ORGANOMETALLICS

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Oxidative Addition of a Diphosphine Anhydride to Iron(0) and Nickel(0): A Simple Approach to Installing Four Ligands

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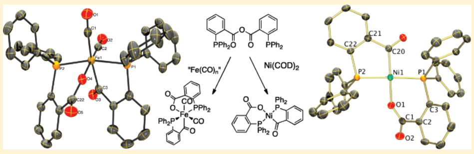
Supporting Information

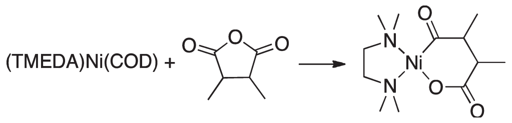


ABSTRACT: The diphosphine anhydride $(PCO)_2O$ was prepared in high yield by DCC coupling of 2-diphenylphosphinobenzoic acid. The diphosphine oxidatively adds to Fe(0) carbonyls to give the acyl carboxylate $Fe(PCO)(PCO_2)(CO)_2$ (**1**). The complex adopts a distorted octahedral geometry with trans phosphines and cis carbonyl ligands. Treatment of $Ni(COD)_2$ with $(PCO)_2O$ afforded the square-planar acyl carboxylate $Ni(PCO)(PCO_2)$ (**2**) with trans phosphine ligands. Upon treatment with PMe_3, **1** gives the monocarbonyl $Fe(PCO)(PCO_2)(CO)(PMe_3)$, whereas **2** and PMe_3 react to give the pentacoordinate adduct **2**PMe_3. Both **1** and **2** give 1:1 adducts with $B(C_6F_5)_3$ ($BPh^F{}_3$). Crystallographic analysis revealed that the borane binds to the noncoordinated carboxylate oxygen in both cases. The value of ν_{CO} for the carboxylato ligand decreased by 45 cm^{-1}, and in the case of **1**$BPh^F{}_3$, ν_{CO} for the CO ligands increased by 15 cm^{-1}. In solution, **1**$BPh^F{}_3$ exists as an equilibrium mixture of three isomers, including a kinetic isomer and another isomer that selectively crystallizes.

INTRODUCTION

Oxidative addition (OA) represents one of the most versatile and predictable reactions in synthetic organometallic chemistry. Although myriad pathways exist for installing ligands, OA provides a reliable method for installing two ligands in the coordination sphere of a metal.[1] First described in the 1970s,[2] *chelate-assisted* oxidative addition typically installs three ligands.[2] Such reactions are of interest because the tritopic attachment of the substrate drives OA reactions that are unfavorable in the absence of chelation. Chelate-assisted oxidative additions have received much attention in recent years and have been applied to organic synthesis,[3] including the activation of C−C bonds.[4]

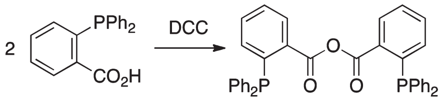
In this paper, we describe the OA of a diphosphine-functionalized carboxylic acid anhydride to low-valent metals. This route enables the installation of *four* ligands. Oxidative addition of the diphosphine anhydride provides an easy way to generate highly unsymmetrical coordination environments from simple reagents. 2-Diphenylphosphinobenzoic anhydride, abbreviated here as $(PCO)_2O$, had been previously generated *in situ* and used to direct allylic substitution,[5] but neither the ligand nor its complexes have been previously characterized, despite the widespread use of diphenylphosphinobenzoic acid.[6] The oxidative addition of carboxylic anhydrides is known in some cases to afford metal acyl-carboxylates.[7] For example, (TMEDA)Ni(COD) oxidatively adds 2,3-dimethylsuccinic anhydride to give the acyl carboxylato nickel(II) derivative (eq 1).[8]



(1)

RESULTS AND DISCUSSION

Phosphine Anhydride $(PCO)_2O$. The $(PCO)_2O$ proligand can be prepared in high yield by coupling of 2-diphenylphosphinobenzoic acid using DCC (eq 2). It exists as a pale yellow, air-stable solid that is sparingly soluble in most organic solvents. The ligand is thermally stable in refluxing THF under an inert atmosphere.



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Oxidative Addition of $(PCO)_2O$ to Fe(0) and Ni(0). Treatment of $(bda)Fe(CO)_3$ or $Fe_2(CO)_9$ with $(PCO)_2O$ afforded the ferrous dicarbonyl **1** in good yield (bda = benzylidene acetone). The ^{31}P NMR and IR spectra of **1** indicate a single unsymmetrical isomer (δ 45, 69, J_{PP} = 125 Hz, eq 3). In the related reaction involving $(bda)Fe(CO)_3$, an intermediate was detected with ν_{CO} = 1938 and 1893 cm^{-1} and possibly a higher energy band obscured by the presence of **1** (ν_{CO} = 2024, 1966 cm^{-1}). The ^{31}P NMR spectrum of this intermediate showed doublets at δ 49 and 64 (J_{P-P} = 125 Hz). Compounds of the type $Fe^0(CO)_3(PR_3)_2$ exhibit comparable IR signatures, e.g., $Fe(CO)_3(dppb)$: ν_{CO} =1981 (s), 1908 (m), 1879 (s).[9]

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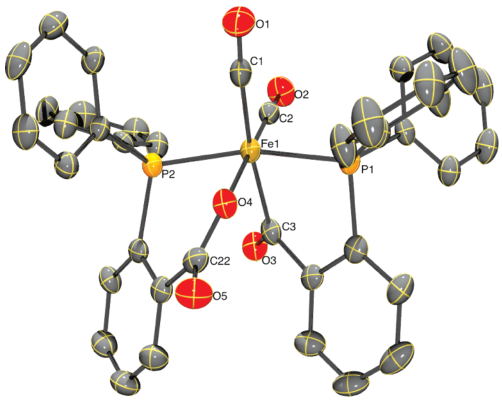


Figure 1. Structure of **1**. Ellipsoids are shown at 50% probability (hydrogen atoms are omitted for clarity). Selected bond lengths (Å): Fe(1)−C(2): 1.741(4); Fe(1)−C(1): 1.805(4); Fe(1)−O(4): 2.004(2); Fe(1)−C(3): 2.010(4); Fe(1)−P(2): 2.2565(10); Fe(1)−P(1): 2.2589(10).

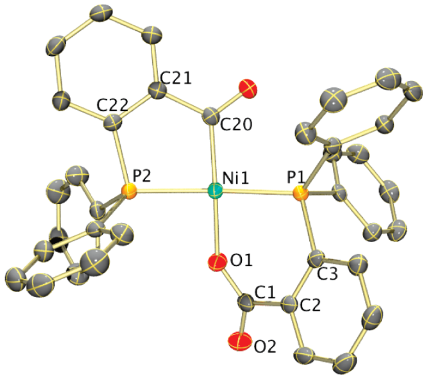
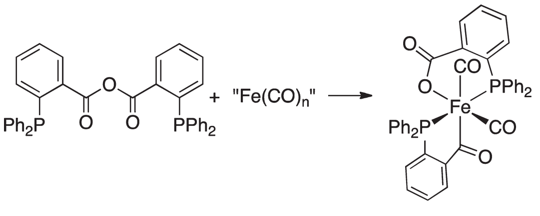


Figure 2. Structure of **2** with thermal ellipsoids shown at the 50% probability level (hydrogen atoms omitted for clarity). Selected bond lengths (Å): Ni(1)−C(20):1.894(2); Ni(1)−O(1): 1.9151(16); Ni(1)−P(2): 2.1786(6); Ni(1)−P(1): 2.1914(6).

Treatment of **1** with CO (1 atm) was found to induce partial reductive elimination of $(PCO)_2O$.



(3)

1

The molecular structure of **1** was determined crystallographically. The molecule can be described as the acyl-carboxylate $Fe(PCO)(PCO_2)(CO)_2$. The complex adopts a distorted octahedral geometry with a P1−Fe1−P2 angle of 165.51(4)°. The carboxylate and acyl groups are mutually cis, and the angle between the two groups C(3)−Fe(1)−O(4) is 89.40(12)°. The acyl−phosphine P(1)−Fe(1)−C(3) and carboxylate−phosphine P(2)−Fe(1)−O(4) chelate bite angles are respectively 80.97(10)° and 80.20(7)°, with $d(\mathrm{Fe-C_{acyl}})$ = 2.011(4) and $d(\mathrm{Fe-O})$ = 2.004(2) Å. The carboxylate and acyl groups are both trans to CO.

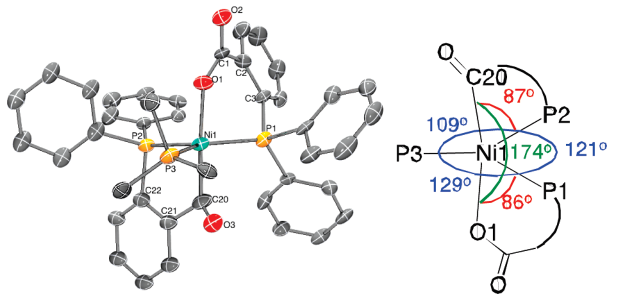
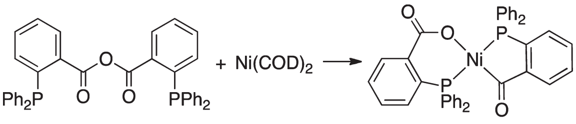


Figure 3. Structure of $\mathbf{2}PMe_3$ with thermal ellipsoids shown at the 50% probability level (hydrogen atoms omitted for clarity). Selected bond lengths (Å): Ni11−C20: 1.871(11); Ni1−O1: 1.980(5); Ni1−P1: 2.217(2); Ni1−P2: 2.281(2); Ni1−P3: 2.259(8).

Treatment of solutions of the cyclooctadiene complex $Ni(COD)_2$ with 1 equiv of $(PCO)_2O$ afforded a single product, $Ni(PCO)(PCO_2)$ (**2**, eq 4). According to the ^{31}P NMR spectrum, the phosphine ligands in this orange-colored product are mutually trans. The value of J_{PP} of 256 Hz indicates trans phosphines,[10] which was confirmed by crystallographic analysis. The distorted square-planar geometry features P1−Ni−O1 and P2−Ni−C20 angles of 89.95° and 86.84°, respectively 8° and 4° wider than the corresponding bite angles in **1**. The angles for P1−Ni−P2 and C20−Ni−O1 are both 165°. The angle between the two chelate rings (C20−Ni−P2 and O1−Ni−P1) is 20°.



(4)

2

PMe₃ Derivatives. Both **1** and **2** react with PMe_3. In the case of **1**, CO substitution was indicated, but in the case of **2** with PMe_3, we obtained the adduct, $\mathbf{2}PMe_3$. Crystallographic analysis of the $\mathbf{2}PMe_3$ revealed a distorted trigonal-bipyrimidal structure in which the three phosphine donors occupy the equatorial positions. The sum of the angles of the three P−Ni−P angles is 359°, where P1−Ni1−P2 is 121°, P2−Ni1−P3 is 109°, and P3−Ni1−P1 is 129°. The chelate angles for P1−Ni1−O1 are 86°, and P2−Ni1−C20 is 87°; the axial ligands are distorted by 6° from linearity. The complex $(PCO)Ni(PMe_3)_2I$ adopts a similarly distorted trigonal-bipyrimidal structure.[11]

Adducts with Lewis Acids. Compound **1** rapidly formed a 1:1 adduct upon treatment with $BPh^F{}_3$. That this adduct retains the stereochemistry of the precursor is indicated by its ^{31}P NMR spectrum, which features doublets at δ 44 and 69 (J_{P-P} = 126 Hz). The IR spectrum showed $\Delta(\nu_{CO})_{av}$ of 15 cm^{-1} upon binding the borane. The value of $\nu_{C=O}$ for the carboxylato ligand decreased by 45 cm^{-1}, which can be compared to $\Delta\nu_{C=O}$ of 49 cm^{-1} for the $BPh^F{}_3$ adduct of ethylbenzoate.[12] Over the course of several minutes in solution, $\mathbf{1}BPh^F{}_3$ converted to a second isomer with cis phosphine ligands (J_{P-P} = 50 Hz).[13] After about 10 h, the ^{31}P NMR spectrum featured yet another pair of doublets at δ 46 and 57 (J_{P-P} = 69 Hz, Scheme 1). A second equivalent of $BPh^F{}_3$ was found not to affect the rate of isomerization. We also observed ready formation of the 1:1 adduct $\mathbf{2}BPh^F{}_3$, which was spectroscopically characterized.

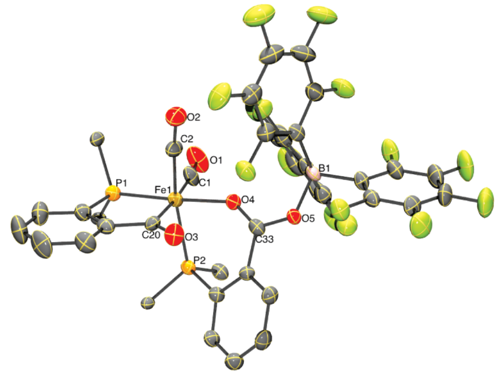
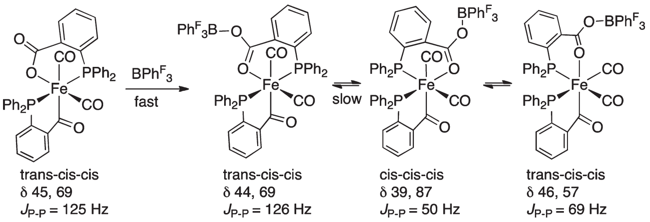


Figure 4. Structure of 1BPh$^F_3$. Ellipsoids are shown at 50% probability. For the sake of clarity, hydrogen atoms and the phenyl groups except the ipso carbon centers are omitted. Selected bond lengths (Å): Fe(1)−C(2): 1.797(4); Fe(1)−C(1): 1.820(4); Fe(1)−C(20): 2.004(4); Fe(1)−O(4): 2.023(3); Fe(1)−P(1): 2.2122(11); Fe(1)−P(2): 2.2964(11).

Scheme 1. Formation and Isomerization of 1BPh$^F_3$



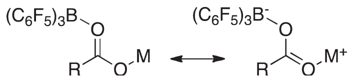
Crystals were obtained of the all-cis isomer of 1BPh$^F_3$ (Figure 4). The crystallographic analysis showed that both carboxylate C−O bonds shorten by 0.05 Å compared with those in **1**. Fe1−O1 bond elongated by 0.019 Å. The *d*(B1−O5) of 1.531(5) Å indicates a strong B−O bond comparable to that in Ni(PCO$_2$BPh$^F_3$)(Me-allyl) (1.541(5) Å).[14] B−O bond distances in related borates vary over a narrow range.[12,15]

Solutions freshly prepared from crystals of 1BPh$^F_3$ exhibited signals for this cis isomer (δ 87, J_{P-P} = 50 Hz) and the starting trans isomer; upon allowing the solution to stand, the third isomer appeared.

CONCLUSIONS

The reaction of (PCO)$_2$O with Fe(0) and Ni(0) reagents installs two different bidentate ligands, κ^2-(2-diphenylphosphinobenzoyl) (PCO) and κ^2-(2-diphenylphosphinobenzoate) (PCO$_2$). In the case of the iron complex, the initial coordination of the phosphine substituents can be detected prior to an apparent intramolecular oxidative addition.

The coordination of Lewis acids to PCO$_2$M centers has been previously examined in the context of the SHOP catalysts.[14] The isomerization of the coordination sphere around Fe caused by the attachment of a Lewis to a carboxylate is an unusual reaction. This rearrangement reflects the dramatic influence of the borane on the donor properties of the carboxylate ligand, consistent with the resonance structures shown in eq 5.



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EXPERIMENTAL SECTION

General Considerations. Tris(pentafluorophenyl)borane was purified by sublimation at 10 mTorr (90 °C).[16] ^{31}P NMR shifts are referenced to H$_3$PO$_4$ (δ 0).

2-Diphenylphosphinobenzoic Anhydride, (PCO)$_2$O. A mixture of 6.02 g (19.7 mmol) of 2-(diphenylphophino)benzoic acid[17] and 2.23 g (10.8 mmol) of dicyclohexylcarbodiimide was treated with 100 mL of CH$_2$Cl$_2$. The solution immediately became yellow, concomitant with the precipitation of the dicyclohexylurea. After stirring for 3 h, the slurry was filtered through a plug of silica gel. The resulting yellow solution was evaporated to yield a yellow powder, which was washed with 20 mL of MeCN. Yield: 4.55 g (77%). ^{31}P NMR (CH$_2$Cl$_2$): δ −3.52. Anal. Calcd (found) for C$_{36}$H$_{30}$O$_3$P$_2$: C, 76.76 (76.17); H, 4.75 (4.82). IR (solid): ν_{CO} 1815 and 1757. Solutions of (PCO)$_2$O in THF oxidize upon exposure to air, as indicated by a ^{31}P NMR signal at δ 42; however, solid (PCO)$_2$O appears to be indefinitely stable.

(2-Diphenylphosphinobenzoyl)(2-diphenylphosphinobenzoato)iron(II)dicarbonyl, Fe(PCO)(PCO$_2$)(CO)$_2$ (1). A solution of 270 mg (0.947 mmol) of (bda)Fe(CO)$_3$ (Fe$_2$(CO)$_9$ can be used instead) in 20 mL of THF was added to a slurry of 324 mg (0.947 mmol) of (PCO)$_2$O in 10 mL of THF. The reaction solution was stirred under argon for 1 h at refluxing temperature. Solvent was removed at reduced pressure to yield a yellow oil, which was triturated with 15 mL of pentane. The resulting yellow powder was dissolved in 5 mL of CH$_2$Cl$_2$, and this solution was layered with 15 mL of pentane to yield crystals after being allowed to stand at −35 °C for 12 h. The yellow microcrystalline solid was collected by filtration and dried under a stream of N$_2$. Yield: 182 mg (30%). Anal. Calcd (found) for C$_{40}$H$_{28}$FeO$_5$P$_2$(CH$_2$Cl$_2$): C, 59.78 (60.52); H, 3.68 (3.64). ^{31}P NMR (CH$_2$Cl$_2$): δ 45, 69 (*d*'s, J_{P-P} = 125 Hz). IR (CH$_2$Cl$_2$): ν_{CO} 2024, 1966 cm^{-1}. X-ray crystals were obtained from vapor diffusion of pentane into a solution of **1** in CH$_2$Cl$_2$. Treatment of **1** with PMe$_3$ gave a new derivative [^{31}P NMR (CH$_2$Cl$_2$): δ 64.4 (dd, J_{P-P} = 22, 129 Hz), 46.3 (dd, J_{P-P} = 22, 129 Hz), −1.81 (t, J_{P-P} = 22 Hz)], which was not characterized further.

(2-Diphenylphosphinobenzoyl)2-diphenylphosphinobenzoatonickel, Ni(PCO$_2$)(PCO) (2). A slurry of 1.32 g (2.218 mmol) of (PCO)$_2$O in 20 mL of THF was added to a yellow solution of 610 mg (2.22 mmol) of Ni(COD)$_2$ in 10 mL of THF. The reaction solution was stirred for 2 h. During this time, the reaction solution became orange and the (PCO)$_2$O dissolved. The solution was concentrated to ~10 mL and then diluted with 30 mL of pentane. The reaction solution was cooled to −35 °C overnight, and the yellow-orange crystals were collected by filtration. The product was washed with 2 × ~10 mL of pentane and dried with a stream of N$_2$. The product was recrystallized by dissolution of the orange crystals in 5 mL of CH$_2$Cl$_2$; this solution was layered with 30 mL of pentane and cooled to −35 °C. Yield: 1.36 g (94%). Anal. Calcd (found) for C$_{38}$H$_{28}$NiO$_3$P$_2$: C, 69.12 (69.35); H, 4.27 (4.10). ^{31}P NMR (CH$_2$Cl$_2$): δ14 (d, J_{P-P} = 256 Hz), 42 (d, J_{P-P} = 256 Hz).

(2-Diphenylphosphinobenzoyl)(2-diphenylphosphinobenzoato)(trimethylphosphine)nickel(II), Ni(PCO)(PCO$_2$)(PMe$_3$), 2PMe$_3$. A solution of 436 mg (0.668 mmol) of **2** in 30 mL of THF was frozen in liquid nitrogen, and the head space was evacuated on a high-vacuum manifold. Onto the frozen solution was condensed ~0.1 mL of PMe$_3$. The solution color changed from orange to red almost immediately upon thawing. After stirring the reaction solution for 0.5 h, solvent and excess PMe$_3$ were removed by distillation at reduced pressure. The resulting red oil was trititurated with 20 mL of a 1:10 mixture of Et$_2$O−pentane to yield a red powder, which was collected by filtration and washed with 10 mL of Et$_2$O and 10 mL of pentane. The red microcrystalline product was dried under a stream of N$_2$ before being extracted into 10 mL of CH$_2$Cl$_2$. Layering this extract with 20 mL of pentane, followed by storing the flask at −35 °C, afforded red crystals, which were washed with 10 mL of Et$_2$O. Yield: 345 mg (71%). Anal. Calcd (found) for C$_{41}$H$_{37}$NiO$_3$P$_3$: C, 67.19 (66.96); H, 5.10 (5.20).

^{31}P NMR (CH_2Cl_2): δ −19 (dd, J_{P-P} = 152 Hz), 9.5 (dd, J_{P-P} = 152 Hz), 27 (t, J_{P-P} = 85 Hz). Upon standing at room temperature, samples decomposed to a new species, an apparent isomer: ^{31}P NMR (CH_2Cl_2): δ 47.65 (J_{P-P} = 50 Hz), 41.43 (s), −14.65 (J_{P-P} = 50, 5 Hz). X-ray crystals were obtained from vapor diffusion of pentane into a solution of **1** in CH_2Cl_2.

BPh^F_3 Adduct of 1. A solution of 70 mg (0.136 mmol) of BPh^F_3 in 5 mL of CH_2Cl_2 was added to a solution of 96 mg (0.134 mmol) of **1** in 10 mL of CH_2Cl_2. Upon addition of the borane, the color of the solution turned from bright yellow to light orange. The reaction solution was stirred for 0.5 h before concentrated to a volume of ∼5 mL. This solution was layered carefully with pentane prior to cooling at −35 °C for 12 h to yield X-ray quality crystals. Anal. Calcd (found) for $C_{58}H_{28}BF_{15}FeO_5P_2$: C, 57.17 (56.05); H, 2.32 (2.35). ^{31}P NMR (CH_2Cl_2): δ 39 (d, J_{P-P}= 50 Hz), 87 (d, J_{P-P} = 50 Hz). IR (CH_2Cl_2): ν_{CO} 2047, 1998, and 1988 cm^{-1}. The isomerization of **1**BPh^F_3 in CH_2Cl_2 was monitored by IR spectroscopy over the course of 10 h. An adduct also formed upon treatment of a CH_2Cl_2 solution of **2** with 1 equiv of BPh^F_3: ^{31}P NMR (CH_2Cl_2, −44 °C): δ 44.00 and 8.9 (dd, 225 Hz).

Crystallography: General Comments. All structures were determined by direct methods. The space group choice was confirmed by successful convergence of the full-matrix least-squares refinement on F^2. Rigid-bond restraints (esd 0.01) were imposed on displacement parameters for disordered sites, and similar displacement amplitudes (esd 0.01) were imposed on disordered sites overlapping by less than the sum of van der Waals radii. Hydrogen atoms were included in the refinement as riding idealized contributors, and their U's were assigned as 1.2 times carrier U_{eq}.

Crystallography of 1. The highest peaks in the final difference Fourier map were in the vicinity of atoms P1 and Fe1; the final map had no other significant features. A final analysis of variance between observed and calculated structure factors showed little dependence on amplitude and resolution. A structural model consisting of the host plus two disordered dichloromethane solvate molecules was developed. All C−Cl distances were restrained as 1.76(1) Å (0.01 esd), and all Cl---Cl distances were restrained as 2.85(2) Å (esd 0.02). Data for **1**: Formula $C_{42}H_{32}Cl_4FeO_5P_2$, M = 876.27, orthorhombic, space group $Pbca$, a = 17.3751(11), b = 19.2388(13), c = 23.6101(15) Å, V = 7892.3(9) Å^3, Z = 8, D_c = 1.475 g cm^{-3}, μ(Mo K) = 0.779 mm^{-3}, $F(000)$ = 3584, T = 193(2) K, $R_1(I > 2\sigma)$ = 0.0462, wR_2(all data) = 0.1068 for 7231 independent reflections with a goodness-of-fit of 1.011.

Crystallography of 1BPh^F_3. A structural model consisting of the host plus three disordered dichloromethane solvate molecules was developed; however, positions for the idealized solvate molecules were poorly determined. This model converged with wR_2 = 0.142 and R_1 = 0.062 for 714 parameters with 0 restraints against 11499 data. Since positions for the solvate molecules were poorly determined, a second structural model was refined with contributions from the solvate molecules removed from the diffraction data using the bypass procedure in PLATON.[18] The electron count from the "squeeze" model converged in good agreement with the number of solvate molecules predicted by the complete refinement. The "squeeze" data are reported here. Data for **1**BPh^F_3: Formula $C_{61}H_{34}BCl_6F_{15}FeO_5P_2$, M = 1473.18, monoclinic, space group $P2_1/c$, a = 15.6244(9), b = 17.9336(11), c = 22.4793(14) Å, β = 98.069(4)°, V = 6236.4(7) Å^3, Z = 4, D_c = 1.569 g cm^{-3}, μ(Mo K) = 0.644 mm^{-3}, $F(000)$ = 2952, T = 193(2) K, $R_1(I > 2\sigma)$ = 0.0598, wR_2(all data) = 0.1264 for 11 499 independent reflections with a goodness-of-fit of 0.894.

Crystallography of 2. The highest peaks in the final difference Fourier map were in the vicinity of the disordered dichloromethane and the Ni atom; the final map had no other significant features. A final analysis of variance between observed and calculated structure factors showed little dependence on amplitude and some dependence on resolution. Data for **2**: Formula $C_{40}H_{32}Cl_4NiO_3P_2$, M = 823.11, triclinic, space group $P\bar{1}$, a = 9.2924(7), b = 12.4785(10), c = 17.5116(14) Å, α = 88.217(5)°, β = 75.154(4)°, γ = 70.221(4)°, V = 1843.5(3) Å^3, Z = 2, qD_c = 1.483 g cm^{-3}, μ(Mo K) = 0.942 mm^{-3}, $F(000)$ = 844, T = 193(2) K, $R_1(I > 2\sigma)$ = 0.0331, wR_2(all data) = 0.0850 for 36 549 independent reflections with a goodness-of-fit of 0.987.

Crystallography of 2PMe$_3$. The highest peaks in the final difference Fourier map were in the vicinity of the nickel atoms; the final map had no other significant features. A final analysis of variance between observed and calculated structure factors showed no dependence on amplitude and little on resolution. For the data crystal, mean $I/\sigma(I)$ was less than 8 for reflections beyond 1 Å resolution. Reflections between 1 and 0.8 Å resolution were removed from least-squares refinement to improve the internal consistency. A structural model consisting of the host plus two dichloromethane solvate molecules was developed. Data for **2**PMe_3: Formula $C_{43}H_{41}Cl_4NiO_3P_3$, M = 899.18, orthorhombic, space group $Pca2_1$, a = 18.842(6), b = 25.205(12), c = 17.491(9) Å, V = 8307(6) Å^3, Z = 8, D_c = 1.438 g cm^{-3}, μ(Mo K) = 0.879 mm^{-3}, $F(000)$ = 3712, T = 193(2) K, $R_1(I > 2\sigma)$ = 0.0502, wR_2(all data) = 0.1114 for 8646 independent reflections with a goodness-of-fit of 1.040.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Spectroscopic and crystallographic information files (cif) are available free of charge via the Internet at http://pubs.acs.org.

■ ACKNOWLEDGMENT

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■ REFERENCES

(1) Hartwig, J. *Organotransition Metal Chemistry: From Bonding to Catalysis*; University Science Books: Sausalito, CA, 2009.

(2) Rauchfuss, T. B.; Roundhill, D. M. *J. Am. Chem. Soc.* **1975**, 97, 3386–3392.

(3) Park, Y. J.; Park, J.-W.; Jun, C.-H. *Acc. Chem. Res.* **2008**, *41*, 222–234.

(4) Rybtchinski, B.; Milstein, D. *Angew. Chem., Int. Ed.* **1999**, *38*, 870–883. Jun, C.-H. *Chem. Soc. Rev.* **2004**, *33*, 610–618. Obenhuber, A.; Ruhland, K. *Organometallics* **2010**, *30*, 171–186. Ruhland, K.; Obenhuber, A.; Hoffmann, S. D. *Organometallics* **2008**, *27*, 3482–3495.

(5) Spangenberg, T.; Schoenfelder, A.; Breit, B.; Mann, A. *Org. Lett.* **2007**, *9*, 3881–3884.

(6) Kuhn, P.; Semeril, D.; Matt, D.; Chetcuti, M. J.; Lutz, P. *Dalton Trans.* **2007**, 515–528.

(7) Yamamoto, A. *J. Organomet. Chem.* **2004**, *689*, 4499–4510.

(8) Fischer, R.; Walther, D.; Kempe, R.; Sieler, J.; Schönecker, B. *J. Organomet. Chem.* **1993**, *447*, 131–136.

(9) Sowa, J. R.; Zanotti, V.; Facchin, G.; Angelici, R. J. *J. Am. Chem. Soc.* **1992**, *114*, 160–165.

(10) Barbaro, P.; Togni, A. *Organometallics* **1995**, *14*, 3570–3573. Keim, W.; Behr, A.; Gruber, B.; Hoffmann, B.; Kowaldt, F. H.; Kuerschner, U.; Limbaecker, B.; Sistig, F. P. *Organometallics* **1986**, *5*, 2356–2359.

(11) Klein, H.-F.; Lemke, U.; Lemke, M.; Brand, A. *Organometallics* **1998**, *17*, 4196–4201.

(12) Parks, D. J.; Piers, W. E. *J. Am. Chem. Soc.* **1996**, *118*, 9440–9441.

(13) Volpe, E. C.; Wolczanski, P. T.; Lobkovsky, E. B. *Organometallics* **2009**, *29*, 364–377.

(14) Komon, Z. J. A.; Bu, X.; Bazan, G. C. *J. Am. Chem. Soc.* **2000**, *122*, 12379–12380.

(15) Danopoulos, A. A.; Galsworthy, J. R.; Green, M. L. H.; Doerrer, L. H.; Cafferkey, S.; Hursthouse, M. B. *Chem. Commun.* **1998**, 2529–2560.

(16) Köster, R.; Binger, P.; Fenzl, W. *Inorg. Synth.* **2007**, *15*, 134–136.

(17) Hoots, J. E.; Rauchfuss, T. B.; Wrobleski, D. A. *Inorg. Synth.* **1982**, *21*, 175.

(18) Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7–13.