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Determination of the Stereoelectronic Parameters of PF_3, PCl_3, PH_3, and $P(CH_2CH_2CN)_3$. The Quantitative Analysis of Ligand Effects (QALE)

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Using the QALE model, we determined the electronic parameters for PF_3 ($\chi_d = 44 \pm 4$, $E_{ar} = 0$, $\pi_p = 14 \pm 1$), PCl_3 ($\chi_d = 42 \pm 1$, $E_{ar} = 4.1 \pm 0.3$, $\pi_p = 5.3 \pm 0.5$), PH_3 ($\chi_d = 17 \pm 1$, $E_{ar} = 0$, $\pi_p = 3.7 \pm 0.7$), and $P(CH_2CH_2CN)_3$ ($\chi_d = 17.0 \pm 0.6$, $E_{ar} = 0$, $\pi_p = 1.2 \pm 0.2$). These values indicate that PF_3 and PCl_3 are comparable in σ donor ability and are the poorest σ donor ligands we have studied. Both PH_3 and $P(CH_2CH_2CN)_3$ are reasonably good σ donors, comparable in strength to $P(p\text{-}ClC_6H_4)_3$. PF_3 is by far the best π acid. The π acidity of PCl_3 is comparable to that of $P[(OCH_2)_3]CEt$, whereas the π acidity of PH_3 is intermediate between $P(O\text{-}p\text{-}XC_6H_4)_3$ and $P(OR)_3$. The analysis of data sets containing $PZ_{3-i}H_i$ sometimes requires the inclusion of "i" as a parameter, which we connect with changes in hybridization of these ligands. There are good correlations of χ_d and π_p with the theoretical results of Gonzalez-Blanco and Branchadell and those of Fantucci. The stereoelectronic parameters for 107 PZ_3 species are listed.

Introduction

The evaluation of π acidity and the separation of σ and π effects of phosphorus(III) ligands has perplexed the chemical community for almost 5 decades and today remains controversial even after years of empirical and theoretical study.[1−21] The original Dewar−Chatt[22,23] model describes M−P bonding in terms of σ donation of the nonbonding phosphorus electrons to the metal and back π donation from the metal to phosphorus via a d_π−d_π bond. More recently, empirical[11,12] and theoretical[19,24−27] studies have led to the consensus that the acceptor orbitals on the phosphorus are the σ* orbitals of PZ_3. The relative σ donor and π acceptor abilities of PZ_3 remains hotly debated, however.

Theory has not yet provided a clear picture of M−P bonding or the partitioning of σ and π effects. Pacchioni and Bagus[19] calculated that the π acidity of PZ_3 increases "markedly" along the series $PMe_3 < PH_3 < P(OMe)_3 < PF_3$ with even PMe_3 having a "remarkable" π acidity. Their calculations also showed that PF_3 is a good σ donor, only moderately weaker than PMe_3. Fantucci[28] calculated that PF_3 should be classified as a stronger σ donor and π acid than PH_3, in apparent contrast to an earlier paper,[27] where it was reported that the σ donicity decreased along the series $PMe_3 > PH_3 > PF_3$ while the π acidity followed the opposite trend. Rolke and Brion suggested that methyl groups are electron attracting relative to hydrogen when bonded to phosphorus.[10] Gonzalez-Blanco and Branchadell[29] claim that PF_3 and $P(pyrrolyl)_3$ are strong and comparable π acids, $P(OMe)_3$ and PH_3 are moderate π acids, whereas PR_3 are weak π acids. They also concluded that

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PF_3 is a weaker σ donor than PH_3.[29] Braga[30] suggested that PCl_3 is a poorer π acceptor and a better σ donor than PF_3, whereas Hillier[31,32] and Topol[33] suggested that PCl_3 has a π acidity similar to PF_3. Most recently, Ziegler reported that PCl_3 is calculated to be a stronger π acid than PF_3.[24]

The separation of σ and π effects has been attempted empirically by a number of groups. Graham[34] and Treichel[35] attempted to separate the σ and π bonding properties of phosphorus(III) ligands by analyses of the force constants of ν_{CO} of a series of molybdenum and tungsten complexes. These analyses led to some curious observations: e.g. PBu_3 is a better π acid than PPh_3. Bodner estimated the donor/acceptor ratios of phosphorus(III) ligands by analyses of ^{13}C chemical shifts of CO carbons in $LNi(CO)_3$ but did not attempt to separate the two effects. On the basis of an analysis of the ^{95}Mo chemical shifts of complexes of the type $L_xMo(CO)_{6-x}$ ($x = 1-3$), Alyea[36] proposed that PCl_3 is not a π acid at all. In the early stages of the development of the QALE model (quantitative analysis of ligand effects), we also proposed that PCl_3 is a pure σ donor.[37] The problem with empirical studies is that the total electron donor capacity of PZ_3 is the result of the combination of at least two electronic properties (σ donicity and π acidity) when PZ_3 is bonded to a transition metal.[1,2,11,12,26,34,36,38−47] No method has been found to separate these electronic effects when only the properties of transition-metal complexes are considered.

Over the past 15 years, we and others have developed and used the QALE model for the interpretation of phosphorus(III) ligand effects.[48−70] Recently, we reported that four stereoelectronic parameters (three electronic and one steric) are needed to describe $P(OR)_3$ and $P(O\text{-}p\text{-}XC_6H_4)_3$.[71] The electronic properties are the σ donor capacity (described by the parameter χ_d), the E_{ar} effect, which we find is not restricted to aryl groups, and the π acidity (π_p) of the phosphorus(III) ligand.[71] We determined values for these parameters by analysis of ν_{CO} for $(\eta\text{-Cp})(CO)(L)Fe(COMe)$, $E°$ and $\Delta H°$ for the $(\eta\text{-Cp})(CO)(L)Fe(COMe)^{+/0}$ couple, and two properties that do not depend on M−P π bonding: namely, the pK_a values of HPR_3^+ and the ionization potentials of PZ_3. With values of π_p for $P(OR)_3$ and $P(O\text{-}p\text{-}XC_6H_4)_3$ in hand, we are in a position to determine the stereoelectronic parameters of other putative π acids. Building on the properties of the phosphites, we recently reported the stereoelectronic parameters for $PPh_x(Pyr)_{3-x}$ (Pyr = pyrrolyl) and $P(NC_4H_8)_3$.[72]

We will use the QALE model and the QALE equations (eqs 1 and 2) to determine the unknown stereoelectronic parameters of PF_3, PCl_3, PH_3, and $P(CH_2CH_2CN)_3$. In the QALE model, each physiochemical property is described by its own equation (e.g., eq 1) in terms of the stereoelectronic parameters of the phosphorus(III) ligands.[54,71] In the absence of a steric threshold this

$$\text{prop} = a\chi_d + b(\theta - \theta_{st})\lambda + cE_{ar} + d\pi_p + e \qquad (1)$$

equation reduces to eq 2. The parameters χ_d, θ, E_{ar}, and

$$\text{prop} = a\chi_d + b\theta + cE_{ar} + d\pi_p + e \qquad (2)$$

π_p were defined earlier. θ_{st} is the steric threshold,[37] and λ is the switching function that turns on the steric term after the size of the ligands surpasses the steric threshold.[37] Normally, we are interested in the values of the coefficients of eqs 1 and 2 for a single property, since these coefficients help us to understand how the property is responding to variations in the stereoelectronic properties of PZ_3. The coefficients are determined by regression analysis of a series of QALE equations (eqs 1 or 2), one for each PZ_3. For a single property and a variety of PZ_3, the coefficients remain constant while

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Table 1. Stereoelectronic Parameters of Phosphorus(III) Compounds (PZ_3) and the A_1 ν_{CO} Values for $(Z_3P)Cr(CO)_5$[a]

no.	PZ_3	χ_d[b]	θ[c]	E_{ar}[d]	π_p[e]	ν_{CO}[f]
1	**PH_3**	**17**	**87**	**0**	**3.7**	
2	**$PMeH_2$**	**14.2**	**97**	**0**	**2.5**	
3	$P[(OCH_2)_3]CEt$	20.2	101	0.2	5	
4	**P(octyl)H_2**	**13**	**103**	**0**	**2.5**	
5	**$PBuH_2$**	**13.1**	**103**	**0**	**2.5**	
6	**PF_3**	**44**	**104**	**0**	**14**	
7	**P(i-Bu)H_2**	**13.2**	**106**	**0**	**2.5**	
8	**$PPhH_2$**	**15.8**	**106**	**1**	**2.5**	
9	$P(OMe)_3$	17.9	107	1	2.8	
10	**PMe_2H**	**11.4**	**108**	**0**	**1.2**	
11	$P(OEt)_3$	15.8	109	1.1	2.9	
12	**$PMeF_2$**	**32.2**	**109**	**0**	**9.3**	
13	$P(OBu)_3$	15.9	110	1.3	2.7	
14	$P(OPr)_3$	15.9	110	1.3	2.7	
15	$P(OCH_2CH_2Cl)_3$	20.3	110	0.4	3.6	
16	$PMe(OEt)_2$	13.4	112	0.7	1.9	
17	**PMe_2F**	**20.4**	**113**	**0**	**4.7**	
18	$PMe_2(OEt)$	11	115	0.4	1	
19	**$PCyH_2$**	**11.8**	**115**	**0**	**2.5**	
20	**$P(CH_2CH_2CN)_2H$**	**17**	**117**	**0**	**2**	
21	PMe_3	8.55	118	0	0	2062.0
22	**P(t-Bu)H_2**	**11.3**	**119**	**0**	**2.5**	
23	**P(Octyl)$_2$H**	**9**	**120**	**0**	**1.2**	
24	**PBu_2H**	**9.2**	**120**	**0**	**1.2**	
25	P(O-i-Bu)$_3$	15.5	120	1.4	3	
26	$P(OMe)_2Ph$	16.4	120	1.7	1.9	
27	**PMe_2Cl**	**19.7**	**120**	**1.4**	**1.8**	
28	$P(OEt)_2Ph$	15	121	1.7	1.9	
29	$PPhMe_2$	10.5	122	1	0	2063.2
30	**$PMeCl_2$**	**30.9**	**122**	**2.7**	**3.5**	
31	PMe_2Et	7.8	123	0	0	
32	**$PMe_2(CH_2CH_2CN)$**	**11.4**	**123**	**0**	**0.4**	
33	**P(i-Bu)$_2$H**	**9.5**	**124**	**0**	**1.2**	
34	**PCl_3**	**42**	**124**	**4.1**	**5.3**	
35	**PPh_2H**	**14.5**	**126**	**2**	**1.2**	
36	$PMeEt_2$	7.1	127	0	0	
37	**$PPrCl_2$**	**29.8**	**127**	**2.7**	**3.5**	
38	**$PMe(CH_2CH_2CN)_2$**	**14.2**	**128**	**0**	**0.8**	
39	P(O-*p*-$MeC_6H_4)_3$	22.4	128	1.4	4.1	
40	P(O-*p*-$MeOC_6H_4)_3$	22.5	128	1.4	3.8	
41	$P(OC_6H_5)_3$	23.6	128	1.3	4.1	
42	P(O-*p*-$ClC_6H_4)_3$	27.2	128	1.3	4	
43	**$PBuCl_2$**	**29.8**	**128**	**2.7**	**3.5**	
44	P(O-*p*-$NCC_6H_4)_3$	31.7	128	1	3.7	
45	P(O-i-Pr)$_3$	13.4	130	1.3	2.9	
46	**P(t-Bu)F_2**	**29.3**	**130**	**0**	**9.3**	
47	**P(O-*p*-$MeOC_6H_4)Cl_2$**	**31.5**	**131**	**3.1**	**3.5**	
48	**$PPhCl_2$**	**32.4**	**131**	**3.7**	**3.5**	
49	PEt_3	6.3	132	0	0	2060.2
50	P(i-Pr)Me_2	6.85	132	0	0	
51	**$PEt_2(CH_2CH_2CN)$**	**9.9**	**132**	**0**	**0.4**	
52	**$PEt(CH_2CH_2CN)_2$**	**13.4**	**132**	**0**	**0.8**	
53	$P(OMe)Ph_2$	14.8	132	2.3	0.9	
54	**$P(CH_2CH_2CN)_3$**	**17**	**132**	**0**	**1.2**	
55	**P(octyl)$(CH_2CH_2CN)_2$**	**13**	**133**	**0**	**0.8**	
56	$P(OEt)Ph_2$	14.1	133	2.4	1	
57	PPr_3	5.4	134	0	0	
58	**$PBu(CH_2CH_2CN)_2$**	**13.1**	**134**	**0**	**0.8**	
59	$PPh(OC_6H_5)_2$	20.2	134	1.9	2.7	
60	PMe(i-Bu)$_2$	6.7	135	0	0	
61	**P(octyl)$_2(CH_2CH_2CN)$**	**9**	**135**	**0**	**0.4**	
62	**$PBu_2(CH_2CH_2CN)$**	**9.2**	**135**	**0**	**0.4**	
63	P(Pent)$_3$	5	136	0	0	
64	P(octyl)$_3$	5	136	0	0	
65	PBu_3	5.25	136	0	0	2059.0
66	$PPhEt_2$	8.6	136	1.1	0	
67	PPh_2Me	12.6	136	2.2	0	2065.0
68	**$PPh(CH_2CH_2CN)_2$**	**15.8**	**136**	**1**	**0.8**	
69	**PPh_2Cl**	**22.8**	**138**	**3.4**	**1.8**	
70	P(t-Bu)Me_2	5.7	139	0	0	
71	$PPhBu_2$	8.1	139	1.3	0	
72	$PPh_2(OC_6H_4)$	16.7	139	2.4	1.4	
73	PPh_2Et	11.1	140	2.3	0	2063.0
74	**$PPh_2(CH_2CH_2CN)$**	**14.5**	**140**	**2**	**0.4**	
75	PPh_2Bu	11.3	142	2.1	0	
76	P(i-Bu)$_3$	5.7	143	0	0	2059.0
77	**P(t-Bu)Cl_2**	**28**	**143**	**2.7**	**3.5**	
78	**PCy_2H**	**6.6**	**144**	**0**	**1.2**	
79	P(*p*-$Me_2NC_6H_4)_3$	5.25	145	2.7	0	
80	P(*p*-$MeOC_6H_4)_3$	10.5	145	2.7	0	2061.0
81	$P(C_6H_5)_2$(*p*-$Me_2NC_6H_4)$	10.6	145	2.7	0	
82	P(*p*-$MeC_6H_4)_3$	11.5	145	2.7	0	2062.0
83	**$PCy(CH_2CH_2CN)_2$**	**11.8**	**145**	**0**	**0.8**	
84	$P(C_6H_5)_2$(*p*-$MeC_6H_4)$	12.1	145	2.7	0	
85	$P(C_6H_5)_2$(*p*-$MeOC_6H_4)$	12.3	145	2.7	0	
86	$P(C_6H_5)_3$	13.25	145	2.7	0	2063.0
87	$P(C_6H_5)_2$(*p*-$ClC_6H_4)$	14.4	145	2.7	0	
88	P(*p*-$FC_6H_4)_3$	15.7	145	2.7	0	
89	P(*p*-$ClC_6H_4)_3$	16.8	145	2.7	0	2065.0
90	PPh_2(Pyr)	19.5	145	3.1	0.6	
91	P(*p*-$F_3CC_6H_4)_3$	20.5	145	2.7	0	2067.3
92	PPh(Pyr)$_2$	25.7	145	3.2	1.3	
93	P(Pyr)$_3$	31.9	145	3.3	1.9	
94	$P(NC_4H_8)_3$	−1.2	146	−0.6	0.9	
95	P(*m*-$MeC_6H_4)_3$	11.3	148	2.7	0	
96	P(*m*-$ClC_6H_4)_3$	19.6	148	2.7	0	
97	**P(t-Bu)$_2$H**	**5.7**	**150**	**0**	**1.2**	
98	P(i-Pr)Ph_2	9.6	150	1.7	0	
99	PPh_2Cy	9.1	153	1.6	0	2060.0
100	**P(t-Bu)$_2$F**	**14.7**	**156**	**0**	**4.7**	
101	**$P(CH_2CH_2CN)Cy2$**	**6.6**	**157**	**0**	**0.4**	
102	P(i-Pr$_3$)	3.45	160	0	0	2058.0
103	$PPhCy_2$	5.7	162	1.6	0	2059.0
104	**P(t-Bu)$_2$Cl**	**14**	**163**	**1.4**	**1.8**	
105	PCy_3	1.4	170	0	0	2056.1
106	P(*o*-$MeC_6H_4)_3$	11.1	178	2.7	0	
107	P(t-Bu)$_3$	0	182	0	0	

[a] The values in Roman type are taken from the literature, whereas the values in boldface are reported here for the first time. The parameters for most mixed ligands (with the exception of PPh_iR_{3-i}) were determined by additivity. [b] χ_d values for the phosphines and phosphites are taken from refs 71−74 or calculated by additivity using the data found in these references. [c] Values for cone angles (θ) are taken from refs 72 and 75 or calculated by additivity using the data found in these references. [d] E_{ar} values are taken from refs 71, 72, and 74. [e] π_p values are taken from refs 71 and 72. [f] Data (cm^{-1}) were measured in dilute cyclohexane solution. Error is estimated to ±0.5 cm^{-1}.

the known values of the stereoelectronic parameters vary as PZ_3 varies. We can turn this approach around and consider a *single* PZ_3 with unknown stereoelectronic parameters and a variety of properties for which we know the coefficients of the QALE equations. Now the stereoelectronic parameters remain constant while the coefficients vary. Using regression analysis we can then obtain values of the parameters of the single PZ_3.

Using this approach, we determined values for the three electronic parameters (χ_d, E_{ar}, and π_p) for PCl_3, $P(CH_2CH_2CN)_3$, PF_3, and PH_3. We present the analysis of PCl_3 in detail. The analyses of $P(CH_2CH_2CN)_3$ and PF_3 are analogous. The analysis of PH_3 is more complex and is discussed separately.

Determination of the Stereoelectronic Parameters of PCl_3

To determine the stereoelectronic parameters of PCl_3, we need a series of QALE equations (with known coefficients) for a variety of properties. To obtain these equations, we use data sets that include the π acidic

Table 2. Systems, Properties, and Ligands Used and Excluded in the QALE Analyses Used to Determine the Coefficients *a*−*e* of Eqs 1 and 2

no.	syst	property	ligands[a]	ligands excluded	refs
1	PZ_3	ionizn potentials	3, 9, 11, 21, 29, 49, 65, 67, 79, 80, 82, 86, 88, 89, 91, 95, 102, 107		76−83
2	$HPZ_3^+ = H^+ + PZ_3$	pK_a	3, 9, 11, 21, 26, 28, 29, 36, 41, 45, 49, 53, 56, 57, 63, 65, 66, 67, 73, 76, 79, 80, 82, 88, 89, 91, 95, 105, 106, 107		84−87
3	$(\eta\text{-Cp})Fe(CO)(PZ_3)COMe^+ + e = (\eta\text{-Cp})Fe(CO)(PZ_3)COMe^0$	E^0	2, 3, 9, 11, 21, 29, 41, 45, 49, 60, 66, 67, 65, 73, 76, 79, 80, 82, 86, 88, 89, 91, 99, 102, 103, 105		88
4	$(\eta\text{-Cp}')Fe(CO)(PZ_3)COMe^+ + e = (\eta\text{-Cp}')Fe(CO)(PZ_3)COMe^0$	E^0	3, 9, 11, 29, 41, 45, 49, 60, 66, 67, 65, 73, 76, 79, 80, 82, 86, 88, 89, 91, 99, 102, 103, 105	65	88
5	$(norbornadiene)Mo(CO)_4 + 2PZ_3 = (Z_3P)_2Mo(CO)_4 + norbornadiene$	$-\Delta H_{rx}$	9, 21, 29, 41, 49, 65, 67, 86		89, 90
6	$Ru(CO)_3(PZ_3)(SiCl_3)_2 = Ru(CO)_2(PZ_3)(SiCl_3)_2 + CO$	log *k*	3, 9, 13, 26, 29, 41, 42, 65, 67, 80, 82, 86, 88, 89, 95, 96, 98	53	91
7	$PhN_3 + PZ_3 = N_2 + Z_3P{=}N$	log *k*	9, 41, 65, 64, 80−82, 89, 84−87, 89		92
8	$(Z_3P)Ru(CO)_4 = (Z_3P)Ru(CO)_3 + CO$	log *k*	3, 11, 21, 41, 49, 65, 66, 73, 80, 82, 86, 89, 105, 107		93
9	$(C_6H_7)Mn(CO)_3^+ + PZ_3 = [C_6H_7(PZ_3)]Mn(CO)_3^+$	log *k*	9, 11, 13, 41, 65, 66, 80, 82, 84, 86, 88, 89, 105, 106		94
10	$CpFe(CO)(PZ_3)COMe$	ν_{CO}	3, 9, 11, 13, 15, 21, 25, 39−42, 44, 49, 65, 80, 82, 86, 88, 89, 91, 102, 105		71, 74, 88, 95
11	$(\eta\text{-Cp}')Fe(CO)(PZ_3)COMe$	ν_{CO}	3, 9, 11, 15, 41, 49, 65, 76, 80, 82, 86, 88, 89, 91, 102, 105		71, 74, 88, 95
12	$(Z_3P)Ni(CO)_3$	ν_{CO}	3, 9, 11, 13, 21, 41, 42, 44, 45, 49, 65, 76, 79, 80, 82, 86, 88, 89, 91, 102, 105, 107		75
13	$(\eta\text{-Cp})Mn(CO)_2(L)$	ν_{CO}	9, 11, 13, 15, 21, 39, 41, 49, 65, 82, 86, 102, 105		96
14	$LMo(CO)_5$	ν_{CO}	3, 9, 11, 21, 41, 49, 65, 86, 95, 105, 107		2, 45
15	$L_2Mo(CO)_4$	ν_{CO}	3, 9, 11, 15, 21, 41, 45, 49, 65, 86, 95	82	45, 82
16	$L_3Mo(CO)_3$	ν_{CO}	3, 9, 11, 15, 21, 41, 45, 49, 65, 86		2, 45
17	$(\eta\text{-Cp})V(CO)_3(PZ_3)$	ν_{CO}	9, 11, 13, 15, 21, 39, 41, 49, 65, 82, 86, 102, 105		96
18	$(Z_3P)Cr(CO)_2(C_6H_3Me_3)$	ν_{CO}	9, 11, 13, 21, 39, 41, 49, 65, 86, 105	15	96
19	$(Z_3P)Cr(CO)_2[C_6H_4(CO_2Me)_2]$	ν_{CO}	9, 11, 13, 21, 39, 41, 49, 65, 86, 102, 105	15	96
20	$(Z_3P)Cr(CO)_5$	ν_{CO}	9, 11, 13, 21, 39, 41, 49, 65, 80, 82, 86, 89, 91, 102, 105	15	96
21	$(Z_3P)Ru(CO)_4$	ν_{CO}	3, 11, 21, 41, 49, 65, 80, 82, 86, 89, 105, 107		93
22	$(PZ_3)Ni(CO)_3$	^{13}C (CO) chem shift	3, 9, 11, 13, 15, 21, 29, 41, 42, 45, 49, 53, 65−67, 71−73, 75, 76, 79, 80, 82, 86, 88, 89, 102, 105, 107		97
23	$(Z_3P)Cr(CO)_5$	^{13}C (cis CO) chem shift	3, 9, 11, 15, 21, 29, 41, 42, 45, 49, 65−67, 73, 76, 86, 99	103, 105	97
24	$(Z_3P)Cr(CO)_5$	^{13}C (trans CO) chem shift	3, 9, 11, 15, 29, 41, 42, 45, 49, 65−67, 73, 76, 86, 99, 103, 105		97
25	$(Z_3P)Mo(CO)_5$	^{13}C (cis CO) chem shift	3, 9, 11, 15, 29, 41, 49, 67, 66, 65, 73, 86, 105, 107		97
26	$MeCo[dgm]_2(PZ_3)$	$J_{H/C}$	9, 21, 29, 41, 45, 49, 65, 66, 73, 79, 80, 82, 86, 88, 89, 98, 102, 105		98

[a] Numbers listed refer to the entry numbers in Table 1.

$P(OR)_3$, and $P(O\text{-}p\text{-}XC_6H_4)_3$, as well as a variety of PR_3, $P(p\text{-}XC_6H_4)_3$, and PPh_iR_{3-i}, for all of which we know values of the four stereoelectronic parameters (χ, θ, E_{ar}, π_d; listed in Table 1):[71] these data sets must also include $PZ_{3-i}Cl_i$ as well. The coefficients *a*−*e* were then obtained from analysis of the subsets of data that exclude $PZ_{3-i}Cl_i$. The properties we consider are listed in Table 2.

We start by determining the regression coefficients (*a*−*e*) for the QALE equations, which will be eventually used to determine the stereoelectronic parameters for PCl_3. We describe this in detail for the particular property of ν_{CO} for $(Z_3P)Mo(CO)_5$ (entry 14 in Table 2). As with all our analyses, we start by graphically examining the data to test their appropriateness for inclusion in the QALE analysis.[57] In general, appropriate data will show a linear dependence on χ_d for $P(p\text{-}XC_6H_4)_3$ as well as for PR_3 (in the absence of a steric threshold) and a linear dependence on *i* for PZ_iY_{3-i}. (When ν_{CO} is plotted versus *i*, the mixed PPh_iR_{3-i} tend to give nonlinear plots. Accordingly, we routinely exclude these *mixed* ligands from the QALE analysis of ν_{CO}. Interestingly, PZ_iCl_{3-i} species give linear results and so later on are included in the analyses of ν_{CO}.) Other outliers that do not fit these general categories of ligands can be detected statistically. In all the analyses presented herein, we found that less than 2% (9 data) of the more than 550 data are outliers.

We have values for the parameters (see Table 1) of 11 ligands in $(Z_3P)Mo(CO)_5$ data set (entry 14, Table 2). Graphical analysis reveals no obvious outliers. We first did the regression analysis on these 11 data using all four of the QALE parameters (Table 1), and the results are summarized below ($s = 1.286$, $r^2 = 98.2\%$, $r^2(\text{adj}) = 96.9\%$):

predictor	coeff	stdev	*t* ratio	*p*
constant	2073.11	5.64	367.69	0.000
χ_d	0.4884	0.2522	1.94	0.101
θ	−0.04867	0.03255	−1.50	0.185
E_{ar}	0.2019	0.8675	0.23	0.824
π_p	1.3840	0.6808	2.03	0.088

On the basis of the low *t* ratio and high *p* value we now

Table 3. Results of Regression Analyses (via Eq 1 or 2) of the Physicochemical Properties Listed in Table 2[a]

no.	a	b	c	d	e	steric threshold	n	r^2	s
1	0.116 ± 0.005	0	−0.49 ± 0.02	0	7.63 ± 0.05		18	0.978	0.1082
2	−0.60 ± 0.02	−0.039 ± 0.007	−0.3 ± 0.1	0	17 ± 1		31	0.981	0.4864
3	0.0158 ± 0.0007	0	0	0.023 ± 0.002	0.112 ± 0.007		25	0.987	0.01381
4	0.0172 ± 0.0005	0.0007 ± 0.0002	0	0.025 ± 0.002	−0.03 ± 0.03		23	0.993	0.01028
5	0	−0.12 ± 0.04	−4.4 ± 0.5	−0.9 ± 0.3	47 ± 5		8	0.979	1.066
6	0	0.063 ± 0.006	0	−0.15 ± 0.04	−4.9 ± 0.1		17	0.968	0.1908
7	−0.18 ± 0.01	−0.039 ± 0.004	0.42 ± 0.005	−0.36 ± 0.06	5.46 ± 0.05		12	0.997	0.0755
8	0	0.133 ± 0.006	0.20 ± 0.03	−0.07 ± 0.02	−3.69 ± 0.06	160	14	0.984	0.1174
9	−0.26 ± 0.03	−0.119 ± 0.005	0.6 ± 0.1	−0.9 ± 0.1	9.2 ± 0.2	128	14	0.989	0.1982
10	1.05 ± 0.01	0.037 ± 0.003	−0.89 ± 0.06	4.28 ± 0.05	1905.1 ± 0.6		22	1.000	0.1848
11	0.87 ± 0.04	0.06 ± 0.02	0	5.1 ± 0.2	1989 ± 0.3		16	0.997	0.7584
12	0.96 ± 0.02	0	0	2.0 ± 0.1	0.4 ± 0.3		22	0.997	0.5866
13	1.4 ± 0.2	0.14 ± 0.04	0	2.5 ± 0.7	1902 ± 6		13	0.984	1.902
14	0.6 ± 0.2	0	0	1.3 ± 0.4	2065.2 ± 0.9		11	0.971	1.39
15	1.3 ± 0.1	0	0	2.2 ± 0.5	2006 ± 1		11	0.998	1.315
16	2.4 ± 0.4	0	0	5 ± 1	1911 ± 4		10	0.983	3.73
17	0.95 ± 0.09	0	0	1.9 ± 0.3	1944.4 ± 0.7		12	0.993	0.9439
18	2.3 ± .1	0.16 ± 0.03	−3.3 ± 0.7	0	1841 ± 5		10	0.994	1.33
19	1.1 ± 0.1	0	0	1.0 ± 0.4	1914.9 ± 0.7		11	0.993	0.9432
20	0.51 ± 0.02	−0.045 ± 0.008	0	1.7 ± 0.1	2063 ± 1		15	0.997	0.3994
21	1.1 ± 0.1	0.06 ± 0.02	−2.4 ± 0.4	0.9 ± 0.3	2045 ± 3		12	0.994	0.6332
22	−0.175 ± 0.009	0	0	−0.10 ± 0.03	6.59 ± 0.09		29	0.982	0.1798
23	−0.16 ± 0.01	0	0.13 ± 0.05	−0.12 ± 0.04	6.9 ± 0.1		17	0.992	0.1202
24	−0.22 ± 0.01	0.013 ± .005	0.71 ± 0.08	0	12.9 ± 0.7		18	0.975	0.2489
25	−0.158 ± 0.009	0	0	0	6.5 ± 0.1		14	0.96	0.2416
26	0.16 ± 0.01	0.067 ± 0.004	0	−0.25 ± 0.05	135.9 ± 0.2	122	18	0.958	0.2038

[a] The letters a−e are the regression coefficients of these equations. Entry numbers correspond to the entry numbers in Table 2.

eliminate E_{ar} as a variable.[99] The results are ($s = 1.196$, $r^2 = 98.1\%$, $r^2(\text{adj}) = 97.3\%$):

predictor	coeff	stdev	t ratio	p
constant	2072.17	3.67	564.51	0.000
χ_d	0.5410	0.1041	5.19	0.000
θ	−0.04356	0.02236	−1.95	0.092
π_p	1.2549	0.3672	3.42	0.011

On the basis again of the low t ratio and high p value, we removed θ as a variable. The final results are ($s = 1.390$, $R^2 = 97.1\%$, $R^2(\text{adj}) = 96.4\%$):

predictor	coeff	stdev	t ratio	p
constant	2065.18	0.89	2320.50	0.000
χ_d	0.6338	0.1075	5.89	0.000
π_p	1.3332	0.4240	3.14	0.014

(We note that the same results are obtained by eliminating θ first and then E_{ar}.) The results of this last analysis are included in entry 14 in Table 3. Each data set for the properties listed in Table 2 was treated by the analogous protocol. The results of these analyses are shown in Table 3.

We continue with the analysis of ν_{CO} for $(Z_3P)Mo(CO)_5$. In general, we take equations such as (1) or (2) for each property, and by dividing each equation by its standard deviation (σ), we weight them and make them dimensionless. We then simplify the resulting equations by setting them equal to zero (eq 3). For PCl_3, eq 3

$$0 = (a/\sigma)\chi_d + (b/\sigma)\theta + (c/\sigma)E_{ar} + (d/\sigma)\pi_p + (e/\sigma - \text{prop}/\sigma) = a'\chi_d + b'\theta + c'E_{ar} + d'\pi_p + e' \quad (3)$$

becomes eq 4 (based on the data presented in entry 14 of Table 3). Equation 4 (as well as eqs 5 and 6) is written

$$0 = (0.6x + (0)124 + (0)y + 1.3z + 2065.2 - 2095)/1.39 \quad (4)$$

in terms of x, y, and z, which stand for the values of the respective parameters χ_d, E_{ar}, and π_p for PCl_3, which we are seeking. Initially, we use Tolman's cone angle[75] for PCl_3 ($\theta = 124°$). For purposes of illustration, we show

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Table 4. Ligands and Their Stereoelectronic Parameters[a]

no.	PZ_3	χ_d	θ, deg	E_{ar}	π_p	comments	n	r^2	σ
1A	**PCl_3**	**42 ± 1**	**124**	**4.1 ± 0.3**	**5.3 ± 0.5**		**48**	**0.995**	**2.573**
1B	PCl_3	42 ± 1	124	3.9 ± 0.4	5.3 ± 0.5	no IP	41	0.995	2.694
1C	PCl_3	42.0 ± 0.9	137 ± 5	4.3 ± 0.3	5.1 ± 0.5		48	0.997	2.394
1D	PCl_3	42 ± 1	137 ± 5	4.3 ± 0.3	5.2 ± 0.5	no IP	41	0.997	2.498
2A	**PF_3**	**44 ± 4**	**104**	**0**	**14 ± 1**		**12**	**0.971**	**3.075**
3A	**$P(CH_2CH_2CN)_3$**	**17.0 ± 0.6**	**132**	**0**	**1.2 ± 0.2**		**23**	**0.996**	**2.099**
3B	$P(CH_2CH_2CN)_3$	17 ± 1	132	0	1.3 ± 0.3	no pK_a	15	0.995	2.645
3C	$P(CH_2CH_2CN)_3$	17.2 ± 0.7	129 ± 3	0	1.2 ± 0.2		23	0.997	2.095
3D	$P(CH_2CH_2CN)_3$	17 ± 1	128 ± 4	0	1.3 ± 0.3	no pK_a	15	0.996	2.660
4A	PH_3	30 ± 1	87	3.0 ± 0.4	−4.1 ± 0.9		33	0.985	2.271
4B	PH_3	19.0 ± 0.7	87	0	2.1 ± 0.5	no pK_a	24	0.990	1.687
4C	**PH_3**	**17. ± 1**	**87**	**0**	**3.7 ± 0.7**	**no pK_a or IP**	**17**	**0.997**	**1.006**
4D	PH_3	19 ± 1	222 ± 36	0	2 ± 1		33	0.978	3.015
4E	PH_3	19.6 ± 0.8	50 ± 29	0	1.8 ± 0.6	no pK_a	24	0.991	1.661
4F	PH_3	17 ± 1	80 ± 20	0	3.5 ± 0.9	no pK_a or IP	17	0.997	1.040

[a] The values of the parameters given in boldface are the ones we suggest that best describe the stereoelectronic properties of the ligands.

Table 5. Data Sets for Systems and Properties Containing $PZ_{3-i}H_i$

no.	syst	property	ligands	$PZ_{3-i}H_i$	ligands excluded	refs
1	HPR_3^+	pK_a	*a*	1, 4, 5, 7, 10, 24, 23, 33, 35, 78		*b*
2	$PZ_3 + (\eta\text{-indenyl})Rh(CO)_2 = (\eta\text{-indenyl})Rh(CO)(PZ_3) + CO$	log *k*	11, 65, 67, 80, 86, 99, 103, 105	35		111
3	$PZ_3 + EtI = EtPZ_3^+I^-$	log *k*	21, 31, 36, 49, 57, 63, 65, 66, 73, 76, 80, 86	23, 24, 33	29, 105	*b*
4	$(CO)_3FeN_4Me_2 + PZ_3 = (CO)_2(PZ_3)FeN_4Me_2 + CO$	log *k*	9, 11, 21, 29, 65−67, 86, 105	8		112
5	$trans\text{-}(NH_3)_4Ru(PZ_3)_2^{3+} + e = trans\text{-}(NH_3)_4Ru(PZ_3)_2^{2+}$	E^0	3, 9, 11, 13−15, 45, 49, 65	19		113
6	$(\eta\text{-Cp})(CO)(L)Fe(COMe)^2 + e = (\eta\text{-Cp})(CO)(L)Fe(COMe)^0$	E^0	*a*	35		*b*
7	$(\eta\text{-}C_5H_4Me)(CO)(L)Fe(COMe)^+ + e = (\eta\text{-}C_5H_4Me)(CO)(L)Fe(COMe)^0$	E^0	*a*	35		*b*
8	$PZ_3 = PZ_3^+ + e$	IP	*a*	1, 2, 8, 10, 22, 35, 97		*b*
9	$trans\text{-}(NH_3)_4Ru(PZ_3)_2^{2+} + H_2O = trans\text{-}(NH_3)_4Ru(PZ_3)_2^{2+} + PZ_3$	log *k*	3, 9, 13−15, 45, 49, 65	19	11	113

[a] All the ligands are listed in Table 2 under the relevant property. [b] References are listed in Table 2.

the θ and y (corresponding to E_{ar}) terms in eqs 4−6 even though their coefficients are zero for this data set.

Where we find data for PZ_iCl_{3-i}, we assume that their parameters are parametrically related to i (additive) and therefore can be calculated from the values for PZ_3 and PCl_3. Each chlorophosphine was incorporated into the analysis by taking advantage of this assumption of additivity, as shown below. Thus, we incorporate $PPhCl_2$ and PPh_2Cl into the analysis (eqs 5 and 6, respectively)

$$0 = [0.6((0.333)13.25 + 0.667x) + 0((0.333)145 + (0.667)124) + 0(1 + 0.667y) + (1.3)0.667z + 2065.2 - 2086]/1.39 \quad (5)$$

$$0 = [0.6((0.667)13.25 + 0.333x) + 0((0.667)145 + (0.333)124) + 0(2 + 0.333y) + (1.3)0.333z + 2065.2 - 2081]/1.39 \quad (6)$$

by using the additional parameters for PPh_3 ($\chi_d = 13.25$; $\theta = 145°$; $E_{ar} = 1$ for one phenyl group, $E_{ar} = 2$ for 2 phenyl groups; $\pi_p = 0$). Other mixed chlorophosphines found in other data sets were treated analogously.

To determine the electronic parameters for PCl_3, we used 17 properties (entries 1, 5−7, 12−20, and 22−25 in Tables 2 and 3), taken from the literature, which have been measured for PR_3 and $P(p\text{-}XC_6H_4)_3$ as well as at least two phosphites in addition to chlorophosphines. When we include data for the mixed $PZ_{3-i}Cl_i$, we are able to write 48 equations for PCl_3 based on the information provided in Table 3. The coefficients ($a' - e'$) of these 48 equations are displayed in Table 1 in the Supporting Information (with θ set to 124°) and Table 2 in the Supporting Information (with θ as a variable).

To obtain values of χ_d, E_{ar}, and π_p for PCl_3, we did a regression analysis using all 48 equations in Table 1 in the Supporting Information (θ set to 124°). The results are displayed in entry 1A in Table 4. We repeated the analysis with θ as a variable (Table 2 in the Supporting Information) and found the electronic parameters (entry 1C in Table 4) to be virtually indistinguishable from the first analysis; however, the calculated value of θ (137 ± 5°) is significantly larger than Tolman's value of 124°.[75]

To compare later these results with the analysis of PH_3 (vide infra), we removed the ionization potential (IP) equations and redid the analyses. These analyses were performed with θ set to 124° (entry 1B in Table 4) as well as with θ as a variable (entry 1D in Table 4). The results we obtained, in both cases, were virtually the same as the results we obtained with the full set of data.

Determination of the Stereoelectronic Parameters of $P(CH_2CH_2CN)_3$ and PF_3

The analysis of $P(CH_2CH_2CN)_3$ was performed in a manner similar to that described above using 23 of the

Table 6. Results of Regression Analyses (with and without the Variable *i* Added to Eq 1 or 2) of the Physicochemical Properties Listed in Table 5[a]

no.	*a*	*b*	*c*	*d*	*f*	*e*	θ_{st}	*n*	r^2	σ
1A	−0.57 ± 0.09	0.01 ± 0.02	0.0 ± 0.4	0		9 ± 4		41	0.773	1.713
1B	−0.60 ± 0.02	−0.041 ± 0.006	−0.3 ± 0.1	0	**−2.7 ± 0.1**	18 ± 1		41	0.985	0.4494
2A	0	−0.05 ± 0.03	0	−1.2 ± 0.5		11 ± 4		9	0.565	0.8151
2B	0	−0.065 ± 0.009	0	−1.3 ± 0.2	**−2.1 ± 0.3**	13 ± 1		9	0.956	0.2131
3A	−0.11 ± 0.4	−0.06 ± 0.04	1.6 ± 0.5	0		3 ± 1	123	15	0.674	0.5180
3B	−0.33 ± 0.07	−0.11 ± 0.01	0.7 ± 0.2	0	**−1.6 ± 0.2**	0.4 ± 0.5	123	15	0.966	0.1759
4A	−0.37 ± 0.09	−0.20 ± 0.03	0	0		4 ± 1	126	10	0.850	0.9525
4B	−0.36 ± 0.05	−0.21 ± 0.02	0	0	**−0.8 ± 0.3**	4.4 ± 0.7	126	10	0.955	0.5637
5A	0.010 ± 0.001	0	−0.019 ± 0.004	0.036 ± 0.004		0.413 ± 0.009		9	0.998	0.005687
5B	0.010 ± 0.002	0	−0.019 ± 0.005	0.036 ± 0.005	**−0.0004 ± 0.004**	0.41 ± 0.01		9	0.998	0.006361
6A	0.0158 ± 0.0007	0	0	0.023 ± 0.002		0.112 ± 0.007		26	0.987	0.013 64
6B	0.0159 ± 0.0007	0	0	0.023 ± 0.002	**−0.006 ± 0.014**	0.112 ± 0.007		26	0.987	0.013 56
7A	0.0163 ± 0.0007	0	0	0.021 ± 0.003		0.084 ± 0.007		25	0.985	0.013 33
7B	0.0167 ± 0.0007	0.0005 ± 0.0003	0	0.024 ± 0.003	**−0.004 ± 0.014**	0.00 ± 0.04		25	0.988	0.013 64
8A	0.131 ± 0.008	0	−0.56 ± 0.04	0		7.6 ± 0.1		26	0.942	0.2081
8B	0.118 ± 0.006	0	−0.48 ± 0.03	0	**0.21 ± 0.04**	7.6 ± 0.07		26	0.973	0.1446
9A	0.1 ± 0.1	0.05 ± 0.03	0.1 ± 0.3	−0.2 ± 0.3		−11 ± 4		9	0.605	0.3988
9B	0.25 ± 0.03	0.072 ± 0.006	0.21 ± 0.06	−0.46 ± 0.6	**1.1 ± 0.1**	−16 ± 1		9	0.986	0.086 41

[a] Entry numbers refer to the entries in Table 5. The letters *a*−*e* are the regression coefficients of these equations, and where present, *f* is the coefficient of *i*, which refers to the number of hydrogens in $PZ_{3-i}H_i$.

24 equations presented in Tables 3 and 4 in the Supporting Information. (One of the equations was shown to be an outlier.) First, we analyzed the equations presented in Table 3 in the Supporting Information, where θ was set to 132°. The results are shown in entry 3A in Table 4. We then analyzed the equations shown in Table 4 in the Supporting Information, where θ was allowed to vary. The results of this analysis are shown in entry 3C and in Table 4. The two methods of analysis give values of the electronic parameters that are virtually indistinguishable. We find that the calculated θ value (129 ± 3°) is statistically indistinguishable from the commonly used value ($\theta = 132°$).

To compare with the PH_3 analysis (vide infra), we removed the pK_a equations and redid the analyses with θ set to 132° as well as with θ as a variable. The results (entries 3B and 3D in Table 4) are indistinguishable from those obtained with the full set of data (entries 3A and 3C in Table 4).

There are only limited data available for the analysis of PF_3 (Table 5 in the Supporting Information). We performed only a single analysis on this set of data using Tolman's value of θ (104°).[75] The results, which are shown in entry 2A of Table 4, have larger errors reflecting the limited set of data.

Analysis of PH_3

Initially, the analysis of PH_3 was performed in a manner analogous to that for PCl_3 with θ set to Tolman's value of 87°.[75] Regression analysis of the full set of 33 equations (Table 6 in the Supporting Information) reveals a large negative value for π_p, suggesting that PH_3 is a much poorer π acid than PR_3 (results are shown in entry 4A in Table 4). We repeated the regression analysis without the pK_a equations (entry 4B in Table 4) and then additionally without the ionization potential equations (entry 4C in Table 4). We obtained significantly different results with each analysis.

We allowed θ for PH_3 to be a variable. Analysis of the full set of equations (Table 7 in the Supporting Information) gave an absurd value of 222° for θ (results are shown in entry 4D in Table 4). We then sequentially eliminated the pK_a and ionization potential equations (entries 4E and 4F in Table 4, respectively). On examining the results, we note that entries 4A and 4D are very different. Entries 4B and 4E are in closer agreement, and finally 4C and 4F are in good agreement. The ramifications of these observations will be discussed below.

Discussion

In the QALE model, analysis of subsets of data should give the same results as the full set. For example, removal of IP equations from the analysis of PCl_3 or the pK_a equations from the analysis of $P(CH_2CH_2CN)_3$, indeed give results that are indistinguishable from the analyses of the full sets (entries 1B and 1D and entries 3B and 3D in Table 4, respectively). In contrast, the sequential removal of the pK_a equations and then the ionization potential equations from the analysis of PH_3 causes a dramatic variation of the values of the parameters. When we eliminate both the pK_a values and ionization potentials, then with θ either fixed or variable we get essentially the same values for χ_d, E_{ar}, and π_p (entries 4C and 4F in Table 4). Furthermore, the calculated value of θ (80 ± 20°, entry 4F) is statistically indistinguishable from Tolman's value[75] of 87°.

The largest variation in parameters occurs when the pK_a equations are removed from the PH_3 analysis. This raises the question as to what is special about the pK_a values of $PZ_{3-i}H_i$. We speculate that hybridization changes play a role in the behavior of $PZ_{3-i}H_i$.[100,101] Protonation of $PZ_{3-i}H_i$ causes a relatively large change in the average bond angles as compared to the protonation of other PZ_3 species.[102−107]

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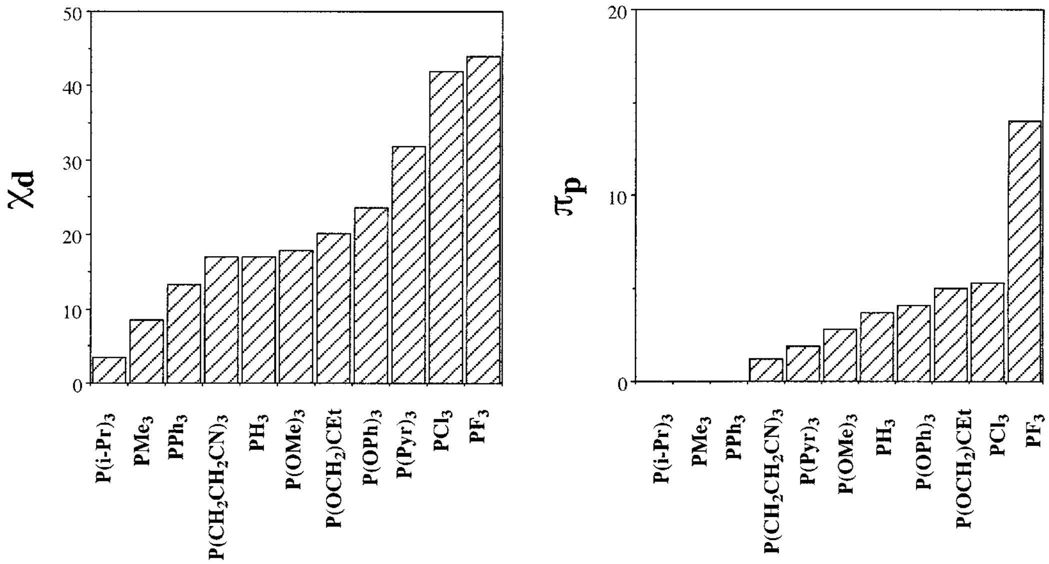

Figure 1. Bar graph presentations of χ_d and π_p for a variety of PZ_3 ligands. Note that that a large value of χ_d indicates a poor σ donor ligand. A large value of π_p indicates a strong π acid.

We introduce into the QALE model the idea of hybridization change in the following way. Since the average bond angle in $PMe_{3-i}H_i$[108−110] decreases monotonically with i, we performed a set of linear regression analyses of pK_a values and of ionization potentials where we used i as a parameter in addition to the parameters listed in entry 4C of Table 4. (We note that these latter parameters are based on the properties of transition-metal complexes where the structures of $PZ_{3-i}H_i$ are not expected to change.) We used data for PR_3, PPh_iR_{3-i}, $P(p\text{-}XC_6H_4)_3$, $P(OR)_3$, and $P(O\text{-}p\text{-}XC_6H_4)_3$ as well as phosphines bearing P−H bonds. First, we analyzed the pK_a values using only χ_d, θ, and E_{ar} (entry 1 in Table 5). The analysis gives a poor fit (shown below), and the coefficients for θ and E_{ar} do not agree with those listed in entry 2 of Table 3 as they should according to the QALE model ($n = 17$, $s = 1.713$, $r^2 = 77.3\%$, $r^2(\text{adj}) = 75.4\%$):

predictor	coeff	stdev	*t* ratio	*p*
constant	9.068	3.475	2.61	0.013
χ_d	−0.57149	0.08695	−6.57	0.000
θ	0.01224	0.02261	0.54	0.592
E_{ar}	0.0264	0.3787	0.07	0.945

The situation improves dramatically when we include the parameter i ($n = 17$, $s = 0.4494$, $r^2 = 98.5\%$, $r^2(\text{adj}) = 98.3\%$):

predictor	coeff	stdev	*t* ratio	*p*
constant	17.6948	0.9897	17.88	0.000
χ_d	−0.59595	0.02284	−26.10	0.000
θ	−0.041180	0.006394	−6.44	0.000
E_{ar}	−0.2900	0.1004	−2.89	0.006
i	−2.7448	0.1226	−22.40	0.000

Not only do we see good statistics but also the coefficients now agree with those listed in entry 2 of Table 3. The large t ratio and small value of p associated with the parameter i clearly demonstrate its importance.

Similar but not as dramatic results were obtained when we performed a similar analysis of the ionization potentials of PZ_3. When we exclude i from the analysis we get ($n = 26$, $s = 0.2081$, $r^2 = 94.2\%$, $r^2(\text{adj}) = 93.7\%$):

predictor	coeff	stdev	*t* ratio	*p*
constant	7.6443	0.1044	73.21	0.000
χ_d	0.130963	0.008456	15.49	0.000
E_{ar}	−0.56253	0.03572	−15.75	0.000

Note that the coefficients of the above analysis agree only marginally with those listed in entry 1 in Table 3. When we include i, we get better statistics and coefficients that agree well with the coefficients listed in entry 1 of Table 3. Again, the large t ratio and the small value of p demonstrate the importance of the parameter i ($n = 26$, $s = 0.1446$, $r^2 = 97.3\%$, $r^2(\text{adj}) = 97.0\%$):

predictor	coeff	stdev	*t* ratio	*p*
constant	7.60371	0.07300	104.16	0.000
χ_d	0.118045	0.006407	18.43	0.000
E_{ar}	−0.48489	0.02918	−16.62	0.000
i	0.20 17	0.04053	5.06	0.000

It stands to reason that the protonation or coordination of $PZ_{3-i}H_i$ results in a thermodynamically unfavorable expansion[100,101] of the bond angles about the phosphorus. This property of $PZ_{3-i}H_i$ is not accounted for in the stereoelectronic parameters of PH_3 (entry 4C in Table 4). Thus, we predict that $PZ_{3-i}H_i$ would give smaller than expected equilibrium constants and smaller than expected rates of reaction when analyzing associative reactions (i.e. protonation, entering-ligand-dependent substitution reactions, S_N2 reactions). Dissociative reactions should show the opposite effect. Accordingly, to incorporate $PZ_{3-i}H_i$ into the QALE analysis the additional parameter i might be required.

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Some examples of data sets that contain $PZ_{3-i}H_i$ are listed in Table 5. (There is a paucity of data for $PZ_{3-i}H_i$. In a number of cases only one representative of this class of ligands is present in a data set.) We performed QALE analyses on these sets of data with and without the parameter *i*. The results of these analyses are shown in Table 6. We have already done the analysis of the pK_a values of HPZ_3^+ (vide supra). We see that the *i* coefficient is negative, indicating that as the number of pendant hydrogens increases, the acidity of HPZ_3^+ increases. On the other hand, the analyses of *E*° values (entries 5−7 in Tables 5 and 6) reveal that the *i* parameter is unnecessary in order to obtain good statistics and agreement of the coefficients. We conclude that the structures of coordinated $PZ_{3-i}H_i$ do not change significantly when the oxidation state of the metal is changed. In contrast, the transformation of $HPZ_{3-i}H_i^+$ to $PZ_{3-i}H_i$ is associated with a large change in structure (vide supra).

With these results in mind, we now consider the analyses of three entering ligand substitution reactions (entries 2−4 in Tables 5 and 6). In each case the parameter *i* is required to get a good fit. We also note that in each case the coefficient of the *i* parameter is negative, indicating that the rate is reduced each time a hydrogen is added to the entering phosphine. It appears that in the transition state $PZ_{3-i}H_i$ species are undergoing a thermodynamically unfavorable expansion of bond angles—a phenomenon that increases the activation energy and retards the rate of reaction.

The analysis of log *k* for the dissociative aquation of $Ru(NH_3)_4(PZ_3)_2^{2+}$ (entry 9 in Tables 5 and 6) shows that the parameter *i* is necessary to obtain a good fit. Furthermore, the positive sign of the *i* coefficient is in harmony with the dissociative nature of this reaction. Thus, it appears that as the $PCyH_2$ ligand is extruded from the coordination sphere of the metal, it undergoes a favorable contraction of the bond angles about the phosphorus.

The ionization potentials of the PZ_3 show a small positive value for the coefficient of *i*. The importance of this observation is not clear to us.

Consideration of the Stereoelectronic Properties of π Acidic PZ₃. We determined the electronic parameters for PCl_3, $P(CH_2CH_2CN)_3$, and PH_3 in two ways. In the first, we set θ equal to Tolman's cone angle and in the second we allowed θ to vary. For $P(CH_2CH_2CN)_3$ and PH_3 we found that the calculated θ values are statistically indistinguishable from Tolman's values. However, for PCl_3 we find a calculated value of 137 ± 5°, which is significantly larger than Tolman's value of 124 ± 2°.[75] The significance of this observation is not yet clear.

For purposes of illustration, we show bar graphs of χ_d and π_p values for a selection of PZ_3 species (Figure 1). We see that σ donor abilities (note that a large χ_d value indicates a poor σ donor) are in the order $P(CH_2CH_2CN)_3 \approx PH_3 > PCl_3 \approx PF_3$. The χ_d values of PCl_3 and PF_3 are the largest (poorest σ donors) that we have yet uncovered.

The π acidity (as measured by π_p) of these ligands spans a large range (0−14; Figure 1). We find that PF_3 is, by far, the strongest π acid with a π acidity that is 2.5 times greater than that of PCl_3, the next strongest π acid. The π acidity of PCl_3 is comparable to that of $P[(OCH_2)_3]CEt$.[71] PH_3 is a stronger π acid than $P(OR)_3$ but slightly weaker than $P(O\text{-}p\text{-}XC_6H_4)_3$. $P(CH_2CH_2CN)_3$ is a weak π acid with a π acidity that is a little less than half that of $P(OR)_3$.

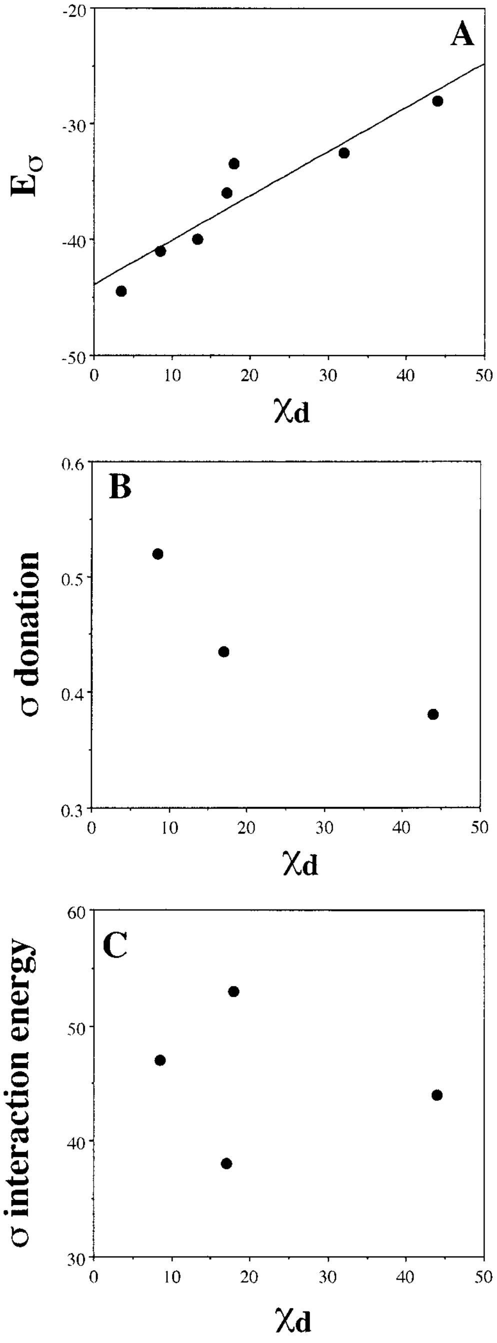

Figure 2. Plots versus χ_d of (A) E_σ for $(Z_3P)Fe(CO)_4$ (model system; Z = H, F, MeO, Me, Ph, i-Pr, Pyr), (B) σ donation for $Pt(PZ_3)_2$ (Z = H, F, Me), and (C) σ interaction energies for $Pd(PZ_3)$ (Z = H, F, MeO, Me). Theoretical data are taken from refs 29, 27, and 19, respectively.

Additionally, PCl_3 shows an E_{ar} effect, which is the largest that we have observed, whereas $P(CH_2CH_2CN)_3$, PH_3, and PF_3 have an E_{ar} parameter of zero.

Comparison of the QALE Parameters with Theoretically Derived Properties. In Figures 2 and 3, we plot the σ donor parameter, χ_d, and the π acceptor parameter, π_p, versus theoretical results from the literature that pertain to σ donicity and π acidity. We

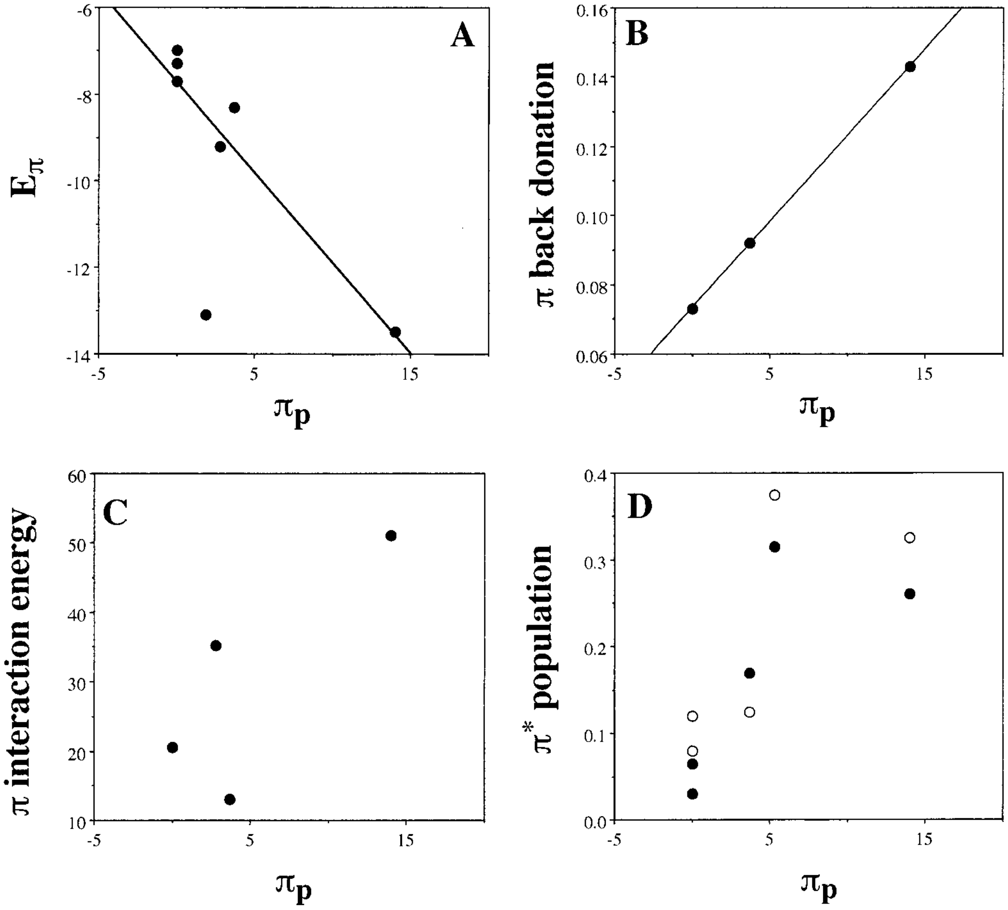

Figure 3. Plots versus π_p of (A) E_π for $(Z_3P)Fe(CO)_4$ (model system; Z = H, F, MeO, Me, Ph, i-Pr, Pyr), (B) π back-donation for $Pt(PZ_3)_2$ (Z = H, F, Me), (C) π interaction energies for $Pd(PZ_3)$ (H, F, MeO, Me), and (D) π* population for $M(CO)_5(PZ_3)$ (M = Cr (open circles), Mo (filled circles); Z = H, F, Me, Cl, Ph) Theoretical data are taken from refs 29, 27, 19, and 24, respectively.

note that there is a strikingly good correlation between our results and those of Gonzalez-Blanco and Branchadell[29] for both χ_d and π_p (except for π_p for $P(Pyr)_3$) (Figures 2A and 3A). There is also reasonably good correlation of our results with those of Fantucci[27] (Figures 1B and 2B). Poorer correlations are observed with the Pacchioni and Bagus data[19] and Ruiz-Morales and Ziegler[24] data (Figures 2C and 3C,D).

Conclusions

Four stereoelectronic parameters appear to be sufficient to describe the stereoelectronic properties of PF_3, PCl_3, PH_3 (in special cases), and $P(CH_2CH_2CN)_3$. PF_3 and PCl_3 are the weakest σ donors, whereas PH_3 and $P(CH_2CH_2CN)_3$ are comparable to $P(p\text{-}ClC_6H_4)_3$. We find that PF_3 is the strongest π acid, around 2.5 times as strong as PCl_3. PH_3 is a modest π acid not very different from the alkyl and aryl phosphites. $P(CH_2CH_2CN)_3$ is a weak π acid with a π acidity less than half that of $P(OR)_3$. PCl_3 has the largest E_{ar} parameter yet uncovered, whereas the E_{ar} parameters for the other three ligands are zero.

These parameters are sufficient to describe properties of PH_3 complexes when the property does not involve a significant change in structure of the PH_3 ligand. When a change does occur, it appears that the parameter *i* (which refers to the number of hydrogens in $PZ_{3-i}H_i$) is required. It further appears that the coefficient of *i* is negative for log *k* for associative reactions and positive for log *k* for dissociative reactions. These observations are in harmony with the idea that the average bond angle of the pendant groups of $PZ_{3-i}H_i$ increases upon coordination. We note that PH_3 is often used in theoretical calculations with the expectation that this ligand would be a good model for PMe_3 and PPh_3. Our work reveals that the stereoelectronic properties of PH_3 are very different from those of PMe_3 and PPh_3.

There is good correlation between our results and theoretical work of Gonzalez-Blanco and Branchadell, as well as the work of Fantucci.

Supporting Information Available: Tables giving the coefficients of eq 3 for the various phosphine complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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