Trinuclear Nickel Complexes with Strong Metal-Arene Interactions Supported by Tris- and Bis(phosphinoaryl)benzene Frameworks

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Supporting Information

Experimental Details
General Considerations 2
Synthesis of 2 2
Synthesis of 3 2
Synthesis of 4 3
Synthesis of 6 3
Synthesis of 7 4
Synthesis of trinickel nonacarbonyl complex supported by ligand 1 4

NMR Spectra
Figure S1. $^1$H NMR (300 MHz, C$_6$D$_6$) spectrum of 2 5
Figure S2. $^{31}$P NMR (121 MHz, C$_6$D$_6$) spectrum of 2 5
Figure S3. $^{13}$C NMR (126 MHz, C$_6$D$_6$) spectrum of 2 5
Figure S4. $^1$H NMR (500 MHz, THF-$d_8$, -30°C) spectrum of 3 6
Figure S5. $^1$H NMR (300 MHz, C$_6$D$_6$) spectrum of 3 6
Figure S6. $^{31}$P NMR (121 MHz, C$_6$D$_6$) spectrum of 3 6
Figure S7. $^{13}$C NMR (126 MHz, THF-$d_8$) spectrum of 3 7
Figure S8. $^1$H NMR (300 MHz, C$_6$D$_6$) spectrum of 4 7
Figure S9. $^{31}$P NMR (121 MHz, C$_6$D$_6$) spectrum of 4 7
Figure S10. $^{13}$C NMR (126 MHz, C$_6$D$_6$) spectrum of 4 8
Figure S11. $^1$H NMR (300 MHz, C$_6$D$_6$) spectrum of 6 8
Figure S12. $^{31}$P NMR (121 MHz, C$_6$D$_6$) spectrum of 6 8
Figure S13. $^{13}$C NMR (126 MHz, C$_6$D$_6$) spectrum of 6 9
Figure S14. $^1$H NMR (300 MHz, C$_6$D$_6$) spectrum of 7 9
Figure S15. $^{31}$P NMR (121 MHz, C$_6$D$_6$) spectrum of 7 9
Figure S16. $^{13}$C NMR (126 MHz, C$_6$D$_6$) spectrum of 7 10
Figure S17. $^1$H NMR (300 MHz, C$_6$D$_6$) spectrum of trinickel nonacarbonyl complex 10
Figure S18. $^{31}$P NMR (121 MHz, C$_6$D$_6$) spectrum of trinickel nonacarbonyl complex 10
Figure S19. Preliminary solid-state structure of trinickel nonacarbonyl complex 12

Crystallographic Information
Table S1. Crystal and refinement data for reported complexes 11

References 12
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 acetonitrile, benzene, dichloromethane, 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). Acetonitrile-d₃ and chloroform-d₃, were purchased from Cambridge Isotopes, dried over calcium hydride, and vacuum transferred prior to use. Benzene-d₆ was also purchased from Cambridge Isotope Laboratories, Inc., dried over sodium/benzophenone ketyl and vacuum transferred prior to use. Unless indicated otherwise, all commercial chemicals were used as received. Ni(COD)₂ and NiI₂ were purchased from Strem. Compound 1 and Na₂Fe(CO)₄ were prepared according to previously published protocol.¹² 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.³ ³¹P NMR chemical shifts are reported with respect to the deuterated solvent used to lock the instrument. Elemental analyses were performed by Robertson Microlit Laboratories, Ledgewood, NJ.

Synthesis of complex 2
A suspension of Ni(COD)₂ (191 mg, 0.693 mmol) in dry THF (10 mL) was added to 1 (300 mg, 0.347 mmol). The solution immediately turned red-orange. The reaction mixture was stirred for 10 minutes then a suspension of NiI₂ (109 mg, 0.347 mmol) in THF (5 mL) was added. The reaction mixture was allowed to stir at room temperature for 4 hours. A color change from red-orange to dark brown was observed over the course of reaction time. The reaction mixture was filtered, and the filtrate was dried in vacuo. The dry residue was triturated with hexanes, diethyl ether, and benzene. The benzene fraction gives the clean product in 60% yield. Recrystallization via vapor diffusion of n-hexanes into benzene yields brown-black crystals. ¹H NMR (300 MHz, C₆D₆) δ 8.81 (s, 2H, aryl-Η), 7.71 (s, 1H, aryl-Η), 7.32 (d, J = 7.8 Hz, 2H, aryl-Η), 7.20 (s, 1H, aryl-Η), 6.99 (d, J = 7.9 Hz, 2H, aryl-Η), 6.85 (d, J = 8.0 Hz, 1H, aryl-Η), 4.61 (s, 2H, central ring-H), 3.35 (s, 1H, central ring-H), 2.72 (s, 4H, CH₄), 2.47 (app d, 2H, CH₂), 1.90 (s, 2H, CH), 1.69 (s, 18H, tert-butyl CH₃), 1.52 (m, 4H, CH₂), 1.36 (s, 9H, tert butyl- CH₃), 1.11 (b, 12H, CH₃), 0.82 (m, 6H, CH₃), 0.70 (m, 12H, CH₃), 0.54 (app dd, 6H, CH₃) ppm; ³¹P NMR (121 MHz, C₆D₆) δ 67.97 (br s, 2P), 11.66 (t, 1P, J = 17.1 Hz) ppm; ¹³C NMR (126 MHz, C₆D₆) δ 149.94 (s), 142.90 (s), 139.62 (d, J = 7.1 Hz), 133.55 (s), 132.25 (d, J = 5.5 Hz), 131.46 (s), 130.50 (s), 129.15 (s), 128.19 (s), 125.94 (s), 123.11 (s), 122.86 (s), 95.29 (d, J = 5.0 Hz), 69.33 (s), 63.08 (s), 34.84 (s), 34.39 (s), 33.53 (s), 32.15 (s), 31.41 (s), 27.48 (d, J = 12.3 Hz), 25.60 (s), 24.71 (d, J = 13.1 Hz), 19.24 (d, J = 20.5 Hz), 18.34 (d, J = 22.3 Hz), 17.04 (s) ppm. Anal. Calcd. for: C₅₁H₇₁I₂Ni₃P₃ (%): C, 52.86; H, 6.77. Found: C, 53.07; H, 6.91.

Synthesis of complex 3
In inert atmosphere glovebox, a solution of Tl(OTf) (13.6 mg, 0.0386 mmol) in THF was added to 2 (50 mg, 0.0386 mmol). The mixture was stirred at room temperature and checked for progress by ³¹P NMR. Formation of thallium iodide as light yellow precipitate was
observed immediately, and Ni$^0$ as black precipitate was observed after 12 hours. The reaction mixture was filtered, and the solvent was removed off the filtrate in vacuo. The residue was triturated with hexanes, diethyl ether, and benzene. The benzene fraction gives the clean product in 50% yield. Recrystallization via vapor diffusion of n-hexanes into benzene yielded the product as brown-black crystals. Complex 3 was observed to decompose overtime in solution and as solid to yield previously characterized mono nickel complex$^1$ and other decomposition products. $^1$H NMR (500 MHz, THF-$d_8$, -30°C) $\delta$ 8.69 (s, 1H, aryl-H), 8.51 (s, 1H, aryl-H), 7.87 (s, 1H, aryl-H), 7.53 (s, 2H, aryl-H), 7.48 (s, 3H, aryl-H), 7.30 (s, 1H, aryl-H), 6.05 (s, 1H, central aryl-H), 5.69 (d, $J = 10.0$ Hz, 1H, central aryl-H), 4.67 (s, 1H, central aryl-H), 3.51 – 3.32 (m, 4H, CH$_2$), 3.25 (app d, $J = 13.9$ Hz, 2H, CH$_2$), 2.77 (app t, $J = 16.4$ Hz, 1H, CH$_3$), 2.44 (app d, $J = 29.1$ Hz, 2H, CH$_2$), 2.05 (br m, 1H, CH$_2$), 1.86 (br m, 2H, CH$_2$), 1.67 (br m, 3H, CH$_3$), 1.54 (s, 9H, tert-butyl CH$_3$), 1.44 (s, 18H, tert-butyl CH$_3$), 1.25 (app m, 12H, CH$_3$), 0.89 (app m, 6H, CH$_3$), 0.73 (app m, 3H, CH$_3$), 0.57 (app m, 3H, CH$_3$), 0.52 – 0.39 (m, 6H, CH$_3$), 0.35 (app m, 3H, CH$_3$). $^3$P NMR (121 MHz, C$_6$D$_6$) $\delta$ 54.03 (d, $J = 91.4$ Hz), 47.13 (d, $J = 97.3$ Hz), 26.90 (t, $J = 91.9$ Hz). $^{13}$C NMR (126 MHz, THF-$d_8$) $\delta$ 151.46 (s), 150.86 (s), 135.08 (s), 133.90 (s), 133.67 (s), 131.71 (s), 130.83 (s), 128.52 (d, $J = 12.7$ Hz), 128.28 (s), 128.09 (d), 127.24 (s), 125.80 (s), 98.84 (s), 85.44 (s), 35.50 (s), 35.15 (s), 31.66 (s), 31.52 (s), 30.43 (s), 20.74 (s), 20.54 (s), 19.21 (s), 18.34 (s), 17.69 – 16.97 (m), 16.70 (s). Anal. Calcd. for: C$_{58}$H$_{92}$F$_3$INi$_2$O$_3$P$_3$S ($3$·THF) (%): C, 55.35; H, 6.97. Anal. Calcd. for: C$_{62}$H$_{94}$F$_3$INi$_2$O$_3$P$_3$S ($3$·THF) (%): C, 56.00; H, 7.13. Found: C, 56.40; H, 7.24.

**Synthesis of complex 4**

In a scintillation vial equipped with a stirbar, a solution of Na$_2$Fe(CO)$_4$ (26 mg, 0.12 mmol) in THF (2 mL) was added to a THF (10 mL) solution of 2 (150 mg, 0.12 mmol). The mixture was stirred at room temperature for 4 hours or monitored by $^3$P NMR spectroscopy. A slight color change was observed from yellow-brown to orange-brown. The mixture was filtered through celite. The filtrate was collected and dried under vacuum. The residue was triturated with hexanes to collect the product. Precipitation of clean product was afforded by cooling a concentrated hexanes solution to -35°C for a few days (47% yield). $^1$H NMR (300 MHz, C$_6$D$_6$) $\delta$ 8.05 (d, $J = 1.4$ Hz, 3H, aryl-H), 7.05 (dd, $J = 7.9$, 1.4 Hz, 3H, aryl-H), 6.98 (d, $J = 8.0$ Hz, 3H, aryl-H), 5.77 (s, 3H, central aryl-H), 3.07 (br s, 3H, CH$_2$), 2.93 (br s, 3H, CH$_2$), 2.57 (br, 3H, CH$_3$), 2.10 (br, 3H, CH$_3$), 1.38 – 1.21 (m, 18H, CH$_3$), 1.13 (s, 27H, tert-butyl CH$_3$), 0.97 (s, 18H, CH$_3$) ppm; $^3$P NMR (121 MHz, C$_6$D$_6$) $\delta$ 61.90 ppm. $^{13}$C NMR (126 MHz, C$_6$D$_6$) $\delta$ 256.34 (s), 148.64 (s), 139.63 (s), 132.98 (s), 130.65 (s), 126.17 (s), 121.91 (s), 76.80 (s), 65.21 (s), 34.08 (s), 31.07 (s), 26.61 (s), 25.44 (s), 21.58 (s), 18.68 (s), 17.25 (s), 16.52 (s), 15.56 (s). IR (CaF$_2$ window, THF, cm$^{-1}$) $\nu$$_{CO}$ : 1847, 1795. Anal. Calcd. for: C$_{60}$H$_{97}$Ni$_3$O$_3$P$_3$ (%): C, 64.04; H, 7.79. Found: C, 64.09; H, 7.63.

**Synthesis of complex 6**

A Schlenk tube fitted with at screw-in Teflon stopper was charged with 1,4-bis(2-diisopropylphosphino)phenyl)benzene (500 mg, 1.08 mmol, 1 equiv) and Ni(COD)$_2$ (891.9 mg, 3.24 mmol, 3 equiv). THF (ca. 60 mL) was added and then the combined reaction mixture was degassed and sealed. After stirring for two hours a color change from yellow to dark red was observed. Following degassing the solution, the reaction mixture was cooled to -78°C and 5 equivalents of CO was admitted using a calibrated gas bulb. The reaction was allowed to slowly warm to room temperature while stirring. During this time the solution turned a bright
red/orange. While stirring for an addition 16 h, the solution slowly turned yellow/brown at which time volatiles were removed under reduced pressure to yield a yellow/brown residue. The residue was dissolved in minimal THF and filtered through a celite pad. The product was recrystallized from the filtrate by the slow vapor diffusion of hexanes over 3 days at room temperature to afford pure product as large dark crystals (37% yield). $^1$H NMR (300 MHz, CD$_{6}$D$_6$) δ 7.42 (d, 2H, aryl-H), 7.09-6.89 (m, 6H, aryl-H), 5.65 (s, 2H, central aryl-H), 4.57 (s, 2H, central aryl-H), 2.30 (m, 2H, CH), 2.12 (m, 2H, CH), 1.25 (dd, 6H, CH$_3$), 1.06 (dd, 12H, CH$_3$), 0.89 (dd, 6H, CH$_3$). $^{31}$P NMR (121 MHz, CD$_{6}$D$_6$) δ 50.32 (s). $^{13}$C NMR (126 MHz, CD$_{6}$D$_6$) δ 246.87 (s), 245.58 (s), 195.08 (s), 151.56 (m), 134.28 (m), 131.62 (s), 129.32 (s), 127.60 (s), 126.33 (s), 91.06 (s), 70.98 (s), 66.64 (s), 26.87 (m), 24.30 (m), 20.18 (s), 18.84 (s), 18.03 (t), 17.58 (s). IR (CaF$_2$ window, THF, cm$^{-1}$) ν$_{CO}$: 2015.4, 1998.0, 1871.9. Anal. Calcd. for: C$_{34}$H$_{40}$Ni$_{3}$O$_{4}$P$_{2}$ (5) (%): C, 54.40; H, 5.37. Found: C, 54.31; H, 5.28.

**Synthesis of complex 7**

In inert atmosphere glovebox, a 20 mL scintillation vial was charged with 5 (102 mg, 0.136 mmol, 1 equiv) and dissolved in THF (ca. 10 mL). While stirring, PMe$_3$ (1 M in THF, 149 µL, 1.1 equiv) was added via syringe. The reaction slowly turned from yellow to bright orange over the 16 h reaction time. Volatiles were removed under reduced pressure to yield an orange residue. Pure product was obtained by the vapor diffusion of hexanes out of a concentrated hexanes/hexamethyldisiloxane solution to yield an orange precipitate (74% yield). $^1$H NMR (300 MHz, CD$_{6}$D$_6$) δ 7.71 (m, 2H, aryl-H), 7.07 (m, 4H, aryl-H), 6.94 (t, 2H, aryl-H), 5.13 (d, 2H, central aryl-H), 4.67 (d, 2H, central aryl-H), 2.41 (m, 2H, CH), 2.24 (m, 2H, CH), 1.38 (dd, 6H, CH$_3$), 1.16 (m, 12H, CH$_3$), 1.00 (d, 9H, CH$_3$), 0.99 (dd, 6H, CH$_3$). $^{31}$P NMR (121 MHz, CD$_{6}$D$_6$) δ 51.50 (d, J = 16.6 Hz), 6.61 (t, J = 16.6 Hz). $^{13}$C NMR (126 MHz, CD$_{6}$D$_6$) δ 259.93 (s), 250.72 (s), 153.21 (m), 135.345 (m), 131.55 (s), 128.87 (s), 127.26 (t), 125.74 (t), 88.31 (s), 68.17 (s), 63.15 (s), 27.01 (m), 24.47 (m), 20.45 (s), 19.11 (t), 18.29 (t), 17.82 (s), 14.48 (d). IR (CaF$_2$ window, THF, cm$^{-1}$) ν$_{CO}$: 1854.3, 1783.0. Anal. Calcd. for: C$_{36}$H$_{49}$Ni$_{3}$O$_{3}$P$_{3}$ (6) (%): C, 54.13; H, 6.18. Found: C, 54.44; H, 6.10.

**Synthesis of trinickel nonacarbonyl complex supported by ligand 1**

Ni(COD)$_2$ (143 mg, 0.520 mmol, 3 equiv) was added to a solution of 1 (150 mg, 0.173 mmol, 1 equiv) in THF (15 mL). The solution was degassed and CO gas (5 equiv) was delivered into the headspace using a volumetric gas bulb. The color of the solution changed from red-orange to almost colorless over 3 hours. The mixture was left to react for 18 h at room temperature or monitored by $^{31}$P NMR spectroscopy. The solvent removed off the reaction mixture in vacuo. The residue was triturated with pentane, and the pentane fraction was collected and dried to give the clean product as a foamy solid (71% yield). Recrystallization of the product via layering of acetonitrile over a concentrated toluene solution at -35 °C yielded crystals. $^1$H NMR (300 MHz, CD$_{6}$D$_6$) δ 7.59 (d, 3H), 7.48 (s, 3H), 7.41 (s, 3H), 7.31 (d, 3H), 3.07 (d, 6H), 1.62 (m, 6H), 1.24 (s, 27H), 0.82 (m, 36H). $^{31}$P NMR (300 MHz, CD$_{6}$D$_6$) δ 54.2 (s). IR (CaF$_2$ window, THF, cm$^{-1}$): 2061.3, 1994.7.
Nuclear Magnetic Resonance Spectra

Figure S1. $^1$H NMR (300 MHz, C$_6$D$_6$) spectrum of 2

Figure S2. $^{31}$P NMR (121 MHz, C$_6$D$_6$) spectrum of 2

Figure S3. $^{13}$C NMR (126 MHz, C$_6$D$_6$) spectrum of 2
Figure S4. $^1$H NMR (500 MHz, THF-$d_8$, -30°C) spectrum of 3

Figure S5. $^1$H NMR (300 MHz, C$_6$D$_6$) spectrum of 3

Figure S6. $^{31}$P NMR (121 MHz, C$_6$D$_6$) spectrum of 3
Figure S7. $^{13}$C NMR (126 MHz, THF-$d_8$) spectrum of 3

Figure S8. $^1$H NMR (300 MHz, C$_6$D$_6$) spectrum of 4

Figure S9. $^{31}$P NMR (121 MHz, C$_6$D$_6$) spectrum of 4
Figure S10. $^{13}$C NMR (126 MHz, C$_6$D$_6$) spectrum of 4

Figure S11. $^1$H NMR (300 MHz, C$_6$D$_6$) spectrum of 6

Figure S12. $^{31}$P NMR (121 MHz, C$_6$D$_6$) spectrum of 6
Figure S13. $^{13}$C NMR (126 MHz, C$_6$D$_6$) spectrum of 6

Figure S14. $^1$H NMR (300 MHz, C$_6$D$_6$) spectrum of 7

Figure S15. $^{31}$P NMR (121 MHz, C$_6$D$_6$) spectrum of 7
Figure S16. $^{13}$C NMR (126 MHz, C$_6$D$_6$) spectrum of 7

Figure S17. $^1$H NMR (300 MHz, C$_6$D$_6$) spectrum of trinickel nonacarbonyl complex supported by 1

Figure S18. $^{31}$P NMR (121 MHz, C$_6$D$_6$) spectrum of trinickel nonacarbonyl complex supported by 1
Crystallographic Information
CCDC 833183, 961094, 961095, 961096 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](http://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, Kα = 0.71073 Å). All diffractometer manipulations, including data collection, integration and scaling were carried out using the Bruker APEXII software. Absorption corrections were applied using SADABS. 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.

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Special refinement details for 2
All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the
estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

**Special refinement details for 3**

3 was crystallized from benzene/hexanes mixture. Accordingly, the compound crystallized with five benzene solvent molecules in the lattice. The structure also contains one outer-sphere trifluoromethanesulfonate counterion that was satisfactorily modeled.

**Special refinement details for 4**

Acetonitrile/toluene layering was used as the solvent to crystallize complex 4. Accordingly, the compound crystallized with one acetonitrile solvent molecule in the lattice.

**Special refinement details for 7**

The compound was crystallized from benzene/hexane mixture. Only a partial data set was collected.

![Diagram](image)

**Figure S18.** Preliminary solid-state structure of trinickel nonacarbonyl complex supported by ligand 1, based on a partial data set.

**References**

(2) *Inorganic Syntheses, Reagents for Transition Metal Complex and Organometallic Syntheses*, 1990; Vol. 28.