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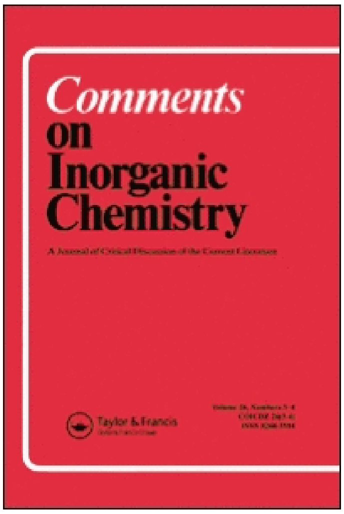

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Re-examination of the Metal Carbonyl Complex Infrared Parameter, v_{co}, and Phosphorus Ligand Parameters, pKa, $\Sigma_{\chi i}$ and $\Sigma\sigma^{ph}$, in Relation to an Evaluation of σ and Ω Components of M-P Bonds

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Re-examination of the Metal Carbonyl Complex Infrared Parameter, ν_{co}, and Phosphorus Ligand Parameters, pKa, $\Sigma\chi_i$ and $\Sigma\sigma^{ph}$, in Relation to an Evaluation of σ and π Components of M-P Bonds

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Detailed analyses of the three phosphorus ligand parameters commonly used as gauges of electronic effects in organophosphorus metal chemistry, pKa, $\Sigma\chi_i$ and $\Sigma\sigma^{ph}$, are presented in terms of their use as σ measures in M-P bonds. The Tolman ligand parameter, $\Sigma\chi_i$, is shown to contain contributions from σ, π and steric factors. Though steric effects can be ignored in the Kabachnik parameter, $\Sigma\sigma^{ph}$, which is a purer σ-parameter than $\Sigma\chi_i$ or ν_{co}, it suffers from its derivation as a Hammett parameter. It is concluded that pKa is the best choice as a σ-only parameter for phosphorus ligands. Furthermore, ν_{co} is shown to be inappropriate as a σ-only or π-only parameter, and the force constant k is deemed to be no better than ν_{co} as an electronic parameter for M-P bonding.

Key Words: *M-P bonding, s-p controversy, phosphorus ligand parameters*

A. INTRODUCTION

The long-standing controversy pertinent to the separation of ligand σ and π electronic and steric effects has been recently evaluated.[1] We

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pointed out that one of the key obstacles to separating the ligand σ and π electronic components in M-P bonding is the failure to use a proper physical parameter for metal complexes. If a parameter of a metal complex such as ν_{co}, or ${}^1J$(M-P), has a parallel response to a weak σ donor or strong π acceptor, it can not be used to distinguish the two effects by correlation analysis. A second obstacle is the suitable identification of a ligand electronic parameter such as pKa, $\Sigma\chi_i$ and $\Sigma\sigma^{ph}$, which are widely employed for the analysis of ligand effects. The nature of these basic ligand parameters is not clearly understood especially in terms of σ and π character, as compared to their use as general electronic parameters. The latter is not enough for the purpose of a quantitative evaluation of M-P bonding. To separate the π-effect from the coexistent σ-component in M-P bonding, the three well-known electronic parameters in organophosphorus metal chemistry, i.e., pKa, $\Sigma\chi_i$ and $\Sigma\sigma^{ph}$, which are usually treated as σ-measures, must be re-examined. This paper presents a detailed analyses of the three parameters in terms of their use as a σ-measure. Then the properties of the infrared parameter, ν_{co}, commonly employed in organometallic chemistry for structural and bonding analysis, are discussed.

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B. ELECTRONIC PARAMETERS

The commonly used electronic measures are pKa for σ-ability,[2] Tolman $\Sigma\chi_i$ for σ and/or mixed σ/π parameters,[2k–n,3a–i] and the Kabachnik $\Sigma\sigma^{ph}$ parameter for mainly the σ-component of phosphorus ligands.[2k–n,4] The pKa values reported in the literature have mostly been determined directly in nitromethane using trivalent phosphorus ligands, PRR_1R_2, though several values for mixed ligands were estimated according to the additive rule if the values for appropriate homogeneous ligands were known.[2b,2f–g] The Tolman electronic parameters, $\Sigma\chi_i$, found to be additive, were derived from the difference of stretching frequencies of carbonyls in $Ni(CO)_3L$ complexes of trivalent phosphorus ligands, $\Delta\nu_{co}(A_1)$, with respect to the $P(t\text{-}Bu)_3$ analogue. The Kabachnik electronic parameters, $\Sigma\sigma^{ph}$, are calculated from pKa values for (O=)P(OH)RR′ by using the Hammett linear equation: $pKa = pKa^o \text{-} \rho\Sigma\sigma$. These three electronic parameters are the ones which have been employed as electronic parameters most often in the studies of the organometallic chemistry of phosphines.

Because of the σ versus π controversy of bonding in metal phosphine compounds, the nature of $\Sigma\chi_i$ obtained from $Ni(CO)_3L$ complexes is also still being debated. As an accurately measured electronic parameter for real organometallic compounds of tertiary phosphines, $\Sigma\chi_i$ has been employed widely by researchers to investigate M-P bonding in various complexes. The general trend of increasing A_1 CO stretching frequency with increasing electronegativity of the substituent on phosphorus has been attributed to either strong π-acceptor properties or to the weak σ-donor ability of PR_3 ligands, each on the basis of the weakening of the metal-CO π-bond. This controversy was typified by the interpretation of Darensbourg and Brown[5] that the decrease in CO force constant upon substitution is due primarily to a weakening of the OC-M σ-bonding and not to an increase in π-bonding, since most phosphorus ligands have the effect of increasing the electron density on the metal. Meanwhile, the phosphorus ligand acts as a π-acceptor and lowers the energy of the π-orbitals on the metal sufficiently so that there is no net increase in M-CO π-bonding. It seems that the variations in $\Sigma\chi_i$, or $\nu_{co}(A_1)$ are mostly thought to be caused by a combination of the π-acceptor and σ-donor ability of a given PR_3 with two extremes of π-only and σ-only interpretation.[6] The steric effect, however, was usually thought not to be operative[2e–j] in $\Sigma\chi_i$, because of the spacious pseudo-T_d geometry of $Ni(CO)_3L$ and the distortionless structure of $Ni(CO)_3P(t\text{-}Bu)_3$,[7] as shown by X-ray crystallography.

To avoid a blind application of the above electronic parameters, especially to a $\sigma/\pi/\theta$ isolation process to be carried out subsequently, the above electronic parameters and the relationships among them as well as the possible steric contribution to any of them were re-examined. A better insight into their identities has been obtained, beneficial in recognizing the real role they play in correlation analyses.

Table I lists the values for the above three electronic parameters with revised Tolman $\Sigma\chi_i$ values, ${}^{FT}X$.[4b] There is little difference between the two sets of data, as demonstrated by Eq. (1) with a correlation coefficient of *r = 0.998* for 27 data points.

$$\Sigma x_i(\mathrm{cm}^{-1}) = 0.944\,{}^{FT}X + 0.08, \quad r = 0.998,\ N = 27 \qquad (1)$$

It is believed, therefore, that the additive role proposed by Tolman is correct and either of the two can be used for other correlation analyses without detectable difference. The ${}^{FT}X$ values might be more precisely measured, as 0.01 cm^{-1} precision was reported. A precision of 0.1 cm^{-1}, however, would satisfy the requirements in most correlation analyses in chemistry.

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TABLE I

Electronic parameters for various phosphorus ligands.

No.	Ligand	pKa[a]	$^{FT}\chi$[b]	$\Sigma\chi_1$[χ]	$\Sigma\sigma^{\Pi\eta}$[δ]
1	$P(mes)_3$	(6.0)[e]	8.5[q]	8.1	
2	$P(o\text{-}Tol)_3$	3.08	10.65	10.5	
3	$P(O\text{-}2,6\text{-}Me_2\text{-}Ph)_3$	(−0.4)			
4	$P(2\text{-}MeO\text{-}Ph)_3$	(9.5)[f]	1.7	2.7	
5	$P(t\text{-}Bu)_3$	11.4	0	0	−4.65
6	$P(O\text{-}t\text{-}Bu)_3$	(4.5)	12.95	12.3[q]	
7	$P(O\text{-}SiMe_3)_3$	(2.4)[g]	15.5[r]		
8	$P(Cy)_3$	9.7	1.4	0.3	−3.57
9	$P(Bz)_3$	(6.0)	10.35	10.5	−2.07
10	$P(i\text{-}Pr)_3$	(9.3)[h]	3.45	3.0	−3.9
11	$P(NMe_2)_3$	(9.4)[i]	5.95	5.7	−3.66
12	$PCyPh_2$	(5.0)[j]	9.1[q]	8.7	−2.37
13	$PBzPh_2$	(3.6)[k]	12.7[q]	12.1	−1.87
14	$P(4\text{-}MeO\text{-}Ph)_3$	4.57	10.50	9.99[q]	−2.22
15	PPh_3	2.73	13.25	12.9	−1.77
16	$P(O\text{-}2\text{-}tol)_3$	−1.83	29.05	27.9	
17	$PPh_2(CH=CH_2)$	(3.4)[l]	13.8[q]	13.1	−1.86
18	PPh_2Et	4.9	11.30	10.4	−2.28
19	PPh_2Cl	(−2.5)[m]	24.65	23.4	−0.25
20	PPh_2Me	4.57	12.10	11.2	−2.14
21	5-PhDBP	(0.5)[n]	13[g]		
22	$PPh_2(C{\equiv}CPh)$	(1.3)[p]	13.8[t]		−0.90
23	$PPh_2(OMe)$	(2.69)	16.30	15.9	−1.30
24	PEt_3	8.69	6.30	5.4	−3.30
25	$P(n\text{-}Bu)_3$	8.43	5.25	4.2	−3.66
26	$P(CH_2CH_2CN)_3$	1.37	22.35	21.9	−1.8
27	PCl_2Ph	(−7.8)[m]	36.40	33.9	1.38
28	PBr_3	(−14)[i]	25.8		(3.1)
29	$P(O\text{-}i\text{-}Pr)_3$	4.08	19.05	18.9	−0.87
30	$P(OPh)_3$	−2.0	30.20	29.1	−0.18
31	$PHPh_2$	0.03[x]	17.35[z]	16.9	−1.18
32	PCl_3	(−13)[i]	48.00	44.4	2.79
33	$PPhMe_2$	6.50	10.60	9.5	−2.40
34	$PPh(OMe)_2$	(2.64)	19.45	18.9	−0.72
35	PMe_3	8.65	8.55	7.8	−2.88
36	$P(OCH_2CF_3)_3$	(−3.5)[w]	36[u]		
37	$P(OCH_2CH_2Cl)_3$	(−0.5)[w]	29.5[q]	27.9	0.09
38	$P(OEt)_3$	3.31	21.60	20.4	−0.63
39	$P(OMe)_3$	2.60	24.10	21.9	−0.36
40	PH_2Ph	(−2.0)[x]	20.85	20.9	−0.48
41	ETPB	1.74	31.20	29.53[q]	
42	PF_3	(−9)[i]	57.8[q]	54.6	1.68
43	PH_3	(−4.3)[y]	26.3[q]	24.9	0.00
44	CO				
45	$P(CF_3)_3$		62.2[q]	58.8	2.10

[a] pKa values are taken from Refs. 2b, 2g and 2f, unless otherwise noted.

[b] Taken from Ref. 4b.

[c] Taken from Ref. 8.

[d] Taken from Ref. 4a.

[e] Calculated from Eq.(2) because all $P(X\text{-}Ph)_3$ ligands should fall on the line (see text).

[f] An average of 10.5 and 8.4, calculated from Eqs. (2) and (2) combined with (5a) according to the recorded $\upsilon_{co}(A_1)$ values of m1-L in this work.

[g] The value of 1.4 was calculated from Eq. (2) in combination with Eq. (5b). However, a value of 2.6 was estimated by other methods [Eqs. (10)–(12)].

[h] An average of 10.2, 9.3 and 8.4, calculated from Eqs. (3), (2) and (2) combined with Eq. (5b) by using the recorded. $\upsilon_{co}(A_1)$ values of c2-L in this work. An estimated value of 9.60 was reported in Ref. 2p.

[i] Estimated from Eq. (3).

[j] An average of 5.05 (via additive rule from PPh_3 and PCy_3), 4.9 [via Eq. (3)], 5.6 [via Eq. (2) and 4.6 [via Eq. (2) combined with Eq. (5b) using the new recorded $\upsilon_{co}(A_1)$ values of c2-L in this work].

[k] An average of 3.8 (by additive rule from PPh_3 and PBz_3), 3.2 [via Eq.(3)], 3.3 [via Eq. (2)] and 4.2 [via Eq. (2) combined with (5b) by using the new recorded $\upsilon_{co}(A_1)$ values of c2-L in this work].

[l] An average of three values: 3.2 [via Eq. (3)], 2.6 [via Eq. (2)] and 4.4 [via Eq.(2)combined with Eqs. (5b) and (5c) using the new recorded $\upsilon_{co}(A_1)$ values for c2-L and f3-L in this work].

[m] -2.5 for PPh_2Cl and-7.9 for $PPhCl_2$ were taken from averaged values of-2.4 [via Eq. (3)] and -2.5 (via additive rule) for the former, -7.8 [via Eq. (3)] and -8.0 (via additive rule) for the latter, respectively. The error in pKa's estimated by extrapolation might be larger for some extra weak bases such as PX_3, but this will not seriously affect the correlation analyses pertinent to the σ/π separation performed here because pKa plays only a minor role in the paramagnetic shielding parameter.

[n] The listed value was taken from Ref. 9. A different value of 3.2 was obtained by averaging 3.3, 4.6 and 1.8 calculated from Eq. (2) combined with Eqs. (5a), (5b) and (5c), respectively, using the $^{-}u_{co}(A_1)$ values in Ref. 10.

[p] An average of -0.1 and 2.6 calculated from Eqs. (3) and (2).

[q] Calculated from Eq. (1).

[r] Calculated from Eq. (5b).

[s] An average of the three values, 12.7, 10.6 and 14.9, calculated from Eqs. (5a), (5b) and (5c), respectively.

[t] Calculated from Eq. (5c).

[u] An average of the two values, 33.8 and 37.2, calculated from Eqs. (5b) and (5c).

[w] Calculated by other methods [from Eqs. (10) and (11) combined with Eq. (14)].

[x] 0.03 for PPh_2H and -2.0 for $PPhH_2$ are taken from Refs 2b, 2g and 2f; meanwhile, 0.39 for PPh_2H and -1.96 for $PPhH_2$ are calculated using the value of -4.3, the new estimated pKa for PH_3in note "y" according to the additive rule. This seems to support the re-estimation of pKa for PH_3.

[y] Reported pKa of PH_3 is -14 (Refs. 2b, 11, 12) which was calculated from kinetic data (see also Ref. 11a). The listed value of-4.3 for PH_3 was estimated by extrapolation from the following three linear correlations of pKa with ^{FT}X for three groups of ligands $PH_{3-n}R_n$(n = 0–3): pKa = A(B-^{FT}X); A = 0.647, B= 18.45 for R = n-Bu; A = 0.624 and B = 17.56 for R = Ph; A = 0.625 and B = 18.54 for R = i-Bu; three pKa's obtained are -4.2, -4.6, and -4.0. It has also been found that the pKa of PH_3 is ca.-4.2 by similar extrapolation from either $PH_{3-n}Me_n$ or $PH_{3-n}Cy_n$ (n = 3 and 2) whose pKa's and ^{FT}X are known. In addition, a value of -4.4 is obtained by averaging -5.6 and -3.2 calculated from Eqs. (2) and (3).

[z] A value of 19.0 calculated from Eqs. (5b) and (5c).

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1. pKa

The pKa values for PR_3 are usually thought to be indicative of only a σ-component because no π-interaction is involved in P-H bonding measured as $[HPR_3]^+$. A slight qualification arises from two points: (i) Solvation effect.[2a–d] It has been shown that the gas phase proton affinities (PA) do not always follow the same trends as the solution pKa's. The typical example is that the sequence $PMe_3 < PPhMe_2 < PPh_3 < PPh_2Me$ is observed for the gas phase proton affinities, but the corresponding solution pKa's are ordered as $PMe_3 > PPhMe_2 > PPh_2Me > PPh_3$. Unfortunately, the gas phase proton affinity values in the literature are very limited, and so are the adiabatic ionization energies (IE). On the other hand, pKa values were found to correlate only very roughly with PA or IE values, although the latter were thought to be preferable-measures for σ-donation ability.[2b] Moreover, some authors recently have even stated that the PA values are not appropriate measures for basicity because the differences in PA are almost entirely due to the electrostatic interaction and not to the covalent σ-donation.[13] (ii) Steric effect. The QALE method[2e–j] has claimed that there is a certain steric contribution to pKa.[1a] It is proposed here that pKa is the best choice as a measure of predominantly σ-interaction without through-space steric effects. The H-P bond involves the least bulky chemical moiety, the H atom. Even if a steric effect could possibly contribute to pKa through bonds, this would have already been reflected in the magnitudes of pKa values because pKa is a net result of inductive effects (no π-interaction involved) through bonds. The solvation effect was thought to strongly affect the interaction between protons and the phosphorus ligands; however, the reported pKa values shall not be considerably distorted by the solvation effect because most of the reported pKa values were determined in a remarkably dilute nitromethane solution (volume ratio is 100:1:0.6 for $CH_3NO_2:HClO_4:H_2O$).[21] Angelici and coworkers have observed an excellent linear relationship between the aqueous pKa's and the protonation enthalpies, ΔH_{HP}, in nonaqueous media[2k] for a wide range of PY_3 ligands. They also concluded that the differences in ΔH_{HP} are not due to steric effects. A similar correlation of pKa with $-\Delta H$, the heats of reaction for forming R_3PHgCl_2 in a nonaqueous (benzene) solution, has been observed[21] except for a few deviations due to steric interactions. Figure 1 presents the relationship between pKa and Tolman cone angle. At a glance, there seems to be a trend of increasing basicity with increased ligand size. It should also, however, be kept in mind that the bulky size of a phosphorus ligand such as $P(t\text{-}Bu)_3$ (#5) or

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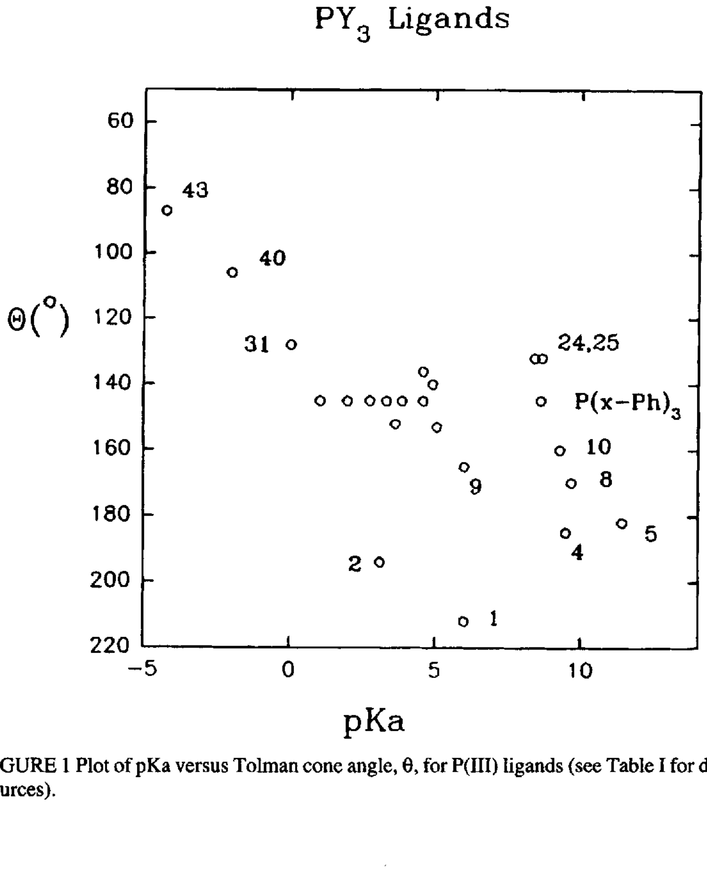

FIGURE 1 Plot of pKa versus Tolman cone angle, θ, for P(III) ligands (see Table I for data sources).

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PCy_3 (#8) is the result of large organic branches. Usually they are electron releasing groups, which certainly contribute to (increase) the basicity *through bonds*. The pKa's of two bulky ligands with electron withdrawing groups, $P(CF_3)_3$ (137°) and $P(C_6F_5)_3$ (184°), have not yet been determined. It is believed that the pKa's for these two F-substituted ligands are immeasurably low. If it is true, the bulk of organic branches could not contribute to the pKa values. In Figure 1, a class of $P(p\text{-}X\text{-}Ph)_3$ ($\theta = 145°$) ligands covers up to 7.6 pKa units with the same ligand size but different electronegativity of the *para*-groups. A common electronegative branch, the MeO- group, actually behaves as an electron releasing substituent at *para*- and *ortho*- positions (#4) on the phenyl ring (pKa = 4.57 for *para*-isomer). In contrast, the extra bulky $P(2\text{-}MeO\text{-}Ph)_3$ (194°)(#2) even has a slightly lower pKa (3.08) than the *para-* analogue. The pKa value of the bulkiest ligand P(mes)$_3$ (212°) is unknown, and the appropriate point #1 in Fig. 1 uses a value of 6.0 estimated from a linear method (see below). Thus, a bulk difference of 67° (212°–145°) corresponds only to a "contribution" of 2.2 pKa units estimated by subtracting 3.84 (for P(p-Tol)$_3$) from 6.0. If the inductive effect is taken into account by assuming that the methyl group has the same effect whether in the *para-* or *ortho-* position (actually the inductive electron-releasing power (+I) of a substituent is greater at the *ortho-* position than at the *para-* position), the appropriate pKa for P(mes)$_3$ will be estimated to be 6.06 (2.73 + 3(3.84 – 2.73)); i.e., the inductive contribution from three methyl groups would be able to increase the basicity by 3.33 pKa units from PPh$_3$ to P(mes)$_3$. Therefore, if the pKa value of 6.0 for P(mes)$_3$ is correct, the increment after the pKa value of P(p-Tol)$_3$ would be due exclusively to electronic effects through bonds and not through space. A pKa value of –4.3 for PH$_3$ in Fig. 1 was re-estimated by extrapolation from five classes of PH$_{3-n}$R$_n$ (see footnotes to Table I). Although the reported value is –14, the real pKa value of PH$_3$ is probably somewhere within –14 and –4. Therefore, it is suggested that there is a predominant σ-effect in the pKa of trivalent phosphorus ligands without steric contribution, in agreement with Hudson's conclusion.[11a] Additionally, the solvent effect does not affect the application of pKa as a σ-measure in correlation analysis.

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2. $\Sigma\chi_i$ or ^{FT}X

The correlation of ^{FT}X with pKa is presented in Fig. 2. A similar correlation was reported before with only a limited number of points (7 P(X-Ph)$_3$'s, total 9 points),[2k] and the authors concluded that ^{FT}X, i.e., ν_{co}, is basically a σ-measure. Figure 2 does show a linear trend between ν_{co} and pKa for a large proportion of phosphorus ligands, except for phosphites (#30, 16, 41, 39, 38, 37) and P(CH$_2$CH$_2$CN)$_3$ (#26). A linear regression for 19 ligands generates Eq. (2):

$$^{FT}X = 17.7 - 1.53\ \text{pKa}, \quad r = 0.980,\ N = 19 \qquad (2)$$

which is shown graphically in Fig. 3. Although many pKa values are as yet unmeasured, Eq. (2) reveals a real linear relationship between ν_{co} and pKa for a specific class of ligands. It should be noted that such a linear correlation between ν_{co} and pKa can be explained by either σ-bonding or π-bonding, as discussed in the literature.[6] In any case, several things can be inferred from Fig. 2. (i) As mentioned before, 7.6 pKa units among

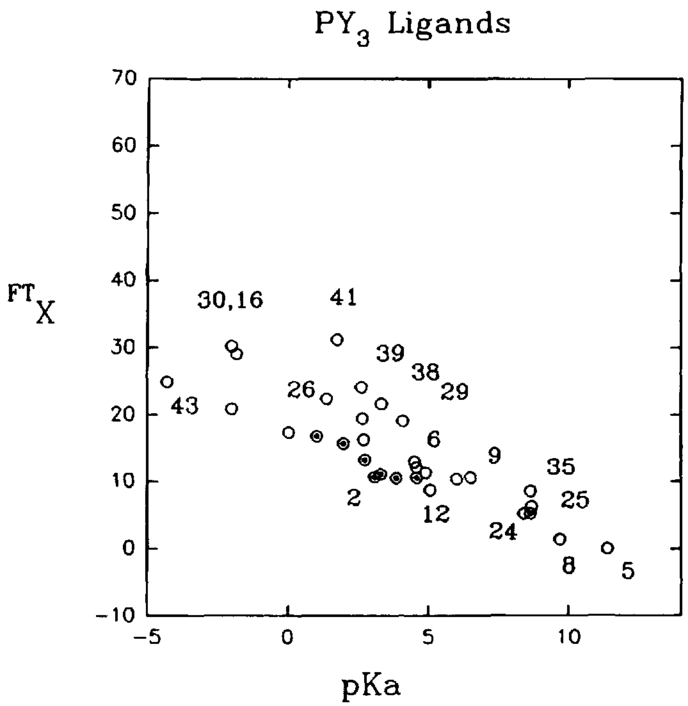

FIGURE 2 Plot of pKa versus ^{FT}X for P(III) ligands. Double points denote arylphosphines ($\theta = 145°$) (see Table I for data sources).

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$P(p\text{-}X\text{-}Ph)_3$ ligands covers half the range of the pKa's (see the double points), while the corresponding variation in $\nu_{co}(Ni(CO)_3L)$ is small for this class of ligands. Moreover, all phosphites with the same pKa values as phosphines have higher ^{FT}X values except for the very bulky P(O-t-Bu)$_3$ ligand (172°) (#6). These observations indicate that the ν_{co} parameter also contains a certain amount of π-character. (ii) The steric effect also operates in the ν_{co} parameter. First, steric size kinetically plays a definite role in substitution reactions going from $Ni(CO)_4$ to $Ni(CO)_{4-n}(PY_3)_n$, as demonstrated clearly by the linear correlation of degree of displacement (DD) with θ in Tolman's Fig. 1.[3a] He states then that "the property of the ligands which primarily determines the stability of the Ni(O) complexes is their size rather than their electronic character". Second, in the pseudo T_d geometry of $Ni(CO)_3L$, the maximum free cone space for the incom-

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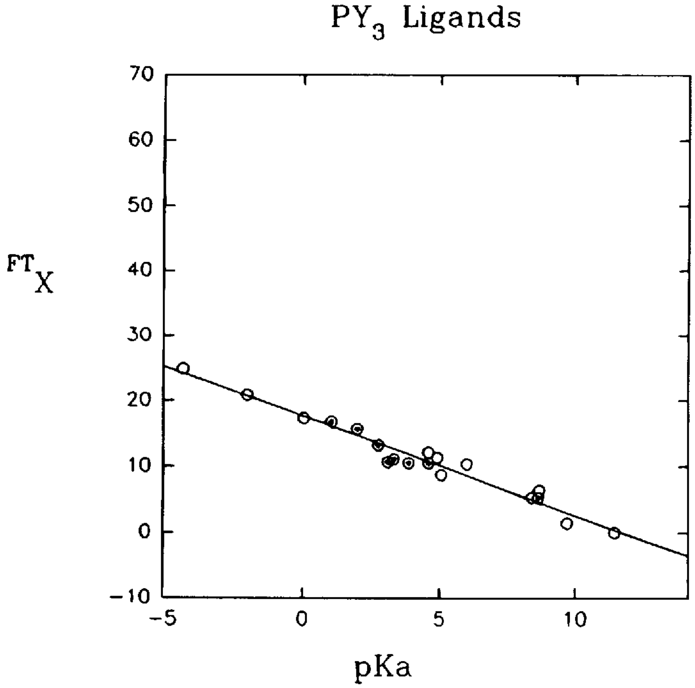

FIGURE 3 Plot of pKa versus ^{FT}X for selected P(III) ligands excluding small phosphites. Double points denote arylphosphines ($\theta = 145°$) (see Table I for data sources).

ing ligand L should be ca. 124° (2{(1/2)109.5° + [(1/2)109.5° − (1/2)95° (for CO, see Ref. 1e)]}). One can expect a steric requirement for most P(III) ligands with $\theta > 124°$. (iii) The deviation of $P(2\text{-}Me\text{-}Ph)_3$ (194°) (#2) down from the line as well as the very low v_{co} value for $P(O\text{-}t\text{-}Bu)_3$ (#6 in Fig. 2) disprove the σ-only mechanism in Ni-P bonding modified by the steric requirement. If σ-character is dominant in the Ni-P bond, the steric factors should *increase* rather than decrease v_{co} values because the weakening of the M-P bond will decrease the electron density on the metal (or depopulate the M-CO π-bonding orbital) and in turn increase v_{co}. On the other hand, if the π-interaction is dominant in the Ni-P bond, steric weakening of that Ni-P bond would indeed result in a *decrease* of v_{co} values due to a population of the CO π^* orbitals via more effective competition by CO, as in the case of $P(O\text{-}t\text{-}Bu)_3$. In other words, steric effects would shift the ν_{co} to two opposite directions in the σ and π mechanisms. As a consequence, steric effects will not evidently be reflected in the i.r. stretching frequencies of *trans* CO's *if the* σ*- and* π*-characters are comparable in M-P bonding*, as already noted.[1b] It will also be seen (later section) that three excellent linear correlations exist between ν_{co} ($Ni(CO)_3L$) and ν_{co} for the Mo-m1, c2, and f3 series although there is a significant bulky ligand repulsion in Mo-P f3, c2, or even in the m1 structures. It is firmly believed that steric effects are an inherent and *implicit* component in ν_{co} or $\Sigma\chi_i$ parameters. Thus, the ν_{co} positions for points #2 and #6 in Fig. 2 prove two points: (i) the steric character does contribute to the ^{FT}X parameter; (ii) ν_{co} is decreased by the increased d_π electron density on the metal due to the weakened Ni-P π-bonding by strong steric interaction. If the steric effect had really been contained in pKa, a σ-measure of a PZ_3 ligand, the weakened Ni-P σ bonding due to the steric requirement would have shifted ν_{co} toward increased values and point #2 should have appeared on the *right side* of the correlation line, according to Fig. 1. (Note: Both pKa and ^{FT}X have a precision of 0.01.) Therefore, a steric component should be assigned to ν_{co}, not pKa. Finally, can the correlation in Fig. 3 be a σ-only line? The answer might be yes in practice; however, as discussed above, the correlation line in Fig. 3 still originates from a combination of σ/π effects on ν_{co}. The π-effect might overlap partially and systematically on the "σ-line". The off-line points in the upper area in Fig. 2 are due to a complicated combination of σ- and π-components with an alleviation of steric effects. It must be pointed out that the nonlinear nature of Fig. 2 was used by Giering and co-workers[2c–j] as a fundamental premise, a pure σ-profile, for the QALE method. The secondary graph of d(ν_{co}) or d(ΔH) against pKa or E^o was treated as π-electronic profiles. When ΔH, measuring the total bonding ability of P(III), is used as one variable in correlation analysis for ligand effects, the second variable must be a single element parameter, σ-only, or π-only or θ. The previously observed two-parameter linear dependence of ΔH on f(θ and ν_{co})[1a] actually encompasses the π-character contribution from the stretching frequency term. The poor two-parameter dependence of ΔH on θ and a σ-dominant parameter, such as pKa, is most likely due to the lack of the appropriate π-component in the later set.[1a] Therefore, $\Sigma\chi_i$ already contains all three factors, σ, π and steric bulk, in which the steric effect is implicit and the σ-component is slightly dominant. Thus, Fig. 3 (not Fig. 2) can be approximately treated as a σ-line, the way many previous proponents of the σ-only viewpoint did in their work.

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3. $\Sigma\sigma^{ph}$

The Kabachnik σ^{ph} parameters[4a] were derived from aqueous pKa values for (O=)P(O-H)RR′ via the Hammett equation, and are usually used as a σ-measure for the R groups. The advantage of this parameter is its extensive scale (more values than for pKa are available for phosphorus ligands[4a]). However, some other features of $\Sigma\sigma^{ph}$ should be noted. (i) The parent P atom is pentavalent, not trivalent, and all s and p orbitals are electronically saturated, so the available orbitals for any "π-back donation" from R groups are 3d orbitals. The $\Sigma\sigma^{ph}$ values for H and alkyl cover up to 4.65 units (from 0.00(H) to –4.65 (t-Bu)), while the electronic effects of such a group correspond to only a very small difference in electronegativities. The typically electronegative $P(OPh)_3$ ligand has a small negative $\Sigma\sigma^{ph}$ value, close to zero for H, and exhibits an electron releasing ability with respect to H. The halogens and the CF_3 group have positive σ^{ph} values (a less positive value occurs for fluorine despite its higher electronegativity). All of these features imply that the acidity of the H-O group in the model compound is sensitive to both I and M effects.[1c,14] The +M effect decreases the σ^{ph} values (toward the negative direction) in the cases of phosphites (e.g., –0.63 for $P(OEt)_3$) and fluorine (1.68 for PF_3, smaller than 2.79 for PCl_3) as an electron-donating group does. This is better attributed to p_π-p_π conjugation, i.e., the resonance component contributes to σ_{ph}, as stated in the original review.[4a] The resonance component will not change the σ-measure of the Kabachnik parameter to π, but acts in the sense of σ-donation, as happened in Hammett constants, σ^H.[1c] In contrast, the Tolman χ_i value for fluorine is normally higher than for chlorine and bromine, and $P(OPh)_3$ has a larger χ_i value (30.2) than hydrogen (24.9). This suggests that in the σ^{ph} parameter, there is a complicated and important resonance effect cooperating in the σ-pathway; while in χ_i or ν_{co}, the σ-character is separate without serious influence from resonance effects. This is why the χ_i or ν_{co} parameters appear to be a σ-measure in many observations.[1a] (ii) The O-H bond in the (O=)P(O-H)RR′ molecule is one more bond away from the P-R interactions than in the $[HPR_3]^+$ case. An inductive influence on the O-H bond from the different substituents, R_i, should be diminished compared with that on $[H\text{-}PR_3]^+$ or $[(OC)_3]Ni\text{-}PR_3$ (*vide infra*). Thus, $\Sigma\sigma^{ph}$ will not be as good as pKa in terms of being a σ-electronic parameter for PR_3. An additional weakness similar to the Hammett constant, σ^H, as discussed earlier,[1c] is its nature as an experimental-error-absorbed parameter. (iii) It can be believed that the steric effect on $\Sigma\sigma^{ph}$ is small.[4a] The remote distance of the O-H bond from

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the substituents should lessen any possible steric interaction. (iv) In the structure of the model compound, (O=)P(O-H)RR′, the limited number of substituents (R or R′) is two. Whether the additive role is applicable for tertiary phosphines in calculating $\Sigma\sigma^{ph}$ for up to *three* substituents has not been verified. The correlation of $\Sigma\sigma^{ph}$ with pKa is shown in Fig. 4. It looks very similar to Fig. 2 with the linearity being slightly improved. In agreement with the above discussion, steric factors can be reasonably diminished or eliminated along both x and y coordinates in Fig. 4; the π-character operates much less significantly along the y axis in Fig. 4 than it does in Fig. 2. These features suggest that Fig. 4 is more of a σ-correlation. A similar linear regression for Fig. 5 generates Eq. (3):

$$\Sigma\sigma^{ph} = -0.290 \text{ pKa} - 0.939, \quad r = 0.984, N = 17 \qquad (3)$$

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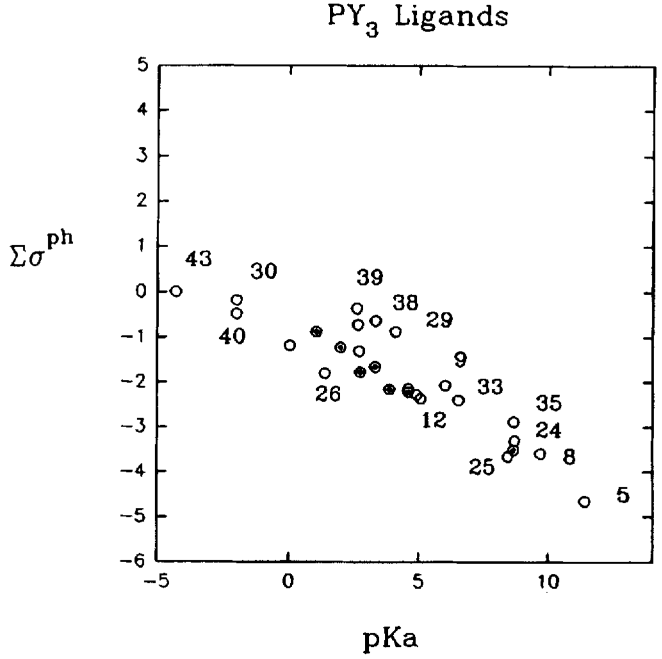

FIGURE 4 Plot of pKa of P(III) ligands versus the Kabachnik parameter, $\Sigma\sigma^{ph}$. Double points denote arylphosphines (θ = 145°) (see Table I for data sources).

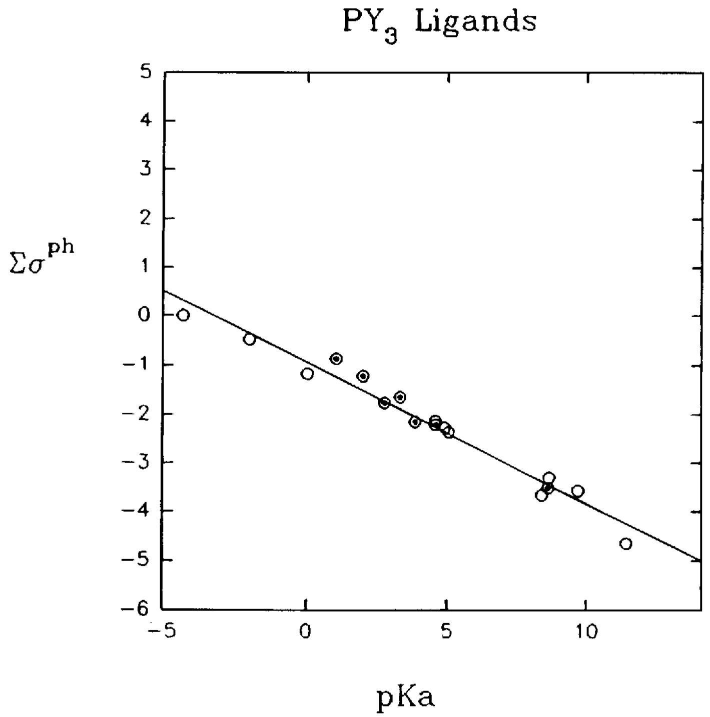

FIGURE 5 Plot of pKa for selected P(III) ligands excluding small phosphites versus the Kabachnik parameter, $\Sigma\sigma^{ph}$. Double points denote arylphosphines ($\theta = 145°$) (see Table I for data sources).

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Two points for $P(OPh)_3$(#30) and $P(CH_2CH_2CN)_3$(#26) fall under the line, implying that *if the two* $\Sigma\sigma^{ph}$ values are not incorrect, then the ν_{co} parameter in Fig. 2 is more sensitive to a ligand σ-effect than the σ^{ph} is in Fig. 4. Similarly, many phosphites deviate upward from the line, reflecting their weak σ- or strong π-acceptor properties. So, if Fig. 3 and Fig. 5 reasonably reflect an inherent σ-correlation between pKa and ν_{co} or σ^{ph}, the latter two parameters still include some non-σ effects.

4. Relationship Between ^{FT}X and $\Sigma\sigma^{ph}$

To obtain further insight into the difference between ν_{co} and $\Sigma\sigma^{ph}$, the interdependence of the two parameters was re-examined in Fig. 6. This is like Tolman's Fig. 2 (only 9 points there).[8] The data for ^{FT}X are taken

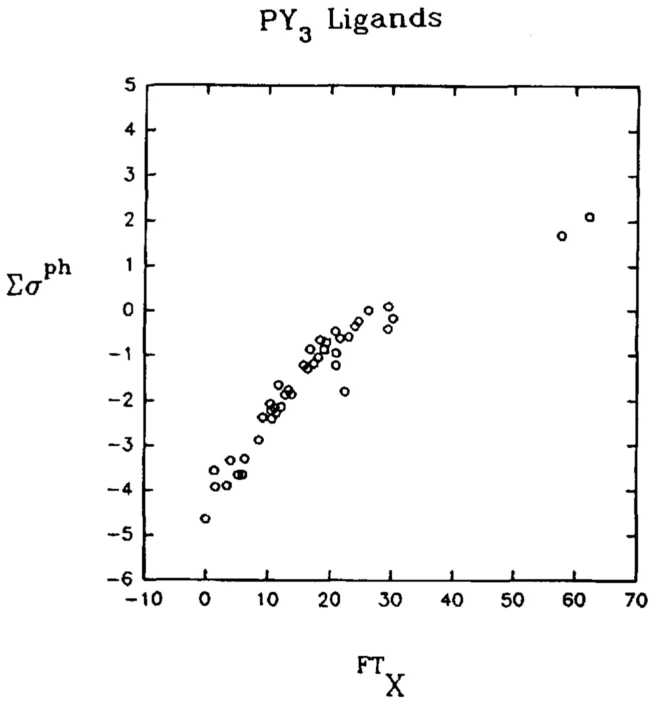

FIGURE 6 Correlation between CO stretching frequencies (A_1) for $Ni(CO)_3(PY_3)$ and the Kabachnik parameter, $\Sigma\sigma^{ph}$. ^{FT}X is taken simply because of the number of data available (see text). This figure uses more data from the literature.

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here simply because of the larger number available than for χ_i. A curve-fitting equation (4) describes the relationship between ^{FT}X and $\Sigma\sigma^{ph}$.

$$\Sigma\sigma^{ph} = 0.944(^{FT}X)^{1/2} - 5.12, \quad r^2 = 0.954, N = 42 \qquad (4)$$

Obviously, the coefficient for the ^{FT}X term in Eq. (4) will approach one if the Tolman's $\Sigma\chi_i$ parameter is used [see Eq. (1)]. The points for $P(CH_2CH_2CN)_3$ (#26) and PCy_3 (#8) seriously deviate from the curve, demonstrating again that $P(CH_2CH_2CN)_3$ seems to be a very anomalous ligand[2e–j] (see Fig. 7). Notably, this relationship becomes more complicated after the inclusion of several more points for the chlorophosphines (see Fig. 7). Based on the previous analyses for individual parameters associated with pKa, the curving in Fig. 6 is most likely caused by the

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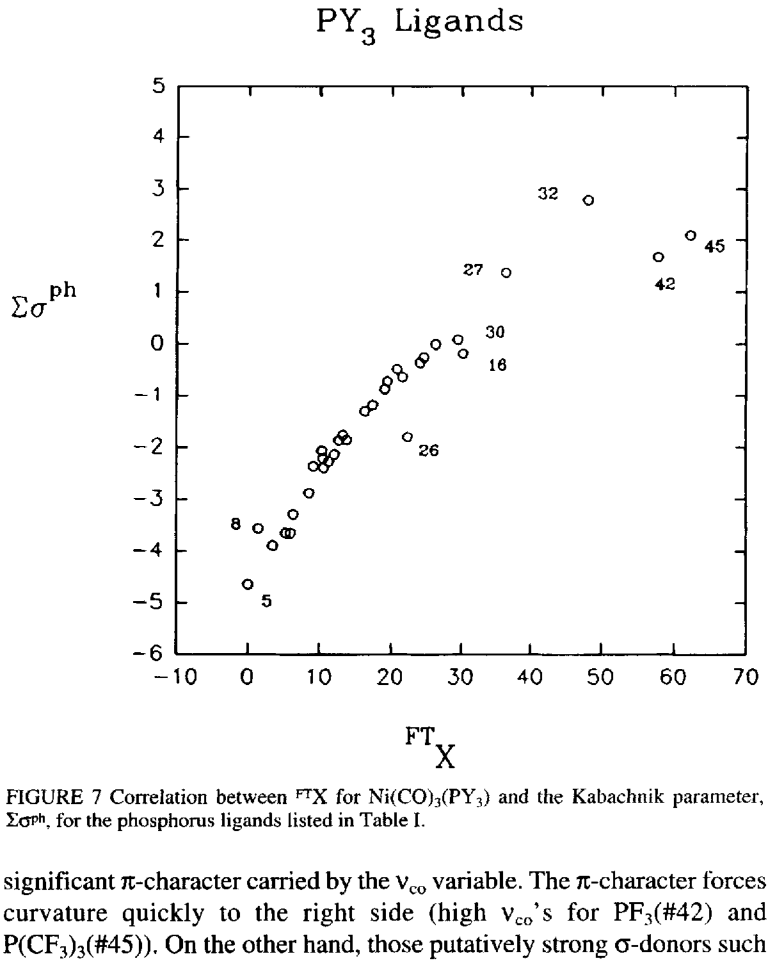

FIGURE 7 Correlation between ${}^{FT}X$ for $Ni(CO)_3(PY_3)$ and the Kabachnik parameter, $\Sigma\sigma^{ph}$, for the phosphorus ligands listed in Table I.

significant π-character carried by the ν_{co} variable. The π-character forces curvature quickly to the right side (high ν_{co}'s for PF_3(#42) and $P(CF_3)_3$(#45)). On the other hand, those putatively strong σ-donors such as PEt_3 have not pushed the curve toward the left side (they would do so if the σ-only interaction were dominant) but exhibit a slight tendency toward the high ν_{co} direction. This suggests that these alkylphosphine ligands might also have considerable π-characters.[1e] Of particular importance is the point for PCl_3(#32). This ligand has been assigned *qualitatively* as a weak σ- and weak π-ligand.[1d] It is predicted here that the weaker σ-only ligands PBr_3 or PI_3 would lie somewhere along an extrapolation from the strong σ-donors such as $P(alkyl)_3$. The estimated $\Sigma\sigma^{ph}/{}^{FT}X$ values for PBr_3 and PI_3 are 3.1/41 and 3.3/39, respectively. If the second curve is drawn along $P(alkyl)_3$ toward PCl_3 (#32), the two curves in Fig. 7 [which coincide at one end (bottom) and open at the other end (top)] exactly reflect the electronic difference between ν_{co} and $\Sigma\sigma^{ph}$, as discussed in previous sections; that is, the i.r. stretching frequency contains more π-character while Kabachnik's parameter, $\Sigma\sigma^{ph}$, contains less or no π-character. The steric effects are implicit on ν_{co} (Ref. 1b and next section) and do not affect σ^{ph}. As a consequence, ν_{co}, or $\Sigma\chi_i$ cannot be used as a good σ-measure in detailed correlation analyses since they are parameters of combined σ- and π-components.

C. I.R. PARAMETERS FOR $MO(CO)_{6-N}L_N$ COMPLEXES

1. Stretching Frequency ν_{co}

The i.r. bands in the carbonyl region have been important parameters for indirectly evaluating the electronic nature of M-P bonding since the 1950's. Cotton and Kraihanzel's detailed theoretical treatment[15] of various geometries for metal carbonyl complexes was a major step forward in i.r. studies of organometallic compounds. The "π-acceptor series" was then set up according to the results of this type of calculation. Consequently, many further studies of σ- and π-bonding ability for organic ligands (mainly N and P donors) were carried out on the basis of CO i.r. parameters.[5] The first scale of σ- and π-parameters for ligands was developed by Graham[16] using the Cotton–Kraihanzel model for $Mn(CO)_5L$ and $Mo(CO)_5L$, as described earlier.[1a] The π-acceptor series and the σ/π scale based on the i.r. model are still cited in recent inorganic textbooks[6a] and monographs.[3h]

As pointed out in previous papers, it seems that the i.r. stretching frequencies of *trans* CO's are not suited for studying the σ/π ability of *trans* ligands, especially in a quantitative sense.[1a,d] Reported assignments for i.r. bands vary, and in many cases, such as for nitrogen or phosphorus complexes of $M(CO)_5L$ and *cis*-$M(CO)_4L_2$ geometries, poor resolution very often negates band assignments. In some other cases, either more[17] or fewer[18] bands than expected have been observed (distorted geometry may also lift degeneracy and cause band splitting). Reported values for $\nu_{co}(A_1$ highest), the sharpest band, for the same compound differ by up to 16–25 cm^{-1} (this is not from a single fortuitous error) which is about 20% of the whole range of $\nu_{co}(A_1)$ variation (see footnotes to Table IV). In the literature, most authors just reported the observed i.r. bands with or without the assignments, and only some calculated the stretching

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force constants. It is also noted here that the order of force constants is sensitive to the band assignments (see footnote "b" for Table II). Therefore, it is felt that further examination of the ν_{co}'s and k's of the title complex series in terms of σ/π characters is worthwhile.

The data for all three sets of complexes $Mo(CO)_5L$, *cis*-$Mo(CO)_4L_2$ and *fac*-$Mo(CO)_3L_3$ are compiled in Tables II–IV. The force constants were recalculated by computer program based on Cotton and Kraihanzel's theoretical treatment.[15] Several critical points about the

TABLE II

CO i.r. parameters for $Mo(CO)_5PY_3$ derivatives.[a]

No.	Ligand	$A_1^{(2)}$	B_1	$A_1^{(1)}$	E	k_1	k_2	k_1
1	$P(mes)_3$							
2	$P(o\text{-}Tol)_3$							
3	$P(O\text{-}2,6\text{-}Me_2\text{-}Ph)_3$							
4	$P(2\text{-}MeO\text{-}Ph)_3$	2068m	1985w	1937s	1937[b]	15.36	15.79	0.32
5	$P(t\text{-}Bu)_3$	2064m		1935s	1935[b]	15.33	15.75	0.31
6	$P(O\text{-}t\text{-}Bu)_3$							
7	$P(O\text{-}SiMe_3)_3$	2075m	1987s	1947s	1947[b]	15.60	15.89	0.31
8	$P(Cy)_3$	2066	1989	1941	1937[c]	15.43	15.78	0.31
9	$P(Bz)_3$	2071m		1943s	1943[d]	15.45	15.87	0.31
10	$P(i\text{-}Pr)_3$							
11	$P(NMe_2)_3$	2073	1986	1949	1942	15.56	15.86	0.32
12	$PCyPh_2$							
13	$PBzPh_2$	2070m		1942s	1942[d]	15.44	15.85	0.31
14	$P(4\text{-}MeO\text{-}Ph)_3$							
15	PPh_3	2075	1988	1949	1949[e,f]	15.55	15.95	0.31
16	$P(O\text{-}2\text{-}tol)_3$							
17	$PPh_2(CH=CH_2)$							
18	PPh_2Et	2073m	1985w	1952sh	1945vs[e]	15.61	15.90	0.31
19	PPh_2Cl	2081	2020	1969	1962[g]	15.86	16.12	0.29
20	PPh_2Me	2074m	1985w	1951sh	1946vs	15.59	15.91	0.31
21	5-PhDBP	2073	1993sh	1952	1952[h]	15.58	15.98	0.30
22	$PPh_2(C\equiv CPh)$							
23	$PPh_2(OMe)$	2075m	1984s	1950vs	1950[d]	15.56	15.97	0.30
24	PEt_3	2069	1980	1945	1944	15.48	15.87	0.30
25	$P(n\text{-}Bu)_3$	2070	1982	1943	1938	15.47	15.81	0.32
26	$P(CH_2CH_2CN)_3$	2077		1965sh	1952vs[f]	15.82	15.99	0.30
27	PCl_2Ph	2086	2011	1969	1969[d]	15.85	16.23	0.29
28	PBr_3							
29	$P(O\text{-}i\text{-}Pr)_3$							
30	$P(OPh)_3$	2084	2000	1974	1965	15.95	16.17	0.29
31	$PHPh_2$							
32	PCl_3	2095	2022	2000	1986	16.36	16.46	0.27
33	$PPhMe_2$	2068w	1982w	1940vs	1940	15.41	15.82	0.31

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TABLE II

(*continued*)

No.	Ligand	$A_1^{(2)}$	B_1	$A_1^{(1)}$	E	k_1	k_2	k_1
34	$PPh(OMe)_2$	2070w	1988w	1946vs	1946[i]	15.49	15.90	0.30
35	PMe_3	2071	1986	1952	1943	15.61	15.86	0.31
36	$P(OCH_2CF_3)_3$							
37	$P(OCH_2CH_2Cl)_3$							
38	$P(OEt)_3$	2080	1995	1966	1952	15.84	16.00	0.31
39	$P(OMe)_3$	2081	1995	1968	1953[f]	15.88	16.02	0.31
40	PH_2Ph							
41	ETPB	2085	2001	1962	1962	15.75	16.15	0.30
42	PF_3	2103	2026	2011	1989[j]	16.57	16.53	0.28
43	PH_3	2081	1994	1962	1950	15.78	15.99	0.32

[a] The stretching frequency data are taken from three main sources: Ref. 15a–f, 5 and 19, unless otherwise indicated; the assignment of the bands has been well studied for the highest $A_1^{(2)}$ and lowest E mode. The $A_1^{(1)}$ and E are very close and often unresolvable, so an additional value from the $A_1^{(1)}$ band has to be taken as the E mode to perform the force constants calculation if this band could not be observed. The largest difference in the $A_1^{(2)}$ mode is 5 cm^{-1} for different authors or solvents; so a set of values at the middle position is taken from the literature values, such as for PPh_3.

[b] Shoulders at 1910 cm^{-1} for $Mo(CO)_5L$ (#4 and #5) and 1905 cm^{-1} for m1-#7 were observed; if these shoulders are assigned as the E modes, the calculated k_1 would be greater than k_2. For example, k_1 and k_2 would be 15.67 and 15.45, respectively, when using 1905 cm^{-1} as the E mode for m1-#7.

[c] Taken from Ref. 18.

[d] Recorded in this work in methylene dichloride.

[e] Ref. 20.

[f] Ref. 21.

[g] Taken from Ref. 22.

[h] Taken from Ref. 23.

[i] Ref. 24.

[j] Ref. 25.

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assignment of bands and calculation of k's have been noted at the bottom of the tables. More information is available in Figs. 8–10.

Three linear correlations of the A_1 CO stretching frequency of each series, $Mo(CO)_5L$, *cis*-$Mo(CO)_4L_2$ or *fac*-$Mo(CO)_3L_3$, with the Tolman electronic parameters, $\Sigma\chi_i$, or $\nu_{co}(A_1)$ of $Ni(CO)_3L$ complexes are expressed by Eqs. (5). They must reflect some common factors which influence this traditional parameter.

$$\nu_{co}(A_1^{(2)})(cm^{-1}) = A + B^{FT}X, \tag{5}$$

$$\text{ml}: \ (Mo(CO)_5P) \quad : A = 2065, B = 0.63, (r = 0.976, N = 26) \tag{5a}$$

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TABLE III

CO i.r. parameters for *cis*-$Mo(CO)_4L_2$ derivatives.[a]

No.	Ligand	$A_1^{(2)}$	$A_1^{(1)}$	B_1	B_2	k_1	k_2	k_i
1	$P(mes)_3$							
2	$P(o\text{-}Tol)_3$							
3	$P(O\text{-}2,6\text{-}Me_2\text{-}Ph)_3$							
4	$P(2\text{-}MeO\text{-}Ph)_3$							
5	$P(t\text{-}Bu)_3$							
6	$P(O\text{-}t\text{-}Bu)_3$							
7	$P(O\text{-}SiMe_3)_3$	2026m	1920sh	1904vs	1880sh^{b}	14.66	15.41	0.39
8	$P(Cy)_3$	2007		1863^{c}				
9	$P(Bz)_3$	2018m		1886vs^{b}				
10	$P(i\text{-}Pr)_3$	2011m	1942m	1896s	1872s^{b}	14.52	15.24	0.36
11	$P(NMe_2)_3^{d}$	2022	1917	1903	1900	14.94	15.35	0.36
12	$PCyPh_2$	2019m	1932m	1884s	1877s^{b}	14.64	15.16	0.41
13	$PBzPh_2$	2020m	1918s	1907s	1876sh^{b}	14.58	15.41	0.36
14	$P(4\text{-}MeO\text{-}Ph)_3$							
15	PPh_3^{b}	2022	1926	1906	1902	14.96	15.38	0.36
16	$P(O\text{-}2\text{-}tol)_3$							
17	$PPh_2(CH{=}CH_2)$	2019m	1933sh	1905s	1872sh^{b}	14.52	15.39	0.37
18	PPh_2Et	2017	1922	1896	1896^{b}	14.88	15.25	0.37
19	PPh_2Cl	2035	1950	1925	1907^{b}	15.04	15.66	0.35
20	PPh_2Me	2020	1925	1902	1891	14.81	15.34	0.37
21	5-PhDBP	2019	1930	1908	1908^{f}	15.04	15.37	0.34
22	$PPh_2(C{\equiv}CPh)$							
23	$PPh_2(OMe)$	2025m		1912s^{b}				
24	PEt_3	2016	1916	1895	1896	14.86	15.24	0.36
25	$P(n\text{-}Bu)_3^{g,c}$	2013	1910	1895	1879	14.63	15.24	0.37
26	$P(CH_2CH_2CN)_3$	2025m	1939s	1930s	1930^{b}	15.33	15.62	0.29
27	$PCl_2Ph^{g,a}$	2052m	1980s	1960s	1942s^{b}	15.53	16.11	0.30
28	PBr_3							
29	$P(O\text{-}i\text{-}Pr)_3$	2029	1946	1918	1887^{b}	14.74	15.57	0.36
30	$P(OPh)_3$	2047	1958	1943	1935	15.45	15.90	0.33
31	$PHPh_2$	2028	1938	1922	1913	15.11	15.58	0.33
32	PCl_3^{d}	2072	2004	1994	1986	16.18	16.56	0.25
33	$PPhMe_2$	2011	1912	1895	1878	14.60	15.23	0.36
34	$PPh(OMe)_2$	2030m	1939s	1915sh	1915^{b}	15.16	15.51	0.35
35	PMe_3^{d}	2016	1910vs	1896vs	1874sh	14.56	15.27	0.38
36	$P(OCH_2CF_3)_3$	2052m	1960sh	1950s	1935sh^{b}	15.64	15.99	0.35
37	$P(OCH_2CH_2Cl)_3$	2040m	1952s	1929sh	1929^{b}	15.37	15.71	0.34
38	$P(OEt)_3^{c}$	2031m	1934sh	1913s	1913^{b}	15.17	15.46	0.37
39	$P(OMe)_3$	2037	1945	1926	1921	15.25	15.67	0.34
40	PH_2Ph							
41	ETPB[a]	2044m	1952sh	1932vs	1932^{b}	15.42	15.76	0.34
42	PF_3^{e}	2086	2013	2010	1989	16.23	16.82	0.26
43	PH_3	2036	1946	1932	1923	15.26	15.72	0.33

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[a] The υ_{co} values are taken from Ref. 15a–f, 19, 26, 27, 17, unless otherwise noted; superscripts in the second column indicate other sources. The largest difference in the $A_1^{(2)}$ υ_{co}

$$c2 : (cis\text{–}Mo(CO)_4P_2) : A = 2004, B = 1.42, (r = 0.975, N = 43) \quad (5b)$$

$$f3^*: (fac\text{–}Mo(CO)_3P_2): A = 1905, B = 2.82, (r = 0.990, N = 23) \quad (5c)$$

*Simple A_1 model only for *fac*-(C_{3v})-derivative.

Of importance is the fact that the steric interaction is more severe in f3 geometry and even considerable in $M(CO)_5L$ compared to $Ni(CO)_3L$,[1e] but this is never reflected obviously in the ν_{co} values.[1b] Thus, it is inferred that in the M-P bonds not only the σ-character is operating but also that the π-character plays an important role because steric weakening of the M-P σ-bonding would certainly decrease the electron density on the metal and in turn depopulate CO π^* orbitals. Consequently, the ν_{co} values should remain high. In other words, if the σ-only theory is correct, the three correlation lines in Figs. 8–10 would not be linear. A curving-up at the low frequency end should be expected, most seriously in the f3-Mo/Ni plot (Fig. 10). On the other hand, if the π-only theory is operative, then the steric weakening of π-bonding in the M-P bonds would lead to a larger population of CO π^* orbitals. Conversely, a curving-down might have occurred at the left end of the correlations. Therefore, there must be a cooperation of both σ- and π-characters in M-P bonding, which balances the expected shift of ν_{co} toward the two opposite directions. And *as a consequence of such a balance, the points at the left end have moved up along the lines due to steric effects*. Three plots in Fig. 11 are drawn for the PY_3 ligands whose Mo complexes are all known and characterized by i.r. spectroscopy. The steep dropping-down of the f3 line, especially for $P(alkyl)_3$ ligands, may indicate that in the most congested f3 geometry, Mo-P π-bonding is greatly decreased, resulting in a greater d-electron population in the *trans* M-CO bonds. A

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is up to 25 cm^{-1} (such as for the $PPhMe_2$ case) from different authors; usualy the set of values in the middle position is taken if the i.r. data reported several times for the same complex. More c2 complexes were measured by i.r. in Ref. 27, which are not included in this table but have been used in plotting [Fig. 9 and Eq. (5b)].

[b] Recorded in this work.

[c] Ref. 18.

[d] Ref. 28.

[e] Ref. 25.

[f] Ref. 10.

[g] Ref. 29.

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TABLE IV

CO i.r. parameters for *fac*-$Mo(CO)_3L_3$ derivatives.[a]

No.	Ligand	A_1	E	k_1	k_i
1	$P(mes)_3$				
2	$P(o\text{-}Tol)_3$				
3	$P(O\text{-}2,6\text{-}Me_2\text{-}Ph)_3$				
4	$P(2\text{-}MeO\text{-}Ph)_3$				
5	$P(t\text{-}Bu)_3$				
6	$P(O\text{-}t\text{-}Bu)_3$				
7	$P(O\text{-}SiMe_3)_3$				
8	$P(Cy)_3$				
9	$P(Bz)_3$				
10	$P(i\text{-}Pr)_3$				
11	$P(NMe_2)_3$				
12	$PCyPh_2$				
13	$PBzPh_2$	1922	1858	14.27	0.326
14	$P(4\text{-}MeO\text{-}Ph)_3$				
15	PPh_3[b,c]	1948	1848	14.30	0.511
16	$P(O\text{-}2\text{-}tol)_3$	1984	1904	15.06	0.419
17	$PPh_2(CH = CH_2)$	1936	1837	14.13	0.503
18	PPh_2Et	1932	1827	14.01	0.531
19	PPh_2Cl[c]	1971	1883	14.78	0.457
20	PPh_2Me[b]	1937	1842	14.19	0.483
21	5-PhDBP	1947	1853[d]	14.35	0.481
22	$PPh_2(C \equiv CPh)$	1944	1851	14.31	0.475
23	$PPh_2(OMe)$[e]	1949	1857	14.40	0.471
24	PEt_3[b]	1926	1820	13.91	0.535
25	$P(n\text{-}Bu)_3$[b]	1922	1816	13.85	0.533
26	$P(CH_2CH_2CN)_3$	1937	1821	13.98	0.587
27	PCl_2Ph	2016	1943[c]	15.64	0.389
28	PBr_3				
29	$P(O\text{-}i\text{-}Pr)_3$	1966	1876	14.68	0.465
30	$P(OPh)_3$[b,e]	1989	1911	15.16	0.409
31	$PHPh_2$	1965	1869[f]	14.60	0.495
32	PCl_3[b]	2040	1983	16.19	0.309
33	$PPhMe_2$[b]	1935	1830[e]	14.06	0.532
34	$PPh(OMe)_2$	1963	1874[e]	14.64	0.460
35	PMe_3[b]	1931	1830	14.04	0.511
36	$P(OCH_2CF_3)_3$	2010	1931	15.48	0.419
37	$P(OCH_2CH_2Cl)_3$	1977	1889	14.87	0.458
38	$P(OEt)_3$[b]	1961	1867	14.56	0.484
39	$P(OMe)_3$[b]	1970	1880[e]	14.74	0.466
40	PH_2Ph				
41	ETPB	1988	1904	15.08	0.440
42	PF_3[g]	2064	2011[b]	16.62	0.291
43	PH_3	1971	1892[b]	14.87	0.411

[a] Most of the i.r. spectra in this table were measured in methylene dichloride [f3-PPh_3 and f3-$P(CH_2CH_2CN)_3$ complexes were recorded in nujol] in this work, unless otherwise

slight curving-up at the left ends of the c2 and m1 lines may suggest the attenuated M-P σ-bonding by steric hindrance, because $A_1^{(2)}$ bands in c2 and m1 complexes are basically a *cis*-parameter and respond more to M-P σ-bonding. The A_1 mode in f3 geometry contains both *trans*- and *cis*- influences.

If the M-P σ-bonding is paramount, then the f3 line shape should be similar to c2's and m1's. Therefore, σ- and π-bonding have comparable contributions to the M-P bond in both $Ni(CO)_3L$ and Mo complexes. Interestingly, it is also noted that the slopes of the three lines in Figs. 8–10 are in the ratio 1.00:2.25:4.48, which is more like 1:2:4 than 1:2:3 which was predicted earlier.[29b] In fact, the original gradients reflect the re-distribution of transferred electrons to the CO ligands through metal from the *trans* phosphorus ligands, according to the calculation:

$M(CO)_mL_n$	m	n	[m(Ni)/m(Mo)]n	Obs. Slopes
$Ni(CO)_3L$	3	1		
$Mo(CO)_5L$	5	1	0.6	0.63
$Mo(CO)_4L_2$	4	2	1.5	1.42
$Mo(CO)_3L_3$	3	3	3.0	2.82

Thus the $\nu_{co}1(A_1)$ can be simply expressed as a function of n and ^{FT}X for $Mo(CO)_{6-n}(PY_3)_n$ complexes:

$$\nu_{co}(A_1)(n,{}^{FT}X) = A + (3n/6 - n)^{FT}X \qquad (6)$$

$$m1: \quad A = 2071 \qquad (6a)$$

$$c2: \quad A = 2004 \qquad (6b)$$

$$f3: \quad A = 1905 \qquad (6c)$$

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noted. Two sharp-lined bands are readily and unambiguously observed and assigned. Some υ_{co} values reported elsewhere are noted in the second column. The variation of the A_1 mode for the same complex was up to 16 cm^{-1} for different authors or solvents, and thus the middle values are taken when the literature data are needed.

[b] Ref. 19, 29b and 24.

[c] Ref. 30.

[d] Ref. 10.

[e] Ref. 31.

[f] Ref. 32.

[g] Ref. 25.

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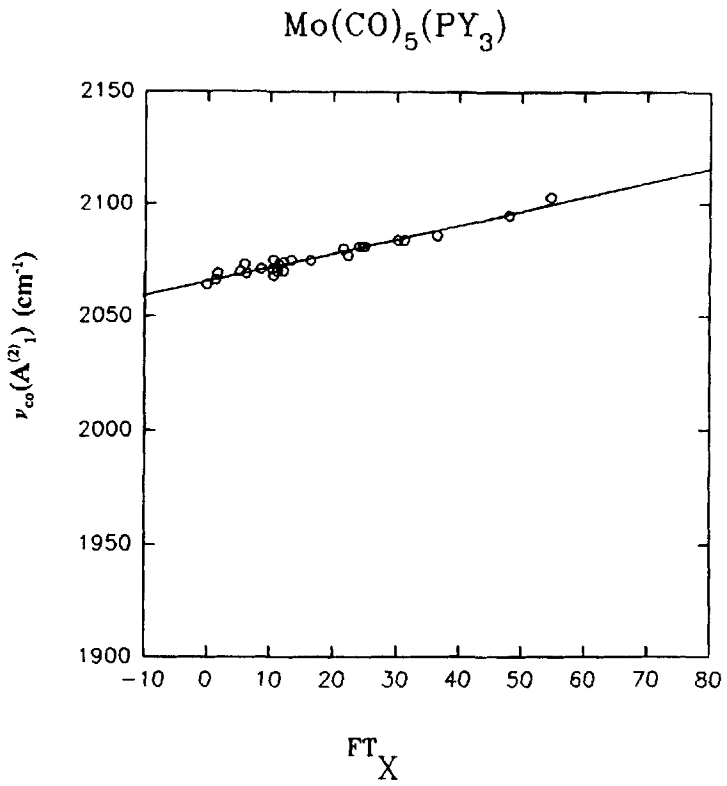

FIGURE 8 Correlations between $\nu_{co}(A_1)$ for $Mo(CO)_5(PY_3)$ complexes and ^{FT}X from $Ni(CO)_3(PY_3)$ (see Table II and Table I for data sources).

A correlation coefficient of *0.997* from a complete set of 83 data points indicates that Eq. (6) is a viable one (see Fig. 12).

It should be pointed out that although these results reasonably support the σ-only theory, the π-pathway is not ruled out by any means.

On the basis of the three excellent correlations, some unreported ^{FT}X values can be indirectly calculated from Eq. (5) or (6) with confidence. Also, Eq. (5) or (6) suggests that other values for A_1 CO stretching frequencies for any phosphorus-metal-carbonyl complexes may be estimated for pseudo-octahedral or tetrahedral or even square-planar geometries. Actually, some analogous linear relationships between ν_{co}'s for different metal complexes have been reported.[2j]

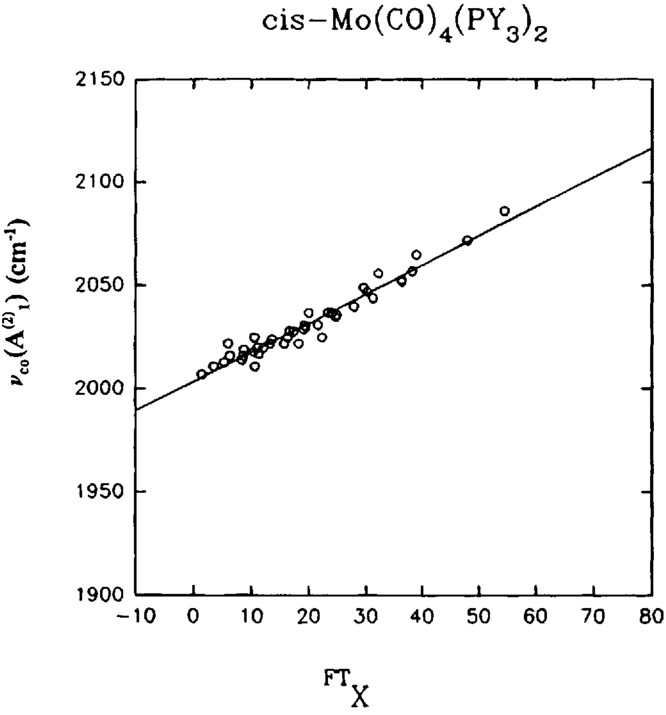

FIGURE 9 Correlations between $\nu_{co}(A_1)$ for *cis*-Mo(CO)$_4$(PY$_3$)$_2$ complexes and ^{FT}X from Ni(CO)$_3$(PY$_3$) (see Table III and Table I for data sources).

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2. Stretching Force Constants

The force constant, k, was once recommended as a better parameter for correlation analysis than ν_{co}.[15] Plots of ν_{co} versus k_2(*cis*) or k_1(*trans*) demonstrate that there is no evident advantage in using force constants rather than stretching frequencies. As seen from Figs. 13 and 14, as well as from their corresponding equations (7), (8) and (9), all ν_{co} bands and k's are related in a linear fashion.

$$\nu_{co}(A_1^{(2)})(\mathrm{ml}) = 44.92k_2 + 1358 \quad (r = 0.978, N = 26) \quad (7a)$$

$$\text{or} \quad = 29.83k_1 + 1609 \quad (r = 0.971, N = 26) \quad (7b)$$

$$\nu_{co}(A_1^{(2)})(\mathrm{c2}) = 45.39k_2 + 1324 \quad (r = 0.985, N = 29) \quad (8a)$$

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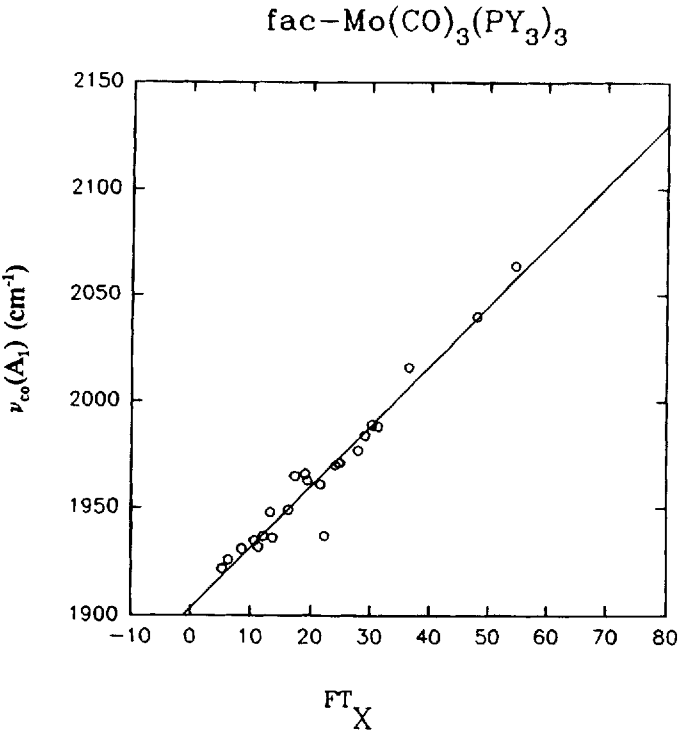

FIGURE 10 Correlations between $\nu_{co}(A_1)$ for *fac*-$Mo(CO)_3(PY_3)_3$ complexes and ^{FT}X from $Ni(CO)_3(PY_3)$ (see Table IV and Table I for data sources).

$$\text{or} \quad = 37.25k_1 + 1470 \quad (r = 0.934,\ N = 29) \qquad (8b)$$

$$\nu_{co}(A_1)(f3) = 50.94k_1 + 1218 \quad (r = 0.998,\ N = 27) \qquad (9a)$$

$$\nu_{co}(E)(f3) = 71.04k_1 + 832.8 \quad (r = 1.000,\ N = 27) \qquad (9b)$$

This has been proved, in particular, by the ν_{co}/k plots for the *fac*-$Mo(CO)_3L_3$ derivatives because two strong and sharp bands can be easily and unambiguously assigned for this geometry. The k_1 values are the most accurately calculated. It is believed that the slight scatter in the correlations of ν_{co} with k for $Mo(CO)_5L$ and *cis*-$Mo(CO)_4L_2$ derivatives stems from one of the following: incorrect assignments,

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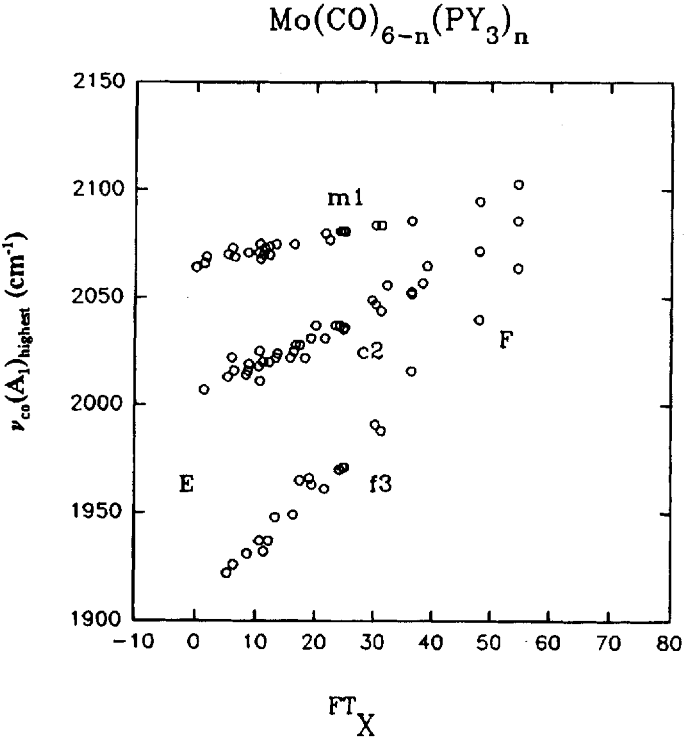

FIGURE 11 An overview of the correlations between ν_{co} for $Mo(CO)_{6-n}(PY_3)_n$ complexes and ν_{co} for $Ni(CO)_3PY_3$ complexes. The ν_{co} data are all available for m1, c2 and f3 Mo complexes for each P(III) ligand in the three plots. The ν_{co} data for $Mo(CO)_6$ and $Ni(CO)_4$ are taken from Ref. 25e.

missed bands (see the footnotes to Table II and previous papers), or recording errors. For example, in $M(CO)_5L$ complexes, the $A_1^{(1)}$ and E bands are very often recorded as a single peak (see Table II). The same problem happens for B_1 and B_2 bands in *cis*-$M(CO)_4L_2$ complexes, and also very often the $A_1^{(1)}$ and B_2 bands are only observed as shoulders. These measurement errors would undoubtedly be incorporated into the calculated k values. Thus, the sharp-lined A_1 band frequencies should be a preferable i.r. parameter for the purpose of correlation analyses or other comparison studies if a series of related ligands is involved.

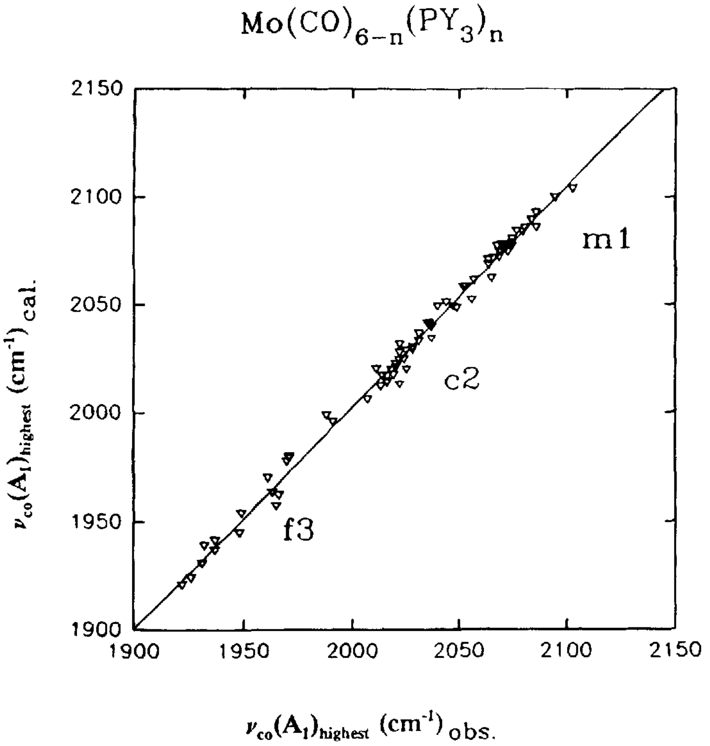

FIGURE 12 Correlation between observed stretching frequencies and predicted stretching frequencies for m1, c2 and f3 Mo complexes.

D. EXPERIMENTAL

The complexes were prepared by literature methods with slight modifications. The infrared spectra were recorded in methylene chloride solution on either a Bomem MB-100 or a Nicolet 20SX/C FTIR spectrometer with a resolution of 4 cm^{-1}. Detailed description has been given in previous publications.[1]

E. CONCLUSIONS

(1) Detailed correlation analyses among the most commonly used electronic parameters of phosphorus ligands, pKa, $\Sigma\chi_i$, and $\Sigma\sigma^{ph}$ permits an

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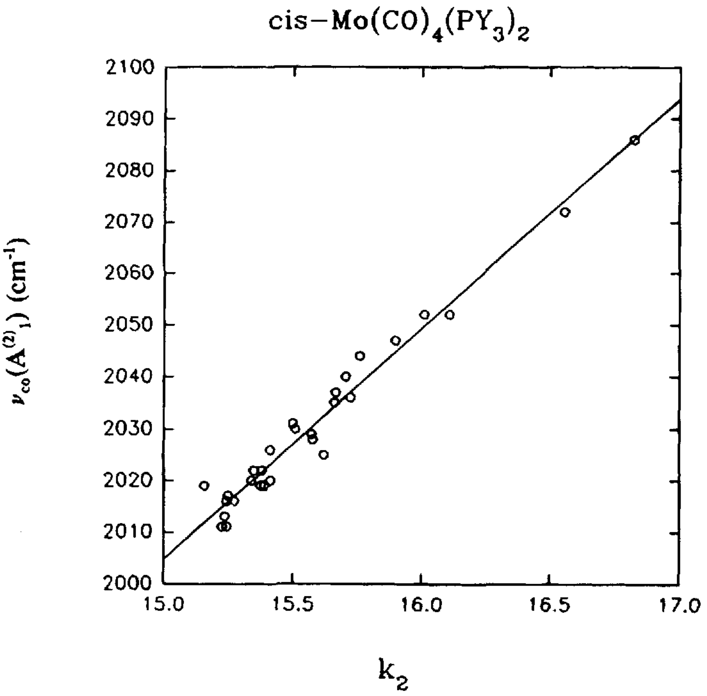

FIGURE 13 Correlation between ν_{co} ($A_1^{(2)}$) and force constants, k_2, for *cis*-$Mo(CO)_4(PY_3)_2$ complexes.

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identification of each of them in terms of σ and π character. The Tolman ligand electronic parameter, $\Sigma\chi_i$, contains the contributions from all the three factors, σ, π and steric bulk. The steric component is implicit in $\Sigma\chi_i$ because of the reverse effects on the *trans* CO infrared stretching frequency via both σ and π pathways. The Kabachnik parameter, $\Sigma\sigma^{ph}$, has some incompatibilities to trivalent phosphorus ligands and numerous drawbacks, as does σ^H. The steric effect can be ignored in $\Sigma\sigma^{ph}$. It is purer than $\Sigma\chi_i$ or ν_{co} as a single-character electronic parameter. It is concluded that the pKa value does not have π and steric components. The solvent effect is undetectable in correlation analysis. With measurement accuracy pKa should be a best choice as a σ-only measure of phosphorus ligands. (2) The *trans* CO stretching frequencies in metal-phosphine complexes have been shown to not be suitable for judging the ligand effects. This is due to this parameter's like response to both a strong

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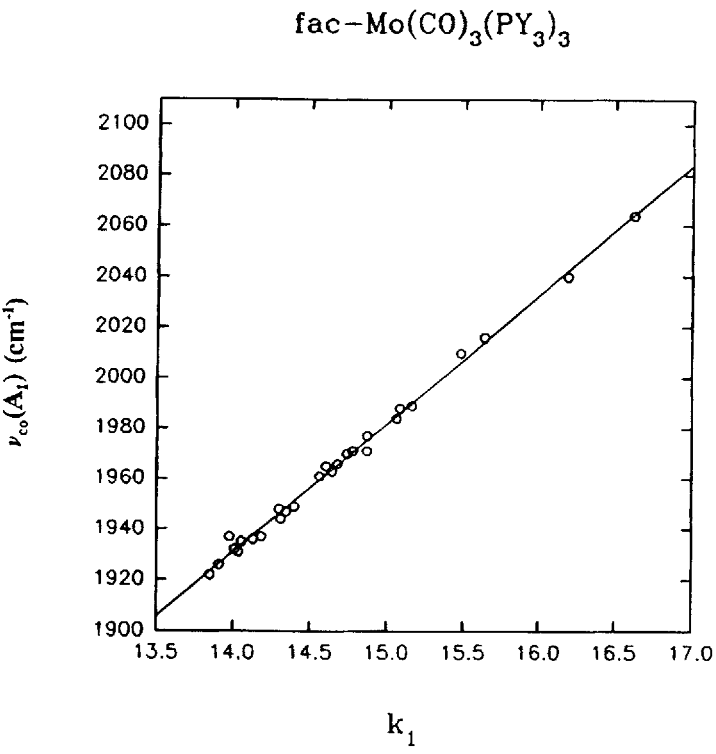

FIGURE 14 Correlation between $\nu_{co}(A_1)$ and force constants, k_1, for *fac*-Mo(CO)$_3$(PY$_3$)$_3$ complexes.

π-character and a weak σ-character, thus allowing no resolution of the σ/π controversy. Such an ambiguous feature of ν_{co} had led to two extreme views, i.e., σ-only and π-only explanations. There seemed to be no simple way to evaluate the steric effects using the stretching frequencies even if ν_{co} is indeed also affected by a steric requirement. Detailed correlation analyses presented here have revealed that the stretching frequency is neither a σ-only nor a π-only parameter. It is really determined by a combined contribution from the three important ligand effects, σ (slightly dominant), π and steric factors, with the steric contribution acting as an implicit one. The excellent linear relationships found between ν_{co} and k suggest that the force constant, k, is not a better electronic parameter than the stretching frequency, as has been supposed by others.[15]

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