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Structural studies of iron phosphonate complex, (.eta.5-C5H5)(CO)2FeP(O)(OEt)2, and its reactivity

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Table V. Intramolecular Nonbonded Distances (Å) Involving Alkyne Substituents in 5a[a]

C(6)···C(1)	3.259 (5)	C(9)···C(1)	3.456 (5)
O(1)	3.745 (5)	C(2)	3.451 (5)
C(4)	3.223 (6)	C(4)	3.797 (5)
O(4)	3.624 (5)		
C(5)	3.183 (5)	C(10)···C(2)	3.536 (5)
O(5)	3.581 (6)	O(2)	3.752 (5)
		C(19)	3.726 (6)

[a] Only distances shorter than 3.9 Å are given.

analogue so far reported, $\mathrm{Cp(CO)_2}\overline{\mathrm{Mo(\mu\text{-}CF_3C_2CF_3)Co}}\mathrm{(CO)_3}$,[23] the alkyne C–C distance (1.371 (7) Å) compares well with the C(7)–C(8) bond length of 1.381 (5) Å in **5a**, in spite of the different electron-withdrawing character of the two alkynes. The C–C–CF_3 bond angles (average 133.7 (1)°) in the MoCo complex are significantly narrower than the C–C–Ph and C–C–Me angles (136.0 (3) and 139.1 (4)°, respectively) in **5a**. However, all of these values are in the typical ranges of bond lengths (1.3–1.4 Å) and angles (130–150°) found in binuclear complexes in which the metal–metal bond is transversely spanned by an alkyne ligand.[27]

As expected from intramolecular steric interactions, the Cp ring is forced to the side opposite the alkyne ligand, which in turn adopts the usual cis-bent structure. The atoms C(6), C(9) and C(7), C(14) are nearly eclipsed (torsion angles C(6)–C(7)–C(8)–C(9) = –9.6° and C(7)–C(8)–C(9)–C(14) = 0.7°).

This brings us to the most noteworthy structural aspect of the molecule, namely, the orientation of the PhC_2Me fragment with respect to the rigid dimetal moiety. Of the two possible isomers, i.e. one with Me trans to Cp and the other with Me cis to Cp, only the former is present in the crystal, together with its enantiomer. One might think that this arrangement derives from intraligand steric repulsions; however, inspection of nonbonded distances involving the alkyne substituents (Table V) shows that the Me carbon atom C(6) forms closer contacts than the Ph carbon atom C(9). The Me group is nestled among C(1), C(4), and C(5) at a short distance of 3.22 Å (av). Models indicate that transposition of the Me and Ph groups should relieve these repulsive steric interactions. Since there is no electronic reason for the observed geometry, it may be that the trapping of the Me group stabilizes this isomer or that its formation is kinetically favored.

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Registry No. **1a**, 111635-09-7; **1b**, 111635-10-0; **2**, 111635-11-1; **3a**, 111635-12-2; **3b**, 111635-13-3; 4, 111635-14-4; **5a**, 111635-15-5; **5a**-*d*, 111689-07-7; **5b**, 111635-16-6; **5b**-*d*, 111635-18-8; **6**, 111635-17-7; $CpFe(CO)_2CH_2C{\equiv}CPh$, 33114-75-9; $Co_2(CO)_8$, 10210-68-1; $CpFe(CO)_2CH_2C{\equiv}CMe$, 34822-36-1; $Mn(CO)_5CH_2C{\equiv}CPh$, 23626-46-2; $CpW(CO)_3CH_2C{\equiv}CPh$, 32993-03-6; $Co(O_2CCF_3)_2$, 6185-58-6; $\mathrm{(CO)_3}\overline{\mathrm{Co(\mu\text{-}PC_2Me)Co}}\mathrm{(CO)_3}$, 53556-74-4; $CpW(CO)_3CH_2C{\equiv}CMe$, 32877-63-7; $CpMo(CO)_3CH_2C{\equiv}CPh$, 32877-62-6; $CpFe(CO)_2OC(O)CF_3$, 37048-23-0.

Supplementary Material Available: Listings of anisotropic thermal parameters and hydrogen atom coordinates for complex **5a** (3 pages); a listing of structure factors for complex **5a** (16 pages). Ordering information is given on any current masthead page.

Structural Studies of Iron Phosphonate Complexes, $(\eta^5\text{-}C_5H_5)(CO)_2FeP(O)(OEt)_2$, and Its Reactivity

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The structure of $(\eta^5\text{-}C_5H_5)(CO)_2FeP(O)(OEt)_2$ has been determined by X-ray diffraction. It crystallized in the triclinic space group $P\bar{1}$ with unit cell parameters a = 15.494 (4) Å, b = 13.668 (3) Å, c = 7.890 (2) Å, α = 85.78 (2)°, β = 80.26 (2)°, γ = 64.77 (1)°, and D_{calcd} = 1.464 g cm^{-3} for Z = 4. One of the main features of the molecule of the complex is the unequal coordination of the two carbonyl groups: one is trans and the other is gauche to the phosphoryl group in the Newman projection along the P–Fe bond and the bond length between Fe and CO is shorter in the trans CO than in the gauche CO. Thus, the trans CO is linked to the Fe atom more strongly than the gauche CO. ^{13}C NMR measurements in a chloroform at room temperature revealed that the two carbonyl groups can be resolved. The carbonyl groups of the complex cannot be displaced by $P(n\text{-}Bu)_3$ or $P(OEt)_3$ under refluxing conditions in benzene and cannot be oxidized to CO_2 by Me_3NO. The iron phosphonate complex reacts readily with a Lewis acid, R^+ (R^+ = Me^+, CPh_3^+, H^+), to afford the corresponding iron phosphite complex, $[(\eta^5\text{-}C_5H_5)(CO)_2FeP(OR)(OEt)_2]^+$.

Introduction

Transition-metal phosphonate complexes are of interest because the pentavalent phosphorus atom is covalently bonded to the transition metal. Phosphonate complexes are usually prepared by reacting trialkyl phosphite, $P(OR)_3$, with complexes containing a labile nucleophilic ligand, X (eq 1).[4]

$$L_nM\text{–}X + P(OR)_3 \rightarrow L_nM\text{–}P(O)(OR)_2 + RX \quad (1)$$

Although the reaction mechanism of the Arbuzov-like dealkylation reaction has been investigated,[5,6] X-ray

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(4) See, e.g.; Brill, T. B.; Landon, S. J. *Chem. Rev.* 1984, *84*, 577.

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structural studies of phosphonate complexes are limited to Hg, Co, Cr, and Pt complexes, $Hg\{P(O)(OEt)_2\}_2$, $HgCl\{P(O)(OEt)_2\}$,[7] $Cp\{P(OMe)_3\}Co\{P(O)(OMe)_2\}_2$,[8] $Cp(dppe)Co\{P(O)(OMe)_2\}^+$,[9] $Cp(CO)_2Cr\{P(OMe)_3\}\{P(O)(OMe)_2\}$,[10] and $Pt\{P(OH)(OMe)_2\}_2\{P(O)(OMe)_2\}_2$,[11] where Cp and dppe stand for a η^5-cyclopentadienyl group and bis(diphenylphosphino)ethane, respectively. In addition, the reactivity of transition-metal phosphonate complexes is not well-known.

In this paper, we focus on the iron phosphonate complex $Cp(CO)_2Fe\{P(O)(OEt)_2\}$ (1). We report its structure in the solid state as determined by X-ray analysis and in solution by NMR measurements as well as some reactivity studies.

Experimental Section

General Remarks. All reactions were carried out under an atmosphere of dry nitrogen. All solvents used were purifed by distillation: Et_2O, THF, benzene, and hexane were distilled from sodium metal, CH_2Cl_2 was distilled from P_2O_5, and acetone was dried with anhydrous $CaSO_4$ and distilled. All solvents were stored under a nitrogen atmosphere. CF_3SO_3H, Ph_3CPF_6, and Me_3OSbCl_6 were purchased from Aldrich. Ph_3CPF_6 was recrystallized according to the literature method.[12] CF_3SO_3H and Me_3OSbCl_6 were used without further purification.

IR spectra were recorded on a Shimadzu FTIR-4000 spectrometer. JEOL PMX-60 and JEOL FX-100 spectrometers were used to obtain ^1H NMR and ^{31}P NMR spectra, respectively. ^{13}C NMR spectra were measured on a JEOL GX-270 (67.8 MHz) and a Hitachi R-42 (22.6 MHz) spectrometers. ^1H NMR and ^{13}C NMR data were referred to $(CH_3)_4Si$ and ^{31}P NMR data was referred to 85% H_3PO_4.

Preparation of $[Cp(CO)_2FeP(O)(OEt)_2]$ (1). Complex 1 was prepared according to the literature method[13] with some modification. To $[CpFe(CO)_2Cl]$ (9.0 g, 42.4 mmol) dissolved in 100 mL of C_6H_6 was added $P(OEt)_3$ (7.3 mL, 7.1 g, 42.6 mmol). The solution was stirred for 4 days at room temperature. An yellowish brown powder was formed that was filtered off. The filtrate was put on a silica gel column and eluted with a 2:2:1 mixture of acetone/Et_2O/CH_2Cl_2 and then eluted with EtOH. The yellow fraction eluted with EtOH was collected and vacuum dried. The yellowish brown oil obtained was extracted with hexane. Upon concentration of the hexane extract, complex 1 was deposited as a yellow powder (5.7 g, 18.1 mmol, 43%). Data: IR (cm^{-1}, C_6H_6) ν_{CO} 2035 s, 1985 s; ^1H NMR (δ, acetone-d_6) 5.20 (s, 5 H), 3.97 (m, 4 H), 1.22 (t, $J = 6.8$ Hz, 6 H); ^{31}P NMR (δ, acetone) 89.94 (s); ^{13}C NMR (δ, $CDCl_3$) 211.47 (d, $J = 40.9$ Hz), 85.82 (s), 59.85 (d, $J = 8.5$ Hz), 16.63 (d, $J = 6.7$ Hz).

Anal. Calcd for $C_{11}H_{15}FeO_5P$: C, 42.27; H, 4.80. Found: C, 42.36; H, 4.87.

Reaction of 1 with Me_3OSbCl_6. To a solution of 1 (90 mg, 0.287 mmol) in 7 mL of CH_2Cl_2 was added Me_3OSbCl_6 (120 mg, 0.303 mmol). The mixture was stirred for 5 h at room temperature. The resulting yellow homogeneous solution was concentrated to 3 mL. Addition of 5 mL of hexane afforded a yellow oil which was washed with hexane and redissolved in 3 mL of CH_2Cl_2. The resulting solution was filtered to remove some insoluble materials and concentrated to ca. 1 mL. Hexane (2.5 mL) was added to give a bright yellow powder which was washed with hexane and dried in vacuo: yield 166 mg (0.250 mmol, 83%) of $[Cp(CO)_2FeP(OMe)(OEt)_2]\cdot SbCl_6$ ($2\cdot SbCl_6$).

Table I. Summary of Crystal Data, Intensity Collection, and Structure Solution and Refinement for $Cp(CO)_2FeP(O)(OEt)_2\bullet H_2O$

formula	$C_{11}H_{17}FeO_6P$
cryst system	triclinic
space group	$P\bar{1}$
cell constants	
a, Å	15.494 (4)
b, Å	13.668 (3)
c, Å	7.980 (2)
α, deg	85.78 (2)
β, deg	80.26 (2)
γ, deg	64.77 (1)
V, Å^3	1506.9 (6)
Z	4
D_{calcd}, g cm^{-3}	1.464
μ_{calcd}, cm^{-1}	4.9
cryst size, mm	0.25 × 0.30 × 0.18
radiatn	Mo Kα ($\lambda = 0.71073$ Å) graphite monochromator
scan technique	ω–2θ
scan range	$2° < 2\theta < 55°$
scan rate, deg min^{-1}	16
unique data	6925
unique data, $F_o > 3\sigma(F_o)$	4820
R_1	0.063
R_2	0.063

Anal. Calcd for $C_{12}H_{18}Cl_6FeO_5PSb$ ($2\cdot SbCl_6$): C, 25.87; H, 3.26. Found: C, 25.92; H, 3.18.

Reaction of 1 with Ph_3CPF_6. To a solution of 1 (81 mg, 0.258 mmol) in 5 mL of CH_2Cl_2 was added Ph_3CPF_6 (103 mg, 0.264 mmol). The mixture was stirred overnight at room temperature. The color of the mixture changed from light yellow to green. The solvent was removed under reduced pressure to give $[Cp(CO)_2FeP(OCPh_3)(OEt)_2]\cdot PF_6$ ($3\cdot PF_6$) (181 mg) as a yellow oil in quantitative yield.

Anal. Calcd for $C_{30}H_{30}F_6FeO_5P_2$ ($3\cdot PF_6$): C, 51.30; H, 4.31. Found: C, 51.04; H, 4.22.

Reaction of 1 with CF_3SO_3H. To a solution of 1 (110 mg, 0.351 mmol) in 4 mL of C_6H_6 was added 70 μL (120 mg, 0.791 mmol) of CF_3SO_3H. A brown oil formed immediately. The mixture was stirred for 2 h at room temperature, and the oil part was washed several times with benzene and was dried under vacuum to afford $[Cp(CO)_2FeP(OH)(OEt)_2]\cdot CF_3SO_3$ ($4\cdot CF_3SO_3$) in quantitative yield. Attempts to isolate the product in the solid state by adding Me_4NPF_6 or $NaBPh_4$ proved unsuccessful.

Anal. Calcd for $C_{12}H_{16}F_3FeO_8PS$ ($4\cdot CF_3SO_3$): C, 31.05; H, 3.47. Found: C, 30.62; H, 3.28.

X-ray Data Collection of $[Cp(CO)_2FeP(O)(OEt)_2]\cdot H_2O$ ($1\cdot H_2O$). Single crystals of $1\cdot H_2O$ were grown from hexane. The single crystal with the dimensions of 0.25 × 0.30 × 0.18 mm was sealed under N_2 in a thin-walled glass capillary and used for the data collection. The determination of cell constants and the intensity data collection were carried out at 20 °C on a Rigaku AFC-5 automated four-circle diffractometer with Mo Kα radiation made monochromatic by a graphite plate ($\lambda = 0.7107$ Å). No systematic absences suggested the space group $P\bar{1}$. The cell constants were determined by a least-squares method using 24 independent reflections with $22.2° < 2\theta < 28.6°$ and are recorded with other crystal data in Table I. Three reference reflections monitored after every cycle of 200 measurements showed no significant variation in intensity during the data collection. Out of 6925 unique reflections measured, 4820 reflections with $|F_o| > 3\sigma(|F_o|)$ were used for the structure determination. They were corrected for Lorentz-polarization factors, but no absorption correction was applied (μ(Mo Kα) = 4.9 cm^{-1}).

Structure Determination and Refinement. The position of the Fe atom was located by using the results of MULTAN direct-method analysis (MULTAN 78).[14] All other computations

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Table II. Fractional Atomic Coordinates ($\times 10^4$) and Thermal Parameters (Å^2) for the Non-Hydrogen Atoms

atom	x	y	z	B_{eq}
Fe1	2344 (1)	3044 (1)	2167 (1)	3.7
Fe2	2611 (1)	7002 (1)	6668 (1)	3.7
P1	1047 (1)	2732 (1)	2446 (2)	3.4
P2	3909 (1)	7136 (1)	7170 (2)	3.9
O1	3496 (4)	945 (4)	3469 (8)	8.2
O2	2735 (4)	2364 (5)	−1361 (6)	7.6
O3	263 (3)	3451 (3)	1474 (5)	4.4
O4	524 (3)	2781 (3)	4384 (4)	4.1
O5	1408 (3)	1484 (3)	1938 (5)	4.4
O6	1918 (5)	7224 (5)	10287 (6)	9.0
O7	1634 (4)	9276 (4)	5952 (9)	9.0
O8	4568 (3)	6248 (4)	8136 (6)	5.6
O9	4603 (3)	7242 (3)	5507 (5)	4.8
O10	3516 (3)	8280 (4)	8107 (6)	5.4
OW1	−797 (4)	5661 (4)	1813 (6)	6.8
OW2	4863 (4)	4099 (4)	8687 (6)	6.8
C1	3033 (4)	1774 (5)	2928 (9)	5.3
C2	2586 (5)	2624 (6)	2 (8)	5.5
C3	2197 (5)	3969 (5)	4266 (8)	5.6
C4	3089 (4)	3783 (5)	3188 (9)	5.5
C5	2854 (5)	4246 (6)	1623 (9)	5.8
C6	1852 (5)	4700 (5)	1711 (9)	5.5

were carried out by using the Universal Crystallographic Computation Program System, UNICS III.[15] Subsequent diffrence Fourier maps revealed the positions of the remaining non-hydrogen atoms. After all the non-hydrogen atoms were refined isotropically, a series of refinements using anisotropic thermal parameters for all non-hydrogen atoms reduced an R_1 value, $(|F_o| - |F_c|)/|F_o|$, to 0.0662 and R_2 value, $[(|F_o| - |F_c|)^2/|F_o|^2]^{1/2}$, to 0.0715. All hydrogen atoms except those of water were located from subsequent difference Fourier maps. All atoms except hydrogen atoms of water molecules were further refined, non-hydrogen atoms anisotropically and hydrogen atoms isotropically. A final refinement converged R_1 to 0.0632 and R_2 to 0.0626. All the atomic scattering factors were taken from Cromer and Waber.[16] The anomalous dispersion coefficients of Cromer and Liberman[17] were used for Fe and P. The final atomic coordinates for non-hydrogen and hydrogen atoms and the final thermal parameters are given in Tables II, III, and IV, respectively, according to the atom labels of Figure 1. (Tables III and IV are given in the supplementary material). Observed and calculated structure factors are listed in Table V (also supplementary material). All the computations including ORTEP drawings[18] were carried out by a HITAC M-200 computer at the Hiroshima University Information Processing Center.

Results and Discussion

Description of the Structure of [$Cp(CO)_2FeP(O)(OEt)_2$]$\cdot H_2O$. There are two crystallographically independent molecules in the asymmetric unit and two asymmetric units per cell giving $Z = 4$. An ORTEP drawing of the two molecules with atom labels is shown in Figure 1. In the figure, the thermal ellipsoids have been drawn to include 20% of the probability distribution. The structures of the two crystallographically independent molecules are basically identical. The only difference is the orientation of one of the ethyl groups. Intramolecular bond distances and bond angles, with estimated standard deviations, are listed in Table VI.

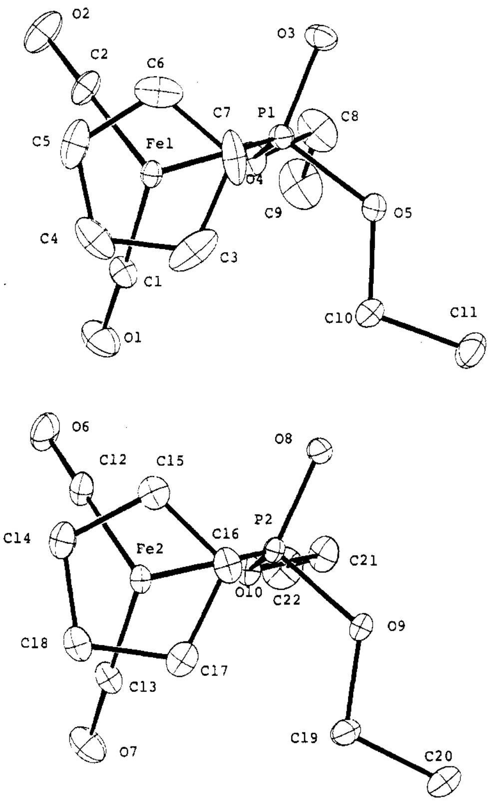

Figure 1. ORTEP drawings of the two crystallographically independent molecules in the asymmetric unit of $Cp(CO)_2FeP(O)(OEt)_2$ (1) showing labeling scheme (top, molecule 1; bottom, molecule 2). Thermal ellipsoids are drawn at 20% probability level.

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

Bond Distances			
Fe1–P1	2.199 (2)	Fe2–P2	2.199 (2)
Fe1–C1	1.734 (6)	Fe2–C12	1.764 (7)
Fe1–C2	1.789 (7)	Fe2–C13	1.735 (7)
Fe1–C3	2.096 (8)	Fe2–C14	2.059 (12)
Fe1–C4	2.109 (9)	Fe2–C15	2.057 (8)
Fe1–C5	2.098 (9)	Fe2–C16	2.076 (8)
Fe1–C6	2.083 (7)	Fe2–C17	2.079 (9)
Fe1–C7	2.097 (6)	Fe2–C18	2.082 (12)
C1–O1	1.151 (8)	C12–O6	1.132 (8)
C2–O2	1.124 (9)	C13–O7	1.147 (8)
P1–O3	1.495 (4)	P2–O8	1.477 (5)
P1–O4	1.611 (4)	P2–O9	1.600 (5)
P1–O5	1.612 (4)	P2–O10	1.606 (5)
O4–C8	1.445 (8)	O9–C19	1.436 (8)
C8–C9	1.488 (11)	C19–C20	1.468 (13)
C5–C10	1.445 (11)	O10–C21	1.449 (14)
C10–C11	1.466 (12)	C21–C22	1.375 (15)
Bond Angles			
P1–Fe1–C1	92.9 (3)	P2–Fe2–C12	88.1 (3)
P1–Fe1–C2	87.5 (3)	P2–Fe2–C13	92.1 (3)
C1–Fe1–C2	95.0 (3)	C12–Fe2–C13	94.5 (3)
Fe1–P1–O3	116.9 (2)	Fe2–P2–O8	117.2 (3)
Fe1–P1–O4	113.8 (2)	Fe2–P2–O9	114.8 (2)
Fe1–P1–O5	106.7 (2)	Fe2–P2–O10	105.1 (2)
Dihedral Angles			
O3–P1–Fe1–C1	18.2 (4)	O8–P2–Fe1–C12	66.9 (4)
O3–P1–Fe1–C2	66.9 (4)	O8–P2–Fe1–C13	18.7 (4)

The molecules are well separated by normal van der Waals distances in the crystal, whereas one of the water hydrogens is hydrogen bonded to the phosphoryl oxygen (OW1-O3 and OW2-O8 lengths are 2.763 and 2.786 Å, respectively). The water is believed to come from air since

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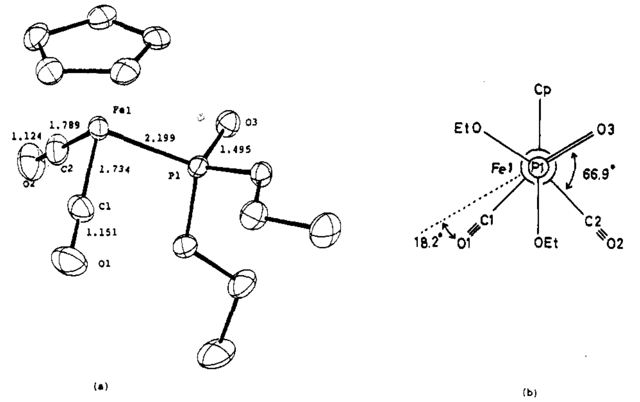

Figure 2. (a) ORTEP drawing of the molecule 1 for 1 showing selected bond distances. (b) Newman projection along the P–Fe bond for molecule 1.

the hexane solution of 1 was kept at 50 °C on a water bath in the process of obtaining crystals for X-ray analysis. Several trials to obtain the single crystals in a dry nitrogen atmosphere were unsuccessful. Thus, we presume that one water molecule might be necessary for crystalline packing.

The possibility that the iron complex analyzed by X-ray diffraction is formulated as $[Cp(CO)_2FeP(OH)(OEt)_2]^+OH^-$ instead of $[Cp(CO)_2P(O)(OEt)_2]\cdot H_2O$ is ruled out by the IR data. The ν_{CO} values in a solid state for the crystals are 2035 and 1983 cm^{-1}, which are exactly the same as those in an acetone solution for the complex prepared in a dry nitrogen atmosphere. The ν_{CO} values for $[Cp(CO)_2Fe(OH)(OEt)_2]^+SO_3CF_3^-$ prepared from $[Cp(CO)_2FeP(O)(OEt)_2]$ and HSO_3CF_3 are 2062 and 2017 cm^{-1} (vide infra).

The X-ray analysis of $1\cdot H_2O$ reveals two interesting features. Figure 2 depicts ORTEP drawing of the molecule 1 for 1 with selected bond distances, and the Newman projection along the P–Fe bond. The first point noted is that one of the carbonyl groups, Fe atom, and phosphoryl group (O1–C1–Fe1–P1–O3 for molecule 1 and O7–C13–Fe2–P2–O8 for molecule 2) are located almost on the same plane; dihedral angles are 18.2° and 18.7° for molecule 1 and molecule 2, respectively. In other words, one carbonyl group (C1–O1 for molecule 1 and C13–O7 for molecule 2) is trans to the P=O bond whereas the other carbonyl group (C2–O2 for molecule 1 and C12–O6 for molecule 2) is gauche (dihedral angles are 66.9° and 66.9° for molecule 1 and molecule 2, respectively). The second point noted is that the bond lengths concerning the two carbonyl groups are different: Fe1–C1 = 1.734 Å vs Fe1–C2 = 1.789 Å and C1–O1 = 1.151 Å vs C2–O2 = 1.124 Å for molecule 1; Fe2–C13 = 1.735 Å vs Fe2–C12 = 1.764 Å and C13–O7 = 1.147 Å vs C12–O6 = 1.132 Å for molecule 2.

The X-ray analyses of the related iron complexes $[Cp(CO)_2FeP(O)(CF_3)_2]$ and $[Cp(CO)_2FeP(CF_3)_2]$ were already reported.[19] In these complexes, Fe–CO bond distances are between 1.763 and 1.786 Å and FeC–O bond lengths are between 1.131 and 1.141 Å. The Fe—CO and FeC—O bond lengths gauche to P=O in the complex analyzed in the present work are in the range of the bond distances mentioned above or very close to the range, whereas the Fe—CO bond lengths trans to the P=O are significantly shorter and the FeC—O bond distances trans to the P=O are longer than those for the two precedents. Since the increase of the back-donation from a central metal atom to a carbonyl group causes a shortening of the Fe—CO bond and a lengthening of the FeC—O bond, it can be considered that the phosphoryl group promotes a back-donation from the iron atom to the carbonyl group trans to the P=O and does not affect the carbonyl group gauche to the P=O.

Table VII. ^{13}C NMR Data in the Terminal Carbonyl Region

complex[a]	δ	$^2J_{PMC}$, Hz	ref
$Cp^*(CO)_2Fe\overline{PN(Me)CH_2CH_2N}(Me)$	217.9	3.0	20
$Cp^*(CO)_2FeP(SiMe_3)_2$	218.5	0	21
$Cp^*(CO)_2FeP(SiMe_3)(t\text{-}Bu)$	219.8	0	21
$Cp^*(CO)_2FeP(t\text{-}Bu)_2$	220.9	0	21
$Cp^*(CO)_2RuP\{C(O)\text{-}t\text{-}Bu\}_2$	202.5	0	22
$Cp^*(CO)_2RuP(SiMe_3)_2$	204.5	0	22
$Cp^*(CO)_2RuP(SiMe_3)Ph$	204.6	0	23

[a] Cp* stands for $\eta^5\text{-}C_5Me_5$.

NMR Study of 1. An apparent inequality of the two carbonyl groups in 1 was found in the solid state. In order to know whether the phosphonate ligand rotates freely along the Fe–P bond in a solution or whether it is fixed as in a solid state, we measured the ^{13}C NMR on a 67.8-MHz JEOR GX-270 spectrometer. $CDCl_3$ was used as a solvent.

The methyl group gives rise to a doublet at 16.63 ppm (J = 6.7 Hz), the methylene groups to a doublet at 59.85 ppm (J = 8.5 Hz), and the cyclpentadienyl group to a singlet at 85.82 ppm. In addition, two signals due to the CO ligands are observed in the range 211–212 ppm. If the C–P coupling constant is not enough large to be detected, then two signals would arise from magnetically different two carbonyl ligands, indicating that the phosphonate does not rotate freely along the Fe–P bond. On the other hand, if the two carbonyl signals are a doublet caused by a C–P coupling, the two carbonyls would be magnetically identical, indicating that the phosphonate does rotate freely in a solution. In order to determine whether the two carbonyl signals are due to the C–P coupling through the Fe atom or not, 1 was subjected to ^{13}C NMR measurement at 22.6 MHz. At both field strengths the two-carbonyl signal difference is 40.9 Hz. Thus we can conclude that the carbonyl carbons and phosphonate phosphorus are coupled each other by 40.9 Hz at 211.47 ppm and that the phosphonate group therefore rotates freely along the Fe–P bond in a solution at room temperature on the NMR time scale.

To our knowledge, no data about coupling constants between coordinating terminal carbonyl carbons and ligating phosphonate phosphorus through a transition metal have been reported. Some ^{13}C NMR data for phosphide transition-metal complexes containing terminal carbonyl ligands have been known, which are listed in Table VII. As can be seen, the coupling constants are less than 3 Hz. Therefore, the large coupling constant (40.9 Hz) appears to be unusual.

Character of Transition-Metal-Bonded Diethyl Phosphonate Group. From the X-ray analysis of 1, the phosphonate group seems to strengthen the Fe—CO bond trans to the phosphoryl group (P=O) and weaken the FeC—O bond, whereas the phosphonate group does not to affect the Fe—CO bond and the FeC—O bond distances gauche to the phosphoryl group. One possible explanation is that the electron in the P=O bond flow into the iron d orbital through presumably a phosphorus d orbital, followed by flowing into a π^* orbital of the CO ligand trans to the phosphoryl group. This electron flow does not affect

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Table VIII. IR, ^{1}H NMR, and ^{31}P NMR Data

complex	IR ν_{CO}, cm^{-1}	^{1}H NMR δ	^{31}P NMR δ
$Cp(CO)_2FeP(O)(OEt)_2$ (1)	2035, 1983, 1177^a (in acetone)	5.20 (s, 5 H, Cp), 3.97 (m, 4 H, OCH_2CH_3), 1.22 (t, J = 6.8 Hz, 6 H, OCH_2CH_3), (in acetone-d_6)	89.94 (s) in acetone
$[Cp(CO)_2FeP(OMe)(OEt)_2]\cdot SbCl_6$ ($2\cdot SbCl_6$)	2065, 2021 (in acetone)	5.72 (s, 5 H, Cp), 4.31 (m, 4 H, OCH_2CH_3), 3.94 (d, J = 12.4 Hz, 3 H, OCH_3), 1.40 (t, J = 7.2 Hz, 6 H, OCH_2CH_3) (in $CDCl_3$)	154.46 (s) (in CH_2Cl_2)
$[Cp(CO)_2FeP(OCPh_3)(OEt)_2]\cdot PF_6$ ($3\cdot PF_6$)	2056, 2009 (in acetone)	7.0–7.2 (m, 15 H, Ph), 5.42 (br, 5 H, Cp), 4.10 (m, 4 H, OCH_2CH_3), 1.30 (m, 6 H, OCH_2CH_3) (in acetone-d_6)	141.23 (s), −145.15 (sep, J = 712 Hz) (in CH_2Cl_2)
$[Cp(CO)_2FeP(OH)(OEt)_2]\cdot SO_3CF_3$ ($4\cdot SO_3CF_3$)	2062, 2017 (in acetone)	5.55 (d, J = 1.2 Hz, 5 H, Cp), 4.02 (m, 4 H, OCH_2CH_3), 1.36 (t, J = 6.8 Hz, 6 H, OCH_2CH_3) (in acetone-d_6)	146.80 (s) (in CH_2Cl_2)

^{a} $\nu_{P=O}$.

the CO group gauche the phosphoryl group because of orthogonal situation between a π^* orbital of the gauche CO and the relevant d orbital of the Fe atom. A diethyl phosphonate group may be said to have a π-donating character.

In contrast, $P(O)(CF_3)_2$ group does not show the π-donating character. The X-ray analysis data of $Cp(CO)_2FeP(O)(CF_3)_2$ reveal that the two Fe–CO bond distances and the two FeC–O bond distances are equal within estimated standard deviation, though one carbonyl group is located trans to the phosphoryl group and the other is gauche to it.[19] It can be thought that $P(O)(CF_3)_2$ group has two very strong electron-withdrawing groups, CF_3, on the phosphorus, thus electrons on the phosphorus atom flow into CF_3 groups instead of flowing into the iron atom.

Reactivity of 1 with $P(n\text{-}Bu)_3$, $P(OEt)_3$, and Me_3NO. The reaction of 1 with phosphine or phosphite was performed in order to examine the possibility of replacement of one carbonyl group of 1 by a neutral donor. Since Haines reported that 1 does not react with $P(OMe)_3$,[13] more basic phosphorus compounds were chosen. Complex 1 and 4 equiv of $P(n\text{-}Bu)_3$ were dissolved in benzene, and the solution was refluxed for 50 h. IR and GC measurements revealed that the starting materials remained. 1 also did not react with $P(OEt)_3$ at all (eq 2). It has been reported that in the reaction of $Cp(CO)_2FeCl$ with PPh_3 one carbonyl ligand is readily replaced with the phosphine to give $Cp(CO)(PPh_3)FeCl$ together with $[Cp(CO)_2Fe(PPh_3)]^+Cl^-$[24] (eq 3). The reaction with $P(OEt)_3$ affords $Cp(CO)\{P(OEt)_3\}FeCl$ together with 1 and $Cp(CO)\{P(OEt)_3\}FeP(O)(OEt)_2$ which come from $[Cp(CO)_2Fe\{P(OEt)_3\}]^+Cl^-$ via the Arbuzov-like dealkylation reaction (eq 4).[13] Thus the two carbonyl groups in 1 can be considered to coordinate more strongly to the central iron atom than those in $Cp(CO)_2FeCl$.

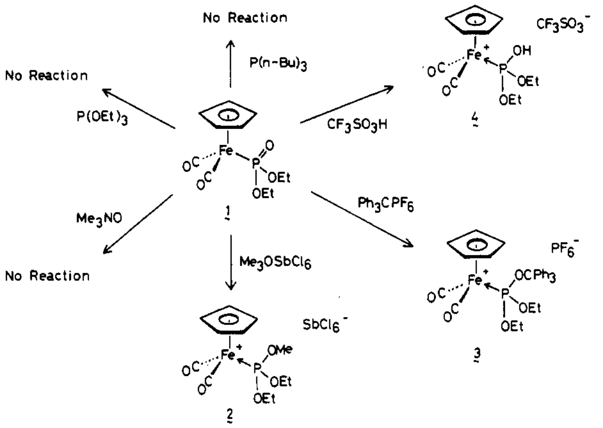
$$Cp(CO)_2FeP(O)(OEt)_2 \xrightarrow{P(OEt)_3} \text{no reaction} \quad (2)$$

$$Cp(CO)_2FeCl \xrightarrow{PPh_3} Cp(CO)(PPh_3)FeCl + [Cp(CO)_2Fe(PPh_3)]^+Cl^- \quad (3)$$

$$Cp(CO)_2FeCl \xrightarrow{P(OEt)_3} Cp(CO)\{P(OEt)_3\}FeCl + [Cp(CO)_2Fe\{P(OEt)_3\}]^+Cl^- + Cp(CO)_2FeP(O)(OEt)_2 + Cp(CO)\{P(OEt)_3\}FeP(O)(OEt)_2 \quad (4)$$

It has been reported that Me_3NO removes the terminal carbonyl ligand by oxidation to CO_2 for some transition-metal complexes.[25] Therefore we attempted to remove the CO ligand of 1 with Me_3NO. The benzene solution containing 1 and 3 equiv of Me_3NO was refluxed for 8 h. However 1 did not react at all with Me_3NO.

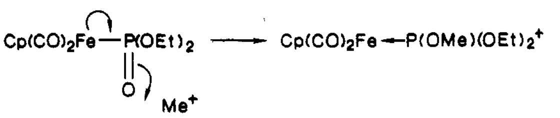
Scheme I



The stability of 1 toward phosphine, phosphite, and Me_3NO is compatible with the fact mentioned above that the Fe-bonded phosphonate group strengthens the Fe–CO bond.

Reactivity of 1 with Some Lewis Acids. Although 1 does not react with phosphine, phosphite, and Me_3NO, it readily reacts with some Lewis acids such as Me^+, CPh_3^+, and H^+ (Scheme I).

In the reaction with Me^+, the product has spectroscopic characteristics which imply that it is a cationic compound; on going from 1 to the product, ν_{CO} absorptions in IR move to higher frequency by about 30–40 cm^{-1}, the Cp resonance in ^{1}H NMR shifts to a lower field by about 0.5 ppm. The ^{31}P NMR resonance at 154.46 ppm indicates that a phosphite coordinates to a transition metal through its lone pair. In the ^{1}H NMR spectrum, a doublet at 3.94 ppm (J = 12.4 Hz) can be ascribed to a OMe group coupled to the phosphorus atom. These data are tabulated in Table VIII. We propose that 1 reacts with Me^+ to give $[Cp(CO)_2Fe\{P(OMe)(OEt)_2\}]^+$ (2) (eq 5). In the reaction, the Fe–P



(5)

bond character changes from covalent to dative, and the

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formal oxidation state of the phosphorus changes from pentavalent to trivalent.

A more bulky electrophile, CPh_3^+, also attacks the phosphoryl oxygen of 1 to give $[Cp(CO)_2FeP(OCPh_3)(OEt)_2]^+$ (3; spectroscopic data are listed in Table VIII). If the conformation of 1 is the same as that found in the solid state (i.e., the Fe–P bond does not rotate in a solution), the bulky CPh_3^+ does not appear to be able to approach the phosphoryl oxygen of 1 close enough to form the O–CPh_3 bond owing to the steric repulsion between phenyl groups of CPh_3^+ and the cyclopentadienyl group of 1. When 1 has the conformation in which the Cp and the phosphoryl oxygen are s-trans to each other with respect to the Fe–P bond, CPh_3^+ can approach close enough to form the O–CPh_3 bond. The formation of 3 is further support for free rotation around the Fe–P bond in 1 in solution.

H^+ also reacts with 1 in the same manner as the other two Lewis Acids, Me^+ and CPh_3^+. The formation of $[Cp(CO)_2FeP(OH)(OEt)_2]^+$ (4) was established from the spectroscopic data in Table VIII. The ν_{CO} (2062 and 2017 cm^{-1}) are very close to those for 2 and 3. The ^{31}P NMR resonance (146.80 ppm) is between those for 2 and 3. The ^1H NMR resonances due to the Cp, methylene, and methyl groups of OCH_2CH_3 group correspond to those for 2 and 3. A signal due to the hydroxy group was not detected. Failure to observe OH is not uncommon; e.g., the ^1H NMR signal attributable to the EH group of $[Cp(CO)_2FeP(EH)(CF_3)_2]^+$ (E = O, S, Se) prepared from $Cp(CO)_2FeP(E)(CF_3)_2$ and a mixture of HCl and $SnCl_4$ was not detected even at −20 °C.[26]

Pyridine deprotonates $4{\cdot}SO_3CF_3$ to afford 1. The spectroscopic data of the resulting product in solution were identical with those of 1 in pyridine. Therefore, we conclude that 4 is relatively acidic.

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Registry No. 1, 35025-44-6; 1·H_2O, 111469-94-4; 2, 111469-97-7; 3, 111469-99-9; 4, 111469-95-5; [$CpFe(CO)_2Cl$], 12107-04-9; P-$(OEt)_3$, 122-52-1.

Supplementary Material Available: Tables of calculated hydrogen atom parameters and anisotropic thermal parameters for 1 (Tables III and IV) (4 pages); a listing of observed and calculated structure factors for 1 (Table V) (24 pages). Ordering information is given on any current masthead page.

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Reaction of Active Uranium and Thorium with Aromatic Carbonyls and Pinacols in Hydrocarbon Solvents[1]

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Highly reactive uranium and thorium metal powders have been prepared by reduction of the anhydrous metal(IV) chlorides in hydrocarbon solvents. The reduction employs the crystalline hydrocarbon-soluble reducing agent $[(TMEDA)Li]_2[Nap]$ (TMEDA = *N,N,N′,N′*-tetramethylethylenediamine, Nap = naphthalene). The resulting active metal powders have been shown to be extremely reactive with oxygen-containing compounds and have been used in the reductive coupling of aromatic ketones giving tetraarylethylenes. Reactions with pinacols have given some mechanistic insight into the ketone coupling reaction. These finely divided metal powders activate very weakly acidic C–H bonds forming metal hydrides, which can be transferred to organic substrates.

Introduction

Highly dispersed and reactive metal powders have commanded a great deal of interest for their applications in catalytic and stoichiometric chemical syntheses, as well as their uses in materials science. Numerous methods exist for the preparation of these metal powders. Most of these methods for preparing metal powders involve the reduction of a metal salt or oxide by hydrogen (usually at high temperatures)[2-4] or by other chemical or electrochemical means.[3,5-10] In addition to reductive techniques, pyrolyses[3,11,12] and metal atom vaporization[13-19] have been employed. An excellent review of the preparation, reactivity,

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