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Separation of Phosphorus(III) Ligands into Pure σ-Donors and σ-Donor/π-Acceptors: Comparison of Basicity and σ-Donicity[1]

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The separation of phosphorus(III) ligands into two distinct groups identified as pure σ-donor ligands and σ-donor/π-acceptor ligands for the acetyl and methyl complexes, (η-Cp)FeL(CO)COMe, (η-Cp′)FeL(CO)COMe (Cp′ = MeC_5H_4), and (η-Cp)FeL(CO)Me, is accomplished by correlation of the terminal carbonyl stretching frequencies with the $E_L{}^{\circ\prime}$ values. The basicity (pK_a value of $HPR_3{}^+$) is related primarily to the σ-donicity (the ability of a ligand to donate σ-electrons to a transition metal) and to a lesser degree to the size of the ligand. We conclude that pK_a values are reasonable measures of the σ-donicity for those ligands that are pure σ-donor ligands; a better measure are the χ values for those ligands that are pure σ-donors for both the iron complex and $LNi(CO)_3$.

Introduction

It has long been thought that the stereo-electronic properties of phosphorus(III) ligands can be parameterized into electronic and steric components. Introduction of Tolman's cone angle (θ) and electronic parameter (χ values)[2] of phosphorus(III) ligands, respectively, was the first step toward this quantification. Since the introduction of the cone angle, it has been shown that many chemical and spectroscopic properties of organometallic complexes correlate with this measure of size,[2] although there is controversy concerning the manner in which θ is determined especially for ligands of the type PR_2R' and PRR′R″.[3] The separation of the electronic parameter into σ and π components is, however, complicated by the concept of synergic bonding which requires the electronic factors to be mutually dependent.[4] The χ values, which are derived from the infrared data for $LNi(CO)_3$, are thought to reflect the collective electron donor/acceptor properties of the ligands.[2] pK_a values (for $HPR_3{}^+$) or half-wave neutralization potentials[5] have been used as measures of σ-donicity (the ability of a ligand to donate σ-electrons to a transition metal) of the ligands (see ref 1 and 6 and references therein). The pK_a values, however, may not be appropriate because they are dependent upon the interactions between the phosphorus and the hard acid, H^+, rather than a soft acid such as a low-valent metal center in an organometallic complex. In addition, pK_a values must be sensitive to solvation energies of the phosphorus compounds.[7] A comparison of the gas-phase protonation and photoelectron spectra with the solution basicities further complicates the situation.[7] For example, in the gas phase it appears that the electron donor ability of the phosphorus(III) ligands is ordered: $PPh_3 > PPh_2Me > PPhMe_2 > PMe_3$. In solution the order of basicity is reversed with PMe_3 being the most basic. It was suggested that PMe_3 is the most basic in solution because it forms the smallest cation ($HPMe_3{}^+$) with presumably the largest solvation energy. On the other hand, there appear to be good correlations between kinetic and thermodynamic properties of organometallic complexes and these pK_a values.[1,6] Because of the gas-phase results, the unresolved problem concerning solvation and solution basicities, and the hard and soft acid/base problem, the employment of

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[1] This is the third paper in a series on the Quantitative Analysis of Ligand Effects (QALE). Earlier papers are: (a) Rahman, Md. M.; Liu, H.-Y.; Prock, A.; Giering, W. P. *Organometallics* **1987**, *6*, 650–58. (b) Golovin, M. N.; Rahman, Md. M.; Belmonte, J. E.; Giering, W. P. *Organometallics* **1985**, *4*, 1981–91.

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pK_a values as a measure of σ-donicity must be suspect. Owing to the importance of phosphorus(III) ligands in organometallic chemistry and catalysis,[8] an evaluation of the stereoelectronic properties has been attacked with an impressive arsenal of techniques including IR,[10] NMR,[11] UV-vis,[12] photoelectron,[9,13] and Mössbauer spectroscopy[14] as well as theoretical[15] and electrochemical[16] methods and X-ray crystallography.[17]

Over the past 3 years we have been exploring the quantification of σ, π, and steric properties of phosphorus(III) ligands through the development of an analytical method—the quantitative analysis of ligand effects (QALE).[1] QALE has led us to some important conclusions: The phosphorus(III) ligands appear to be divided into at least two different classes (σ-donors and σ-donors/π-acceptors, vide infra) depending on the stereoelectronic nature of the metal fragment and the phosphorus(III) ligand. The identification of the pure σ-donor ligands was based on correlations of chemical properties with the pK_a values of the ligands.[1] However, it required some chemical judgement on our part. In this paper we present a method for classiying the phosphorus(III) ligands into pure σ-donor ligands and σ-donor/π-acceptor ligands for a given complex in a way that does not rely on scales of σ-donicity (σ_d) or π-acidity (π_a).

Method

It has been observed that the kinetics and thermodynamics of certain organometallic reactions are linearly related to the Brønsted basicities (pK_a values of R_3PH^+—a measure of σ_d), cone angles, and $E_{\pi a}$ values (a measure of π_a) of ancillary or incipient phosphorus(III) ligands.[1,6] It seems reasonable that other properties of organometallic complexes bearing phosphorus(III) ligands should display similar empirical relationships with σ_d and π_a. In order to achieve the separation of σ-donor and σ-donor/π-acceptor ligands (without reliance on pK_a values), we propose a model in which certain properties of the complexes are linearly related to the σ-donicities and π-acidities of the ligands. We will show that this simple model leads to chemically meaningful results.

The method begins with a correlation of appropriate properties of the *same* family of complexes. Such a pair of properties is the terminal carbonyl stretching frequencies, ν_{CO}, and the reduction potentials, $E_L{}^{\circ\prime}$ (which, for convenience, we will write as E°). *This separation of ligands requires no a priori knowledge of σ-donor (σ_d) and π-acceptor (π_a) properties of the ligands.* The method is described below. For purposes of the following discussion, both σ_d and π_a are used in a formal sense to express the relationship between ligand properties and properties of the complexes.

The linear relationships between the properties of the complexes and σ_d and π_a are expressed in eq 1 and 2 (for σ-donor ligands) and eq 3 and 4 (for π-acceptor ligands). For purposes of clarity, we consider only those ligands that do not display steric effects.

σ-Donor Ligands

$$\nu_{CO} = a\sigma_d + c \tag{1}$$

$$E^\circ = a'\sigma_d + c' \tag{2}$$

π-Acceptor Ligands

$$\nu_{CO} = A\sigma_d + B\pi_a + C \tag{3}$$

$$E^\circ = A'\sigma_d + B'\pi_a + C' \tag{4}$$

We draw simple but important conclusions from eq 1–4 which lead to a separation of the ligands into two classes. Elimination of σ_d from eq 1 and 2 gives eq 5, while combination of eq 3 and 4 gives eq 6. Equations 5 and 6 relate one measured property (ν_{CO}) to the other (E°). Equation

$$\nu_{CO} = (a/a')E^\circ + c - ac'/a' \tag{5}$$

$$\nu_{CO} = (A/A')E^\circ + (B - AB'/A')\pi_a + C - AC'/A' \tag{6}$$

5 predicts that, for those complexes containing pure σ-donor ligands, a plot of E° versus ν_{CO} gives a straight line which should show a small degree of scatter arising only from experimental error. On the other hand, when π-effects are operative, the picture becomes more complex—ν_{CO} is a function of two variables, $E_L{}^\circ$ and π_a, thereby giving a plot of ν_{CO} versus $E_L{}^\circ$ with considerable scatter. *Thus,*

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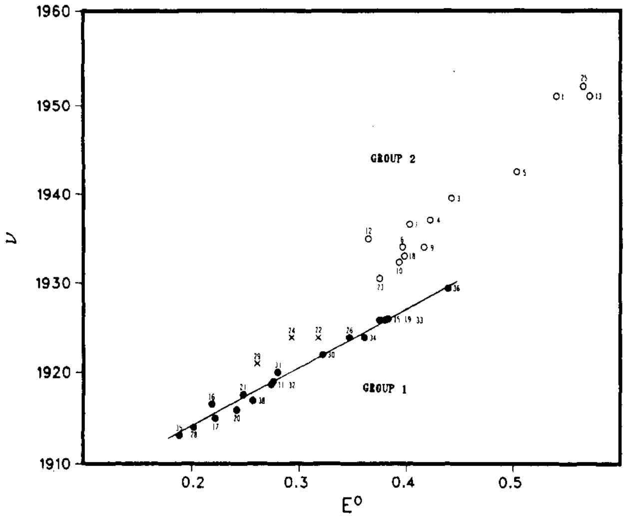

Figure 1. Plot of the terminal carbonyl stretching frequencies, ν_{CO} (cm^{-1}), of (η-Cp)Fe(CO)LCOMe versus the reduction potentials, $E°$ (V), of the (η-Cp)Fe(CO)LCOMe$^{0,+}$ couple. The numbers next to the data points refer to the phosphorus(III) compounds given in the table. The line is drawn through the open circles for the group 1 (σ-donor) ligands. The solid circles represent the group 2 (σ-donor/π-acceptor) ligands. The X's are the data points for the anomalous ligands as discussed in the text.

different relationships between ν_{CO} and $E°$ should be observed for the two groups of ligands. A single linear relationship between ν_{CO} and $E°$, valid over the entire range of ligands, would result only if $E_L°$ were proportional to π_a and the coefficients and intercepts of the resulting equations were equal to those of eq 5. We are not aware of any reason why this should generally be the case. This analysis is applicable even if synergic bonding is operative since "cross terms" involving σ_d and π_a would appear in eq 3 and 4 but not in eq 1 and 2, thereby still giving rise to groups of ligands. Thus, by plotting ν_{CO} versus $E°$, it should be possible to distinguish between σ-donor and π-acceptor ligands without prior knowledge of either σ_d or π_a. This method, which is independent of the ligand, should be generally applicable and not restricted to phosphorus(III) ligands.

Results

The above concepts are applied to the analyses of the terminal carbonyl stretching frequencies and $E_L°$ values of the acetyl complexes (η-Cp)Fe(CO)LCOMe (L = phosphorus(III) ligand) and (η-Cp′)Fe(CO)LCOMe (Cp′ = MeC$_5$H$_4$) and the methyl complexes (η-Cp)Fe(CO)LMe. These complexes were chosen for three reasons: simplicity of preparation, the existence of a single terminal carbonyl ligand which precludes coupling problems with other terminal carbonyls, and generally uncomplicated electrochemical behavior. The values of ν_{CO} and $E°$ for the iron complexes are given in Tables I (acetyl complexes) and II (methyl complexes). Many of the acetyl complexes containing large (θ > 153°) trialkyl and mixed alkyl/aryl phosphines exist in solution as rapidly interconverting isomers as evidenced by the appearance of two or three terminal carbonyl bands in their IR spectra although the NMR spectra at ambient temperature show the presence of a single species. Therefore, we systematically excluded these acetyl complexes bearing large ligands from the analyses. For similar reasons, the data for the large trialkyl phosphite acetyl complexes P(O-*i*-Pr)$_3$ and P(OCy)$_3$ were also not included. The acetyl complexes containing the largest ligands PPh(*t*-Bu)$_2$ and P(*t*-Bu)$_3$ as well as (η-Cp′)Fe(P(OCy)$_3$(CO)COMe (Cy = cyclohexyl) could not be prepared. Surprisingly, (η-Cp)FeL(CO)Me containing P(OMe)$_3$ and P(OEt)$_3$ ligands also exhibit two closely spaced terminal carbonyl absorptions (Table II). Accordingly these data were not included in the analysis of (η-Cp)FeL(CO)Me. (The origins of this phenomenon are currently under study.) This leaves a total of 33 data points for the analysis of each family of acetyl complexes and 18 data points for the methyl complexes.

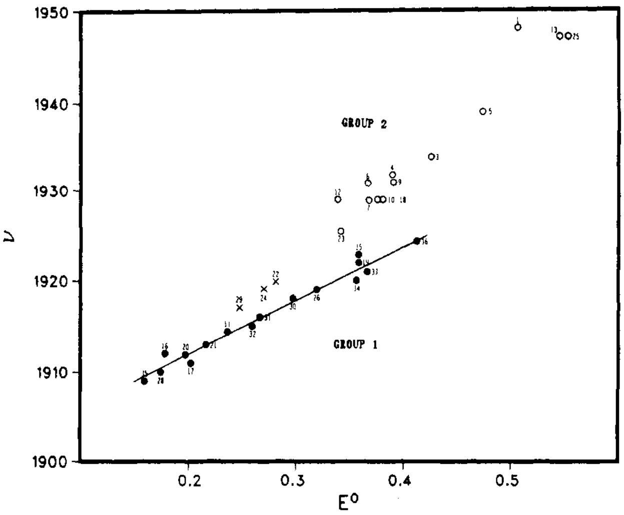

Figure 2. Plot of ν_{CO} versus $E°$ for (η-Cp′)FeL(CO)COMe.

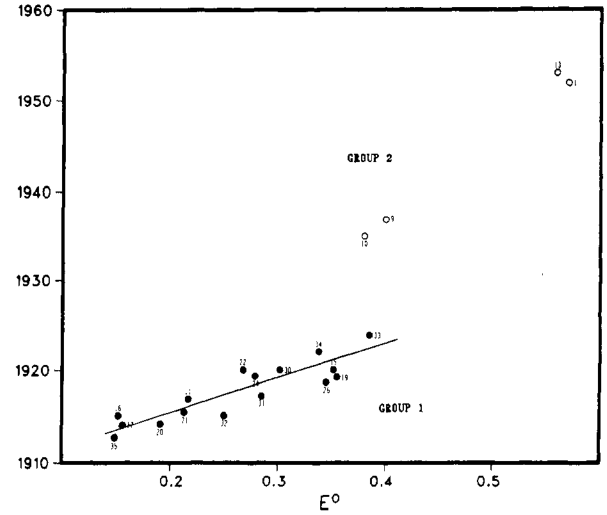

Figure 3. Plot of ν_{CO} versus $E°$ for (η-Cp)FeL(CO)Me.

Plots of ν_{CO} versus $E°$ divide the ligands into two groups, 1 and 2 (Figures 1–3). For the two families of acetyl complexes, each set of group 1 ligands defines a line with very little scatter. It is noteworthy that each line passes through the data points for all seven triarylphosphines (entries 30–36 in Table 1). Only the data for PCy$_2$H (Cy = cyclohexyl), PPh$_2$Et, and PPh$_2$Me fall 4–6 cm^{-1} above the line for both families of acetyl complexes. This anomaly is discussed below. The group 2 ligands are separated from the group 1 ligands. Although the ν_{CO} values for this group are linearly correlated with $E°$, the slope is steeper and there is more scatter than observed for group 1. The plot of ν_{CO} versus $E°$ for the more limited set of methyl complexes shows a similar division of ligands.

Discussion

The nature of the metal phosphorus bond has a strong influence on the electron density on the metal center; strong σ-donors enhance the electron density whereas strong π-acids decrease the electron density. We believe

Table I. Terminal Carbonyl Stretching Frequencies (ν_{CO}) and Formal Reduction Potentials ($E°$) for (η-Cp)Fe(CO)LCOMe and (η-Cp′)Fe(CO)LCOMe and Stereoelectronic Properties of Phosphorus(III) Ligands

no.	L	θ^a	$pK_a{}^b$	χ^c	ν^d	$E^{\circ e}$	ν^f	$E^{\circ g}$
1	$P(OCH_2)_3CEt$	101	1.74	31.20	1951.0	0.540	1948.0	0.506
2	$PPhH_2$	106	(−2.0)	20.85	...	...	1932.0	irrev
3	$P(OMe)_3$	107	2.6	24.10	1939.5	0.442	1934.0	0.425
4	$P(OEt)_3$	109	3.31	21.60	1937.0	0.422	1931.9	0.389
5	$P(OCH_2CH_2Cl)_3$	110			1942.5	0.503	1939.0	0.473
6	$PMe(OEt)_2$	112			1934.0	0.396	1930.9	0.366
7	$P(CH_2CH_2CN)_2H$	117	(−0.6)		1936.5	0.403	1928.9	0.367
8	PMe_3	118	8.65	8.55	...	...	...	...
9	$P(OMe)_2Ph$	120	(2.64)	19.45	1934.0	0.416	1931.0	0.390
10	$P(OEt)_2Ph$	121	(3.1)	18.10	1932.3	0.393	1929.0	0.380
11	PMe_2Ph	122	6.5	10.60	1918.7	0.274	1914.4	0.236
12	PPh_2H	126	0.03	17.35	1934.9	0.364	1929.0	0.338
13	$P(OPh)_3$	128	−2.00	30.20	1951.0	0.571	1947.0	0.545
14	$P(O\text{-}i\text{-}Pr)_3$	130	4.08	19.50	1938.9^h 1930.0^h 1921.0^h	0.384^h	1936.6^h 1925.9^h 1918.6^h	0.352^h
15	$P(OMe)Ph_2$	132	(2.69)	16.30	1926.1	0.383	1922.9	0.358
16	PEt_3	132	8.69	6.30	1916.6	0.219	1912.0	0.178
17	PBu_3	132	8.43	5.25	1915.1	0.222	1911.0	0.202
18	$P(CH_2CH_2CN)_3$	132	1.36	22.35	1933.0	0.398	1929.0	0.375
19	$P(OEt)Ph_2$	133	(2.91)	15.60	1926.0	0.375	1922.0	0.358
20	$PMe(i\text{-}Bu)_2$	135			1916.0	0.242	1911.9	0.197
21	PEt_2Ph	136	6.25	9.30	1917.6	0.248	1913.0	0.216
22	$PMePh_2$	136	4.57	12.10	1924.0	0.318	1919.9	0.281
23	$PPh(CH_2CH_2CN)_2$	136	1.82		1930.5	0.375	1925.5	0.341
24	$PEtPh_2$	140	4.9	11.30	1924.0	0.293	1919.1	0.270
25	$P(O\text{-}o\text{-}tol)_3$	141	−1.83	27.7	1952.0	0.565	1947.0	0.553
26	$PPh_2(CH_2CH_2CN)$	141	2.27		1924.0	0.347	1919.0	0.319
27	$P(OCy)_3$	141		18.00	1938.4^h 1928.0^h 1920.3^h	0.378^h	*i*	*i*
28	$P(i\text{-}Bu)_3$	143	7.97	5.70	1914.1	0.202	1910.0	0.174
29	PCy_2H	143	4.55	9.10	1921.0	0.261	1917.0	0.247
30	PPh_3	145	2.73	13.25	1922.0	0.322	1918.0	0.297
31	$P(p\text{-}MePh)_3$	145	3.84		1920.0	0.280	1916.0	0.266
32	$P(p\text{-}MeOPh)_3$	145	4.59	10.50	1919.0	0.276	1915.0	0.259
33	$P(p\text{-}ClPh)_3$	145	1.03	16.80	1926.0	0.380	1921.0	0.366
34	$P(p\text{-}FPh)_3$	145	1.97	15.70	1924.0	0.361	1920.0	0.356
35	$P(p\text{-}Me_2NPh)_3$	145	8.65	5.25	1913.2	0.189	1909.0	0.159
36	$P(p\text{-}CF_3Ph)_3$	145			1929.4	0.439	1924.4	0.412
37	$PBzPh_2$	152		12.30	1937.0^h 1926.0^h 1920.0^h	0.282^h	1931.0^h 1922.0^h 1915.8^h	0.250^h
38	$PCyPh_2$	153	(5.05)		1917.0	0.257	1911.0	0.225
39	$P(i\text{-}Pr)_3$	160		3.45	1915.0^h	0.158^h	1910.0^h	0.137^h
40	PCy_2Ph	162			1916.5^h	0.202^h	1911.0^h	0.184^h
41	PBz_3	165		10.35	1928.1^h 1910.3^h	0.255^h	1923.3^h 1907.6^h	0.228^h
42	$P(m\text{-}tolyl)_3$	165	3.30		1920.6^h	0.305^h	1916.0^h	0.278^h
43	PCy_3	170	9.70	1.40	1914.9^h 1911.0^h	0.130^h	1908.8^h	0.114^h
44	$P(t\text{-}Bu)_2Ph$	170		4.95	*i*	*i*	*i*	*i*
45	$P(t\text{-}Bu)_3$	182	11.40	0.0	*i*	*i*	*i*	*i*

[a] Cone angles in deg, taken from ref 2 or calculated from data provided therein. [b] pK_a values are taken from ref 1 and 5, unless otherwise stated; those in parentheses were estimated on the basis of additivity plots if the pK_a values of other members of the homologous series are known. [c] Data are taken from ref 10a. [d] Stretching frequencies (cm^{-1}) of terminal CO of (η-Cp)Fe(CO)LCOMe in cyclohexane at ambient temperatures. [e] $E_L{}^{\circ\prime}$ (V) vs SCE, of (η-Cp)Fe(CO)LCOMe$^{0,+}$ in CH_3CN (0.2 M $LiClO_4$) at 0 °C. [f] Stretching frequencies (cm^{-1}) of terminal CO of (η-Cp′)Fe(CO)LCOMe in cyclohexane at ambient temperatures. [g] $E_L{}^{\circ\prime}$ (V) vs SCE, of (η-Cp′)Fe(CO)LCOMe$^{0,+}$ in CH_3CN (0.2 M $LiClO_4$) at 0 °C. [h] Iron complexes that exhibited more than one absorption band in the terminal CO region in the FTIR spectrum and those containing L with a cone angle greater than 153° were not included in the analysis. [i] Iron complex could not be synthesized under the experimental conditions followed for other ligands.

that it is possible to distinguish between pure σ-donor ligands and σ-donor/π-acceptor ligands within a family of complexes by a correlation of two appropriate properties of a family of complexes when these properties are sensitive to the electron density on the metal. Undoubtedly, the terminal carbonyl stretching frequencies are directly dependent on the electron density of the metal to which the carbon monoxide is bonded. The formal reduction potentials are a measure of the free energy difference between two oxidation states; it has long been recognized that the ease of oxidation increases with the electron donor ability of the ancillary ligands as long as the nature of the ligands remains basically unchanged.[16]

Our model predicts that in plots of ν_{CO} versus $E°$, the data for the pure σ-donor ligands will lie on a line (eq 5) with little scatter whereas that for the σ-donor/π-acid ligands will lie in a different region and show considerable scatter (eq 6). Indeed, examination of the data displayed in Figures 1 and 2 (acetyl complexes) shows that the more basic ligands lie on a line with little scatter as predicted for the pure σ-donor ligands. The basicities of the group 1 ligands range from 8.69 (PEt_3) to 1.03 ($P(p\text{-}ClPh)_3$) to probably an even smaller value for $P(p\text{-}CF_3Ph)_3$. Significantly, the group 1 ligands are not restricted to those

Table II. Terminal Carbonyl Stretching Frequencies (ν_{CO}) and Formal Reduction Potentials ($E°$) for (η-Cp)FeL(CO)(Me)

no.	L	ν^a	$E°^b$
1	$P(OCH_2)_3CEt$	1951.9	0.570
3	$P(OMe)_3$	1930.7 1942.1	0.388
4	$P(OEt)_3$	1926.8 1939.4	0.387
9	$P(OMe)_2Ph$	1936.9	0.400
10	$P(OEt)_2Ph$	1935.0	0.380
11	PMe_2Ph	1916.8	0.217
13	$P(OPh)_3$	1953.0	0.559
15	$P(OMe)Ph_2$	1920.0	0.352
16	PEt_3	1915.0	0.152
17	PBu_3	1914.0	0.156
19	$P(OEt)Ph_2$	1919.2	0.355
20	PMe(i-Bu)$_2$	1914.1	0.191
21	PEt_2Ph	1915.4	0.213
22	$PMePh_2$	1920.0	0.268
24	$PEtPh_2$	1919.3	0.279
26	$PPh_2(CH_2CH_2CN)$	1918.6	0.345
30	PPh_3	1920.0	0.302
31	P(*p*-MePh)$_3$	1917.1	0.285
32	P(*p*-MeOPh)$_3$	1915.0	0.250
33	P(*p*-ClPh)$_3$	1924.0	0.385
34	P(*p*-FPh)$_3$	1922.1	0.338
35	P(*p*-Me$_2$NPh)$_3$	1912.7^c	0.149

[a] Carbonyl stretching frequencies (cm^{-1}) of (η-Cp)Fe(CO)(Me)L in cyclohexane at ambient temperatures. [b] $E_L°'$ (V) vs SCE, of (η-Cp)FeL(CO)(Me)$^{0,+}$ in acetone (0.1 M $LiClO_4$) at 0 °°C. [c] Insoluble in cyclohexane; datum obtained from calibration curve between cyclohexane and methylene chloride solutions.

ligands which contain only P–C bonds but also include $P(OMe)Ph_2$ and $P(OEt)Ph_2$. Because group 1 includes some of the most basic ligands[5] and because the correlation between ν_{CO} and $E°$ exhibits such a small degree of scatter, we designate all the group 1 ligands as pure σ-donor ligands with no π-acceptor character.

Generally, the less basic ligands lie above the line defined by the group 1 ligands in Figures 1 and 2 and show considerable scatter of the data. This scatter is predicted by eq 6 for the relationship between ν_{CO} and $E°$ for σ-donor/π-acceptor ligands (vide supra). Consonant with this interpretation, the group 2 ligands include those that are generally thought to be strong π-acceptors such as $P(OR)_3$. Therefore, we designate the group 2 ligands as σ-donor/π-acceptor ligands. Importantly, this group is not restricted to ligands containing phosphorus–oxygen bonds but includes PPh_2H, $P(CH_2CH_2CN)_3$, and $PPh(CH_2CH_2CN)_2$ as well. It is noteworthy that at least two sets of homologous complexes are respresented in both groups ($PPh_{3-x}(CH_2CH_2CN)_x$ and $PPh_{3-x}(OMe)_x$, group 1 when $x = 0$ or 1 and group 2 when $x = 2$ or 3).

We were surprised that the data for the acetyl complexes containing PCy_2H, PPh_2Me, and PPh_2Et were 4–6 cm^{-1} above the line for the other group 1 ligands. A reviewer suggested that the ligands of these three anomalous complexes may actually belong to group 2; i.e., they are σ-donor/π-acceptors. If this is correct, then the iron–phosphorus bond of each of these complexes should be significantly shorter than that for the group 1 complexes. We find that the bond lengths for two of the anomalous complexes, (η-Cp′)(CO)(PPh_2Me)FeCOMe (2.183 Å)[18] and (η-Cp′)(CO)(PPh_2Et)FeCOMe (2.199 Å),[18] are very similar to the iron–phosphorus bond lengths for ligands we have classified as pure σ-donors, (η-Cp)(CO)(PPh_3)FeCOMe (2.202 Å)[18] and (η-Cp)(CO)[P(*p*-CF_3Ph)$_3$]FeCOMe (2.183 Å),[18] and considerably longer than those found in the complexes containing the π-acid ligands (η-Cp)(CO)[P($OCH_2)_3$CEt]FeCOMe (2.09 Å)[18] and (η-Cp)(CO)[P(OPh_3)]FeCOR (2.106–2.110 Å).[19] This is not unexpected since electronically and sterically there is nothing to distinguish PCy_2H, PPh_2Me, and PPh_2Et from the other group 1 ligands. The reason for this anomalous behavior is still an open question.

The question arises whether the group 2 ligands deviate from the lines drawn in Figures 1 and 2 because of conformism due to rotation about the acetyl–iron bond. If this is true, then a series of complexes that lacks the acetyl group will not show two groups of ligands. Accordingly, we examined the methyl complexes, (η-Cp)FeL(CO)Me (Figure 3). Qualitatively, this plot resembles those shown in Figures 1 and 2 in that the ligands are divided clearly into two different groups. The complexes containing the trialkyl, mixed alkyl/aryl, and triaryl ligands appear to fall on a line. Significantly, methyl complexes containing two of the ligands (PPh_2Me and PPh_2Et) of the anomalous acetyl complexes now fall within the band of points for the group 1 methyl complexes. The second group of methyl complexes deviates from the group 1 complexes in the same manner as for the acetyl complexes. Clearly, the separations of the group 1 and 2 acetyl and methyl complexes are not associated with the rotation of the acetyl ligand. Thus, we are led to conclude that the separation of the two groups of ligands is due to electronic rather than steric factors.

The separation of complexes is consistent with the concept of an electronic threshold (π_t) for the onset of phosphorus–metal multiple bonding.[1a] There does not appear to be a continuum between pure σ and σ/π bonding. We believe that these results are consonant with the existence of a double potential energy minimum in the metal–phosphorus bond similar to that proposed for the rarely observed bond-stretch (distortional) isomers.[20]

Steric effects become important for the largest ligands. For example, these effects are apparently so severe that we are unable to prepare complexes containing the large and strong σ-donor ligands PPh(*t*-Bu)$_2$ ($\theta = 170°$) and P(*t*-Bu)$_3$ ($\theta = 182°$). Many of the complexes containing slightly smaller ligands (θ = 152–170°) display multiple terminal carbonyl absorptions which we believe are a manifestation of steric effects.

The onset of steric effects for the π-acid ligands occurs at smaller θ as evidenced by the appearance of three terminal carbonyl bands in the IR spectra of the P(O-*i*-Pr)$_3$ ($\theta = 130°$) and $P(OCy)_3$ ($\theta = 141°$) cyclopentadienyl complexes. The methylcyclopentadienyl ligand in Cp′FeL(CO)COMe creates a slightly more crowded environment around the iron than does the cyclopentadienyl ligand. This increased congestion is sufficient to preclude the synthesis of the $P(OCy)_3$ complex. These observations are consonant with the π-acid ligands possessing shorter metal–phosphorus bonds.[1a]

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(18) Structures determined in our laboratories. Results will be reported elsewhere.

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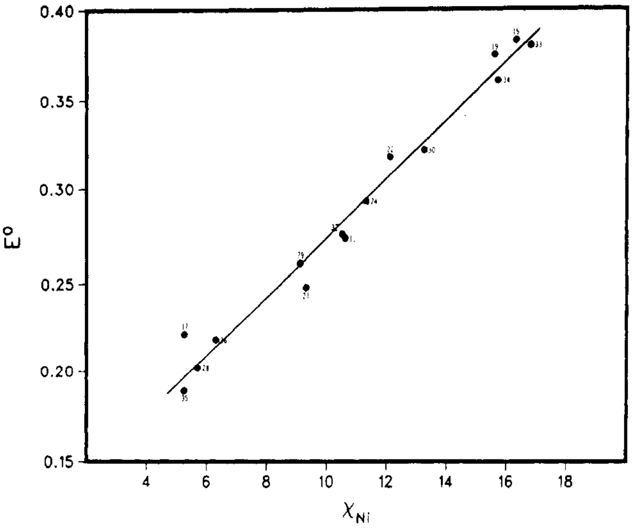

Figure 4. Plot of $E°$ for (η-Cp)Fe(CO)LCOMe for the group 1 ligands (see Figure 1) versus the χ values for $LNi(CO)_3$ as reported by Bartik[10a] et al. The numbers next to the data points refer to the phosphorus(III) compounds given in the Table I.

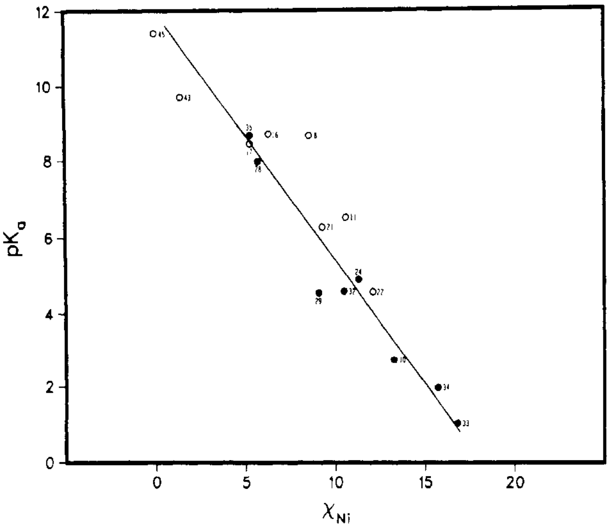

Figure 5. Plot of the pK_a values[5] of HPR_3^+ versus the χ values[10a] of $LNi(CO)_3$ for the ligands of the group 1 complexes (see Figure 1). The line is drawn through the points (solid circles) for the ligands with cone angles[2] between 140° and 145°.

The Relationship between Basicity and σ-Donicity of Phosphorus(III) Ligands

The basicities of the phosphorus(III) ligands (pK_a values or half-wave neutralization potentials) have been used often as measures of σ-donicities of these ligands toward transition metals.[1,5,6] Having identified the group 1 ligands as pure σ-donor ligands, we are in a position to assess the appropriateness of this usage of pK_a values. Either ν_{CO} or $E°$ for (η-Cp)Fe(CO)LCOMe for pure σ-donor ligands can serve as a scale of σ-donicity (see eq 1 and 2). However, because of the large body of χ values[2,10a] available for $LNi(CO)_3$,[2,10a] we examined the feasibility of using the χ values as a measure of σ-donicity. The excellent linear relationship between the $E°$ values [(η-Cp)FeL(CO)-COMe)] and χ for the group 1 ligands (Figure 4) demonstrates that these ligands are also σ-donor ligands toward the $Ni(CO)_3$ fragment. In order to compare the pK_a values and σ-donicity, the pK_a values of the group 1 ligands were plotted against Bartik's χ values[10a] (Figure 5). The plot clearly shows that there is a correlation between the two parameters although there is a good deal of scatter. (We found that pK_a values measured in our laboratory for several of the phosphorus(III) compounds are in agreement with the values[5a] reported earlier.) Linear regression analysis of pK_a versus χ (for 16 data points) yields

$$pK_a = -0.603\chi + 11.6 \qquad r = 0.95 \tag{7}$$

Inclusion of the cone angle, θ, in the analysis improves the correlation and yields

$$pK_a = -0.675\chi - 0.047\theta + 18.9 \qquad r = 0.98 \tag{8}$$

Assuming that the errors are normally distributed, we applied the sequential F-test,[21] which shows that the coefficient of θ in eq 8 is indeed nonzero with a risk of being wrong of less than 1%. (The 95% confidence interval for the coefficient of θ is -0.047 ± 0.027). Significantly, the pK_a values of the phosphorus(III) ligands diminish with increasing size (θ). This is consistent with the idea that the smaller HPR_3^+ are more highly solvated. The enhanced solvation increases the thermodynamic stability of the protonated form, thereby making the smaller ligands more basic. This phenomenon is readily apparent in Figure 5; there is a good linear correlation between pK_a and χ for nearly isosteric ligands (θ = 140–145°). The ligands with smaller cone angles lie to the more basic side of this line, whereas the larger ligands generally lie to the less basic side. Clearly, the pK_a values depend on both the σ-donicity and the size of the ligand, with θ contributing about 3 pK_a units over the range of cone angles, 118° (PMe_3) to 182° ($P(t\text{-}Bu)_3$). The magnitude of this contribution is in harmony with the result of our estimates of free energy of solvation based on a simple electrostatic model of HPR_3^+ as a charged sphere of appropriate size representing the PH^+ fragment, surrounded by a medium of two different dielectric constants subtending different solid angles around the central iron atom, one representing the solvent and the other representing the pendent groups on the phosphorus. In conclusion, since σ_d is the major contributor to the basicity of the phosphorus(III) compounds, the pK_a values retain their validity as a reasonable measure of the σ-donicity of the ligands. However, the χ values are a better measure of σ_d. Equating χ values with σ_d is at present limited to those ligands that are included in group 1 of Figures 1–3 and other closely related ligands. Even without their being included in the present analysis, the following ligands may safely be assumed to be σ-donor ligands for $LNi(CO)_3$: the simple trialkyl, mixed alkyl/aryl, and triaryl ligands including the weakly basic $P(p\text{-}ClPh)_3$. This is gratifying since the χ values, which are widely used in organometallic chemistry, are known already for a large number of these ligands.[2,10a]

Finally, it was reported recently that the order of σ-donicity of the family of ligands PPh_xMe_{3-x} decreased as x decreased.[7] These interpretations were based on gas-phase protonation and photoelectron spectroscopy of the phosphines. Our results and those of others[11j] do not lead us to believe that the gas-phase results can be extrapolated to solution species.

Conclusion

We have described a method for classifying phosphorus(III) ligands into σ-donors and σ-donor/π-acceptors

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based on a correlation of properties of a given family of organometallic complexes containing ligands of both classes. Although some questions remain to be resolved, we have illustrated the method by using the data for three families, (η-Cp)Fe(CO)LCOMe, (η-Cp′)Fe(CO)LCOMe, and (η-Cp)FeL(CO)Me, and have shown that the results are indeed obtainable without a priori knowledge of a scale of σ-donicity (i.e. pK_a). As a corollary, we have shown that the ν_{CO} values of (η-Cp)FeL(CO)COMe are a measure of σ-donicity as are the χ values when restricted to those ligands that are pure σ-donors in both complexes.

Experimental Section

The complexes (η-Cp)Fe(CO)LCOMe and (η-Cp′)FeL(CO)COMe were prepared by refluxing (η-Cp)Fe(CO)$_2$Me or (η-Cp′)Fe(CO)$_2$Me with a slight excess of ligand in acetonitrile as described by Green.[22] Complexes containing P(*t*-Bu)$_3$ and PPh(*t*-Bu)$_2$ and (η-Cp′)Fe(P(OCy)$_3$(CO)COMe could not be synthesized. The methyl complexes were synthesized by photolyzing refluxing acetonitrile solutions of phosphorus(III) compounds and (η-Cp)Fe(CO)$_2$Me. Compounds were characterized by proton NMR and IR spectroscopy. Infrared data were collected on degassed cyclohexane solutions at ambient temperature on a Perkin-Elmer Model 1800 FT infrared spectrometer. The samples were progressively diluted with cyclohexane until limiting values of the terminal carbonyl stretching frequencies were obtained. These limiting values, which are accurate to 0.3 cm^{-1}, are reported in Tables I and II. The $E_{\mathrm{L}}^{\circ\prime}$ values for the acetyl complexes (acetonitrile) and methyl complexes (acetone) were determined at 0 °C by cyclic voltammetry (EG and G Princeton Applied Research 174A polarographic analyzer) on 0.2 M LiClO$_4$ solutions containing approximately 1 mmol of complex. The $E_{\mathrm{L}}^{\circ\prime}$ were found to be independent of scan rate in the range 50–500 mV s^{-1} for the acetyl complexes. The methyl complexes containing less basic ligands exhibited cyclic voltammograms that are scan rate dependent. The cathodic return waves were observed at intermediate scan rates consistent with solvent incorporation as described elsewhere.[23] The E° values for these complexes were measured in the usual manner ($(E_{\mathrm{pa}} + E_{\mathrm{pc}})/2$). Computer simulation of this type of system shows that the experimental E° values differ from the true E° by less than 10 mV.

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Registry No. 1, 824-11-3; **2**, 638-21-1; **3**, 121-45-9; **4**, 122-52-1; **5**, 140-08-9; **6**, 15715-41-0; **7**, 4023-49-8; **8**, 594-09-2; **9**, 18351-42-3; **10**, 4894-60-4; 11, 672-66-2; **12**, 829-85-6; **13**, 101-02-0; **14**, 116-17-6; **15**, 3577-87-5; **16**, 554-70-1; **17**, 998-40-3; **18**, 4023-53-4; **19**, 2161-16-2; **20**, 117227-81-3; **21**, 1605-53-4; **22**, 1486-28-8; **23**, 15909-92-9; **24**, 607-01-2; **25**, 2622-08-4; **26**, 5032-65-5; **27**, 15205-58-0; **28**, 4125-25-1; **29**, 829-84-5; **30**, 603-35-0; **31**, 1038-95-5; **32**, 855-38-9; **33**, 1159-54-2; **34**, 18437-78-0; **35**, 1104-21-8; **36**, 13406-29-6; **37**, 7650-91-1; **38**, 6372-42-5; **39**, 6476-36-4; **40**, 6476-37-5; **41**, 7650-89-7; **42**, 6224-63-1; **43**, 2622-14-2; **44**, 32673-25-9; **45**, 13716-12-6; (η-Cp)Fe(CO)$_2$Me, 12080-06-7; (η-Cp′)Fe(CO)2Me, 64023-11-6; (η-Cp)Fe(CO)[P(OCH$_2$)$_3$CEt]COMe, 117227-82-4; (η-Cp)Fe(CO)[P(OMe)$_3$]COMe, 77307-42-7; (η-Cp)Fe(CO)[P(OEt)$_3$]COMe, 117306-61-3; (η-Cp)Fe(CO)[P(OCH$_2$CH$_2$Cl)$_3$]COMe, 117227-83-5; (η-Cp)Fe(CO)[P(OEt)$_2$]COMe, 117227-84-6; (η-Cp)Fe(CO)[P(CH$_2$CH$_2$CN)$_2$H]COMe, 117227-85-7; (η-Cp)Fe(CO)[P(OMe)$_2$Ph]COMe, 117227-86-8; (η-Cp)Fe(CO)[P(OEt)$_2$]Ph]COMe, 117227-87-9; (η-Cp)Fe(CO)(PMe$_2$Ph)COMe, 32993-87-6; (η-Cp)Fe(CO)(PPh$_2$H)COMe, 117227-88-0; (η-Cp)Fe(CO)[P(O-Ph)$_3$]COMe, 12213-20-6; (η-Cp)Fe(CO)[P(O-i-Pr)$_3$]COMe, 117227-89-1; (η-Cp)Fe(CO)[P(OMe)Ph$_2$]COMe, 117227-90-4; (η-Cp)Fe(CO)PEt$_3$)COMe, 117227-91-5; (η-Cp)Fe(CO)(PBu$_3$)COMe, 12190-08-8; (η-Cp)Fe(CO)[P(CH$_2$CH$_2$CN)$_3$]COMe, 117227-92-6; (η-Cp)Fe(CO)[P(OEt)Ph$_2$]COMe, 117227-93-7; (η-Cp)Fe(CO)[PMe(*i*–Bu)$_2$]COMe, 117227-94-8; (η-Cp)Fe(CO)(PEt$_2$Ph)COMe, 117227-95-9; (η-Cp)Fe(CO)(PMePh$_2$)COMe, 117227-96-0; (η-Cp)Fe(CO)[PPh(CH$_2$CH$_2$CN)$_2$]COMe, 117227-97-1; (η-Cp)Fe(CO)(PEtPh$_2$)COMe, 117227-98-2; (η-Cp)Fe(CO)[P(O-*o*-tol)$_3$]COMe, 117227-99-3; (η-Cp)Fe(CO)[PPh$_2$(CH$_2$CH$_2$CN]COMe, 117228-00-9; (η-Cp)Fe(CO)[P(OCy)$_3$]COMe, 117228-01-0; (η-Cp)Fe(CO)[P(*i*-Bu)$_3$]COMe, 117228-02-1; (η-Cp)Fe(CO)(PCy$_2$H)COMe, 117228-03-2; (η-Cp)Fe(CO)(PPh$_3$)COMe, 12101-02-9; (η-Cp)Fe(CO)[P(*p*-MePh)$_3$]COMe, 117228-04-3; (η-Cp)Fe(CO)[P(*p*-MeOPh)$_3$]COMe, 117228-05-4; (η-Cp)Fe(CO)[P(*p*-ClPh)$_3$]COMe, 117228-06-5; (C-Cp)Fe(CO)[P(*p*-FPh)2]COMe, 117228-07-6; (η-Cp)Fe(CO)[P(*p*-Me$_2$NPh)$_2$]COMe, 117228-08-7; (η-Cp)Fe(CO)[P(*p*-CF$_3$Ph)$_3$]COMe, 117228-09-8; (η-Cp)Fe(CO)(PBzPh$_2$)COMe, 59140-17-9; (η-Cp)Fe(CO)(PCyPh$_2$)COMe, 117228-10-1; (η-Cp)Fe(CO)[P(*i*-Pr)$_3$]COMe, 117228-46-3; (η-Cp)Fe(CO)(PCy$_2$Ph)COMe, 117228-47-4; (η-Cp)Fe(CO)(PBz$_3$)COMe, 59140-18-0; (η-Cp)Fe(CO)[P(*m*-tolyl)$_3$]COMe, 117228-48-5; (η-Cp)Fe(CO)(PCy$_3$), 32610-55-2; (η-Cp′)Fe(CO)[P(OCH$_2$)$_3$CEt]COMe, 117228-11-2; (η-Cp′)Fe(CO)(PPhH$_2$)COMe, 117228-12-3; (η-Cp′)Fe(CO)[P(OMe)$_3$]COMe, 117228-13-4; (C-Cp′)Fe(CO)[P(OEt)$_3$]COMe, 117228-14-5; (η-Cp′)Fe(CO)[P(OCH$_2$CH$_2$Cl)$_3$]COMe, 117228-15-6; (η-Cp′)Fe(CO)[PMe(OEt)$_2$]COMe, 117228-16-7; (η-Cp′)Fe(CO)[P(CH$_2$CH$_2$CN)$_2$H]COMe, 117228-17-8; (η-Cp′)Fe(CO)[P(OMe)$_2$Ph]COMe, 117228-18-9; (η-Cp′)Fe(CO)(P(OEt)$_2$Ph]COMe, 117228-19-0; (η-Cp′)Fe(CO)(PMe$_2$Ph)COMe, 117228-20-3; (η-Cp′)Fe(CO)(PPh$_2$H)COMe, 117228-21-4; (η-Cp′)Fe(CO)[P(OPh)$_3$]COMe, 117228-22-5; (η-P′)Fe(CO)[P(O-*i*-Pr)$_3$]COMe, 117228-23-6; (η-Cp′)Fe(CO)[P(OMe)Ph$_2$]COMe, 117228-24-7; (η-Cp′)Fe(CO)(PEt)3)COMe, 117228-25-8; (η-Cp′)Fe(CO)(PBu$_3$)COMe, 117228-26-9; (η-Cp′)Fe(CO)[P(CH$_2$CH$_2$CN)$_3$]COMe, 117228-27-0; (η-Cp′)Fe(CO)[P(OEt)Ph$_2$]COMe, 117228-28-1; (η-Cp′)Fe(CO)[PMe(*i*-Bu)$_2$]COMe, 117228-29-2; (η-Cp′)Fe(CO)(PEt$_2$Ph)COMe, 117228-30-5; (η-Cp′)Fe(CO)(PMePh$_2$)COMe, 117228-31-6; (η-Cp′)Fe(CO)[PPh(CH$_2$CH$_2$CN)$_2$]COMe, 117228-32-7; (η-Cp′)Fe(CO)(PEtPh$_2$)COMe, 117228-33-8; (η-Cp′)Fe(CO)[P(O-*o*-tol)$_3$]COMe, 117228-34-9; (η-Cp′)Fe(CO)[PPh$_2$(CH$_2$CH$_2$CN)]COMe, 117228-35-0; (η-Cp′)Fe(CO)[P(*i*-Bu)$_3$]COMe, 117251-12-4; (η-Cp′)Fe(CO)(PCy$_2$H)COMe, 117228-36-1; (η-Cp′)Fe(CO)(PPh$_3$)COMe, 117228-37-2; (η-Cp′)Fe(CO)[P(*p*-MePh)$_3$]COMe, 117228-38-3; (η-Cp′)Fe(CO)[P(*p*-MeOPh)$_3$]COMe, 117228-39-4; (η-Cp′)Fe(CO)[P(*p*-ClPh)$_3$]COMe, 117228-40-7; (η-Cp′)Fe(CO)[P(*p*-FPh)$_3$]COMe, 117228-41-8; (η-Cp′)Fe(CO)[P(*p*-Me$_2$NPh)$_3$]COMe, 117228-42-9; (η-Cp′)Fe(CO)P(*p*-CF$_3$Ph)$_3$]COMe, 117228-43-0; (η-Cp′)Fe(CO)(PBzPh$_2$)COMe, 117228-44-1; (η-Cp′)Fe(CO)(PCyPh$_2$)COMe, 117228-45-2; (η-Cp′)Fe(CO)[P(*i*-Pr)$_3$COMe, 117228-49-6; (η-Cp′)Fe(CO)(PCy$_2$Ph)COMe, 117228-50-9; (η-Cp′)Fe(CO)(PBz$_3$)COMe, 117228-51-0; (η-Cp′)Fe(CO)[P(*m*-tolyl)$_3$]COMe, 117228-52-1; (η-Cp′)Fe(CO)(PCy$_3$)COMe, 117228-53-2; (η-Cp)Fe[P(OCH$_2$)$_3$CEt](CO)(Me), 80409-89-8; (η-Cp)Fe[P(OMe)$_3$](CO)(Me), 32680-12-9; (η-Cp)Fe[P(OEt)$_3$](CO)(Me), 117228-54-3; (η-Cp)Fe[P(OMe)$_2$Ph[(CO)(Me), 117228-55-4; (η-Cp)Fe[P(OEt)$_2$Ph](CO)(Me), 117228-56-5; (η-Cp)Fe(PMe$_2$Ph)(CO)(Me), 117228-57-6; (η-Cp)Fe[)P(OPh)$_3$](CO)(Me), 12290-98-1; (η-Cp)Fe[P(OMe)Ph$_2$](CO)(Me), 117228-58-7; (η-Cp)Fe(PEt$_3$)(CO)(Me), 117228-59-8; (η-Cp)Fe(PBu$_3$)(CO)(Me), 52928-70-8; (η-Cp)Fe[P(OEt)ph$_2$](CO)(Me), 117228-60-1; (η-Cp)Fe[PMe(*i*-Bu)$_2$](CO)(Me), 117228-61-2; (η-Cp)Fe(PEt$_2$Ph)(CO)(Me), 117228-62-3; (η-Cp)Fe(PMePh$_2$)(CO)(Me), 117228-63-4; (η-Cp)Fe(PEtPh$_2$)(CO)(Me), 117228-64-5; (η-Cp)Fe[PPh$_2$(CH$_2$CH$_2$CN)](CO)(Me), 117228-65-6; (η-Cp)Fe(PPh$_3$)(CO)(Me), 12100-51-5; (η-Cp)Fe[P(*p*-MePh)$_3$](CO)(Me), 117228-66-7; (η-Cp)Fe[P(*p*-MeOPh)$_3$](CO)(Me), 117228-67-8; (η-Cp)Fe[P(*p*-ClPh)$_3$](CO)(Me), 117228-68-9; (η-Cp)Fe[P(*p*-FPh)$_3$](CO)(Me), 117228-69-0; (η-Cp)Fe[P(*p*-Me$_2$NPh)$_3$](CO)(Me), 117251-13-5.