$H_8)_2CH_2$ by fractional distillation through a −22 °C U-trap, through which 1-MeB_5H_8 passed. The ^{11}B NMR spectrum for (1-B_5H_8)$_2CH_2$ is as follows: B(1), −41.18 ppm (singlet); B(2–5), −13.85 ppm (doublet, J = 160.7 Hz). The ^1H NMR spectrum shows the following resonances: −2.38 ppm (very broad, intensity 8); +0.24 ppm (broad, intensity 2); +2.48 ppm (quartet, J = 161.6 Hz, intensity 8).

A 2-day 65 °C reaction in a 30-mL stainless steel bomb containing $HfCl_4$ (2.5 mmol), CH_2Cl_2 (5.09 mmol), and B_5H_9 (10.68 mmol) produced a 2% yield of (1-B_5H_8)$_2CH_2$ and 1% of 1-MeB_5H_8.

R. Reactions between 2,3-$Cl_2C_4H_8$ and B_5H_9. A typical reaction, run as noted in procedure C, contained 0.82 mmol of $ZrCl_4$, 3.5 mmol of 2,3-dichlorobutane (2,3-$Cl_2C_4H_8$), and 7 mmol of B_5H_9. The (butyl)pentaborane product, separated by gas chromatography with the 8-ft column, was primarily 1-(*i*-C_4H_9)B_5H_8, in 7% yield, whose ^{11}B NMR spectrum is as follows: B(1), −44.22 ppm (singlet); B(2–5), −13.87 ppm (J = 159.4 Hz). The ^1H NMR spectrum exhibits the following resonances: −2.47 ppm (very broad, intensity 4); +0.90 ppm (broad multiplet, intensity 2); +1.04 ppm (doublet, J = 6.40 Hz, intensity 6); +1.71 ppm (broad multiplet, intensity 1); +2.40 ppm (quartet, J = 162.5 Hz, intensity 4). The mass spectrum of 1-(*i*-C_4H_9)B_5H_8 has a parent ion peak at m/e 119.2 (calculated for $^{12}C_4H_{17}{}^{10}B^{11}B_4$ 119.235).

In another reaction between 2,3-$Cl_2C_4H_8$ (3.5 mmol), B_5H_9 (7 mmol), and $ZrCl_4$ (0.7 mmol) in a 100-mL reaction flask at 50 °C for 2 h, the (butyl)pentaborane products, separated by gas chromatography with the 8-ft column, consisted of 1-(*i*-C_4H_9)B_5H_8 (42%) and 1-(s-C_4H_9)B_5H_8 (7%).

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Registry No. B_5H_9, 19624-22-7; $AlCl_3$, 7446-70-0; $FeCl_3$, 7705-08-0; $NbCl_5$, 10026-12-7; $TaCl_5$, 7721-01-9; $ZrCl_4$, 10026-11-6; $HfCl_4$, 13499-05-3; BF_3, 7637-07-2; Pd, 7440-05-3; $TiCl_4$, 7550-45-0; $SnCl_4$, 7646-78-8; $ZnBr_2$, 7699-45-8; $(C_5H_5)_2ZrCl_2$, 1291-32-3; $(C_5H_5)_2Zr(H)Cl$, 37342-97-5; YCl_3, 10361-92-9; 1-(*i*-C_3H_7)B_5H_8, 37838-05-4; 1-(*n*-C_3H_7)B_5H_8, 34692-67-6; 2-(*n*-C_3H_7)B_5H_8, 126724-90-1; 1-EtB_5H_8, 23753-61-9; 2-ClC_3H_7, 75-29-6; 2-BrC_3H_7, 75-26-3; 2-IC_3H_7, 75-30-9; *n*-ClC_3H_7, 540-54-5; *n*-ClC_4H_9, 109-69-3; *s*-ClC_4H_9, 78-86-4; *t*-ClC_4H_9, 507-20-0; 1-(*s*-C_4H_9)B_5H_8, 92276-87-4; CH_2Cl_2, 75-09-2; 2,3-$Cl_2C_4H_8$, 7581-97-7; 1-(c-C_5H_9)B_5H_8, 126724-91-2; 1-(C_6H_{11})B_5H_8, 126724-92-3; (1-B_5H_8)$_2CH_2$, 93659-46-2; 1-(*i*-C_4H_9)B_5H_8, 126724-93-4; 2-(*i*-C_3H_7)B_5H_8, 126724-94-5; 1-butene, 106-98-9; *cis*-2-butene, 590-18-1; *trans*-2-butene, 624-64-6; ethyl chloride, 75-00-3; cyclopentyl chloride, 930-28-9; cyclohexyl chloride, 542-18-7; methyl chloride, 74-87-3.

Supplementary Material Available: Spectra for 1-(*i*-C_3H_7)B_5H_8 (^{11}B NMR, ^1H NMR, and mass spectra), 1-(*n*-C_3H_7)B_5H_8 (^1H NMR and mass spectra), and 1-(s-C_4H_9)B_5H_8 and 1-(*i*-C_4H_9)B_5H_8 (^1H NMR spectra) (7 pages). Ordering information is given on any current masthead page.

Quantitative Analysis of Ligand Effects (QALE). Systematic Study of Iron–Phosphorus Bond Lengths and Their Relationship to Steric Thresholds

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Systematic determination of Fe–P bond lengths for the set of complexes (η-Cp)(CO)(L)FeCOMe containing "sterically unencumbered" σ-donor phosphorus(III) ligands shows that the Fe–P bond lengths vary over a narrow range (2.195 ± 0.015 Å) and are only slightly dependent on the σ-donicity and size of the ligand. π-Acid ligands (i.e. $P(OR)_3$) exhibit significantly shorter Fe–P bond lengths around 2.10 Å. In light of this virtual constancy of σ bond length for a family of complexes, it is reasonable to expect steric thresholds to be manifest. We report on five systems that can be analyzed in terms of sharp thresholds.

Introduction

Although ligand effects have been employed in organometallic chemistry for nearly 20 years, only recently have there been attempts to extract information about the stereoelectronic factors that influence the thermodynamics and kinetics of reactions by quantitative analysis of ligand effects (for which we use the acronym QALE).[1–13] QALE is based on the premise that certain thermodynamic, kinetic, and structural properties of a complex and its reactions can be expressed in terms of steric and electronic parameters assigned to the ligands involved. This leads to a correlation method, often made linear in the stereoelectronic parameters, from which insights about structure or reactivity may be drawn. A complicating feature is the type of bonding (σ or π) that exists between the ligand and the metal fragment. Dose the bond type range smoothly, with no abrupt transition, from one end

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of the scale of ligands to the other? If it does not, then a correlation scheme might give misleading results unless applied to ligands of the same bond type. Another complicating feature is that steric effects might not be continuously operative for all sizes of ligands. Below we discuss briefly the evidence from the literature that has led us to the view that there are discontinuities in electronic and steric effects of ligands. Then we report new results from a systematic study of Fe–P bond lengths that lends support to the concepts of different M–P bond types and steric thresholds. Finally, we consider the sharpness of the steric threshold.

Electronic Factors. The idea that transition-metal–phosphorus(III) bonding involves a σ and a π component is deeply entrenched in the tradition of organometallic chemistry.[14] The well-known contraction of the M–P bond that occurs with increasing electronegativity of the α-atom (C, O, F) of the pendent groups on phosphorus is consonant with increasing π bonding as one moves across the series.[15] This simple picture may not be entirely accurate since there is accumulating evidence that phosphorus(III) ligands may act as pure σ donors, depending on the the nature of the pendent groups, the length of the M–P bond, and crowding about the metal.

Part of this evidence comes from correlations of properties of phosphorus(III) complexes and the pK_a values of HPR_3^+. The pK_a values are related to the strength of the P–H bond, which cannot possess a π component. Therefore, a linear correlation of properties of phosphorus(III) complexes with pK_a values suggests (but does not prove) a lack of an M–P π interaction; i.e., those phosphorus(III) ligands are acting as pure σ donors. For example, a plot of the χ values for $Ni(CO)_3(PR_3)$ against the pK_a values shows that the data separate into two groups: one group (trialkylphosphines, mixed alkylarylphosphines, and triarylphosphines) shows a nearly linear relationship,[3] whereas the remainder (primarily those ligands containing P–O bonds) create a scatter diagram.[16] This leads us to the conclusion that the first group possesses no π component in their Ni–P bond. On the other hand, the lack of correlation with pK_a for the second group suggests that there is a second component to the Ni–P bond, probably a π interaction. A similar division of ligands is seen in the plot of the $E°$ values for $(\eta\text{-Cp})Mn(CO)_2L$ versus pK_a.[1] More recently we have shown that a correlation of properties that depend on the electron-donor ability of the phosphorus(III) ligands also serves to divide the ligands into what we have classified as σ donors and π acids, thereby obviating the necessity to use pK_a values.[3] Thus, a plot of ν_{CO} versus $E°$ for $(\eta\text{-Cp})(CO)(L)FeCOMe$ divides the ligands into the same groups as seen in the pK_a correlation described above. Furthermore, we have recently shown that stereoelectronic parameters (χ and θ) of trialkylphosphines, mixed alkylarylphosphines, and triarylphosphines are transferable to the analogous silyl groups and, thus, allow the separation of the steric and electronic factors influencing the chemistry of allylsilanes.[17] Since there is no possibility in allylsilanes of π bonding that in any way resembles Ni–P π bonding, we conclude that the χ values for this group of ligands contain no π component and, therefore, the phosphines form only σ bonds to nickel.

Additional support for our conclusion comes from analyses of kinetic and thermodynamic data for reactions involving phosphorus(III) ligands. It has long been known that the rates (log k) of associative entering ligand (PR_3) dependent substitution reactions are linearly related to the pK_a values of HPR_3^+ (with a steric contribution for the larger ligands).[18] This linear relationship is consistent with the phosphines behaving as σ donors in the transition states of the reactions. It is important to note that even the kinetic data for phosphorus(III) compounds bearing P–O bonds correlate with pK_a.[1,5–7] This observation suggests that in the transition state of this reaction these potentially strong π acids also behave as σ donors. This interpretation finds further support in the analyses of heats of reaction data where, in one case, the phosphites behave as π acids and, in another case, appear to behave as σ donors. For example, the heats of addition of phosphorus(III) compounds to $((\eta\text{-}C_5H_7)NiMe)_2$ increase with larger χ (more π acidic and less basic) values of the ligands.[2,19] In fact, the reaction with $P(OPh)_3$ exhibits the largest heat of reaction. These results are consistent with the presence of an important π component to the $Ni\text{–}P(OPh)_3$ bond in the product. In contrast the heats of substitution of toluene from $(\eta\text{-tol})Mo(CO)_3$ increase as χ decreases, with $P(OPh)_3$ exhibiting the smallest heat of reaction.[11] This led Nolan and Hoff to conclude that Mo–P σ bonding is more important than π bonding. Since we find that the data for the molybdenum system correlate quite well with pK_a and θ alone, we suggest that the π component is completely attenuated, leaving only a σ bond.[2] Thus, it appears that, in the sterically congested $Mo(CO)_3(PR_3)_3$, the phosphite ligands behave as σ-donor ligands.

Steric Factors. In his seminal papers, Tolman showed that the size of phosphorus(III) ligands plays a central role in the chemistry of their complexes.[20] Schenkluhn and co-workers took the concept of the cone angle one step further when they analyzed product distributions and heats of reaction via linear and nonlinear regression analysis in terms of the cone angle and Tolman's electronic parameter, ν.[19] Somewhat later, Kochi[9] showed that the rates of some organometallic reactions may be separated into electronic (pK_a) and steric (θ) components. It now appears that steric effects may be ushered in at a particular θ (steric threshold). The seeds of the steric threshold idea can be found in two papers. Trogler and Marzilli observed that the chemical shift of the methyl (methanol) resonance for $(MeOH)Co(DMG)_2L^+$ correlates linearly with cone angle.[21] The steric effect disappears, however, for ligands with cone angles less than approximately 118°, suggesting that there is a steric threshold near this value. Cotton and Darensbourg noted that the structure of $(CO)_5WPMe_3$ showed no signs of steric distortion.[22] Since $(CO)_5WP(t\text{-}Bu)_3$ is sterically distorted,[23] there must be a value of θ between the cone angles for PMe_3 and $P(t\text{-}Bu)_3$ where steric effects become operative.

Our group[1] concurrently with Poe et al.[5] noted that steric thresholds are particularly obvious in the kinetic data for entering ligand (PR_3) dependent substitution reactions. The analysis of these kinetic data leading to the observation of steric thresholds builds on the premise, first noted

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by Kochi,[9] that the free energy of activation is divisible into steric (log k_{st}), electronic (log k_{el}), and intrinsic (C, independent of the stereoelectronic properties of PR_3) components such that

$$\log k = \log k_{el} + \log k_{st} + C \qquad (1)$$

Construction of electronic and steric profiles allows the separation of the two effects. An electronic profile is a plot of log k for a series of isosteric ligands (or small ligands that do not exhibit steric effects) versus a measure of the σ donicity (commonly pK_a values) of the phosphorus(III) ligands. log k_{st} is the difference (at the same pK_a) between data points for the remaining ligands and the electronic profile. The steric profile is generated by plotting log k_{st} versus the cone angle (θ) of the ligand.

These steric profiles[1,5-7] often show regions of no steric effects for small ligands followed by steric thresholds, after which the rate (log k_{st}) for reaction declines linearly as a function of θ. We suggested that the value of the steric threshold (θ_{st}) is a measure of the congestion about the metal in the transition state and the slope (steric sensitivity) of the steric profile after θ_{st} is related to the flexibility of the transition-state complex. A large slope indicates a stiff complex, whereas a smaller slope indicates a more flexible complex. Subsequently, we have shown that steric thresholds may also be observed in heat of reaction data,[2] and kinetic data for reactions that involve spectator phosphorus(III) ligands.[4]

Although the aforementioned evidence provides strong support for the separation of ligands into pure σ donors and π acids, it is indirect. Certainly, the most direct method of studying metal–ligand bonding is the systematic X-ray diffraction study of phosphorus(III) complexes. We are aware of only two reported systematic studies: These involve the sterically congested complexes $L_2Mo(CO)_4$[24] and $ClCo(dmg)_2L$.[25] In each case it was observed that the M–P bond lengths increase linearly with θ. In order to better understand the electronic factors that influence M–P bonding, we have determined the structures of 10 complexes of the type (η-Cp)(CO)(L)FeCOMe which are predicted to be sterically uncongested.[3] Seven of the complexes posses ligands that were classified as pure σ donors, and three contain putative π acids.[3]

Table I. Stereoelectronic Properties of Phosphorus(III) Ligands

no.	ligand	θ,[a] deg	pK_a[b]	χ[c]	χ_d
1	$P(OCH_2)_3CEt$	101	1.74	31.20	18.39
2	$PPhH_2$	106	(−2.0)	20.85	20.85
3	$P(OMe)_3$	107	2.60	24.10	16.70
4	$P(OEt)_3$	109	3.31	21.60	15.51
5	PMe_3	118	8.65	8.55	8.55
6	$P(OMe)_2Ph$	120	(2.64)	19.45	15.73
7	$P(OEt)_2Ph$	121	(3.1)	18.10	14.98
8	$PPhMe_2$	122	6.5	10.60	10.60
9	PCl_3	124		48.00	48.0
10	PPh_2H	126	0.03	17.35	17.35
11	$P(OPh)_3$	128	−2.0	30.20	22.05
12	P(O-*i*-Pr)$_3$	130	4.08	19.5	12.9
13	PCl_2Ph	131		36.40	36.4
14	$P(OMe)Ph_2$	132	(2.69)	16.3	14.82
15	PEt_3	132	8.69	6.30	6.30
16	$P(CH_2CH_2CN)_3$	132	1.36	22.35	16.79
17	$P(OEt)Ph_2$	133	(2.91)	15.60	14.43
18	PBu_3	136	8.43	5.25	5.25
19	$PMePh_2$	136	4.57	12.10	12.10
20	PEt_2Ph	136	6.25	9.30	9.30
21	$PClPh_2$	138		24.65	24.65
22	$PEtPh_2$	140	4.9	11.30	11.30
23	P(*i*-Bu)$_3$	143	7.97	5.70	5.70
24	P(*p*-$CF_3Ph)_3$	145		20.2	20.2
25	P(*p*-ClPh)$_3$	145	1.03	16.80	16.80
26	P∞*p*-FPh)$_3$	145	1.97	15.70	15.70
27	PPh_3	145	2.73	13.25	13.25
28	P(*p*-MePh)$_3$	145	3.84	11.5	11.5
29	P(*p*-MeOPh)$_3$	145	4.59	10.50	10.50
30	P(*p*-$Me_2NPh)_3$	145	8.65	5.25	5.25
31	P(*i*-Pr)Ph_2	150		10.85	10.85
32	$PBzPh_2$	152		12.30	12.30
33	$PCyPh_2$	153		9.40	9.40
34	P(*t*-Bu)Ph_2	157		8.95	8.95
35	P(*i*-Pr)$_3$	160		3.45	3.45
36	PCy_2Ph	162		5.55	5.55
37	PBz_3	165		10.35	10.35
38	P(*m*-MePh)$_3$	165	3.30		
39	P(*o*-MeOPh)Ph_2	170		10.30	10.30
40	PCy_3	170	9.70	1.40	1.40
41	P(*t*-Bu)$_2$Ph	170		4.95	4.95
42	P(*t*-Bu)$_3$	182	11.40	0.00	0.00

[a] Cone angles are taken from ref 20 or calculated from data given therein. [b] See ref 1 and references therein. [c] χ values are taken from ref 26.

Results and Discussion

New Measure of σ Donicity: χ_d Values. Before describing our studies of Fe–P bond lengths, we take the opportunity to introduce a measure of σ donicity, the χ_d values, which we will use in analyses of the data presented below. As we reported, the pK_a values appear to contain a steric component (from solvation?) that is linearly related to the cone angle of the phosphorus(III) compound[3] (eq 2, based on data for 17 PR_3 ligands). We noted[3] that the

$$pK_a = -[0.68\ (\pm 0.03)]\chi - [0.047\ (\pm 0.010)]\theta + 18.9\ (\pm 1.6) \qquad (2)$$

χ values,[20,26] which reflect no steric influences,[20] for $LNi(CO)_3$ (L = trialkylphosphines, mixed alkylarylphosphines, and triarylphosphines) are better measures of their σ donicity when restricted to this group of ligands. (Standard errors are shown in parentheses). An important conclusion extracted from this relationship is that pK_a values overestimate the σ donicity of the smallest ligands (i.e. $P(OMe)_3$, $PPhH_2$). Unfortunately, χ values cannot generally be used as measures of σ donicity of the ligand since χ may contain a π component as well as a σ component, depending on the nature of the substituents attached to the phosphorus.[3,20,26] Accordingly, we used eq 2 to calculate from known pK_a values[27] and Tolman's cone angles[20] a new set of χ values (χ_d) that would be expected for the π acids where they behave as only σ-donor ligands (vide infra). Table I displays the commonly encountered phosphorus(III) ligands, their cone angles (θ), pK_a values, χ values, and χ_d values. The χ_d values for the trialkylphosphines, mixed alkylarylphosphines, and triarylphosphines are taken directly as their χ values since they are presumed to have no π component (vide supra).

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Table II. Fe-P Bond Lengths for (η-Cp)(PR_3)(CO)FeCOMe

no.	ligand	Fe-P bond length, Å
1	$P(OCH_2)_3CEt$	2.08
6	$P(OMe)_2Ph$	2.122 (1)
8	$PPhMe_2$	2.180 (1)[28b]
11	$P(OPh)_3$	2.110 (1)[29]
16	$P(CH_2CH_2CN)_3$	2.188 (2)
19	PPh_2Me^{a}	2.185 (2)[28b]
22	PPh_2Et^{a}	2.200 (2)[28a]
24	$P(p\text{-}CF_3Ph)_3$	2.184 (2)[28b]
27	PPh_3	2.202 (2)[28a]
27	PPh_3^{a}	2.195 (2)[28a]
30	$P(p\text{-}Me_2NPh)_3$	2.211 (3)[28b]
	$PPh_2(NH(CH(Me)Ph)$	2.188 (2)[30]

^{a} Structure was done on η-$MeC_5H_4(PR_3)(CO)FeCOMe$.

Predicated on structural, NMR, and electrochemical studies (vide infra), it now appears to us that $PPhH_2$ and PPh_2H act only as σ donors toward the $Ni(CO)_3$ fragment. Second, on the basis of the thermodynamic data (vide infra) it appears that PCl_3 also is a pure σ donor toward $Ni(CO)_3$. Accordingly, the χ_d values for these hydrides and chlorides are set equal to their χ values. We believe that the use of χ_d values has significant advantages over the use of pK_a values. First, a large number of χ values have been measured[20,26] precisely for trialkylphosphines, mixed alkylarylphosphines, and triarylphosphines and can be used directly as the χ_d values. Second, the χ values can be determined for extremely weak σ donors for which pK_a values cannot be measured. Third, we claim that the χ_d values are free of steric influences in contrast to the pK_a values of HPR_3^+.

Analysis of the Fe-P Bond Lengths in (η-Cp)(CO)(L)FeCOMe. In an earlier paper we presented electrochemical and spectroscopic evidence that supports the separation of phosphorus(III) ligands into σ donors and π acids.[3] In order to see if the division of ligands is manifest in terms of Fe-P bond lengths, we determined the structures of 10 complexes containing ligands that span a wide range of stereoelectronic properties (see Table II).[28]

We selected complexes that contain sterically unencumbered σ-donor ligands[3] ranging in size from $PPhMe_2$ ($\theta = 122°$) to PAr_3 ($\theta = 145°$), as well as strong ($P(p\text{-}Me_2NPh)_3$, $\chi_d = 5.25$) and weak ($P(p\text{-}CF_3Ph)_3$, $\chi_d = 20.2$) σ donors, in addition to several ligands with intermediate properties. Putative π-acid ligands included $P(OCH_2)_3CEt$, $PPh(OMe)_2$, and $P(CH_2CH_2CN)_3$. The Fe-$P(OPh)_3$ and Fe-$PPh_2(NHCH(Me)Ph)$ bond lengths were obtained from the literature for ((η-Cp)(CO)($P(OPh)_3$)FeCOC(Me) = C(Me)SPh)[29] and ((η-Cp)(CO)($PPh_2(NHCH(Me)Ph)$)FeCOMe),[30] respectively.

The Fe-P bond lengths were plotted against the χ_d values and cone angles (θ) of the phosphorus(III) ligands in Figures 1 and 2, respectively. In Figure 1 it can be seen that the Fe-P bond lengths for those ligands that were previously designated as σ donors span a narrow range between 2.180 and 2.210 Å. There is a slight decrease of the Fe-P bond length as χ_d increases for the isosteric triaryl ligands. This probably arises due to a slight contraction of the covalent radius of the phosphorus as the pendent groups on the phosphorus are made more electronegative. The plot of the Fe-P bond lengths versus θ in Figure 2 shows that there is only a slight increase in length over the range of 23° (vide infra). The π acids ($PPh(OMe)_2$, $P(OCH_2)_3CEt$, $P(OPh)_3$) all have bonds that are significantly shorter than those of the σ donors. Surprisingly, the Fe-$P(CH_2CH_2CN)_3$ bond length of 2.188 Å places it with the σ donors (vide infra). From these data we draw the important conclusion that, in the absence of π bonding and steric encumbrance, length of the M-P bond is essentially constant and independent of the electron donor capacity of the ligand.

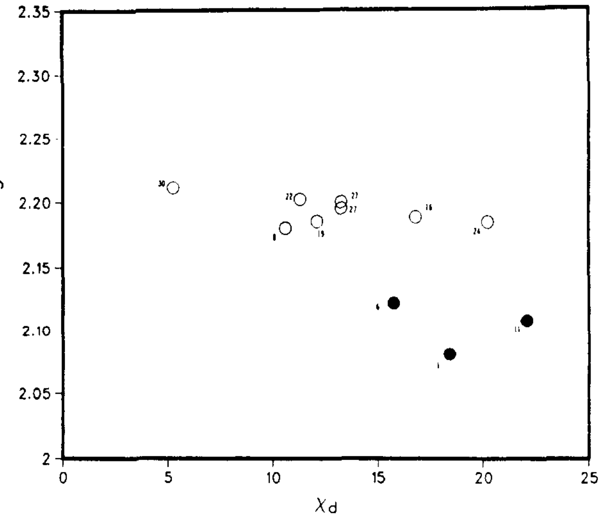

Figure 1. Plot of Fe-P bond lengths for (η-Cp)(CO)(L)FeCOMe versus χ_d. Bond length data are displayed in Table II. Open and filled circles represent ligands designated as σ donors and π acids,[3] respectively. Numbers in this and subsequent figures refer to ligands listed in Table I.

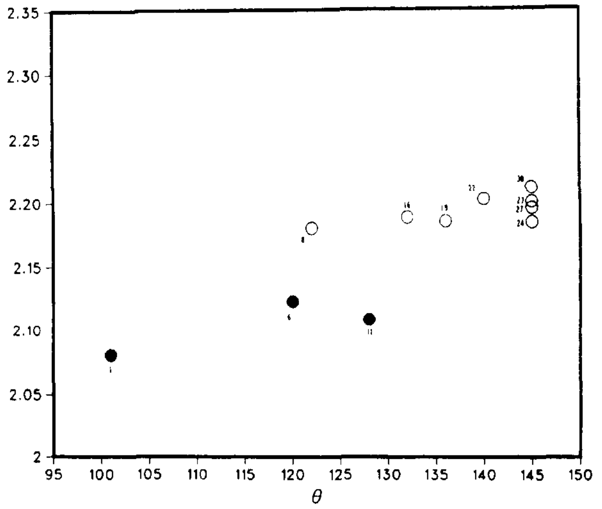

Figure 2. Plot of Fe-P bond lengths (Table II) versus θ. Symbols have the same meaning as in Figure 1.

This small dependence of the Fe-P bond length on θ is contrasted with the large dependence of the M-P bond observed in $ClCo(dmg)_2L$[25] and $L_2Mo(CO)_4$[24] (Figure 3). Each of these complexes has been found to be sterically crowded. For the molybdenum family, our QALE analysis of the heat of reaction data[31] (vide infra) shows a sharp steric threshold at 126°. Accordingly, we have drawn the line through the points for those ligands with θ greater than the steric threshold. On the basis of the NMR data[21] for $(MeOH)Co(dmg)_2L^+$, it appears that the steric threshold for $ClCo(dmg)_2L$ is less than 120°, the cone angle for the smallest ligand, whose Co-P bond length is displayed in

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(28) (a) Liu, H.-Y.; Rahman, M. M.; Koh, L. L.; Eriks, K.; Giering, W. P.; Prock, A. *Acta Crystallogr., Sect. C* **1989**, *C45*, 1683-6. Liu, H.-Y.; Koh, L. L.; Eriks, K.; Giering, W. P.; Prock, A. *Acta Crystallogr., Sect. C* **1990**, *C46*, 51-4. (b) Submitted for publication.

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(31) Mukerjee, S. L.; Nolan, S. P.; Hoff, C. D.; Lopez de la Vega, R. *Inorg. Chem.* **1988**, *27*, 81-5.

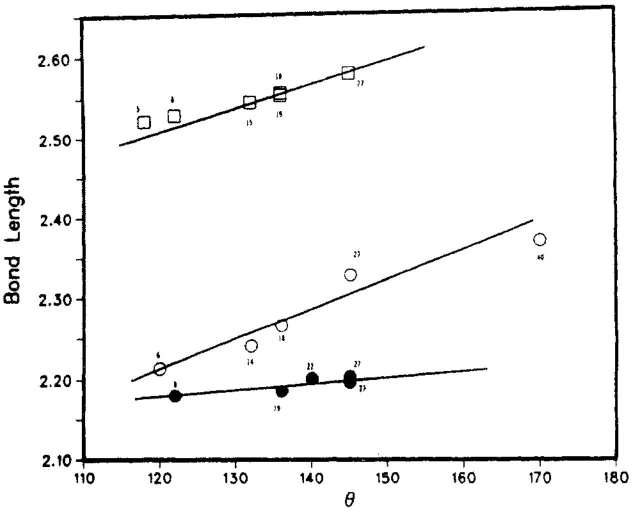

Figure 3. Plot of Fe–P ((η-Cp)(CO)(L)FeCOMe, filled circles), Mo–P ($L_2Mo(CO)_4$, open squares), and Co–P ($Co(Cl)(dmg)_2L$, open circles) bond lengths versus cone angle, θ. Data for the Co–P and Mo–P bond lengths were taken from ref 25 and 24, respectively. The line for the Mo data is drawn through the points for the four largest ligands (θ > 126°) since the thermodynamic data show a steric threshold at 126° (see text).

Figure 3. The slopes of the the data for the Mo and Co complexes relative to the slope for the data of the iron family are 4.3 and 5.4, respectively.

This linear relationship between M–P bond length and θ for sterically congested complexes is consistent with the M–P bonding being entirely of σ character. This follows from the notion that the M–P bond length for a family of complexes can be viewed as a function of three variables, the π acidity, the σ donicity, and the size (θ) of the ligand. We now know that the σ contribution is constant, and we assume that increasing size can only increase the M–P bond length whereas an increasing π contribution causes a contraction of the M–P distance. Since there is a simple linear relationship between bond length and θ, π bonding could be involved only if there were an inverse relationship between π bonding and θ. We know of no fundamental reason why this should be true for the M–P bond lengths of the alkyl- and arylphosphines shown in Figure 3. Thus, it seems likely that all of these ligands are pure σ donors.

Classification of Phosphorus(III) Ligands. Since we have shown that ligands which we have classified as σ-donor ligands have essentially constant Fe–P bond lengths that fall in the region between 2.180 and 2.210 Å, it follows that other ligands with bond lengths in this region are also likely to be σ donors. Thus, predicated on this reasoning we now classify $P(CH_2CH_2CN)_3$ as a σ donor since its Fe–P bond length is 2.188 Å. This is opposite to our assignment based on a correlation of ν_{CO} and $E°$ values for (η-Cp)(CO)(L)FeCOMe, which predicted $P(CH_2CH_2CN)_3$ to be a π acid.[3] This original π classification is primarily a result of the exceptionally high ν_{CO} value of the complex. Other evidence does suggest, however, that this ligand should be considered a σ donor. For example, $P(CH_2CH_2CN)_3$ behaves as a σ donor in a correlation plot of $E°$((η-Cp)(CO)(L)FeCOMe) and χ_d. In addition, its heat of reaction[32] with $MePt(PPhMe_2)(THF)^+$ places it with the other σ donors used in the study. Thus, three pieces of information, in particular in Fe–P bond length, indicate that this ligand is a σ donor. The ν_{CO} datum ((η-Cp)(L)(CO)FeCOMe) for this ligand appears to be misleading. We do not understand the origin of this anomaly. It should be noted that the $(CO)_5Mo$– and $(CO)_5W$–$P(CH_2CH_2CN)_3$ bond lengths are 0.06 Å shorter than the corresponding bond lengths for PPh_3.[33] It seems reasonable that in these group VI complexes $P(CH_2CH_2CN)_3$ is acting as a π acid. The Fe–P bond length of the aminophosphine complex[30] (η-Cp)(CO)(PPh_2(NHCH(Me)Ph)FeCOMe is 2.187 Å, thereby indicating that this ligand is a σ donor. Predicated on thermodynamic[11,31] and kinetic[34] evidence (vide infra) and NMR data to the published later, it appears that PCl_3 and $PPhH_2$ are σ donors toward $Ni(CO)_3$. These observations lead us to speculate that the presence of a P–O (or P–F) bond is required for phosphorus(III) ligands to function as π acids toward $Ni(CO)_3$ and (η-Cp)(CO)FeCOMe.

Comparison of pK_a and χ_d in QALE Analyses. If unemcumbered M–P σ bonds are of nearly the same length, then, for a given family of complexes, it is reasonable that steric effects could turn on over a narrow range of θ. Thus, one might expect to see a fairly sharp threshold in entering-ligand-dependent substitution reactions.

Recently, Poe et al. questioned the sharpness of the steric thresholds for entering-ligand-dependent substitution reactions.[7] Although agreeing that there should be a region of no steric effects for sufficiently small ligands,[5,7] they suggested that there may not be a sharp break in the steric profile but rather a curved region around the threshold. Furthermore, the magnitude of this curvature might be dependent on the flexibility of the transition-state complex; a rigid complex would show a sharper threshold, while a flexible complex would show a large region of curvature before the profile becomes linear again at larger cone angles. The issue of the sharpness of the steric thresholds is important since sharp thresholds will allow a quantitative assessment of the congestion about a metal center in a particular energy state.

One of the problems with assessing the sharpness of steric thresholds is the dearth of data for ligands with θ near the steric threshold. For this reason one must examine many systems and look for the pattern of the steric profile that emerges. In the examples that follow, we present analyses of data sets, each of which have sufficient data near the steric thresholds to show the character of the threshold. We have analyzed each set of data for the entering–ligand-dependent substitution reactions using both pK_a and χ_d values to generate the steric profiles and to compare the results. The results are comparable except that the substitution of χ_d values for pK_a values changes the values of the steric thresholds and the steric sensitivities (d(log k_{st})/dθ). This is not surprising because of the steric dependence of the pK_a values.[3] We believe that the steric parameters extracted from the QALE analysis based on χ_d values more truly reflect the steric properties of the complexes. For example, the steric profiles (Figure 4) for reaction 3[34] are similar, except the steric threshold changes

$$Me_2N_4Fe(CO)_3 + PR_3 \rightarrow Me_2N_4Fe(CO)_2(PR_3) + CO \qquad (3)$$

from 128 to 124° when χ_d values are used. The datum for $PPhH_2$ falls on the steric profile when its χ value is used for its χ_d value. This result is consistent with its classification as a σ donor (vide supra). For reaction 4[18] (Figure

$$Co(NO)(CO)_3 + PR_3 \rightarrow Co(NO)(CO)_2(PR_3) + CO \qquad (4)$$

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(32) Manzer, L. E.; Tolman, C. A. *J. Am. Chem. Soc.* **1975**, *97*, 1955–6.

(33) Cotton, F. A.; Darensbourg, D. J.; Ilsey, W. H. *Inorg. Chem.* **1981**, *20*, 578–83.

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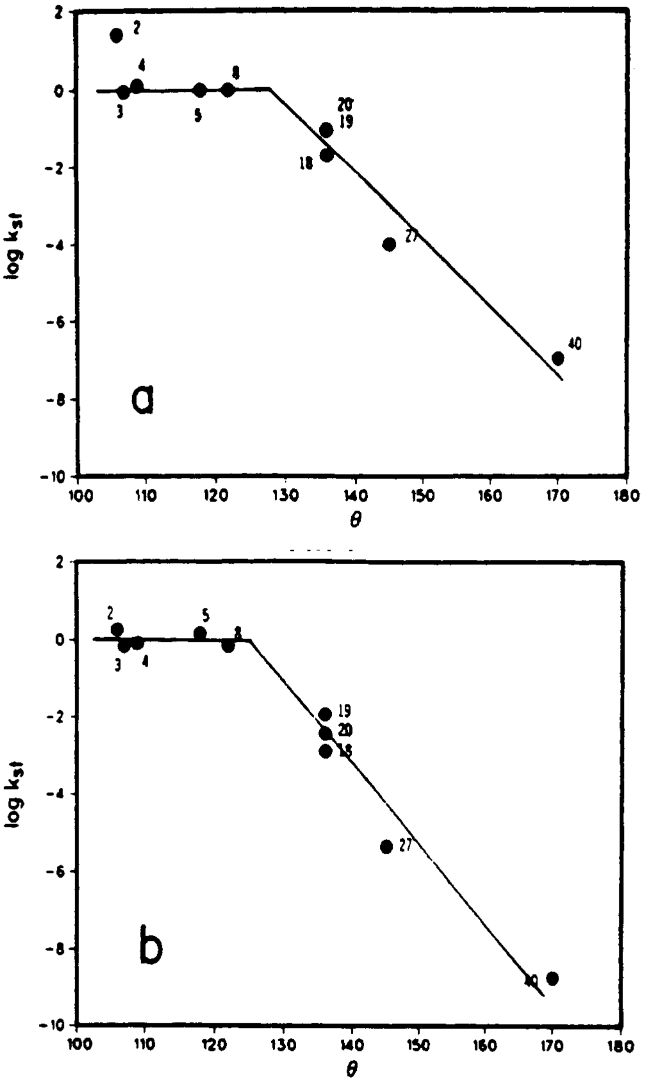

Figure 4. Steric profiles (a) based on pK_a values (R_3PH^+) and (b) based on χ_d values (see text and Table I) for the entering-ligand-dependent substitution reaction between $Me_2N_4Fe(CO)_3$ and phosphorus(III) compounds. Kinetic data used in the QALE analysis were taken from ref 34. log k_{st} is the deviation of the data from an electronic profile for either isosteric ligands or ligands that do not exhibit steric effects.[1-7]

5) the steric profile based on pKa values shows a plateau region of no steric effects. We see that there is a steric threshold since the datum for PCy_3 (θ = 170°) lies well below the plateau. When χ_d values are used in the QALE analysis, the resulting steric profile again shows the plateau region, but here the steric threshold is more clearly defined and is followed by a linearly declining region.

The steric thresholds (Figure 6) based on pK_a and χ_d values also show a good correspondence for the recently reported[10] kinetic data for reaction 5.

$$Fe_2(CO)_7(\mu\text{-}PPh_2) + PR_3 \rightarrow Fe_2(CO)_6(PR_3)(\mu\text{-}PPh_2) + CO \quad (5)$$

The aforementioned examples deal with changes in free energy. Application of QALE to heat of reaction data again shows sharp steric thresholds, suggesting that steric effects may be divided between the enthalpy and entropy components of the free energy. For example, analysis of the recently reported heat of reaction data[31] for reaction 6 produces a steric profile (Figure 7) that exhibits a steric

$$(NBD)Mo(CO)_4 + 2PR_3 \rightarrow L_2Mo(CO)_4 + NBD \quad (6)$$

threshold at 126°. It is unexpected and interesting to note

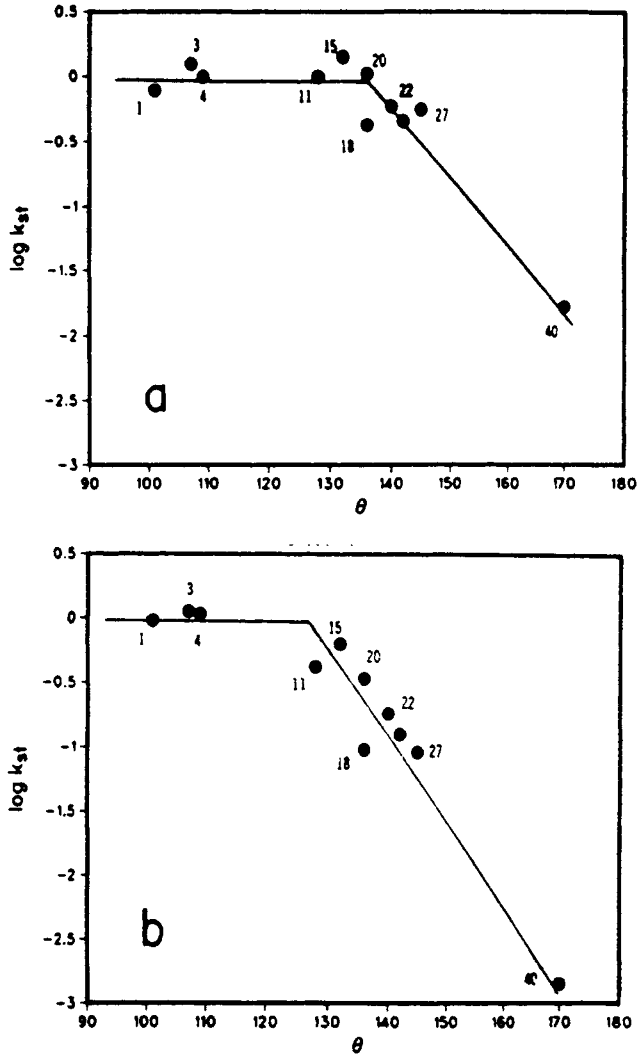

Figure 5. Steric profiles (a) based on pK_a values and (b) based on χ_d values for the entering-ligand-dependent substitution reaction between $Co(NO)(CO)_3$ and phosphorus(III) compounds. Kinetic data used in the QALE analysis were taken from ref 18. Stereoelectronic properties of $P(OEt)_3$ were substituted for those of $P(OBu)_3$. The unlabeled point is PPh_2Bu (χ_d = 11.1, θ = 142°).

that PCl_3 fits this analysis (and that for the heats of formation of $L_3Mo(CO)_3$, vide infra) when its χ value is used as its χ_d value (vide supra). This preliminary result suggests that PCl_3 is acting only as a σ donor toward the $Ni(CO)_3$ fragment.

A final example is the QALE analysis of the heat of reaction data for the addition of acetyl chloride to $IrL_2(CO)Cl$[35] (eq 7). This system differs from those described

$$IrL_2(CO)Cl + CH_3COCl \rightarrow IrL_2(CO)(CH_3CO)(Cl)_2 \quad (7)$$

earlier in that the phosphorus(III) ligands play the role of spectator ligands and do not directly participate in the reaction. Because the phosphorus(III) ligands are present both in the reactant and the product, thresholds exist for both states. The steric profile (Figure 8) shows a plateau region and a sharp steric threshold at 132°, after which it declines linearly to 165°. (The datum for $P(OPh)_3$ does not fit this analysis (vide infra).) The steric threshold at 132° must correspond to the onset of steric destabilization of the more crowded hexacoordinate product. Since another threshold is not observed, the threshold for the

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(35) Yoneda, G.; Lin, S.-M.; Wang, L.-P.; Blake, M. D. *J. Am. Chem. Soc.* **1981**, *103*, 5768–71.

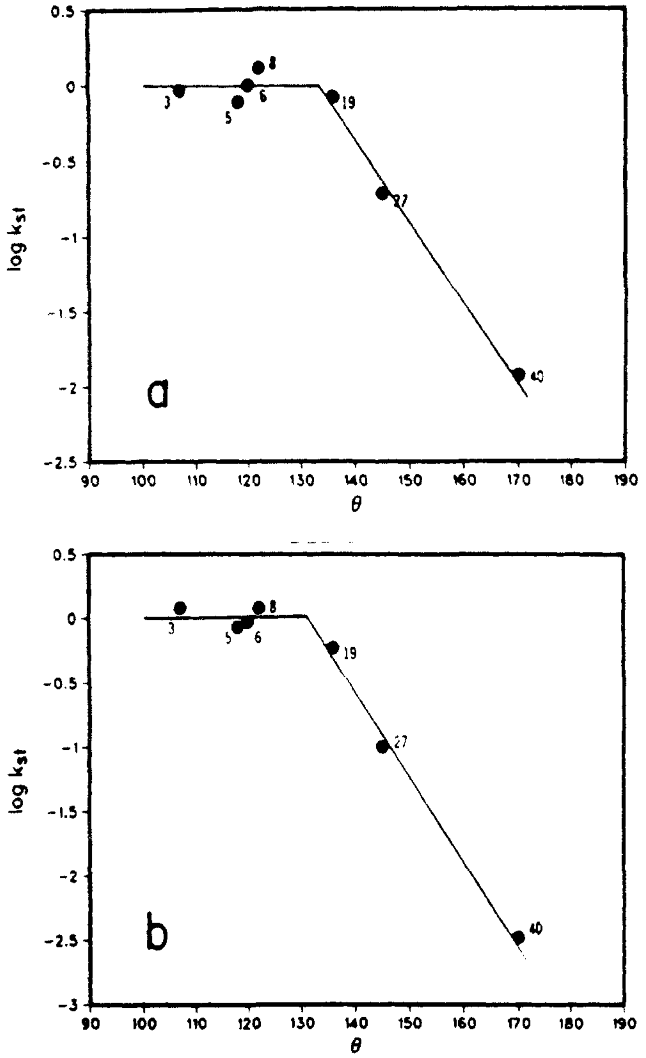

Figure 6. Steric profiles (a) based on pK_a values and (b) based on χ_d values for the entering-ligand-dependent substitution reactions of $Fe_2(CO)_7(\mu\text{-}PPh_2)$. Kinetic data used in the QALE analysis were taken from ref 10.

reactant, $IrL_2(CO)Cl$, must be greater than 165°—the cone angle for the largest (PBz_3) ligand used in the study.

Some Interpretations via QALE. The apparent existence of sharp thresholds allows a quantitative analysis of the data for the aforementioned reactions via linear equations shown in generalized form in eq 8. The coefficients a and b and the constant term c convey fundamental information about the nature of the transition state relative to that of the ground state. The coefficient a of the χ_d term is related to the change in metal–phosphorus bonding. The coefficient b is related to the relative flexibility of the ground and transition states. θ_{st} is the steric threshold for the reaction, and λ is a switching function that turns on the steric effect when the size of the ligand exceeds the steric threshold; i.e., λ equals 0 when θ is less than θ_{st}, and λ equals 1 when θ is greater than θ_{st}. The constant term c contains information about the "intrinsic reactivity" of the system. A meaningful comparison of the c terms for different systems can be made for the special case where the a coefficients are the same. In this case the difference in intrinsic reactivity refers to the amount of bond-breaking and other endoergic processes in the formation of the transition state which are independent

$$\log k = a(\chi_d) + b(\theta - \theta_{st})\lambda + c \qquad (8)$$

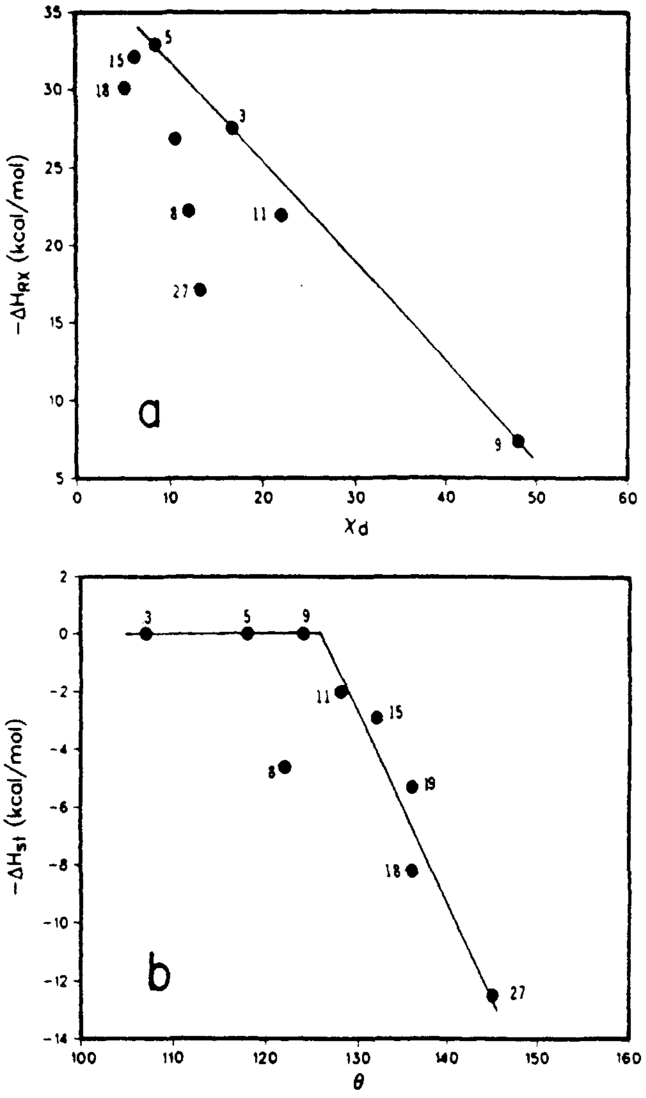

Figure 7. Electronic (a) and steric (b) profiles for the heats of reaction for the formation of $L_2Mo(CO)_4$ from $(NBD)Mo(CO)_4$ (NBD = norbornadiene). Data used in the QALE analysis were taken from ref 31.

of χ_d and θ. Comparison of the following QALE analyses of the kinetics of reactions 5 and 10[36] illustrate the use of

$$Fe_2(CO)_7(\mu\text{-}PPh_2) + PR_3 \rightarrow Fe_2(CO)_6(PR_3)(\mu\text{-}PPh_2) + CO \qquad (5)$$

$$\log k = [-0.102\ (\pm 0.012)]\chi_d - [0.064\ (\pm 0.004)](\theta - 131°)\lambda + 4.01\ (\pm 0.17) \qquad (9)$$

$$FeCo(CO)_7(\mu\text{-}AsMe_2) + PR_3 \rightarrow FeCo(CO)_7(PR_3)(\mu\text{-}AsMe_2) \qquad (10)$$

$$\log k = [-0.107\ (\pm 0.015)]\chi_d - [0.028\ (\pm 0.011)](\theta - 142°)\lambda - 0.85\ (\pm 0.24) \qquad (11)$$

the method. Reaction 5, which involves the odd-electron species $Fe_2(CO)_7(\mu\text{-}PPh_2)$, is orders of magnitude faster than reaction 10 for corresponding ligands. The QALE analyses show that the transition state in the $Fe_2(CO)_7(\mu\text{-}PPh_2)$ reaction is more congested with a steric threshold of 131° as compared to the steric threshold of 142° for the $FeCo(CO)_7(\mu\text{-}AsMe_2)$ transition state. This is probably a

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[36] Jackson, R. A.; Kanluen, R.; Poe, A. *Inorg. Chem.* **1981**, *20*, 1130–3.

[37] Meriwether, L. S.; Fiene, M. L. *J. Am. Chem. Soc.* **1959**, *81*, 4200.

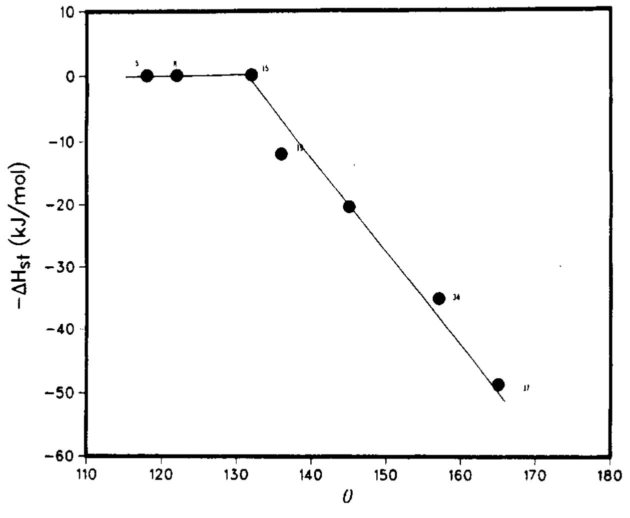

Figure 8. Steric profile for the heats of reaction for the addition of acetyl chloride to $IrL_2(CO)Cl$. The unlabeled point is PPh_2-(*p*-MePh) (χ_d = 11.9, θ = 145°). Data were taken from ref 35.

result of increased crowding attributable to the phenyl groups in $Fe_2(CO)_7(\mu\text{-}PPh_2)$. Because there is only one data point beyond the steric threshold for $FeCo(CO)_7(\mu\text{-}AsMe_2)$, 142° is a lower limit. (For this reason we cannot compare the coefficients of the θ terms.) The coefficients of the χ_d terms reflect the degree of entering ligand–metal bonding in the transition state. Since these coefficients in eqs 9 and 11 are virtually the same, we conclude that the bonding is very similar. Furthermore, because the *a* coefficients are virtually the same, we can compare the *c* terms of eqs 9 and 11. Their difference reflects the large difference in intrinsic reactivity of the two systems. $Fe_2(CO)_7(\mu\text{-}PPh_2)$ is intrinsically more reactive, probably because there is less bond breaking in the transition state of reaction 5 than in that of reaction 10.

With the recent report[31] of the heat of reaction data for reaction 6 we are in a position to make a quantitative comparison of those data with the data for the formation of $(PR_3)_3Mo(CO)_3$ (reaction 13).[11] (The datum for

$$(NBD)Mo(CO)_4 + 2PR_3 \rightarrow L_2Mo(CO)_4 + NBD \quad (6)$$

$$-\Delta H_{RX} = [-0.68\ (\pm 0.03)]\chi_d - [0.68\ (\pm 0.008)](\theta - 126°)\lambda + 124.7\ (\pm 1.1) \quad (12)$$

$PPhMe_2$, which inexplicably does not correlate, was not included in the analysis of reaction 6). $L_2Mo(CO)_4$ is a crowded complex with a steric threshold of 126°, but not as crowded as $L_3Mo(CO)_3$, where the QALE analysis[2] of heats of reaction 13 shows that the steric threshold is less

$$(tol)Mo(CO)_3 + 3PR_3 \rightarrow L_3Mo(CO)_3 + tol \quad (13)$$

$$-\Delta H_{RX} = [-0.57\ (\pm 0.04)]\chi_d - [0.39\ (\pm 0.06)]\theta + 97.9\ (\pm 7.7) \quad (14)$$

than 107°—the cone angle for the smallest ligand used in the study. Interestingly, comparison of the steric sensitivities (coefficient of the θ terms in eqs 12 and 14) of the two complexes indicates that $L_2Mo(CO)_4$ is more rigid than $L_3Mo(CO)_3$ although it is less crowded. Undoubtedly, this has to do with the greater compressibility of the phosphorus(III) ligands as compared to that of CO ligands. It is noteworthy that PCl_3 fits the correlation scheme (for both sets of data) quite well when for its χ_d value we use its χ value directly. This indicates to us that PCl_3 is only a σ-donor ligand toward $Ni(CO)_3$. Designation of PCl_3 as a very weak σ donor accounts for the high lability of the ligand in $(Cl_3P)Ni(CO)_3$.[38] While the phosphite ligands are treated as σ donors in reactions 3–6 and 13, such is not the case for $P(OPh)_3$ in reaction 7. In fact, when $P(OPh)_3$ is treated as a σ-donor ligand in the QALE analysis of reaction 7, the predicted heat of reaction is 51 kJ/mol more negative than the experimental value. The reason for this discrepancy is likely to lie in changes in the mode of M–P bonding in the reactant and product. It seems reasonable that $P(OPh)_3$ is multiply bonded to the iridium in $Ir(P(OPh)_3)_2(CO)Cl$ but that this π acidity is diminished in the congested product. The 51 kJ/mol difference between experimental and calculated heats of reaction is attributed to the difference in the energy between the multiple bond and σ bond for $P(OPh)_3$ ligands in $Ir(P(OPh)_3)_2(CO)Cl$.

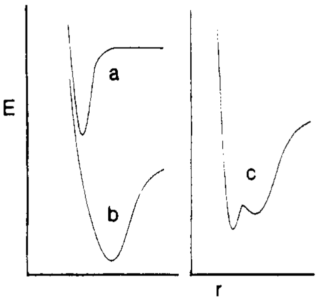

Figure 9. Hypothetical potential energy curves describing the M–P bond. Curves a and b represent the energies for the σ and π bonds, respectively, and are displaced vertically for clarity. Curve c is the sum of curves a and b.

Below we describe a model for the M–P bond that may account for the difference in behavior of phosphine ligands.

Model of the Metal–Phosphorus Bond. It must be emphasized that in the QALE analyses of the kinetic data for entering-ligand-dependent substitution reactions[1,5–7] (including reactions 3–5) as well as the heat of reaction data for reactions 6 and 13 all the phosphorus(III) ligands appear to behave as σ-donor ligands, including ligands that are normally viewed as strong π acids, e.g. $P(OR)_3$. It appears that even the trialkyl phosphites act as pure σ donors under appropriate conditions. We believe that this behavior is determined by the shape of the potential energy curve describing the M–P bond (Figure 9). We propose a model that begins with the well-accepted notion that the M–P bond is described by σ and π components.[14] These components are plotted separately in Figure 9 (curves a and b) and then combined to give the total potential energy curve c for the bond. (The sharpness of the barrier is not important; it results merely from the curve shapes selected for curves a and b, which are displaced vertically for clarity.) Importantly, we make use of the idea that the π component reaches its minimum energy at a shorter internuclear distance than the σ bond. The total potential energy curve exhibits one or two minima, depending on the π acidity of the phosphorus(III) ligand. The σ-bond minimum occurs at a constant, longer internuclear distance. Its depth is probably a measure of the σ donicity of the ligand. An M–P multiple bond forms only when the stabilization provided by the formation of the π bond is

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[38] (a) Stohrer, W.-D.; Hoffmann, R. *J. Am. Chem. Soc.* **1972**, *94*, 1661. (b) Schleyer, P. v. R.; Sax, A. F.; Kalcher, J.; Janoschek, R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 364. (c) Weighardt, K.; Backes-Dahmann, G.; Nuber, B.; Weiss, J. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 777. (d) Chatt, J.; Manojlovic-Muir, L.; Muir, K. W. *J. Chem. Soc. D* **1971**, 655. (e) Manojlovic-Muir, L.; Muir, K. W. *J. Chem. Soc., Dalton Trans.* **1972**, 686. (f) Manojlovic-Muir, L. *J. Chem. Soc. A* **1971**, 2796. (g) Cotton, F. A.; Diebold, N. P.; Roth, W. J. *Inorg. Chem.* **1987**, *26*, 2848. (h) Wieghardt, K.; Backes-Dahmann, G.; Holzbach, W. *Z. Anorg. Allg. Chem.* **1983**, *499*, 44–58. (i) Jean, Y.; Lledos, A.; Burdett, J. K.; Hoffmann, R. *J. Chem. Soc., Chem. Commun.* **1988**, 140–2. (j) Jean, Y.; Lledos, A.; Burdett, J. K.; Hoffmann, R. *J. Am. Chem. Soc.* **1988**, *110*, 4506–16.

sufficient to compensate for the destabilization of the π bond that accompanies the decrease of the internuclear distance. The multiple bond may be destabilized by reduced π acidity of the ligand or by steric interaction between the ligand and the metal fragment, which would be manifest as an additional potential energy curve not shown in Figure 9. If the multiple-bond minimum rises above the σ-bond minimum, then the ligand "jumps" to the outer minimum. In this model, it is possible that a ligand might be sterically destabilized when multiply bonded and not sterically destabilized when it serves as a pure σ donor in the same complex.

With this model in mind, it is understandable why incipient phosphorus(III) ligands behave only as σ donors in the transition states of entering-ligand-dependent substitution reactions. In this case, the M–P bond in the transition state is expected to be quite long and would only possess σ-bond character. L$_2$Mo(CO)$_4$ and L$_3$Mo(CO)$_3$ are families of relatively crowded complexes even for σ-donor ligands. Such steric congestion appears to prevent potential π-acid ligands (P(OMe)$_3$ and P(OPh)$_3$) from approaching close enough to form a Mo–P p bond. Accordingly, these potential π acids reside in the less sterically demanding σ-bond positions.

The idea that the potential energy curve for the M–P bond is described by a double potential energy minimum suggests that these compounds are related to the extremely rare class of compounds called bond stretch isomers. These isomers exist in two isomeric forms that differ only in the length of one or more bonds.[38] If our model of the M–P bond is correct, then bond stretch isomerism will be found to be more widespread in organometallic and inorganic chemistry than is now observed.

Conclusion

From the results described herein, we conclude that in the absence of π-bonding and steric effects the length of the M–P σ bond is virtually constant. These σ-donor ligands include the trialkylphosphines, mixed alkylarylphosphines, and triarylphosphines, P(CH$_2$CH$_2$CN)$_3$, PPh$_x$H$_{3-x}$, and PPh$_x$Cl$_{3-x}$ for (η-Cp)(CO)(L)FeCOMe and LNi(CO)$_3$. The Fe–P bonds are significantly shorter for those ligands possessing P–O bonds. We find that the results of the QALE analyses presented herein and elsewhere[1-7] are compelling evidence for the existence of steric thresholds that are sharp enough to allow the use of a switching function to describe the onset of these effects.

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A Stable Titanacyclo-2-pentene: Synthesis and Structure of 3,3-Bis(η^5-cyclopentadienyl)-4,5-diphenyl-3-titanatetracyclo[5.5.1.0^{2,6}.0^{8,12}]trideca-4,8,11-triene

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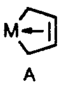
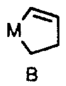
The title compound was synthesized by the reduction of Cp$_2$TiCl$_2$ with Mg in the presence of tricyclo[5.2.1.0^{2,6}]deca-2,5,8-triene and diphenylacetylene. The compound crystallizes in the orthorhombic space group $P2_12_12_1$ with a = 8.447 (2) Å, b = 18.389 (4) Å, c = 19.210 (4) Å, and V = 2984 (1) Å^3. The final agreement for all data was $R(F)$ = 5.73%. ^{1}H and ^{13}C NMR spectral assignments are made with the aid of 2D-COSY and HETCOR NMR studies.

Introduction

A relatively large number of group 4 metallacyclo-3-pentenes have been reported; most of these are zirconocene and hafnocene derivatives,[1-5] although a few titanocene derivatives are known.[5] These complexes are related to metallacycles of conjugated cis dienes, and their general structures are illustrated by structure A. The synthesis and chemistry of these metallacyclo-3-pentenes have been reviewed.[6,7]



A



B

Metallacyclo-2-pentenes arise from cyclization reactions of a reduced metal center with an alkyne and alkene. The general structure of these species is shown by B.

Numerous examples of group 4 metallacyclo-2-pentenes are known, particularly zirconaindans, which are prepared from the stepwise cyclization reactions of (η^2-dehydrobenzene)dicyclopentadienylzirconium with various alkenes. Analogous metallacyclo-2-pentenes from cyclohexyne and

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[†] X-ray structure determination.

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