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Supporting Information

Cationic Functionalisation by Phosphenium Ion Insertion

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Experimental Procedures

General Considerations

All manipulations were carried out using standard Schlenk techniques at a Stock apparatus with N₂ as an inert gas or in a glove box with Ar atmosphere. All glassware was dried with a heat gun (600 °C) for at least 30 min prior to use. *o*-DFB was distilled from P₂O₅, CD₂Cl₂ was distilled from CaH₂ and other solvents were directly taken from an MB SPS-800 solvent purification system and degassed at room temperature. Solution ¹H (400.130 MHz), ¹⁹F (376.498 MHz) and ³¹P (161.976 MHz) NMR spectra were recorded at an Avance400 (Bruker) spectrometer using (H₃C)₄Si (¹H), CFCI₃ (¹⁹F) or 85% phosphoric acid (³¹P), respectively, as external standards. Chemical shifts (δ) are provided in parts per million (ppm) and coupling constants (J) are reported in Hertz (Hz). Chemical shifts and coupling constants for all ³¹P{¹H} and ³¹P NMR spectra were derived from spectral simulation. The following abbreviations are used: s = singlet, d = doublet, dd = doublet of doublets, ddd = doublet of doublets of doublets, t = triplet, br = broad and m = multiplet. ESI mass spectra were recorded at the internal mass spectrometry department using a ThermoQuest Finnigan TSQ 7000 mass spectrometer and peak assignment was performed using the Molecular weight calculator 6.50.^[1] Elemental analysis of the products was conducted by the elemental analysis department at the University of Regensburg using an Elementar Vario EL. The starting materials [Cp''Ni(η³-P₃)] (**1**),^[2] Ti[TEF]^[3], [(Et₃Si)₂(μ-H)][BARF]^[4], (2,2'-biphen)PCl^[5] and tBuPCl₂^[6] were synthesized following literature procedures. All other chemicals were purchased from commercial vendors. GaCl₃ was sublimed and all purchased halogenophosphanes were distilled before use.

Synthesis:

 $[\text{Cp}''\text{Ni}(\eta^3\text{-P}_4\text{Ph}_2)]\text{[OTf]}$ (**2a**[OTf])

A colourless solution of Ph₂PCl (0.1 mmol, 22 mg, 17.9 μL, 1 eq.) in 1 mL of toluene was added to an orange solution of **1** (0.1 mmol, 38 mg, 1 eq.) and Ti[OTf] (0.1 mmol, 35 mg, 1 eq.) in 5 mL of *o*-DFB at room temperature. Immediate precipitation of small amounts of white solid occurred and a colour change to dark red could be observed upon stirring for 24 h. The mixture was then filtered through glass fibre filter paper and upon addition of 50 mL of *n*-hexane a dark red oil was precipitated. This oil was washed three times with 10 mL of *n*-hexane, each, and dried under reduced pressure (10⁻³ mbar). Dissolving the residue in *o*-DFB and layering with *n*-hexane (ratio of 1:8) yielded [Cp''Ni(η³-P₄Ph₂)] [OTf] (**2a**[OTf]) after five days at room temperature as small red plates suitable for single crystal X-ray analysis.

Yield:	45 mg (0.063 mmol, 63%)
Elemental analysis:	calc. (%) for [Cp''Ni(η ³ -P ₄ Ph ₂)] [OTf] (C ₃₀ H ₄₁ O ₃ F ₃ P ₄ SNi): C: 50.09 H: 5.47 found (%): C: 50.01 H: 5.32
ESI(+)-MS (<i>o</i> -DFB):	<i>m/z</i> (%) = 569.1 (100%) [Cp''Ni(η ³ -P ₄ Ph ₂)] ⁺

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NMR (CD₂Cl₂, 298 K): ¹H: δppm = 1.21 (s, 9 H, C(CH₃)₃), 1.31 (s, 18 H, C(CH₃)₃), 5.92 (s, 2 H, C₅H₂BU₃), 7.54–7.86 (br, 10 H, Ph)
³¹P{¹H}: (AMM'X spin system) δppm = 12.4 (ddd, ¹J_{PX-PM/PM'} = 270.3 Hz, ²J_{PX-PA} = 14.2 Hz, 1 P, P^X), 57.8 (ddd, ¹J_{PM/PM'-PX} = 270.3 Hz, ¹J_{PM/PM'-PA} = 288.1 Hz, 2 P, P^{MM}), 73.8 (ddd, ¹J_{PA-PM/PM'} = 288.1 Hz, ²J_{PA-PX} = 14.2 Hz, 1 P, P^A)
³¹P: (AMM'X spin system) δppm = 12.4 (t, ¹J_{PX-PM/PM'} = 270.3 Hz, 1 P, P^X), 57.8 (ddd, ¹J_{PM/PM'-PX} = 270.3 Hz, ¹J_{PM/PM'-PA} = 288.1 Hz, 2 P, P^{MM}), 73.8 (ddd, ¹J_{PA-PM/PM'} = 288.1 Hz, ²J_{PA-PX} = 14.2 Hz, 1 P, P^A)
¹⁹F{¹H}: δppm = -78.75 (s, [OTf]⁻)

[Cp''Ni(η³-P₄Ph₂)] [SbF₆] (2a[SbF₆])

A colourless solution of Ph₂PCI (0.1 mmol, 22 mg, 17.9 μL, 1 eq.) in 1 mL of toluene was added to an orange solution of [Cp''Ni(η³-P₃)] (0.1 mmol, 38 mg, 1 eq.) and Ag[SbF₆] (0.1 mmol, 34 mg, 1 eq.) in 5 mL of *o*-DFB at room temperature. Immediate precipitation of small amounts of white solid and a colour change to red could be observed. After stirring for 24 h at room temperature the mixture was filtered through glass fibre filter paper and upon addition of 50 mL of *n*-hexane, a dark red solid precipitated. The precipitate was washed three times with 10 mL of *n*-hexane, each, and dried under reduced pressure (10⁻³ mbar). Recrystallisation from *o*-DFB/*n*-hexane (1:8) at room temperature yielded [Cp''Ni(η³-P₄Ph₂)] [SbF₆] (**2a**[SbF₆]) as red platelets, suitable for X-ray analysis after one week.

Yield: 27 mg (0.037 mmol, 37%)
 Elemental analysis: calc. (%) for [Cp''Ni(η³-P₄Ph₂)] [SbF₆] (C₂₉H₄₁F₆P₄NiSb): C: 43.22 H: 4.88
 found (%): C: 43.55 H: 4.62
 ESI(+)-MS (*o*-DFB): *m/z* (%) = 569.1 (100%) [Cp''Ni(η³-P₄Ph₂)]⁺
 NMR (CD₂Cl₂, 298 K): ¹H: δppm = 1.21 (s, 9 H, C(CH₃)₃), 1.31 (s, 18 H, C(CH₃)₃), 5.92 (s, 2 H, C₅H₂BU₃), 7.54–7.86 (br, 10 H, Ph)
³¹P{¹H}: (AMM'X spin system) δppm = 12.4 (ddd, ¹J_{PX-PM/PM'} = 270.3 Hz, ²J_{PX-PA} = 14.2 Hz, 1 P, P^X), 57.8 (ddd, ¹J_{PM/PM'-PX} = 270.3 Hz, ¹J_{PM/PM'-PA} = 288.1 Hz, 2 P, P^{MM}), 73.8 (ddd, ¹J_{PA-PM/PM'} = 288.1 Hz, ²J_{PA-PX} = 14.2 Hz, 1 P, P^A)
³¹P: (AMM'X spin system) δppm = 12.4 (t, ¹J_{PX-PM/PM'} = 270.3 Hz, 1 P, P^X), 57.8 (ddd, ¹J_{PM/PM'-PX} = 270.3 Hz, ¹J_{PM/PM'-PA} = 288.1 Hz, 2 P, P^{MM}), 73.8 (ddd, ¹J_{PA-PM/PM'} = 288.1 Hz, ²J_{PA-PX} = 14.2 Hz, 1 P, P^A)
¹⁹F{¹H}: δppm = -122.7 (br, [SbF₆]⁻)

[Cp''Ni(η³-P₄Ph₂)] [TEF] (2a[TEF])

A colourless solution of Ph₂PCI (0.1 mmol, 22 mg, 17.9 μL, 1 eq.) in 1 mL of toluene was added to an orange solution of **1** (0.1 mmol, 38 mg, 1 eq.) and Ti[TEF] (0.1 mmol, 117 mg, 1 eq., [TEF]⁻ = [Al(OC(CF₃)₃)₄]⁻) in 5 mL of *o*-DFB at room temperature. Immediate precipitation of small amounts of white solid and a slow colour change to red could be observed. After stirring for 24 h at room temperature the mixture was filtered through glass fibre filter paper and the solvent was removed *in vacuo*. The oily red residue was washed three times with 10 mL of *n*-hexane, each, and dried under reduced pressure (10⁻³ mbar). Dark red crystals of [Cp''Ni(η³-P₄Ph₂)] [TEF] (**2a**[TEF]), suitable for X-ray analysis could be obtained by slowly evaporating CH₂Cl₂ from a concentrated solution. Performing the same reaction with Ag[TEF] instead of Ti[TEF] results in diminished yields.

Yield: 80 mg (0.052 mmol, 52%)
 Elemental analysis: calc. (%) for [Cp''Ni(η³-P₄Ph₂)] [TEF] (C₄₅H₄₁O₄F₃₆AlP₄Ni): C: 35.16 H: 2.56
 found (%): C: 35.17 H: 2.53
 ESI(+)-MS (*o*-DFB): *m/z* (%) = 569.1 (100%) [Cp''Ni(η³-P₄Ph₂)]⁺
 NMR (CD₂Cl₂, 298 K): ¹H: δppm = 1.21 (s, 9 H, C(CH₃)₃), 1.31 (s, 18 H, C(CH₃)₃), 5.92 (s, 2 H, C₅H₂BU₃), 7.54–7.86 (br, 10 H, Ph)
³¹P{¹H}: (AMM'X spin system) δppm = 12.4 (ddd, ¹J_{PX-PM/PM'} = 270.3 Hz, ²J_{PX-PA} = 14.2 Hz, 1 P, P^X), 57.8 (ddd, ¹J_{PM/PM'-PX} = 270.3 Hz, ¹J_{PM/PM'-PA} = 288.1 Hz, 2 P, P^{MM}), 73.8 (ddd, ¹J_{PA-PM/PM'} = 288.1 Hz, ²J_{PA-PX} = 14.2 Hz, 1 P, P^A)
³¹P: (AMM'X spin system) δppm = 12.4 (t, ¹J_{PX-PM/PM'} = 270.3 Hz, 1 P, P^X), 57.8 (ddd, ¹J_{PM/PM'-PX} = 270.3 Hz, ¹J_{PM/PM'-PA} = 288.1 Hz, 2 P, P^{MM}), 73.8 (ddd, ¹J_{PA-PM/PM'} = 288.1 Hz, ²J_{PA-PX} = 14.2 Hz, 1 P, P^A)
¹⁹F{¹H}: δppm = -75.62 (s, [TEF]⁻)

[Cp''Ni(η³-P₄Ph₂)] [BAR^F] (2a[BAR^F])

A colourless solution of [(Et₃Si)₂(μ-H)][BAR^F] (0.1 mmol, 91 mg, 1 eq., [BAR^F]⁻ = [B(C₆F₅)₄]⁻) in 3 mL of *o*-DFB was added to an orange solution of **1** (0.1 mmol, 38 mg, 1 eq.) and Ph₂PCI (0.1 mmol, 22 mg, 17.9 μL, 1 eq.) in 4 mL of *o*-DFB at room temperature. Immediate colour change to red could be observed. After stirring for 6 h at room temperature the solvent was removed *in vacuo*. The oily red residue was washed three times with 10 mL of *n*-hexane, each, and dried under reduced pressure (10⁻³ mbar) leading to solidification. [Cp''Ni(η³-P₄Ph₂)] [BAR^F] (**2a**[BAR^F]) was isolated as an orange to red powder. All attempts to obtain (**2a**[BAR^F]) as a single crystalline material failed.

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Yield: 45 mg (0.037 mmol, 37%)
 Elemental analysis: calc. (%) for $[\text{Cp}^{\text{***}}\text{Ni}(\eta^3\text{-P}_4\text{Ph}_2)][\text{BAr}^{\text{F}}](\text{C}_6\text{H}_4\text{F}_2)_{1.5}$ ($\text{C}_{62}\text{H}_{47}\text{BF}_{23}\text{P}_4\text{Ni}$): C: 51.98 H: 3.18
 found (%): C: 52.35 H: 2.87 (Signals for $\text{C}_6\text{H}_4\text{F}_2$ are also found in the ^1H NMR of the isolated product)
 ESI(+) MS (*o*-DFB): m/z (%) = 569.1 (100%) $[\text{Cp}^{\text{***}}\text{Ni}(\eta^3\text{-P}_4\text{Ph}_2)]^+$
 NMR (CD_2Cl_2 , 298 K): ^1H : δ ppm = 1.21 (s, 9 H, $\text{C}(\text{CH}_3)_3$), 1.31 (s, 18 H, $\text{C}(\text{CH}_3)_3$), 5.92 (s, 2 H, $\text{C}_5\text{H}_2\text{Bu}_3$), 7.54–7.86 (br, 10 H, Ph)
 $^{31}\text{P}\{^1\text{H}\}$: (AMM'X spin system) δ ppm = 12.4 (ddd, $^1J_{\text{P}_X\text{-P}_M/\text{P}_M} = 270.3$ Hz, $^2J_{\text{P}_X\text{-P}_A} = 14.2$ Hz, 1 P, P^{X}), 57.8 (ddd, $^1J_{\text{P}_M/\text{P}_M\text{-P}_X} = 270.3$ Hz, $^1J_{\text{P}_M/\text{P}_M\text{-P}_A} = 288.1$ Hz, 2 P, $\text{P}^{\text{M/M}}$), 73.8 (ddd, $^1J_{\text{P}_A\text{-P}_M/\text{P}_M} = 288.1$ Hz, $^2J_{\text{P}_A\text{-P}_X} = 14.2$ Hz, 1 P, P_A)
 ^{31}P : (AMM'X spin system) δ ppm = 12.4 (t, $^1J_{\text{P}_X\text{-P}_M/\text{P}_M} = 270.3$ Hz, 1 P, P^{X}), 57.8 (ddd, $^1J_{\text{P}_M/\text{P}_M\text{-P}_X} = 270.3$ Hz, $^1J_{\text{P}_M/\text{P}_M\text{-P}_A} = 288.1$ Hz, 2 P, $\text{P}^{\text{M/M}}$), 73.8 (ddd, $^1J_{\text{P}_A\text{-P}_M/\text{P}_M} = 288.1$ Hz, $^2J_{\text{P}_A\text{-P}_X} = 14.2$ Hz, 1 P, P^A)
 $^{19}\text{F}\{^1\text{H}\}$: δ ppm = -167.4 (t, 2 F, $[\text{BAr}^{\text{F}}]^-$), -163.6 (t, 1 F, $[\text{BAr}^{\text{F}}]^-$), -133.0 (br, 2 F, $[\text{BAr}^{\text{F}}]^-$)

 $[\text{Cp}^{\text{***}}\text{Ni}(\eta^3\text{-P}_4\text{Ph}_2)][\text{GaCl}_4]$ (**2a** $[\text{GaCl}_4]$)

A colourless solution of GaCl_3 (0.1 mmol, 18 mg, 1 eq.) in 4 mL of *o*-DFB was added to an orange solution of **1** (0.1 mmol, 38 mg, 1 eq.) and Ph_2PCI (0.1 mmol, 22 mg, 17.9 μL , 1 eq.) in 3 mL of *o*-DFB at room temperature. A rapid colour change to dark red occurred. After stirring for 4 h at room temperature the solvent was removed *in vacuo* and the oily red residue was washed three times with 10 mL of *n*-hexane, each. Drying under reduced pressure (10^{-3} mbar) lead to solidification and dark red crystals of $[\text{Cp}^{\text{***}}\text{Ni}(\eta^3\text{-P}_4\text{Ph}_2)][\text{GaCl}_4]$ (**2a** $[\text{GaCl}_4]$), suitable for X-ray analysis could be obtained by recrystallisation from *o*-DFB/*n*-hexane (1:6) at room temperature after seven days.

Yield: 55 mg (0.071 mmol, 71%)
 Elemental analysis: calc. (%) for $[\text{Cp}^{\text{***}}\text{Ni}(\eta^3\text{-P}_4\text{Ph}_2)][\text{GaCl}_4]$ ($\text{C}_{29}\text{H}_{41}\text{P}_4\text{Cl}_4\text{NiGa}$): C: 44.56 H: 5.03
 found (%): C: 44.49 H: 5.11
 ESI(+) MS (*o*-DFB): m/z (%) = 569.1 (100%) $[\text{Cp}^{\text{***}}\text{Ni}(\eta^3\text{-P}_4\text{Ph}_2)]^+$
 NMR (CD_2Cl_2 , 298 K): ^1H : δ ppm = 1.21 (s, 9 H, $\text{C}(\text{CH}_3)_3$), 1.31 (s, 18 H, $\text{C}(\text{CH}_3)_3$), 5.92 (s, 2 H, $\text{C}_5\text{H}_2\text{Bu}_3$), 7.54–7.86 (br, 10 H, Ph)
 $^{31}\text{P}\{^1\text{H}\}$: (AMM'X spin system) δ ppm = 12.4 (ddd, $^1J_{\text{P}_X\text{-P}_M/\text{P}_M} = 270.3$ Hz, $^2J_{\text{P}_X\text{-P}_A} = 14.2$ Hz, 1 P, P^{X}), 57.8 (ddd, $^1J_{\text{P}_M/\text{P}_M\text{-P}_X} = 270.3$ Hz, $^1J_{\text{P}_M/\text{P}_M\text{-P}_A} = 288.1$ Hz, 2 P, $\text{P}^{\text{M/M}}$), 73.8 (ddd, $^1J_{\text{P}_A\text{-P}_M/\text{P}_M} = 288.1$ Hz, $^2J_{\text{P}_A\text{-P}_X} = 14.2$ Hz, 1 P, P^A)
 ^{31}P : (AMM'X spin system) δ ppm = 12.4 (t, $^1J_{\text{P}_X\text{-P}_M/\text{P}_M} = 270.3$ Hz, 1 P, P^{X}), 57.8 (ddd, $^1J_{\text{P}_M/\text{P}_M\text{-P}_X} = 270.3$ Hz, $^1J_{\text{P}_M/\text{P}_M\text{-P}_A} = 288.1$ Hz, 2 P, $\text{P}^{\text{M/M}}$), 73.8 (ddd, $^1J_{\text{P}_A\text{-P}_M/\text{P}_M} = 288.1$ Hz, $^2J_{\text{P}_A\text{-P}_X} = 14.2$ Hz, 1 P, P^A)

 $[\text{Cp}^{\text{***}}\text{Ni}(\eta^3\text{-P}_4\text{Mes}_2)][\text{GaCl}_4]$ (**2b** $[\text{GaCl}_4]$)

A colourless solution of GaCl_3 (0.1 mmol, 18 mg, 1 eq.) in 4 mL of *o*-DFB was added to an orange solution of **1** (0.1 mmol, 38 mg, 1 eq.) and Mes_2PCI (0.1 mmol, 30 mg, 1 eq.) in 3 mL of *o*-DFB at room temperature. A rapid colour change to red occurred. After stirring for 6 h at room temperature the solvent was removed *in vacuo* and the oily red residue was washed three times with 10 mL of *n*-hexane, each. Drying under reduced pressure (10^{-3} mbar) lead to solidification of the product $[\text{Cp}^{\text{***}}\text{Ni}(\eta^3\text{-P}_4\text{Mes}_2)][\text{GaCl}_4]$ (**2b** $[\text{GaCl}_4]$), which was isolated as a red powder. All attempts to recrystallise the product ended in the formation of red oil at the bottom of the flask.

Yield: 46 mg (0.053 mmol, 53%)
 Elemental analysis: calc. (%) for $[\text{Cp}^{\text{***}}\text{Ni}(\eta^3\text{-P}_4\text{Mes}_2)][\text{GaCl}_4]$ ($\text{C}_{35}\text{H}_{51}\text{P}_4\text{Cl}_4\text{NiGa}$): C: 48.72 H: 5.96
 found (%): C: 48.29 H: 5.79
 ESI(+) MS (*o*-DFB): m/z (%) = 653.2 (100%) $[\text{Cp}^{\text{***}}\text{Ni}(\eta^3\text{-P}_4\text{Mes}_2)]^+$
 NMR (CD_2Cl_2 , 298 K): ^1H : δ ppm = 1.14 (s, 9 H, $\text{C}(\text{CH}_3)_3$), 1.29 (s, 18 H, $\text{C}(\text{CH}_3)_3$), 2.32 (s, 6 H, Me), 2.64 (s, 6 H, Me), 2.73 (s, 6 H, Me), 5.92 (d, $^4J = 1.4$ Hz, 2 H, $\text{C}_5\text{H}_2\text{Bu}_3$), 6.98 (d, $^4J = 4.2$ Hz, 2 H, Mes), 7.01 (d, $^4J = 4.6$ Hz, 2 H, Mes)
 $^{31}\text{P}\{^1\text{H}\}$: (AA'MX spin system) δ ppm = -3.1 (t, $^1J_{\text{P}_X\text{-P}_A/\text{P}_A} = 267.7$ Hz, 1 P, P^{X}), 45.6 (t, $^1J_{\text{P}_M\text{-P}_A/\text{P}_A} = 294.8$ Hz, 1 P, P^{M}), 103.7 (dd, $^1J_{\text{P}_A/\text{P}_A\text{-P}_X} = 267.7$ Hz, $^1J_{\text{P}_A/\text{P}_A\text{-P}_M} = 294.8$ Hz, 2 P, P^A/A)
 $^{31}\text{P}\{^1\text{H}\}$: (AA'MX spin system) δ ppm = -3.1 (t, $^1J_{\text{P}_X\text{-P}_A/\text{P}_A} = 267.7$ Hz, 1 P, P^{X}), 45.6 (t, $^1J_{\text{P}_M\text{-P}_A/\text{P}_A} = 294.8$ Hz, 1 P, P^{M}), 103.7 (dd, $^1J_{\text{P}_A/\text{P}_A\text{-P}_X} = 267.7$ Hz, $^1J_{\text{P}_A/\text{P}_A\text{-P}_M} = 294.8$ Hz, 2 P, P^A/A)

 $[\text{Cp}^{\text{***}}\text{Ni}(\eta^3\text{-P}_4\text{Mes}_2)][\text{TEF}]$ (**2b** $[\text{TEF}]$)

A colourless solution of $\text{Ti}[\text{TEF}]$ (0.1 mmol, 117 mg, 1 eq., $[\text{TEF}]^- = [\text{Al}(\text{OC}(\text{CF}_3)_3)_4]^-$) in 2 mL of *o*-DFB was added to an orange solution of **1** (0.1 mmol, 38 mg, 1 eq.) and Mes_2PCI (0.1 mmol, 30 mg, 1 eq.) in 3 mL of *o*-DFB at room temperature. A rapid colour change to red occurred and formation of white solid could be observed. After stirring for 24 h at room temperature, the mixture was filtered, and the solvent removed *in vacuo*. The oily red residue was washed three times with 10 mL of *n*-hexane, each. Drying under reduced

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pressure (10^{-3} mbar) lead to solidification of the product $[\text{Cp}^{\text{***}}\text{Ni}(\eta^3\text{-P}_4\text{Mes}_2)][\text{TEF}]$ (**2b**[TEF]), which was isolated as a red powder. All attempts to recrystallise the product ended in the formation of red oil at the bottom of the flask.

Yield: 75 mg (0.046 mmol, 46%)

Elemental analysis: calc. (%) for $[\text{Cp}^{\text{***}}\text{Ni}(\eta^3\text{-P}_4\text{Mes}_2)][\text{TEF}]$ ($\text{C}_{51}\text{H}_{51}\text{O}_4\text{F}_{36}\text{AlP}_4\text{Ni}$): C: 37.77 H: 3.17
found (%): C: 38.05 H: 3.08

ESI(+)-MS (*o*-DFB): m/z (%) = 653.2 (100%) $[\text{Cp}^{\text{***}}\text{Ni}(\eta^3\text{-P}_4\text{Mes}_2)]^+$

NMR (CD_2Cl_2 , 298 K): ^1H : δ ppm = 1.14 (s, 9 H, $\text{C}(\text{CH}_3)_3$), 1.29 (s, 18 H, $\text{C}(\text{CH}_3)_3$), 2.32 (s, 6 H, Me), 2.64 (s, 6 H, Me), 2.73 (s, 6 H, Me), 5.92 (d, $^4J = 1.4$ Hz, 2 H, $\text{C}_5\text{H}_2\text{Bu}_3$), 6.98 (d, $^4J = 4.2$ Hz, 2 H, Mes), 7.01 (d, $^4J = 4.6$ Hz, 2 H, Mes)
 $^{31}\text{P}\{\text{H}\}$: (AMXX' spin system) δ ppm = -3.1 (t, $^1J_{\text{P}_X\text{-PA/PA}'} = 267.7$ Hz, 1 P, P^{X}), 45.6 (t, $^1J_{\text{P}_M\text{-PA/PA}'} = 294.8$ Hz, 1 P, P^{M}), 103.7 (dd, $^1J_{\text{PA/PA}'}\text{-PX} = 267.7$ Hz, $^1J_{\text{PA/PA}'}\text{-PM} = 294.8$ Hz, 2 P, $\text{P}^{\text{A/A}'}$)
 $^{31}\text{P}\{\text{H}\}$: (AMXX' spin system) δ ppm = -3.1 (t, $^1J_{\text{P}_X\text{-PA/PA}'} = 267.7$ Hz, 1 P, P^{X}), 45.6 (t, $^1J_{\text{P}_M\text{-PA/PA}'} = 294.8$ Hz, 1 P, P^{M}), 103.7 (dd, $^1J_{\text{PA/PA}'}\text{-PX} = 267.7$ Hz, $^1J_{\text{PA/PA}'}\text{-PM} = 294.8$ Hz, 2 P, $\text{P}^{\text{A/A}'}$)
 $^{19}\text{F}\{\text{H}\}$: δ ppm = -75.62 (s, [TEF] $^-$)

$[\text{Cp}^{\text{***}}\text{Ni}(\eta^3\text{-P}_4\text{Cy}_2)][\text{GaCl}_4]$ (**2c**[GaCl₄])

A colourless solution of GaCl_3 (0.1 mmol, 18 mg, 1 eq.) in 4 mL of *o*-DFB was added to an orange solution of **1** (0.1 mmol, 38 mg, 1 eq.) and Cy_2PCl (0.1 mmol, 23 mg, 22 μL , 1 eq.) in 3 mL of *o*-DFB at room temperature. A rapid colour change to red occurred. After stirring for 6 h at room temperature the solvent was removed *in vacuo* and the oily red residue was washed three times with 10 mL of *n*-hexane, each. Drying under reduced pressure (10^{-3} mbar) lead to solidification of the product $[\text{Cp}^{\text{***}}\text{Ni}(\eta^3\text{-P}_4\text{Cy}_2)][\text{GaCl}_4]$ (**2c**[GaCl₄]), which was then recrystallised from *o*-DFB/*n*-hexane (1:8) at -30 °C to give dark red crystals of X-ray analysis quality after two weeks.

Yield: 47 mg (0.059 mmol, 59%)

Elemental analysis: calc. (%) for $[\text{Cp}^{\text{***}}\text{Ni}(\eta^3\text{-P}_4\text{Cy}_2)][\text{GaCl}_4] \cdot (\text{C}_6\text{H}_4\text{F}_2)_{0.2}$ ($\text{C}_{30.2}\text{H}_{51.8}\text{P}_4\text{Cl}_4\text{NiGa}$): C: 44.42 H: 6.39
found (%): C: 44.38 H: 6.12

ESI(+)-MS (*o*-DFB): m/z (%) = 581.2 (100%) $[\text{Cp}^{\text{***}}\text{Ni}(\eta^3\text{-P}_4\text{Cy}_2)]^+$

NMR (CD_2Cl_2 , 298 K): ^1H : δ ppm = 1.26 – 2.56 (several broad multiplets, 22 H, Cy), 1.29 (s, 9 H, $\text{C}(\text{CH}_3)_3$), 1.45 (s, 18 H, $\text{C}(\text{CH}_3)_3$), 5.92 (d, $^4J = 1.4$ Hz, 2 H, $\text{C}_5\text{H}_2\text{Bu}_3$)
 $^{31}\text{P}\{\text{H}\}$: (AMXX' spin system) δ ppm = 35.0 (m, $^1J_{\text{P}_X\text{-PM}} = 270.9$ Hz, $^1J_{\text{P}_X\text{-PM}} = 261.8$ Hz, $^1J_{\text{P}_X\text{-PA}} = 286.6$ Hz, $^1J_{\text{P}_X\text{-PA}} = 296.7$ Hz, $^2J_{\text{P}_X\text{-PX}'} = 22.7$ Hz, 2 P, $\text{P}^{\text{X/X}'}$), 48.5 (ddd, $^1J_{\text{P}_M\text{-PX}} = 270.9$ Hz, $^1J_{\text{P}_M\text{-PX}} = 261.8$ Hz, $^2J_{\text{P}_M\text{-PA}} = 12.3$ Hz, 1 P, P^{M}), 84.3 (ddd, $^1J_{\text{PA-PX}} = 286.6$ Hz, $^1J_{\text{PA-PX}'} = 296.7$ Hz, $^2J_{\text{PA-PM}} = 12.3$ Hz, 1 P, P^{A})
 ^{31}P : (AMXX' spin system) δ ppm = 35.0 (m, $^1J_{\text{P}_X\text{-PM}} = 270.9$ Hz, $^1J_{\text{P}_X\text{-PM}} = 261.8$ Hz, $^1J_{\text{P}_X\text{-PM}} = 286.6$ Hz, $^1J_{\text{P}_X\text{-PA}} = 296.7$ Hz, $^2J_{\text{P}_X\text{-PX}'} = 22.7$ Hz, 2 P, $\text{P}^{\text{X/X}'}$), 48.5 (m, 1 P, P^{M}), 84.3 (ddd, $^1J_{\text{PA-PX}} = 286.6$ Hz, $^1J_{\text{PA-PX}'} = 296.7$ Hz, $^2J_{\text{PA-PM}} = 12.3$ Hz, 1 P, P^{A})

$[\text{Cp}^{\text{***}}\text{Ni}(\eta^3\text{-P}_4\text{Cy}_2)][\text{TEF}]$ (**2c**[TEF])

A colourless solution of $\text{Ti}[\text{TEF}]$ (0.1 mmol, 117 mg, 1 eq.) in 2 mL of *o*-DFB was added to an orange solution of **1** (0.1 mmol, 38 mg, 1 eq.) and Cy_2PCl (0.1 mmol, 23 mg, 22 μL , 1 eq.) in 3 mL of *o*-DFB at room temperature. A rapid colour change to red occurred and formation of white solid could be observed. After stirring for 24 h at room temperature, the mixture was filtered, and the solvent removed *in vacuo*. The oily red residue was dissolved in 3 mL of CH_2Cl_2 , precipitated with 30 mL of *n*-hexane and washed three times with 10 mL of *n*-hexane, each. Drying under reduced pressure (10^{-3} mbar) lead to solidification of the product $[\text{Cp}^{\text{***}}\text{Ni}(\eta^3\text{-P}_4\text{Cy}_2)][\text{TEF}]$ (**2c**[TEF]), which was isolated as an orange to red powder. All attempts to recrystallise the product ended in the formation of red oil at the bottom of the flask.

Yield: 88 mg (0.057 mmol, 57%)

Elemental analysis: calc. (%) for $[\text{Cp}^{\text{***}}\text{Ni}(\eta^3\text{-P}_4\text{Cy}_2)][\text{TEF}]$ ($\text{C}_{45}\text{H}_{51}\text{O}_4\text{F}_{36}\text{AlP}_4\text{Ni}$): C: 35.16 H: 2.56
found (%): C: 35.04 H: 3.06

ESI(+)-MS (CH_2Cl_2): m/z (%) = 581.2 (100%) $[\text{Cp}^{\text{***}}\text{Ni}(\eta^3\text{-P}_4\text{Cy}_2)]^+$

NMR (CD_2Cl_2 , 298 K): ^1H : δ ppm = 1.26 – 2.56 (several broad multiplets, 22 H, Cy), 1.29 (s, 9 H, $\text{C}(\text{CH}_3)_3$), 1.45 (s, 18 H, $\text{C}(\text{CH}_3)_3$), 5.92 (d, $^4J = 1.4$ Hz, 2 H, $\text{C}_5\text{H}_2\text{Bu}_3$)
 $^{31}\text{P}\{\text{H}\}$: (AMXX' spin system) δ ppm = 35.0 (m, $^1J_{\text{P}_X\text{-PM}} = 270.9$ Hz, $^1J_{\text{P}_X\text{-PM}} = 261.8$ Hz, $^1J_{\text{P}_X\text{-PA}} = 286.6$ Hz, $^1J_{\text{P}_X\text{-PA}} = 296.7$ Hz, $^2J_{\text{P}_X\text{-PX}'} = 22.7$ Hz, 2 P, $\text{P}^{\text{X/X}'}$), 48.5 (ddd, $^1J_{\text{P}_M\text{-PX}} = 270.9$ Hz, $^1J_{\text{P}_M\text{-PX}} = 261.8$ Hz, $^2J_{\text{P}_M\text{-PA}} = 12.3$ Hz, 1 P, P^{M}), 84.3 (ddd, $^1J_{\text{PA-PX}} = 286.6$ Hz, $^1J_{\text{PA-PX}'} = 296.7$ Hz, $^2J_{\text{PA-PM}} = 12.3$ Hz, 1 P, P^{A})
 ^{31}P : (AMXX' spin system) δ ppm = 35.0 (m, $^1J_{\text{P}_X\text{-PM}} = 270.9$ Hz, $^1J_{\text{P}_X\text{-PM}} = 261.8$ Hz, $^1J_{\text{P}_X\text{-PM}} = 286.6$ Hz, $^1J_{\text{P}_X\text{-PA}} = 296.7$ Hz, $^2J_{\text{P}_X\text{-PX}'} = 22.7$ Hz, 2 P, $\text{P}^{\text{X/X}'}$), 48.5 (m, 1 P, P^{M}), 84.3 (ddd, $^1J_{\text{PA-PX}} = 286.6$ Hz, $^1J_{\text{PA-PX}'} = 296.7$ Hz, $^2J_{\text{PA-PM}} = 12.3$ Hz, 1 P, P^{A})
 $^{19}\text{F}\{\text{H}\}$: δ ppm = -75.62 (s, [TEF] $^-$)

$[\text{Cp}^{\text{***}}\text{Ni}(\eta^3\text{-P}_4\text{biphen})][\text{GaCl}_4]$ (**2d**[GaCl₄])

A colourless solution of GaCl_3 (0.1 mmol, 18 mg, 1 eq.) in 4 mL of CH_2Cl_2 was added to an orange solution of **1** (0.1 mmol, 38 mg, 1 eq.) and biphen PCl (0.1 mmol, 22 mg, 1 eq.) in 3 mL of CH_2Cl_2 at room temperature. Rapid colour change to dark red occurred. After

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stirring the solution for 1.5 h, it was constrained to a total of 4 mL, layered with 20 mL of *n*-hexane, and stored at $-30\text{ }^{\circ}\text{C}$. After one week, formation of red microcrystalline $[\text{Cp}^{\text{***}}\text{Ni}(\eta^3\text{-P}_4\text{biphen})][\text{GaCl}_4]$ (**2d** $[\text{GaCl}_4]$) could be observed. Recrystallisation from $\text{CH}_2\text{Cl}_2/n$ -hexane (1:5) at $-30\text{ }^{\circ}\text{C}$ yielded light red crystals of X-ray quality after two weeks.

Yield: 55 mg (0.07 mmol, 70 %)
 Elemental analysis: calc. (%) for $[\text{Cp}^{\text{***}}\text{Ni}(\eta^3\text{-P}_4\text{biphen})][\text{GaCl}_4]\cdot(\text{C}_6\text{H}_{14})_{0.6}$ ($\text{C}_{32.6}\text{H}_{45.4}\text{P}_4\text{Cl}_4\text{NiGa}$): C: 47.09 H: 5.50
 found (%): C: 47.56 H: 5.11
 ESI(+) MS (*o*-DFB): m/z (%) = 567.1 (100%) $[\text{Cp}^{\text{***}}\text{Ni}(\eta^3\text{-P}_4\text{biphen})]^+$, 895.2 (8%) $[(\text{Cp}^{\text{***}}\text{Ni})(\mu_3\eta^3\eta^1\eta^1\text{-P}_4\text{biphenCl})]^+$
 NMR (CD_2Cl_2 , 298 K): ^1H : δ ppm = 1.36 (s, 9 H, $\text{C}(\text{CH}_3)_3$), 1.52 (s, 18 H, $\text{C}(\text{CH}_3)_3$), 6.25 (d, $^4J_{\text{H-H}} = 1.5$ Hz, 2 H, $\text{C}_5\text{H}_2\text{Bu}_3$), 7.72 (m, 2 H, biphen), 7.83 (m, 2 H, biphen), 7.96 (m, 2 H, biphen), 8.28 (m, 2 H, biphen)
 $^{31}\text{P}\{^1\text{H}\}$: (AA'MX spin system) δ ppm = 17.1 (m, $^1J_{\text{P-X-PA}} = 292.8$ Hz, $^1J_{\text{P-X-PA}'} = 274.2$ Hz, $^2J_{\text{P-X-PM}} = 24.8$ Hz, 1 P, P^X), 63.8 (m, $^1J_{\text{PM-PA}} = 277.2$ Hz, $^1J_{\text{PM-PA}'} = 282.5$ Hz, $^2J_{\text{PM-PX}} = 24.8$ Hz, 1 P, P^M), 70.0 (m, $^1J_{\text{PA-PX}} = 292.8$ Hz, $^1J_{\text{PA}'-PX} = 274.2$ Hz, $^1J_{\text{PA-PM}} = 277.2$ Hz, $^1J_{\text{PA}'-PM} = 282.5$ Hz, 2 P, P^{A/A'}})
 ^{31}P : (AA'MX spin system) δ ppm = 17.1 (t, $^1J_{\text{P-X-PA/A}'} = 282.4$ Hz, 1 P, P^X), 63.8 (m, $^1J_{\text{PM-PA}} = 277.2$ Hz, $^1J_{\text{PM-PA}'} = 282.5$ Hz, $^2J_{\text{PM-PX}} = 24.8$ Hz, 1 P, P^M), 70.0 (m, $^1J_{\text{PA-PX}} = 292.8$ Hz, $^1J_{\text{PA}'-PX} = 274.2$ Hz, $^1J_{\text{PA-PM}} = 277.2$ Hz, $^1J_{\text{PA}'-PM} = 282.5$ Hz, 2 P, P^{A/A'}})

$[\text{Cp}^{\text{***}}\text{Ni}(\eta^3\text{-P}_4\text{biphen})][\text{TEF}]$ (**2d** $[\text{TEF}]$)

A colourless solution of $\text{Ti}[\text{TEF}]$ (0.1 mmol, 117 mg, 1 eq.) in 2 mL of *o*-DFB was added to an orange solution of **1** (0.1 mmol, 38 mg, 1 eq.) and biphen $\text{P}(\text{Cl})$ (0.1 mmol, 22 mg, 1 eq.) in 3 mL of *o*-DFB at room temperature. A rapid colour change to dark red occurred and formation of white solid could be observed. After stirring for 24 h at room temperature, the mixture was filtered, and the solvent removed *in vacuo*. The dark red residue was washed three times with 10 mL of *n*-hexane, each, and then dried under reduced pressure (10^{-3} mbar) to yield $[\text{Cp}^{\text{***}}\text{Ni}(\eta^3\text{-P}_4\text{biphen})][\text{TEF}]$ (**2d** $[\text{TEF}]$) as an orange to red powder.

Yield: 84 mg (0.055 mmol, 55%)
 Elemental analysis: calc. (%) for $[\text{Cp}^{\text{***}}\text{Ni}(\eta^3\text{-P}_4\text{biphen})][\text{TEF}]$ ($\text{C}_{45}\text{H}_{37}\text{O}_4\text{F}_{36}\text{AlP}_4\text{Ni}$): C: 35.20 H: 2.43
 found (%): C: 35.02 H: 2.47
 ESI(+) MS (CH_2Cl_2): m/z (%) = 567.1 (100%) $[\text{Cp}^{\text{***}}\text{Ni}(\eta^3\text{-P}_4\text{biphen})]^+$
 NMR (CD_2Cl_2 , 298 K): ^1H : δ ppm = 1.36 (s, 9 H, $\text{C}(\text{CH}_3)_3$), 1.52 (s, 18 H, $\text{C}(\text{CH}_3)_3$), 6.25 (d, $^4J_{\text{H-H}} = 1.5$ Hz, 2 H, $\text{C}_5\text{H}_2\text{Bu}_3$), 7.72 (m, 2 H, biphen), 7.83 (m, 2 H, biphen), 7.96 (m, 2 H, biphen), 8.28 (m, 2 H, biphen)
 $^{31}\text{P}\{^1\text{H}\}$: (AA'MX spin system) δ ppm = 17.1 (m, $^1J_{\text{P-X-PA}} = 292.8$ Hz, $^1J_{\text{P-X-PA}'} = 274.2$ Hz, $^2J_{\text{P-X-PM}} = 24.8$ Hz, 1 P, P^X), 63.8 (m, $^1J_{\text{PM-PA}} = 277.2$ Hz, $^1J_{\text{PM-PA}'} = 282.5$ Hz, $^2J_{\text{PM-PX}} = 24.8$ Hz, 1 P, P^M), 70.0 (m, $^1J_{\text{PA-PX}} = 292.8$ Hz, $^1J_{\text{PA}'-PX} = 274.2$ Hz, $^1J_{\text{PA-PM}} = 277.2$ Hz, $^1J_{\text{PA}'-PM} = 282.5$ Hz, 2 P, P^{A/A'}})
 ^{31}P : (AA'MX spin system) δ ppm = 17.1 (t, $^1J_{\text{P-X-PA/A}'} = 282.4$ Hz, 1 P, P^X), 63.8 (m, $^1J_{\text{PM-PA}} = 277.2$ Hz, $^1J_{\text{PM-PA}'} = 282.5$ Hz, $^2J_{\text{PM-PX}} = 24.8$ Hz, 1 P, P^M), 70.0 (m, $^1J_{\text{PA-PX}} = 292.8$ Hz, $^1J_{\text{PA}'-PX} = 274.2$ Hz, $^1J_{\text{PA-PM}} = 277.2$ Hz, $^1J_{\text{PA}'-PM} = 282.5$ Hz, 2 P, P^{A/A'}})
 $^{19}\text{F}\{^1\text{H}\}$: δ ppm = -75.54 (s, $[\text{TEF}]^-$)

$[\text{Cp}^{\text{***}}\text{Ni}(\eta^3\text{-P}_4\text{Me}_2)][\text{TEF}]$ (**2e** $[\text{TEF}]$)

A colourless solution of $\text{Ti}[\text{TEF}]$ (0.1 mmol, 117 mg, 1 eq.) in 2 mL of *o*-DFB was added to an orange solution of **1** (0.1 mmol, 38 mg, 1 eq.) and $\text{Me}_2\text{P}(\text{Cl})$ (0.1 mmol, 10 mg, 10 μL , 1 eq.) in 3 mL of *o*-DFB at room temperature. A rapid colour change to red occurred and formation of white solid could be observed. After stirring for 24 h at room temperature, the mixture was filtered, and the solvent removed *in vacuo*. The oily red residue was washed three times with 10 mL of *n*-hexane, each. Drying under reduced pressure (10^{-3} mbar) lead to solidification. Recrystallisation from *o*-DFB/*n*-hexane (1:10) at $4\text{ }^{\circ}\text{C}$ gave $[\text{Cp}^{\text{***}}\text{Ni}(\eta^3\text{-P}_4\text{Me}_2)][\text{TEF}]$ (**2e** $[\text{TEF}]$) as a single crystalline material after 10 days.

Yield: 73 mg (0.052 mmol, 52%)
 Elemental analysis: calc. (%) for $[\text{Cp}^{\text{***}}\text{Ni}(\eta^3\text{-P}_4\text{Me}_2)][\text{TEF}]$ ($\text{C}_{35}\text{H}_{35}\text{O}_4\text{F}_{36}\text{AlP}_4\text{Ni}$): C: 29.74 H: 2.50
 found (%): C: 29.95 H: 2.42
 ESI(+) MS (CH_2Cl_2): m/z (%) = 445.1 (100%) $[\text{Cp}^{\text{***}}\text{Ni}(\eta^3\text{-P}_4\text{Me}_2)]^+$
 NMR (CD_2Cl_2 , 298 K): ^1H : δ ppm = 1.30 (s, 9 H, $\text{C}(\text{CH}_3)_3$), 1.44 (s, 18 H, $\text{C}(\text{CH}_3)_3$), 2.01 (d, $^2J_{\text{HP}} = 12.2$ Hz, 3 H, Me), 2.30 (d, $^2J_{\text{HP}} = 12.4$ Hz, 3 H, Me), 5.96 (s, 2 H, $\text{C}_5\text{H}_2\text{Bu}_3$)
 $^{31}\text{P}\{^1\text{H}\}$: (AMM'X spin system) δ ppm = 14.7 (ddd, $^1J_{\text{P-X-PM}} = 257.1$ Hz, $^1J_{\text{P-X-PM}'} = 255.4$ Hz, $^2J_{\text{P-X-PA}} = 18.6$ Hz, 1 P, P^X), 64.0 (m, $^1J_{\text{PM-PX}} = 257.1$ Hz, $^1J_{\text{PM}'-PX} = 255.4$ Hz, $^1J_{\text{PM-PA}} = 295.4$ Hz, $^1J_{\text{PM}'-PA} = 279.5$ Hz, 2 P, P^{MM'}}), 83.5 (ddd, $^1J_{\text{PA-PM}} = 295.4$ Hz, $^1J_{\text{PA-PM}'} = 279.5$ Hz, $^2J_{\text{PA-PX}} = 18.6$ Hz, 1 P, P^A)
 ^{31}P : (AMM'X spin system) δ ppm = 14.7 (m, 1 P, P^X), 64.0 (m, $^1J_{\text{PM-PX}} = 257.1$ Hz, $^1J_{\text{PM}'-PX} = 255.4$ Hz, $^1J_{\text{PM-PA}} = 295.4$ Hz, $^1J_{\text{PM}'-PA} = 279.5$ Hz, 2 P, P^{MM'}}), 83.5 (ddd, $^1J_{\text{PA-PM}} = 295.4$ Hz, $^1J_{\text{PA-PM}'} = 279.5$ Hz, $^2J_{\text{PA-PX}} = 18.6$ Hz, 1 P, P^A)
 $^{19}\text{F}\{^1\text{H}\}$: δ ppm = -75.60 (s, $[\text{TEF}]^-$)

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[Cp^{'''}Ni(η³-P₄PhCl)]][TEF] (2f[TEF])

A colourless solution of Ti[TEF] (0.1 mmol, 117 mg, 1 eq.) in 2 mL of *o*-DFB was added to an orange solution of **1** (0.1 mmol, 38 mg, 1 eq.) and PhPCl₂ (0.1 mmol, 18 mg, 14 μL, 1 eq.) in 3 mL of *o*-DFB at room temperature. A rapid colour change to dark red occurred and formation of white solid could be observed. After stirring for 20 h at room temperature, the mixture was filtered, and the solvent removed *in vacuo*. The oily red residue was washed three times with 10 mL of *n*-hexane, each. Drying under reduced pressure (10⁻³ mbar) lead to formation of [Cp^{'''}Ni(η³-P₄CiPh)]][TEF] (**2f**[TEF]) as a brownish red solid. NMR spectroscopy studies revealed that **2f**[TEF] is formed in two isomeric forms, *endo*-Ph and *exo*-Ph, respectively. According to the ¹H and ³¹P NMR spectrum the two isomers are formed in a ratio of 1:7. Crystals of the *endo*-Ph isomer of **2f**[TEF] could be obtained in X-ray analysis quality, by recrystallisation from *o*-DFB/*n*-hexane (1:6) at 4 °C for two weeks.

Yield: 93 mg (0.06 mmol, 60%)
 Elemental analysis: calc. (%) for [Cp^{'''}Ni(η³-P₄Me₂)]][TEF]·(C₆H₄F₂)_{0.6} (C_{42.6}H_{36.4}O₄F_{37.2}AlP₄Ni): C: 32.72 H: 2.35
 found (%): C: 32.89 H: 2.52 (Signals for C₆H₄F₂ are also found in the ¹H NMR of the isolated product)
 ESI(+)-MS (*o*-DFB): *m/z* (%) = 527.1 (100%) [Cp^{'''}Ni(η³-P₄PhCl)]⁺
 NMR (CD₂Cl₂, 298 K): ¹H: δppm = 1.21 (s, 9 H, C(CH₃)₃ (**2f**⁺*exo*)), 1.29 (s, 18 H, C(CH₃)₃ (**2f**⁺*exo*)), 1.39 (s, 9 H, C(CH₃)₃ (**2f**⁺*endo*)), 1.49 (s, 18 H, C(CH₃)₃ (**2f**⁺*endo*)), 5.91 (d, ⁴J_{H-H} = 2.7 Hz, 2 H, C₅H₂BU₃ (**2f**⁺*exo*)), 6.05 (s, 2 H, C₅H₂BU₃ (**2f**⁺*endo*)), 7.73 (m, 2.3 H, Ph (**2f**⁺)), 7.81 (m, 1.1 H, Ph (**2f**⁺)), 7.9 – 8.0 (m, 2.3 H, Ph (**2f**⁺)), **2f**⁺*endo*: **2f**⁺*exo* = 7:1
³¹P{¹H}: (two AA'MX spin systems) δppm = 34.3 (ddd, ¹J_{PX-PA} = 274.1 Hz, ¹J_{PX-PA'} = 273.6 Hz, ²J_{PX-PM} = 36.8 Hz, 1 P, P^X (**2f**⁺*endo*)), 42.3 (ddd, ¹J_{PX-PA} = 331.1 Hz, ¹J_{PX-PA'} = 330.2 Hz, ²J_{PX-PM} = 18.7 Hz, 1 P, P^X (**2f**⁺*exo*)), 59.5 (ddd, ¹J_{PM-PA} = 346.4 Hz, ¹J_{PM-PA'} = 338.5 Hz, ²J_{PM-PX} = 36.8 Hz, 1 P, P^M (**2f**⁺*endo*)), 73.9 (ddd, ¹J_{PM-PA} = 285.0 Hz, ¹J_{PM-PA'} = 282.3 Hz, ²J_{PM-PX} = 18.7 Hz, 1 P, P^M (**2f**⁺*exo*)), 94.1 (m, ¹J_{PA-PX} = 331.1 Hz, ¹J_{PA'-PX} = 330.2 Hz, ¹J_{PA-PM} = 285.0 Hz, ¹J_{PA'-PM} = 282.3 Hz, 2 P, P^{A/A'} (**2f**⁺*exo*)), 113.5 (ddd, ¹J_{PA-PM} = 346.4 Hz, ¹J_{PA'-PM} = 338.5 Hz, ¹J_{P2-PX} = 274.1 Hz, ¹J_{P4-PX} = 273.6 Hz, 2 P, P^{A/A'} (**2f**⁺*endo*))
³¹P: (two AA'MX spin systems) δppm = 34.3 (ddd, ¹J_{PX-PA} = 274.1 Hz, ¹J_{PX-PA'} = 273.6 Hz, ²J_{PX-PM} = 36.8 Hz, 1 P, P^X (**2f**⁺*endo*)), 42.3 (t (broad), ¹J_{P-P} = 339.8 Hz, 1 P, P^X (**2f**⁺*exo*)), 59.5 (t (broad), ¹J_{P-P} = 342.4 Hz, 1 P, P^M (**2f**⁺*endo*)), 73.9 (ddd, ¹J_{PM-PA} = 285.0 Hz, ¹J_{PM-PA'} = 282.3 Hz, ²J_{PM-PX} = 18.7 Hz, 1 P, P^M (**2f**⁺*exo*)), 94.1 (m, ¹J_{PA-PX} = 331.1 Hz, ¹J_{PA'-PX} = 330.2 Hz, ¹J_{PA-PM} = 285.0 Hz, ¹J_{PA'-PM} = 282.3 Hz, 2 P, P^{A/A'} (**2f**⁺*exo*)), 113.5 (ddd, ¹J_{PA-PM} = 346.4 Hz, ¹J_{PA'-PM} = 338.5 Hz, ¹J_{PA-PX} = 274.1 Hz, ¹J_{PA'-PX} = 273.6 Hz, 2 P, P^{A/A'} (**2f**⁺*endo*)),
 Integration: **2f**⁺*endo*: **2f**⁺*exo* = 7:1
¹⁹F{¹H}: δppm = -75.57 (s, [TEF]⁻)

[Cp^{'''}Ni(η³-P₄BuCl)]][TEF] (2g[TEF])

A colourless solution of Ti[TEF] (0.1 mmol, 117 mg, 1 eq.) in 2 mL of *o*-DFB was added to an orange solution of **1** (0.1 mmol, 38 mg, 1 eq.) and ^tBuPCl₂ (0.1 mmol, 16 mg, 1 eq.) in 3 mL of *o*-DFB at room temperature. Precipitation of white solid and a colour change to red could be observed within one hour. Stirring for 20 h lead to darkening of the mixture. The solution was then filtered of the white solid, and the solvent removed *in vacuo*. The dark red to brown precipitate was washed three times with 10 mL of *n*-hexane, each. After drying under vacuum (10⁻³ mbar) [Cp^{'''}Ni(η³-P₄Ci^tBu)]][TEF] (**2g**[TEF]) could be isolated as a brown powder.

Yield: 74 mg (0.05 mmol, 50%)
 Elemental analysis: calc. (%) for [Cp^{'''}Ni(η³-P₄^tBuCl)]][TEF]·(C₆H₄F₂)_{0.4} (C_{39.4}H_{39.6}O₄F_{36.8}AlP₄CiNi): C: 31.11 H: 2.63
 found (%): C: 31.01 H: 2.50 (Signals for C₆H₄F₂ are also found in the ¹H NMR of the isolated product)
 ESI(+)-MS (*o*-DFB): *m/z* (%) = 507.1 (100%) [Cp^{'''}Ni(η³-P₄^tBuCl)]⁺
 NMR (CD₂Cl₂, 298 K): ¹H: δppm = 1.32 (s, 9 H, C(CH₃)₃), 1.46 (s, 18 H, C(CH₃)₃), 1.47 (d, ³J_{PH} = 22.0 Hz, 9 H, ^tBu), 6.01 (s, 2 H, C₅H₂BU₃)
³¹P{¹H}: δppm = 57.1 (ddd, ¹J_{PX-PM} = 288.6 Hz, ¹J_{PX-PM'} = 270.0 Hz, ²J_{PX-PA} = 41.9 Hz, 1 P, P^X), 85.9 (ddd, ¹J_{PM-PA} = 357.9 Hz, ¹J_{PM-PA'} = 324.8 Hz, ¹J_{PM-PX} = 288.6 Hz, ¹J_{PM'-PX} = 270.0 Hz, 2 P, P^{M/M'}), 107.2 (ddd, ¹J_{PA-PM} = 357.9 Hz, ¹J_{PA-PM'} = 324.8 Hz, ²J_{PA-PX} = 41.9 Hz, 1 P, P^A)
³¹P: δppm = 57.1 (ddd, ¹J_{PX-PM} = 288.6 Hz, ¹J_{PX-PM'} = 270.0 Hz, ²J_{PX-PA} = 41.9 Hz, 1 P, P^X), 85.9 (ddd, ¹J_{PM-PA} = 357.9 Hz, ¹J_{PM-PA'} = 324.8 Hz, ¹J_{PM-PX} = 288.6 Hz, ¹J_{PM'-PX} = 270.0 Hz, 2 P, P^{M/M'}), 107.2 (br, 1 P, P^A)
¹⁹F{¹H}: δppm = -75.60 (s, [TEF]⁻)

[(Cp^{'''}Ni)₂(μ;η³:η¹:η¹-P₄Br₃)]][TEF] (3a[TEF])

Addition of a solution of Ti[TEF] (0.1 mmol, 117 mg, 1 eq.) in 3 mL of CH₂Cl₂ to a solution of **1** (0.1 mmol, 38 mg, 1 eq.) and PBr₃ (0.1 mmol, 27 mg, 10 μL, 1 eq.) in 4 mL of CH₂Cl₂ at -80 °C lead to an immediate colour change to dark red and the precipitation of white solid. ³¹P NMR spectra (*o*-DFB/tol-*d*⁸ capillary, r. t., Figure SI 7) taken 1 h after the addition revealed the initial formation of

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$[(Cp^*Ni(\eta^3-P_4Br_2))][TEF]$ (**2h**[TEF]) besides P_4 and the final product $[(Cp^*Ni)_2(\mu;\eta^3:\eta^1:\eta^1-P_4Br_3)][TEF]$ (**3a**[TEF]). Attempts to isolate the intermediate **2h**[TEF] by filtration of the cold ($-80^\circ C$) solution and washing three times with cold *n*-hexane (10 mL each, $-80^\circ C$) failed. Isolated batches of (**2h**[TEF]) always carried impurities of the final product **3a**[TEF]. The latter was obtained, by letting the reaction mixture warm to room temperature overnight and stirring for three more days. The now dark brown mixture was filtered, and the solvent removed *in vacuo*. The brown precipitate was washed with 10 mL of *n*-hexane, each, and then dried under reduced pressure (10^{-3} mbar). Recrystallisation from CH_2Cl_2/n -hexane (1:6) at room temperature for six days yielded large blackish red crystals of **3a**[TEF] in X-ray quality. These crystals were washed with toluene, dried under reduced pressure and then isolated. Conducting the reaction in *o*-DFB, but only cooling to $-30^\circ C$ yielded similar results.

Yield: 92 mg (0.048 mmol, 90% based on **1**)
 Elemental analysis: calc. (%) for $[(Cp^*Ni)_2(\mu;\eta^3:\eta^1:\eta^1-P_4Br_3)][TEF]\cdot(TiBr)_{0.5}$ ($C_{50}H_{58}O_4F_{36}AlP_4Ni_2Br_{3.5}Ti_{0.5}$): C: 29.24 H: 2.85 found (%): C: 29.16 H: 2.56 (even after several filtration steps, TiBr precipitates after layering *o*-DFB solutions of the product and covers the surface of the crystals)
 ESI(+)-MS (*o*-DFB): m/z (%) = 332.2 (100) $[Cp^*Ni(H_3CCN)]^+$, 373.2 (20) $[Cp^*Ni(H_3CCN)_2]^+$, 947.0 (5) $[(Cp^*Ni)_2(\mu;\eta^3:\eta^1:\eta^1-P_4Br_3)]^+$; Acetonitrile molecules are from the purging solution of the diffractometer.
 NMR (CD_2Cl_2 , 298 K): 1H : δ ppm = 1.25 (s, 9 H, $C(CH_3)_3$), 1.41 (s, 9 H, $C(CH_3)_3$), 1.42 (s, 9 H, $C(CH_3)_3$), 1.46 (s, 18 H, $C(CH_3)_3$), 1.48 (s, 9 H, $C(CH_3)_3$), 4.91 (m, 1 H, $C_5H_2^tBu_3$), 5.35 (m, 1 H, $C_5H_2^tBu_3$), 5.43 (s, 1 H, $C_5H_2^tBu_3$), 5.91 (s, 1 H, $C_5H_2^tBu_3$)
 $^{31}P\{^1H\}$: (AMNX spin system) δ ppm = -1.1 (t (br), $^1J_{P-X-PN} = 347.0$ Hz, $^1J_{P-X-PM} = 379.2$ Hz, 1 P, P^X), 128.0 (td, $^1J_{P_2-PA} = 353.1$ Hz, $^1J_{PN-PX} = 347.0$ Hz, $^2J_{PN-PM} = 71.3$ Hz, 1 P, P^N), 134.2 (ddd, $^1J_{PM-PX} = 379.2$ Hz, $^2J_{PM-PA} = 281.7$ Hz, $^2J_{PM-PN} = 71.3$ Hz, 1 P, P^M), 182.0 (dd, $^1J_{PA-PN} = 353.1$, $^2J_{PA-PM} = 281.7$ Hz, 1 P, P^A)
 $^{31}P\{^1H\}$: (AMNX spin system) δ ppm = -1.1 (t (br), $^1J_{P-X-PN} = 347.0$ Hz, $^1J_{P-X-PM} = 379.2$ Hz, 1 P, P^X), 128.0 (td, $^1J_{P_2-PA} = 353.1$ Hz, $^1J_{PN-PX} = 347.0$ Hz, $^2J_{PN-PM} = 71.3$ Hz, 1 P, P^N), 134.2 (ddd, $^1J_{PM-PX} = 379.2$ Hz, $^2J_{PM-PA} = 281.7$ Hz, $^2J_{PM-PN} = 71.3$ Hz, 1 P, P^M), 182.0 (dd, $^1J_{PA-PN} = 353.1$, $^2J_{PA-PM} = 281.7$ Hz, 1 P, P^A)
 $^{19}F\{^1H\}$: δ ppm = -75.50 (s, [TEF] $^-$)

$[(Cp^*Ni)_2(\mu;\eta^3:\eta^1:\eta^1-P_4biphenCl)][GaCl_4]$ (**3b**[GaCl₄])

Following the same synthetic protocol as for (**2d**[GaCl₄]) but performing the reaction in *o*-DFB and stirring for 20 h again leads to a dark red solution of (**2d**[GaCl₄]), by NMR spectroscopy. When this solution was concentrated to 4 mL, layered with *n*-hexane (6:1), and then stored at room temperature for two weeks $[(Cp^*Ni)_2(\mu;\eta^3:\eta^1:\eta^1-P_4biphenCl)][GaCl_4]$ (**3b**[GaCl₄]) crystallised as light brown plates of X-ray quality. Alternatively, **2d**[GaCl₄] can be stirred in *o*-DFB solution (4 mL) for two weeks. When the resulting solution is layered with *n*-hexane, crystals of **3b**[GaCl₄] can be obtained in similar yield. Decanting off the solvent followed by washing steps (3 x 10 mL *n*-hexane) and drying under reduced pressure (10^{-3} mbar) gives pure **3b**[GaCl₄].

Yield: 41 mg (0.037 mmol, 74% based on **1**)
 Elemental analysis: calc. (%) for $[(Cp^*Ni)_2(\mu;\eta^3:\eta^1:\eta^1-P_4biphenCl)][GaCl_4]$ ($C_{46}H_{66}P_4Cl_5NiGa$): C: 49.90 H: 6.01 found (%): C: 50.02 H: 5.94
 ESI(+)-MS (*o*-DFB): m/z (%) = 895.2 (100) $[(Cp^*Ni)_2(\mu;\eta^3:\eta^1:\eta^1-P_4biphenCl)]^+$
 NMR (CD_2Cl_2 , 298 K): 1H : δ ppm = 0.89 (s, 9 H, $C(CH_3)_3$), 1.11 (s, 9 H, $C(CH_3)_3$), 1.25 (s, 9 H, $C(CH_3)_3$), 1.38 (s, 9 H, $C(CH_3)_3$), 1.40 (s, 9 H, $C(CH_3)_3$), 1.42 (s, 9 H, $C(CH_3)_3$), 4.69 (s, 1 H, $C_5H_2^tBu_3$), 5.20 (s, 1 H, $C_5H_2^tBu_3$), 5.54 (s, 1 H, $C_5H_2^tBu_3$), 5.60 (s, 1 H, $C_5H_2^tBu_3$), 7.53 (m, 2 H, biphen), 7.61 – 7.80 (m (br), 4 H, biphen), 8.00 (m, 2 H, biphen)
 $^{31}P\{^1H\}$: δ ppm = -31.9 (br, 1 P), 80.6 (br, 1 P), 84.1 (dd, $^1J_{PP} = 246.9$, $^2J_{PP} = 112.1$ Hz, 1 P), 146.6 (ddd, $^1J_{PP} = 392.2$ Hz, $^2J_{PP} = 112.1$ Hz, $^2J_{PP} = 69$ Hz, 1 P)
 ^{31}P : δ ppm = 84.1 (br, 1 P), 146.6 (m, 1 P); other signals are not observed due to significant line broadening

$[(Cp^*Ni)_2(\mu;\eta^3-\eta^3-P_3)][GaCl_4]$ (**4**)

A colourless solution of $GaCl_3$ (36 mg, 0.2 mmol, 1 eq.) in *o*-DFB (4 mL) was added to a bright orange solution of **1** (78 mg, 0.2 mmol, 1 eq.) in *o*-DFB (4 mL), which resulted in an immediate colour change to a dark greenish brown. This solution was stirred for 1 h and then 40 mL of *n*-pentane were added to precipitate a dark brown oil. The slightly yellowish solvent mixture was decanted, the oil washed three times with 10 mL of toluene and another three times with 10 mL of *n*-pentane, each and then dissolved in 3 mL of *o*-DFB again. This solution was layered with 25 mL of *n*-pentane and stored for four weeks at room temperature, affording dark greenish brown crystals of $[(Cp^*Ni)_2(\mu;\eta^3-\eta^3-P_3)][GaCl_4]$ (**4**) in X-ray analysis quality.

Yield: 72 mg (0.074 mmol, 74% based on **1**)
 Elemental analysis: calc. (%) for $[(Cp^*Ni)_2(\mu;\eta^3-\eta^3-P_3)][GaCl_4]\cdot(GaCl_3)_{0.5}$ ($C_{34}H_{58}P_3Cl_{5.5}Ni_2Ga_{1.5}$): C: 41.81 H: 5.99 found (%): C: 42.17 H: 5.82
 ESI(+)-MS (*o*-DFB): m/z (%) = 675.2 (80) $[(Cp^*Ni)_2(\mu;\eta^3-\eta^3-P_3)]^+$, below 300 (several peaks that could not be assigned to certain molecular fragments)
 NMR (CD_2Cl_2 , 298 K): 1H : δ ppm = 1.02 (s, 18 H, $C(CH_3)_3$), 1.36 (s, 36 H, $C(CH_3)_3$), 4.66 (s, 2 H, $C_5H_2^tBu_3$)
 $^{31}P\{^1H\}$: δ ppm = 139.5 (s)
 ^{31}P : δ ppm = 139.5 (s)

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Tested reactions and conditions

Attempts to employ $t\text{Bu}_2\text{PCl}$ or $(\text{Et}_2\text{N})_2\text{PCl}$ under identical conditions (*o*-DFB, $\text{Ti}[\text{TEF}]$ equimolar) as for the synthesis of **2a-2e**[TEF] failed as no observable colour change or precipitation of a white solid occurred. ^{31}P NMR spectra of the reaction mixtures revealed unreacted halogenophosphanes and **1** at $\delta = -168.8$ ppm. Using two equivalents of Ph_2PCl (0.2 mmol, 44 mg, 35.8 μL , 2 eq.) and $\text{Ti}[\text{TEF}]$ (0.2 mmol, 234 mg, 2 eq.) with only one equivalent of **1** (0.1 mmol, 38 mg, 1 eq.) under identical conditions did not lead to the anticipated second insertion of $[\text{Ph}_2\text{P}]^+$ into **2a**⁺. This reaction rather yielded **2a**[TEF] in similar yields to the reported procedure (*vide supra*) accompanied by $[\text{Ph}_2\text{ClPPPh}_2][\text{TEF}]$, identified by ^{31}P NMR spectra of the reaction solutions. When **1** (0.1 mmol, 38 mg, 1 eq.) is reacted with dihalogenophosphanes R_2PCl_2 ($\text{R} = \text{Ph}, t\text{Bu}$; 0.1 mmol) in the presence of two equivalents of $\text{Ti}[\text{TEF}]$ (0.2 mmol, 234 mg, 2 eq.) the second chloride atom is not abstracted and the reaction outcome are the products **2f**[TEF] and **2g**[TEF]. Excess of $\text{Ti}[\text{TEF}]$ crystallises from the reaction mixtures upon layering with *n*-hexane and cooling to -30 °C.

NMR spectroscopic investigations

Assignment of the signals in the ^{31}P NMR spectra (CD_2Cl_2 , r. t.) of the compounds **2a-g** is simplified by the broadening of the signal of the former phosphonium ion (P1) compared to the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. The other signals can then be assigned by following the $^1J_{\text{PP}}$ couplings around the P_4 ring. For simplification, the $^{31}\text{P}\{^1\text{H}\}$ and ^{31}P NMR spectra of **2a-e** and **2f/g** are compared in Figure S11 and Figure S12, respectively. The signals are labelled according to Figure S11b.

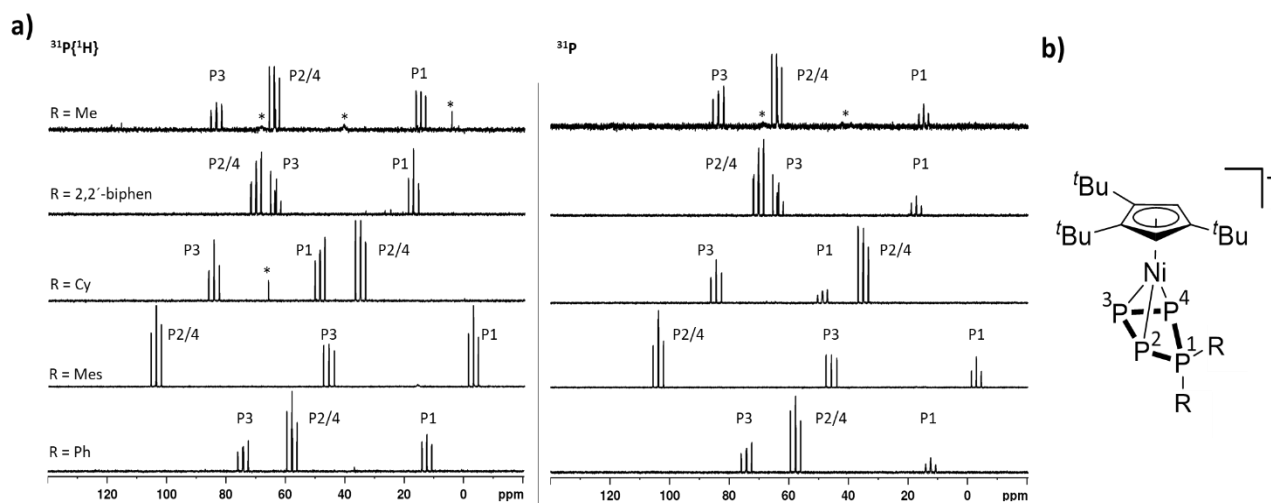


Figure S1: ^{31}P and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **2f-2g**[TEF] in CD_2Cl_2 recorded at 298 K with signal assignment corresponding to Figure S1 1b); The endo/exo labelling for **2f** refers to the position of the Ph ring on the P_4 ring.

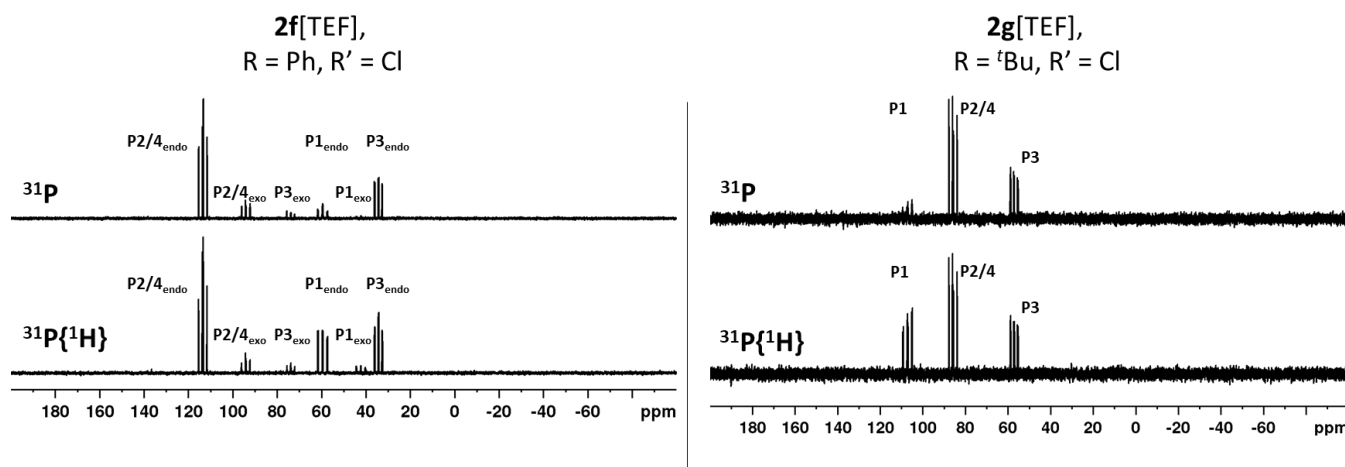


Figure S2: a) $^{31}\text{P}\{^1\text{H}\}$ (left) and ^{31}P NMR spectra (right) of **2a-2e**[TEF] in CD_2Cl_2 recorded at 298 K; signal assignment is done according to the structure shown in b) to illustrate the variation of the sequence of the signals with the corresponding P atoms.

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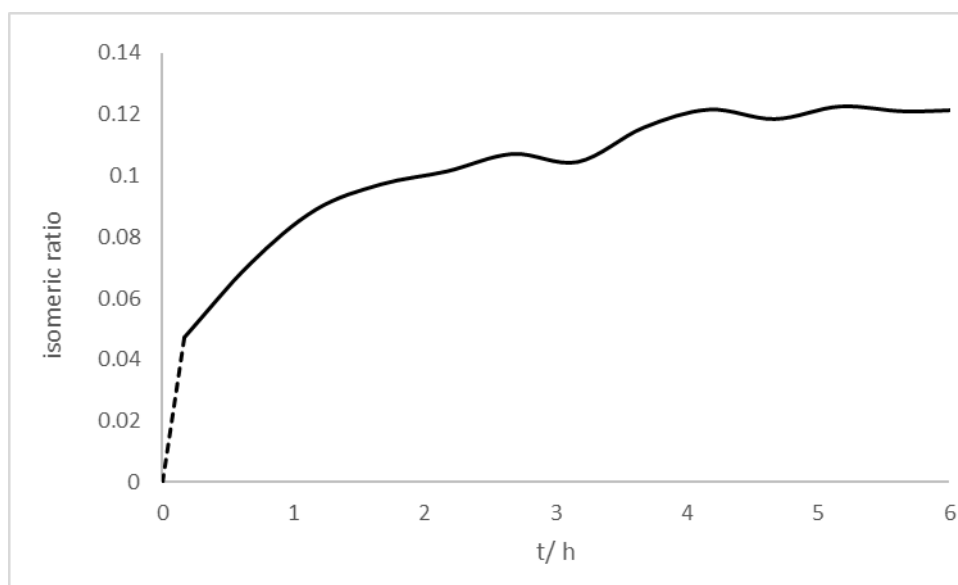


Figure SI 3: Plot of the isomeric ratio $2f_{\text{endo}}:2f_{\text{exo}}$ against the time after dissolving crystals of $2f_{\text{endo}}[\text{TEF}]$ in CD_2Cl_2 obtained from ^{31}P NMR spectra recorded every 30 min for 6 h; The final ratio after 6 h is 8:1, which is very close to that observed for spectra of precipitated $2f$ (7:1).

As both isomers of $2f$ are formed during the reaction of 1 with Ph_2PCI and $\text{Ti}[\text{TEF}]$, the question arises if they exist in equilibrium or if the observed isomeric ratio of 7:1 ($2f_{\text{endo}}:2f_{\text{exo}}$) is due to kinetic factors during the reaction. Thus, crystals of $2f_{\text{endo}}[\text{TEF}]$ were subjected to ^{31}P NMR spectroscopic measurements to gather information about the formation of both isomers of $2f$. Crystals of $2f_{\text{endo}}[\text{TEF}]$ were dissolved in 0.8 mL of CD_2Cl_2 and ^{31}P NMR spectra of this sample were recorded every 30 min for 6 h. The plot of the isomeric ratio during this time (Figure SI 3) shows that the initially present endo isomer slowly interconverts to the exo isomer until an isomeric ratio of 7:1 ($2f_{\text{endo}}:2f_{\text{exo}}$) is approached after 6 h. This clearly supports the assumption that both isomers exist in equilibrium (in solution) and their formation is not based on kinetic factors during the initial synthesis of $2f$.

The room temperature ^{31}P and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of $3a$ in CD_2Cl_2 are identical and express an AMNX spin system. An expected similar spectrum is not observed for $3b$ in CD_2Cl_2 , which is probably caused by a dynamic effect involving rotation of the $\text{Cp}^{\text{***}}$ ligands. Thus, the complete set of four resonances in the spectrum of $3b$ is only observed at very high scan numbers (6144), but two of them are significantly broadened (Figure SI 4).

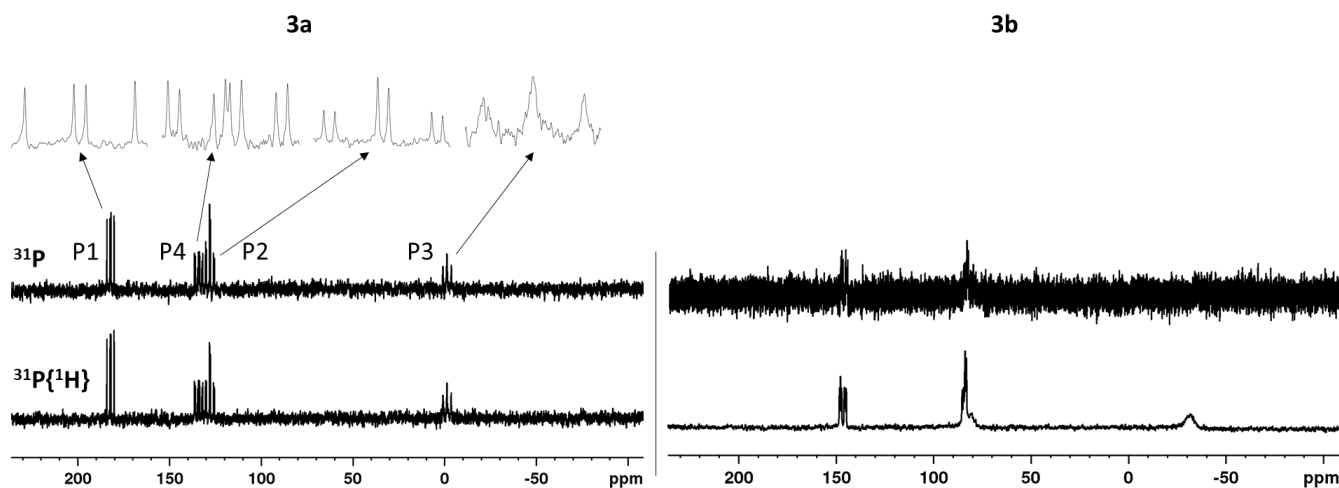


Figure SI 4: ^{31}P (top) and $^{31}\text{P}\{^1\text{H}\}$ (bottom) NMR spectra of $3a$ and $3b$ in CD_2Cl_2 recorded at 298 K with zoomed in signals for the spectra of $3a$; The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $3b$ was recorded with 6144 scans to be able to see the full set of four signals, which is not visible for the ^{31}P NMR spectrum (512 scans).

Only when the solution is cooled to -80°C sharp signals can be observed. However, at this temperature two sets of signals are found in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (Figure SI 5), thus indicating the presence of two isomeric forms of $3b_{1/2}$. We attribute these isomers to differently rotated $\text{Cp}^{\text{***}}$ ligands at both Ni centres. As the number of scans needed for recording this spectrum was still very high (8192), the corresponding ^{31}P spectrum could not be recorded and signal assignment was conducted as for $3a$ (most downfield shifted signal

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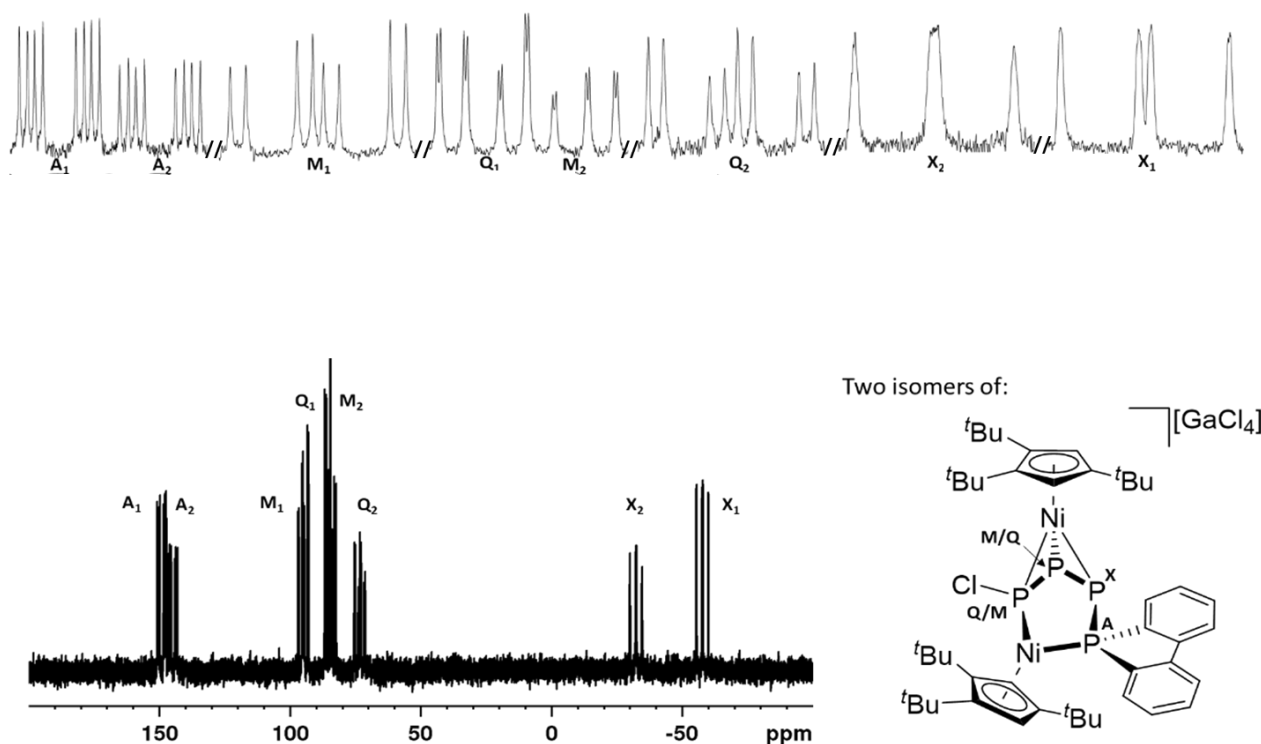


Figure SI 5: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **3b** in CD_2Cl_2 recorded at 193 K with 8192 scans (bottom), zoomed in signal with assignment (top) and structure of **3b** with assigned P atoms (right); Isomerism in the cation **3b** is most probably caused by hindered rotation of the Cp^* ligands at this temperature; Spectral parameters: **3b**₁: $\delta/\text{ppm} = 149.1$ (ddd, $^1J_{\text{PA-PX}} = 397.1$ Hz, $^2J_{\text{PA-PQ}} = 108.2$ Hz, $^2J_{\text{PA-PM}} = 57.3$ Hz, 1 P, P^{A}), 94.8 (ddd, $^1J_{\text{PM-PX}} = 346.9$ Hz, $^1J_{\text{PM-PQ}} = 247.2$ Hz, $^2J_{\text{PM-PA}} = 57.3$ Hz, 1 P, P^{M}), 85.7 (ddd, $^1J_{\text{PQ-PM}} = 247.2$ Hz, $^2J_{\text{PQ-PA}} = 108.2$ Hz, $^2J_{\text{PQ-PX}} = 11.7$ Hz, 1 P, P^{Q}), -57.8 (ddd, $^1J_{\text{PX-PA}} = 397.13$ Hz, $^1J_{\text{PX-PM}} = 346.9$ Hz, $^2J_{\text{PX-PQ}} = 11.7$ Hz, 1 P, P^{X}); **3b**₂: $\delta/\text{ppm} = 144.7$ (ddd, $^1J_{\text{PA-PX}} = 391.2$ Hz, $^2J_{\text{PA-PM}} = 113.2$ Hz, $^2J_{\text{PA-PQ}} = 60.6$ Hz, 1 P, P^{A}), 83.4 (ddd, $^1J_{\text{PM-PQ}} = 246.2$ Hz, $^2J_{\text{PM-PA}} = 113.2$, $^2J_{\text{PM-PX}} = 11.7$ Hz, 1 P, P^{M}), 73.4 (ddd, $^1J_{\text{PQ-PX}} = 360.4$ Hz, $^1J_{\text{PQ-PM}} = 246.2$ Hz, $^2J_{\text{PQ-PA}} = 60.6$ Hz, 1 P, P^{Q}), -32.4 (ddd, $^1J_{\text{PX-PA}} = 391.2$ Hz, $^1J_{\text{PX-PQ}} = 360.4$ Hz, $^2J_{\text{PX-PM}} = 11.7$ Hz, 1 P, P^{X}).

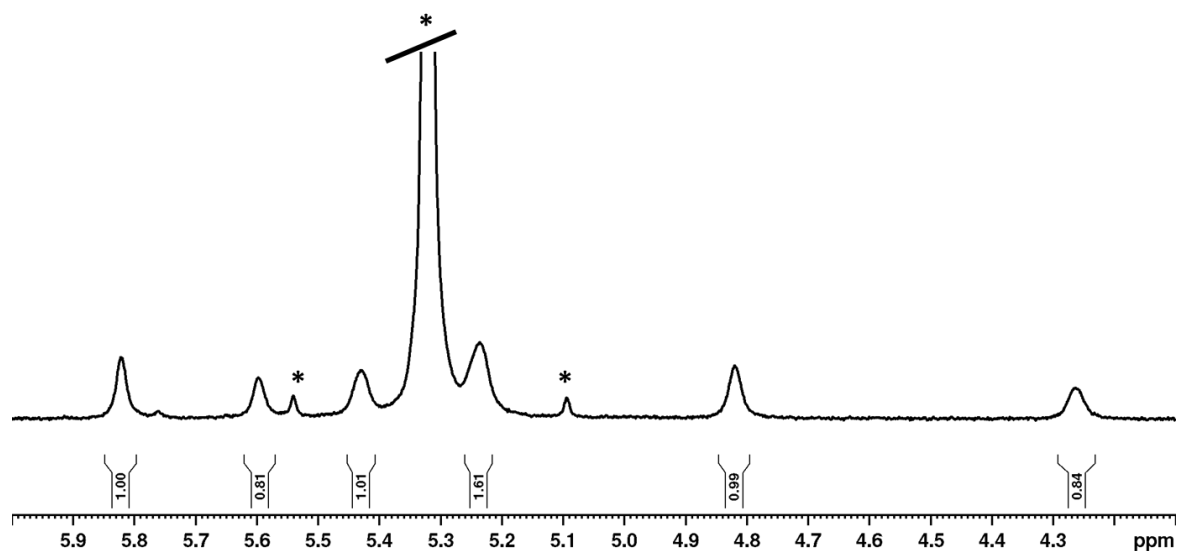


Figure SI 6: ^1H NMR spectrum of **3b** in CD_2Cl_2 recorded at 193 K showing two sets of signals for the $\text{C}_5\text{H}_2\text{Bu}_3$ protons, thus indicating the presence of two isomers of **3b**_{1,2} in a ratio of 1.25:1; One of the expected signals is probably overlapped by the large solvent signal caused by residual CH_2Cl_2 (*).

should be that of P^{A} due to the similarity with the starting material (2,2'-biphen)PCl). However, the corresponding ^1H NMR shows signals in accordance with two isomers of **3b** being present. While the respective signals of the ^tBu and the biphen moieties overlap and thus avoid further interpretation, the region for the $\text{C}_5\text{H}_2\text{Bu}_3$ protons is well resolved and allows for integration (Figure SI 6), which affords an isomeric ratio of 1:1.25.

The allylic distortion of the P_3 middle deck in **4** leads to inequivalent P atoms and thus its ^{31}P NMR spectrum should show multiple (two) signals. Similar behaviour is found for the isoelectronic complex $[(\text{Cp}^*\text{Co})(\text{Cp}^*\text{Ni})(\mu, \eta^3\text{-P}_3)]$.^[7] However, in the room temperature ^{31}P

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NMR spectrum of **4** in CD_2Cl_2 only one sharp singlet is found, located at $\delta = 139.5$ ppm, which hints towards a dynamic process of the P_3 middle deck in solution. A $^{31}\text{P}\{^1\text{H}\}$ VT NMR study of **4** in CD_2Cl_2 (Figure SI 7) revealed that this dynamic behaviour is retained even at temperatures as low as 193 K. The only noticeable change in these spectra is the slight shift of the singlet upon cooling of the sample.

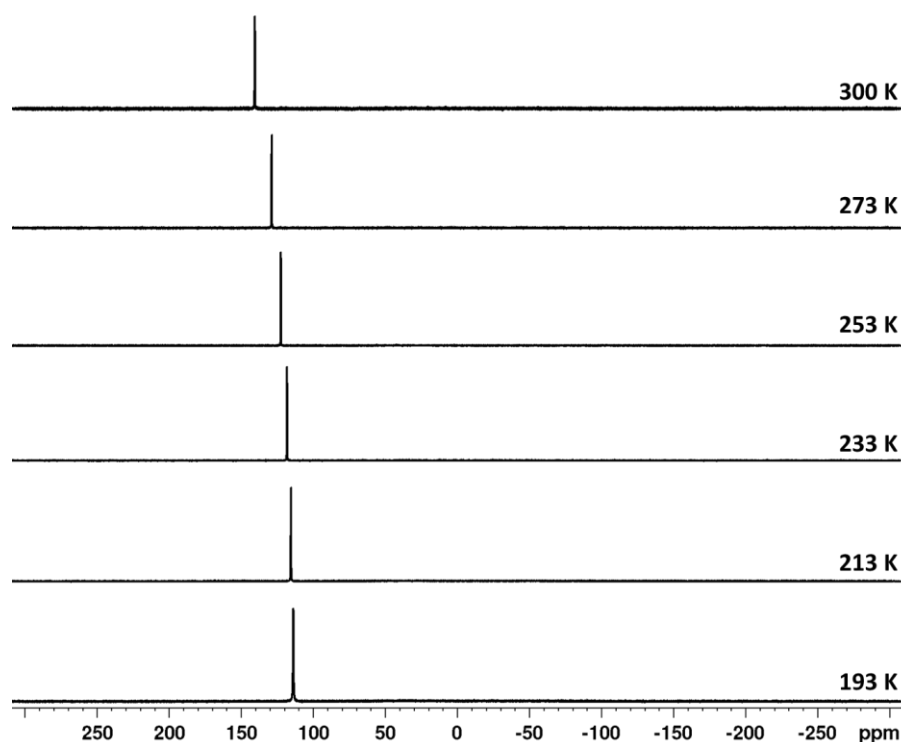


Figure SI 7: $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **4** in CD_2Cl_2 recorded at different temperatures.

To get insight into the formation of the dinuclear products **3** an NMR study was carried out to elucidate possible intermediates. Thus, PBr_3 (10 μL , 0.1 mmol, 1 eq.) was added to a freshly prepared solution of **1** (38 mg, 0.1 mmol, 1 eq.) and $\text{Ti}[\text{TEF}]$ (117 mg, 0.1 mmol, 1 eq.) in 1 mL of *o*-DFB. A capillary with toluene- d^8 and PPh_3 (standard) was added, the NMR tube closed and then shaken. Immediately

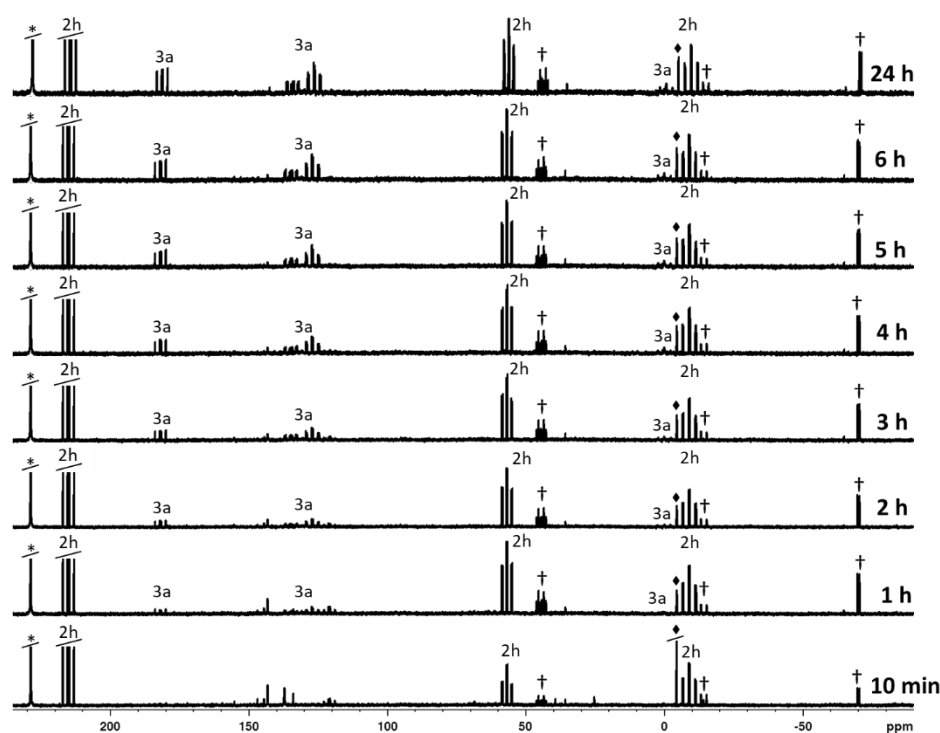


Figure SI 8: $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of a reaction solution containing 0.1 mmol of **1**, PBr_3 and $\text{Ti}[\text{TEF}]$ in *o*-DFB with a capillary containing toluene- d^8 and PPh_3 (*); Spectra were measured hour-wise and additionally another spectrum was measured 24 h after addition of PBr_3 ; Signals are assigned to the corresponding species **2h**, **3a**, † (unidentified side product) and * (residual PBr_3).

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the solution turned dark brown and the sample was subjected to the first measurement (10 min). Afterwards, $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the solution were recorded every hour and a final one was collected 24 h after the reaction was started (Figure SI 8). In the first spectrum the immediate formation of **2h** can be seen, alongside the complete consumption of the starting material **1**. After one hour the formation of **3a** is visible in the spectra and a third species (**†**) also appears but so far eludes structural assignment.

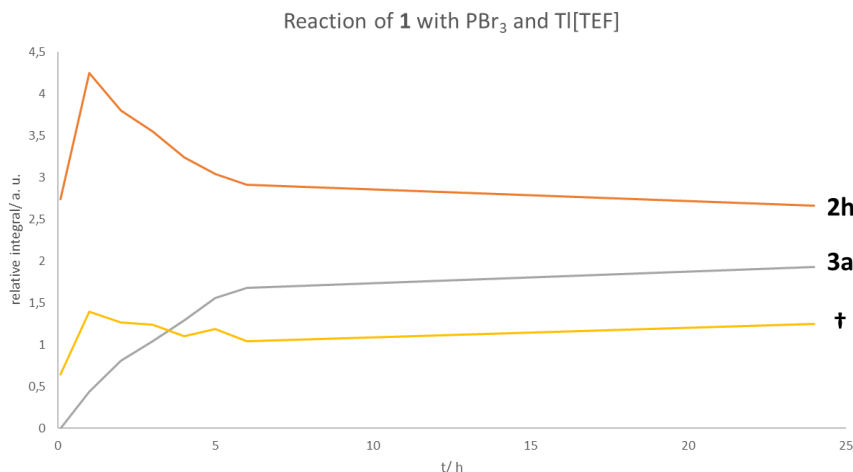


Figure SI 9: Relative signal intensities of **2h**, **3a** and **†** compared to the standard PPh_3 over the course of 24 h; The flattening of the plot is probably caused by the absence of mixing in between the measurements.

While the intensity of the signals corresponding to **2h** slowly decrease, the ones for **3a** increase and that of **†** stays the same (Figure SI 9). This data may suggest that **2h** is an intermediate during the reaction of **1** with “ $[\text{Br}_2\text{P}][\text{TEF}]$ ” which finally affords **3a**. Further insight into this reaction could however not be obtained as the precipitation of TiCl and the elongated reaction times (three days with stirring) caused severe problems during NMR spectroscopic investigations. Thus, the plot in figure SI 7 can only be seen having qualitative character.

In one more attempt to get an understanding of this reaction we recorded $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of reaction solutions (*o*-DFB, C_6D_6 capillary) with a very broad ppm range (Figure SI 10). Thus, we were able to find P_4 as one of the by-products of the reaction yielding **3a**. Accordingly, a reaction mechanism involving the initial formation of **2h** followed by its fragmentation into P_4 and a $\{\text{Cp}'''\text{Ni}\}$ containing species and the formation of **3a** from this species and another equivalent of **2h** seems to be plausible. However, this complicated reaction pathway involving several species eludes further study so far.

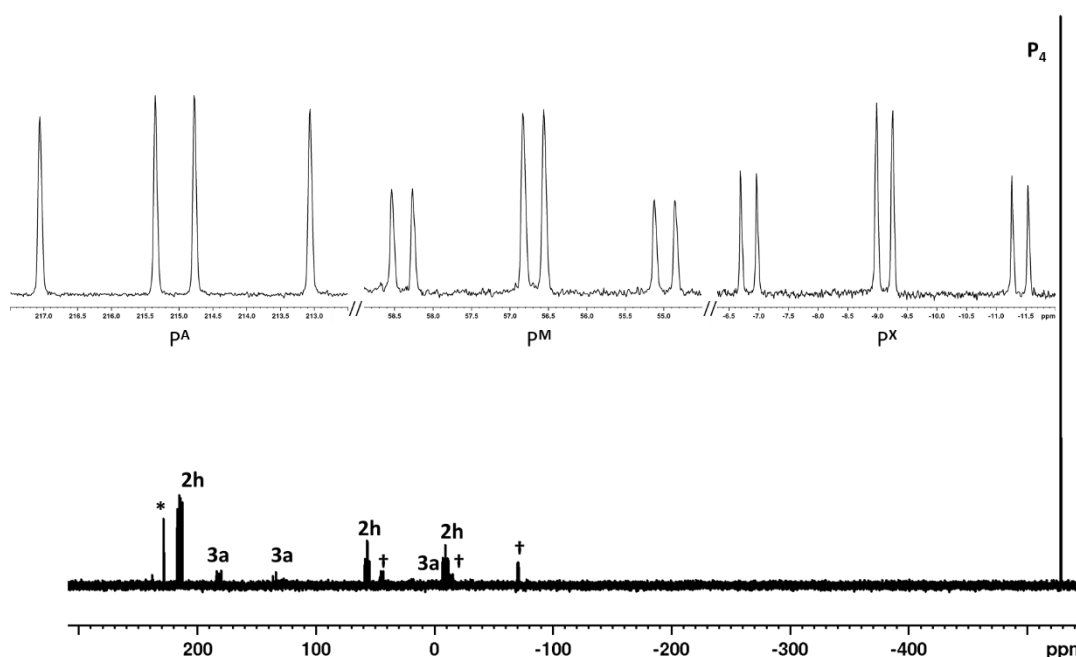


Figure SI 10: Bottom: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction mixture (0.1 mmol **1**, PBr_3 and $\text{Ti}[\text{TEF}]$) in *o*-DFB (C_6D_6 capillary) recorded at 298 K with a broad ppm range; The singlet at $\delta = -528.3$ ppm clearly shows the formation of P_4 during the reaction; Top: Zoomed in signals assigned to **2h**, which shows a typical A_2MX spectrum; Spectral parameters: $\delta/\text{ppm} = 215.1$ (dd, $^1J_{\text{PA-PX}} = 370.6$ Hz, $^1J_{\text{PA-PM}} = 277.5$ Hz, 2P, P^{A}), 56.7 (td, $^1J_{\text{PM-PA}} = 277.5$ Hz, $^2J_{\text{PM-PX}} = 44.1$ Hz, 1P, P^{M}), -9.1 (td, $^1J_{\text{PX-PA}} = 370.6$ Hz, $^2J_{\text{PX-PM}} = 44.1$ Hz, 1P, P^{X}).

SUPPORTING INFORMATION

X-ray crystallographic information

The crystallographic data for all synthesised compounds was collected on either an Xcalibur Gemini (Agilent technologies, AT) with an Atlas^{S2} detector using Mo-K α (**2a**[SbF₆], **2a**[GaCl₄], **2a**[TEF], **2g**[TEF], **3a**[TEF]) radiation (sealed tube), on a SuperNova diffractometer (AT) with a Titan^{S2} detector using Cu-K β radiation (**2a**[OTf], **2c**[GaCl₄], **2e**[TEF], **3b**[GaCl₄], **4**[GaCl₄]), obtained by using customised optics, or on another SuperNova diffractometer (AT) with a Titan^{S2} detector using a standard Cu-K α (**2d**[GaCl₄]) sealed tube microfocus source. Data reduction and absorption correction were performed with the CrysAlisPro software package.^[8] Structure solution and refinement was conducted in Olex2 (1.3-alpha)^[9] with ShelXT^[10] (solution) and ShelXL-2014^[11] (least squares refinement (F^2)) or olex2.refine (Gauss-Newton).^[9] All non-H atoms were refined with anisotropic displacement parameters and H atoms were treated as riding models with isotropic displacement parameters and fixed C-H bond lengths (sp³: 0.96 (CH₃), 0.97 (CH₂); sp²: 0.93 (CH)). Residual electron density arising from disordered solvent molecules was treated with the integrated solvent mask procedure of Olex2 (1.3 alpha) and visualisation of the crystal structures was done with this program as well.^[9]

CCDC-2015036 (**1**), CCDC-2015037 (**2a**[OTf]), CCDC-2015038 (**2a**[SbF₆]), CCDC-2015039 (**2a**[TEF]), CCDC-2015040 (**2a**[GaCl₄]), CCDC-2015041 (**2c**[GaCl₄] oDFB), CCDC-2015042 (**2d**[GaCl₄]), CCDC-2015043 (**2e**[TEF]), CCDC-2015044 (**2fendo**[GaCl₄]), CCDC-2015045 (**3a**[TEF]), CCDC-2015046 (**3b**[GaCl₄]) and CCDC-2015047 (**4**[GaCl₄] oDFB), contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/contents/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336-033; e-mail: deposit@ccdc.com.ac.uk).

Table S1: X-ray crystallographic data on all crystallographically characterised compounds.

Compound	1 ^[12]	2a [OTf]	2a [SbF ₆]
Empirical formula	C ₁₇ H ₂₉ NiP ₃	C ₃₀ H ₃₉ F ₃ NiO ₃ P ₄ S	C ₂₉ H ₃₉ F ₆ NiP ₄ Sb
Formula weight	385.02	719.26	805.94
Temperature/K	123.00(10)	122.98(17)	293(2)
Crystal system	monoclinic	monoclinic	monoclinic
Space group	P2 ₁ /n	P2 ₁ /n	P2 ₁ /n
a/Å	19.2653(9)	10.49870(10)	10.6938(2)
b/Å	14.6055(3)	26.0828(2)	25.2128(4)
c/Å	9.2674(4)	12.95300(10)	13.2668(2)
α /°	90	90	90
β /°	133.487(8)	109.4820(10)	110.963(2)
γ /°	90	90	90
Volume/Å ³	1891.9(2)	3343.91(5)	3340.25(10)
Z	4	4	4
ρ_{calc} /cm ³	1.352	1.429	1.603
μ /mm ⁻¹	7.840	5.520	1.616
F(000)	816.0	1496.0	1624.0
Crystal size/mm ³	0.352 × 0.245 × 0.151	0.383 × 0.293 × 0.111	0.402 × 0.224 × 0.165
Radiation	Cu K β (λ = 1.39222)	Cu K β (λ = 1.39222)	Mo K α (λ = 0.71073)
2 θ range for data collection/°	7.906 to 149.05	6.12 to 148.27	6.582 to 64.626
Index ranges	-26 ≤ h ≤ 22, -12 ≤ k ≤ 20, -11 ≤ l ≤ 12	-13 ≤ h ≤ 14, -35 ≤ k ≤ 30, -17 ≤ l ≤ 16	-15 ≤ h ≤ 15, -34 ≤ k ≤ 37, -19 ≤ l ≤ 19
Reflections collected	10908	28827	31775
Independent reflections	5090 [R _{int} = 0.0372, R _{sigma} = 0.0466]	9012 [R _{int} = 0.0409, R _{sigma} = 0.0359]	10913 [R _{int} = 0.0322, R _{sigma} = 0.0417]
Data/restraints/parameters	5090/0/199	9012/63/420	10913/0/379
Goodness-of-fit on F ²	1.017	1.044	1.061
Final R indexes [$I \geq 2\sigma(I)$]	R ₁ = 0.0345, wR ₂ = 0.0864	R ₁ = 0.0380, wR ₂ = 0.1046	R ₁ = 0.0343, wR ₂ = 0.0702
Final R indexes [all data]	R ₁ = 0.0386, wR ₂ = 0.0906	R ₁ = 0.0396, wR ₂ = 0.1064	R ₁ = 0.0501, wR ₂ = 0.0773
Largest diff. peak/hole / e Å ⁻³	0.65/-0.49	0.54/-0.73	0.87/-1.15

2a [TEF]	2a [GaCl ₄]	2c [GaCl ₄]·(o-DFB) _{0.5}
C ₉₀ H ₇₈ Al ₂ F ₇₂ Ni ₂ O ₈ P ₈	C ₂₉ H ₃₉ Cl ₄ GaNiP ₄	C ₆₄ H ₁₀₆ Cl ₈ F ₂ Ga ₂ Ni ₂ P ₈
3074.66	781.71	1701.70
122.7(4)	293(2)	123.00(12)
monoclinic	monoclinic	monoclinic
P2 ₁ /n	P2 ₁ /n	P2 ₁ /n
20.99150(10)	10.3088(18)	10.30213(12)
22.23550(10)	37.3289(11)	16.4498(2)
25.32560(10)	17.239(3)	23.1565(3)
90	90	90
96.6970(10)	149.06(5)	95.0842(12)
90	90	90
11740.23(9)	3411(2)	3908.84(9)
4	4	2
1.740	1.522	1.446

SUPPORTING INFORMATION

3.115 6128.0 0.322 × 0.208 × 0.175 Cu Kα (λ = 1.54184) 7.028 to 147.352 -24 ≤ h ≤ 26, -27 ≤ k ≤ 27, -23 ≤ l ≤ 31 101791 23503 [R _{int} = 0.0302, R _{sigma} = 0.0226] 23503/655/2095 1.019 R ₁ = 0.0351, wR ₂ = 0.0873 R ₁ = 0.0382, wR ₂ = 0.0900 0.62/-0.41	1.862 1600.0 0.681 × 0.324 × 0.126 Mo Kα (λ = 0.71073) 7.028 to 64.43 -14 ≤ h ≤ 15, -30 ≤ k ≤ 53, -24 ≤ l ≤ 18 18408 10619 [R _{int} = 0.0384, R _{sigma} = 0.0815] 10619/0/361 1.076 R ₁ = 0.0514, wR ₂ = 0.0861 R ₁ = 0.0744, wR ₂ = 0.0965 0.88/-0.66	6.657 1764.0 0.339 × 0.205 × 0.082 Cu Kβ (λ = 1.39222) 5.958 to 139.876 -13 ≤ h ≤ 13, -21 ≤ k ≤ 18, -30 ≤ l ≤ 30 27605 9585 [R _{int} = 0.0304, R _{sigma} = 0.0298] 9585/36/458 1.028 R ₁ = 0.0309, wR ₂ = 0.0824 R ₁ = 0.0336, wR ₂ = 0.0845 0.57/-0.51
2d[GaCl₄]⁻(<i>n</i>-hex)_{0.4} C ₁₅₇ Cl ₂₀ GasH ₂₁₃ Ni ₅ P ₂₀ 4070.81 122.9(3) monoclinic P2 ₁ /n 23.5978(3) 26.0263(3) 31.9826(3) 90 107.3890(10) 90 18744.8(4) 4 1.442 5.898 8360.0 0.272 × 0.077 × 0.057 Cu Kα (λ = 1.54184) 6.792 to 148.454 -29 ≤ h ≤ 29, -23 ≤ k ≤ 32, -29 ≤ l ≤ 39 104837 36561 [R _{int} = 0.0598, R _{sigma} = 0.0597] 36561/288/1975 1.022 R ₁ = 0.0543, wR ₂ = 0.1327 R ₁ = 0.0739, wR ₂ = 0.1437 0.92/-0.73	2e[TEF] C ₁₄₀ H ₁₄₀ Al ₄ F ₁₄₄ Ni ₄ O ₁₆ P ₁₆ 5652.79 123.01(10) triclinic P-1 19.4947(11) 24.9584(14) 25.7834(14) 64.002(6) 73.289(5) 71.681(5) 10538.0(12) 2 1.781 4.384 5616.0 0.242 × 0.23 × 0.179 Cu Kβ (λ = 1.39222) 4.752 to 150.572 -21 ≤ h ≤ 27, -33 ≤ k ≤ 34, -35 ≤ l ≤ 34 110292 56269 [R _{int} = 0.0648, R _{sigma} = 0.0843] 56269/4534/4740 1.029 R ₁ = 0.0714, wR ₂ = 0.1818 R ₁ = 0.1111, wR ₂ = 0.2293 0.99/-0.91	2f_{endo}[TEF] C ₃₉ H ₃₄ AlClF ₃₆ NiO ₄ P ₄ 1495.68 293(2) monoclinic P2 ₁ /n 15.4562(5) 12.8245(4) 28.0794(11) 90 96.820(3) 90 5526.5(3) 4 1.798 0.693 2968.0 0.702 × 0.659 × 0.368 Mo Kα (λ = 0.71073) 6.568 to 64.97 -19 ≤ h ≤ 22, -18 ≤ k ≤ 19, -42 ≤ l ≤ 40 53485 18349 [R _{int} = 0.0236, R _{sigma} = 0.0300] 18349/1072/1457 1.038 R ₁ = 0.0778, wR ₂ = 0.2092 R ₁ = 0.0958, wR ₂ = 0.2252 1.85/-1.30
3a[TEF] C ₅₀ H ₅₈ AlBr ₃ F ₃₆ Ni ₂ O ₄ P ₄ 1914.97 293(2) triclinic P $\bar{1}$ 10.5753(4) 17.8782(7) 20.7325(8) 108.035(3) 103.509(3) 101.557(3) 3462.9(2) 2 1.837 2.518 1896 0.328 × 0.177 × 0.141 Mo Kα (λ = 0.71073) 6.538 to 64.868 -13 ≤ h ≤ 15, -18 ≤ k ≤ 26, -31 ≤ l ≤ 29 31980 21606 [R _{int} = 0.0258, R _{sigma} = 0.0680] 21606/18/974 1.053 R ₁ = 0.0497, wR ₂ = 0.0865 R ₁ = 0.0799, wR ₂ = 0.0978 1.00/-0.58	3b[GaCl₄] C ₄₆ H ₆₆ Cl ₅ Ga ₃ Ni ₂ P ₄ 1107.25 122.99(13) triclinic P-1 10.4773(5) 14.5388(8) 18.7053(11) 105.393(5) 105.799(5) 97.951(5) 2574.3(3) 2 1.428 7.587 1148.0 0.3 × 0.2 × 0.1 (estimated) Cu Kβ (λ = 1.39222) 4.676 to 119.1 -11 ≤ h ≤ 12, -17 ≤ k ≤ 17, -22 ≤ l ≤ 12 16125 9775 [R _{int} = 0.0394, R _{sigma} = 0.0718] 9775/151/646 1.026 R ₁ = 0.0561, wR ₂ = 0.1344 R ₁ = 0.0761, wR ₂ = 0.1493 0.83/-0.51	4[GaCl₄]⁻(<i>o</i>-DFB)_{0.33}⁻(<i>n</i>-pent)_{0.33} C ₁₁₃ Cl ₁₂ F ₂ Ga ₃ H ₁₉₀ Ni ₆ P ₉ 2852.19 293(2) trigonal R-3 62.3366(8) 62.3366(8) 17.8833(5) 90 90 120 60182(2) 18 1.417 5.121 26748.0 0.538 × 0.351 × 0.292 CuKα (λ = 1.54184) 6.572 to 149.804 -75 ≤ h ≤ 76, -71 ≤ k ≤ 77, -20 ≤ l ≤ 17 98135 26099 [R _{int} = 0.0603, R _{sigma} = 0.0432] 26099/408/1556 1.047 R ₁ = 0.0477, wR ₂ = 0.1250 R ₁ = 0.0532, wR ₂ = 0.1326 0.92/-0.63

SUPPORTING INFORMATION

1

A different polymorph of **1** has already been described previously.^[12] Compound **1** crystallised from a concentrated *n*-hexane solution, which was stored at $-30\text{ }^{\circ}\text{C}$ for one day. It forms large bright red blocks with the space group $P2_1/n$ containing a single molecule in the asymmetric unit. The respective solid state structure is shown in Figures SI 11.

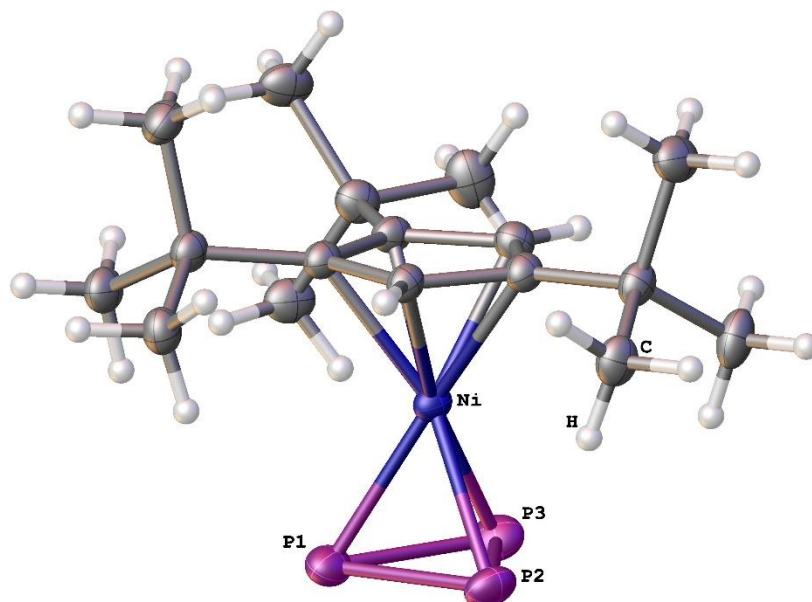


Figure SI 11: The asymmetric unit of **1**, ADPs are drawn at the 50% probability level; Selected bond lengths [\AA] and angles [$^{\circ}$]: P1-P2 2.1410(8), P1-P3 2.1425(7), P2-P3 2.1488(8), Ni-P1 2.2427(5), Ni-P2 2.2455(6), Ni-P3 2.2357(6), P1-P2-P3 59.93(3), P2-P3-P1 59.86(3), P2-P1-P3 60.22(3).

2a[OTf]

Compound **2a[OTf]** crystallised from a concentrated solution in *o*-DFB, which was layered with *n*-hexane (8:1) and stored for several days at room temperature. It crystallises as large dark red plates with the space group $P2_1/n$ containing one anion and one cation in the asymmetric unit. The solid state structure is shown in Figure SI 12.

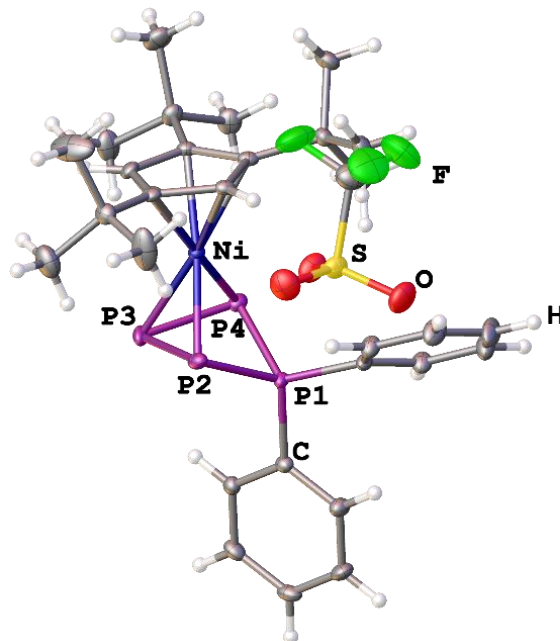


Figure SI 12: The asymmetric unit of **2a[OTf]**, ADPs are drawn at the 50% probability level; Selected bond lengths [\AA] and angles [$^{\circ}$]: P1-P2 2.1723(6), P1-P4 2.1740(5), P2-P3 2.1984(6), P3-P4 2.1889(6), P2-Ni 2.2743(5), P3-Ni 2.2154(5), P4-Ni 2.2778(5), P1-P2-P3 83.66(2), P2-P3-P4 87.48(2), P3-P4-P1 83.84(2), P2-P1-P4 88.51(2), P3-P4-P2-P1 136.21(4).

SUPPORTING INFORMATION

2a[SbF₆]

Compound **2a**[SbF₆] crystallised from a concentrated solution in *o*-DFB, which was layered with *n*-hexane (8:1) and stored for several days at room temperature. It crystallises as large dark red plates with the space group $P2_1/n$ containing one anion and one cation in the asymmetric unit. The solid state structure is shown in Figure SI 13.

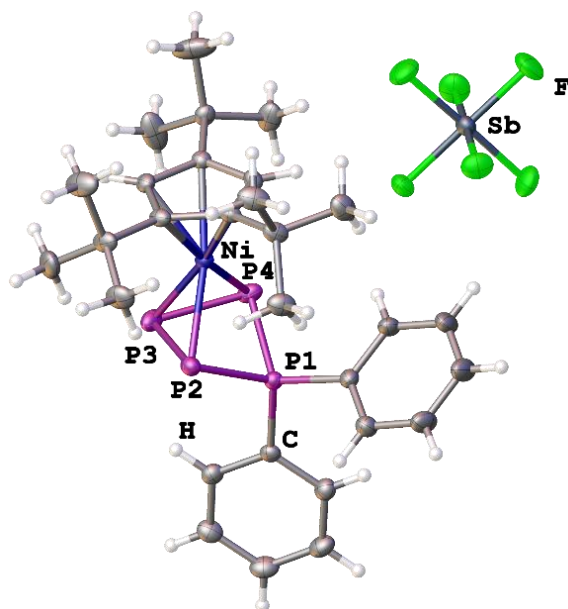


Figure SI 13: Asymmetric unit of **2a**[SbF₆], ADPs are drawn at the 50% probability level; Selected bond lengths [Å] and angles [°]: P1-P2 2.1727(7), P1-P4 2.1737(7), P2-P3 2.1946(8), P3-P4 2.2002(8), P2-Ni 2.2787(6), P3-Ni 2.2130(6), P4-Ni 2.2786(6), P1-P2-P3 83.39(3), P2-P3-P4 87.58(3), P3-P4-P1 83.23(3), P2-P1-P4 88.80(3), P3-P4-P2-P1 135.47(4).

2a[TEF]

Compound **2a**[TEF] crystallised by slowly evaporating the solvent of a CH₂Cl₂ solution. Thus, a few red platelets of **2a**[TEF] could be obtained, which crystallises in the monoclinic space group $P2_1/n$ with two anions and two cations in the asymmetric unit. The structure in solid state is shown in Figure SI 14. The severe disorder within one of the anions was treated with restraints. The cations are enantiomers to each other and besides that their structural parameters differ only very slightly. Thus, these structural parameters are given for only one of them.

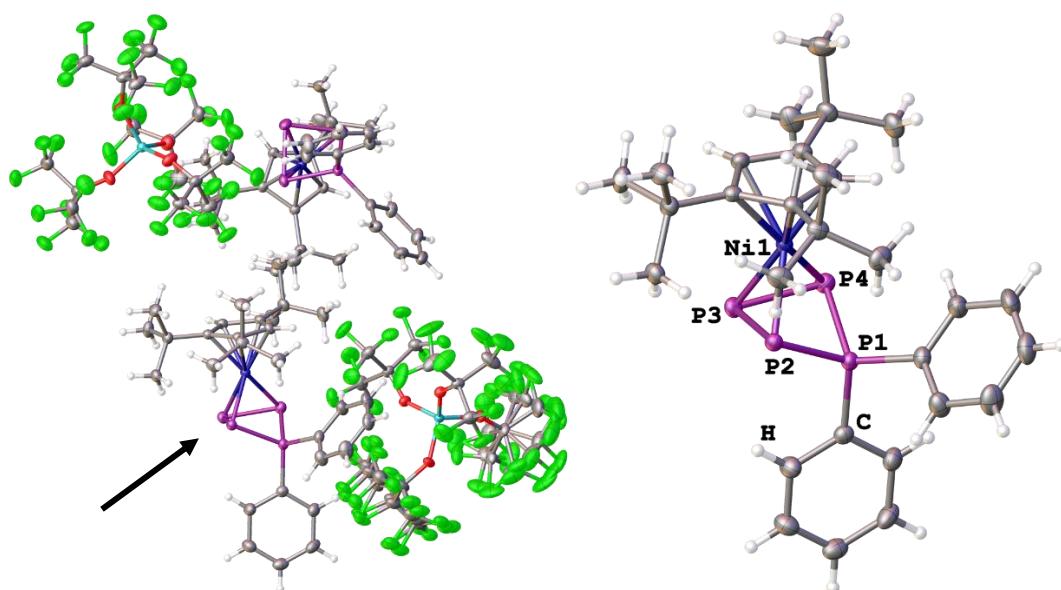


Figure SI 14: Asymmetric unit of **2a**[TEF] (left) and the marked cation denoted with Ni1 (right), ADPs are drawn at the 50% probability level; Selected bond lengths [Å] and angles [°]: P1-P2 2.1659(6), P1-P4 2.1733(6), P2-P3 2.1988(6), P3-P4 2.1967(6), P2-Ni1 2.2598(5), P3-Ni1 2.2192(5), P4-Ni1 2.2867(5), P1-P2-P3 83.56(2), P2-P3-P4 86.93(3), P3-P4-P1 83.44(2), P2-P1-P4 88.35(3), P3-P4-P2-P1 134.70(3).

SUPPORTING INFORMATION

2a[GaCl₄]

Compound **2a**[GaCl₄] crystallised from a concentrated solution in *o*-DFB, which was layered with *n*-hexane (6:1) and stored for several days at room temperature. It crystallises as large dark red plates with the space group $P2_1/n$ containing one anion and one cation in the asymmetric unit. The structure in solid state is shown in Figure SI 15.

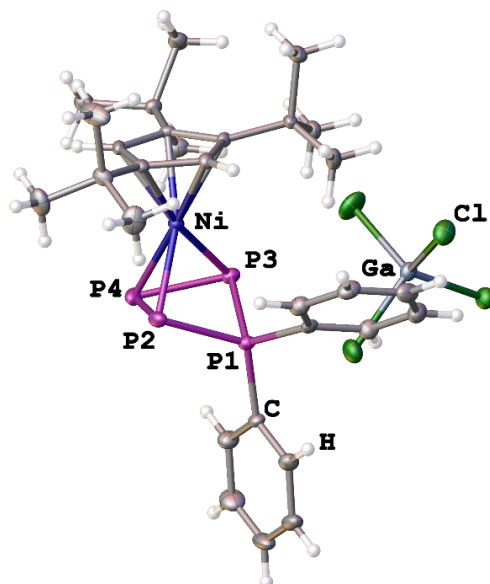


Figure SI 15: Asymmetric unit of **2a**[GaCl₄], ADPs are drawn at the 50% probability level; Selected bond lengths [Å] and angles [°]: P1-P2 2.1790(20), P1-P4 2.1731(14), P2-P3 2.1862(16), P3-P4 2.1940(20), P2-Ni 2.2873(12), P3-Ni 2.2281(9), P4-Ni 2.2780(20), P1-P2-P3 84.85(9), P2-P3-P4 87.54(11), P3-P4-P1 84.80(8), P2-P1-P4 88.17(9), P3-P4-P2-P1 138.83(11).

2c[GaCl₄](*o*-DFB)_{0.5}

Compound **2c**[GaCl₄] crystallised as an *o*-DFB solvate from a concentrated solution in *o*-DFB, which was layered with *n*-hexane (6:1) and stored at −30 °C for several days. It forms large dark red plates with the space group $P2_1/n$ containing one anion, one cation and half a molecule of *o*-DFB in the asymmetric unit. Slight disorder within the [GaCl₄][−] anion could be refined without restraints, but DFIX restraints were used for two of the C–H bonds in the disordered *o*-DFB molecule. The structure in solid state is shown in Figure SI 16.

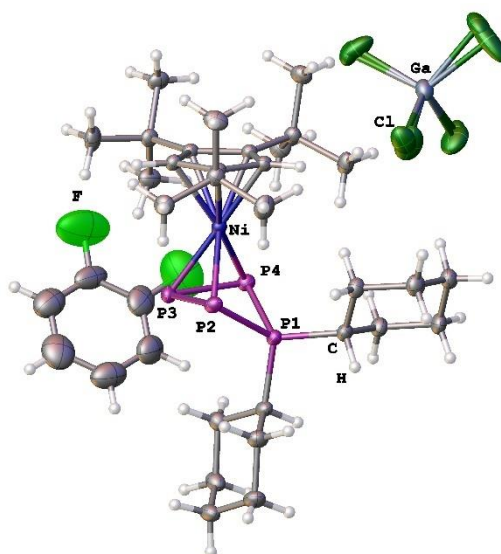


Figure SI 16: Asymmetric unit of **2c**[GaCl₄](*o*-DFB)_{0.5}, ADPs are drawn at the 50% probability level; Selected bond lengths [Å] and angles [°]: P1-P2 2.1738(6), P1-P4 2.1827(5), P2-P3 2.1922(5), P3-P4 2.1951(6), P2-Ni 2.2788(4), P3-Ni 2.2186(5), P4-Ni 2.2854(4), P1-P2-P3 83.59(2), P2-P3-P4 86.98(2), P3-P4-P1 83.32(2), P2-P1-P4 87.75(2), P3-P4-P2-P1 133.96(3).

SUPPORTING INFORMATION

2d[GaCl₄] \cdot (*n*-hex)_{0.4}

Layering a concentrated CH₂Cl₂ solution of **2d**[GaCl₄] with *n*-hexane (5:1) and storing it at $-30\text{ }^{\circ}\text{C}$ for two weeks leads to formation of light red crystals of **2d**[GaCl₄] \cdot (*n*-hex)_{0.4}. It crystallises in the monoclinic space group P2₁/n with five cations, five anions and two *n*-hexane molecules in the asymmetric unit. Disorder within the [GaCl₄]⁻ anions and one of the Cp^{'''} ligands was treated with restraints. Both *n*-hexane molecules are too disordered for proper modelling and thus have been treated with the implemented solvent mask procedure in Olex2.^[9] As the structural parameters within the cations only differ very slightly, just those for one of them (Ni1) are given and the structure of the asymmetric unit and the respective cation are provided in Figure SI 17.

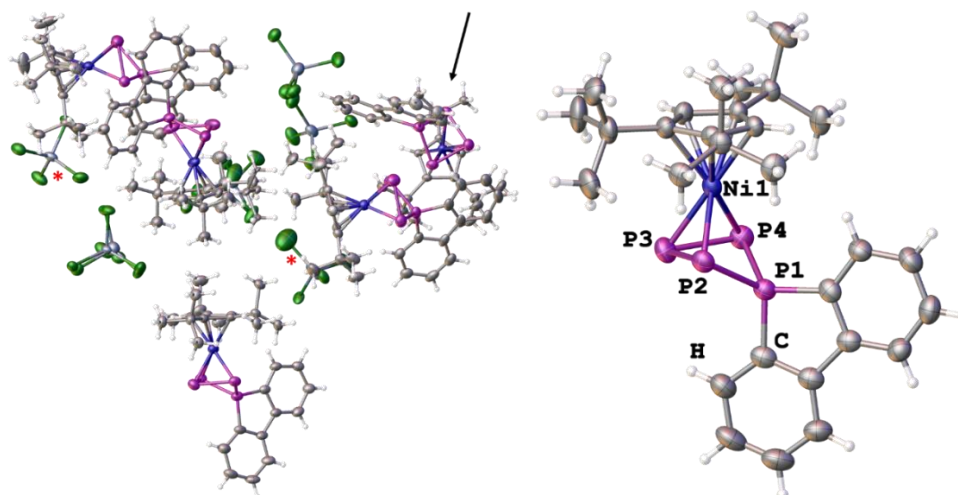


Figure SI 17: Asymmetric unit of **2d**[GaCl₄](*n*-hex)_{0.4}, where * marks two disordered parts of one [GaCl₄]⁻ anion and the arrow points to the cation denoted with Ni1 (left) and the respective structure of this cation (right), ADPs are drawn at the 50% probability level; Selected bond lengths [Å] and angles [°]: P1-P2 2.1629(14), P1-P4 2.1620(14), P2-P3 2.2078(15), P3-P4 2.1919(14), P2-Ni 2.2642(12), P3-Ni 2.2343(13), P4-Ni 2.2952(12), P1-P2-P3 82.59(6), P2-P3-P4 87.53(5), P3-P4-P1 82.97(6), P2-P1-P4 89.46(5), P3-P4-P2-P1 134.74(8).

2e[TEF]

Red crystals of **2e**[TEF] could be obtained from layering a concentrated solution in *o*-DFB with *n*-hexane (1:10) and storing it at $4\text{ }^{\circ}\text{C}$ for ten days. **2e**[TEF] crystallises in the triclinic space group $P\bar{1}$ with four cations and four anions in the asymmetric unit. Heavy disorder within the anions was treated with restraints, but still leads to comparably bad R values. Thus, structural parameters were considered carefully. As the structural parameters within the cations only differ very slightly, just those for one of them (Ni1) are given and the structure of the asymmetric unit and the respective cation are provided in Figure SI 18.

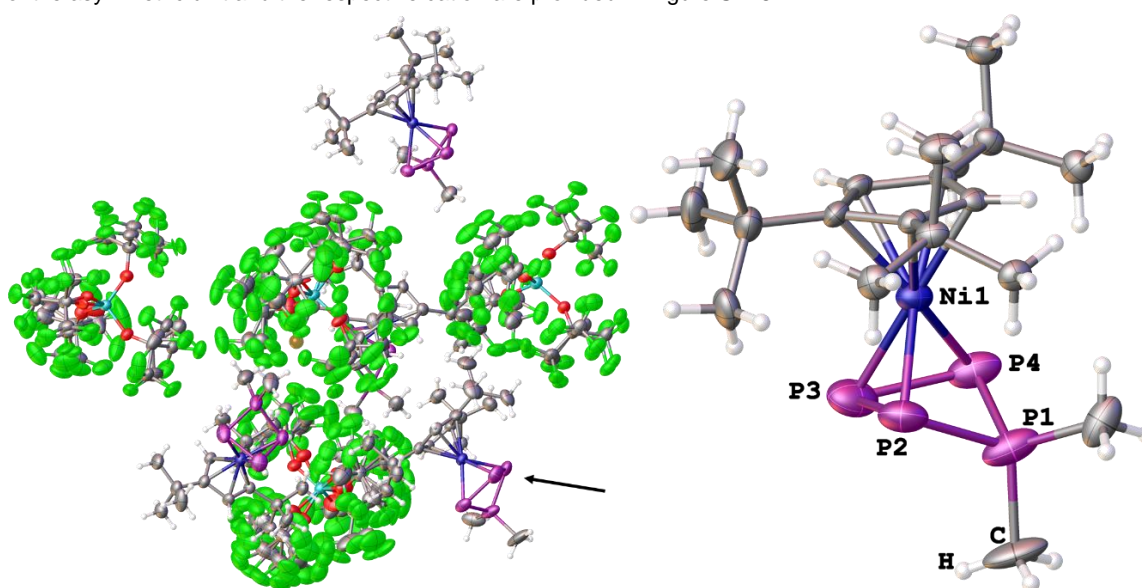


Figure SI 18: Asymmetric unit of **2e**[TEF], where the arrow points to the cation denoted with Ni1 (left) and the respective structure of this cation (right), ADPs are drawn at the 50% probability level; Selected bond lengths [Å] and angles [°]: P1-P2 2.153(2), P1-P4 2.149(2), P2-P3 2.188(2), P3-P4 2.195(2), P2-Ni 2.260(1), P3-Ni 2.199(1), P4-Ni 2.274(1), P1-P2-P3 84.37(9), P2-P3-P4 87.50(8), P3-P4-P1 84.28(10), P2-P1-P4 89.58(7), P3-P4-P2-P1 139.25(9).

SUPPORTING INFORMATION

2f_{endo}[TEF]

Layering a concentrated solution of **2f**[TEF] in *o*-DFB with *n*-hexane and storing the solution at 4 °C for two weeks, yields bright red crystals of the *endo*-Ph isomer of **2f**[TEF] (Figure SI 19). The X-ray structural analysis of **2f_{endo}**[TEF] revealed its incommensurate modulated structure in the solid state (Figure SI 20), but the solution and refinement of the average structure yielded a reasonable structural model ($R_1 = 7.8\%$), which may be discussed. Structural parameters were considered carefully. The average structure of **2f_{endo}**[TEF] forms a monoclinic lattice with the space group $P2_1/n$, where the asymmetric unit contains one anion and one cation. As a result of the modulation, the structure appears heavily disordered, which especially counts for the [TEF]⁻ anion. Disorder has been treated with restraints.

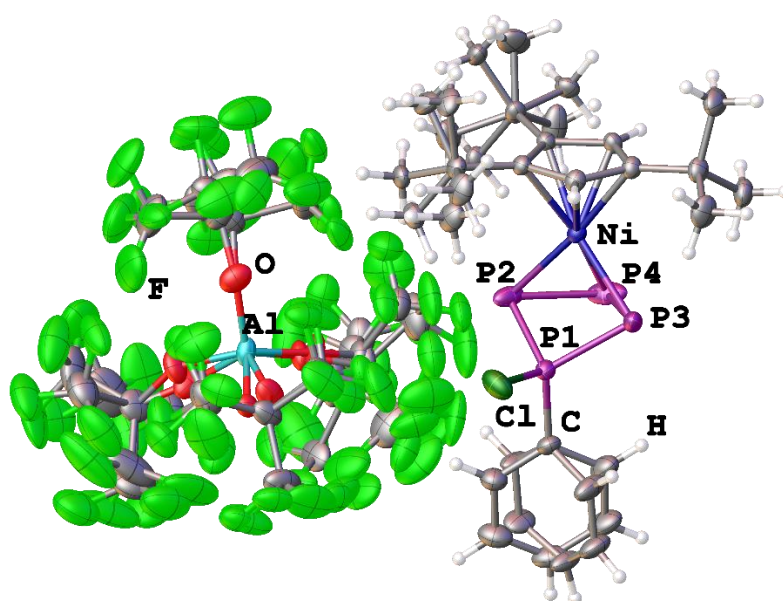


Figure SI 3: Asymmetric unit of the average structure solution of **2f_{endo}**[TEF] with ADPs drawn at the 50% probability level; Selected bond lengths [Å] and angles [°]: P1-P2 2.1462(11), P1-P4 2.1471(11), P2-P3 2.1966(17), P3-P4 2.2038(16), P2-Ni 2.2684(9), P3-Ni 2.2141(9), P4-Ni 2.2708(9), P1-Cl 2.0227(11), P1-P2-P3 79.86(5), P2-P3-P4 88.76(5), P3-P4-P1 79.68(4), P2-P1-P4 91.60 (5), P2-P3-P4-P1 130.52(7).

SUPPORTING INFORMATION

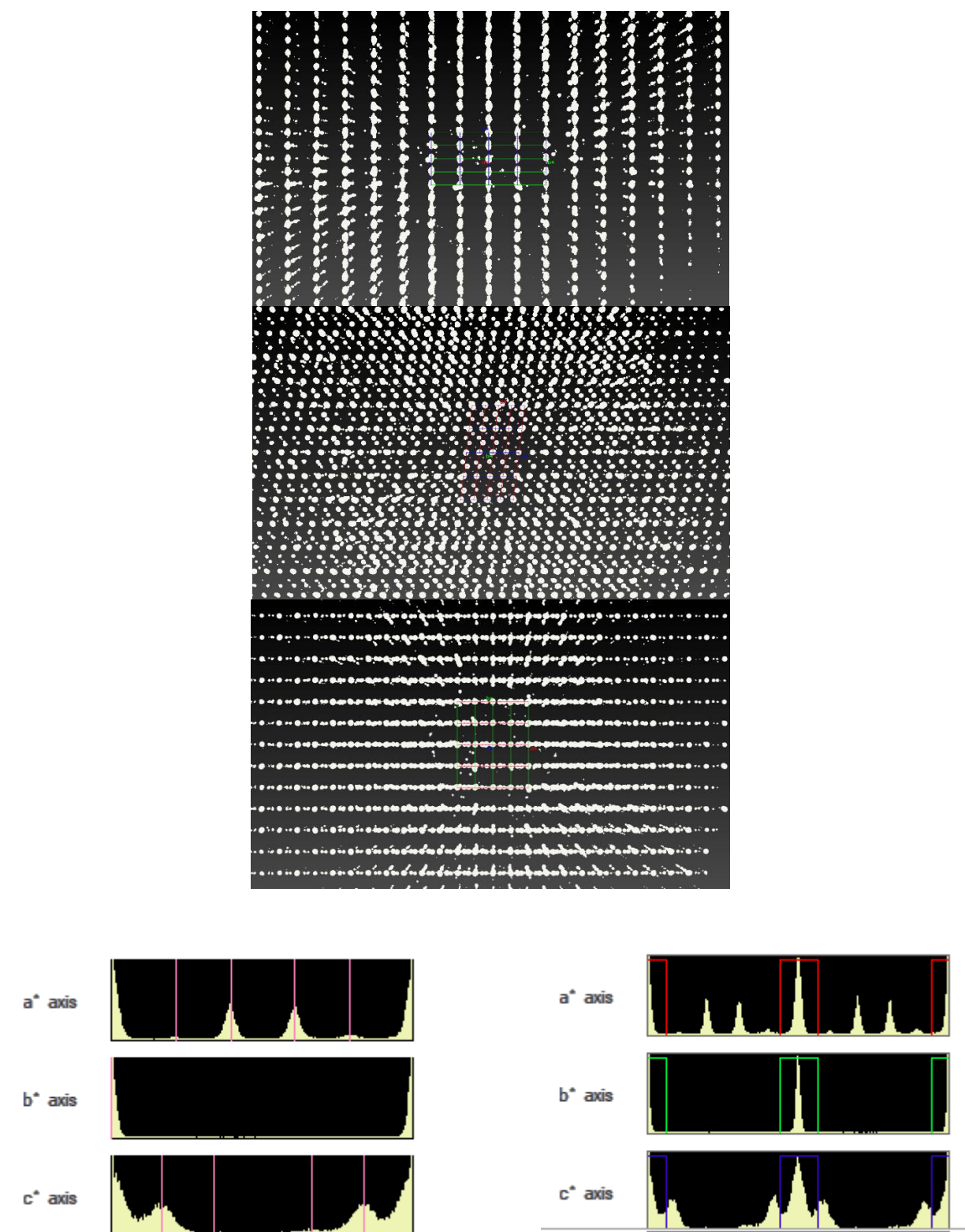


Figure SI 20: Views of the reciprocal space of $2f_{\text{endo}}[\text{TEF}]$ along the a^* (top), b^* (middle) and c^* (bottom) axis, with clearly visible satellite peaks (along a^* and c^*) arising from the incommensurate structure of this compound; Bottom: Intensity distribution histograms with (left) and without (right) the refined modulation vector $0.393, 0.0, 0.169$ of order 2.

SUPPORTING INFORMATION

3a[TEF]

Storing a solution of **3a**[TEF] in CH₂Cl₂ layered with *n*-hexane at room temperature for six days yield dark blackish red crystals. **3a**[TEF] crystallises in the triclinic space group $P\bar{1}$ with one cation and one anion in the asymmetric unit. Disorder within the [TEF]⁻ anion was treated with SIMU restraints and the solid state structure is shown in Figure SI 21.

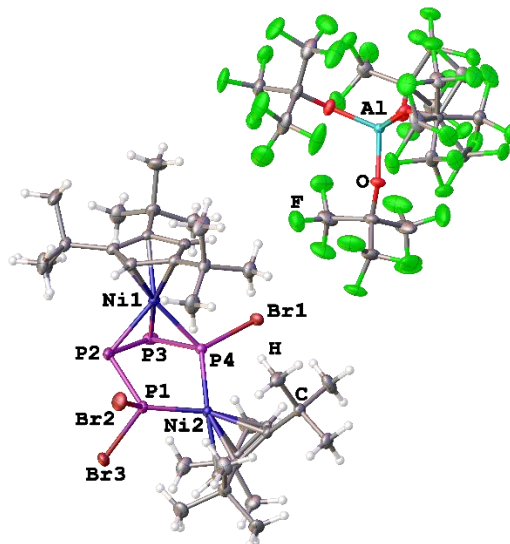


Figure SI 21: Asymmetric unit of **3a**[TEF], ADPs are drawn at the 50% probability level; Selected bond lengths [Å] and angles [°]: P1-P2 2.2228(11), P2-P3 2.1653(12), P3-P4 2.1623(10), P2-Ni1 2.2562(8), P3-Ni1 2.2691(8), P4-Ni1 2.2209(8), P1-Ni2 2.1035(8), P4-Ni2 2.1573(8), P1-Br2 2.2161(8), P1-Br3 2.2194(8), P4-Br1 2.2146(8), P1-P2-P3 100.82(4), P2-P3-P4 86.47(4), P3-P4-Ni2 116.62(4), P1-Ni2-P4 84.96(3), P2-P1-Ni2 117.12(4), Br2-P1-Br3 100.82(3), P3-P4-P2-P1 135.30(6), P3-P4-P2-Ni2 126.93(7).

3b[GaCl₄]

Brownish crystals of **3b**[GaCl₄] are obtained from layering a concentrated solution in *o*-DFB with *n*-hexane (6:1) and storing it for two weeks at room temperature. **3b**[GaCl₄] crystallises in the triclinic space group $P\bar{1}$ with one cation and one anion in the asymmetric unit (Figure SI 22). Disorder within the 'Bu groups and the anion were treated with DFIX and SIMU restraints. The crystal movie recording before the X-ray diffraction experiment failed due to issues with the camera. Thus, the dimensions of the crystal are therefore estimated and only multi-scan absorption correction was applied.

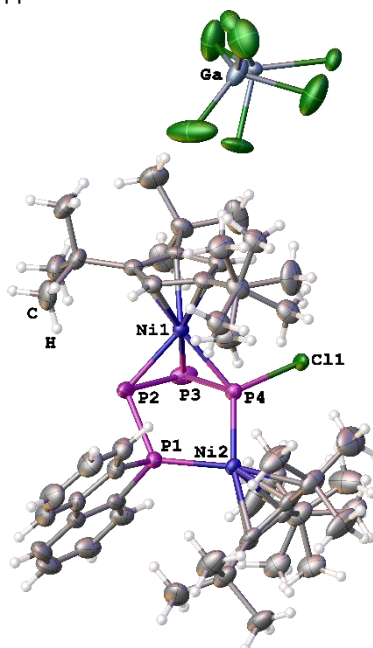


Figure SI 22: Asymmetric unit of **3b**[GaCl₄], ADPs are drawn at the 50% probability level; Selected bond lengths [Å] and angles [°]: P1-P2 2.2387(16), P2-P3 2.1450 (20), P3-P4 2.1444(16), P2-Ni1 2.2525(13), P3-Ni1 2.2617(13), P4-Ni1 2.2167(12), P1-Ni2 2.1420(12), P4-Ni2 2.1470(13), P4-Cl1 2.0738(16), P1-P2-P3 100.66(7), P2-P3-P4 85.34(6), P3-P4-Ni2 116.16(7), P1-Ni2-P4 85.79(5), P2-P1-Ni2 113.88(5), P3-P4-P2-P1 -130.58(8), P3-P4-P2-Ni2 -124.67(9).

SUPPORTING INFORMATION

 $4[\text{GaCl}_4] \cdot (\text{o-DFB})_{0.33} \cdot (\text{n-pent})_{0.33}$

Layering a concentrated solution of $4[\text{GaCl}_4]$ with *n*-pentane (8:1) and storing it for four weeks at room temperature afforded dark brownish green crystals of the solvate $4[\text{GaCl}_4] \cdot (\text{o-DFB})_{0.33} \cdot (\text{n-pent})_{0.33}$. This compound has the space group $R\bar{3}$ and the asymmetric unit contains three cations, three anions, an *o*-DFB and a strongly disordered *n*-pentane molecule, which was treated with the implemented solvent mask procedure in Olex2 (Figure SI 23).^[9] Disorder within the Cp''' ligands, the anions and two of the three P_3 middle decks was treated with restraints and the cation without disorder is selected for description of structural parameters.

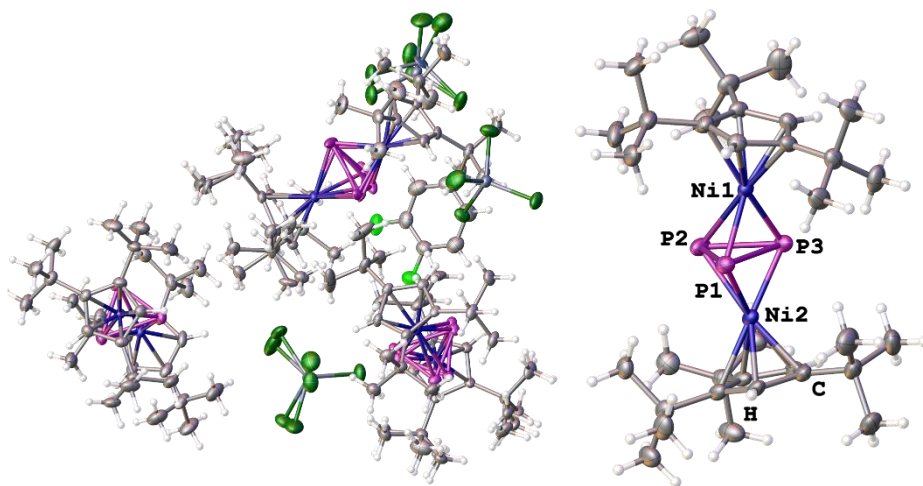


Figure SI 23: Asymmetric unit of $4[\text{GaCl}_4] \cdot (\text{o-DFB})_{0.33} \cdot (\text{n-pent})_{0.33}$ (left) and the cation without disorder (right), ADPs are drawn at the 50% probability level; Selected bond lengths [Å] and angles [°]: P1-P2 2.2021(11), P1-P3 2.5385(10), P2-P3 2.1975(11), P1-Ni1 2.1842(9), P2-Ni1 2.3566(9), P3-Ni1 2.1831(9), P1-Ni2 2.1746(8), P2-Ni2 2.3920(9), P3-Ni2 2.1786(9), P1-P2-P3 70.48(5), P2-P3-P1 54.84(4), P3-P1-P2 54.68(5), P2-P1-P3-Ni1 82.51(5), P2-P3-P1-Ni2 84.28(6), fold angle in between the planes of the Cp''' ligands: 24.48(15).

SUPPORTING INFORMATION

Details on computational results

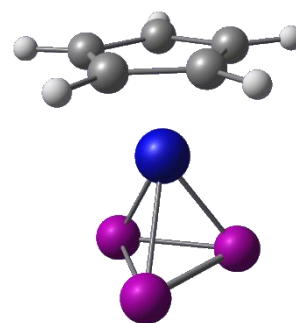
Calculations were carried out using the Gaussian09 software package^[13] at the DFT level by means of either the density functional BP86^[14] or the hybrid density functional B3LYP.^[14,15] The def2SVP^[16] basis set was used for calculations involving both isomers of **2f** and **2g** and the structures of **3a** and **3b**. The def2TZVP^[16] basis set was used for calculations on the possible reaction mechanism. Implicit solvent correction was applied via a polarisable continuum model for CH₂Cl₂.^[17] NBO analysis of **3a** and **3b** was conducted with the NBO6 software package.^[18] Stationary points were verified by analytical frequency calculations. The transition state **TS2** was verified by slightly changing its molecular geometry along its imaginary frequency and then performing geometry optimisations on the obtained structures.

Cartesian coordinates for all optimised structures:

[CpNi(η^3 -P₃)]:

BP86/def2TZVP: Energies/H = -2726.415940, Enthalpies/H = -2726.414996, Free Energies/H = -2726.462662, ZPVE/ kJ/mol = 227.85 (ZPVE = zero point vibrational energies)

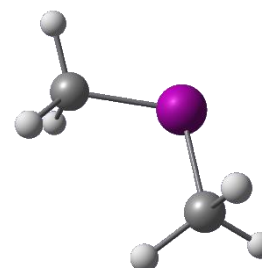
Symbol	X	Y	Z
Ni	0.2315880	0.0003550	-0.0002530
P	-1.6581020	0.1405030	1.2453800
P	-1.6588170	-1.1486330	-0.5009340
P	-1.6599450	1.0076390	-0.7439290
C	1.9482110	-1.2180120	-0.0684430
C	1.9470460	0.9456500	0.7719540
C	1.9476030	-0.4439540	1.1363480
H	1.9453280	-0.8386160	2.1488960
C	1.9472350	-0.3099050	-1.1810320
C	1.9493720	1.0258080	-0.6589600
H	1.9451030	1.9402720	-1.2462460
H	1.9476710	1.7873270	1.4593890
H	1.9452950	-2.3031370	-0.1298310
H	1.9483070	-0.5859450	-2.2320710



[Me₂P]⁺:

BP86/def2TZVP: Energies/H = -420.933417, Enthalpies/H = -420.932473, Free Energies/H = -420.966318, ZPVE/ kJ/mol = 182.86

Symbol	X	Y	Z
C	1.3970920	-0.4638670	-0.0245410
H	2.2782590	-0.0007810	-0.4883890
H	1.6232810	-0.5021650	1.0746510
H	1.2053900	-1.4928920	-0.3534430
C	-1.3971220	-0.4638380	0.0245590
H	-2.2786000	-0.0005020	0.4875270
H	-1.6224530	-0.5030140	-1.0747920
H	-1.2055490	-1.4926400	0.3542600

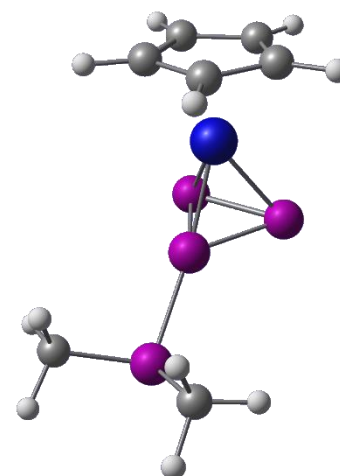


SUPPORTING INFORMATION

 $[\text{CpNi}(\eta^3\text{-P}_4\text{Me}_2)]^+$ (**I2**):

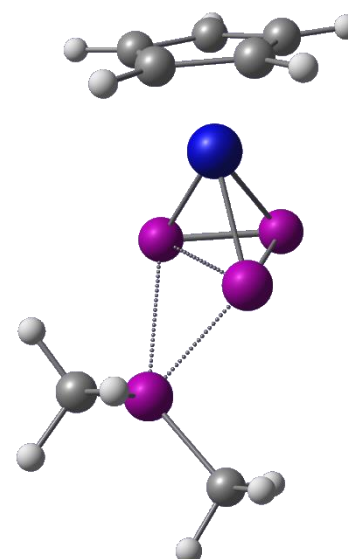
BP86/def2TZVP: Energies/H = -3147.407361, Enthalpies/H = -3147.406417, Free Energies/H = -3147.467349, ZPVE/ kJ/mol = 424.86

Symbol	X	Y	Z
Ni	-1.1354880	0.0281460	-0.0004480
P	3.2133650	-0.0222500	0.0308580
P	-0.1746150	-1.7721380	1.1066150
P	1.0156070	-0.3347520	0.0516700
P	-0.1268880	-1.7511780	-1.0851130
C	-2.0787760	1.6676670	0.9182250
C	-3.2114140	0.0616430	-0.3109570
C	-2.9171680	0.5176520	1.0209600
H	-3.2587120	0.0533110	1.9418490
C	-1.8646440	1.9345840	-0.4837250
C	-2.5725560	0.9507550	-1.2396520
H	-2.6069620	0.8771180	-2.3228540
C	3.3926220	1.2146770	1.3918260
C	3.3771280	1.0295710	-1.4799650
H	4.4457130	1.2900930	-1.5432480
H	3.1137260	0.4437930	-2.3698380
H	2.7870510	1.9536960	-1.4392070
H	2.7873060	2.1181790	1.2467240
H	3.1569080	0.7450120	2.3551140
H	4.4580050	1.4950690	1.3970920
H	-3.8151020	-0.8044620	-0.5682400
H	-1.6742630	2.2431000	1.7461380
H	-1.2631750	2.7424850	-0.8917120

 $[\text{CpNi}(\eta^3\text{-P}_4\text{Me}_2)]^+$ (**TS2**):

BP86/def2TZVP: Energies/H = -3147.399502, Enthalpies/H = -3147.398558, Free Energies/H = -3147.458166, ZPVE/ kJ/mol = 422.58

Symbol	X	Y	Z
Ni	-1.1158950	-0.0587770	-0.0207480
P	2.8839640	0.2073760	0.4226840
P	0.4276800	-0.7474120	1.3923110
P	0.9364150	-0.3681810	-0.8503960
P	-0.0803630	-2.1539330	-0.1211310
C	-1.9847070	1.8377560	-0.2372500
C	-3.1046150	-0.0092440	0.5885650
C	-2.4581740	1.2220070	0.9584250
H	-2.3363370	1.6004450	1.9692870
C	-2.3647010	1.0024850	-1.3555270
C	-3.0651360	-0.1246470	-0.8465860
H	-3.4696500	-0.9472030	-1.4295780
C	2.5662740	2.0261340	0.5041300



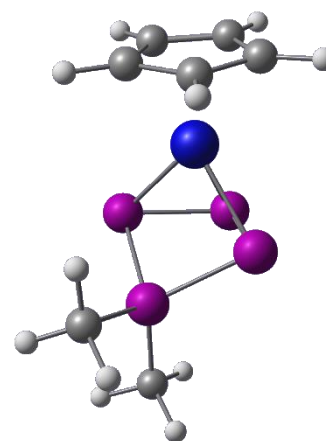
SUPPORTING INFORMATION

C	3.9787380	0.0923470	-1.0732940
H	4.9648770	0.4650240	-0.7501060
H	4.0908910	-0.9586340	-1.3696080
H	3.6188640	0.6901840	-1.9218420
H	2.2284000	2.4575710	-0.4478800
H	1.8372730	2.2453140	1.2949390
H	3.5258180	2.4904640	0.7824410
H	-3.5588960	-0.7209510	1.2727400
H	-1.4342030	2.7723220	-0.3019010
H	-2.1434750	1.2024630	-2.4003390

$[\text{CpNi}(\eta^3\text{-P}_4\text{Me}_2)]^+$ (**P2**):

BP86/def2TZVP: Energies/H = -3147.439393, Enthalpies/H = -3147.438449, Free Energies/H = -3147.496319, ZPVE/ kJ/mol = 427.63

Symbol	X	Y	Z
Ni	-0.9306060	-0.1157720	-0.0000030
P	2.0928060	0.4372400	0.0000010
P	0.7404110	-0.3961710	1.5208370
P	0.7404220	-0.3961780	-1.5208400
P	0.3468100	-1.9608900	-0.0000010
C	-2.1183220	1.4635440	-0.7131780
C	-2.6708930	0.2064030	1.1546360
C	-2.1182840	1.4636190	0.7130680
H	-1.7690020	2.2662400	1.3563070
C	-2.6709550	0.2062820	-1.1545870
C	-3.0272070	-0.5552070	0.0000740
H	-3.4612400	-1.5511810	0.0001370
C	2.2680680	2.2462300	-0.0000080
C	3.7713560	-0.2658940	0.0000130
H	4.3042870	0.0786920	0.8975770
H	3.7115030	-1.3609100	0.0000340
H	4.3042880	0.0786580	-0.8975650
H	2.8222660	2.5580460	-0.8969830
H	1.2723840	2.7059170	-0.0000470
H	2.8222020	2.5580630	0.8970000
H	-2.7949230	-0.1038260	2.1886960
H	-1.7690700	2.2660940	-1.3565210
H	-2.7950410	-0.1040530	-2.1886090

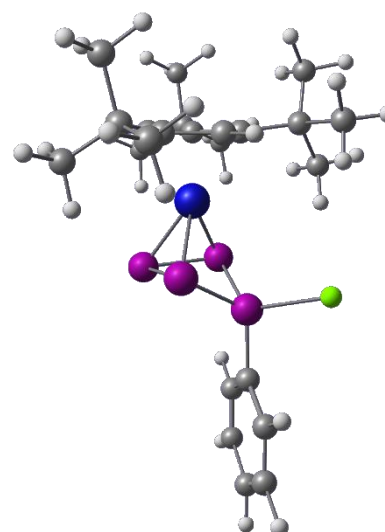


SUPPORTING INFORMATION

$[\text{Cp}^* \text{Ni}(\eta^3\text{-P}_4\text{PhCl})]^+$ (**2f_{endo}**):

B3LYP/def2SVP: Energies/H = -4228.944626, Enthalpies/H = -4228.943682, Free Energies/H = -4229.043422, ZPVE/ kJ/mol = 1366.27

Symbol	X	Y	Z
Ni	-0.6055810	0.3257590	0.2996010
P	2.3200890	-0.1159040	-0.3697060
P	1.1873620	1.7385380	-0.0530340
P	0.9835470	-1.1957870	1.0023560
P	0.8255180	0.8235620	1.9506710
C	-2.1020130	-0.7204590	-0.8298670
C	-2.2643850	1.5495960	-0.1990790
C	-1.9589300	0.6314310	-1.2641200
H	-1.6844300	0.9353530	-2.2679190
C	-2.4753900	-0.6482140	0.6082740
C	-2.5828850	0.7454250	0.9280690
H	-2.8612410	1.1340260	1.9026140
C	-0.9531250	-2.9411430	-1.5459320
H	0.0504950	-2.5024910	-1.6366150
H	-1.0267580	-3.7547360	-2.2844480
H	-1.0423020	-3.3869200	-0.5518670
C	-3.4336080	-2.5463150	-1.9283720
H	-3.7116930	-3.0679380	-1.0045050
H	-3.4386780	-3.2895510	-2.7406870
H	-4.2138290	-1.8010640	-2.1484150
C	-2.4510790	3.0575910	-0.3087710
C	-1.7222180	-1.3331080	-3.2592330
H	-2.4997510	-0.6438630	-3.6209460
H	-1.6742010	-2.1745300	-3.9662250
H	-0.7504160	-0.8188220	-3.2940880
C	-2.9443040	-1.6769070	1.6613270
C	-2.0363220	-1.8823080	-1.8476140
C	-2.3765040	-3.0998510	1.5236260
H	-2.6894100	-3.5995850	0.6004040
H	-2.7487530	-3.7104360	2.3598750
H	-1.2775800	-3.1081160	1.5750620
C	-2.5742190	-1.1931200	3.0856490
H	-1.4871860	-1.0604040	3.1995990
H	-2.8973080	-1.9475840	3.8181040
H	-3.0653600	-0.2500370	3.3620850
C	-4.4927450	-1.7350610	1.5649240
H	-4.9402480	-0.7468370	1.7510980
H	-4.8845480	-2.4339630	2.3207990
H	-4.8300640	-2.0792030	0.5773860
C	-1.9241810	3.7824970	0.9451240
H	-2.3976780	3.4129770	1.8672570
H	-2.1393160	4.8596460	0.8721990



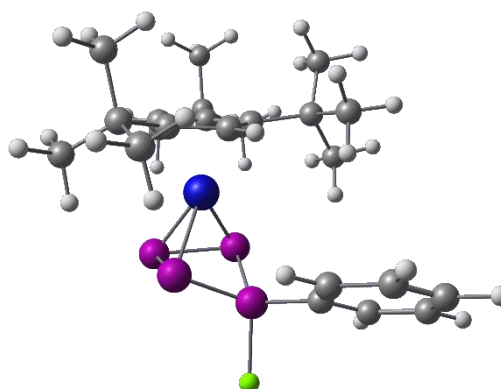
SUPPORTING INFORMATION

H	-0.8339770	3.6684830	1.0517830
C	-1.7662080	3.6269620	-1.5647850
H	-0.6811120	3.4441440	-1.5596020
H	-1.9226690	4.7154700	-1.6101620
H	-2.1836190	3.1976540	-2.4884310
C	-3.9802170	3.2938340	-0.4255060
H	-4.3979650	2.7716860	-1.3002640
H	-4.1827090	4.3703100	-0.5414580
H	-4.5120830	2.9401360	0.4709930
C	4.0852880	-0.1212200	0.0449840
C	4.9879660	0.6182050	-0.7412350
C	4.5373350	-0.8409800	1.1630630
C	6.3398140	0.6352540	-0.3994720
C	5.8953480	-0.8195110	1.4915170
C	6.7934410	-0.0823820	0.7143870
H	7.0428510	1.2093740	-1.0068600
H	6.2493380	-1.3831770	2.3573140
Cl	2.2879980	-0.7214080	-2.3554720
H	4.6432220	1.1720540	-1.6172070
H	7.8541170	-0.0674110	0.9755350
H	3.8422460	-1.4193830	1.7757340

$[\text{Cp}^{\text{***}}\text{Ni}(\eta^3\text{-P}_4\text{ClPh})]^{\text{+}}$ (**2f_{exo}**):

B3LYP/def2SVP: Energies/H = -4228.942000, Enthalpies/H = -4228.941056, Free Energies/H = -4229.037902, ZPVE/ kJ/mol = 1368.80

Symbol	X	Y	Z
Ni	-0.5924970	-0.5354360	-0.3188020
P	2.2987130	-0.8281050	-0.8802510
P	0.8914180	-2.3023750	-0.0791030
P	0.7229040	0.0512030	-2.1315490
P	-0.1978040	-1.9732490	-1.9991920
C	-1.3172230	1.2739020	0.6013300
C	-1.9622430	-0.8991660	1.2606660
C	-1.1242600	0.2315880	1.5565660
H	-0.4665750	0.2931250	2.4159140
C	-2.2904240	0.7439970	-0.3906760
C	-2.6654090	-0.5617320	0.0717010
H	-3.3851690	-1.2062250	-0.4230900
C	0.3127610	3.0969480	-0.2652300
H	1.1999490	2.4476560	-0.2398050
H	0.6504170	4.1268040	-0.0695810
H	-0.1026880	3.0687780	-1.2770620
C	-1.8273830	3.7215140	0.9518750
H	-2.3635330	3.8896240	0.0109470
H	-1.3942530	4.6859990	1.2586160



SUPPORTING INFORMATION

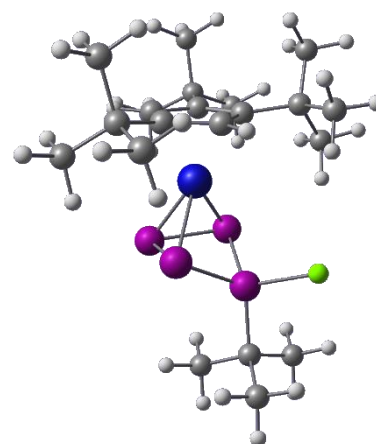
H	-2.5603310	3.4233500	1.7175640
C	-2.2343680	-2.0982030	2.1596430
C	0.0748100	2.7006570	2.1665510
H	-0.5814870	2.4925680	3.0249400
H	0.4999780	3.7046650	2.3117350
H	0.9114840	1.9876160	2.1809720
C	-3.0641310	1.3593220	-1.5776220
C	-0.6948950	2.6727470	0.8253740
C	-2.3009480	2.4187330	-2.3915220
H	-2.0616760	3.3180370	-1.8143040
H	-2.9271340	2.7380770	-3.2380930
H	-1.3667760	2.0126180	-2.8073570
C	-3.4895820	0.2573820	-2.5795990
H	-2.6238100	-0.2864420	-2.9871760
H	-4.0169930	0.7255310	-3.4237380
H	-4.1801070	-0.4775610	-2.1429100
C	-4.3612800	1.9828220	-0.9946610
H	-4.9678780	1.2229200	-0.4785880
H	-4.9671580	2.4033320	-1.8127310
H	-4.1489510	2.7889240	-0.2802840
C	-2.4663360	-3.3806280	1.3372400
H	-3.2952760	-3.2707780	0.6217270
H	-2.7202680	-4.2137350	2.0103620
H	-1.5650280	-3.6705740	0.7745870
C	-1.0940070	-2.3258120	3.1685750
H	-0.1389900	-2.5377080	2.6646410
H	-1.3337390	-3.1877030	3.8094660
H	-0.9523890	-1.4566060	3.8288580
C	-3.5316780	-1.7578470	2.9408240
H	-3.4116900	-0.8380340	3.5340340
H	-3.7756030	-2.5804180	3.6314050
H	-4.3851700	-1.6179840	2.2599770
C	3.1938150	0.2012260	0.3105940
C	3.0677800	-0.0519830	1.6864110
C	4.0175420	1.2438370	-0.1510770
C	3.7664900	0.7429500	2.5988170
H	2.4370400	-0.8653510	2.0525140
C	4.7026150	2.0359820	0.7703150
H	4.1291110	1.4340430	-1.2209340
C	4.5784540	1.7858140	2.1425520
H	3.6757300	0.5435340	3.6687000
H	5.3395940	2.8490820	0.4155940
H	5.1210290	2.4062810	2.8595070
Cl	3.8146580	-1.6433910	-2.0441400

SUPPORTING INFORMATION

$[\text{Cp}^* \text{Ni}(\eta^3\text{-P}_4\text{tBuCl})]^+$ (**2g_{endo}**):

B3LYP/def2SVP: Energies/H = -4155.171882, Enthalpies/H = -4155.170938, Free Energies/H = -4155.268938, ZPVE/ kJ/mol = 1447.38

Symbol	X	Y	Z
Ni	0.3450650	0.3379170	-0.3107430
P	-2.6130210	-0.1260560	0.1254290
P	-1.4803510	1.7430840	-0.0630890
P	-1.1860410	-1.1562480	-1.1961550
P	-0.9432860	0.8906860	-2.0547910
C	1.7742210	-0.7775190	0.8474630
C	1.9318960	1.5388610	0.4222660
C	1.5662680	0.5286320	1.3803290
H	1.2081460	0.7408260	2.3813360
C	2.2514060	-0.5774700	-0.5484570
C	2.3566820	0.8397270	-0.7394940
H	2.7045670	1.3150820	-1.6516350
C	0.6140420	-3.0589030	1.2988150
H	-0.3987300	-2.6367910	1.3647250
H	0.6523480	-3.9349950	1.9652270
H	0.7684270	-3.4130250	0.2761870
C	3.0623970	-2.6804860	1.8692860
H	3.4009340	-3.1307440	0.9284750
H	3.0298370	-3.4811880	2.6242450
H	3.8192240	-1.9471500	2.1887540
C	2.0731570	3.0348110	0.6738410
C	1.2605170	-1.5992300	3.1890340
H	2.0054400	-0.9344860	3.6516520
H	1.1855170	-2.4979110	3.8189560
H	0.2805960	-1.1005800	3.2115440
C	2.8167530	-1.5087930	-1.6439330
C	1.6637630	-2.0233300	1.7569640
C	2.2629970	-2.9442160	-1.6688200
H	2.5091990	-3.5183670	-0.7690850
H	2.7078480	-3.4791420	-2.5213400
H	1.1715850	-2.9578430	-1.8068610
C	2.5466900	-0.9154120	-3.0487220
H	1.4688550	-0.7994850	-3.2408350
H	2.9493970	-1.5986550	-3.8110240
H	3.0295700	0.0584270	-3.2076120
C	4.3542640	-1.5583080	-1.4347680
H	4.7978210	-0.5529580	-1.4987940
H	4.8139610	-2.1839510	-2.2161460
H	4.6221340	-1.9841670	-0.4579380
C	1.6291500	3.8569360	-0.5522310
H	2.1791330	3.5743100	-1.4624890
H	1.8161460	4.9266670	-0.3717540



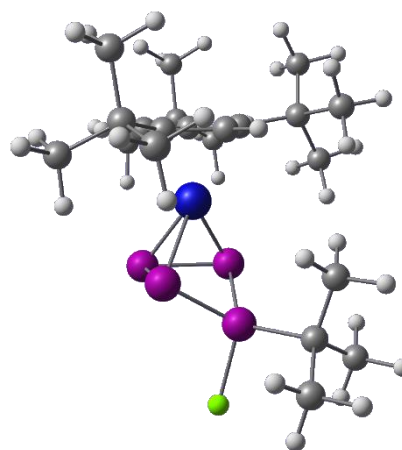
SUPPORTING INFORMATION

H	0.5528370	3.7375650	-0.7527110
C	1.2767130	3.4805610	1.9137670
H	0.2014180	3.2732340	1.8053740
H	1.3964950	4.5645940	2.0614090
H	1.6329110	2.9840230	2.8292200
C	3.5823690	3.2859900	0.9305200
H	3.9449670	2.6977300	1.7878360
H	3.7504860	4.3518480	1.1519640
H	4.1885350	3.0193580	0.0511030
C	-4.4503060	-0.1260410	-0.3434640
C	-5.1880790	0.8062220	0.6328760
H	-6.2498610	0.8412420	0.3404750
H	-5.1354180	0.4458720	1.6696590
H	-4.7981060	1.8352600	0.5954950
C	-4.9665680	-1.5716440	-0.2470600
H	-6.0308590	-1.5779220	-0.5319960
H	-4.4340690	-2.2468020	-0.9343200
H	-4.8884900	-1.9719840	0.7734590
C	-4.5640320	0.3989300	-1.7853670
H	-4.2010630	1.4328590	-1.8840210
H	-4.0305520	-0.2362450	-2.5081320
H	-5.6299310	0.3944690	-2.0640580
Cl	-2.6140240	-0.8422690	2.0780280

$[\text{Cp}^* \text{Ni}(\eta^3\text{-P}_3\text{Cl}^t\text{Bu})]^+$ (**2g_{exo}**):

B3LYP/def2SVP: Energies/H = -4155.165046, Enthalpies/H = -4155.164101, Free Energies/H = -4155.262553, ZPVE/ kJ/mol = 1446.79

Symbol	X	Y	Z
Ni	0.2879420	0.2664310	-0.3633960
P	-2.7704400	-0.1484860	-0.3778990
P	-1.5501270	1.6531000	-0.6850400
P	-1.1247550	-1.3807440	-1.1777160
P	-0.6867860	0.4592850	-2.3649790
C	1.7526130	-0.6891830	0.9283690
C	1.6663240	1.6305590	0.5141100
C	1.3479750	0.5830030	1.4390620
H	0.9063680	0.7463630	2.4152940
C	2.3065340	-0.4329150	-0.4236380
C	2.2437440	0.9876080	-0.6187650
H	2.5984670	1.5033870	-1.5056020
C	0.7809730	-3.0620100	1.3390580
H	-0.2703010	-2.7429600	1.3983090
H	0.8955080	-3.9491710	1.9813680
H	0.9784290	-3.3676090	0.3070110
C	3.1626300	-2.4976380	1.9957330
H	3.5505490	-2.9552530	1.0787890
H	3.1634160	-3.2762000	2.7738540



SUPPORTING INFORMATION

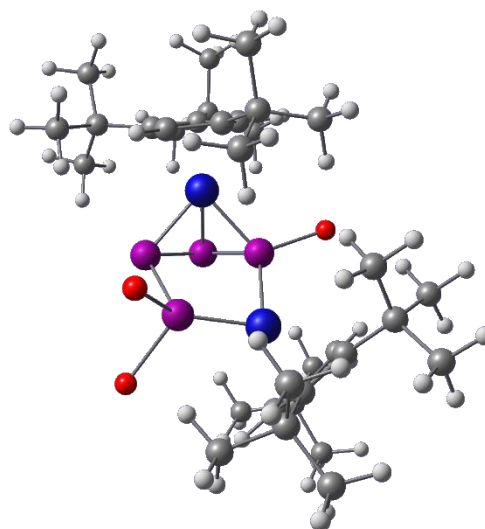
H	3.8615240	-1.7076310	2.3113960
C	1.6462730	3.1287370	0.7877300
C	1.2551660	-1.5627420	3.2595320
H	1.9306010	-0.8366700	3.7364080
H	1.2460960	-2.4669500	3.8858620
H	0.2371160	-1.1493440	3.2723590
C	3.0730650	-1.2937290	-1.4524940
C	1.7244940	-1.9441170	1.8353820
C	2.6066680	-2.7562830	-1.5699770
H	2.7698240	-3.3370550	-0.6558690
H	3.1785110	-3.2504650	-2.3697750
H	1.5412670	-2.8235440	-1.8391500
C	2.9649510	-0.6821850	-2.8708060
H	1.9211560	-0.6127830	-3.2119780
H	3.5070560	-1.3259930	-3.5790190
H	3.4167950	0.3169910	-2.9414100
C	4.5736350	-1.2501180	-1.0539700
H	4.9478750	-0.2148760	-1.0492950
H	5.1657730	-1.8219030	-1.7858510
H	4.7566480	-1.6788910	-0.0607700
C	1.3927230	3.9389190	-0.4980710
H	2.1494190	3.7361820	-1.2708700
H	1.4347060	5.0154490	-0.2725450
H	0.4003010	3.7285140	-0.9260090
C	0.6028110	3.5023190	1.8567740
H	-0.4181650	3.2421210	1.5396090
H	0.6321670	4.5871620	2.0404980
H	0.8036020	3.0038360	2.8174180
C	3.0601330	3.4751270	1.3278350
H	3.2872770	2.9124650	2.2466450
H	3.1151470	4.5498190	1.5629610
H	3.8398640	3.2470710	0.5849090
C	-3.5906340	-0.4868140	1.2909720
Cl	-4.3624740	-0.1877760	-1.7149600
C	-2.5039500	-0.3957630	2.3744590
H	-1.7108750	-1.1410780	2.2271030
H	-2.0465350	0.6034340	2.4246500
H	-2.9740320	-0.5981620	3.3500010
C	-4.1984760	-1.8997750	1.2436040
H	-4.6837520	-2.1005480	2.2121690
H	-4.9606340	-1.9956930	0.4574230
H	-3.4302550	-2.6732110	1.0890160
C	-4.6705170	0.5853590	1.5219060
H	-5.1232350	0.4070080	2.5104870
H	-4.2496910	1.6028400	1.5279590
H	-5.4694980	0.5379690	0.7697260

SUPPORTING INFORMATION

 $[(Cp''Ni)_2(\mu;\eta^3:\eta^1:\eta^1-P_4Br_3)]^+ (3a)$

B3LYP/def2SVP: Energies/H = -13431.720505, Enthalpies/H = -13431.719561, Free Energies/H = -13431.862697, ZPVE/ kJ/mol = 2238.06

Symbol	X	Y	Z
Br	0.4276270	-3.2108310	-0.9767950
Br	-1.7734950	3.3687370	-1.5796430
Br	-0.6430860	2.9114590	1.6925810
Ni	-1.8540770	-0.1688950	-0.2675090
Ni	2.1710910	-0.0228290	-0.0661190
P	0.1980350	-0.9820290	-0.6017910
P	-0.8911990	1.7716430	-0.2492840
P	1.3179120	-0.0123730	-2.2139420
P	1.2345360	1.8252680	-1.0197630
C	3.4205370	-1.4313050	0.8363200
H	3.2623850	-2.5039240	0.7874840
C	-3.0242700	-1.8426840	-0.6265850
H	-2.5916550	-2.8078670	-0.8690220
C	-3.9084590	-0.1140010	0.6083700
C	-3.4107050	-0.8753860	-1.6010230
C	2.8770810	-0.5844290	1.8626970
C	3.2912630	0.7248010	1.5205670
H	3.0378520	1.6191450	2.0795770
C	-3.8282730	0.2271790	-0.8311640
H	-4.1441360	1.1824360	-1.2405390
C	-3.4187640	-1.4442860	0.7290730
C	4.2594910	-0.6958510	-0.0646960
C	4.1589260	0.7025420	0.3508660
C	-4.6960960	-2.6624210	2.5641490
H	-5.0633030	-1.7702650	3.0836780
H	-4.6242010	-3.4684010	3.3113430
H	-5.4510330	-2.9610250	1.8200690
C	2.2029600	-1.0280920	3.1517760
C	-3.4431690	-1.0231490	-3.1187470
C	-3.3153400	-2.4498120	1.9012450
C	-4.6533930	0.8526050	1.5540420
C	4.9198790	1.9817780	-0.0711430
C	-4.5913220	2.3077910	1.0320210
H	-3.5589460	2.6709310	0.9393660
H	-5.1066760	2.9660850	1.7472070
H	-5.0934360	2.4365280	0.0631470
C	-6.1499040	0.4395600	1.5415840
H	-6.5556660	0.4642540	0.5180080
H	-6.7342260	1.1466270	2.1522560
H	-6.3096540	-0.5689330	1.9427560
C	5.1288540	-1.4808300	-1.0723170
C	-2.2728050	-2.0199370	2.9547360



SUPPORTING INFORMATION

H	-1.2709930	-1.9831270	2.5058010
H	-2.2442500	-2.7526420	3.7774690
H	-2.4820930	-1.0363460	3.3875310
C	-2.5349950	-2.1738960	-3.5874350
H	-1.4842700	-2.0012590	-3.3096920
H	-2.5822380	-2.2640960	-4.6836930
H	-2.8459890	-3.1420080	-3.1652020
C	5.5338770	-0.7277690	-2.3508350
H	4.6514900	-0.3854440	-2.9118970
H	6.0949470	-1.4140600	-3.0029610
H	6.1863690	0.1311660	-2.1585190
C	1.6353250	-2.4520490	3.0216280
H	0.9002250	-2.5244640	2.2070410
H	1.1332100	-2.7420510	3.9567910
H	2.4276160	-3.1920400	2.8315870
C	-4.1233050	0.8852340	2.9992700
H	-4.2643170	-0.0616260	3.5316530
H	-4.6664240	1.6559750	3.5675920
H	-3.0539110	1.1433490	3.0230520
C	-4.9058930	-1.3466870	-3.5128670
H	-5.2533470	-2.2729310	-3.0285990
H	-4.9867790	-1.4808200	-4.6037350
H	-5.5870660	-0.5330860	-3.2179560
C	4.6832390	2.4195240	-1.5339210
H	4.8420150	1.6193670	-2.2601970
H	5.3721620	3.2421890	-1.7814440
H	3.6600060	2.7998790	-1.6672780
C	-3.0095780	0.2795880	-3.8163990
H	-3.6439150	1.1318350	-3.5288780
H	-3.0864120	0.1658160	-4.9092460
H	-1.9666850	0.5349590	-3.5735480
C	1.0906600	-0.0495900	3.5674840
H	1.4743060	0.9729990	3.7024280
H	0.6515840	-0.3663490	4.5260690
H	0.2868540	-0.0126910	2.8184120
C	6.4066120	-1.9196250	-0.3067730
H	6.9964770	-1.0604520	0.0411210
H	7.0455020	-2.5243300	-0.9697650
H	6.1523900	-2.5334960	0.5709580
C	6.4308260	1.7475600	0.1820480
H	6.6137380	1.4067340	1.2131700
H	6.9751150	2.6937570	0.0381030
H	6.8651350	1.0101780	-0.5038180
C	3.3088850	-1.0306570	4.2403680
H	4.1333600	-1.7095730	3.9724240
H	2.8857580	-1.3701790	5.1990260
H	3.7281170	-0.0237090	4.3890610

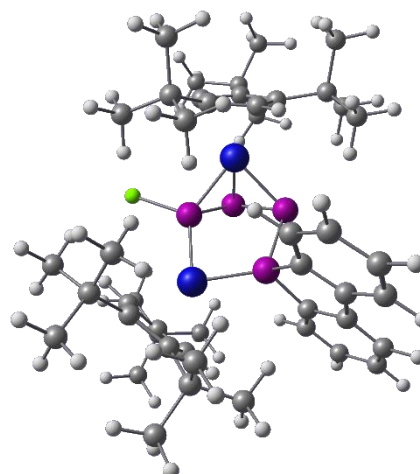
SUPPORTING INFORMATION

C	-2.8723070	-3.8369780	1.3793830
H	-3.5805460	-4.2474080	0.6430760
H	-2.8296990	-4.5408810	2.2241950
H	-1.8715110	-3.8114640	0.9247150
C	4.3968950	-2.7620210	-1.5401390
H	4.1924790	-3.4667760	-0.7223020
H	5.0332140	-3.2927250	-2.2637680
H	3.4452370	-2.5248940	-2.0381780
C	4.4998360	3.1780070	0.8151450
H	3.4238050	3.3940030	0.7356980
H	5.0397530	4.0756460	0.4792960
H	4.7506020	3.0220540	1.8749860

$[(Cp''Ni)_2(\mu;\eta^3:\eta^1:\eta^1-P_4biphenC)]^+ (\mathbf{3b})$:

B3LYP/def2SVP: Energies/H = -6631.766303, Enthalpies/H = -6631.765358, Free Energies/H = -6631.918303, ZPVE/ kJ/mol = 2656.45

Symbol	X	Y	Z
Ni	1.7698811	-0.6463039	0.3271271
Ni	-2.2512149	-0.2667362	0.2133180
P	-0.3025568	-1.3049820	0.6963321
P	0.9694810	1.4211141	0.2737259
Cl	-0.6460077	-3.3539850	1.1295232
P	-1.1571260	1.5448410	1.0978159
P	-1.3107119	-0.2578070	2.3183080
C	1.3617919	3.7259250	-1.0405592
C	3.2041432	-1.9757749	-0.7643889
C	2.8035032	-2.4268218	0.5666302
H	2.2939133	-3.3654998	0.7576772
C	3.2920552	-1.5626357	1.5936841
C	3.8073211	-0.6999218	-0.5681399
C	-4.4141279	-0.5917233	0.3922930
C	-4.1248510	0.6537597	-0.3320301
C	-3.1503128	-1.1158433	-1.5423280
C	1.7132639	2.8284541	1.1800609
C	3.7877081	-0.4494687	0.8925381
H	4.1963920	0.4450003	1.3542470
C	-3.3400579	0.2840407	-1.4945790
H	-3.0059810	0.9846567	-2.2521171
C	1.8341388	3.9599281	0.3368958
C	0.8673889	2.4172270	-1.2558541
C	-3.7547268	-1.6275203	-0.3390229
H	-3.7507147	-2.6755873	-0.0598149
C	3.3434802	-1.8282657	3.0953121
C	0.3893940	2.0251269	-2.5078851
H	0.0169260	1.0128058	-2.6668630



SUPPORTING INFORMATION

C	2.0992179	2.8867512	2.5208989
H	1.9926019	2.0166203	3.1693069
C	-5.3011689	-0.9340623	1.6141710
C	1.3651528	4.6385639	-2.1042492
H	1.7429047	5.6532800	-1.9620353
C	2.3663338	5.1467272	0.8575897
H	2.4725117	6.0299691	0.2242127
C	-2.6872788	-1.9343243	-2.7387249
C	-4.6992660	2.0867277	-0.2659811
C	2.6262158	4.0796503	3.0279208
H	2.9336578	4.1347464	4.0745848
C	2.7606557	5.1999693	2.1976487
H	3.1751977	6.1270043	2.6006517
C	4.6336011	0.2468582	-1.4659290
C	0.3970179	2.9466778	-3.5604791
H	0.0272470	2.6505517	-4.5447491
C	2.9642553	-2.8775609	-1.9987178
C	-4.8595749	-0.2626062	2.9341580
H	-4.7045130	0.8163058	2.8441459
H	-5.6298719	-0.4296232	3.7037240
H	-3.9222739	-0.7053041	3.2988010
C	0.8829018	4.2451039	-3.3558342
H	0.8881468	4.9583708	-4.1833983
C	6.0772141	-0.3209127	-1.5224219
H	6.1196192	-1.3044698	-2.0066919
H	6.7260161	0.3666463	-2.0891100
H	6.4984861	-0.4237306	-0.5099979
C	1.9313862	-2.2669811	-2.9700379
H	2.2352872	-1.2880671	-3.3564329
H	1.7750663	-2.9374681	-3.8307048
H	0.9656892	-2.1405461	-2.4607479
C	4.7356650	1.6580612	-0.8415531
H	5.2873750	1.6633493	0.1089200
H	5.2808970	2.3197922	-1.5310581
H	3.7474740	2.1034742	-0.6685311
C	-4.9553281	2.6411257	1.1463878
H	-4.0337621	2.6540688	1.7477838
H	-5.3116472	3.6792377	1.0635968
H	-5.7234981	2.0820647	1.6919129
C	4.0877331	0.4385281	-2.8928500
H	3.0614551	0.8343890	-2.8761730
H	4.7175570	1.1659721	-3.4282200
H	4.0937451	-0.4840730	-3.4831159
C	-1.7074758	-1.1415173	-3.6187259
H	-0.7951908	-0.8841872	-3.0621130
H	-1.4100158	-1.7460863	-4.4889389
H	-2.1545389	-0.2119324	-4.0018950

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C	-6.0336530	2.0573675	-1.0626691
H	-6.7759980	1.3863205	-0.6126551
H	-6.4641681	3.0709075	-1.0916142
H	-5.8663450	1.7311705	-2.1007661
C	4.2885013	-3.1772959	-2.7376988
H	5.0324243	-3.6150148	-2.0537358
H	4.1038424	-3.9049420	-3.5438808
H	4.7321502	-2.2876189	-3.1989068
C	-3.7725591	3.0984657	-0.9832482
H	-3.6674931	2.8929256	-2.0576322
H	-4.2087132	4.1044737	-0.8942852
H	-2.7698811	3.1269068	-0.5339052
C	-3.9697578	-2.2359365	-3.5603789
H	-4.4540858	-1.3075715	-3.9001120
H	-3.7113157	-2.8337475	-4.4489669
H	-4.7004647	-2.8065535	-2.9665649
C	2.4003674	-4.2491240	-1.5575448
H	1.4263123	-4.1589210	-1.0553788
H	2.2542714	-4.8815270	-2.4463937
H	3.0898794	-4.7805869	-0.8835567
C	-6.7711989	-0.5634974	1.2984990
H	-7.0949309	-0.9946694	0.3382680
H	-7.4265719	-0.9652234	2.0868000
H	-6.9340490	0.5206516	1.2612559
C	-5.2721468	-2.4579383	1.8770181
H	-4.2545018	-2.8182992	2.0920751
H	-5.8926108	-2.6804222	2.7580401
H	-5.6791857	-3.0355673	1.0333451
C	-2.0462177	-3.2662223	-2.3151788
H	-2.7414827	-3.8941193	-1.7376488
H	-1.7505637	-3.8384973	-3.2076798
H	-1.1499747	-3.1047782	-1.7012088
C	4.8016552	-2.2151875	3.4461382
H	5.5005441	-1.3980905	3.2076281
H	4.8913882	-2.4377415	4.5220102
H	5.1204943	-3.1084856	2.8861432
C	2.4159572	-2.9916287	3.4898962
H	2.7026823	-3.9299297	2.9901782
H	2.4766142	-3.1662196	4.5754452
H	1.3657722	-2.7811458	3.2395522
C	2.9493471	-0.5748056	3.8977601
H	1.9124671	-0.2762537	3.6761390
H	3.0231811	-0.7743756	4.9785541
H	3.6113460	0.2758134	3.6745730

SUPPORTING INFORMATION

Selected canonical molecular orbitals of **3a**

To obtain further insight into the electronic structure of **3a** we performed a Mulliken population analysis on its optimized geometry. While most of the canonical frontier orbitals (HOMO-5 to LUMO+1, Figure SI 24) are smeared across large parts of the cation, the orbital contributions of P1 and P4 in the HOMO-4 (Significant orbital contributions: Ni2(d) = 20 %, P1(p) = 7 %, P4(p) = 6 %) may yield a possible explanation for the relatively high $^2J_{P-P}$ coupling constant found in the ^{31}P NMR spectra of **3a**. The bonding motif found for P1-Ni2-P4 in the HOMO-4 resembles an allylic-type interaction.

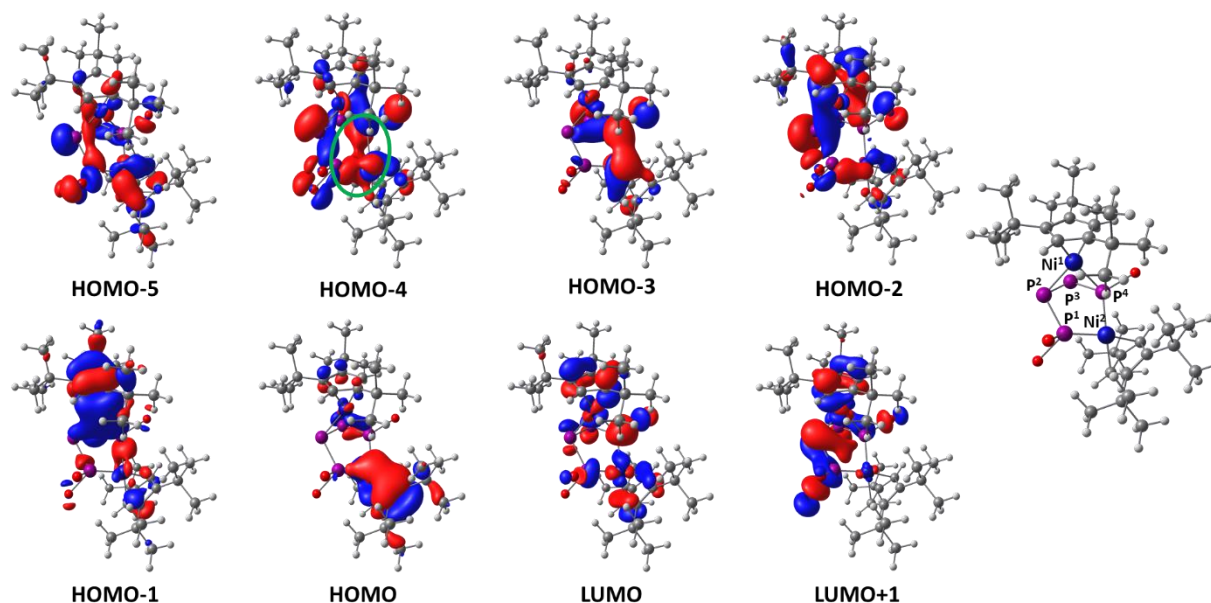


Figure SI 24: Canonical frontier orbitals of **3a**; The allylic part of the HOMO-4, which is stretched across P1, Ni2 and P4 is marked in green, isosurfaces are drawn with both signs and at a 0.03 contour value.

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