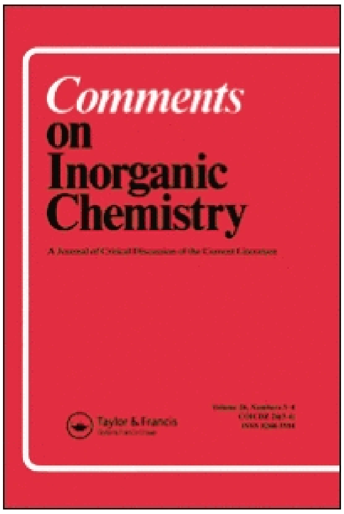

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An Assessment of the Parameters Relevant to the Subdivision of σ and Ω Electronic Effects in M-P Bonds

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An Assessment of the Parameters Relevant to the Subdivision of σ and π Electronic Effects in M-P Bonds

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The origin of the σ and π controversy in inorganic and organometallic chemistry, particularly with respect to M-P bonds, is comprehensively analyzed. It is concluded that traditionally used physical parameters such as ν_{CO}, $\delta(^{13}CO)$, $^1J(M\text{-}P)$, E^0 and r(M-P) of metal carbonyl complexes can not be used to resolve the σ and π controversy due to the parallel influence of weak σ and strong π bonding. In contrast, the parameters ΔE, bond strength and metal NMR isotropic chemical shift should be useful to distinguish σ and π effects because they respond to the weak σ and strong π effects in opposite directions. The metal NMR isotropic chemical shift is undoubtedly the best probe due to the high accuracy of experimental measurement. Its application in the separation of σ, π and steric effects in M-P bonding should be possible.

Key Words: *M-P bonding, σ-π controversy,* ^{95}*Mo NMR chemical shift*

INTRODUCTION

The metal–phosphorus bond plays an important role in inorganic and organometallic chemistry and is a crucial component of many catalytic species.[1] The formation of a transition metal–phosphorus bond is viewed

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as a result of three contributions: σ-donation, π-backbonding and the steric hindrance that weakens the σ- and/or π-interaction.[2] Such a bonding pattern is generally employed by inorganic chemists to explain qualitatively both chemical reactions and structures.[2a,3] Meanwhile, quantitative analyses of the three bonding factors have also been carried out by several groups[2a,4] and many ligand parameters have been proposed. Electronic parameters include χ_i(Tolman's electronic parameter),[2a] $\Delta\sigma$ and $\Delta\pi$ (Graham's σ and π measures),[4a] $\pi_{M\text{-}P}$ (Meek's π bond order),[2b] σ (Bodner's σ/π ratio),[4b] E^o_L (Lever's ligand parameter),[5] $\pi_{a,b}$ and χ_d (Giering's π and σ measures).[4c–h] Steric parameters include θ (cone angle by Tolman),[2a] Θ (solid angle by Immirzi and Musco),[6] SAF (solid angle factor by L. Xing-Fu *et al.*),[7] LP (ligand profile by Ferguson and Alyea),[8] θ_N (cone angle for amines by Seligson and Trogler),[9] and E_r (steric parameters by T. L. Brown).[10] Any success in separating and quantifying the σ and π components as well as isolating the superimposed steric effects would be extremely important to obtain an understanding of the nature of the M-P bond.

The scaling of the bulkiness of phosphine ligands by Tolman's θ parameter is well accepted. However, description of the ligand electronic nature in terms of σ and π ability remains quite controversial.[2d,11] In fact, this long-argued issue has not been substantially solved so far in spite of persistent efforts. This work will explore the origin of the σ/π controversy and present an assessment of the parameters relevant to the separation of ligand σ and π electronic effects in M-P bonds and then propose several potential parameters which could be used to resolve the σ and π controversy.

THE ORIGIN OF THE σ/π CONTROVERSY

The σ/π controversy arises from attempts to interpret various physical parameters of metal complexes in terms of either σ- or π-bonding ability. The progress and discussion over the past three decades can be seen in many review articles.[2a,4,11] The alternative terms in the literature related to the σ/π controversy include the "synergic effect",[12] "σ/π parallel",[2a,4b,13] σ-paramount[14] and π-paramount.[4a,15] Even in recent publications, including theoretical calculations, quite different conclusions that apparently support either the extreme or intermediate views have emerged.[16] Some workers have concluded that the subdivision of σ and π effects is "extremely difficult"[2c] or has "no clear way"[11c,e] of being resolved.

The main reason for this failure is the parallel nature of the *strong* π *and weak* σ effects. In a OC-M-P bond framework, a weak σ donor induces the same spectral response on the trans CO as a strong π acceptor does. For example, the increase in ν_{CO} or decrease in $\delta(^{13}CO)$ can be caused by strong π or weak σ interaction in the M-P bond.[17] At one extreme, the variation of ν_{CO} or $\delta(^{13}CO)$ can be explained solely by σ theory without invoking π bonding, as shown in Fig. 1. This is most likely the origin of the σ/π controversy and the barrier that prevented previous workers from separating the two effects using i.r. or ^{13}CO NMR parameters.

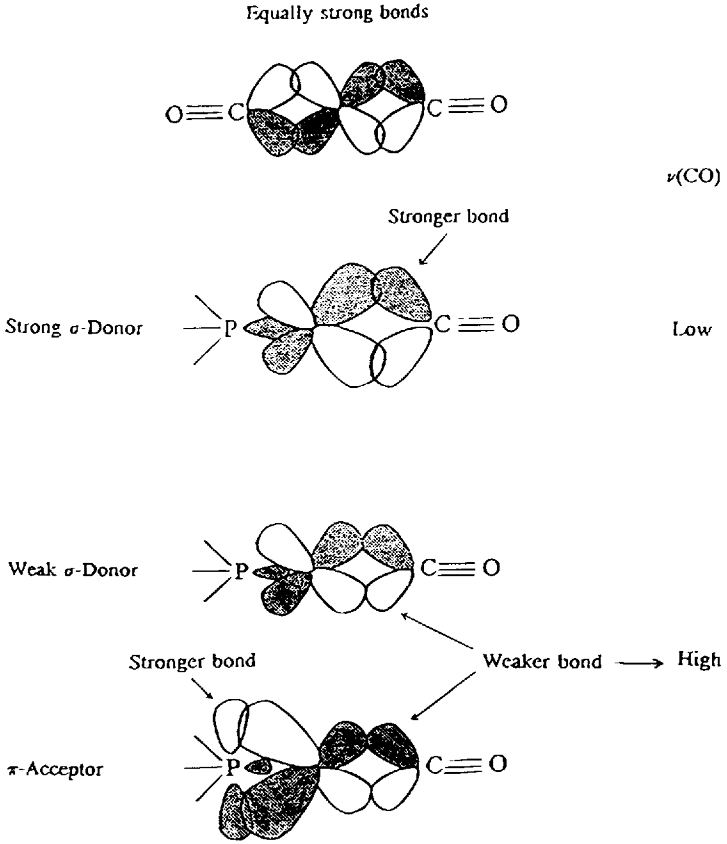


FIGURE 1 Electronic effects (σ and π) of phosphine ligands on the stretching frequencies for carbonyls in OC-M-PZ_3 complexes.

Correspondingly, it is such a subtle mechanism that leads to the "σ-only" and "π-only" theories in the literature. Figure 2 presents a typical correlation between a complex parameter, Tolman's χ_i (Bartik's data, ^{FT}X,[18] are used here because of the greater number available), and a ligand σ-measure, pKa. This correlation is often used by proponents of both σ-theory and π-theory to support their disparate viewpoints.[11] In the σ-view, phosphite ligands are weak σ-donors and give rise to a high stretching frequency, ν_{CO}, of trans CO, while alkylphosphine ligands are strong σ-donors and cause a low ν_{CO}. On the other hand, the π-theory views phosphites as good π-acceptors which induce a high ν_{CO} and alkylphosphines as weak π-acceptors and hence induce a low ν_{CO}. Thus, the resultant lin-

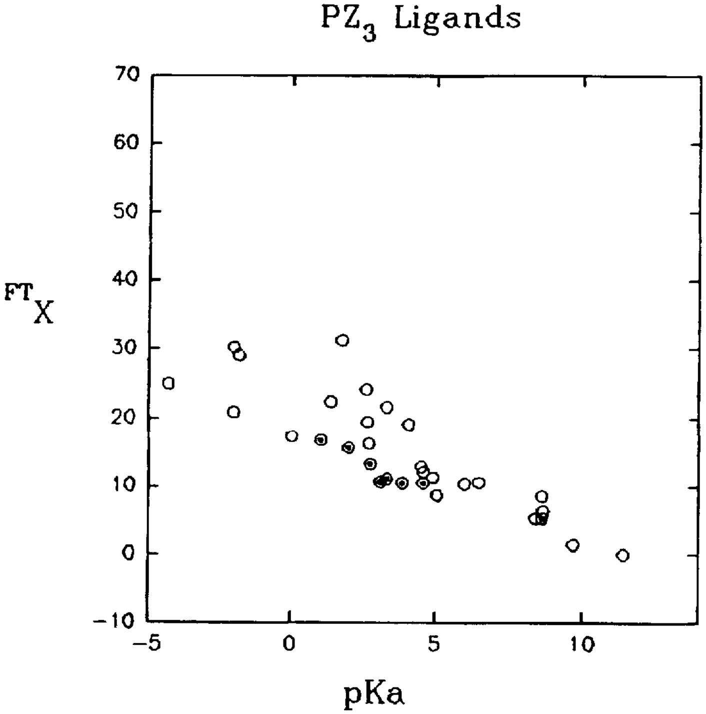


FIGURE 2 A plot of pKa versus ^{FT}X for P(III) ligands. Double points denote $(p\text{-X-}C_6H_4)_3P$ $(\theta \equiv 145^\circ)$. The up-left points are for phosphites and down-right points are for alkylphosphines. Similar correlations will be obtained when ^{FT}X is replaced by k (force constants), $\delta(^{13}CO)$, $^1J(M\text{-}P)$, E° and $r(M\text{-}P)$. The points trend will turn around 90° counterclockwise if $\delta(^{13}CO)$ and $r(M\text{-}P)$ are used as complex parameters along Y axis (see text).

ear correlation can be reasonably interpreted by either σ bonding or π bonding. It should be pointed out here that the alkylphosphines, with their high pKa values, are undoubtedly strong σ-donors, but it has not yet been firmly proved that they are *not* strong π-acceptors.

Two other physical parameters widely used to estimate the π bonding are $^1J(M\text{-}P)$ coupling constant and M-P bond length. $^1J(M\text{-}P)$ varies in a similar way to ν_{CO} in terms of σ/π interaction, i.e., a large coupling constant can be associated with weak σ or strong π bonding on the basis of substituent electronegativity. However, it is only observed that there is a linear dependence of ^1J coupling constant (in Hz) on σ interaction or s character, as briefly described by Eqs. (1)–(8), although people still conventionally attribute the large coupling constants, at least partially, to π bonding:

$$^1J(C-H)(C_2H_{6-2n}, n = 0-2) = 5.7(s\%(C)) - 18.4 \qquad N = 3, r = 0.99, \qquad (1)^{19}$$

$$^1J(C_x-C_y)(C_2H_{6-2n}, n = 0-2) = 0.073(s\%(x)s\%(y)) - 17 \qquad N = 3, r = 0.97, \qquad (2)^{20}$$

$$^1J(C-H)(CH_{4-n}Cl_n, n = 0-3) = 28.3\Sigma EN - 64.3 \qquad N = 4, r = 0.99, \qquad (3)^{21}$$

$$^1J(Ag-P)([Ag(PBu_3)_n]^+, n = 2-4) = 992(1/n) - 36 \qquad N = 3, r = 0.99, \qquad (4)^{22}$$

$$^1J(Mo-P)(Mo(CO)_5L) = 0.254\,{}^1J(P-H) + 5.73 \qquad N = 11, r = 0.98, \qquad (5)^{17}$$

$$^1J(Mo-P)(cis-Mo(CO)_4L_2) = 0.236\,{}^1J(P-H) + 18.4 \qquad N = 11, r = 0.99, \qquad (6)^{17}$$

$$^1J(Mo-P)(fac-Mo(CO)_3L_3) = 0.229\,{}^1J(P-H) + 27.6 \qquad N = 11, r = 0.99, \qquad (7)^{17}$$

$$^1J(W-P)(W(CO)_5L) = 0.390\,{}^1J(P-H) + 58.9 \qquad N = 11, r = 0.98. \qquad (8)^{23}$$

In Eqs. (1)–(8), s% (C) denotes the percentage of carbon atom's hybrid in C-H bond and s%(*x*) and s%(*y*) the percentage of carbon *x*'s and *y*'s hybrids in the C-C bond; EN denotes the Pauling group electronegativity and ^1J(P-H) is for $[HPZ_3]^+$.[24] Moreover, the tendency of decreasing coupling constants for strong π acceptors like PF_3 observed in the correlation of ^1J(Pt-P) for *cis*-$[PtCl_2(PEt_3)L]$ with ^1J(P-H) suggests that π bonding does not seem to be contributing.[25]

Importantly, a short M-P bond distance could be determined either by strong π or by *weak* σ bonding. The latter possibility sounds unacceptable initially but can easily be rationalized. In a M-P σ bond, the relative greater proportion of the ns orbital, which is contracted by comparison with the np orbital, will lead to a shorter bond distance, i.e., "more phosphorus *s*-character produces a shorter M-P bond".[3a] On the other hand, it has also been well accepted that "the *p*-character of a lone pair stabilizes the metal—phosphorus σ-bond".[26] These ideas suggest that a σ-only P → M bond becomes weak with an increase of s character in the lone pair due to stabilization or "penetration" of s electrons. The M-P bond length could very possibly be correlated to σ bonding or s character and also parallel with the bond strength in the absence of π contribution. As a comparison, the *heterolysis* (not homolysis) of the C-H bond in acetylene is much easier than in ethane and ethene even though the C(sp)-H bond is much shorter than C(sp^2)-H or C(sp^3)-H bond.[27] The difficulty in convincing people of the existence of such a correlation of *short distance with weak σ bonding* lies mainly in two facts. First, the M-P bond strength data are very limited and the crystallographically observed short M-P bonds are conventionally attributed to π interaction, as occurred in the interpretation of ^1J(M-P) values, without association with bond strength data. Second, most theoretical calculations mostly pay attention to π bonding and any short bonds are usually simply interpreted by π theory in terms of the electronegativity effects on orbital interactions; i.e., the hyperconjugation principle is overemphasized as a cure-all (*vide infra*).

Redox potential, E^o, is also often used to study the electronic nature of M-P or M-N bonds,[4c–h,5,28] however, it has not been clarified that E^o is *not* a measure of the integrated electron density around metal. In fact, the E^o value for a given metal complex will shift to a more positive direction if the ligand is a good π acceptor or weak σ donor due to the decreased electron density on the metal center. Notably, many linear correlations of E^o with ν_{CO} and ^1J(M-P) have been reported.[4c–f,28,29] Hence, like ν_{CO}, ^1J(M-L) and *r*(M-L), neither is E^o able to distinguish the parallel strong π and weak σ effects. Equations (9–14) present other important correlations from the literature in addition to Eqs. 1–8, indicating that these commonly used complex parameters ν_{CO}, $\delta(^{13}CO)$, k, E^{o}, $^{1}J(M\text{-}P)$, $^{1}J(H\text{-}P)$, $r(M\text{-}P)$ are all roughly linearly related to each other and also correlated to ligand pKa. It must also be kept in mind that these parameters respond to a strong π or a weak σ effect *in the same direction* and, therefore, can *not* be used practically to resolve the σ/π controversy.

$$\delta(^{13}CO) = ak + b, \qquad (9)^{4b,\,30}$$

$$E^{\circ} = a\nu_{CO\,(or\,N2)}\,(\text{or } k) + b, \qquad (10)^{4c,\,28}$$

$$^{1}J(M - P) = a\nu_{CO} + b, \qquad (11)^{29}$$

$$^{1}J(M - L) \sim r, \qquad (12)^{21}$$

$$r(M - P) = a\nu_{CO} + b, \qquad (13)^{31}$$

$$\nu_{CO}(A_1)(O_h) = a\chi_i + b \quad (N = 26, r = 0.96). \qquad (14)^{17}$$

In Eqs. (9–14), a and b are constants; k is force constant; ν_{CO} is carbonyl or dinitrogen infrared frequency; r is M-L bond distance; and χ_i is the Tolman electronic parameter. Equation (9) applies to $Ni(CO)_3L$ and $M(CO)_5L$ (M = Cr and Mo), Eq. 10 to $Cr(C_6Me_6)(CO)_2L$, $Mn(C_5H_4Me)(CO)_2L$, *cis*-$Cr(CO)_4L_2$, *trans*-$Mo(CO)(dppe)_2L$ and η-$MeCpMo(CO)_2L$, Eq. (11) to $W(CO)_5L$, Eq. (12) to $[(PPh_3)_nAgNO_3]$ (n = 1–4), Eq. (13) to $Cr(CO)_5L$ and Eq. (14) to $Mo(CO)_{6-n}(PY_3)_n$(n = 1–3).

PREVIOUS ATTEMPTS TO SEPARATE σ AND π EFFECTS

(a) Graham's Δσ and Δπ Parameters

The first attempt to separate and scale the σ- and π-abilities for a wide range of phosphorus ligands was made by Graham in 1968.[4a] His method employed the parameters Δk_1 (*trans*) and Δk_2 (*cis*) for the CO bonds *trans* and *cis* to the donor ligands in $Mo(CO)_5L$ derivatives in comparison with their corresponding values for the cyclohexylamine analogue. On the assumptions that the change in the π-acceptor property (Δπ) in going from L to L′ (CO's) will affect Δk_1 more than Δk_2 by a factor of 2, and that cyclohexylamine is incapable of π-bonding, two equations were developed to calculate each set of Δσ and Δπ parameters:

$$\Delta k_1\,(trans) = \Delta\sigma + 2\Delta\pi, \qquad (15)$$

$$\Delta k_2\,(cis) = \Delta\sigma + \Delta\pi. \qquad (16)$$

Some representative Graham's values ($\Delta\sigma/\Delta\pi$) are: PF_3(–0.09/0.79), CO(–0.06/0.74), PCl_3(–0.09/0.71), $P(OMe)_3$(–0.38/0.58), P(*n*-Bu)$_3$(–0.48/0.48), $P(OPh)_3$(–0.13/0.48), PPh_3(–0.15/0.27).

Graham considered that his $\Delta\pi$ values give a more practical order of π-acceptor abilities than his $\Delta\sigma$ parameters, and consequently these $\Delta\pi$ values have been applied by others to their own data analyses.[29] Some authors, however, questioned the $\Delta\pi$ parameter since the $\Delta\pi$ value for P(*n*-Bu)$_3$ is the same as that for $P(OPh)_3$,[11b] even though no quantitative studies indicated that P(*n*-Bu)$_3$, or other P(alkyl)$_3$, are *not* strong π-acceptors. More importantly, the π-ability of PCl_3 was deemed by the Graham approach to be only slightly weaker than that of PF_3 and much higher than those for phosphites and other phosphines. This is contrary to conclusions based on the more recently measured M-PCl_3 bond strength data,[32] and the earlier observed labile property of PCl_3 ligand in nickel carbonyl complexes.[33] We have also recently concluded from $\delta(^{95}Mo)$ data that PCl_3 is a much weaker π-acceptor.[34] The very poor π-acceptor ability of PCl_3 as compared to PF_3 was suggested earlier by two other groups.[4g,35]

Graham's assumption of a more sensitive CO response to a *trans* donor ligand's electronic effects is unambiguous, but three qualifications should be considered further. First, the factor of 2 in Eq. (15) might be underestimated. The three d_π orbitals should be anisotropic, not "equally" affected in π-effect transmission. The equatorial d_{xy} orbital which directly links the four *cis* CO's in a $M(CO)_5L$ complex (L located at d_{z2}) should have much less contribution in transmitting the π-interaction due to the mismatched symmetry. Thus a factor of over 4, as estimated by Cotton,[36] might be more reasonable when taking into account the fact that the other two d_π (d_{xz} and d_{yz}) orbitals are shared by the four planar CO's and one axial CO. Second, the σ-donicity of L should also contribute. To whatever extent it does, this σ-component should be distinguished from π-components. Significantly, the view that stretching frequencies are usually considered to be determined mainly by π-bonding with the metal makes little sense (see next section). Finally, and most importantly, a weak σ-donor would have the same effect as a strong π-acceptor, resulting in a high ν_{CO} value even if its intrinsic π-ability is very weak, as demonstrated before. Consequently, this effect, from the point of view of *trans* CO, is equivalent to a strong π-competition from L. Graham's method did not take such a secondary effect into account.

(b) Bodner's Donor/Acceptor Ratio[4b]

Bodner and co-workers studied many sets of M-P complexes by ^{13}C NMR in the 1970's.[4b,30] They proposed a set of substituent parameters for trivalent phosphorus ligands, PZ_3, denoted as σ.[4b] They rationalized that the carbonyl chemical shift in M-P complexes should reflect the donor/acceptor character of phosphorus ligands as there is an apparent deshielding of carbonyl resonances with increasing M-C π back-bonding, and the back-bonding increases as electron density on the metal increases.[37] The σ values were calculated by dividing $\delta(^{13}CO)$ of the $Y_3PNi(CO)_3$ complexes by three, and scaling these data so that the substituent parameter for Y = H is equal to zero. A single set of σ-parameters was used as a measure for the σ-donor/π-acceptor ratio, based on the assumption that the net donation of electron density increases as the electron-withdrawing power of the substituent on phosphorus decreases. Obviously, the increase in π-acceptor ability or decrease in σ-donor power had been related to the electron withdrawing power of Z groups, and the single set of σ values suggests that σ-ability and π-ability operate coincidentally but in opposite directions, i.e., the σ and π controversy. An increasing order of donor/acceptor ratio for PZ_3 ligands was proposed to be: $PCl_3 < P(OPh)_3 < P(SR)_3 < P(OR)_3 < PPh_3 < P(NR_2)_3 \leq PR_3$. It can be expected from the previous linear relationship between $\delta(^{13}CO)$ and force constant k for $Ni(CO)_3L$ complexes[4b] that a similar linear correlation of Bodner's substituent parameter, σ, and Tolman's electronic parameter, χ_i, would exist:

$$\sigma(\text{Bodner}) = 0.150\,\chi_i - 1.05, \quad r = 0.962,\ N = 30. \tag{17}$$

Thus, if the $\delta(^{13}CO)$ or Bodner's σ is an overall electronic parameter, then so is ν_{CO} or χ_i. The point here is that the latter shows a very similar trend to pKa. Therefore, Bodner's σ-parameters can not provide more than Tolman's χ_i[2a] in terms of the ligand σ- and/or π-electronic effects.

(c) The "QALE"[4c–h]

The "QALE" (Quantitative Analysis of Ligand Effects) method was developed by Giering *et al.* in 1985.[4c] Since then, they have been attempting to quantify the three important factors: σ, π and steric effects. They classified phosphorus ligands into three electronic groups: class I, σ-donor/π-donor; class II, σ-donor; and class III, σ-donor/π-acceptor.[4d] They also concluded that many different steric thresholds exist in various model complexes based on the non-linear trends observed in their correlation analyses. The QALE method states that the ligands in different classes can be transformed due to the attenuation of electronic effects by steric hindrance. Similar observations were reported by Hoff and other workers.[38] For example, there is a decreasing dependence of ΔH (heat of reaction) on steric factors on going from $(Z_3P)_3Mo(CO)_3$ (1.42) to $(Z_3P)_2Mo(CO)_4$ (0.81). Poë and co-workers[38c–e] made attempts to quantitatively separate electronic and steric contributions of P-donor nucleophiles in associative substitution reactions, developing both electronic and steric profiles for the reactions of certain carbonyl clusters with PZ_3. Although the definition and evaluation of steric threshold in Giering's work make a lot of sense, QALE only classifies P(III) ligands into several groups in an approximate and qualitative, not quantitative, manner. For example, most phosphites are usually assigned as π-acceptors, arylphosphines as weak π-acceptors and alkylphosphines as strong σ-donors with some π-character. Actually, such a qualitative classification has been known for years.

A key limitation in QALE is that it employs *two "appropriate properties"* in the relevant correlation analyses, as the authors themselves realized in a later paper.[4e] Ligand properties, such as pKa or cone angle θ (noted as X for simplicity here), and complex spectroscopic, thermodynamic, kinetic, or electrochemical properties (noted as Y here for simplicity) comprise these "appropriate properties". pKa was reasonably used as a σ-parameter to distinguish "ligand effects" by graphing against a Y parameter. Unfortunately, QALE does not take into account the importance of Y parameters for the delineation of σ- and π-effects. Instead, QALE employs an arbitrary pair of data sets in their primary σ-correlations, and even two Y parameters for other correlation analyses.[4e–g] Some credible results, however, were obtained,[4d] when ΔH was used as a Y parameter since ΔH reflects better the total bonding in the M-P(III) linkage.[2a]

Table I lists many multi-parameter linear expressions for ligand effects. Tolman's electronic parameter is roughly linearly related to ligand aqueous pKa, as shown by Eq. #1. Equation #2 indicates an improved linearity of Eq. #1 after including the ligand bulk term, θ. The steric factor could either contribute to pKa or χ_i though QALE claimed the former. Equation #10 is similar to Eq. #1 due to a Hammett relation between pKa and $\Sigma\sigma^{ph}$.[39] All the remaining equations are virtually the same as Tolman's original expression (#4) with alternative use of pKa, ΔHNP, $\delta(^{13}CO)(Ni(CO)_3L)$ or χ_i as a (total) electronic measure. Undoubtedly, the inclusion of a steric factor improves the linearity of the correlations for both chemical and

TABLE I

Multi-parameter linear equations for ligand effects.

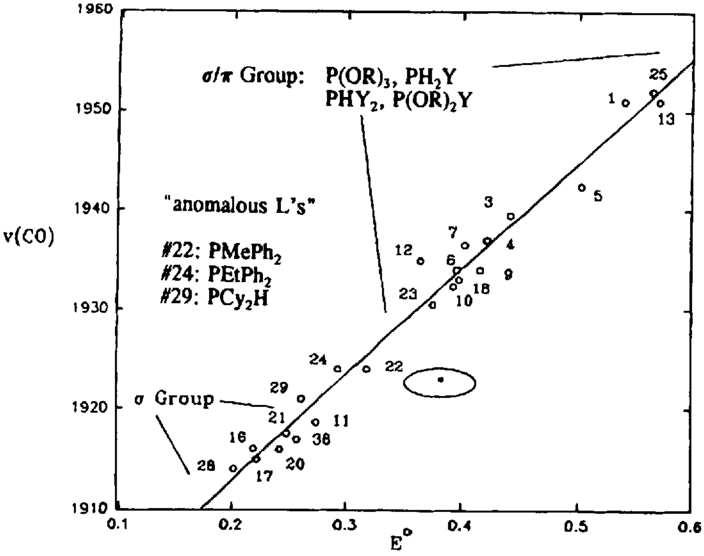
No.	Linear Expressions[a]	Mode[b]	r^c	N^e	Ref.
1.	$\mathrm{pKa} = f(\chi_i)$	PZ_3	0.95	16	4e
2.	$\mathrm{pKa} = f(\chi_i, \theta)$	PZ_3	0.98	16	4g
					4e
3.	$\nu_{CO}(A_1 = f(\mathrm{pKa}, \theta)$	f3-Mo	0.99		4d
4.	$\Delta H^\circ = f(\nu_{CO}, \theta)$	$Ni(CO)_3L$	0.85–0.97		1g,2a
5.	$\Delta H = f(\mathrm{pKa}, \theta)$	f3-Mo	0.97		4d
6.	$\Delta H = f(\chi_i, \theta)$	η^3-NiMeL			4d
7.	$\Delta H = f(\nu_{co}, \theta)$	Q_2PtMeL	0.84		4d
8a.	$\Delta H = f(\nu_{CO}, \theta)$	f3-Mo			4d
					32a
			0.95		38a
8b.	$\Delta H = f(\chi_d, \theta)$	f3-Mo			4g
9a.	$\Delta H = f(\nu_{CO}, \theta)$	c2-Mo	0.86		32b
9b.	$\Delta H = f(\chi_d, \theta)$	c2-Mo			4g
10a.	$\Sigma\sigma^{ph} = f(\chi_i)$	$P(x\text{-}Ph)_3$	0.974	7	4h
10b.	$\Sigma\sigma^{ph} = f(\chi_i, \theta)$	PZ_3	0.949	28	4h
10c.	$\Sigma\sigma^{ph} = f(\chi_i, \theta, E_{ary})$	PZ_3	0.985	28	4h
11a.	$\log k = f(\chi_i)^d$	$HSiR_3{}^d$	0.949	4	4h
11b.	$\log k = f(\chi_i, \theta)$	$HSiR_3$	0.76	19	4h
11c.	$\log k = f(\chi_i, \theta, E_{ary})$	$HSiR_3$	0.961	19	4h
12.	$\log k = f(\delta(^{13}C), \theta)$	$Re(CO)_4LX$			10f
13.	$\log k_2 = f(\Delta HNP, \theta)$	$Ir_4(CO)_{11}L$			38c
14.	$\log K = f(\mathrm{pKa}, \theta)$	$PtPh_2(CO)L$			38b

a: χ_i is the Tolman electronic parameter ($\Delta\nu_{CO}(A_1)$ of $Ni(CO)_3L$ relative to $L = P(t\text{-}Bu)_3$); θ is the Tolman cone angle; ν_{CO} is the appropriate stretching frequency; χ_d is a measure of σ-donicity proposed by QALE (Ref. 4g); $\Sigma\sigma^{ph}$ is the Kabachnik parameter; E_{ary} is the aryl effect proposed by QALE and the values are 0, 1, 2 and 2.7 for PR_3, $PPhR_2$, PPh_2R and PPh_3, respectively; ΔH is the heat of reaction in forming appropriate model compounds. b: PZ_3 denotes all P(III) ligands; f3-Mo = *fac*-$Mo(CO)_3P_3$, c2-Mo = *cis*-$Mo(CO)_4P_2$, η^3-NiMeL is a pseudo-tetrahedral Ni complex, η^3-C_5H_9NiMeL; Q_2PtMeL is a pseudo-square planar Pt complex. c: r is correlation coefficient; the r values for Eqs. 10 to 11 are r^2. d: Equation (11) is for reaction: $B^+ + HSiR_3 \rightarrow BH + SiR_3{}^+$, the χ_i and θ are for R in $HSiR_3$. e: N is the number of data points; blanks indicate that values were not given in the original papers.

mathematical significance. It needs to be clarified that there is no steric contribution in pKa, ΔHNP, $\delta(^{13}CO)(Ni(CO)_3L)$ or χ_i. Otherwise, the steric effects will be repeatedly considered. The QALE method transfers some "deviations" between a single- and a dual-parameter correlation into an extra ligand parameter, which can then be used to develop a multi-parameter equation. The improved coefficient thus obtained proves that the method is, in principle, correct. These deviations have been noted previously and they are not deemed to be due to experimental error. For example, PF_3 or phosphites usually deviate from a single parameter correlation toward the strong M-P bonding side. However, the uncertainty in the ΔH or log(k) data should not be ignored. For example, the error of ΔH is about 10%,[32e] as stated by Hoff, which is probably comparable to "the improvement" or "the deviations" in many correlations. The use of ν_{CO} and E^o (oxidation potential of the metal complexes) in QALE is another problem, as pointed out before (*vide supra*). As a matter of fact, the nature or identity of the Y parameters such as ν_{CO}, E^o, χ_i, ΔH or log(k) had not been clarified in terms of ligand electronic and steric effects when QALE adopted them. These Y parameters have a lot in common, and many of them are linearly related to one another. It was the similarity of many Y parameters and the similarity of most Y parameters to ligand σ electronic measures that blocked the practical separation of the three important parameters (σ,π,θ) during the past 30 years. In particular, the *trans* CO stretching frequency can not differentiate σ- and π-effects of L since ν_{CO} responds to both electronic effects in the same direction. It is, therefore, not surprising that there are a number of self-inconsistencies in the QALE work. Many ligands had to be designated as "anomalous" (PPh_2Me, PPh_2Et and PCy_2H)[4e] or "borderline" (PPh_3, $PPhEt_2$ and PMe_3).[4d] Some $PPh_2(OR)$ ligands were assigned as anomalous[4d] but pure σ-donors later.[4e] The ligands $P(CH_2CH_2CN)_3$, $PPhH_2$ and PPh_2H were designated as σ-donor/π-acceptor (class III)[4e] but as pure σ-donors later.[4g] A redrawn Fig. 1 of Ref. 4g, that includes many class-II ("group I", σ-only donors) and those "anomalous" ligands as well, is presented here as Fig. 3. Obviously, it is still linear ($r = 0.991$, $N = 23$). If the proposed "aryl effects"[4h] for arylphosphines are taken into account, one will see a linear plot for ν_{CO} versus E^o (oxidation potential for the complexes) for a wide range of P(III) ligands with the one exception of $P(CH_2CH_2CN)_3$. So the QALE does not yet seem to be able to successfully classify the phosphorus ligands and quantify the ligand effects in terms of σ and π bonding.

HYPERCONJUGATION IN M-P BONDING

Recent detailed molecular orbital calculations of PZ_3 and their metal complexes reiterate the importance of π-character in M-P bonding (although the extreme cases of σ-only and π-only bonding are still being reported[16]). The main feature of these new theoretical treatments is that the phosphorus accepting orbitals have mainly the P-Z σ* character, rather than in-



* excluding $P(X\text{-}Ph)_3$,
PPh_2L', L' = OR & CH_2CH_2CN

#23: $PPh(CH_2CH_2CN)_2$
#18: $P(CH_2CH_2CN)_3$

FIGURE 3 The re-plotted main correlation of ν_{CO} with E^0 which was used by QALE to classify P(III) ligands into two different groups. The correlation coefficient found here is $r = 0.991$ for $N = 23$. See Ref. 4g for the numbering.

volve only the traditionally accepted 3d orbitals.[40–44] Significantly, this P-Z σ^*-LUMO description has received strong experimental support by electron transmission spectroscopy (ETS) and X-ray crystallography. ETS results indicate that the energy of the LUMO orbital in PZ_3 ligands is very sensitive to the Z group, suggesting that this orbital is largely P-Z σ^* in character.[42] A survey of the molecular structures of a number of M-P complexes in different oxidation states by Orpen *et al.*[43] clearly shows that strong π-bonding with metals in low oxidation states always leads to shorter M-P and longer P-Z bond distances as well. The interaction of a phosphine ligand with a low oxidation state metal (an "anion") and the acceptance of charge into the P-Z σ^* orbital has been considered as a kind of hyperconjugation process essentially analogous to the hyperconjugation in organic chemistry.[44] Thus the effectiveness of the d_π-σ^* interaction is determined by the nature of the substituents on phosphorus. An electronegative substituent Z on P has been thought to increase the d_π-σ^* overlap for two reasons.[41d] First, the P-Z σ_e^* orbitals (actually *all* orbitals) are lowered in energy by the strong inductive effect of Z and more pyramidal Z-P-Z angles (see the Walsh diagram[44c]), making the PZ_3 molecule a better π-acceptor. Second, because the P-Z filled σ_e bonds are highly polar toward Z, the σ_e^* orbitals must necessarily be highly polar toward P, and hence the M-P π-back-bonding is enhanced. It is also concluded[40] that P 3p character increases in σ_e^* and decreases in σ_e orbitals with increasing electronegativity of Z, accounting for the sensitivity of d_π-p interaction or hyperconjugation with substituent electronegativity. It is difficult to refute such an elegant interpretation. However, hyperconjugation concerns only π bonding and not σ bonding. The increased electronegativity of the substituents also lowers the energy level of the ligand σ orbital, enlarging the energy difference between the other pair of frontier orbitals, metal LUMO and ligand HOMO (a_1), and making the ligand a poorer σ-donor. Just as the increase in positive charge on the metal freezes π-electrons on the metal (M-HOMO),[43] the increase in positive charge on the phosphorus ligand due to the introduction of electronegative group(s) freezes the σ-electrons on the phosphorus (P-HOMO). According to the calculation of Xiao *et al.*, the phosphorus LUMO orbital decreases by 1.9 eV but the HOMO orbital decreases by 3.0 eV from PMe_3 to PF_3.[40] Therefore, an electronegative substituent on the ligand has a dual effect: enhancing π interaction through hyperconjugation but weakening the σ interaction through an inductive effect. There still remains, therefore, the issue of σ/π controversy. Also, it should be noted that the hyperconjugation process is contradictory to the traditional "synergic effect", in which σ-bonding is considered to be enhanced by increased M-P π-bonding.

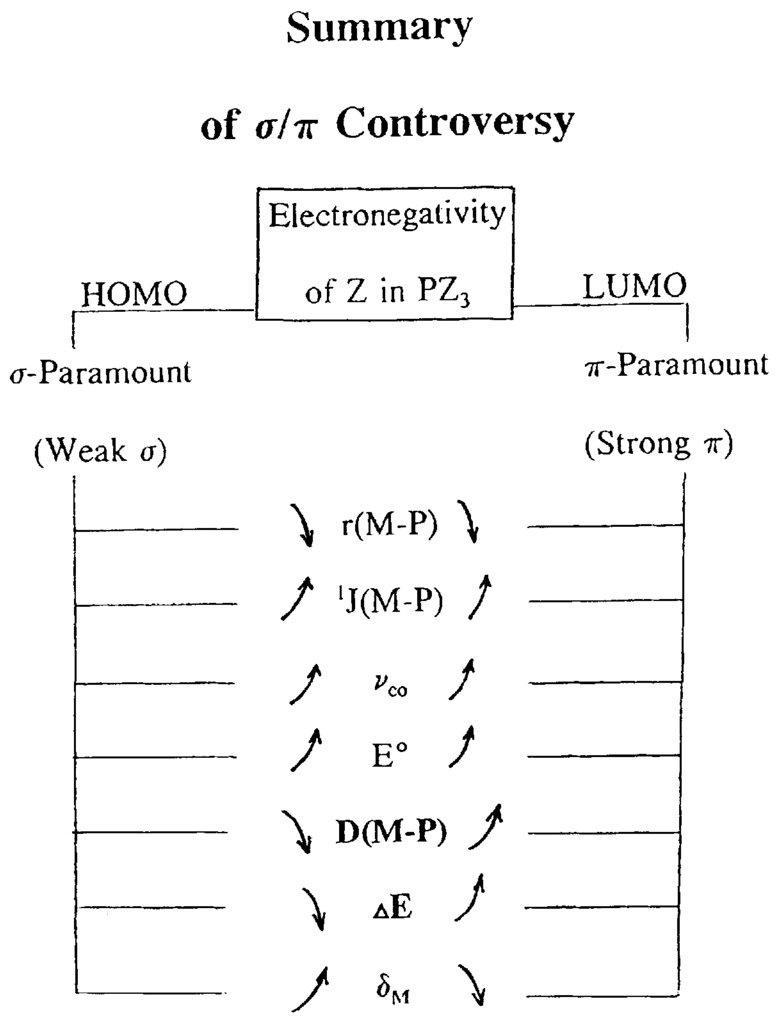
It must be pointed out that the strong π interaction results in a strong bond strength and a large ligand field electronic transition energy, ΔE, and the weak σ interaction results in a weak bond strength and small ΔE. In contrast to the above-mentioned physical parameters such as ν_{CO} and ^1J(M-P) which respond to the strong π/weak σ in the same direction, the bond strength and ΔE have an opposite response to strong π and weak σ interactions in M-P bonds and can very possibly be used to resolve the σ/π controversy. Unfortunately, no attempt has ever been made to apply bond strength and ΔE data to the separation of σ- and π-effects in M-P bonding. Part of the reason is surely the unavailability of data, particularly the difficulty of obtaining ΔE values.

THE APPLICATION OF METAL NMR CHEMICAL SHIFT TO THE RESOLUTION OF THE σ/π CONTROVERSY

Transition metal NMR spectroscopy has been greatly developed during the past 15 years.[45] A voluminous number of chemical shift data has been reported.[46] It is well accepted that metal NMR spectral data provide extremely sensitive evidence about the disposition of valence electrons in molecules.[46–50] The direct bonding between the metal and the phosphorus ligands obviously makes the metal NMR shielding parameter, δ_M, a much better probe for the nature of M-P bond than other parameters like ν_{CO}. In solution, the dipolar interaction, chemical shift anisotropy and the quadrupolar interaction are completely averaged out by isotropic motion.[51] Only sharp resonance lines characterized by isotropic chemical shifts, δ_{iso} or σ_{iso}, and indirect spin–spin couplings can be observed. The orientation-dependent interactions in solids would not affect the isotropic parameter, δ_{iso}. The physical significance of δ_{iso} has been closely related to the bonding and structure of metal complexes by the modified Ramsey equation (18).[46]

$$\sigma_p = -\text{const.}(\Delta E)^{-1} < r^{-3} >_{(n-1)d} \langle 0 | L^2 | 0 \rangle \qquad (18)$$

in which ΔE is the mean excitation energy, r is the average d-electron distance from the nucleus and $\langle 0|L^2|0\rangle$ is the angular imbalance of charge (where L is the angular momentum operator). A great number of previous observations have confirmed qualitatively the theoretical prediction.[45–50] For a series of closely related metal complexes of a given class of ligands, such as PZ_3, the only influences on the M-P bond or metal δ_{iso} arise from the indirect substituent (electronic and steric) effects via the same donor atom of phosphorus. So, the paramagnetic contribution associated with valence electrons as described by the Ramsey equation can be considered with confidence to dominate the isotropic chemical shielding. The energy term is related to the ligand spectroscopic effect and the radial term to the ligand nephelauxetic effect. Both strong π and strong σ bonding will shift metal δ_{iso} to lower frequency due to the increased ΔE, delocalization of d electrons and decreased spin-orbital interaction. In contrast, weak π and weak σ bonding will shift metal δ_{iso} to high frequency (i.e., deshielded metal nucleus). Steric hindrance destabilizes σ and π interactions and hence causes a high frequency shift.[17,52] The most remarkable feature is that strong π bonding will shift δ_M to low frequency *but* weak σ bonding will shift δ_M to high frequency.[34] In other words, the



SCHEME 1

metal NMR chemical shift parameter, δ_{iso}, has a *distinguishable dependence* on weak σ and strong π electronic effects and therefore can be used to resolve the σ/π controversy surrounding M-P bonding. The utilization of ^{95}Mo NMR chemical shifts to the separation of weak σ-bonding effects for PCl_3 and related ligands from the strong π-acceptor ability of the PF_3

ligand was recently demonstrated in our laboratory.[34a] Further applications of ^{95}Mo NMR spectroscopy to the separation of σ, π and steric effects in a wide range of $Mo(CO)_{6-n}L_n$ complexes are underway.

CONCLUSION

Traditionally used physical parameters, ν_{CO}, $\delta(^{13}CO)$, $^1J(M\text{-}P)$, E^0 and r(M-P), are demonstrated to be unable to resolve the σ/π controversy for M-P bonding due to the parallel influence of weak σ and strong π bonding. In contrast, the parameter ligand field separation energy (ΔE), bond strength and metal NMR chemical shift should be useful for separating σ and π effects because all three parameters respond to the weak σ and strong π effects *in opposite directions*, as summarized in Scheme 1. For the first four parameters, the arrows indicate that both weak σ bonding and strong π bonding (as caused by an increase in electronegativity of the Z substituent in PZ_3) have the same effect on the parameters. For the last three parameters, the arrows indicate that weak σ bonding and strong π bonding affect the parameter in the opposite direction. The metal NMR chemical shift is undoubtedly the best probe of the three due to the high accuracy of experimental measurement, and thus should be useful for the separation of σ, π and steric effects in M-P bonding.

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