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Cone angles: Tolman's and Plato's

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Contents

Abstract

The successful application of Tolman cone angles for P-donor and other ligands in accounting quantitatively for steric effects in a wide variety of physicochemical processes is contrasted with the variability of cone angles obtained from crystallographic studies. It is maintained that the latter are not relevant in describing steric effects for reactions in solution. Problems with cone angles for ligands with conformational uncertainties are best dealt with by systematic measurement of deviations of data for those ligands from trends defined by ligands with less ambiguous cone angles. In fact a body of cone angles for all ligands could be obtained by adjusting cone angles to give perfect fits to individual steric profiles and then averaging the values obtained from a large number of such studies. In this way a set of cone angles could be obtained that are divorced from their origins in Tolman's models and justified solely by their successful quantitative application. Although it is tempting to relate these cone angles to some Platonically perfect set, consideration given here to even a small number of sets of data of this sort suggests that there may always be some ligands with uncertain cone angles. Thus, a combination of eight sets of data that include $P(OMe)_3$ as a ligand suggests that it should have its Tolman cone angle increased by ca. 10°. A much larger proposed increase is disputed. Another set of data suggests that its Tolman cone angle is appropriate when it is a nucleophile but that $P(O-i\text{-}Pr)_3$ as a nucleophile should have its Tolman cone angle reduced by ca. 5°. Thus the deviant behaviour of conformationally ambiguous ligands may be systematic, and could depend on whether the P-donors are acting as ligands or nucleophiles. However, the concept of a Platonically perfect set of cone angles is probably justified for many ligands that are conformationally unambiguous and these ideal cone angles may be essentially identical with Tolman's values. In the course of these analyses a new set of π-acidity parameters was developed and values are tabulated.

Keywords: P-donor ligands; Deviant cone angles; Substitution reactions; Addition reactions; Group transfer reactions; Steric effects; Electronic effects

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1. Introduction

Quantitative evidence for steric effects in reactions of metal carbonyls and other organometallic compounds first became available in 1966 [1] when Basolo and Schuster-Woldan showed that the logarithms of the

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second order rate constants for associative substitution of P-donor ligands into $CpRh(CO)_2$ and $Co(CO)_3(NO)$ were linearly related to Δhnp, the half neutralization potentials of the nucleophiles and a measure of their proton basicities [2]. While this relationship was adhered to by most of the nucleophiles used, the value of log k_2 for the largest nucleophile PCy_3 lay well below the linear plot for the other data and this was easily ascribed to steric effects.

More relationships of this sort were discovered during the subsequent few years and Poë and Twigg [3] quantified steric effects by measuring any differences between the log k_2 values observed for larger ligands (such as PPh_3 as well as PCy_3) and those predicted simply according to their basicity. Application of this method continued [4] until Kochi and coworkers [5], Giering and coworkers [6] and Poë and coworkers [7] found a significant number of sets of data that fitted well to analogues of Tolman's equation (Eq. (1)) [8] relating a property of a complex

$$\text{Property} = a + b(\chi) + c(\theta) \quad (1)$$

(logs of rate constants or equilibrium constants etc.) to the electronic and steric properties of the ligands. In this case, χ is a measure of the net electron donicity of the ligand (as measured by the $A_{1(CO)}$ stretching frequency of $Ni(CO)_3L$ as compared to that of $Ni(CO)_3(P{-}t{-}Bu_3)$, and θ is a measure of the size of the ligands provided by their cone angles [8].

It was evident from the early studies of Basolo [1] that there are some associative substitution reactions that do not show a steric effect at all. It follows that, as cone angles decrease and steric effects become smaller, there must be [6,7] a transition from Eq. (1) to another in which $c = 0$. So called steric profiles can be obtained from plots of log $k_2 - b(\chi)$, or its equivalent, (i.e. the values of log k_2 adjusted for the electronic effects) against the nucleophile cone angles. These will therefore generally consist of a horizontal line that changes to a downward linear plot as θ increases. Since it seemed likely that steric effects would come into play quite gradually, it was thought that the transition between the horizontal and downwardly linear parts of the steric profile would also be quite gradual, i.e. the steric threshold (θ_{th}) [6], above which the linear plot is found, would be quite vaguely defined [9]. However, Giering and coworkers showed [10] that the steric thresholds were quite sharply defined and this counterintuitive observation needed some rationalization. This was provided [11] by the introduction of the concept of a 'transition state isomer', i.e. a form of the complex that contains a quite sharply defined opening, related in size to θ_{th}, and created when the nucleophile approaches closely enough to the metal carbonyl. Nucleophiles that fit into this space without nucleophile–ligand repulsions will lie below the steric threshold but larger ligands will experience nucleophile–ligand repulsions that will result in higher energy barriers to reaction.

Tolman's equation Eq. (1) has therefore been replaced by Eq. (2) where a can be

$$\text{Property} = a + b(\text{el}) + c(\theta - \theta_{th})\lambda \quad (2)$$

defined in ways related to an intrinsic or standard reactivity [11] and el is a measure of the ligands' electronic properties that can include (χ [8,12], δ_{co} [13]) contributions from π-acidity effects, or that measure only σ-donor effects (χ_d [14], pK'_a [11] and Δhnp [2]). More recently, el has been adapted to take account of separate 'aryl' [14,15] and π-acidity effects [14,16] through the introduction of the parameters E_{Ar} and π_p, respectively. The value of λ, the switching factor, is either 1 when $\theta > \theta_{th}$ or zero when $\theta \leq \theta_{th}$. Values of θ, with minor exceptions, are still those provided by Tolman [8c] in spite of the complete absence of any understanding of why free energies of ligand–ligand repulsion effects, and a wide range of other physicochemical parameters, should be linearly related to a cone angle in degrees, and why the admittedly crude methodology used to derive cone angles should be so successful! The reason for the continued use of Tolman's cone angles is the obviously pragmatic one that their use is successful [11,14,16]; i.e. they allow a quantitative description of the dependence of a great many disparate physicochemical properties on the electronic and steric natures of the ligands involved.

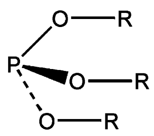
In spite of this success, there have very properly been a number of strenuous critical efforts made to probe the validity of the concept of cone angles. Fergusson and coworkers [17] focussed on the nature of the ligands as irregular conic cogs and the concept of ligand profiles was introduced. The profiles were found to be quite compatible with Tolman's cone angles, but their origins in crystallographic data ensured, at that time, that they would be available for only relatively few ligands. Some crystallographic studies were also directed towards measuring the changes in cone angles as the cone was extended out from the metal [18]. This has obvious relevance to the choice of cone angles appropriate to nucleophilic attack by P-donors since the metal–P bond in the transition states will be longer than when the P-donor is present as a fully bonded ligand. This study has not, unfortunately, been extended to enough ligands to be useful. However, the use of solid angles, Ω, [19] has been investigated and this study included an examination of the changes in effective sizes with increasing distance of the ligand from the metal. Calculations of inter ligand repulsive energies [20] have provided a large number of ligand steric parameters, E_R, that have a patina of theoretical respectability compared with crude cone angles. Some E_R values correlate linearly quite well with Tolman's cone angles and therefore, in a sense, provide some retrospective theoretical justification of the success of cone angles. The correlations allow the derivation of ‘cone angle equivalents’, θ' [21], which are directly related to E_R values but which have a scale change so that data can be analyzed in terms of either θ or θ' ($\theta = \theta' = 145°$ for PPh_3 and its para-substituted derivatives) and the results compared. However, neither the E_R values nor the cone angle equivalents provide generally improved fits to equations such as Eq. (2).

A fundamentally important point that has been raised with respect to Tolman’s cone angles is whether the choice of conformations of ligands with various possible conformations and internal strain was correctly made [22]. This problem was implicit in the earlier changes of cone angle for $P(OPh)_3$ from an original value of 121 ± 10° [8b] to a finally accepted value of 128° [8c]. Later it was emphasized [22] that alkyl phosphites were assumed by Tolman to have a conformation such that all the P–O–R moieties were bent in the same way so as to give a minimum cone angle. This is a conformation that had never actually been detected in crystallographic studies [23] and it was suggested therefore that these cone angles had been incorrectly underestimated. A combination of crystallography and trends in some equilibrium constant data led to the suggestion that the true cone angles of $P(OMe)_3$ and $P(OEt)_3$ were actually larger than Tolman’s by 20 and 25°, respectively (see below).

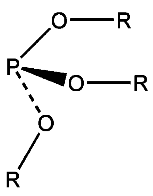
The explosion of crystallographic data (available on the Cambridge Crystallographic Data Base) has led to a very thorough analysis of crystallographic cone angles derived from structures of more than 4000 phosphine-containing compounds [24]. This method has very recently been applied to large numbers of conformationally flexible phosphite complexes [25] and, more specifically, to phosphite complexes with well defined ligand environments [26].

Without attempting to provide a detailed critique of this methodology some points deserve comment. Although the 1507 cone angles for PPh_3, in particular, do have a mean value of 148°, the standard deviation is ±5° and the spread is from 129 to 168°. Data of this sort attest to the ability of PPh_3 and similar ligands to adjust to their individual environments. However, it is also interesting to note that the cone angles of PPh_3 for complexes of the Groups 5–9 metals spread only from 142.3 to 147.2° (144.5 to 147.2° for Groups 6–9, as read from Fig. 3(a) in Ref. [24]). Those for osmium and ruthenium complexes are identical at close to 144.5° (Fig. 3(a) in Ref. [24]) while those for iron complexes are close to 146.5°, both well within the uncertainty assigned by Tolman. Since so many of the analyses of kinetic and other data involve these metals, the use of 145° for the cone angle of PPh_3 is well justified crystallographically if, indeed, it needs justification (see below). However, the 560 cone angles of PMe_3 have a quite precise average of 111.1 ± 2.4°, which is significantly lower than Tolman’s 118 ± 2°, so not all Tolman’s cone angles have crystallographic justification. The point that crystallographic cone angles vary with the group of the metal to which is attached is interesting and must be borne in mind.

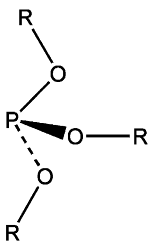
The results obtained in a similar way by Coville and co-workers [25,26] are also of great interest. Crystallographic cone angles for 316 $P(OMe)_3$ structures fall clearly into two groups centred at 117 and 130° and these appear to correspond to the two conformations shown in structures **B** and **C**. The 33 structures of $P(OEt)_3$ hint strongly at *three* maxima centred at 119, 124 and 132°, again showing the flexibility of this ligand, but the two lower maxima both correspond to conformation **B**, while the highest corresponds to **C**. Only one structure with conformation **D** is reported and none of **A**. It is concluded that ‘the metal–ligand environment appears to play a role in establishing the observed conformation’. It is also acknowledged that ‘packing effects certainly cannot be discounted in determining the conformation’ and that ‘the size of the phosphite ligand in the solid state may not *exactly* (our italics) correspond with that in solution’. No estimates were provided



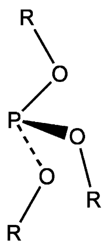
A



B



C



D

for the energetic contributions of these various factors, and calculations of relative energies of various conformations, such as those provided by Bart et al. [23], suffer from involvement of small differences between large values and may now be methodologically outdated.

It is this absence of any 'feel' for relative energetics that underlies the ambiguity in using crystallographic cone angles in the quantitative correlation of kinetic, thermodynamic and other data pertaining to behaviour of isolated molecules in solution. It is our belief that the use of such cone angles is fortunately unnecessary and inappropriate, and that another and superior method is available. This method involves the use of Tolman cone angles as a *starting point* in analyzing electronic and steric effects, but then allows for their adjustment by repeated tests of their 'goodness of fit' to a large number of data sets when they are treated as variables. The electronic parameters, e.g. χ_d, π_p, E_{ar} etc. are accepted in the first instance as fundamental to the analyses, and the cone angles are then eventually determined by the need for their values to provide the best possible fits of a wide range of data to the appropriate equations.

Adjustment of cone angles to give better fits with trends in data is not, of course, a new practice. Some of Tolman's cone angles, while originating in the use of molecular models, were adjusted to 'more suitable' values. Apart from the cone angle for $P(OPh)_3$ mentioned above, that for $P(O\text{-}i\text{-}Pr)_3$ was increased from 114 to 130° [8b] because of a reconsideration of the effect of internal steric strain, and that for PCy_3 was decreased from 179 to 170° [8c] to improve the fit with data for the substitution of other ligands into $Ni(CO)_4$. And even the calculated E_R values for the archetypal substituted PPh_3 ligands were adjusted to improve the fit to some kinetic data [27]. The cone angle of $P\text{-}n\text{-}Bu_3$ was also upgraded from 132 to 136° by Giering and co-workers [28], for no explicit reason, but all these modifications were relatively minor and did not disturb the general pattern of the parameters. More recently [22], cone angles of $P(OMe)_3$ and $P(OEt)_3$ were adjusted upwards by over 20° (see above) on the basis of a combination of crystallographic data and data trends for the equilibria, in THF:

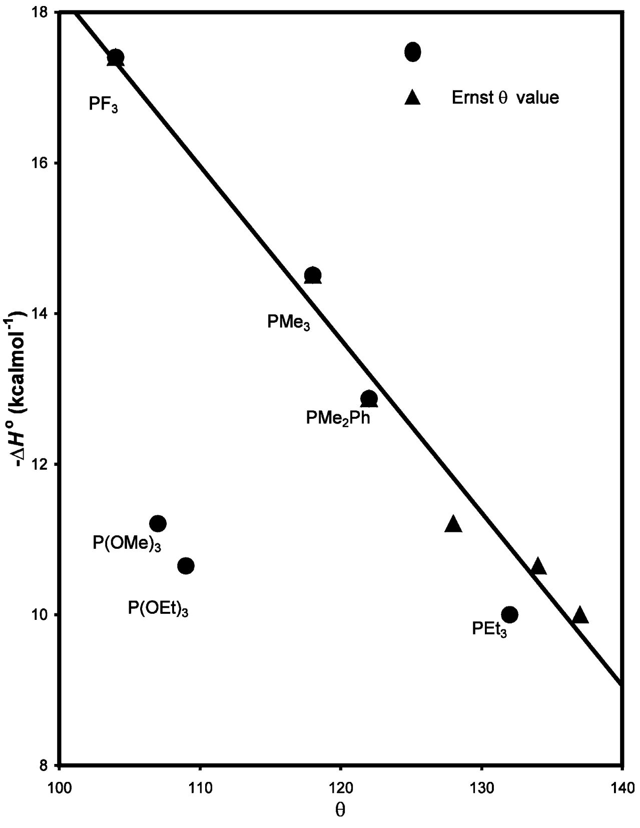


Fig. 1. Dependence of $-\Delta H°$ for reaction (3) on the Tolman and Ernst cone angles for the added ligand. (No $\Delta H°$ value is available for the ligand etpb).

$$Ti(2,4\text{-}Me_2pd)_2 + L \rightleftharpoons Ti(2,4\text{-}Me_2pd)_2L \quad (3)$$

where $L = PF_3$, $P(OMe)_3$, $P(OEt)_3$, PMe_3, $PPhMe_2$ and PEt_3. Equilibrium constants were obtained by using NMR techniques over a range of temperatures so that enthalpies and entropies of ligand addition could be calculated. Entropy changes were taken to be fairly constant and a plot of $-\Delta H°$ against Tolman's and Ernst's cone angles is shown in Fig. 1. This reveals that, *provided electronic effects are ignored*, the cone angles that Ernst et al. derived from their crystallographic studies allow a much better fit to the data. However, the proviso that electronic effects are negligible for such a widely differing set of ligands seems to us to be unreasonable and we have therefore reexamined the data for the equilibrium in Eq. (3).

2. The cone angles of phosphites

2.1. $P(OMe)_3$ and $P(OEt)_3$ as ligands in some titanium(II) complexes

As mentioned above, the enthalpy changes for the equilibria in Eq. (3) were assumed by Ernst and Stahl to depend entirely on steric effects due to the different ligands and as a result proposed large upward adjustments to the cone angles for $P(OMe)_3$ and $P(OEt)_3$ However, we believe that this is unlikely. We have recalculated the thermodynamic parameters for the equilibria (and our values agree well with those of Ernst and Stahl [22]) and from them we calculate the equilibrium constants at 25 °C shown in Table 1. Values for the Tolman and Ernst ligand cone angles are also given, as are the values of pK'_a [11]. Those for pK'_a are directly related to Giering's χ_d values [14,16] in a way that has been described in detail elsewhere [11]. We have chosen to use pK'_a as the electronic parameter because it inherently has the high precision of the IR

Table 1
Ligand parameters and equilibrium constants for the formation of ligand adducts of (2,4-$Me_2pd)_2Ti$ in THF at 25 °C [a]

L	θ_T (°)	θ_E (°)	$pK'_a(\sigma)$	$pK'_a(\pi)$ [b]	π_p [c]	log K
Etpb	101	101	−0.30	8.5	5.0	4.137
PF_3	104	104	−10.01 [d]	20.4	13.2	5.928
$P(OMe)_3$	107	128	0.83	4.85	2.8	1.858
$P(Oet)_3$	109	134	1.64	3.98	2.9	1.812
PMe_3	118	118	6.45	0	0	3.175
$PPhMe_2$	122	122	5.07	0	0	2.197
PEt_3	132	137	7.96	0	0	0.293

[a] The data for the ligand etpb ($P(OCH_2)_3CEt$) were not available in the original publication [22] but were kindly provided later by Professor Ernst.

[b] See Ref. [30].

[c] See Refs. [14,16]; the value for etpb is taken as an arbitrary standard.

[d] Derived in the usual way [11] from the value of χ_d reported by Giering and coworkers [16b] and now preferred to the value given in Ref. [11b].

frequencies used in deriving χ_d [11]. In doing this we ignore possible small contributions from solvation effects (THF vs. a paraffin solvent) [11] in this system.

Analysis of the data using Ernst's cone angles and no electronic effect shows that the data for etpb fit very poorly. The value of K that is needed for a good fit to the data for the other ligands is ca. 100 times larger than that observed. Alternatively an upward adjustment of its cone angle of almost 10° would be required for it to fit, yet etpb is a ligand for which the cone angle is generally accepted to be unambiguous. Equally, using Tolman's cone angles and only the σ-donor electronic parameter pK'_a leads to a very poor fit and the data for ν_{co} in some closely related Ti(II) complexes [29] show that π-bonding effects must be included. Estimates of useful π-bonding parameters, with that for etpb ($P(OCH_2)_3CEt$) being taken arbitrarily as 5, have been made [16] but other estimates are available [30]. These were obtained by measuring the deviation of the pK'_a values for π-acid ligands from the values predicted for pK'_a from the correlation between pK'_a and χ for purely sigma donors. The latter measure the net donicity (sigma donicity offset by π-acidity) of the π-acids while the former measure the sigma donicity alone. The relevant values of the π-acidity parameter, $pK'_a(\pi)$, are given in Table 1 and the complete set is given in Appendix A.

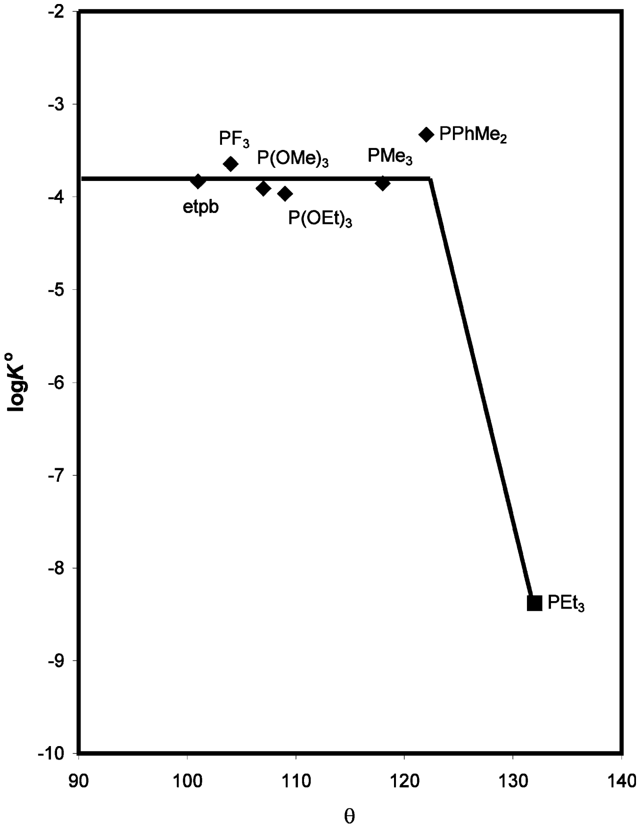


Fig. 2. The steric profile for reaction (3) with σ-donor and π-acidity parameters chosen as described in the text.

The values of $pK'_a(\pi)$ correlate quite well with the values of π_p derived by Giering and coworkers [16] as shown by Eq. (4) where R^2 is 0.947.

$$pK'_a(\pi) = (1.78 \pm 0.13)\pi_p - 1.11 \pm 0.37 \qquad (4)$$

When the data are analyzed in terms of Eq. (5) it is found that only the largest ligand,

$$\log K = \alpha + \beta_\sigma\, pK'_a(\sigma) + \beta_\pi\, pK'_a(\pi) + \gamma(\theta - \theta_{th})\lambda \qquad (5)$$

PEt_3, shows any steric inhibition and the resulting steric profile is shown in Fig. 2. The values of the coefficients are $\alpha = -3.8 \pm 0.9$, $\beta_\sigma = 1.09 \pm 0.17$, $\beta_\pi = 1.00 \pm 0.13$, $122° \le \theta_{th} < 132°$ and $-\gamma \ge 0.34$ deg^{-1}, while $R^2 = 0.979$ and $\sigma(\log K) = 0.30$. In Eq. (5) we have renamed pK'_a as $pK'_a(\sigma)$, to emphasize its significance with respect to sigma donation, while the effective π-acidity parameter is given, by analogy, the symbol $pK'_a(\pi)$. The fit of the data to the analogous equation using Giering's π_p values is not quite as good in this case. The form of the steric profile is nevertheless exactly the same as that in Fig. 2 and this demonstrates the dramatic fact that, except for the largest ligand *there are no steric effects at all on the equilibrium constants for* Eq. (3). This set of data, far from providing evidence for the need to increase the cone angles for $P(OMe)_3$ and $P(OEt)_3$ by substantial amounts, has nothing at all to contribute to this question.

2.2. $P(OMe)_3$ as a ligand in some 17-electron $Re(CO)_4L$ complexes

Relevant data of a quite different sort are available [31] for the reactions of some 17-electron $Re(CO)_4L$ radicals generated by flash photolysis of the parent dinuclear, Re–Re-bonded $[Re(CO)_4L]_2$ complexes. In all, complexes with nine different ligands ($L = CO$, $P(OMe)_3$, PMe_3, $AsEt_3$, $P(O{-}i{-}Pr)_3$, $P(n{-}Bu)_3$, $P(i{-}Bu)_3$, $P(i{-}Pr)_3$ and PCy_3) were reacted with eight different reagents in a variety of solvents at 22 °C, viz: CH_2Br_2 in acetonitrile, CH_2Br_2, $CHCl_3$, and CCl_4, $HSn(n{-}Bu)_3$, $[S(nBu)]_2$, and $MeSSiMe_3$ in hexane, $MCP^+BF_4^-$ (MCP^+ = methyl-4-cyanopyridinium) in acetonitrile and maleic anhydride in toluene. These reactions include halogen, hydride and sulfur group-transfer reactions and two electron transfer reactions.

In analyzing the kinetic data a different choice of electronic parameter has to be made and we follow the procedure adopted by Brown and coworkers [31] in this regard. Because of the high electron density and low oxidation state of the complexes, and the π-acidity of some of the ligands (particularly CO), an electronic parameter that reflects this property is needed. Although χ values do reflect this property, no χ value is available for CO and the only suitable parameter available is $\delta(^{13}CO)$, the ^{13}C chemical shift in $Ni(CO)_3L$ complexes [32]. This parameter has the advantage of being available also for $AsEt_3$ so data involving this ligand can also be included in the analyses. The balance between σ-donor and π-acceptor strengths of the ligands is appropriate only to these particular 18-electron Ni(0) complexes so any difference in this balance in the 17-electron Re(0) complexes of interest might show up as deviations of the data involving π-acid ligands from the regular trends. However, no deviations ascribable to this difference are observed. Analysis of data involving only those ligands for which separate sigma and π parameters are known was not successful, probably because of the small number of degrees of freedom available.

The data were analyzed according to the equation:

$$\log k = \alpha + \beta\delta(^{13}CO) + \gamma\theta \quad (6)$$

and the steric profile found for reactions of $Re(CO)_4L$ with $CHCl_3$ in hexane is shown in Fig. 3 where data involving the ligands $P(OMe)_3$ and $P(i{-}Bu)_3$ were not included in the analysis since they seem to deviate significantly from the trends shown by data for the other ligands. However, the data for $P(i{-}Bu)_3$ need not be considered deviant if a straightforward steric effect is

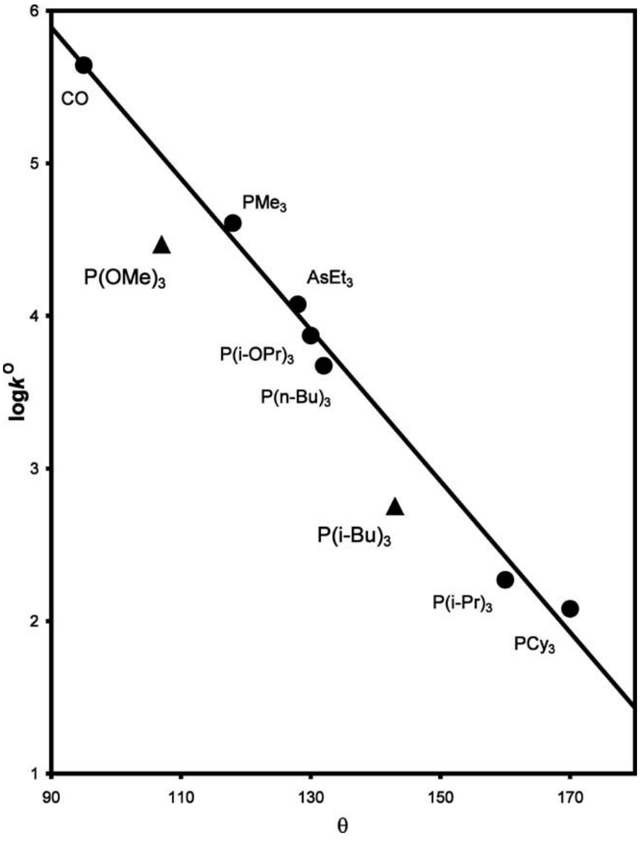


Fig. 3. The steric profile for reactions of $Re(CO)_4L$ with $CHCl_3$ in hexane at 22 °C. (Data taken from Ref. [31a]; data for $L = P(OMe)_3$ or $P(i{-}Bu)_3$ not included in the analysis).

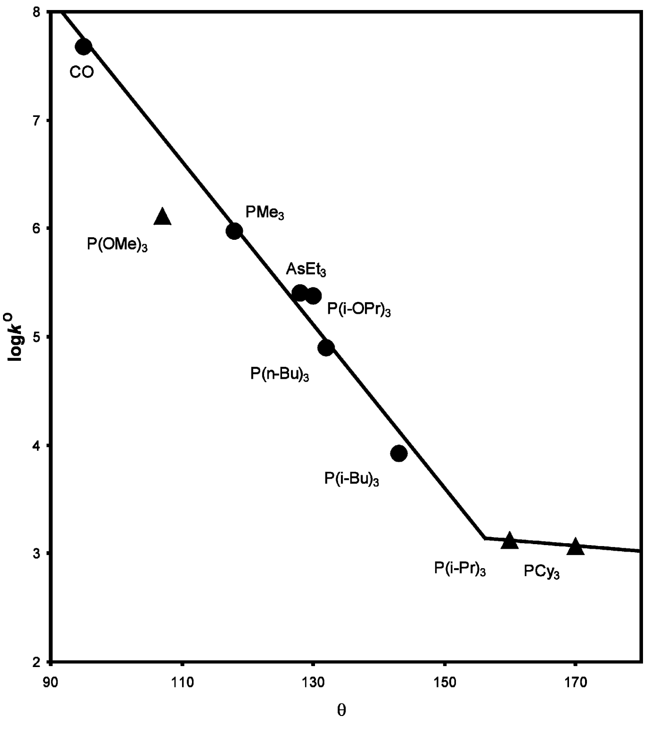


Fig. 4. The steric profile for reactions of $Re(CO)_4L$ with CH_2Br_2 in hexane at 22 °C derived by omitting data for $P(OMe)_3$ (see text; data taken from Ref. [31a]).

Table 2
Analysis of the data of Brown and coworkers [31] according to Eq. (6) but without data for $P(OMe)_3$, $P(i\text{-}Pr)_3$ and PCy_3

Reactant	α	β (ppm^{-1})	γ (deg^{-1})	R^2	RMSD(θ) (deg)	$\Delta P(OMe)_3$ (deg) [a]
CH_2Br_2 in hexane	15.2(12)	0.67(9)	0.078(12)	0.947	2.0	10.1
CH_2Br_2 in CH_3CN	15.1(7)	0.61(5)	−0.078(7)	0.978	1.2	10.4
$CHCl_3$ in hexane	12.4(9)	0.65(7)	0.071(10)	0.964	1.8	10.5
CCl_4 in hexane	14.0(13)	0.64(10)	0.065(13)	0.931	2.6	8.1
$HSn(n\text{-}Bu)_3$ in hexane	13.8(6)	0.41(5)	−0.064(7)	0.970	1.3	7.1
(n-Bu)SS(n-Bu) in hexane	15.3(6)	0.69(5)	−0.086(7)	0.986	1.0	10.5
$MeSSiMe_3$ in hexane	12.4(8)	0.54(6)	−0.069(8)	0.962	1.5	10.9
$MCP^+BF_4^-$ in CH_3CN	12.1(16)	0.16(12)	−0.04(2)	0.760	4.8	4.8
MA in toluene	15.0(30)	0.39(23)	−0.07(3)	0.658	5.2	4.6

[a] Deviation of Tolman cone angle for $P(OMe)_3$ from that required for the data to fit exactly on the steric profile.

invoked. A steric threshold between the data for $P(i\text{-}Bu)_3$ and $P(i\text{-}Pr)_3$ could occur if steric repulsions involving those ligands in the ground state of $Re(CO)_4L$ diminish the steric effect shown in the transition state for the transfer of the chlorine atom so that the gradient of the steric profile becomes less negative.

The steric profile obtained in this way from similar data for one of the other reactions is shown in Fig. 4 where it can be seen that even the ligand $P(i\text{-}Pr)_3$ may fit below the steric threshold. The result of this analysis suggests that now only the data for the complex containing $P(OMe)_3$ is deviant. The increase in the cone angle required to make this ligand fit exactly on the steric profile is 10.1° and the RMSD(θ) value for the remaining ligands is $\pm 2.0°$. All the reactions show this same behaviour and the results obtained are summarized in Table 2. The average deviation of the data for reactions of the $P(OMe)_3$ complex from the steric profiles is $9.7 \pm 0.5°$ when results for seven of the nine sets of reactions are considered. The data for the two electron transfer reactions show a much poorer fit to the model as well as smaller, and less precise, deviations for the $P(OMe)_3$ complexes.

2.3. $P(O\text{–}i\text{-}Pr)_3$ as a nucleophile in substitution reactions of $Ir_4(CO)_{12}$

The carbonyl cluster $Ir_4(CO)_{12}$ was the first to show excellent adherence ($R^2 >$ ca. 0.98) to an equation such as Eq. (1) and the θ_T values ranged from 101 to 170° without obvious deviations of any nucleophiles, *including* $P(OEt)_3$, from the steric profiles at temperatures ranging from 40 to 100 °C [7]. We have modified the analysis of those data by using $pK'_a(\sigma)$ as the σ-donor parameter, and by taking into account the possibility of some effects on the rates due to π-acidity [16,30] or the 'aryl' effect [15] of the nucleophiles. Values of the rate constants at 25–100 °C were calculated by use of the activation parameters, and data for the nucleophile $P(O\text{–}i\text{-}Pr)_3$ ($\theta_T = 130°$), obtained subsequently [33] to the original set, were also included. In the event, no aryl effect was detected but small improvements of the fits of the data were observed when the π-acidity parameter, π_p, was included (Eq. (7)). The results obtained are shown in Table 3 where it can be seen

$$\log k_2 = \alpha + \beta\, pK'_a(\sigma) + \gamma\theta_T + \phi\pi_p \tag{7}$$

that the fits to the equation are very good. Inclusion of the parameter π_p improves the R^2 values by ca. 0.032–0.009 as the temperature increases from 25 to 100 °C but all the coefficients of the electronic and steric parameters decrease with increasing temperature. Use of the π-acidity parameter, $pK'_a(\pi)$, led to even smaller improvements in the fit and the corresponding coefficients were barely significant compared with their uncertainties.

The rates were measured over quite different temperature ranges, depending on the particular nucleophile

Table 3
Analysis of second order rate constants for associative substitution of P-donor nucleophiles into $Ir_4(CO)_{12}$ according to Eq. (7)

T (°C)	β	γ (deg^{-1})	ϕ	$\sigma(\log k_2)$	$\sigma(\theta_T)$ (deg) [a]	R^2
25.0	0.37(4)	−0.082(8)	0.23(11)	0.267	2.51	0.984
40.0	0.34(4)	−0.080(7)	0.22(9)	0.235	2.27	0.986
60.0	0.31(4)	−0.077(7)	0.18(10)	0.241	2.40	0.984
80.0	0.28(4)	−0.075(8)	0.15(11)	0.286	2.95	0.976
100.0	0.26(5)	−0.072(10)	0.12(14)	0.349	3.69	0.961

[a] From a plot of θ_T against $\log k_2 - \beta pK'_a(\sigma) - \phi\pi_p$.

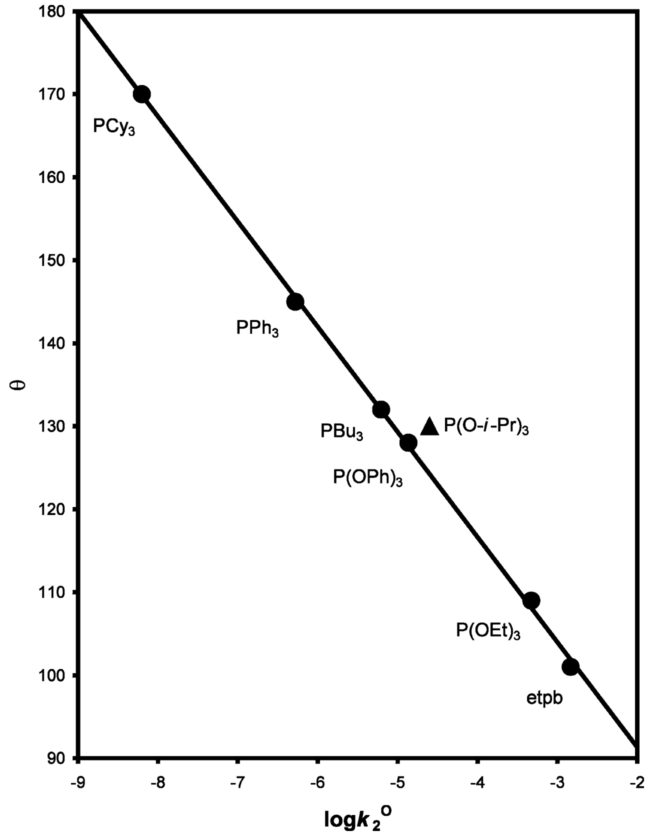


Fig. 5. The inverse steric profile for reactions of $Ir_4(CO)_{12}$ at 60 °C. The data for L = P(O–*i*-Pr)₃ were not included in the calculations (see text).

involved and, although there was no temperature common to all the nucleophiles, the data at 40 and 60 °C needed the least adjustment for temperature differences. The analyses of the data at those temperatures are probably the most reliable and this is supported by the better fit of the data at these temperatures.

The values of $\sigma(\theta_T)$ are all quite good but, when the deviations of the individual values of θ_T from the inverse steric profile (i.e. the plot of θ_T vs. log $k_2 - \beta$ p$K'_a(\sigma) - \phi\pi_p$) are considered, the largest deviation is always that due to the P(O–*i*-Pr)₃ nucleophile. Thus the deviations suggest that the value $\theta_T = 130°$ is high by 3.9 and 4.5°, respectively, at 40 and 60 °C, whereas the next highest deviations are 2.2 and 2.5°, both for etpb. Omitting the data for P(O–*i*-Pr)₃ from the analysis has a negligible effect on the coefficients obtained but the deviations of its θ_T value from the inverse steric profiles (Fig. 5) are now 4.9 and 5.7° at 40 and 60 °C, respectively. The value of $\sigma(\theta)$ for the other nucleophiles is 0.7°. The deviations of the θ_T values for etpb and P(OEt)₃ at 60 °C are both only −0.9° so that it is clearly only P(O–*i*-Pr)₃ that appears to be a 'sterically deviant' nucleophile in this series of reactions. However, it deviates in a way that suggests its cone angle was perhaps over adjusted by Tolman (see above) and that it should be *smaller* than θ_T.

3. Discussion

The above applications of the methodology for separating electronic and steric effects on thermodynamic or kinetic data involving P-donor ligands show some important features. The most dramatic is that conclusions about steric effects can depend crucially on a correct assessment of any electronic effects. In the case of adduct formation by Ti(2,4-Me₂pd)₂ the arbitrary exclusion of any electronic effects at all leads to totally different results from those obtained if both σ-donor and π-acidity effects are, quite reasonably, allowed for. Disregard of electronic effects allows the equilibrium data to be fitted only by gross modifications of the cone angles of two of the seven ligands involved, and moderate modification of that of a third. The large adjustments proposed by Ernst and Stahl [22] and, unwisely in our view, set in stone in a well regarded undergraduate text book [34], are therefore quite unjustified and it seems much more likely that there are in fact no steric effects at all for six out of the seven ligands.

Our fit of the data to Eq. (5) draws attention to an advantage of the p$K'_a(\pi)$ parameter compared with Giering's π_p values. The parameters p$K'_a(\sigma)$ and p$K'_a(\pi)$ are both dimensionless and their coefficients can be directly compared to obtain the relative contributions of sigma and pi-bonding to the strength of the bonding of the P-donors to the Ti(II) centre. In this case the two contributions are both essentially the same and rather large, the sigma donicity involved being quantitatively comparable, in view of the way in which the parameters are derived, to the proton basicity of the ligands.

The kinetic data reported by Brown and coworkers [31] for the various reactions of $Re(CO)_4L$ also involve the presence of ligands completely bound to a metal. However, in these cases, there are no suitable σ-donor and π-acidity parameters for four out of the nine ligands used. The data for the remaining ligands do not give a good fit to any suitable equation partly because at least one of them lies above a steric threshold and too many parameters need derivation from the few data left. We, therefore, are limited to following Brown's example [31] and use $\delta(^{13}CO)$ as the electronic parameter. The successful use of this parameter for the many reactions reported suggests that the balance between σ-donor and π-acidity effects on the rates must be similar to those on $\delta(^{13}CO)$. While the need to rely on this coincidence is regrettable the data analyses do provide a good example of what should be done when more suitable ligand selections are available.

In these reactions the effects due to the ligands are shown up in the differences between ground state effects on five-coordinate complexes, and effects on transition states that involve a variety of processes in essentially six-coordinate species. In the event, the ground state steric effects are only evident for the two largest substituents, and possibly for only one (provided their cone angles are correct) and the analysis of any uncertainties in cone angles depends on the other seven ligands.

The results of the analysis of the seven group transfer reactions all indicate that $P(OMe)_3$ is a clear outlier and that its Tolman cone angle has to be increased by close to 9 or 10° *in each case* in order for its data to fit the steric profile. However, $P(i\text{-Bu})_3$ is not the outlier that Brown and coworkers suspected [31]. The results for the electron transfer reactions [31c] fit less well to Eq. (6) but they also suggest that the cone angle of $P(OMe)_3$ needs increasing, though to an extent that seems to be smaller than for the group transfer reactions but that is not so precisely defined.

The associative reactions of the cluster $Ir_4(CO)_{12}$ necessarily involve electronic and steric effects of the P-donors as nucleophiles in transition states where the Ir–P bonds are presumably not fully formed. The ligands used are more conventional and closely related to each other than those in the above two studies and their electronic parameters are therefore probably more reliable. It has previously been believed [11,21] that contributions due to π acidity in associative reactions of this sort are negligible, and it appears that, at most, only a very small and not well defined contribution is operative here. Allowing for this small effect, the steric profile is still quite linear and $P(OMe)_3$ is not an outlier in this case. If the *relative* effective values of the cone angles remain the same in the kinetics of associative reactions as in other types of reaction, or in other types of physicochemical measurements, then linear steric profiles should still be obtained but with the steric coefficient, γ, being smaller. On the other hand, when P-donors such as $P(OMe)_3$ show enhanced cone angles when present as ligands, but do not show such an effect when present as nucleophiles in associative transition states, this might be indicative of a genuinely smaller effective cone angle when the metal–P bond are longer [18]. In other words, cone angles might vary with the type of interaction the P-donors are having within a complex. That seems to be the case here and it is possible that the smaller enhancement of the cone angle for $P(OMe)_3$ required for electron transfer reactions of the complexes $Re(CO)_4L$ is a genuine indication that its cone angle is effectively smaller because the reactant approaches the Re atom less closely than in the group transfer reactions. The only possible deviant in this analysis is the nucleophile $P(O\text{–}i\text{-Pr})_3$ and this deviates in a way that suggests its cone angle should be slightly but significantly smaller than Tolman's. This brings us back to the fact, mentioned above, that Tolman adjusted his cone angle upwards by a considerable amount as a result of reconsidering the large variation of steric strain with conformation of the ligand. This contrasts surprisingly with the case of $P(OMe)_3$ where the cone angle did not seem to vary at all with changing internal strain [8] but it does emphasize that some ligands might change their effective cone angles more with changing circumstances than others.

The analyses considered here represent a very small and not necessarily ideal selection. Although we have emphasized deviations of cone angles from otherwise linear steric profiles, most P-donors (and some other donors as well) do usually fit on linear steric profiles and Tolman's cone angles are remarkably successful in representing steric effects [14,16]. Some, however, do need adjustment and some adjustments may be necessary in some circumstances but not in others. Sometimes, of course, ligands may lie below steric thresholds in which case the whole question of their cone angles is irrelevant. This is often the case with the smaller phosphites acting as nucleophiles.

There is, however, a way in which a widely applicable set or sets of cone angles can be obtained, and the approach followed above suggests what this might be. One would start with Tolman cone angles, adjusted if necessary in the ways outlined above, and in every analysis the cone angles required for a perfect fit to the steric profile would be tabulated. This would be repeated each time a new set of data was analyzed (or old ones reanalyzed) and the effective cone angles averaged. In time a set of cone angles applicable to particular situations would be accumulated, rather in the way the Cambridge Data Base has been used to derive crystallographic cone angles, but on a smaller scale! These new cone angles would then have risen above their humble origins in simple molecular models. They would have taken on an independent existence of their own that would be strictly relevant to the kinetic, thermodynamic or other environments in which the measurements are made, rather than in the quite different solid environments characteristic of crystallographic cone angles. If these new cone angles are applicable in all circumstances then they would justify their description as ideal or Platonic. This need not be denied them even if some fall into sub groups, characteristic of different circumstances of the sort implied above. It would certainly not detract from their basis in a very wide range of diverse experimental data rather than in simple molecular models. Provided their relative values stay the same they could be re-scaled to any convenient values and referred to simply as 'steric parameters' so as to emphasize their distinction from model-based cone angles. However, it would probably be more correct to recognize their historic origins and leave the values close to or exactly equal to Tolman's cone angles from which they evolved.

This process assumes, as was done above, that the electronic parameters that are used are essentially correct and that any adjustments needed are due entirely to faulty assignments of cone angles. If this is not true it should become apparent during the process outlined, and for ligands with reliable cone angles, but dubious electronic ones, the electronic ones can be refined. Such an iterative process would be similar to that used by Giering and coworkers [16] for a restricted set of ligands. The approach is also fundamentally different from the type of data analysis proposed by Drago and coworkers [35], which generally minimizes contributions from steric effects. It has been extensively and, we believe, convincingly criticized by Giering and coworkers [36] and we do not consider that further consideration of that approach is necessary here.

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Appendix A

The π-acidity parameters, $pK'_a(\pi)$ and π_p, for relevant P-donor ligands are given in Table A1.

Table A1 π-acidity parameters, $pK'_a(\pi)$ and π_p, for relevant P-donor ligands

L	$pK'_a(\pi)$ [a]	π_p [b]
etpb	8.50	5.0
PF_3	20.43[c]	13.2
$P(OMe)_3$	4.85	2.8
$P(OBu)_3$	3.47	2.7
$P(OEt)_3$	3.97	2.9
$PPh(OMe)_2$	2.37	1.9
$PPh(OEt)_2$	1.97	1.97
$P(OPh)_3$	5.33	4.1
$P(O-i\text{-}Pr)_3$	4.00	2.9
$P(CH_2CH_2CN)$	3.60	1.2
$PPh_2(OMe)$	0.86	0.80
$PPh_2(OEt)$	0.65	1.0
$PPh(OPh)_2$	3.11	2.7
$P(OCy)_3$	3.37	–
$PPh_2(OPh)$	1.42	1.4
$P(O-o\text{-}MeC_6H_4)_3$	5.33	–
$P(O-o\text{-}PhC_6H_4)_3$	5.74	–
$P(O-t\text{-}Bu)_3$	2.26	–

[a] Taken from Ref. [30] and derived as described in the text.

[b] Taken from Refs. [14,16].

[c] Derived from the relationship, $pK'_a(\pi) = (1.78 \pm 0.13)\pi_p - 1.11 \pm 0.37$ using Giering's π_p value of 13.2. This value is now preferred to that reported in Ref. [11b].

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