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Molecular mechanics (MM2) calculations and cone angles of phosphine ligands

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Abstract

Molecular mechanics (MM2) calculations were performed on 54 conformations of 18 phosphines (PH_3; $PH_{3-n}R_n$, where $n = 1,\ldots,3$, and R = Me and Et, n = 1 or 2 and R = ^{i}Pr, and n = 1 and R = ^{t}Bu, PMe_2Et, $PMeEt_2$, $PPhMe_2$, and PPh_2R where R = Me, Et, ^{i}Pr, ^{t}Bu and Ph). The results are compared to those previously obtained from MINDO/3 and MNDO calculations, and to experimental data. Single conformer cone angles and weighted average cone angles were calculated from MM2 optimized geometries employing Tolman's general definition, and they are compared to Tolman's values, MINDO/3 results, and T.L. Brown's E_R values. Of the cone angle definitions used, the weighted average values are suggested as the best single representation of phosphine ligand sizes. The steric parameters (cone angle and E_R values) alone, and in conjunction with electronic parameters, are correlated with experimental data.

Key words: Phosphine; Molecular mechanics

1. Introduction

The widespread use of phosphorus-containing ligands in low oxidation state transition metal complexes and organometallics has resulted in many reports of their structures and properties. Several electron diffraction, microwave and X-ray crystallographic investigations have been published [1]; the effects of phosphorus ligand electronic and steric properties upon transition metal complexes have been studied [2]; and phosphorus compounds have been the subject of several computational reports [3–11].

Computational studies have included *ab initio*, semi-empirical and molecular mechanics techniques. The *ab initio* calculations have necessarily been performed only on small ligands [3]. Even semi-empirical calculations, as exemplified by MINDO/3 [4] and MNDO [4c,e], have been restricted to relatively small molecules. In contrast, molecular mechanics calculations can include very large ligands. Allinger and von Voithenberg [5] have reported the results of MM1 (1973 force field) calculations on a series of acyclic phosphines ($PH_{3-n}Me_n$, where n = 0, 1, 2 or 3; PH_2R, where R = Et, ^{i}Pr and ^{t}Bu; PMe_2Et, $P(^tBu)_3$, and PPh_3) and phosphorus-containing heterocyclic compounds. Rithner and Bushweller [6] have reported their results from MM2 on the series of phosphines $P(^tBu)_2R$, where R = H, Me, Et, Bz, ^{i}Pr, ^{t}Bu and Ph. However, their calculations made use of phosphorus parameters derived from the earlier force field (MM1), since MM2 values had not been published. Bowen and Allinger subsequently reported MM2 values of the parameters for phosphorus and included calculations for the same phosphines reported earlier using MM1

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[7]. The MM2 force field has been extended by Robinet *et al.* [8a] to include five-coordinate phosphorus, and by Ugliengo *et al.* [8b] to include the P=O moiety. Li *et al.* [9] have used MM2 generated data to study hydrolysis of P=O containing compounds. Eckert *et al.* [10] have used MM2 to compute conformational energy differences in the complexes $W(CO)_3[P(^iPr)_3]_2(H_2)$, but they did not optimize bond angles or bond lengths. Most recently, Brown and co-workers have reported the use of MM2 to examine energy differences associated with the binding of phosphines and phosphites to $Cr(CO)_5$ (*vide infra*) [11].

TABLE 1. Conformational energies and conformational energy differences (kcal/mol) for alkyl phosphines

Compound	Conformation	No.	MM2 SE [a]	MM2 ΔSE [a,b]	MINDO/3 $\Delta(\Delta H_f)$ [b,c]	MNDO $\Delta(\Delta H_f)$ [b,d]
PH_3			0			
PH_2Me			0.26			
$PHMe_2$			0.36			
PMe_3			0.32			
PH_2Et	t	1	0.06	0	0.04	0.36
	g_r; g_1	2	0.63	0.57	0	0
$PHEt_2$	t,t	1	3.70	2.62	1.03	1.97
	t,g_1; g_r,t	2	2.09	1.01	0.67	1.02
	t,g_r; g_1,t	3	1.71	0.63	0.46	0.57
	g_1,g_r	4	1.08	0	0	0
	g_1,g_1; g_r,g_r	5	1.68	0.60	0.24	0.28
	g_r,g_1	6	3.38	2.30	0.62	0.87
PEt_3	t,t,t	1	9.61	6.36	1.52	6.89
	t,t,g_r; t,t,g_1; t,g_r,t; t,g_1,t; g_r,t,t; g_1,t,t	2	6.59	3.34	0.78	3.00
	t,g_1,g_r; g_r,t,g_1; g_1,g_r,t	3	3.76	0.51	0.32	1.32
	t,g_r,g_r; t,g_1,g_1; g_r,t,g_r; g_1,t,g_1; g_r,g_r,t; g_1,g_1,t	4	3.88	0.63	0.29	1.01
	t,g_r,g_1; g_1,t,g_r; g_r,g_1,t	5	4.95	1.70	0.54	1.26
	g_r,g_r,g_r; g_1,g_1,g_1	6	3.25	0	0	0
	g_r,g_1,g_1; g_1,g_r,g_r; g_r,g_r,g_1; g_1,g_1,g_r; g_r,g_1,g_r; g_1,g_r,g_1	7	4.48	1.23	0.25	– [e]
$PH_2(^iPr)$	tg_r; tg_1	1	0.37	0	0.05	0.15
	$g_r$gl	2	0.89	0.53	0	0
$PH(^iPr)_2$	tg_1,tg_r	1	5.08	2.12	0.41	– [e]
	tg_r,tg_1	2	6.74	3.78	0.65	3.53
	tg_r,tg_r; tg_1,tg_1	3	5.61	2.65	0.54	0.89
	tg_r,$g_r g_1$; $g_r g_1$,tg_r	4	4.58	1.62	0.14	1.55
	tg_1,$g_r g_1$; $g_r g_1$,tg_r	5	2.96	0	0	0
	$g_r g_1$,$g_r g_1$	6	4.41	1.46	0.13	1.22
$PH_2(^tBu)$			0.64			
PMe_2Et	t	1	2.21	0.96	0.28 [d]	0.95
	g_r; g_1	2	1.25	0	0 [d]	0
$PMeEt_2$	t,t	1	5.52	3.32	0.77 [d]	2.79
	t,g_1; g_r,t	2	2.97	0.77	0.42 [d]	0.96
	t,g_r; g_l,t	3	3.10	0.90	0.32 [d]	0.70
	g_1,g_r	4	2.20	0	0 [d]	0.11
	g_r,g_1	5	3.36	1.14	0.26 [d]	13.24
	g_1,g_1; g_r,g_r	6	2.21	0.01	0.06 [d]	0

[a] Steric energy, see Section 2.
[b] Energy difference between listed conformer and conformer with the lowest energy.
[c] From ref. 4d, except where noted.
[d] From ref. 4e.
[e] Data not available, see ref. 4e.

Part of the purpose of the research reported here is to extend the number of compounds studied using MM2 to include additional ligands that are potentially interesting in transition metal complexes. Another purpose of this paper is to report the use of MM2 results to estimate phosphorus ligand sizes.

In order to quantify ligand sizes, Tolman introduced the idea of a cone angle, θ [12]. It was defined as the apex angle of a right cylindrical cone centered 2.28 Å from the center of a phosphorus atom which just touched the van der Waals radii of the outermost atoms. For unsymmetrical ligands, Tolman introduced the concept of a half cone angle, $\theta/2$ [2]. This was defined as the angle between the metal-phosphorus vector and the vector that just touched the van der Waals radii of the outermost atoms of a substituent. Cone angles were computed from the half cone angles by averaging the $\theta/2$ values for the three phosphorus substituent groups and multiplying the result by 2. Using Tolman's definitions of cone angles, different investigators have assigned quantitative size values to phosphorus ligands through three data sources. Tolman used CPK models [2,12], some groups (particularly Alyea and Ferguson) [13] have utilized X-ray crystallographic data, and we [4d] have used MINDO/3 optimized geometries. Each method has drawbacks, however. Tolman restricted himself to the single conformation that produced the smallest cone angle for a ligand. Alyea and Ferguson were similarly restricted to the single ligand conformations dictated in part by crystal-packing forces. Our computer modeling approach provided for the examination of all unique ligand conformations; consequently, it allowed the computation of weighted average cone angles based on conformer energy differences. This was restricted to relatively small phosphines, however.

As noted above, recently Brown and co-workers have reported MM2 computed energies for several phosphites, phosphines, and their $Cr(CO)_5$ complexes [11a,b]. Their interests were especially directed towards the energy differences between the free and complexed ligand. For their comparisons, they chose the lowest energy conformation of the ligand in each of the respective environments. As a result of this work, Brown has also introduced the concept of ligand repulsive energy (E_R), which "may be thought of as the repulsive force experienced by the ligand in the energy-minimized structure, scaled by its equilibrium distance from the metal center" [11d]. He found good correlations between E_R and experimental kinetic and thermodynamic data.

Our interest in investigating ways of representing phosphorus ligand sizes was initially prompted by inconsistencies between equilibrium *cis/trans* ratios in phosphine $W(CO)_4LL'$ (which are believed to be a function of the sizes of L and L′) and the Tolman cone angle values for some of the ligands [14]. Therefore, one purpose of the research reported here is to determine whether MM2 optimized geometries and conformer energies can be used to obtain a set of cone angles that is more consistent with our experimental data.

In this paper we report results of MM2 calculations for the conformations of 18 phosphorus ligands that correspond to all plausible energy minima. Also reported are cone angles and weighted average cone angles calculated from the MM2 optimized geometries and conformer energies using Tolman's general definitions. The geometries and cone angles are compared to Tolman's values, MINDO/3 and MNDO results, Brown's E_R values, and experimental data. Of the approaches based on using various definitions of cone angles, weighted average θ's are the best single representation of phosphorus ligand sizes.

2. Methods

MM2 calculations [7,15*] were performed on 54 conformations of 18 phosphine ligands. Since some phosphorus bond parameters required for calculating heats of formation were unavailable, steric energies calculated by MM2 were used in place of heats of formation as measures of relative conformer energies (see also Section 3).

The compounds and conformers of the alkyl phosphines are listed in Table 1. Symmetry-related, energetically identical conformations are listed together as one unique conformation. Single conformations were used for PH_3, PH_2Me, $PHMe_2$, PMe_3, and $PH_2(^tBu)$, with staggered hydrogens on methyl substituents and staggered methyls on the tert-butyl group. Three conformations were considered for cases involving ethyl and isopropyl substituents. They are depicted below (phosphorus is the front atom), and named according to the system cited by Hanack [16], where *trans* and *gauche* refer to the relationship between the back-carbon substituent and the phosphorus lone pair of electrons. In Table 1, the individual substituent orientations of a given ligand conformation are separated by commas and listed in counterclockwise order as viewed from the phosphorus lone pair. The symmetry-related, equal-energy conformations are separated by semicolons.

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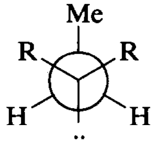
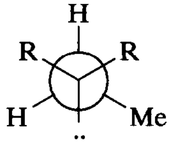
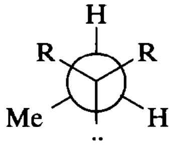
* Reference number with asterisk indicates a note in the list of references.



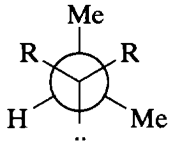
trans
(t)



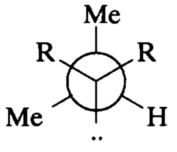
gauche-right
(g_r)



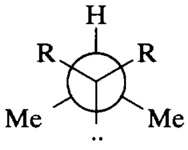
gauche-left
(g_l)



trans gauche-right
(tg_r)



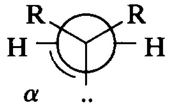
trans gauche-left
(tg_l)



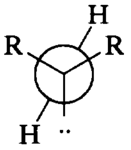
gauche-right gauche-left
(g_rg_l)

Input coordinate data for the alkyl phosphines were idealized bond lengths (P–H = 1.4 Å, P–C = 1.8 Å, C–C(alkyl) = 1.5 Å, C–H = 1.1 Å), bond angles (R–P–R′ = 109.5°, R–C–R′(alkyl) = 109.5°), and dihedral angles (multiples of 60°). All bond lengths, bond angles, and dihedral angles were then optimized.

For ligands containing phenyl groups, input geometries which possessed α angles of 90° and 0° were utilized initially (see below, however). The input geometries for $PPhMe_2$ used the idealized bond lengths and angles described above plus C–C(aryl) = 1.4 Å, and R–C–R′(aryl) = 120°. For diphenyl alkyl phosphines, the atomic coordinates for the phenyl groups were generated using the MM2 coordinate calculation option [15]: a hydrogen atom in the corresponding monophenyl phosphine was replaced by the phenyl group. The phenyl groups were then rotated so that the α angles were all possible combinations of 0° and 90°. The starting geometry for triphenyl phosphine was obtained similarly. All bond lengths, bond angles, and dihedral angles were allowed to optimize through two different methods. In the first, the optimization was completed in the usual manner, using MM2 parameters appropriate for benzene rings. For the second, self-consistent field (SCF) calculations of conjugated π-systems were used for the phenyl groups.



$\alpha = 90°$



$\alpha = 0°$

As described in Section 3, there was concern that, for the phenyl substituted phosphines, stable conformations might have been missed. Therefore, additional approaches for locating low energy conformers were utilized. All of these additional computations were completed without SCF calculations. For $PPhMe_2$, the

TABLE 2. Conformational energies and energy differences (kcal/mol) for aryl-containing phosphines

Compound	Alkyl conformation	Aryl α angle [a]	Conformer number	Multiplicity	Steric energy (SE)	ΔSE
$PPhMe_2$ [b]	–	88	1	1	0.10	0.13
	–	0	2	1	−0.13	0
PPh_2Me	–	87, 7	–	–	−2.07	
PPh_2Et	t	81, 25	1	2	0.39	1.71
	g_r	84, 4	2	2	−0.40	0.92
	g_r	−6, −85	3	2	−1.32	0
$PPh_2(^iPr)$	tg_l	84, 23	1	2	1.19	0.46
	tg_l	−21, 84	2	2	3.32	2.59
	g_rg_l	38, 11	3	2	0.73	0
$PPh_2(^tBu)$	–	−80, −21	1	2	5.08	0
	–	−32, −22	2	2	5.67	0.59
PPh_3	–	−30, −78, 0	1	6	−3.65	0.06
	–	−15, 90, 19	2	6	−3.71	0
	–	−41, −26, −47	3	2	−3.12	0.59

[a] Angles reported are from the phosphorus lone pair of electrons (see Section 2) to the closest *ortho* carbon atom. A positive value indicates a clockwise rotation of α.

[b] Previously reported conformer energy value differences are 0 and 0.89 kcal, respectively, for 1 and 2 from MINDO/3; 3.02 and 0, respectively, from MNDO (ref. 4d).

phenyl ring was rotated with α angles of 0–180° in 1° increments using the MM2 dihedral driver option. At each α angle all bond lengths, bond angles and dihedral angles were allowed to optimize. For the diphenyl-substituted phosphines, both phenyl groups were incremented from 0 to 180° in 10° steps. One phenyl was held at 0° while the other phenyl was incremented from 0 to 180°. The first phenyl was then moved to and held at 10° while the second was incremented from 0 to 180°, and so on. The resulting 361 conformers were used to generate energy contour plots using SURFER [17]. The plot for $PPh_2(^tBu)$ revealed an additional conformer (and its mirror image) that had been missed by the previously described method. Subsequently, this conformation was input by adjusting the α angles so that the energy minimization process began close to the minimum predicted from the SURFER plots. Geometries and energies calculated are listed in Table 2.

A related approach was used for PPh_3. Thus, two of the phenyl groups were incremented from 0 to 180°, but this was done in 30° steps, and a two-stage optimization was used. In the first stage the two phenyl groups to be incremented were input at the appropriate α angles. Those angles were not allowed to vary while the third phenyl group was optimized. Upon completion of this optimization, the output geometry was used as input into the second stage. Here all three rings were allowed to optimize. With the aid of SYBYL [18] to visualize the geometries, the 36 computational results were examined for similar and dissimilar conformations. Three clearly different conformers were observed; they are listed in Table 2.

The dihedral angles M–P–C–C (or lone pair-P–C–C) were obtained using the MM2 optimized coordinates for the phosphorus and carbons, and an estimate of the position of the metal. To estimate the metal atom location a plane was constructed that contained the three atoms directly attached to phosphorus, and a perpendicular to this plane was dropped through the phosphorus atom and extended. In tabulating the data the convention used is that the dihedral angle is positive if, when looking through P towards C, R is clockwise from M. Thus for phenyl groups, the dihedral angle is the same as the α angle defined above.

The resulting MM2 optimized geometries for the various phosphine ligands were used as input for a computer program described in our earlier paper [4d] which calculates half cone angles. For each unique conformation, cone angles were determined by Tolman's method. Thus, the maximum half cone angle was found for each of the three substituent groups, averaged, and multiplied by 2.

For ligands with multiple conformations, weighted average cone angles were calculated from the equation

$$\text{weighted average } \theta = n_A\theta_A + n_B\theta_B + \cdots + n_i\theta_i$$

where θ_i is the cone angle for each contributing conformer, i, and n_i is the mole fraction of that conformer. Reference 4d includes a method for computing these mole fractions from steric energies.

3. Results and discussion

Input conformations for the alkyl phosphines studied (using idealized geometries, see Section 2) and steric energies for the final output geometries are listed in Table 1. For the aryl containing ligands, the final output geometries and steric energies are contained in Table 2. Steric energies, rather than heats of formation, are listed in the tables because our version of MM2 did not contain the necessary parameters for P–H and P–C bonds needed for computations of ΔH. Since these parameter values are constant for a given ligand, irrespective of conformation, differences in steric energies provide the same information as differences in heats of formation.

Before proceeding to a detailed discussion of the geometries and energies of the molecules, a few generalizations are appropriate. First, our energies for those ligands previously reported by Bowen and Allinger [7] (PH_2Me, $PHMe_2$, PMe_3, PH_2Et, $PH_2(^iPr)$, $PH_2(^tBu)$ and PPh_3, although only one conformer of the latter was reported) are essentially identical to theirs. Therefore, except for PPh_3, further discussion of these is minimal. Second, no unusual bond lengths or bond angles are observed for the additional compounds we examined. Third, for alkyl groups, the general input geometries (*gauche vs. trans* relationships to the phosphorus lone pair) are maintained in all output geometries. However, some rotation about the P–C bond is observed, especially in cases where there is more than one *trans* Me group. For example, in conformer 1 of PEt_3 (all three groups *trans* to the lone pair), the methyl groups rotate 22° into a "propeller" arrangement. Fourth, terminal Me groups (*i.e.*, of Et, ^{i}Pr and ^{t}Bu substituents) generally adopt staggered conformations. Exceptions to this occur for those conformers of $PHEt_2$, PEt_3 and $PH(^iPr)_2$ that contain more than one methyl group *trans* to the lone pair. Rotations of up to 45° (conformer 1 of $PHEt_2$) occur in these as a means of relieving steric interactions. Fifth, phenyl groups sometimes rotate a great deal, resulting in output geometries that are substantially different from the original input. Therefore, additional approaches to locating low energy conformations were attempted. These are described in the Section 2 and discussed in greater detail below, following descriptions of the behavior of the alkyl phosphines. Sixth, there is very little difference in computed geometries and conformer energy differences between those calculations that included SCF calculations and those that did not (*e.g.*, typical conformational energy differences between the two computational methods are less than 0.05 kcal). Energy and conformational data listed in the tables were obtained without the SCF option.

Conformational energy differences (the differences in energy between the lowest energy conformer and each of the other conformers) computed by MM2, MINDO/3 [4d] and MNDO [4e] are also listed in Table 1 for the alkyl phosphines. In general, the energy differences from MM2 and MNDO are more similar to each other and larger than those obtained from MINDO/3. For PH_2Et, MM2 predicts the *trans* geometry (conformer 1) to be more stable, which is consistent with experimental results [1m,n], but in contrast to both MINDO/3 and MNDO. Both MINDO/3 and MNDO predict conformer 2 of $PH_2(^iPr)$ to be the more stable, whereas 1 is more stable according to MM2 calculations. The three computational methods predict similar results for $PHEt_2$: conformer 4, where the two *gauche* groups are pointed away from each other, is the lowest in energy; and conformer 1, with two *trans* methyl groups, is the highest in energy. In the crystal structure of a tungsten complex, however, conformer 2 of $PHEt_2$ was observed [19]. The three computational methods predict the same low energy conformer of $PH(^iPr)_2$, 5, and the same highest energy conformer, 2 (although conformer 1 was not maintained by MNDO during geometry optimization). All three methods predict conformer 2 of PMe_2Et to be the more stable. Agreement is also good for conformers 1–5 of $PMeEt_2$, with 4 and 5 being similarly low in energy. Results for the sixth conformer, however, are quite different; the unusually large value obtained from MNDO has been described in an earlier paper [4e].

Of the seven unique conformations of PEt_3, number 6 (all methyl groups *gauche* to the lone pair in a head-to-tail arrangement) is computed by all three methods to be the lowest in energy. Examinations of 18 crystal structures [20] of transition metal complexes containing the PEt_3 ligand indicate that conformer 6, although observed [20a], is not common. Instead, conformer 3, in which one group is *trans* and the other two *gauche* and pointed away from each other, is the most common arrangement [20b–o]. Four crystal structures contain the arrangement of 4 [20e,o–q], where one group is *trans* and the two *gauche* groups are arranged head-to-tail, and one structure has two *trans* groups with one *gauche* (conformer 2) [20r]. None of the crystal structures contain conformations in which *gauche* groups point towards each other (conformers 5 and 7), or in which all groups are *trans* (conformer 1). The latter is the highest energy conformation for all three computational methods, although number 7 was not maintained by MNDO.

The only other ligand for which MINDO/3 and MNDO results are available is $PPhMe_2$. For the MM2 calculations two input geometries were used initially, one with α angle of 90° and the other with 0°. These conformations were maintained in the optimized geometries (output α angles of 88° and 0°, respectively). Since there is no obvious reason why phenyl groups should be stable at only those α angles, the phenyl unit was also driven from 0 to 180° in 1° increments while optimizing the other atom positions. No additional low energy conformations were observed. Rotation about the $P-CH_3$ bond is minimal for the low energy conformer ($\alpha = 0°$). Rotations of about 8° are observed for both methyl groups of the $\alpha = 88°$ conformer, presumably to reduce steric interactions between the phenyl and methyl groups. As listed in Table 2, the MM2 calculated energy differences between the two conformers is in the same direction, but smaller than that obtained from MNDO, and in the opposite direction of the MINDO/3 results.

Initially the phenyl groups of PPh_2R ligands (R = alkyl) were input with plausible α angles of (0°, 0°), (0°, 90°) and (90°, 90°). The output geometries often did not resemble the input, however. Therefore, an alternate approach was used to locate low energy conformations. For each alkyl conformer, both phenyl groups were incremented from 0 to 180° in 10° steps producing 361 output steric energies. Using these data and the program SURFER [17], contour and three-dimensional plots were generated to help locate minima. These are illustrated in Figs. 1(a) and (b), respectively, for tg_1-$PPh_2(^iPr)$. (The zero points on the axes are chosen arbitrarily for convenience of display. They are related to, but do not equal the α angles.) Two minima are readily seen in the figures: 3.32 kcal at about (40°, 80°) and 1.19 kcal at (100°, 150°).

Using a similar approach, only a single conformation (and its mirror image) was found for PPh_2Me, three unique conformations each for PPh_2Et and $PPh_2(^iPr)$, and two for $PPh_2(^tBu)$. In all cases the input conformation of the alkyl group was maintained, although some P-alkyl and/or $C-CH_3$ bond rotation occurred. The single low energy conformer of PPh_2Me, for example, has a $P-CH_3$ rotation of about 10°.

The P-alkyl bond of PPh_2Et conformers 1 and 3 are rotated relatively little, although the $C-CH_3$ bond of the former is moved about 6° from staggered. In contrast, conformer 2 has a P-alkyl rotation of about 30° away from the phenyl with $\alpha = 4°$. Rotation of the $C-CH_3$ bond is minimal in this conformer. The energy of conformer 2 is higher than that of 3, by about 1 kcal. In several crystal structure determinations of compounds that contain PPh_2Et, there is nearly an even split between *trans* and *gauche* orientations [20o,21].

The behavior of $PPh_2(^iPr)$ is similar to the ethyl compound. Three conformers were obtained. Substantial P–alkyl rotation is absent for conformers 1 and 3, although $C-CH_3$ bond rotations of 6–10° are observed in all cases. Conformer 2 has a P–alkyl rotation of about 20° and $C-CH_3$ rotation of about 8°. An interesting feature of this structure is that the Ph group with $\alpha = 84°$ bisects the two methyl groups; the P–alkyl rotation helps accommodate this bisection. As is the case with the PPh_2Et analog, conformer 2 is higher in energy.

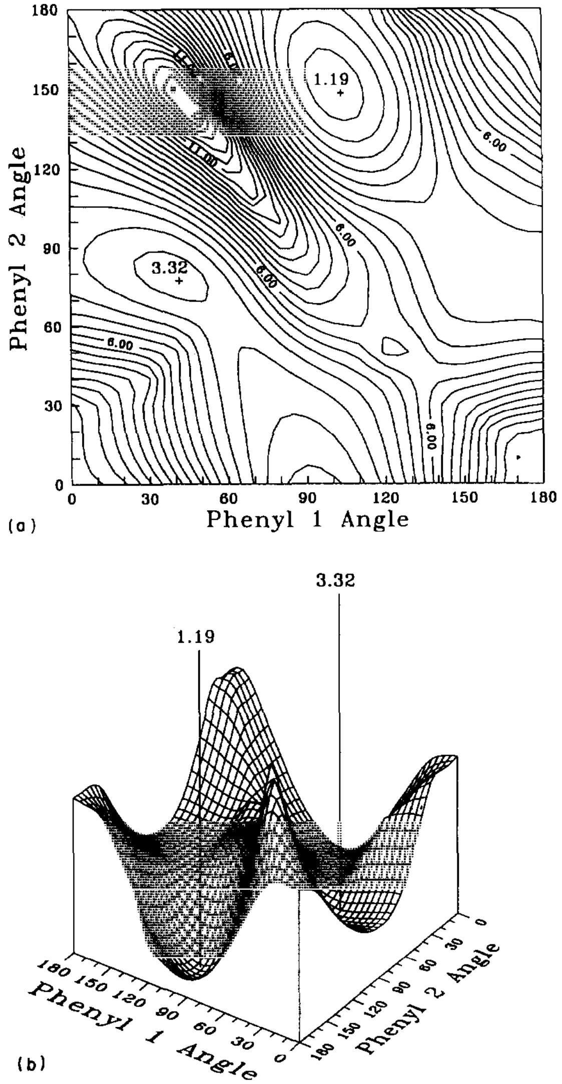


Fig. 1. Energy plot for tg_1-$PPh_2(^iPr)$ as a function of phenyl dihedral angles. Note that the dihedral angles are related to, but do not equal α angles. (a) Contour plot. (b) Energy surface plot.

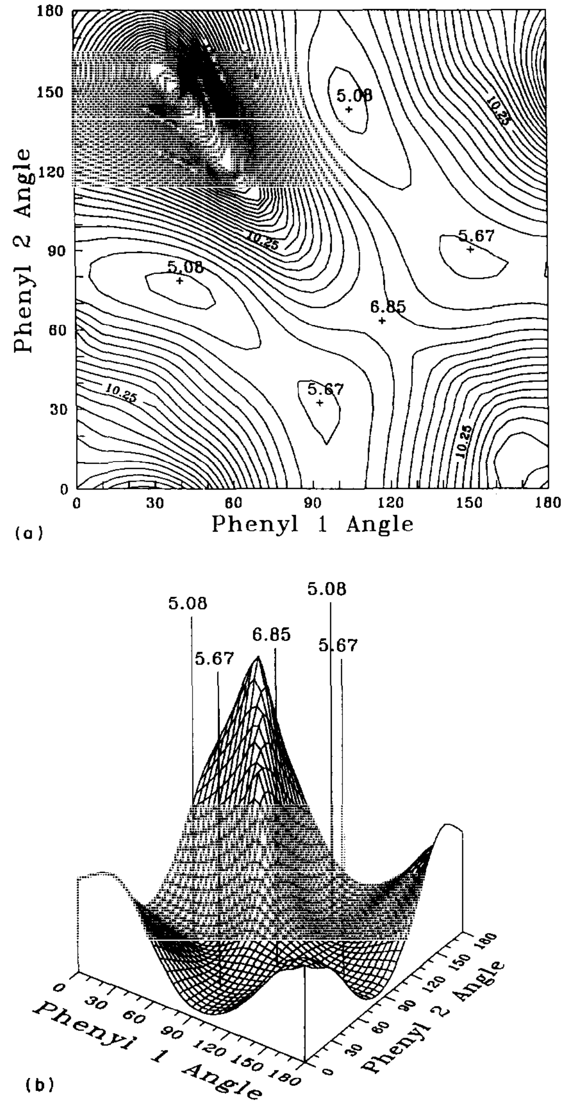


Fig. 2. Energy plot for $PPh_2(^tBu)$ as a function of phenyl dihedral angles. Note that the dihedral angles are related to, but do not equal α angles. (a) Contour plot. (b) Energy surface plot.

Two interesting phenomena are provided by PPh_2 (^tBu). One of these is our inadvertent discovery of a saddle point that we initially misidentified as a conformer. When the α angles were input in the initial fashion (see Section 2), one of the input "conformers" had α angles of (0°, 0°). Optimization provided output angles of (−5°, 6°). However, examination of the contour plots reveals that this is a saddle point, not a minimum. (See Figs. 2(a) and (b). As was the case for Figs. 1(a) and (b), the zero points on the axes are arbitrarily chosen for convenience of display. Thus, they are related to, but do not equal α angles. The saddle point of 6.85 kcal, for example, appears at about

(120°, 60°).) The second interesting feature of $PPh_2(^tBu)$ is the existence of an additional conformer (and its mirror image). It is about 1.2 kcal lower than the saddle point (at 5.67 kcal), and is located between the saddle point and the lower energy conformation (5.08 kcal). It may be viewed as an intermediate in the interconversion between the mirror-image low energy conformers. Thus, looking at Fig. 2(a), if one begins at (40°, 80°) and proceeds "southeast" through the valley, the intermediate is encountered at about (90°, 30°). Proceeding "south" from that point through the bottom of the plot at (0°, 95°) causes one to re-enter at the top (180°, 100°). Continuing south results in locating the mirror image of the original low energy point at about (110°, 140°). It should be noted further that the low energy barrier to rotation follows this path, and does not involve crossing the saddle point located on the symmetry plane. Analogous intermediate conformations are not present with the other PPh_2R ligands.

For both conformations of $PPh_2(^tBu)$, some rotation is observed about P–alkyl and $C-CH_3$ bonds. The lower energy conformer has P–alkyl rotations of about 10°, and $C-CH_3$ of about 5°. The analogous values are 25° and 7°, respectively, for the higher energy conformation. In both cases one of the phenyl groups bisects two methyl groups ($\alpha = 80°$ and $-32°$ for the lower and higher energy conformers, respectively).

A different approach was used to locate minimum energy conformers for PPh_3. Instead of attempting to optimize geometries while incrementing three phenyl groups, a two step optimization approach was used in conjunction with two incremented phenyl groups. The latter were taken from 0 to 180° in 30° steps. In the first stage of the optimization, the two incremented phenyl groups were fixed and the third allowed to optimize. For the second stage, all atom positions were allowed to optimize. It was hoped that by using this approach, (a) the molecule would find a relatively low energy position after the first optimization, and (b) subsequent optimization of that conformation would not lead to passing over a minimum energy conformation. Although this approach does not guarantee that a conformer(s) was not missed, we chose not to undertake additional calculations. Of the 36 potentially unique conformations this approach provided, only three different low energy output geometries were observed: those exemplified by conformers 1, 2 and 3 in Table 2. Conformer 1 has a phenyl group eclipsing the lone pair of electrons ($\alpha = 0°$). Although it was observed from 28 of the 36 output geometries, it is not the lowest energy conformation. That designation belongs to conformer 2, which has one phenyl perpendicular to the lone pair ($\alpha = 90°$); it was observed in 5 of the 36 output conformers. The highest energy conformation (3) is a propeller arrangement, and occurs in three of the output conformations. This is the conformation reported in the crystal structure [1r].

Atom positions from the MM2 optimized geometries of each conformation of each ligand were used to compute cone angles, as described in Section 2. Thus, half-cone angles were obtained by taking the largest $\theta/2$ value for each substituent group, averaging the three values, and multiplying by two to give θ. The values are listed in Table 3. Also listed are the corresponding cone angles previously reported from MINDO/3 calculations [4d]. Table 4 contains the cone angle values reported by Tolman (those derived from CPK models of the conformation with the smallest cone angle) [2], cone angles from the smallest conformer predicted by MM2 and by MINDO/3 [4d] (which we will refer to as Tolman-like cone angles), the cone angle of the conformer that MM2 calculated to have the lowest energy, and MM2 weighted average cone angles.

The idea of weighted average cone angles was introduced by us in an earlier paper as an approach for reporting sizes of ligands having multiple conformations [4d]. (The contribution of each conformer is weighted according to its energy, the weighting is multiplied by the cone angle of that conformer, and the products summed to provide the weighted average cone angle for the ligand; see Section 2.) For the alkyl phosphines the identification of symmetry related conformers is unambiguous, as listed in Table 1. Among the PPh_2R (where R = alkyl) ligands, each conformer listed in Table 2 is assumed to have a mirror image. The case of PPh_3 is more complex, however. Multiplicities of six, six, and two were used for conformers 1, 2, and 3, respectively. The choice of a multiplicity of two for conformer 3 is arbitrary. Based on the fact that one α angle is calculated to be significantly different from the other two, a multiplicity of six is reasonable. However, it was decided that since this conformation is similar to the propeller arrangement of the crystal structure, a multiplicity of 2 (it and its mirror image) would be used.

As seen from Table 4, there is generally very close agreement between Tolman's values and the MM2-derived Tolman-like cone angle values, especially for the smaller ligands. As the ligands become larger, however, our values increase more rapidly than his. These differences probably arise from the fact that the MM2 calculations involved minimization of energies through bond stretching, bending, and conformational rotations to relieve steric interactions, whereas Tolman constructed his conformations with the substituent groups packed as tightly as possible in order to minimize the size.

There are significant differences between our previously reported MINDO/3 calculations and the MM2 results. For phosphines containing only alkyl and H substituents, the MINDO/3 values are generally 5–10° larger for each conformation than those from MM2 (Table 3). This is probably due primarily to a flattening of phosphorus (increased R–P–R angles, or decreased lone pair-P–R angles) in the output geometries from MINDO/3 compared to those of MM2. For the alkylphosphines, $PH_{3-n}R_n$, the P–H $\theta/2$ values directly reflect the degree of flattening, since the P–H bond lengths are nearly constant. The flattening increases with the number of alkyl substituents. For example, from MM2 results, the P–H $\theta/2$ values for PH_3, PH_2Me, and $PHMe_2$ are 43.3, 44.0, and 44.7, respectively. This trend is consistent with that from MINDO/3 (45.6, 47.1 and 49.0, respectively) [4d], although the increments for the latter are larger. Similar results are observed for the Et phosphine series. MM2-based half cone angles for the monosubstituted phosphines, PH_2R, differ very little (Me = 44.0; Et = 44.0, 44.2; ^{i}Pr = 44.0, 44.2; ^{t}Bu = 44.2). This is in contrast to results from MINDO/3 [4d], wherein the P–H half cone angles range from 46.4 for $PH_2(^tBu)$ to 47.1 for PH_2Me.

TABLE 3. Cone angles derived from MM2 and MINDO/3 optimized geometries for all phosphine conformations (deg)

Compound	No.	MM2	MINDO/3 [a]
PH_3		87	91
PH_2Me		97	104
$PHMe_2$		107	118
PMe_3		117	137
PH_2Et	1	97	105
	2	111	114
$PHEt_2$	1	114	122
	2	122	132
	3	126	132
	4	137	140
	5	136	142
	6	139	144
PEt_3	1	135	141
	2	144	153
	3	149	161
	4	151	162
	5	156	165
	6	162	173
	7	167	176
$PH_2(^iPr)$	1	112	116
	2	111	115
$PH(^iPr)_2$	1	146	154
	2	138	146
	3	137	148
	4	142	147
	5	141	148
	6	140	144
$PH_2(^tBu)$		112	118
PMe_2Et	1	120	
	2	133	
$PMeEt_2$	1	127	
	2	135	
	3	142	
	4	148	
	5	151	
	6	148	
$PPhMe_2$	1	118	140
	2	139	156
PPh_2Me		138	
PPh_2Et	1	140	
	2	156	
	3	150	
$PPh_2(^iPr)$	1	156	
	2	160	
	3	169	
$PPh_2(^tBu)$	1	161	
	2	181	
PPh_3	1	159	
	2	157	
	3	164	

[a] From ref. 4d.

TABLE 4. Single conformer cone angles from MM2, MINDO/3 and Tolman, and weighted average cone angles from MM2 (deg) [a]

Compound	Tolman-like			Lowest energy MM2	Weighted-average MM2
	MM2	MINDO /3 [b]	Tolman [c]		
PH_3	87	91	87	87	87
PH_2Me	97	104		97	97
$PHMe_2$	107	118		107	107
PMe_3	117	137	118	117	117
PH_2Et	97	105		97	103
$PHEt_2$	114	122		137	132
PEt_3	135	141	132	162	156
$PH_2(^iPr)$	111	115		112	112
$PH(^iPr)_2$	137	144		141	141
$PH_2(^tBu)$	112	118		112	112
PMe_2Et	120			133	131
$PMeEt_2$	127			148	146
$PPhMe_2$	118	140	122	139	130
PPh_2Me	138		136	138	138
PPh_2Et	140		140	150	151
$PPh_2(^iPr)$	156		150	169	165
$PPh_2(^tBu)$	161		157	161	166
PPh_3	157		145	157	159

[a] For compounds containing phenyl groups, data from the SCF calculations are reported.

[b] From ref. 4d.

[c] From ref. 2.

For a given ligand, different conformations provide a relatively small effect on flattening. Thus, the P–H $\theta/2$ values for PH_2Et are 44.2 (*trans*) and 44.0 (*gauche*); for $PHEt_2$ they are 44.7–44.8 (conformers 4, 5 and 6) and 45.3–45.4 (conformers 1, 2 and 3); and for $PH_2(^iPr)$ the values are 44.2 (t, g conformers) and 44.0 (g, g conformers).

In most cases, MM2 and MINDO/3 provide similar, but not always identical, relative size orderings for the conformations of a given ligand. More importantly, there is a difference in the ligand ordering for $PHMe_2$, $PHEt_2$, $PH_2(^iPr)$, and $PH_2(^tBu)$ (Table 4). Our earlier MINDO/3 calculations provide for comparison to only one phenyl containing ligand, $PPhMe_2$. For both input conformations ($\alpha = 0°$ and $\alpha = 90°$), the cone angles from MINDO/3 are much larger than those of MM2.

To assess the best representation of ligand sizes (the conformer with the smallest cone angle *vs.* the one with the lowest energy *vs.* a weighted average), the Tolman and MM2 data listed in Table 4 were compared to equilibrium *cis/trans* ratios of $W(CO)_4LL'$ complexes. These ratio data were taken from an earlier paper, which reported that they are a function of ligand sizes [14]. The L ligands are $PPhMe_2$, PPh_2Et and $P(p\text{-Tol})_3$, and L' ligands are $P(p\text{-Tol})_3$, $PPh_2(^tBu)$, $PPh_2(^iPr)$, PPh_2Et, PPh_2Me, $PPhMe_2$, PEt_3 and PMe_3. (We did not do MM2 calculations on $P(p\text{-Tol})_3$. Consequently, we assigned the relative conformational energies and cone angles computed for PPh_3 to it.)

Three types of linear regressions were performed using ABSTAT [22]: *cis/trans* ratios as a function of electronic parameter values (eqn. (1)); *cis/trans* ratios as a function of steric parameter values (eqn. (2)); and *cis/trans* ratios as a function of both electronic and steric parameter values (eqn. (3)).

$$\ln(cis/trans) = a(E) + c \qquad (1)$$

$$\ln(cis/trans) = b(S) + c \qquad (2)$$

$$\ln(cis/trans) = a(E) + b(S) + c \qquad (3)$$

(E = electronic parameter, S = steric parameter, and a, b and c are coefficients). Equation (3) is analogous to the linear free energy relationship used by Brown and others [23] based on the work of Hammett [24], Taft [25] and Schenkluhn [26].

Equation (2) was applied to 15 cases: S values from Tolman θs, Tolman-like θs, lowest energy θs, weighted average θs, and Brown's E_R values were correlated to ln (*cis/trans*) values from the three ligand data sets. Table 5 lists the resulting $\bar{R}^2$ values ($\bar{R}^2$ represents an adjusted R^2) [27].

Figures 3–5 help visualize the reasons for the correlation trends. These three figures are plots of ln(*cis/trans*) *vs.* Tolman-like, lowest energy, and weighted average cone angles, respectively, where L = PPh_2Et. As can be seen in Fig. 3 (smallest conformer or Tolman-like θ data), ln(*cis/trans*) generally decreases as the cone angle increases, although there is some scatter of points. A striking exception to the trend occurs with PEt_3 (point e on all three figures), which has been assigned a cone angle that is too small to fit with the other points. (This behavior is also observed with the other two L ligands.) The location of PEt_3 is much better in Fig. 4, wherein the cone angle data are from lowest energy conformers. PEt_3 is an example of a ligand where the smallest cone angle conformer (1) is substantially higher in energy than the lowest energy conformer (6). Choosing the lowest en-

TABLE 5. $\bar{R}^2$ values from eqn. (2) (ln(*cis/trans*) *vs.* steric parameter only)

L ligand	Tolman	Tolman-like	Lowest energy	Weighted-average	E_R
$PPhMe_2$	0.728	0.672	0.656	0.829	0.819
PPh_2Et	0.775	0.773	0.732	0.911	0.809
$P(p\text{-Tol})_3$	0.667	0.701	0.811	0.921	0.664

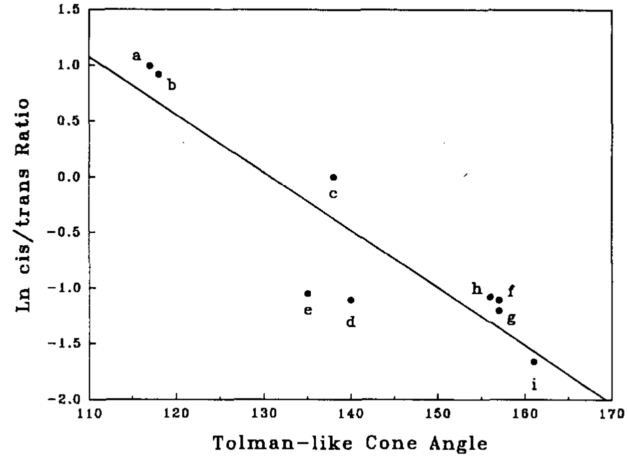


Fig. 3. Plot of ln(*cis/trans*) ratio of $W(CO)_4LL'$ complexes *vs.* Tolman-like cone angles. L = PPh_2Et, L' = PMe_3 (a), $PPhMe_2$ (b), PPh_2Me (c), PPh_2Et(d), PEt_3 (e), $P(p\text{-Tol})_3$ (f), PPh_3 (g), $PPh_2(^iPr)$ (h), and $PPh_2(^tBu)$ (i).

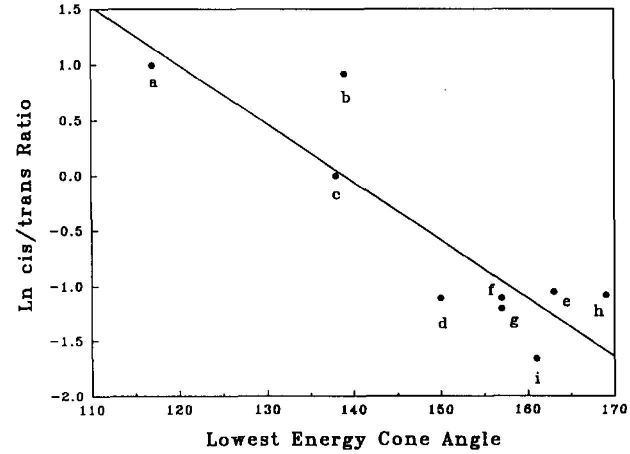


Fig. 4. Plot of ln(*cis/trans*) ratio of $W(CO)_4LL'$ complexes *vs.* lowest energy conformer cone angle. See legend to Fig. 3 for ligand identifications.

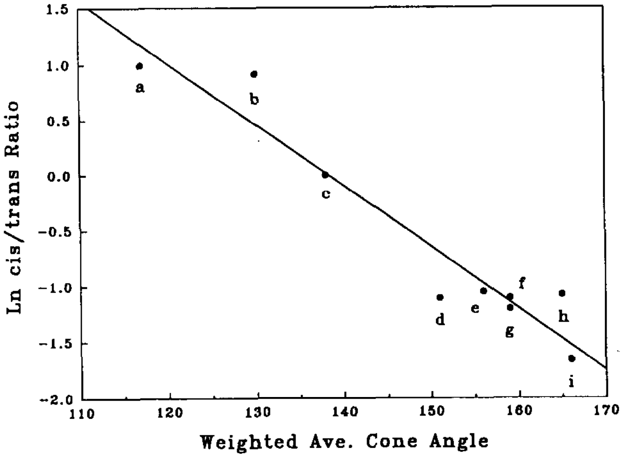


Fig. 5. Plot of ln(*cis*/*trans*) ratio of $W(CO)_4LL'$ complexes *vs.* weighted average cone angle. See legend to Fig. 3 for ligand identifications.

ergy conformation provides a much better representation of PEt_3 size. The use of lowest energy conformers introduces other problems, however. For example, the location of $PPhMe_2$ (point b) is not nearly as appealing in Fig. 4 as on the smallest cone angle plot (Fig. 3). $PPhMe_2$ is a ligand that MM2 predicts has little difference in energy between its two conformers, but a fairly large difference between the two cone angles. Use of the lowest energy conformer overemphasizes the large cone angle conformation. This ligand is better suited to the smallest conformer approach.

The weighted average cone angles (Fig. 5) are compromises between smallest cone angle and lowest energy conformers, and are improvements over both. Like Fig. 4, Fig. 5 shows that PEt_3 is handled well. $PPhMe_2$, however, is displaced from the more ideal location of Fig. 3, but not as severely as in Fig. 4.

Linear regressions using eqn. (1) were applied to 12 cases: the electronic parameters (E) were assigned from pK_a [28], ν [2], χ [29] and $\Delta\delta^{13}C$ [30] values, and correlated to the three ln(*cis*/*trans*) ligand data sets. The results are unimpressive, with $\bar{R}^2$ values ranging from -0.167 to $+0.111$.

Two parameter fittings (eqn. (3)) were completed for 60 cases: the four E sets (pK_a, ν, χ and $\Delta\delta^{13}C$) with the five S sets (Tolman, Tolman-like, smallest energy and weighted average θs, and Brown's E_R) *vs.* the ln(*cis*/*trans*) data sets from the three ligands. As seen from the $\bar{R}^2$ values listed in Table 6, with two dramatic exceptions, at best the two parameter fits provide only moderate improvements over the steric-only calculations of eqn. (2). The exceptions occur with pK_a and both the Tolman θ and Brown E_R values, where $\bar{R}^2$ increases by an average of 0.19 and 0.16 units, respectively. The reasons for the unique behavior of pK_a with these two steric parameters is not understood.

Although the linear free energy relationship represented by eqn. (3) has been generally accepted, we chose to examine alternative mathematical relationships as well. Thus, the seven additional correlations represented by eqns (4)–(10) were also computed.

$$(cis/trans) = a(E) + b(S) + c \tag{4}$$

$$(cis/trans) = a(E) + b[\ln(S)] + c \tag{5}$$

$$(cis/trans) = a[\ln(E)] + b(S) + c \tag{6}$$

$$(cis/trans) = a[\ln(E)] + b[\ln(S)] + c \tag{7}$$

$$\ln(cis/trans) = a(E) + b[\ln(S)] + c \tag{8}$$

$$\ln(cis/trans) = a[\ln(E)] + b(S) + c \tag{9}$$

$$\ln(cis/trans) = a[\ln(E)] + b[\ln(S)] + c \tag{10}$$

As illustrated by representative data contained in Table 7, the small differences among most of the $\bar{R}^2$ values

TABLE 6. $\bar{R}^2$ values from eqn. (3) (ln(*cis*/*trans*) *vs.* both electronic and steric parameters)

E parameter	L ligand	Tolman	Tolman-like	Lowest energy	Weighted-average	E_R
p*K*a	$PPhMe_2$	0.899	0.572	0.705	0.863	0.844
	PPh_2Et	0.942	0.770	0.720	0.902	0.962
	P(*p*-Tol)$_3$	0.897	0.676	0.700	0.910	0.956
ν	$PPhMe_2$	0.824	0.743	0.588	0.806	0.829
	PPh_2Et	0.775	0.810	0.709	0.896	0.781
	P(*p*-Tol)$_3$	0.685	0.726	0.783	0.905	0.612
χ	$PPhMe_2$	0.830	0.732	0.594	0.814	0.824
	PPh2Et	0.792	0.814	0.690	0.898	0.784
	P(*p*-Tol)$_3$	0.697	0.722	0.773	0.908	0.613
$\Delta\delta^{13}C$	$PPhMe_2$	0.863	0.791	0.588	0.808	0.870
	PPh_2Et	0.822	0.872	0.700	0.898	0.808
	P(*p*-Tol)$_3$	0.762	0.815	0.774	0.914	0.664

TABLE 7. Representative $\bar{R}^2$ values from eqns. (3)–(10) averaged from the three ligands sets

Equation	$E = \mathrm{p}K_a$		$E = \chi$	
	S = weighted-average	S = E_R	S = weighted-average	$S = E_R$
(4)	0.876	0.857	0.849	0.588
(5)	0.886	0.929	0.871	0.749
(6)	0.875	0.873	0.846	0.589
(7)	0.886	0.939	0.869	0.754
(3)	0.892	0.921	0.873	0.740
(8)	0.886	0.951	0.877	0.851
(9)	0.892	0.955	0.873	0.751
(10)	0.885	0.955	0.878	0.860

do not make a choice of equation obvious. This leads us to question the validity of statistical treatments that utilize limited data sets, such as those we used in the preceding paragraphs, and/or an empirically based selection of eqn. (3) over one of the other relationships (4)–(10).

4. Summary

Molecular mechanics calculations provide atom positions that can be useful for determining ligand cone angles. The choice of ligand conformation or conformations, however, can substantially affect the θ values. Particular care is needed when computing conformational energies of phenyl groups. Based on correlations to *cis/trans* ratios in $W(CO)_4LL'$ complexes, we have found weighted average cone angles to provide the best representation of a single θ value. The use of weighted average cone angles has the accompanying requirement that all relatively low energy conformations be included, however. Locating the conformations can be difficult when there are aromatic substituents.

For the tungsten complex data, correlations with weighted average θs are somewhat better than Brown's E_R values. However, that need not be the case for other data sources. Brown reported that the correlation of Tolman θs to be better than E_R for the tungsten system, but E_R to be better for several others. He has also calculated E_R values for many more ligands than we have computed weighted average θs. Consequently, we cannot make meaningful comparisons to the other systems that Brown used.

Inclusion of electronic parameters with the tungsten data generally has little effect on $\bar{R}^2$ values. This is consistent with the *cis/trans* ratios being largely steric in origin. However, unusually large values of $\bar{R}^2$ are observed when the electronic parameter $\mathrm{p}K_a$ is used with Tolman θ and Brown E_R values.

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