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Phosphorus−Phosphorus Coupling Constants in Mixed-Phosphine Tricarbonyl Iron Complexes, $Fe(CO)_3LL'$. Crystal Structure of *trans*-$Fe(CO)_3(PEt_3)(PPh_3)$

Richard L. Keiter,* John William Benson,[†] Ellen A. Keiter, Travis A. Harris, Matthew W. Hayner, Laura L. Mosimann, Eric E. Karch, Carol A. Boecker, Donna M. Olson, Jennaver VanderVeen, and Douglas E. Brandt

Department of Chemistry, Eastern Illinois University, Charleston, Illinois 61920

Arnold L. Rheingold* and Glenn P. A. Yap

Department of Chemistry, University of Delaware, Newark, Delaware 19716

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Mixed-ligand complexes, *trans*-$Fe(CO)_3LL'$ ($L = PPh_3$, $L' = PPh_2Me$, $PPhMe_2$, PMe_3, PPh_2Et, PEt_3, $PPh_2CH{=}CH_2$, PPh_2H, $AsPh_3$, $P(OPh)_3$; $L = PMe_3$, $L' = PEt_3$, PPh_2Et, PCy_3, PPh_2Me, $PPhMe$; $L = PEt_3$, $L' = PPh_2Me$; $L = PPh_2H$, $L' = PPh_2CH{=}CH_2$, PPh_2Et; $L = AsPh_3$, $L' = PPhMe_2$, $P(OPh)_3$, $P(OMe)_3$, $P(OEt)_3$), have been obtained from the stepwise reaction of phosphines with $Fe(CO)_3(BDA)$ (BDA = benzylideneacetone) or $Fe(CO)_3(AsPh_3)_2$ and from the reaction of phosphine with $Fe(CO)_4PPh_3$ in the presence of base. A strong negative correlation exists between $^2J_{PP}$ coupling constant values and the sum of the phosphine pK_a values. By application of quantitative analysis of ligand effects, it has been shown that $^2J_{PP}$ for the mixed-ligand complexes correlates strongly with both χ and E_{ar}, but not with θ. Although a near perfect fit is obtained from the three-parameter equation, a statistical analysis suggests that for this small data set there are no predictive advantages over the one-parameter pK_a model. It is possible to calculate reliable $^2J_{PP}$ values for *trans*-$Fe(CO)_3L_2$ complexes with either model. An X-ray structure of solid-state *trans*-$Fe(CO)_3(PEt_3)(PPh_3)$ shows equal $Fe-PEt_3$ and $Fe-PPh_3$ bond distances, implying that bond strength equalization may occur when two rather different phosphines occupy trans coordination sites.

Introduction

Although reliable methods recently have become available for the synthesis of $Fe(CO)_3L_2$ ($L = PR_3$) complexes,[1] preparation of disubstituted $Fe(CO)_3LL'$ ($L = PR_3$; $L' = PR_3'$) complexes remains difficult, as shown by the scarcity of literature examples.[2] The most systematic approach, reported by Cardaci's group, utilized a hydrosilyl derivative, $Fe(CO)_3L(H)(SiPh_3)$, from which $HSiPh_3$ is displaced by L′:[2c]

$$Fe(CO)_4L + HSiPh_3 \rightarrow Fe(CO)_3L(H)(SiPh_3) + CO \qquad (1)$$

$$Fe(CO)_3L(H)(SiPh_3) + L' \rightarrow Fe(CO)_3LL' + HSiPh_3 \qquad (2)$$

Highest yields (35%) were obtained when $L = PMe_3$ and $L' = PPh_3$, but for $L' = PMe_2Ph$, $PMePh_2$, or PEt_3, all of the possible disubstituted products resulted and product separation was not achieved. It is noteworthy that no crystal structures of mixed-ligand phosphine tricarbonyl complexes have been reported.

In the course of their investigations, Cardaci et al. obtained phosphorus−phosphorus coupling constants for several mixed-phosphine-ligand complexes. Particularly intriguing to us was the linear relationship that was shown to exist between $^2J_{PP}$ and pK_a values of L in $Fe(CO)_3(PMe_3)L$. If the validity of the relationship could be established for a wider range of compounds, it would be possible to determine phosphorus−phosphorus coupling constants for complexes containing two identical phosphines [e.g., $Fe(CO)_3(PPh_3)_2$], for which direct determination is experimentally difficult.

In this work, we have investigated several synthetic approaches for production of $Fe(CO)_3LL'$ and have established that Cardaci's coupling constant/pK_a correlation holds even when L′ is sterically demanding. The results have been further analyzed within the context of Giering and Prock's quantitative analysis of ligand effects (QALE).[3] In addition, we have succeeded in obtaining the crystal structure of *trans*-$Fe(CO)_3(PEt_3)(PPh_3)$, which permits assessment of the bonding ca-

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* To whom correspondence should be addressed. E-mail: cfrlk@eiu.edu; arnrhein@udel.edu.

[†] Current address: Department of Chemistry, Rockford College, Rockford, IL 61108.

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pacities of two rather different phosphines in a competitive environment.

Experimental Section

General Considerations. All reactions were carried out under dry, oxygen-free nitrogen with standard Schlenk techniques. Phosphines were obtained from Aldrich and used without further purification. Solvents were purged with N_2 prior to use. Starting materials, $Fe(CO)_4(PPh_3)$ and $Fe(CO)_3(BDA)$ (BDA = benzylideneacetone), were prepared as described in the literature.[4,5] Infrared spectra were recorded on a Nicolet 20 DX-B FT spectrometer. Phosphorus-31 NMR spectra were obtained from CD_2Cl_2 or $CDCl_3$ solutions with a General Electric QE-300 FT NMR spectrometer. Microanalyses were performed at the University of Illinois Microanalytical Laboratory, Urbana, IL.

Stepwise Reactions of Phosphines with $Fe(CO)_3(BDA)$. Synthesis of *trans*-$Fe(CO)_3(PEt_3)(PPh_3)$. To a solution of $Fe(CO)_3(BDA)$ (0.319 g, 1.12 mmol) in toluene (15 mL, distilled from CaH_2 under N_2) chilled to ice temperature was added dropwise over 20 min a toluene solution (10 mL) of PEt_3 (0.165 mL, 1.12 mmol). The ice bath was removed after 4 h, and PPh_3 (0.291 g, 1.11 mmol) dissolved in toluene (10 mL) was added dropwise over 20 min. After the solution was stirred for 64 h, the solvent was removed and the residue was chromatographed on alumina (Brockman, Activity I from Aldrich, deactivated with 5% w/w water) using a 3:1 mixture of hexanes/CH_2Cl_2. The first light yellow band was collected and found to be a mixture of $Fe(CO)_3(PPh_3)_2$, $Fe(CO)_3(PEt_3)(PPh_3)$, and $Fe(CO)_3(PEt_3)_2$ by its $^{31}P\{^1H\}$ NMR spectrum. Evaporation of the eluate and recrystallization from CH_2Cl_2/C_5H_{12} (1:10) gave large, feathery, yellow crystals and small, yellow blocks. The feathery crystals were separated manually and found to be pure *trans*-$Fe(CO)_3(PEt_3)(PPh_3)$ (0.339 g, 58.4%; mp 160−161 °C). IR (hexane): ν_{CO} 1886 cm^{-1}. Anal. Calcd for $C_{27}H_{30}FeO_3P_2$: C, 62.33; H, 5.81. Found: C, 62.41; H, 5.83.

Mixed-ligand complexes *trans*-$Fe(CO)_3(PMe_3)(PPh_3)$, *trans*-$Fe(CO)_3(PPh_2H)(PPh_2CH{=}CH_2)$, *trans*-$Fe(CO)_3(PEt_3)(PPh_2Me)$, *trans*-$Fe(CO)_3(PMe_3)(PPh_2Et)$, *trans*-$Fe(CO)_3(PMe_3)(PCy_3)$, *trans*-$Fe(CO)_3(PPh_2H)(PPh_2Et)$, and *trans*-$Fe(CO)_3(PMe_3)(PEt_3)$ were prepared by similar procedures and identified by their $^{31}P\{^1H\}$ NMR spectra.

Reactions of Phosphines with $Fe(CO)_4(PPh_3)$ in the Presence of NaOH. *trans*-$Fe(CO)_3(PPh_3)(PPh_2Et)$. To 50 mL of 1-butanol was added $Fe(CO)_4(PPh_3)$ (1.00 g, 2.33 mmol), NaOH (0.22 g, 5.3 mmol), and PPh_2Et (0.50 mL, 2.3 mmol). The solution was heated at reflux for 2 h, cooled to room temperature, and filtered to give a solid product shown by $^{31}P\{^1H\}$ NMR spectral integration to consist of *trans*-$Fe(CO)_3(PPh_3)(PPh_2Et)$ (70%), *trans*-$Fe(CO)_3(PPh_2Et)_2$ (19%), and *trans*-$Fe(CO)_3(PPh_3)_2$ (11%). Attempts to separate these complexes by chromatography were not successful.

The reaction of $Fe(CO)_4(PPh_3)$ with PPh_2Me, prepared as described above, gave *trans*-$Fe(CO)_3(PPh_3)(PPh_2Me)$, *trans*-$Fe(CO)_3(PPh_2Me)_2$, and *trans*-$Fe(CO)_3(PPh_3)_2$ in a spectral ratio of 4.4:1.8:1.0 and with $PPh_2CH{=}CH_2$ gave *trans*-$Fe(CO)_3(PPh_3)(PPh_2CH{=}CH_2)$, *trans*-$Fe(CO)_3(PPh_3)_2$, and *trans*-$Fe(CO)_3(PPh_2CH{=}CH_2)_2$ in a ratio of 12:7.0:1.0.

Synthesis of *trans*-$Fe(CO)_3(AsPh_3)_2$. (a) The reaction of $Fe(CO)_5$ (6.5 g, 33 mmol) with $AsPh_3$ (20.4 g, 66.6 mmol) and $NaBH_4$ (1.26 g, 33.3 mmol) in refluxing 1-butanol (100 mL) for 2 h gave a precipitate consisting of $Fe(CO)_4AsPh_3$ and *trans*-$Fe(CO)_3(AsPh_3)_2$.[1a] Separation of the two complexes was achieved by extracting the solid residue with boiling heptane, in which the monosubstituted complex is soluble.[6] The undissolved portion was recrystallized from a CH_2Cl_2/CH_3OH solution to give the disubstituted product (10.1 g, 40%). Substituting sodium hydroxide[1d] for sodium borohydride did not improve the yield. (b) The triphenylarsine displacement of BDA from $Fe(CO)_3(BDA)$ provided a more selective synthesis of this compound.[1e,7] A solution of $Fe(CO)_3(BDA)$ (6.11 g, 21.4 mmol) and $AsPh_3$ (13.1 g, 42.8 mmol) in CH_2Cl_2 (55 mL) was stirred at room temperature for 24 h. The tan precipitate was collected by filtration and recrystallized from CH_2Cl_2/CH_3OH to give pure product (9.66 g, 60%; dec 200−202 °C[6a]). IR (toluene): ν_{CO} 1886 cm^{-1}.

Synthesis of *trans*-$Fe(CO)_3(PPh_3)_2$. A toluene solution (25 mL) of *trans*-$Fe(CO)_3(AsPh_3)_2$ (0.500 g, 0.665 mmol) and PPh_3 (0.349 g, 1.33 mmol) was heated under reflux for 12 h. The solvent was removed under vacuum, and the product was recrystallized from CH_2Cl_2/CH_3OH to give 0.38 g (86%) of spectroscopically pure *trans*-$Fe(CO)_3(PPh_3)_2$. IR ($CHCl_3$): ν_{CO} 1884 cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$): 82.5 ppm.[1a]

Stepwise Reactions of Phosphines with *trans*-$Fe(CO)_3(AsPh_3)_2$. Synthesis of *trans*-$Fe(CO)_3(AsPh_3)(PPh_3)$ and *trans*-$Fe(CO)_3(PPh_3)(PPhMe_2)$. The formation of the arsine intermediate was maximized when the reaction was carried out by dropwise addition (85 min) of PPh_3 (0.174 g, 0.663 mmol) in toluene (10 mL) to a refluxing toluene solution (20 mL) containing *trans*-$Fe(CO)_3(AsPh_3)_2$ (0.500 g, 0.664 mmol). The total reaction time was 4 h. Analysis of the crude reaction mixture by $^{31}P\{^1H\}$ NMR showed formation of *trans*-$Fe(CO)_3(AsPh_3)(PPh_3)$ and *trans*-$Fe(CO)_3(PPh_3)_2$ (2:1). Separation of the two compounds by recrystallization and by column chromatography was attempted but not achieved. No improvement in mixed-ligand product formation was noted when reaction times were increased to 8 h. When the reaction was carried out in lower boiling solvents (cyclohexane, acetone, isopropyl alcohol, or THF), *trans*-$Fe(CO)_3(PPh_3)_2$ formed exclusively. The 4 h preparation described above was repeated, and to the resulting crude reaction mixture, $PPhMe_2$ (0.091 g, 0.664 mmol) was added. After the solution was heated at reflux temperature for 4 h, the solvent was removed and the crude reaction mixture was shown by $^{31}P\{^1H\}$ NMR analysis to contain all of the possible disubstituted products, including *trans*-$Fe(CO)_3(PPh_3)(PPhMe_2)$. Also prepared by this method were *trans*-$Fe(CO)_3(PPh_3)(PPh_2H)$ and *trans*-$Fe(CO)_3(PPh_3)[P(OPh)_3]$.

Reactions of $P(OR)_3$ (R = Me, Et, Ph) with *trans*-$Fe(CO)_3(AsPh_3)_2$. A toluene solution (25 mL) of *trans*-$Fe(CO)_3(AsPh_3)_2$ (0.50 g, 0.66 mmol) and $P(OMe)_3$ (0.08 g, 0.66 mmol) was refluxed (oil-bath temperature thermostated at 120 °C) for 8 h. The solvent was removed from the solution, and the residue was placed on a silica gel column and eluted with toluene. The first fraction collected was the mixed-ligand product, *trans*-$Fe(CO)_3(AsPh_3)[P(OMe)_3]$, followed by *trans*-$Fe(CO)_3[P(OMe)_3]_2$, and a third fraction consisting of $AsPh_3$. The mixed-ligand product was further purified by recrystallization from CH_2Cl_2/CH_3OH to give 0.025 g (6.5%) of yellow *trans*-$Fe(CO)_3(AsPh_3)[P(OMe)_3]$; mp 201−202 °C, dec. Anal. Calcd for $C_{24}H_{24}AsFeO_6P$: C, 50.56; H, 4.24. Found: C, 50.35; H, 4.12. By the same procedure, *trans*-$Fe(CO)_3(AsPh_3)[P(OEt)_3]$ and *trans*-$Fe(CO)_3(AsPh_3)[P(OPh)_3]$ were prepared.

A 1:5 molar ratio of *trans*-$Fe(CO)_3(AsPh_3)_2$ (0.5 g, 0.66 mmol) to $P(OR)_3$ (R = Me, Et, Ph) (3.2 mmol) in 25 mL of toluene was refluxed (oil-bath temperature thermostated at 120 °C) for 24 h. The solvent was removed, and integral product percentages were obtained from the $^{31}P\{^1H\}$ NMR spectra (Table 1). Carbonyl stretching frequencies of the *trans*-$Fe(CO)_3(AsPh_3)[P(OR)_3]$ and *trans*-$Fe(CO)_3[P(OR)_3]_2$ complexes, separated by chromatography as described above, are given in Table 2.

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Table 1. Relative Yields (%) from Reactions of *trans*-$Fe(CO)_3(AsPh_3)_2$ with $P(OR)_3$[a]

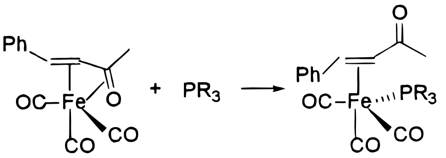
ligand	reactant ratio[b]	$Fe(CO)_3$-$(AsPh_3)[P(OR)_3]$	$Fe(CO)_3$-$[P(OR)_3]_2$	$Fe(CO)_2$-$[P(OR)_3]_3$
$P(OMe)_3$	1:1	74.2	25.8	0
$P(OEt)_3$	1:1	80.2	19.8	0
$P(OPh)_3$	1:1	87.6	12.4	0
$P(OMe)_3$	1:5	53.7	42.9	3.4
$P(OEt)_3$	1:5	43.8	53.2	3.0
$P(OPh)_3$	1:5	66.0	33.0	1.0

[a] The reactions with a 1:1 mole ratio were carried out for 8.0 h, and the reactions with a 1:5 mole ratio were carried out for 24.0 h, both in refluxing toluene. [b] Complex/phosphite.

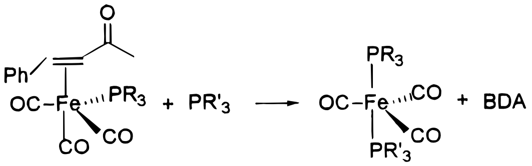
Crystallographic Structural Determination of $Fe(CO)_3(PEt_3)(PPh_3)$. A suitable crystal of *trans*-$Fe(CO)_3(PEt_3)(PPh_3)$ was obtained by diffusion of a layer of pentane into a CH_2Cl_2 solution of $Fe(CO)_3(PEt_3)(PPh_3)$ at −18 °C under nitrogen. Crystallographic data are given in Table 3. Photographic evidence and systematic absences in the diffraction data uniquely identified the space group. No correction for absorption was required. The structure was refined with all non-hydrogen atoms anisotropic and all hydrogen atoms idealized. All computations used SHELXTL, version 5, software (G. Sheldrick, Siemans XRD, Madison, WI).

Results and Discussion

Synthetic Aspects. Vessieres and Dixneuf found that $Fe(CO)_3(BDA)$ reacts with 1 mol of $PPhMe_2$ to give $Fe(CO)_3(BDA)(PPhMe_2)$, a complex in which BDA is bound as a monodentate ligand.[8] In addition, Cardaci and Sorriso were able to isolate $Fe(CO)_3(BDA)(SbPh_3)$.[9] However, the reaction of PPh_3 (less basic than PMe_2Ph) with $Fe(CO)_3(BDA)$ gave a mixture of $Fe(CO)_3(BDA)(PPh_3)$ and $Fe(CO)_2(BDA)(PPh_3)$.[10] More recently, it has been demonstrated that 2 mol of PR_3 displace BDA from $Fe(CO)_3(BDA)$ rapidly and cleanly to give *trans*-$Fe(CO)_3(PR_3)_2$.[1e,h,7] These results suggested a potential method for the preparation of mixed-ligand phosphine complexes from $Fe(CO)_3(BDA)$ via a two-step reaction:



(3)



(4)

Even without isolation of the intermediate $Fe(CO)_3L(BDA)$ in these reactions, the major product for eight reactions was the mixed-ligand derivative. In all cases, the symmetrical derivatives, $Fe(CO)_3L_2$ and $Fe(CO)_3L'_2$, were present as minor products. Although traces of $Fe(CO)_2L(BDA)$ were present in product mixtures, its formation was minimized by adding the more nucleophilic phosphine first (e.g., PMe_3 before PPh_3) at 0 °C.

Table 2. Infrared Data (CO Stretching Frequencies) for Phosphite Complexes of Iron Tricarbonyl[a]

L	*trans*-$Fe(CO)_3AsPh_3L$	*trans*-$Fe(CO)_3L_2$	ref
$P(OMe)_3$	1900(s), 1910(s)	1913(s), 1922(s)	30
$P(OEt)_3$	1898(s), 1910(s)	1907(s), 1917(s)	30a
$P(OPh)_3$	1909(s)	1926(s)	30, 6b

[a] In hexane, cm^{-1}.

Table 3. Crystal Data and Structure Refinement for *trans*-$Fe(CO)_3(PEt_3)(PPh_3)$

empirical form	$C_{27}H_{30}FeO_3P_2$
fw	520.3
temp	296(2) K
wavelength	0.710 73 Å
cryst syst	monoclinic
space group	$P2_1/n$
unit cell dimens	$a = 11.314(3)$ Å, $\alpha = 90°$ $b = 16.042(4)$ Å, $\beta = 93.58(2)°$ $c = 14.813(4)$ Å, $\gamma = 90°$
volume, Z	2683(1) $Å^3$, 4
density (calcd)	1.288 g/cm^3
abs coeff	0.706 mm^{-1}
$F(000)$	1088
cryst size	0.40 × 0.37 × 0.35 mm
θ range for data collection	2.20−25.00°
limiting indices	$-13 \le h \le 12$, $0 \le k \le 19$, $-17 \le l \le 0$
no. reflns collected	4611
no. indep reflns	4443 ($R_{int} = 0.0439$)
refinement method	full-matrix least-squares on F^2
data/restraints/ parameters	4400/0/298
goodness-of-fit on F^2	1.064
final R indices [$I > 2\sigma(I)$]	R1 = 0.660, wR2 = 0.1626
final R indices (all data)	R1 = 0.1285, wR2 = 0.2246
largest diff. peak and hole	0.846 and −0.373 e $Å^{-3}$

Identification of the $Fe(CO)_3LL'$, $Fe(CO)_3L_2$, and $Fe(CO)_3L'_2$ complexes by $^{31}P\{^1H\}$ NMR spectroscopy is straightforward. The mixed-ligand complexes give the expected two doublets with $^2J_{PP}$ values ranging from 22.9 to 33.2 Hz (Table 4). When all three complexes are present, the two doublets tend to lie between singlets arising from the two symmetrical products. For example, the ^{31}P chemical shifts of *trans*-$Fe(CO)_3(PPh_3)_2$ and *trans*-$Fe(CO)_3(PMe_3)_2$ are singlets at 82.6 and 39.3 ppm, respectively, while the chemical shifts of *trans*-$Fe(CO)_3(PMe_3)(PPh_3)$ are 81.8 and 42.9 ppm. The signal for PPh_3 shifts to a lower frequency when the more basic PMe_3 occupies the trans position, while the signal for PMe_3, when it is trans to the less basic PPh_3, shifts to higher frequency.

Our second approach for preparing mixed-ligand complexes was based on a synthesis developed for $Fe(CO)_3(PR_3)_2$ complexes. When $Fe(CO)_5$ is heated under reflux in 1-butanol with 2 mol of PR_3 in the presence of $NaBH_4$, *trans*-$Fe(CO)_3(PR_3)_2$ is formed selectively.[1a,i] When $Fe(CO)_4PPh_3$ is substituted for $Fe(CO)_5$, but conditions are otherwise unchanged, no reaction occurs. However, if sodium hydroxide is used in place of sodium borohydride, conversion of $Fe(CO)_4PPh_3$ to *trans*-$Fe(CO)_3(PPh_3)_2$ takes place in high yield.[1a,d] Thus, it appeared that it would be possible to prepare $Fe(CO)_3LL'$ complexes from $Fe(CO)_4L$ and L′ by this method:

$$Fe(CO)_4(PR_3) + OH^- \rightarrow [HFe(CO)_3PR_3]^- + CO_2 \quad (5)$$

$$[HFe(CO)_3(PR_3)]^- + PR'_3 \rightarrow trans\text{-}Fe(CO)_3(PR_3)(PR'_3) + H_2 \quad (6)$$

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Table 4. $^{31}P\{^1H\}$ NMR (CD_2Cl_2) and pK_a Data for Carbonyl Complexes of Iron[a]

trans-$Fe(CO)_3LL'$

L	L′	δ_L (ppm)	$\delta_{L'}$ (ppm)	$^2J_{PP}$ (Hz)	$(pK_a + pK_a')^a$
PPh_3	$PPh_2CH{=}CH_2$	83.1	76.7	33.2	2.73 + (?)
PPh_3	PPh_2Me	82.5	66.3	31.8	2.73 + 4.57
PPh_3	PPh_2H	82.1	55.6	31.1	2.73 + 0.03
PPh_3	PPh_2Et	82.9	77.8	30.9	2.73 + 4.9
PPh_3	$PPhMe_2$	82.0	52.2	30.0	2.73 + 6.50
PPh_3	PMe_3	81.8	42.9	28.7	2.73 + 8.65
PPh_3	PEt_3	82.5	71.4	27.8	2.73 + 8.69
PPh_2Et	PPh_2H	77.1	55.4	29.4	4.9 + 0.03
$PPh_2CH{=}CH_2$	PPh_2H	76.3	55.1	28.8	(?) + 0.03
PPh_2Me	PMe_3	67.0	44.2	26.8[b]	4.57 + 8.65
PPh_2Et	PMe_3	76.4	42.3	26.7	4.9 + 8.65
PPh_2Me	PEt_3	70.6	65.4	25.9	4.57 + 8.69
$PPhMe_2$	PMe_3	52.1	43.2	24.5[b]	6.50 + 8.65
PEt_3	PMe_3	72.1	43.9	22.9	8.69 + 8.65
PMe_3	PCy_3	45.0	88.1	23.5	8.65 + 9.7
PPh_3	$P(OPh)_3$	79.3	186.0	86.3	2.73 + (−2.0)
$AsPh_3$	$PPhMe_2$		55.6		
$AsPh_3$	PPh_3		85.3		
$AsPh_3$	$P(OPh)_3$		185.6		
$AsPh_3$	$P(OMe)_3$		192.2		
$AsPh_3$	$P(OEt)_3$		185.3		

trans-$Fe(CO)_3L_2$

L	δ (ppm)	ref	L	δ (ppm)	ref
$P(OMe)_3$	190.7		PPh_2Me	65.4	1a
$P(OEt)_3$	185.0		PPh_2H	54.3	1a
$P(OPh)_3$	182.0		PPh_2Et	77.3	1a
PPh_3	82.6	1a	PMe_3	39.3	1b
$PPhMe_2$	50.3	1f	PEt_3	70.5	
$PPh_2CH{=}CH_2$	76.7	1a			

$Fe(CO)_2L_3$

L	δ (ppm)	ref	L	δ (ppm)	ref
$P(OPh)_3$	165.8	31	$P(OMe)_3$	188.6	31
$P(OEt)_3$	182.8	31			

[a] pK_a values were taken from ref 15. [b] Data taken from ref 2c.

The harsh reaction conditions required (strong base, >90 °C) led to some product scrambling such that, in each case, both symmetrical products were produced along with the mixed-ligand complex (60−70%). At temperatures lower than 90 °C, essentially no reaction took place over the 2 h reaction time employed. Substitution of $[Et_4N]OH$ for NaOH did not lead to greater product selectivity.

Kinetic studies of the reaction of *trans*-$Fe(CO)_3(AsPh_3)_2$ with CO, reported by Modi and Atwood, showed that $AsPh_3$ is replaced by CO to give $Fe(CO)_4(AsPh_3)$ ($k = 4.57 \times 10^{-5}$ s^{-1} at 90 °C).[6b] Furthermore, their work revealed that the reaction of *trans*-$Fe(CO)_3(PPh_3)_2$ with CO is much slower and requires a much higher temperature in order to achieve a rate comparable to that of the arsine reaction ($k = 2.64 \times 10^{-5}$ s^{-1} at 136 °C). These reactions proceed by a dissociative mechanism and indicate that the Fe−$AsPh_3$ bond is significantly weaker than the Fe−PPh_3 bond, a conclusion verified by Luo and Nolan from thermodynamic studies.[1h] These and other results[11] indicated that stepwise replacement of $AsPh_3$ from *trans*-$Fe(CO)_3(AsPh_3)_2$ by phosphines may provide easy access to mixed-ligand complexes:

$$\textit{trans}\text{-}Fe(CO)_3(AsPh_3)_2 + PR_3 \rightarrow \textit{trans}\text{-}Fe(CO)_3(AsPh_3)(PR_3) + AsPh_3 \quad (7)$$

$$\textit{trans}\text{-}Fe(CO)_3(AsPh_3)(PR_3) + PR'_3 \rightarrow \textit{trans}\text{-}Fe(CO)_3(PR_3)(PR'_3) + AsPh_3 \quad (8)$$

Although 2 mol of PPh_3 displace $AsPh_3$ from *trans*-$Fe(CO)_3(AsPh_3)_2$ in refluxing toluene to give *trans*-$Fe(CO)_3(PPh_3)_2$ in essentially quantitative yield, 1 mol of PPh_3 gives a 2:1 mixture of *trans*-$Fe(CO)_3(AsPh_3)(PPh_3)$ and *trans*-$Fe(CO)_3(PPh_3)_2$. The latter reaction was performed under a variety of conditions in an attempt to optimize the formation of the mixed-ligand product. The ratio was not improved in favor of the mixed-ligand complex by changing reaction times from 4 h to 2, 6, or 8 h. On the premise that lower temperatures might discourage displacement of both arsine ligands, lower boiling solvents (cyclohexane, isopropyl alcohol, THF, and acetone) were substituted for toluene. However, only *trans*-$Fe(CO)_3(PPh_3)_2$ was produced from these lower temperature reactions. Although these observations could be explained in terms of ligand scrambling occurring at higher temperatures but not lower, separate experiments showed that a mixture of *trans*-$Fe(CO)_3(AsPh_3)_2$ and *trans*-$Fe(CO)_3(PPh_3)_2$ does react to give mixed-ligand complexes. Furthermore, no reaction occurs when *trans*-$Fe(CO)_3(PPh_3)_2$ and $AsPh_3$ are heated under similar conditions. We conclude that the activation energy for the conversion of *trans*-$Fe(CO)_3(AsPh_3)(PPh_3)$ to *trans*-$Fe(CO)_3(PPh_3)_2$ is lower than that for the conversion of *trans*-$Fe(CO)_3(AsPh_3)_2$ to *trans*-$Fe(CO)_3(AsPh_3)(PPh_3)$, but as the temperature is increased, the slower reaction becomes relatively more favorable, which accounts for the appearance of the mixed-ligand complex in the crude reaction mixtures produced at higher temperatures.

A number of reactions were carried out between *trans*-$Fe(CO)_3(AsPh_3)_2$ and $P(OMe)_3$, $P(OEt)_3$, or $P(OPh)_3$.

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(11) (a) Wovkulich, M. J.; Atwood, J. D. *Organometallics* **1982**, *1*, 1316. (b) Fontaine, X. L. R.; Fowles, E. H.; Layzell, T. P.; Shaw, B. L.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.* **1991**, 1519.

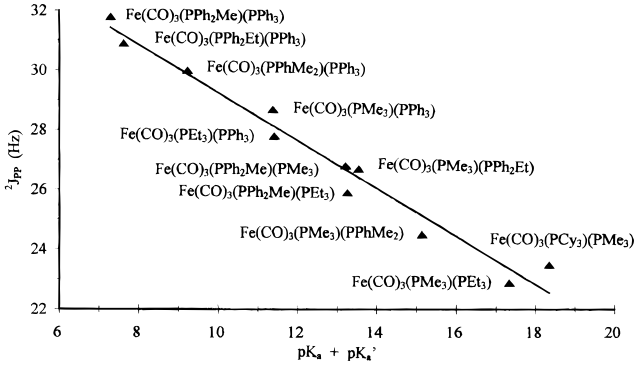

Figure 1. Plot of experimentally determined phosphorus−phosphorus coupling constants vs the sum of the pK_a values for the two phosphines in *trans*-Fe(CO)$_3$LL′.

Whereas phosphines displace arsines quantitatively, phosphites do not. Even when *trans*-Fe(CO)$_3$(AsPh$_3$)$_2$ was heated under reflux in toluene for 24 h with a 5-fold excess of phosphite, formation of *trans*-Fe(CO)$_3$[(P(OR)$_3$]$_2$ was incomplete (Table 1). When 1:1 mole ratios of the reactants were heated under reflux in toluene for 8 h, mixtures of *trans*-Fe(CO)$_3$[P(OR)$_3$](AsPh)$_3$ and *trans*-Fe(CO)$_3$[P(OR)$_3$]$_2$ were obtained (Table 1). Although the reactions most likely proceed primarily by AsPh$_3$ dissociation, the data in Table 1 suggest that the incoming ligands play a role in the substitution process (cone angles[12] for P(OMe)$_3$, P(OEt)$_3$, and P(OPh)$_3$ are 107°, 109°, and 128°, respectively, and pK_a values[13] are 2.60, 3.31, and −2.0, respectively). The better nucleophiles, P(OMe)$_3$ and P(OEt)$_3$ (and sterically less hindered), lead to higher conversions to di- and trisubstituted products than does P(OPh)$_3$.

Relationship between $^2J_{PP}$ and pK_a. It has been noted that absolute values of the phosphorus−phosphorus coupling constants for the complexes *trans*-Fe(CO)$_3$(PMe$_3$)L (L = PMe$_3$, PEt$_3$, PMe$_2$Ph, PMePh$_2$, PPh$_3$) are linearly related to the pK_a values of the ligands, L,[2c] with less basic ligands associated with larger values of $^2J_{PP}$. This correlation is in agreement with the general rule that the magnitude of $^2J_{PP}$ increases as the electronegativities of groups attached to phosphorus increase[14] and that the affinities of phosphines for protons lessen (and pK_a values decrease) as substituent electronegativities increase.[15]

We have examined the $^2J_{PP}$/pK_a relationship for a range of Fe(CO)$_3$LL′ complexes in which both phosphines are allowed to vary. To take into account these ligand combinations, we have plotted $^2J_{PP}$ vs the sum of the two pK_a values, pK_a + pK_a′ (Figure 1, Table 4). The plot shows that the strong $^2J_{PP}$/pK_a correlation remains intact for the much larger and more diverse data set. The equation describing the relationship is

$$^2J_{PP} = (-0.80 \pm 0.05)(pK_a + pK_a') + (37.3 \pm 0.6) \qquad (9)$$

$$n = 11 \quad R^2 = 0.968$$

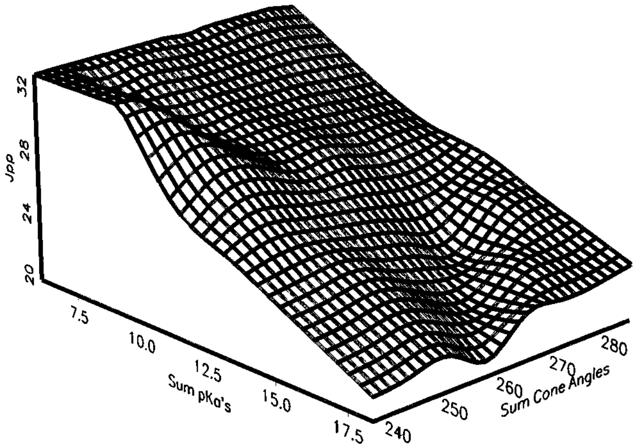

Figure 2. Three-dimensional plot showing correlations between $^2J_{PP}$, pK_a, and phosphine cone angle, θ, for *trans*-Fe(CO)$_3$LL′.

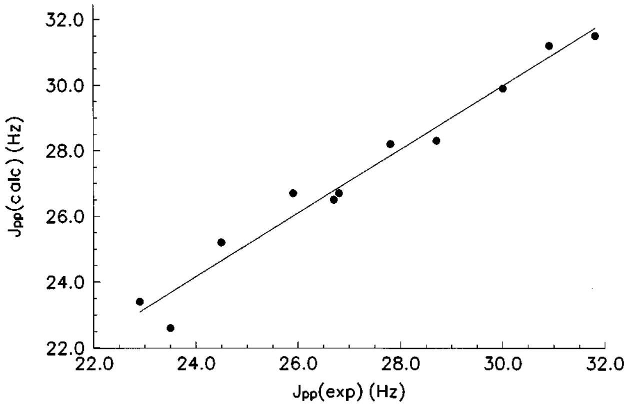

Figure 3. Plot of $^2J_{PP}$ (calculated) vs $^2J_{PP}$ (experimental) for *trans*-Fe(CO)$_3$LL′ complexes (eq 9).

Notably, even *trans*-Fe(CO)$_3$(PMe$_3$)(PCy$_3$), a complex containing a sterically demanding phosphine (cone angle = 170°), does not depart significantly from the other data collected. Correlations with pK_as and cone angles are displayed in three dimensions in Figure 2. The two-dimensional contour reveals a strong negative correlation of J_{PP} with pK_a, but an insignificant correlation with phosphine cone angles. Equation 9 allows the calculation of $^2J_{PP}$ coupling constants to within 2% of the experimental values (shown graphically in Figure 3). Data collected for phosphite and secondary phosphine complexes deviated substantially from those for mixed-ligand tertiary phosphine complexes and were not included in Figures 1, 2, or 3. In addition, complexes of PPh$_2$CH=CH$_2$ were omitted because experimental values of pK_a are not available.

Quantitative Analysis of Ligand Effects. The pK_a values used in eq 9 are based on proton dissociation from R$_3$PH$^+$ in polar aprotic media and are referenced to aqueous solution. Evidence has been presented by Giering[16] and more recently by Poë[17] that these values have a steric component. Modified pK_a values, from which the steric contributions have been deducted, are thought to better account for the nucleophilic behavior

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[12] (a) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313. (b) Rahman, M.; Liu, H. Y.; Prock, A.; Giering, W. P. *Organometallics* **1987**, *6*, 650.

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[14] Jameson, C. J. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds.; VCH: Deerfield Beach, FL, 1993.

[15] Bush, R. C.; Angelici, R. J. *Inorg. Chem.* **1988**, *27*, 681.

[16] Liu, H.-Y.; Eriks, K.; Prock, A. Giering, W. P. *Organometallics* **1990**, *9*, 1758.

[17] Hudson, R. H. E.; Poë, A. J. *Organometallics* **1995**, *14*, 3238.

Table 5. Parameters Used for Determination of Equation 11

L	L′	${}^2J_{PP}$ (Hz)	χ	θ	E_{ar}
PPh_3	PPh_2Me	31.8	25.35	281	4.7
PPh_3	PPh_2Et	30.9	24.55	285	4.7
PPh_3	$PPhMe_2$	30.0	23.85	267	3.7
PPh_3	PMe_3	28.7	21.80	263	2.7
PPh_3	PEt_3	27.8	19.55	277	2.7
PPh_2Me	PMe_3	26.8	20.65	254	2.0
PPh_2Et	PMe_3	26.7	19.85	258	2.0
PPh_2Me	PEt_3	25.9	18.4	268	2.0
$PPhMe_2$	PMe_3	24.5	19.15	240	1.0
PEt_3	PMe_3	22.9	14.85	250	0.0
PMe_3	PCy_3	23.5	9.95	288	0.0

of phosphines in nonpolar solvents. When the scaled values from Poë's work were used in eq 9, a straight line with a R^2 value of 0.869 was obtained. This poorer correlation may in fact demonstrate that the better correlation given by traditional pK_a values results from an inherent steric component that is built into traditional pK_as.

Giering and Prock have shown that many physiochemical properties can be related by the equation

$$\text{property} = a\chi + b(\theta - \theta_{st}) + cE_{ar} + d \qquad (10)$$

in which χ is an electronic factor, θ is Tolman's cone angle, θ_{st} is the steric threshold, and E_{ar} is an aryl effect parameter.[3b] Analysis of data from many kinetic studies suggests that the steric term is of no consequence until the cone angle reaches the steric threshold, at which point it turns on and has a significant bearing on the observed rate.

Nolan[18] has applied the QALE analysis to heats of reaction obtained for the formation of $Fe(CO)_3(PR_3)_2$ from phosphine and $Fe(CO)_3(BDA)$. Excellent correlations were found between ΔH and both the electronic and steric factors, with a steric threshold of 135°. It was of interest to determine if eq 10 could be also applied to our ${}^2J_{PP}$ data.

The following equation was determined by multiple linear regression using the experimental phosphorus−phosphorus coupling values, ${}^2J_{PP}$, and literature values of χ, θ, and E_{ar} (Table 5):

$$ {}^2J_{PP} = (2.15 \pm 0.58)\chi + (0.286 \pm 0.076)\theta - (4.80 \pm 1.8)E_{ar} - (80.2 \pm 28) \qquad (11)$$

$$n = 11 \quad R^2 = 0.992$$

This appears to be an unusually excellent fit of the QALE model to the data. Caution must be used, however, before declaring this a meaningful result. The standard linear regression procedures used to fit the model equation to the data assume no uncertainty in the independent variables. However, the uncertainties in the experimental values of ${}^2J_{PP}$ and in the independent variables will lead to an expected sum of square residuals, even for an exact model. To estimate this value requires a knowledge of the uncertainties in the values of ${}^2J_{PP}$, χ, θ, and E_{ar}. Our ${}^2J_{PP}$ values have an uncertainty of ±0.1 Hz, and θ has an uncertainty of at least ±2°.[12a] A value of ±3° or more may be more reasonable for some of the ligands. Unfortunately, the values of E_{ar} are reported in the literature with no estimate of their uncertainty. Examining Giering and Prock's method of determining E_{ar},[3a] it does not seem unreasonable and seems even conservative to estimate an uncertainty of ±0.3 in the values of E_{ar}. A reasonable estimate of the uncertainty in χ is 0.1. If the error in each variable is assumed to be independent and normally distributed, a calculation of the expected sum of square residuals for eq 11 results in a value of about 7 Hz. The actual sum of square residuals for the fitted equation is 0.7 Hz. Why is the difference between the expected sum of square residuals and the actual sum of square residuals important? The fitting process cannot distinguish between two different models when it yields for both a sum of square residuals that is less than the expected sum for each model. Any sum of square residuals that is less than the expected value for a perfect model is less only because of an accidental fit of the particular data set. As an example, consider the model

$$ {}^2J_{PP} = AE_{ar} + B \qquad (12)$$

a linear correlation using only the E_{ar} parameter. Linear regression applied to our ${}^2J_{PP}$ data results in

$$ {}^2J_{PP} = (1.79 \pm 0.09)E_{ar} + (23.1 \pm 0.3) \qquad (13)$$

$$n = 11 \quad R^2 = 0.976$$

A calculation of the expected sum of square residuals results in 2.1 Hz, which is identical to the actual sum (2.1 Hz). Thus, the model accounts for all of the variations in the data except that expected due to uncertainties inherent in the data itself. Even though the QALE model results in a higher correlation coefficient than the simpler one (eqs 12 and 13), there is no statistical basis for using the correlation coefficient to accept one model over the other. This in no way implies that the QALE model is inappropriate, only that this particular set of data cannot be used to distinguish between the complete QALE model and some other simpler model with fewer parameters by simply comparing the coefficient of correlation between the experimental values and model predicted values. It only points out the importance of considering more than correlation coefficients in deciding between competing models. A more complete analysis is possible using analysis of variance techniques, but that would require more detailed information about the uncertainties in the independent variables.

The QALE analysis of our data does not reveal a steric threshold, perhaps surprising in view of Nolan's thermochemical results, but our largest cone angle sum is 288°, or 144°/ligand, which is not an extreme value. It is possible that a threshold is present at some greater cone angle sum. Cone angle changes could influence ${}^2J_{PP}$ if these changes were accompanied by changes in the R−P−R bond angle (and consequently changes in the s character present in the metal−phosphorus bond) or if steric repulsion prevented maximum overlap of the phosphorus and iron bonding orbitals. As seen in the crystallographic section which follows, the Fe−P distances and R−P−R angles change minimally at best as the substituents on phosphorus are changed, and therefore, one is led to expect that cone angle changes do not have much bearing on ${}^2J_{PP}$ within the range of ligands employed in this study.

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[18] Li, C.; Stevens, E. D.; Nolan, S. P. *Organometallics* **1995**, *14*, 3791.

Table 6. $^2J_{PP}$ for $Fe(CO)_3L_2$[a] Calculated from pK_a Values[a] and QALE Factors[b]

complex	exptl	calcd (eq 9)	calcd (eq 11)
$Fe(CO)_3(PPh_3)_2$		32.9	33.6
$Fe(CO)_3[\eta^1\text{-}PPh_2CH_2CH_2PPh_2]_2$	30.4[c]	31.1	
$Fe(CO)_3(PPh_2Me)_2$		30.0	30.4
$Fe(CO)_3(PPh_2Et)_2$		29.5	29.3
$Fe(CO)_3(PPhMe_2)_2$		26.9	25.6
$Fe(CO)_3(PMe_3)_2$	23.5[d]	23.5	24.1
$Fe(CO)_3(PEt_3)_2$		23.4	22.4
$Fe(CO)_3(PCy_3)_2$		21.8	23.0

[a] $^2J_{PP} = (-0.80 \pm 0.05)(pK_a + pK_a') + (37.3 \pm 0.6)$. [b] $^2J_{PP} = (2.15 \pm 0.58)\chi + (0.286 \pm 0.076)\theta - (4.8 \pm 1.8)E_{ar} - (80.2 \pm 28)$. [c] Analysis of second-order proton spectrum, ref 19. [d] Analysis of second-order phosphorus spectrum, ref 20.

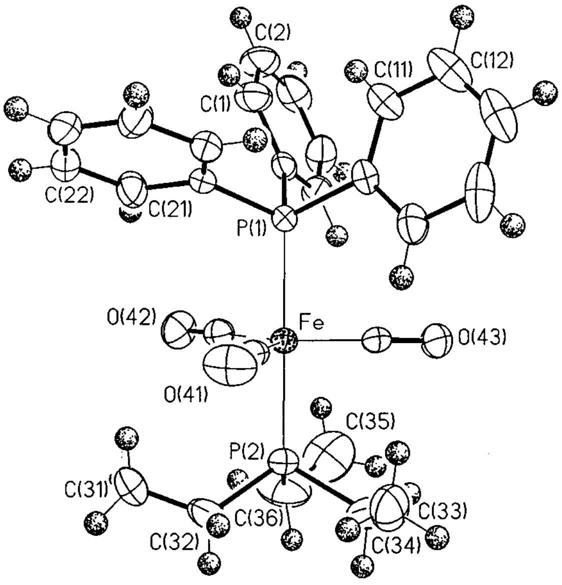

Figure 4. Molecular structure of *trans*-$Fe(CO)_3(PEt_3)(PPh_3)$.

Equations 9 and 11 allow one to calculate three important types of data: (1) $^2J_{PP}$ for *trans*-$Fe(CO)_3L_2$ complexes in which the phosphines are equivalent; (2) $^2J_{PP}$ values for mixed-phosphine complexes not yet synthesized; and (3) phosphine pK_a values not yet experimentally measured. Whereas $^2J_{PP}$ has been determined for *trans*-$Fe(CO)_3(PMe_3)_2$ by proton NMR analysis of its $X_9AA'X'_9$ spin system[2c,19] and for *trans*-$Fe(CO)_3(\eta^1\text{-}PPh_2CH_2CH_2PPh_2)_2$ by phosphorus NMR analysis of its XAA′X′ spin system,[20] obtaining values by similar methods for more complex systems such as *trans*-$Fe(CO)_3(PPh_3)_2$ is not straightforward. Values of $^2J_{PP}$ for several bis(phosphine) complexes, calculated from eqs 9 and 11, are shown in Table 6. Similar calculations enable one to obtain $^2J_{PP}$ for mixed-ligand complexes not yet synthesized. An example of the pK_a determination is provided by $PPh_2CH{=}CH_2$, for which the estimated value (eq 9) is 2.4 based on the $^2J_{PP}$ for *trans*-$Fe(CO)_3(PPh_3)(PPh_2CH{=}CH_2)$ (33.2 Hz) and the pK_a for PPh_3 (2.73).

Structure of *trans*-$Fe(CO)_3(PEt_3)(PPh_3)$. The structure of *trans*-$Fe(CO)_3(PEt_3)(PPh_3)$ is shown in Figure 4; selected structural parameters are given in Table 7. This is the first structurally characterized example of an $Fe(CO)_3$ fragment bound to two different phosphine ligands, and it provides a comparison to recently reported structures of complexes with two identical phosphines, $(Fe(CO)_3(PPh_3)_2$,[21] $Fe(CO)_3(PPh_2Cy)_2$,[18] and $Fe(CO)_3(PPh_2Me)_2$.[22]

Table 7. Selected Bond Lengths (Å) and Angles (deg) for *trans*-$Fe(CO)_3(PEt_3)(PPh_3)$

Distances			
Fe−P(1)	2.204(2)	Fe−C(41)	1.773(8)
Fe−P(2)	2.201(2)	Fe−C(42)	1.768(8)
C(41)−O(41)	1.137(8)	Fe−C(43)	1.767(8)
C(42)−O(42)	1.153(8)	P(1)−C(6)	1.836(7)
C(43)−O(43)	1.151(8)	P(1)−C(16)	1.834(7)
P(2)−C(32)	1.781(10)	P(1)−C(26)	1.836(7)
P(2)−C(34)	1.866(11)	P(2)−C(36)	1.843(12)
Angles			
P(1)−Fe−P(2)	177.34(9)	C(43)−Fe−C(42)	118.6(3)
C(43)−Fe−C(41)	123.6(4)	Fe−C(41)−O(41)	178.0(7)
C(42)−Fe−C(41)	117.(3)	C(41)−Fe−P(1)	88.7(2)
C(42)−Fe−P(1)	92.1(2)	C(43)−Fe−P(1)	91.9(2)
C(41)−Fe−P(2)	88.8(2)	C(42)−Fe−P(2)	89.7(2)
C(43)−Fe−P(2)	88.9(2)	Fe−C(42)−O(42)	178.6(7)
Fe−C(43)−O(43)	177.8(7)		

The geometry about iron is approximately trigonal bipyramidal, with equatorial CO ligands and axial phosphine ligands (P−Fe−P angle = 177.34(9)°). Two of the C−Fe−C angles (118.6(3)°, 117.7(3)°) are nearly equivalent, while the third is substantially larger (123.6(4)°), a trend observed previously in bis(phosphine) derivatives and ascribed to packing effects.[21,22]

The Fe atom and the three CO groups are nearly coplanar, but the three CO groups are bent slightly toward the triethylphosphine ligand (average C−Fe−P angle = 89.1(2)°) and away from the triphenylphosphine ligand (average C−Fe−P angle = 90.9(2)°), suggesting a slight mutual steric awareness of the two phosphines.

The most unusual feature of the structure is the Fe−P bond distances, which are identical within experimental error (2.204(2) and 2.201(2) Å).[24] If bond length correlates with bond strength, a concept which has been recently questioned,[23] the $Fe{-}PPh_3$ and $Fe{-}PEt_3$ bonds are of equal strength. Support for equal strength is provided by the positive correlation between the Fe−P bond length and bond energy data.[18] When PPh_3, PPh_2Cy, and PPh_2Me react with $Fe(CO)_3(BDA)$ to give disubstituted *trans*-$Fe(CO)_3(PR_3)_2$ complexes, 26.9, 27.5, and 34.1 kcal are liberated, respectively, with Fe−P bond lengths in the resulting complexes of 2.2173(9), 2.218(1), and 2.2059(14) Å, respectively. In other words, the significantly shorter Fe−P bond in $Fe(CO)_3(PPh_2Me)_2$ is associated with a significantly larger Fe−P bond energy.

Increasing the basicities of ligands (L) trans to triphenylphosphine in $Fe(CO)_3(PPh_3)L$ would be expected to increase the $Fe{-}PPh_3$ bond strength. Substituting the CO group trans to PPh_3 in *trans*-$Fe(CO)_4PPh_3$ with a second PPh_3 ligand gives *trans*-$Fe(CO)_3(PPh_3)_2$, in which the average Fe−P distance (2.2173(9) Å) is significantly

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[19] Harris, R. K. *Can. J. Chem.* **1964**, *42*, 2275.

[20] Keiter, R. L.; Rheingold, A. L.; Hamerski, J. J.; Castle, C. K. *Organometallics* **1983**, *2*, 1635.

[21] The structure of $Fe(CO)_3(PPh_3)_2$ has been reported by two groups (the latter one is reported with crystallized ether): (a) Glaser, R.; Yoo, Y.-H.; Chen, G. S.; Barnes, C. L. *Organometallics* **1994**, *13*, 2578. (b) Lane, H. P.; Godfrey, S. M.; McAuliffe, C. A.; Pritchard, R. G. *J. Chem. Soc., Dalton Trans.* **1994**, 3249.

[22] Glaser, R.; Haney, P. E.; Barnes, C. L. *Inorg. Chem.* **1996**, *35*, 1758.

[23] (a) Alyea, E. C.; Song, S. *Inorg. Chem.* **1995**, *34*, 3864. (b) Ernst, R. D.; Freeman, J. W.; Stahl, L.; Wilson, D. R.; Arif, A. M.; Nuber, B.; Ziegler, M. L. *J. Am. Chem. Soc.* **1995**, *117*, 5075.

[24] Riley, P. E.; Davis, R. E. *Inorg. Chem.* **1980**, *19*, 159.

shorter than the Fe−P distance in $Fe(CO)_4PPh_3$ (2.244(1) Å).[24] Replacing one PPh_3 of *trans*-$Fe(CO)_3(PPh_3)_2$ with the more basic PEt_3 shortens the Fe−PPh_3 distance even further. Thus, the equal Fe−P distances in *trans*-$Fe(CO)_3(PEt_3)(PPh_3)$ may be the result of a significantly enhanced π-acceptance by PPh_3 induced by the very basic trans PEt_3. This is not the first time that equalization of metal−phosphorus bond lengths of dissimilar phosphines trans to one another has been observed: the Cr−P bond distances in *trans*-$Cr(CO)_4(PBu_3)(PPh_3)$ are and 2.344(4) and 2.349(4) Å, respectively.[25] An exception to bond length equalization is found, however, in *trans*-$[Ru(NO_2)(terpy)(PMe_3)(PPh_3)]^+$, where the Ru−$PMe_3$ distance (2.347(2) Å) is substantially shorter than the Ru−PPh_3 distance (2.458(2) Å).[26] Perhaps the difference is associated with the fact that when phosphines are coordinated to ruthenium in the +2 oxidation state, they receive only minimal π-donation from ruthenium.

The P−C distances (average 1.830(9) Å) of the PPh_3 ligand found in $Fe(CO)_3(PPh_3)(PEt_3)$ are virtually unchanged compared to those in the free ligand (average 1.831(2) Å) and those in $Fe(CO)_4PPh_3$ (average 1.831(3) Å). Likewise, the average C−P−C bond angles (102.9(3)°) for PPh_3 in our mixed-ligand complex are identical to those in the free ligand (102.767(924)°) and only slightly less than those (103.9(5)°) in $Fe(CO)_4PPh_3$. The invariance of P−C distances and C−P−C angles for free PPh_3 compared to transition-metal-coordinated PPh_3 has been well-documented in the comprehensive study by Orpen's group.[27]

The range of Fe−C distances in the mixed-ligand complex is 1.767(8)−1.773(8) Å (average = 1.769 Å), almost identical to that in the bis(triphenylphosphine) derivative at 1.765(4)−1.776(4) Å (average = 1.770 Å). Replacement of PPh_3 with the more basic PEt_3 would be expected to add electron density and lead to longer CO bonds. However, the CO bond lengths in *trans*-$Fe(CO)_3(PEt_3)(PPh_3)$ range from 1.137(8) to 1.153(8) Å (average 1.147(8) Å) compared to 1.132(5)−1.154(5) Å (average = 1.140(5) Å) in $Fe(CO)_3(PPh_3)_2$,[21] a change that is not significant. Moreover, variation in the CO stretching frequencies (ν_{CO}(hexane) = 1885 cm^{-1} for $Fe(CO)_3(PPh_3)_2$; 1886 cm^{-1} for $Fe(CO)_3(PEt_3)(PPh_3)$) is insignificant, further revealing an insensitivity of the carbonyl groups to the nature of the phosphine.

The *ipso* carbons of the PPh_3 group and the methylene carbons of the PEt_3 group are eclipsed, giving an approximate D_{3h} symmetry. Viewed along the P−Fe−P axis, these C atoms are in a gauche conformation relative to the three CO ligands, with torsional angles of 77° and 43° on average. The deviation from the staggered (60°/60°) structure, expected based on steric interactions between the PR_3 and CO ligands, cannot be attributed to weak bonding interactions because there are no close contacts that support the argument. Structures of the similar complexes $Fe(CO)_3(PPh_3)_2$,[21] $Fe(CO)_3$(*trans*-$PPh_2CH{=}CHPPh_2)_2$,[28] and $Ru(CO)_3(PPh_3)_2$[29] also have an eclipsed/gauche arrangement of phosphine ligands.

Summary. In this work we have shown that a good negative correlation exists between $^2J_{PP}$ coupling constants in $Fe(CO)_3LL'$ complexes and the sum of the pK_a values for the free phosphine ligands. An even better correlation is obtained when $^2J_{PP}$ is related to the QALE factors, χ, θ, and E_{ar}, but statistical analysis leads us to conclude that this model is no more reliable for estimating phosphorus−phosphorus coupling constants in *trans*-$Fe(CO)_3L_2$ than the simpler one-parameter pK_a approach. The QALE model is potentially useful for determining the relative importance of the χ, θ, and E_{ar} contributions to $^2J_{PP}$ but, because these parameters themselves are strongly correlated for the particular phosphines chosen for our study, this data set is of limited value for drawing fundamental conclusions. It is apparent from these studies, however, that $^2J_{PP}$ is strongly dependent on the electronic properties of the phosphine ligands but rather insensitive to their cone angles.

The molecular structure of *trans*-$Fe(CO)_3(PEt_3)(PPh_3)$ has revealed two Fe−P bonds of equal length, implying equal metal−phosphorus bond strengths for the two different phosphines. Equalization of bond strengths may occur because the electron density provided to iron by PEt_3 enhances the π interaction between Fe and PPh_3.

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Supporting Information Available: Tables of crystal data and structure refinement, final atomic positional parameters, interatomic distances and angles, anisotropic displacement parameters, and hydrogen coordinates (5 pages). Ordering information is given on any current masthead page.

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