N-9 seem to be significantly different for ATP than the ratio of N_3 to N_1 shifts in 1-methylimidazole. Given the limited available data and the number of possible interpretations, we simply note these discrepancies without speculating as to their origins.

Contribution from the Department of Chemistry,
University of Wisconsin, Madison, Wisconsin 53706

Synthesis of a Metal Complex of Benzenethiol, [Fe(C5H5)(CO)2(PhSH)]BF4, and Its Characterization as a Strong Acid

P. M. Treichel* and L. D. Rosenhein

The acid-base chemistry of metal thiolate complexes has attracted some attention. The recent paper by Gingerich and Angelici[1] described the attempted protonation of PPN[W(C-O)5SH]. This reaction was intended to form the known compound W(CO)5(SH2)[2] by protonation at sulfur but gave instead a thiolato-bridged complex, μ-HS[W(CO)5]2$^-$. That W(CO)5(SH2) is a very strong acid is supported by the fact[2] that loss of a proton occurs even on treatment with [N(C2-H5)4]Br; bromide ion is of course a very weak base. Interestingly [W(CO)5SH]$^-$ does not give up its proton even to very strong bases. In contrast μ-HS[W(CO)5]2$^-$ can be deprotonated with sodium ethoxide.[1]

In addition, the reaction of [Mn(C5H4CH3)(CO)2SEt]$^-$ with strong acid to give [Mn2(C5H4CH3)2(CO)4SEt]$^+$ is noted.[3] This dimerization reaction resembles the reaction of [W(C-O)5SH]$^-$ with acid in that a thiolato-bridged product is formed.

The only instances of simple protonation at sulfur in thiolato complexes involve non-organometallic species such as [Ru-(NH3)5SR]$^+$ (R = H, C2H5). Values of pK_a for the complexes [Ru(NH3)5(RSH)]$^{2+}$ were determined to be 4.0 (for the H2S complex) and 9.2 (for the C2H5SH complex). The acidity is increased moderately over the free ligand pK_a values of 7 and 12, respectively.[4]

We describe here an organometallic complex of benzenethiol, having the formula [Fe(C5H5)(CO)2(PhSH)]BF4 (I). The synthesis of this complex was accomplished with use of the method developed by Reger and Coleman.[5] Of particular interest in this work was the ability of this complex to function as a strong acid, and experiments were carried out to attempt to further define this property.

Experimental Section

The compound [Fe(C5H5)(CO)2(THF)]BF4 was prepared by the literature method.[5] Reactions were routinely carried out under N2.

Infrared data were recorded on a Beckman Acculab 7 spectrophotometer; NMR spectra were run on a Jeol NM-MH-100 spectrometer. Optical absorbance measurements were made on Cary 14 and 118 instruments using 1.0-cm quartz cells. The analysis of I was done by Galbraith Laboratories, Knoxville, Tenn.

Preparation of [Fe(C5H5)(CO)2(PhSH)]BF4 (I). A 2.0-g (6.0 mmol) sample of [Fe(C5H5)(CO)2(THF)]BF4[5] was dissolved in 50

(1) Gingerich, R. G. W.; Angelici, R. J. *J. Am. Chem. Soc.* **1979**, *101*, 5604-5608.
(2) Herberhold, M.; Suss, G. *J. Chem. Res. Miniprint* **1977**, 2720-2743.
(3) Burkett-St. Laurent, J. C. T. R.; Caira, M. R.; English, R. B.; Haines, R. J.; Nassimbeni, L. R. *J. Chem. Soc., Dalton Trans.* **1977**, 1077-1081.
(4) Kuehn, C. G.; Taube, H. *J. Am. Chem. Soc.* **1976**, *98*, 689-702.
(5) Reger, D. L.; Coleman, C. *J. Organomet. Chem.* **1977**, *131*, 153-162.

Table I. Equilibrium Data for the Systems I + Base ⇌ II + BH$^+$ in CH$_2$Cl$_2$

$C_B^b \times 10^3$	C_{II} (measd)$^c \times 10^3$	$[B]^d \times 10^3$	$C_I^e \times 10^3$	K_e^f	K_{assoc}^g
(a) B = THF, C_T^a = 2.56 × 10^3 M					
9.08	0.620	8.46	1.94	2.34	37.8
18.2	0.939	17.2	1.62	3.16	33.6
27.2	1.17	26.1	1.39	3.75	32.2
36.3	1.35	35.0	1.21	4.33	32.0
45.4	1.48	43.9	1.08	4.64	31.3
54.5	1.61	52.9	0.948	5.19	32.2
(b) B = Me$_2$SO, C_T^a = 4.27 × 10^3 M					
0.471	0.378	0.0938	3.89	0.391	1030
0.943	0.719	0.223	3.55	0.652	907
1.41	1.07	0.342	3.20	1.05	980
1.89	1.35	0.539	2.92	1.15	855
2.36	1.70	0.659	2.57	1.70	1000
2.83	2.10	0.726	2.17	2.81	1340
(c) B = Ph$_2$NH, C_T^a = 4.89 × 10^3 M					
0.708	0.530	0.178	4.36	0.362	683
1.42	1.21	0.209	3.68	1.90	1570
2.12	1.90	0.220	2.99	5.52	2900
2.38	2.31	0.522	2.58	3.96	1720
4.25	3.05	1.20	1.84	4.22	1380
5.66	3.65	2.02	1.24	5.32	1460

^{a} $C_T = C_I + C_{II}$. ^{b} $C_B = [B] + [BH^+]$. ^{c} Determined spectrophotometrically; see text. ^{d} $[B] = C_B - C_{II}$. ^{e} $C_I = C_T - C_{II}$. ^{f} Equilibrium constant for the reaction I + B ⇌ II + [BH]$^+$; $K_e = [II][BH^+]/[I][B]$. ^{g} Equilibrium constant for the reaction I + B ⇌ [II···H-B]$^+$; $K_e = [II]/[I][B]$; see text for discussion.

mL of CH$_2$Cl$_2$, and 1.30 g (12.0 mmol) of PhSH was added. The solution was stirred at room temperature for 3 h. A brown solid was then precipitated from solution by addition of hexane. Purification by recrystallization from CH$_2$Cl$_2$/hexane gave yellow crystals; 0.80 g (40%), mp 133-136 °C.

Anal. Calcd for C$_{13}$H$_{11}$BF$_4$FeS: C, 41.75; H, 2.97; Fe, 14.93. Found: C, 42.05; H, 2.89; Fe, 14.73.

IR: ν(CO) 2055, 2015 cm^{-1} in CH$_3$NO$_2$. NMR (CD$_2$Cl$_2$): δ 7.49 (C$_6$H$_5$), 5.39 (C$_5$H$_5$). The S-H resonance occurs between δ 5.0 and 6.0, its position dependent upon concentration.

The product could be handled only in CH$_2$Cl$_2$ and CH$_3$NO$_2$. It was not soluble in nonpolar solvents and was deprotonated in typical polar solvents (acetone, acetonitrile), giving Fe(C$_5$H$_5$)(CO)$_2$SPh (II); ν(CO) = 2030, 1987 cm^{-1}.[6]

Equilibrium Studies. We hoped to determine more quantitatively the acidity of I by studying its reaction with several weak bases, viz., eq 1. This could be done by taking advantage of the different

[Fe(C$_5$H$_5$)(CO)$_2$(PhSH)]BF$_4$ + B ⇌
$$\text{Fe(C}_5\text{H}_5\text{)(CO)}_2\text{SPh} + [\text{BH}]\text{BF}_4 \quad (1)$$
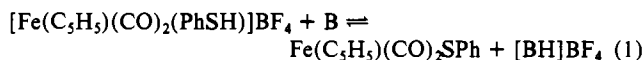
absorption spectra of the starting material and product. The product of deprotonation, II, is maroon and shows a maximum at 560 nm having an extinction coefficient ϵ_{II} of 278 cm^{-1} M^{-1} (CH$_2$Cl$_2$). In contrast, yellow I has a maximum in the ultraviolet region of the spectrum which trails into the visible region. At 560 nm the extinction coefficient for this compound, ϵ_I, is 24 cm^{-1} M^{-1}. (This measured value, which was presumed to be somewhat uncertain due to its small magnitude, was verified by the method of Rose and Drago.[7])

The measurements of equilibrium concentrations were carried out as follows. A solution of I in CH$_2$Cl$_2$ between 0.01 and 0.03 M was prepared. A measured quantity of the base used was added to 5.00 mL of this solution. The resulting mixture was diluted to 25.0 mL, and C_T (total concentration of I and II) and C_B (total concentration of B and BH$^+$) were calculated. The concentration of species II, C_{II}, was related to the absorbance, A, by the relationship $C_{II} = (A - \epsilon_I b C_T)/[(\epsilon_{II} - \epsilon_I)b]$. Knowing C_{II}, one can determine the value of C_I ($C_I = C_T - C_{II}$). The equilibrium concentration of base is assumed

(6) Ahmad, M.; Bruce, R.; Knox, G. R. *J. Organomet. Chem.* **1966**, *6*, 1-10.
(7) Rose, N. J.; Drago, R. S. *J. Am. Chem. Soc.* **1959**, *81*, 6138-6145.

to be the initial concentration of base (C_B) minus C_{II}, and the concentration of BH^+ equals C_{II}. Data for equilibria, with the bases THF, Me_2SO, and Ph_2NH at several different concentrations are given in Table I.

In the experiments using Me_2SO and Ph_2NH the absorbance of the solution changed slowly with time. The absorbance listed is the value determined by extrapolation of a plot of log A vs. t to $t = 0$.

Discussion

The absence of organometallic complexes having thiols, RSH, as ligands is noteworthy. Many reactions have been carried out between thiols and organometallic precursors, but in each case the product is found to contain only thiolate groups, RS, serving as either bridging or terminal ligands. In these reactions the thiol proton is lost in a fashion which is unknown but probably not directly related to its acidity, since most of these reactions are run in nonpolar media.

It was apparent to us that the synthesis of organometallic complexes with thiol ligands would require very mild conditions. One possible route was the protonation of a compound having a terminal SR ligand group. This route had been used successfully in the synthesis of the ruthenium complexes mentioned above,[4] but it was also known to have failed in two instances when the attempted protonation gave a dinuclear product.[1,3] We were persuaded that a better route might be the substitution of an easily replaced ligand in the metal coordination sphere by a thiol. The compound [Fe(C_5H_5)(CO)$_2$(THF)]BF_4 seemed an ideal precursor since it is known that THF is readily replaced by a wide range of ligands.[5] The reaction of this species with benzenethiol, in CH_2Cl_2 at room temperature, was successful, and we were able to isolate the complex [Fe(C_5H_5)(CO)$_2$(PhSH)]BF_4 (I), a yellow crystalline solid, which was characterized by infrared and NMR data and by elemental analyses. Notably, this compound is reasonably stable as a solid, melting at 133–136 °C without decomposition. It is reactive toward water and other basic substances and must be handled with the exclusion of such materials.

The strongly acidic character of this compound was immediately evident. Typical of ionic compounds this species dissolved in most polar solvents, but in this process the solvent was also protonated. This fact was evident from the shift of ν(CO) by 20–30 cm^{-1} to the values for the known compound Fe(C_5H_5)(CO)$_2$SPh (II).[6] The only common solvents in which this compound could be dissolved without reaction were CH_2Cl_2 and CH_3NO_2; these solvents were used in further studies.

Protonation of II to give I occurred in CH_2Cl_2 when HBF_4(aq) or HBr(g) was added. This fact was determined by the appearance of the ν(CO) peaks for I. It was not possible to isolate pure I from these reaction systems however; only oils were obtained upon workup of the HBr reaction, while it proved impossible to remove water from the product of the HBF_4 reaction.

A more precise determination of the acidity of I appeared desirable. However, severe limitations were imposed by the solubility of I and its reactivity toward most polar solvents. Ultimately we chose to study the behavior of I with various weak bases in the solvent CH_2Cl_2. This choice was not ideal; since CH_2Cl_2 is not often used for such studies, there would be little basis for precise comparison of the acidity of I with other species. Furthermore, CH_2Cl_2 has a low dielectric constant, and it presumably does not strongly solvate either acidic or basic reactants. As a consequence, association between acidic and basic species in the equilibrium system was likely either by ion pairing or by hydrogen bonding, thus complicating an analysis of the system.[8] Indeed the data presented here are in much better accord with an equilibrium

of the sort in eq 2 for which $K_{assoc} = $ [Fe(C_5H_5)(CO)$_2$PhS$\cdots$HB]$^+$/[Fe(C_5H_5)(CO)$_2$(PhSH)]$^+$[B] than they are with a conventional equilibrium expression (vide infra).

$$[Fe(C_5H_5)(CO)_2(PhSH)]^+ + B \rightleftharpoons$$
$$[Fe(C_5H_5)(CO)_2PhS\cdots HB]^+ \quad (2)$$
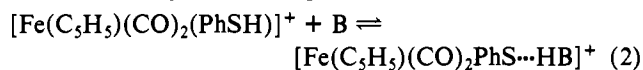
In order for this study to be carried out, measured quantities of a base (THF, Me_2SO, or Ph_2NH) and of I were dissolved in CH_2Cl_2. The concentration of II was then determined spectrophotometrically, taking advantage of its absorption maximum at 560 nm (ϵ = 278 cm^{-1} M^{-1}). The association of II with the acidic species, BH^+, did not appreciably change the absorption spectrum. With the concentration of II and the initial concentrations known, the equilibrium concentrations of the species could be ascertained (Table I).

It can be seen that these data are in best accord with the equilibrium defined above (K_{assoc}) in which there is association between I and BH^+. The conventional K_e expression is clearly inadequate, varying monotonically as the amount of added base is varied. The best results for K_{assoc} were obtained with THF as the base. Average values of K_{assoc} are

base	K_{assoc} (av dev)
THF	33.2 (1.7)
Me_2SO	1.0 (0.1) $\times$ 10^3
Ph_2NH	1.6 (0.5) $\times$ 10^3

For expression of these results in a different form, in equimolar solutions of I with each base (at the concentrations used in these experiments), there is 8% association with THF, 62% association with Me_2SO, and 70% association with Ph_2NH.

While the calculated values of K_{assoc} are somewhat imprecise, they certainly express the general magnitude of the acidity, conveying clearly the strong-acid nature of I. (The pK_a values for N(C_6H_5)$_2H_2^+$, (Me_2SO)H$^+$, and (THF)H$^+$ are 0.80,[9] -1.80,[10] and -2.08,[11] respectively, determined in water or aqueous ethanol. Although precise pK_a values of these species are undoubtedly different in CH_2Cl_2, the general magnitude of these values is probably reasonable for the sake of these comparisons. Certainly one can argue that I must be quite a strong acid to effect protonation to the extent observed.) Lack of precision could be a consequence of the fact that other possible equilibria such as homoconjugation and association with the BF_4^- counterion were not taken into account. In addition spectrophotometric measurements of the concentration of II were complicated because the absorption at 560 nm slowly changed with time, a change of 0–20% being observed over 10 min or so for the Me_2SO and Ph_2NH complexes. Possibly, this change was the consequence of a slow substitution of PhSH by these bases. We have established that both [Fe(C_5H_5)(CO)$_2$(Me_2SO)]$^+$ and [Fe(C_5H_5)(CO)$_2$(Ph_2NH)]$^+$ can be prepared from the THF compound. Displacement of PhSH by THF is unlikely since the reverse reaction is known to be favored by the synthesis of I from the THF complex. It is noted that the equilibrium data for B = THF is substantially better, which indirectly supports the idea that substitution reactions are involved in the uncertainties in K_{assoc}.

The pK_a value of C_6H_5SH is 6.62,[12] measured in aqueous methanol. Upon coordination to the metal the acidity of this group is increased by many orders of magnitude. The acidity of compound I is closer to the acidity of $C_6H_5SH_2^+$ than to C_6H_5SH. The extent of this increase in acidity is quite striking. An increase in acidity upon coordination seems likely to be a general phenomenon, arising because of delocalization of the

(8) Davis, M. M. "The Chemistry of Non-Aqueous Solvent Systems"; Lagowski, J. J., Ed.; Academic Press: New York, 1970; Vol. 3.

(9) Reynard, R.; Rumpf, P. *Bull. Chem. Soc. Fr.* **1963**, 1805–1810.
(10) Landini, D.; Modena, G.; Scorrano, G.; Taddei, F. *J. Am. Chem. Soc.* **1969**, *91*, 6703–6707.
(11) Arnett, E. M.; Wu, C. Y. *J. Am. Chem. Soc.* **1962**, *84*, 1684–1688.
(12) De Maria, P.; Fini, A.; Hall, F. M. *J. Chem. Soc., Perkins Trans. 2* **1973**, 1969–1971.

available lone pair in the deprotonated form over the metal and other ligands.[6,13] The extent of the increase is no doubt related to factors such as the net charge on the complex (consider $[Ru(NH_3)_5(RSH)]^{2+})$[4] and the donor–acceptor character of other ligands. This seems to us to be a subject which has not yet been sufficiently studied, and we hope that our work, albeit qualitative, will encourage further consideration of this topic.

Registry No. I, 76136-83-9; II, 12110-44-0; THF, 109-99-9; Me₂SO, 67-68-5; Ph₂NH, 122-39-4; [Fe(C₅H₅)(CO)₂(THF)]BF₄, 63313-71-3.

---

(13) Treichel, P. M.; Dean, W. K.; Douglas, W. M. *Inorg. Chem.* **1972**, *11*, 1615–1618.

Contribution from the Guelph-Waterloo Centre for Graduate Work in Chemistry, Guelph Campus, University of Guelph, Guelph, Ontario, Canada N1G 2W1

Steric Control in the Synthesis and Reactions of [Pt₂Cl₂(μ-Cl)₂(PCy₃)₂]

G. K. Anderson, H. C. Clark,* and J. A. Davies

Dimeric halide-bridged complexes[1] of platinum(II) of the type [Pt₂Cl₂(μ-Cl)₂(ER₃)₂] (E = P, As, Sb; R = alkyl, aryl) are generally prepared by heating a slurry of platinum(II) chloride with the appropriate *cis*-[PtCl₂(ER₃)₂] complex in an inert solvent.[2,3] If the cis isomer of the [PtCl₂(ER₃)₂] complex is not available, two alternative methods may be employed; the trans isomer may be fused with the platinum(II) halide[4,5] or the ER₃ ligand may be reacted with the dimeric ethylene complex [Pt₂Cl₂(μ-Cl)₂(C₂H₄)₂].[4] The former method requires a high degree of thermal stability from both reactants and products while the latter method is generally employed only for tertiary stibines, since phosphines and arsines yield mainly monomeric products via bridge cleavage.[1b] Neither method is available when ER₃ is a sterically demanding phosphine ligand. Our interest in platinum complexes of such ligands[6,7] has led us to develop an efficient synthesis of the dimeric complex [Pt₂Cl₂(μ-Cl)₂(PCy₃)₂] (Cy = cyclohexyl), a synthesis in which a high degree of steric control is observed. In addition, bridge-cleavage reactions with neutral ligands are now reported which yield several interesting products of trans geometry; the reaction with carbon monoxide yields an exceptionally stable trans complex which shows little tendency to isomerize to the more common, thermodynamically preferred, cis isomer. Cleavage by large nucleophiles is slow; a probable consequence of steric hindrance during an associative process.[8]

Experimental Section

[K][PtCl₃(C₂H₄)] was prepared by the literature method.[9] Phosphine ligands were obtained from Strem Chemicals and 90% ¹³C-enriched carbon monoxide from Prochem. Spectrograde acetone was distilled from activated 3-Å molecular sieve immediately prior to use. All manipulations involving tertiary phosphines were performed under strictly anaerobic conditions. ¹³C and ³¹P NMR spectra were obtained on a Bruker WP60 instrument operating in the Fourier transform mode at 15 (¹³C) or 24 MHz (³¹P). Infrared spectra were obtained on a Perkin-Elmer 180 spectrometer either as Nujol mulls with use of CsI optics or as chloroform solutions with use of KBr solution cells of 0.1-mm path length.

Synthesis of [Pt₂Cl₂(μ-Cl)₂(PCy₃)₂]. A solution of PCy₃ (0.280 g, 1.0 mmol) in acetone (500 mL) was added dropwise over 48 h to a vigorously stirred solution of [K][PtCl₃(C₂H₄)] (0.369 g, 1.0 mmol) in acetone (500 mL). The solution was stirred for a further 24 h and then reduced to dryness in vacuo at room temperature. The residue was extracted with chloroform (3 × 15 mL aliquots), and the extracts were filtered and reduced to small volume in vacuo. Careful addition of petroleum ether (bp 30–40 °C) caused a yellow solid to crystallize which was filtered, recrystallized from chloroform–petroleum ether, and dried in vacuo. The yield was 0.358 g (70%). Anal. Calcd for Pt₂Cl₄P₂C₃₆H₆₆: C, 39.56; H, 6.09. Found: C, 39.53; H, 6.00.

Cleavage Reactions of [Pt₂Cl₂(μ-Cl)₂(PCy₃)₂]. (A) SMe₂ and C₅H₅N. A 10-fold excess of the ligand was added to a solution of the dimer (~30 mg) in CDCl₃, and the solution was examined spectroscopically after 15 min and again after being treated at 55 °C for 2 h.

(B) PCy₃, P(o-CH₃C₆H₄)₃, PMePh₂, AsPh₃, and t-BuNC. A stoichiometric amount of the ligand was added to a solution of the dimer (~30 mg) in CDCl₃, and the solution was examined spectroscopically. Reactions of PMePh₂, AsPh₃, and t-BuNC were complete within ~15 min while reactions with PCy₃ and P(o-CH₃C₆H₄)₃ required several hours.

(C) CO and ¹³CO. Solutions of the dimer (~30 mg) in CDCl₃ were either purged with a gentle stream of CO for 1 h or stirred under an atmosphere of ¹³CO for 2 h and then examined spectroscopically.

Results and Discussion

The slow addition of PCy₃ to [K][PtCl₃(C₂H₄)] under anaerobic conditions gives the dimeric complex [Pt₂Cl₂(μ-Cl)₂(PCy₃)₂] in high yield. Its far infrared spectrum shows bands at 353 cm⁻¹ and 326, 250 cm⁻¹ attributed largely to terminal and bridging metal–chlorine vibrations.[1c] The ³¹P{¹H} NMR spectrum is entirely typical of the AA′XX′ spin system,[10] characteristic of dimeric complexes of this type (δ(P) = 20.2, ¹*J*(Pt, P) = 3875 Hz, ³*J*(Pt, P) = 20 Hz, ⁴*J*(P, P) < 2 Hz, ²*J*(Pt, Pt) = 138 Hz).[11]

The preparative route described here is specific for sterically demanding phosphine ligands, and attempts to utilize this method in the preparation of dimeric analogues of less bulky ligands such as PEt₃ and PPh₃[12] lead to the isolation of other products. Thus, the slow addition of dilute solutions of these ligands to [K][PtCl₃(C₂H₄)] yields *trans*-[PtCl₂(PR₃)₂] as the only phosphine-containing products. Similar experiments at low temperature (−60 °C) also yield only these monomeric species. The trans geometry of the [PtCl₂(PR₃)₂] complexes

---

(1) F. R. Hartley, "The Chemistry of Platinum and Palladium", Applied Science, New York, 1973: (a) p 133; (b) p 130; (c) p 244.
(2) R. J. Goodfellow and L. M. Venanzi, *J. Chem. Soc.*, 7533 (1965).
(3) A. C. Smithies, M. Rycheck, and M. Orchin, *J. Organomet. Chem.*, **12**, 199 (1968).
(4) J. Chatt, *J. Chem. Soc.*, 652 (1951).
(5) J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 2787 (1955).
(6) H. C. Clark, *Isr. J. Chem.*, **15**, 210 (1976–1977).
(7) H. C. Clark, A. B. Goel, and C. Billard, *J. Organomet. Chem.*, **182**, 431 (1979).

(8) Nucleophilic attack on bridged [Pt₂X₂(μ-X)₂L₂] (X = halide, L = neutral ligand) complexes follows the same rate law as ligand displacement reactions of mononuclear complexes and is thus assumed to be associative. See R. G. Pearson and M. M. Muir, *J. Am. Chem. Soc.*, **88**, 2163 (1966).
(9) P. B. Chock, J. Halpern, and F. E. Paulik, *Inorg. Synth.*, **14**, 90 (1973).
(10) A. A. Kiffen, C. Masters, and J. P. Visser, *J. Chem. Soc., Dalton Trans.*, 1311 (1975).
(11) ³¹P{¹H} and ¹³C{¹H} NMR data are relative to external H₃PO₄ and internal Me₄Si, respectively. More positive values of δ represent deshielding.
(12) The cone angle data of Tolman allow some relative comparisons of ligand steric effects to be made. Cone angles of ligands employed here, or used in discussion, are as follows: ~95° for CO, 122° for PMe₂Ph, 132° for PEt₃ and P-n-Bu₃, 136° for PMePh₂, 145° for PPh₃, 170° for PCy₃, and 194° for P(o-CH₃C₆H₄)₃. See for discussion C. A. Tolman, *Chem. Rev.*, **77**, 313 (1977).