Organometallics **1991**, *10*, 766-770

Reaction of the Iron Phosphorane Complex $(\eta^5\text{-}C_5H_5)(CO)_2Fe\{P(O)(NEt_2)(OMe)\}$ with Boron Trihalides. Preparation, X-ray Structure Analysis, and Reactivity of the Iron Chloro-Substituted-Phosphorane Complex

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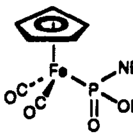
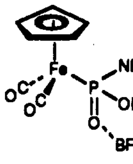
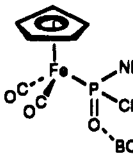
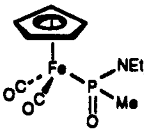
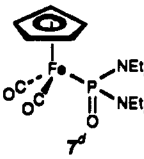
Received July 12, 1990

The iron phosphorane complex $(\eta^5\text{-}C_5H_5)(CO)_2Fe\{P(O)(NEt_2)(OMe)\}$ (**1**) reacts with 1 equiv of BX_3 (X = F, Cl) to generate an adduct of **1** with BX_3 (**2** (X = F), **5** (X = Cl)) through the lone pair of the phosphoryl oxygen. The treatment of **1** with 2 equiv of BF_3 yields **2**, whereas the reaction with 2 equiv of BCl_3 gives an iron chloro-substituted-phosphorane complex, $[(\eta^5\text{-}C_5H_5)(CO)_2Fe\{P(O)(NEt_2)(Cl)\}]\cdot BCl_3$ (**3**), which crystallizes in the monoclinic space group $P2_1/n$ with $a = 9.080$ (3) Å, $b = 14.689$ (3) Å, $c = 14.363$ (3) Å, $\beta = 102.65$ (2)°, and $Z = 4$. X-ray diffraction has revealed that the Fe–P and P–Cl bonds are covalent in nature and the chloroaminophosphorane group interacts with BCl_3 through the lone pair of the phosphoryl oxygen in **3**. The Cl atom of **3** is readily replaced by OMe, Me, and NEt_2 groups to give **1**, **6**, and **7**, respectively.

Introduction

Transition-metal phosphorane complexes are attracting considerable attention due to the presence of a covalent bond between a transition metal and a pentavalent phosphorus atom and have been studied for a variety of transition metals.[1] However, the substituents on the phosphorus atom of phosphorane complexes have been limited to OR and R (R = alkyl or aryl). Recently, amino-substituted phosphorane complexes have been reported.[2] We have been seeking phosphorane complexes containing a good leaving group such as a halogen atom on the phosphorus, because such complexes may be a good precursor to introduce a desired group on the phosphorus. It has been shown that boron trihalides, BX_3, can abstract an OR group on a carbon or a phosphorus atom as an anion to give cationic compounds or OR/X exchange products.[3-5]

Table I. Spectroscopic Data

complex	IR[a] (ν_{CO}), cm^{-1}	^1H NMR[b] (δ), ppm	^{31}P NMR[a] (δ), ppm
 **1**	2030 1978	1.13 (t, J = 7.0 Hz, 6 H, CH_2CH_3) 3.07 (m, 4 H, CH_2CH_3) 3.44 (d, J = 11.0 Hz, 3 H, OCH_3) 5.03 (s, 5 H, C_5H_5)	103.3 (s)
 **2**	2058 2008	1.18 (t, J = 7.0 Hz, 6 H, CH_2CH_3) 3.15 (m, 4 H, CH_2CH_3) 3.57 (d, J = 12.0 Hz, 3 H, OCH_3) 5.19 (d, J = 1.0 Hz, 5 H, C_5H_5)	131.6 (2)
 **3**	2071 2026	1.27 (t, J = 7.0 Hz, 6 H, CH_2CH_3)[c] 3.50 (m, 4 H, CH_2CH_3) 5.70 (s, 5 H, C_5H_5)	147.8 (s)
 **6**	2018 1962	1.13 (t, J = 7.0 Hz, 6 H, CH_2CH_3) 1.75 (d, J = 8.0 Hz, 3 H, PCH_3) 3.09 (m, 4 H, CH_2CH_3) 4.96 (s, 5 H, C_5H_5)	107.1 (s)
 **7**[d]	2022 1968	1.10 (t, J = 7.0, 12 Hz, CH_3) 3.07 (m, 8 H, CH_2) 4.93 (s, 5 H, C_5H_5)	98.2 (s)

[a] In CH_2Cl_2. [b] In $CDCl_3$. [c] In acetone-d_6. [d] See ref 2d.

These results stimulated us to attempt the reaction of transition-metal phosphorane complexes with BX_3. In this paper, we report the preparation of a chloro-substituted-phosphorane complex, $[Cp(CO)_2Fe\{P(O)(NEt_2)(Cl)\}]\cdot BCl_3$ (**3**), by the OMe/Cl substitution reaction of $Cp(CO)_2Fe\{P(O)(NEt_2)(OMe)\}$ (**1**) with BCl_3, where Cp stands for $\eta^5\text{-}C_5H_5$; we also determined its structural features by an X-ray analysis and its reactivity with some nucleophiles.

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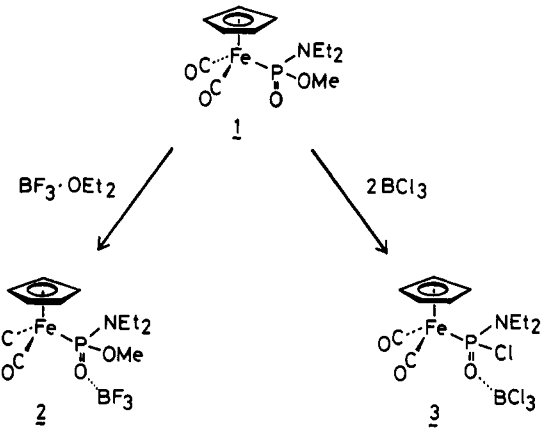
Scheme I



Results and Discussion

Reaction of Cp(CO)$_2$Fe{P(O)(NEt$_2$)(OMe)} (1) with BF$_3$·OEt$_2$. Treatment of Cp(CO)$_2$Fe{P(O)(NEt$_2$)(OMe)} (1) with BF$_3$·OEt$_2$ in THF gave a yellow oil (2). The spectroscopic data for 2 are given in Table I. The IR absorptions in the ν_{CO} region appeared at 2058 and 2008 cm^{-1}, which are 30 cm^{-1} higher than those of 1. The ^{1}H NMR spectral pattern of 2 is similar to that of 1, but all signals are observed at a field slightly lower than those for 1. The ^{31}P NMR resonance of 2 (131.6 ppm) is also observed at a field lower than that of 1 (103.3 ppm).

It has been reported that *fac*-[Mo(bpy)(CO)$_3${$\overline{\mathrm{PN(Me)CH_2CH_2N}}$Me(OMe)}] reacts with 2 equiv of BF$_3$·OEt$_2$ in CH$_2$Cl$_2$ at −78 °C to give *fac*-[Mo(bpy)(CO)$_3${$\overline{\mathrm{PN(Me)CH_2CH_2N}}$Me(OMe)}]·2BF$_3$ (eq 1), which exhibits IR

$$fac\text{-}[\mathrm{Mo(bpy)(CO)_3\{\overline{PN(Me)CH_2CH_2N}Me(OMe)\}}] \xrightarrow[-78\ ^\circ\mathrm{C}]{2\mathrm{BF_3\cdot OEt_2}} fac\text{-}[\mathrm{Mo(bpy)(CO)_3\{\overline{PN(Me)CH_2CH_2N}Me(OMe)\}}]\cdot 2\mathrm{BF_3} \quad (1)$$

signals in the ν_{CO} region at frequencies higher by 30–50 cm^{-1} than those of the starting complex.[5b] Therefore, 2 seems to be the adduct of 1 with BF$_3$ where BF$_3$ presumably interacts with the lone pair on the oxygen of the phosphoryl or methoxy group or on the nitrogen in 1. The adduct with the lone pair of the phosphoryl oxygen donated to BF$_3$, as depicted in Scheme I, is most likely (vide infra). Complex 2 was not changed either by further treatment with BF$_3$·OEt$_2$ or by refluxing in CH$_2$Cl$_2$.

Reaction of 1 with 2 Equiv of BCl$_3$. The treatment of 1 with BCl$_3$ in place of BF$_3$·OEt$_2$ was attempted. In this reaction, pale yellow crystals of 3 were obtained. Its IR spectrum showed patterns characteristic of two terminal carbonyl groups. The ^{1}H NMR spectrum showed that 3 has no OMe group. The ^{31}P NMR signal showed a singlet at 147.8 ppm, lower by 45 ppm than that for 1.

Molybdenum complexes containing a phosphite as a ligand react with 2 equiv of BF$_3$·OEt$_2$ to afford single OR/F exchange products (eq 2) and with 2 equiv of BCl$_3$ to give a double OR/Cl exchange product (eq 3).[5] In contrast,

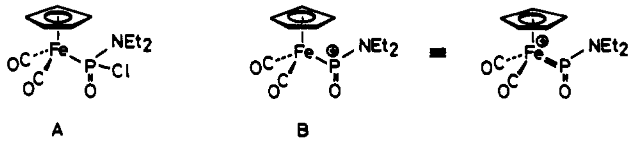
$$fac\text{-}[\mathrm{Mo(bpy)(CO)_3\{P(OR)_3\}}] \xrightarrow{2\mathrm{BF_3\cdot OEt_2}} fac\text{-}[\mathrm{Mo(bpy)(CO)_3\{P(OR)_2F\}}] \quad (2)$$

$$fac\text{-}[\mathrm{Mo(bpy)(CO)_3\{P(OMe)_3\}}] \xrightarrow{2\mathrm{BCl_3}} mer\text{-}[\mathrm{Mo(bpy)(CO)_3\{P(OMe)Cl_2\}}] \quad (3)$$

treatment of molybdenum complexes containing a chelated diaminophosphine as a ligand with 2 equiv of BF$_3$·OEt$_2$ or BCl$_3$ results in the formation of a cationic phosphenium complex (eq 4), where the OR group on a phosphorus is abstracted as an anion.[5b]

$$fac\text{-}[\mathrm{Mo(bpy)(CO)_3\{\overline{PN(Me)CH_2CH_2N}Me(OR)\}}] \xrightarrow{2\mathrm{BF_3\cdot OEt_2}\ \text{or}\ 2\mathrm{BCl_3}} fac\text{-}[\mathrm{Mo(bpy)(CO)_3\{\overline{PN(Me)CH_2CH_2N}Me\}}]^+ \quad (4)$$

On the basis of the above-mentioned experimental results on the molybdenum complexes and the spectroscopic data for 3, there are two possible structures for 3: A, which corresponds to the OR/Cl exchange product, and B, which corresponds to the OR$^-$ abstraction product.



X-ray Structure Determination of 3. In order to determine the structure of 3, an X-ray analysis was carried out. Crystal data are given in Table II. Figure 1 illustrates

Table II. Summary of Crystal Data for [Cp(CO)$_2$Fe{P(O)(NEt$_2$)Cl}]•BCl$_3$

formula	C$_{11}$H$_{15}$BCl$_4$FeNO$_3$P
cryst syst	monoclinic
space group	$P2_1/n$
cell const	
a, Å	9.080 (3)
b, Å	14.689 (3)
c, Å	14.363 (3)
β, deg	102.65 (2)
V, Å^3	1869.2 (8)
Z	4
D_{calcd}, g cm^{-3}	1.595
μ_{calcd}, cm^{-1}	14.7
cryst size, mm	0.40 × 0.30 × 0.09
radiation	Mo Kα (λ = 0.71069 Å), graphite monochromator
scan technique	ω
scan range, deg	$3 < 2\theta < 55$
no. of unique data	4820
no. of unique data, $F_o > 3\sigma(F_o)$	2337
R_1	0.064
R_2	0.065

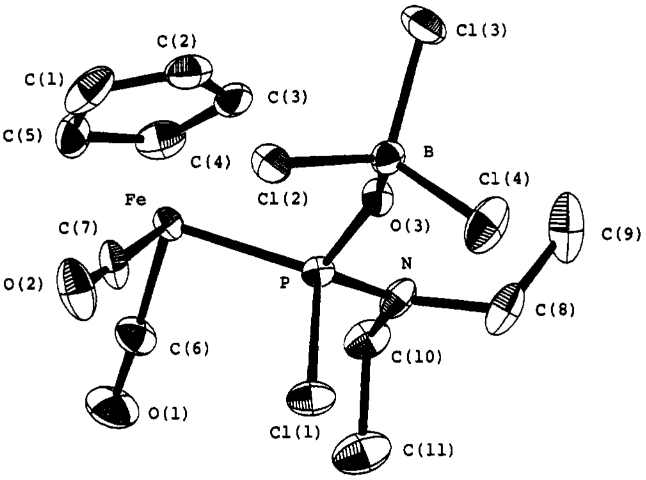


Figure 1. ORTEP drawing of the molecular structure of 3 with atomic labels. All hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 30% probability lebel.

Table III. Fractional Atomic Coordinates (×10^4) and Thermal Parameters (Å^2) for the Non-Hydrogen Atoms

atom	x	y	z	B_{eq}
Fe	1566 (1)	5957 (1)	2673 (1)	3.5
Cl(1)	3056 (3)	4545 (1)	1129 (2)	5.7
Cl(2)	4926 (3)	4152 (2)	3698 (2)	5.2
Cl(3)	7156 (3)	5692 (2)	4127 (2)	6.9
Cl(4)	7185 (3)	4425 (2)	2464 (2)	8.4
P	3381 (2)	5754 (1)	1908 (1)	3.3
O(1)	−890 (8)	5953 (6)	995 (5)	8.9
O(2)	1160 (8)	4016 (4)	2982 (6)	8.2
O(3)	4979 (5)	5638 (3)	2544 (4)	3.9
N	3662 (8)	6537 (4)	1156 (4)	4.4
C(1)	1482 (16)	6189 (7)	4098 (7)	8.0
C(2)	2874 (11)	6410 (8)	3959 (7)	6.6
C(3)	2719 (12)	7100 (7)	3307 (7)	6.5
C(4)	1186 (13)	7302 (6)	3009 (7)	6.3
C(5)	410 (12)	6755 (8)	3471 (8)	7.1
C(6)	93 (9)	5948 (7)	1644 (7)	5.4
C(7)	1345 (6)	4756 (6)	2860 (7)	5.5
C(8)	5069 (12)	6525 (7)	793 (7)	6.4
C(9)	6078 (14)	7303 (9)	1148 (11)	9.8
C(10)	2436 (11)	7101 (6)	610 (6)	5.5
C(11)	1640 (15)	6690 (8)	−339 (7)	8.3
B	5953 (11)	5014 (7)	3146 (6)	4.2

Table IV. Bond Distances (Å) and Angles (deg) with Estimated Standard Deviations in Parentheses

	Bond Distances		
Fe–P	2.193 (3)	C(3)–C(4)	1.398 (15)
Fe–C(1)	2.091 (11)	C(4)–C(5)	1.344 (16)
Fe–C(2)	2.071 (9)	P–O(3)	1.545 (5)
Fe–C(3)	2.079 (10)	P–Cl(1)	2.085 (3)
Fe–C(4)	2.079 (12)	P–N	1.636 (7)
Fe–C(5)	2.083 (10)	N–C(8)	1.486 (14)
Fe–C(6)	1.759 (8)	N–C(10)	1.472 (11)
Fe–C(7)	1.802 (9)	C(8)–C(9)	1.490 (16)
C(6)–O(1)	1.145 (10)	C(10)–C(11)	1.525 (13)
C(7)–O(2)	1.119 (11)	B–O(3)	1.428 (10)
C(1)–C(2)	1.365 (18)	B–Cl(2)	1.853 (11)
C(1)–C(5)	1.434 (15)	B–Cl(3)	1.870 (9)
C(2)–C(3)	1.364 (15)	B–Cl(4)	1.854 (11)
	Bond Angles		
P–Fe–C(6)	95.5 (3)	N–C(10)–C(11)	113.9 (8)
P–Fe–C(7)	93.6 (3)	P–O(3)–B	143.8 (5)
C(6)–Fe–C(7)	91.6 (4)	O(3)–B–Cl(2)	113.3 (6)
Fe–C(6)–O(1)	178.1 (9)	O(3)–B–Cl(3)	107.2 (6)
Fe–C(7)–O(2)	177.6 (9)	O(3)–B–Cl(4)	110.2 (6)
O(3)–P–Fe	115.5 (2)	Cl(2)–B–Cl(3)	107.9 (5)
O(3)–P–N	101.9 (3)	Cl(2)–B–Cl(4)	109.1 (5)
O(3)–P–Cl	103.1 (2)	Cl(3)–B–Cl(4)	109.1 (5)
N–P–Cl(1)	105.6 (3)	C(1)–C(2)–C(3)	108.6 (9)
C(8)–N–P	119.8 (6)	C(2)–C(3)–C(4)	108.5 (10)
C(10)–N–P	122.6 (6)	C(3)–C(4)–C(5)	108.2 (9)
C(8)–N–C(10)	115.4 (7)	C(4)–C(5)–C(1)	107.7 (10)
N–C(8)–C(9)	112.2 (9)	C(5)–C(1)–C(2)	107.0 (10)

the structure with atom labels. The final atomic coordinates for non-hydrogen atoms are given in Table III. Intramolecular bond distances and bond angles, with estimated standard deviations, are listed in Table IV.

The X-ray results revealed that **3** is an adduct of the iron chloroaminophosphorane complex with BCl_3 through the phosphoryl oxygen. The Fe–P bond distance (2.193 (3) Å) falls in the range of normal Fe–P single-bond lengths, and the P–Cl bond is a covalent bond.[6] The P–O(3) bond (1.545 (5) Å) is slightly longer than those in $Cp(CO)_2Fe\{P(O)(CF_3)_2\}$ (1.478 Å),[7] $Cp(CO)_2Fe\{P(O)(OEt)_2\}$ (1.495 Å),[1p] and $[Cp(CO)_2Fe\{P(O)(NEt_2)_2\}]_2FeCl_2$ (1.514 Å),[2a] and the B–Cl bonds (average 1.859 Å) are longer than those for free BCl_3 (1.75 Å), due to the interaction of the phosphorus oxygen with an electron-deficient BCl_3 molecule.

The chlorophosphorane complex **3** can be regarded as a piano-stool complex, as are other $Cp(CO)_2Fe$(phosphorane) type complexes: $Cp(CO)_2Fe\{P(O)(CF_3)_2\}$,[7] $Cp(CO)_2Fe\{P(O)(OEt)_2\}$,[1p] and $[Cp(CO)_2Fe\{P(O)(NEt_2)_2\}]_2FeCl_2$.[2a] The nitrogen atom of **3** is nearly planar,[8] which is consistent with the fact that at least one of the nitrogen atoms directly bonded to a phosphorus atom has a trigonal-planar geometry irrespective of the phosphorus valency and the coordination number.[2a]

Removal of BCl_3 from 3. The BCl_3 molecule in **3** is tightly bonded to the phosphoryl oxygen in noncoordinating solvents such as CH_2Cl_2. However, the BCl_3 molecule can be removed to give BCl_3-free $Cp(CO)_2Fe\{P(O)(NEt_2)Cl\}$ (**4**) by a 1-h reflux in a coordinating solvent such as THF. ^{31}P NMR spectroscopy for **3** just dissolved in THF shows a singlet at 150.8 ppm corresponding to the chemical shift (147.8 ppm) observed in CH_2Cl_2, indicating that the adduct form is kept in THF. The solution after a 1-h reflux showed an intense singlet at 127.3 ppm with a very weak singlet at 150.8 ppm. The former signal is attributed to **4** (eq 5). The BCl_3 molecule in **3** can be removed to give

$$\underset{\mathbf{3}}{Cp(CO)_2Fe\{P(O)(NEt_2)(Cl)\}\cdot BCl_3} \xrightarrow[\text{in THF}]{\Delta} \underset{\mathbf{4}}{Cp(CO)_2Fe\{P(O)(NEt_2)(Cl)\}} + THF\cdot BCl_3 \quad (5)$$

4 even in CH_2Cl_2 by adding a Lewis base such as an amine. A CH_2Cl_2 solution of **3** with a 25-fold excess of NEt_3 showed a singlet at 126.0 ppm due to **4** in the ^{31}P NMR spectrum (eq 6).

$$\underset{\mathbf{3}}{Cp(CO)_2Fe\{P(O)(NEt_2)(Cl)\}\cdot BCl_3} \xrightarrow[\text{in } CH_2Cl_2]{\text{excess } NEt_3} \underset{\mathbf{4}}{Cp(CO)_2Fe\{P(O)(NEt_2)(Cl)\}} + NEt_3\cdot BCl_3 \quad (6)$$

The difference in ^{31}P NMR chemical shifts between **3** and **4** is 23.5 ppm in THF and 21.8 ppm in CH_2Cl_2. The corresponding difference between **1** and **2** is 28.3 ppm; thus, **2** may be assigned to the adduct of **1** with BF_3 through the phosphoryl oxygen.

Reaction of 1 with 1 Equiv of BCl_3. The OMe/Cl exchange for **1** takes place in the reaction with 2 equiv of BCl_3, whereas the exchange does not occur with 1 equiv of BCl_3. We attempted to elucidate what happens in the reaction of **1** with 1 equiv of BCl_3. The CH_2Cl_2 solution containing **1** and 1 equiv of BCl_3 prepared at −78 °C was subjected to ^{31}P NMR measurement. The spectrum showed two intense signals at 108.2 ppm (assigned to **1**) and 131.2 ppm with almost equal intensity and two weak unidentified singlets at 137.1 and 137.7 ppm. The difference between the two intense signals is 23.0 ppm, close to the difference between **3** and **4**. Thus, the signal at 131.2 ppm is attributed to an adduct of **1** with BCl_3 through the phosphoryl oxygen, **5** (eq 7). Raising the temperature of

$$\underset{\mathbf{1}}{Cp(CO)_2Fe\{P(O)(NEt_2)(OMe)\}} + BCl_3 \rightleftharpoons \underset{\mathbf{5}}{Cp(CO)_2Fe\{P(O)(NEt_2)(OMe)\}\cdot BCl_3} \quad (7)$$

the solution caused broadening of the two singlets with coalescence at 27 °C. Cooling the solution reproduced the

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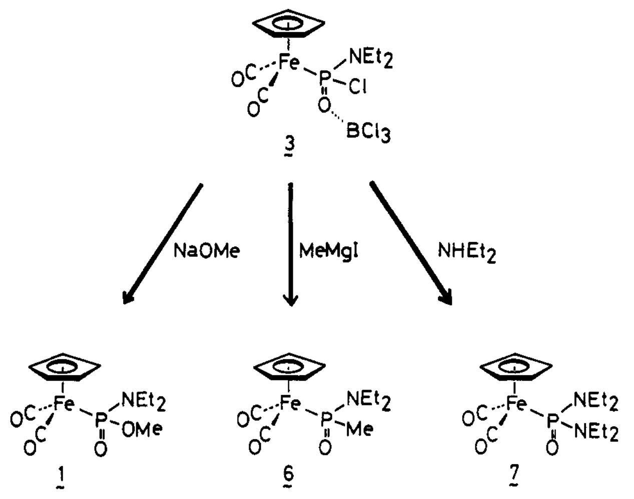
[6] The P–Cl bond distance is not known for chlorophosphorane complexes but is known for the iron chlorophosphide complex $(\eta^5\text{-}C_5Me_5)(CO)_2Fe\{P(CMe_3)Cl\}$: Malisch, W.; Angerer, W.; Cowley, A. H.; Norman, N. C. *J. Chem. Soc., Chem. Commun.* **1985**, 1811.

[7] Barrow, M. J.; Sim, G. A. *J. Chem. Soc., Dalton Trans.* **1975**, 291.

[8] The angle of C(8)–N–C(10) in the Newman projection down the N–P bond is 162.3°. If the nitrogen atom were ideally planar, the angle should be 180°.

Scheme II



two intense singlets at 108.2 and 131.2 ppm, indicating that **5** is in equilibrium with **1** in CH_2Cl_2. The adduct of **1** with BF_3, i.e., **2**, is stable in CH_2Cl_2 at room temperature, while the adduct with BCl_3, i.e., **5**, is in equilibrium with **1**. This indicates that the acceptor ability toward the phosphoryl oxygen of **1** is stronger for BF_3 than for BCl_3.

Brown and Holmes reported that the acceptor properties increase in the order $BF_3 < BCl_3 < BBr_3$.[9] The reason for the reversed order obtained here is not clear now, but one possible explanation is on steric grounds. The phosphoryl phosphorus in **1** has relatively bulky groups such as $Cp(CO)_2Fe$, NEt_2, and OMe, and BCl_3 is bulkier than BF_3 (the bond distances of B–Cl in BCl_3 and B–F in BF_3 are 1.75 and 1.30 Å, respectively[10]). Thus, the Lewis acid–base interaction between **1** and BCl_3 may suffer some steric repulsion, which makes the $P{=}O{\cdots}BCl_3$ bond weak.

The treatment of **1** with 1 equiv of BCl_3 does not promote the OMe/Cl exchange reaction, while that with 2 equiv of BCl_3 does. Therefore, **3** may be formed by the reaction of **5** with BCl_3; that is, the replacement of the OMe group of **1** by Cl requires two BCl_3 molecules, as was shown in the previous report on Mo complexes having phosphite ligands.[5]

Reaction of 3 with Lewis Bases. After the iron chloroaminophosphorane complex was isolated as detailed above, its reactivity was examined. Described here are the reactions with OMe^-, Me^-, and $NHEt_2$ as typical nucleophiles (Scheme II).

Treatment of **3** with 2.5 equiv of NaOMe in methanol at room temperature gave **1** in 84% yield, where the Cl atom on phosphorus is replaced by an OMe group. The substitution of the Cl atom in **3** by a methyl group was attempted in the reactions with MeMgI and MeLi. Treatment with 3 equiv of MeMgI in THF at −78 °C led to the isolation of $Cp(CO)_2Fe\{P(O)(NEt_2)(Me)\}$ (**6**) in 56% yield, whereas the reaction with MeLi in THF at −78 °C caused a complicated reaction. Thus, a Grignard reagent seems to be an adequate alkylating reagent for **3**. Reflux of the THF solution of **3** in the presence of excess $NHEt_2$ caused the formation of $Cp(CO)_2Fe\{P(O)(NEt_2)_2\}$ (**7**) in 75% yield accompanied by the formation of an ammonium salt, NH_2Et_2Cl. As was mentioned above, the Cl atom on the phosphorus of **3** is readily replaced by OMe, Me, and NEt_2 groups; thus, it can be said that **3** is a good precursor to obtain a substituted-phosphorane complex.

Experimental Section

General Remarks. All reactions were carried out under dry nitrogen by using Schlenk-tube techniques. Hexane and THF were distilled from sodium metal, dichloromethane was distilled from P_2O_5, and methanol was dried over molecular sieves (Type 4A) and then distilled. All solvents were stored under a nitrogen atmosphere. $BF_3{\cdot}OEt_2$ and BCl_3 (hexane solution) purchased were used without further purification. $Cp(CO)_2Fe\{P(O)(NEt_2)(OMe)\}$ (**1**) was prepared by the reported method.[2b]

IR spectra were recorded on a Shimadzu FTIR-4000 spectrometer. NMR spectra were recorded on a JEOL PMX-60 spectrometer for ^1H spectra with $(CH_3)_4Si$ as an internal standard and on a JEOL FX-100 spectrometer for ^{31}P spectra with 85% H_3PO_4 as an external standard.

The complexes **2**, **3**, and **6**, prepared in the course of this work, were so air-sensitive that the correct elemental analysis data could not be obtained, though satisfactory spectroscopic data were obtained.

$[Cp(CO)_2Fe\{P(O)(NEt_2)(OMe)\}]{\cdot}BF_3$ (2). A solution of **1** (41 mg, 0.13 mmol) in THF (3 mL) was cooled at −78 °C, and then $BF_3{\cdot}OEt_2$ (15.6 μL, 0.13 mmol) was added. The reaction mixture was warmed to room temperature. The solvent was removed under reduced pressure to give **2** as a yellow oil, yield 37 mg (75%).

$[Cp(CO)_2Fe\{P(O)(NEt_2)Cl\}]{\cdot}BCl_3$ (3). To a solution of **1** (263 mg, 0.81 mmol) in CH_2Cl_2 (25 mL) was added BCl_3 (1.6 mL of BCl_3, 1.0 M hexane solution, 1.6 mmol). The reaction mixture was stirred for 1 h at room temperature. The solvent was removed under reduced pressure. CH_2Cl_2 (15 mL) was added to the residue, and the solution was filtered to remove some insoluble materials. The solvent was removed from the filtrate under reduced pressure to give pale yellow crystals (**3**) as a crude product; yield 361 mg (100%). The complex was recrystallized from CH_2Cl_2/hexane to obtain single crystals for X-ray analysis.

Reaction of 3 with NaOMe. To a solution of **3** (125 mg, 0.28 mmol) in MeOH (20 mL) was added NaOMe (38 mg, 0.70 mmol). After 10 min of stirring at room temperature, the solvent was removed under reduced pressure. The residue was dissolved in CH_2Cl_2 (20 mL) and the solution was filtered to remove unreacted NaOMe. The solvent was removed from the filtrate under reduced pressure to give a yellow oil, which was purified by passing through a silica gel column to give **1**, yield 77 mg (84%).

Reaction of 3 with MeMgI. A solution of **3** (679 mg, 1.51 mmol) in THF (20 mL) was cooled to −78 °C, and an ether solution (5 mL) containing MeMgI (4.75 mmol) was added. The mixture was warmed to room temperature. After filtration to remove some insoluble materials, the filtrate was put on an alumina column and eluted with CH_2Cl_2/MeCOOEt (4/1) and CH_2Cl_2/MeCOOEt/EtOH (6/1/1) in that order. The band eluted with the last eluent was collected, and the solvents were removed under reduced pressure to give **6** as a brown oil (263 mg, 0.85 mmol, 56%).

Reaction of 3 with $NHEt_2$. To a solution of **3** (198 mg, 0.44 mmol) in THF (15 mL) was added $NHEt_2$ (0.5 mL, 4.38 mmol). The solution was refluxed for 1 h. After removal of $NHEt_2{\cdot}HCl$ by filtration, the solution was loaded on an alumina column and eluted with EtOH. Removal of the solvent in the yellow eluate gave **7** (122 mg, 0.33 mmol, 75%). Anal. Calcd for $C_{15}H_{25}FeN_2O_3P$: C, 48.93; H, 6.84; N, 7.61. Found: C, 48.74; H, 6.81; N, 7.55.

X-ray Data Collection, Structure Determination, and Refinement. A single crystal of **3** was sealed under N_2 in a thin-walled glass capillary. Determination of cell constants and collection of intensity data were carried out on a Syntex R3 diffractometer with Mo Kα radiation. The space group was determined as $P2_1/n$. Unit cell constants were determined by the least-squares refinement of 25 reflections. Three reference reflections monitored after every cycle of 200 measurements showed no significant variation in intensity during the data collection. Of 4820 unique reflections measured, 2337 reflections with $|F_o| > 3\sigma(|F_c|)$ were used for the structure determination. The data were corrected for Lorentz-polarization factors, but no absorption correction was applied (μ(Mo Kα) = 14.7 cm^{-1}).

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The position of the Fe atom was determined by direct methods (MULTAN 78).[11] All other computations were carried out by use of the Universal Crystallographic Computation Program System, UNICS III.[12] Subsequent difference Fourier maps revealed the positions of the remaining non-hydrogen atoms. After all the non-hydrogen atoms had been refined isotropically, a series of refinements with anisotropic thermal parameters for all non-hydrogen atoms reduced R_1 ($\sum(|F_o| - |F_c|)/\sum|F_o|$) to 0.078 and R_2 ($[\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$) to 0.081. All hydrogen atoms were placed at idealized positions. In the final stage, non-hydrogen atoms were refined anisotropically, including hydrogen atoms whose positions were fixed (B = 4.0 Å^2). In the final refinement R_1 converged to 0.064 and R_2 to 0.065: unit weighting was used. All atomic scattering factors were taken from Cromer and Weber.[13] All the computations, including the ORTEP drawing,[14] were carried out by a HITAC M-680H computer at the Hiroshima University Information Processing Center.

Acknowledgment. We thank Mr. Akira Mizuno and Mr. Yoshihisa Toda at the Materials Science & Analysis Laboratories, Mitsui Petrochemical Industry, Ltd., for ^{31}P NMR measurements. We acknowledge financial support from the Ministry of Education under Grant No. 01470052 and 02640479.

Supplementary Material Available: Tables of calculated hydrogen atom parameters and anisotropic thermal parameters for 3 (Tables V and VI) (2 pages); a listing of observed and calculated structure factors (Table VII) (12 pages). Ordering information is given on any current masthead page.

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Bonding Mode of Nitrogen Heterocyclic Ligands to (η^5-Cyclopentadienyl)ruthenium Cation and Reactivity Studies of the Nitrogen and π-Bonded Complexes: Mechanistic Aspects of a Nitrogen to π Rearrangement

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Received August 10, 1990

The nitrogen heterocyclic ligands pyridine (**1**), 2-methylpyridine (**2**), 2,4-dimethylpyridine (**3**), 2,4,6-trimethylpyridine (**4**), quinoline (**5**), isoquinoline (**6**), 2-methylquinoline (**7**), and 1,2,3,4-tetrahydroquinoline (**8**) were reacted with (η^5-cyclopentadienyl)ruthenium cation, $[CpRu(CH_3CN)_3](PF_6)$, to ascertain the mode of bonding as a function of structure, i.e., nitrogen (η^1(N)) versus π (η^6) bonding. Ligands **1**–**3**, **5**, and **6** formed N-bonded complexes, while **4**, **7**, and **8** only formed π-bonded complexes. Thus, it appears that steric and electronic effects influence the bonding mode of nitrogen heterocyclic compounds to CpRu$^+$. An interesting N (η^1) to π (η^6) rearrangement occurred with the N-bonded CpRu$^+$ complexes of ligands **2**, **3**, and **5**, and mechanistic aspects were studied by ^{1}H NMR spectroscopy. Crossover experiments with $[CpRu(\eta^1(N)\text{-2-methylpyridine})(CH_3CN)_2]^+$ (**11**) and $[MeCpRu(\eta^1(N)\text{-2-methylpyridine-}d_7)(CH_3CN)_2]^+$ (**21**-d_7) clearly show that N(η^1)-bonded complexes undergo ligand exchange much faster than the N to π rearrangement at 21 °C (NMR probe temperature). Furthermore, neither N- and π-bonded complexes nor π- and π-bonded complexes undergo ligand exchange with each other; however, both types of bonding modes did undergo facile exchange with free nitrogen ligand. These exchange reaction rates were found to be concentration-dependent. Consequently, our attempts to use the former result with N- and π-bonded complexes to prove the intramolecular nature of the N to π rearrangement, i.e., rearrangement of **11** in the presence of $[MeCpRu(\eta^6\text{-2-methylpyridine-}d_7)]^+$ (**22**-d_7), were not successful; exchange of any free **2** that might form, i.e., at low concentrations, with **22**-d_7 was found to be slower than the N to π rearrangement. The role of the acetonitrile ligand in the N to π rearrangement and in the displacement of η^1- and η^6-bonded nitrogen heterocyclic ligands will also be discussed.

The bonding mode of nitrogen heterocyclic ligands to rhodium and ruthenium complexes that act as homogeneous catalysts has been of considerable interest due to its pivotal role in the regioselective hydrogenation of the nitrogen-containing ring of these model coal compounds.[1] We recently communicated our initial results on the bonding mode of polynuclear heteroaromatic nitrogen ligands with (η^5-pentamethylcyclopentadienyl)rhodium dicationic complexes (Cp*Rh^{2+}) and (η^5-cyclopentadienyl)ruthenium cationic complexes (CpRu$^+$), i.e., nitrogen (N) versus π bonding, and have shown that the regioselectivity of nitrogen ring reduction is in fact dependent on the ligand being N-bonded to the Rh or Ru metal centers.[2]

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