

Arene Non-Innocence in Dinuclear Complexes of Fe, Co, and Ni Supported by a *para*-Terphenyl Diphosphine

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Experimental Details

General Considerations

Unless otherwise specified, all air- and moisture-sensitive compounds were manipulated using glovebox or using standard Schlenk line techniques with an N₂ atmosphere. Anhydrous tetrahydrofuran (THF) was purchased from Aldrich in 18 L Pure-Pac™ containers. Anhydrous pentane, hexanes, benzene, toluene, diethyl ether, and THF were purified by sparging with nitrogen for 15 minutes and then passing under nitrogen pressure through a column of activated A2 alumina (Zapp's). Benzene-*d*₆, tetrahydrofuran-*d*₈, and toluene-*d*₈ was purchased from Cambridge Isotope Laboratories, Inc., dried over sodium/benzophenone ketyl and vacuum transferred prior to use. Compound **1**, **5**, and NaCo(CO)₄ were prepared according to previously published protocol.¹ Unless otherwise indicated, all commercial chemicals were used as received. Nickel bis(1,5-cyclooctadiene) (Ni(COD)₂) and Fe₃(CO)₁₂ stabilized with 10 wt. percent methanol were purchased from Strem Chemicals, Inc.. Co₂(CO)₈, [*n*Bu₄N][PF₆], and ferrocene were purchased from Alfa Aesar. Ferrocenium hexafluorophosphate and carbon monoxide were purchased from Sigma Aldrich. ¹H, ¹³C, and ³¹P NMR spectra were recorded on Varian Mercury 300 or Varian INOVA-500 spectrometers at room temperature unless indicated otherwise. Chemical shifts for ¹H and ¹³C NMR data are reported relative to residual solvent peaks.² ³¹P NMR chemical shifts are reported with respect to the deuterated solvent used to lock the instrument. IR spectra were obtained as solution samples using a CaF₂ window cell on a Thermo Scientific Nicolet 6700 FT-IR spectrometer or as thin films on a Bruker Alpha FT-IR spectrometer with a diamond ATR attachment. Elemental analyses were performed by Robertson Microlit Laboratories, Ledgewood, NJ.

Synthesis of Complex 2

Compound **1** (300 mg, 0.648 mmol, 1 equiv) was transferred as a solution in *ca.* 10 mL THF into a quartz Schlenk tube fitted with a screw-in Teflon stopper along with a magnetic stir bar. Fe₃(CO)₁₂ (10 wt % MeOH stabilizer) (359.3 mg, 0.648 mmol, 1 equiv) was then added as a solution in *ca.* 20 mL THF. The reaction mixture was then thoroughly degassed and allowed to stir for 1 hr, during which time the solution turned from green to a deep red. The reaction mixture was then subjected to UV photolysis under a 200 W Hg-Xe lamp for 2-3 days until the desired product was determined to be the majority species by ³¹P NMR. During photolysis, the solution was degassed every few hours. Volatiles were then removed under reduced pressure. The dark red/orange residue was washed with hexanes then diethyl ether until only a pale orange color remained in washes. The remaining material was dissolved in THF and filtered through a Celite pad and the filtrate dried under reduced pressure. The solid was then recrystallized by the vapor diffusion of hexanes into a concentrated THF solution. Resulting dark red/orange crystals were washed with hexanes and dried under reduced pressure. Yield: 48.4 mg (11 %) ¹H NMR (300 MHz, C₆D₆) δ 7.57 (d, 2H, aryl-*H*), 7.10 (t, 2H, aryl-*H*), 6.97 (t, 2H, aryl-*H*), 6.88 (t, 2H, aryl-*H*), 3.76 (s, 4H, central aryl-*H*), 2.20 (m, 4H, *CH*), 0.98 (dd, 12H, *CH*₃), 0.82 (dd, 12H, *CH*₃) ppm. ³¹P NMR (121 MHz, C₆D₆) δ 90.59 (s) ppm. ¹³C NMR (126 MHz, C₆D₆) δ 221.3 (d), 149.4 (d), 139.0 (d), 130.2 (d), 129.3 (s), 129.0 (s), 126.84 (s), 96.8 (s), 57.6 (s), 26.7 (d), 17.2 (d) ppm. IR (ATR film, cm⁻¹) ν_{CO}:

1966, 1914, 1903, 1880. Anal. Calcd. for: C₃₄H₄₀Fe₂O₄P₂ (**2**) (%): C, 59.50; H, 5.87. Found: C, 59.29; H, 5.74.

Synthesis of Complex 3

Compound **1** (100 mg, 0.216 mmol, 1 equiv) was transferred as a solution in *ca.* 15 mL toluene into a Schlenk tube fitted with a screw-in Teflon stopper along with a magnetic stir bar. Co₂(CO)₈ (74 mg, 0.216 mmol, 1 equiv) was then added as a solution in *ca.* 15 mL toluene. The brown reaction mixture was heated to 110 °C for 1 hour. The solution was then degassed, 1 atm of fresh N₂ readmitted, and then heated at 110 °C for an additional 2-3 hours. During this time the solution turned green. The reaction mixture was then dried under reduced pressure. The green powder was washed with *ca.* 10 mL of ether and the remaining material dissolved in THF and filtered through a Celite pad and dried under reduced pressure to yield a green powder as the clean product. Yield: 78 mg (54 %). ¹H NMR (300 MHz, C₆D₆) δ 7.51 (d, 2H, aryl-*H*), 7.14 (t, 2H, aryl-*H*), 7.05 (t, 2H, aryl-*H*), 6.93 (m, 2H, aryl-*H*), 4.29 (broad s, 2H, central aryl-*H*), 3.95 (d, 2H, central aryl-*H*), 2.90 (m, 2H, *CH*), 2.19 (m, 2H, *CH*), 1.15 (m, 12H, *CH*₃), 0.99 (dd, 6H, *CH*₃), 0.89 (dd, 6H, *CH*₃) ppm. ³¹P NMR (121 MHz, C₆D₆) δ 80.20 (s) ppm. ¹³C NMR (126 MHz, C₆D₆) δ 271.45 (s), 215.4 (s), 153.21 (d), 135.25 (d), 130.40 (s), 129.46 (s), 127.65 (s), 127.42 (m), 87.39 (s), 61.65 (d), 60.15 (s), 27.29 (t), 24.51 (s), 18.32 (s), 18.13 (s), 17.86 (s), 17.28 (s) ppm. IR (CaF₂ window, THF, cm⁻¹) ν_{CO}: 1946, 1928, 1771. Anal. Calcd. for: C₃₃H₄₀Co₂O₃P₂ (**3**) (%): C, 59.65; H, 6.07. Found: C, 59.90; H, 6.07.

Synthesis of Complex 4

Complex **5** (100.0 mg, 0.154 mmol, 1 equiv) was transferred as a solution in *ca.* 6 mL of THF into a 20 mL scintillation vial along with a magnetic stir bar. NaCo(CO)₄ (29.8 mg, 0.154 mmol, 1 equiv) was then added as a solution in *ca.* 4 mL of THF. The reaction mixture was stirred for 30 minutes at room temperature during which time the solution turned from green to brown/yellow. The solution was then dried under reduced pressure, and the resulting solid was triturated with diethyl ether, filtered through a Celite pad, and then dried under reduced pressure. The solid from the filtrate was recrystallized by the vapor diffusion of pentane into a concentrated THF solution to yield ruby red rectangular crystals. Complex **4** is *unstable* in solution and slowly decomposes to two different products by ³¹P NMR at 50.32 (P₂Ni₃(CO)₄) and 32.31 ppm.³ Yield: 11 mg (11 %) ¹H NMR (300 MHz, C₆D₆) δ 7.26 (broad d, 2H, aryl-*H*), 7.15-6.96 (broad m, 6H, aryl-*H*), 5.85 (broad s, 4H, central aryl-*H*), 2.32 (m, 4H, *CH*), 1.44-0.80 (broad m, 24H, *CH*₃) ppm. ³¹P NMR (121 MHz, C₆D₆) δ 34.80 (s) ppm. ¹³C NMR (126 MHz, C₆D₆) δ 235.66 (s), 196.96 (s), 151.41 (d), 133.72 (d), 130.41 (s), 129.37 (s), 128.56 (d), 126.92 (s), 118.51 (d), 105.64 (broad s), 73.93 (broad s), 25.66 (broad s), 18.00 (broad s) ppm. IR (CaF₂ window, THF, cm⁻¹) ν_{CO}: 1972, 1956.4, 1803. Anal. Calcd. for: C₃₃H₄₀Ni₂O₃P₂ (**4**) (%): C, 59.69; H, 6.07. Found: C, 59.61; H, 6.10.

Synthesis of Complex 4 from 1

Compound **1** (20 mg, 0.039 mmol, 1 equiv) and Ni(COD)₂ (21.2 mg, 0.077 mmol, 2 equiv) were transferred as a solution in *ca.* 5 mL of THF into a Schlenk tube fitted with a screw-in Teflon stopper along with a magnetic stirbar. The solution was stirred for *ca.* 20 minutes at room temperature during which time the solution turned deep red. The

reaction mixture was then thoroughly degassed. The solution was cooled to $-78\text{ }^{\circ}\text{C}$, and *ca.* 4 equivalents of CO were admitted using a calibrated gas bulb. The solution was then allowed to slowly warm to room temperature while stirring over 30 minutes during which time the color changed from red to orange and finally to pale yellow. The volatiles were then removed under reduced pressure. While complex **4** was found to be the majority product, a significant quantity of impurities of $\text{P}_2\text{Ni}_3(\text{CO})_4$ as well as a transfacial polycarbonyl dinickel complex, with each phosphine coordinated to a $\text{Ni}(\text{CO})_3$ or $\text{Ni}(\text{CO})_2$ fragment, were observed which proved difficult to remove by recrystallization.^{1a, 3} Synthesis from complex **5** was therefore pursued as the predominant route to complex **4**.

Synthesis of Complex **2**·[PF₆]

Complex **2** (30.0 mg, 0.043 mmol, 1 equiv) was transferred as a solution in *ca.* 6 mL of THF to a 20 mL scintillation vial along with a magnetic stir bar. Ferrocenium hexafluorophosphate (14.5 mg, 0.043 mmol, 1 equiv) was then added as a solution in *ca.* 4 mL of THF. The reaction mixture was stirred for 30 minutes during which time the solution changed from red/orange to green/brown. The reaction mixture was then concentrated under reduced pressure, and *ca.* 5 mL of diethyl ether was added to precipitate out the product. The solid was washed with additional diethyl ether and then dissolved in minimal THF before filtering through a Celite pad and removing volatiles under reduced pressure. The emerald green residue was recrystallized by vapor diffusion of pentane into a concentrated THF solution at $-35\text{ }^{\circ}\text{C}$ to yield dark green crystalline needles. Complex **2**·[PF₆] is *unstable* in THF solution and decomposes overnight at room temperature to ill-defined species. Complex **2**·[PF₆] also immediately decomposes in acetonitrile. As a crystalline solid, complex **2**·[PF₆] is indefinitely stable at room temperature. Yield: 14.7 mg (41 %). ¹H NMR (300 MHz, *d*₈-THF) shows no signals between 200 and -70 ppm consistent with a paramagnetic compound with a weakly associated PF₆ counteranion. ³¹P NMR (121 MHz, *d*₈-THF) shows no signals between 200 and -200 ppm consistent with a paramagnetic compound with a weakly associated PF₆ counteranion. ¹⁹F NMR (282 MHz, *d*₈-THF) shows a broadened doublet centered at -70.32 ppm consistent with a weakly associated PF₆ counteranion. IR (ATR film, cm^{-1}) ν_{CO} : 2010, 1972, 1938, 1917. Anal. Calcd. for: $\text{C}_{34}\text{H}_{40}\text{F}_6\text{Fe}_2\text{O}_4\text{P}_3$ (**2**·[PF₆]) (%): C, 49.13; H, 4.85. Found: C, 49.40; H, 4.85.

Nuclear Magnetic Resonance Spectra

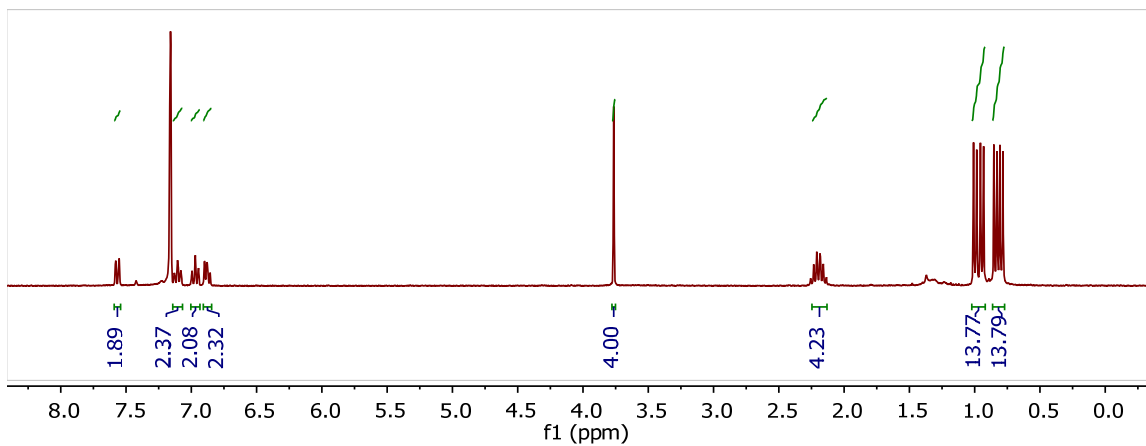


Figure S1. ^1H NMR (300 MHz, C_6D_6) spectrum of **2**.

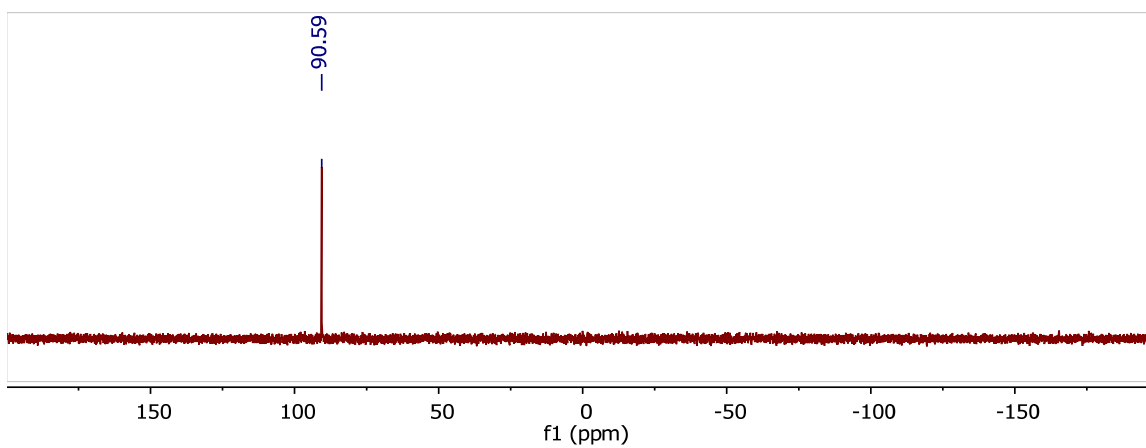


Figure S2. ^{31}P NMR (121 MHz, C_6D_6) spectrum of **2**.

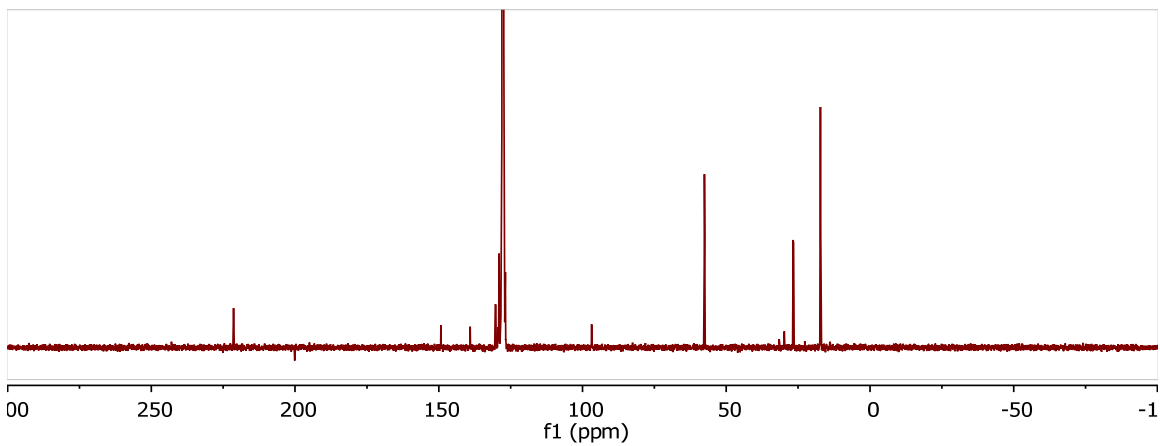


Figure S3. ^{13}C NMR (126 MHz, C_6D_6) spectrum of **2**.

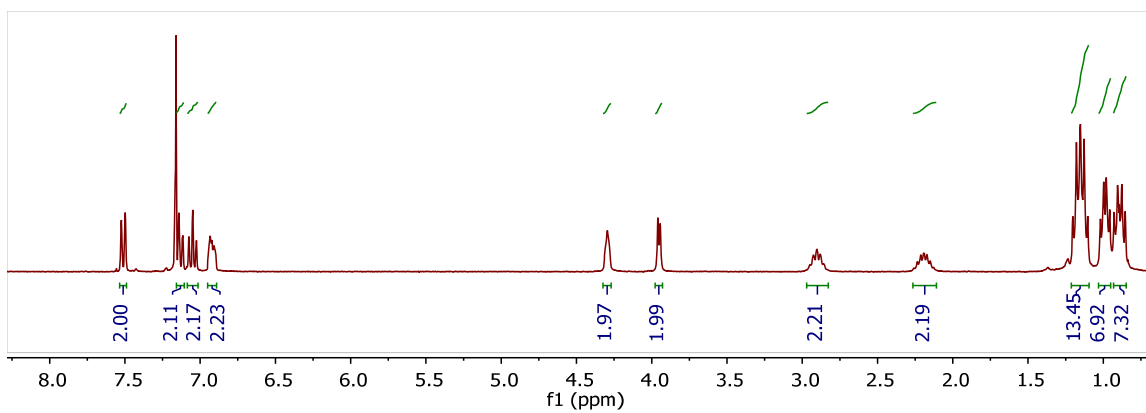


Figure S4. ^1H NMR (300 MHz, C_6D_6) spectrum of **3**.

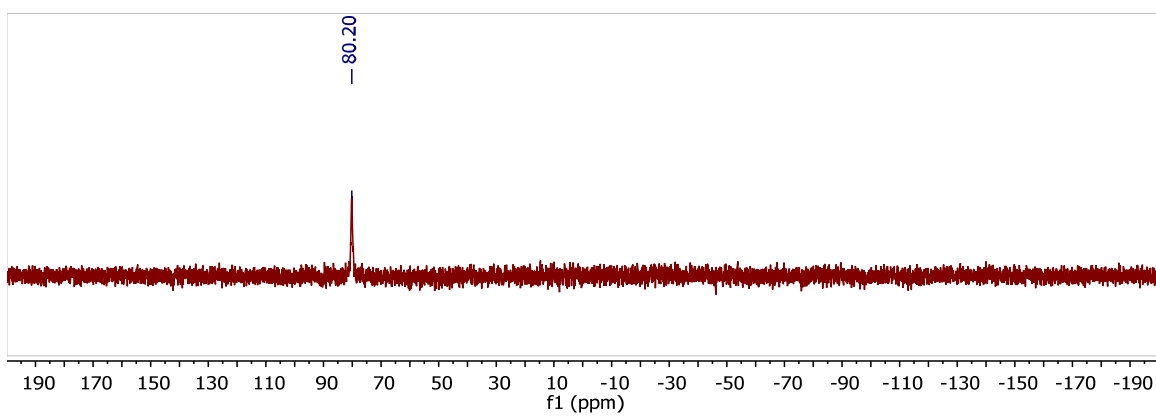


Figure S5. ^{31}P NMR (121 MHz, C_6D_6) spectrum of **3**.

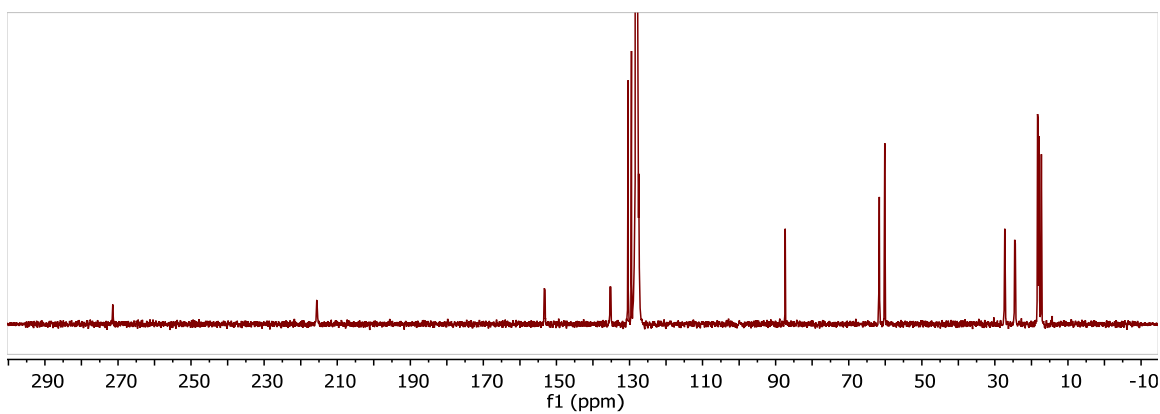


Figure S6. ^{13}C NMR (126 MHz, C_6D_6) spectrum of **3**.

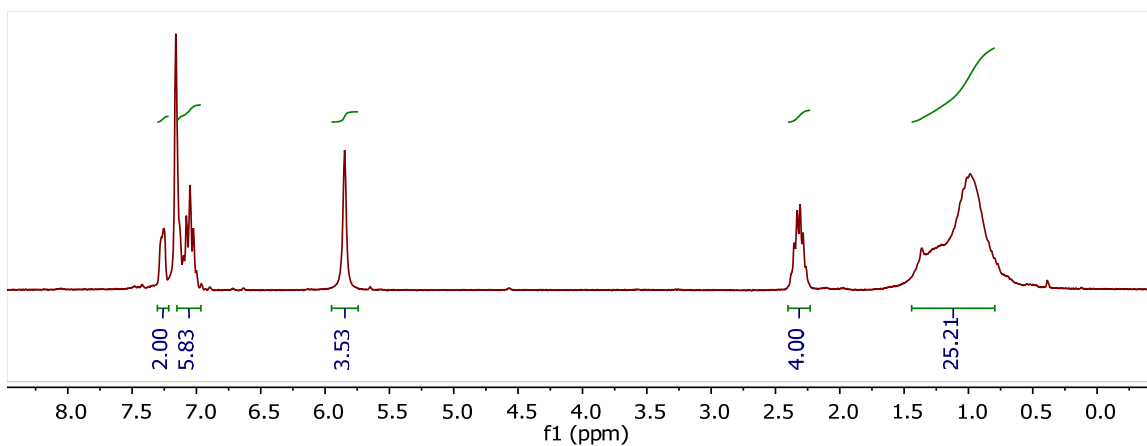


Figure S7. ^1H NMR (300 MHz, C_6D_6) spectrum of **4**.

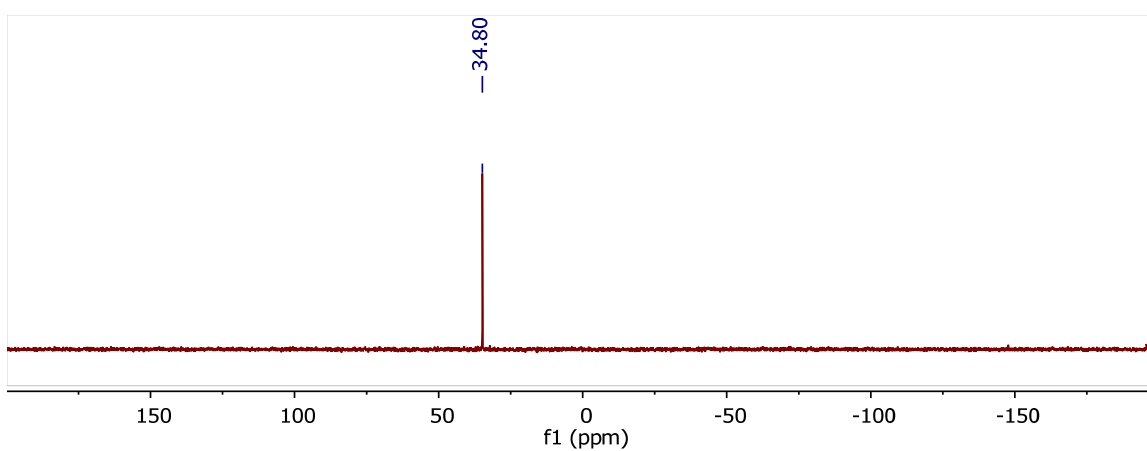


Figure S8. ^{31}P NMR (121 MHz, C_6D_6) spectrum of **4**.

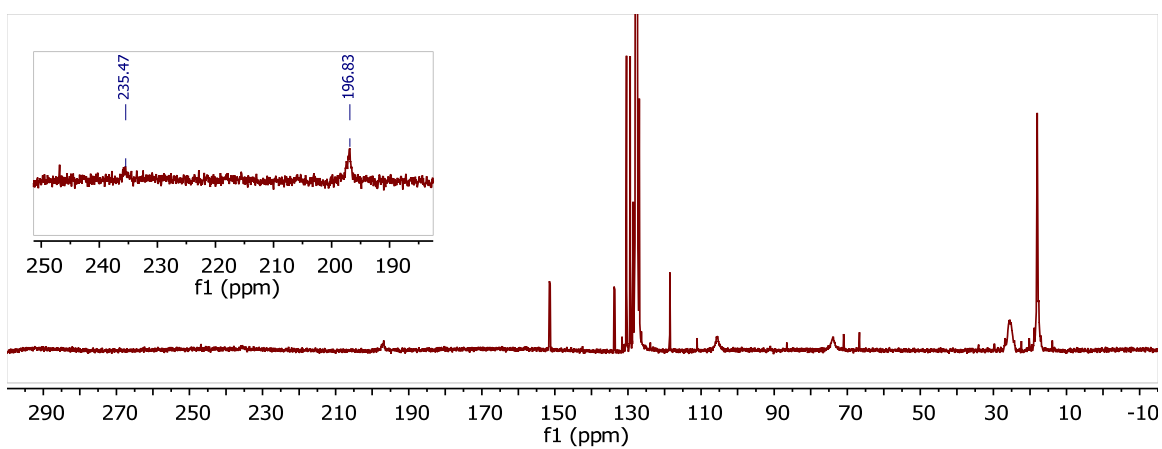


Figure S9. ^{13}C NMR (126 MHz, C_6D_6) spectrum of **4**.

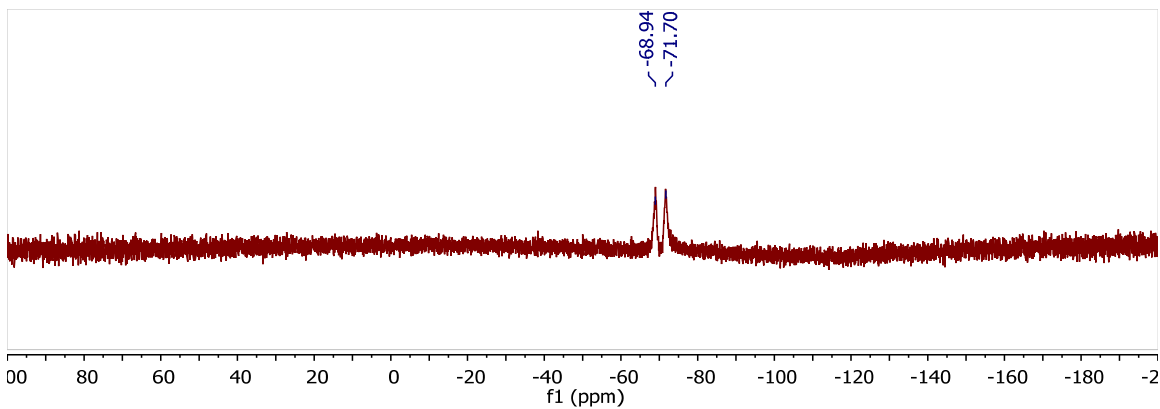


Figure S10. ^{19}F NMR (282 MHz, d_8 -THF) spectrum of $2\cdot[\text{PF}_6]$.

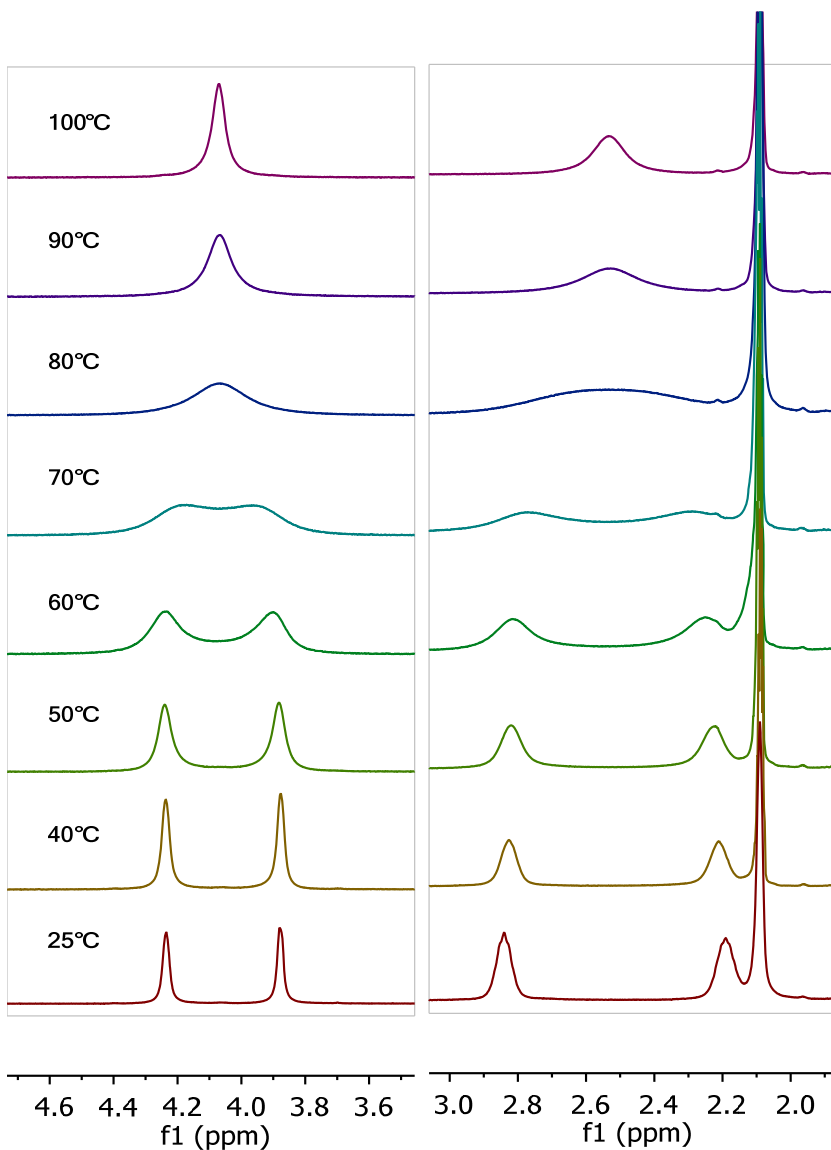


Figure S11. VT ^1H NMR (500 MHz, d_8 -PhMe) spectra of 3 with central arene protons (Left) and methine protons (Right) shown.

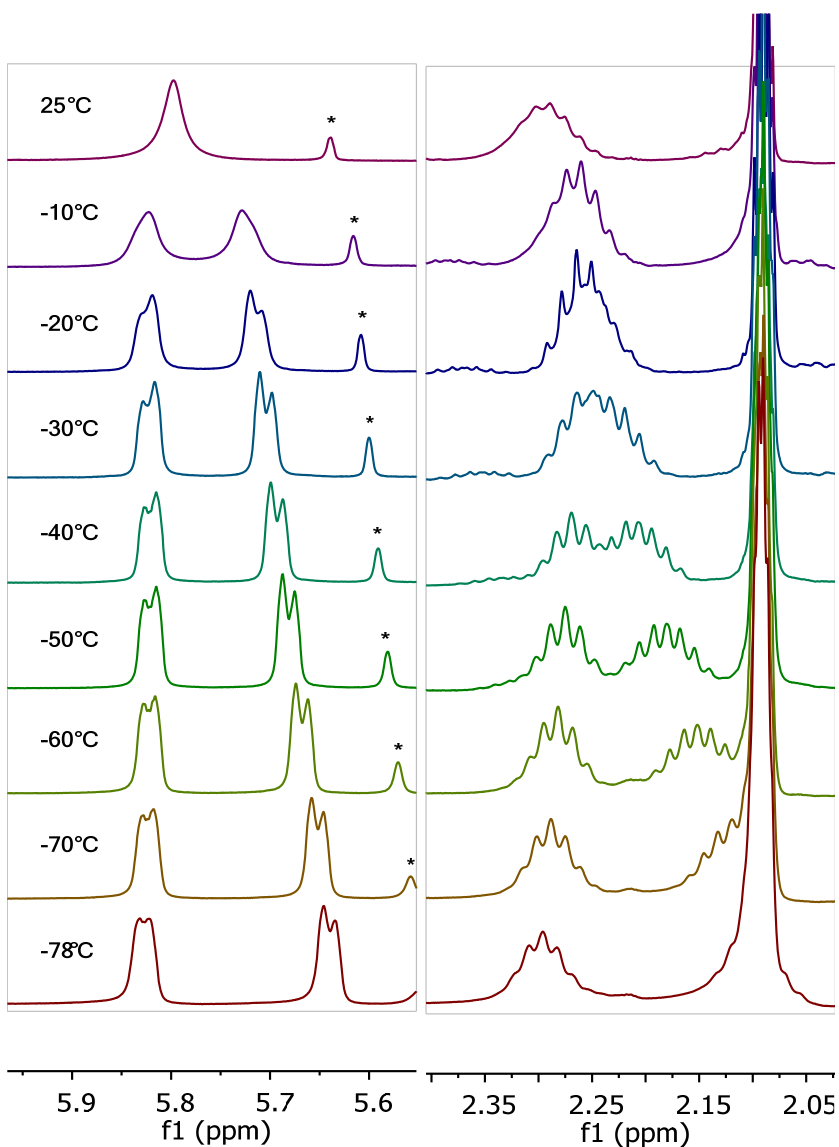


Figure S12. VT ¹H NMR (500 MHz, *d*₈-PhMe) spectra of **4** with central arene protons (Left) and methine protons (Right) shown. Starred peak corresponds to decomposition of **4** to P₂Ni₃(CO)₄ over course of experiment.

Electrochemistry Details

Electrochemical measurements of complex **2** were taken on a Pine Instrument Company biopotentiostat model AFCBP1 as 3 millimolar solutions in THF using 0.1 molar [*n*Bu₄N][PF₆] as the electrolyte with a platinum wire counter electrode, a platinum working electrode, and a silver/silver nitrate reference electrode. Electrochemical measurements of compounds were internally referenced to ferrocene.

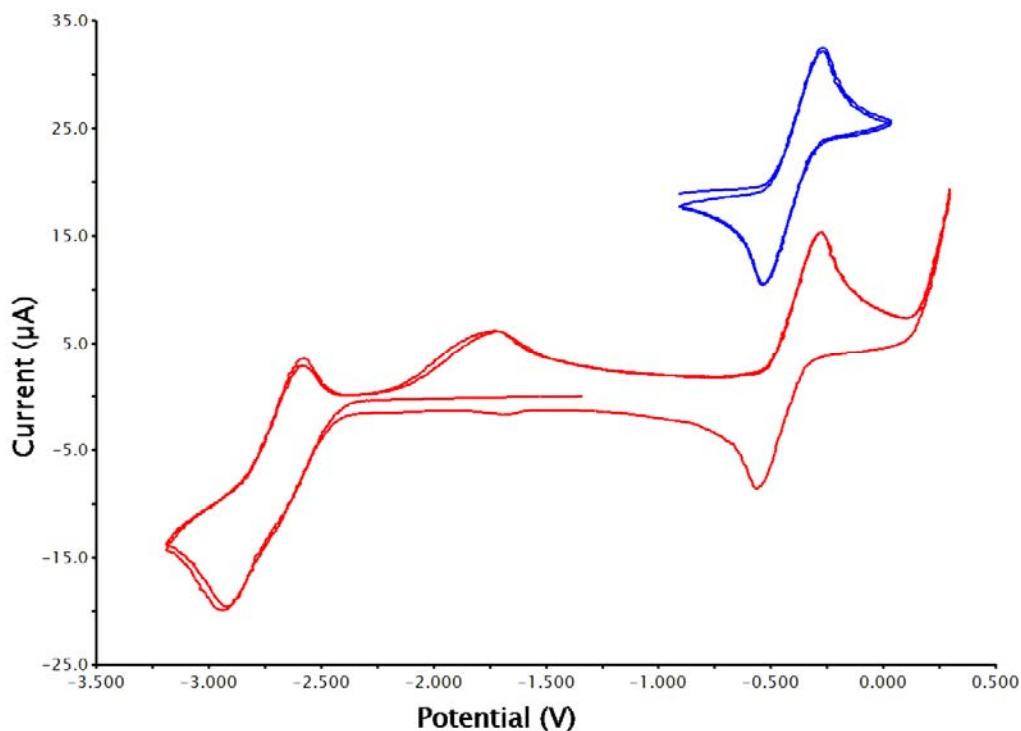


Figure S13. Cyclic voltammogram of **2** with potentials referenced to the Fc/Fc⁺ couple.

Crystallographic Information

CCDC 981915, 737475, 981916, and 981917 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Refinement details

In each case, crystals were mounted on a glass fiber or nylon loop using Paratone oil, then placed on the diffractometer under a nitrogen stream. Low temperature (100 K) X-ray data were obtained on a Bruker APEXII CCD based diffractometer (Mo sealed X-ray tube, $K_{\alpha} = 0.71073 \text{ \AA}$). All diffractometer manipulations, including data collection, integration and scaling were carried out using the Bruker APEXII software.⁴ Absorption corrections were applied using SADABS.⁵ Space groups were determined on the basis of systematic absences and intensity statistics and the structures were solved by direct methods using XS (incorporated into SHELXTL) and refined by full-matrix least squares on F^2 . All non-hydrogen atoms were refined using anisotropic displacement parameters. Hydrogen atoms were placed in idealized positions and refined using a riding model. The structure was refined (weighted least squares refinement on F^2) to convergence.

Table S1. Crystal and refinement data for reported complexes.

| Complex | 2 | 3 | 4 | 2·[PF₆] |
|---|---|---|---|---|
| empirical formula | C ₃₄ H ₄₀ O ₄ P ₂ Fe ₂ | C ₃₉ H ₄₆ Co ₂ O ₃ P ₂ | C ₃₃ H ₄₀ Ni ₂ O ₃ P ₂ | C ₃₆ H ₄₄ F ₆ Fe ₂ O _{4.50} P ₃ |
| formula wt | 686.33 | 742.56 | 664.01 | 867.32 |
| T (K) | 100 | 100 | 100 | 100 |
| a, Å | 14.3107(5) | 10.0645(4) | 14.1146(4) | 8.8633(4) |
| b, Å | 11.4723(4) | 11.1061(5) | 15.1785(4) | 15.6066(7) |
| c, Å | 20.2029(7) | 32.262(1) | 15.6000(4) | 27.166(1) |
| α, deg | 90 | 90 | 90 | 90 |
| β, deg | 108.029(2) | 91.975(2) | 115.380(1) | 98.310(2) |
| γ, deg | 90 | 90 | 90 | 90 |
| V, Å ³ | 3154.0(2) | 3604.0(3) | 3019.6(1) | 3718.4(3) |
| Z | 4 | 4 | 4 | 4 |
| cryst syst | Monoclinic | Monoclinic | Monoclinic | Monoclinic |
| space group | P2 ₁ /c | P2 ₁ /n | P2 ₁ /c | P2 ₁ /c |
| d _{calc} , g/cm ³ | 1.4453 | 1.369 | 1.461 | 1.549 |
| θ range, deg | 3 to 73.66 | 1.94 to 36.81 | 1.972 to 30.656 | 2.000 to 30.598 |
| μ, mm ⁻¹ | 1.058 | 1.045 | 1.386 | 0.980 |
| abs cor | Semi-empirical from equivalents | Semi-empirical from equivalents | Semi-empirical from equivalents | Semi-empirical from equivalents |
| GOF ^c | 1.076 | 1.517 | 0.983 | 1.602 |
| R1, ^a wR2 ^b (I > 2σ(I)) | 0.0302, 0.1373 | 0.0373, 0.0624 | 0.0321, 0.1090 | 0.0267, 0.0732 |

$$^a R1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|} \quad ^b wR2 = \left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)]} \right\}^{1/2} \quad ^c GOF = S = \left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{(n-p)} \right\}^{1/2}$$

Special refinement details for 2·[PF₆]

2·[PF₆] was crystallized from a THF-hexanes vapor diffusion at -35 °C in an inert atmosphere glovebox. It was found to crystallize with a disordered THF solvent molecule with one oxygen modeled isotropically. The structure also contains an outer-sphere hexafluorophosphate anion that was satisfactorily modeled.

References

- (a) A. Velian, S. Lin, A. J. M. Miller, M. W. Day and T. Agapie, *J. Am. Chem. Soc.*, 2010, **132**, 6296-6297; (b) W. F. Edgell and J. Lyford, *Inorg. Chem.*, 1970, **9**, 1932-1933.
- G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw and K. I. Goldberg, *Organometallics*, 2010, **29**, 2176-2179.
- S. Suseno, K. T. Horak, M. W. Day and T. Agapie, *Organometallics*, 2013, **32**, 6883-6886.
- APEX2, Version 2 User Manual, M86-E01078, Bruker Analytical X-ray Systems, Madison, WI, June 2006.
- Sheldrick, G. M. "SADABS (Version 2008/1): Program for Absorption Correction for Data from Area Detector Frames", University of Göttingen, 2008.