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Evaluation of the Stereoelectronic Parameters of Fluorinated Phosphorus(III) Ligands. The Quantitative Analysis of Ligand Effects (QALE)

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Using the QALE model, we determined the QALE stereoelectronic parameters for the following ligands: $P(CF_3)_3$ ($\chi_d = 33 \pm 2$, $\theta = 137 \pm 13°$, $E_{ar} = 0$, $\pi_p = 11.1 \pm 0.6$), $P(CH_2CH_2C_6F_{13})_3$ ($\chi_d = 9 \pm 3$, $\theta = 137 \pm 2°$, $E_{ar} = 0$, $\pi_p = 2.5 \pm 0.4$), $P[p\text{-}(F_{13}C_6)C_6H_4]_3$ ($\chi_d = 23 \pm 1$, $\theta = 145°$, $E_{ar} = 2.7$, $\pi_p = 0$), and $P(C_6F_5)_3$ ($\chi_d = 34 \pm 2$, $\theta = 191 \pm 13°$, $E_{ar} = 4.3 \pm 0.5$, $\pi_p = 0$). In addition, we evaluated the parameters for $P[Pyr\text{-}3,4\text{-}(CO_2Et)_2]_3$ (Pyr = pyrrolyl; $\chi_d = 43 \pm 2$, $\theta = 145°$, $E_{ar} = 3.3$, $\pi_p = 2 \pm 1$). Revised parameters for PF_3 are also presented: $\chi_d = 33 \pm 2$, $\theta = 110 \pm 24°$, $E_{ar} = 0$, $\pi_p = 13.2 \pm 0.5$. The absence of an indicated error means that these values were assigned initially to the particular parameters in the analyses or that the parameters are statistically indistinguishable from zero. Where a comparison can be made, we find that our calculated values of θ are indistinguishable from those of Tolman; therefore, we suggest the continued use of Tolman's values. It is observed that the perfluoroalkyl groups are highly π acidifying and that this effect is transmitted through intervening CH_2 groups.

Introduction

There has been an explosive growth of the application of fluorinated phosphorus(III) ligands in biphasic catalysis.[1−9] The coordination of ligands such as $P(CH_2CH_2C_6F_{13})_3$ imparts solubility in liquid and supercritical CO_2 as well as fluorocarbon solvents.[10] Furthermore, the electron-withdrawing effects of the C_6F_{13} group should increase the oxidative stability of the phosphine, while the ethylene group tends to insulate the phosphorus atom from the extreme electron-withdrawing effects of the C_6F_{13} group.[10] The relative inertness of the C−F groups further enhances the stability of the ligand.[10] It has been observed that the electronic effect of the fluoroalkyl group on the ligating atom can be "fine-tuned" by varying the number of CH_2 groups between the phosphorus atom and the fluoroalkyl groups.[11,12]

It has long been thought that pendant fluoro- or trifluoromethyl groups impart unusual stereoelectronic properties to the phosphorus(III) ligands.[13] For example, fluorine directly attached to phosphorus is thought to make PF_3 a π acid comparable to CO.[14] Indeed, we recently reported that the π acidity of PF_3 is almost 3 times that of PCl_3 and 5 times that of $P(OR)_3$ (R = alkyl).[14,15] We now extend our evaluation of the stereoelectronic properties of phosphorus(III) ligands to the series of fluorinated ligands $P(CF_3)_3$, $P(CH_2CH_2C_6F_{13})_3$, $P[p\text{-}(C_6F_{13})C_6H_4]_3$, and $P(C_6F_5)_3$. We also include an evaluation of the stereoelectronic properties of $P[Pyr\text{-}3,4\text{-}(CO_2Et)_2]_3$ (Pyr = pyrrolyl) as well as a reassessment of the stereoelectronic properties of PF_3.

Methodology

Recently, we reported our method for determining the stereoelectronic parameters of phosphorus(III) ligands.[14] In the QALE model, each physicochemical property is described by its own QALE equation (e.g., eq 1) in terms of the stereoelectronic parameters of the phosphorus(III) ligands.[15,16] In these equations, χ_d is the σ donor capacity of the ligand, θ is Tolman's

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

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Table 1. Stereoelectronic Parameters of Phosphorus(III) Compounds (PZ$_3$, Z = Any Pendant Group)[a]

no.	PZ$_3$	χ_d[b]	θ[c]	E_{ar}[d]	π_p[e]	no.	PZ$_3$	χ_d[b]	θ[c]	E_{ar}[d]	π_p[e]
1	PH$_3$	17	87	0	3.7	70	PBu$_2$(CH$_2$CH$_2$CN)	9.2	135	0	0.4
2	PMeH$_2$	14.2	97	0	2.5	**71**	**PEt(CF$_3$)$_2$**	**24.1**	**135**	**0**	**7.4**
3	P(OCH$_2$)$_3$CEt	20.2	101	0.2	5	72	P(Pent)$_3$	5	136	0	0
4	P(Oct)H$_2$	13	103	0	2.5	73	P(Octyl)$_3$	5	136	0	0
5	PBuH$_2$	13.1	103	0	2.5	74	PBu$_3$	5.25	136	0	0
6	**P(CF$_3$)H$_2$**	**22.3**	**104**	**0**	**6.2**	75	PPhEt$_2$	8.6	136	1.1	0
7	**PF$_3$**	**33**	**104**	**0**	**13.2**	76	PPh$_2$Me	12.6	136	2.2	0
8	P(i-Bu)H$_2$	13.2	106	0	2.5	77	PPh$_2$Vi	13.65	136		0
9	PPhH$_2$	15.8	106	1	2.5	78	PPh(CH$_2$CH$_2$CN)$_2$	15.8	136	1	0.8
10	P(OMe)$_3$	17.9	107	1	2.8	**79**	**P(CH$_2$CH$_2$C$_6$F$_{13}$)$_3$**	**9**	**137**	**0**	**2.5**
11	PMe$_2$H	11.4	108	0	1.2	**80**	**P(CF$_3$)$_3$**	**33**	**137**	**0**	**11.1**
12	P(OEt)$_3$	15.8	109	1.1	2.9	81	PPhPr$_2$	8	138	1	0
13	**PMeF$_2$**	**24.9**	**109**	**0**	**8.8**	82	PPh$_2$Cl	22.8	138	3.4	1.8
14	P(OBu)$_3$	15.9	110	1.3	2.7	83	P(t-Bu)Me$_2$	5.7	139	0	0
15	P(OPr)$_3$	15.9	110	1.3	2.7	84	PPhBu$_2$	8.1	139	1.3	0
16	P(OCH$_2$CH$_2$Cl)$_3$	20.4	110	0.4	3.6	85	PPh$_2$(OC$_6$H$_4$)	16.7	139	2.4	1.4
17	PMe(OEt)$_2$	13.4	112	0.7	1.9	86	PPh$_2$Et	11.1	140	2.3	0
18	**PMe$_2$F**	**16.7**	**113**	**0**	**4.4**	87	PPh$_2$(CH$_2$CH$_2$CN)	14.5	140	2	0.4
19	PMe$_2$(OEt)	11	115	0.4	1	**88**	**PMe$_2$(C$_6$F$_5$)**	**17.3**	**140**	**1.4**	**0**
20	PCyH$_2$′	11.8	115	0	2.5	89	PPh$_2$Pr	10.6	141	2	0
21	P(CH$_2$CH$_2$CN)$_2$H	17	117	0	2	90	PPh$_2$Bu	11.3	142	2.1	0
22	PMe$_3$	8.55	118	0	0	**91**	**PPh$_2$(CH$_2$CH$_2$C$_6$F$_{13}$)**	**11.8**	**142**	**2**	**0.8**
23	P(t-Bu)H$_2$	11.3	119	0	2.5	92	P(i-Bu)$_3$	5.7	143	0	0
24	P(Oct)$_2$H	9	120	0	1.2	93	P(t-Bu)Cl$_2$	28	143	2.7	3.5
25	PBu$_2$H	9.2	120	0	1.2	94	PCy$_2$H	6.6	144	0	0.4
26	P[O(i-Bu)]$_3$	15.5	120	1.4	3	**95**	**PCl$_2$(C$_6$F$_5$)**	**39.6**	**144**	**4.1**	**3.5**
27	P(OMe)$_2$Ph	16.4	120	1.7	1.9	96	P(*p*-Me$_2$NC$_6$H$_4$)$_3$	5.25	145	2.7	0
28	PMe$_2$Cl	19.7	120	1.4	1.8	97	P(*p*-MeOC$_6$H$_4$)$_3$	10.5	145	2.7	0
29	**PH(CF$_3$)$_2$**	**27.7**	**120**	**0**	**8.6**	98	PPh$_2$(*p*-Me$_2$NC$_6$H$_4$)	10.6	145	2.7	0
30	P(OEt)$_2$Ph	15	121	1.7	1.9	99	P(*p*-MeC$_6$H$_4$)$_3$	11.5	145	2.7	0
31	PPhMe$_2$	10.5	122	1	0	100	PCy(CH$_2$CH$_2$CN)$_2$	11.8	145	0	0.8
32	PMeCl$_2$	30.9	122	2.7	3.5	101	PPh$_2$(*p*-MeC$_6$H$_4$)	12.1	145	2.7	0
33	PMe$_2$Et	7.8	123	0	0	102	PPh$_2$(*p*-MeOC$_6$H$_4$)	12.3	145	2.7	0
34	PMe$_2$(CH$_2$CH$_2$CN)	11.4	123	0	0.4	103	P(C$_6$H$_5$)$_3$	13.25	145	2.7	0
35	P(i-Bu)$_2$H	9.5	124	0	1.2	104	PPh$_2$(*p*-ClC$_6$H$_4$)	14.4	145	2.7	0
36	**PMe$_2$(CF$_3$)**	**16.7**	**124**	**0**	**3.7**	105	P(*p*-FC$_6$H$_4$)$_3$	15.7	145	2.7	0
37	PCl$_3$	42	124	4.1	5.3	**106**	**PPh$_2$[*p*-(F$_{13}$C$_6$)C$_6$H$_4$]**	**16.5**	**145**	**2.7**	**0**
38	PPh$_2$H	14.5	126	2	0.4	107	P(*p*-ClC$_6$H$_4$)$_3$	16.8	145	2.7	0
39	**PF(CF$_3$)$_2$**	**33**	**126**	**0**	**11.8**	**108**	**PPh[*p*-(F$_{13}$C$_6$)C$_6$H$_4$]$_2$**	**19.8**	**145**	**2.7**	**0**
40	PMeEt$_2$	7.1	127	0	0	109	PPh$_2$(Pyr)[f]	19.5	145	3.1	0.6
41	PPrCl$_2$	29.8	127	2.7	3.5	110	P(*p*-F$_3$CC$_6$H$_4$)$_3$	20.5	145	2.7	0
42	PMe(CH$_2$CH$_2$CN)$_2$	14.2	128	0	0.8	**111**	**P[*p*-(F$_{13}$C$_6$)C$_6$H$_4$]$_3$**	**23**	**145**	**2.7**	**0**
43	P(O-*p*-MeC$_6$H$_4$)$_3$	22.4	128	1.4	4.1	112	PPh(Pyr)$_2$[f]	25.7	145	3.2	1.3
44	P(O-*p*-MeOC$_6$H$_4$)$_3$	22.5	128	1.4	3.8	113	P(Pyr)$_3$[g]	31.9	145	3.3	1.9
45	P(OC$_6$H$_5$)$_3$	23.6	128	1.3	4.1	**114**	**P[Pyr-3,4-(CO$_2$Et)$_2$]$_3$**[f]	**43**	**145**	**3.3**	**2**
46	P(O-*p*-ClC$_6$H$_4$)$_3$	27.2	128	1.3	4	**115**	**PPh[Pyr-3,4-(CO$_2$Et)$_2$]$_2$**[f]	**33.1**	**145**	**3.2**	**1.4**
47	PBuCl$_2$	29.8	128	2.7	3.5	**116**	**PPh$_2$[Pyr-3,4-(CO$_2$Et)$_2$]**[f]	**23.2**	**145**	**3.1**	**0.7**
48	P(O-*p*-NCC$_6$H$_4$)$_3$	31.7	128	1	3.7	117	P(NC$_4$H$_8$)$_3$[g]	−1.2	146	−0.6	0.9
49	**P(CF$_3$)Cl$_2$**	**39**	**128**	**2.7**	**7.2**	118	P(*m*-MeC$_6$H$_4$)$_3$	11.3	148	2.7	0
50	P(O-i-Pr)$_3$	13.4	130	1.3	2.9	119	P(*m*-ClC$_6$H$_4$)$_3$	19.6	148	2.7	0
51	**P(t-Bu)F$_2$**	**22**	**130**	**0**	**8.8**	120	PEt$_2$(t-Bu)$_2$	4.2	149	0	0
52	**PMe(CF$_3$)$_2$**	**24.9**	**131**	**0**	**7.4**	121	P(t-Bu)$_2$H	5.7	150	0	1.2
53	P(p-MeOC$_6$H$_4$)Cl$_2$	31.5	131	3.7	3.5	122	P(i-Pr)Ph$_2$	9.6	150	1.7	0
54	PPhCl$_2$	32.4	131	3.7	3.5	**123**	**P(i-Pr)$_2$(CH$_2$CH$_2$C$_6$F$_{13}$)**	**5.3**	**152**	**0**	**0.8**
55	PEt3	6.3	132	0	0	124	PPh$_2$Cy	9.1	153	1.6	0
56	PMe$_2$(i-Pr)	6.9	132	0	0	125	PPh(i-Pr)$_2$	10	155	2	0
57	PEt$_2$(CH$_2$CH$_2$CN)	9.9	132	0	0.4	**126**	**P(t-Bu)$_2$F**	**11**	**156**	**0**	**4.4**
58	PEt(CH$_2$CH$_2$CN)$_2$	13.4	132	0	0.8	127	P(CH$_2$CH$_2$CN)Cy$_2$	6.6	157	0	0.4
59	P(OMe)Ph$_2$	14.8	132	2.3	0.9	128	PPh$_2$(t-Bu)	8.8	157	2	0
60	P(CH$_2$CH$_2$CN)$_3$	17	132	0	1.2	**129**	**PPh$_2$(C$_6$F$_5$)**	**20.4**	**158**	**3.4**	**0**
61	P(octyl)(CH$_2$CH$_2$CN)$_2$	13	133	0	0.8	**130**	**PCy$_2$(CH$_2$CH$_2$C$_6$F$_{13}$)**	**3.9**	**159**	**0**	**0.8**
62	P(OEt)Ph$_2$	14.1	133	2.4	1	131	P(i-Pr$_3$)	3.45	160	0	0
63	**P(OMe)$_2$(C$_6$F$_5$)**	**23.5**	**133**	**2.0**	**1.9**	132	PPhCy$_2$	5.7	162	1.6	0
64	**PCl(CF$_3$)$_2$**	**36**	**133**	**1.4**	**9.2**	133	P(t-Bu)$_2$Cl	14	163	1.4	1.8
65	PPr$_3$	5.4	134	0	0	134	PCy$_3$	1.4	170	0	0
66	PBu(CH$_2$CH$_2$CN)$_2$	13.1	134	0	0.8	**135**	**PPh(C$_6$F$_5$)$_2$**	**27.6**	**171**	**3.7**	**0**
67	PPh(OC$_6$H$_5$)$_2$	20.2	134	1.9	2.7	136	P(*o*-MeC$_6$H$_4$)	10.65	178	2.7	0
68	PMe(i-Bu)$_2$	6.7	135	0	0	137	P(t-Bu)$_3$	0	182	0	0
69	P(Oct)$_2$(CH$_2$CH$_2$CN)	9	135	0	0.4	**138**	**P(C$_6$F$_5$)$_3$**	**34.8**	**184**	**4.1**	**0**

[a] The values in lightface type are taken from the literature, whereas the values in boldface are reported here for the first time. Ligands are listed in order of increasing cone angle. [b] χ_d values for the lightface phosphorus(III) compounds are taken from refs 14, 15, and 19−21 or calculated by additivity using the data found in these references. [c] Values for cone angles (θ, deg) for the lightface phosphorus(III) compounds are taken from ref 22 or calculated by additivity using the data found in these references. θ values for the pyrrolyl- and pyrrolidinylphosphines are taken from ref 21. [d] E_{ar} values for the lightface phosphorus(III) compounds are taken from refs 14, 15, 20, and 21. [e] π_p values for the lightface phosphorus(III) compounds are taken from refs 14, 15, and 21. [f] Pyr = pyrrolyl. [g] NC$_4$H$_8$ = pyrrolidinyl.

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

no.	syst	property	ligands used	ligands excluded	refs
1	PZ_3	vertical ionization potentials	3, 10, 12, 22, 28, 31, 32, 37, 54, 55, 74, 76, 93, 96, 97, 99, 103, 105, 107, 110, 131, 136, 137	$PZ_{3-i}H_i$[a]	23−32
2	$Cr(CO)_5(PZ_3)$	ν_{CO}	3, 10, 12, 14, 22, 37, 43, 45, 55, 74, 97, 99, 103, 107, 110, 131, 134		15, 33, 34
3	*trans*-$Cr(CO)_4(PZ_3)_2$	ν_{CO}	7, 10, 12, 22, 45,74, 99, 103, 118		35−37
4	$Cr(1,3,5\text{-}MeC_6H_3)(CO)_2(PZ_3)$	ν_{CO}	10, 12, 14, 22, 37, 38, 43, 45, 55, 74, 103, 134		33
5	$Fe(CO)_4(PZ_3)$	ν_{CO}	10, 12, 22, 37, 45, 55, 74, 103, 105, 110, 134, 136, 137		33, 39−41
6	$Fe(CO)_3(PZ_3)_2$	$-\Delta H_{rx}$	22, 31, 55, 74, 76, 86, 97, 99, 103, 105, 107, 109, 110, 112, 113, 117, 124, 131, 132, 134		42−45
7	$Fe(CO)_3(PZ_3)_2$	ν_{CO}	10, 22, 55, 74, 97, 99, 103, 105, 107, 109, 110, 112, 113, 117, 131, 134, 137		42, 43, 45−47
8	$Ir(CO)(Cl)(PZ_3)_2$	ν_{CO}	10, 45, 55, 74, 96, 97, 99, 103, 105, 107, 110, 131, 134		48−50
9	$Mn(Cp)(CO)_2(PZ_3)$	ν_{CO}	10, 12, 14, 22, 37, 43, 45, 55, 74, 99, 103, 131, 134		33
10	$Mo(CO)_5(PZ_3)$	ν_{CO}	1, 3, 10, 12, 22, 37, 45, 55, 60, 74, 103, 118, 137, 134		51
11	$Mo(CO)_4(PZ_3)_2$	ν_{CO}	1, 3, 10, 12, 22, 37, 45, 50, 55, 60, 74, 99, 103, 118, 131, 134		51, 52
12	$Mo(CO)_3(PZ_3)_3$	ν_{CO}	1, 3, 10, 12, 22, 37, 45, 50, 54, 55, 74, 82, 103	60[b]	51
13	$[(CO)_2RhCl]_2 + 4\ PZ_3 = 2Rh(CO)(Cl)(PZ_3)_2 + 2\ CO$	$-\Delta H_{rx}$	10, 22, 31, 45, 55, 76, 97, 99, 103, 105, 107, 109, 110, 112, 131, 134	113[c]	53−55
14	$Rh(CO)(Cl)(PZ_3)_2$	ν_{CO}	10, 22, 45, 55, 97, 99, 103, 105, 107, 109, 110, 112, 113, 131, 134	117[d]	53−55
15	$Rh(CO)(Cl)(PZ_3)_2$	Rh−P bond length	22, 31, 76, 77, 99, 103, 105, 113, 117, 131, 134		53, 56−66
16	$Ru(Cp)(cod)Cl + 2PZ_3 = Ru(Cp)(Cl)(PZ_3)_2 + cod$	$-\Delta H_{rx}$	3, 22, 31, 45, 50, 55, 74, 76, 97, 99, 105, 107, 109, 110, 112, 113, 117	10[e]	67−69
17	$Ru(Cp^*)(cod)Cl + 2PZ_3 = Ru(Cp^*)(Cl)(PZ_3)_2 + cod$	$-\Delta H_{rx}$	3, 22, 31, 45, 50, 55, 74, 76, 97, 105, 107, 109, 110, 112, 113		67−69
18	$W(CO)_5(PZ_3)$	ν_{CO}	3, 12, 22, 22, 37, 45, 55, 74, 103, 134, 136		33, 34, 36, 70
19	$Os_3(CO)_{11}(PZ_3)$	Os−P bond length	3, 10, 27, 45.55, 77, 99, 103, 105, 110, 134, 136, 137		71
20	$Ni(CO)_3(PZ_3)$	ν_{CO}	3, 10, 12, 26, 22, 37, 45, 46, 48, 50, 55, 60, 74, 92, 96, 97, 99, 103, 105, 107, 131, 134, 137		25
21	$Fe_2Cp_2(CO)_3 + PZ_3 = Fe_2Cp_2(CO)_3PZ_3$	log *k*	10, 45, 50, 74, 103, 129, 131, 134, 137, 135		72
22	*t*-$BuOOH + PZ_3 = O{=}PZ_3 + t\text{-}BuOH$	log *k*	10, 12, 27, 45, 50, 55, 59, 74, 97, 99, 103, 105, 107		73

[a] $PZ_{3-i}H_i$ are excluded because their inclusion might require an additional parameter *i*, which refers to the number of hydrogens.[14]
[b] Deviates from the line determined by the other ligands by 8σ.
[c] Deviates from the line determined by the other ligands by 7σ.
[d] Deviates from the line determined by the other ligands by 5σ.
[e] Deviates from the line determined by the other ligands by 14σ.

cone angle and is a measure of the size of the ligand, E_{ar} is an extra electronic effect originally associated with the number of aromatic pendant groups but is now thought to be more general,[15] and π_p is a measure of the π acidity. In eq 1, θ_{st} is the steric threshold[17] and λ is the switching function that turns on the steric term after the size of the ligand surpasses the steric threshold.[17] In the absence of a steric threshold, this equation can be reduced to eq 2. In the QALE model, eqs 1

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

and 2 are generally applicable to all phosphorus(III) ligands.

Normally, in a QALE analysis we examine the manner in which a physicochemical property changes as the nature of the phosphorus(III) ligand changes. Beginning with the known parameters of the ligands in the particular data set, we then determine the values of the coefficients (*a*−*e*) of the QALE equations via regression analysis. On the other hand, if we want to determine the parameters of a given ligand, we can turn this procedure around. Beginning with a number of QALE equations with known coefficients for a number of different properties of a given ligand, we can determine the unknown parameters for this ligand. With a view toward obtaining the parameters of the fluorinated phosphorus(III) ligands, we obtained the QALE equations listed in Table 3 by regression analysis for 22 physicochemical properties (Table 2). We chose these properties because they have been measured not only for the fluorinated ligands of interest but also for a number of other π acidic phosphorus(III) ligands as well as alkyl- and arylphosphines. In deriving the QALE equations, we omit the fluorinated ligands but include alkyl- and arylphosphines (PR_3 and $P(p\text{-}XC_6H_4)_3$, respectively), alkyl and aryl phosphites ($P(OR)_3$ and $P(O\text{-}p\text{-}XC_6H_4)_3$, respectively), and the π acidic ligands PH_3, PCl_3, $P(CH_2CH_2CN)_3$, and P(Pyr)$_3$, for which the stereoelectronic parameters are known (see Table 1).

Before using the QALE equations in Table 3 to determine the parameters for PZ_3 (Z and Y are used to indicate any pendant group), we weighted them and made them dimensionless by dividing each one by its estimated standard deviation (*s*). We then put them into the standard form of eq 3. a'−d'

$$a'\chi_d + b'\theta + c'E_{ar} + d'\pi_p + e' = 0 \qquad (3)$$

are the QALE coefficients divided by the estimated standard deviation (*s*). e' is the sum of all constant terms divided by *s*. Regression analysis of the collection of equations for a single phosphorus(III) ligand gives estimated values of the QALE parameters and e'_{calcd}. We used the "Minitab" program for all statistical calculations. For illustrative purposes, we have displayed the output, which shows the standard deviation (standard error), "*t* ratios" and "*p* values" of the parameters as well as the estimated standard deviation (*s*) and r^2 value of the analysis.

Occasionally, within a set of data or within a set of equations, we find an outlier. A data point is identified

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

no.	a	b	c	d	e	θ_{st} (deg)	n	σ	r^2
1	0.115 ± 0.003	0	−0.47 ± 0.03	0	7.63 ± 0.05		23	0.1185	0.985
2	0.50 ± 0.02	−0.047 ± 0.007	0	1.67 ± 0.09	2063 ± 1		17	0.3842	0.998
3	1.6 ± 0.2	0.24 ± 0.05	0	7.2 ± 0.4	133 ± 6		9	1.777	0.999
4	2.1 ± 0.1	0.16 ± 0.04	−2.2 ± 0.9	0	1842 ± 6		12	1.907	0.993
5	0.66 ± 0.09	−0.06 ± 0.01	−1.6 ± 0.5	2.0 ± 0.3	2054 ± 2		13	0.7684	0.996
6	−0.78 ± 0.07	−0.45 ± 0.02	−1.4 ± 0.3	−1.3 ± 0.6	46.7 ± 0.5	134	20	0.8994	0.991
7	1.40 ± 0.08	−0.13 ± 0.02	4.5 ± 0.4	12.3 ± 0.5	1875 ± 3		16	1.053	0.999
8	1.42 ± 0.09	−0.13 ± 0.03	4.9 ± 0.4	6.5 ± 0.4	1951 ± 4		13	1.091	0.998
9	1.8 ± 0.1	0.15 ± 0.02	−2.0 ± 0.6	1.5 ± 0.5	1899 ± 3		13	1.140	0.998
10	0.51 ± 0.06			1.6 ± 0.3	2066.1 ± 0.6		14	1.350	0.979
11	1.3 ± 0.1			2.4 ± 0.5	2006 ± 1		16	2.238	0.984
12	2.6 ± 0.2			4.8 ± 0.9	1911 ± 2		13	3.701	0.990
13	−1.4 ± 0.1	−0.40 ± 0.03	−2.5 ± 0.7	−1.5 ± 0.6	136 ± 5		16	1.501	0.990
14	1.7 ± 0.1	−0.24 ± 0.03	4.1 ± 0.5	5.8 ± 0.5	1980 ± 4		15	1.276	0.998
15	−0.0011 ± 0.0002	0.000 69 ± 0.00009		−0.011 ± -003	2.24 ± 0.01		11	0.004 04	0.969
16		−0.90 ± 0.07	0.9 ± 0.3		36.3 ± 0.5	135	18	1.15	0.962
17		−0.72 ± 0.7	1.0 ± 0.4		31.8 ± 0.05	127	15	1.069	0.959
18	0.54 ± 0.05			1.5 ± 0.2	2064.6 ± 0.5		11	0.8137	0.994
19	−0.0026 ± 0.0009	0.0015 ± 0.0003		−0.006 ± 0.003	2.17 ± 0.05		14	0.016 27	0.940
20	0.92 ± 0.04			2.0 ± 0.2	2057		23	1.1111	0.993
21	−0.04 ± 0.01	−0.032 ± 0.004	0.35 ± 0.07		9.7 ± 0.6		8	0.1234	0.983
22	−0.9 ± 0.2	−0.08 ± 0.1	0.20 ± 0.08	−0.52 ± 0.07	1.7 ± 0.2	128	13	0.1344	0.982

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

Table 4. List of Ligands and Equations Used To Determine the Stereoelectronic Parameters of the Phosphorus(III) Compounds Listed in Column 2

no.	PZ$_3$	χ_d	θ (deg)	E_{ar}	π_p	n^a	σ	r^2	eqs[b]	ligands used[c]	ligands excluded[c]	refs
1	PF$_3$	33 ± 2	110 ± 24	0	13.2 ± 0.5	19	4.876	0.992	1	7, 13, 18, 51, 126		28, 31
									2, 5,[d] 7,[d] 9, 10, 12, 18	7		24, 33, 36, 37, 41, 52, 70, 71, 74
									11	7, 13, 18, 51, 126		52
									19	7, 126		71
2	P(CF$_3$)$_3$	33 ± 2	137 ± 13	0	11.1 ± 0.6	20	2.352	0.992	1	36, 49, 52, 64, 80		75, 76
									2	52, 80	36[e]	77
									3, 10, 11, 18	36, 52, 80		77
									5	80		78
3	P(CH$_2$CH$_2$-C$_6$F$_{13}$)$_3$	9 ± 3	137 ± 2	0	2.5 ± 0.4	14	1.667	0.999	6	91, 123, 130		47
									8		79[f]	
									13	79, 123, 130	91[g]	79
									14	79, 91, 123, 130		79
									15	79, 91		79, 80
									16, 17	79		80, 81
4[h]	P(*p*-(F$_{13}$C$_6$)-C$_6$H$_4$)$_3$	22.7 ± 1.1	145	2.7	0	4			8, 14	111		82
5[d]	P(C$_6$F$_5$)$_3$	34 ± 2	184 ± 13	4.1 ± 0.5	0	13	3.002	0.987	1	63, 88, 95, 129		83, 84
									13,27,28	138		22, 71, 85
									21	129, 135, 138		86
									29	129 , 135		72
									30	129		73
6	P[Pyr-3,4-(CO$_2$Et)$_2$]$_3$	43 ± 2	145	3.3	2 ± 1	6	0.8308	1.000	20	114−116		87
									21	114−116		87

[a] Numbers of equations from Table 3 that were used in the analyses. [b] Numbers refer to the properties and equations listed in Tables 2 and 3. [c] Numbers refer to the entry numbers in Table 1. [d] We found in the literature three values of ν_{CO} for Fe(CO)$_4$(PF$_3$) and two values of ν_{CO} for Fe(CO)$_3$(PF$_3$)$_2$. Each of these values was included as a separate data point. [e] Deviates by 3.6 standard deviations (3.6σ) (see text). [f] Deviates by 9.4σ. [g] Deviates by 5.6σ. [h] See text for the method of analysis.

statistically as an outlier in the following manner.[18] We obtain the predicted values and the residuals of the property based on regression analysis, where we omit the suspect data point. Using the regression equation, we calculate the predicted value of the suspect data point. If the difference between the predicted value and the experimental value is greater than 3.5 standard deviations from the set of residuals, then it is an outlier. Within the 22 data sets listed in Table 2 we found only 4 outliers out of 324 data. (The range of r^2 is 0.940−0.999 with a median of 0.990.) In the analyses listed in Table 4, we found 3 outliers out of the 76 equations.

Results

Reevaluation of the Stereoelectronic Parameters of PF$_3$. Our original analysis of PF$_3$ was based on a limited set of data.[14] Accordingly, we revisited this ligand and added 6 new properties to the analysis.

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This gave us 19 equations. (The total number of equations is obtained by summing the product of the number of equations by the number of ligands involved.). In addition, we found 3 values for ν_{CO} for $Fe(CO)_4(PZ_3)$ and 2 values for $Fe(CO)_3(PZ_3)_2$. Each of these values was included in the analysis as a separate equation, bringing the total number of equations to 22 (see entry 1, Table 4). The output of the Minitab program for the analysis of this set of equations gives the results

predictor	coeff	st dev	*t* ratio	*p*
χ_d	30.671	5.531	5.55	0.000
θ	119.87	31.37	3.82	0.001
E_{ar}	0.817	1.561	0.52	0.607
π_p	13.894	1.459	9.52	0.000

with *s* (estimated standard deviation) = 4.977 and r^2 = 0.992. This regression analysis shows that E_{ar} is statistically indistinguishable from zero by virtue of its small *t* ratio and large *p* value. Hence, E_{ar} was set to zero and dropped from the final analysis. Repeating the analysis in terms of χ_d, θ, and π_p only, we obtained

predictor	coeff	st dev	*t* ratio	*p*
χ_d	33.029	3.146	10.50	0.000
θ	109.55	23.91	4.58	0.000
π_p	13.1882	0.5480	24.07	0.000

with *s* = 4.876 and r^2 = 0.992. We see that χ_d (33 ± 3) is smaller than our earlier reported value of 44 ± 4; π_p decreased slightly from 14 ± 1 to 13.2 ± 0.5. The analysis provides θ = 110 ± 24°, which overlaps Tolman's value[22] of 104°. We suggest the continued use of Tolman's value. This new value of χ_d indicates that its σ donor capacity is between that of PCl_3 and P(O-*p*-$CNC_6H_4)_3$ (see Table 1). Its π_p value of 13.2 indicates that PF_3 is the most π acidic phosphorus(III) ligand in our present listing of ligands.

The new stereoelectronic parameters for PF_3 and those for the other ligands considered in this study are presented in Table 4.

Determination of the Stereoelectronic Parameters of $P(CF_3)_3$. We used the equations listed in entry 2 of Table 4 for the determination of the parameters of $P(CF_3)_3$. To include the small set of data for ν_{CO} for *trans*-$Cr(CO)_4L_2$, we added the data point for PF_3 to obtain the QALE equation (entry 3, Table 3). Combining the appropriate data for $P(CF_3)_3$ with data for the mixed ligands containing the CF_3 groups gave us 20 equations. When we performed the analysis of these equations in terms of the four QALE parameters, we found E_{ar} to be indistinguishable from zero. The results of the regression analysis using χ_d, θ, and π_p gave the results

predictor	coeff	st dev	*t* ratio	*p*
χ_d	33.188	2.413	13.75	0.000
θ	137.31	12.51	10.97	0.000
π_p	11.0629	0.5636	19.63	0.000

with *s* = 2.352 and r^2 = 0.992. Therefore, the values of χ_d, θ and π_p are 33 ± 2, 137 ± 13°, and 11.1 ± 0.6, respectively.

Determination of the Stereoelectronic Parameters of $P(CH_2CH_2C_6F_{13})_3$. Initial inspection of the 14 equations listed in entry 3 of Table 4 revealed a correlation between the coefficients of the electronic terms. As a result, we were unable to evaluate the separate contributions of the electronic parameters without assigning a value to one of the parameters. Accordingly, we assigned a value of zero to E_{ar} since $P(CF_3)_3$ has this value, as do the other PR_3 species (R = alkyl). The final regression analysis gives the results

predictor	coeff	st dev	*t* ratio	p
χ_d	8.880	1.678	5.29	0.000
θ	137.054	1.801	76.08	0.000
π_p	2.4553	0.4307	5.70	0.000

with *s* = 1.667 and r^2 = 0.999. Thus, we obtain values of 9 ± 2, 137 ± 3°, and 2.5 ± 0.4 for χ_d, θ, and π_p, respectively.

Determination of the Stereoelectronic Parameters of P[*p*-$(C_6F_{13})C_6H_4]_3$. Only two properties of this ligand have been reported.[82] Accordingly, the results we report must be considered tentative. We performed the analysis in the following manner. We assumed that this para-substituted triarylphosphine behaves in no exceptional way as compared to other P(*p*-$XC_6H_4)_3$ species.

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Thus, we assigned values of 145°, 2.7, and 0 to θ, $E_{\rm ar}$, and $\pi_{\rm p}$, respectively. The lack of π acidity for $P(C_6F_5)_3$ supports the assumption that $\pi_{\rm p}$ is zero for $P[p\text{-}(C_6F_{13})\text{-}C_6H_4]_3$ (vide infra). We then used the $\chi_{\rm d}$ dependence of $\nu_{\rm CO}$ for $M(CO)Cl[P(p\text{-}XC_6H_4)_3]_2$ (M = Rh, Ir) (eqs 3 and 4, respectively) to calculate $\chi_{\rm d}$ for this ligand. Using

$$\nu_{\rm CO}({\rm Rh}) = (1.70 \pm 0.02)\chi_{\rm d} + (1955.5 \pm 0.3) \quad n = 6,\ r^2 = 0.999 \quad (3)$$

$$\nu_{\rm CO}({\rm Ir}) = (1.46 \pm 0.02)\chi_{\rm d} + (1945.7 \pm 0.3) \quad n = 7,\ r^2 = 0.999 \quad (4)$$

these two experimental $\nu_{\rm CO}$ values for $P[p\text{-}(C_6F_{13})C_6H_4]_3$, (1993 and 1979 cm^{-1}, respectively), we calculated the corresponding values for $\chi_{\rm d}$. We repeated this operation for all variations of the standard errors and averaged the extreme results to obtain 23 ± 1 for $\chi_{\rm d}$. This is noteworthy (vide infra), since the $\chi_{\rm d}$ value of 23 is close to the value of 20.5 for $P(p\text{-}F_3CC_6H_4)_3$.

Determination of the Stereoelectronic Parameters of $P(C_6F_5)_3$. We found 7 sets of data that included $P(C_6F_5)_3$ or related phosphines. This gave us 13 equations (entry 5, Table 4). Regression analysis in terms of the four QALE parameters showed that $\pi_{\rm p}$ was indistinguishable from zero. Accordingly, it was dropped from the final analysis, which gave the following results

predictor	coeff	st dev	*t* ratio	*p*
$\chi_{\rm d}$	33.915	1.622	20.91	0.000
θ	190.63	13.14	14.51	0.000
$E_{\rm ar}$	4.2595	0.5418	7.86	0.000

with $s = 3.020$ and $r^2 = 0.987$. Thus, we obtain values of 34 ± 2, 191 ± 13°, and 4.3 ± 0.5 for $\chi_{\rm d}$, θ, and $E_{\rm ar}$, respectively.

Determination of the Stereoelectronic Parameters of $P[Pyr\text{-}3,4\text{-}(CO_2Et)_2]_3$ (Pyr = Pyrrolyl). Our results for this analysis must be considered tentative, since there are only two reported properties on which to base our analysis (entry 6 in Table 4). This gave us six equations. Since $E_{\rm ar}$ does not change for $P(p\text{-}XC_6H_4)_3$ as X is varied, we assumed that this is also true for substituted pyrrolylphosphines. Accordingly, for $P[Pyr\text{-}3,4\text{-}(CO_2Et)_2]_3$ we set $E_{\rm ar} = 3.3$ (the value[21] for $P(Pyr)_3$). Nolan[87] suggested that this ligand is isosteric with $P(Pyr)_3$. Thus, we assigned θ a value of 145°. The results of the regresssion analysis are

predictor	coeff	st dev	*t* ratio	*p*
$\chi_{\rm d}$	42.829	2.443	17.53	0.000
$\pi_{\rm p}$	2.0029	0.9722	2.06	0.131

with $s = 0.8308$ and $r^2 = 100.0$. Thus, the parameters for this ligand are 43 ± 2, 145°, 3.3, and 2 ± 1 for $\chi_{\rm d}$, θ, $E_{\rm ar}$ and $\pi_{\rm p}$, respectively. We discuss the π acidity of this ligand below.

Discussion

It is noteworthy the values of θ that we obtained for PF_3 (110°), $P(CF_3)_3$ (137°), and $P(C_6F_5)_3$ (191°) are remarkably similar to the values reported by Tolman. Tolman does not report θ for $P(CH_2CH_2C_6F_{13})_3$. Even so, the value θ (137°) which we report for $P(CH_2CH_2C_6F_{13})_3$ is close to the value of θ (136°) that we find works well for PBu_3 in QALE analyses (e.g., see the appropriate analyses in Tables 2 and 3).

PF_3 is the most π acidic of the phosphorus(III) ligands. Our analysis also reveals that $P(CF_3)_3$ has a large value of $\pi_{\rm p}$, consonant with Grobe's assertion[13] that this ligand is a strong π acid. Interestingly, $P(CH_2CH_2C_6F_{13})_3$ also exhibits a significant π acidity, although it is as good a σ donor as PMe_3. We also note that there appears to be no π acidity associated with $P(C_6F_5)_3$. Furthermore, in the absence of π acidity, we expect that the $\chi_{\rm d}$ value should be the same as Tolman's value of χ (34.8), as indeed it is. Therefore, we suggest that Tolman's value be used for $\chi_{\rm d}$. $P(C_6F_5)_3$ does appear to have one of the largest $E_{\rm ar}$ values of any of the phosphorus(III) ligands.

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The lack of π acidity for $P(C_6F_5)_3$ reinforces our contention that $P[p\text{-}(C_6F_{13})C_6H_4]_3$ is not a π acid.

The χ_d value for $P[Pyr\text{-}3,4\text{-}(CO_2Et)_2]_3$ is the largest that we have determined, making it the poorest σ donor ligand, so far. Interestingly, even though π_p has a large error, its value is very close to the π_p value (1.9) of $P(Pyr)_3$, and thus we believe that it is real. The similarity of π_p for $P[Pyr\text{-}3,4\text{-}(CO_2Et)_2]_3$ and $P(Pyr)_3$ is reminiscent of the $P(O\text{-}p\text{-}XC_6H_4)_3$ ligands, whose π_p parameters are independent of the para substituent.[15]

The availability of the stereoelectronic parameters of the fluorinated phosphorus(III) compounds gives us the opportunity to explore how the electronic influence of the fluoroalkyl group is attenuated by intervening atoms (spacers). To accomplish this, we treat the C_6F_{13} like a CF_3 group. Certainly, the similarity of χ_d and π_p for $P[p\text{-}(C_6F_{13})C_6H_4]_3$ ($\chi_d = 23$ and $\pi_p = 0$) and $P(p\text{-}F_3CC_6H_4)_3$ ($\chi_d = 20.5$ and $\pi_p = 0$) suggests that this is possible. In support of our view, we note that Hope also concluded that CF_3 and C_6F_{13} have similar electronic properties.[82] By treating perfluoroalkyl groups as trifluoromethyl groups, we can generate a homologous series of fluorinated phosphorus(III) ligands. For example, $P(CH_2CH_2C_6F_{13})_3$ is treated like $P(CH_2CH_2CF_3)_3$. To incorporate PF_3 into the analysis, we multiplied its π_p value by 3, since all the other ligands possess the equivalent of nine fluorine atoms.

Examination of the data presented in Table 4 reveals that the π acidifying effect of the CF_3 group does not end abruptly as “spacers” are inserted between the phosphorus and the perfluoroalkyl group. Rather, the π effect is smoothly attenuated as the number of atoms separating phosphorus and fluorine increases. This is shown in Figure 1, where we plot π_p vs “n”, the number of atoms between phosphorus and the fluorines. We note that the π_p contribution of CF_3 appears to have vanished by the time there are five intervening atoms separating the fluorine and phosphorus atoms. Qualitatively, our observation agrees with that of Gladysz, who noted that the (total) electronic effect of the fluoroalkyl group is still observable with five intervening CH_2 groups and nearly disappears with six CH_2 groups.[12]

This essentially smooth monotonic attenuation of the π effect is not mirrored in the changes in χ_d. For example, the para CF_3 group in $P(p\text{-}F_3CC_6H_4)_3$ causes a nine unit increase in χ_d as compared with $P(p\text{-}MeC_6H_4)_3$. In contrast, the C_6F_3 group (which is closer to the phosphorus) in $P(CH_2CH_2C_6F_{13})_3$ causes only a 3.6 unit increase in χ_d as compared to PPr_3.

Hope compared the ν_{CO} values for $Ir(CO)(Cl)[P(CH_2CH_2C_6F_{13})_3]_2$ with $Ir(CO)(Cl)[PEt_3]_2$ and, similarly, ν_{CO} for $Ir(CO)(Cl)[P[p\text{-}(F_{13}C_6)C_6H_4]_3]_2$ with $Ir(CO)(Cl)(PPh_3)_2$. He noted that the phenyl ring better insulates the phosphorus from the $F_{13}C_6$ than does the array of two CH_2 groups.[82] We note that Hope's conclusion is based on the total electronic effect of the phosphine on ν_{CO}. However, ν_{CO} is strongly influenced by both σ and π effects. When the electronic effect is separated into its components, we see that two CH_2 groups, indeed, strongly attenuate the effect on χ_d more so than does the phenyl group. However, because there is a significant π contribution to ν_{CO} and since $P(CH_2CH_2C_6F_{13})_3$ is a π acid, its relative effect on ν_{CO} is greater than that for $P[p\text{-}(F_{13}C_6)C_6H_4]_3$.

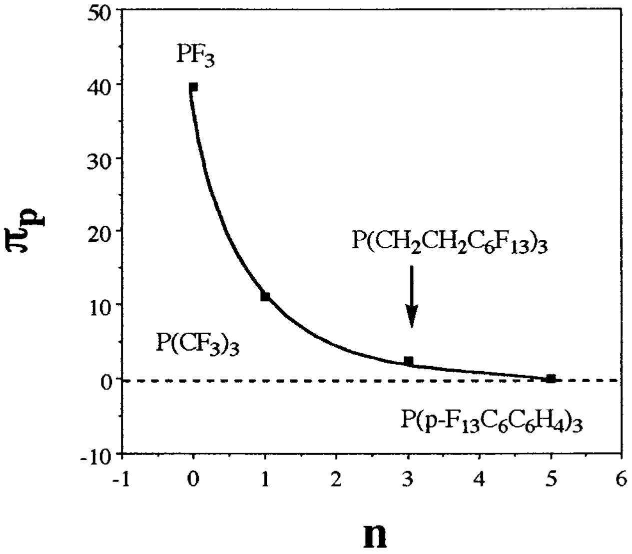

Figure 1. Plot of the π_p values of fluorinated phosphorus(III) ligands vs the number of atoms (n) separating the phosphorus and fluorine atoms.

Conclusions

The QALE parameters for a series of fluorinated phosphorus(III) compounds are reported. PF_3 and $P(CF_3)_3$ are by far the most π acidic ligands we have encountered. The π acidifying effect of the fluorine atoms is transmitted to the phosphorus through at least three bonds and appears to have vanished by five bonds. $P(CH_2CH_2C_6F_{13})_3$ is unique in that it is a good σ donor as well as a modest π acid. $P(C_6F_5)_3$, which is not a π acid, is a very large and very poor σ donor ligand. The calculated values of θ for PF_3, $P(CF_3)_3$, and $P(C_6F_5)_3$ are in excellent agreement with Tolman's values. The calculated value of θ for $P(CH_2CH_2C_6F_{13})_3$ is virtually the same as θ for PBu_3.

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