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Bond Character between Iron and Phosphorus in Fe−P(E)YZ (E = O, S; Y, Z = Alkoxy, Amino, Phenyl) As Inferred from ^{57}Fe Mössbauer Measurements

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A series of (η^5-C_5R_5)(CO)$_2$Fe{P(E)YZ} complexes (R = H, Me; E = O, S; Y, Z = OMe, OEt, NEt$_2$, MeNCH$_2$CH$_2$NMe, Ph), (η^5-C_5H_5)(CO)$_2$FeX (X = Cl, Br, I), and (η^5-C_5Me_5)(CO)$_2$FeCl were prepared, and the ^{57}Fe Mössbauer spectra together with IR(ν_{CO}) and ^{31}P NMR spectra were measured. The Fe−P bond in (η^5-C_5R_5)(CO)$_2$Fe{P(E)YZ} is found to be as covalent as the Fe−Me bond in (η^5-C_5H_5)Fe(CO)$_2$Me. There are linear correlations between isomer shifts (IS) and quadrupole splittings (QS) in the ^{57}Fe Mössbauer spectra, between IS and chemical shifts in the ^{31}P NMR spectra (δ), between IS and the IR stretching frequencies in the CO region (ν_{CO}), and between δ and ν_{CO}. These correlations indicate that the electron-donating group on the phosphorus atom (Y, Z) increases the electron density on the phosphorus atom, increases π-donation from P(E)YZ to the Fe, and concomitantly increases π-back-donation from iron to the CO ligands. The systematic replacement of the carbonyl group by phosphine or phosphites shows the large shift in IS and QS, indicating a large change in the d-electron density of the iron atom. Especially for the complexes having no carbonyl ligand, the d-electron density is much accumulated on the iron atom.

Introduction

Transition-metal phosphonate complexes, which are generally described as L$_n$M{P(O)(OR)$_2$}, are attracting considerable attention due to the presence of a covalent bond between a transition metal and a pentavalent phosphorus atom. We have been engaged in the study on piano-stool iron complexes containing a phosphonate ligand, such as Cp(CO)$_2$Fe{P(O)(OR)$_2$} (Cp = η^5-C_5H_5) and the derivatives. Although the Fe−P bond is formally covalent, the covalency may depend on the substituents on both the phosphorus and the iron.

^{57}Fe Mössbauer spectroscopy has been widely used in bond character studies of iron complexes.[1] The isomer shifts (IS) provide us with a sensitive indication of metal s-electron density. It is well-known that (i) an increase in the s-electron density at an iron nucleus results in a decrease in the IS, and (ii) an increase in the p- and/or d-electron density results in an increase in the IS because the increased electron density decreases the s-electron density at an iron nucleus (shielding effect).[2] It is roughly said that when a ligand on an Fe serves as a σ donor, a decrease in the IS is observed because the effect i is greater than the effect ii. When a ligand serves as a π acceptor, a decrease in the IS is observed because of electron transfer from a filled d orbital of Fe into an empty ligand orbital. Relating the observed quadrupole splitting (QS) as well as IS with other spectroscopic data provides us with an overall picture of the bond character between a ligand and an iron center.

In this paper, we report the ^{57}Fe Mössbauer spectroscopic data for a series of piano-stool iron complexes containing a P(E)YZ ligand (E = O, S; Y, Z = OMe, OEt, NEt$_2$, Ph, NMeCH$_2$CH$_2$NMe). This constitutes, to our knowledge, the first ^{57}Fe Mössbauer spectroscopic data for iron phosphonate complexes and their derivatives. On the basis of these data, together with ^{31}P NMR chemical shifts (δ) and IR absorption bands in the CO stretching region (ν_{CO}), the bond character between the iron and the phosphorus is discussed.

Results and Discussion

Preparation and ^{57}Fe Mössbauer Measurement of Iron Complexes. Piano-stool iron complexes subjected to the ^{57}Fe Mössbauer measurements in this paper are listed in Chart 1. Complexes **6**−**12** and **14**−**16** were prepared in the reaction of Cp(CO)$_2$FeCl or [Cp*(CO)$_2$Fe(THF)]PF$_6$, where Cp and Cp* stand for η^5-C_5H_5 and η^5-C_5Me_5, respectively, with PYZ(OR) by the Arbuzov-like dealkylation reaction (eq 1). Thiophosphonate complexes (**13** and **17**) were obtained in the

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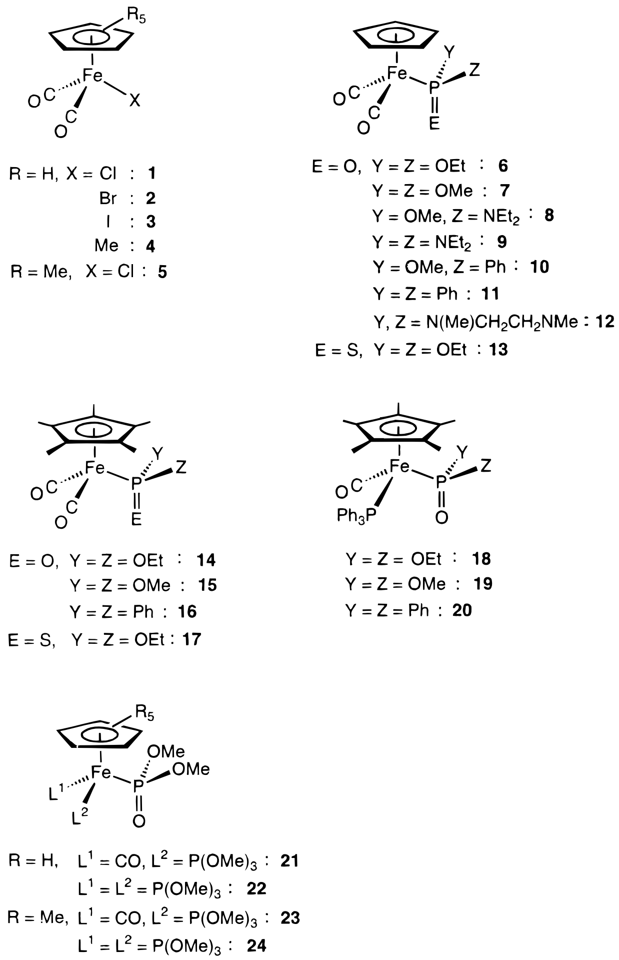
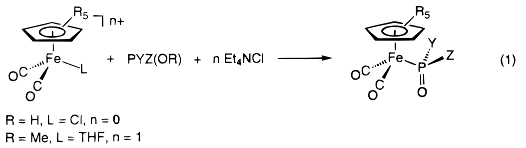
(1) (a) Gibb, T. C. In *Principles of Mössbauer Spectroscopy*; Chapman and Hall: London, 1976. (b) Parish R. V. In *Mössbauer Spectroscopy*; Dickson, D. P. E., Berry, F. J., Eds.; Cambridge University Press: Cambridge, 1986; Chapter 2.

(2) (a) Shenoy, G. K. In *Mössbauer Spectroscopy Applied to Inorganic Chemistry*; Long, G. J., Ed.; Plenum: New York, 1984; Chapter 5. (b) Long, G. J.; Alway D. G.; Barnett, K. W. *Inorg. Chem.* **1978**, *17*, 486, and references cited therein.

10.1021/om980433z CCC: $15.00

Chart 1

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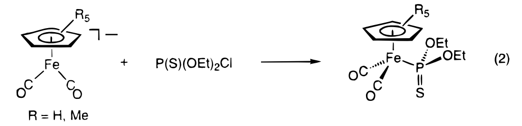
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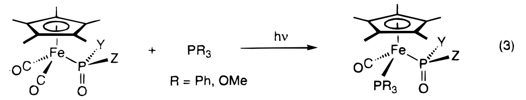
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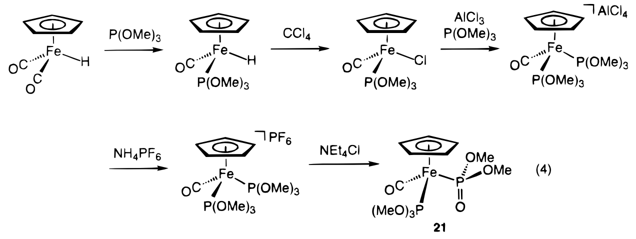
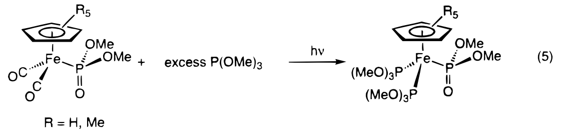

(4)


(5)

reaction of $[Cp(CO)_2Fe]^-$ or $[Cp^*(CO)_2Fe]^-$ with $P(S)(OEt)_2Cl$ (eq 2). Complexes $Cp^*(CO)(PPh_3)Fe\{P(O)YZ\}$ (**18**−**20**) were prepared by the photolysis of $Cp^*(CO)_2Fe\{P(O)YZ\}$ (**14**−**16**) in the presence of PPh_3 (eq 3). Preparation of **21** was attempted by the photolysis of **7** in the presence of 1 equiv of $P(OMe)_3$. However, the isolated yellow powder was a mixture of monosubstituted (**21**) and disubstituted (**22**) complexes, and the separation was found to be difficult. The reaction of **7** with 0.5 equiv of $P(OMe)_3$ did not improve the situation. Therefore, we sought another preparative method and found the following route (eq 4). $Cp(CO)_2FeH$ readily reacts with $P(OMe)_3$ to give $Cp(CO)\{P(OMe)_3\}FeH$, which then reacts with CCl_4 to yield $Cp(CO)\{P(OMe)_3\}FeCl$. The Cl is displaced by $P(OMe)_3$ in the presence of $AlCl_3$ to give $[Cp(CO)Fe\{P(OMe)_3\}_2]AlCl_4$. After the conversion into the PF_6 salt, the Arbuzov-like dealkylation reaction of $[Cp(CO)Fe\{P(OMe)_3\}_2]PF_6$ with NEt_4Cl yields the desired complex **21**. In the sequence, the product was not contaminated by **22**. In contrast, **23**, which is a Cp* derivative of **21**, can be prepared from **15** and 1 equiv of $P(OMe)_3$ by a simple substitution promoted by photolysis (eq 3). Complex **22** was prepared either from **21** and $P(OMe)_3$ or from **7** and excess $P(OMe)_3$. Complex **24** was also prepared either from **23** and $P(OMe)_3$ or from **15** and excess $P(OMe)_3$ (eq 5).

^{57}Fe Mössbauer measurements were undertaken at room temperature unless otherwise noted. The spectrum of $CpFe(CO)_2\{P(O)(OMe)_2\}$ (**7**), which is a typical example of iron phosphonate complexes in this paper, is shown in Figure 1. The parameters are calculated as IS = -0.046 mm s^{-1}, QS = 1.731 mm s^{-1} (relative to α-Fe). The small deviation from a symmetric doublet may be attributed to the preferred orientation. The half-line width is 0.25 mm s^{-1}, and the error limits of IS and QS are 0.003 mm s^{-1} and 0.007 mm s^{-1}, respectively.

All compounds in the present study showed similar spectra, half-line widths, and error limits. The Mössbauer parameters, together with the ^{31}P NMR and IR(ν_{CO}) data, are summarized in Table 1.

Comparison of (η^5-C_5R_5)(CO)$_2$Fe{P(E)YZ} with (η^5-C_5R_5)(CO)$_2$FeX (R = H, Me; X = Cl, Br, I) and (η^5-C_5H_5)(CO)$_2$FeMe. The relationship between the IS and QS obtained in the ^{57}Fe Mössbauer measurements is shown in Figure 2 for Fp{P(E)YZ}, Fp*{P(E)YZ}, FpX (X = Cl, Br, I), and Fp*Cl, where Fp and Fp* stand for $Cp(CO)_2Fe$ and $Cp^*(CO)_2Fe$, respectively. The data for FpX agree with the results reported by Long,[2b] although they are slightly different from those reported by Heber.[3]

It can be said from Figure 2 that Fp{P(E)YZ} and Fp*{P(E)YZ} make one colony and FpX and Fp*X make another colony. Complexes in the former colony exhibit lower IS values than those in the latter, indicating that an Fe−P(E)YZ bond has less ionic character than the Fe−halogen bond which bears $Fe^{\delta+}-X^{\delta-}$ charge polarization. This interpretation is consistent with the fact that a phosphorus atom is less electronegative than halogen atoms.

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[3] Herber, R. H.; King, R. B.; Wertheim; G. K. *Inorg. Chem.* **1964**, *3*, 101.

Table 1. Spectroscopic Data

complex	Mössbauer data[a] IS (mm s^{-1})	Mössbauer data[a] QS (mm s^{-1})	IR[d] ν_{CO} (cm^{-1})	^{31}P NMR δ (ppm)
1: FpCl	0.148	1.836		
2: FpBr	0.148	1.849		
3: FpI	0.128	1.830		
4: FpMe	0.069[b]	1.746[b]		
	−0.008[c]	1.753[c]		
5: Fp*Cl	0.130	1.894		
6: Fp{P(O)(OEt)$_2$}	−0.044	1.742	2036 1981	106.2[e]
	0.033[b]	1.753[b]		
7: Fp{P(O)(OMe)$_2$}	−0.046	1.731	2038 1978	109.2[e]
	0.030[b]	1.711[b]		
8: Fp{P(O)OMe)(NEt$_2$)}	−0.018	1.715	2028 1971	103.3[e]
9: Fp{P(O)(NEt$_2$)$_2$}	−0.026	1.713	2018 1965	98.2[e]
10: Fp{P(O)Ph(OMe)}	−0.062	1.761	2031 1977	121.1[e]
11: Fp{P(O)Ph$_2$}	0.002	1.703	2018 1968	89.1[e]
12: Fp{P(O)N(Me)CH$_2$CH$_2$NMe}	−0.010	1.713	2014 1958	97.2[e]
13: Fp{P(S)(OEt)$_2$}	−0.008	1.703	2041 1989	177.7[e]
14: Fp*{P(O)(OEt)$_2$}	−0.054	1.809	2011 1960	110.6[f]
15: Fp*{P(O)(OMe)$_2$}	−0.049	1.802	2014 1962	113.5[f]
	0.032[b]	1.804[b]		
16: Fp*{P(O)Ph$_2$}	−0.042	1.751	2000 1964	88.5[f]
17: Fp*{P(S)(OEt)$_2$}	−0.038	1.771	2018 1970	190.3[f]
18: Cp*(CO)(PPh$_3$)Fe{P(O)(OEt)$_2$}	0.054	1.894	1933[f]	121.2 (d)[f] 76.7 (d) (J = 88.6 Hz)
19: Cp*(CO)(PPh$_3$)Fe{P(O)(OMe)$_2$}	0.072	1.916	1934[f]	125.8 (d)[f] 76.6 (d) (J = 88.2 Hz)
20: Cp*(CO)(PPh$_3$)Fe{P(O)Ph$_2$}	0.078	1.906	1933[f]	121.6 (d)[f] 76.7 (d) (J = 88.6 Hz)
21: Cp(CO){P(OMe)$_3$}Fe{P(O)(OMe)$_2$}	0.060[b]	1.778[b]	1960	124.9 (d)[e] 181.8 (d) (J = 140.3 Hz)
22: Cp{P(OMe)$_3$}$_2$Fe{P(O)(OMe)$_2$}	0.164[b]	1780[b]		136.6 (t)[e] 186.8 (d) (J = 149.6 Hz)
23: Cp*(CO){P(OMe)$_3$}Fe{P(O)(OMe)$_2$}	0.071[b]	1890[b]	1942	130.6 (d)[e] 182.2 (d) (J = 134.3 Hz)
24: Cp*{P(OMe)$_3$}$_2$Fe{P(O)(OMe)$_2$}	0.201[b]	1.906[b]		138.6 (t)[e] 183.0 (d) (J = 143.4 Hz)

[a] Isomer shift data are reported with respect to α-Fe. [b] Measured at 78 K. [c] Evaluated values at 298 K. [d] KBr disk. [e] In CH_2Cl_2. [f] In THF.

Next we attempted to measure the ^{57}Fe Mössbauer spectrum of FpMe because it is the simplest alkyl complex involving an Fp fragment. The methyl complex shows IS = 0.069 mm s^{-1} and QS = 1.746 mm s^{-1} at 78 K, agreeing with the data reported.[4] The complex does not show a clear doublet at room temperature presumably due to the extremely decreased recoil-free fraction near room temperature. Therefore, we estimated the IS value at room temperature for FpMe based on the assumption that the second-order Doppler shift of FpMe is the same as that of Fp{P(O)(OEt)$_2$}. Since Fp{P(O)-

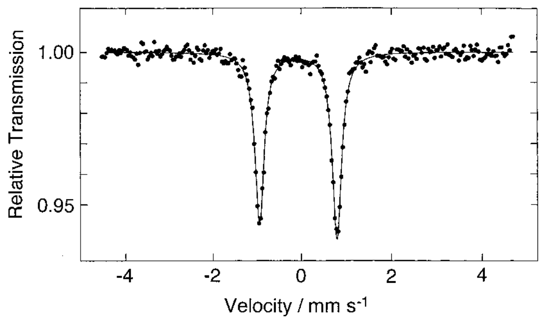

Figure 1. ^{57}Fe Mössbauer spectrum of Cp(CO)$_2$Fe{P(O)(OEt)$_2$} at room temperature.

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[4] Pannel, K. H.; Wu, C. C.; Long, G. J. *J. Organomet. Chem.* **1980**, *186*, 85.

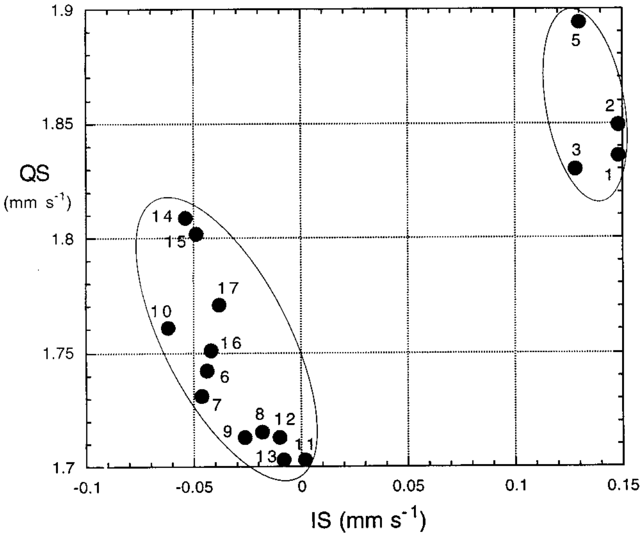

Figure 2. Relationship between IS and QS of the ^{57}Fe Mössbauer spectra for complexes **1**−**17** except **4**. Two colonies are roughly observed.

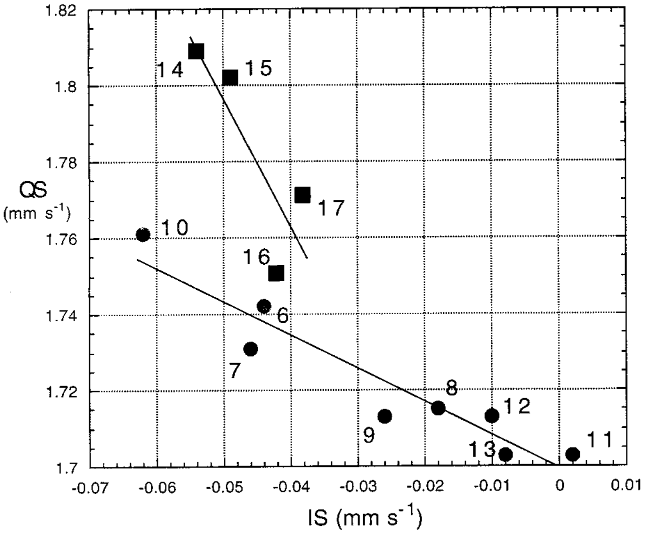

Figure 3. Relationship between IS and QS for complexes **6**−**17**. Fp{P(E)YZ} complexes (**6**−**13**) are linearly correlated, and Fp*{P(O)YZ} complexes (**14**−**17**) make another straight line.

(OEt)$_2$} showed an IS of −0.044 mm s^{-1} at room temperature and an IS of 0.033 mm s^{-1} at 78 K, the IS at room temperature for FpMe is estimated as −0.008 mm s^{-1}. If the estimated parameter is plotted in Figure 2, the point is situated in the colony for Fp{P(E)YZ} complexes. Therefore, we can say that the Fe−P bond in Fp{P(E)YZ} is as covalent as the Fe−C bond in FpMe from the Mössbauer spectroscopic point of view.

The Effect of the Phosphorus Substituents (Y and Z) in Fp{P(E)YZ} and Fp*{P(E)YZ} on the Fe−P Bond Character. In Figure 2, Fp{P(E)YZ} and Fp*{P(E)YZ} make one colony. However, a closer look reveals the following three notable trends (see Figure 3). (i) Fp*{P(E)YZ} complexes (**14**−**17**) show lower IS and higher QS values than the corresponding Fp{P(E)YZ} complexes (**6**, **7**, **11**, and **13**). (ii) Thiophosphonate complexes (**13** and **17**) exhibit higher IS and lower QS values than the corresponding phosphonate ones (**6** and **14**). (iii) For both Fp{P(E)YZ} and Fp*{P(E)YZ} a linear correlation between IS and QS is observed: The QS increases with the decrease in the IS, and the slope is steeper for Fp*{P(E)YZ} than for Fp{P(E)YZ}. The origins of these trends are unclear now.

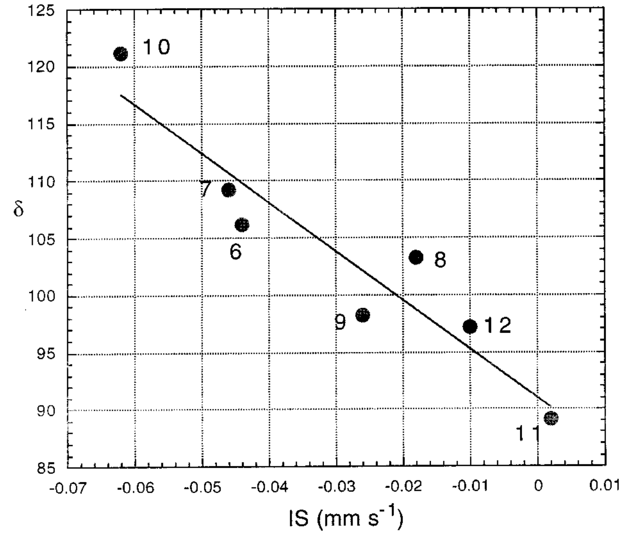

Figure 4. Relationship between IS and δ (the chemical shift of the ^{31}P NMR spectra).

Next we examined the relationship between IS and the chemical shift of the ^{31}P NMR spectra (δ) for Fp{P(O)YZ} (**6**−**12**). Figure 4 shows that there is roughly a linear correlation: the IS increases in the order YZ = (Ph)(OMe) < (OMe)$_2$ ≤ (OEt)$_2$ < (NEt$_2$)$_2$ ≤ (OMe)(NEt$_2$) ≤ MeNCH$_2$CH$_2$NMe < (Ph)$_2$, and the δ moves upfield in almost the same order: YZ = (Ph)(OMe) < (OMe)$_2$ ≤ (OEt)$_2$ ≤ (OMe)(NEt$_2$) ≤ (NEt$_2$)$_2$ ≤ MeNCH$_2$CH$_2$NMe < (Ph)$_2$. These orders are basically consistent with the generally known trend in terms of relative electron-donating effects of substituents on phosphorus: OR < NR$_2$ < Ph.[5] An upfield shift in the ^{31}P NMR chemical shift indicates an increase in electron density on the phosphorus if the magnetic anisotropy of its substituents can be neglected, and a higher IS corresponds directly to a decrease in s-electron density and indirectly to an increase in p- and/or d-electron density at the Fe. The relationship in Figure 4 indicates that electron density afforded on the phosphorus from its substituents (Y, Z) is donated to the Fe by π-donation in a certain ratio.

Infrared spectra in the carbonyl stretching region are characterized by two intense absorption bands (ν_{CO}) for Fp complexes. The relationship between IS and ν_{CO} for Fp{P(O)YZ} is shown in Figure 5. It can be seen that the ν_{CO} values for the two absorptions decrease roughly with an increase in the IS. It is well-known that π-back-donation from a filled d orbital of a transition metal to an empty π* orbital of a CO ligand causes a decrease in ν_{CO}. Thus, Figure 5 indicates that a low ν_{CO} value correlates to much electron density in the d orbital(s) of Fe. In other words, it can be said that d-electron density on the Fe flows into the π* orbital of a CO ligand in a certain ratio.

Figure 6 shows the relationship between ν_{CO} and δ for Fp{P(O)YZ}. Except for **10** and **11**, there is a linear correlation; ν_{CO} decreases with an upfield shift of δ. The correlation can be understood to suggest that electron-donating substituent(s) increase electron density on the

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[5] Emsley, J.; Hall, D. In *The Chemistry of Phosphorus*; Harper & Row Ltd.: New York, 1976; Chapter 2.

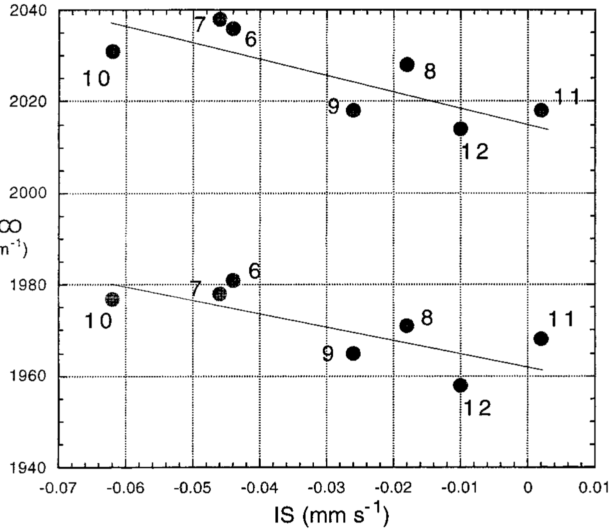

Figure 5. Relationship between IS and ν_{CO} (the CO stretching absorption of the IR spectra).

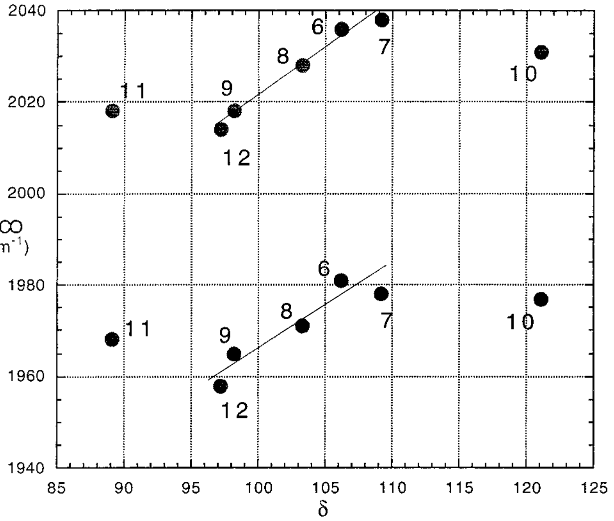

Figure 6. Relationship between δ and ν_{CO} for Fp{P(E)YZ}.

phosphorus, leading to an upfield chemical shift. This also causes electron donation from P to Fe, resulting in great π-back-donation from Fe to CO ligand(s), which leads to a lower ν_{CO}. Since both **10** and **11** have phenyl group(s) on the phosphorus, the deviation of these complexes from the correlation line may arise from the magnetic anisotropy of a phenyl ring, which additionally influences the ^{31}P NMR chemical shift.

It was found that there are roughly linear correlations between IS vs QS, IS vs δ, IS vs ν_{CO}, and δ vs ν_{CO}. These correlations can be compatibly explained in terms of π-donation of a P(O)YZ ligand toward Fe. An increase in electron-donating ability of phosphorus substituents (Y and Z) makes electron density high on the phosphorus. A part of the increased electron density stays on the phosphorus, which induces an upfield chemical shift in the ^{31}P NMR spectra. The rest of the electron density flows into d orbital(s) of the Fe through π-donation. The increased electron density of the Fe stays in the d orbital(s) to some extent, leading to a higher IS. The rest of the electron density is donated to a π* orbital of CO ligand(s) (π-back-donation), causing a lower ν_{CO}.

The Effect of the Carbonyl Ligands. From the above discussion a P(O)YZ ligand has been proposed to have π-donating character in Cp(CO)$_2$Fe{P(O)YZ}. In order to elucidate the role of the carbonyl ligands in Cp(CO)$_2$Fe{P(O)YZ}, **18**−**20** and **21**−**24** were subjected to ^{57}Fe Mössbauer measurements.

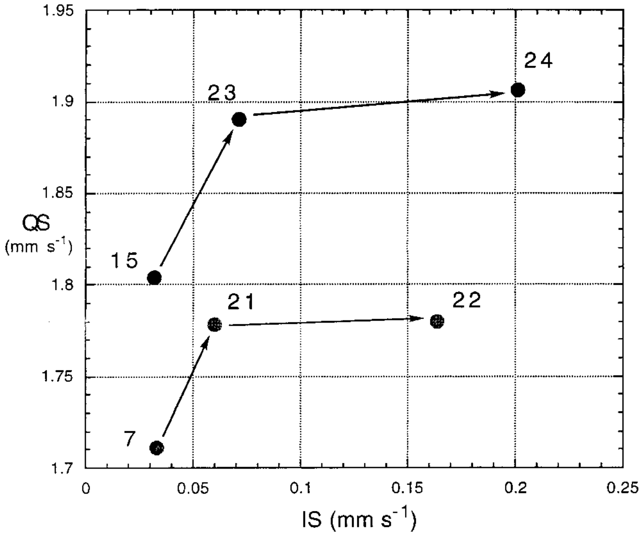

Figure 7. Relationship between IS and QS at 78 K by replacing the carbonyl ligand of Fp{P(O)(OMe)$_2$} and Fp*-{P(O)(OMe)$_2$} with P(OMe)$_3$ systematically.

For complexes Cp*(CO)(PPh$_3$)Fe{P(O)YZ} (Y = Z = OEt, **18**; OMe, **19**; Ph, **20**) the isomer shifts were observed in the range 0.054−0.078 mm s^{-1}, which are higher by 0.108−0.121 mm s^{-1} than those for the corresponding dicarbonyl complexes. The relatively high IS values are consistent with the well-supported concept that CO is a significantly better π-accepter ligand than PPh$_3$. The QS values were observed in the range 1.894−1.916 mm s^{-1}, which are higher by 0.085−0.155 mm s^{-1} than those for the corresponding dicarbonyl complexes. This can be attributed to the reduced symmetry around the iron by the replacement of CO by PPh$_3$. We tried in vain to introduce the second PPh$_3$. It is presumably due to the steric hindrance. So we used P(OMe)$_3$ in place of PPh$_3$ because of the small cone angle (cone angles are 107° and 145° for P(OMe)$_3$ and PPh$_3$, respectively[6]) to study the role of the CO ligand systematically.

For the Cp series (**7**, **21**, and **22**) and the Cp* series (**15**, **23**, and **24**), the Mössbauer parameters obtained at 78 K are plotted in Figure 7. For the Cp series, the first CO substitution causes a +0.030 mm s^{-1} IS shift (**7** → **21**), while the second CO substitution leads to a +0.104 mm s^{-1} IS shift (**21** → **22**). The Cp* series show similar trends (a +0.039 mm s^{-1} IS shift for **15** → **23**, and a +0.130 mm s^{-1} IS shift for **23** → **24**). These tendencies can be explained as follows. A certain ratio of the electron density afforded by π-donation from P(O)(OMe)$_2$ to Fe is equally donated to two CO ligands for **7**. In the case of **21**, the amount of π-back-donation from Fe to CO is not the same as that to one CO in **7**, but more than that, because a CO ligand can accept more electron density when the d-electron density on a central metal increases. In contrast, since **22** has no CO ligand, the electron density afforded by the P(O)(OMe)$_2$ ligand may be accumulated on the Fe, leading to a significantly high shift in IS. The series of **15** → **23** → **24** shows the same tendencies for the same reason.

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(6) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

In terms of QS values there is a comparatively large difference between the nonsubstituted and monosubstituted derivatives, whereas there is no significant difference between the monosubstituted and disubstituted derivatives. This indicates that the QS value is not determined solely by the symmetry around the iron atom.

Experimental Section

General Remarks. All reactions were carried out under an atmosphere of dry nitrogen by using Schlenk tube techniques. Column chromatography was done quickly in the air. Benzene, hexane, and THF were purified by distillation from sodium metal, CH_2Cl_2 was distilled from P_2O_5, and these solvents were stored under a nitrogen atmosphere. Dichloromethane, acetone, and ethanol as eluents were obtained from common commercial sources and were used without further purification. Complexes **6**,[7] **8**,[8] **9**,[9] **11**,[10] **12**,[8] and **13**[11] were prepared by the literature procedures.

IR spectra were recorded on a Shimadzu FTIR-8100A spectrometer. JEOL EX-270, EX-400, and LA-300 spectrometers were used to obtain ^1H and ^{31}P NMR spectra. ^1H NMR data were referenced to Me_4Si, and ^{31}P NMR data were referenced to 85% H_3PO_4. ^{57}Fe Mössbauer spectra were obtained by using a Toyo Research spectrometer where a $^{57}Co(Rh)$ source moving in a constant-acceleration mode was used. The Mössbauer parameters were obtained by least-squares fitting to Lorentzian peaks. The isomer shift values are referred to α-Fe.

Preparation of 7 and 10. The complexes were prepared in a manner similar to that of $Cp(CO)_2Fe\{P(O)(OEt)_2\}$ (**6**) from $Cp(CO)_2FeCl$ and $P(OMe)_3$ or $P(OMe)_2Ph$. For **7**: Yield 40%. Anal. Calcd for $C_9H_{11}FeO_5P$: C, 37.80; H, 3.88. Found: C, 37.59; H, 3.78. Data: IR (cm^{-1}, KBr disk) ν_{CO} 2038, 1978; ^1H NMR (δ, $CDCl_3$) 3.66 (d, J_{PH} = 10.8 Hz, 6H, CH_3), 5.07 (s, 5H, C_5H_5); ^{31}P NMR (δ, CH_2Cl_2) 109.2 (s). For **10**: Yield 62%. Anal. Calcd for $C_{14}H_{13}FeO_4P$: C, 50.64; H, 3.95. Found: C, 50.35; H, 3.92. Data: IR (cm^{-1}, KBr disk) ν_{CO} 2031, 1977; ^1H NMR (δ, $CDCl_3$) 3.55 (d, J_{HP} = 11.4 Hz, 3H, CH_3), 4.85 (s, 5H, C_5H_5), 7.41 (m, 5H, C_6H_5); ^{31}P NMR (δ, CH_2Cl_2) 121.1 (s).

Preparation of 14, 15, and 16. $P(OEt)_3$ (0.60 mL, 3.50 mmol) was added to a solution of $[Cp^*(CO)_2Fe(THF)]PF_6$ (1602 mg, 3.45 mmol) in CH_2Cl_2 (20 mL). The reaction mixture was stirred for 19 h at room temperature. The solvent was removed under reduced pressure to give a reddish yellow powder, which was washed with hexane several times to give $[Cp^*(CO)_2Fe\{P(OEt)_3\}]PF_6$ (1773 mg, 3.18 mmol, 92%). NEt_4Cl (3000 mg, 18.1 mmol) was added to a suspension of the complex in benzene. After the reaction mixture was refluxed for 1 h, the solvent was removed under reduced pressure. The residue was charged on a silica gel column and eluted with acetone and EtOH in this order. The band eluted with EtOH was collected and the solvent was removed under reduced pressure to give **14** (1003 mg, 2.61 mmol, 82%). Anal. Calcd for $C_{16}H_{25}FeO_5P$: C, 50.02; H, 6.05. Found: C, 49.76; H, 6.38. Data: IR (cm^{-1}, KBr disk) ν_{CO} 2011, 1960; ^1H NMR (δ, $CDCl_3$) 1.23 (t, J_{HH} = 6.0 Hz, 6H, CH_2CH_3), 1.86 (s, 15H, $C_5(CH_3)_5$), 3.95 (m, 4H, CH_2); ^{31}P NMR (δ, THF) 110.6 (s).

Complex **15** was prepared in a manner similar to that of **14** from $[Cp^*(CO)_2Fe(THF)]PF_6$, $P(OMe)_3$, and NEt_4Cl. Yield: 80%. Anal. Calcd for $C_{14}H_{21}FeO_5P$: C, 47.22; H, 5.94. Found: C, 47.16; H, 5.82. Data: IR (cm^{-1}, KBr disk) ν_{CO} 2014, 1962; ^1H NMR (δ, $CDCl_3$) 1.88 (s, 15H, $C_5(CH_3)_5$), 3.57 (d, J_{HP} = 12.0 Hz, 6H, OCH_3); ^{31}P NMR (δ, THF) 113.5 (s).

Complex **16** was prepared in a manner similar to that of **14** from $[Cp^*(CO)_2Fe(THF)]PF_6$, $PPh_2(OMe)$, and NEt_4Cl. Yield: 65%. Anal. Calcd for $C_{24}H_{25}FeO_3P$: C, 64.30; H, 5.62. Found: C, 64.25; H, 5.90. Data: IR (cm^{-1}, KBr disk) ν_{CO} 2000, 1964; ^1H NMR (δ, acetone-d_6) 1.74 (s, 15H, $C_5(CH_3)_5$), 7.26 (m, 10H, C_6H_5); ^{31}P NMR (δ, THF) 88.5 (s).

Preparation of 17. The complex was prepared in a manner similar to that of **13** from $K[Cp^*(CO)_2Fe]$ and $P(S)(OEt)_2Cl$. Yield: 62%. Anal. Calcd for $C_{16}H_{25}FeO_4PS$: C, 48.01; H, 6.30. Found: C, 47.79; H, 6.18. Data: IR (cm^{-1}, KBr disk) ν_{CO} 2018, 1970; ^1H NMR (δ, acetone-d_6) 1.18 (t, J_{HH} = 6.8 Hz, 6H, OCH_2CH_3), 1.89 (s, 15H, $C_5(CH_3)_5$), 4.01 (m, 4H, CH_2); ^{31}P NMR (δ, THF) 190.3 (s).

Preparation of 18, 19, and 20. Complex **14** (1280 mg, 3.33 mmol), PPh_3 (4500 mg, 17.2 mmol), and benzene (30 mL) were put in a Pyrex Schlenk tube, and the solution was irradiated with a 400 W medium-pressure mercury arc lamp at 0 °C for 2 h. After the solvent was removed, the residue was loaded on a silica gel column and eluted with acetone and then EtOH/acetone (1/10). The band eluted with EtOH/acetone (1/10) was collected, and the solvents were removed in vacuo to give an orange powder of **18** (510 mg, 0.83 mmol, 25%). Anal. Calcd for $C_{33}H_{40}FeO_4P_2$: C, 64.09; H, 6.53. Found: C, 64.31; H, 5.70. Data: IR (cm^{-1}, THF) ν_{CO} 1933; ^1H NMR (δ, $CDCl_3$) 1.20 (t, J_{HP} = 6.4 Hz, 6H, OCH_2CH_3), 1.45 (s, 15H, $C_5(CH_3)_5$), 3.58 (m, 4H, CH_2), 7.49 (m, 15H, C_6H_5); ^{31}P NMR (δ, THF) 76.7 (d, J_{PP} = 88.6 Hz, PPh_3), 121.2 (d, J_{PP} = 88.6 Hz, $P(O)(OEt)_2$).

Complex **19** was prepared in a manner similar to that of **18** from **15**. Yield: 24%. Anal. Calcd for $C_{31}H_{35}FeO_4P$: C, 63.06; H, 6.15. Found: C, 63.01; H, 5.98. Data: IR (cm^{-1}, THF) ν_{CO} 1934; ^1H NMR (δ, $CDCl_3$) 1.48 (s, 15H, $C_5(CH_3)_5$), 2.64 (d, J_{HP} = 9.0 Hz, 6H, OCH_3), 7.50 (m, 15H, C_6H_5); ^{31}P NMR (δ, THF) 76.6 (d, J_{PP} = 88.2 Hz, PPh_3), 125.8 (d, J_{PP} = 88.2 Hz, $P(O)(OMe)_2$).

Complex **20** was prepared in a manner similar to that of **18** from **16**. Yield: 25%. Anal. Calcd for $C_{41}H_{40}FeO_2P_2$: C, 72.23; H, 5.91. Found: C, 72.14; H, 5.88. Data: IR (cm^{-1}, THF) ν_{CO} 1933; ^1H NMR (δ, $CDCl_3$) 1.38 (s, 15H, $C_5(CH_3)_5$), 7.45 (m, 25H, C_6H_5); ^{31}P NMR (δ, THF) 76.7 (d, J_{PP} = 88.6 Hz, PPh_3), 121.6 (d, J_{PP} = 88.6 Hz, $P(O)Ph_2$).

Preparation of 21. $P(OMe)_3$ (1.2 mL, 10.1 mmol) was added to a solution of $Cp(CO)_2FeH$ in THF (40 mL), which was prepared in situ from $[Cp(CO)_2Fe]_2$ (1.5 g, 4.2 mmol), $NaK_{2.8}$, and CH_3COOH, to give $Cp(CO)\{P(OMe)_3\}FeH$ (IR; ν_{CO} 1940 cm^{-1}). Addition of CCl_4 (30 mL) to the solution caused the color to change from orange to green to yield $Cp(CO)\{P(OMe)_3\}FeCl$ (IR; ν_{CO} 1971 cm^{-1}). After the volatile materials were removed from the green solution under reduced pressure, benzene (80 mL), $AlCl_3$ (2.26 g, 17.0 mmol), and then $P(OMe)_3$ (3 mL, 25.4 mmol) were added in this order. Stirring the mixture for 1 h at room temperature caused the formation of a reddish yellow powder of $[Cp(CO)Fe\{P(OMe)_3\}_2]AlCl_4$. After the supernatant was removed by decantation, the powder was dissolved in H_2O. NH_4PF_6 (2.76 g, 17.0 mmol) was added to the solution to give a powder of $[Cp(CO)Fe\{P(OMe)_3\}_2]PF_6$, which was extracted by CH_2Cl_2 (50 mL). The solvent was removed from the CH_2Cl_2 solution in vacuo. Benzene (100 mL) and NEt_4Cl (2.0 g, 12.1 mmol) were added to the residue, and the resulting suspension was heated at the reflux temperature for 6 h to give a yellow homogeneous solution. The solvent was removed under reduced pressure. The residue was loaded on a silica gel column and eluted with CH_2Cl_2, acetone, and then acetone/EtOH (1/1) in this order. The reddish yellow band eluted with acetone/EtOH (1/1) was collected to give **21** (1.24 g, 3.26 mmol, 39% based on $[Cp(CO)_2Fe]_2$). Anal. Calcd for $C_{11}H_{20}FeO_7P_2$: C, 34.58; H, 5.28. Found: C, 34.41; H, 5.22. Data: IR (cm^{-1}, KBr disk) ν_{CO} 1960; ^1H NMR (δ, $CDCl_3$) 3.51

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(d, J_{HP} = 11.2 Hz, 6H, P(O)(OCH$_3$)$_2$), 3.67 (dd, J_{HP} = 11.7 & 2.0 Hz, 9H, P(OCH$_3$)$_3$), 4.75 (s, 5H, C$_5$H$_5$); ^{31}P NMR (δ, CH$_2$Cl$_2$) 124.9 (d, J_{PP} = 140.3 Hz, P(O)(OMe)$_2$), 181.8 (d, J_{PP} = 140.3 Hz, P(OMe)$_3$).

Preparation of 22. P(OMe)$_3$ (0.2 mL, 1.68 mmol) was added to a solution of **21** (534 mg, 1.60 mmol) in benzene (100 mL). The reaction mixture was irradiated with a 400 W medium-pressure mercury arc lamp at 0 °C for 2 h. The solvent was removed under reduced pressure. The resulting yellow oil was loaded on a silica gel column and eluted with CH$_2$Cl$_2$, acetone, and then acetone/EtOH (1/1) in this order. The yellow band eluted with acetone/EtOH (1/1) was collected, and the solvents were removed in vacuo to give **22** (561 mg, 1.17 mmol, 73%). Anal. Calcd for C$_{13}$H$_{29}$FeO$_9$P$_3$: C, 32.66; H, 6.11. Found: C, 32.42; H, 6.30. Data: ^{1}H NMR (δ, CDCl$_3$) 3.55 (d, J_{HP} = 10.1 Hz, 6H, P(O)(OCH$_3$)$_2$), 3.69 (m, 18H, P(OCH$_3$)$_3$), 4.52 (s, 5H, C$_5$H$_5$); ^{31}P NMR (δ, CH$_2$Cl$_2$) 136.6 (t, J_{PP} = 149.6 Hz, P(O)(OMe)$_2$), 186.8 (d, J_{PP} = 149.6 Hz, P(OMe)$_3$).

Preparation of 23. P(OMe)$_3$ (0.24 mL, 2.08 mmol) was added to a solution of **15** (741 mg, 2.08 mmol) in benzene (50 mL). The reaction mixture was irradiated with a 400 W medium-pressure mercury arc lamp at 0 °C for 3 h. The solvent was removed under reduced pressure. The resulting reddish yellow oil was loaded on a silica gel column and eluted with CH$_2$Cl$_2$, acetone, and then EtOH in this order. The yellow band eluted with the last eluent was collected, and the solvent was removed in vacuo to give a yellow powder of **23** (414 mg, 1.02 mmol, 49%). Anal. Calcd for C$_{16}$H$_{30}$FeO$_7$P$_2$: C, 42.31; H, 6.66. Found: C, 42.70; H, 6.80. Data: IR (cm^{-1}, KBr disk) ν_{CO} 1942; ^{1}H NMR (δ, CDCl$_3$) 1.77 (s, 15H, C$_5$(CH$_3$)$_5$), 3.55 (d, J_{HP} = 10.0 Hz, 6H, P(O)(OCH$_3$)$_2$), 3.68 (d, J_{HP} = 10.0 Hz, 9H, P(OCH$_3$)$_3$); ^{31}P NMR (δ, CH$_2$Cl$_2$) 130.6 (d, J_{PP} = 134.3 Hz, P(O)(OMe)$_2$), 182.2 (d, J_{PP} = 134.3 Hz, P(OMe)$_3$).

Preparation of 24. The complex **24** was prepared in a manner similar to that of **22** from **23** and P(OMe)$_3$ by a photoreaction. In this case the irradiation was performed for 19.5 h. After a column purification, complex **24** was obtained as a yellow powder in 76%. Anal. Calcd for C$_{18}$H$_{39}$FeO$_9$P$_3$: C, 39.43; H, 7.17. Found: C, 39.29; H, 7.02. Data: ^{1}H NMR (δ, CDCl$_3$) 1.65 (s, 15H, C$_5$(CH$_3$)$_5$), 3.52 (d, J_{HP} = 9.8 Hz, 6H, P(O)(OCH$_3$)$_2$), 3.67 (m, 18H, P(OCH$_3$)$_3$); ^{31}P NMR (δ, CH$_2$Cl$_2$) 138.9 (t, J_{PP} = 143.4 Hz, P(O)(OMe)$_2$), 183.0 (d, J_{PP} = 143.4 Hz, P(OMe)$_3$).

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