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Pentafluoroaryl Transfer from Tris(pentafluorophenyl)boron Hydrate to Nickel. Synthesis and X-ray Crystal Structure of $(PPh_2CH_2C(O)Ph)Ni(C_6F_5)_2$

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The reaction of tris(pentafluorophenyl)boron trihydrate, $B(C_6F_5)_3{\cdot}3H_2O$ (**1**), with the nickel dimer $[(PPh_2CH{=}C(O)Ph)Ni(Ph)]_2$ (**3**) (synthesized by phosphine abstraction from $(PPh_2CH{=}C(O)Ph)Ni(Ph)(PPh_3)$ (**2**)) yields $(PPh_2CH_2C(O)Ph)Ni(C_6F_5)_2$ (**4**). In this reaction a number of processes occur: fragmentation of the dimer **3**, transfer of two protons from **1**, and transfer of two C_6F_5 groups from boron to nickel. In solution, **4** loses one C_6F_5 ligand as pentafluorobenzene due to proton transfer from the chelating ligand, forming the dimer $[(PPh_2CH{=}C(O)Ph)Ni(C_6F_5)]_2$ (**5**). Compounds **4** and **5** were characterized by NMR and MS techniques. Compound **4** was independently synthesized by the reaction of $PPh_2CH_2C(O)Ph$ and $(\eta^6\text{-toluene})Ni(C_6F_5)_2$. The crystal structure of **4** was determined using single-crystal X-ray diffraction methods. Details concerning the synthesis and characterization of **1**−**3** are also given.

Introduction

Tris(pentafluorophenyl)boron, owing to its pentafluorophenyl substituents, is a very strong Lewis acid.[1] As such, this reagent is effective in a number of chemical transformations. Among them are aldol and Michael reactions of silyl enol ethers with carbonyls,[2] the Diels−Alder addition of dienes with α,*β*-unsaturated aldehydes,[3] and the stereoselective rearrangement of epoxides.[4]

Tris(pentafluorophenyl)boron plays an active role in polymerizations. It can initiate the propagation of cationically polymerizable monomers such as vinyl ethers, *N*-vinylcarbazole,[5] and styrene.[6]

Tris(pentafluorophenyl)boron probably has found the most utility as an activator in olefin polymerization. Marks and co-workers have shown that $B(C_6F_5)_3$ can abstract the methyl group from $(Me_5C_5)_2ZrMe_2$ to form a cationic zirconocene complex.[7] Others have reported related reactions with different group 4 alkyl complexes[8] which yield catalysts active in styrene,[9] propylene,[10] and functional olefin polymerization[11] among others.[12]

While $B(C_6F_5)_3$ can readily be employed in aromatic hydrocarbon solvents, Siedle and co-workers recognized the limitations of $B(C_6F_5)_3$ in aliphatic hydrocarbons and sought methods of increasing the solubility of this type of reagent in such media.[13] This objective was achieved by forming adducts of $B(C_6F_5)_3$ with, for example, long-chain alcohols and mercaptans. In addition, water complexes such as $B(C_6F_5)_3{\cdot}3H_2O$ (**1**) were also reported. These adducts of $B(C_6F_5)_3$ transform this strong Lewis acid into a Br*ϕ*nsted acid which can react with dialkylmetallocene complexes to form the same catalytically active, cationic species made with $B(C_6F_5)_3$. Of course, Br*ϕ*nsted acids derived from $B(C_6F_5)_3$ generate the cationic metallocenium complexes by protonation of the metal−alkyl bond with concomitant formation of, in the case of the alcohol adduct, $[ROB(C_6F_5)_3]^-$ as the anion rather than by the alkyl abstraction reaction preferred by $B(C_6F_5)_3$.

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The success of metallocenium catalysts in olefin polymerization is in part due to the ability of the gegenion to remain stable and relatively weakly coordinating. Early attempts by Jordan et al. to access cationic zirconocene complexes by reacting Cp_2ZrMe_2 with $AgPF_6$ resulted in transfer of the fluoride from PF_6 to zirconium.[14] To circumvent this problem, BPh_4^- was employed as the counterion.[15] However, anions of this type can form π-complexes with coordinately unsaturated metal centers[16] and are susceptible to electrophilic attack.[17] Boron-containing anions supported by fluorinated aryl groups, on the other hand, are thought to be relatively inert[18] and form the basis for a growing number of patents and publications on metallocene olefin polymerization catalysis.[19,20]

Despite the increasing interest in the reactivity patterns of $B(C_6F_5)_3$ and Brϕnsted acids derived from $B(C_6F_5)_3$ with group 4 metallocenes, relatively few reports have appeared involving later transition metal complexes and $B(C_6F_5)_3$ or its Brϕnsted acid derivatives.[21] In the late 1980s workers at DuPont described nickel complexes which, in the presence of phosphine acceptors, yielded high-molecular-weight polyethylene.[22] Given the ability of $B(C_6F_5)_3$ to form donor/acceptor complexes with phosphine,[23] we investigated the interaction of several nickel complexes of the type described by Klabunde et al. with $B(C_6F_5)_3$ as well as with the water adduct of $B(C_6F_5)_3$. In particular, we found that $B(C_6F_5)_3 \cdot 3H_2O$ reacts with the dimer complex $[(PPh_2CH{=}C(O)Ph)Ni(Ph)]_2$ by first protonation of the chelating ligand and the Ni−Ph bond followed by transfer of an unprecedented two pentafluorophenyl groups from boron to nickel.

Experimental Section

General Considerations. All manipulations of organometallic complexes were carried out under an atmosphere of prepurified argon or nitrogen using standard Schlenk or drybox techniques. Toluene was dried by refluxing over sodium benzophenone ketyl, distilled under nitrogen, and stored over 4A molecular sieves. THF was dried over sodium benzophenone ketyl under nitrogen, vacuum-transferred, and stored over 4A molecular sieves. Cyclohexane was dried by refluxing over sodium under nitrogen, distilled, and stored over 4A molecular sieves.

Tris(pentafluorophenyl)boron was obtained from Akzo-Nobel as a 3.15 wt % solution in Isopar E. $Ni(COD)_2$ and $Rh(acac)(C_2H_4)_2$ were purchased from Strem. $PPh_3{=}CHC(O)Ph$ was purchased from SPECS. (η^6-toluene)$Ni(C_6F_5)_2$ was synthesized according to a literature procedure.[24] $PPh_2CH_2C(O)Ph$ was synthesized by a known procedure[25] but was isolated from a 5% ethyl acetate in cyclohexane solution followed by washing with pentane.

Instrumental Analysis. The ^1H, ^{19}F, and ^{31}P NMR spectra were recorded on a Bruker AMX-500 NMR spectrometer operating at 500.14, 470.53, and 202.47 MHz, respectively, unless otherwise specified. Chemical shifts for ^1H NMR spectra were referenced using internal solvent resonances and are reported relative to tetramethylsilane. The ^{19}F NMR spectra were referenced to external $CFCl_3$, while the ^{31}P NMR spectra were referenced to external H_3PO_4.

The infrared spectra were recorded on a Perkin-Elmer Model 1800 spectrometer using polystyrene film as a standard. Samples were prepared as Nujol mulls on KBr salt plates in the drybox.

The mass spectra (FD, FI, and CI) were recorded on a Finnegan MAT 95Q instrument.

$B(C_6F_5)_3$. Solid $B(C_6F_5)_3$ was prepared by the following method.[26] A 3.15 wt % solution of $B(C_6F_5)_3$ in Isopar E (75.0 mL, 3.33 mmol) was placed in a 200 mL Kjeldahl flask equipped with a magnetic stirbar. The solution was removed in vacuo to give a white powder. The powder was sublimed (95 °C, approximately 0.1 mmHg) to yield white needles. ^{19}F NMR (C_6D_6): δ −129.1 (s, 2F), −142.0 (s, 1F), and −160.3 (s, 2F). IR (Nujol): 2953 sh, 2924 vs, 2855 m, 1648 m, 1524 m, 1475 s, 1383 m, 1321 m, 1166 m, 1151 w, 1020 m, 973 s, 784 w, 667 w, 620 w cm^{-1}.

$B(C_6F_5)_3 \cdot 3H_2O$ (1). The synthesis of **1** reported here is based on a prior publication.[27] A 3.15 wt % solution of $B(C_6F_5)_3$ in Isopar E (50 mL, 2.22 mmol) was placed in a 200 mL Kjeldahl flask equipped with a magnetic stirbar. Approximately 50 mL of dry, degassed cyclohexane was added to this solution followed by 3 equiv of degassed, demineralized water (0.120 mL, 6.68 mmol). Precipitation of a white, microcrystalline solid occurred. The slurry was stirred for 30 min, after which time the solution was decanted and the solid was dried in vacuo. Yield: 0.826 g (66%). ^{19}F NMR (C_6D_6): δ −134.7 (apparent d, 2F), −154.7 (apparent t, 1F), −162.6 (apparent t, 2F). FI-MS: *m/z* 512 [M^+]; evidently loss of water occurred in the mass spectrometer. IR (Nujol): 3666 m, 3597 m, 3499 m, 2950 sh, 2920 s, 1647 m, 1602 m, 1520 s, 1468 s, 1379 m, 1288 m, 1111 m, 1098 m, 969 s, 859 w, 797 w, 771 w, 676 w, 614 w cm^{-1}.

$(PPh_2CH{=}C(O)Ph)Ni(Ph)(PPh_3)$ (2). The synthesis of **2** reported here is based on two previous publications.[28] A toluene slurry (150 mL) of PPh_3 (5.00 g, 19.1 mmol) and the ylide $PPh_3{=}CHC(O)Ph$ (7.30 g, 19.1 mmol) was added to a chilled (0 °C) toluene slurry (80 mL) of $Ni(COD)_2$ (5.30 g, 19.1 mmol). Afterward, the mixture became a red-brown slurry. The mixture was warmed to room temperature and stirred for 21 h. This mixture was then heated to 50 °C for 2 h, cooled to room temperature, and stirred for an additional 16 h. The mixture was filtered to give a red-brown filtrate which upon removal of solvent in vacuo gave a brown residue. The residue was dissolved in toluene (50 mL), and from this solution a tan precipitate began to form upon addition of 50 mL of hexane. The mixture was cooled at −20 °C to give a gold-tan solid which was filtered, washed with hexane, and dried. Yield: 10.5 g (79%). ^1H NMR (C_6D_6): δ 7.57 (m, 12H), 7.00 (m, 20 H), 6.60

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(m, 3H), 5.19 (s, 1H). $^{31}P\{^1H\}$ NMR (C_7D_8): δ 22.2, 20.5 (second-order AB quartet, $^2J_{P_AP_B} = 285$ Hz).

$[(PPh_2CH{=}C(O)Ph)Ni(Ph)]_2$ (3). The synthesis of **3** is derived from a previous report.[29] In the drybox both compound **2** (1.00 g, 1.43 mmol) and $Rh(acac)(C_2H_4)_2$ (0.180 g, 0.700 mmol) were weighed into two separate flasks and capped. On the Schlenk line, toluene was added to each compound: for the rhodium compound about 5 mL and for the nickel compound about 20 mL. The solution of $Rh(acac)(C_2H_4)_2$ was added to the nickel solution. A precipitate began to form immediately. The mixture was stirred for 4 h and then filtered and dried in vacuo to give a brown-yellow solid. Yield: 0.500 g (79%). ^1H NMR (C_6D_6): δ 7.70 (d of d, 4H), 7.45 (d, 2H), 7.30 (d, 2H), 7.05 (m, 6H), 6.90 (m, 3H), 6.55 (t, 1H), 6.46 (t, 2H), 4.87 (s, 1H). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 21.3 (s).

$(PPh_2CH_2C(O)Ph)Ni(C_6F_5)_2$ (4). Method A. Compound **3** (0.150 g, 0.171 mol) was weighed into a 100 mL Kjeldahl flask in the drybox. Also in the drybox, 0.194 g of $B(C_6F_5)_3{\cdot}3H_2O$ (0.342 mol) was weighed into a separate flask. After each solid was dissolved separately in a minimum of toluene (about 15 mL each), the solution of $B(C_6F_5)_3{\cdot}3H_2O$ was added to the solution/slurry of the nickel dimer (it was not completely soluble in toluene). The mixture changed from cloudy orange to a translucent red-brown upon addition of the boron reagent. The solution was stirred for approximately 1 h, after which time the toluene was removed in vacuo. The yellowish brown solid was redissolved in a small amount of toluene and cooled to −20 °C. A yellow solid formed which was filtered and dried in vacuo. Yield: 0.108 g (45%). ^1H NMR (CD_2Cl_2): δ 7.90 (d, 2H), 7.67 (t, 3H), 7.48 (m, 4 H), 7.20 (m, 6 H), 4.19 (d, $J_{PH} =$ 5 Hz, 2 H). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 26.8 (s). ^{19}F NMR (C_6D_6): δ −115.8 (m, 2F), −119.0 (m, 2F), −159.8 (t, 1F), −160.9 (t, 1F), −162.9 (apparent t of d, 2F), −163.7 (apparent t, 2F). FD-MS: m/z 696 [M^+]; exhibited expected isotope pattern for nickel. CI-MS: m/z 529 [$M^+ - C_6F_5$]; exhibited expected isotope pattern for nickel.

Method B. (η^6-toluene)$Ni(C_6F_5)_2$ (0.1 g, 0.2 mmol) was dissolved in 10 mL of toluene under an inert atmosphere. To this solution was added dropwise $PPh_2CH_2C(O)Ph$ (0.063 g, 0.2 mmol) in 10 mL of toluene. The solution turned yellow-brown after 10 min, and a yellow powder precipitated. After it was stirred at room temperature for 1 h, the solvent was removed in vacuo, resulting in a yellow solid. This was dissolved in 10 mL of CH_2Cl_2, filtered, and kept in the freezer at −20 °C. Bright yellow crystals of **4** were obtained in quantitative yield after 2 days. Anal. Calcd for $C_{33}H_{18}POF_{10}Ni{\cdot}{}^1/_3CH_2Cl_2$: C, 53.62; H, 2.32. Found: C, 53.84; H, 3.03. The presence of methylene chloride was confirmed by ^1H NMR spectroscopy.

$[(PPh_2CH{=}C(O)Ph)Ni(C_6F_5)]_2$ (5). Compound **4** (0.39 g, 0.56 mmol) was dissolved in approximately 50 mL of 1,2-dichloroethane. The yellow solution was refluxed for 42 h. An orange color developed during this time. Cooling the solution to room temperature resulted in an orange powder. The solvent was removed in vacuo to give an orange solid. Yield: 0.28 g (93%). Alternatively, large well-shaped crystals of compound **5** can be isolated after allowing **4** to stand in methylene chloride for several days. ^1H NMR (CD_2Cl_2): δ 7.75 (m, 4H), 7.57 (m, 2H), 7.43 (m, 4H), 7.31 (d, 2H), 7.11 (m, 3H), 4.54 (s, 1H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 19.8 (s). ^{19}F NMR (CD_2Cl_2): δ −118.1 (m, 2F), −161.3 (m, 1F), −165.8 (m, 2F). FD-MS: m/z 1058 [M^+]; exhibited expected isotope pattern for two nickel atoms. Anal. Calcd for $C_{52}H_{32}P_2O_2F_{10}Ni_2{\cdot}1^1/_3CH_2Cl_2$: C, 54.73; H, 2.99. Found: C, 54.69; H, 3.07. The presence of methylene chloride in the above ratio was confirmed by ^1H NMR spectroscopy.

$(PPh_2CH{=}C(O)Ph)Ni(C_6F_5)(pyridine)$ (6). Approximately 0.20 g of **5** (0.18 mmol) was dissolved in toluene. An excess (5.0 mL, 5.1 g, 65 mmol) of pyridine was added to the solution. The solution was stirred for about 15 min. Removal of the solvent in vacuo resulted in a yellow powder. ^1H NMR (CD_2Cl_2): δ 8.66 (br s, 2 H), 7.81−7.30 (m, 18 H), 4.70 (s, 1 H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 24.8 (s). ^{19}F NMR (CD_2Cl_2): δ −119.1 (m, 2F), −163.5 (m, 1F), −165.0 (m, 2F). FD-MS: m/z 607 [M^+]; exhibited expected isotope pattern for nickel. Anal. Calcd for $C_{31}H_{21}NPOF_5Ni$: C, 61.22; H, 3.48. Found: C, 61.28; H, 3.68.

Reaction of 5 with Ethylene. Compound **5** (0.0056 g, 0.0053 mmol) was dissolved in $CDCl_3$. Ethylene was bubbled through this orange solution for about 5 min. The solution was then allowed to stand at room temperature for about 15 h and heated to 65 °C overnight to give a cloudy, green-yellow mixture. ^{19}F NMR analysis of the solution exhibited resonances consistent with pentafluorostyrene.

X-ray Crystallography. Single crystals of $(PPh_2CH_2C(O)Ph)Ni(C_6F_5)_2{\cdot}CH_2Cl_2$ (**4**), grown from methylene chloride at −20 °C, are, at 20 ± 1 °C, monoclinic, space group $P2_1/c\text{-}C_{2h}^5$ (No. 14) with $a = 14.773$ (3) Å, $b = 11.174$ (3) Å, $c = 21.175$ (6) Å, $\beta = 110.84$ (2)°, $V = 3267$ (2) Å^3, and $Z = 4$ ($d_{\text{calcd}} = 1.590$ g cm^{-3}; μ_a(Mo Kα) = 0.89 mm^{-1}). A total of 4491 independent reflections having 2θ(Mo Kα) < 45.8° (the equivalent of 0.6 limiting Cu Kα spheres) were collected on a computer-controlled Nicolet autodiffractometer using full (1.20° wide) scans and graphite-monochromated Mo Kα radiation. The structure was solved using "Direct Methods" techniques with the Siemens SHELXTL-PC software package as modified at Crystalytics Co. The resulting structural parameters have been refined to convergence (R1(unweighted, based on F) = 0.041 for 2239 independent reflections having 2θ(Mo Kα) < 45.8° and $I > 3\sigma(I)$) using counter-weighted full-matrix least-squares techniques and a structural model which incorporated anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for all hydrogen atoms. The hydrogen atoms were fixed at idealized sp^3- or sp^2-hybridized positions using a C−H bond length of 0.96 Å. The isotropic thermal parameter of each hydrogen was fixed at 1.2 times the equivalent isotropic thermal parameter of the carbon atom to which it is covalently bonded.

Bond lengths and angles for **4** are found in Tables 1 and 2, respectively. Atomic coordinates and anisotropic thermal parameters for non-hydrogen atoms for **4** are found in Tables 3 and 4, while atomic coordinates for hydrogen atoms are found in Table 5 (see the Supporting Information for Tables 3−5).

Results and Discussion

Synthesis of Starting Materials. The previous synthetic method employed for $B(C_6F_5)_3{\cdot}3H_2O$ (**1**), gas-phase transfer of water to solid $B(C_6F_5)_3$ under a static vacuum,[30] was somewhat cumbersome for the production of larger quantities. Thus, the addition of 3 equiv of deoxygenated water to a solution of commercially available $B(C_6F_5)_3$ (in Isopar E and cyclohexane) was attempted (eq 1) and found to yield colorless microcrystals that were insoluble in aliphatic hydrocarbons.

$$B(C_6F_5)_3 + 3\ H_2O \rightarrow \underset{\textbf{1}}{B(C_6F_5)_3{\cdot}3H_2O} \qquad (1)$$

Despite the fact that the synthesis and the crystal structure of **1**, albeit with sparse details, are available, no spectroscopic characterization of $B(C_6F_5)_3{\cdot}3H_2O$ has been reported until now.

The FI-MS of **1** was rather confusing at first since a molecular ion of m/z 512, consistent with $B(C_6F_5)_3$ and not its trihydrate, was observed. It is clear, however, from the IR spectrum of **1** that it contained complexed

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(29) See ref 22a.

(30) See ref 13a.

Table 1. Bond Lengths (Å) Involving Non-Hydrogen Atoms in Crystalline $(PPh_2CH_2C(O)Ph)Ni(C_6F_5)_2 \cdot CH_2Cl_2$ (4)[a]

Complex			
Ni1−P1	2.184(3)	Ni1−O1	1.939(5)
Ni1−C21	1.886(7)	Ni1−C31	1.931(8)
P1−C1	1.821(8)	P1−C3	1.810(7)
		P1−C9	1.810(7)
O1−C2	1.252(10)		
		C1−C2	1.498(10)
C2−C15	1.468(10)		
C3−C4	1.390(11)	C9−C10	1.400(11)
C3−C8	1.372(12)	C9−C14	1.382(12)
C4−C5	1.389(11)	C10−C11	1.384(12)
C5−C6	1.373(15)	C11−C12	1.358(16)
C6−C7	1.368(15)	C12−C13	1.369(14)
C_7−C8	1.377(11)	C13−C14	1.374(12)
C15−C16	1.387(11)	C17−C18	1.364(15)
C15−C20	1.386(13)	C18−C19	1.373(15)
C16−C17	1.381(11)	C19−C20	1.369(11)
C21−C22	1.372(12)	C31−C32	1.370(11)
C21−C26	1.373(10)	C31−C36	1.363(10)
C22−C23	1.381(13)	C32−C33	1.348(12)
C23−C24	1.379(12)	C33−C34	1.364(9)
C24−C25	1.350(15)	C34−C35	1.367(11)
C25−C26	1.372(12)	C35−C36	1.379(12)
C22−F22	1.376(9)	C32−F32	1.365(8)
C23−F23	1.349(11)	C33−F33	1.360(9)
C24−F24	1.406(11)	C34−F34	1.353(10)
C25−F25	1.354(9)	C35−F35	1.369(8)
C26−F26	1.355(10)	C36−F36	1.375(9)
Solvent of Crystallization			
Cl1−C1s	1.706(12)	Cl2−C1s	1.729(12)

[a] The numbers in parentheses are the estimated standard deviations in the last significant digit. Atoms are labeled in agreement with Figure 1.

Table 2. Bond Angles (deg) Involving Non-Hydrogen Atoms in Crystalline $(PPh_2CH_2C(O)Ph)Ni(C_6F_5)_2 \cdot CH_2Cl_2$ (4)[a]

Complex			
P1−Ni1−O1	82.9(2)	C21−Ni1−C31	89.0(3)
P1−Ni1−C21	97.4(3)	O1−Ni1−C21	176.7(3)
O1−Ni1−C31	91.2(3)	P1−Ni1−C31	170.4(2)
Ni1−P1−C1	98.8(3)	C1−P1−C3	106.8(3)
Ni1−P1−C3	129.4(3)	C1−P1−C9	103.6(3)
Ni1−P1−C9	110.5(3)	C3−P1−C9	104.9(3)
Ni1−O1−C2	124.0(4)	O1−C2−C1	117.8(6)
		O1−C2−C15	119.7(7)
P1−C1−C2	107.0(5)	C1−C2−C15	122.4(7)
P1−C3−C4	116.4(6)	P1−C9−C10	118.8(6)
P1−C3−C8	124.3(5)	P1−C9−C14	122.2(6)
C4−C3−C8	119.3(7)	C10−C9−C14	119.0(7)
C3−C4−C5	119.0(8)	C9−C10−C11	119.1(9)
C4−C5−C6	120.5(9)	C10−C11−C12	120.8(8)
C5−C6−C7	120.6(8)	C11−C12−C13	120.5(8)
C6−C7−C8	119.0(9)	C12−C13−C14	120.0(10)
C3−C8−C7	121.6(8)	C9−C14−C13	120.7(8)
C2−C15−C16	118.9(7)	C16−C17−C18	120.4(8)
C2−C15−C20	121.6(7)	C17−C18−C19	121.4(8)
C16−C15−C20	119.5(7)	C18−C19−C20	118.6(10)
C15−C16−C17	118.9(8)	C15−C20−C19	121.1(8)
Ni1−C21−C22	124.6(5)	Ni1−C31C32	128.0(5)
Ni1−C21−C26	121.7(6)	Ni1−C31−C36	119.0(6)
C22−C21−C26	113.7(7)	C32−C31−C36	113.0(7)
C21−C22−C23	124.5(7)	C31−C32−C33	124.5(6)
C21−C22−F22	118.6(7)	C31−C32−F32	117.8(7)
C23−C22−F22	117.0(8)	C33−C32−F32	117.8(7)
C22−C23−C24	118.1(9)	C32−C33−C34	120.3(7)
C22−C23−F23	120.4(7)	C32−C33−F33	121.7(6)
C24−C23−F23	121.5(9)	C34−C33−F33	118.0(7)
C23−C24−C25	120.1(9)	C33−C34−C35	118.9(8)
C23−C24−F24	119.2(9)	C33−C34−F34	121.1(7)
C25−C24−F24	120.6(7)	C35−C34−F34	120.0(6)
C24−C25−C26	119.0(7)	C34−C35−C36	117.8(6)
C24−C25−F25	119.0(8)	C34−C35−F35	119.2(7)
C26−C25−F25	122.0(8)	C36−C35−F35	123.1(7)
C21−C26−C25	124.6(8)	C31−C36−C35	125.6(7)
C21−C26−F26	119.3(7)	C31−C36−F36	119.5(8)
C25−C26−F26	116.1(7)	C35−C36−F36	114.9(6)
Solvent of Crystallization			
Cl1−C1s−Cl2	113.0(8)		

[a] The numbers in parentheses are the estimated standard deviations in the last significant digit. Atoms are labeled in agreement with Figure 1.

water. Three sharp, medium-intensity bands were observed at 3666, 3597 (with a shoulder), and 3499 cm^{-1} and are assigned to OH vibrations. A medium-intensity band was observed at 1602 cm^{-1}, which was assigned to a H_2O bending mode. The sharpness of the stretching vibrations is taken as evidence for the highly ordered environment of the water. In the crystal structure of **1**, one water is coordinated to boron and the other two waters participate in hydrogen bonding to the bound water molecule.[31] Further evidence that **1** was indeed distinct from $B(C_6F_5)_3$ came from its ^{19}F NMR spectrum. While $B(C_6F_5)_3$ exhibited resonances at −134.7, −154.7, and −162.6 ppm, $B(C_6F_5)_3 \cdot 3H_2O$ resonances appeared at −128.9, −142,3, and −160.4 ppm. Addition of pure $B(C_6F_5)_3$ to a solution of $B(C_6F_5)_3 \cdot 3H_2O$ results in the disappearance of the ^{19}F resonances for $B(C_6F_5)_3 \cdot 3H_2O$ and the growth of new, broader peaks at −133.3, −151.7, and −162.8 ppm. Evidently, the water molecules complexed to $B(C_6F_5)_3$ undergo a dynamic exchange that is fast on the NMR time scale. However, given the following data which show that **1** is indeed distinct from $B(C_6F_5)_3$, the *m*/*z* 512 molecular ion can be explained by complete loss of complexed water from **1** under the high vacuum of the MS experiment. Furthermore, repeating the reported synthetic method[32] for **1** yielded colorless crystals that exhibited the same ^{19}F NMR spectral pattern for **1** synthesized by the addition of water to a solution of $B(C_6F_5)_3$. Evidently **1** loses water of hydration in the high vacuum of the MS experiment and therefore only exhibits a molecular ion for $B(C_6F_5)_3$.

Although the synthesis of $(PPh_2CH{=}C(O)Ph)Ni(Ph)(PPh_3)$ (**2**) has been known for 20 years,[33] its spectroscopic data were not reported until 1988.[34] While the ^1H NMR spectrum of **2** is consistent with that published previously, it was not entirely clear if the ^{31}P NMR data obtained by us were identical with those reported. For **2**, an AB spin system is expected with large phosphorus−phosphorus coupling since, on the basis of the crystal structure of **2**, the phosphorus atoms are *trans*. The ^{31}P NMR pattern for **2** is of higher order; the two inner lines are much more intense than the outer two lines. This indicates that the coupling constant between P_A and P_B is greater than the difference between their chemical shifts (i.e., $J_{AB} > \Delta\delta_{AB}$). This spectrum was successfully simulated using the calculated chemical shifts of 22.2

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[31] See ref 13a.
[32] See ref 13a.
[33] See ref 28a.
[34] See ref 28b.

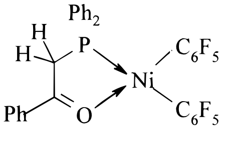
and 20.5 ppm and a $^2J_{P_AP_B}$ value of 285 Hz (see the Supporting Information).[35,36]

The complex [(PPh$_2$CH=C(O)Ph)Ni(Ph)]$_2$ (**3**) can be synthesized from (PPh$_2$CH=C(O)Ph)Ni(Ph)(PEt$_3$) according to the method of Klabunde et al.[37] A similar procedure was followed for **2**, the triphenylphosphine analogue. Thus, addition of the phosphine acceptor Rh(acac)(C$_2$H$_4$)$_2$ to **2** gave the dimer complex **3** in good yield (eq 2). Since no spectroscopic data have been published

$$\underset{\mathbf{2}}{(PPh_2CH{=}C(O)Ph)Ni(Ph)(PPh_3)} + Rh(acac)(C_2H_4)_2 \rightarrow \underset{\mathbf{3}}{[(PPh_2CH{=}C(O)Ph)Ni(Ph)]_2} + Rh(acac)(PPh_3)_2 + 2C_2H_4 \quad (2)$$

previously for **3**, this material was subjected to ^{31}P and ^{1}H NMR analysis, which is consistent with the known solid-state structure. The results are presented in the Experimental Section.

Reaction of B(C$_6$F$_5$)$_3$·3H$_2$O with 3. The reaction of 2 equiv of B(C$_6$F$_5$)$_3$·3H$_2$O (or 1 equiv of B per Ni) with [(PPh$_2$CH=C(O)Ph)Ni(Ph)]$_2$ was carried out in toluene at room temperature and gave yellow microcrystals in 45% isolated yield. The solid was soluble in methylene chloride and was moderately soluble in toluene. The ^{31}P NMR spectrum of the product exhibited a single resonance at 26.8 ppm, a shift of only ca. 5 ppm downfield from that of the starting material. Its ^{1}H NMR spectrum exhibited aryl resonances between 7.90 and 7.20 ppm and a methylene doublet at 4.19 ppm in a 15:2 ratio, respectively. The ^{19}F NMR spectrum of the solid is most revealing. Two distinct pentafluorophenyl groups in a 1:1 ratio are observed and seem to be in similar chemical environments, given that their chemical shifts are so similar. A molecular ion of m/z 696 was observed in the FD-MS of the product, which exhibited the expected isotopic ratios for nickel. On the basis of these data, the structure of the reaction product is proposed to be



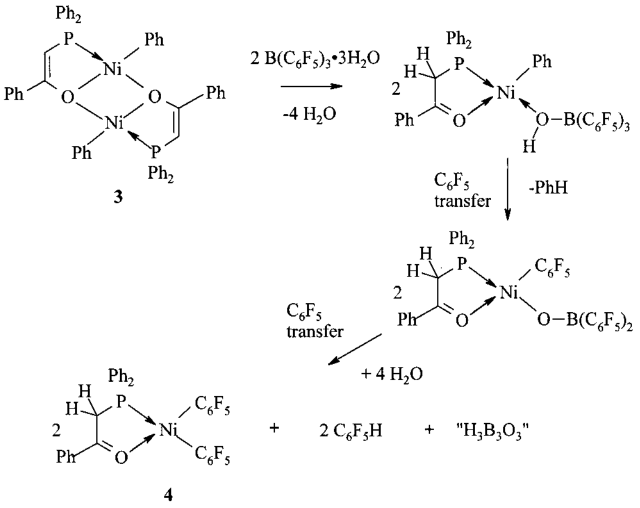
4

This proposal was confirmed by independent synthesis and single-crystal X-ray analysis (see below).

To track down the fate of the missing phenyl group attached to the starting dimer **3**, the volatiles from the reaction with **1** carried out in toluene-d_8 were collected. NMR analysis of the volatiles showed a significant amount of benzene, consistent with the loss of the phenyl ligand in **3** by protonation of the Ni−Ph bond.

The fate of the third pentafluorophenyl group originating from boron was established by monitoring the reaction between **1** and **3** using ^{19}F NMR methods. Besides the resonances for the product, complex **4**, three new resonances appeared at −138.8 (2F), −153.7 (1F), −162.0 (2F) ppm, in agreement with data published previously for C$_6$F$_5$H.[38]

Scheme 1



A reaction sequence for the formation of **4** is presented in Scheme 1. The proposal takes into account the production of benzene and pentafluorobenzene. The Brϕnsted acid B(C$_6$F$_5$)$_3$·3H$_2$O first protonates the methine carbon of the phosphorus/oxygen chelate ligand in complex **3**. A nickel cation and a HOB(C$_6$F$_5$)$_3$$^-$ anion are formed along with loss of 4 equiv of water. The ionic intermediate is probably a zwitterion or at least a contact ion pair. Such species arguably would be favored in toluene.[39] The zwitterion could be formed by virtue of an oxygen donor bond to the nickel between the anion and cation as shown in Scheme 1. The oxygen donor bond from the anion replaces the oxygen−nickel donor bond in the starting material **3**, serving to break up the dimer into its constituent monomeric parts. The close proximity of the HOB(C$_6$F$_5$)$_3$$^-$ anion to the Ni−Ph bond of the cation increases the probability that a second, seemingly unfavored, protonation can occur. Loss of PhH followed by C$_6$F$_5$ transfer from boron to nickel creates the proposed neutral nickel boronoxy intermediate in Scheme 1. Reaction of this complex with the liberated water molecules along with a second C$_6$F$_5$ transfer from boron to nickel generates the observed final reaction products: **4**, C$_6$F$_5$H, and, presumably, H$_3$BO$_3$.

Precedent for double protonation of an organometallic complex by a related boron-containing reagent can be found for a dimethylzirconocene complex. Siedle et al.[40] revealed that [Et$_3$NH][HOB(C$_6$F$_5$)$_3$] reacts with [(Me$_5$C$_5$)$_2$ZrMe$_2$] to yield 2 equiv of methane: first, by proton transfer from the stronger triethylammonium conjugate acid and, second, by proton transfer from the weaker boronoxy acid.

Furthermore, Green and co-workers have explored reactions of group 4 transition-metal complexes[41] and late-transition-metal complexes[42] with B(C$_6$F$_5$)$_3$, which resulted in transfer of *one pentafluorophenyl group* from

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[35] Becker, E. D., *High-Resolution NMR, Theory and Chemical Applications*, 2nd ed.; Academic Press: New York, 1980; p 138.

[36] The simulation was carried out using a PC-adapted version of the program LAOCOON with a 5 Hz line broadening: Castellano, S. M.; Bothner-By, A. A. *J. Chem. Phys.* **1964**, *41*, 3863.

[37] See ref 22a.

[38] Bruce, M. I. *J. Chem. Soc. A* **1968**, 1459.

[39] Eisch, J. J.; Pombrik, S. L.; Gurtzgen, S.; Rieger, R. *Stud. Surf. Sci. Catal.* **1994**, *89*, 221.

[40] Siedle, A. R.; Newmark, R. A.; Lamanna, W. M.; Huffman, J. C. *Organometallics* **1993**, *12*, 1491.

[41] Gomez, R.; Green, M. L. H.; Haggit, J. L. *J. Chem. Soc., Chem. Commun.* **1994**, 2607.

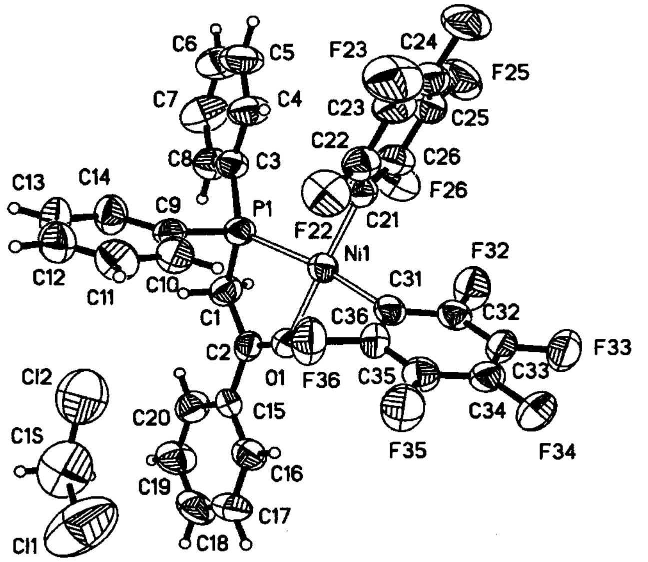

Figure 1. ORTEP drawing of $(PPh_2CH_2C(O)Ph)Ni(C_5F_6)_2\cdot CH_2Cl_2$ (**4**).

the boron to the transition metal. In the former case, $B(C_6F_5)_3$ reacts with a zirconium dimethyl species to yield a $Zr-C_6F_5$ bond, while in the latter case $CpFe(CO)_2Me$ reacts with $B(C_6F_5)_3$ to yield iron−tetrafluorophenyl derivatives. The synthesis of **4** is the first example of the transfer of *two pentafluorophenyl groups* from $B(C_6F_5)_3$ to a transition metal. In contrast, Puddephatt and co-workers have shown that $B(C_6F_5)_3$ reacts with a dimethylplatinum species by the more traditional alkyl abstraction route.[43]

Independent Synthesis of 4. Complex **4** can be synthesized by an independent route that involved the addition of the P∼O chelate ligand $PPh_2CH_2C(O)Ph$ to a $Ni(C_6F_5)_2$ precursor. The chelate ligand was synthesized by a known procedure (see Experimental Section) and was added as a toluene solution to $(\eta^6\text{-toluene})Ni(C_6F_5)_2$. An immediate color change from red-brown to yellow occurred. Removal of the solvent in vacuo gave a yellow solid. This solid exhibited the exact NMR spectral characteristics that were observed for the reaction product of the trihydrate of $B(C_6F_5)_3$ and dimer **3** (eq 3). The ability to make **4** by this independent route

$$PPh_2CH_2C(O)Ph + (\eta^6\text{-toluene})Ni(C_6F_5)_2 \rightarrow \underset{\mathbf{4}}{(PPh_2CH_2C(O)Ph)Ni(C_6F_5)_2} \quad (3)$$

enabled us to access larger amounts for a thermolysis study (see below).

Crystal and Molecular Structure of 4. Crystals of **4** suitable for X-ray analysis were grown from methylene chloride solution. A perspective plot of the complex is shown in Figure 1; selected distances and angles are given in Tables 1 and 2.

The nickel adopts a square-planar geometry involving the P and O atoms of the chelating phosphino−ketone ligand and the *ipso* carbons of the pentafluoroaryl groups. As expected for a square-planar geometry, the bond angles involving the nickel and ligand atoms bonded to nickel total near 360° (observed, 360.5°). However, there are significant deviations from the idealized ligand bond angles expected for a square-planar geometry. For example, the P1−Ni−O1 angle is more acute than normal (82.9(2)°) and the P1−Ni−C21 angle significantly more obtuse than usual (97.4(3)°). These deviations are undoubtedly due to the chelate ligand that ties together the P and O atoms of the coordination sphere, thus decreasing the angle from the idealized 90°. Similar, but less dramatic, deviations are observed for nickel complexes coordinated to P∼O enolate chelates. For complex **2** and the related complex $(PPr^i_2CH{=}C(O)Ph)Ni(Ph)(PPh_3)$ the corresponding P−Ni−O angle measured 86.5°.

The Ni−P1 distance measures 2.184(3) Å and is comparable to those found for related compounds. For example, it is somewhat shorter than the Ni−P distances in *trans*-$NiBr(C_6F_5)(PPh_2Me)_2$ and *trans*-$Ni(C_6F_5)_2(PPh_2Me)_2$ which average 2.2156(13) and 2.206(1) Å, respectively.[44] The Ni−P1 distance in **4** is somewhat longer than in **2** (2.168 Å) and in $(PPr^i_2CH{=}C(O)Ph)Ni(Ph)(PPh_3)$ (2.1756(7) Å). The Ni−O1 distance in **4** is 1.939(5) Å and is significantly longer than that found for the Ni−O bond (1.895(3) Å) in a related Ni(II) species with a chelating ketonic ligand, $[Ni(HOCMe_2CH_2C(O)Me)_2]^{2+}$.[45]

The two $Ni-C_{ipso}(C_6F_5)$ distances differ significantly from one another. The Ni−C bond *trans* to phosphorus (Ni−C31) is significantly longer (1.931(8) Å) than the Ni−C bond *trans* to oxygen (Ni−C21, 1.886(7) Å). These distances are in agreement with the strong *trans* influence of phosphorus.[46] There are two crystal structures of complexes containing *cis*-oriented bis(pentafluorophenyl) ligands, but they both exhibit $Ni-C_{ipso}(C_6F_5)$ distances that are shorter than the Ni−C (Ni−C31) bond *trans* to phosphorus in **4**: for (norbornadiene)$Ni(C_6F_5)_2$, $Ni-C(C_6F_5) = 1.914(2)$ and 1.921(2) Å, and for (cycloocta-1.5-diene)$Ni(C_6F_5)_2$, $Ni-C(C_6F_5) = 1.902(2)$ Å.[47] The shorter distances are due to the coordination of olefinic ligands *trans* to the pentafluorophenyl groups which are known to exhibit a weaker *trans* influence than phosphorus. The least-squares plane containing the immediate nickel coordination environment (Ni, P1, O1, C21, and C31) forms dihedral angles of 77.4 and 72.3° with the least-squares planes defined by the pentafluorophenyl rings, C21−C26 and C31−C36, respectively. This angle, defined as ϕ by Eyring and Radonovich, has been correlated with the relative degree of nickel to C_6F_5 back-bonding in a series of related *cis*-bis(pentafluorophenyl)nickel complexes. As ϕ approaches 90° for these complexes, the nickel−pentafluorophenyl bond length decreases. For example, $\phi = 72°$ and $Ni-C_{ipso}(C_6F_5) = 1.917(2)$ Å in $(\eta^4\text{-norbornadiene})Ni(C_6F_5)_2$, $\phi = 83°$ and $Ni-C_{ipso}(C_6F_5) = 1.902(4)$ Å in $(\eta^4\text{-cycloocta-1,5,diene})Ni(C_6F_5)_2$, and $\phi = 89°$ and $Ni-C_{ipso}(C_6F_5) = 1.891(4)$ Å in $(\eta^6\text{-toluene})Ni(C_6F_5)_2$. For complex **4**, on the basis of the ϕ parameter alone, one would expect the $Ni-C_{ipso}(C_6F_5)$ bond distances to hover around 1.92

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(42) Green, M. L. H.; Haggit, J. L.; Mehnert, C. P. *J. Chem. Soc., Chem. Commun.* **1995**, 1853.

(43) Hill, G. S.; Rendina, L. M.; Puddephatt, R. J. *J. Chem. Soc., Dalton Trans.* **1996**, 1809.

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(45) Foxman, B. M.; Mazurek, H. *Inorg. Chem.* **1979**, *18*, 113.

(46) Purcell, K. F.; Kotz, J. C. *Inorganic Chemistry*, Saunders: Philadelphia, PA, 1977; p 705.

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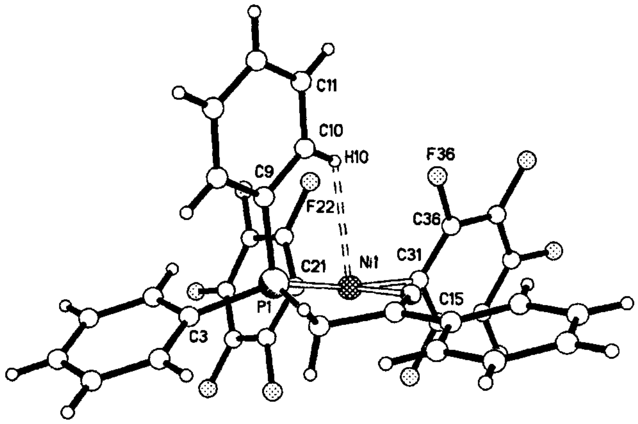
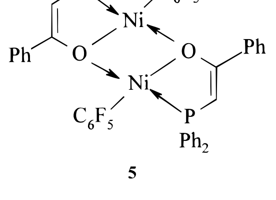


Figure 2. Ball and stick drawing of **4**.

Å. The fact that the bond lengths are longer (Ni−C31, 1.931(8) Å) and shorter (Ni−C21, 1.886(7) Å) suggests that the *trans* influences of phosphorus and oxygen override the relatively weak nickel to pentafluorophenyl back-bonding interaction. However given the relatively high standard deviations of these distances, a definitive conclusion cannot be made.

Figure 2 presents a side view of complex **4** that bisects the P1−Ni−O1 angle. This perspective accentuates the puckering of the five-membered P∼O chelate ligand. This conformation forces the C9-containing phenyl ring attached to P1 to position ortho hydrogen H10 above the metal at one of the two axial sites of an octahedral nickel coordination sphere. While the Ni−H10 separation, 2.753 Å, is beyond bonding distance, one axial position of nickel is nevertheless effectively blocked by the phenyl ring (see the space-filling drawing in the Supporting Information). Approach to the opposite axial position is unencumbered. Although the X-ray data suggest that the methylene protons of the P∼O chelate are inequivalent, solution NMR data at room temperature exhibit only one resonance for these protons. Evidently, the P∼O ligand undergoes a dynamic process, presumably flipping of the methylene carbon in the puckered ring from one side of the square plane to the other, rendering the methylene protons equivalent. This process would then force the C3-containing phenyl substituent attached to phosphorus to cover access to the opposite axial site from that hidden by the C9-containing phenyl group shown in the static structure of Figure 2.

Thermolysis of $(PPh_2CH_2C(O)Ph)Ni(C_6F_5)_2$ (4). In the solid state, **4** undergoes no significant reaction after 1 day of exposure to atmospheric oxygen and moisture (^1H NMR spectroscopy). However, when a 1,2-dichloroethane solution of **4** is maintained at 65 °C for approximately 40 h, an orange precipitate forms. Spectral data taken of the orange solid are in agreement with the synthesis of $[(PPh_2CH{=}C(O)Ph)Ni(C_6F_5)]_2$ (**5**). Compound **5** exhibits a single set of peaks in its ^{19}F NMR spectrum and a single phosphorus resonance. Integration of the ^1H NMR spectrum of **5** is in agreement with loss of one methylene proton from the P∼O chelate in **4** and formation of 1 equiv of pentafluorobenzene (^{19}F NMR). Formulation of compound **5** as a dimer is based on (1) the observed molecular ion (*m*/*z* 1058) in the MS experiment, which exhibited isotopic ratios consistent with two nickel atoms per molecule, and (2) the results of a preliminary X-ray structure determination for crystals of **5**. Unfortunately, the small size and poor quality of the crystals for **5** limited the quality and quantity of the diffraction data and prevented a high-precision structure determination.[48] The data were, however, of sufficient quality to unambiguously identify **5** as a dimeric species with crystallographic C_2 symmetry in the solid state. Furthermore, the qualitative and semiquantitative structural parameters which resulted from the X-ray structure determination are totally consistent with the proposed structure of **5** and the other spectroscopic and analytical data for the compound. As shown in Figure 3, not only does the P∼O ligand form a chelate to each nickel, it also holds the dimer together through a dative oxygen to nickel bond that bridges the two nickel centers. The structure of **5** is analogous to that reported for the starting material,



5

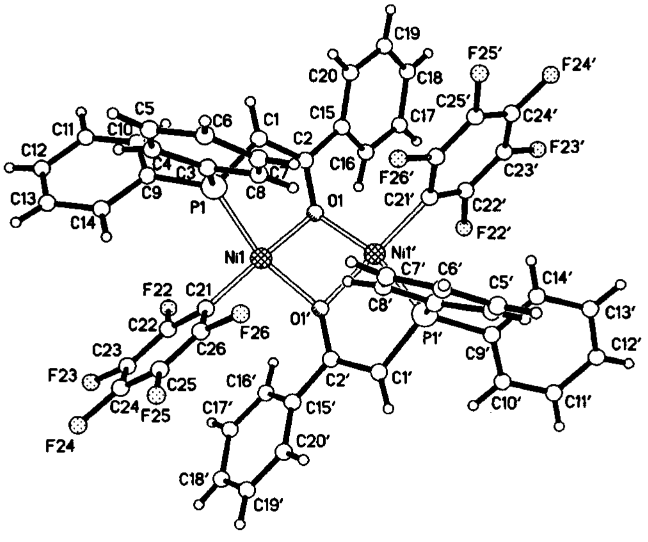


Figure 3. Ball and stick drawing of $[(PPh_2CH{=}C(O)Ph)]$-$Ni(C_6F_5)]_2$ (**5**).

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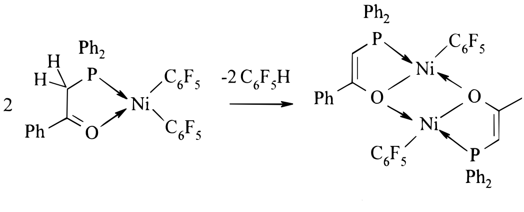
[48] Crystals of $[Ni(C_6F_5)\{(C_6H_5)_2PCHCO(C_6H_5)\}]_2{\cdot}C_2H_4Cl_2$ are, at 20 °C, monoclinic, space group $P2/c$-C_h (No. 13), with $a = 15.512(7)$ Å, $b = 8.957(4)$ Å, $c = 20.828(9)$ Å, $\beta = 117.80(4)°$, $V = 2560(2)$ Å^3, and $Z = 2$ dimeric formula units ($d_{calcd} = 1.483$ g cm^{-3}; μ_a(Cu Kα) = 3.14 mm^{-1}). The crystals were not only quite small (maximum dimension 0.26 mm) but also invariably twinned. Several crystals were examined before a relatively single one was found which was used for subsequent data collection. A total of 2353 independent reflections having 2θ(Cu Kα) < 95.04° (the equivalent of 0.4 limiting Cu Kα sphere) were collected on a computer-controlled Syntex P single-crystal diffractometer using $\theta/2\theta$ scans with fixed scan rates of 6 or 3°/min and Ni-filtered Cu Kα radiation. "Direct methods" techniques were used to solve the structure, and the resulting structural parameters have been refined to convergence (R1(unweighted, based on F) = 0.105 for 1117 independent reflections having 2θ(Cu Kα) < 95.04° and $I > 2\sigma(I)$) using counterweighted full-matrix least-squares techniques and a structural model which incorporated anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for all included hydrogen atoms. Selected bond distances: Ni1−O1 = 1.901(10) Å; Ni1−O1′ = 1.912(12) Å; Ni1−P1 = 2.116(6) Å; Ni1−C21 = 1.91(2) Å; Ni1···Ni1′ = 2.723(5) Å. Selected bond angles: O1−Ni1−O1′ = 78.1(5)°; C21−N1−O1′ = 99.7(6)°; O1−Ni1−P1 = 88.4(4)°; C21−Ni1−P1 = 94.1(5)°.

Scheme 2

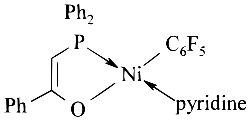


4 **5**

dimer **3**. Unfortunately, no details regarding the structure of **3** are available for comparison purposes.

A possible route to **5** involves the protonation of one of the Ni$-$C$_6$F$_5$ bonds in **4** to form the observed pentafluorobenzene product by transfer of one of the acidic methylene protons of the phosphorus/oxygen chelate. This transformation is detailed in Scheme 2. Therefore, the chelating ligand is amphoteric in nature; it can accept protons from strong Brϕnsted acids (i.e., $B(C_6F_5)_3\cdot 3H_2O$) and can donate protons to suitably basic substrates (i.e., Ni$-$C$_6$F$_5$ bonds). In related palladium chemistry, Braunstein and co-workers found that the phosphino$-$ketone ligand $PPh_2CH_2C(O)Ph$ can be deprotonated with NaH to give the chelating ylide ligand found in **2** and **3**.[49] The loss of H$^+$ from $PPh_2CH_2C(O)$-Ph to form the corresponding chelating ylide has been described for related nickel systems.[50]

Reactivity of [(PPh$_2$CH$_2$C(O)Ph)Ni(C$_6$F$_5$)]$_2$ (5). Addition of an excess of pyridine to a toluene solution of dimer **5** gave a yellow powder after the solvent was removed under vacuum. The yellow material exhibited a single resonance at 24.8 ppm in the ^{31}P NMR experiment and a single set of pentafluorophenyl resonances (*ortho, meta,* and *para*) in the ^{19}F NMR spectrum. The molecular ion observed in the mass spectrum of the yellow complex is consistent with the formation of the pyridine adduct $(PPh_2CH_2C(O)Ph)Ni(C_6F_5)$(pyridine) (**6**). The two-electron-donor pyridine replaces the oxygen bridges that hold dimer **5** together, forming mononuclear complex **6** in the process.



6

Given the propensity of complexes such as **3** to react with ethylene to form oligomers and in some cases polymers, ethylene was bubbled through a solution of dimer **5**. After 15 h at room temperature, no reaction was visible. This was confirmed by NMR analysis of the solution. However, when the ethylene-saturated solution was heated to 65 °C overnight, the orange solution became a cloudy yellow-green mixture. While the ^{1}H NMR spectrum of this solution was quite complex and indecipherable, the ^{19}F NMR spectrum showed resonances at -143.4 (2F), -157.9 (1F), and -164.3 (2F) which are very close to those resonances associated with pentafluorostyrene.[51] Other unidentified resonances are also observed in this spectrum.

The formation of pentafluorostyrene is consistent with the migratory insertion of ethylene into the Ni$-$C$_6$F$_5$ bond, followed by β-hydride elimination. In this process, a nickel$-$hydride species should also be generated which is the purported active catalyst in oligomerization/polymerization of ethylene. Similar migratory insertion$-\beta$-hydride elimination processes have been observed in related Ni$-$Ph and Ni$-$C$_6$F$_5$ complexes.[52] To the extent that this nickel$-$hydride species is formed, complex **5** should be an active catalyst for the oligomerization and/or polymerization of ethylene under the right conditions (e.g., increased pressure and temperature).[53]

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Supporting Information Available: Figures giving experimental and simulated ^{31}P NMR spectra of complex **2** and space-filling diagrams of complex **4**, tables of atomic coordinates and anisotropic thermal parameters for complex **4**, and tables of bond lengths, bond angles, atomic coordinates, and anisotropic thermal parameters for complex **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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