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Ligand steric properties*

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CONTENTS

ABSTRACT

Methods of estimating the steric requirements of ligands are reviewed. The most widely employed measure is the cone angle, Θ, first proposed by Tolman. Elaborations on the cone angle concept include mathematical methods for its estimation, estimates based on X-ray structural data, and solid cone angle measures. The ligand repulsive parameter, E_R, is based upon molecular mechanics calculations of the structures of $Cr(CO)_5$ complexes of the various ligands. The Θ and E_R parameters correlate reasonably well, but significant disparities are found among a large group of phosphorus, arsenic and nitrogen ligands for which both Θ and E_R values are available. Consideration of the various approaches to estimating ligand steric requirements indicates that each ligand has a *range* of steric requirements relative to other

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ligands, depending on the details of the particular complex or reaction involved. Applications of ligand steric requirements include quantitative linear free energy relationships. Given the relative imprecision with which the steric (and probably also the electronic) parameters can be determined, the use of additional parameters to account for the relative importances of σ and π bonding, or the existence of a steric threshold may not be justified by the number and variety of data available. Nevertheless, despite their lack of high precision, linear free energy relationships can provide important information regarding the electronic and steric demands of the transition state relative to the ground state in chemical reactions.

1. INTRODUCTION

The properties of metal-coordinated compounds, whether in classical inorganic coordination complexes or in organometallic compounds, are determined in large measure by the ligands bound to the metal. A ligand is any atom, molecule or ion bound to one or more metals, and which, along with other ligands, forms the primary set of bonds for that metal. For purposes of the present discussion, the term can also be extended to molecules or ions acting as reagents approaching a reaction center and involved in an intermediate or transition state in the course of a reaction.

It would be desirable to be able to describe ligand effects in terms of a small number of parameters relating to steric and electronic properties, with characteristic values for each ligand. The electronic property of a ligand refers to the electronic character of the ligand–metal bond, i.e. to the extent of overlap of orbitals and amount of net charge transfer between ligand and metal.

The concern in this review is primarily with the steric properties of ligands, with an emphasis on organometallic systems. The steric effect is a measure not merely of a ligand's size, but of its spatial requirements in the coordination environment. We will review and compare various methods proposed for quantitatively assessing ligand steric requirements. On the basis of such comparative analyses, the advantages and limitations of differing approaches can be evaluated. In addition, the comparative results also provide a basis for considering the precision with which a characteristic steric parameter value can be assigned to a given ligand.

2. METHODS OF EVALUATING LIGAND STERIC REQUIREMENTS*

2.1 Cone angle

The most widely used quantitative measure of the amount of space occupied by a ligand is the so-called "cone angle", Θ, as defined and measured by Tolman [2–4]. The cone angle concept was originally applied to phosphorus ligands, but has since been extended to amines [5]. For symmetrical ligands (those with all three organic substituents the same), the cone angle Θ is defined as the apex angle of a cylindrical cone, with origin 2.28 Å from the center of the phosphorus atom, whose

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* See also an earlier review of Group 15 ligands covering some of the same ground [1].
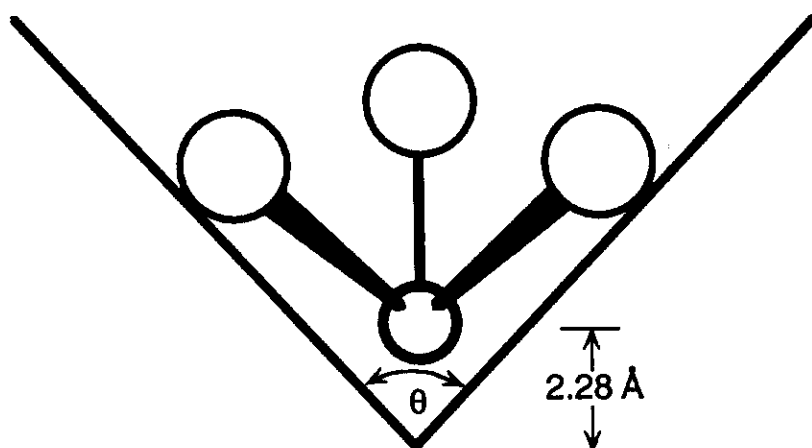
Fig. 1. Geometrical definition of the cone angle.

sides just touch the van der Waals surfaces of the outermost atoms of the organic substituents (Fig. 1). Tolman constructed space-filling (CPK) models of various phosphines and measured their cone angles using a special jig and protractor. In cases where various conformations of the groups bound to phosphorus are possible, the groups were folded back to give the smallest possible cone angle while still maintaining a nominal three-fold symmetry axis. In cases where Θ is difficult to measure with models (e.g. PCy_3), values were estimated by employing relative dissociation constants, K_d, for the reaction $NiL_4 \rightleftharpoons NiL_3 + L$.

For unsymmetrical phosphines PRR'_2 and $PRR'R''$, Tolman [4] suggested that an "effective" cone angle can be obtained using the "half-angles", or semicone angles, $\theta_i/2$, illustrated in Fig. 2. The effective cone angle is defined in terms of the average of the maximum half-angles $\theta_i/2$ (eqn. (1)).

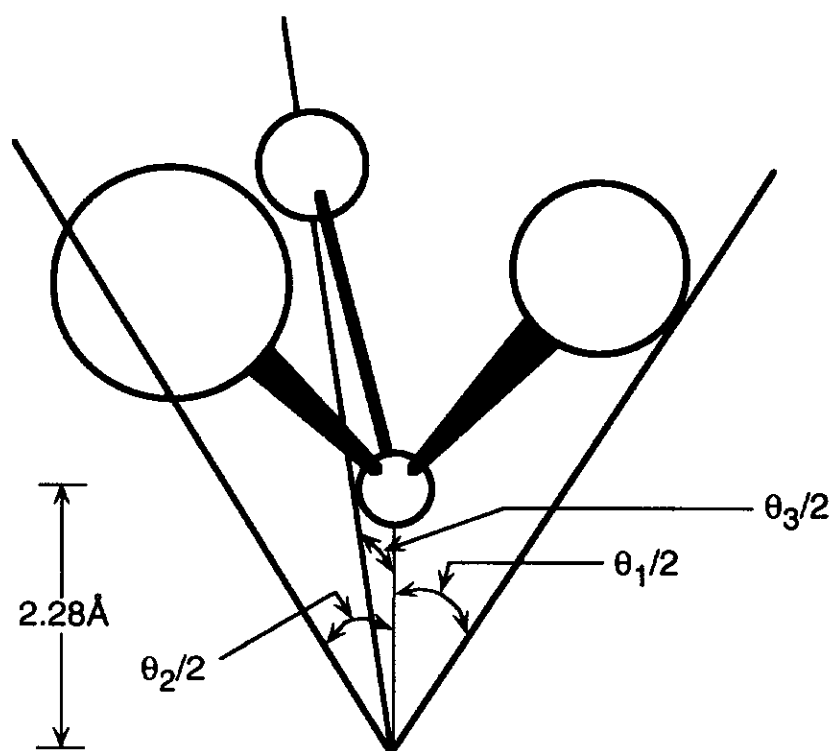$$\Theta = \frac{2}{3} \sum_{i=1}^{3} \frac{\theta_i}{2} \tag{1}$$

Fig. 2. Geometrical definition of the semicone angle, $\theta/2$.

For example, for a ligand such as PMeEt(t-Bu), Θ is 144°, the average of that for PMe$_3$ ($\Theta = 118°$), PEt$_3$ ($\Theta = 132°$), and P(t-Bu)$_3$ ($\Theta = 182°$). The cone angle values of a selection of phosphorus ligands evaluated by Tolman are listed in Table 1.

The cone angle model used by Tolman has the advantages of being simple and generally applicable. However, the approach does have limitations, some of which have been noted by Tolman [2].

(1) The space-filling models employed are inflexible, and assume tetrahedral geometries about carbon and phosphorus. In real molecules, low-energy bending distortions can occur when the ligand environment becomes crowded.

(2) Where the substituent group conformations are variable, Tolman employed the conformation which gives the smallest cone angle. This conformation may be a poor approximation of the one found in the free ligand or when it is bound in a metal complex.

(3) The van der Waals surface formed from the outermost atoms of the substituents on phosphorus or other central atom is irregular. Substituent groups on ligands bound to the same metal center can sometimes mesh with one another, permitting closer packing of ligands than would be expected based on cone angle values.

(4) Tolman has suggested using the sum of the half-angles to estimate appropriate cone angles for phosphorus ligands in which the substituent groups are different. The values thus obtained may not reflect the properties of the ligand, particularly when the substituent groups differ greatly.

TABLE 1

Cone angles for phosphorus ligands [2]

Ligand	Θ (degrees)	Ligand	Θ (degrees)
PH$_3$	87	PPh$_2$(i-Pr)	150
PH$_2$Ph	101	P(i-Pr)$_3$	160
Me$_2$PCH$_2$CH$_2$PMe$_2$	107	P(sec-Bu)$_3$	160
Et$_2$PCH$_2$CH$_2$PEt$_2$	114	PBz$_3$	165
PMe$_3$	118	PCy$_3$[a]	170
PMe$_2$Ph	122	P(neopentyl)$_3$	~180
PHPh$_2$	128	P(t-Bu)$_3$	182
PEt$_3$	132	P(C$_6$F$_5$)$_3$	184
P(n-Bu)$_3$	132	P(o-Tol)$_3$	194
PMePh$_2$	136	P(mesityl)$_3$	212
PEt$_2$Ph	136	P(OMe)$_3$	107
PEtPh$_2$	140	P(OPh)$_3$	128
P(i-Bu)$_3$	143	P(O-i-Pr)$_3$	130
PPh$_3$	143	P(O-o-tolyl)$_3$	141
P(p-tol)$_3$	145	P(O-t-Bu)$_3$	172

[a]Cy = c-C$_6$H$_{11}$, cyclohexyl.

(5) It is not clear how to extend the cone angle concept to ligands such as sulfides, olefins and other organic ligands (however, the use of solid cone angles goes some way toward circumventing this limitation, as described below).

2.2 Variants of the cone angle concept

Following the publication of Tolman's innovative approach, several modifications and extensions of the cone angle concept were made in an attempt to overcome some of the limitations of the original method.

2.2.1 Mathematical models

Imyanitov [6] has developed a mathematical procedure for determining the cone angle of any ligand AB_n (A and B are atoms with A coordinated to the metal) provided that the covalent radii of A, B and M are known, the van der Waals radius of B is known and the molecular geometry is known. Using a graphical representation of $M-AB_n$, shown in Fig. 3, Imyanitov derived the equation

$$\theta/2 = \text{arc } \sin(R_B/(a^2 + b^2)^{1/2}) + \text{arc } \tan(-b/a) \tag{2}$$

where $a = r_M + r'_A + (r_A + r_B) \sin(\alpha - 90)$ and $-b = (r_A + r_B) \cos(\alpha - 90)$. Here, r_M, r_A, r'_A, and r_B are the covalent radii of the subscript atoms $(AB = r_A + r_B; MA = r'_A + r_M)$. R_B is the van der Waals radius of atom B, θ is the cone angle and α is the angle MAB shown in Fig. 3.

Imyanitov extended the use of this equation to more bulky and complex ligands AB'_3, where B' is a polyatomic organic group [7], by using geometrical constructions to measure an "effective" covalent radius, r_e, and an "effective" van der
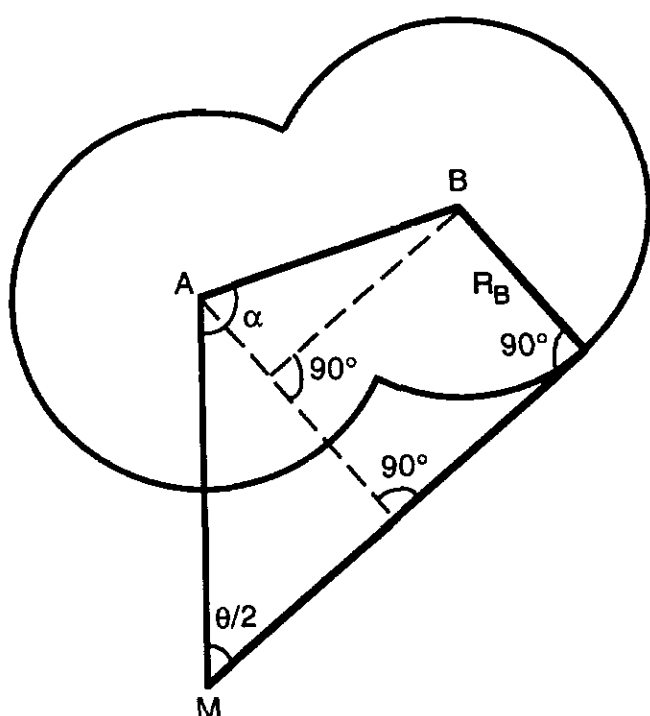

Fig. 3. Graphical model for computation of the semicone angle, $\theta/2$.

Waals radius, R_e, for the substituent group. Because Imyanitov elected to use a shorter metal–phosphorus distance of 2.23 Å, his calculated phosphine cone angles are systematically 5° higher than those of Tolman.

2.2.2 Cone angles based on X-ray structural data

Several research groups have used X-ray crystal structure data as a basis for estimating angles. Ferguson and co-workers [8–10] have devised a method of calculating the maximum semicone angles $(\theta/2)$ of phosphine ligands from the atomic coordinates observed in the crystal structures of transition metal phosphine compounds (Fig. 4). $\theta/2$ is the angle between the M–P axis and a vector X emanating from the center of the metal and tangent to the van der Waals spheres of the outermost atoms of the ligand as it is rotated around the M–P axis. The average of the maximum $\theta/2$ values found for the three phosphine substituents is doubled to give the cone angle for the ligand. The cone angles obtained by this method are listed in Table 2 along with Tolman's values for comparison. The agreement with Tolman's values is reasonably good. On the other hand, for some ligands, the cone angles obtained by this method show considerable variation. For example, for PCy_3, θ varies from 163° in $[PtI_2(PCy_3)_2]$ to 181° in $[Hg(NO_3)_2(PCy_3)]_2$.

To better visualize the sizes of the phosphine ligands, Ferguson and co-workers introduced the "ligand profile", a cartesian plot of the $\theta/2$ values vs. the degree of rotation around the M–P axis (ϕ in Fig. 4). These ligand profiles for bulky phosphines graphically display the gaps between the phosphine substituents and the overall "cog-like" nature of the phosphine. An example is shown in Fig. 5. A variation of the ligand profile has been reported by Smith and Oliver [11] who opted to plot $\theta/2$ vs. ϕ using a polar coordinate system.

Payne and Stepaniak [12] have used X-ray crystal structure data of phosphines in square-planar complexes to compute "variable" cone angles which describe the
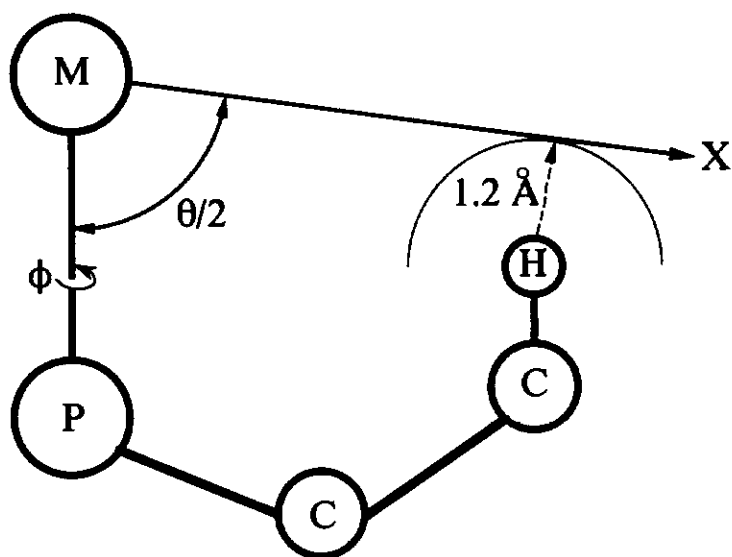

Fig. 4. Schematic diagram for calculation of the semicone angle $\theta/2$ from crystal structure data. The cone-generating vector X is co-planar with the metal, phosphorus and hydrogen, and is tangent to the van der Waals radius of the outermost hydrogen atom, 1.2 Å from the H atom center. Adapted from ref. 9.

TABLE 2

Cone angle data determined from the analysis of X-ray crystal structures [8–10]

Compound	Maximum semicone angles, $\theta/2$ (degrees)	Estimated cone angle (degrees)
$[Cy_3PHg(SCN)_2]_n$	86.7, 87.3, 91.9	177[a]
$[Cy_3PHg(NO_3)_2]_2$	89.9, 90.5, 90.9	181
$[Cy_3PHg(OAc)_2]_2$	84.5, 88.9, 95.1	179
$(Cy_3P)_2Hg(OAc)_2$	83.0, 86.3, 86.9	171
	78.5, 85.5, 89.0	170
$(Cy_3P)_2Hg(ClO_4)_2$	79.1, 82.6, 87.2	166
	78.2, 82.9, 86.2	165
$(Cy_3)_3Pt$	76.3, 84.3, 85.0	164
$(Cy_3P)_2PtI_2$	74.9, 84.3, 85.9	163
$(t\text{-}Bu)_3PHg(OAc)_2$	91.9, 93.9, 95.1	187[b]
$(t\text{-}Bu)_3PHg_2(SCN)_4$	92.9, 94.2, 96.5	189
$(t\text{-}Bu)_3PNiBr_3^-$	88.0, 88.2, 88.2	176
$[(o\text{-}tol)_3PHgCl \cdot ClO_4]_2$	93.6, 101.4, 102.0	198[c]
$[(o\text{-}tol)_3PHg(OAc)_2]_2$	86.6, 99.7, 99.8	191
$((o\text{-}tol)_3P)_2PtI_2$	82.8, 88.6, 103.8	183
$((o\text{-}tol)_3P)_2IrClCO$	87, 89, 102	183
$[HgP(mesityl)_3(NO_3)_2]_2$	102.7, 103.1, 106.4	212[d]
	103.2, 103.7, 104.2	207

[a]Tolman cone angle = 170°.
[b]Tolman cone angle = 182°.
[c]Tolman cone angle = 194°.
[d]Tolman cone angle = 212°.
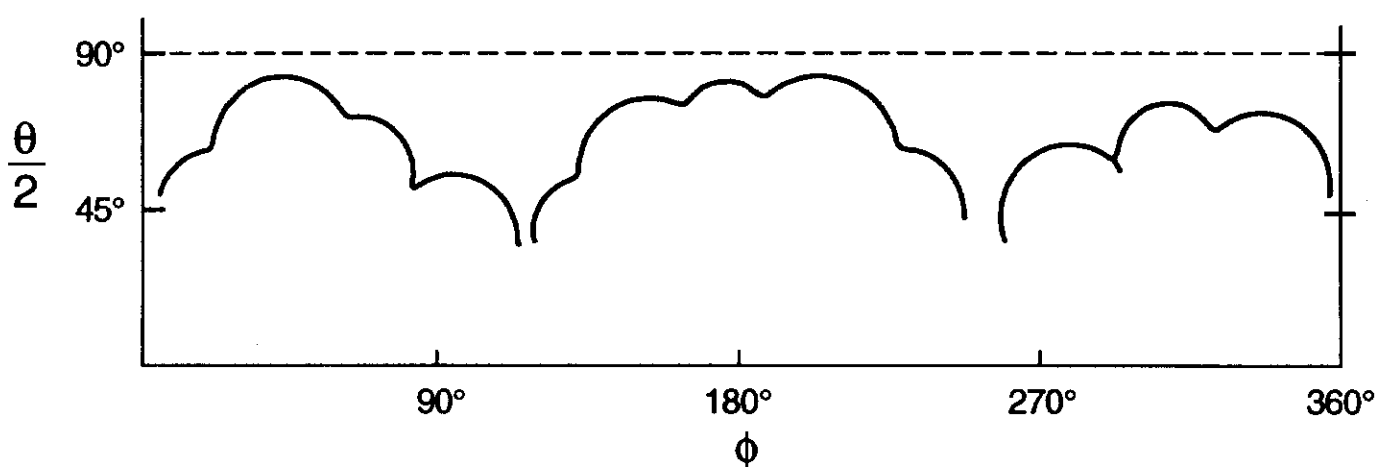
Fig. 5. Ligand profile for $P(c\text{-}C_6H_{11})_3$ in $[P(c\text{-}C_6H_{11})_3]_3Pt$. Adapted from ref. 9.

change in the ligand steric demand as it is rotated about the metal–phosphorus bond axis. The calculations reveal that there is wide variation in the steric requirement of the phosphine as it is rotated around the metal–phosphorus bond. For example, the cone angle for PCy_3 was found to vary from a minimum of 113° to a maximum of 169° with a mean value of 145° for the three sets of data examined.

2.2.3 Applications of semi-empirical molecular orbital calculations to conformational analysis

Mosbo and co-workers [13] investigated the use of alternative cone angle definitions using MINDO/3-computed optimized geometries and heats of formation (ΔH_f) data for 15 different phosphines. In cases such as PEt_3, in which multiple ligand conformations are possible, calculations were carried out on all possible low-energy conformations. From the optimized geometry, half-cone angles ($\theta/2$) were calculated for each conformation using a computer program. A metal atom is positioned 2.23 Å from the center of the phosphorus atom along a vector passing through the center of the phosphorus atom which is normal to the plane defined by three points located 1.00 Å along each P–R bond axis. The half-cone angle ($\theta/2$) values to the outermost van der Waals radii of the organic groups attached to phosphorus were computed at 1° increments for the 360° rotation (ϕ) about the metal–phosphorus bond. Plots of $\theta/2$ vs. ϕ gave the ligand profiles for the phosphines as defined by Ferguson and co-workers [8–10].

In the method deemed optimal for calculating a cone angle from the computed $\theta/2$ data, the average maximum $\theta/2$ values obtained for each of the groups on phosphorus was doubled. For ligands with multiple configurations, weighted-average cone angles were calculated using eqn. (3) where θ_i is the cone angle characteristic of conformer i, and n_i is the corresponding mole fraction. The mole fraction of conformer A is expressed by eqn. (4), where g_A is the

$$\theta = n_1\theta_1 + n_2\theta_2 + \ldots + n_i\theta_i \tag{3}$$

$$n_A = \frac{g_A}{g_A + g_B e^{-\Delta E_{AB}/RT} + \ldots + g_i e^{-\Delta E_{Ai}/RT}} \tag{4}$$

number of conformers with that conformation, ΔE_{Ai} is the difference in the heat of formation between conformers i and A, and $T = 298$ K. The cone angles thus obtained are listed in Table 3. Since the weighted average of all conformations was used rather than just the conformation that gives the smallest cone angle, the values calculated in this manner are generally larger than those reported by Tolman.

The advantage this method offers for determining cone angles is that it considers the energy-weighted contributions from various conformations of the free ligand. However, program and computational requirements limit application of the method to relatively simple ligands.

2.2.4 Cluster cone angles

Mingos [14] defines a "cluster cone angle" to describe the steric interactions of ligands bound to large transition metal cluster polyhedral more accurately. In contrast to mononuclear complexes, the ligands in large cluster complexes form a "shell" around a metal framework. The steric requirements of ligands that fit around the metal cluster polyhedron are better represented by a cone angle based on a cone with

TABLE 3

Conformer-weighted average cone angles, $\langle\theta\rangle$, determined from MINDO/3 optimized geometries and heats of formation data [13]

Ligand	$\langle\theta\rangle$ (degrees)	Θ^a (degrees)
PH$_3$	91.2	87
PH$_2$Me	103.4	97
PH$_2$Et	108.0	102
PH$_2$(i-Pr)	111.6	111
PH$_2$(t-Bu)	116.4	119
PH$_2$Ph	106.3	106
PH$_2$(o-tol)	110.2	123
PHMe$_2$	117.7	108
PHEt$_2$	126.8	117
PH(i-Pr)$_2$	135.3	136
PHMePh	117.5	117
PHEtPh	121.5	121
PMe$_3$	134.4	118
PEt$_3$	148.2	132
PMe$_2$Ph	139.3	127

$^a \Theta$ = Tolman cone angle.

apex at the center of the metal polyhedron rather than the vertex metal atom to which each ligand is bound. Since the cone apex-to-phosphorus distance is much greater in the cluster than as defined for Tolman's cone angle, the cluster cone angle for a given phosphine is invariably smaller than the Tolman cone angle. Cluster cone angles must be calculated for each particular metal framework (see, for example, ref. 15).

2.3 Solid angle measures of ligand steric requirement

The Tolman cone angle and its various elaborations is a two-dimensional quantity, an angle measured in a plane. To the extent that a group of ligands approach nominal three-fold axial symmetry, the relative cone angles are reasonably accurate measures of their relative three-dimensional space-filling properties. For unsymmetrical ligands, the averaging of semicone angles, as described, is a means for extending the cone angle concept. However, ligands that depart substantially from an approximate three-fold symmetry, such as sulfides or olefins, are not readily handled in terms of the cone angle concept.

By generalizing the cone angle notion to three dimensions, one obtains a solid angle measure of the ligand's steric properties. Figure 6 shows the projection of the solid cone angle generated by a ligand onto a hypothetical spherical surface surrounding the metal. The solid cone angle could be taken to be either that encompassed
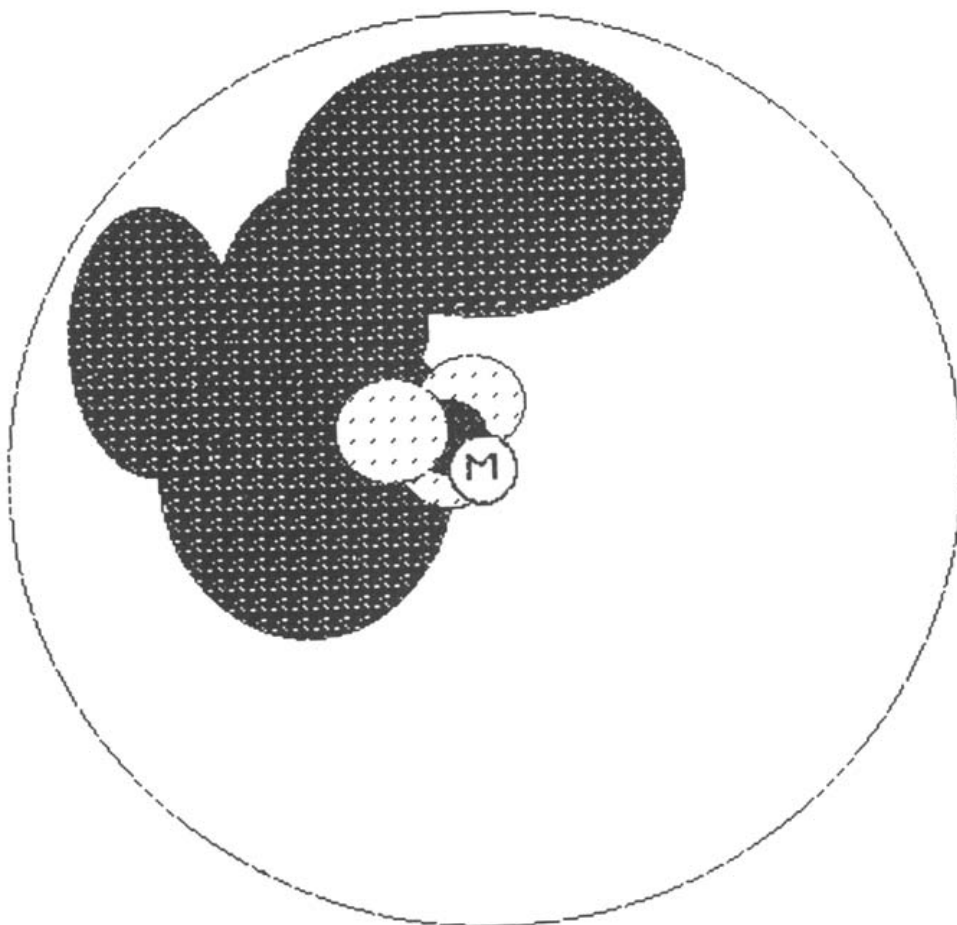
Fig. 6. Illustration of the solid angle generated by a ligand bound to a metal. The reader must imagine that the circle encloses the inside surface of a sphere, against which the "shadow" of the ligand is projected, with the light source centered at the metal.

by the symmetrical cone that includes the "shadow" of the ligand, or it could be defined in terms of just the shaded area.

The first attempts to define cone angles based on solid angles were made by Immirzi and Musco [16]. Sets of $\theta/2$ as a function of ϕ data were obtained from X-ray crystal structure data in a manner similar to that of Ferguson and co-workers. From the data sets, the solid angle Ω of a generalized non-circular cone was calculated using eqn. (5). An equivalent circular cone angle Θ', in degrees rather than steradians, was then calculated using eqn. (6). Θ' values for several phosphorus ligands are listed in Table 4. Since this procedure yields essentially the *average* value of $\theta/2$ multiplied by 2, the cone angles Θ' are systematically lower than those reported by Tolman, and even more substantially lower than the values based on maximum semicone angles (Table 3).

$$\Omega = \int_{\phi=0}^{2\pi} (1 - \cos(\theta/2))\mathrm{d}\theta \tag{5}$$

$$\Theta' = 2 \text{ arc } \cos(1 - \Omega/2\pi) \tag{6}$$

The concept of a solid cone angle as a measure of ligand steric effects has been applied to organometallic and organic compounds [16–23]. However, the methods

TABLE 4

Solid cone angles (Ω) (steradians) and values of Θ' (eqn. 6) for some phosphines [16]

Ligand	Complex	Ω	Θ' (degrees)	Tolman cone angle, Θ (degrees)
PEt$_3$	trans-HPdClL$_2$	3.60, 3.72	130, 132	132
PEt$_3$	PtL$_4$	3.09, 3.14	119, 120	132
PMe$_2$Ph	[Ir(CO)$_3$L$_3$]ClO$_4$	3.06, 3.03	118, 118	122
PMe$_2$Ph	cis-PdCl$_2$L$_2$	2.90	125	122
PMe$_2$Ph	PtL$_4$	2.82, 2.81	113, 113	122
		2.79, 2.88	112, 115	
PPh$_2$Me	[AuL$_2$]PF$_6$	3.44	126	136
PPh$_2$Me	MoH$_4$L$_4$	2.99, 2.99	117, 117	136
		3.05, 3.10	118, 119	
PPh$_2$Me	[IrL$_4$]BF$_4$	3.31, 3.27	123, 123	136
PPh$_3$	AuCl$_3$L	3.75	132	145
PPh$_3$	Co(CO)$_2$NOL	3.58	129	145
PPh$_3$	[CuClL]$_2$	3.57	129	145
PPh$_3$	Rh(C$_2$H$_4$)(Cp*)L	3.54	128	145
PPh$_3$	cis-PtCl(dtt)L$_2$[a]	3.82, 3.72	134, 132	145
PPh$_3$	CuClL$_3$	3.70	132	145
PPh$_3$	Ir(NO)L$_3$	3.59	129	145
PPh$_3$	[CuL$_3$]BF$_4$	3.77	133	145
PPh$_3$	PdL$_4$	3.44, 3.43	126, 126	145
PPh$_3$	RuH$_2$L$_4$	3.31, 3.32	124, 124	145
		3.35, 3.38	124, 125	
P(i-Pr)$_3$	IrHL$_2$(C$_4$H$_6$)	3.89, 3.96	135, 137	160
P(i-Pr)$_3$	IrL$_2$(C$_3$H$_5$)	4.02	138	160
PCy$_3$	PdL$_2$	4.48	147	170
PCy$_3$	PtH$_2$L$_2$(monocl.)	4.61	149	170
PCy$_3$	PtH$_2$L$_2$(tricl.)	4.40	145	170
PCy$_3$	PtL$_3$	4.18	141	170
P(t-Bu)$_2$Ph	PdL$_2$	4.94	155	170
P(t-Bu)$_2$Ph	cis-PtCl$_2$L$_2$	4.61, 4.50	149, 147	170
P(methyl)$_2$(i-Pr)	PdL$_2$	6.09	177	209

[a] dtt = di-p-tolyltriazenido.

for estimating the ligand steric profile vary widely. In a recent evaluation of organic steric substituent constants, the appropriate conformation of the substituent was evaluated using molecular mechanics methods, and the solid angle projected by the substituent from the perspective of a defined "reaction center" was then computed [22]. The resulting steric parameters for 12 alkyl substituents of widely varying size correlated well with Taft E_s steric parameters [24]. More recently, a computational method of computing the solid cone angles for ligands has been proposed and applied to phosphines, phosphites, amines, alkyl and aryl groups, and η^5-C$_5$H$_{5-n}$R$_n$

[23]. The solid cone angles are computed as the solid angle encompassed within only the projection of the ligand itself (the shaded area in Fig. 6). The ligand conformations assumed were determined by molecular mechanics methods (see Sect. 2.5). Representative values are listed in Appendix Tables A1 and A2.

2.4 Angular symmetric deformation coordinate

Recently, Orpen and co-workers [25] proposed a new parameter to describe the steric bulk of phosphines. Using crystal structure data retrieved from the Cambridge Structural Database, the "angular symmetric deformation coordinate," $S4'$, defined as the sum of the Z–P–C angles minus the sum of the C–P–C angles (Z = any element), was calculated for 18 different phosphine ligands coordinated to Z. The mean $S4'$ values, listed in Table 5, are small for phosphines having large cone angles, and large for phosphines having small cone angles. Phosphines with large cone angles tend to give relatively small sums of Z–P–C angles and relatively large sums of C–P–C angles, i.e. the ligands are considerably flattened. Conversely, in phosphines of small cone angles, the ligands are more pyramidal.

TABLE 5

Angular symmetric deformation coordinate, $S4'$, for various phosphine ligands [25]

Phosphine ligand	Mean $S4'$ (degrees)
PMe_3	46.5
$PPhMe_2$	39.2
$PHPh_2$	47.1
$P(n\text{-Pr})_3$	23.8
$P(CH_2CH_2CN)_3$	30.7
PEt_3	33.2
$P(n\text{-Bu})_3$	28.2
PPh_2Me	33.7
$P(CF_3)_3$	75.8
PPh_3	27.6
$P(p\text{-}C_6H_4Me)$	34.3
$P(i\text{-Pr})_3$	26.1
$P(s\text{-Bu})_3$	19.0
$P(CH_2Ph)_3$	27.2
PCy_3	17.9
$P(t\text{-Bu})_3$	2.6
$P(o\text{-tol})_3$	14.6
$P(\text{mesityl})_3$	−17.9

2.5 Ligand repulsive energy parameter, E_R

The measures of ligand steric requirement we have considered are all geometric in nature. The magnitude of either the two-dimensional cone angle or the solid cone angle is intuitively appealing as a measure of steric requirement. However, for ligands that depart significantly from cylindrical symmetry about the M–L bond axis, the angular measure is less clearly related to the property of interest.

For ligands that possess energetically accessible conformational states with significantly different steric properties, there is a question of which conformer is the appropriate one to employ in evaluating the cone angle. The elegant studies based on solid-state crystal-structure data not withstanding, for most ligands it is necessary to assume a conformer to evaluate the cone angle. The convention has been to employ a ligand conformer that leads to the smallest feasible cone angle.

The ligand repulsive energy parameter, E_R, is based on a molecular mechanics computational model [26]. The ligand is "bound" to a prototypical metal complex $Cr(CO)_5$, as illustrated in Fig. 7 for triethyl phosphite. Based on a set of assumed force field parameters, an energy-minimized structure is computed for the complex. Generally, the energy-minimized structure, including the resulting ligand conformation, does not change significantly with variations in the detailed assumptions regarding force constants or strain-free values for bond distances and angles involved in the metal–ligand interaction so long as chemically reasonable values are chosen.

Ligand conformations in the complexes often differ dramatically from those computed for the free ligands, as illustrated in Fig. 7, and are seldom close to the folded-back conformations assumed in computing cone angles. The energy-minimized
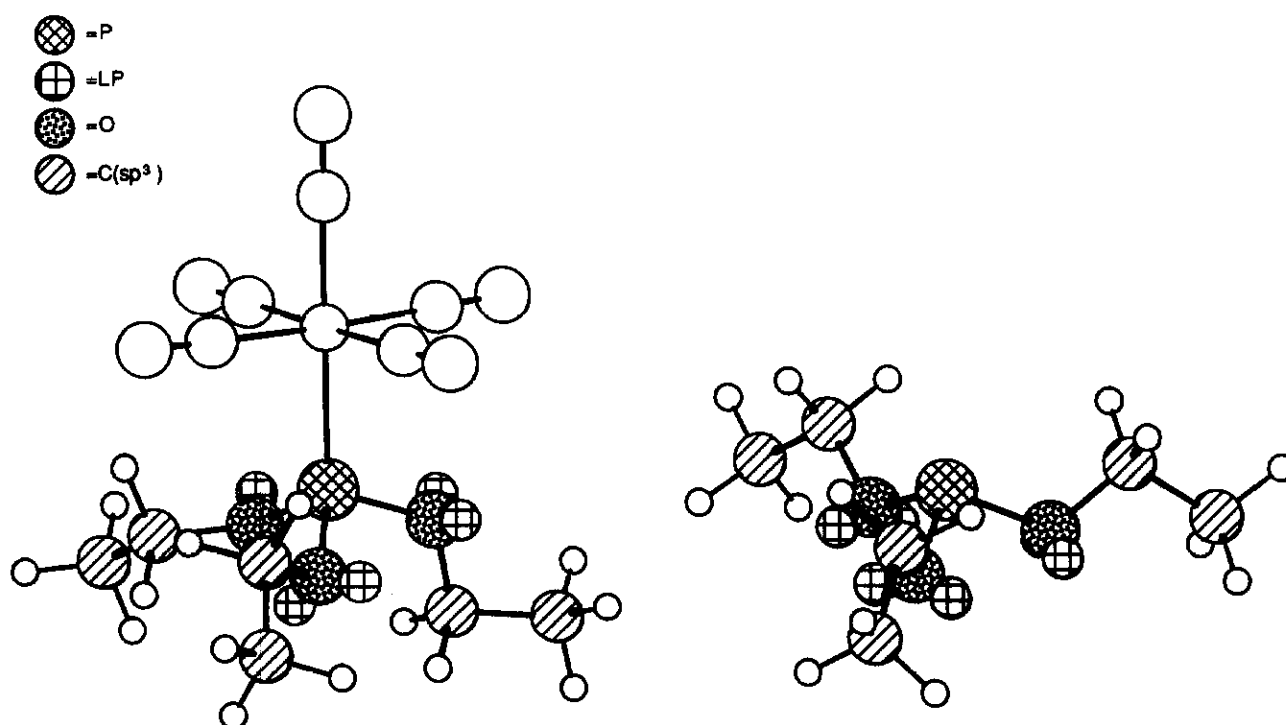

Fig. 7. Conformation of triethylphosphite, free and bound to $Cr(CO)_5$, as computed by molecular mechanics [30(a)].

structure provides a starting point for computing E_R. With all coordinates of the lowest energy structure frozen, the metal–ligand distance is varied about the equilibrium value. For each value of metal–ligand distance, the repulsive van der Waals energy in the $Cr(CO)_5$ complex is computed. The variation in this quantity with metal–ligand distance, $dE_{VDW(repulsive)}/dr$, represents the van der Waals repulsive force acting between ligand and metal complex. E_R is defined as the product of this force and the equilibrium metal–ligand bond distance (eqn. (7)). It is expressed in units of kcal mol^{-1}.

$$E_R = r_e[dE_{VDW(repulsive)}/dr_e] \tag{7}$$

E_R can be computed for any ligand provided that a reasonable molecular mechanics model can be formulated for its interaction with $Cr(CO)_5$. To date, E_R values have been computed for many phosphines, phosphites and arsenic ligands [26], amines [27], and sulfides [28]. Values are listed in Appendix Tables A1–A3.

In spite of their very different origins, E_R values correlate moderately well with Tolman cone angles. For example, a correlation of E_R vs. Θ values is illustrated in Fig. 8 for phosphines containing alkyl and aryl groups. However, significant differences are seen in the two sets of parameters when the comparisons are extended to phosphites and arsenic ligands [26]. Comparisons of linear free energy correlations of kinetic data as well as other properties data for phosphorus ligands shows that
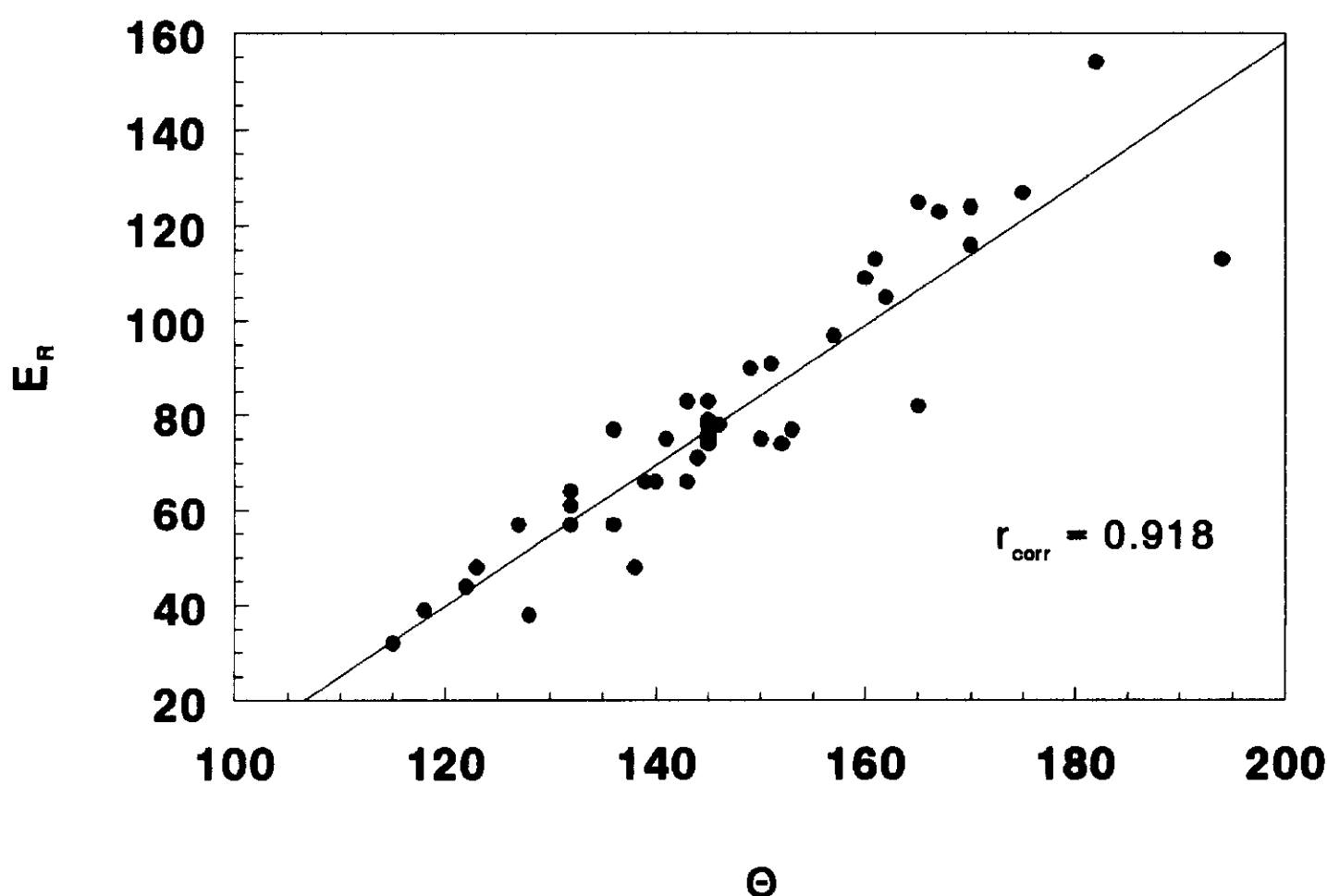

Fig. 8. Correlation of E_R values with Tolman cone angle values for alkyl, aryl, and mixed alkyl/aryl phosphines [26].

cone angles and E_R values lead to comparable correlation coefficients overall as measures of ligand steric requirements [26], although there are often substantial differences in correlation coefficients for a particular set of kinetics or properties data.

Figure 9 shows the correlation of E_R with solid angle values computed by White et al. for 60 phosphorus ligands, including alkyl, aryl and alkoxy groups on phosphorus (Table A1). The correlation ($r_{corr} = 0.837$) is somewhat less satisfactory than that with Tolman cone angles ($r_{corr} = 0.859$) for the same set of ligands.

E_R values are based on computations involving energies and forces, whereas the cone angle is a geometric construct. Nevertheless, both parameters are concerned with the van der Waals "surface" of the ligand. The cone angle represents a measure of how wide the ligand appears from the viewpoint of a point in space corresponding to a metal center to which the ligand is bound. E_R values are based on the magnitude of the repulsive interactions of the ligand's exterior surface atoms with a prototypical metal center, $Cr(CO)_5$, for the ligand in a conformation appropriate to binding to that center.

$Cr(CO)_5$ was chosen as the prototype center for computing E_R values in part because it has comparatively high-order rotational symmetry about the metal–ligand axis. Variations in molecular mechanics energy with rotation of the ligand about the metal–ligand axis tend to be rather small. The question arises as to how much the relative values of E_R would vary for binding of the ligands to a metal center of different shape and symmetry. This question is related to the broader issue of how much variation may be expected in the relative steric effects of ligands from one reaction system to another, with substantial variations in symmetry and steric requirements of the reaction center.
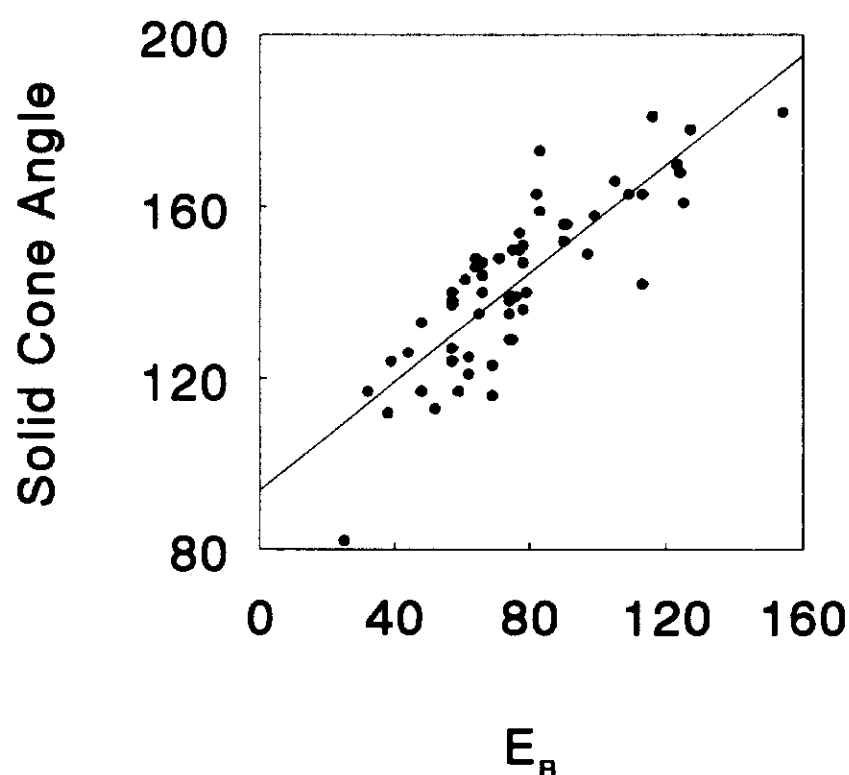

Fig. 9. Correlation of E_R values with solid cone angle values [23] for 60 phosphorus ligands.

To address this question, repulsive energy parameters have been computed for a selection of phosphorus ligands bound to CpRh(CO), a metal center with substantially different symmetry and steric requirements than $Cr(CO)_5$ [29]. The resulting E'_R values are graphed vs. the corresponding E_R values in Fig. 10. The correlation is generally quite good; only $P(OPh)_3$ departs substantially from the linear relationship. From this we may conclude that, for nearly all ligands, E_R values are rather robust as general measures of ligand steric requirements.

3. HOW CONSTANT ARE THE RELATIVE VALUES OF LIGAND STERIC PARAMETERS?

It is too much to expect that a single set of ligand steric parameters will reflect accurately the relative steric requirements of ligands in markedly different situations. To interpret properly the results of linear free energy correlations employing ligand steric parameters, and to assess the potential utility of the parameters in other applications, it is important to have some sense of the precision that may be attached to the parameter values.

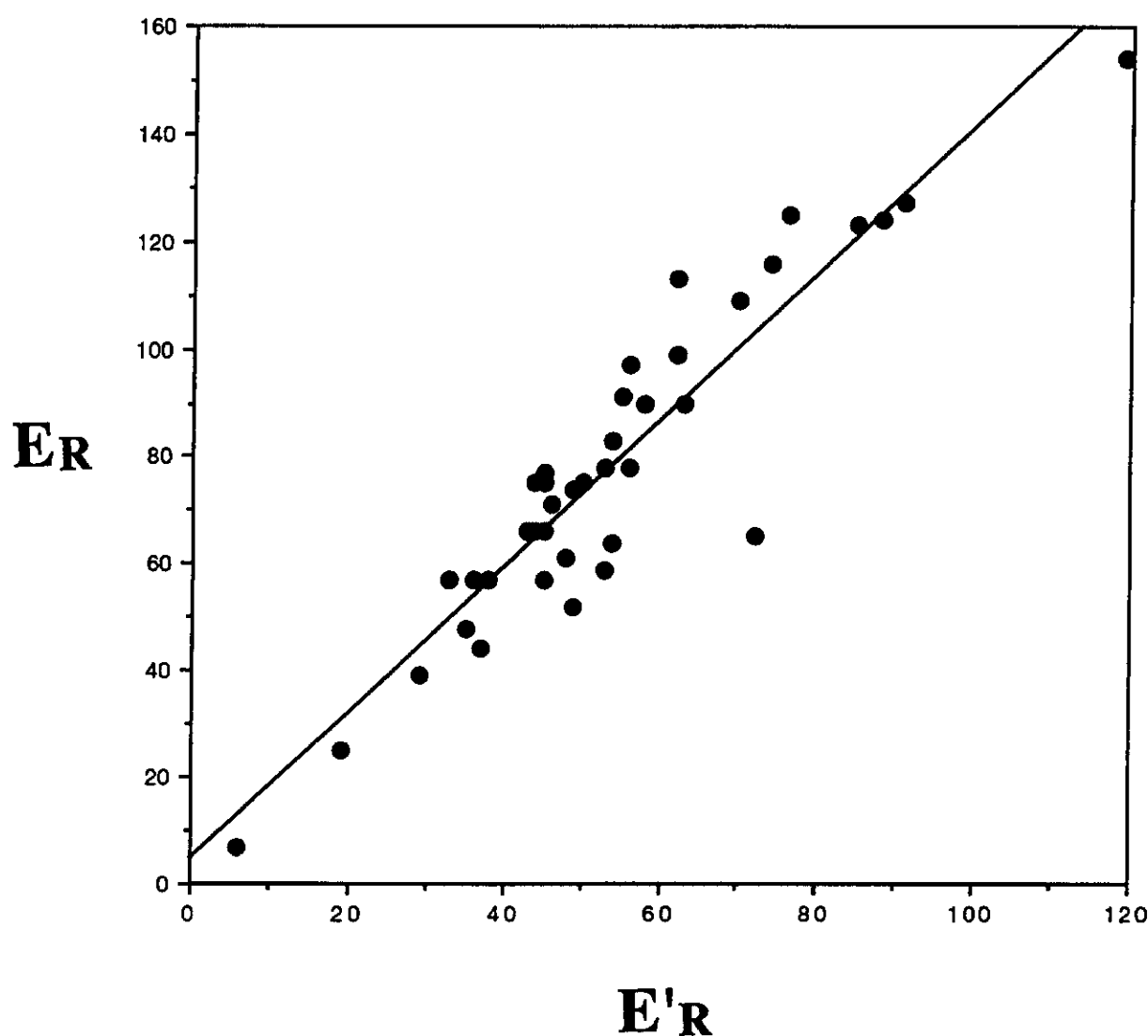Some ligands are compact and exist in a small number of conformational

Fig. 10. Correlation of E_R values computed for phosphorus ligands bound to $Cr(CO)_5$ with E'_R values computed for the same ligands bound to CpRh(CO) [27].

states, all of which have similar steric requirements. Examples include PMe_3, $P(i-Pr)_3$, $P(t-Bu)_3$; to a lesser extent, PPh_3 and $P(c-C_6H_{11})_3$. Others have the potential for existing in several conformational states of comparable energy but significantly different steric requirement. Examples include $P(n-Bu)_3$, $P(OEt)_3$, $P(CH_2Ph)_3$ and $PPhEt_2$, either as free ligands or when bound to a metal center. Molecular mechanics computations indicate that, for most ligands bound to $Cr(CO)_5$, a single conformational substate leads to an energy-minimized structure that lies significantly below (i.e. on the order of 1 kcal mol^{-1} or more) the energies of other conformers [26,30]. This lowest energy structure is employed in computing E_R values.

Aside from conformational variations, the steric requirement for a particular ligand depends also on the degree to which other groups on the metal center can intermesh with the groups bound to the central atom of the ligand [9]. For example, it has been noted that there is considerable space between the cyclohexyl groups of $P(c-C_6H_{11})_3$ [31].

A further important question is whether a given ligand, bound to two metal centers with differing symmetry, might not have different lowest energy conformations, with significantly different steric requirements, in the two sites. If the effective conformation of a ligand varies from one reaction or binding situation to another, with substantial consequences for the free energies involved, a single steric parameter, however arrived at, may not be useful.

In a given reaction system, ligands may react as reagents (for example, as attacking reagents in an associative displacement step, or as leaving groups in a dissociative reaction) or, on the other hand, may be bound to a metal center undergoing a reaction that does not directly involve the ligands. In the latter case, the ligands are termed "spectator" ligands [32]. They exert an influence on the reaction through their electronic properties as well as their steric characteristics. Notable examples of important spectator-ligand influences are the effects of phosphines on hydroformylation catalysis [33], and asymmetric hydrogenation and synthesis [34] involving transition metal centers. It may be asked whether a single set of parameters suffices to deal with ligand steric effects in both kinds of reaction situations.

Linear free energy correlations involving reaction sets in which phosphorus ligands are attacking reagents in substitution, isomerization, decarbonylation and atom transfer reactions, reveal comparable distributions of correlation coefficients [26]. The data analyzed to date suggest that Θ or E_R parameters are equally applicable to the ligands as reagents or spectator ligands. The attempts to estimate cone angle values from crystal structure data provide an indication of variability. As shown in Table 2, the cone angle values estimated for $P(c-C_6H_{11})_3$ from data on a series of mercury and platinum complexes vary over a range of 18°. The cone angle for even a compact ligand such as $P(t-Bu)_3$ is seen to vary over 13°. The solid cone angle estimates based on X-ray structural data also show variations for a given ligand from one complex to the next (Table 4). For example, the solid cone angle for

PPh_3 varies over 10° among ten complexes of varied character. (Because the basis on which the cone angles are calculated differ in these studies, comparisons of the absolute values among the studies are not useful in this context, only the variation within each study.)

The particular criteria employed in measuring cone angles in these studies probably exaggerate the variations for a given ligand among the complexes, particularly where the *maximum* semicone angles were estimated. Further, the variations in ligand conformation may be greater in the solid state, where intermolecular contacts are more variable than for complexes surrounded by solvent. Nevertheless, these studies show that, even for ligands that are fairly compact and symmetric, significant variations in steric parameters occur from one binding situation to another.

In a rather similar vein, the Tolman cone angles for certain phosphite ligands have been questioned on the grounds that the prevalent conformations are at variance with the assumptions on which the cone angle estimate is based, and because the empirical evidence favors a larger estimate [35].

Another measure of the variable steric properties of ligands as the binding site changes is found in the scatter in the values of the angular symmetric deformation coordinate, $S4'$ [25]. For example, for $P(n\text{-}Bu)_3$, the mean value of $S4'$ is 28.2°, with a standard deviation of 12.2° in a series of 32 complexes. This level of scatter in $S4'$, which is typical of the data in general, is in part the result of solid-state packing effects, as well as variations in electronic factors related to ligand binding. However, the major contributions appear to arise from variations in the steric interactions between the ligands and the metal complexes to which they are bound.

The scatter in relative values of ligand repulsive energy parameters for ligands in two different binding situations, $Cr(CO)_5$ and $CpRh(CO)$ (Fig. 10) also provides an indication of the sensitivity of the E_R parameter to the specifics of ligand binding site [29]. While for most ligands the relative values are well-correlated between the two binding sites, there is some scatter, reflecting the differing symmetries and steric requirements of the two metal centers.

In summary, the evidence based entirely on the methods for estimating steric effects themselves suggests that, while each ligand may be assigned a steric parameter value, the parameter has a range of values, depending on the reaction involved or structural situation. For some ligands with a limited range of conformational possibilities, the range is quite narrow; for others it may be larger. In general, *the precision with which the steric parameter for a ligand can be applied is substantially lower than the precision with which it can be estimated by any given methodology.* Each ligand has not one, but a range of steric requirement values, depending on the reaction or structural context.

4. APPLICATIONS

Quantitative measures of relative ligand steric requirements are useful in a variety of qualitative assessments, such as in selection of ligands for trial in a

homogeneous catalytic system or synthetic procedure. Interpretations and predictions of changes in coordination number, rough comparative equilibrium constants or reaction rates provide further examples of qualitative uses [2]. Most importantly, however, quantitative measures of ligand steric effects provide the basis for establishing quantitative relationships with rate constants, equilibrium constants or physical and chemical properties data. Such quantitative relationships, properly established, have predictive power and provide the basis for deeper understanding of the experimental data.

Linear free energy relationships. Among the most important quantitative relationships are the so-called linear free energy relationships (lfer), in which the free energy difference (in equilibrium systems) or free energy barrier (in kinetics systems) in a series of equilibria or reactions is linearly related to one or more properties that vary systematically throughout the series. For a reaction series involving several ligands, an lfer of the form of eqn. (8) is often employed [26,36–44].

$$\ln k_i = aE_i + bS_i + c \tag{8}$$

Here, k_i is the rate constant of the ith ligand, E_i is a measure of the electronic character of the ith ligand, and S_i is a measure of the steric requirement of the ith ligand. The coefficients a and b are measures of the sensitivity of the rate constant to variations in the electronic and steric characteristics, respectively, of the ligand. For phosphorus ligands, E_i might be taken as the frequency of the totally symmetric stretching mode of the CO groups in $Ni(CO)_3L$, referenced to the value for $L = P(t\text{-Bu})_3(\chi)$ [2,45]. Alternatively, the ^{13}CO chemical shift of the same CO groups, referenced to the value for $Ni(CO)_4$, might be chosen [46]. The steric parameter might be chosen to be the cone angle, by one or another definition, as described above, or E_R.

To illustrate the application of eqn. (8), consider the rate constants for the associative substitution of CO by L in $Fe(NO)_2(CO)_2$ complexes [47].

$$Fe(NO)_2(CO)_2 + L \rightarrow Fe(NO)_2(CO)L + CO \tag{9}$$

Table 6 lists various lfer expressions of the form of eqn. (8), the corresponding correlation coefficients and number of cases in the set (χ is not listed for $AsPh_3$). Figure 11 illustrates the relationships graphically.

These lfer are based on data for nine or ten different ligands, which afford a reasonable range of ligand types. The quality of fit is probably a bit better than average. For the ligand set employed in this study, the correlation between Θ and E_R is not particularly good ($r = 0.804$); however, the correlation between δ and χ values is excellent ($r = 0.966$). In this particular case, the lfer fit using Θ is slightly better than for E_R; however, in many cases the reverse is true.

The rate datum for $AsPh_3$ is an outlier in both correlations. The correlations are much improved by omitting the data for this ligand, as shown in Fig. 11(e) and (f). The origin of the failure of $AsPh_3$ to follow the lfer is not entirely clear; Morris

TABLE 6

Linear free relationships applied to rate data for reaction (9) [47]

	LFER	n^a	r^b
a	$\ln k = a\delta + bE_R + c$	10	0.800
b	$\ln k = a\delta + b\Theta + c$	10	0.882
c	$\ln k = a\chi + bE_R + c$	9^c	0.928
d	$\ln k = a\chi + b\Theta + c$	9^c	0.993
e	$\ln k = a\delta + bE_R + c$	9^c	0.961
f	$\ln k = a\delta + b\Theta + c$	9^c	0.978

[a] The ligands in the set are $P(n\text{-Bu})_3$, $PPhEt_2$, PCy_3, $P(O\text{-Bu})_3$, PPh_2Et, $P[(p\text{-OCH}_3)C_6H_5]_3$, PPh_3, $P(OCH_2)_3CCH_3$, $P(OPh)_3$, $AsPh_3$.

[b] Correlation coefficient.

[c] Omitting datum for $AsPh_3$.
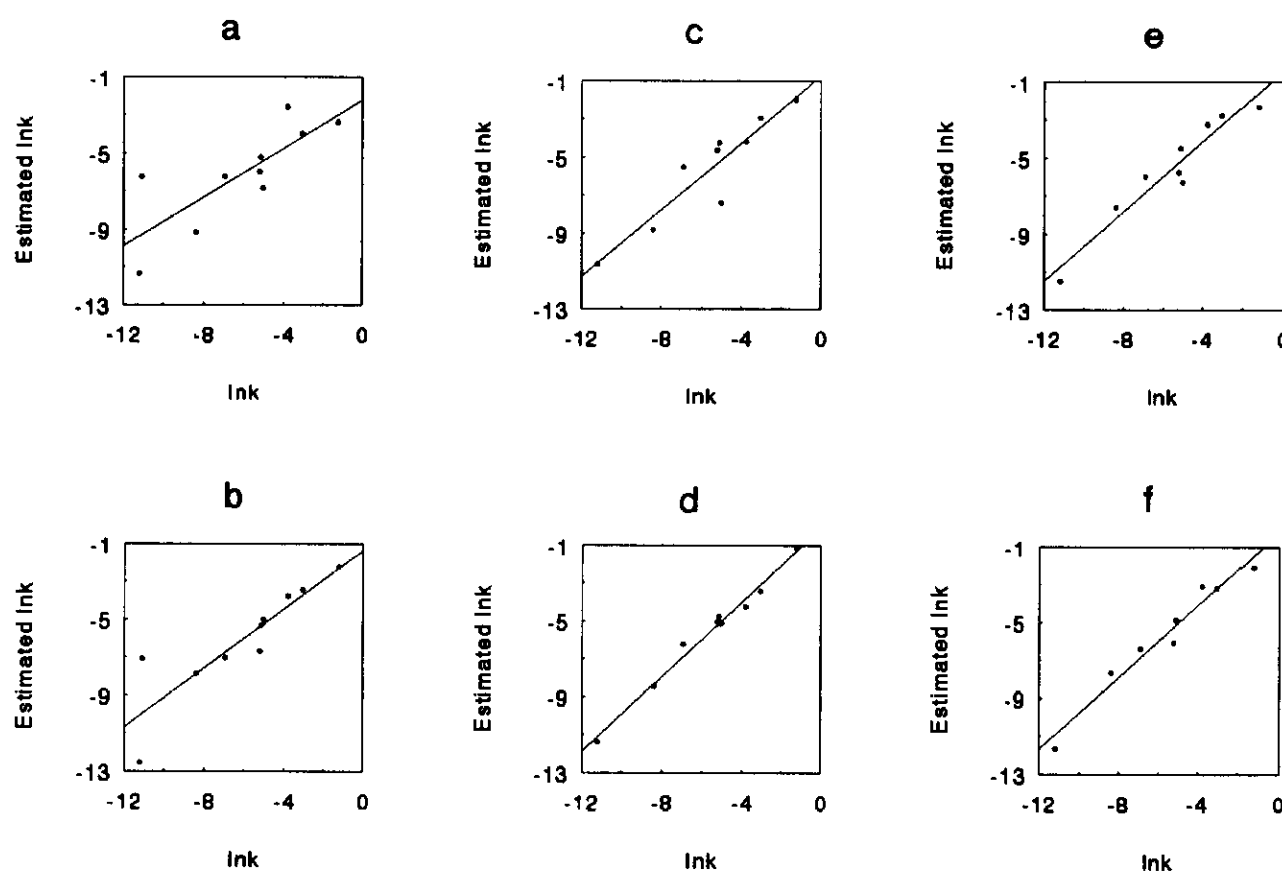
Fig. 11. Linear free energy correlations for the lfer expressions listed in Table 6 for the reaction of eqn. (9).

and Basolo speculate, on the basis of the comparatively positive measured entropy of activation, that the mechanism may have changed toward a dissociative interchange type of process [47].

Various elaborations on eqn. (8) have been proposed to permit distinguishing σ and π components of the electronic term [48], or to take into account characteristics of the reaction system that give rise to a threshold for the onset of steric effects. Giering and co-workers have proposed the use of the equation

$$\ln k = a\chi_d + b(\Theta - \Theta_{st})\lambda + c \tag{10}$$

in which Θ_{st} represents a steric threshold below which variation in ligand cone angle does not affect the rate [32]. Thus, $\lambda = 0$ for $\Theta < \Theta_{st}$, and $= 1$ for $\Theta \geqslant \Theta_{st}$. The parameter χ_d in this expression represents a measure of ligand σ donor character, derived from the A_1 symmetry IR CO stretching frequencies in $Ni(CO)_3L$ complexes, "corrected" for π acidity [49]. χ_d differs from the parameter directly derived from the observed IR frequency, for ligands containing alkoxy groups bound to phosphorus, but inexplicably, not for ligands containing another electron-withdrawing group, Cl. The estimation of χ_d is based on a presumed relationship between pK_a, χ and the Tolman cone angle, Θ.

Often, data available in a given reaction series do not admit of determining the number of parameters in eqn. (10), or other expressions in which added parameters are involved (for example, through separately identifying σ and π components of the electronic term), with statistically significant levels of uncertainty. However, even when copious data are available, the interpretations of the added parameters rest on the assumption that the steric and electronic parameters are known with quite good precision. We have seen, however, that the variation in the steric parameter for a given ligand can be fairly high from one coordination situation to the next.

The fact that lfers based on eqn. (8) lack high precision does not mean that they are without value. The signs and magnitudes of the coefficients a and b in eqn. (8) are of considerable interest. In kinetics systems, the sign of a indicates whether the rate constant increases or decreases as a result of increasing electron release on the part of the ligand, whether the ligand is a spectator ligand or the attacking reagent. Similarly, the sign of b indicates whether the rate constant increases or decreases as a result of an increase in steric requirement of the ligand. It might, for example, be increased if the ligand is a spectator ligand, and the reaction involves a dissociative process (steric acceleration of dissociation). It might be decreased if the ligand, as a spectator ligand, impedes access to the reaction center.

The magnitudes of a and b depend, of course, on the particular variables chosen to represent the steric or electronic components. However, for a given set of ligands studied, one can ask what fraction of the total change in $\ln k$ is due to the electronic component, $(a\Delta E_i)$, and what fraction to the steric component $(b\Delta S_i)$.

The variations in the values of a and b over a wide range of reaction systems provide an indication of the way in which the comparative importance of steric and electronic terms varies with the overall free energy changes in reactions. For example, in a series of atom transfer reactions of the form

$$Re(CO)_4L + X-R \rightarrow Re(CO)_4LX + R \tag{11}$$

where L represents a phosphine or phosphite, and X–R is an organic halide or pseudo-halide (R–SCN, R–SR), the ratio a/b for a series of reactions involving a fixed X–R and variable L was found to vary in a systematic way with the overall ergonicity of the reaction [50]. The results could be understood in terms of a Marcus-type model for atom transfer. A similar model is applicable to substitution reactions,

TABLE 7

"Ideal" ligand set for use in linear free energy studies

Ligand	δ (ref. 46)	χ (ref. 45)	Θ (ref. 2)	Θ' (ref. 23)	E_R (ref. 26)
P(n-Bu)$_3$	5.69	5.25	132	148	64
P(i-Bu)$_3$	5.40	5.70	143	173	83
P(i-Pr)$_3$	6.20	3.45	160	163	109
P(CH$_2$Ph)$_3$	3.98	10.35	165	163	82
P(OMe)$_3$	3.18	24.0	107	113	52
P(O–i-Pr)$_3$	3.90	19.05	130	138	74
P(OPh)$_3$	1.69	30.20	128	135	65
PPh$_3$	4.30	13.25	145	129	75
PPh$_2$Me	4.53	12.10	136	124	57
PPhMe$_2$	4.76	10.60	122	126	44

and probably also to a number of other reaction types familiar in organometallic and inorganic chemistry.

To facilitate comparative studies involving various different reactions, it would be advantageous if workers chose their ligands from a common small set. The ideal set is one in which the ligand steric and electronic properties vary over a wide range, the ligands are available at reasonable cost, and each is relatively easy to handle. Table 7 lists a set of ten ligands which embody the desired range, variety and availability. Clearly, many substitutions could be made and still preserve the range of parameters (e.g. P(OEt)$_3$ for P(OMe)$_3$, PPh$_2$Et for PPh$_2$Me, and P(c-C$_6$H$_{11}$)$_3$ for P(i-Pr)$_3$).

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APPENDIX

Tables of ligand parameters.

TABLE A1

Steric and electronic parameters of phosphorus and arsenic ligands

Ligand	δ^a	Tolman cone angle[b] (degrees)	$E_R{}^c$	Solid cone angle[d] (degrees)
CO	0	95	7	
PMe₃	5.05	118	39	124
PEt₃	5.54	132	61	143
P(n-Bu)₃	5.69	132	64	148
P(i-Bu)₃	5.40	143	83	173
P(i-Pr)₃	6.20	160	109	163
P(Cy)₃[e]	6.32	170	116	181
P(t-Bu)₃	6.37	182	154	182
PMe₂Et	5.21	123	48	133
PMe₂(i-Pr)	5.43	132	57	140
PMe₂(t-Bu)	5.48	139	66	144
PEt₂Me	5.36	127	57	138
PEt₂(i-Pr)	5.77	141	75	150
PEt₂(t-Bu)	5.82	149	90	156
P(i-Pr)₂Me	5.82	146	78	151
P(i-Pr)₂Et	5.99	151	91	156
P(i-Pr)₂(t-Bu)	6.26	167	123	170
P(t-Bu)₂Me	5.92	161	113	163
P(t-Bu)₂Et	6.09	165	125	161
P(t-Bu)₂(i-Pr)	6.31	175	127	178
P(Cy)₂H	5.35	143	66	147
P(Cy)H₂	4.07	115	32	117
PPh₃	4.30	145	75	129
P(p-ClPh)₃	3.54	145	74	129
P(m-CH₃Ph)₃	4.48	145	79	140
P(m-ClPh)₃	3.40	145	78	136
P(p-MePh)₃	4.50	145	74	135
P(p-(OCH₃)Ph)₃	4.43	145	76	139
P(p-FPh)₃	3.77	145	74	129
P(m-t-BuPh)₃	4.60	145	83	159
P(o-CH₃Ph)₃	3.67	194	113	142
PPh₂H	3.93	128	38	112
PPh₂Me	4.53	136	57	124
PPh₂Et	4.78	140	66	140
PPh₂(n-Bu)	4.74	140	66	140
PPh₂(i-Bu)	4.76	144	71	148

TABLE A1 (*continued*)

Ligand	δ^a	Tolman cone angle[b] (degrees)	$E_R{}^c$	Solid cone angle[d] (degrees)
PPh$_2$(i-Pr)	4.78	150	75	139
PPh$_2$Cy	5.07	153	77	150
PPh$_2$Bz[f]	4.20	152	74	139
PPh$_2$(*t*-Bu)	4.80	157	97	149
PPh$_2$Cl	2.49	138	48	117
PPhMe$_2$	4.76	122	44	126
PPhEt$_2$	5.36	136	57	137
PPh(*n*-Bu)$_2$	5.29	136	77	154
PPh(Cy)$_2$	5.80	162	105	166
PPh(*t*-Bu)$_2$	5.35	170	124	168
PBz$_3$[e]	3.98	165	82	163
P(OCH$_2$)$_3$CCH$_3$	2.60	101	25	82
P(OMe)$_3$	3.18	107	52	113
P(OEt)$_3$	3.61	109	59	117
P(O–*n*-Bu)$_3$	3.95	110	64	146
P(O–i-Pr)$_3$	3.90	130	74	138
P(O–i-Pr)$_2$(O–*t*-Bu)	3.90	144	78	147
P(O–i-Pr)(O–*t*-Bu)$_2$	3.90	158	90	152
P(O-*t*-Bu)$_3$	3.90	172	99	158
P(OPh)$_3$	1.69	128	65	135
PPh$_2$(OMe)	3.96	132	62	125
PPh$_2$(OEt)	4.27	132	62	121
PMe$_2$(OPh)	3.90	121	57	127
PPh(OMe)$_2$	3.48	120	69	116
PEt(OMe)$_2$	4.36	115	69	123
AsMe$_3$	4.46	114	27	126
AsEt$_3$	5.33	128	40	134
As(*n*-Bu)$_3$	5.26	128	44	151
AsPh$_3$	4.16	141	44	128
AsPhMe$_2$	4.80	123	30	124
AsPhEt$_2$	4.89	132	36	134
As(OEt)$_3$	3.22	105	40	117
As(OPh)$_3$	1.55	124	42	128

[a] ^{13}C chemical shift in LNi(CO)$_3$ complexes, down-field in ppm, from Ni(CO)$_4$.
[b] Ref. 2.
[c] kcal mol^{-1}.
[d] Ref. 23. The values listed are for an energy-minimized ligand conformation yielding minimum cone angle.
[e] Cy = cyclohexyl, C$_6$H$_{11}$.
[f] Bz = benzyl, CH$_2$Ph.

TABLE A2

Steric parameters for amines

Ligand	Cone angle[a] (degrees)	Solid cone angle[b] (degrees)	E_R[c]
NH_3	94	87	10
NH_2Me	106	105	30
NH_2Et	106	109	31
$NH_2(n\text{-}Pr)$	106	112	31
$NH_2(i\text{-}Pr)$	106	116	41
$NH_2(i\text{-}Bu)$	106		33
$NH_2(neopentyl)$	106	123	35
$NH_2(s\text{-}butyl)$	113	111	43
$NH_2(Cy)$	115	127	41
$NHMe_2$	119	116	64
NHMeEt	119	121	62
Piperidine	121	139	61
$NH_2(t\text{-}Bu)$	123	119	53
$NHEt_2$	125	128	73
$NH_2(ada)$[d]	127	138	53
$NH(n\text{-}Pr)_2$	127	137	81
NMe_3	132	124	93
Quinuclidine	132	129	104
NMe_2Et	132	128	81
$NHCy_2$	133	164	113
$NH(i\text{-}Pr)_2$	137	144	105
$NH(i\text{-}Bu)_2$	138	145	85
$NMeEt_2$	145	140	93
NEt_3	150	142	109
$NH(s\text{-}Bu)_2$	158	146	88
$N(n\text{-}Pr)_3$	160	161	112
$N(i\text{-}Pr)_3$	220	161	179
NH_2Ph		110	
NHMePh		124	
$NHPh_2$		127	
NEt_2Ph		144	
NBz_3[e]		173	

[a] Ref. 5.

[b] Ref. 23. Values listed are for an energy-minimized ligand conformation yielding minimum cone angle.

[c] Ref. 27.

[d] ada = adamantyl.

[e] Bz = benzyl.

TABLE A3

Ligand repulsive energy parameters for sulfur ligands [29]

Ligand	E_R	Ligand	E_R	
SMe$_2$	44	S(n-Pr)(s-Bu)	55	
SEt$_2$	60	S(n-Pr)(t-Bu)	71	
S(n-Pr)$_2$	64	S(i-Pr)(n-Bu)	60	
S(i-Pr)$_2$	69	S(i-Pr)(i-Bu)	57	
S(n-Bu)$_2$	63	S(i-Pr)(s-Bu)	62	
S(i-Bu)$_2$	66	S(i-Pr)(t-Bu)	73	
S(s-Bu)$_2$	75	S(n-Bu)(i-Bu)	59	
S(t-Bu)$_2$	91	S(n-Bu)(s-Bu)	59	
SMeEt	50	S(n-Bu)(t-Bu)	70	
SMe(n-Pr)	47	S(i-Bu)(s-Bu)	47	
SMe(i-Pr)	48	S(i-Bu)(t-Bu)	72	
SMr(n-Bu)	49	S(s-Bu)(t-Bu)	62	
SMe(i-Bu)	52	S(benzyl)(Me)	61	
SMe(s-Bu)	48	S(benzyl)(Et)	63	
SMe(t-Bu)	56	S(benzyl)(n-Pr)	71	
SEt(n-Pr)	62	S(benzyl)(i-Pr)	63	
SEt(i-Pr)	54	S(benzyl)(n-Bu)	68	
SEt(n-Bu)	54	S(benzyl)(i-Bu)	56	
SEt(i-Bu)	63	S(benzyl)(s-Bu)	65	
SEt(s-Bu)	61	S(benzyl)(t-Bu)	77	
SEt(t-Bu)	68	2,5-DHT[a]	40	
S(n-Pr)(i-Pr)	56	THT[b]	40	
S(n-Pr)(n-Bu)	62	THTP[c]	50	
S(n-Pr)(i-Bu)	65			

[a] 2,5-DHT = 2,5-dihydrothiophene.
[b] THT = tetrahydrothiophene.
[c] THTP = tetrahydrothiopyran.