Supporting Information

for

Synthesis of Pyridylimido Complexes of Tantalum and Niobium by Reductive Cleavage of the N=N Bond of 2,2'-Azopyridine: Precursors for Early-Late Heterobimetallic Complexes

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Contents:

1. Electrochemical Analyses of Complexes 2a and 2b

In an argon-filled glovebox, complex **2a** (8.3 mg, 0.010 mmol) was dissolved in CH_2Cl_2 (2 mL) and an electrolyte ([^{n}Bu$_4$N][BAr$^F_4$] (Ar^F = 3,5-(CF$_3$)$_2$C$_6$H$_3$), 221 mg, 0.20 mmol) was added. The solution which contained 1 mM of **2a** and 0.1 M of [^{n}Bu$_4$N][BAr$^F_4$] was used for measurement of cyclic voltammogram with a glassy carbon working electrode, a platinum wire auxiliary electrode, a silver wire electrode, and scan rate of 100 mV/s. In a similar manner, cyclic voltammogram of complex **2b** was measured.

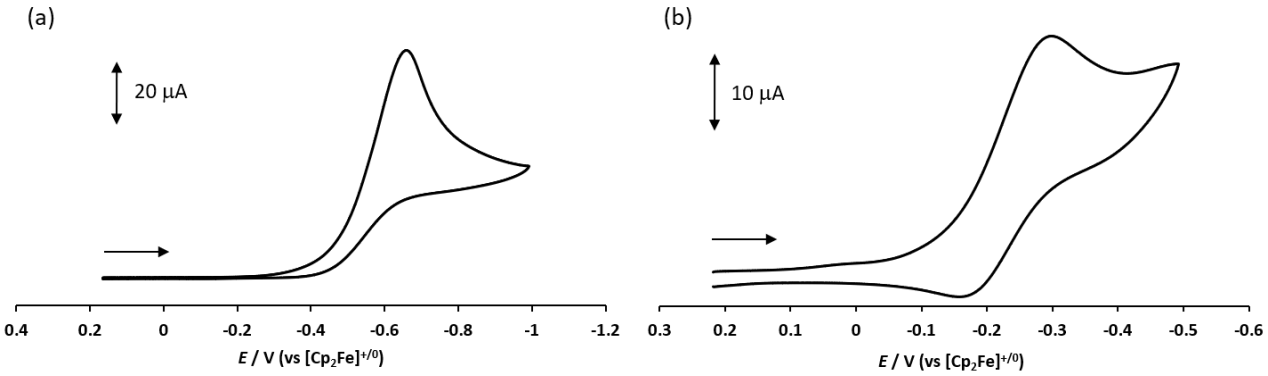
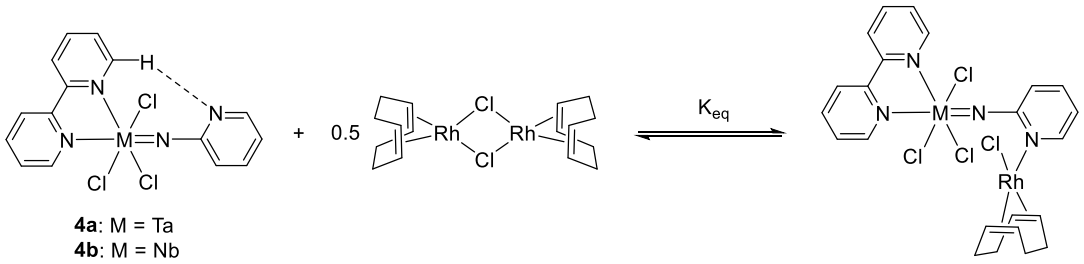


Figure S1. Cyclic voltammograms of (a) **2a** and (b) **2b**.

2. van't Hoff Plot

The relative concentrations of the equilibrium species were determined by ^{1}H NMR analysis in CD_2Cl_2. Figure S2 shows a standard van't Hoff plot for the temperature range from 263 to 303 K for **4a** and 243 to 303 K for **4b**, giving ΔH =-5.3(2) kcal mol^{-1}, ΔS = -9.5(8) e.u., ΔG_{303K} = -2.4(5) kcalmol^{-1} for **5a**; ΔH = -7.2(4) kcal mol^{-1}, ΔS = -17(2) e.u. ΔG_{303K} = -2.1(9) kcal mol^{-1} for **5b**.



4a: M = Ta
4b: M = Nb

5a: M = Ta
5b: M = Nb

$$K_{eq} = \frac{[\mathbf{5}]}{[\mathbf{4}][RhCl(cod)]_2]^{0.5}}$$

$$\ln K_{eq} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}$$

$$\Delta G = T\Delta H - \Delta S$$

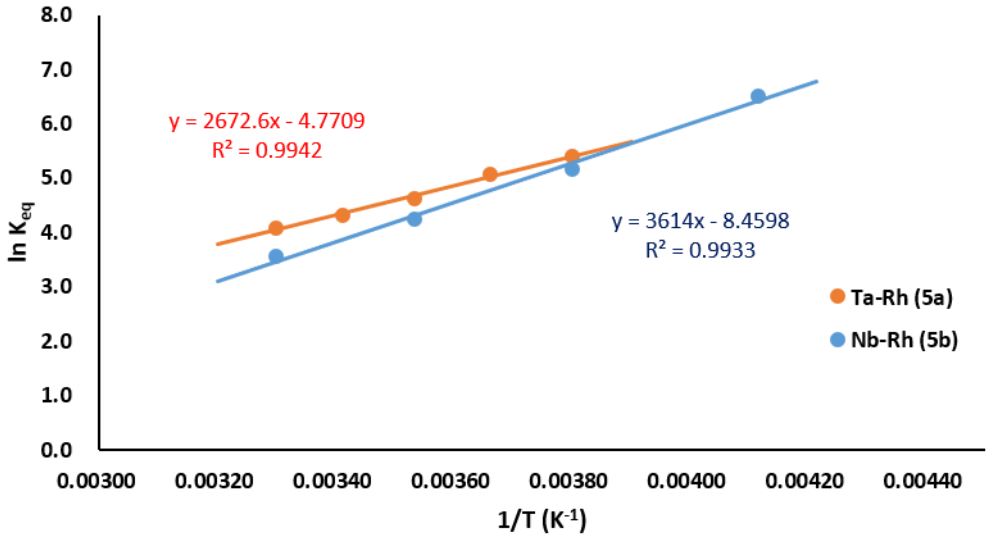


Figure S2. van't Hoff plot for the equilibria between (bipy)MCl_3(μ-Npy)RhCl(cod) (**5a**: M = Ta, **5b**: M = Nb) and a mixture of M(=Npy)Cl_3(bipy) (**4a**: M = Ta, **4b**: M = Nb) and $[RhCl(cod)]_2$.

3. ^{1}H and ^{13}C NMR Spectra of Complexes 2b, 4a, 5a, and 5b

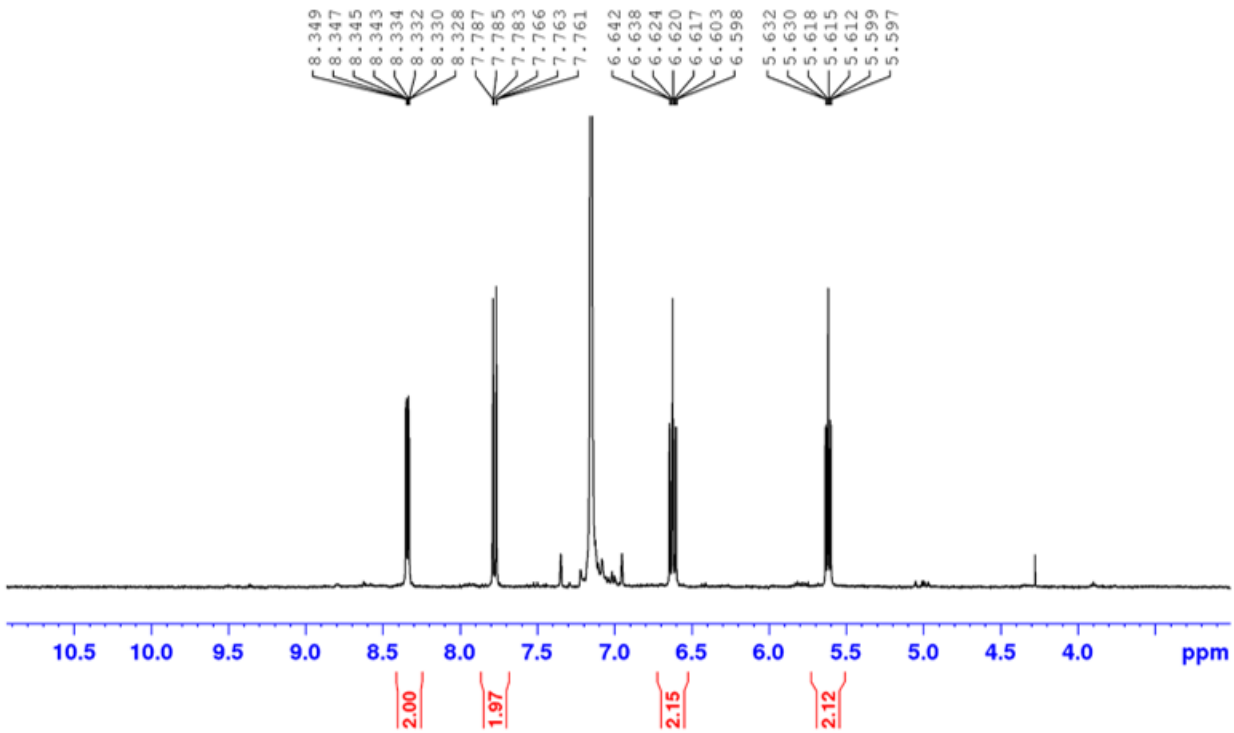


Figure S3. ^{1}H NMR spectrum of complex **2b** in C_6D_6 at 303 K.

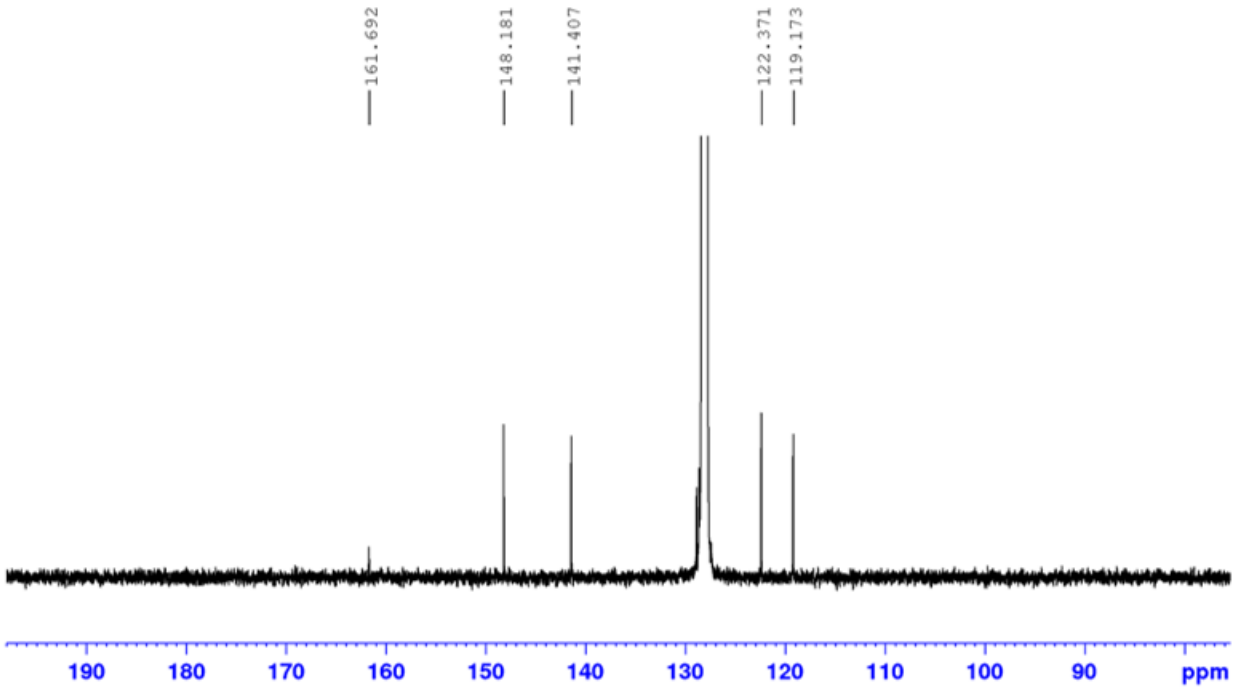


Figure S4. ^{13}C NMR spectrum of complex **2b** in C_6D_6 at 303 K.

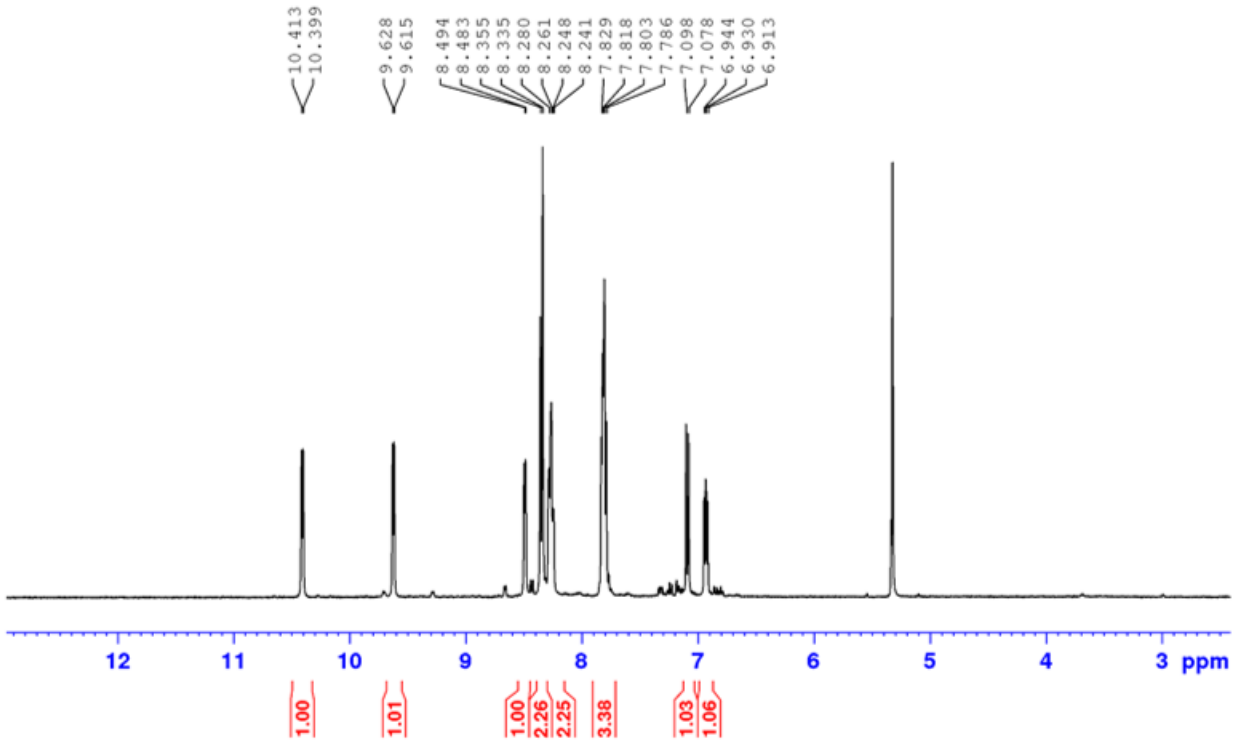


Figure S5. ^{1}H NMR spectrum of complex **4a** in CD_2Cl_2 at 303 K.

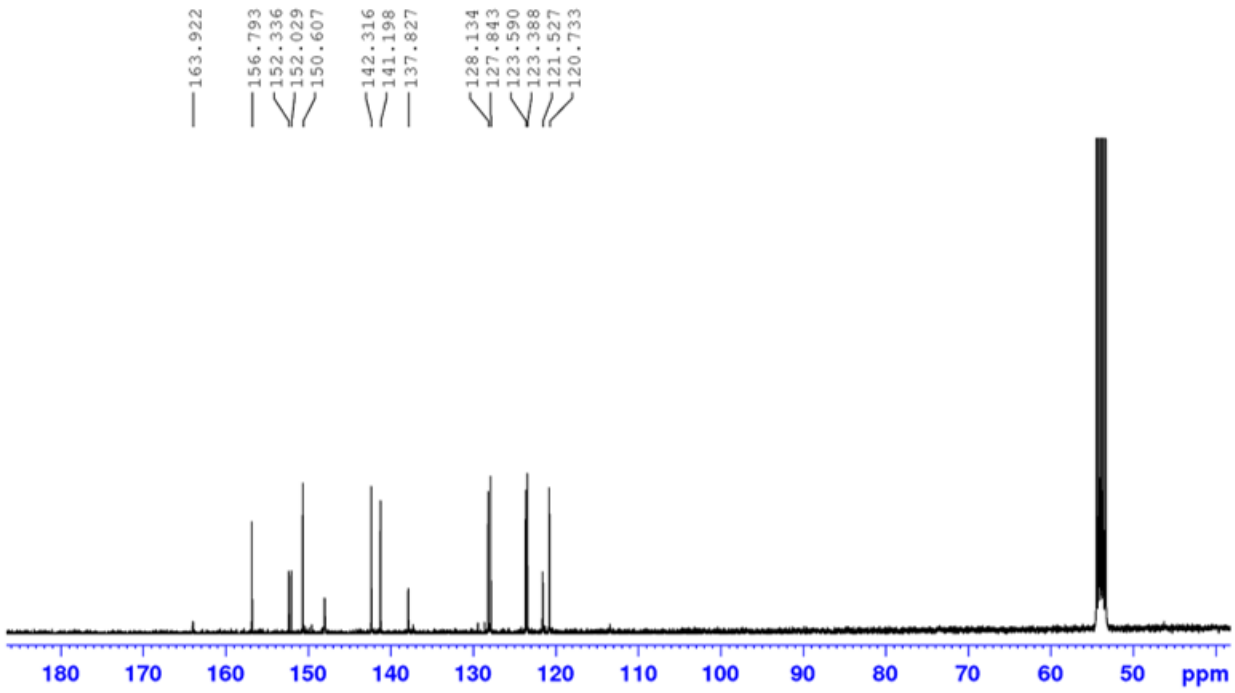


Figure S6. ^{13}C NMR spectrum of complex **4a** in CD_2Cl_2 at 303 K.

4. Molecular Structures of Complexes 2b, 4b, and 5b

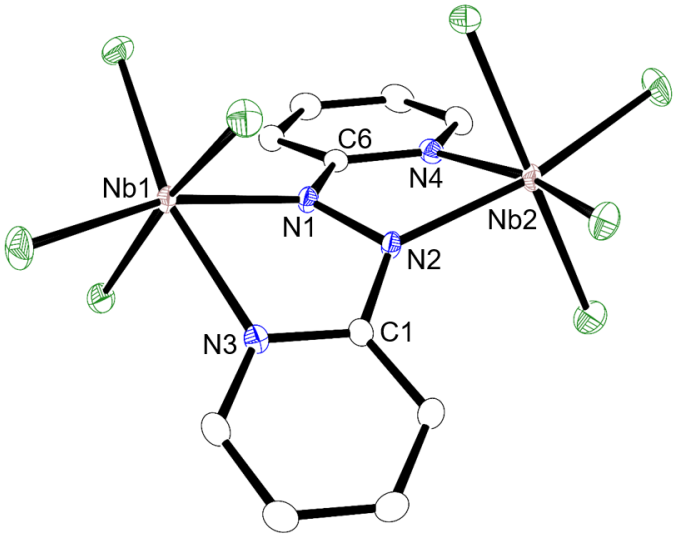


Figure S7. Molecular structure of complex **2b** with 50% thermal ellipsoids. All hydrogen atoms and solvent molecules are omitted for clarity. Selected bond distances (Å) and angle (deg): N1—N2, 1.4026(16); C1—N2, 1.3910(19); C6—N1, 1.3935(18); Nb1—N1, 2.0731(12); Nb2—N2, 2.0829(12); Nb1—N3, 2.2255(13); Nb2—N4, 2.2164(12); C1—N2—N1—C6, 33.02.

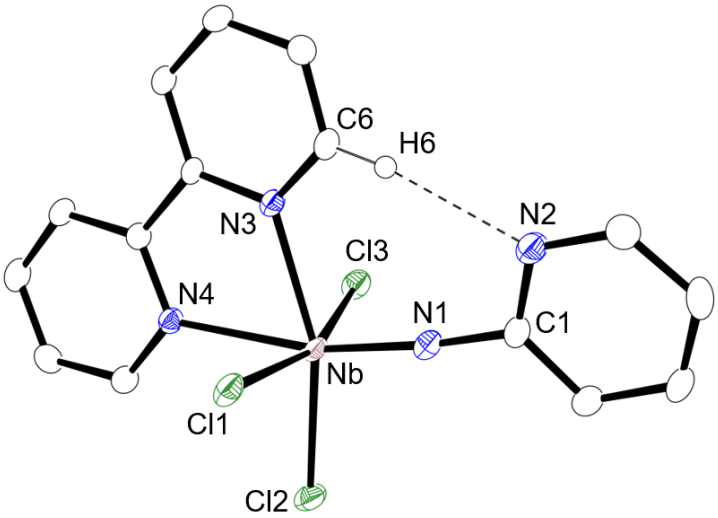


Figure S8. Molecular structure of complex **4b** with 50% thermal ellipsoids. All hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Nb—N1, 1.774(2); N1—C1, 1.391(3); Nb—N3, 2.259(3); Nb—N4, 2.370(2); Nb—Cl1, 2.3993(9); Nb—Cl2, 2.3749(9); Nb—Cl3, 2.3922(8); N1—Nb—N4, 167.30(9); N3—Nb—Cl2, 160.57(6); Nb—N1—C1, 174.2(2).

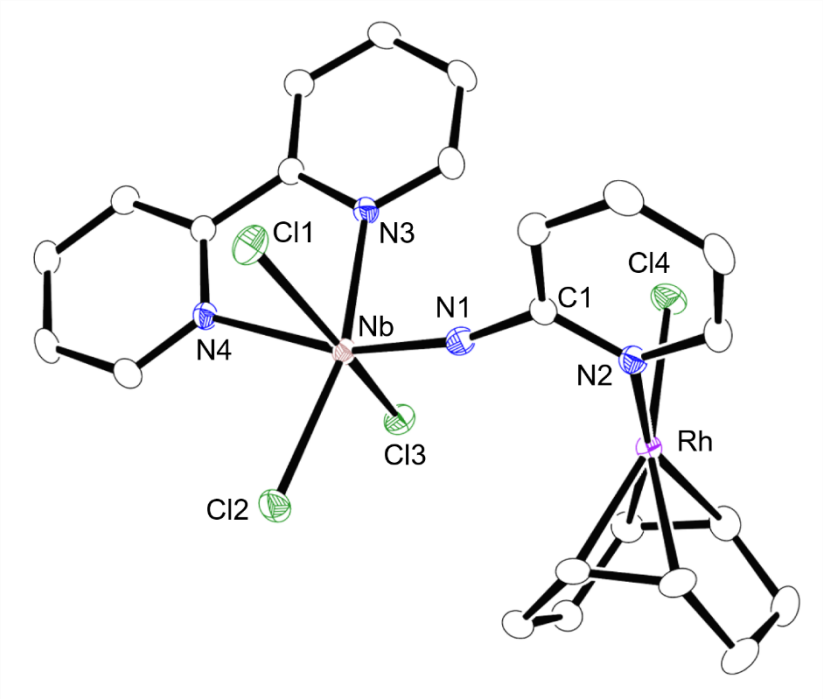


Figure S9. Molecular structure of complex **5b** with 50% thermal ellipsoids. All hydrogen atoms and solvent molecules are omitted for clarity. Selected bond distances (Å) and angles (deg): Nb—N1, 1.7804(14); N1—C1, 1.383(2); Nb—N3, 2.2531(14); Nb—N4, 2.3545(14); Nb—Cl1, 2.3876(5); Nb—Cl2, 2.3710(5); Nb—Cl3, 2.4054(5); Rh—N2, 2.0999(15); Rh—Cl4, 2.3909(5); N1—Nb—N4, 163.29(5); Nb—N1—C1, 165.92(12).

5. X-ray Crystallographic analysis

Table S1. Crystal Data and Data Collection Parameters for **2a**, **2b**, **3a**, **4a**, **4b**, **5a**, and **5b**.

	2a·C$_6$H$_6$	**2b·C$_6$H$_6$**
empirical formula	$C_{16}H_{14}Cl_8N_4Ta_2$	$C_{16}H_{14}Cl_8N_4Nb_2$
formula weight	907.83	731.75
crystal system	*monoclinic*	*monoclinic*
space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
a, Å	11.428(5)	11.4367(11)
b, Å	16.150(6)	16.1110(14)
c, Å	13.616(5)	13.5646(13)
α, deg.	-	-
β, deg.	103.749(4)	103.8899(19)
γ, deg.	-	-
V, Å^3	2441.0(16)	2426.3(4)
Z	4	4
D_{calcd}, g/cm^3	2.470	2.003
μ [Mo-$K\alpha$], mm^{-1}	69.833	18.378
T, K	113(2)	113(2)
crystal size, mm	0.20 × 0.12 × 0.12	0.24 × 0.09 × 0.08
θ range for data collection (deg.)	3.12 to 27.48	3.10 to 27.50
no. of reflections measured	22584	23304
unique data (R_{int})	5350 (0.0640)	5538 (0.0167)
data / restraint / parameters	5350 / 0 / 271	5538 / 0 / 271
$R1$ ($I > 2.0\sigma(I)$)	0.0650	0.0145
$wR2$ ($I > 2.0\sigma(I)$)	0.1238	0.0359
$R1$ (all data)	0.0707	0.0177
$wR2$ (all data)	0.1280	0.0366
GOF on F^2	1.242	1.030
$\Delta\rho$, e Å^{-3}	3.38, -1.99	0.33, -0.35

a) $R1 = (\Sigma||Fo| - |Fc||)/(\Sigma|Fo|)$ b) $wR2 = [\{\Sigma w(Fo^2\text{-}Fc^2)^2\}/\{\Sigma w(Fo^4)\}]^{1/2}$

Table S1. (continued)

	3a	**4a**
empirical formula	$C_{52}H_{88}Cl_{14}N_{10}Ta_4$	$C_{15}H_{12}Cl_3N_4Ta$
formula weight	2073.47	535.59
crystal system	*triclinic*	*monoclinic*
space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)
a, Å	8.9723	8.3470(11)
b, Å	18.162	13.7603(13)
c, Å	23.217	14.8577(16)
α, deg.	89.6120	-
β, deg.	79.2850	93.947(5)
γ, deg.	89.9550	-
V, Å^3	3717.3	1702.5(3)
Z	2	4
D_{calcd}, g/cm^3	1.852	2.089
μ [Mo-*K*α], mm^{-1}	6.401	6.919
T, K	113(2)	113(2)
crystal size, mm	0.20 × 0.20 × 0.20	0.30 × 0.26 × 0.25
θ range for data collection (deg.)	3.20 to 27.40	3.10 to 27.48
no. of reflections measured	32110	15938
unique data (R_{int})	16029 (0.0481)	3862 (0.0451)
data / restraint / parameters	16029 / 56 / 718	3862 / 0 / 208
*R*1 ($I > 2.0\sigma(I)$)	0.0625	0.0632
*wR*2 ($I > 2.0\sigma(I)$)	0.1445	0.1351
*R*1 (all data)	0.1243	0.0669
*wR*2 (all data)	0.1692	0.1383
GOF on F^2	0.966	1.176
$\Delta\rho$, e Å^{-3}	3.41, -0.96	3.40, -3.66

a) $R1 = (\Sigma||Fo| - |Fc||)/(\Sigma|Fo|)$ b) $wR2 = [\{\Sigma w(Fo^2\text{-}Fc^2)^2\}/\{\Sigma w(Fo^4)\}]^{1/2}$

Table S1. (continued)

	4b	**5a·CH_2Cl_2**
empirical formula	$C_{15}H_{12}Cl_3N_4Nb$	$C_{24}H_{26}Cl_6N_4RhTa$
formula weight	447.55	867.07
crystal system	*monoclinic*	*triclinic*
space group	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
a, Å	8.334(2)	10.2852(18)
b, Å	13.735(4)	10.4153(17)
c, Å	14.794(4)	14.428(3)
α, deg.	-	105.088(3)
β, deg.	93.159(7)	103.114(3)
γ, deg.	-	91.360(3)
V, Å^3	1690.9(8)	1447.7(5)
Z	4	2
D_{calcd}, g/cm^3	1.758	1.989
μ [Mo-$K\alpha$], mm^{-1}	1.188	4.914
T, K	113(2)	113(2)
crystal size, mm	0.12 × 0.04 × 0.02	0.09 × 0.03 × 0.01
θ range for data collection (deg.)	3.10 to 27.50	3.00 to 27.50
no. of reflections measured	23073	25103
unique data (R_{int})	3885 (0.0525)	6609 (0.0370)
data / restraint / parameters	3885 / 0 / 208	6609 / 0 / 325
$R1$ ($I > 2.0\sigma(I)$)	0.0323	0.0255
$wR2$ ($I > 2.0\sigma(I)$)	0.0642	0.0416
$R1$ (all data)	0.0464	0.0391
$wR2$ (all data)	0.0698	0.0443
GOF on F^2	1.109	1.009
$\Delta\rho$, e Å^{-3}	0.47, -0.51	0.67, -0.88

a) $R1 = (\Sigma||Fo| - |Fc||)/(\Sigma|Fo|)$ b) $wR2 = [\{\Sigma w(Fo^2\text{-}Fc^2)^2\}/\{\Sigma w(Fo^4)\}]^{1/2}$

Table S1. (continued)

	5b·CH_2Cl_2
empirical formula	$C_{24}H_{26}Cl_6N_4NbRh$
formula weight	779.03
crystal system	*triclinic*
space group	$P\bar{1}$ (No. 2)
a, Å	10.3047(9)
b, Å	10.4035(10)
c, Å	14.4157(14)
α, deg.	105.493(2)
β, deg.	102.8873(19)
γ, deg.	91.1763(16)
V, $Å^3$	1446.5(2)
Z	2
D_{calcd}, g/cm^3	1.788
μ [Mo-*K*α], mm^{-1}	1.541
T, K	113(2)
crystal size, mm	0.14 × 0.10 × 0.10
θ range for data collection (deg.)	3.00 to 27.50
no. of reflections measured	24040
unique data (R_{int})	6624 (0.0266)
data / restraint / parameters	6624 / 0 / 325
*R*1 ($I > 2.0\sigma(I)$)	0.0198
*wR*2 ($I > 2.0\sigma(I)$)	0.0516
*R*1 (all data)	0.0235
*wR*2 (all data)	0.0523
GOF on F^2	1.080
$\Delta\rho$, e $Å^{-3}$	0.91, -0.85

a) $R1 = (\Sigma||Fo| - |Fc||)/(\Sigma|Fo|)$ b) $wR2 = [\{\Sigma w(Fo^2\text{-}Fc^2)^2\}/\{\Sigma w(Fo^4)\}]^{1/2}$