–O).
** The difference of the *E* ν(C–O) vibration in $[Mo/W(^{13}CO)_5(NO)]^+$ and $[Mo/W(^{12}CO)_5(NO)]^+$ is about 45 cm^{-1}.

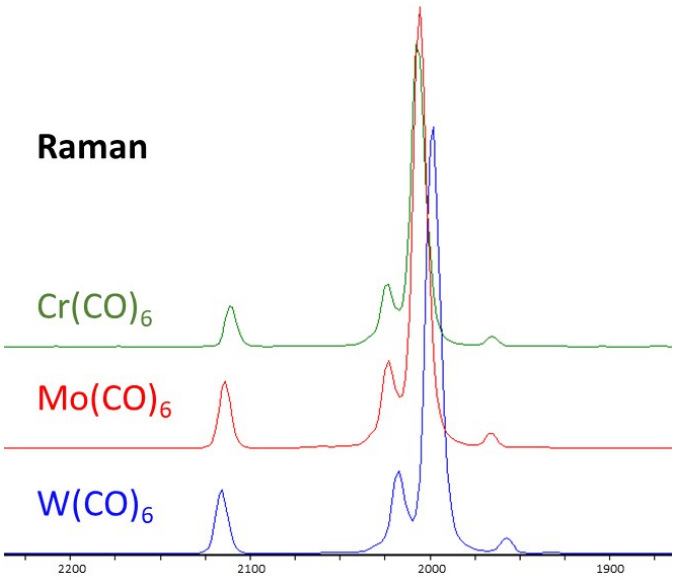
Supplementary Table 2. Full assignment of all IR and Raman vibrations for complexes **3** and **4**.

$[Mo(CO)_6][F\text{-}\{Al(OR^F)_3\}_2]$ (3)		**$[W(CO)_6][F\text{-}\{Al(OR^F)_3\}_2]$ (4)**		**$[Mo(CO)_6]^+$ calcd.[a)]**		**$[W(CO)_6]^+$ calcd.[a)]**		**$[F\text{-}\{Al(OR^F)_3\}_2]^-$ [35]**	**Assignment [34,35] b)**
IR	Raman	IR	Raman	IR	Raman	IR	Raman	IR	
	84 (vvs) 112 (vvs)		88 (s)		76 (vvs)		77		δ(Mo–C) E_g δ(W–C) E_g
			174 (vvw)						C–C
	233 (vvw)		233 (vvw)						C–C
			293 (vvw)						C–C
	294 (vw)								C–C, Al–O
	325 (w)		327 (w)						*C–C, Al–O
						340 (vvw)			ν(W–C) E_u
				344 (vvw)					ν(Mo–C) A_{2u} ν(Mo–C) E_u
					347 (vvw)				ν(Mo–C) E_g
			345 (vvw)				369 (vvw)		ν(W–C) E_{1g}
	361 (vw)				385 (w)				ν(Mo–C) A_{1g}
			393 (mw)				403 (vw)		ν(W–C) A_{1g}
							416 (vvw)		δ(C–O) A_{1g}
						455 (vvw)			δ(C–O) A_{2u}
				463 (vvw)					δ(C–O) A_{2u}
	539 (vw)		540 (vw)						C–C, C–O
						551 (vvw)			δ(C–O) E_u
				565 (vvw)					δ(C–O) E_u
568 (w)	572 (vvw)	568 (w)	572 (vvw)					572 (m)	Al–O, C–C
638 (w)		*638 (w)*						*639 (m)*	*Al–F–Al*
726 (vvs)	730 (vvw)	726 (vvs)						728 (s)	C–C, C–O
	753 (mw)		*753 (m)*						- [Anion]
760 (vvw)		760 (vvw)							C–C, C–O
									C–C, C–O
	818 (mw)		*818 (vw)*						- [Anion]
865 (w)		*865 (w)*						*865 (w)*	*Al–O, Al–F–Al*
972 (vvs)	981 (vvw)	972 (vvs)	983 (vvw)					975 (s)	C–C, C–F
1129 (vw)	1131 (vvw)	1129 (vw)	1088 (vvw)						C–C, C–F
1184 (vs)	1179 (vvw)	1183 (s)						1183 (m)	C–C, C–F
1216 (vvs)		1215 (vvs)						1218 (s)	C–C, C–F
1247 (vvs)		1247 (vvs)						1249 (s)	C–C, C–F
1278 (ms)	1280 (vvw)	1277 (m)	1276 (vvw)					1268 (m)	C–C, C–F
1300 (mw)		1301 (mw)						1301 (m)	C–C, C–F
1355 (vw)	1365 (vvw)	1355 (vw)						1355 (m)	C–C, C–F
2089 (vvs)[d)]		2075 (vvs)[d)]		2072 (vvs)		2062 (vvs)			ν(C–O) A_{2u} ν(C–O) E_u
			1879 (vvw, br)[e)]						ν(C–O)
	2118 (mw, br)	2117 (vvw)[c)]	2075 (vww, br)[e)]		2074 (ms)		2064 (m)		ν(C–O) E_g
	2175 (vss)		2174 (vvs)		2158 (vw)		2155 (vw)		ν(C–O) A_{1g}

[a)] BP86-D3BJ/def2-TZVPP, D_{3d} symmetry, **no scale factor was applied**. w: weak, m: medium, s: strong, v: very, sh: shoulder, br: broad.
[b)] The assignments of the respective anion bands and their intensities are based on $[N(Bu)_4][Al(OR^F)_4]$ (IR and Raman) in ref.[34] and $[CBr_3][F\text{-}\{Al(OR^F)_3\}_2]$ (IR only) in ref.[35]. The characteristic IR bands that are suited best for differentiation between $[Al(OR^F)_4]^-$ and $[F\text{-}\{Al(OR^F)_3\}_2]^-$ are given in italics; in Raman spectroscopy, the difference is subtle and shows best in the (roughly) 1:1 intensity of the bands at 747 and 795 cm^{-1} ($[Al(OR^F)_4]$) compared to a (roughly) 1:3 intensity for the bands at 753 and 817 cm^{-1} ($[F\text{-}\{Al(OR^F)_3\}_2]^-$).
[c)] The additional band in the IR of $[W(CO)_6][F\text{-}\{Al(OR^F)_3\}_2]$ at 2117 cm^{-1} is either the Raman-active E_g vibration or a contamination which coincidentally vibrates at that same wavenumber.
[d)] Small ^{13}CO shoulders are visible in the spectrum.
[e)] The spectrum consists of two very broad bands that span over 300 cm^{-1}.
* *Note*: Due to partial overlap with the anion bands, the ν(Mo–C) A_{2u}/E_u vibrations cannot be assigned unambiguously.

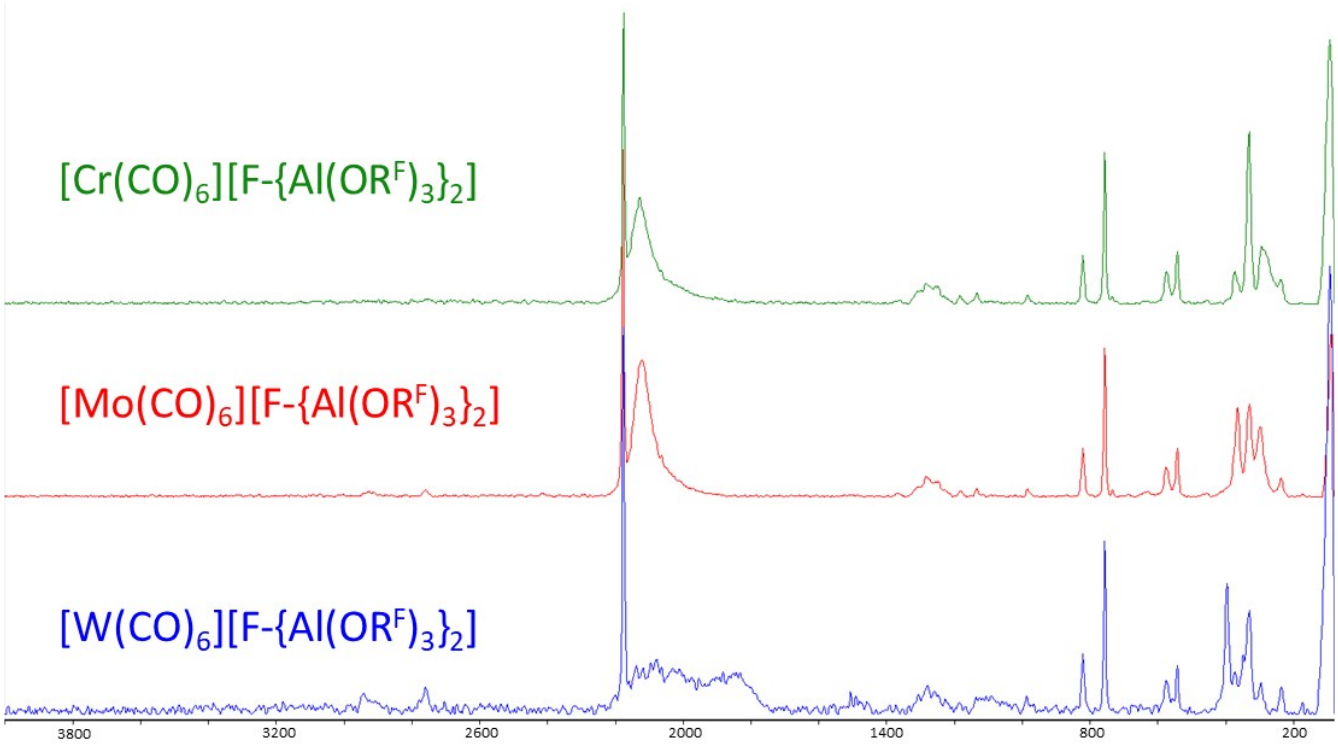
Comparison of the CO vibrations

Raman spectra of the neutral Cr/Mo/W(CO)$_6$ triad



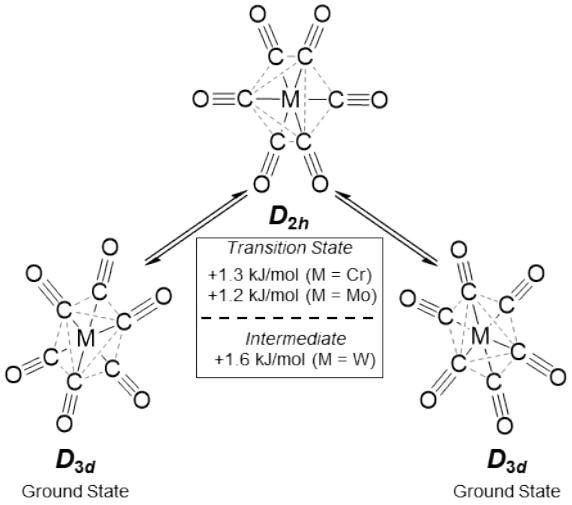
Supplementary Figure 20. Stacked Raman spectra of the neutral Cr/Mo/W(CO)$_6$ triad.

Stacked Raman spectra of the cationic [Cr/Mo/W(CO)$_6$]$^+$ triad

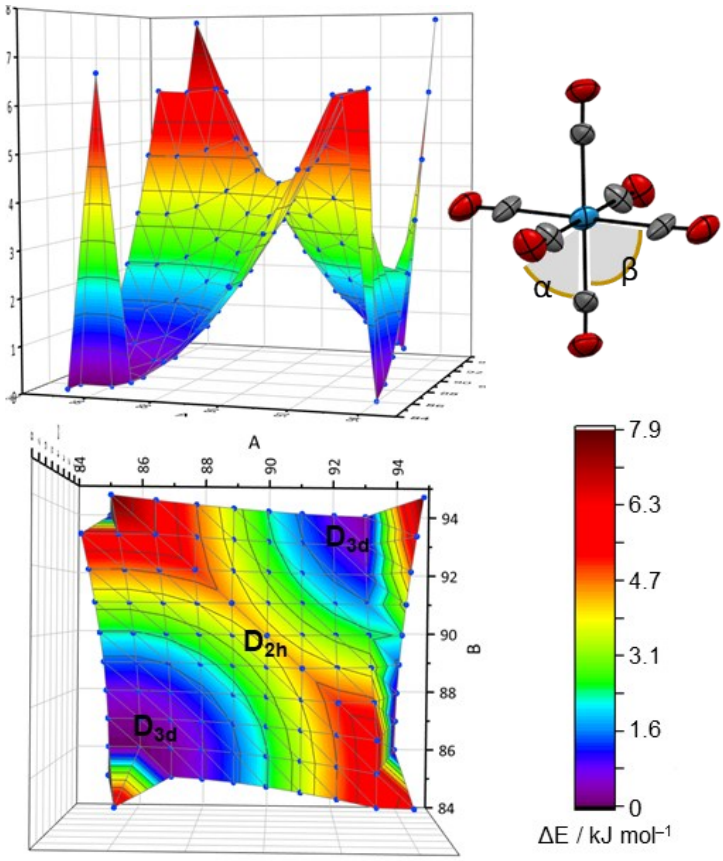


Supplementary Figure 21. Stacked Raman spectra of the cationic [Cr/Mo/W(CO)$_6$]$^+$ triad.

Discussion of the $D_{3d}/D_{2h}/D_{3d}$ fluctuation



In order to evaluate our previous findings on the fluctuation of $[Cr(CO)_6]^+$, we conducted an initial (pseudo-relaxed) energy surface scan (BP86-D3BJ/def2-SVP) along the two '*cis*' C_{eq}-W-C_{ax} angles for $[W(CO)_6]^+$ which only gave a reasonable output for *trans* C-W-C angles fixed at 180°. It gave a D_{2h}-symmetric transition state at about +4.5 kJ mol^{-1} between two D_{3d} ground states (see picture below) which would be in agreement with our previous findings on the Cr system.



Supplementary Figure 22. Energy surface scan along two angles for $[W(CO)_6]^+$.

However as we looked further into detail, single-point calculations with vibrational analysis of the alleged D_{2h} transition state showed no imaginary vibration. A geometry optimization without geometry restrictions (in C_1) led to the D_{3d} ground state; a geometry optimization in D_{2h} led to a D_{2h} local minimum about +5 kJ mol^{-1} above the D_{3d} structure.

On BP86-D3BJ/def2-TZVPP level of theory, the D_{2h} symmetric structure is also a local minimum for $[W(CO)_6]^+$ (+9.5 kJ mol^{-1}) and not a transition state any more. This is the same for $[Mo(CO)_6]^+$ (D_{2h} +8.2 kJ mol^{-1}) and Cr (D_{2h} +8.2 kJ mol^{-1}).

As an alternative approach, an *ad hoc* QST2 transition state search for $[Mo(CO)_6]^+$ between the two D_{3d} and D_{2h} structures failed with BP86.

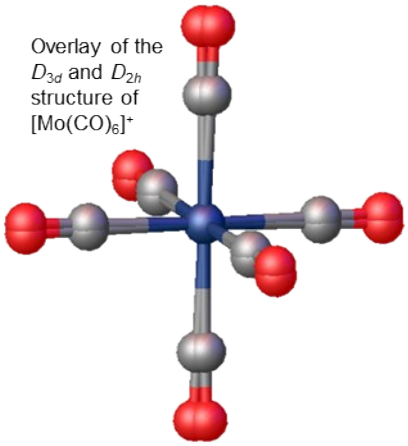
We then conducted a third study with the TPSSh (D3BJ/def2-TZVPP) functional (that we also used in the $[Cr(CO)_6]^+$ publication). Here, we found a D_{2h}-symmetric transition state (TS), that connected the two isomeric D_{3d} ground states, for Cr ($D_{2h,\,TS}$ = +3.4 kJ mol^{-1}) and Mo ($D_{2h,\,TS}$ = +4.8 kJ mol^{-1}). However, for W, the D_{2h} structure is again a local minimum (+4.8 kJ mol^{-1}).

We then fed the TPSSh structures into a DPLNO-CCSD(T) calculation for more exact energetics.

	$\Delta E(D_{2h}–D_{3d})$				
	BP86-D3BJ/def2-TZVPP	D_{2h} = TS	TPSSh- D3BJ/def2-TZVPP	DPLNO-CCSD(T)/def2-TZVPP	D_{2h} = TS
$[Cr(CO)_6]^+$	+8.2	no	+3.4	+1.3	yes
$[Mo(CO)_6]^+$	+9.0	no	+4.8	+1.2	yes
$[W(CO)_6]^+$	+9.5	no	+4.8	+1.6	no

From these findings, we summarize and conclude the following:

a) Although superficially similar, the electronic and structural fluctuations of $[Cr/Mo/W(CO)_6]^+$ differ in their devilish details
b) The structural differences for D_{3d} and D_{2h} are very small



c) The results and trends of the calculations are dependent on the software (Orca, Gaussian, Turbomole), functionals (TPSSH, BP86, …) and basis set (SVP vs TZVPP) that we used
d) Possible changes in the electronic occupation in the ground state and the possible transition states in these delicate systems highly complicate the calculations and might give different results.
e) Two D_{3d}-Isomers for Cr and Mo equilibrate via a D_{2h} intermediate/transition state. We were unable to find a transition state for W between the D_{3d} and D_{2h} local minimum even with the TPSSh functional
f) The coupled-cluster calculations based on the TPSSh-structures show that the energy-barrier between D_{3d}-D_{2h}-D_{3d} is small enough for a fast equilibration. One should note that the calculated small T1-diagnostic values around 0.02 suggest that the DPLNO-CCSD(T) give valid and reliable energies.

To summarize, a proper and correct description of these systems is very complex, especially since we got different results from different functionals and methods.

We believe that a thorough and large scale theoretical investigation carried out by expert specialists is needed and should be part of a future report.

CO vibrations of all literature-known homoleptic hexacarbonyl complexes

Supplementary Table 3. CO vibrations of all literature-known homoleptic hexacarbonyl complexes, taken from [36] and references therein.

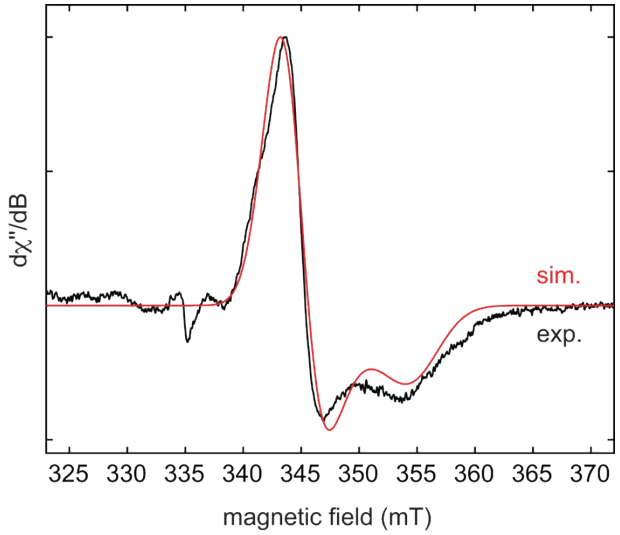
		Raman		IR	Comment
		A_{1g}	E_g	E_u/A_{2u} (D_{3d}) / T_{1u} (O_h)	
Gr. IV	$[Ti(CO)_6]^{2-}$	-	-	1748	CH_3CN solution
	$[Zr(CO)_6]^{2-}$	-	-	1757	CH_3CN solution
	$[Hf(CO)_6]^{2-}$	-	-	1757	CH_3CN solution
Gr. V	$V(CO)_6$	2102	2038	1984	Ar-Matrix, 12K
	$[V(CO)_6]^-$	2020	1894	1858	CH_3CN solution
	$[Nb(CO)_6]^-$	2023	1885	1864	Ra solid, IR acetone solution
	$[Ta(CO)_6]^-$	2025	1881	1859	Ra solid, IR acetone solution
Gr VI	$Cr(CO)_6$	2112	2018	1984	CCl_4 solution
	$Mo(CO)_6$	2117	2019	1986	CCl_4 solution
	$W(CO)_6$	2117	2010	1977	CS_2 solution
	$[Cr(CO)_6]^+$	2173	2128	2096	Solid
	$[Mo(CO)_6]^+$	2174	2127	2089	Solid
	$[W(CO)_6]^+$	2173	2128	2075	Solid
Gr VII	$[Mn(CO)_6]^+$	2192	2125	2095	CH_3CN solution
	$[Tc(CO)_6]^+$	-	-	2095	CH_3CN solution
	$[Re(CO)_6]^+$	2197	2122	2085	CH_3CN solution
Gr VIII	$[Fe(CO)_6]^{2+}$	2241	2220	2204	Solid
	$[Ru(CO)_6]^{2+}$	2254	2222	2199	Solid
	$[Os(CO)_6]^{2+}$	2259	2218	2190	Solid
Gr IX	$[Ir(CO)_6]^{3+}$	2295	2276	2254	Solid

Comparison of Turbomole vs Gaussian calculations

Supplementary Table 4. Comparison of selected calculated stretch vibrations with Turbomole (TM) (*BP86-D3BJ/def2-TZVPP*) vs Gaussian (G) (*BP86/def2-TZVPP*).

	$Cr(CO)_6$	$[Cr(CO)_6]^+$	$[Cr(CO)_5(NO)]^+$	$Mo(CO)_6$	$[Mo(CO)_6]^+$	$[Mo(CO)_5(NO)]^+$	$W(CO)_6$	$[W(CO)_6]^+$	$[W(CO)_5(NO)]^+$
A_{1g} CO TM	2104	2158	-	2106	2158	-	2104	2155	-
A_{1g} CO G	2098	2152	-	2100	2151	-	2098	2148	-
E_g CO TM	2015	2074	-	2013	2074	-	2008	2067	-
E_g CO G	2009	2067	-	2007	2068	-	2002	2061	-
A_{2u}/E_u TM	1994	2080	-	1990	2073	-	1985	2062	-
A_{2u}/E_u G	1988	2077	-	1985	2065	-	1980	2056	-
A_1 NO TM	-	-	1903	-	-	1877	-	-	1868
A_1 NO G	-	-	1895	-	-	1870	-	-	1861
E CO TM	-	-	2085	-	-	2078	-	-	2070
E CO G	-	-	2079	-	-	2072	-	-	2064
A_1 M–C TM	406	364	-	418	385	-	435	403	-
A_1 M–C G	401	358	-	414	381	-	431	400	-
A_1 M–N TM	-	-	667	-	-	570	-	-	537
A_1 M–N G	-	-	662	-	-	566	-	-	535
A_1 M–N TM	-	-	506	-	-	485	-	-	498
A_1 M–N G	-	-	503	-	-	484	-	-	497

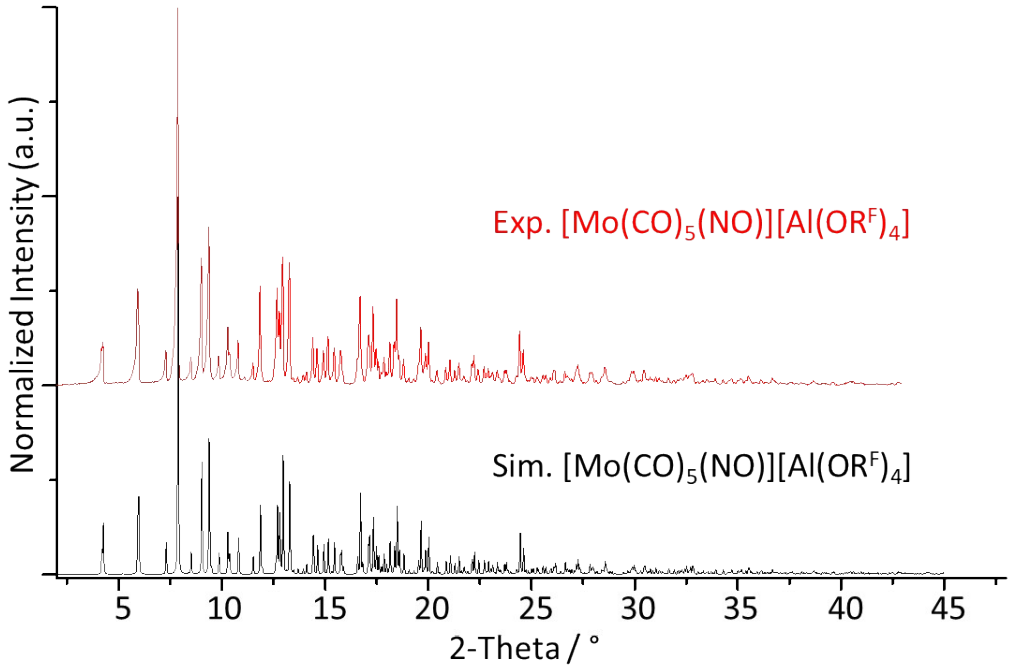
5. EPR Spectrum and simulation of the Impurity found in the sample of 3



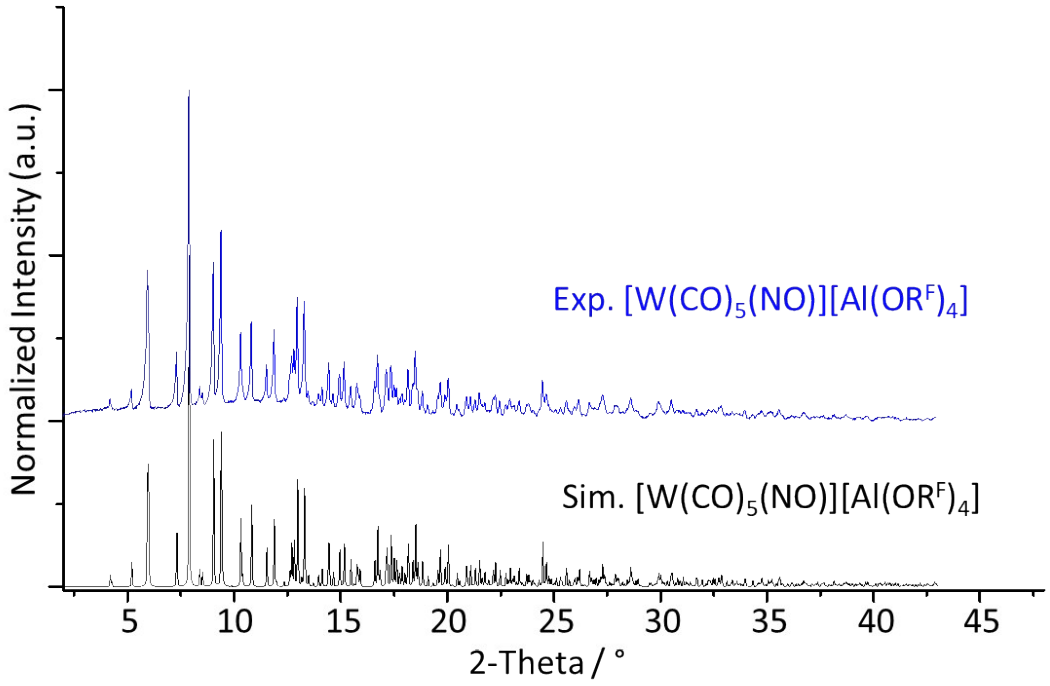
Supplementary Figure 23: Experimental and simulated EPR spectra of the small impurity present in **3** at 100 K. Simulation parameters: $g_{\perp} = 1.948$, $g_{/\!/} = 1.891$.

6. Powder XRD Data

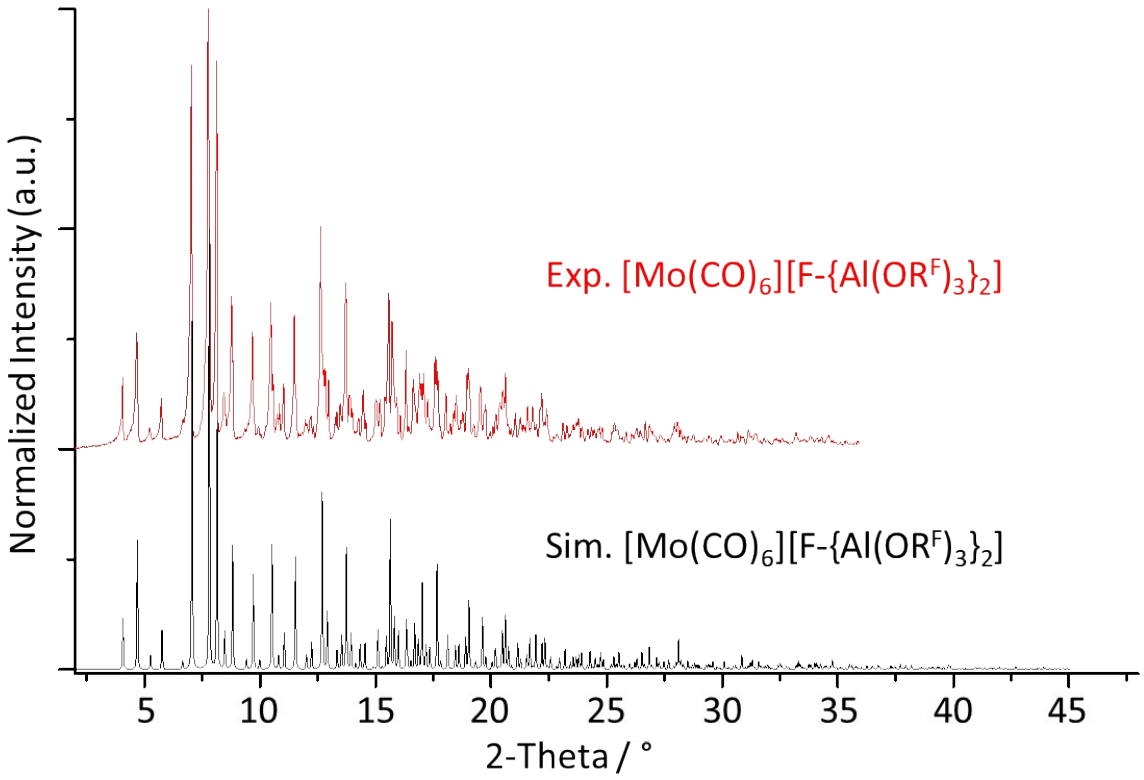
In order to evaluate the phase purity of the bulk materials **1**, **2**, **3** and **4**, powder XRD measurements were conducted at 100K. They confirm the absence of crystalline impurities for both bulk materials.



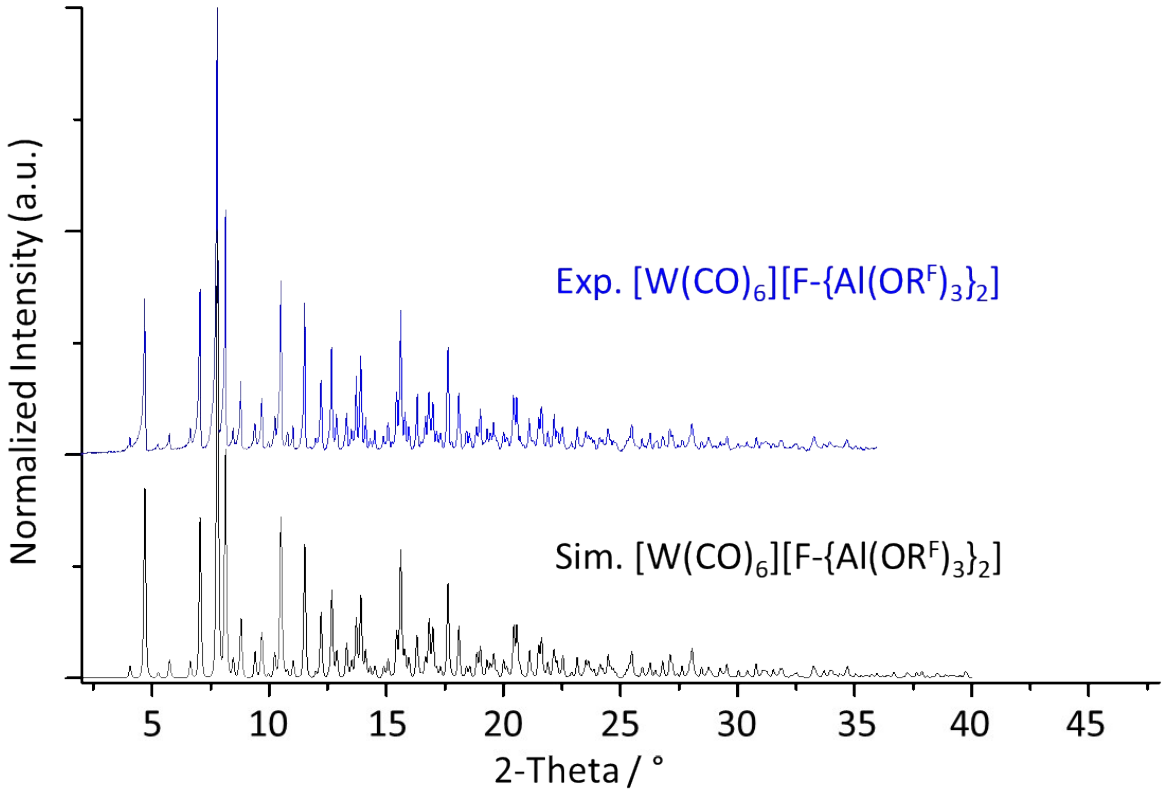
Supplementary Figure 24. Experimental (Exp., red) and simulated (Sim., black) powder XRD diffractogram of **1**.



Supplementary Figure 25. Experimental (Exp., blue) and simulated (Sim., black) powder XRD diffractogram of **2**.



Supplementary Figure 26. Experimental (Exp., red) and simulated (Sim., black) powder XRD diffractogram of **3**.



Supplementary Figure 27. Experimental (Exp., blue) and simulated (Sim., black) powder XRD diffractogram of **4**.

7. Single-Crystal XRD Data of Compounds 1 to 4

$[Mo(CO)_5(NO)][Al(OR^F)_4]$ (1)

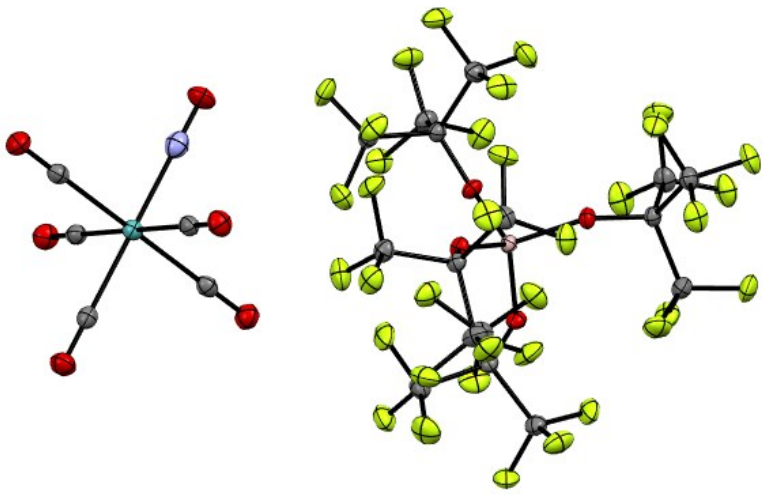


Table 1 Crystal data and structure refinement for p4n_a.

CCDC Deposition Number	1952379
Identification code	p4n_a
Empirical formula	$C_{21}NO_{10}F_{36}AlMo$
Formula weight	1233.14
Temperature/K	99.99
Crystal system	tetragonal
Space group	P4/n
a/Å	13.7152(3)
b/Å	13.7152(3)
c/Å	9.5418(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1794.88(10)
Z	2
ρ_{calc}g/cm^3	2.282
μ/mm^{-1}	0.632
F(000)	1184.0
Crystal size/mm^3	0.15 × 0.1 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.97 to 66.212
Index ranges	$-19 \leq h \leq 16$, $-21 \leq k \leq 13$, $-11 \leq l \leq 13$
Reflections collected	22133
Independent reflections	3368 [R_{int} = 0.0225, R_{sigma} = 0.0155]
Data/restraints/parameters	3368/0/163
Goodness-of-fit on F^2	1.029
Final R indexes [I>=2σ (I)]	R_1 = 0.0226, wR_2 = 0.0555
Final R indexes [all data]	R_1 = 0.0242, wR_2 = 0.0565
Largest diff. peak/hole / e Å^{-3}	0.57/-0.70

Table 2 Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for p4n_a. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Mo1	2500	2500	3710.5(2)	17.68(5)
N1	2500	2500	1564(3)	27.3(4)
Al1	7500	2500	0	12.34(11)
O1	2500	2500	7085(2)	27.5(4)
C1	2500	2500	5909(3)	18.8(4)
O2	3493.1(9)	4623.3(8)	3710.3(11)	27.0(2)
C2	3143.5(10)	3881.0(10)	3712.3(13)	19.6(2)
O3	2500	2500	380(2)	30.1(4)
O1_1	6848.6(6)	3320.2(6)	1012.4(10)	16.46(16)
C1_1	6871.2(9)	4162.8(8)	1746.0(13)	14.95(19)
C2_1	5833.3(9)	4336.8(9)	2367.6(14)	20.1(2)
F1_1	5220.7(6)	4650.9(7)	1383.4(10)	27.54(19)
F2_1	5832.3(7)	4996.1(7)	3400.4(10)	28.16(18)
F3_1	5464.0(7)	3511.6(7)	2881.1(10)	29.9(2)
C3_1	7613.0(10)	4102.6(10)	2971.7(14)	22.4(3)
F4_1	8444.2(7)	3702.7(8)	2539.7(11)	31.6(2)
F5_1	7268.9(8)	3559.0(8)	4013.3(10)	33.7(2)
F6_1	7831.6(7)	4984.2(8)	3513.0(10)	30.7(2)
C4_1	7142.9(10)	5039.7(10)	787.7(16)	20.8(2)
F7_1	8100.9(7)	5075.6(7)	569.8(11)	29.0(2)
F8_1	6877.6(8)	5893.5(6)	1349.7(10)	30.4(2)
F9_1	6712.8(7)	4964.4(7)	-456.1(9)	30.5(2)

Table 3 Anisotropic Displacement Parameters (Å²×10³) for p4n_a. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mo1	17.86(6)	17.86(6)	17.34(9)	0	0	0
N1	23.8(6)	23.8(6)	34.2(12)	0	0	0
Al1	11.43(14)	11.43(14)	14.2(3)	0	0	0
O1	31.4(6)	31.4(6)	19.6(8)	0	0	0
C1	16.3(5)	16.3(5)	23.8(10)	0	0	0
O2	29.7(5)	22.8(5)	28.4(6)	1.3(4)	2.0(4)	-3.4(4)
C2	19.0(5)	23.6(6)	16.2(6)	0.9(4)	1.3(4)	2.4(5)
O3	36.8(6)	36.8(6)	16.5(8)	0	0	0
O1_1	15.6(4)	13.8(3)	19.9(4)	-3.3(3)	1.8(3)	1.3(3)
C1_1	14.7(4)	14.2(4)	16.0(5)	-0.9(4)	-0.2(4)	2.1(4)
C2_1	18.1(5)	20.2(5)	22.0(6)	-2.8(4)	1.7(4)	2.4(4)
F1_1	17.9(4)	32.3(5)	32.4(5)	-5.3(4)	-5.9(3)	9.1(3)
F2_1	25.8(4)	31.1(4)	27.5(4)	-12.7(4)	3.5(3)	6.1(3)
F3_1	26.5(4)	26.6(4)	36.8(5)	0.6(4)	13.5(4)	-2.3(3)
C3_1	22.0(6)	23.5(5)	21.7(6)	-3.3(4)	-5.6(5)	3.7(5)
F4_1	19.7(4)	38.4(5)	36.9(5)	-9.1(4)	-9.1(4)	11.1(3)
F5_1	41.9(6)	37.0(5)	22.2(4)	8.2(4)	-5.5(4)	5.8(4)
F6_1	28.4(4)	32.3(5)	31.3(5)	-13.3(4)	-8.2(4)	0.2(3)
C4_1	24.4(5)	15.1(5)	22.8(6)	0.1(4)	1.7(5)	-0.8(4)
F7_1	24.9(4)	24.6(4)	37.4(5)	-3.0(4)	7.9(4)	-8.0(3)
F8_1	39.5(5)	12.7(3)	39.1(6)	-2.0(3)	4.4(4)	3.3(3)
F9_1	40.6(5)	30.3(4)	20.6(4)	7.0(4)	-4.6(4)	-0.4(4)

Table 4 Bond Lengths for p4n_a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Mo1	N1	2.049(3)	C1_1	C3_1	1.5524(18)
Mo1	C1	2.098(2)	C1_1	C4_1	1.5561(18)
Mo1	C2	2.0897(14)	C2_1	F1_1	1.3316(16)
Mo1	C2[1]	2.0896(14)	C2_1	F2_1	1.3375(15)
Mo1	C2[2]	2.0896(14)	C2_1	F3_1	1.3332(16)
Mo1	C2[3]	2.0896(14)	C3_1	F4_1	1.3305(16)
N1	O3	1.129(3)	C3_1	F5_1	1.3290(17)
O1	C1	1.122(3)	C3_1	F6_1	1.3486(16)
O2	C2	1.1252(18)	C4_1	F7_1	1.3311(17)
O1_1	Al1	1.7312(9)	C4_1	F8_1	1.3383(16)
O1_1	C1_1	1.3514(14)	C4_1	F9_1	1.3293(17)
C1_1	C2_1	1.5605(17)			

[1]1/2-X,1/2-Y,+Z; [2]1/2-Y,+X,+Z; [3]+Y,1/2-X,+Z

Table 5 Bond Angles for p4n_a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N1	Mo1	C1	180.0	O1_1	C1_1	C2_1	107.86(10)
N1	Mo1	C2[1]	90.04(4)	O1_1	C1_1	C3_1	111.09(10)
N1	Mo1	C2[2]	90.04(4)	O1_1	C1_1	C4_1	111.23(10)
N1	Mo1	C2[3]	90.04(4)	C3_1	C1_1	C2_1	108.64(10)
N1	Mo1	C2	90.05(4)	C3_1	C1_1	C4_1	109.08(10)
C2[3]	Mo1	C1	89.96(4)	C4_1	C1_1	C2_1	108.88(10)
C2	Mo1	C1	89.95(4)	F1_1	C2_1	C1_1	110.91(11)
C2[1]	Mo1	C1	89.96(4)	F1_1	C2_1	F2_1	107.48(10)
C2[2]	Mo1	C1	89.96(4)	F1_1	C2_1	F3_1	107.10(11)
C2[2]	Mo1	C2[3]	90.0	F2_1	C2_1	C1_1	112.61(11)
C2[1]	Mo1	C2	90.0	F3_1	C2_1	C1_1	110.87(10)
C2[3]	Mo1	C2	90.0	F3_1	C2_1	F2_1	107.63(11)
C2[2]	Mo1	C2[1]	90.0	F4_1	C3_1	C1_1	110.49(11)
C2[3]	Mo1	C2[1]	179.91(7)	F4_1	C3_1	F6_1	107.32(12)
C2[2]	Mo1	C2	179.91(7)	F5_1	C3_1	C1_1	111.13(11)
O3	N1	Mo1	180.0	F5_1	C3_1	F4_1	107.75(11)
O1_1[4]	Al1	O1_1[5]	112.16(6)	F5_1	C3_1	F6_1	107.19(11)
O1_1[5]	Al1	O1_1	108.14(3)	F6_1	C3_1	C1_1	112.74(10)
O1_1[4]	Al1	O1_1	108.15(3)	F7_1	C4_1	C1_1	110.90(11)
O1_1[4]	Al1	O1_1[6]	108.14(3)	F7_1	C4_1	F8_1	107.37(12)
O1_1[5]	Al1	O1_1[6]	108.14(3)	F8_1	C4_1	C1_1	112.07(12)
O1_1[6]	Al1	O1_1	112.16(6)	F9_1	C4_1	C1_1	111.00(11)
O1	C1	Mo1	180.0	F9_1	C4_1	F7_1	107.55(13)
O2	C2	Mo1	179.73(14)	F9_1	C4_1	F8_1	107.76(11)
C1_1	O1_1	Al1	146.39(8)				

[1]1/2-Y,+X,+Z; [2]1/2-X,1/2-Y,+Z; [3]+Y,1/2-X,+Z; [4]1-Y,-1/2+X,-Z; [5]1/2+Y,1-X,-Z; [6]3/2-X,1/2-Y,+Z

$[W(CO)_5(NO)][Al(OR^F)_4]$ (2)

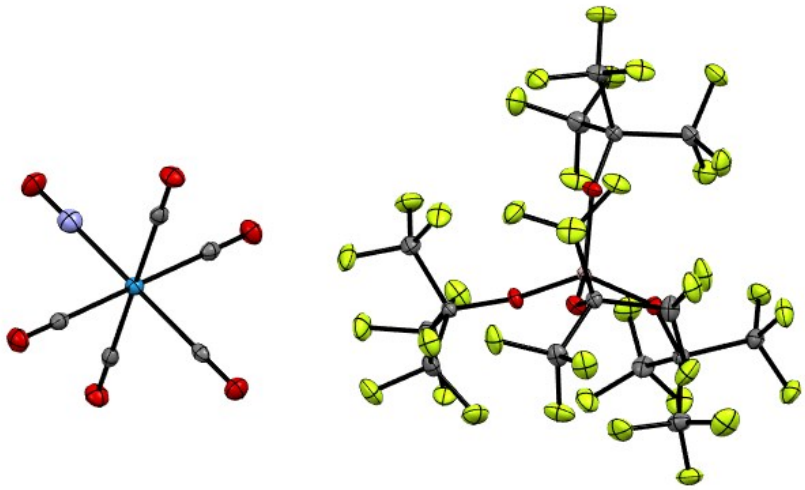


Table 1Crystal data and structure refinement for p4n_a.

CCDC Deposition Number	1952378
Identification code	p4n_a
Empirical formula	$C_{21}NO_{10}F_{36}AlW$
Formula weight	1321.00
Temperature/K	99.99
Crystal system	tetragonal
Space group	P4/n
a/Å	13.6990(7)
b/Å	13.6990(7)
c/Å	9.5293(5)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1788.29(16)
Z	2
ρ_{calc}g/cm^3	2.4531
μ/mm^{-1}	3.497
F(000)	1248.3
Crystal size/mm^3	0.2 × 0.2 × 0.15
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.2 to 54.16
Index ranges	$-13 \le h \le 17$, $-17 \le k \le 16$, $-9 \le l \le 11$
Reflections collected	12595
Independent reflections	1924 [R_{int} = 0.0462, R_{sigma} = 0.0297]
Data/restraints/parameters	1924/0/163
Goodness-of-fit on F^2	1.129
Final R indexes [I>=2σ (I)]	R_1 = 0.0236, wR_2 = 0.0736
Final R indexes [all data]	R_1 = 0.0236, wR_2 = 0.0737
Largest diff. peak/hole / e Å^{-3}	1.25/-0.64

Table 2 Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for p4n_a. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
W1	2500	2500	3707.0(2)	14.39(11)
N1	2500	2500	1574(7)	25.2(14)
Al1	7500	2500	10000	9.3(3)
O1	1511(3)	380(3)	3707(3)	23.0(7)
C1	1859(3)	1127(4)	3712(3)	16.1(9)
O2	2500	2500	7076(5)	23.3(11)
C2	2500	2500	5897(8)	14.0(12)
O3	2500	2500	377(5)	27.4(12)
O1_1	6680(2)	1847(2)	8987(3)	13.9(5)
C1_1	5837(2)	1869(3)	8246(4)	11.7(6)
C2_1	4961(3)	2141(3)	9213(5)	18.4(8)
F1_1	5032.4(18)	1712.7(19)	10455(2)	26.3(5)
F2_1	4104(2)	1878(2)	8647(3)	27.5(7)
F3_1	4921.6(19)	3100.1(19)	9430(3)	25.2(6)
C3_1	5897(3)	2613(3)	7022(4)	20.0(8)
F4_1	6440(2)	2268(2)	5978(3)	29.8(6)
F5_1	6297(2)	3443.0(18)	7456(3)	28.2(6)
F6_1	5015(2)	2832(2)	6481(3)	26.4(6)
C4_1	5659(3)	826(3)	7632(4)	17.4(7)
F7_1	6484.1(18)	462.1(17)	7115(3)	25.8(5)
F8_1	4997(2)	828.8(19)	6596(3)	25.2(5)
F9_1	5345(2)	217(2)	8611(2)	24.5(6)

Table 3 Anisotropic Displacement Parameters (Å²×10³) for p4n_a. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
W1	13.74(12)	13.74(12)	15.67(16)	-0	-0	0
N1	24(2)	24(2)	28(3)	-0	-0	0
Al1	7.7(5)	7.7(5)	12.3(8)	-0	-0	0
O1	22.8(17)	17.1(17)	29.1(18)	-4.1(14)	-1.7(11)	-0.7(10)
C1	15.5(19)	20(2)	12(2)	3.1(18)	-1.1(12)	-0.0(12)
O2	25.5(16)	25.5(16)	19(3)	-0	-0	0
C2	10.7(17)	10.7(17)	21(3)	-0	-0	0
O3	33.0(18)	33.0(18)	16(3)	-0	-0	0
O1_1	11.4(12)	12.2(12)	18.2(11)	-1.2(10)	-3.5(10)	-1.9(10)
C1_1	10.2(15)	11.7(15)	13.2(16)	-0.6(13)	-0.2(14)	0.4(14)
C2_1	11.0(17)	22.6(18)	22(2)	0.3(14)	-0.2(16)	-1.3(16)
F1_1	25.8(12)	33.4(14)	19.7(12)	0.2(11)	7.4(10)	3.8(10)
F2_1	13.3(13)	33.8(17)	35.5(17)	-4.1(11)	-1.5(9)	-4.3(10)
F3_1	20.8(12)	21.8(12)	33.1(15)	7.2(10)	-2.1(11)	-5.7(10)
C3_1	19.5(16)	20(2)	19.9(16)	-3.5(16)	-3.3(13)	5.9(16)
F4_1	31.1(14)	38.4(18)	20.0(10)	-5.8(11)	8.2(10)	4.5(11)
F5_1	34.6(14)	15.8(11)	34.2(13)	-9.6(10)	-9.1(11)	7.9(10)
F6_1	29.0(15)	23.0(13)	27.3(12)	0.8(11)	-12.8(10)	8.2(9)
C4_1	17.3(17)	16.0(17)	18.7(17)	-3.1(14)	-4.2(14)	-0.6(14)
F7_1	21.4(12)	21.7(12)	34.3(14)	1.0(9)	0.1(10)	-13.3(10)
F8_1	27.7(14)	24.5(13)	23.4(10)	-6.8(11)	-11.9(11)	-2.7(11)
F9_1	29.5(15)	15.0(13)	28.9(14)	-8.4(11)	-5.9(9)	6.0(9)

Table 4 Bond Lengths for p4n_a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
W1	N1	2.033(7)	O1_1	C1_1	1.354(4)
W1	C1[1]	2.075(5)	C1_1	C2_1	1.557(5)
W1	C1	2.075(5)	C1_1	C3_1	1.551(5)
W1	C1[2]	2.075(5)	C1_1	C4_1	1.562(5)
W1	C1[3]	2.075(5)	C2_1	F1_1	1.325(5)
W1	C2	2.087(7)	C2_1	F2_1	1.342(5)
N1	O3	1.140(8)	C2_1	F3_1	1.332(5)
Al1	O1_1[4]	1.731(3)	C3_1	F4_1	1.330(5)
Al1	O1_1	1.731(3)	C3_1	F5_1	1.328(5)
Al1	O1_1[5]	1.731(3)	C3_1	F6_1	1.347(5)
Al1	O1_1[6]	1.731(3)	C4_1	F7_1	1.330(5)
O1	C1	1.129(6)	C4_1	F8_1	1.340(4)
O2	C2	1.124(9)	C4_1	F9_1	1.324(5)

[1]1/2-Y,+X,+Z; [2]1/2-X,1/2-Y,+Z; [3]+Y,1/2-X,+Z; [4]1-Y,-1/2+X,2-Z; [5]3/2-X,1/2-Y,+Z; [6]1/2+Y,1-X,2-Z

Table 5 Bond Angles for p4n_a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	W1	N1	90.14(9)	C2_1	C1_1	O1_1	110.7(3)
C1[1]	W1	N1	90.14(9)	C3_1	C1_1	O1_1	111.1(3)
C1[2]	W1	N1	90.14(9)	C3_1	C1_1	C2_1	109.2(3)
C1[3]	W1	N1	90.14(9)	C4_1	C1_1	O1_1	108.0(3)
C1[3]	W1	C1[1]	90.0	C4_1	C1_1	C2_1	108.7(3)
C1[2]	W1	C1[1]	179.73(18)	C4_1	C1_1	C3_1	109.1(3)
C1[3]	W1	C1	179.73(18)	F1_1	C2_1	C1_1	111.5(3)
C1[3]	W1	C1[2]	90.0	F2_1	C2_1	C1_1	111.9(3)
C1[2]	W1	C1	90.0	F2_1	C2_1	F1_1	107.7(3)
C1[1]	W1	C1	90.0	F3_1	C2_1	C1_1	111.1(3)
C2	W1	N1	180.0	F3_1	C2_1	F1_1	107.5(4)
C2	W1	C1[1]	89.86(9)	F3_1	C2_1	F2_1	107.0(4)
C2	W1	C1	89.86(9)	F4_1	C3_1	C1_1	111.1(3)
C2	W1	C1[3]	89.86(9)	F5_1	C3_1	C1_1	110.5(3)
C2	W1	C1[2]	89.86(9)	F5_1	C3_1	F4_1	107.8(3)
O3	N1	W1	180.0	F6_1	C3_1	C1_1	112.7(3)
O1_1[4]	Al1	O1_1[5]	108.14(9)	F6_1	C3_1	F4_1	107.1(3)
O1_1	Al1	O1_1[5]	108.14(9)	F6_1	C3_1	F5_1	107.4(3)
O1_1[6]	Al1	O1_1	108.14(9)	F7_1	C4_1	C1_1	110.5(3)
O1_1[6]	Al1	O1_1[5]	112.16(19)	F8_1	C4_1	C1_1	112.3(3)
O1_1[4]	Al1	O1_1	112.16(19)	F8_1	C4_1	F7_1	107.7(3)
O1_1[6]	Al1	O1_1[4]	108.14(9)	F9_1	C4_1	C1_1	111.2(3)
O1	C1	W1	179.6(3)	F9_1	C4_1	F7_1	107.5(3)
O2	C2	W1	180.0	F9_1	C4_1	F8_1	107.5(3)
C1_1	O1_1	Al1[6]	146.5(3)				

[1]1/2-Y,+X,+Z; [2]+Y,1/2-X,+Z; [3]1/2-X,1/2-Y,+Z; [4]3/2-X,1/2-Y,+Z; [5]1-Y,-1/2+X,2-Z; [6]1/2+Y,1-X,2-Z

$[Mo(CO)_6[F\text{-}\{Al(OR^F)_3\}_2]$ (3)

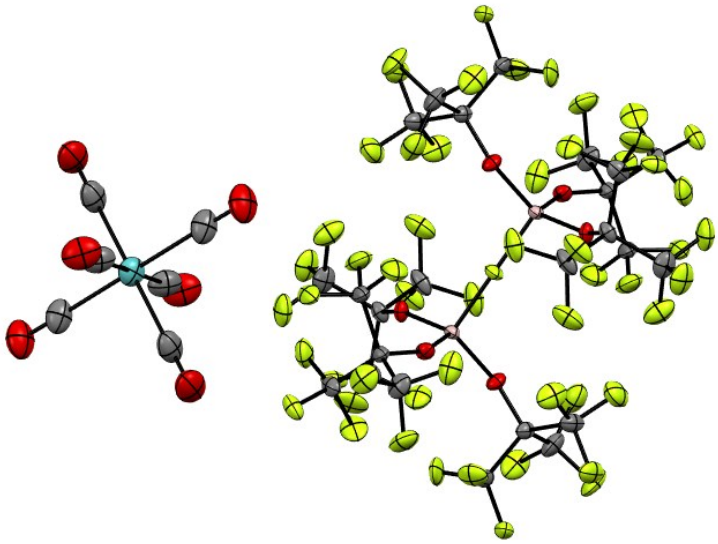


Table 1 Crystal data and structure refinement for pa-3_a.

CCDC Deposition Number	1952385
Identification code	pa-3_a
Empirical formula	$C_{30}O_{12}F_{55}Al_2Mo$
Formula weight	1747.20
Temperature/K	99.99
Crystal system	cubic
Space group	Pa-3
a/Å	17.285(3)
b/Å	17.285(3)
c/Å	17.285(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	5164(2)
Z	4
ρ_{calc}g/cm^3	2.247
μ/mm^{-1}	0.544
F(000)	3356.0
Crystal size/mm^3	0.15 × 0.1 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.082 to 50.154
Index ranges	$-20 \le h \le 20$, $-20 \le k \le 20$, $-20 \le l \le 20$
Reflections collected	35822
Independent reflections	1541 [R_{int} = 0.0829, R_{sigma} = 0.0244]
Data/restraints/parameters	1541/1135/279
Goodness-of-fit on F^2	1.191
Final R indexes [I>=2σ (I)]	R_1 = 0.0537, wR_2 = 0.1469
Final R indexes [all data]	R_1 = 0.0671, wR_2 = 0.1549
Largest diff. peak/hole / e Å^{-3}	0.81/-0.86

Table 2 Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for pa-3_a. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Mo1	5000	5000	5000	40.3(4)
F1	5000	0	5000	20.0(13)
Al1	5587.6(7)	587.6(7)	4412.4(7)	14.4(5)
O1	4138(3)	3430(3)	5524(3)	63.6(14)
C1	4438(4)	3978(4)	5351(4)	48.9(15)
O1_2	5871(13)	1340(15)	4981(15)	19(4)
C1_2	6440(7)	1701(7)	5391(7)	20(2)
C2_2	6108(6)	2471(5)	5693(5)	31(2)
F1_2	6056(6)	2998(4)	5132(5)	41(2)
F2_2	6534(8)	2772(6)	6256(7)	41(3)
F3_2	5390(8)	2362(15)	5960(15)	44(4)
C3_2	6688(5)	1193(6)	6085(5)	29(2)
F4_2	6774(15)	458(8)	5865(15)	42(5)
F5_2	6184(9)	1204(8)	6661(8)	45(3)
F6_2	7369(5)	1416(8)	6369(7)	39(3)
C4_2	7144(5)	1863(5)	4865(5)	25(2)
F7_2	7561(4)	1222(5)	4769(5)	38.8(19)
F8_2	7623(11)	2406(13)	5112(17)	29(3)
F9_2	6875(16)	2061(15)	4167(7)	43(5)
O1_1	5900(12)	1272(14)	5036(14)	25(4)
C1_1	6500(7)	1624(6)	5402(6)	21(2)
C2_1	7130(5)	1020(5)	5622(5)	25.9(19)
F1_1	6799(13)	368(7)	5864(13)	40(4)
F2_1	7606(5)	1263(7)	6175(6)	37(2)
F3_1	7570(4)	841(4)	5015(4)	33.1(16)
C3_1	6876(5)	2255(5)	4889(5)	29(2)
F4_1	6413(4)	2881(4)	4853(5)	38.2(18)
F5_1	6995(13)	2013(12)	4174(7)	38(3)
F6_1	7543(10)	2468(12)	5203(16)	42(5)
C4_1	6190(5)	1999(5)	6153(5)	30(2)
F7_1	5526(7)	2370(12)	6017(13)	41(3)
F8_1	6683(7)	2520(6)	6437(6)	45(3)
F9_1	6058(8)	1471(7)	6690(7)	42(3)

Table 3 Anisotropic Displacement Parameters (Å²×10³) for pa-3_a. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mo1	40.3(4)	40.3(4)	40.3(4)	-10.0(3)	-10.0(3)	-10.0(3)
F1	20.0(13)	20.0(13)	20.0(13)	4.8(13)	4.8(13)	-4.8(13)
Al1	14.4(5)	14.4(5)	14.4(5)	2.1(5)	2.1(5)	-2.1(5)
O1	53(3)	46(3)	92(4)	-2(3)	-14(3)	-15(2)
C1	39(3)	42(3)	66(4)	-10(3)	-15(3)	-3(3)
O1_2	23(7)	13(5)	23(6)	-2(4)	-5(5)	-1(5)
C1_2	20(5)	20(5)	21(5)	6(4)	-6(4)	-3(4)
C2_2	35(5)	30(5)	29(5)	-8(3)	-13(4)	0(4)
F1_2	55(6)	23(4)	47(5)	5(3)	-15(4)	9(4)
F2_2	52(6)	32(5)	39(6)	-17(4)	-17(4)	-3(4)
F3_2	34(5)	58(8)	39(7)	-17(5)	-5(5)	8(5)
C3_2	24(5)	29(4)	33(5)	15(4)	-11(3)	-6(4)
F4_2	47(10)	27(5)	51(10)	13(5)	-20(7)	2(5)
F5_2	45(6)	57(8)	34(5)	18(5)	1(4)	-10(6)

F6_2	34(5)	50(7)	32(6)	20(4)	-18(4)	-13(5)
C4_2	25(5)	29(5)	20(5)	2(4)	-7(3)	-9(3)
F7_2	19(3)	43(4)	55(5)	-4(4)	7(3)	1(3)
F8_2	25(5)	39(6)	22(5)	-5(4)	4(4)	-14(4)
F9_2	47(11)	69(10)	12(5)	8(5)	-5(4)	-8(6)
O1_1	16(6)	24(7)	36(8)	-10(6)	-5(5)	-2(5)
C1_1	21(5)	18(5)	25(5)	-4(4)	-1(4)	-5(3)
C2_1	22(4)	26(4)	29(4)	5(3)	-5(3)	-8(3)
F1_1	43(9)	24(5)	54(9)	10(5)	-2(7)	-12(5)
F2_1	42(5)	36(5)	34(5)	7(3)	-14(4)	-6(4)
F3_1	23(3)	39(4)	38(3)	-4(3)	-3(2)	11(3)
C3_1	22(4)	28(5)	36(5)	7(4)	-4(4)	-4(3)
F4_1	38(4)	17(3)	60(5)	8(3)	-14(3)	-8(3)
F5_1	28(6)	54(8)	31(6)	7(5)	3(4)	-18(5)
F6_1	33(6)	45(7)	48(11)	11(6)	-6(6)	-24(5)
C4_1	28(4)	27(4)	36(4)	-7(3)	0(4)	-5(3)
F7_1	34(5)	42(6)	46(7)	-21(5)	4(5)	7(4)
F8_1	48(5)	50(6)	36(5)	-20(4)	-5(4)	-15(5)
F9_1	43(6)	57(7)	26(4)	2(4)	14(4)	-12(5)

Table 4 Bond Lengths for pa-3_a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Mo1	C1[1]	2.105(7)	C3_2	F6_2	1.333(11)
Mo1	C1[2]	2.105(7)	C4_2	F7_2	1.333(11)
Mo1	C1[3]	2.105(7)	C4_2	F8_2	1.323(12)
Mo1	C1	2.105(7)	C4_2	F9_2	1.338(13)
Mo1	C1[4]	2.105(7)	O1_1	Al1	1.689(17)
Mo1	C1[5]	2.105(7)	O1_1	C1_1	1.358(11)
F1	Al1	1.759(2)	C1_1	C2_1	1.555(11)
F1	Al1[6]	1.759(2)	C1_1	C3_1	1.549(11)
O1	C1	1.120(8)	C1_1	C4_1	1.548(11)
O1_2	Al1	1.702(19)	C2_1	F1_1	1.333(12)
O1_2	C1_2	1.364(12)	C2_1	F2_1	1.329(10)
C1_2	C2_2	1.542(12)	C2_1	F3_1	1.332(9)
C1_2	C3_2	1.546(11)	C3_1	F4_1	1.346(10)
C1_2	C4_2	1.543(12)	C3_1	F5_1	1.322(13)
C2_2	F1_2	1.333(10)	C3_1	F6_1	1.327(12)
C2_2	F2_2	1.327(11)	C4_1	F7_1	1.335(12)
C2_2	F3_2	1.336(13)	C4_1	F8_1	1.334(10)
C3_2	F4_2	1.335(13)	C4_1	F9_1	1.321(11)
C3_2	F5_2	1.324(12)			

[1]+Y,+Z,+X; [2]+Z,+X,+Y; [3]1-X,1-Y,1-Z; [4]1-Z,1-X,1-Y; [5]1-Y,1-Z,1-X; [6]1-X,-Y,1-Z

Table 5 Bond Angles for pa-3_a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	Mo1	C1[1]	90.7(3)	F1_2	C2_2	F3_2	106.6(12)
C1[2]	Mo1	C1[3]	89.3(3)	F2_2	C2_2	C1_2	112.3(9)
C1[2]	Mo1	C1[4]	90.7(3)	F2_2	C2_2	F1_2	107.6(9)
C1	Mo1	C1[2]	180.0	F2_2	C2_2	F3_2	108.5(14)
C1	Mo1	C1[4]	89.3(3)	F3_2	C2_2	C1_2	109.9(14)
C1[1]	Mo1	C1[2]	89.3(3)	F4_2	C3_2	C1_2	110.5(13)
C1[1]	Mo1	C1[3]	89.3(3)	F5_2	C3_2	C1_2	113.2(9)

C1	Mo1	C1[5]	89.3(3)	F5_2	C3_2	F4_2	107.4(13)
C1[5]	Mo1	C1[3]	180.00(19)	F5_2	C3_2	F6_2	107.5(11)
C1[1]	Mo1	C1[5]	90.7(3)	F6_2	C3_2	C1_2	111.5(9)
C1[1]	Mo1	C1[4]	180.0	F6_2	C3_2	F4_2	106.3(13)
C1[2]	Mo1	C1[5]	90.7(3)	F7_2	C4_2	C1_2	110.4(8)
C1[3]	Mo1	C1[4]	90.7(3)	F7_2	C4_2	F9_2	106.7(12)
C1	Mo1	C1[3]	90.7(3)	F8_2	C4_2	C1_2	115.6(14)
C1[5]	Mo1	C1[4]	89.3(3)	F8_2	C4_2	F7_2	107.0(13)
Al1[6]	F1	Al1	180.0	F8_2	C4_2	F9_2	109.0(15)
O1_2[7]	Al1	F1	105.9(10)	F9_2	C4_2	C1_2	107.8(13)
O1_2	Al1	F1	105.9(10)	C1_1	O1_1	Al1	148.7(19)
O1_2[8]	Al1	F1	105.9(10)	O1_1	C1_1	C2_1	110.4(13)
O1_2	Al1	O1_2[7]	112.8(8)	O1_1	C1_1	C3_1	111.7(13)
O1_2[7]	Al1	O1_2[8]	112.8(8)	O1_1	C1_1	C4_1	108.2(13)
O1_2	Al1	O1_2[8]	112.8(8)	C3_1	C1_1	C2_1	108.6(8)
O1_1[7]	Al1	F1	102.7(9)	C4_1	C1_1	C2_1	108.6(8)
O1_1	Al1	F1	102.7(9)	C4_1	C1_1	C3_1	109.2(8)
O1_1[8]	Al1	F1	102.7(9)	F1_1	C2_1	C1_1	110.1(12)
O1_1	Al1	O1_2[7]	118.1(15)	F2_1	C2_1	C1_1	113.5(8)
O1_1[7]	Al1	O1_2[7]	5.4(18)	F2_1	C2_1	F1_1	107.8(12)
O1_1	Al1	O1_2[8]	110.1(15)	F2_1	C2_1	F3_1	106.7(7)
O1_1[8]	Al1	O1_2[7]	110.1(15)	F3_1	C2_1	C1_1	111.2(7)
O1_1[8]	Al1	O1_2[8]	5.4(18)	F3_1	C2_1	F1_1	107.2(10)
O1_1[7]	Al1	O1_2[8]	118.1(15)	F4_1	C3_1	C1_1	110.1(8)
O1_1[7]	Al1	O1_1[8]	115.3(6)	F5_1	C3_1	C1_1	112.1(12)
O1_1	Al1	O1_1[8]	115.3(6)	F5_1	C3_1	F4_1	107.7(11)
O1_1	Al1	O1_1[7]	115.3(6)	F5_1	C3_1	F6_1	109.5(14)
O1	C1	Mo1	178.7(6)	F6_1	C3_1	C1_1	109.0(13)
C1_2	O1_2	Al1	149(2)	F6_1	C3_1	F4_1	108.2(12)
O1_2	C1_2	C2_2	107.6(14)	F7_1	C4_1	C1_1	110.6(12)
O1_2	C1_2	C3_2	110.1(14)	F8_1	C4_1	C1_1	111.7(9)
O1_2	C1_2	C4_2	110.2(14)	F8_1	C4_1	F7_1	106.9(11)
C2_2	C1_2	C3_2	109.3(9)	F9_1	C4_1	C1_1	111.1(8)
C2_2	C1_2	C4_2	109.6(9)	F9_1	C4_1	F7_1	107.9(11)
C4_2	C1_2	C3_2	110.0(8)	F9_1	C4_1	F8_1	108.6(10)
F1_2	C2_2	C1_2	111.7(8)				

[1]1-Y,1-Z,1-X; [2]1-X,1-Y,1-Z; [3]1-Z,1-X,1-Y; [4]+Y,+Z,+X; [5]+Z,+X,+Y; [6]1-X,-Y,1-Z; [7]1-Z,-1/2+X,1/2-Y; [8]1/2+Y,1/2-Z,1-X

$[W(CO)_6[F\text{-}\{Al(OR^F)_3\}_2]$ (4)

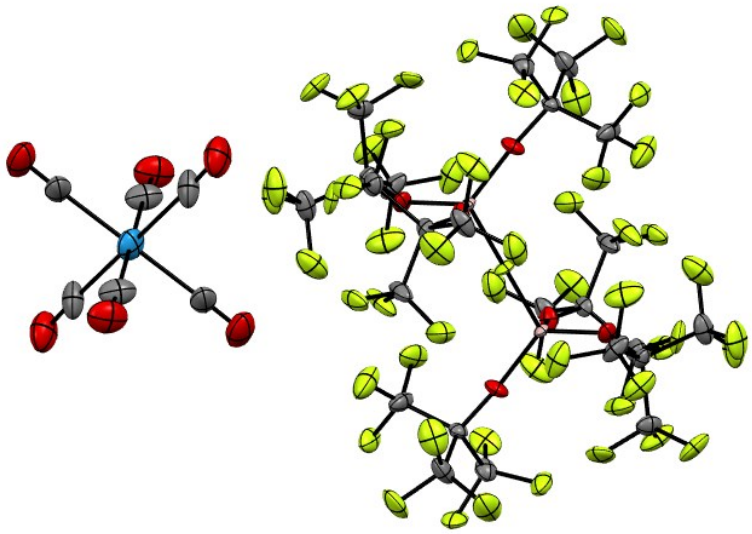


Table 1 Crystal data and structure refinement for pa-3_a.

CCDC Deposition Number	1952383
Identification code	pa-3_a
Empirical formula	$C_{30}O_{12}F_{55}Al_2W$
Formula weight	1835.11
Temperature/K	99.99
Crystal system	cubic
Space group	Pa-3
a/Å	17.3168(3)
b/Å	17.3168(3)
c/Å	17.3168(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	5192.8(3)
Z	4
ρ_{calc}g/cm^3	2.347
μ/mm^{-1}	2.513
F(000)	3484.0
Crystal size/mm^3	0.1 × 0.1 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.074 to 56.328
Index ranges	-23 ≤ h ≤ 23, -23 ≤ k ≤ 23, -23 ≤ l ≤ 23
Reflections collected	184672
Independent reflections	2130 [R_{int} = 0.0659, R_{sigma} = 0.0109]
Data/restraints/parameters	2130/1136/267
Goodness-of-fit on F^2	1.375
Final R indexes [I>=2σ (I)]	R_1 = 0.0762, wR_2 = 0.1448
Final R indexes [all data]	R_1 = 0.0822, wR_2 = 0.1474
Largest diff. peak/hole / e Å^{-3}	1.25/-1.20

Table 2 Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for pa-3_a. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
W1	5000	5000	5000	46.4(3)
O1	5864(4)	6546(4)	4450(5)	64(2)
C1	5574(5)	6018(5)	4665(6)	48(2)
F1	5000	10000	5000	21.8(17)
Al1	4412.1(9)	9412.1(9)	5587.9(9)	11.8(5)
O1_2	4136(13)	8661(13)	5017(16)	22.6(15)
C1_2	3575(8)	8303(7)	4607(7)	18.6(12)
C2_2	3902(8)	7526(7)	4306(7)	33(3)
F1_2	4614(9)	7637(16)	4033(16)	50(5)
F2_2	3473(10)	7221(8)	3747(9)	48(4)
F3_2	3951(8)	7004(6)	4867(7)	50(3)
C3_2	2861(7)	8130(7)	5117(7)	28(3)
F4_2	2440(5)	8771(7)	5221(7)	38(3)
F5_2	3051(19)	7872(15)	5814(9)	42(5)
F6_2	2397(14)	7613(15)	4778(18)	41(6)
C4_2	3324(7)	8805(7)	3914(8)	32(3)
F7_2	3227(16)	9541(9)	4126(16)	45(5)
F8_2	2649(7)	8572(10)	3623(9)	39(4)
F9_2	3829(11)	8793(11)	3341(11)	53(5)
O1_1	4088(10)	8718(10)	4970(12)	22.6(15)
C1_1	3487(6)	8379(6)	4598(6)	18.6(12)
C2_1	3117(6)	7754(6)	5123(6)	26(2)
F1_1	3574(5)	7127(4)	5163(6)	37(2)
F2_1	2423(10)	7537(12)	4886(13)	29(3)
F3_1	3046(16)	8045(12)	5834(7)	36(3)
C3_1	2867(5)	8985(5)	4374(5)	22(2)
F4_1	3200(13)	9634(7)	4132(12)	39(4)
F5_1	2421(4)	9166(5)	4976(5)	33.4(18)
F6_1	2396(6)	8739(7)	3816(6)	36(3)
C4_1	3813(6)	8000(6)	3858(6)	29(2)
F7_1	3946(9)	8522(7)	3319(7)	42(3)
F8_1	3317(7)	7480(7)	3571(7)	44(3)
F9_1	4473(7)	7630(10)	4002(11)	42(3)

Table 3 Anisotropic Displacement Parameters (Å²×10³) for pa-3_a. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
W1	46.4(3)	46.4(3)	46.4(3)	-11.9(2)	-11.9(2)	-11.9(2)
O1	49(4)	47(4)	97(6)	-7(4)	-13(4)	-14(3)
C1	25(4)	39(4)	79(6)	-10(4)	-1(4)	-3(3)
F1	21.8(17)	21.8(17)	21.8(17)	8.1(18)	8.1(18)	-8.1(18)
Al1	11.8(5)	11.8(5)	11.8(5)	2.7(6)	2.7(6)	-2.7(6)
O1_2	16(3)	21(3)	31(3)	-7(3)	-5(2)	-4(2)
C1_2	16(3)	17(3)	23(3)	0(2)	-4(2)	-5(2)
C2_2	36(6)	28(5)	35(6)	-11(4)	-17(5)	7(5)
F1_2	39(6)	61(12)	50(11)	-11(8)	-4(6)	20(6)
F2_2	65(9)	36(8)	43(7)	-21(6)	-23(6)	0(7)
F3_2	69(9)	26(5)	53(7)	0(5)	-23(6)	12(6)
C3_2	19(5)	37(6)	27(6)	-2(5)	-3(4)	-5(4)
F4_2	11(4)	50(6)	53(7)	-9(5)	7(4)	0(4)
F5_2	42(9)	57(13)	28(6)	17(6)	-5(6)	-25(8)

F6_2	37(8)	42(8)	43(13)	14(8)	-8(7)	-27(7)
C4_2	26(6)	30(5)	40(6)	20(5)	-12(4)	-8(5)
F7_2	48(12)	28(6)	59(12)	18(6)	-29(8)	-2(6)
F8_2	33(6)	49(9)	36(8)	18(6)	-20(5)	-14(6)
F9_2	44(7)	75(12)	41(7)	28(8)	0(5)	-6(8)
O1_1	16(3)	21(3)	31(3)	-7(3)	-5(2)	-4(2)
C1_1	16(3)	17(3)	23(3)	0(2)	-4(2)	-5(2)
C2_1	29(5)	29(5)	22(5)	8(4)	-7(4)	-7(4)
F1_1	40(5)	16(3)	55(6)	9(3)	-11(4)	-10(3)
F2_1	34(5)	37(6)	14(4)	14(4)	-10(4)	-17(4)
F3_1	52(8)	39(7)	18(4)	4(4)	3(4)	-21(6)
C3_1	18(4)	22(5)	28(5)	6(4)	-2(3)	-6(3)
F4_1	47(9)	20(4)	52(9)	12(5)	-2(7)	-13(5)
F5_1	20(4)	43(5)	38(4)	0(4)	2(3)	9(3)
F6_1	42(6)	35(5)	32(5)	7(4)	-19(4)	-5(5)
C4_1	28(5)	28(5)	32(5)	-9(4)	4(4)	-8(4)
F7_1	45(7)	58(7)	24(4)	1(4)	12(4)	-18(5)
F8_1	48(6)	49(7)	37(6)	-21(5)	1(4)	-22(5)
F9_1	38(5)	44(7)	45(7)	-31(5)	5(5)	9(5)

Table 4 Bond Lengths for pa-3_a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
W1	C1[1]	2.105(9)	C3_2	F6_2	1.338(13)
W1	C1[2]	2.105(9)	C4_2	F7_2	1.336(13)
W1	C1[3]	2.105(9)	C4_2	F8_2	1.336(12)
W1	C1	2.105(9)	C4_2	F9_2	1.324(13)
W1	C1[4]	2.105(9)	O1_1	Al1	1.705(9)
W1	C1[5]	2.105(9)	O1_1	C1_1	1.357(11)
O1	C1	1.108(11)	C1_1	C2_1	1.552(11)
F1	Al1[6]	1.763(3)	C1_1	C3_1	1.550(11)
F1	Al1	1.763(3)	C1_1	C4_1	1.546(11)
O1_2	Al1	1.703(12)	C2_1	F1_1	1.345(10)
O1_2	C1_2	1.353(12)	C2_1	F2_1	1.325(12)
C1_2	C2_2	1.550(13)	C2_1	F3_1	1.337(12)
C1_2	C3_2	1.548(12)	C3_1	F4_1	1.330(12)
C1_2	C4_2	1.545(12)	C3_1	F5_1	1.335(10)
C2_2	F1_2	1.333(13)	C3_1	F6_1	1.335(10)
C2_2	F2_2	1.329(12)	C4_1	F7_1	1.320(11)
C2_2	F3_2	1.329(12)	C4_1	F8_1	1.339(10)
C3_2	F4_2	1.339(12)	C4_1	F9_1	1.333(12)
C3_2	F5_2	1.329(13)			

[1]+Y,+Z,+X; [2]+Z,+X,+Y; [3]1-X,1-Y,1-Z; [4]1-Z,1-X,1-Y; [5]1-Y,1-Z,1-X; [6]1-X,2-Y,1-Z

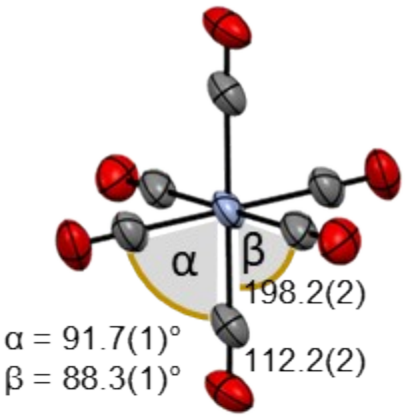
Table 5 Bond Angles for pa-3_a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	W1	C1[1]	92.0(4)	F2_2	C2_2	F1_2	108.4(15)
C1[2]	W1	C1[3]	88.0(4)	F3_2	C2_2	C1_2	111.5(11)
C1[4]	W1	C1[5]	88.0(4)	F3_2	C2_2	F1_2	107.3(14)
C1	W1	C1[2]	180.0	F3_2	C2_2	F2_2	107.3(12)
C1[1]	W1	C1[5]	180.0	F4_2	C3_2	C1_2	110.6(10)
C1[1]	W1	C1[2]	88.0(4)	F5_2	C3_2	C1_2	112.6(16)
C1[1]	W1	C1[3]	88.0(4)	F5_2	C3_2	F4_2	107.0(14)

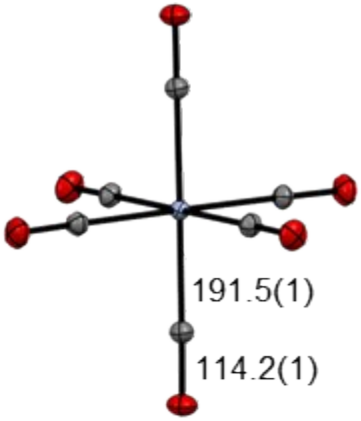
C1	W1	C1[4]	88.0(4)	F5_2	C3_2	F6_2	108.7(16)
C1[4]	W1	C1[3]	180.0(3)	F6_2	C3_2	C1_2	111.0(15)
C1[1]	W1	C1[4]	92.0(4)	F6_2	C3_2	F4_2	106.7(15)
C1[2]	W1	C1[5]	92.0(4)	F7_2	C4_2	C1_2	111.0(15)
C1[2]	W1	C1[4]	92.0(4)	F8_2	C4_2	C1_2	111.7(11)
C1[3]	W1	C1[5]	92.0(4)	F8_2	C4_2	F7_2	106.4(14)
C1	W1	C1[3]	92.0(4)	F9_2	C4_2	C1_2	112.8(12)
C1	W1	C1[5]	88.0(4)	F9_2	C4_2	F7_2	107.7(15)
O1	C1	W1	176.3(9)	F9_2	C4_2	F8_2	106.9(14)
Al1[6]	F1	Al1	180.00(8)	C1_1	O1_1	Al1	148.8(15)
O1_2[7]	Al1	F1	105.6(11)	O1_1	C1_1	C2_1	109.9(12)
O1_2	Al1	F1	105.6(11)	O1_1	C1_1	C3_1	110.9(11)
O1_2[8]	Al1	F1	105.6(11)	O1_1	C1_1	C4_1	107.3(10)
O1_2[7]	Al1	O1_2[8]	113.1(9)	C3_1	C1_1	C2_1	109.4(8)
O1_2[7]	Al1	O1_2	113.1(9)	C4_1	C1_1	C2_1	109.8(8)
O1_2[8]	Al1	O1_2	113.1(9)	C4_1	C1_1	C3_1	109.5(8)
O1_2	Al1	O1_1[7]	109.5(14)	F1_1	C2_1	C1_1	110.5(8)
O1_2[8]	Al1	O1_1[7]	118.2(13)	F2_1	C2_1	C1_1	113.0(12)
O1_2[7]	Al1	O1_1[7]	5.2(16)	F2_1	C2_1	F1_1	108.7(12)
O1_1	Al1	F1	103.6(9)	F2_1	C2_1	F3_1	108.0(14)
O1_1[8]	Al1	F1	103.6(9)	F3_1	C2_1	C1_1	108.4(12)
O1_1[7]	Al1	F1	103.6(9)	F3_1	C2_1	F1_1	108.1(11)
O1_1[8]	Al1	O1_1	114.7(6)	F4_1	C3_1	C1_1	110.5(11)
O1_1[7]	Al1	O1_1	114.7(6)	F4_1	C3_1	F5_1	107.3(11)
O1_1[7]	Al1	O1_1[8]	114.7(6)	F4_1	C3_1	F6_1	107.8(12)
C1_2	O1_2	Al1	148.9(18)	F5_1	C3_1	C1_1	111.4(8)
O1_2	C1_2	C2_2	108.1(11)	F6_1	C3_1	C1_1	112.9(9)
O1_2	C1_2	C3_2	111.3(15)	F6_1	C3_1	F5_1	106.7(9)
O1_2	C1_2	C4_2	110.5(15)	F7_1	C4_1	C1_1	111.0(9)
C3_2	C1_2	C2_2	108.5(10)	F7_1	C4_1	F8_1	108.0(11)
C4_2	C1_2	C2_2	109.3(10)	F7_1	C4_1	F9_1	108.2(12)
C4_2	C1_2	C3_2	109.1(10)	F8_1	C4_1	C1_1	111.1(9)
F1_2	C2_2	C1_2	109.5(14)	F9_1	C4_1	C1_1	111.2(11)
F2_2	C2_2	C1_2	112.6(11)	F9_1	C4_1	F8_1	107.2(11)

[1]1-Y,1-Z,1-X; [2]1-X,1-Y,1-Z; [3]1-Z,1-X,1-Y; [4]+Z,+X,+Y; [5]+Y,+Z,+X; [6]1-X,2-Y,1-Z; [7]1-Z,1/2+X,3/2-Y; [8]-1/2+Y,3/2-Z,1-X

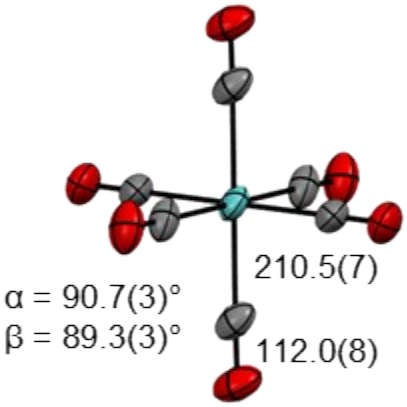
Comparison of structure metrics of the homoleptic carbonyl cation triad with their neutral congeners



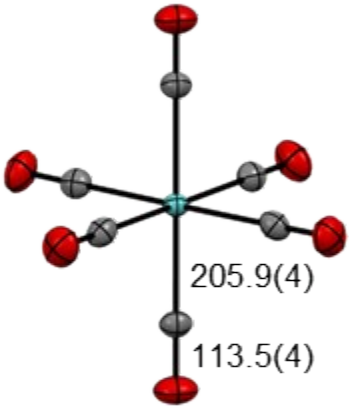
$[Cr(CO)_6]^+$



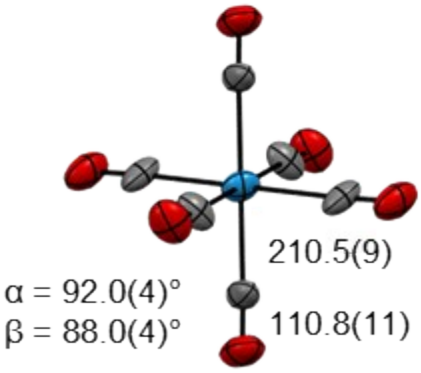
$Cr(CO)_6$



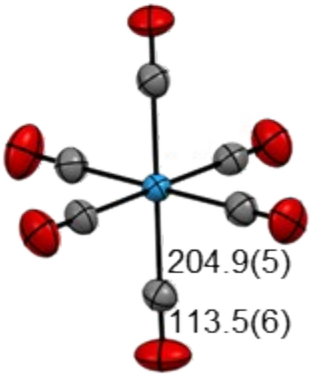
$[Mo(CO)_6]^+$



$Mo(CO)_6$



$[W(CO)_6]^+$



$W(CO)_6$

8. Single-Crystal XRD Data of the side Products

Due to space-saving reasons, for the side products only atomic coordinates are deposited here. For additional information, please check the CCDC numbers 1952378 to 1952389 .

$[Mo(CO)_6][Al(OR^F)_4]$

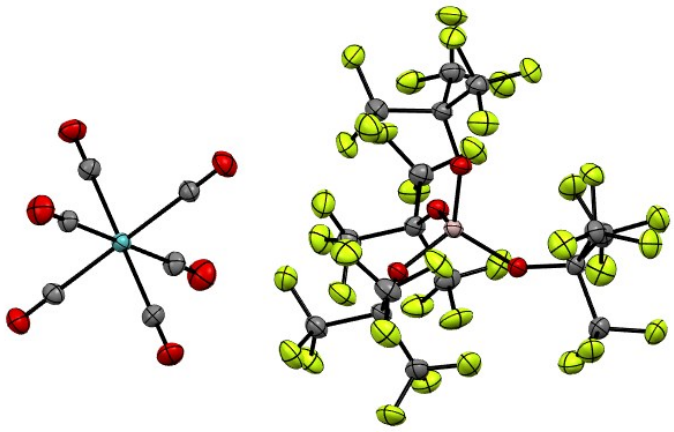


Table 1 Crystal data and structure refinement for p4n_a.

CCDC Deposition Number	1952381
Identification code	p4n_a
Empirical formula	$C_{22}O_{10}F_{36}AlMo$
Formula weight	1231.14
Temperature/K	373.15
Crystal system	tetragonal
Space group	P4/n
a/Å	13.7590(6)
b/Å	13.7590(6)
c/Å	9.5821(7)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1814.0(2)
Z	2
ρ_{calc}g/cm^3	2.254
μ/mm^{-1}	0.624
F(000)	1182.0
Crystal size/mm^3	0.2 × 0.2 × 0.2
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.622 to 61.002
Index ranges	$-19 \le h \le 19$, $-19 \le k \le 19$, $-13 \le l \le 13$
Reflections collected	71711
Independent reflections	2766 [R_{int} = 0.0650, R_{sigma} = 0.0175]
Data/restraints/parameters	2766/0/163
Goodness-of-fit on F^2	1.114
Final R indexes [I>=2σ (I)]	R_1 = 0.0380, wR_2 = 0.0932
Final R indexes [all data]	R_1 = 0.0412, wR_2 = 0.0951
Largest diff. peak/hole / e Å^{-3}	0.60/-1.43

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for p4n_a. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Mo1	7500	7500	6274.4(4)	22.34(10)
Al1	7500	2500	10000	21.5(2)
O1	7500	7500	9625(4)	48.9(10)
C1	7500	7500	8479(5)	29.2(9)
O2	6496.3(18)	5371.6(17)	6277(2)	38.4(5)
C2	6846(2)	6103(2)	6275(3)	27.0(5)
C3	7500	7500	4061(4)	24.4(8)
O3	7500	7500	2916(4)	44.1(9)
O1_1	6680.4(13)	1850.2(13)	8994(2)	26.7(4)
C1_1	5844.7(18)	1871.3(19)	8261(3)	25.0(5)
C2_1	4967(2)	2137(2)	9215(4)	32.3(6)
F1_1	5039.8(14)	1711.9(14)	10447(2)	41.8(4)
F2_1	4115.5(13)	1871.1(16)	8653(2)	43.6(5)
F3_1	4927.1(14)	3095.4(14)	9430(2)	41.0(5)
C3_1	5905(2)	2611(2)	7035(3)	34.9(6)
F4_1	6446.1(16)	2270.3(16)	5996(2)	46.7(5)
F5_1	6297.7(16)	3442.6(13)	7469(2)	44.5(5)
F6_1	5022.2(16)	2828.1(14)	6496(2)	42.6(4)
C4_1	5670(2)	839(2)	7641(3)	30.9(5)
F7_1	6494.2(13)	468.7(14)	7121(2)	41.9(4)
F8_1	5014.6(15)	833.4(14)	6607(2)	40.3(4)
F9_1	5360.1(15)	224.7(13)	8621(2)	39.2(4)

$[Mo(CO)_6][Mo_2(CO)_8I_3][Al(OR^F)_4]_2$

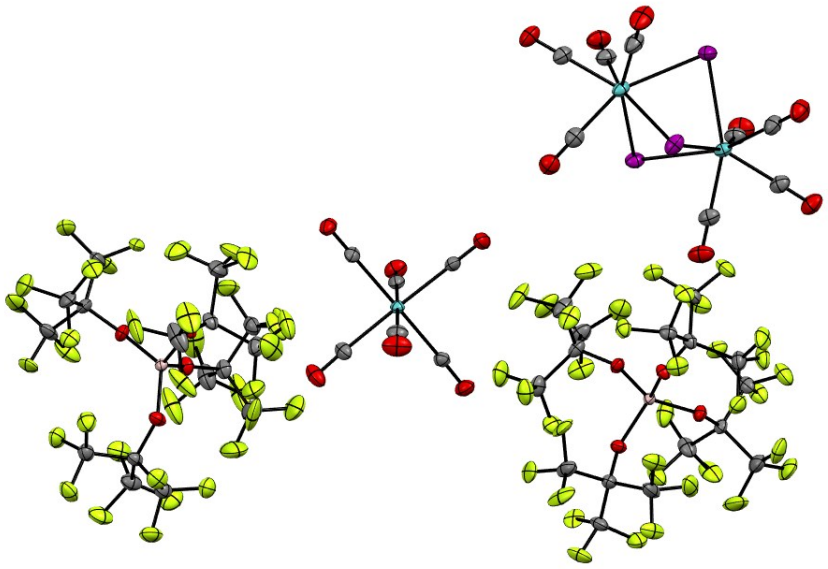


Table 1 Crystal data and structure refinement for p21n_a.

CCDC Deposition Number	1952380
Identification code	p21n_a
Empirical formula	$C_{46}O_{22}F_{72}Al_2Mo_3I_3$
Formula weight	2994.95
Temperature/K	100.01
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	13.9703(4)
b/Å	28.8124(9)
c/Å	20.6169(6)
α/°	90
β/°	90.4430(10)
γ/°	90
Volume/Å^3	8298.4(4)
Z	4
ρ_{calc}g/cm^3	2.397
μ/mm^{-1}	1.812
F(000)	5644.0
Crystal size/mm^3	0.2 × 0.15 × 0.15
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	1.414 to 61.054
Index ranges	$-17 \le h \le 19$, $-41 \le k \le 40$, $-29 \le l \le 29$
Reflections collected	279748
Independent reflections	25308 [R_{int} = 0.0295, R_{sigma} = 0.0191]
Data/restraints/parameters	25308/4922/2007
Goodness-of-fit on F^2	1.060
Final R indexes [I>=2σ (I)]	R_1 = 0.0340, wR_2 = 0.0837
Final R indexes [all data]	R_1 = 0.0418, wR_2 = 0.0884
Largest diff. peak/hole / e Å^{-3}	1.43/-1.21

Table 2 Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for p21n_a. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
I1	1087.0(2)	9032.1(2)	1877.1(2)	31.55(5)
Mo1	7133.4(2)	6211.2(2)	2446.2(2)	17.41(4)
Al1	7339.3(5)	8723.6(2)	4888.8(4)	14.32(13)
O1	8882.5(18)	5484.5(9)	2362.1(13)	39.5(6)
C1	8261(2)	5728.1(10)	2391.3(15)	27.0(6)
I2	2374.7(2)	8716.6(2)	3492.5(2)	29.84(5)
Al2	7693.1(5)	3739.3(3)	4974.8(4)	14.51(13)
Mo2	2914.5(2)	9287.7(2)	2413.4(2)	23.08(5)
O2	7208(2)	6156.2(12)	4009.9(12)	46.9(7)
C2	7183(2)	6177.1(12)	3472.5(15)	30.3(6)
Mo3	1832.5(2)	8173.1(2)	2380.0(2)	24.08(5)
I3	3634.7(2)	8446.7(2)	1853.1(2)	26.86(4)
O3	8765.4(17)	7004.1(8)	2442.8(12)	33.3(5)
C3	8187(2)	6732.7(10)	2447.0(14)	23.3(5)
O4	5430.5(17)	6967.3(8)	2541.2(12)	33.5(5)
C4	6022(2)	6707.0(10)	2506.3(14)	24.3(5)
O5	7097.3(19)	6244.7(9)	879.4(11)	35.4(5)
C5	7100(2)	6234.5(10)	1421.4(15)	24.1(5)
O6	5532.5(16)	5400.8(8)	2428.1(12)	30.6(5)
C6	6088(2)	5681.3(10)	2436.4(14)	23.2(5)
O7	3152(2)	9541.1(11)	928.3(12)	45.0(6)
C7	3070(2)	9456.5(13)	1453.9(16)	33.1(7)
O8	1501(2)	9961.6(9)	3163.9(14)	43.9(6)
C8	2011(3)	9724.2(11)	2899.2(16)	32.9(7)
O9	3912(2)	10259.7(9)	2407.2(12)	39.4(6)
C9	3546(2)	9909.5(12)	2407.6(15)	31.3(6)
O10	4909.3(19)	9162.9(11)	3134.7(12)	42.5(6)
C10	4202(2)	9209.2(12)	2884.2(15)	30.6(6)
O11	3292.2(19)	7506.6(9)	3116.2(12)	38.6(5)
C11	2771(2)	7739.7(11)	2855.3(15)	30.8(6)
O12	926.3(19)	7182.8(8)	2289.8(12)	36.6(5)
C12	1256(2)	7540.5(11)	2320.5(15)	29.5(6)
O13	1553.8(19)	7979.6(10)	874.9(12)	41.1(6)
C13	1652(2)	8042.5(12)	1408.4(16)	32.1(6)
O14	-152(2)	8237.2(11)	3107.9(17)	55.3(8)
C14	554(3)	8212.5(13)	2853.6(18)	37.8(8)
O1_14	8260(20)	8450(14)	5300(20)	21(6)
C1_14	8787(15)	8369(6)	5834(13)	20.6(5)
C2_14	8636(12)	8773(7)	6315(9)	34(4)
F1_14	8590(30)	9180(14)	6040(30)	45(8)
F2_14	9312(17)	8810(18)	6749(13)	35(5)
F3_14	7845(13)	8743(7)	6637(10)	38(4)
C3_14	8459(13)	7903(6)	6127(8)	37(4)
F4_14	8774(15)	7552(6)	5804(11)	45(4)
F5_14	7549(17)	7805(13)	6150(20)	41(6)
F6_14	8781(19)	7849(9)	6719(10)	50(6)
C4_14	9846(13)	8344(5)	5624(8)	28(3)
F7_14	10050(20)	8113(8)	5102(13)	31(5)
F8_14	10350(20)	8156(10)	6086(15)	41(6)
F9_14	10180(13)	8752(6)	5508(10)	42(4)
O1_13	7360(15)	3333(6)	4413(9)	21.4(4)
C1_13	6936(13)	2926(7)	4247(9)	23.0(6)

C2_13	7739(18)	2618(8)	3954(10)	32(4)
F1_13	8310(19)	2861(9)	3571(12)	48(6)
F2_13	7350(20)	2279(9)	3612(14)	50(7)
F3_13	8292(16)	2430(8)	4414(10)	36(5)
C3_13	6520(14)	2705(7)	4871(12)	31(4)
F4_13	5700(14)	2902(8)	5046(15)	44(6)
F5_13	7120(14)	2751(7)	5370(9)	31(4)
F6_13	6345(19)	2258(7)	4788(15)	53(7)
C4_13	6134(17)	3031(8)	3743(12)	33(4)
F7_13	5619(17)	3391(8)	3935(16)	39(6)
F8_13	5550(20)	2672(11)	3650(20)	49(8)
F9_13	6501(18)	3133(10)	3175(11)	52(6)
O1_12	6679(13)	3956(6)	5338(12)	19.5(8)
C1_12	6171(12)	4116(5)	5847(9)	23.9(5)
C2_12	6511(8)	4602(4)	6063(6)	35(3)
F1_12	7453(9)	4628(5)	6085(9)	65(4)
F2_12	6191(9)	4711(5)	6651(5)	60(3)
F3_12	6180(20)	4906(9)	5626(10)	54(6)
C3_12	5101(10)	4135(5)	5649(7)	45(3)
F4_12	4781(14)	3698(6)	5670(9)	56.1(10)
F5_12	4999(14)	4322(6)	5070(8)	67(4)
F6_12	4587(12)	4386(5)	6063(10)	54(4)
C4_12	6317(10)	3772(5)	6416(7)	49(3)
F7_12	6293(14)	3339(5)	6198(10)	76(5)
F8_12	5638(9)	3823(4)	6853(7)	61.8(11)
F9_12	7190(16)	3866(10)	6650(18)	55(5)
O1_11	7650(30)	9281(7)	4673(19)	21.1(9)
C1_11	8112(15)	9563(6)	4253(11)	20.0(8)
C2_11	7455(12)	9648(5)	3664(9)	27.6(14)
F1_11	7416(10)	9267(5)	3278(5)	45(3)
F2_11	7740(30)	10014(7)	3308(14)	46(6)
F3_11	6554(7)	9735(5)	3830(7)	51(4)
C3_11	8330(11)	10022(6)	4604(9)	32(3)
F4_11	8695(11)	9948(5)	5194(7)	52(4)
F5_11	7544(9)	10282(4)	4642(9)	58(4)
F6_11	8990(20)	10272(14)	4284(18)	44(6)
C4_11	9032(15)	9327(6)	4025(10)	30(3)
F7_11	9724(14)	9357(6)	4473(9)	39(3)
F8_11	9390(30)	9492(10)	3465(12)	36(4)
F9_11	8903(10)	8872(5)	3918(8)	35(3)
O1_10	7670(20)	9270(6)	4638(16)	21.1(9)
C1_10	8131(11)	9529(6)	4198(9)	20.0(8)
C2_10	7392(8)	9761(3)	3729(6)	27.6(14)
F1_10	6791(11)	9431(6)	3507(13)	33(3)
F2_10	7821(15)	9930(4)	3192(8)	32(3)
F3_10	6928(6)	10107(3)	4011(4)	40.8(18)
C3_10	8684(7)	9923(3)	4562(5)	36(2)
F4_10	9478(6)	9744(3)	4836(5)	64(3)
F5_10	8117(13)	10095(9)	5024(8)	46(4)
F6_10	8935(18)	10269(10)	4163(14)	47(6)
C4_10	8873(7)	9245(3)	3796(5)	32.4(19)
F7_10	9373(17)	8953(5)	4177(11)	41(3)
F8_10	9505(18)	9535(9)	3514(11)	47(5)
F9_10	8416(7)	9008(3)	3326(5)	44(2)

O1_9	8010(20)	4033(10)	4283(10)	25.0(10)
C1_9	8146(8)	4439(7)	3970(7)	24.4(7)
C2_9	7188(6)	4675(3)	3844(4)	31.2(15)
F1_9	6509(10)	4383(5)	3642(7)	65(4)
F2_9	7250(17)	4997(5)	3368(8)	46(3)
F3_9	6878(5)	4891(2)	4359(3)	49.9(18)
C3_9	8801(7)	4756(3)	4361(6)	52(2)
F4_9	9719(5)	4629(3)	4321(6)	90(3)
F5_9	8558(12)	4734(4)	4981(6)	67(4)
F6_9	8735(15)	5196(5)	4164(11)	66(5)
C4_9	8670(8)	4321(4)	3345(6)	40.6(13)
F7_9	9347(8)	4007(3)	3434(5)	71(3)
F8_9	9084(17)	4696(6)	3073(11)	71(5)
F9_9	8063(8)	4149(2)	2894(3)	80(3)
O1_8	7700(20)	9262(5)	4619(13)	21.1(9)
C1_8	8183(10)	9508(5)	4169(7)	20.0(8)
C2_8	9247(7)	9345(4)	4133(5)	32(2)
F1_8	9738(7)	9502(4)	4637(5)	48(2)
F2_8	9691(11)	9484(7)	3593(9)	47(3)
F3_8	9246(16)	8882(5)	4134(9)	44(4)
C3_8	7697(6)	9452(3)	3490(4)	29.7(15)
F4_8	6749(9)	9474(6)	3558(11)	49(4)
F5_8	7980(8)	9051(3)	3221(4)	53(2)
F6_8	7961(9)	9797(3)	3085(5)	38(2)
C4_8	8149(6)	10027(3)	4367(4)	26.7(15)
F7_8	7291(5)	10208(2)	4230(4)	45.2(17)
F8_8	8805(11)	10281(6)	4048(9)	36(3)
F9_8	8337(11)	10081(8)	4996(6)	40(3)
O1_7	6434.3(14)	8788.9(6)	5444.1(9)	19.6(4)
C1_7	5615.7(19)	9006.0(9)	5602.5(12)	19.4(5)
C2_7	4888(2)	9004.5(10)	5029.4(14)	25.6(5)
F1_7	5327.3(15)	9122.6(8)	4485.1(9)	37.4(4)
F2_7	4165.3(14)	9299.5(7)	5115.8(11)	37.4(4)
F3_7	4515.8(14)	8583.4(7)	4941.2(9)	31.9(4)
C3_7	5177(2)	8736.2(10)	6185.0(13)	23.0(5)
F4_7	5622.3(14)	8838.4(7)	6737.1(8)	32.5(4)
F5_7	5238.5(13)	8283.2(6)	6094.2(9)	27.6(4)
F6_7	4242.3(13)	8837.5(7)	6265.6(9)	32.0(4)
C4_7	5821(2)	9515.5(10)	5812.3(15)	29.2(6)
F7_7	6608.7(15)	9539.6(7)	6177.8(10)	36.7(4)
F8_7	5106.3(15)	9701.0(7)	6155.1(11)	40.6(5)
F9_7	5962.1(16)	9783.6(6)	5295.6(11)	38.6(5)
O1_6	8252(4)	8430(2)	5284(3)	19.2(10)
C1_6	8748(3)	8376.0(14)	5845(3)	20.6(5)
C2_6	9555(3)	8015.6(13)	5719.6(18)	33.0(8)
F1_6	9207(3)	7590.2(11)	5691(2)	53.8(10)
F2_6	10243(4)	8026.7(16)	6179(2)	41.6(11)
F3_6	9953(4)	8095(2)	5158(2)	55.5(15)
C3_6	9209(3)	8835.8(13)	6072(2)	38.8(10)
F4_6	8600(6)	9182(2)	6006(5)	57.3(19)
F5_6	9957(3)	8942.2(13)	5711(2)	59.9(11)
F6_6	9525(4)	8817(3)	6684(3)	56.8(16)
C4_6	8091(3)	8195.0(17)	6392.6(18)	39.8(10)
F7_6	7592(3)	8531.0(19)	6658.8(17)	61.2(12)

F8_6	8590(4)	7985(2)	6870.3(18)	59.0(14)
F9_6	7468(3)	7902(2)	6153(4)	59.3(17)
O1_5	7016.8(14)	8398.7(6)	4221.9(9)	20.8(4)
C1_5	6884(2)	7981.4(9)	3939.3(13)	23.0(5)
C2_5	7699(2)	7631.7(10)	4130.0(15)	30.6(6)
F1_5	8542.5(14)	7832.8(7)	4107.4(10)	36.0(4)
F2_5	7721.0(18)	7264.9(7)	3723.7(11)	45.3(5)
F3_5	7559.7(18)	7469.3(7)	4725.5(10)	40.5(5)
C3_5	5910(3)	7770.2(12)	4143.5(16)	35.3(7)
F4_5	5188.6(15)	7998.3(9)	3849.0(12)	49.7(6)
F5_5	5791.6(16)	7810.4(7)	4779.4(10)	39.8(5)
F6_5	5834.4(18)	7321.1(8)	3990.9(12)	50.9(6)
C4_5	6905(2)	8057.2(11)	3193.3(15)	32.4(6)
F7_5	6378.1(18)	8424.9(8)	3030.0(10)	44.1(5)
F8_5	6548.1(19)	7692.1(8)	2865.8(10)	49.2(6)
F9_5	7794.3(16)	8116.1(8)	2992.1(9)	41.8(5)
O1_4	7972(15)	4007(7)	4256(7)	25.0(10)
C1_4	8056(6)	4411(5)	3932(5)	24.4(7)
C2_4	7134(5)	4484(2)	3505(3)	41.0(13)
F1_4	7121(4)	4181.9(16)	3020(2)	63.1(15)
F2_4	7088(13)	4910(4)	3257(6)	53(3)
F3_4	6373(7)	4416(4)	3869(4)	51.7(19)
C3_4	8183(4)	4846.1(19)	4371(3)	36.5(12)
F4_4	8776(7)	4748(4)	4854(4)	61(2)
F5_4	7352(4)	4977.6(14)	4619(2)	47.1(11)
F6_4	8531(10)	5208(3)	4047(7)	58(3)
C4_4	8949(6)	4363(3)	3480(4)	40.6(13)
F7_4	9740(3)	4423.5(17)	3825(3)	55.2(12)
F8_4	8897(13)	4654(5)	2978(7)	68(3)
F9_4	8981(4)	3945.8(19)	3219(3)	40.3(11)
O1_3	6756(3)	4044.9(13)	5307(3)	19.5(8)
C1_3	6190(4)	4099.6(18)	5830(3)	23.9(5)
C2_3	6788(3)	4186.5(17)	6455.0(19)	36.3(9)
F1_3	7133(5)	3784(3)	6704(5)	48.9(16)
F2_3	6274(2)	4392.4(16)	6924.7(15)	59.4(11)
F3_3	7515(2)	4469.9(14)	6326.7(18)	42.4(8)
C3_3	5542(3)	4529.5(14)	5693(2)	32.6(9)
F4_3	5200(4)	4512.5(14)	5092.9(19)	42.3(9)
F5_3	6054(6)	4925(3)	5764(3)	43.5(13)
F6_3	4793(3)	4552.7(16)	6096(2)	46.0(10)
C4_3	5535(3)	3666.9(16)	5932(2)	41.3(11)
F7_3	4860(3)	3648.1(16)	5452(2)	56.1(10)
F8_3	5098(3)	3682.7(12)	6513(2)	61.8(11)
F9_3	6048(3)	3282.7(13)	5919(2)	45.3(10)
O1_2	7434.4(16)	3164.6(7)	4804.8(10)	21.4(4)
C1_2	7113(2)	2856.0(10)	4362.8(15)	23.0(6)
C2_2	6087(3)	2979.8(12)	4133(2)	35.3(8)
F1_2	5450.0(17)	2872.9(10)	4588.4(16)	48.4(6)
F2_2	5828(3)	2757.6(13)	3588(2)	51.8(9)
F3_2	6014(2)	3433.6(9)	4017.3(14)	40.9(6)
C3_2	7797(3)	2833.4(12)	3770.0(17)	30.6(7)
F4_2	8699.0(16)	2870.9(8)	3954.8(12)	38.7(5)
F5_2	7611(2)	3181.0(8)	3364.5(10)	43.5(6)
F6_2	7708(2)	2438.9(9)	3434.0(13)	41.3(6)

C4_2	7096(3)	2368.6(11)	4700.5(19)	33.1(7)
F7_2	7982.5(17)	2198.1(7)	4753.4(13)	40.8(6)
F8_2	6588.0(17)	2062.4(8)	4343.6(14)	43.7(6)
F9_2	6733.7(19)	2391.2(8)	5280.8(12)	44.2(6)
O1_1	8605.3(15)	3735.3(7)	5539.8(10)	24.5(4)
C1_1	9437.0(19)	3548.9(10)	5747.9(13)	21.6(5)
C2_1	9306(2)	3033.6(10)	5953.9(14)	27.6(6)
F1_1	8480.5(15)	2977.6(7)	6256.5(10)	36.8(4)
F2_1	10004.6(16)	2887.1(7)	6355.7(10)	38.0(4)
F3_1	9304.7(16)	2754.5(7)	5440.5(10)	37.4(4)
C3_1	10223(2)	3580.1(12)	5216.8(15)	31.4(6)
F4_1	10543.7(16)	4011.8(8)	5153.7(11)	43.8(5)
F5_1	9862.7(15)	3452.2(8)	4645.7(9)	38.0(5)
F6_1	10970.1(14)	3307.2(8)	5346.0(11)	42.9(5)
C4_1	9764(2)	3838.3(11)	6345.2(14)	27.5(6)
F7_1	9657.4(15)	4287.9(7)	6241.8(10)	34.1(4)
F8_1	10692.9(14)	3767.3(8)	6496.5(11)	39.9(5)
F9_1	9258.3(15)	3728.8(7)	6865.4(9)	33.8(4)

$[W(CO)_4(OR^F)_2][F\text{-}\{Al(OR^F)_3\}_2]$

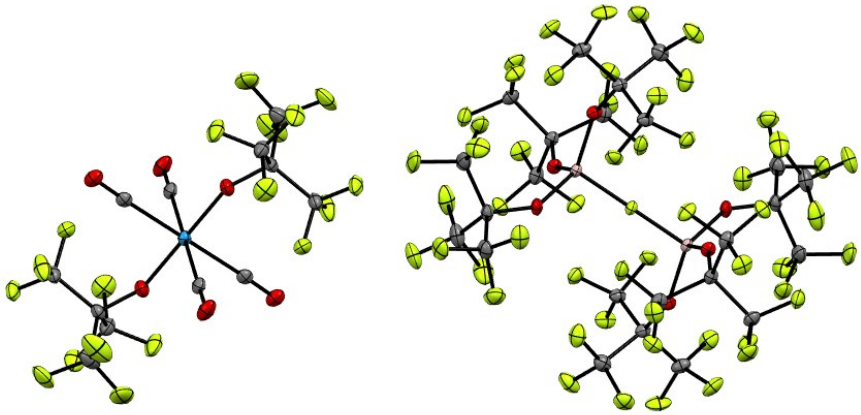


Table 1 Crystal data and structure refinement for p-1_a.

CCDC Deposition Number	1952382
Identification code	p-1_a
Empirical formula	$C_{36}O_{12}F_{73}Al_2W$
Formula weight	2249.17
Temperature/K	99.95
Crystal system	triclinic
Space group	P-1
a/Å	11.5888(8)
b/Å	11.5986(8)
c/Å	12.7755(8)
α/°	82.965(2)
β/°	67.136(2)
γ/°	87.863(2)
Volume/Å^3	1570.27(18)
Z	1
ρ_{calc}g/cm^3	2.378
μ/mm^{-1}	2.141
F(000)	1069.0
Crystal size/mm^3	0.1 × 0.08 × 0.06
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.484 to 54.32
Index ranges	-14 ≤ h ≤ 14, -14 ≤ k ≤ 14, -16 ≤ l ≤ 16
Reflections collected	37611
Independent reflections	6968 [R_{int} = 0.0367, R_{sigma} = 0.0295]
Data/restraints/parameters	6968/0/562
Goodness-of-fit on F^2	0.993
Final R indexes [I>=2σ (I)]	R_1 = 0.0242, wR_2 = 0.0532
Final R indexes [all data]	R_1 = 0.0274, wR_2 = 0.0548
Largest diff. peak/hole / e Å^{-3}	0.96/-0.62

Table 2 Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for p-1_a. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
W1	10000	5000	10000	13.97(5)
O1	9959.3(16)	7424.2(15)	11056.3(14)	21.9(4)
C1	9991(2)	6584(2)	10702.3(19)	16.8(5)
F1	5000	0	5000	12.9(4)
Al1	4602.1(6)	820.1(6)	6173.7(5)	10.70(13)
C2	11552(2)	5573(2)	8434(2)	17.8(5)
O2	12348.5(17)	5861.8(16)	7622.4(15)	26.6(4)
O1_4	8853.6(15)	5728.9(15)	9407.7(14)	19.9(4)
C1_4	8207(2)	5971(2)	8694(2)	17.6(5)
C2_4	8503(2)	7257(2)	8146(2)	22.7(5)
F1_4	8508.8(16)	7920.9(13)	8916.7(14)	34.0(4)
F2_4	7672.7(16)	7651.0(14)	7724.9(14)	34.4(4)
F3_4	9632.5(15)	7335.4(14)	7312.1(14)	35.2(4)
C3_4	8624(2)	5133(2)	7765(2)	21.7(5)
F4_4	8199.2(17)	4062.9(13)	8240.6(15)	35.6(4)
F5_4	9862.9(14)	5073.9(14)	7307.0(13)	30.7(4)
F6_4	8211.9(15)	5447.2(13)	6945.5(13)	28.8(4)
C4_4	6790(2)	5810(3)	9463(2)	30.8(6)
F7_4	6609.5(16)	4844.6(18)	10177.1(16)	51.2(5)
F8_4	6114.4(14)	5744.9(17)	8836.2(15)	41.2(4)
F9_4	6380.9(15)	6689.7(19)	10077.0(14)	46.5(5)
O1_3	4076.0(14)	-102.3(13)	7416.7(13)	13.9(3)
C1_3	3082(2)	-585.0(19)	8323.3(18)	14.2(5)
C2_3	2534(2)	284(2)	9234(2)	19.0(5)
F1_3	3280.6(14)	379.1(13)	9790.0(12)	25.2(3)
F2_3	1401.3(13)	-55.2(13)	10005.3(12)	26.0(3)
F3_3	2431.1(13)	1332.8(12)	8732.8(12)	23.4(3)
C3_3	2037(2)	-941(2)	7936(2)	19.0(5)
F4_3	2541.4(13)	-1344.1(13)	6928.1(12)	24.9(3)
F5_3	1324.7(13)	-47.0(13)	7838.7(13)	24.9(3)
F6_3	1273.7(13)	-1783.2(13)	8677.4(12)	25.1(3)
C4_3	3552(2)	-1678(2)	8869.8(19)	17.7(5)
F7_3	3723.7(13)	-2561.1(12)	8237.8(12)	22.5(3)
F8_3	2730.2(14)	-2058.7(13)	9921.3(11)	24.6(3)
F9_3	4630.9(13)	-1475.6(12)	8939.6(12)	22.4(3)
O1_2	6034.1(14)	1400.9(14)	5921.6(13)	15.6(3)
C1_2	6661(2)	1955(2)	6430(2)	16.4(5)
C2_2	6936(3)	1107(2)	7333(2)	26.4(6)
F1_2	5914.5(16)	940.5(16)	8297.7(13)	37.3(4)
F2_2	7849.0(16)	1498.2(15)	7596.9(14)	34.8(4)
F3_2	7283.4(18)	78.2(14)	6960.3(16)	38.3(4)
C3_2	7916(2)	2423(2)	5472(2)	22.3(5)
F4_2	7732.7(14)	2933.1(13)	4558.4(12)	28.4(3)
F5_2	8711.5(14)	1561.5(14)	5137.6(14)	32.9(4)
F6_2	8464.8(14)	3208.0(13)	5821.1(13)	28.9(4)
C4_2	5885(2)	2992(2)	7003(2)	24.1(6)
F7_2	5947.4(15)	3894.6(13)	6234.6(15)	34.2(4)
F8_2	6256.7(15)	3346.3(15)	7777.4(14)	36.6(4)
F9_2	4678.3(13)	2673.1(14)	7539.8(13)	29.6(4)
O1_1	3419.2(15)	1701.6(14)	6097.1(13)	15.6(3)
C1_1	2984(2)	2464(2)	5446.1(19)	14.8(5)
C2_1	3936(2)	2626(2)	4180(2)	17.3(5)

F1_1	5098.4(12)	2670.8(13)	4149.0(11)	23.0(3)
F2_1	3751.8(13)	3591.1(12)	3588.4(12)	23.4(3)
F3_1	3870.1(13)	1726.3(13)	3649.1(11)	23.0(3)
C3_1	1715(2)	2001(2)	5513(2)	20.8(5)
F4_1	809.9(13)	2123.5(13)	6529.7(12)	26.2(3)
F5_1	1788.4(15)	878.5(13)	5385.7(13)	28.9(3)
F6_1	1364.6(14)	2560.9(14)	4710.7(13)	30.3(4)
C4_1	2786(2)	3658(2)	5922(2)	20.1(5)
F7_1	2248.2(14)	3508.8(13)	7069.4(12)	26.2(3)
F8_1	2052.8(14)	4355.0(13)	5548.9(13)	30.0(4)
F9_1	3870.1(14)	4205.1(12)	5640.9(13)	26.2(3)

$[W(CO)_6(OR^F)][F\text{-}\{Al(OR^F)_3\}_2]$

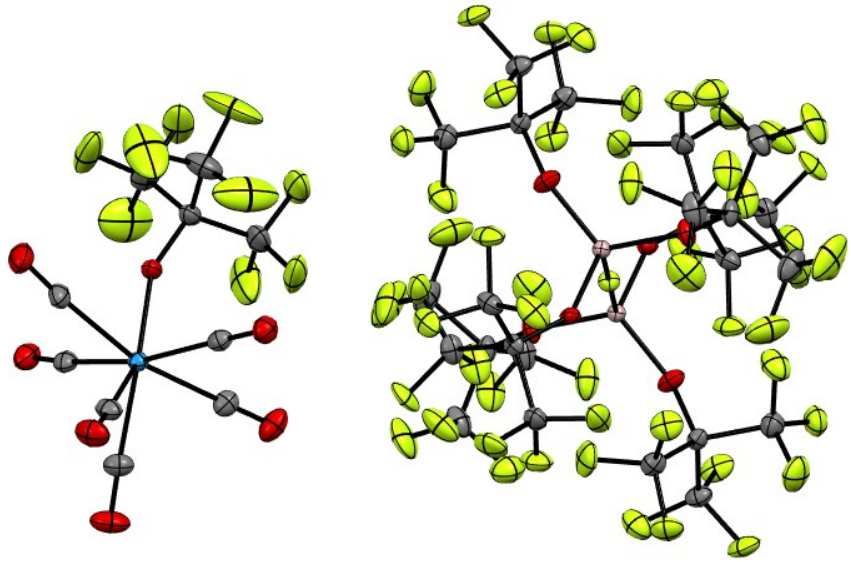


Table 1 Crystal data and structure refinement for IK_JB130_0m_a.

CCDC Deposition Number	1952384
Identification code	IK_JB130_0m_a
Empirical formula	$C_{68}Al_4F_{128}O_{26}W_2$
Formula weight	4140.30
Temperature/K	99.99
Crystal system	triclinic
Space group	P-1
a/Å	15.848(3)
b/Å	17.229(3)
c/Å	22.395(4)
α/°	94.072(3)
β/°	102.240(3)
γ/°	101.653(3)
Volume/Å^3	5811.1(17)
Z	2
ρ_{calc}g/cm^3	2.366
μ/mm^{-1}	2.283
F(000)	3936.0
Crystal size/mm^3	0.1 × 0.08 × 0.08
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	1.874 to 62.084
Index ranges	$-22 \le h \le 22$, $-24 \le k \le 24$, $-32 \le l \le 32$
Reflections collected	382640
Independent reflections	37090 [R_{int} = 0.0638, R_{sigma} = 0.0311]
Data/restraints/parameters	37090/39550/3206
Goodness-of-fit on F^2	1.018
Final R indexes [I>=2σ (I)]	R_1 = 0.0303, wR_2 = 0.0611
Final R indexes [all data]	R_1 = 0.0519, wR_2 = 0.0698
Largest diff. peak/hole / e Å^{-3}	1.23/-1.18

Table 2 Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for IK_JB130_0m_a. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
W1	4072.7(2)	-1375.2(2)	2682.4(2)	16.20(2)
O1	2675.0(15)	-251.6(14)	2272.4(10)	38.1(5)
C1	3123.2(18)	-665.3(17)	2408.8(12)	25.1(5)
F1	5000	5000	0	20.2(4)
Al1	4609.8(5)	5858.4(4)	175.4(3)	14.87(14)
O2	3717.8(15)	-1692.7(12)	1174.0(9)	32.1(5)
C2	3812.3(18)	-1615.0(16)	1718.3(12)	23.0(5)
F2	5000	5000	5000	14.8(4)
Al2	5486.3(5)	4513.8(4)	4486.1(3)	12.25(13)
W2	-1002.5(2)	3609.4(2)	2614.8(2)	15.57(2)
Al4	390.4(5)	9140.8(4)	-172.7(3)	12.45(13)
O4	4852.4(13)	-663.8(12)	4122.5(8)	27.9(4)
C4	4562.5(17)	-904.9(16)	3621.5(11)	21.2(5)
F4	0	10000	0	16.8(4)
Al3	9453.4(4)	498.8(4)	5464.7(3)	12.05(13)
O3	5851.5(15)	-2045.4(14)	3109.4(9)	35.0(5)
C3	5241.1(19)	-1819.2(17)	2948.7(12)	24.0(5)
F3	10000	0	5000	15.8(4)
C6	3052.2(18)	-1802.1(16)	3091.9(13)	24.4(5)
O6	2488.4(14)	-2007.1(13)	3316.4(11)	35.3(5)
C5	3687.8(19)	-2602.9(16)	2531.3(13)	25.7(5)
O5	3515.9(17)	-3276.8(13)	2446.1(11)	40.2(5)
C12	-1504.2(19)	2399.5(16)	2357.5(11)	23.7(5)
O12	-1753.3(16)	1739.8(12)	2210.6(9)	34.9(5)
C11	-2133.5(19)	3199.6(16)	2912.6(13)	25.4(5)
O11	-2758.2(15)	2992.3(13)	3074.4(11)	39.5(5)
C10	-1830.1(18)	4419.0(17)	2337.2(12)	23.4(5)
O10	-2230.2(14)	4870.8(14)	2214.3(11)	36.7(5)
C9	-601.2(19)	4014.6(16)	3580.9(12)	23.9(5)
O9	-335.7(17)	4258.5(13)	4075.8(9)	38.3(5)
C8	84.8(19)	3064.2(16)	2928.4(11)	22.8(5)
O8	672.5(15)	2815.4(14)	3114.9(9)	33.9(5)
C7	-1167.1(17)	3442.2(15)	1643.5(12)	20.4(5)
O7	-1261.3(14)	3353.2(12)	1131.9(8)	29.2(4)
O1_1	4761.0(15)	-392.7(13)	2422.8(10)	19.7(5)
C1_1	5455(3)	242(3)	2498(2)	21.3(5)
C2_1	5335(4)	921(3)	2937(3)	40.7(8)
F1_1	5418(5)	732(4)	3500(2)	94(2)
F2_1	5909(4)	1589(3)	2981(4)	89(2)
F3_1	4537(4)	1061(3)	2767(3)	113(3)
C3_1	5424(3)	518(3)	1846(2)	33.3(10)
F4_1	5405(4)	-79(3)	1451(2)	88.0(19)
F5_1	4699(2)	770(2)	1645.5(17)	71.6(12)
F6_1	6100(2)	1116(2)	1850.6(16)	58.4(10)
C4_1	6346(3)	5(3)	2736(2)	35.6(10)
F7_1	6436(2)	-576(2)	2358.2(18)	69.2(12)
F8_1	7033.4(19)	610(2)	2816.7(16)	54.7(9)
F9_1	6365(2)	-268(2)	3271.4(15)	60.1(10)
O1_2	41.5(15)	4528.2(13)	2681.8(10)	20.0(5)
C1_2	481(3)	5187(3)	2488.0(19)	22.6(6)
C2_2	1468(3)	5114(3)	2611(2)	45.7(11)
F1_2	1514(4)	4377(3)	2399(2)	68.0(13)

F2_2	1964.9(19)	5635(3)	2375(2)	107.9(17)
F3_2	1784.9(19)	5188.6(18)	3212.1(13)	52.9(8)
C3_2	182(3)	5236(2)	1800.6(17)	34.9(9)
F4_2	-712.1(15)	5158.5(15)	1635.6(10)	40.4(6)
F5_2	324(2)	4634.6(17)	1458.0(11)	46.5(7)
F6_2	536(2)	5914.9(16)	1620.6(13)	53.8(8)
C4_2	376(4)	5931(3)	2863(3)	47.8(14)
F7_2	-416(4)	6060(4)	2680(3)	112(3)
F8_2	987(3)	6570.4(18)	2819(2)	92.1(15)
F9_2	535(3)	5855(2)	3453.6(14)	60.4(9)
O1_3	6420(4)	5241(4)	4519(4)	18.0(5)
C1_3	7110(4)	5454(4)	4248(3)	21.6(6)
C2_3	7161(3)	4772(2)	3775.6(19)	27.6(9)
F1_3	6579(5)	4727(4)	3245(3)	38.3(15)
F2_3	7962(3)	4853(4)	3642.0(19)	39.3(10)
F3_3	6971(5)	4083(3)	3995(4)	41.6(16)
C3_3	7976(3)	5650(4)	4758(2)	48.8(14)
F4_3	7877(6)	6078(5)	5243(3)	81(3)
F5_3	8196(5)	4992(5)	4943(3)	70(2)
F6_3	8676(4)	6055(5)	4579(4)	64(2)
C4_3	7021(4)	6198(3)	3908(2)	41.0(12)
F7_3	7200(6)	6846(4)	4303(3)	77(2)
F8_3	7571(4)	6309(3)	3529(3)	53.2(14)
F9_3	6208(7)	6113(7)	3586(6)	57(2)
O1_4	5607.6(11)	3631.7(10)	4751.3(7)	17.8(3)
C1_4	5848.9(16)	3207.5(14)	5221.1(11)	18.0(5)
C2_4	6756.6(19)	3639.0(16)	5639.9(13)	28.9(6)
F1_4	7417.2(11)	3548.8(11)	5384.5(10)	42.5(5)
F2_4	6899.7(14)	3371.1(11)	6191.1(8)	46.2(5)
F3_4	6792.7(12)	4417.4(9)	5731.6(8)	32.7(4)
C3_4	5144.1(19)	3112.4(16)	5610.8(12)	26.1(6)
F4_4	4332.9(11)	2927.3(11)	5261.4(8)	32.8(4)
F5_4	5232.9(14)	3784.5(11)	5970.5(8)	38.0(4)
F6_4	5217.4(13)	2529.4(11)	5981.1(8)	38.2(4)
C4_4	5909.5(18)	2372.2(15)	4939.9(12)	23.7(5)
F7_4	5103.3(11)	1911.5(10)	4716.4(8)	32.2(4)
F8_4	6343.4(11)	1994.7(10)	5366.0(8)	32.0(4)
F9_4	6324.0(12)	2439.2(10)	4487.7(8)	32.6(4)
O1_5	4786.1(11)	4368.3(10)	3776.1(7)	18.5(3)
C1_5	4147.0(16)	3849.3(14)	3345.6(10)	16.7(4)
C2_5	3316.0(16)	3558.9(16)	3602.7(11)	20.9(5)
F1_5	2836.6(11)	4112.9(11)	3599.0(8)	31.9(4)
F2_5	2784.1(11)	2895.3(10)	3283.5(7)	30.9(4)
F3_5	3559.7(11)	3420.0(10)	4184.4(7)	27.3(3)
C3_5	4489.9(18)	3108.4(15)	3149.7(11)	22.8(5)
F4_5	5320.3(12)	3329.7(11)	3091.1(9)	37.1(4)
F5_5	4489.6(12)	2601.6(9)	3574.1(7)	28.0(3)
F6_5	4002.7(13)	2710.0(10)	2616.5(7)	34.4(4)
C4_5	3907.0(18)	4301.1(15)	2780.2(11)	21.6(5)
F7_5	4560.1(12)	4417.1(10)	2488.7(7)	31.3(4)
F8_5	3174.5(11)	3903.6(10)	2379.8(7)	31.9(4)
F9_5	3781.1(12)	5015.4(10)	2954.8(7)	28.9(4)
O1_6	4548(3)	6305(2)	-482.6(18)	29.4(9)
C1_6	4743(4)	6983(4)	-743(3)	20.7(7)

C2_6	4013(4)	6908(3)	-1352(2)	40.3(13)
F1_6	3270(3)	7020(4)	-1209(3)	78.3(17)
F2_6	4221(3)	7412(2)	-1738.5(16)	63.9(14)
F3_6	3859(4)	6185(3)	-1658.0(17)	64.9(13)
C3_6	5649(4)	7060(4)	-921(3)	40.0(15)
F4_6	6250(3)	6948(3)	-446.4(18)	66.5(13)
F5_6	5600(6)	6508(4)	-1379(3)	56.0(19)
F6_6	5939(3)	7774(3)	-1087(2)	60.0(13)
C4_6	4794(6)	7740(4)	-310(4)	27.0(17)
F7_6	5569(5)	7963(4)	79(2)	30.5(11)
F8_6	4687(6)	8353(5)	-627(4)	42.8(14)
F9_6	4173(6)	7625(6)	7(5)	56(2)
O1_7	5345(4)	6442(3)	777(2)	14.4(9)
C1_7	5963(6)	6491(5)	1309(4)	17.6(15)
C2_7	6798(5)	6242(6)	1181(4)	20.6(15)
F1_7	6632(9)	5447(5)	1073(5)	25.2(14)
F2_7	7495(4)	6476(4)	1654(3)	30.6(12)
F3_7	6997(5)	6554(5)	692(3)	33.4(12)
C3_7	6223(7)	7374(5)	1612(4)	31.5(19)
F4_7	5480(8)	7648(12)	1596(8)	46(2)
F5_7	6702(4)	7835(5)	1307(4)	42.1(14)
F6_7	6652(10)	7452(9)	2199(4)	47(3)
C4_7	5577(5)	5945(4)	1753(3)	28.8(14)
F7_7	5034(4)	6271(5)	2027(3)	42.0(13)
F8_7	6203(5)	5791(4)	2195(2)	44.1(14)
F9_7	5107(4)	5252(2)	1444(3)	35.7(11)
O1_8	3531(4)	5572(6)	153(4)	20.6(15)
C1_8	2825(8)	5440(7)	411(6)	22(2)
C2_8	1982(6)	5070(8)	-98(6)	45(3)
F1_8	1964(12)	4307(8)	-238(8)	49(4)
F2_8	1261(5)	5124(8)	90(6)	74(3)
F3_8	2008(8)	5426(7)	-604(5)	63(3)
C3_8	2703(9)	6244(6)	705(5)	30(3)
F4_8	3480(9)	6675(10)	1032(7)	41(3)
F5_8	2420(9)	6677(11)	270(8)	43(3)
F6_8	2138(12)	6133(16)	1068(9)	39(4)
C4_8	2963(8)	4875(6)	912(4)	38(2)
F7_8	3500(7)	5272(6)	1434(3)	49.7(19)
F8_8	2220(8)	4541(4)	1060(4)	63(2)
F9_8	3317(10)	4300(5)	728(3)	63(3)
O1_9	8623(5)	-214(6)	5616(5)	15.2(12)
C1_9	7746(5)	-566(5)	5468(4)	15.5(12)
C2_9	7179(5)	-19(4)	5692(3)	24.0(12)
F1_9	7270(4)	36(5)	6306(2)	37.3(11)
F2_9	6303(5)	-277(6)	5451(5)	30(2)
F3_9	7425(6)	721(3)	5556(3)	32.3(12)
C3_9	7391(5)	-789(5)	4759(3)	23.9(14)
F4_9	8010(5)	-1035(6)	4523(5)	39.5(13)
F5_9	7221(5)	-157(4)	4489(3)	35.0(14)
F6_9	6648(6)	-1358(8)	4607(7)	32(2)
C4_9	7636(5)	-1336(4)	5791(3)	23.7(12)
F7_9	7884(6)	-1908(5)	5488(3)	33.5(13)
F8_9	6802(6)	-1619(7)	5800(6)	37(2)
F9_9	8139(5)	-1199(4)	6361(2)	34.0(13)

O1_10	9073(4)	1186(3)	5045(3)	23.0(4)
C1_10	9111(3)	1767(3)	4676(2)	16.3(9)
C2_10	8881(2)	2511(2)	4988.8(16)	22.9(7)
F1_10	9567(3)	2929(3)	5408.5(19)	35.7(9)
F2_10	8621.1(19)	2995.2(16)	4575.2(15)	33.4(6)
F3_10	8221(4)	2272(4)	5260.8(17)	31.0(10)
C3_10	8424(2)	1463(2)	4057.8(15)	25.9(8)
F4_10	8451(4)	721(3)	3867(5)	37.8(13)
F5_10	7608(4)	1450(3)	4116(3)	31.6(12)
F6_10	8577(2)	1912(2)	3609.6(12)	40.0(7)
C4_10	10052(2)	2000(2)	4551.3(15)	22.4(7)
F7_10	10167(3)	1453(2)	4148(2)	32.3(8)
F8_10	10184(7)	2691(3)	4319(3)	31.1(12)
F9_10	10668(4)	2057(5)	5070(3)	36.0(18)
O1_11	10299.7(11)	825.9(11)	6100.3(7)	20.6(4)
C1_11	10505.9(17)	1202.8(16)	6683.3(10)	21.3(5)
C2_11	10997(2)	689(2)	7119.1(13)	36.1(7)
F1_11	11809.8(13)	732.7(14)	7030.2(9)	48.1(5)
F2_11	11065.0(17)	927.0(15)	7706.3(8)	60.8(7)
F3_11	10572.7(16)	-70.5(12)	7004.1(9)	52.3(6)
C3_11	9660.5(19)	1313.6(19)	6892.8(12)	30.6(6)
F4_11	9098.6(11)	1514.7(13)	6425.6(8)	39.2(4)
F5_11	9230.4(14)	636.1(13)	7050.1(9)	47.6(5)
F6_11	9826.1(12)	1879.7(12)	7363.0(8)	39.4(4)
C4_11	11114.5(19)	2032.2(18)	6708.2(13)	30.1(6)
F7_11	10646.0(14)	2525.9(11)	6439.1(8)	39.8(4)
F8_11	11504.2(13)	2360.9(13)	7283.0(8)	47.0(5)
F9_11	11746.7(12)	1980.2(12)	6409.8(9)	42.7(5)
O1_12	98.1(15)	8578.5(11)	378.6(9)	29.8(4)
C1_12	168.2(17)	7933.6(14)	681.3(10)	17.9(5)
C2_12	260.8(19)	7225.9(15)	252.7(12)	23.9(5)
F1_12	-503.3(14)	6882.1(12)	-131.7(8)	45.2(5)
F2_12	552.0(14)	6668.3(11)	558.9(8)	38.8(4)
F3_12	818.6(14)	7487.8(12)	-92.4(9)	45.5(5)
C3_12	974.6(18)	8154.7(18)	1237.3(13)	29.1(6)
F4_12	1003.0(14)	8846.4(12)	1548.0(10)	51.4(6)
F5_12	1725.0(12)	8222.4(14)	1046.9(10)	50.8(6)
F6_12	979.3(13)	7621.7(12)	1639.8(8)	39.8(4)
C4_12	-695.4(18)	7684.5(17)	915.5(12)	26.1(6)
F7_12	-717.5(13)	8219.3(12)	1364.5(8)	41.0(5)
F8_12	-752.2(13)	6981.7(11)	1131.7(9)	39.6(4)
F9_12	-1407.1(12)	7633.5(13)	469.9(9)	41.0(5)
O1_13	1498.9(11)	9471.6(12)	-76.3(9)	24.9(4)
C1_13	2242.0(16)	9594.2(14)	-296.8(11)	18.8(5)
C2_13	2380.5(17)	8785.0(15)	-560.6(12)	21.7(5)
F1_13	2643.6(13)	8360.2(10)	-111.8(8)	35.2(4)
F2_13	2975.0(11)	8871.8(11)	-903.4(8)	33.4(4)
F3_13	1622.9(11)	8351.2(9)	-914.4(7)	27.3(3)
C3_13	2186(2)	10156.1(17)	-798.6(14)	34.6(7)
F4_13	1812.5(18)	10743.0(12)	-645.2(10)	57.9(6)
F5_13	1684.4(14)	9765.9(12)	-1334.7(8)	42.5(5)
F6_13	2974.3(16)	10479.3(12)	-892.4(10)	54.5(6)
C4_13	3040.4(17)	9972.7(17)	258.8(13)	26.7(6)
F7_13	3074.4(12)	10737.5(10)	395.6(9)	37.6(4)

F8_13	3808.8(11)	9904.4(13)	134.8(10)	46.3(5)
F9_13	2962.0(12)	9617.0(12)	757.5(8)	37.9(4)
O1_14	-126.2(13)	8755.8(13)	-909.0(8)	30.4(5)
C1_14	-850.4(16)	8560.8(15)	-1382.0(10)	18.8(5)
C2_14	-1668.1(18)	8777.5(17)	-1195.4(12)	26.0(6)
F1_14	-1602.1(12)	9564.6(11)	-1163.8(8)	35.2(4)
F2_14	-2422.1(11)	8423.5(12)	-1585.9(9)	40.8(5)
F3_14	-1695.9(13)	8575.8(12)	-639.1(8)	39.7(5)
C3_14	-1054.8(18)	7652.9(16)	-1589.7(11)	24.4(5)
F4_14	-305.1(12)	7405.4(11)	-1600.7(8)	34.1(4)
F5_14	-1440.1(14)	7238.4(11)	-1208.3(9)	42.7(5)
F6_14	-1574.4(12)	7454.9(11)	-2152.1(8)	35.4(4)
C4_14	-640(2)	9023.5(18)	-1924.0(13)	32.4(6)
F7_14	-85.5(14)	8706.9(12)	-2189.4(9)	43.5(5)
F8_14	-1355.5(15)	9016.5(14)	-2352.1(9)	51.4(6)
F9_14	-243.7(15)	9776.7(11)	-1721.5(11)	51.8(6)
O1_15	8593(17)	-190(20)	5587(19)	15.2(12)
C1_15	7725(16)	-551(16)	5528(13)	15.5(12)
C2_15	7690(20)	-1280(17)	5890(14)	21(3)
F1_15	7940(40)	-1860(30)	5610(20)	33.5(13)
F2_15	6860(20)	-1550(30)	5930(20)	37(2)
F3_15	8190(30)	-1100(20)	6454(15)	34.0(13)
C3_15	7250(20)	35(19)	5799(14)	29(4)
F4_15	7410(50)	790(20)	5670(20)	44.0(19)
F5_15	7460(30)	70(30)	6406(14)	37.3(11)
F6_15	6380(20)	-250(40)	5624(18)	41(8)
C4_15	7320(20)	-790(20)	4835(12)	21(4)
F7_15	7100(30)	-160(30)	4587(19)	48(9)
F8_15	6580(20)	-1330(20)	4733(15)	32(8)
F9_15	7860(30)	-1070(40)	4530(30)	39.5(13)
O1_16	9041(11)	1190(9)	5031(7)	23.0(4)
C1_16	9115(9)	1726(8)	4613(6)	20(2)
C2_16	9938(6)	2411(5)	4864(4)	24.1(19)
F1_16	9794(7)	2928(7)	5278(5)	30(2)
F2_16	10165(18)	2844(9)	4418(8)	24(3)
F3_16	10618(10)	2104(12)	5095(7)	25(3)
C3_16	9180(5)	1309(5)	4002(4)	21.4(18)
F4_16	8613(9)	603(8)	3853(13)	33(3)
F5_16	9974(6)	1180(6)	4016(5)	26(2)
F6_16	8973(6)	1737(5)	3531(3)	33.8(17)
C4_16	8256(6)	2046(5)	4528(4)	24.4(19)
F7_16	7560(11)	1550(9)	4179(10)	40(4)
F8_16	8346(5)	2714(4)	4258(4)	34.6(18)
F9_16	8082(11)	2242(11)	5069(5)	34(3)
O1_17	6444(8)	5199(9)	4513(7)	18.0(5)
C1_17	7161(9)	5437(7)	4273(6)	21.6(6)
C2_17	7760(6)	6197(6)	4667(4)	43(2)
F1_17	7396(8)	6821(8)	4546(6)	56(3)
F2_17	8527(8)	6338(9)	4498(8)	49(3)
F3_17	7896(13)	6154(8)	5255(5)	56(4)
C3_17	7684(5)	4774(5)	4286(4)	31.2(18)
F4_17	7160(11)	4040(8)	4133(8)	44(3)
F5_17	8184(12)	4764(9)	4834(6)	55(3)
F6_17	8190(6)	4837(8)	3873(4)	39(2)

C4_17	6844(5)	5602(5)	3606(4)	30.8(18)
F7_17	6542(11)	4923(7)	3234(7)	35(3)
F8_17	7489(7)	6020(5)	3393(4)	39(2)
F9_17	6188(12)	5980(14)	3533(11)	48(4)
O1_18	5116(5)	-465(4)	2695(4)	19.7(5)
C1_18	5496(10)	257(8)	2548(7)	21.3(5)
C2_18	5293(9)	917(7)	2958(8)	40.7(8)
F1_18	5689(9)	880(13)	3524(8)	60(5)
F2_18	5535(11)	1628(10)	2809(11)	58(5)
F3_18	4466(8)	786(8)	2954(8)	49(4)
C3_18	5158(8)	328(8)	1868(5)	43(3)
F4_18	5152(9)	-302(9)	1482(7)	55(4)
F5_18	4325(7)	418(9)	1744(6)	73(4)
F6_18	5650(10)	938(8)	1672(6)	61(4)
C4_18	6500(8)	304(8)	2688(5)	31(3)
F7_18	6707(7)	-100(7)	2236(5)	48(3)
F8_18	6960(7)	1046(6)	2742(6)	60(3)
F9_18	6793(7)	32(8)	3205(4)	48(3)
O1_20	8565(7)	-111(9)	5620(8)	16(3)
C1_20	7704(9)	-518(8)	5467(6)	19(2)
C2_20	7520(6)	-1041(6)	5976(4)	36(2)
F1_20	7474(4)	-598(5)	6472(3)	51.2(19)
F2_20	6748(9)	-1585(9)	5826(7)	36(4)
F3_20	8154(6)	-1433(5)	6134(4)	44(2)
C3_20	7514(7)	-1050(6)	4848(4)	29(2)
F4_20	7920(6)	-658(4)	4455(4)	39.4(18)
F5_20	7786(4)	-1720(3)	4904(3)	48.3(18)
F6_20	6652(9)	-1255(16)	4570(15)	41(5)
C4_20	7111(5)	93(5)	5396(4)	26.8(18)
F7_20	7070(4)	403(4)	4879(3)	37.7(14)
F8_20	6287(7)	-246(12)	5400(8)	44(5)
F9_20	7419(9)	677(6)	5861(4)	44.0(19)
O1_21	4920(7)	6447(6)	-366(4)	29.4(9)
C1_21	4816(10)	7054(9)	-714(7)	20.7(7)
C2_21	4767(13)	7782(9)	-293(8)	22(4)
F1_21	4240(20)	7504(19)	75(15)	60(6)
F2_21	4434(11)	8320(12)	-588(11)	42(4)
F3_21	5521(15)	8100(13)	110(8)	52(6)
C3_21	5600(8)	7234(7)	-1036(5)	28(3)
F4_21	5450(14)	6680(8)	-1504(6)	61(5)
F5_21	6344(6)	7272(6)	-656(5)	39(2)
F6_21	5600(7)	7926(6)	-1263(5)	31(2)
C4_21	3913(8)	6810(8)	-1180(6)	42(2)
F7_21	3734(11)	6081(6)	-1475(5)	64.9(13)
F8_21	3825(9)	7298(6)	-1601(5)	63.9(14)
F9_21	3234(6)	6832(8)	-922(6)	67(3)
O1_22	3596(3)	5402(4)	294(3)	18.3(11)
C1_22	2808(6)	5431(6)	430(4)	19.5(17)
C2_22	2064(5)	5197(6)	-174(3)	25.0(15)
F1_22	1875(9)	4428(6)	-369(6)	36.4(17)
F2_22	1309(4)	5399(5)	-114(3)	41.5(14)
F3_22	2320(4)	5573(4)	-632(2)	29.2(12)
C3_22	2812(7)	6278(5)	717(3)	22.3(17)
F4_22	3595(7)	6604(8)	1095(5)	29.0(17)

F5_22	2673(6)	6771(8)	295(5)	34.1(16)
F6_22	2210(9)	6276(12)	1059(6)	30.7(19)
C4_22	2631(5)	4816(4)	889(3)	30.0(15)
F7_22	3128(5)	5117(4)	1451(2)	40.5(13)
F8_22	1791(4)	4659(3)	925(2)	41.9(14)
F9_22	2816(5)	4143(2)	722(2)	43.3(13)
O1_23	5183(5)	6266(7)	910(4)	25.6(18)
C1_23	5936(8)	6508(8)	1361(6)	19(2)
C2_23	6737(7)	6334(9)	1125(6)	24(3)
F1_23	6741(15)	5558(8)	1072(10)	37(3)
F2_23	7520(6)	6712(8)	1485(5)	39(2)
F3_23	6711(9)	6536(8)	565(5)	36(2)
C3_23	6098(10)	7410(6)	1555(5)	22(2)
F4_23	5354(13)	7632(17)	1616(11)	33(3)
F5_23	6414(10)	7833(7)	1155(6)	48(3)
F6_23	6664(14)	7625(13)	2101(7)	39(3)
C4_23	5827(9)	6030(6)	1909(5)	33(2)
F7_23	5294(8)	6312(7)	2219(5)	42(2)
F8_23	6589(10)	6086(8)	2310(4)	50(3)
F9_23	5469(10)	5273(4)	1722(7)	56(3)
O1_24	4811(12)	6335(12)	-441(8)	29.4(9)
C1_24	4584(12)	6920(12)	-788(8)	32(3)
C2_24	4936(11)	7723(12)	-371(8)	22(4)
F1_24	4712(12)	7685(11)	179(8)	25(4)
F2_24	4720(30)	8380(30)	-570(20)	42.8(14)
F3_24	5826(9)	7898(12)	-198(9)	68(7)
C3_24	5004(13)	6848(11)	-1354(7)	60(6)
F4_24	4450(20)	6299(13)	-1765(10)	91(8)
F5_24	5767(17)	6660(20)	-1217(18)	115(14)
F6_24	5060(20)	7544(13)	-1565(11)	88(9)
C4_24	3568(11)	6795(10)	-966(8)	38(2)
F7_24	3107(15)	6073(9)	-1183(8)	75(7)
F8_24	3341(13)	7250(10)	-1387(8)	34(5)
F9_24	3191(11)	7044(11)	-531(8)	40(4)
O1_19	-232(6)	4610(5)	2418(4)	20.0(5)
C1_19	492(9)	5237(9)	2555(7)	22.6(6)
C2_19	304(10)	5904(7)	2967(6)	29(3)
F1_19	-322(9)	6184(11)	2627(7)	42(4)
F2_19	997(8)	6484(8)	3220(8)	66(4)
F3_19	-29(10)	5636(6)	3421(5)	52(4)
C3_19	1304(6)	4957(7)	2906(5)	34(3)
F4_19	1372(15)	4297(9)	2600(8)	53(4)
F5_19	1231(8)	4787(8)	3460(4)	55(3)
F6_19	2069(6)	5479(7)	2945(7)	52(3)
C4_19	657(8)	5528(8)	1946(6)	40(3)
F7_19	970(11)	4998(7)	1651(7)	76(5)
F8_19	1230(7)	6203(6)	2029(6)	66(4)
F9_19	-92(8)	5617(9)	1603(5)	59(3)

$[Mo_2(CO)_8I_2][F\text{-}\{Al(OR^F)_3\}_2]$

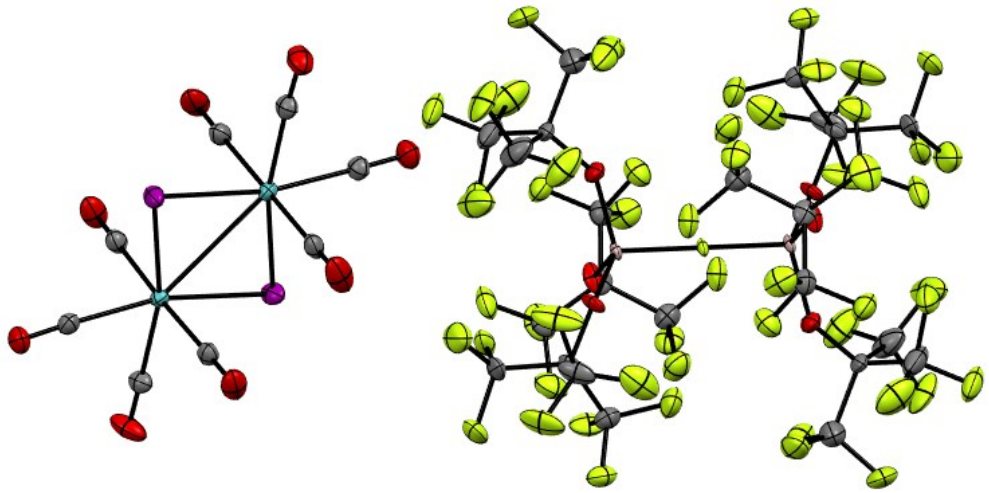


Table 1 Crystal data and structure refinement for p-1_a.

CCDC Deposition Number	1952385
Identification code	p-1_a
Empirical formula	$C_{96}O_{42}F_{165}Al_6Mo_6I_6$
Formula weight	6458.88
Temperature/K	100.01
Crystal system	triclinic
Space group	P-1
a/Å	13.3850(11)
b/Å	21.4285(17)
c/Å	31.305(3)
α/°	85.822(3)
β/°	81.782(3)
γ/°	83.840(3)
Volume/Å^3	8820.3(12)
Z	2
ρ_{calc}g/cm^3	2.432
μ/mm^{-1}	1.740
F(000)	6090.0
Crystal size/mm^3	0.1 × 0.08 × 0.02
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	1.316 to 54.968
Index ranges	$-17 \le h \le 17$, $-27 \le k \le 27$, $-40 \le l \le 40$
Reflections collected	220441
Independent reflections	40469 [R_{int} = 0.0683, R_{sigma} = 0.0589]
Data/restraints/parameters	40469/37017/2893
Goodness-of-fit on F^2	1.102
Final R indexes [I>=2σ (I)]	R_1 = 0.0698, wR_2 = 0.1668
Final R indexes [all data]	R_1 = 0.1007, wR_2 = 0.1822
Largest diff. peak/hole / e Å^{-3}	5.74/-2.29

With a better (numerical) absorption correction, the quality of the structure would certainly improve greatly.

Table 2 Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for p-1_a. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
I001	9538.7(5)	14164.4(3)	8760.4(2)	24.20(13)
I002	4513.9(5)	143.6(3)	10698.7(2)	23.95(13)
I003	4297.2(5)	7052.5(3)	7328.3(2)	24.05(13)
I004	5775.3(5)	6564.8(3)	6014.0(2)	25.75(13)
I005	389.9(5)	9057.6(3)	4735.9(2)	24.24(13)
I006	10726.5(5)	12453.9(3)	8057.5(2)	25.07(13)
Mo07	5583.1(5)	601.6(3)	9959.5(2)	13.28(13)
Mo08	509.6(5)	9762.9(3)	5406.8(2)	13.45(14)
Mo09	9586.9(5)	13576.7(3)	8015.4(2)	15.81(14)
Mo0A	10672.6(5)	13033.2(3)	8800.5(2)	15.03(14)
Mo0B	5587.6(5)	7415.4(3)	6625.1(2)	15.14(14)
Mo0C	4495.6(5)	6185.8(3)	6716.2(2)	16.40(14)
Al0D	9385.9(16)	7883.6(10)	8048.3(7)	8.5(4)
Al0E	4435.5(16)	4819.7(10)	9552.0(7)	8.2(4)
Al0F	555.4(17)	5448.6(10)	5341.2(7)	11.2(4)
Al0G	10492.8(16)	8959.5(10)	8594.5(7)	9.4(4)
Al0H	5658.2(17)	12024.5(11)	7047.0(7)	11.9(4)
Al0I	4502.8(17)	11530.6(11)	6197.3(7)	12.5(4)
F00J	5000	5000	10000	10.6(11)
F00K	0	5000	5000	12.0(12)
F00L	9948(3)	8427(2)	8315.4(14)	14.5(9)
F00M	5093(3)	11780(2)	6616.8(14)	16.6(9)
O1P	9308(6)	13183(3)	7080(2)	35.4(16)
O04M	8647(5)	12412(3)	9218(2)	34.5(16)
O04Q	6093(5)	1694(3)	10511(2)	28.6(14)
O04T	8238(6)	14785(3)	7688(2)	36.9(16)
O052	7497(5)	6646(3)	6998(3)	38.2(17)
O053	1737(5)	8556(3)	5799(2)	34.6(16)
O054	3590(5)	1451(3)	9732(3)	42.3(19)
O057	-1602(5)	9311(3)	5890(2)	35.4(16)
O05D	11119(5)	13341(3)	9735(2)	29.9(15)
O05E	12673(5)	13682(4)	8377(2)	44(2)
O05G	3703(5)	8125(3)	6204(2)	38.2(17)
O05I	6360(6)	5454(3)	7145(3)	43.0(19)
O05L	919(5)	10245(3)	6298(2)	31.0(15)
O05M	5814(5)	8616(3)	7143(2)	32.7(15)
O05O	7575(5)	-232(3)	10209(3)	42.8(19)
O05S	6926(5)	1451(3)	9274(2)	35.5(16)
O05U	2615(5)	10245(4)	4948(2)	48(2)
O05W	4309(5)	5016(3)	6171(2)	34.2(16)
O05X	2565(6)	6905(3)	6331(3)	48(2)
O05Y	11983(6)	11788(4)	9104(2)	45(2)
O05Z	7096(6)	8180(3)	5957(3)	41.7(19)
O060	11572(6)	14251(4)	7605(2)	44(2)
O061	3004(5)	5399(3)	7383(2)	38.1(17)
O063	7589(5)	12918(4)	8413(2)	48(2)
C066	-874(6)	9469(4)	5713(3)	19.4(16)
C068	9350(6)	12624(4)	9067(3)	19.0(16)
C06A	6447(7)	1131(4)	9506(3)	21.4(17)
C06F	10886(7)	14013(5)	7750(3)	27.7(19)
C06I	8693(7)	14366(4)	7813(3)	23.4(17)
C06K	8285(7)	13149(5)	8279(3)	27.2(19)

C06M	1307(7)	8967(4)	5654(3)	22.3(17)
C06W	1868(7)	10068(5)	5099(3)	26.2(19)
C06X	11526(7)	12223(4)	8986(3)	23.6(17)
C070	3541(7)	5691(4)	7155(3)	24.3(17)
C073	6888(7)	43(4)	10118(3)	24.1(18)
C074	5713(7)	5716(4)	6992(3)	24.8(18)
C075	6572(7)	7901(4)	6186(3)	23.5(17)
C079	4284(7)	1152(4)	9810(3)	23.5(17)
C07H	3241(7)	6661(4)	6464(3)	26.5(18)
C07J	9416(7)	13311(4)	7416(3)	25.4(18)
C07M	6819(7)	6914(4)	6875(3)	24.8(18)
C07O	4355(7)	7876(4)	6354(3)	22.6(17)
C07T	758(6)	10094(4)	5979(3)	18.5(15)
C07U	5902(6)	1305(4)	10325(3)	20.1(16)
C07Z	10939(7)	13254(4)	9402(3)	22.5(17)
C080	4393(7)	5431(4)	6357(3)	23.5(17)
C084	11971(7)	13449(5)	8522(3)	28.1(19)
C08E	5724(7)	8185(4)	6970(3)	22.8(17)
O1_21	-79(4)	6186(2)	5347.8(18)	20.5(12)
C1_21	-63(5)	6802(3)	5211(2)	18.8(14)
C2_21	704(6)	7113(3)	5436(3)	32.7(19)
F1_21	347(6)	7238(3)	5837.1(19)	55.9(19)
F2_21	944(5)	7666(2)	5230(2)	45.9(16)
F3_21	1561(4)	6744(2)	5451(2)	40.9(14)
C3_21	259(6)	6873(4)	4716(2)	25.4(16)
F4_21	-144(5)	6443(3)	4521.1(18)	40.1(14)
F5_21	1254(4)	6766(3)	4612.5(18)	36.0(13)
F6_21	-32(4)	7442(2)	4549.7(17)	33.3(12)
C4_21	-1139(6)	7134(4)	5330(3)	36(2)
F7_21	-1750(4)	6971(3)	5069(2)	51.4(17)
F8_21	-1152(5)	7753(2)	5298(2)	51.6(18)
F9_21	-1514(5)	6959(3)	5732(2)	58(2)
O1_20	310(5)	5062(3)	5837.8(17)	22.7(12)
C1_20	328(5)	5072(3)	6266(2)	22.6(15)
C2_20	-391(7)	5633(4)	6464(3)	47(2)
F1_20	66(7)	6168(3)	6370(2)	73(2)
F2_20	-598(5)	5534(4)	6895.7(17)	55.9(19)
F3_20	-1258(5)	5684(4)	6308(2)	57.3(19)
C3_20	-16(7)	4449(4)	6493(3)	42(2)
F4_20	430(6)	3966(3)	6269(2)	49.9(17)
F5_20	-1037(5)	4480(4)	6533(2)	59(2)
F6_20	278(6)	4362(3)	6888.4(19)	57(2)
C4_20	1419(7)	5148(5)	6354(3)	45(2)
F7_20	1985(5)	4578(4)	6299(2)	59.1(19)
F8_20	1456(5)	5343(3)	6747.4(18)	48.4(17)
F9_20	1842(5)	5586(3)	6072.3(19)	47.9(17)
O1_19	5242(5)	11720(3)	5727.4(18)	28.4(14)
C1_19	5305(5)	12041(3)	5338(2)	19.8(15)
C2_19	4771(7)	11703(4)	5023(2)	35.2(19)
F1_19	5331(6)	11177(3)	4898(2)	65(2)
F2_19	4599(5)	12061(3)	4671.7(18)	52.1(18)
F3_19	3875(5)	11548(3)	5224(2)	45.4(16)
C3_19	4825(6)	12730(4)	5374(3)	32.2(18)
F4_19	5040(5)	12953(3)	5726(2)	51.1(17)

F5_19	3823(4)	12758(3)	5385(2)	48.5(17)
F6_19	5184(4)	13094(3)	5032.1(19)	40.0(14)
C4_19	6446(6)	12044(4)	5152(2)	34.7(19)
F7_19	6873(5)	12452(3)	5352(2)	52.3(17)
F8_19	6585(5)	12206(3)	4728.0(17)	43.1(15)
F9_19	6948(5)	11476(3)	5206(2)	58(2)
O1_18	3350(4)	11941(3)	6228.8(19)	26.7(13)
C1_18	2462(5)	12154(4)	6461(2)	28.3(17)
C2_18	2628(6)	12755(4)	6681(3)	37(2)
F1_18	3134(5)	12598(3)	7021(2)	49.6(17)
F2_18	1756(4)	13075(3)	6834(2)	49.9(17)
F3_18	3167(5)	13135(3)	6412(2)	53.6(17)
C3_18	1658(6)	12318(4)	6149(3)	33.7(19)
F4_18	1678(5)	11853(3)	5883(2)	52.5(18)
F5_18	1845(5)	12844(3)	5910(2)	51.1(16)
F6_18	725(4)	12422(3)	6356(2)	44.8(16)
C4_18	2103(6)	11645(4)	6807(2)	30.7(18)
F7_18	1725(5)	11191(3)	6640(2)	47.5(16)
F8_18	1394(5)	11880(3)	7113(2)	52.6(18)
F9_18	2884(4)	11386(3)	7003.1(19)	45.5(15)
O1_17	4574(5)	10740(3)	6305(2)	27.9(14)
C1_17	4463(5)	10147(3)	6223(2)	21.0(15)
C2_17	3812(6)	10128(4)	5845(2)	26.5(17)
F1_17	3059(4)	10590(2)	5872.4(18)	31.4(12)
F2_17	3414(4)	9590(2)	5848.4(18)	34.2(13)
F3_17	4386(4)	10217(3)	5465.2(16)	36.1(13)
C3_17	5507(6)	9788(4)	6101(3)	30.7(18)
F4_17	5986(4)	9642(3)	6446.5(19)	41.5(14)
F5_17	6105(4)	10126(3)	5821.4(19)	41.4(14)
F6_17	5424(5)	9244(3)	5924(2)	45.8(16)
C4_17	3903(6)	9829(4)	6641(2)	29.8(18)
F7_17	4244(5)	9984(3)	6986.9(17)	46.6(16)
F8_17	4002(5)	9205(3)	6635(2)	46.4(16)
F9_17	2911(4)	10012(3)	6678.4(19)	42.5(15)
O1_16	5475(5)	12824(3)	6988(2)	29.0(14)
C1_16	5601(5)	13414(3)	7080(2)	24.8(16)
C2_16	6314(6)	13414(4)	7436(3)	29.8(18)
F1_16	5820(5)	13286(3)	7824.0(19)	48.2(16)
F2_16	6702(4)	13954(3)	7442(2)	40.3(14)
F3_16	7077(4)	12967(3)	7371(2)	41.3(14)
C3_16	6082(7)	13776(4)	6663(3)	38(2)
F4_16	5664(6)	13661(3)	6327(2)	60(2)
F5_16	7072(5)	13601(3)	6590(2)	56.4(18)
F6_16	5966(6)	14399(3)	6698(2)	55.5(18)
C4_16	4567(6)	13768(4)	7247(3)	33.6(19)
F7_16	4013(5)	13932(3)	6923(2)	44.9(16)
F8_16	4666(5)	14285(3)	7440(2)	54.5(19)
F9_16	4024(5)	13397(3)	7528(2)	53.0(17)
O1_15	6867(4)	11688(3)	6993.9(19)	27.0(14)
C1_15	7744(5)	11510(3)	6744(2)	22.0(15)
C2_15	7605(6)	10902(4)	6525(3)	28.4(17)
F1_15	7140(5)	10496(3)	6801(2)	47.4(16)
F2_15	8473(4)	10605(3)	6352.1(19)	38.1(14)
F3_15	7044(4)	11036(3)	6199.7(19)	38.5(14)

C3_15	8008(6)	12030(4)	6390(2)	28.5(17)
F4_15	8397(4)	12494(2)	6541.3(19)	37.7(13)
F5_15	7146(5)	12292(3)	6236.8(19)	41.5(14)
F6_15	8639(5)	11825(3)	6059(2)	51.4(18)
C4_15	8606(6)	11373(4)	7028(3)	29.8(18)
F7_15	8575(5)	11822(3)	7296.3(19)	42.7(15)
F8_15	9522(4)	11344(4)	6786(2)	55.2(18)
F9_15	8546(5)	10826(3)	7248(2)	54.4(18)
O1_14	4955(5)	11750(3)	7503.3(19)	34.4(16)
C1_14	4907(5)	11413(3)	7885(2)	23.6(16)
C2_14	3768(7)	11364(5)	8058(3)	57(3)
F1_14	3238(7)	11914(4)	8007(4)	119(4)
F2_14	3652(6)	11190(4)	8482(2)	77(3)
F3_14	3404(5)	10944(4)	7843(3)	76(2)
C3_14	5436(6)	10732(4)	7842(3)	37(2)
F4_14	6435(4)	10745(4)	7807(3)	76(3)
F5_14	5251(7)	10517(4)	7483(3)	77(2)
F6_14	5125(5)	10347(3)	8169(2)	54.1(18)
C4_14	5416(8)	11747(5)	8205(3)	67(3)
F7_14	6294(7)	11931(4)	8013(2)	84(3)
F8_14	5593(8)	11374(4)	8549(2)	96(3)
F9_14	4792(10)	12256(4)	8330(3)	135(5)
O1_12	1788(4)	5450(3)	5121(2)	24.2(13)
C1_12	2651(5)	5180(3)	4905(2)	22.3(15)
C2_12	2993(6)	4551(4)	5144(2)	27.5(17)
F1_12	3404(4)	4642(3)	5490.1(17)	35.2(13)
F2_12	3680(4)	4195(3)	4888.5(18)	39.3(14)
F3_12	2205(4)	4221(3)	5268.1(19)	36.7(13)
C3_12	2464(6)	5051(4)	4440(2)	28.4(17)
F4_12	1898(5)	5531(3)	4278.0(18)	39.1(14)
F5_12	1971(4)	4535(3)	4452.1(18)	33.7(12)
F6_12	3318(4)	4967(3)	4171.8(17)	35.4(13)
C4_12	3478(6)	5641(4)	4877(3)	29.3(17)
F7_12	3264(4)	6132(3)	4607(2)	42.5(15)
F8_12	4394(4)	5389(3)	4735(2)	43.9(15)
F9_12	3489(4)	5862(3)	5265.1(18)	39.1(14)
O1_10	8212(4)	7839(3)	8338.8(17)	15.4(11)
C1_10	7198(5)	7990(3)	8361(2)	14.5(13)
C2_10	6966(5)	8708(3)	8252(2)	21.5(15)
F1_10	7569(4)	9030(2)	8435.8(19)	36.3(13)
F2_10	6012(4)	8915(3)	8394.3(19)	34.9(13)
F3_10	7132(4)	8846(2)	7828.6(16)	28.5(11)
C3_10	6779(5)	7611(3)	8030(2)	19.3(15)
F4_10	6759(4)	7013(2)	8168.1(17)	29.3(12)
F5_10	7367(4)	7632(2)	7649.5(15)	24.5(11)
F6_10	5844(4)	7842(3)	7965.1(17)	30.1(12)
C4_10	6691(5)	7814(3)	8823(2)	20.7(15)
F7_10	7104(4)	7262(2)	8967.2(17)	30.8(12)
F8_10	5696(4)	7775(3)	8837.1(17)	36.1(14)
F9_10	6805(4)	8245(3)	9099.0(16)	32.7(12)
O1_9	10185(4)	7212(2)	8101.7(19)	18.6(12)
C1_9	10281(5)	6575(3)	8142(2)	14.0(13)
C2_9	10025(6)	6302(4)	7730(2)	29.4(18)
F1_9	9187(5)	6611(3)	7607(2)	45.3(16)

F2_9	9871(5)	5695(2)	7794(2)	45.8(16)
F3_9	10773(5)	6362(3)	7399.0(17)	45.9(15)
C3_9	11402(5)	6360(3)	8200(2)	19.5(15)
F4_9	11583(4)	6497(2)	8587.8(16)	28.7(11)
F5_9	12036(4)	6662(2)	7906.3(18)	30.9(12)
F6_9	11633(4)	5745(2)	8157.8(17)	28.2(11)
C4_9	9570(5)	6336(3)	8544(2)	20.7(15)
F7_9	9570(4)	6689(3)	8873.2(16)	35.2(13)
F8_9	9851(4)	5739(2)	8668.8(18)	33.7(13)
F9_9	8629(4)	6365(2)	8452(2)	36.8(14)
O1_8	9335(4)	8186(3)	7536.6(16)	19.0(12)
C1_8	9714(5)	8424(3)	7146(2)	17.1(14)
C2_8	10846(5)	8529(4)	7140(2)	25.7(16)
F1_8	10938(4)	9025(3)	7360.3(18)	34.0(13)
F2_8	11337(4)	8614(3)	6742.6(17)	40.5(15)
F3_8	11333(4)	8031(3)	7329.8(19)	37.6(13)
C3_8	9615(6)	7971(4)	6793(2)	28.9(17)
F4_8	8702(4)	7758(3)	6857.3(18)	39.1(14)
F5_8	10308(5)	7483(3)	6801(2)	45.5(15)
F6_8	9734(5)	8257(3)	6395.8(16)	37.7(14)
C4_8	9096(6)	9065(3)	7049(2)	25.5(16)
F7_8	8190(4)	8981(3)	6947.8(18)	35.6(13)
F8_8	9582(5)	9402(3)	6723.1(19)	43.2(15)
F9_8	8957(4)	9408(2)	7392.4(19)	37.0(13)
O1_7	9673(4)	9629(2)	8573.4(19)	18.8(11)
C1_7	9582(5)	10261(3)	8508(2)	16.6(14)
C2_7	9855(6)	10561(3)	8907(2)	28.1(17)
F1_7	9120(5)	10519(3)	9244.0(16)	38.7(14)
F2_7	9987(5)	11174(2)	8823.9(18)	39.4(15)
F3_7	10708(4)	10271(3)	9023.1(18)	38.4(14)
C3_7	10265(5)	10484(3)	8095(2)	19.4(15)
F4_7	10299(4)	10090(2)	7784.4(16)	30.5(12)
F5_7	11212(4)	10507(2)	8175.7(18)	30.9(12)
F6_7	9936(4)	11057(2)	7939.5(16)	28.3(11)
C4_7	8454(5)	10466(3)	8456(2)	23.7(16)
F7_7	8260(4)	10295(3)	8079.7(17)	33.2(12)
F8_7	8230(4)	11090(2)	8471.9(19)	37.3(14)
F9_7	7826(4)	10196(2)	8766.0(17)	30.4(12)
O1_6	11651(4)	9044(3)	8302.6(17)	16.5(11)
C1_6	12670(5)	8902(3)	8286(2)	19.0(14)
C2_6	12913(6)	8189(3)	8395(2)	25.3(16)
F1_6	12762(4)	8051(2)	8817.8(16)	28.0(11)
F2_6	13877(4)	7988(3)	8251.0(19)	37.2(13)
F3_6	12321(4)	7860(3)	8213.6(19)	35.5(13)
C3_6	13180(6)	9079(4)	7823(2)	29.1(17)
F4_6	12746(4)	9629(3)	7675.2(17)	34.7(13)
F5_6	13067(4)	8644(3)	7548.0(17)	34.2(13)
F6_6	14165(4)	9130(3)	7808.9(18)	38.8(14)
C4_6	13080(5)	9294(4)	8613(2)	23.4(16)
F7_6	13083(4)	9891(3)	8472.7(18)	36.9(13)
F8_6	14021(4)	9078(3)	8677.9(18)	34.9(13)
F9_6	12491(4)	9275(2)	8994.8(15)	28.0(11)
O1_5	10573(4)	8635(3)	9098.4(17)	19.4(12)
C1_5	10212(5)	8395(3)	9493(2)	16.5(14)

C2_5	9070(5)	8297(4)	9507(2)	24.8(16)
F1_5	8575(4)	8802(3)	9334(2)	41.4(15)
F2_5	8606(4)	8193(3)	9907.3(17)	39.2(14)
F3_5	8968(4)	7814(3)	9279.7(18)	35.1(13)
C3_5	10832(6)	7753(3)	9579(2)	23.8(16)
F4_5	11747(4)	7834(3)	9667.1(19)	34.2(13)
F5_5	10944(4)	7419(2)	9237.1(19)	36.7(13)
F6_5	10376(5)	7418(3)	9912.7(19)	41.0(15)
C4_5	10315(6)	8857(4)	9840(2)	27.0(17)
F7_5	11247(4)	9042(3)	9784.4(18)	39.9(14)
F8_5	10153(5)	8586(3)	10239.7(16)	46.6(16)
F9_5	9672(5)	9364(3)	9820(2)	47.5(16)
O1_4	5215(4)	5122(3)	9127.7(16)	18.2(11)
C1_4	5280(5)	5383(3)	8718(2)	14.5(13)
C2_4	6412(5)	5509(3)	8576(2)	20.5(15)
F1_4	6634(4)	5979(2)	8788.6(16)	28.0(11)
F2_4	6599(4)	5660(3)	8152.6(15)	30.8(12)
F3_4	7035(4)	5006(2)	8666.0(17)	31.6(12)
C3_4	4971(6)	4933(4)	8408(2)	31.8(18)
F4_4	4130(5)	4675(3)	8590(2)	44.1(15)
F5_4	5692(5)	4463(3)	8321(2)	48.6(16)
F6_4	4772(5)	5222(3)	8031.7(17)	46.4(16)
C4_4	4599(5)	6018(3)	8700(2)	21.1(15)
F7_4	3631(4)	5912(3)	8702.4(18)	35.7(14)
F8_4	4850(4)	6375(2)	8341.7(16)	31.7(12)
F9_4	4646(4)	6344(2)	9034.5(17)	34.9(13)
O1_3	3262(4)	5224(2)	9625.2(17)	14.2(10)
C1_3	2257(5)	5190(3)	9742(2)	14.6(13)
C2_3	1724(5)	5866(3)	9792(2)	21.3(15)
F1_3	1852(4)	6092(2)	10166.2(16)	26.5(11)
F2_3	722(3)	5898(3)	9778(2)	33.4(13)
F3_3	2111(4)	6257(2)	9479.2(17)	26.5(11)
C3_3	1802(5)	4881(3)	9385(2)	18.9(15)
F4_3	2402(3)	4368(2)	9256.6(16)	21.7(10)
F5_3	1744(4)	5273(2)	9037.0(16)	31.2(12)
F6_3	883(4)	4706(2)	9520.7(18)	29.6(12)
C4_3	2054(5)	4800(3)	10177(2)	18.8(15)
F7_3	2232(4)	4190(2)	10122.5(16)	25.9(11)
F8_3	1107(4)	4904(2)	10371.4(17)	28.5(12)
F9_3	2667(4)	4947(3)	10449.5(16)	30.1(12)
O1_2	4403(4)	4025(2)	9575.4(19)	18.6(12)
C1_2	4809(5)	3422(3)	9615(2)	14.4(13)
C2_2	4692(6)	3092(3)	9204(2)	27.9(17)
F1_2	3768(4)	3221(3)	9096.3(18)	36.5(13)
F2_2	4858(5)	2466(2)	9260.8(19)	37.9(14)
F3_2	5357(5)	3273(3)	8872.3(17)	41.5(14)
C3_2	5948(5)	3395(3)	9670(2)	22.0(15)
F4_2	6048(4)	3541(3)	10067.3(16)	28.8(12)
F5_2	6403(4)	3809(3)	9392.7(18)	36.2(13)
F6_2	6437(4)	2824(2)	9606(2)	34.9(13)
C4_2	4209(5)	3096(3)	10016(2)	21.2(15)
F7_2	4080(4)	3454(3)	10350.7(16)	30.4(12)
F8_2	4696(4)	2547(2)	10136.3(19)	37.5(14)
F9_2	3296(4)	2979(2)	9936.5(18)	28.9(12)

$[W_2(CO)_8Cl_3][F\text{-}\{Al(OR^F)_3\}_2]$

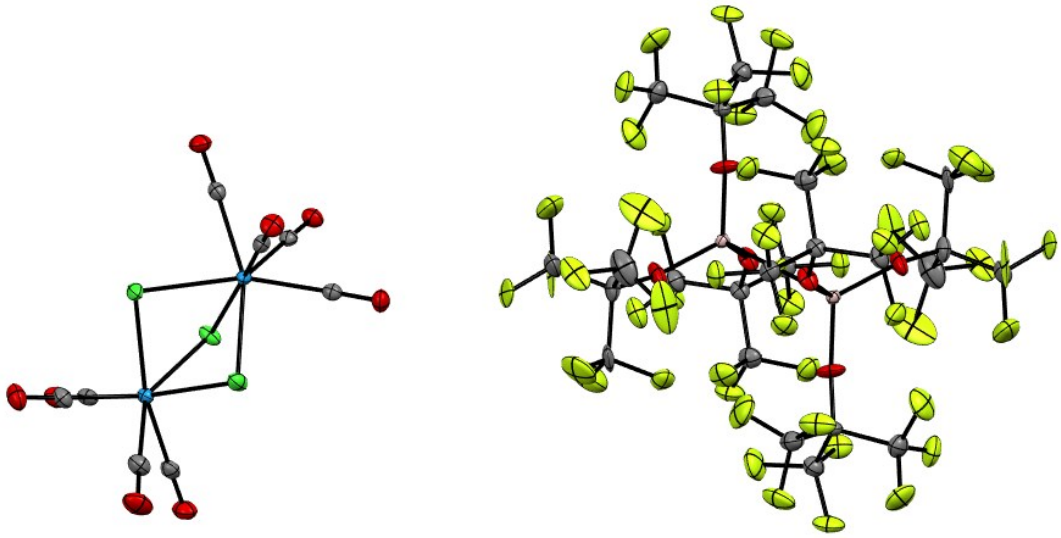


Table 1 Crystal data and structure refinement for p-1_crystscale_a.

CCDC Deposition Number	1952387
Identification code	p-1_crystscale_a
Empirical formula	$C_{32}O_{14}F_{55}Al_2Cl_3W_2$
Formula weight	2181.33
Temperature/K	100.02
Crystal system	triclinic
Space group	P-1
a/Å	11.3269(6)
b/Å	12.2795(6)
c/Å	23.4349(11)
α/°	76.8830(10)
β/°	86.1610(10)
γ/°	66.4850(10)
Volume/Å^3	2909.8(3)
Z	2
ρ_{calc}g/cm^3	2.490
μ/mm^{-1}	4.354
F(000)	2048.0
Crystal size/mm^3	0.2 × 0.08 × 0.05
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	1.784 to 56.564
Index ranges	$-15 \le h \le 15$, $-16 \le k \le 16$, $-31 \le l \le 31$
Reflections collected	76325
Independent reflections	14432 [R_{int} = 0.0278, R_{sigma} = 0.0219]
Data/restraints/parameters	14432/9027/1206
Goodness-of-fit on F^2	1.034
Final R indexes [I>=2σ (I)]	R_1 = 0.0190, wR_2 = 0.0382
Final R indexes [all data]	R_1 = 0.0260, wR_2 = 0.0406
Largest diff. peak/hole / e Å^{-3}	0.92/-0.83

Table 2 Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for p-1_crystscale_a. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
W1	10777.7(2)	8672.8(2)	2664.9(2)	13.96(2)
Al1	4302.9(6)	1519.8(6)	4606.9(3)	10.94(12)
F2	5000	5000	0	16.1(4)
O1	9651.0(18)	11537.6(16)	2485.9(8)	27.8(4)
C1	10069(2)	10518(2)	2546.4(11)	19.7(5)
Cl1	10964.4(6)	6502.7(5)	2887.0(3)	22.29(12)
Cl3	10355.7(6)	8335.6(6)	1683.2(2)	21.55(12)
O3	13572.5(18)	7220.2(18)	3232.9(9)	36.4(5)
C3	12577(2)	7760(2)	3022.2(12)	24.2(5)
O6	8715.7(17)	4933.8(16)	3058.9(8)	24.1(4)
C6	8817(2)	5747(2)	2754.3(10)	16.7(5)
C5	9943(2)	5705(2)	1816.0(10)	18.0(5)
O5	10410.8(18)	4890.1(16)	1610.9(8)	26.3(4)
C4	10660(2)	8944(2)	3498.5(11)	20.7(5)
O4	10582.6(18)	9088.9(18)	3960.8(8)	29.8(4)
O7	6112.9(16)	7981.0(15)	2383.6(8)	21.8(4)
C7	7182(2)	7666(2)	2308.8(10)	16.3(4)
O8	7817.8(17)	8019.1(16)	930.2(8)	24.8(4)
C8	8241(2)	7717(2)	1391.5(11)	17.8(5)
W2	9098.2(2)	7155.1(2)	2200.9(2)	12.46(2)
Al2	5885.8(6)	3845.5(6)	595.5(3)	10.71(12)
F1	5000	0	5000	19.0(4)
O2	12690.3(18)	9536.3(17)	1836.2(8)	30.4(4)
C2	12019(2)	9224(2)	2141.6(11)	21.0(5)
Cl2	8499.1(5)	8926.0(5)	2712.3(3)	19.89(12)
O1_8	5380(30)	2160(30)	4495(18)	28.7(6)
C1_8	6496(16)	2160(12)	4263(7)	23(3)
C2_8	6258(16)	3381(14)	3828(7)	34(4)
F1_8	5727(17)	3412(17)	3336(5)	66(5)
F2_8	7321(15)	3590(20)	3731(7)	43(4)
F3_8	5397(15)	4299(11)	4036(8)	57(4)
C3_8	7381(15)	2058(13)	4776(6)	32(3)
F4_8	7291(10)	1223(11)	5222(4)	31(3)
F5_8	6855(15)	3091(14)	4961(8)	60(4)
F6_8	8587(14)	1644(17)	4576(8)	57.5(8)
C4_8	7245(16)	1044(14)	3992(7)	48(4)
F7_8	7789(12)	74(9)	4451(8)	70(5)
F8_8	8230(20)	1180(30)	3687(13)	43(6)
F9_8	6461(14)	890(20)	3653(8)	73(6)
O1_7	7435(8)	3525(14)	440(5)	15.9(11)
C1_7	8660(11)	2749(9)	385(4)	18.5(5)
C2_7	8961(6)	2449(6)	-230(3)	30.3(15)
F1_7	8032(13)	2173(15)	-396(6)	58(4)
F2_7	10084(5)	1520(6)	-226(3)	41.2(14)
F3_7	9022(10)	3402(10)	-623(4)	45(2)
C3_7	9501(6)	3405(6)	511(3)	29.6(15)
F4_7	9563(11)	3339(12)	1085(4)	53(2)
F5_7	9000(20)	4567(9)	257(8)	53(4)
F6_7	10702(9)	2910(14)	343(5)	31(2)
C4_7	8933(5)	1565(5)	849(2)	21.4(13)
F7_7	8367(14)	1767(13)	1352(6)	40(3)
F8_7	10183(6)	966(6)	984(4)	43.8(18)

F9_7	8523(17)	814(13)	677(5)	26.4(19)
O1_6	7392(5)	3515(9)	295(3)	15.9(11)
C1_6	8665(7)	2742(6)	393(3)	18.5(5)
C2_6	8869(4)	1614(4)	148(2)	32.1(11)
F1_6	8466(12)	862(9)	519(3)	37.3(17)
F2_6	10110(3)	1003(4)	41(2)	47.5(10)
F3_6	8221(8)	1938(10)	-358(4)	47.7(19)
C3_6	9467(4)	3433(5)	44(2)	35.6(12)
F4_6	9082(12)	4532(6)	145(5)	45.8(19)
F5_6	9324(7)	3551(8)	-531(3)	58.4(19)
F6_6	10720(6)	2861(11)	170(3)	38.4(18)
C4_6	9137(4)	2311(4)	1046.1(18)	24.8(10)
F7_6	9305(7)	3188(6)	1228(2)	39.8(12)
F8_6	10228(4)	1330(4)	1140(2)	33.4(9)
F9_6	8215(8)	2076(8)	1373(3)	28.3(15)
O1_5	5508.7(19)	4475.5(15)	1191.6(7)	25.0(4)
C1_5	5370(2)	5350(2)	1481.6(10)	16.2(4)
C2_5	5486(3)	6476(2)	1058.5(11)	23.1(5)
F1_5	6464.6(18)	6114.6(15)	706.5(7)	39.1(4)
F2_5	5666.4(16)	7224.9(13)	1341.6(7)	30.3(4)
F3_5	4435.8(17)	7103.8(14)	720.1(7)	37.3(4)
C3_5	4022(3)	5725(2)	1758.7(12)	29.2(6)
F4_5	4009.0(18)	4883.2(15)	2225.5(7)	41.0(4)
F5_5	3130.2(16)	5862.5(16)	1379.7(9)	47.4(5)
F6_5	3678.9(17)	6780.9(15)	1924.8(9)	46.2(5)
C4_5	6417(3)	4847(2)	1974.1(12)	28.0(6)
F7_5	6609.7(18)	3713.2(14)	2234.6(7)	39.8(4)
F8_5	6101.6(19)	5513.1(15)	2380.4(7)	41.8(4)
F9_5	7539.4(17)	4843.9(18)	1759.1(9)	50.1(5)
O1_4	5398.4(16)	2685.5(14)	651.2(7)	16.7(3)
C1_4	4795(2)	1981(2)	955.8(10)	15.4(4)
C2_4	5536(2)	1227(2)	1542.3(10)	20.4(5)
F1_4	6627.8(15)	316.2(13)	1447.1(7)	30.3(3)
F2_4	4852.0(16)	729.3(13)	1912.8(6)	29.7(3)
F3_4	5875.0(15)	1909.3(13)	1809.6(6)	26.2(3)
C3_4	3393(2)	2782(2)	1090.2(11)	23.3(5)
F4_4	2849.0(15)	3666.1(14)	626.3(7)	35.3(4)
F5_4	3380.2(15)	3303.2(14)	1532.5(7)	29.6(3)
F6_4	2663.7(15)	2143.5(15)	1233.4(8)	36.1(4)
C4_4	4780(3)	1099(2)	575.4(11)	23.6(5)
F7_4	3878.8(16)	1676.5(14)	151.4(7)	32.6(4)
F8_4	4540.4(18)	162.9(14)	893.4(7)	34.8(4)
F9_4	5898.1(16)	657.4(13)	322.1(7)	31.4(4)
O1_3	3171.9(16)	2208.3(15)	5067.5(8)	21.7(4)
C1_3	2746(2)	3056(2)	5401.2(10)	16.7(4)
C2_3	2710(2)	4305(2)	5048.2(12)	24.5(5)
F1_3	3895.7(15)	4291.2(14)	5005.5(7)	33.2(4)
F2_3	1981.8(15)	5218.0(13)	5293.6(7)	31.5(4)
F3_3	2249.0(18)	4533.9(15)	4507.8(7)	40.2(4)
C3_3	1364(2)	3184(2)	5588.1(11)	21.3(5)
F4_3	1310.0(14)	2104.4(14)	5789.5(7)	29.7(3)
F5_3	546.6(14)	3745.9(14)	5134.4(7)	30.1(3)
F6_3	942.0(15)	3815.3(15)	6008.4(7)	35.1(4)
C4_3	3632(2)	2634(2)	5953.9(11)	25.2(5)

F7_3	3427.7(16)	1749.7(15)	6342.8(7)	35.2(4)
F8_3	3439.3(16)	3531.3(15)	6228.2(7)	33.9(4)
F9_3	4862.9(14)	2188.3(16)	5813.6(7)	35.8(4)
O1_2	3686.0(17)	1371.6(17)	4002.5(7)	26.7(4)
C1_2	2761(2)	1761(2)	3580.2(10)	16.3(4)
C2_2	1407(3)	2058(3)	3848.8(11)	28.7(6)
F1_2	1459.4(19)	1259(2)	4335.5(8)	54.0(5)
F2_2	558.2(15)	2053.4(18)	3481.4(8)	43.5(5)
F3_2	950.2(15)	3155.4(17)	3976.3(7)	40.1(4)
C3_2	2771(3)	2909(2)	3141.6(12)	27.4(6)
F4_2	3770.8(17)	2620.0(16)	2793.5(7)	39.3(4)
F5_2	2867.2(18)	3683.1(15)	3431.5(9)	45.5(5)
F6_2	1698.7(17)	3483.9(15)	2804.8(7)	42.4(4)
C4_2	3082(2)	722(2)	3248.8(11)	24.8(5)
F7_2	4321.3(15)	238.1(14)	3145.2(7)	31.8(4)
F8_2	2434.1(16)	1103.9(16)	2734.2(7)	35.7(4)
F9_2	2765.4(18)	-166.7(15)	3566.3(8)	44.8(5)
O1_1	5486(4)	2047(5)	4476(3)	28.7(6)
C1_1	6515(3)	2184(3)	4191.0(15)	18.4(7)
C2_1	6934(3)	1410(3)	3720.6(16)	28.9(7)
F1_1	6896(3)	325(2)	3935.9(16)	59.6(9)
F2_1	8121(5)	1233(6)	3536(2)	57.7(15)
F3_1	6172(2)	1922(2)	3249.1(9)	42.4(6)
C3_1	6132(4)	3546(4)	3891.8(18)	30.8(9)
F4_1	6035(3)	4197(2)	4281.4(12)	50.0(7)
F5_1	5014(3)	3984(2)	3612.0(15)	62.2(9)
F6_1	7004(4)	3691(4)	3505.7(12)	51.5(9)
C4_1	7637(4)	1790(4)	4635.9(19)	45.3(11)
F7_1	7209(3)	2212(4)	5117.3(11)	66.1(10)
F8_1	8531(2)	2220(3)	4434.1(13)	57.5(8)
F9_1	8190(3)	607(3)	4790.0(15)	92.0(12)

$[W(CO)_6I][Al(OR^F)_4]$

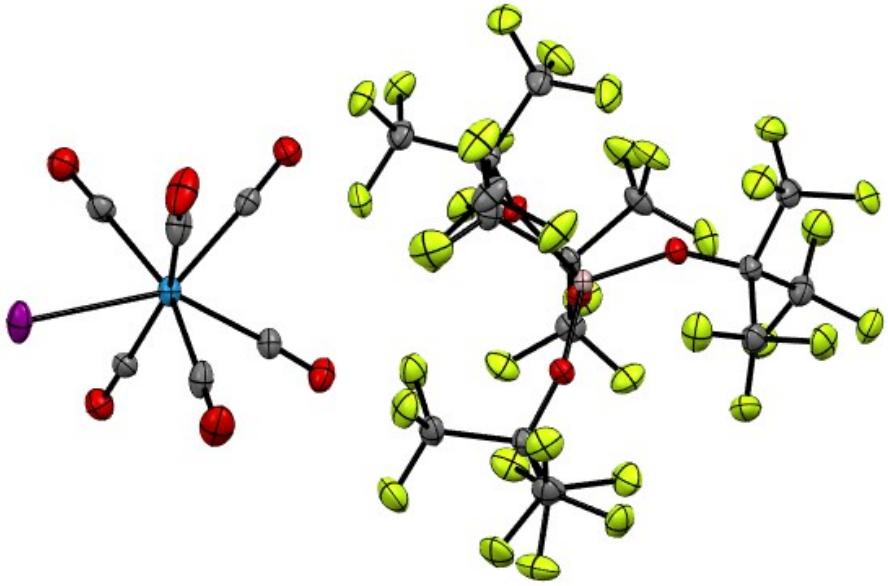


Table 1 Crystal data and structure refinement for p21c_neu_a.

CCDC Deposition Number	1952389
Identification code	p21c_neu_a
Empirical formula	$C_{44}O_{20}F_{72}Al_2I_2W_2$
Formula weight	2891.90
Temperature/K	100.0
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	16.4380(6)
b/Å	28.3511(10)
c/Å	17.5878(6)
α/°	90
β/°	110.764(2)
γ/°	90
Volume/Å^3	7664.2(5)
Z	4
ρ_{calc}g/cm^3	2.506
μ/mm^{-1}	4.070
F(000)	5408.0
Crystal size/mm^3	0.15 × 0.12 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.65 to 52.86
Index ranges	$-20 \le h \le 20$, $-35 \le k \le 35$, $-22 \le l \le 21$
Reflections collected	199573
Independent reflections	15706 [R_{int} = 0.0353, R_{sigma} = 0.0220]
Data/restraints/parameters	15706/1956/1273
Goodness-of-fit on F^2	1.054
Final R indexes [I>=2σ (I)]	R_1 = 0.0427, wR_2 = 0.1162
Final R indexes [all data]	R_1 = 0.0503, wR_2 = 0.1208
Largest diff. peak/hole / e Å^{-3}	4.91/-2.19

Table 2 Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for p21c_neu_a. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
W1	4375.5(2)	8886.2(2)	2405.4(2)	16.60(7)
O1	5313(4)	7886.5(19)	2835(4)	40.1(14)
C1	4967(5)	8237(2)	2657(5)	27.4(15)
I1	3700.4(3)	9614.4(2)	3051.6(3)	26.42(11)
W2	-728.9(2)	6269.5(2)	1888.0(2)	19.37(8)
O2	5968(3)	9069(2)	4089(3)	36.3(13)
C2	5417(4)	8987(3)	3511(4)	25.2(14)
I2	-1740.7(3)	5700.5(2)	2475.9(3)	32.99(12)
Al05	8285.6(11)	6182.1(6)	6054.6(11)	11.8(3)
O5	3040(3)	8282.4(18)	3004(3)	27.0(9)
C5	3504(4)	8479(3)	2862(5)	27.0(9)
C4	3180(4)	8989(2)	1435(4)	18.3(12)
O4	2547(3)	9054.7(17)	929(3)	25.9(10)
C3	5080(4)	9449(2)	2156(4)	20.4(12)
O3	5449(3)	9764.0(17)	2058(3)	27.7(11)
Al06	3256.7(11)	6461.9(6)	1169.3(11)	13.8(3)
O6	4723(4)	8530(2)	827(3)	38.4(13)
C6	4607(5)	8650(3)	1402(5)	28.5(14)
C12	-321(5)	5613(3)	1599(5)	27.8(14)
O12	-96(4)	5255(2)	1465(4)	42.4(14)
C11	-396(4)	6404(2)	882(4)	21.1(13)
O11	-246(3)	6464.3(19)	315(3)	29.1(11)
C10	-1930(4)	6319(2)	920(4)	21.5(13)
O10	-2581(3)	6339.7(19)	414(3)	30.2(11)
C9	-1366(4)	6787(2)	2346(4)	24.4(14)
O9	-1698(3)	7045.6(19)	2615(3)	32.2(11)
C8	81(4)	6850(2)	2141(4)	20.1(12)
O8	509(3)	7168.5(19)	2304(3)	28.6(11)
C7	239(5)	6077(3)	2994(5)	31.2(16)
O7	749(4)	5960(3)	3592(3)	45.9(16)
O1_8	2561(3)	6845.5(15)	475(3)	17.0(9)
C1_8	2191(4)	7276(2)	342(4)	18.0(11)
C2_8	1675(4)	7377(2)	919(4)	23.2(13)
F1_8	1283(3)	6982.4(15)	1028(3)	32.2(9)
F2_8	1056(3)	7704.4(15)	622(3)	33.5(10)
F3_8	2188(3)	7517.8(15)	1650(2)	32.3(9)
C3_8	2902(4)	7664(2)	491(4)	23.7(13)
F4_8	3224(3)	7666.2(15)	-96(3)	32.2(9)
F5_8	3566(3)	7582.5(14)	1183(3)	30.0(9)
F6_8	2601(3)	8096.8(14)	544(3)	36.3(10)
C4_8	1549(4)	7301(2)	-557(4)	23.6(13)
F7_8	1906(3)	7115.0(15)	-1048(2)	29.7(9)
F8_8	1327(3)	7745.9(15)	-803(3)	31.1(9)
F9_8	827(3)	7065.1(15)	-642(3)	30.7(9)
O1_7	2999(3)	5892.1(15)	819(3)	19.1(9)
C1_7	2383(4)	5591(2)	367(4)	20.2(12)
C2_7	2822(5)	5106(2)	370(5)	26.5(13)
F1_7	3281(3)	5107.7(15)	-122(3)	33.0(10)
F2_7	2252(3)	4748.9(14)	135(3)	35.8(10)
F3_7	3375(3)	5004.9(14)	1118(3)	31.6(9)
C3_7	1646(4)	5528(2)	732(4)	24.9(13)
F4_7	1426(3)	5949.5(15)	945(3)	32.9(10)

F5_7	1938(3)	5271.7(15)	1410(3)	34.8(10)
F6_7	942(3)	5322.8(17)	228(3)	40.7(11)
C4_7	1957(5)	5768(2)	-527(4)	26.1(13)
F7_7	1343(3)	6086.8(15)	-594(3)	33.1(10)
F8_7	1601(3)	5415.6(16)	-1041(3)	39.3(11)
F9_7	2552(3)	5964.0(16)	-775(3)	31.7(9)
O1_6	3111(3)	6555.7(16)	2084(3)	19.3(9)
C1_6	3423(4)	6484(2)	2896(4)	20.4(12)
C2_6	4142(4)	6852(3)	3317(4)	27.9(14)
F1_6	4883(3)	6732(2)	3216(3)	43.3(12)
F2_6	4313(3)	6880.9(18)	4118(2)	37.1(11)
F3_6	3921(3)	7277.7(17)	2999(3)	41.9(11)
C3_6	2649(5)	6555(3)	3204(4)	25.4(13)
F4_6	1941(3)	6336.9(17)	2716(3)	35.3(10)
F5_6	2447(3)	7010.5(15)	3195(3)	30.4(9)
F6_6	2821(3)	6394.5(16)	3956(2)	31.7(9)
C4_6	3789(5)	5977(3)	3106(4)	32.6(15)
F7_6	3141(4)	5661.5(16)	2917(3)	44.0(12)
F8_6	4255(3)	5923.7(19)	3892(3)	43.3(12)
F9_6	4287(3)	5868.2(18)	2678(3)	43.3(12)
O1_5	4331(3)	6570.7(16)	1296(3)	20.2(9)
C1_5	5004(4)	6507(2)	1052(4)	19.5(12)
C2_5	4884(5)	6811(3)	274(4)	26.2(13)
F1_5	4074(3)	6759.8(17)	-254(3)	35.6(10)
F2_5	5425(3)	6683.1(16)	-105(3)	33.0(10)
F3_5	5012(3)	7262.8(15)	453(3)	34.3(10)
C3_5	5845(4)	6680(3)	1742(4)	27.2(14)
F4_5	6083(3)	6365.9(18)	2353(3)	37.3(10)
F5_5	5705(3)	7084.1(17)	2043(3)	34.5(10)
F6_5	6519(3)	6737.1(17)	1496(3)	36.4(10)
C4_5	5122(4)	5983(3)	858(5)	25.5(13)
F7_5	4984(3)	5702.9(15)	1404(3)	33.9(10)
F8_5	5917(3)	5886.4(15)	850(3)	33.2(10)
F9_5	4553(3)	5859.3(15)	132(3)	32.2(9)
O1_4	8278(3)	6717.5(15)	5597(3)	18.7(9)
C1_4	7821(4)	7051(2)	5066(4)	20.3(12)
C2_4	7104(5)	7263(3)	5332(5)	32.5(15)
F1_4	6686(3)	6928.2(18)	5573(3)	40.3(11)
F2_4	6530(3)	7519.1(19)	4762(3)	49.9(13)
F3_4	7470(4)	7548.7(17)	5986(3)	47.5(13)
C3_4	8479(5)	7440(2)	5042(4)	26.7(14)
F4_4	8943(3)	7313.1(15)	4603(3)	34.4(10)
F5_4	9034(3)	7528.5(15)	5797(3)	42.4(12)
F6_4	8085(3)	7848.9(14)	4748(3)	34.7(10)
C4_4	7395(5)	6843(3)	4189(4)	25.9(13)
F7_4	7929(3)	6552.4(15)	4019(3)	32.7(10)
F8_4	7175(3)	7184.1(16)	3631(2)	34.8(10)
F9_4	6680(3)	6602.6(17)	4129(3)	37.4(10)
O1_3	7601(3)	5814.8(15)	5330(3)	19.3(9)
C1_3	7146(4)	5400(2)	5195(4)	20.8(12)
C2_3	7780(5)	4980(2)	5537(5)	27.2(14)
F1_3	8255(3)	4898.9(15)	5078(3)	32.5(10)
F2_3	7360(3)	4579.7(15)	5561(3)	38.2(11)
F3_3	8326(3)	5069.6(15)	6281(3)	35.3(10)

C3_3	6459(5)	5403(3)	5612(6)	41.4(18)
F4_3	6071(3)	5813(2)	5526(4)	58.8(16)
F5_3	6836(4)	5319.4(19)	6416(3)	51.6(13)
F6_3	5851(3)	5076(2)	5304(4)	64.8(18)
C4_3	6700(5)	5347(3)	4261(5)	31.2(15)
F7_3	6015(3)	5630.0(18)	3990(3)	55.3(15)
F8_3	6406(3)	4903.7(15)	4058(3)	36.6(11)
F9_3	7238(3)	5447.7(18)	3882(3)	41.0(11)
O1_2	7905(3)	6206.4(15)	6851(3)	17.7(9)
C1_2	8066(4)	6325(2)	7636(4)	19.1(12)
C2_2	8883(4)	6635(3)	7990(4)	25.0(13)
F1_2	9599(3)	6360.4(18)	8203(3)	38.1(11)
F2_2	8917(3)	6870.5(15)	8654(2)	27.6(9)
F3_2	8962(3)	6938.6(14)	7454(2)	26.4(8)
C3_2	7266(5)	6622(3)	7650(5)	29.7(14)
F4_2	6528(3)	6425.5(17)	7163(3)	35.7(10)
F5_2	7300(3)	7063.0(16)	7419(3)	40.3(11)
F6_2	7203(3)	6624.1(19)	8399(3)	43.8(12)
C4_2	8154(5)	5875(3)	8145(5)	34.6(15)
F7_2	7348(3)	5681.6(17)	7995(3)	41.8(11)
F8_2	8508(4)	5961(2)	8948(3)	56.0(15)
F9_2	8662(3)	5558.0(16)	7956(3)	42.4(11)
O1_1	9349(3)	5991.5(16)	6430(3)	18.0(9)
C1_1	10114(4)	5964(2)	6304(4)	15.7(11)
C2_1	9990(4)	6030(2)	5390(4)	20.2(12)
F1_1	9278(3)	5813.0(15)	4916(2)	28.3(9)
F2_1	10671(3)	5852.6(16)	5224(2)	28.9(9)
F3_1	9923(3)	6482.7(15)	5185(2)	27.7(9)
C3_1	10753(4)	6345(2)	6826(4)	21.0(12)
F4_1	11049(3)	6228.2(16)	7607(2)	29.4(9)
F5_1	10350(3)	6757.3(14)	6750(3)	28.2(9)
F6_1	11441(2)	6407.0(14)	6596(3)	25.9(8)
C4_1	10507(4)	5463(2)	6584(4)	23.5(13)
F7_1	10402(3)	5343.0(15)	7267(3)	29.9(9)
F8_1	11357(2)	5447.8(15)	6710(3)	30.6(9)
F9_1	10109(3)	5139.8(14)	6028(3)	30.3(9)

$[W(CO)_6I][F\text{-}\{Al(OR^F)_3\}_2]$

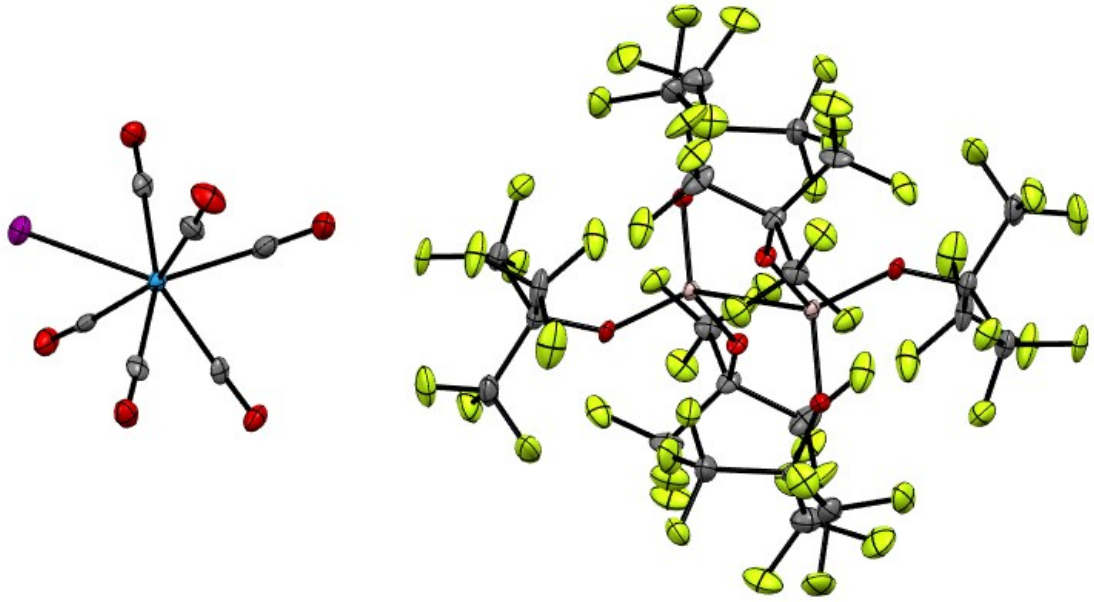


Table 1 Crystal data and structure refinement for p-1_a.

CCDC Deposition Number	1952388
Identification code	p-1_a
Empirical formula	$C_{30}O_{12}F_{55}Al_2IW$
Formula weight	1962.01
Temperature/K	100.05
Crystal system	triclinic
Space group	P-1
a/Å	10.5119(7)
b/Å	12.5617(8)
c/Å	21.1226(15)
α/°	85.595(2)
β/°	76.545(3)
γ/°	78.485(2)
Volume/Å^3	2656.7(3)
Z	2
ρ_{calc}g/cm^3	2.453
μ/mm^{-1}	3.038
F(000)	1848.0
Crystal size/mm^3	0.2 × 0.15 × 0.15
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	1.984 to 50.698
Index ranges	$-12 \le h \le 12$, $-15 \le k \le 15$, $-25 \le l \le 25$
Reflections collected	56910
Independent reflections	9734 [R_{int} = 0.0756, R_{sigma} = 0.0569]
Data/restraints/parameters	9734/1431/913
Goodness-of-fit on F^2	1.061
Final R indexes [I>=2σ (I)]	R_1 = 0.0424, wR_2 = 0.0867
Final R indexes [all data]	R_1 = 0.0615, wR_2 = 0.0933
Largest diff. peak/hole / e Å^{-3}	2.01/-2.16

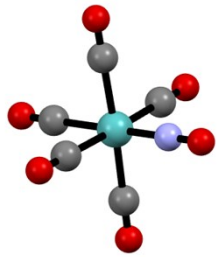
Table 2 Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for p-1_a. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
W1	2897.8(3)	179.6(2)	7450.6(2)	13.82(8)
F1	10000	5000	5000	13.3(10)
Al1	10116.5(17)	3676.7(13)	4732.8(8)	11.1(4)
O1	2265(5)	-470(3)	6126(2)	24.0(10)
C1	2498(6)	-235(5)	6579(3)	18.5(13)
I1	450.2(4)	-431.8(3)	7921.8(2)	22.89(11)
O3	4368(5)	1690(4)	6367(2)	32.4(12)
C3	3872(6)	1150(6)	6756(3)	23.2(14)
O4	5906(4)	-31(3)	7567(2)	22.7(10)
C4	4848(6)	29(5)	7531(3)	16.3(13)
O5	2632(5)	540(3)	8984(2)	23.8(10)
C5	2733(6)	422(5)	8454(3)	17.8(13)
O6	3787(4)	-2451(3)	7469(2)	25.8(11)
C6	3526(6)	-1547(5)	7465(3)	18.6(13)
C2	1665(7)	1722(5)	7564(3)	22.3(14)
O2	968(5)	2525(4)	7623(2)	33.3(12)
Al2	4746.8(17)	6409.8(13)	114.5(8)	11.3(4)
F2	5000	5000	0	14.9(10)
O1_6	5598(4)	6969(3)	-573.2(19)	17.9(9)
C1_6	6673(6)	7409(5)	-875(3)	15.1(12)
C2_6	6527(7)	8577(6)	-636(3)	25.5(14)
F1_6	5619(4)	9279(3)	-879(2)	36.7(10)
F2_6	7678(4)	8941(3)	-808(2)	34.4(10)
F3_6	6130(4)	8606(3)	7.6(19)	37.1(10)
C3_6	7980(7)	6705(5)	-751(4)	27.4(14)
F4_6	7918(4)	5659(3)	-754(3)	49.1(13)
F5_6	8159(4)	6900(4)	-167(2)	48.3(12)
F6_6	9052(4)	6885(3)	-1198(2)	35.6(10)
C4_6	6729(6)	7484(5)	-1614(3)	21.4(13)
F7_6	7164(4)	6519(3)	-1877.4(19)	36.6(10)
F8_6	7516(4)	8160(3)	-1936.4(17)	24.8(8)
F9_6	5520(4)	7848(3)	-1727.9(19)	34.3(10)
O1_5	3065(4)	6716(3)	189(2)	20.2(10)
C1_5	1963(6)	7500(5)	195(3)	18.2(12)
C2_5	1666(6)	7658(5)	-487(3)	23.4(13)
F1_5	2560(4)	8182(3)	-884.8(18)	29.7(9)
F2_5	462(4)	8238(3)	-484(2)	31.5(9)
F3_5	1770(4)	6721(3)	-752(2)	36.9(10)
C3_5	784(6)	7106(5)	684(3)	26.0(14)
F4_5	1141(4)	6710(4)	1230(2)	43.5(11)
F5_5	376(4)	6336(3)	438(2)	40.4(11)
F6_5	-243(4)	7935(3)	848(2)	41.6(11)
C4_5	2154(6)	8603(5)	427(3)	24.1(14)
F7_5	2076(4)	8572(3)	1060(2)	40.7(11)
F8_5	1252(4)	9437(3)	282(2)	31.0(9)
F9_5	3352(4)	8794(3)	132(2)	33.5(10)
O1_4	5337(4)	6572(3)	775.4(19)	21.0(10)
C1_4	5436(6)	6337(5)	1401(3)	17.1(12)
C2_4	4817(7)	5331(5)	1680(3)	24.7(14)
F1_4	3658(4)	5413(3)	1500(2)	37.9(10)
F2_4	4589(4)	5236(3)	2320.4(18)	37.5(10)
F3_4	5603(4)	4421(3)	1429.4(19)	34.1(10)

C3_4	6930(7)	6114(6)	1418(3)	26.1(14)
F4_4	7403(4)	7040(3)	1343(2)	34.1(10)
F5_4	7643(4)	5473(3)	942(2)	35.5(10)
F6_4	7151(4)	5628(4)	1975(2)	44.2(11)
C4_4	4715(7)	7337(5)	1819(3)	25.4(14)
F7_4	4949(4)	8256(3)	1493.2(19)	33.0(10)
F8_4	5126(4)	7321(3)	2379.0(18)	37.9(10)
F9_4	3402(4)	7387(3)	1970(2)	40.3(11)
O1_3	9305(4)	3788(3)	4116.3(19)	15.7(9)
C1_3	8998(6)	4264(5)	3561(3)	15.8(12)
C2_3	10046(7)	4934(5)	3205(3)	26.1(14)
F1_3	9847(5)	5883(3)	3509(2)	39.3(11)
F2_3	10006(4)	5171(3)	2583.7(18)	28.9(9)
F3_3	11263(4)	4424(3)	3226.2(19)	31.6(9)
C3_3	8965(7)	3358(5)	3103(3)	24.6(14)
F4_3	8335(4)	2602(3)	3435.4(18)	29.8(9)
F5_3	10199(4)	2875(3)	2832.9(19)	33.3(10)
F6_3	8340(4)	3757(3)	2628.0(19)	35.4(10)
C4_3	7609(7)	5022(6)	3732(3)	28.0(14)
F7_3	6641(4)	4421(4)	3861(2)	40.7(11)
F8_3	7386(4)	5735(3)	3254(2)	38.7(10)
F9_3	7499(4)	5571(3)	4255.1(19)	35.2(10)
O1_2	9444(4)	2919(3)	5386.6(19)	14.6(9)
C1_2	8316(6)	2535(5)	5683(3)	17.8(12)
C2_2	7199(7)	3492(5)	5954(3)	26.3(14)
F1_2	7391(4)	3850(3)	6498(2)	42.0(11)
F2_2	5987(4)	3235(3)	6102(2)	37.2(11)
F3_2	7180(4)	4326(3)	5524(2)	36.5(10)
C3_2	7855(6)	1922(5)	5193(3)	20.2(13)
F4_2	8891(4)	1344(3)	4800.5(18)	26.6(9)
F5_2	7200(4)	2607(3)	4813.5(19)	29.6(9)
F6_2	7053(4)	1245(3)	5488.1(19)	29.7(9)
C4_2	8641(7)	1727(5)	6248(3)	26.7(14)
F7_2	9336(4)	784(3)	6011(2)	35.0(10)
F8_2	7537(4)	1531(3)	6662.2(19)	37.5(10)
F9_2	9367(5)	2109(3)	6578.2(19)	40.8(11)
O1_1	11809(4)	3266(3)	4522.9(19)	13.4(9)
C1_1	12806(6)	2374(5)	4415(3)	15.8(12)
C2_1	12734(6)	1751(5)	3821(3)	20.6(13)
F1_1	11497(4)	1651(3)	3849.6(18)	26.5(9)
F2_1	13490(4)	754(3)	3800.5(18)	28.1(9)
F3_1	13159(4)	2271(3)	3265.0(17)	28.2(9)
C3_1	14139(6)	2792(6)	4274(3)	26.8(14)
F4_1	14382(4)	3099(4)	4813(2)	39.9(11)
F5_1	14133(4)	3630(3)	3847(2)	35.7(10)
F6_1	15181(3)	2016(3)	4017(2)	32.4(10)
C4_1	12721(6)	1589(5)	5024(3)	24.3(14)
F7_1	12388(4)	2146(3)	5570.6(18)	32.0(9)
F8_1	13862(4)	903(3)	5028(2)	37.8(10)
F9_1	11779(4)	1004(3)	5047.7(18)	28.7(9)

9. Additional Information on the DFT Calculations

$[Mo(CO)_5(NO)]^+$ (C_{4v} symmetry @BP86-D3BJ/def2-TZVPP)



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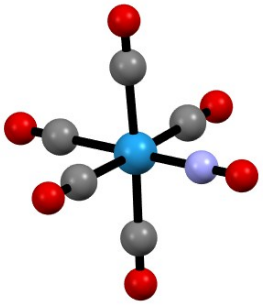
     3                      -0.00         0.00000         -       -
     4                       0.00         0.00000         -       -
     5                       0.00         0.00000         -       -
     6                       0.00         0.00000         -       -
     7        e             51.94         0.00191       YES     YES
     8        e             51.94         0.00191       YES     YES
     9        b1            63.04         0.00000       NO      YES
    10        b2            77.76         0.00000       NO      YES
    11        e             78.63         0.19554       YES     YES
    12        e             78.63         0.19554       YES     YES
    13        a1            84.29         1.23255       YES     YES
    14        e             85.28         0.43183       YES     YES
    15        e             85.28         0.43183       YES     YES
    16        e            318.26         0.02940       YES     YES
    17        e            318.26         0.02940       YES     YES
    18        a1           327.20        20.85486       YES     YES
    19        a2           328.70         0.00000       NO      NO
    20        e            355.82        39.64616       YES     YES
    21        e            355.82        39.64616       YES     YES
    22        b1           369.37         0.00000       NO      YES
    23        a1           384.18         1.19842       YES     YES
    24        e            424.64         1.83503       YES     YES
    25        e            424.64         1.83503       YES     YES
    26        b2           453.30         0.00000       NO      YES
    27        b1           464.53         0.00000       NO      YES
    28        a1           485.22         3.38567       YES     YES
```

```
    29        e              521.42        24.19389       YES      YES
    30        e              521.42        24.19389       YES      YES
    31        a1             570.49        85.30854       YES      YES
    32        e              629.93        40.44970       YES      YES
    33        e              629.93        40.44970       YES      YES
    34        a1            1877.24      1100.05878       YES      YES
    35        e             2077.62      1147.11919       YES      YES
    36        e             2077.62      1147.11919       YES      YES
    37        b1            2092.48         0.00000       NO       YES
    38        a1            2121.37       234.88359       YES      YES
    39        a1            2162.27       109.87714       YES      YES
$end
```

$[W(CO)_5(NO)]^+$ (C_{4v} symmetry @BP86-D3BJ/def2-TZVPP)

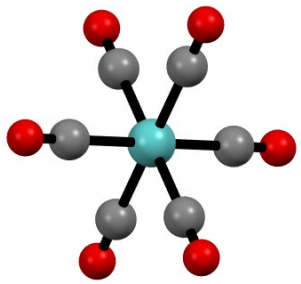


```
$coord
   -0.00000000000000      0.00000000000000      0.16408012946431  w
    0.00000000000000      0.00000000000000      3.73610638653136  n
    0.00000000000000      0.00000000000000     -3.91103579450310  c
   -0.00000000000000     -3.96763375642796      0.04737839894420  c
    0.00000000000000      3.96763375642796      0.04737839894420  c
    3.96763375642796     -0.00000000000000      0.04737839894420  c
   -3.96763375642796      0.00000000000000      0.04737839894420  c
    0.00000000000000      0.00000000000000      5.91129247093002  o
    6.12260688497221     -0.00000000000000     -0.00822252816875  o
   -0.00000000000000     -6.12260688497221     -0.00822252816875  o
    0.00000000000000      6.12260688497221     -0.00822252816875  o
    0.00000000000000      0.00000000000000     -6.05706667552446  o
   -6.12260688497221      0.00000000000000     -0.00822252816875  o


$vibrational spectrum
#  mode     symmetry     wave number   IR intensity    selection rules
#                         cm**(-1)       km/mol          IR     RAMAN
     1                      -0.00         0.00000        -       -
     2                      -0.00         0.00000        -       -
     3                      -0.00         0.00000        -       -
     4                       0.00         0.00000        -       -
     5                       0.00         0.00000        -       -
     6                       0.00         0.00000        -       -
     7        e             51.93         0.00040       YES      YES
     8        e             51.93         0.00040       YES      YES
     9        b1            63.12         0.00000       NO       YES
    10        e             77.33         0.07908       YES      YES
    11        e             77.33         0.07908       YES      YES
    12        b2            79.40         0.00000       NO       YES
    13        a1            80.03         0.39943       YES      YES
    14        e             84.67         0.06788       YES      YES
    15        e             84.67         0.06788       YES      YES
    16        e            328.53         0.21518       YES      YES
    17        e            328.53         0.21518       YES      YES
    18        a1           332.86        30.67683       YES      YES
    19        a2           339.48         0.00000       NO       NO
    20        e            348.77        49.17700       YES      YES
    21        e            348.77        49.17700       YES      YES
```

```
    22        b1            388.10         0.00000       NO       YES
    23        a1            403.53         1.23417       YES      YES
    24        e             426.67         1.04433       YES      YES
    25        e             426.67         1.04433       YES      YES
    26        b2            449.05         0.00000       NO       YES
    27        b1            471.73         0.00000       NO       YES
    28        a1            497.96         5.91232       YES      YES
    29        e             523.51        20.33481       YES      YES
    30        e             523.51        20.33481       YES      YES
    31        a1            536.63        61.18063       YES      YES
    32        e             603.49        24.55595       YES      YES
    33        e             603.49        24.55595       YES      YES
    34        a1           1867.69      1108.52180       YES      YES
    35        e            2070.26      1233.83312       YES      YES
    36        e            2070.26      1233.83312       YES      YES
    37        b1           2085.68         0.00000       NO       YES
    38        a1           2113.73       271.01490       YES      YES
    39        a1           2159.60       111.76938       YES      YES
$end
```

$[Mo(CO)_6]^+$ (D_{3d} symmetry @BP86-D3BJ/def2-TZVPP)



```
$coord
    0.00000000000000      -0.00000000000000       0.00000000000000  mo
    2.91589332682140      -1.68349179716858       2.09617714017994  c
   -2.91589332682140       1.68349179716858      -2.09617714017994  c
   -2.91589332682140      -1.68349179716858       2.09617714017994  c
    2.91589332682140       1.68349179716858      -2.09617714017994  c
    0.00000000000000      -3.36698359433713      -2.09617714017994  c
    0.00000000000000       3.36698359433713       2.09617714017994  c
    4.51417666910794      -2.60626111507899       3.20507652102789  o
    0.00000000000000      -5.21252223015800      -3.20507652102789  o
   -4.51417666910794      -2.60626111507899       3.20507652102789  o
    4.51417666910794       2.60626111507899      -3.20507652102789  o
   -4.51417666910794       2.60626111507899      -3.20507652102789  o
    0.00000000000000       5.21252223015800       3.20507652102789  o


$vibrational spectrum
#  mode     symmetry     wave number   IR intensity    selection rules
#                         cm**(-1)      km/mol          IR     RAMAN
     1                      -0.00        0.00000        -       -
     2                       0.00        0.00000        -       -
     3                       0.00        0.00000        -       -
     4                       0.00        0.00000        -       -
     5                       0.00        0.00000        -       -
     6                       0.00        0.00000        -       -
     7        eu            49.68        0.39120       YES      NO
     8        eu            49.68        0.39120       YES      NO
     9        a2u           65.79        0.38918       YES      NO
    10        a1u           66.46        0.00000       NO       NO
    11        a1g           72.70        0.00000       NO       YES
    12        eg            76.24        0.00000       NO       YES
    13        eg            76.24        0.00000       NO       YES
```

```
    14        eu             83.23         0.99784       YES     NO
    15        eu             83.23         0.99784       YES     NO
    16        eg            313.70         0.00000       NO      YES
    17        eg            313.70         0.00000       NO      YES
    18        a2g           327.50         0.00000       NO      NO
    19        eu            343.80        34.10063       YES     NO
    20        eu            343.80        34.10063       YES     NO
    21        a2u           343.89        21.27280       YES     NO
    22        eg            346.74         0.00000       NO      YES
    23        eg            346.74         0.00000       NO      YES
    24        a1g           385.02         0.00000       NO      YES
    25        a1g           406.84         0.00000       NO      YES
    26        eu            434.66         1.27602       YES     NO
    27        eu            434.66         1.27602       YES     NO
    28        eg            444.15         0.00000       NO      YES
    29        eg            444.15         0.00000       NO      YES
    30        a2u           463.18        55.11007       YES     NO
    31        a1u           507.06         0.00000       NO      NO
    32        eu            564.58        76.63279       YES     NO
    33        eu            564.58        76.63279       YES     NO
    34        eu           2071.50      1131.70585       YES     NO
    35        eu           2071.50      1131.70585       YES     NO
    36        a2u          2072.61       876.82727       YES     NO
    37        eg           2074.00         0.00000       NO      YES
    38        eg           2074.00         0.00000       NO      YES
    39        a1g          2157.70         0.00000       NO      YES
$end
```

$[Mo(CO)_6]^+$ (D_{3d} symmetry @TPSSh-D3BJ/def2-TZVPP)

```
   -0.00000000000000     -0.00000000000000      0.00000000000000  mo
    2.93734205882835      1.69587522836653     -2.09012689431936  c
    4.52952372180140      2.61512174008285     -3.17923454488749  o
    2.93734205882835     -1.69587522836653      2.09012689431936  c
    4.52952372180140     -2.61512174008285      3.17923454488749  o
   -2.93734205882835     -1.69587522836653      2.09012689431936  c
   -4.52952372180140     -2.61512174008285      3.17923454488749  o
   -2.93734205882835      1.69587522836653     -2.09012689431936  c
   -4.52952372180140      2.61512174008285     -3.17923454488749  o
    0.00000000000000      3.39175045673311      2.09012689431936  c
    0.00000000000000      5.23024348016567      3.17923454488749  o
    0.00000000000000     -3.39175045673311     -2.09012689431936  c
    0.00000000000000     -5.23024348016567     -3.17923454488749  o
```

$[Mo(CO)_6]^+$ (D_{4h} symmetry @TPSSh-D3BJ/def2-TZVPP)

```
    0.00000000000000      0.00000000000000      0.00000000000000  mo
    0.00000000000000      0.00000000000000     -3.92749382034803  c
    0.00000000000000      0.00000000000000     -6.07015118331336  o
   -2.83849374489425      2.83849374489425      0.00000000000000  c
   -4.34752557581842      4.34752557581842      0.00000000000000  o
    0.00000000000000      0.00000000000000      3.92749382034803  c
    0.00000000000000      0.00000000000000      6.07015118331336  o
    2.83849374489425     -2.83849374489425      0.00000000000000  c
    4.34752557581842     -4.34752557581842      0.00000000000000  o
   -2.83849374489425     -2.83849374489425      0.00000000000000  c
   -4.34752557581842     -4.34752557581842      0.00000000000000  o
    2.83849374489425      2.83849374489425      0.00000000000000  c
    4.34752557581842      4.34752557581842      0.00000000000000  o
```

$[Mo(CO)_6]^+$ (D_{3d} symmetry @DLPNO-CCSD(T)/def2-TZVPP)

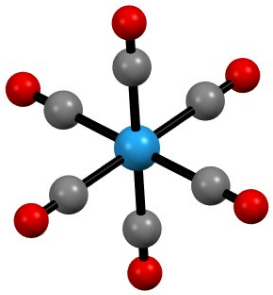
```
  Mo -0.00000000000000      0.00000000000000      0.00000000000000
  C   1.55402920000000      0.89721920000000     -1.10650640000000
  O   2.39587650000000      1.38326000000000     -1.68418510000000
  C   1.55402920000000     -0.89721920000000      1.10650640000000
```

```
  O   2.39587650000000     -1.38326000000000      1.68418510000000
  C  -1.55402920000000     -0.89721920000000      1.10650640000000
  O  -2.39587650000000     -1.38326000000000      1.68418510000000
  C  -1.55402920000000      0.89721920000000     -1.10650640000000
  O  -2.39587650000000      1.38326000000000     -1.68418510000000
  C  -0.00000000000000      1.79443840000000      1.10650640000000
  O  -0.00000000000000      2.76651990000000      1.68418510000000
  C  -0.00000000000000     -1.79443840000000     -1.10650640000000
  O   0.00000000000000     -2.76651990000000     -1.68418510000000
FINAL SINGLE POINT ENERGY      -746.922299529868
T1 diagnostic                                  ...      0.020366323
```

[Mo(CO)$_6$]$^+$ (D_{2h} symmetry @DLPNO-CCSD(T)/def2-TZVPP)

```
  Mo  0.00000000000000      0.00000000000000      0.00000000000000
  C   1.41262630000000      0.00000000000000      1.55273830000000
  C  -1.41262630000000      0.00000000000000      1.55273830000000
  C  -1.41262630000000      0.00000000000000     -1.55273830000000
  C   0.00000000000000      2.12635380000000      0.00000000000000
  C   1.41262630000000      0.00000000000000     -1.55273830000000
  C   0.00000000000000     -2.12635380000000      0.00000000000000
  O   0.00000000000000      3.25534010000000      0.00000000000000
  O  -2.15919250000000      0.00000000000000     -2.40328210000000
  O  -2.15919250000000      0.00000000000000      2.40328210000000
  O   0.00000000000000     -3.25534010000000      0.00000000000000
  O   2.15919250000000      0.00000000000000      2.40328210000000
  O   2.15919250000000      0.00000000000000     -2.40328210000000
FINAL SINGLE POINT ENERGY      -746.921851067340
T1 diagnostic                                  ...      0.020375013
```

[W(CO)$_6$]$^+$ (D_{3d} symmetry @BP86-D3BJ/def2-TZVPP)



```
$coord
    0.00000000000000     -0.00000000000000      0.00000000000000  w
   -2.92199099492087      1.68701228748725      2.10536672229622  c
    2.92199099492087     -1.68701228748725     -2.10536672229622  c
   -0.00000000000000      3.37402457497444     -2.10536672229622  c
   -0.00000000000000     -3.37402457497444      2.10536672229622  c
   -2.92199099492087     -1.68701228748725     -2.10536672229622  c
    2.92199099492087      1.68701228748725      2.10536672229622  c
   -4.51853940839188      2.60877994377900      3.22250123174188  o
   -4.51853940839188     -2.60877994377900     -3.22250123174188  o
   -0.00000000000000      5.21755988755796     -3.22250123174188  o
   -0.00000000000000     -5.21755988755796      3.22250123174188  o
    4.51853940839188     -2.60877994377900     -3.22250123174188  o
    4.51853940839188      2.60877994377900      3.22250123174188  o


$vibrational spectrum
#  mode     symmetry     wave number   IR intensity    selection rules
#                         cm**(-1)        km/mol          IR     RAMAN
     1                        0.00         0.00000        -       -
     2                        0.00         0.00000        -       -
```

```
     3                      0.00         0.00000        -       -
     4                      0.00         0.00000        -       -
     5                      0.00         0.00000        -       -
     6                      0.00         0.00000        -       -
     7        eu            49.74         0.32617      YES      NO
     8        eu            49.74         0.32617      YES      NO
     9        a2u           62.00         0.03922      YES      NO
    10        a1u           66.97         0.00000      NO       NO
    11        a1g           75.07         0.00000      NO       YES
    12        eg            77.82         0.00000      NO       YES
    13        eg            77.82         0.00000      NO       YES
    14        eu            79.98         0.28881      YES      NO
    15        eu            79.98         0.28881      YES      NO
    16        eg           323.81         0.00000      NO       YES
    17        eg           323.81         0.00000      NO       YES
    18        a2g          338.28         0.00000      NO       NO
    19        eu           339.58        46.66963      YES      NO
    20        eu           339.58        46.66963      YES      NO
    21        a2u          341.67        34.70887      YES      NO
    22        eg           368.51         0.00000      NO       YES
    23        eg           368.51         0.00000      NO       YES
    24        a1g          403.14         0.00000      NO       YES
    25        a1g          416.16         0.00000      NO       YES
    26        eg           439.42         0.00000      NO       YES
    27        eg           439.42         0.00000      NO       YES
    28        eu           441.66         0.74766      YES      NO
    29        eu           441.66         0.74766      YES      NO
    30        a2u          455.25        39.09420      YES      NO
    31        a1u          515.56         0.00000      NO       NO
    32        eu           551.47        55.44791      YES      NO
    33        eu           551.47        55.44791      YES      NO
    34        eu          2062.27      1226.82834      YES      NO
    35        eu          2062.27      1226.82834      YES      NO
    36        a2u         2062.72       958.61374      YES      NO
    37        eg          2066.97         0.00000      NO       YES
    38        eg          2066.97         0.00000      NO       YES
    39        a1g         2154.59         0.00000      NO       YES
$end
```

$[W(CO)_6]^+$ (D_{3d} symmetry @TPSSh-D3BJ/def2-TZVPP)

```
  -0.00000000000000      0.00000000000000      0.00000000000000  w
   2.93817085158138      1.69635373208562     -2.09887899330716  c
   4.52698638835355      2.61365680993369     -3.19972461663019  o
   2.93817085158138     -1.69635373208562      2.09887899330716  c
   4.52698638835355     -2.61365680993369      3.19972461663019  o
  -2.93817085158138     -1.69635373208562      2.09887899330716  c
  -4.52698638835355     -2.61365680993368      3.19972461663019  o
  -2.93817085158138      1.69635373208562     -2.09887899330716  c
  -4.52698638835355      2.61365680993368     -3.19972461663019  o
  -0.00000000000000      3.39270746417125      2.09887899330716  c
   0.00000000000000      5.22731361986739      3.19972461663019  o
  -0.00000000000000     -3.39270746417125     -2.09887899330716  c
```

$[W(CO)_6]^+$ (D_{4h} symmetry @TPSSh-D3BJ/def2-TZVPP)

```
   0.00000000000000      0.00000000000000      0.00000000000000  w
   0.00000000000000      0.00000000000000     -3.93992290111083  c
   0.00000000000000      0.00000000000000     -6.08508912125128  o
  -2.83908142561367      2.83908142561367      0.00000000000000  c
  -4.35014799922503      4.35014799922503      0.00000000000000  o
   0.00000000000000      0.00000000000000      3.93992290111083  c
   0.00000000000000      0.00000000000000      6.08508912125128  o
   2.83908142561367     -2.83908142561367      0.00000000000000  c
   4.35014799922503     -4.35014799922503      0.00000000000000  o
  -2.83908142561367     -2.83908142561367      0.00000000000000  c
  -4.35014799922503     -4.35014799922503      0.00000000000000  o
   2.83908142561367      2.83908142561367      0.00000000000000  c
```

```
    4.35014799922503      4.35014799922503      0.00000000000000  o
```

[W(CO)$_6$]$^+$ (D_{3d} symmetry @DLPNO-CCSD(T)/def2-TZVPP)

```
  W   0.00000000000000      0.00000000000000      0.00000000000000
  C   1.55525940000000      0.89792950000000     -1.10975670000000
  O   2.39684660000000      1.38382000000000     -1.69069860000000
  C   1.55525940000000     -0.89792950000000      1.10975670000000
  O   2.39684660000000     -1.38382000000000      1.69069860000000
  C  -1.55525940000000     -0.89792950000000      1.10975670000000
  O  -2.39684660000000     -1.38382000000000      1.69069860000000
  C  -1.55525940000000      0.89792950000000     -1.10975670000000
  O  -2.39684660000000      1.38382000000000     -1.69069860000000
  C   0.00000000000000      1.79585890000000      1.10975670000000
  O  -0.00000000000000      2.76764000000000      1.69069860000000
  C   0.00000000000000     -1.79585890000000     -1.10975670000000
  O   0.00000000000000     -2.76764000000000     -1.69069860000000
FINAL SINGLE POINT ENERGY      -745.720888493062
T1 diagnostic                                 ...      0.019198053
```

[W(CO)$_6$]$^+$ (D_{2h} symmetry @DLPNO-CCSD(T)/def2-TZVPP)

```
  W   0.00000000000000      0.00000000000000      0.00000000000000
  C   1.41523810000000      0.00000000000000      1.55572630000000
  C  -1.41523810000000      0.00000000000000      1.55572630000000
  C  -1.41523810000000      0.00000000000000     -1.55572630000000
  C   0.00000000000000      2.12660680000000      0.00000000000000
  C   1.41523810000000      0.00000000000000     -1.55572630000000
  C   0.00000000000000     -2.12660680000000      0.00000000000000
  O   0.00000000000000      3.25705850000000      0.00000000000000
  O  -2.16785170000000      0.00000000000000     -2.40281820000000
  O  -2.16785170000000      0.00000000000000      2.40281820000000
  O   0.00000000000000     -3.25705850000000      0.00000000000000
  O   2.16785170000000      0.00000000000000      2.40281820000000
  O   2.16785170000000      0.00000000000000     -2.40281820000000
FINAL SINGLE POINT ENERGY      -745.720292810443
T1 diagnostic                                 ...      0.019187954
```

[Cr(CO)$_6$]$^+$ (D_{3d} symmetry @DLPNO-CCSD(T)/def2-TZVPP)

```
  Cr  0.00000000000000     -0.00000000000000      0.00000000000000
  C   1.44476510000000      0.83413550000000     -1.05747920000000
  O   2.27891760000000      1.31573370000000     -1.64814440000000
  C   1.44476510000000     -0.83413550000000      1.05747920000000
  O   2.27891760000000     -1.31573370000000      1.64814440000000
  C  -1.44476510000000     -0.83413550000000      1.05747920000000
  O  -2.27891760000000     -1.31573370000000      1.64814440000000
  C  -1.44476510000000      0.83413550000000     -1.05747920000000
  O  -2.27891760000000      1.31573370000000     -1.64814440000000
  C  -0.00000000000000      1.66827100000000      1.05747920000000
  O   0.00000000000000      2.63146730000000      1.64814440000000
  C   0.00000000000000     -1.66827100000000     -1.05747920000000
  O  -0.00000000000000     -2.63146730000000     -1.64814440000000
FINAL SINGLE POINT ENERGY     -1722.635701647553
T1 diagnostic                                 ...      0.026540659
```

[Cr(CO)$_6$]$^+$ (D_{2h} symmetry @DLPNO-CCSD(T)/def2-TZVPP)

```
  Cr  0.00000000000000      0.00000000000000      0.00000000000000
  C   1.32901730000000      0.00000000000000      1.44726990000000
  C  -1.32901730000000      0.00000000000000      1.44726990000000
  C  -1.32901730000000      0.00000000000000     -1.44726990000000
```

```
  C   0.00000000000000      1.99589300000000      0.00000000000000
  C   1.32901730000000      0.00000000000000     -1.44726990000000
  C   0.00000000000000     -1.99589300000000      0.00000000000000
  O   0.00000000000000      3.12371360000000      0.00000000000000
  O  -2.08309760000000      0.00000000000000     -2.29007150000000
  O  -2.08309760000000      0.00000000000000      2.29007150000000
  O   0.00000000000000     -3.12371360000000      0.00000000000000
  O   2.08309760000000      0.00000000000000      2.29007150000000
  O   2.08309760000000      0.00000000000000     -2.29007150000000
FINAL SINGLE POINT ENERGY     -1722.635225255617
T1 diagnostic                                ...      0.026540357
```

NBO and AIM analysis

For the QTAIM calculations (QTAIM = Quantum Theory of Atoms In Molecules) the multifunctional wavefunction analyzer Multiwfn was employed.[37] wfn input files were generated by single-point calculations on the B3LYP-D3BJ/def2-TZVPP level of theory employing TURBOMOLE. A basin analysis (options 17 + 1) has been performed on the electron density (option 1) employing a high quality grid (spacing = 0.06 Bohr, option 3). The electron density has been integrated with atomic-center + uniform grids and with exact refinement of the basin boundaries (options 7 + 2 + 1). As a result, the atomic charges after normalization are given. NBO analysis[38] was carried out with the implemented feature of TURBOMOLE with standard inputs based also on B3LYP-D3BJ/def2-TZVPPmsingle-point calculations.

NBO

Summary of Natural Population Analysis:

$[Cr(CO)_6]^+$

			Natural Population			
Atom	No	Natural Charge	Core	Valence	Rydberg	Total
1	cr	-0.94560	17.97683	6.89783	0.07095	24.94560
2	c	0.67020	1.99942	3.27829	0.05209	5.32980
3	o	-0.34593	1.99975	6.31152	0.03466	8.34593
4	c	0.67020	1.99942	3.27829	0.05209	5.32980
5	o	-0.34593	1.99975	6.31152	0.03466	8.34593
6	c	0.67020	1.99942	3.27829	0.05209	5.32980
7	o	-0.34593	1.99975	6.31152	0.03466	8.34593
8	c	0.67020	1.99942	3.27829	0.05209	5.32980
9	o	-0.34593	1.99975	6.31152	0.03466	8.34593
10	c	0.67020	1.99942	3.27829	0.05209	5.32980
11	o	-0.34593	1.99975	6.31152	0.03466	8.34593
12	c	0.67020	1.99942	3.27829	0.05209	5.32980
13	o	-0.34593	1.99975	6.31152	0.03466	8.34593
* Total *		1.00000	41.97188	64.43667	0.59146	107.00000

$[Mo(CO)_6]^+$

Atom	No	Natural Charge	Natural Population: Core	Valence	Rydberg	Total
1	mo	-0.56976	7.96606	6.56952	0.03419	14.56976
2	c	0.60270	1.99947	3.34871	0.04912	5.39730
3	c	0.60270	1.99947	3.34871	0.04912	5.39730
4	c	0.60270	1.99947	3.34871	0.04912	5.39730
5	c	0.60270	1.99947	3.34871	0.04912	5.39730
6	c	0.60270	1.99947	3.34871	0.04912	5.39730
7	c	0.60270	1.99947	3.34871	0.04912	5.39730
8	o	-0.34107	1.99975	6.30663	0.03469	8.34107
9	o	-0.34107	1.99975	6.30663	0.03469	8.34107
10	o	-0.34107	1.99975	6.30663	0.03469	8.34107
11	o	-0.34107	1.99975	6.30663	0.03469	8.34107
12	o	-0.34107	1.99975	6.30663	0.03469	8.34107
13	o	-0.34107	1.99975	6.30663	0.03469	8.34107
* Total *		1.00000	31.96139	64.50157	0.53703	97.00000

$[W(CO)_6]^+$

Atom	No	Natural Charge	Natural Population: Core	Valence	Rydberg	Total
1	w	-0.33753	7.96728	6.33174	0.03850	14.33753
2	c	0.55991	1.99949	3.39296	0.04764	5.44009
3	c	0.55991	1.99949	3.39296	0.04764	5.44009
4	c	0.55991	1.99949	3.39296	0.04764	5.44009
5	c	0.55991	1.99949	3.39296	0.04764	5.44009
6	c	0.55991	1.99949	3.39296	0.04764	5.44009
7	c	0.55991	1.99949	3.39296	0.04764	5.44009
8	o	-0.33699	1.99975	6.30179	0.03545	8.33699
9	o	-0.33699	1.99975	6.30179	0.03545	8.33699
10	o	-0.33699	1.99975	6.30179	0.03545	8.33699
11	o	-0.33699	1.99975	6.30179	0.03545	8.33699
12	o	-0.33699	1.99975	6.30179	0.03545	8.33699
13	o	-0.33699	1.99975	6.30179	0.03545	8.33699
* Total *		1.00000	31.96272	64.50023	0.53705	97.00000

AIM

The atomic charges after normalization and atomic volumes:

$[Cr(CO)_6]^+$

1	(Cr)	Charge:	1.290665	Volume:	61.207 Bohr^3
2	(C)	Charge:	1.047795	Volume:	75.368 Bohr^3
3	(O)	Charge:	-1.096250	Volume:	129.135 Bohr^3
4	(C)	Charge:	1.047798	Volume:	75.368 Bohr^3
5	(O)	Charge:	-1.096253	Volume:	129.135 Bohr^3
6	(C)	Charge:	1.047799	Volume:	75.368 Bohr^3
7	(O)	Charge:	-1.096254	Volume:	129.135 Bohr^3
8	(C)	Charge:	1.047791	Volume:	75.368 Bohr^3
9	(O)	Charge:	-1.096246	Volume:	129.135 Bohr^3
10	(C)	Charge:	1.047794	Volume:	75.348 Bohr^3
11	(O)	Charge:	-1.096215	Volume:	129.133 Bohr^3
12	(C)	Charge:	1.047796	Volume:	75.348 Bohr^3
13	(O)	Charge:	-1.096217	Volume:	129.133 Bohr^3

$[Mo(CO)_6]^+$

1	(Mo)	Charge:	1.490151	Volume:	96.091 Bohr^3
2	(C)	Charge:	1.011291	Volume:	80.463 Bohr^3
3	(C)	Charge:	1.011293	Volume:	80.463 Bohr^3
4	(C)	Charge:	1.011292	Volume:	80.463 Bohr^3
5	(C)	Charge:	1.011294	Volume:	80.463 Bohr^3
6	(C)	Charge:	1.010499	Volume:	80.437 Bohr^3
7	(C)	Charge:	1.010485	Volume:	80.437 Bohr^3
8	(O)	Charge:	-1.092874	Volume:	129.178 Bohr^3

```
     9 (O )    Charge:   -1.092405     Volume:   129.181 Bohr^3
    10 (O )    Charge:   -1.092875     Volume:   129.178 Bohr^3
    11 (O )    Charge:   -1.092876     Volume:   129.178 Bohr^3
    12 (O )    Charge:   -1.092876     Volume:   129.178 Bohr^3
    13 (O )    Charge:   -1.092392     Volume:   129.181 Bohr^3
```

$[W(CO)_6]^+$

```
     1 (W )    Charge:    1.659214     Volume:   101.396 Bohr^3
     2 (C )    Charge:    0.976235     Volume:    80.477 Bohr^3
     3 (C )    Charge:    0.976235     Volume:    80.477 Bohr^3
     4 (C )    Charge:    0.976236     Volume:    80.477 Bohr^3
     5 (C )    Charge:    0.976235     Volume:    80.477 Bohr^3
     6 (C )    Charge:    0.975868     Volume:    80.483 Bohr^3
     7 (C )    Charge:    0.975865     Volume:    80.483 Bohr^3
     8 (O )    Charge:   -1.086016     Volume:   128.919 Bohr^3
     9 (O )    Charge:   -1.085912     Volume:   128.903 Bohr^3
    10 (O )    Charge:   -1.086017     Volume:   128.919 Bohr^3
    11 (O )    Charge:   -1.086015     Volume:   128.919 Bohr^3
    12 (O )    Charge:   -1.086016     Volume:   128.919 Bohr^3
    13 (O )    Charge:   -1.085908     Volume:   128.903 Bohr^3
```

Reaction Enthalpies

$H°_g = E_{SCF} + E_{ZPE} + RT = E_{SCF} + E_{ZPE} + 2.48\ kJ\ mol^{-1}$

	Enthalpy H (kJ mol^{-1})		Reaction	$\Delta_R H°_g$ (kJ mol^{-1})	
	BP86	B3LYP		BP86	B3LYP
CO (C_{6v})	-297620.9347443340	-297476.31921281	$Cr(CO)_6 + [NO]^+ \rightarrow [Cr(CO)_6]^+ + NO$	-71	-143
NO (C_{2v})	-341192.7487023620	-341010.51564983	$Cr(CO)_6 + [NO]^+ \rightarrow [Cr(CO)_5(NO)]^+ + CO$	-240	-245
$[NO]^+$ (C_{6v})	-340264.7504791870	-340084.09190075	$Mo(CO)_6 + [NO]^+ \rightarrow [Mo(CO)_6]^+ + NO$	-82	-121
$Cr(CO)_6$ (O_h)	-4529249.5821833200	-4527504.71515699	$Mo(CO)_6 + [NO]^+ \rightarrow [Mo(CO)_5(NO)]^+ + CO$	-252	-255
$[Cr(CO)_6]^+$ (D_{3d})	-4528392.4375271400	-4526721.08755285	$W(CO)_6 + [NO]^+ \rightarrow [W(CO)_6]^+ + NO$	-84	-119
$[Cr(CO)_5(NO)]^+$ (C_{4v})	-4572133.5112971100	-4570357.91460443	$W(CO)_6 + [NO]^+ \rightarrow [W(CO)_5(NO)]^+ + CO$	-254	-255
$Cr(CO)_6OR^F$ (C_1) (OR^F-CO)	-7487368.3936561300	-7484337.11257795	$[AgI_2]^+ + Cr(CO)_6 \rightarrow [Cr(CO)_6I]^+ + AgI$	58	66
$Mo(CO)_6$ (O_h)	-1965943.7390771100	-1964569.79225696	$[AgI_2]^+ + Mo(CO)_6 \rightarrow [Mo(CO)_6I]^+ + AgI$	8	14
$[Mo(CO)_6]^+$ (D_{3d})	-1965097.5849938200	-1963764.53838315	$[AgI_2]^+ + W(CO)_6 \rightarrow [W(CO)_6I]^+ + AgI$	-8	-6
$[Mo(CO)_5(NO)]^+$ (C_{4v})	-2008839.8657202900	-2007432.12259521	$Si(CH_3)_3F + [Cr(CO)_6]^+ \rightarrow [Si(CH_3)_3]^+ + Cr(CO)_6F$	247	314
$W(CO)_6$ (O_h)	-1963059.7220820500	-1961635.52508363	$Si(CH_3)_3F + [Cr(CO)_6]^+ \rightarrow [Si(CH_3)_3]^+ + Cr(CO)_6F$	218	288
$[W(CO)_6]^+$ (D_{3d})	-1962215.9139033300	-1960828.22510894	$Si(CH_3)_3F + [Mo(CO)_6]^+ \rightarrow [Si(CH_3)_3]^+ + Mo(CO)_6F$	243	296
$[W(CO)_5(NO)]^+$ (C_{4v})	-2005957.0447520600	-2004498.36133313	$Si(CH_3)_3F + [W(CO)_6]^+ \rightarrow [Si(CH_3)_3]^+ + W(CO)_6F$	217	266
Ag^+	-385075.1025665400	-385075.10256654	$[Al(OR^F)_4]^- + [Cr(CO)_6]^+ \rightarrow Al(OR^F)_3 + Cr(CO)_6OR^F$	-185	-97
$[Cr(CO)_6I]^+$ (C_2)	-5310487.4438307900	-5308346.64203146	$[Al(OR^F)_4]^- + [Mo(CO)_6]^+ \rightarrow Al(OR^F)_3 + Mo(CO)_6OR^F$	-152	-82
$[Mo(CO)_6I]^+$ (C_{2v})	-2747231.3588399100	-2745463.49754842	$[Al(OR^F)_4]^- + [W(CO)_6]^+ \rightarrow Al(OR^F)_3 + W(CO)_6OR^F$	-173	-108
$[W(CO)_6I]^+$ (C_{2v})	-2744363.3335535200	-2742549.07355968	$[OR^F]^- + Cr(CO)_6F \rightarrow F^- + Cr(CO)_6OR^F$	227	197
I^- (O_h)	-782263.0457087000	-781865.11752138	$[OR^F]^- + Mo(CO)_6F \rightarrow F^- + Mo(CO)_6OR^F$	236	229
$[AgI_2]^+$ (C_s)	-1949695.6811259600	-1948545.73619812	$[OR^F]^- + W(CO)_6F \rightarrow F^- + W(CO)_6OR^F$	240	233

AgI (C_{6v})	-1168399.8024311200	-1167637.83368086	$Si(CH_3)_3I + [Cr(CO)_6]^+ \rightarrow [Si(CH_3)_3]^+ + Cr(CO)_6I$	84	145
F^- (O_h)	-262226.4367354260	-262120.52624459	$Si(CH_3)_3I + [Mo(CO)_6]^+ \rightarrow [Si(CH_3)_3]^+ + Mo(CO)_6I$	80	115
$[OR^F]^-$ (C_3)	-2958450.5137634500	-2957149.17012822	$Si(CH_3)_3I + [W(CO)_6]^+ \rightarrow [Si(CH_3)_3]^+ + W(CO)_6I$	82	111
$[FAl(ORF)_3]^-$ (C_1)	-9774696.2332965300	-9770616.09924771			
$[Al(OR^F)_4]^-$ (S_4)	-12470685.2959277000	-12465424.04199000			
$Al(OR^F)_3$ (C_1)	-9511894.7414240200	-9507905.22665207			
$[Si(CH_3)_3]^+$ (C_{3h})	-1073759.6016105100	-1073349.74637593			
$Si(CH_3)_3F$ (C_{3v})	-1336956.2113476900	-1336447.37701712			
$Si(CH_3)_3I$ (C_{3v})	-1856680.6808195500	-1855863.25381724			
$Cr(CO)_6F$ (C_{2v}) (F-Cr)	-4791341.9391892800	-4789505.19414006			
$Cr(CO)_6F$ (C_1) (F-CO)	-4791371.2350889100	-4789531.15403589			
$Mo(CO)_6F$ (C_{2v})	-2228051.3136591000	-2226566.03190243			
$W(CO)_6F$ (C_{2v})	-2225195.0587594300	-2223659.60758187			
$W(CO)_6OR^F$ (C_1)	-4921179.2108438400	-4918454.90350666			
$[W(CO)_6OR^F]^+$ (C_1)	-4920504.6611423600	-4917809.17463674			
$Cr(CO)_6I$ (C_{3v})	-5311229.3059130400	-5309089.31058798			
$Mo(CO)_6I$ (C_{3v})	-2747938.2591119400	-2746163.49078459			
$W(CO)_6I$ (C_1)	-2745055.1229314600	-2743230.29893051			
$Mo(CO)_6OR^F$ (C_1)	-4924039.7784719100	-4921365.43342563			
$[Cr(CO)_6I]^+$ (C_2)	-5310487.4438307900	-5308346.64203146			
$[Mo(CO)_6I]^+$ (C_{2v})	-2747231.3588399100	-2745463.49754842			
$[W(CO)_6I]^+$ (C_{2v})	-2744363.3335535200	-2742549.07355968			
$[W_2(CO)_{12}]^{2+}$ (C_1)	-3924247.9571920700	-			

	E_{SCF} (kJ mol^{-1})		E_{ZPE} (kJ mol^{-1})	
	BP86	**B3LYP**	**BP86**	**B3LYP**
CO (C_{6v})	-297642.3247443340	-297498.2292128050	18.910	19.430
NO (C_{2v})	-341212.6987023620	-341031.0156498320	17.470	18.020
$[NO]^+$ (C_{6v})	-340287.5504791870	-340107.6219007530	20.320	21.050
$Cr(CO)_6$ (O_h)	-4529419.4121833200	-4527677.0951569900	167.350	169.900
$[Cr(CO)_6]^+$ (D_{3d})	-4528563.4575271400	-4526891.4575528500	168.540	167.890
$[Cr(CO)_5(NO)]^+$ (C_{4v})	-4572303.7412971100	-4570530.8846044300	167.750	170.490
$Cr(CO)_6OR^F$ (C_1) (OR^F-CO)	-7487712.0736561300	-7484687.6326	341.200	348.040
$Mo(CO)_6$ (O_h)	-1966110.3890771100	-1964739.4022569600	164.170	167.130
$[Mo(CO)_6]^+$ (D_{3d})	-1965263.4049938200	-1963933.5183831500	163.340000	166.500
$[Mo(CO)_5(NO)]^+$ (C_{4v})	-2009007.2157202900	-2007602.6725952100	164.870	168.070
$W(CO)_6$ (O_h)	-1963226.0520820500	-1961804.9450836300	163.850	166.940
$[W(CO)_6]^+$ (D_{3d})	-1962381.6539033300	-1960997.2551089400	163.260	166.550
$[W(CO)_5(NO)]^+$ (C_{4v})	-2006124.0447520600	-2004668.6713331300	164.520	167.830
Ag^+	-385081.3010018080	-385081.3010018080	3.718435	3.718435
$[Cr(CO)_6I]^+$ (C_2)	-5310664.9038307900	-5308526.7520314600	174.980	177.630
$[Mo(CO)_6I]^+$ (C_{2v})	-2747406.4088399100	-2745641.9475484200	172.570	175.970
$[W(CO)_6I]^+$ (C_{2v})	-2744538.1635535200	-2742727.4535596800	172.350	175.900
I^- (O_h)	-782269.2441439680	-781871.3160	3.718435	3.718435
$[AgI_2]^+$ (C_s)	-1949713.3511259600	-1948563.3961981200	15.190	15.180
AgI (C_{6v})	-1168411.1424311200	-1167649.1636808600	8.860	8.850
F^- (O_h)	-262232.6351706940	-262126.7247	3.718435	3.718435
$[OR^F]^-$ (C_3)	-2958615.2337634500	-2957319.2601282200	162.240	167.610
$[FAl(ORF)_3]^-$ (C_1)	-9775236.4432965300	-9771172.1892477100	537.730	553.610

$[Al(OR^F)_4]^-$ (S_4)	-12471389.5759277000	-12466151.7219900000	701.800	725.200
$Al(OR^F)_3$ (C_1)	-9512427.4514240200	-9508453.7666520700	530.230	546.060
$[Si(CH_3)_3]^+$ (C_{3h})	-1074061.0916105100	-1073658.0263759300	299.010	305.800
$Si(CH_3)_3F$ (C_{3v})	-1337270.4313476900	-1336768.4370171200	311.740	318.580
$Si(CH_3)_3I$ (C_{3v})	-1856992.5908195500	-1856182.0138172400	309.430	316.280
$Cr(CO)_6F$ (C_{2v}) (F-Cr)	-4791516.0891892800	-4789680.9541400600	171.670	173.280
$Cr(CO)_6F$ (C_1) (F-CO)	-4791548.6250889100	-4789710.3240358900	174.910	176.690
$Mo(CO)_6F$ (C_{2v})	-2228224.1336591000	-2226742.0219024300	170.340	173.510
$W(CO)_6F$ (C_{2v})	-2225367.7787594300	-2223835.3875818700	170.240	173.300
$W(CO)_6OR^F$ (C_1)	-4921517.6708438400	-4918801.5435	335.980	344.160
$[W(CO)_6OR^F]^+$ (C_1)	-4920847.5711423600	-4918160.8346	340.430	349.180
$Cr(CO)_6I$ (C_{3v})	-5311405.3559130400	-5309267.9005879800	173.570	176.110
$Mo(CO)_6I$ (C_{3v})	-2748111.7791119400	-2746340.0307845900	171.040	174.060
$W(CO)_6I$ (C_1)	-2745228.3829314600	-2743406.7489305100	170.780	173.970
$Mo(CO)_6OR^F$ (C_1)	-4924378.1284719100	-4921711.9134	335.870	344.000
$[Cr(CO)_6I]^+$ (C_2)	-5310664.9038307900	-5308526.7520314600	174.980	177.630
$[Mo(CO)_6I]^+$ (C_{2v})	-2747406.4088399100	-2745641.9475484200	172.570	175.970
$[W(CO)_6I]^+$ (C_{2v})	-2744538.1635535200	-2742727.4535596800	172.350	175.900
$[W_2(CO)_{12}]^{2+}$ (C_1)	-3924587.3571920700		336.920	

			CH_2Cl_2, ε = 8.93	*o*DFB, ε = 13.8		$\Delta_R G°_{solv}$ (kJ mol^{-1})	
	freeH energy	freeH entropy	COSMO energy	COSMO energy		CH_2Cl_2	*o*DFB
$[Cr(CO)_6]^+$	168.540	0.48268	-1724.9131867961	-1724.9179398358	$[Cr(CO)_6]^+ + F^- \rightarrow Cr(CO)_6F$	-193	-161
$[Mo(CO)_6]^+$	163.340	0.52888	-748.5987773403	-748.6034025769	$[Mo(CO)_6]^+ + F^- \rightarrow Mo(CO)_6F$	-205	-172
$[W(CO)_6]^+$	163.260	0.53149	-747.5013733330	-747.5060141437	$[W(CO)_6]^+ + F^- \rightarrow W(CO)_6F$	-225	-192
$Cr(CO)_6F$	171.670	0.53566	-1825.0013990964	-1825.0022286007			
$Mo(CO)_6F$	170.340	0.56849	-848.6943115051	-848.6949895849	$[Cr(CO)_6]^+ + [OR^F]^- \rightarrow Cr(CO)_6OR^F$	-107	-83
$W(CO)_6F$	170.240	0.56043	-847.6057656844	-847.6063768114	$[Mo(CO)_6]^+ + [OR^F]^- \rightarrow Mo(CO)_6OR^F$	-94	-71
$Cr(CO)_6OR^F$	338.720	0.81835	-2851.9162740079	-2851.9169858902	$[W(CO)_6]^+ + [OR^F]^- \rightarrow W(CO)_6OR^F$	-112	-88
$Mo(CO)_6OR^F$	335.870	0.82241	-1875.6029149053	-1875.6034320887			
$W(CO)_6OR^F$	335.980	0.81962	-1874.5129048990	-1874.5133718026	$[Cr(CO)_6]^+ + [Al(OR^F)_4]^- \rightarrow Cr(CO)_6OR^F + Al(OR^F)_3$	90	107
$[OR^F]^-$	162.240	0.46395	-1126.9488506488	-1126.9536740721	$[Mo(CO)_6]^+ + [Al(OR^F)_4]^- \rightarrow Mo(CO)_6OR^F + Al(OR^F)_3$	102	119
F^-	3.718	0.14558	-100.0082631972	-100.0165816745	$[W(CO)_6]^+ + [Al(OR^F)_4]^- \rightarrow W(CO)_6OR^F + Al(OR^F)_3$	84	102
$Al(OR^F)_3$	530.230	1.06111	-3623.0945327556	-3623.0947315153			
$[FAl(OR^F)_3]^-$	537.730	1.13293	-3723.2362119343	-3723.2392236424	$Al(OR^F)_3 + F^- \rightarrow [FAl(OR^F)_3]^-$	-335	-320
$[Al(OR^F)_4]^-$	701.800	1.31981	-4750.1410726992	-4750.1436636479	$Al(OR^F)_3 + ORF- \rightarrow [Al(OR^F)_4]^-$	-196	-190
$[W_2(CO)_{12}]^{2+}$	336.920	0.88236		-1495.0203856200	$2\ W(CO)_6 \rightarrow [W_2(CO)_{12}]^{2+}$		32
$[Si(CH_3)_3]^+$	299.010	0.35986	-409.1648123711	-409.1697952226			
$Si(CH_3)_3F$	311.740	0.35439	-509.3434162118	-509.3437257407	$[Si(CH_3)_3]^+ + F^- \rightarrow Si(CH_3)_3F$	-404	-370
AgI	8.860	0.26479	-445.0349925725	-445.0359568253			
$[AgI_2]^+$	15.190	0.35391	-742.6812244109	-742.6861734862	$[Cr(CO)_6]^+ + [FAl(OR^F)_3]^- \rightarrow Cr(CO)_6F + Al(OR^F)_3$	142	159
$[Cr(CO)_6I]^+$	174.980	0.56120	-2022.7923023640	-2022.7968327612	$[Mo(CO)_6]^+ + [FAl(OR^F)_3]^- \rightarrow Mo(CO)_6F + Al(OR^F)_3$	130	148
$[Mo(CO)_6I^+$	172.570	0.57757	-1046.4990846028	-1046.5036100238	$[W(CO)_6]^+ + [FAl(OR^F)_3]^- \rightarrow W(CO)_6F + Al(OR^F)_3$	110	128
$[W(CO)_6I]^+$	172.350	0.57783	-1045.4065689803	-1045.4110750947			
$Cr(CO)_6$	167.350	0.48268	-1725.1687419034	-1725.1690568614	$[Cr(CO)_6]^+ + Si(CH_3)_3F \rightarrow [Si(CH_3)_3]^+ + Cr(CO)_6F$	210	208
$Mo(CO)_6$	164.170	0.50448	-748.8555039709	-748.8557813820	$[Mo(CO)_6]^+ + Si(CH_3)_3F \rightarrow [Si(CH_3)_3]^+ + Mo(CO)_6F$	199	197
$W(CO)_6$	163.850	0.50870	-747.7570121896	-747.7572970954	$[W(CO)_6]^+ + Si(CH_3)_3F \rightarrow [Si(CH_3)_3]^+ + W(CO)_6F$	179	177
					$Cr(CO)_6 + [AgI_2]^+ \rightarrow [Cr(CO)_6I]^+ + AgI$	64	63
					$Mo(CO)_6 + [AgI_2]^+ \rightarrow [Mo(CO)_6I]^+ + AgI$	14	13
					$W(CO)_6 + [AgI_2]^+ \rightarrow [W(CO)_6I]^+ + AgI$	-1	-1

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