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Solid angles
III. The role of conformers in solid angle calculations

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Abstract

The values of the solid angles Ω for a range of commonly encountered ligands in organometallic chemistry (phosphines, phosphites, amines, arsines and cyclopentadienyl rings) have been determined. The solid angles were derived from a single energy conformer in a geometry constrained in a prototypical metal environment, i.e. with the ligand attached to $Cr(CO)_5$. This choice permits comparison with recent ligand repulsive energies E_R reported by Brown. Correlations between Ω, E_R and θ for the range of ligands studied typically gave correlation coefficients greater than 0.8. The values of the weighted average solid angle $\overline{\Omega}$, using an extension of the methodology by Brown and Mosbo, have also been determined. The minimum conformer solid angle values are correlated with the weighted average solid angle ($r = 0.96$), suggesting that the minimum-energy conformation is a good approximate measure of steric size.

Keywords: Phosphorus ligands; Arsenic ligands; Solid angles; Cone angles; Steric size; Molecular mechanics calculation

1. Introduction

The evaluation of steric effects in chemistry has been recognized as important in understanding chemical reactivity [1]. Although quantification of the size of ligands in inorganic chemistry and functional groups in organic chemistry should logically be assessed by the same procedures, historically this has not been the case [2]. Only in recent years have attempts been made to consider the common features of the two disciplines and to measure sizes using the same procedures.

For example, we and others have been evaluating steric size (ligands, and organic groups) by use of a solid angle Ω [3,4]. The solid angle of an object is the area of the "shadow" of the object projected onto a surface, the shadow area being a measure of the steric size of the object. More rigorously, the solid angle of an element of area dS, subtended at a point O is

$$\mathrm{d}\Omega = \frac{\boldsymbol{r} \cdot \mathrm{d}\boldsymbol{S}}{r^3} \qquad (1)$$

where $\boldsymbol{r}$ is the vector from O to ds and r is its magnitude [5]. This equation has been solved numerically [4] and analytically [3]. When the object is a ligand, then the shadow of the sphere is brought about by atomic spheres using van der Waals and covalent radii where appropriate. If the ligand covers the entire unit sphere, then the solid angle is 4π sr. Steradians are often not the units of choice to express the solid angle; so a pure number Ω_s is defined Eq. 2 which gives the steric size of the ligand as the fraction of unit sphere occupied:

$$\Omega_s = \frac{\Omega}{4\pi} \qquad (2)$$

It is possible to derive a linear or cone angle from the solid angle measure. If the solid angle Ω is assumed to

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Table 1
Steric sizes of Group 15 donor ligands

Ligand	θ [a] (°)	θ [b] (°)	Ω [c] (sr)	Ω [c] (°)	Ω_S [c]	E_R [d]
PH_3	87	91.2 [e]	1.26	74	0.100	
PH_2Ph	101	106.4 [e]	2.12	97	0.168	
PH_2Me		104.5 [e]	2.09	96	0.166	
PF_3	104		2.12	97	0.169	
$Me_2PCH_2CH_2PMe_2$	107					
PH_2Et		111.0 [e]	2.21	99	0.176	
$PH_2(o\text{-}MePh)$		113.3 [e]	2.40	104	0.191	
$Et_2PCH_2CH_2PEt_2$	115					
$PCyH_2$	115		2.98	117	0.234	32
$PH_2(^iPr)$		115.7 [e]	2.51	106	0.200	
$PHMe_2$		117.9 [e]	2.82	113	0.224	
$PH_2(^tBu)$		118.3 [e]	2.88	114	0.229	
PMe_3	118	136.9 [e]	3.35	124	0.267	39
$PHMePh$		120.2 [e]	2.86	114	0.227	
$Ph_2PCH_2PPh_2$	121					
PMe_2Ph	122	141.7 [e]	3.45	126	0.274	44
		112–118 [f]	2.79–3.06 [f]			
PMe_2Et	123		3.76	133	0.299	48
PCl_3	124		2.51	106	0.199	
$PMe_2(CF_3)$	124		3.92	136	0.312	
$Ph_2PCH_2CH_2PPh_2$	125					
$Ph_2P(CH_2)_3PPh_2$	127					
PEt_2Me	127		4.04	138	0.322	57
$PHPh_2$	128		2.75	112	0.219	38
$PHEtPh$		129.9 [e]	2.93	116	0.233	
PBr_3	131		2.66	110	0.212	
$PPhCl_2$		131 [g]	2.77	112	0.221	
$PMe_2(^iPr)$	132		4.15	140	0.331	57
$P(CH_2CHCH_2)_3$		132 [g]	4.29	143	0.341	
PEt_3	132	166.4 [e]	4.31	143	0.344	61
		137 [h]	3.09–3.72 [f]			
		119–130 [f]				
$P(n\text{-}Pr)_3$	132		4.53	148	0.360	
$P(n\text{-}Bu)_3$	132		4.53	148	0.360	64
$P(CH_2CH_2CN)_3$		132 [g]	4.69	151	0.373	
PPh_2Me	136	117–126 [f]	3.34	124	0.266	57
			2.99–3.44 [f]			
$PPhEt_2$	136		3.96	137	0.316	57
$PPh(n\text{-}Bu)_2$	136		4.85	154	0.386	77
$PH(Et)_2$		137.3 [e]	3.24	122	0.258	
$P(CF_3)_3$	137		4.64	150	0.369	
PPh_2Cl	138	137 [g]	2.99	117	0.238	48
$PMe_2(^tBu)$	139		4.32	144	0.344	66
PPh_2Et	140		4.12	140	0.328	66
$PPh_2(n\text{-}Bu)$	140		4.13	140	0.329	66
$PEt_2(^iPr)$	141		4.64	150	0.369	75
$Cy_2PCH_2CH_2PCy_2$	142					
PCy_2H	143		4.49	147	0.358	66
$P(^tBu)_3$	143		5.91	173	0.470	83
$PPh_2(^tBu)$	144		4.54	148	0.361	71
$P(p\text{-}ClPh)_3$	145		3.58	129	0.285	74
$P(p\text{-}FPh)_3$	145		3.59	129	0.286	74
$P(p\text{-}MePh)_3$	145		3.60	129	0.286	74
PPh_3	145	120 [i]	3.60	129	0.286	75
		123–134 [f]	3.31–3.82 [f]			
$P(p\text{-}OMePh)_3$	145		3.60	129	0.286	76
$P(m\text{-}FPh)_3$	145		3.78	133	0.301	
$P(m\text{-}ClPh)$	145	165 [g]	3.91	136	0.311	78
$P(m\text{-}^tBuPh)_3$	145		5.12	159	0.407	83
$P(^iPr)_2Me$	146		4.72	151	0.375	78
$PH(^iPr)^2$		147.5 [e]	3.93	136	0.312	

Table 1 (continued)

Ligand	θ [a] (°)	θ [b] (°)	Ω [c] (sr)	Ω [c] (°)	Ω_S [c]	E_R [d]
$P(m\text{-}MePh)_3$	148 [g]	165 [g]	4.16	140	0.331	79
$PEt_2(^{t}Bu)$	149		5.00	156	0.398	90
$PPh_2(^{i}Pr)$	150	151 [g]	4.07	139	0.324	75
$P(^{i}Pr)_2Et$	151		5.00	156	0.398	91
$P(NMe_2)_3$	152		5.40	164	0.430	
PPh_2Bz	152		4.06	139	0.323	74
PPh_2Cy	153		4.65	150	0.371	77
$PPh_2(^{t}Bu)$	157		4.60	149	0.366	97
$PPh_2(C_6F_5)$	158		3.93	136	0.312	
$P(^{i}Pr)_3$	160	135–137 [f]	5.34	163	0.425	109
			3.89–4.02 [f]			
$P(^{t}Bu)_3$	160		5.83	172	0.464	
$P(^{t}Bu)_2Me$	161		5.33	163	0.424	113
$PPhCy_2$	162		5.51	166	0.439	105
$P(^{t}Bu)_2Et$	165		5.25	161	0.418	125
PBz_3	165		5.38	163	0.428	82
$P(^{i}Pr)_2(^{t}Bu)$	167		5.71	170	0.454	123
$PPh(^{t}Bu)_2$	170	147–155 [f]	5.61	168	0.447	124
			4.50–4.94 [f]			
PCy_3	170	163–181 [k]	6.33	181	0.504	116
		138–149 [f]	4.02–4.61 [f]			
$PPh_2(o\text{-}OMePh)$		171 [g]	3.63	130	0.289	
$P(^{t}Bu)_2(^{i}Pr)$	175		6.18	178	0.492	127
$P(neopentyl)_3$	≈ 180		5.91	173	0.470	
$P(^{t}Bu)_3$	182	176–189 [k]	6.37	182	0.507	154
$P(C_6F_5)_3$	184		4.87	154	0.388	
$P(o\text{-}MePh)_3$	194		4.22	142	0.336	113
$P(menthyl)_2(^{i}Pr)$	209 [f]	176.5 [f]	7.12	195	0.566	
			6.09 [f]			
$P(mesityl)_3$	212	203–208 [l]	6.01	175	0.479	
$P(OCH_2)_3CMe$	101		1.55	82	0.124	25
$P(OMe)_2Et$	106		3.30	123	0.262	69
$P(OMe)_3$	107		2.83	113	0.225	52
	128 [h]					
$P(OEt)_3$	109		3.01	117	0.239	59
	134 [h]					
$P(OCH_2CH_2Cl)_3$	110		3.18	121	0.253	
$P(O\text{-}n\text{-}Bu)_3$	110		4.46	146	0.355	64
$P(OMe)_2Ph$	115		2.95	116	0.235	69
$P(OEt)_2Ph$	116		3.43	126	0.273	
$P(OPh)Me_2$	121		3.49	127	0.278	57
$P(O\text{-}p\text{-}MePh)_3$	128		3.15	120	0.251	
$P(OPh)_3$	128		3.85	135	0.307	65
$P(O\text{-}^{i}Pr)_3$	130		4.01	138	0.319	74
$P(OMe)Ph_2$	132		3.39	125	0.270	62
$P(OEt)Ph_2$	133		3.18	121	0.253	62
$P(O\text{-}o\text{-}MePh)_3$	141		4.49	147	0.357	
$P(O\text{-}^{i}Pr)_2(O\text{-}^{t}Bu)$	144		4.52	147	0.359	78
$P(O\text{-}o\text{-}^{i}PrPh)_3$	148		5.26	161	0.418	
$P(O\text{-}o\text{-}PhPh)_3$	152		5.42	164	0.431	
$P(O\text{-}^{i}Pr)(O\text{-}^{t}Bu)_2$	158		4.69	151	0.373	90
$P(O\text{-}^{t}Bu)_3$	172		5.10	158	0.406	99
$P(O\text{-}o\text{-}^{t}BuPh)_3$	175		5.43	164	0.432	

be that of a cone, then the solid cone angle $\Omega°$ is obtained from the relationship [6]

$$\Omega° = 2\arccos\left(1 - \frac{\Omega}{2\pi}\right) \qquad (3)$$

There are significant similarities and differences associated with the solid angle measure when compared with the more common steric measure of size in inorganic chemistry, namely the Tolman [7] cone angle θ. These similarities or differences have been highlighted elsewhere and will not be discussed here [2]. This

Notes to Table 1
[a] From [7].
[b] Modifications to the Tolman cone angle.
[c] The solid angle Ω is measured in steradians. The measure in degrees refers to a right circular cone with that solid angle which hence corresponds to a linear vertex cone angle. Ω_s is $\Omega/4\pi$ and gives the fraction of a sphere occupied. Σ_{total}, the total strain energy measured in kilocalories per mole with the MM2 force field is as follows:
$PH_3 = -2.54$; PMe_2Ph, -1.54; PEt_3, -2.56; PPh_3, 3.58; PBz_3, -6.38; $P(^tBu)_3$, 33.6; $P(OEt)_3$, 1.870; $P(OPh)_3$, 1.89; $P(O^iPr)_3$, 1.54.
[d] From [8a]; E_R is measured in kilocalories per mole.
[e] From [9].
[f] From [6]; based on crystal structure data for a wide variety of metals.
[g] From [18d].
[h] From [17].
[i] From [13]; based on Mo systems.
[j] From [14].
[k] From [15]; measurement based on Hg, Pt, Ni and Ir systems.
[l] From [16]; measurement based on the Ag system.

publication does, however, address an issue common to both measures of steric size, i.e. the matter of ligand or group conformation.

This problem has been considered previously for both solid and cone angle measurements, and a solution to the problem has been made possible by the advent of recent developments in molecular mechanics. Further, the recent approach to measurements of ligands when attached to prototypical metal fragments provides a more realistic steric measurement of the steric size of ligands as found in inorganic (organometallic) complexes [8]. It is these issues that are addressed in the present paper.

It appears that the first attempt to evaluate conformer-independent cone angles was made by Mosbo and coworkers [9a]. This initial study was restricted to phosphorus donor ligands which had limited conformational degrees of freedom about the P–C bond, the ligand not being attached to a metal fragment. The ligand with the largest conformational space considered was PEt_3 (27 different conformers). In the methodology the ligand was placed in a series of pseudo-staggered conformations relative to an apex (a metal atom). Heats of formation for each conformer were calculated using MINDO/3, and a Boltzmann-type analysis was used to define a weighted mean cone angle. Importantly, both P and the metal size were ignored in the calculation of the weighted mean cone angles.

More recently Mosbo and coworkers [9b] have calculated conformer-independent cone angles for a series of phosphine ligands using molecular mechanics (MM2) calculations. From the above two related studies the above authors suggest that weighted mean cone angles are superior to single conformer cone angles as a method of evaluation of steric size.

2. Results and discussion

2.1. Measurement of solid angles: single conformers

The recent solutions to Eq. (1) (numerical and analytical) have permitted the generation of Ω for a wide range of ligands and organic groups. The methodology does require that atoms be placed in specific positions, i.e. a specific conformer, relative to some apex. Solid

Table 2
Correlations between steric, electronic and physical parameters for a series of literature reported reactions or data [a]

Reaction data	Reference	Ω_s [b]		θ [b]	
		R^2	MSE	e^2	MSE
$Ru(CO)_4L + L' \rightarrow Ru(CO)_3(L)(L')$ [c]	19	0.995	0.601	0.998	0.209
$(\eta^5\text{-}C_5H_5)Mo(CO)_2(L)HgX$ [d]	20	0.972	2.561	0.995	460
trans-$W(CO)_4(L)(L') \rightarrow$ *cis*-$W(CO)_4(L)(L')$ [e]	21a	0.652	8.59	0.760	5.94
$Ru(CO)_3(L)(SiCl_3)_2 + L' \rightarrow Ru(CO)_2(L)(L')(SiCl_3)_2$ [f]	21b	0.988	4.45	0.999	0.524

[a] The electronic measure for L and L′ was taken from the work of Tolman [7]. The steric data were taken from the work of Tolman [7] (θ values) or Table 1 (Ω_s).
[b] Non-intercept model used. Intercept model gives poor R^2 and MSE values, particularly for Ω.
[c] log k used, where k is the rate constant. See Figs. 3(a) and 3(b).
[d] ^{199}Hg NMR spectral resonance recorded. See Figs. 4(a) and 4(b).
[e] The equilibrium constant k was used in the correlation.
[f] log k used, where k is the rate constant.

angle data generated are available in the literature [3a,4] and correspond to the maximum, minimum [10] and "Tolman equivalent" conformers.

Recent work by Brown [8a] on steric measurements using ligand repulsive energies suggests a more appropriate approach to using energy-minimized conformers. In this method the size of the ligand is evaluated in an energy-minimized conformation after being placed in a more realistic organometallic environment. The metal–ligand fragment chosen was $Cr(CO)_5$, a fragment for which the molecular mechanics force field has been thoroughly paramatized.

Using Brown's approach we have generated single-conformer (energy-minimum) solid angles for a range of typical organometallic ligands (phosphines, phosphites, amines, arsines and cyclopentadienyl groups). For comparative purposes both the generic SYBYL [11] and MMP2 [12] force fields were used, but the results were identical. The solid angles (Ω, $\Omega°$ and Ω_s) for a range of phosphines and phosphites are given in Table 1 [2]. A set of values for other types of ligand (amines, cyclopentadienyl ligands, and arsines) can be found elsewhere [2]. Also included in Table 1 are some comparative cone angles, ligand repulsive energies, and total molecular mechanics energies (ΣE_{total}) measured with the MMP2 force field.

Correlations have been made between the various steric measurements available, namely θ, E_R, $\Omega°$ and Ω_s. Initially relationships between the above measures were examined by an interactive outlier process. In the preliminary correlations all data falling outside two standard deviations were rejected (see Table 3 for the statistical analysis). The correlation coefficient r was monitored as each outlier was rejected.

2.1.1. Combined correlations with phosphines, phosphites, amines and arsines

As an overall test as to the utility of Ω_s as a general steric parameter the relationships between Ω_s and E_R or θ were investigated. The graphs of Ω_s vs. θ and E_R for all the ligands studied (140 data points) are shown in Figs. 1 and 2. In general, the correlations are both good ($r > 0.8$ in all cases), although Ω_s correlates better with θ than with E_R. To explore the correlation in greater detail the analysis was broken down further.

2.1.2. Individual correlations with phosphines, phosphites, amines and arsines

In the relationship between Ω_s and E_R or θ only three of the 85 phosphines investigated appeared problematic: $P(^tBu)_3$, $P(o\text{-}MePh)_3$ and $PPh_2(o\text{-}MePh)$. In all cases the correlation coefficient improved significantly after rejection of these points (e.g. Ω vs. θ changed from $r = 0.831$ to $r = 0.862$). One general feature appears to arise from the P- and N-donor data, namely Ω_s correlates better with E_R than with θ. This

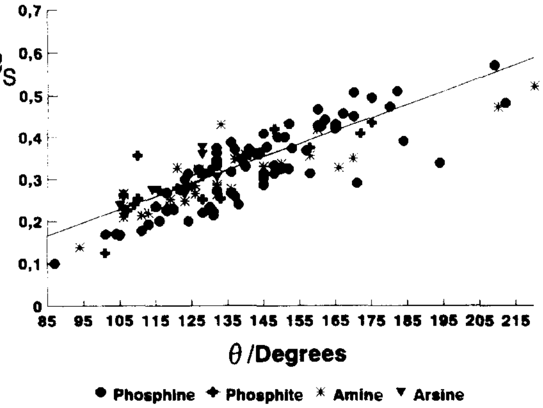

Fig. 1. Plot of Ω_s against the Tolman cone angle θ, for phosphines, phosphites, amines and arsines.

is not unexpected as both E_R and Ω_s were measured relative to the $Cr(CO)_5$ fragment in the molecular mechanics minimization procedures. Surprisingly, for AsR_3 and $As(OR)_3$ ligands, the opposite is true; Ω_s correlates better with θ for arsines than with E_R. Brown [8a] has also noted anomalous behavior with $AsPh_3$. The only anomalous data points in the relationship between Ω_s and θ are for $As(n\text{-}Pr)_3$ and $As(n\text{-}Bu)_3$. Owing to the small sample set (nine data points) these data affect the correlation significantly and could explain why this effect is not seen for the equivalent phosphine data. This anomalous behaviour can be associated with the repulsion between the long arms of the butyl (and to a lesser extent to the propyl) chains, which may be non-trivial. Thus the ligand opens up from its minimum conformer to relieve this unfavorable interaction. This feature is not seen for the Tolman cone angle but is generally seen for the Brown data.

The relationships between the steric parameters for the phosphites is generally better than for the phosphines. This is probably because of the limited phos-

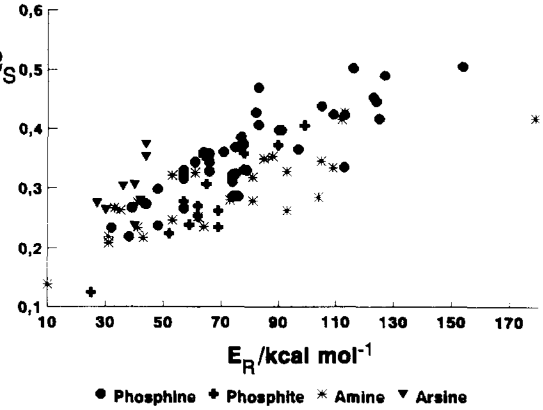

Fig. 2. Plot of Ω_s against E_R for phosphines, phosphites, amines and arsines.

phite data set (only 20 data points). Only the behavior of $P(OEt)_3$ appeared anomalous. The general trend for better correlations between Ω_s and E_R than between Ω_s and θ is again observed. This trend is also observed for the amine data.

2.2. Correlations with experimental reaction rates

A number of reaction rates and equilibrium constants involving organometallic reagents containing ligands such as phosphines and phosphites have been suggested

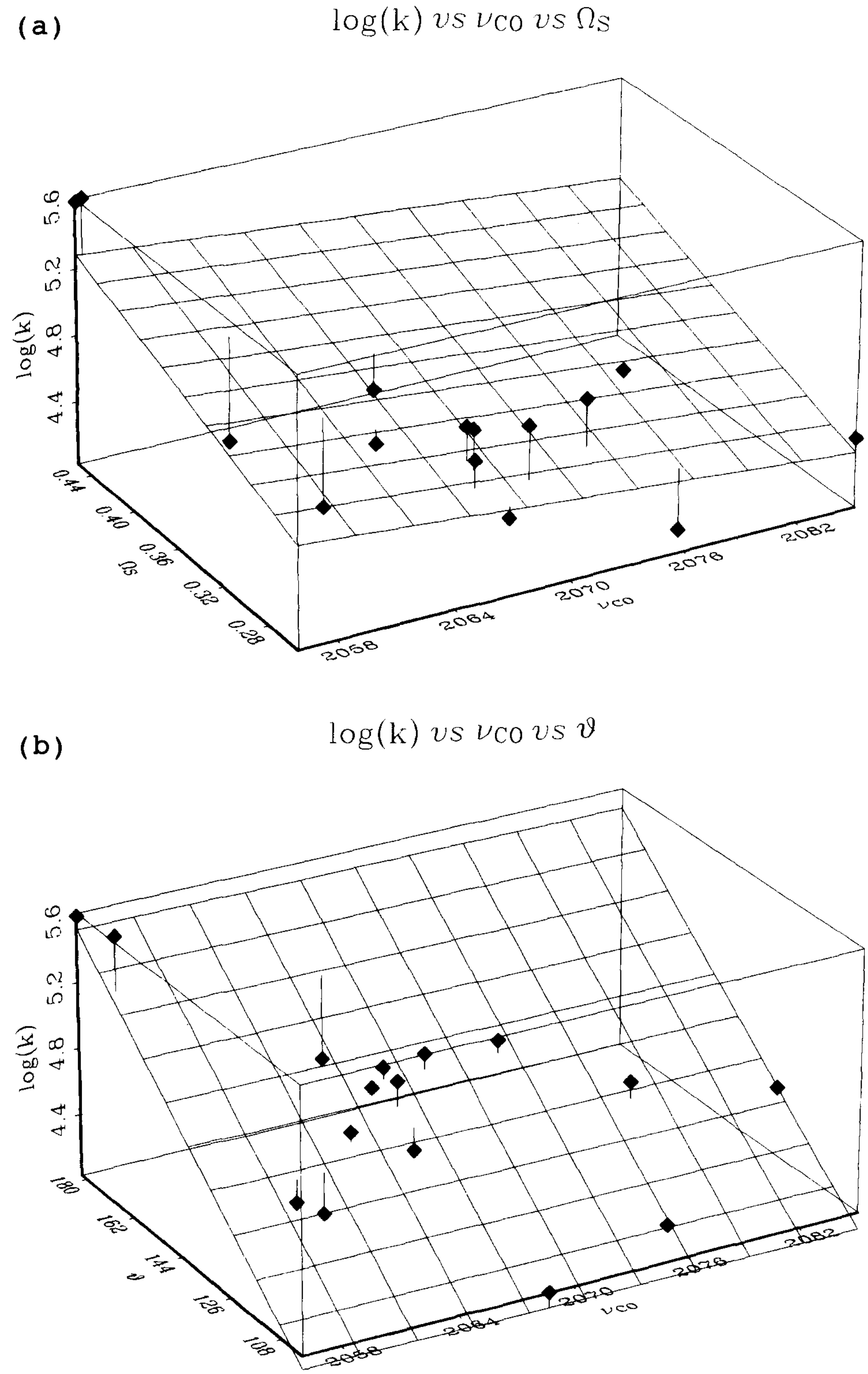

Fig. 3. Three-dimensional correlation plots for the reaction between $Ru(CO)_4L$ and L′ [19]: (a) plot of Ω_s, ν(CO) and log k; (b) plot of θ, ν(CO) and log k (k is the rate constant).

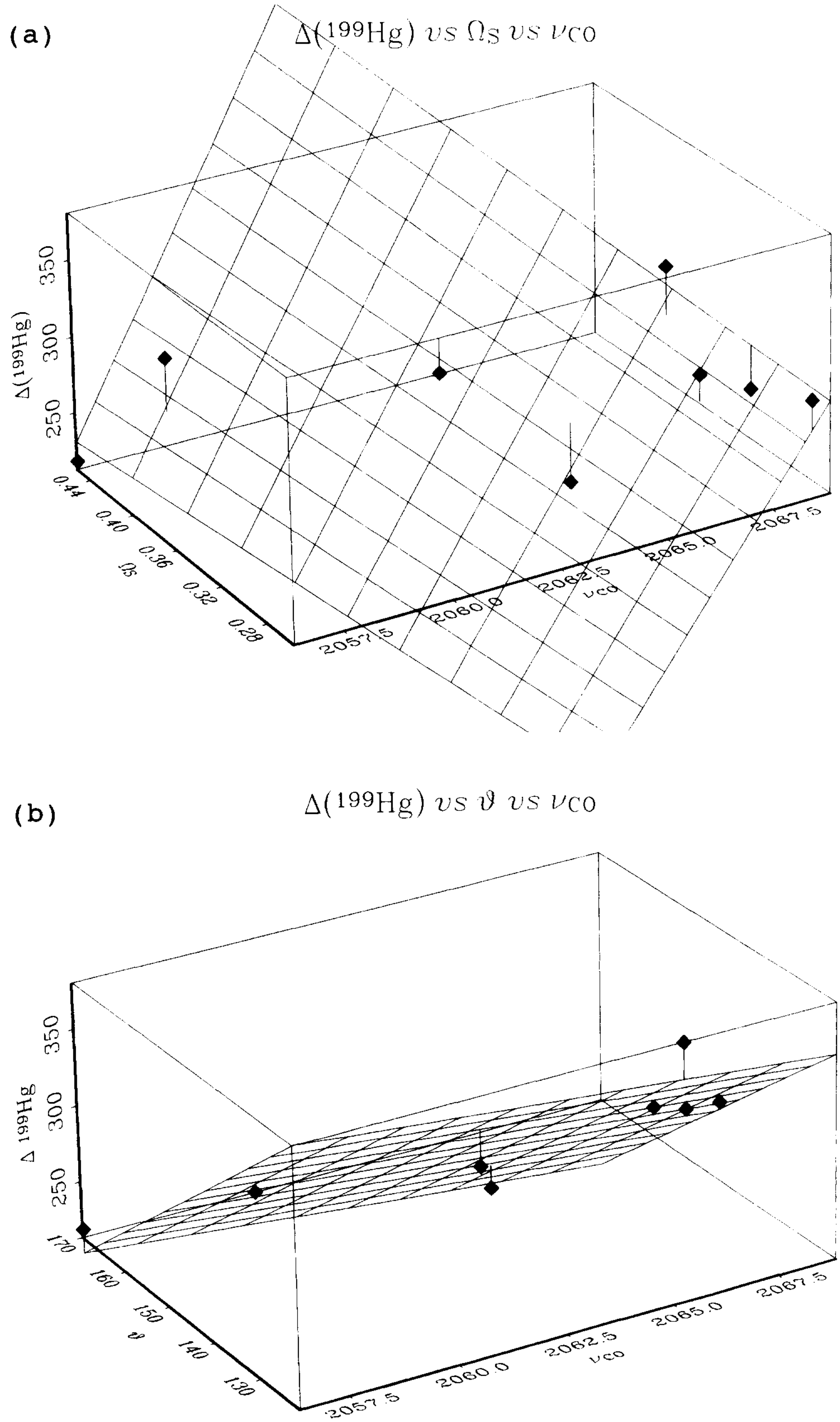

Fig. 4. Three-dimensional correlation plots for the complexes (η^5-C_5H_5)Mo(CO)$_2$(L)HgX: (a) plot of Ω_s, ν(CO) and ^{119}Hg resonance; (b) plot of θ, ν(CO) and ^{119}Hg resonance.

to be under steric control. Correlations of the rates and constants, with for instance Tolman cone angles, have been successfully performed [18]. We thus attempted to correlate solid angles with similar reported literature data.

2.2.1. Correlations of Ω and θ with rate constants

The reaction between $Ru(CO)_4L$ and L′ to give $Ru(CO)_3(L)(L')$ has been investigated by Chen and Poë [19]. We have attempted to correlate the kinetic data with steric, electronic and sterio–electronic factors. The latter gave the most significant correlations. A three-dimensional plot showing the correlations between Ω_s, ν(CO) [7] and log k as well as θ, ν(CO) and log k are shown in Figs. 3(a) and 3(b) respectively (k is the rate constant for the reaction). It is interesting to note the different slopes obtained on changing the steric parameter (Ω_s vs. θ). The R^2 and MSE data are given in Table 2 where it can be noted that the Tolman cone angle gives a better correlation than the solid angle data.

2.2.2. Correlation of Ω and θ with NMR parameters

The position of the ^{119}Hg resonance for a series of $(\eta^5\text{-}C_5H_5)Mo(CO)_2(L)HgX$ complexes has been reported by Cotton and Miles [20]. Correlated data for Ω_s and θ (and ν(CO)) vs. the ^{119}Hg resonance are shown in Figs. 4(a) and 4(b) respectively. Again remarkable changes in slopes with the change in the steric factor (Ω_s vs. θ) are seen. Values for R^2 and MSE are given in Table 2 and again θ proves to a superior steric measure in the correlation.

2.2.3. Correlations for two other sets of experimental data [21]

Other correlations were also performed using θ and Ω (and ν(CO)), and the data are shown in Table 2. Again it appears that θ is a better steric measure than Ω_s for the data.

2.2.4. General comments

The four analyses suggest that the values obtained for the solid angles give an underestimate of the steric size of phosphines and phosphites. Conversion of Ω_s to $\Omega°$ (i.e. solid angle expressed in degrees) reveals that the $\Omega°$ values are smaller than the θ values. The reason for the smaller size relates to the method of measurement as well as to the sizes of the van der Waals and covalent radii used in the two methods [3]. This issue will need to be explored further in future extensions of the solid angle methodology.

2.3. Measurement of solid angles: multiple conformers

We now turn our attention to the case of the existence of a ligand with many conformers of similar energy corresponding to many different solid angles. Since the solid angle is additive [3a], it is possible to obtain a weighted average solid angle which represents the entire conformation space of the ligand. Mosbo and coworkers [9] have attempted an equivalent weighted average analysis of cone angle and E_R methodologies using a small conformation space. In this approach a weighted average obtained from a Boltzmann-type analysis, as described below, was used.

If g_A is the number of conformers with conformation A, and ΔE_{Ai} is the change in enthalpy of formation between conformers A and i, then the mole fraction n_A of conformer is given by

$$n_A = \frac{g_A}{g_A + g_B \exp(-\Delta E_{AB}/RT) + \ldots + g_i \exp(-\Delta E_{Ai}/RT)} \quad (4)$$

The mole fraction n_A of the ligand in conformation A, n_A, is then multiplied by the steric measure, e.g. the cone angle θ_A of that conformer, and summed over all conformers to give the total cone angle θ for the ligand [9]:

$$\theta = n_A\theta_A + n_B\theta_B + \ldots + n_i\theta_i \quad (5)$$

In this analysis, metal and phosphorus atoms were ignored (the radii were set to zero) and hence only ligand effects in free space were considered.

We have modified the approach of Mosbo and coworkers to obtain an energy-weighted conformer averaged solid angle. This has been achieved by the following modifications.

(1) As discussed above, the point apex in the approach of Mosbo and coworkers has been replaced by a $Cr(CO)_5$ fragment apex.

(2) In the approach of Mosbo and coworkers, only a small number of conformers of low energy were considered. As a ligand changes conformation, the ligand will spend time in a conformation between the two lower energy conformations. In our calculations these conformers have been included.

(3) A large conformational space (between 500 and 1000 conformers per ligand) was sampled using the Monte Carlo method with random variation in key dihedral angles.

The weighted average solid angles, $\overline{\Omega}$ and $\overline{\Omega}_s$, were calculated by an approach similar to those used by Mosbo and coworkers but incorporating the above added features (Table 3):

$$\overline{\Omega} = n_A\Omega_A + n_B\Omega_B + \ldots + n_i\Omega_i \quad (6)$$

$$\overline{\Omega}_s = \frac{\overline{\Omega}}{4\pi}. \quad (7)$$

Comparison of solid angle data in Tables 3 and 4 for values measured relative to the $Cr(CO)_5$ fragment in the minimum-energy conformation and as a weighted average solid angle reveals small differences in the solid

Table 3
Statistical data for correlations between solid angle and θ or E_R [a]

Relationship	Data Set	r [b]	MSE	Significance level
Ω_s vs. E_R	**Phosphine**	**0.890**	**0.00149**	**0.0000**
Ω° vs. E_R	Phosphine	0.887	86.3	0.0000
Ω_s vs. θ	Phosphine	0.878	0.00301	0.0003
Ω vs. θ	**Phosphine**	**0.862**	**197**	**0.0307**
Ω_s vs. Ω°	Phosphine	0.998	0.000225	0.0000
Ω_s vs. E_R	**Phosphite**	**0.895**	**0.00157**	**0.0000**
Ω° vs. E_R	Phosphite	0.901	77.4	0.0000
Ω_s vs. θ	Phosphite	0.896	0.00216	0.134
Ω° vs. θ	**Phosphite**	**0.863**	**151.6**	**0.0896**
Ω_s vs. Ω°	Phosphite	0.998	0.0000341	0.0000
Ω vs. E_R	**Amine**	**0.840**	**0.00159**	**0.0000**
Ω° vs. E_R	Amine	0.839	104.5	0.0000
Ω_s vs. θ	Amine	0.873	0.00168	0.0000
Ω° vs. θ	**Amine**	**0.862**	**115.3**	**0.0000**
Ω vs. Ω°	Amine	0.9986	0.0000207	0.0000
Ω_s vs. E_R	**Arsine**	**0.558**	**0.00169**	**0.167**
Ω° vs. E_R	Arsine	0.558	104	0.152
Ω_s vs. θ	Arsine	0.751	0.00111	0.422
Ω° vs. θ	**Arsine**	**0.761**	**65.5**	**0.461**
Ω_s vs. Ω°	Arsine	0.9997	0	0.0000
Ω_s vs. E_R	**P donors**	**0.876**	**0.00174**	**0.0000**
Ω° vs. E_R	P donors	0.859	111.4	0.0000
Ω_s vs. θ	P donors	0.880	0.002809	0.0001
Ω° vs. θ	**P donors**	**0.862**	**189.1**	**0.0024**
Ω_s vs. Ω°	P donors	0.998	0.000204	0.0000
Ω_s vs. E_R	**P and N donors**	**0.867**	**0.002184**	**0.0000**
Ω° vs. E_R	P and N donors	0.860	137.1	0.0000
Ω_s vs. θ	P and N donors	0.878	0.002627	0.0007
Ω° vs. θ	**P and N donors**	**0.864**	**173.4**	**0.0000**
Ω_s vs. Ω°	P and N donors	0.998	0.0001384	0.0000
Ω_s vs. E_R	**All ligands**	**0.828**	**0.00225**	**0.0000**
Ω° vs. E_R	All ligands	0.822	142.07	0.0000
Ω_s vs. θ	All ligands	0.870	0.00257	0.0011
Ω° vs. θ	**All ligands**	**0.858**	**169.3**	**0.0000**
Ω_s vs. Ω°	All ligands	0.998	0.000130	0.0000

[a] Bold type indicates the relationships with the most chemical significance.
[b] The correlation coefficient r is measured after data outside of two standard deviations have been deleted.

angle data. Indeed, the two sets of data are well correlated with regression equation $\Omega_s = \overline{\Omega}_s + 5.34 \times 10^{-3}$ ($r = 0.96$) (Fig. 5). The weighted average solid angles correlate significantly better with the Tolman [7] cone angle ($r = 0.881$) and weighted mean cone angles of Mosbo and coworkers [9] ($r = 0.993$) than with the solid angles in the minimum generated conformation ($r = 0.858$). This trend is also seen with Brown's [8a] E_R values ($r = 0.846$ vs. 0.828). The weighted average solid angle is thus better related to other steric measures than the solid angle of a single low energy conformer. This result is not unexpected since the weighted mean solid angle takes into account possible ligand rotations. It is finally to be noted that, unlike the cone angle measure, the weighted mean solid angle also provides shape information.

3. Methods section

The required ligand was built using ALCHEMY III [22] and submitted to SYBYL for energy minimization [11]. The SYBYL program was parametrized using the data obtained from the literature [8,23]. Low energy structures were found by a method similar to that employed by Brown [8a] with the solid angle calculated from the perspective of the Cr atom ignoring the carbonyl group.

Table 4
Conformer averaged solid angles for phosphines and phosphites

Ligand	Conformers	$\overline{\Omega}$ [a] (sr)	$\overline{\Omega}_s$ [a]	Ω [b] (sr)	Ω_s [b]
PH_2Et	500	2.08	0.166	2.21	0.176
$PH_2(^iPr)$	500	2.30	0.183	2.51	0.200
PH_2Ph	500	2.12	0.169	2.12	0.168
$PH_2(o\text{-tol})$	500	2.37	0.189	2.40	0.191
$PHEt_2$	1000	3.17	0.252	3.24	0.258
$PH(^iPr)_2$	1000	3.63	0.289	3.93	0.312
$PHPh_2$	1000	2.73	0.217	2.75	0.219
$PH(o\text{-tol})_2$	1000	3.12	0.249	–	–
PHMePh	500	2.46	0.196	2.86	0.227
PHEtPh	1000	2.85	0.227	2.93	0.233
$PHMe(o\text{-tol})$	500	3.07	0.244	–	–
PMe_2Et	1000	3.49	0.277	3.76	0.299
$PMe_2(^iPr)$	1000	3.61	0.287	4.15	0.331
PMe_2Ph	1000	3.36	0.268	3.45	0.274
$PMe_2(o\text{-tol})$	1000	3.49	0.278	–	–
$PMeEt_2$	1000	3.62	0.288	4.04	0.322
$PMe(^iPr)_2$	1000	4.40	0.350	4.72	0.375
$PMePh_2$	1000	3.24	0.258	3.34	0.266
$PMe(o\text{-tol})_2$	1000	3.85	0.307	–	–
$PEtPh_2$	1000	3.64	0.289		
$P(^tBu)Ph_2$	1000	4.11	0.327		
$P(^iPr)Ph_2$	1000	3.78	0.301		
PEt_2Ph	1000	3.98	0.317		
PEt_3	1000	4.13	0.329	4.31	0.344
$P(^iPr)_3$	1000	4.89	0.389	5.34	0.425
$P(^nBu)_3$	1000	4.88	0.388		
$P(^iBu)_3$	1000	5.28	0.420		
$P(Cy)_3$	1000	5.69	0.453		
PPh_3 [c]	1000	3.42	0.272	3.60	0.286
$P(m\text{-tol})_3$	1000	3.74	0.297		0.336
$P(m\text{-ClPh})_3$	1000	3.54	0.282		0.225
$P(CH_2CH_2CN)_3$	1000	4.21	0.335		0.239
$P(CH_2CH{=}CH_2)_3$	1000	3.76	0.299		0.319
$P(Bz)_3$	1000	4.57	0.364		0.307
$P(^tBu)_3$	200	5.69	0.453		0.357
$P(o\text{-tol})_3$	1000	4.42	0.352	4.22	
$P(OMe)_3$	1000	2.69	0.214	2.83	
$P(OEt)_3$	1000	3.31	0.264	3.01	
$P(O\text{-}^iPr)_3$	1000	4.35	0.346	4.01	
$P(OPh)_3$	1000	3.22	0.256	3.85	
$P(O\text{-}o\text{-tol})_3$	1000	4.27	0.340	4.49	
$P(O\text{-}n\text{Bu})_3$	1000	3.98	0.317		
$P(O\text{-}p\text{-ClPh})_3$	1000	3.38	0.269		

[a] $\overline{\Omega}$, $\overline{\Omega}_s$; weighted solid angles (see text).
[b] Ω, Ω_s; solid angles measured in minimum conformation.
[c] Identical values calculated for $P(p\text{-RC}_6H_4)$ (R=OMe, F, Cl, or CH_3).

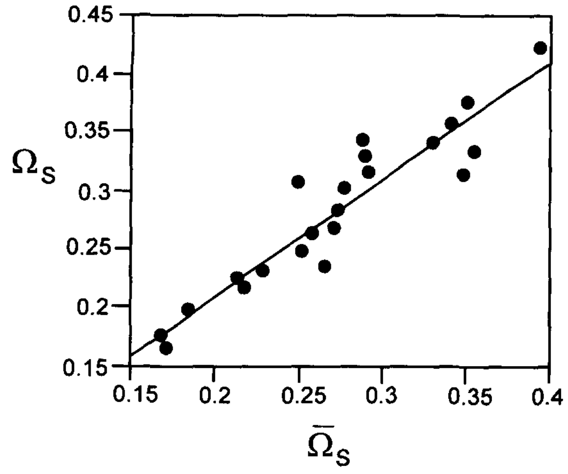

Fig. 5. Plot of Ω against $\bar{\Omega}_s$ for a selected range of phosphines and phosphites.

The energy minimized structure was also submitted to MMP2 to verify the minimum and to calculate an accurate energy for the structure. The solid angles for this conformer were also calculated and are presented in Table 1. For the energy-weighted conformer averaged solid angles, the conformers were generated using BIOGRAF 3.2.1S, a comprehensive molecular mechanics package distributed by Molecular Simulations Inc. [24], with parameters obtained from the literature [8,23]. Energy minimization was carried out using the conjugate gradient 200 minimizer with a step size of 2.00 Å and a termination criterion of 0.100 kcal mol^{-1} $Å^{-2}$. Once the complexes were energy minimized, they were submitted to a stochastic conformational search. Between 500 and 1000 conformers were generated by Monte Carlo variation of several designated torsion angles and each conformer was fully energy minimized. All torsion angles except those governing rotation about the C≡O axis were considered. The range of conformers sampled in the calculation include those predominantly in an energy 'minimum' as well as those on the hypersurface connecting minima, as required.

4. Conclusions

Two sets of data have been provided: the solid angle of a ligand in a representation of the global minimum energy conformation and a weighted average solid angle taken over a large conformational space. Both measures correlate well with standard measures of steric size (Tolman [7] cone angle and Brown's [8a] ligand repulsive energy). Problems recognized by Mosbo and coworkers [9a] in the definition of weighted mean cone angles have been overcome with the solid angle methodology. The method proposed is sufficiently general to be applied to any system which can be modelled by molecular mechanics methods.

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References

[1] M.S. Newman (ed.), *Steric Effects in Organic Chemistry*, Wiley, New York, 1956.
[2] D. White and N.J. Coville, *Adv. Organomet. Chem., 36* (1994) 95.
[3] (a) D. White, B.C. Taverner, P.G.L. Leach and N.J. Coville, *J. Comput. Chem., 14* (1993) 1042; (b) D. White, B.C. Taverner, P.G.L. Leach and N.J. Coville, *J. Organomet. Chem., 478* (1994) 205.
[4] (a) R. Chauvin and H.B. Kagan, *Chirality, 3* (1991) 242; (b) T. Komatsuzaki, K. Sakakibar and M. Hirota, *Tetrahedron Lett., 30* (1989) 3309; (c) T. Komatsuzaki, K. Sakakibara and M. Hirota, *Chemistry Lett.,* (1990) 1913; (d) M. Hirota, K. Sakakibara and T. Komatsuzaki, *Comput. Chem., 15* (1991) 241; (e) I. Akai, K. Sakakibara and M. Hirota, *Chem. Lett.,* (1992) 1317; (f) T. Komatsuzaki, I. Akai, K. Sakakibara and M. Hirota, *Tetrahedron, 48* (1992) 1539.
[5] K.F. Riley, *Mathematical Methods for Physical Sciences*, Cambridge University Press, Cambridge, Cambs., 1974, p. 91.
[6] A. Immirzi and A. Musco, *Inorg. Chim. Acta, 25* (1977) L41.
[7] C.A. Tolman, *Chem. Rev., 77* (1977) 313.
[8] (a) T.L. Brown, *Inorg. Chem., 31* (1992) 1286; (b) M.-G. Choi and T.L. Brown, *Inorg. Chem., 32* (1993) 5603; (c) M.-G. Choi and T.L. Brown, *Inorg. Chem., 32* (1993) 1548; (d) M.-G. Choi, D. White and T.L. Brown, *Inorg. Chem., 33* (1993) 5591.
[9] (a) J.T. de Santo, J.A. Mosbo, B.N. Storhoff, P.L. Block and R.E. Bloss, *Inorg. Chem., 19* (1980) 3086; (b) M. Cin, G.L. Durst, S.R. Head, P.L. Bock and J.A. Mosbo, *J. Organomet. Chem., 470* (1994) 73.
[10] (a) A. Di Nola, H.J.C. Berendsen and O. Edholm, *Macromolecules, 17* (1984) 2044; (b) A.E. Howard and P.A. Kollman, *J. Med. Chem., 31* (1988) 1669; (c) M. Saunders, K.N. Houk, Y.-D. Wu, W.C. Still, M. Lipton, G. Chang and W.C. Guida, *J. Am. Chem. Soc. 112* (1990) 1419; (d) H. Goto and E. Osawa, *J. Chem. Soc., Perkin Trans. II* (1993) 187; (e) D. Wild and P. Willett, *J. Chem. Inf. Comput. Sci., 34* (1994) 224; (f) F. Villamagna and M.A. Whitehead, *J. Chem. Soc., Faraday Trans., 90* (1994) 47.
[11] SYBYL V 5.4, Tripos Associates Inc., St. Louis, MO, 1991.
[12] J.T. Sprague, J.C. Tai, Y. Yuh and N.L. Allinger, *J. Comput. Chem., 8* (1987) 581.
[13] D.F. Mullica, S.L. Gipson, E.L. Sappenfield, C.C. Liu and D.H. Leschnitzer, *Inorg. Chim. Acta, 177* (1990) 89.
[14] D. White, L. Carlton and N.J. Coville, *J. Organomet. Chem., 440* (1992) 15.
[15] G. Ferguson, P.J. Roberts, E.C. Alyea and M. Kheen, *Inorg. Chem., 17* (1978) 2965.
[16] E.C. Alyea, G. Ferguson and A. Somogyvani, *Inorg. Chem., 21* (1982) 1369.
[17] L. Stahl and R.D. Ernst, *J. Am. Chem. Soc., 109* (1987) 5673.
[18] (a) M.N. Golovin, M.M. Rahman, J.E. Belmonte and W.P. Giering, *Organometallics, 4* (1981) 1981; (b) A.A. Tracy, K. Eriks, A. Prock and W.P. Giering, *Organometallics, 9* (1990) 1399; (c) L. Chen and A.J. Poe, *Inorg. Chem., 28* (1989) 3641;

(d) M.M. Rahman, H.Y. Liu, A. Prock and W.P. Giering, *Organometallics, 6* (1987) 650.
[19] L. Chen and A.J. Poë, *Inorg. Chem., 28* (1989) 3641.
[20] J.D. Cotton and E.A. Miles, *Inorg. Chim. Acta, 173* (1990) 129.
[21] (a) M.L. Boyles, D.V. Brown, D.A. Drake, C.K. Hostetler, C.K. Maves and J.A. Mosbo, *Inorg. Chem., 24* (1985) 3126; (b) R.K. Pomeroy and K.L. Chalk, *Inorg. Chem., 23* (1984) 444.
[22] ALCHEMY III, Tripos Associates, St. Louis, MO, 1992.
[23] (a) M.L. Caffery and T.L. Brown, *Inorg. Chem., 30* (1991) 3907; (b) K.J. Lee and T.L. Brown, *Inorg. Chem., 31* (1992) 289.
[24] BIOGRAF 3.2.1S, Molecular Simulations, Inc., Burlington, MA.