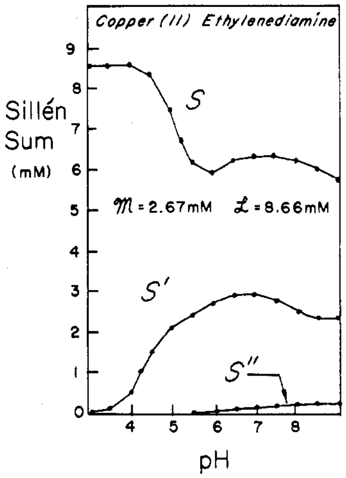

**Figure 6.** Plot of the Sillen sum ($S$) and the residual sums with $enH^+$ and $enH_2^{2+}$ deleted ($S'$) and with $enH^+$, $enH_2^{2+}$, $Cu(en)^{2+}$, $Cu(en)_2^{2+}$, and $Cu_p(OH)_q$ (see text) deleted ($S''$), for the "common point" set.

performing yet another level of residual analysis. The constants for the formation of $Cu(en)^{2+}$ and $Cu(en)_2^{2+}$ determined in this study, along with the literature values[16] for the copper(II) hydrolysis constants, were used to further delete contributions to the Sillen sum. The $S''$ in Table IIIB indicates that up to ~10% of the metal ions participate in the formation of complexes other than $Cu(en)^{2+}$ and $Cu(en)_2^{2+}$. Figure 6 shows the three different Sillen sums $S$, $S'$, and $S''$. The nearest integral values of the $\bar{e}''_m$, $\bar{e}''_l$, and $\bar{e}''_h$ (Table IIIB) suggest the presence of the dimeric species $[(en)Cu(OH)_2Cu(en)]^{2+}$. We fail to see strong evidence for either $Cu(en)_2OH^+$ or $Cu(en)_3^{2+}$ in the pH <9 region for the total concentrations used in this study. The identification of the dimer must at this point remain tentative since its concentration relative to the other species is low enough to make possible errors in data a serious problem.[24] The suggestion of its presence, such as it may be, convinces us that the proposed technique is a valuable addition to other methods in equilibrium analysis.

## Conclusion

The recently described variation methods[4-6] in potentiometric titrations allow one to determine pM and pL values by using only a pH-sensitive electrode, while making no assumptions about the nature of the species present in solution. The present EVM algorithm extends these methods further, while requiring no additional data. That is, having the model-independent pM and pL values, one proceeds to determine the model. Specifically, the average stoichiometric coefficients are determined. The technique should prove to be a valuable addition in the study of complicated equilibrium reactions in aqueous solutions. However, the most important task remains—the acquisition of data of sufficient accuracy so that this technique can be successfully applied.

**Acknowledgment.** The support from the Research and Equipment Fund of Syracuse University is gratefully acknowledged.

**Registry No.** Copper, 7440-50-8; ethylenediamine, 107-15-3.

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[24] The $\bar{n}$ region for pL <6 (pH >7) is particularly sensitive to errors in the total concentration of ethylenediamine. One might suspect that the dip in the $\bar{n}$ curves (Figures 2, 3) in that region (pL 4, 5) is possibly due to analytical errors. For example, suppose the nine metal–ligand formation curves were to have $\bar{n} = 2.00$ (rather than the observed values ~1.90–1.95); in that region solution of eq 33 for $L$ suggests that our ligand stock solution would have to be only 1% less concentrated. The results of our analyses of the stock solution (by independent titrations in the absence of metal ions) indicate an uncertainty of ~0.5%. For this reason, the results of the residual analysis for species other than $Cu(en)^{2+}$ and $Cu(en)_2^{2+}$ must remain tentative.

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# Phosphorus-Ligand Cone Angles. Consequences of Alternate Definitions and Use of MINDO/3 Calculations

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Four specific definitions for cone angles, based on Tolman's general concept, are presented and discussed in terms of idealized phosphine geometries. Cone angles, computed from MINDO/3 optimized geometries and heats of formation data, are reported for the unique conformations and for conformer weighted averages of 15 phosphines: $PH_2R$ (R = H, Me, Et, *i*-Pr, *t*-Bu, Ph, *o*-tol), PHRR′ (R = R′ = Me, Et, *i*-Pr, R = Ph, R′ = Me, Et), and $PRR'_2$ (R = R′ = Me, Et; R = Ph, R′ = Me). The consequences of using MINDO/3 as a data source for cone angle determinations are discussed.

## Introduction

The importance of phosphorus-ligand steric effects in organometallic chemistry and homogeneous catalysis has been reviewed by Tolman.[1] It has been reported, for example, that phosphorus-ligand size affects reaction rates,[2] product distributions,[3,4] and the course of asymmetric syntheses.[5]

In order to quantify phosphorus-ligand sizes, Tolman introduced the concept of cone angle, $\theta$.[1,6] It is generally defined as the apex angle of a right cylindrical cone centered 2.28 Å from the center of a phosphorus atom which just touches the van der Waals radii of the outermost atoms. For unsymmetrical ligands, Tolman introduced the concept of half cone angles, $\theta/2$.[1] These are defined as the angles between the metal–phosphorus vector and the vector that just touches the van der Waals radii of the outermost atoms. To aid in the

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[1] Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.
[2] Darensbourg, D. J.; Graves, A. H. *Inorg. Chem.* **1979**, *18*, 1257.
[3] Trost, B. M.; Weber, L.; Strege, P. E.; Fullerton, T. J.; Dietsche, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 3416.
[4] Ounapu, L. M.; Mosbo, J. A.; Risley, J. M.; Storhoff, B. N. *J. Organomet. Chem.*, in press.
[5] Onuma, K.; Ito, T.; Nakamura, A. *Tetrahedron Lett.* **1979**, 3163.
[6] Tolman, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 2956.

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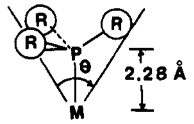
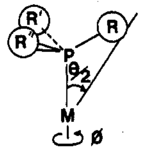
visualization of ligand sizes, Alyea et al.[7] have introduced the use of ligand profiles, which are plots of $\theta/2$ vs. $\phi$, the angle of rotation about the metal–phosphorus vector.





Most[8] cone angles reported in the literature have been obtained by using Tolman's concept. The values listed, however, depend on three additional factors: (1) a specific definition for $\theta$, (2) the choice of substituent conformations, and (3) the source of data. Tolman specifically defined $\theta$ as 2 times the average of the maximum $\theta/2$ values for the three phosphorus substituents (eq 1). For each ligand, he chose the single

$$\theta = \tfrac{2}{3}\sum_{i=1}^{3}\theta_i/2 \tag{1}$$

conformer which minimized $\theta$, with use of CPK models as the source of data.[1,6] Cone angle values have also been reported by using X-ray crystallographic atom positions[7] and Tolman's specific definition for cone angles (eq 1); ligand substituent conformations in these cases are those dictated by crystal packing forces. A second specific definition has been used by Immirzi and Musco with atom positions from crystal structures.[9] The solid angle, $\Omega$, was defined by eq 2, and the cone angle, $\bar{\theta}°$, was obtained from eq 3. (This definition is further

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

$$\bar{\theta}° = 2 \arccos(1 - \Omega/2\pi) \tag{3}$$

discussed in the Results and Discussion.) Thus, to date, most cone angle values have been derived from (1) two specific definitions based on Tolman's concept, (2) single ligand conformations, and (3) data from CPK models or X-ray crystal structures.

This paper reports unique methods for determining ligand cone angles. The general concept of cone angle as described by Tolman is maintained, but three alternative definitions related to eq 1 are posed. Multiple ligand conformations are also considered both individually and as contributors to overall weighted-average cone angles. The latter is uniquely possible through the use of molecular orbital calculations. Heats of formation and atom positions generated by geometry optimization were obtained through application of the semiempirical molecular orbital treatment MINDO/3,[10] which has been recently parameterized to include phosphorus.[11,12] The ramifications of the alternate definitions, the results for single ligand conformations, the weighted averages, and the consequences of using MINDO/3 are discussed.

## Methods Section

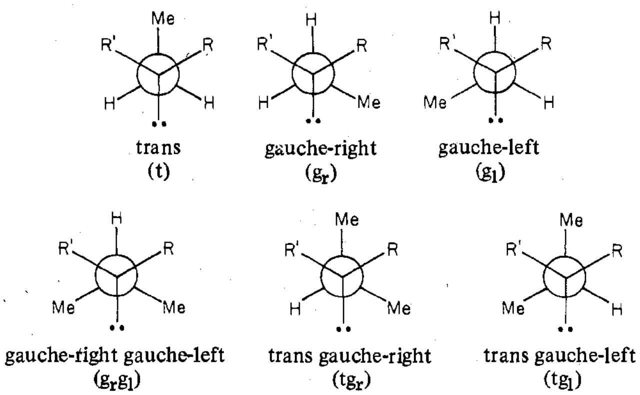
MINDO/3 calculations were performed on all potentially low-energy conformations of 15 phosphorus ligands. The compounds and conformers considered are contained in Table I; symmetry-related, energetically identical conformations are listed together as one unique conformation. For each of the ligands $PH_3$, $PH_2Me$, $PHMe_2$, $PMe_3$, and $PH_2$-*t*-Bu a single conformation was used with staggered hydrogens on methyl substituents and staggered methyls on the *tert*-butyl group. Three conformations were considered for ethyl and isopropyl sub-

Table I. MINDO/3-Derived Heats of Formation and Mole Fractions of All Phosphine Conformers

| compd | unique and contributing conformers[a] | no. | $\Delta H_f$, kcal/mol | mol fracn |
|---|---|---|---|---|
| $PH_3$ | | | 2.52 | unity |
| $PH_2Me$ | | | −10.01 | unity |
| $PH_2Et$ | t | 1 | −4.74 | 0.318 |
| | $g_r$; $g_l$ | 2 | −4.78 | 0.682 |
| $PH_2$-*i*-Pr | $tg_r$; $tg_l$ | 1 | 10.43 | 0.648 |
| | $g_rg_l$ | 2 | 10.38 | 0.352 |
| $PH_2$-*t*-Bu | | | 34.56 | unity |
| $PH_2Ph$ | s | 1 | 52.52 | 0.856 |
| | e | 2 | 53.57 | 0.144 |
| $PH_2$-*o*-tol | $s_r$; $s_l$ | 1 | 57.16 | 0.846 |
| | $e_t$ | 2 | 57.94 | 0.113 |
| | $e_c$ | 3 | 58.53 | 0.042 |
| $PHMe_2$ | | | −19.73 | unity |
| $PHEt_2$ | t, t | 1 | −8.34 | 0.039 |
| | t, $g_l$; $g_r$, t | 2 | −8.70 | 0.146 |
| | t, $g_r$; $g_l$, t | 3 | −8.91 | 0.207 |
| | $g_l$, $g_r$ | 4 | −9.37 | 0.227 |
| | $g_l$, $g_l$; $g_r$, $g_r$ | 5 | −9.13 | 0.302 |
| | $g_r$, $g_l$ | 6 | −8.75 | 0.079 |
| $PH(i\text{-}Pr)_2$ | $tg_l$, $tg_r$ | 1 | 22.85 | 0.083 |
| | $tg_r$, $tg_l$ | 2 | 23.09 | 0.055 |
| | $tg_r$, $tg_r$; $tg_l$, $tg_l$ | 3 | 22.98 | 0.134 |
| | $tg_r$, $g_rg_l$; $g_rg_l$, $tg_l$ | 4 | 22.58 | 0.262 |
| | $tg_l$, $g_rg_l$; $g_rg_l$, $tg_r$ | 5 | 22.44 | 0.333 |
| | $g_rg_l$, $g_rg_l$ | 6 | 22.57 | 0.132 |
| PHMePh | s | 1 | 43.12 | unity |
| | e | 2 | | |
| PHEtPh | t, s | 1 | 48.80 | 0.290 |
| | $g_l$, s | 2 | 48.48 | 0.494 |
| | $g_r$, s | 3 | 48.97 | 0.216 |
| | t, e | 4 | | |
| | $g_l$, e | 5 | | |
| | $g_r$, e | 6 | | |
| $PMe_3$ | | | −27.05 | unity |
| $PEt_3$ | t, t, t | 1 | −8.68 | 0.005 |
| | t, t, $g_r$; t, t, $g_l$; t, $g_r$, t; t, $g_l$, t; $g_r$, t, t; $g_l$, t, t | 2 | −9.42 | 0.113 |
| | t, $g_l$, $g_r$; $g_r$, t, $g_l$; $g_l$, $g_r$, t | 3 | −9.88 | 0.122 |
| | t, $g_r$, $g_r$; t, $g_l$, $g_l$; $g_r$, t, $g_r$; $g_l$, t, $g_l$; $g_r$, $g_r$, t; $g_l$, $g_l$, t | 4 | −9.91 | 0.256 |
| | t, $g_r$, $g_l$; $g_l$, t, $g_r$; $g_r$, $g_l$, t | 5 | −9.66 | 0.085 |
| | $g_r$, $g_r$, $g_r$; $g_l$, $g_l$, $g_l$ | 6 | −10.20 | 0.140 |
| | $g_r$, $g_l$, $g_l$; $g_l$, $g_r$, $g_r$; $g_r$, $g_r$, $g_l$; $g_l$, $g_l$, $g_r$; $g_r$, $g_l$, $g_r$; $g_l$, $g_r$, $g_l$ | 7 | −9.95 | 0.278 |
| $PMe_2Ph$ | s | 1 | 36.70 | 0.882 |
| | e | 2 | 37.59 | 0.118 |

[a] See Methods for a description.

Chart I



trans (t) gauche-right ($g_r$) gauche-left ($g_l$)

gauche-right gauche-left ($g_rg_l$) trans gauche-right ($tg_r$) trans gauche-left ($tg_l$)

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(7) Alyea, E. C.; Dias, S. A.; Ferguson, G.; Restino, R. J. *Inorg. Chem.* **1977**, *16*, 2329.

(8) An alternate cone angle concept by N. C. Payne and P. F. Stepaniak has been cited in: Clark, H. C. *Isr. J. Chem.* **1976/77**, *15*, 210.

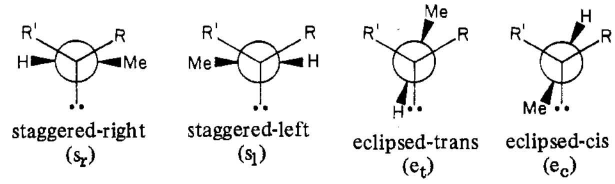
(9) Immirzi, A.; Musco, A. *Inorg. Chim. Acta* **1977**, *25*, L41.

(10) Bingham, R. C.; Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* **1975**, *97*, 1285.

(11) Dewar, M. J. S.; Lo, D. H.; Ramsden, C. A. *J. Am. Chem. Soc.* **1975**, *97*, 1311.

(12) (a) Frenking, G.; Goetz, H.; Marschner, F. *J. Am. Chem. Soc.* **1978**, *100*, 5295. (b) Goetz, H.; Frenking, G.; Marschner, F. *Phosphorus Sulfur* **1978**, *4*, 309.

**Chart II**



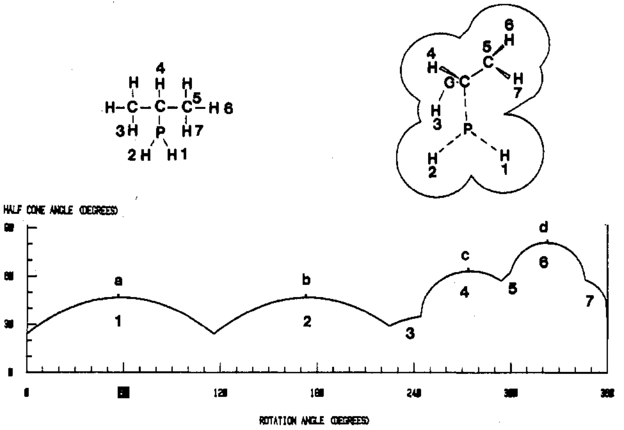
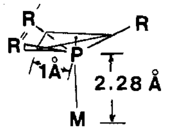


**Figure 1.** $tg_l$ $PH_2$-*i*-Pr: top left, atom number identification; top right, circular trace containing contacted and skeletal atoms; bottom, ligand profile plot.

stituents. They are represented in Chart I (phosphorus is the front atom) and named according to the system cited by Hanack,[13] where trans and gauche refer to the relationship between the back-carbon substituent and the phosphorus lone-pair electrons. For a phenyl group the staggered (s) and eclipsed (e) conformations were used, while for *o*-tolyl there were two staggered and two eclipsed orientations as depicted in Chart II. In Table I, 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.

Input data for MINDO/3 were initial approximate bond lengths (P–H = 1.4 Å, P–C = 1.8 Å, C–C(alkyl) = 1.5 Å, C–C(aryl) = 1.4 Å, C–H = 1.1 Å), bond angles (R–P–R′ = 109.5°, R–C–R′(alkyl) = 109.5°, R–C–R′(aryl) = 120°), and idealized twist angles (staggered groups for alkyl substituents, staggered and eclipsed for aryl substituents). All atom positions were allowed to optimize.

The resulting MINDO/3 optimized geometries of the ligands were used as input for a computer program we wrote which calculates half cone angles. Since the metal atom was not included in the MINDO/3 calculations, it was necessary to position it. Of the several options for its location, we chose a point 2.28 Å from phosphorus on the vector through phosphorus which was normal to a plane defined by the three points 1.00 Å along each P–R bond:



Half cone angles (θ/2) to the van der Waals radii of the outermost atoms were computed at 1° increments for a 360° rotation (φ) about the metal–phosphorus bond. The van der Waals radii used were 1.22 Å for hydrogen and 1.55 Å for carbon while that for phosphorus was set to zero for two reasons: (1) it was desired to observe the effect of substituent groups on the cone angle without interference from phosphorus, and (2) the accepted value of 1.9 Å[14] is too large for transition-metal complexes. These two points are discussed further in the Results and Discussion.

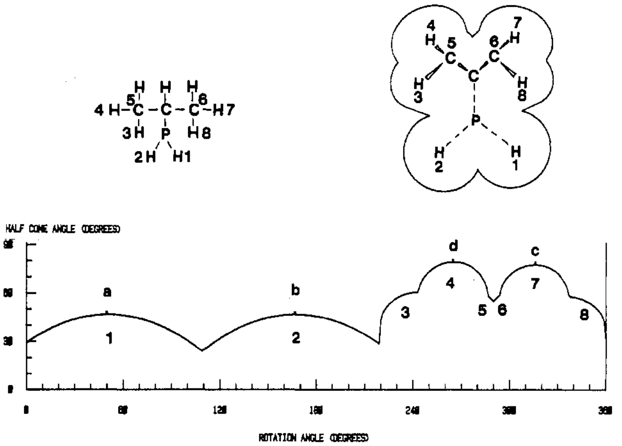


**Figure 2.** $g_rg_l$ $PH_2$-*i*-Pr: top left, atom number identification; top right, circular trace containing contacted and skeletal atoms; bottom, ligand profile plot.

For each unique conformation, cone angles were determined from the four specific definitions described in the following paragraphs. Figures 1 and 2 will be used to introduce and illustrate these definitions. The plots were obtained from MINDO/3 optimized geometries of the two conformations of isopropylphosphine, $tg_l$ and $g_rg_l$, but the concepts discussed apply to other phosphorus ligands and other data sources as well. Both types of graphs indicate where the trace of the θ/2 vector contacts the van der Waals radii of the outermost substituent atoms. The circular traces containing the molecular skeletons indicate which substituent atoms are contacted by the vector. For clarity, only those hydrogens contacted are included inside the trace. The ligand profile graphs (half cone angles (degrees) vs. rotation angles (degrees)) result from plotting the angle the vector makes (the maximum θ/2 value) vs. degrees rotated (φ), in 1° increments. All atom numbers under the plotted line correspond to those within the circular traces.

**Definition I, $\theta_I$.** The maximum θ/2 value ($(\theta/2)_{max}$), point d in Figure 1 or 2, was multiplied by 2 (eq 4).

**Definition II (Tolman's Definition), $\theta_{II}$.** The maximum θ/2 values for each substituent (points a, b, and d) were averaged and multiplied by 2 (eq 5).

**Definition III, $\theta_{III}$.** Averaged maximum θ/2 values obtained for each substituent were averaged and multiplied by 2 (eq 6). Averaged maximum θ/2 values were obtained for alkyl groups by averaging the maximum θ/2 values for the two gauche groups. Thus, for the conformers of isopropylphosphine, points c and d, which correspond to the gauche groups, were first averaged and the resulting θ/2 values then averaged with the values of points a and b. For staggered phenyl groups the maximum θ/2 value was averaged with the maximum θ/2 of its mirrored atom. For the staggered *o*-tolyl groups, the largest θ/2 (which resulted from the *o*-methyl group) was averaged with the maximum θ/2 value from the other half of the ring. For hydrogen and eclipsed aryl substituents, the maximum θ/2 was used without averaging.

**Definition IV, $\theta_{IV}$.** The 360 θ/2 values computed from the 360° rotation of φ in 1° increments were averaged and multiplied by 2 (eq 7). These values are proportional to the areas under the ligand profile curves.

$$\theta_I = 2(\theta/2)_{max} \tag{4}$$

$$\theta_{II} = \tfrac{2}{3}\sum_{i=1}^{3}((\theta/2)_{max})_i \tag{5}$$

$$\theta_{III} = \tfrac{2}{3}\sum_{i=1}^{3}(((\theta/2)_{max})_{av})_i \tag{6}$$

$$\theta_{IV} = \tfrac{2}{360}\sum_{i=1}^{360}(\theta/2)_i \tag{7}$$

For ligands with multiple conformations, eq 8 (in conjunction with

$$\theta = n_A\theta_A + n_B\theta_B + \ldots + n_i\theta_i \tag{8}$$

definitions I–IV) was used to calculate weighted-average cone angles.

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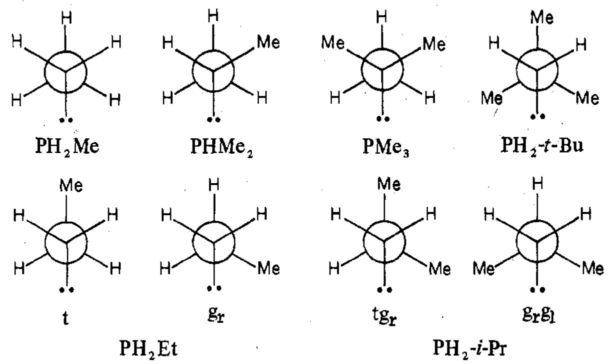
[13] Hanack, M. "Conformation Theory"; Academic Press: New York, 1965; p 68.

[14] Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, N.Y., 1960; p 260.

[15] Whittaker, D. "Stereochemistry and Mechanism"; Clarendon Press: Oxford, 1973; p 36.

Chart III



The contribution of each conformation was determined from its cone angle (i.e., $\theta_A$ for conformer A) and its mole fraction ($n_A$).

The mole fractions are listed in Table I. The values were obtained from eq 9, where $g_A$ is the number of conformers with that unique

$$n_A = \frac{g_A}{g_A + g_B e^{-\Delta E_{AB}/RT} + \ldots + g_i e^{-\Delta E_{Ai}/RT}} \qquad (9)$$

conformation, $\Delta E_{Ai}$ was taken to be the difference in heat of formation between conformers i and A, and $T = 298$ K. The derivation of eq 9 was based on the usual assumption used for conformational analyses of acyclic compounds that the energy distribution within a given conformer is negligibly different from that of another.[13]

## Results and Discussion

Cone angle values of phosphorus ligands depend upon the specific definition used. In this paper the four definitions designated by Roman numerals (see Methods and below, eq 4–7) will be discussed. For ligands with multiple conformations, $\theta$ also depends upon which conformation is chosen. Three options (option A = the conformation which provides the largest $\theta$, option B = the conformation which provides the smallest $\theta$, and option C = the weighted average of all conformations) will be used for the ensuing discussions. From a given definition, I–IV, A and B are the extremes of size and C is intermediate. Values for A–C are identical for ligands with only one conformation.

Definitions I–IV and options A–C will be discussed first in terms of idealized geometries, from which the ramifications of each definition and conformer choice are more easily visualized. The consequences of MINDO/3 use will then be described. The discussion of definitions and choices that follows pertains to any procedure that provides atom positions, however. Deviations produced by a particular procedure (e.g., use of CPK models, crystallographic data, or MINDO/3) are manifestations of the procedure, not the definitions.

**Idealized Conditions.** The term idealized conditions will be a general one meaning that bond lengths of a given type (e.g., P–H, P–C(alkyl), C–C(alkyl), etc.) and bond angles of a given type (e.g., R–P–R′, P–C–C(alkyl), C–C–H(alkyl), etc.) are constant for all conformations and compounds and that twist angles (dihedral angles) are those of perfectly staggered geometries (60, 180, 300°) for alkyl groups or perfectly staggered and eclipsed conformations for aryl groups. Specific values for bond lengths, bond angles, and van der Waals radii are not included in these general discussions. The six phosphines PH$_2$Me, PHMe$_2$, PMe$_3$, PH$_2$Et, PH$_2$-*i*-Pr, and PH$_2$-*t*-Bu will be used to illustrate the facets of each of definitions I–IV and options A–C. Newman projections of the unique conformations are shown in Chart III. (For complete description of PHMe$_2$ one additional projection, the mirrored image of the one shown, would be required; two additional projections, identical with the one depicted, are needed for PMe$_3$.)

**Definition I (Eq 4).** For each conformation of each compound,

$$\theta_I = 2((\theta/2)_{max}) \qquad (4)$$

the maximum $\theta/2$ value ($(\theta/2)_{max}$) is obtained and multiplied by 2. For PH$_2$Me, $(\theta/2)_{max}$ results from contact of the $\theta/2$ vector with either gauche H; the values are identical under the idealized conditions described above. Similarly, $(\theta/2)_{max}$ results from either gauche H of t PH$_2$Et, from any of the four gauche H's of PHMe$_2$ and from any of the six gauche H's of PMe$_3$. The g$_r$ conformer of PH$_2$Et, both conformers of PH$_2$-*i*-Pr, and PH$_2$-*t*-Bu have $(\theta/2)_{max}$ values obtained from contacting a gauche Me. $\theta_I$ for the largest conformer choice (A) can be visualized as defining the smallest right cylindrical cone that will hold any of the conformers so that the metal is at the apex with the phosphorus centered in the cone at a distance 2.28 Å from the apex.

The increasing order of size obtained from idealized conditions, definition I, and option A is PH$_2$Me = PHMe$_2$ = PMe$_3$ < PH$_2$Et = PH$_2$-*i*-Pr = PH$_2$-*t*-Bu. The only order change for the smallest conformer option (B) occurs at PH$_2$Et where PMe$_3$ = PH$_2$Et < PH$_2$-*i*-Pr. The weighted average (C) differs from A and B only for PH$_2$Et, but the precise effect cannot be predicted without knowledge of the relative populations of the two unique conformers. Qualitatively, however, the IC value for PH$_2$Et lies between IA and IB yielding PMe$_3$ < PH$_2$Et < PH$_2$-*i*-Pr, with the remainder of the ordering unchanged. The primary feature of definition I is that it emphasizes the largest group in the ligand. The other three definitions involve averaging, which decreases the emphasis on the largest group.

**Definition II (Eq 5).** For each conformation of each compound,

$$\theta_{II} = \tfrac{2}{3}\sum_{i=1}^{3}((\theta/2)_{max})_i \qquad (5)$$

$(\theta/2)_{max}$ is obtained for each of the three substituents, averaged, and multiplied by 2. Under idealized conditions the $(\theta/2)_{max}$ value for a P–H hydrogen is constant, and alkyl group substituent $(\theta/2)_{max}$ values are characteristic of the larger gauche group. Therefore, cone angles for PH$_2$Me and t PH$_2$Et are identical, and those for g$_r$ PH$_2$Et, both conformations of PH$_2$-*i*-Pr, and PH$_2$-*t*-Bu are the same. Substituent $(\theta/2)_{max}$ values under definition II are strictly additive.

The increasing order of size predicted by IIA is PH$_2$Me < PHMe$_2$ < PH$_2$Et = PH$_2$-*i*-Pr = PH$_2$-*t*-Bu < PMe$_3$. The ordering is partially modified to PH$_2$Me = PH$_2$Et < PHMe$_2$ for IIB and to PH$_2$Me < PH$_2$Et ≈ PHMe$_2$ < PH$_2$-*i*-Pr for IIC. The exact position of PH$_2$Et with respect to PHMe$_2$ is dependent upon the relative population of the two unique conformers of PH$_2$Et.

Definition II, option B, is the method used by Tolman. It emphasizes the maximum size of each substituent but averages the three for the molecular cone angle. Although Tolman has not reported $\theta$ values for PH$_2$-*i*-Pr and PH$_2$-*t*-Bu, he has for P(*i*-Pr)$_3$ and P(*t*-Bu)$_3$. Application of IIB to the latter molecules under idealized conditions would predict identical cone angles, whereas Tolman's values are 160 and 182°, respectively.[1] The difference is a manifestation of the technique he used, not a difference in definition. His use of CPK models necessarily satisfied all criteria of idealized conditions except one, idealized dihedral angles. The differences in reported values for P(*i*-Pr)$_3$ and P(*t*-Bu)$_3$, therefore, are undoubtedly due to different dihedral angles obtained when he rotated groups to minimize $\theta$.

**Definition III (Eq 6).** For each conformation of each

$$\theta_{III} = \tfrac{2}{3}\sum_{i=1}^{3}(((\theta/2)_{max})_{av})_i \qquad (6)$$

compound, an averaged $(\theta/2)_{max}$ is obtained for each of the three substituents, averaged, and multiplied by 2. For alkyl substituents the averaged $(\theta/2)_{\max}$ values are determined by averaging $(\theta/2)_{\max}$ for each gauche group. (See Methods for a detailed description of $((\theta/2)_{\max})_{\mathrm{av}}$ for other groups.) Under ideal conditions the $((\theta/2)_{\max})_{\mathrm{av}}$ value for a P–H hydrogen is constant, and alkyl substituent $((\theta/2)_{\max})_{\mathrm{av}}$ values are characteristic of the two gauche groups. Hence, $((\theta/2)_{\max})_{\mathrm{av}}$ of an Me substituent is the same as that for a t Et, those for $\mathrm{g_r}$ Et and $\mathrm{tg_r}$ *i*-Pr are identical, and those for $\mathrm{g_rg_l}$ *i*-Pr and *t*-Bu are the same. The $((\theta/2)_{\max})_{\mathrm{av}}$ values are strictly additive.

The increasing order of size predicted by IIIA is $PH_2Me < PH_2Et < PHMe_2 < PH_2\text{-}i\text{-}Pr = PH_2\text{-}t\text{-}Bu < PMe_3$. For IIIB, the ordering changes to $PH_2Me = PH_2Et < PH_2\text{-}i\text{-}Pr < PHMe_2 < PH_2\text{-}t\text{-}Bu < PMe_3$, and for IIIC it is $PH_2Me < PH_2Et < PH_2\text{-}i\text{-}Pr \approx PHMe_2 < PH_2\text{-}t\text{-}Bu < PMe_3$. The position of $PH_2$-*i*-Pr with respect to $PHMe_2$ is dependent on the relative populations of the $PH_2$-*i*-Pr unique conformers. Like definition II, III also emphasizes maximum $\theta/2$ values, but, in contrast to II, they are averaged by groups on the substituents, rather than just the substituents themselves.

For symmetrical phosphines with all gauche groups identical (e.g., $PMe_3$), definitions I–III provide identical $\theta$ values under idealized conditions. Unsymmetrical substitution (e.g., $PH_2Me$) will always result in definition I being the largest, and different gauche groups on a substituent (e.g., $PH_2Et$ vs. $PH_2$-*t*-Bu) will make $\theta_{\mathrm{II}}$ greater than $\theta_{\mathrm{III}}$.

**Definition IV (Eq 7).** This definition is much different in

$$\theta_{\mathrm{IV}} = {}^{2}\!/_{360}\sum_{i=1}^{360}(\theta/2)_i \qquad (7)$$

concept than I–III: for each conformation of each compound the 360 $\theta/2$ values obtained for the 360 rotation in 1° increments (see Methods) are averaged and multiplied by 2. Maximum $\theta/2$ values are given no more weighting than any other.

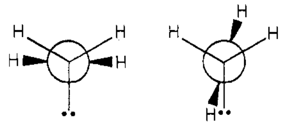
This definition is similar to that of Immirzi and Musco,[9] who, after determining the solid angle ($\Omega$) defined by eq 2, obtained an average cone angle ($\bar{\theta}$°) from eq 3. The relationship between $\Omega$ and their crystallographic data was not specified, however. The quantity $(1 - \Omega/2\pi)$ in eq 3 is an average of cos $(\theta/2)$. In the context of their definition and our procedure, 360 values of cos $(\theta/2)$ would be averaged and the arc cos would be obtained and multiplied by 2. In contrast, under definition IV the 360 values of $\theta/2$ are averaged and multiplied by 2. The results of the two procedures are similar but are slightly different numerically.

Compared to the other three definitions, IV emphasizes the "valleys" between atoms (minimum $\theta/2$). Because minimum as well as maximum $\theta/2$ values are included, definition IV consistently provides smaller angles than the other three definitions. Cone angles should be viewed as indicators of relative rather than absolute sizes, however, making differences in absolute values immaterial. It is the trends produced that are important.

Definition IV trends for alkyl groups are similar to those from III. Thus, a phosphorus H substituent makes a smaller contribution than Me which in turn is less than a *t*-Bu. Minor differences in relative $\theta$ values do occur, however. For example, definition III predicts identical results for $\mathrm{g_r}$ $PH_2Et$ and $\mathrm{tg_r}$ $PH_2$-*i*-Pr, while the latter is slightly larger under definition IV. This is due to the $\theta/2$ vector briefly contacting a hydrogen of the trans Me in $PH_2$-*i*-Pr (a group missing in $\mathrm{g_r}$ $PH_2Et$) during the 360° rotation. Furthermore, group values are not strictly additive under definition IV. Because of the contact with the trans Me in $PH_2$-*i*-Pr, for example, the rotation angle range that includes a tg *i*-Pr group is greater than that which includes a g Et. Concomitantly, the H range of $\mathrm{tg_r}$ $PH_2$-*i*-Pr is reduced compared to that in g $PH_2Et$. These differences are very minor, however. Size orderings for IVA–C are the same as for IIIA–C, respectively.

There is an advantage to using definition IV over III for some ligands. When the three substituents are very complex, it can become difficult and inadvisable to attempt to distinguish among gauche groups of each substituent. In fact, it may become difficult to differentiate among substituent groups. Since definition IV does not require differentiation, cone angles of complex ligands can be unambiguously obtained.

Definition IV differs dramatically from III for aryl substituents, however. With e $PH_2Ph$, for example, definition III averages the single, very large $(\theta/2)_{\max}$ value for the Ph substituent with the two H's making $\theta_{\mathrm{III}}$ much larger for e than for s. Under definition IV the e Ph group also provides very large $\theta/2$ values but covers a very narrow rotation range (ca. 50°). The s Ph group, on the other hand, provides smaller $\theta/2$ values but covers a larger rotation range (ca. 145°). When the rotation ranges and $\theta/2$ values are combined, as under definition IV, the difference between the two conformers is greatly reduced.



s e

$PH_2Ph$

**MINDO/3 Results.** Values for heats of formation, P–H and/or P–C bond lengths, and H–P–H, H–P–C and/or C–P–C bond angles obtained from MINDO/3 have been reported by Frenking, Goetz, and Marschner[12] for $PH_3$, $PH_2Me$, $PHMe_2$, $PMe_3$, $PH_2Et$, $PHEt_2$, $PEt_3$, and $PH_2Ph$, although conformers were not specified for the latter five compounds. Our results (see Table I for heats of formation data) were in general agreement with theirs.

Cone angle values calculated for each unique conformation are listed in Table II, and weighted-average cone angles (option C) are contained in Table III. Although skewing around P–C bonds occurred in numerous conformers (vide infra), all input conformations were maintained except for eclipsed phenyls of PHMePh (conformer **2**) and PHEtPh (conformers **4**–**6**). These four were skewed so severely that they are better described as skewed staggered conformations. Data from them are not included in the tables.

Half cone angles were calculated with the van der Waals radius of phosphorus set to zero. The effect of using the literature value[14] of 1.9 Å can be visualized on the ligand profile plots of Figures 1 and 2 as a horizontal line at 56.4°, which obliterates the P–H hydrogens and removes fine structure in the isopropyl groups. Although phosphorus may make a contribution to the sizes of ligands, in this report it was desired to consider the effects of substituents, not phosphorus, on cone angles. What the appropriate value for the van der Waals radius of phosphorus in a transition-metal complex should be is also unclear. Phosphorus–phosphorus distances obtained from the crystal structures of $[Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)(Ph_2PCH_2PPh_2)]BPh_4$[16] and $PtCl_2(PMe_3)_2$[17] are about 3.1 and 3.3 Å, respectively, suggesting that the radius of phosphorus should be much smaller than 1.9 Å. The effect of setting the radius to zero is potentially important in those compounds with P–H hydrogens and in the procedure described by definition IV. If, for example, an appropriate radius were 1.6 Å, half the average P–P distance in the two complexes above, P–H hydrogens would be hidden

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(16) Cowie, M. *Inorg. Chem.* **1979**, *18*, 286.

(17) Messmer, G. G.; Amma, E. L.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 725.

**Table II.** MINDO/3-Derived Cone Angles for All Phosphine Conformers from Definitions I-IV[a]

| compd | no.[b] | $\theta_{\mathrm{I}}$ | $\theta_{\mathrm{II}}$ | $\theta_{\mathrm{III}}$ | $\theta_{\mathrm{IV}}$ |
|---|---|---|---|---|---|
| $PH_3$ | | 91.2 | 91.2 | 91.2 | 75.9 |
| $PH_2Me$ | | 125.0 | 104.5 | 103.4 | 87.0 |
| $PH_2Et$ | 1 | 128.2 | 105.2 | 104.2 | 87.7 |
| | 2 | 153.6 | 113.7 | 109.8 | 92.4 |
| $PH_2$-*i*-Pr | 1 | 161.8 | 116.1 | 110.2 | 94.6 |
| | 2 | 158.6 | 114.9 | 114.3 | 100.4 |
| $PH_2$-*t*-Bu | | 169.2 | 118.3 | 116.4 | 102.5 |
| $PH_2Ph$ | 1 | 123.4 | 103.8 | 103.7 | 80.3 |
| | 2 | 179.0 | 121.7 | 121.7 | 90.6 |
| $PH_2$-*o*-tol | 1 | 145.2 | 110.9 | 107.2 | 100.0 |
| | 2 | 183.4 | 123.3 | 123.3 | 91.8 |
| | 3 | 220.6 | 135.3 | 135.3 | 104.3 |
| $PHMe_2$ | | 127.8 | 117.9 | 117.7 | 99.6 |
| $PHEt_2$ | 1 | 133.8 | 121.9 | 120.4 | 100.9 |
| | 2 | 167.2 | 131.9 | 124.5 | 106.0 |
| | 3 | 166.6 | 131.7 | 124.7 | 106.4 |
| | 4 | 162.4 | 139.7 | 128.4 | 110.8 |
| | 5 | 164.0 | 142.3 | 128.5 | 111.3 |
| | 6 | 167.4 | 143.8 | 128.5 | 117.0 |
| PH(*i*-Pr)$_2$ | 1 | 185.4 | 154.5 | 129.0 | 120.2 |
| | 2 | 170.2 | 145.8 | 132.7 | 114.0 |
| | 3 | 182.4 | 148.1 | 133.2 | 116.4 |
| | 4 | 174.8 | 146.9 | 135.9 | 119.8 |
| | 5 | 178.4 | 147.7 | 136.5 | 121.4 |
| | 6 | 168.4 | 143.7 | 138.3 | 124.4 |
| PHMePh[c] | 1 | 135.0 | 120.2 | 117.5 | 107.5 |
| PHEtPh[c] | 1 | 135.8 | 122.5 | 119.2 | 108.1 |
| | 2 | 160.0 | 130.7 | 122.8 | 112.9 |
| | 3 | 174.4 | 137.9 | 121.4 | 113.1 |
| $PMe_3$ | | 137.2 | 136.9 | 134.4 | 114.7 |
| $PEt_3$ | 1 | 142.2 | 141.1 | 139.0 | 116.6 |
| | 2 | 176.2 | 153.1 | 142.8 | 121.4 |
| | 3 | 174.2 | 161.1 | 146.7 | 126.4 |
| | 4 | 177.4 | 162.5 | 146.9 | 126.9 |
| | 5 | 178.4 | 164.8 | 147.2 | 127.2 |
| | 6 | 175.0 | 173.0 | 151.0 | 132.2 |
| | 7 | 175.8 | 175.5 | 151.3 | 131.4 |
| $PMe_2Ph$ | 1 | 140.4 | 139.8 | 137.2 | 123.9 |
| | 2 | 198.8 | 155.6 | 154.7 | 118.6 |

[a] See Methods for a description of definitions. [b] See Table I for conformers included under each conformer number. [c] Data for conformers **2** of PHMePh and **4–6** of PHEtPh are not included due to severe P–aryl bond rotation upon MINDO/3 optimization (see MINDO/3 Results subsection).

**Table III.** Weighted-Average Cone Angles for Definitions I–IV from MINDO/3-Optimized Geometries and Heats of Formation Data[a]

| compd | $\theta_{\mathrm{I}}$ | $\theta_{\mathrm{II}}$ | $\theta_{\mathrm{III}}$ | $\theta_{\mathrm{IV}}$ |
|---|---|---|---|---|
| $PH_3$ | 91.2 | 91.2 | 91.2 | 75.9 |
| $PH_2Me$ | 125.0 | 104.5 | 103.4 | 87.0 |
| $PH_2Et$ | 145.5 | 111.0 | 108.0 | 90.9 |
| $PH_2$-*i*-Pr | 160.7 | 115.7 | 111.6 | 96.6 |
| $PH_2$-*t*-Bu | 169.2 | 118.3 | 116.4 | 102.5 |
| $PH_2Ph$ | 131.4 | 106.4 | 106.3 | 81.8 |
| $PH_2$-*o*-tol | 152.7 | 113.3 | 110.2 | 99.3 |
| $PHMe_2$ | 127.8 | 117.9 | 117.7 | 99.6 |
| $PHEt_2$ | 163.7 | 137.3 | 126.8 | 109.4 |
| PH(*i*-Pr)$_2$ | 176.8 | 147.5 | 135.3 | 120.2 |
| PHMePh[b] | 135.0 | 120.2 | 117.5 | 107.5 |
| PHEtPh[b] | 156.1 | 129.9 | 121.5 | 111.6 |
| $PMe_3$ | 137.2 | 136.9 | 134.4 | 114.7 |
| $PEt_3$ | 176.0 | 166.4 | 148.2 | 128.2 |
| $PMe_2Ph$ | 147.3 | 141.7 | 139.3 | 123.3 |

[a] See Methods for a description of definitions and manner of weighted-average calculation. [b] Data for conformers **2** of PHMePh, and **4–6** of PHEtPh were not included in calculations (see MINDO/3 Results subsection).

from the $\theta/2$ vector for P–H $(\theta/2)_{\max}$ values of less than 44.6°. Under those conditions, which did not occur with the phosphines reported here, cone angles calculated from definitions I–III would be erroneous. Definition IV would similarly present a problem for molecules with profiles that have points below 44.6°, since these would be averaged in with the other $\theta/2$ values. All compounds described in this paper have $\theta/2$ values below 44.6°.

The fact that nonideal geometries are generated by MINDO/3 could have manifestations upon cone angles through differences in (1) bond lengths, (2) phosphorus flattening, (3) skewing around P–C bonds, and (4) skewing around C–C bonds. It is not the intent of this report to compare MINDO/3-generated geometries with other computational or experimental techniques; a future paper will discuss those aspects. Rather, it is the intent of this subsection to illustrate how nonidealized geometries, in this case those from MINDO/3, are reflected in cone angle values.

Of the four possible effects on cone angles cited above, bond length is the only one which is unimportant. Analyses of the length differences found in P–C and C–H bonds of the methyl-substituted phosphines, for example, affected cone angles by no more than 0.02°.

As defined here, the degree of flatness at phosphorus, the second effect, is the relative M–P–R bond angle (R = C, H); the smaller the angle, the flatter the phosphorus. This definition holds because in any given phosphine all M–P–R angles are equal, due to the procedure used to locate the metal. Flattening can arise if the H–P–H, H–P–C, or C–P–C bond angles increase.

For the alkylphosphines, $PH_n(R)_{3-n}$, flattening increases with the number of alkyl substituents because MINDO/3-generated bond angles increase in the order H–P–H < C–P–H < C–P–C. Since P–H bond lengths are nearly constant, the P–H $\theta/2$ values directly reflect this degree of flattening. For example, the P–H $\theta/2$ values for $PH_3$, $PH_2Me$, and $PHMe_2$ are 45.6, 47.1, and 49.0°, respectively, which correspond to the respective M–P–R angles of 117.6, 114.5, and 110.4°.

The P–H $\theta/2$ values for $PH_2R$ increase in the order *t*-Bu (46.4°) < *i*-Pr (46.6, 46.5°) < Et (46.9, 46.9°) < Me (47.1°), which is also the order of decreasing M–P–R angles. Since the H–P–H angles in all the phosphines studied are nearly invariant, the flattening necessarily results from increased H–P–C angles. The nearly identical values for the two conformers of both $PH_2$-*i*-Pr and $PH_2Et$ reflect the fact that H–P–C angles are affected little by conformer changes.

Comparison of the compounds with phenyl groups to those with alkyl groups shows that P–H $\theta/2$ values are similar. Thus, those for conformers **1** and **2** of $PH_2Ph$ are 46.5 and 47.0°, respectively, and those for $PH_2$-*o*-tol range from 46.3 to 46.9°. In contrast to $PH_2Ph$, however, the largest value for $PH_2$-*o*-tol, 46.9°, is associated with the staggered conformer, **1**.

Skewing, as defined here, is the result of two effects, changes in the P–C–R or C–C–R bond angles and P–C or C–C rotation. Within any of the compounds $PH_2Me$, $PHMe_2$, or $PMe_3$, the only significant contribution to differences between $\theta/2$ for gauche hydrogens arises from skewing about the P–C bond. Furthermore, the skewing is due almost solely to P–C bond rotation. Thus, the $(\theta/2)_{\max}$ values of 62.5 and 59.4° for the two gauche hydrogens of Me in $PH_2Me$ are due respectively to a 7.9° rotation toward and a 6.9° rotation away from the metal.

Skewing around C–C bonds is more difficult to assess in terms of $(\theta/2)_{\max}$ values, since the latter are also affected by flattening at phosphorus, P–C–C bond angle changes, and P–C bond rotations. The $(\theta/2)_{\max}$ difference of 3.4° between the $g_l$ methyl groups of $g_rg_l$ (point c in Figure 2) and $tg_l$ (point d in Figure 1), for example, is a combined effect due primarily to P–C and C–C skews. This can be visualized as resulting in differing orientations of the planes defined by the three methyl hydrogens; the plane is tilted more toward the metal in the $tg_l$ conformer.

## Conclusion

Currently there is insufficient experimental or theoretical data available to definitely state which definition, I–IV, or which option, A–C, best represents phosphorus-ligand size. There are reasons to expect some definitions and options to be better, however.

Of options A–C, C appears to be the most fitting. When steric effects are important in complexes, a given ligand is unlikely to assume a geometry similar to the largest possible. Therefore, A is a particularly poor option, and B is the more reasonable single conformer choice. Since restricted P–C or C–C bond rotation in phosphine ligands of transition-metal complexes at room temperature is rare, a given ligand would be best described by a weighted average of the contributing conformations. Unfortunately, that information is also not experimentally available. Heat of formation data obtained from MINDO/3 has been presented here, but the reliability of the difference in conformer energies is unknown. Furthermore, the values were obtained for free ligands; relative conformer energies probably change upon complexation.

Of definitions I–IV, it is reasonable to expect that one of the averaging techniques, II–IV, is most appropriate. Definition I emphasizes the largest group and essentially ignores the smaller ones, yet there is no reason to expect, for example, that $PH_2Me$, $PHMe_2$, and $PMe_3$ are essentially the same size. Furthermore, the paucity of examples of restricted rotations about M–P bonds in trisubstituted phosphines at room temperature makes an averaging technique more reasonable. This undoubtedly contributed to Tolman's choice of definition II. It is unclear as to how much averaging is appropriate. Definition III would appear preferable to II since averaging the two gauche Me groups of $g_lg_r$ $PH_2$-*i*-Pr, for example, provides a distinctly different cone angle than the average of gauche Me and H of $g_r$ $PH_2Et$. Another advantage to averaging gauche groups can be visualized with $PMe_3$. A 5° rotation of each methyl group around the P–C bonds produces a difference of about 5° in $\theta_{II}$ but has an insignificant effect on $\theta_{III}$ or $\theta_{IV}$. Therefore, the source of data, whether from models, X-ray crystallography, computation, or other sources, can provide inappropriate information about sizes under definition II. Definition IV has the decided advantage of not requiring the identification of gauche or substituent groups (see Idealized Conditions) but also has two important disadvantages. The extreme averaging of IV causes cone angle differences among ligands to be depressed. More important, however, is the lack of an unambiguous choice for the effective radius of phosphorus (see MINDO/3 Results subsection). If it were not for the latter problem, we would prefer definition IV, but, until the effect of phosphorus size on cone angles is clarified or sufficient data become available to make a choice obvious, we currently prefer definition III with option C.

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**Registry No.** $PH_3$, 7803-51-2; $PH_2Me$, 593-54-4; $PH_2Et$, 593-68-0; $PH_2$-*i*-Pr, 4538-29-8; $PH_2$-*t*-Bu, 2501-94-2; $PH_2Ph$, 638-21-1; $PH_2$-*o*-tol, 53772-59-1; $PHMe_2$, 676-59-5; $PHEt_2$, 627-49-6; PH(*i*-Pr)$_2$, 20491-53-6; PHMePh, 6372-48-1; PHEtPh, 3619-88-3; $PMe_3$, 594-09-2; $PEt_3$, 554-70-1; $PMe_2Ph$, 672-66-2.

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# Conformational Effects of Nucleophilic and Electrophilic Attack on (Arene)chromium Tricarbonyl Complexes

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Nucleophilic and electrophilic substitution in (arene)chromium tricarbonyl complexes was investigated by means of extended Hückel molecular orbital calculations and qualitative considerations from perturbation theory. It was found that the regioselectivity of attack on the arene should be controlled not only by the substituent on the arene but also by the conformation of the $Cr(CO)_3$ unit. It is shown that the arene carbons which are eclipsed with respect to the carbonyl groups are preferentially attacked by nucleophiles. Electrophilic substitution is preferred at the staggered arene carbons. This is a consequence of the intermixing between $\pi^*$ levels induced by the $Cr(CO)_3$ orbitals. Both charge and overlap controlled arguments operate in the same direction for the early stages of the reactions.

Attack by nucleophiles on (polyene)$ML_n$ transition-metal complexes has been extensively investigated by experimental means.[2] The theoretical details of these reactions are also beginning to unfold.[3] In general, the products of nucleophilic attack are thought to be kinetically controlled with exo attack by the nucleophile on the polyene.[3c] However, there do appear to be several exceptions to this rule.[4] Of special concern to

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(1) (a) University of Houston; Camille and Henry Dreyfus Teacher-Scholar, 1979–1984. (b) Cornell University.

(2) (a) For reviews see ref 3a. Also, see: White, D. A. *Organomet. Chem. Rev., Sect. A* **1968**, *3*, 497. (b) Al-Kathumi, K. M.; Kane-Maguire, L. A. P. *J. Organomet. Chem.* **1975**, *102*, C4. John, G. R.; Kane-Maguire, L. A. P. *Ibid.* **1976**, *120*, C45. Mansfield, C. A.; Kane-Maguire, L. A. P. *J. Chem. Soc., Dalton Trans.* **1976**, 2187. John, G. R.; Kane-Maguire, L. A. P.; Sweigart, D. A. *J. Organomet. Chem.* **1976**, *120*, C47. Sweigart, D. A.; Wilker, C. N. *J. Chem. Soc., Chem. Commun.* **1977**, 304.

(3) (a) Schilling, B. E. R.; Hoffmann, R.; Faller, J. W. *J. Am. Chem. Soc.* **1979**, *101*, 592. (b) Davis, S. G.; Green, M. L. H.; Mingos, D. M. P. *Nouv. J. Chim.* **1977**, *1*, 445. (c) Davis, S. G.; Green, M. L. H.; Mingos, D. M. P. *Tetrahdron* **1978**, *34*, 3047. (d) Ephritikhine, M.; Francis, B. R.; Green, M. L. H.; Mackenzie, R. E.; Smith, M. J. *J. Chem. Soc., Dalton Trans.* **1977**, 1131. (e) Clack, D. W.; Monshi, M.; Kane-Maguire, L. A. P. *J. Organomet. Chem.* **1976**, *107*, C40. (f) Clack, D. W.; Monshi, M.; Kane-Maguire, L. A. P. *Ibid.* **1976**, *120*, C25. (g) Clack, D. W.; Kane-Maguire, L. A. P. *Ibid.* **1979**, *174*, 199.

0020-1669/80/1319-3092$01.00/0