Steric Parameters of Conformationally Flexible Ligands from X-ray Structural Data. 2. P(OR)$_3$ Ligands in Multiple Ligand Environments

Jeremy M. Smith and Neil J. Coville*

Department of Chemistry, University of the Witwatersrand, PO Wits 2050, South Africa

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Cone (θ) and solid (Ω) angle data for the alkyl phosphite ligands P(OR)$_3$ (R = Me, Et, ^{i}Pr) were determined from structural data in the Cambridge Structural Database (CSD). The results for the P(OMe)$_3$ and P(OEt)$_3$ ligands are indicative of more than one preferred cone (or solid) angle, suggesting that geometric measurements of steric parameters for these ligands need to be used with care, as is shown in the analysis of some linear free energy relationships.

Introduction

In the analysis of ligand effects, particularly those of phosphorus(III) ligands, the QALE model (eq 1) has found widespread use and application.[1] Typically, physicochemical properties of a chemical system are described in terms of up to four parameters. The electronic properties of ligands are described in terms of a single parameter, χ,[2] while a size parameter, θ (cone angle[3]), is used to describe steric effects. Often steric thresholds, defined as the point at which there is a sudden onset of steric effects, are observed in QALE analyses. The thresholds are described by the parameter $(\theta - \theta_{st})\lambda$, where θ_{st} is the value of the steric threshold, and λ is a switching parameter, zero in the absence of steric effects and unity when they are operative. An aryl effect parameter, E_{ar},[4] which is dependent solely on the number of aryl groups attached to a ligand, may also be included. In addition to statistical analyses, extensive use of graphical analysis is made in the QALE methodology.[5]

$$\text{Property} = a\chi + b\theta + c(\theta - \theta_{st})\lambda + dE_{ar} + e \quad (1)$$

A competing model, the ECW model,[6−8] has been proposed, where only two parameters are used to describe physicochemical properties of phosphorus ligands. In this model, the bonding between Lewis acids (metals) and Lewis bases (ligands) is described in terms of electrostatic (hard) and covalent (soft) interactions. Thus, one parameter corresponds to the portion of bonding that can be ascribed to electrostatic (E_A/E_B) interactions and the other (C_A/C_B) to covalent interactions. Appropriate sets of data are analyzed using the ECW equation, and physicochemical properties are predicted and new parameters derived.

$$\text{Property} = E_AE_B + C_AC_B + W \quad (2)$$

Giering and Prock have shown, in the analysis of isoequilibrium behavior arising from the temperature dependence of $E°/T$ values for the [Fe(η^5-C$_5$H$_5$)(L)(CO)(COMe)]$^+$/[Fe(η^5-C$_5$H$_5$)(L)(CO)(COMe)]^0 couple, that the ECW model does not adequately model stereoelectronic effects of phosphorus ligands. Although the QALE model, in contrast to the ECW model, was sufficiently able to describe the isoequilibrium behavior of alkyl and aryl phosphines, it originally failed in the case of phosphites,[9] until two new parameters describing the "aryl effect" and π-acidity of phosphite ligands were incorporated.[10]

In the previous paper of this series, we examined the steric parameters of a series of alkyl phosphite ligands in a constant ligand environment from the X-ray crystal structure data of [Mo(η^5-C$_5$H$_5$)(CO)$_2$(L)I] and [W(I)$_2$(CO)$_2$(L)(Ph$_2$P(CH$_2$)$_2$PPh$_2$)] complexes.[11] Our study supported previous suggestions[12,13] that the cone angles of these ligands, particularly P(OMe)$_3$ and P(OEt)$_3$, are underestimated. Further, we also suggested that the steric parameters used in quantitative relationships with chemical data need to be carefully considered. Another example of this is shown in the analysis of phosphorus ligand effects on the $^1J_{CH}$ values of the Co−CH$_3$ moiety in a series of methylcobaloxime complexes, [Co(L)(DH)$_2$CH$_3$] (DH = monoanion of dimethylglyoxime).[14] The steric parameters that correlated best

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[1] Fernandez, A.; Reyes, C.; Wilson, M. R.; Woska, D. C.; Prock, A.; Giering, W. P. *Organometallics* **1997**, *16*, 342−348, and references therein.

[2] Bartik, T.; Himmler, T.; Schulte, H.-G.; Seevogel, K. *J. Organomet. Chem.* **1984**, *272*, 29−41.

[3] Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313−348.

[4] Wilson, M. R.; Woska, D. C.; Prock, A.; Giering, W. P. *Organometallics* **1993**, *12*, 1742−1752.

[5] Bartholomew, J.; Fernandez, A. L.; Lorsbach, B. A.; Wilson, M. R.; Prock, A.; Giering, W. P. *Organometallics* **1996**, *15*, 295−301.

[6] Drago, R. S. *Organometallics* **1995**, *14*, 3408−3417.

[7] Drago, R. S.; Joerg, S. *J. Am. Chem. Soc.* **1996**, *118*, 2654−2663.

[8] Joerg, S.; Drago, R. S.; Sales, J. *Organometallics* **1998**, *17*, 589−599.

[9] Fernandez, A. L.; Lee, T. Y.; Reyes, C.; Prock, A.; Giering, W. P. *Organometallics* **1998**, *17*, 3169−3175.

[10] Fernandez, A. L.; Reyes, C.; Prock, A.; Giering, W. P. *J. Chem. Soc., Perkin Trans. 2* **2000**, 1033−1041.

[11] Smith, J. M.; Coville, N. J.; Cook, L. M.; Boeyens, J. C. A. *Organometallics* **2000**, *19*, 5273−5280.

[12] Stahl, L.; Ernst, R. D. *J. Am. Chem. Soc.* **1987**, *109*, 5673−5680.

[13] Stahl, L.; Trakarnpruk, W.; Freeman, J. W.; Arif, A. M.; Ernst, R. D. *Inorg. Chem.* **1995**, *34*, 1810−1814.

[14] Moore, S. J.; Marzilli, L. G. *Inorg. Chem.* **1998**, *37*, 5329−5335.

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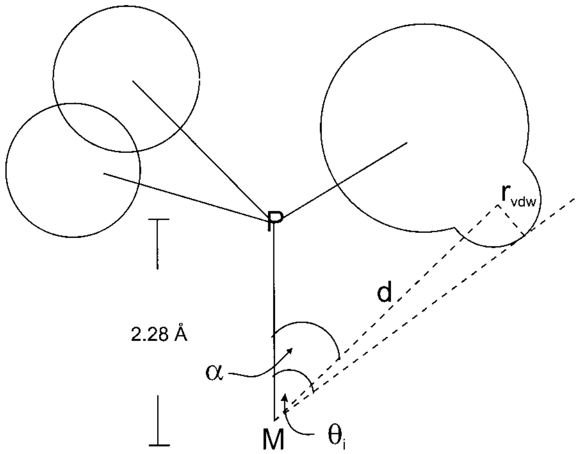

Figure 1. Schematic illustration of the method used for calculating cone angles from data in CSD.

with $^1J_{CH}$ were cone angles calculated from analogous cobaloxime complexes.[15]

In this paper, we have extended our previous work to determining the cone and solid angles of alkyl phosphite ligands in multiple ligand environments, using data from the Cambridge Structural Database (CSD). In a previous study,[16] cone angle values of phosphine ligands determined from structures in the CSD were found in general to be similar to those originally determined by Tolman;[3] however, phosphite ligands were not examined. These ligands, with their conformationally flexible arms, are extensively used in organometallic synthesis,[17,18] and hence a CSD analysis of these ligands would be useful. Herein we report the evaluation of phosphite size from the CSD. The results have been applied to the isoequilibrium behavior of the $[Fe(\eta^5\text{-}C_5H_5)(L)(CO)(COMe)]^+/[Fe(\eta^5\text{-}C_5H_5)(L)(CO)(COMe)]^0$ couple.

Results and Discussion

The cone angles of the ligands $P(OR)_3$ (R = Me, Et, ^{i}Pr) were calculated from data in the CSD. The algorithm used to calculate the Tolman cone angle is based on Figure 1 and is slightly modified from that previously published.[16] The distance, *d*, and the corresponding angle, α, from the metal to each of the surface atoms (oxygen and hydrogen) of each organic substituent of the phosphite ligand are measured from the crystallographic data. The half-cone angle, θ_i, for each atom is then calculated according to eq 3:

$$\theta_i = \alpha + \frac{180}{\pi}\sin^{-1}\left(\frac{r_{vdW}}{d}\right) \tag{3}$$

where r_{vdW} is the van der Waals radius of the element in question (oxygen or hydrogen). For each substituent on phosphorus, the maximum half-cone angle is identified, and the Tolman cone angle is calculated by eq 4:

Table 1. Results of Cone and Solid Angles Determined from Data in the CSD

	$P(OMe)_3$	$P(OEt)_3$	$P(O^iPr)_3$
number of data points	316	33	10
average cone angle, θ_{av}	124	125	137
range of cone angles	103−139	116−138	132−144
Tolman cone angle, θ^3	107	109	130
average solid angle, Ω_{av}	2.15	2.47	3.28
range of solid angles	1.64−2.76	1.55−2.95	3.06−3.52
solid angle, Ω^{27}	2.83	3.01	4.01

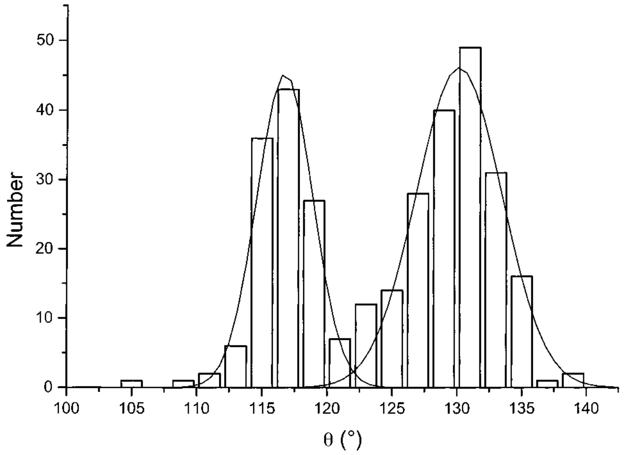

Figure 2. Histogram showing the spread of cone angle values determined from data in the CSD for the $P(OMe)_3$ ligand. Gaussian curves are shown to fit the data.

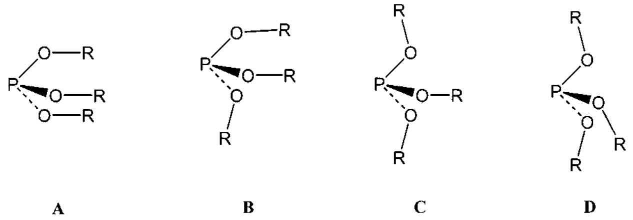

Figure 3. Possible conformations of $P(OR)_3$.

$$\theta = \frac{2}{3}\sum\theta_i \tag{4}$$

For consistency with previous work, the same M−P bond distance (2.28 Å) and van der Waals radii were used. The results of the calculations are listed in Table 1. For other alkyl phosphite ligands, $P(OR)_3$, insufficient data were available for meaningful calculations.

For the $P(OMe)_3$ ligand, which has the most data, the spread of cone angles obtained is shown as a histogram in Figure 2, with a Gaussian fit to the data. *Two maxima are evident*, centered at 117° and 130°, respectively. This is an unexpected result, suggesting that more than one conformation is energetically accessible to this ligand.

The question of ligand conformation to be used in determining cone angle values of the alkyl phosphite ligands has previously been discussed.[11−13,19] Four conformations of $P(OMe)_3$ are possible (Figure 3). The cone angles of 117° and 130° determined from the maxima of the histogram are characteristic of ligand conformations **B** and **C**, respectively, as shown by the conformations of the $P(OMe)_3$ ligand in $[Fe_2(PhC(S)SMe)(CO)_5(P(OMe)_3)]$[20] (117°, conformation **B**) and $[Fe_2(\mu$-

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(15) Trogler, W. C.; Marzilli, L. G. *Inorg. Chem.* **1975**, *14*, 2942−2948.

(16) Müller, T. E.; Mingos, D. M. P. *Transition Met. Chem.* **1995**, *20*, 533−539.

(17) Wilkinson, G. W.; Stone, F. G. A.; Abel, E. W. *Comprehensive Organometallic Chemistry*; Pergamon: Oxford, 1982.

(18) Abel, E. W.; Stone, F. G. A.; Wilkinson, G. W. *Comprehensive Organometallic Chemistry II*; Pergamon: Oxford, 1995.

(19) Chen, L.; Poë, A. J. *Coord. Chem. Rev.* **1995**, *143*, 265−295.

η^3-$RCH_2OC(S)SMe)(CO)_5P(OMe)_3]$[21] (130°, conformation **C**). Of the four conformations, the original Tolman cone angle was determined from the minimum conformation **A**, which gives a cone angle of 107°. As can be seen in Figure 2, there are very few structures giving cone angles of this size. By contrast, a value of 128° for $P(OMe)_3$, based on conformation **C**, has been found to be consistent with equilibrium studies in “open titanocene” complexes.[12,13]

It is notable that all four possible phosphite conformations are energetically accessible, as shown by the complexes giving the smallest and largest cone angles. The smallest cone angle (103°) was measured from the complex $[Co(\eta^5\text{-}C_9H_7)(C_3F_7)(P(OMe)_3)_2]^+SbF_6^-$,[22] which has a phosphite conformation that is somewhat distorted from **A**. There are two phosphite ligands in this complex, one of which is eclipsed by the six-membered ring of the indenyl ligand. As a direct consequence of the limited space available to this particular phosphite ligand, it has to adopt a compact conformation, leading to the small cone angle. Conformation **D** is observed for one of the phosphite ligands in the ruthenium dimer $[Ru_2(\eta^5\text{-}C_5H_5)_2S_6(P(OMe)_3)_2]$,[23] which gives a cone angle of 138°. As expected, in this complex there is relatively little steric repulsion for the phosphite ligand, allowing it to open up, resulting in a larger cone angle. Thus, *the metal–ligand environment appears to play a role in establishing the observed phosphite conformation*, as we have previously suggested.[11] However, electronic and, in the solid state, packing effects certainly cannot be discounted in determining the conformation of the $P(OMe)_3$ ligand. In the above ruthenium example, for instance, two independent molecules are found in the unit cell, and the cone angles of the remaining three phosphite ligands range from 128° to 133°. Their conformations are of type **C**.

While the conformation, and hence size, of the phosphite ligand in the solid state may not exactly correspond with that in solution, it is clear that the $P(OMe)_3$ ligand is more flexible than previously recognized, leading to greater variability in cone angles. Further, it is important to note while a spread of conformations, and hence cone angles, is observed, there are two *preferred* conformations, leading to two characteristic cone angles.

The cone angle data for the $P(OEt)_3$ ligand (Figure 4) show a trend similar to that of $P(OMe)_3$, although the clustering of data points is not quite as dramatic as those of $P(OMe)_3$. This may be due to (i) the greater degrees of freedom in this ligand, leading to blurring of cone angles due to the greater number of available conformations, or (ii) insufficient data. Up to three maxima can be identified from the histogram, with cone angles of 119°, 124°, and 132°, respectively. Examination of representative structures for the two smaller cone angles shows the conformation of the $P(OEt)_3$ ligand to be similar in both cases to type **B**.[24,25] Clearly, the greater degrees of freedom lead to a greater spread of angles, although the observation of two maxima is unexpected. This could reflect the lack of crystallographic data; when sufficient data are available, the two maxima may merge into one new, averaged maximum. Interestingly the solid angle data show only one maximum. For the largest cone angle, the conformation is of type **C**.[26] The data for $P(O^iPr)_3$, on the other hand, can be fitted as a single Gaussian distribution (Supporting Information). More importantly, the maximum of the Gaussian fit, at 137°, is a value larger than that previously reported by Tolman.[3]

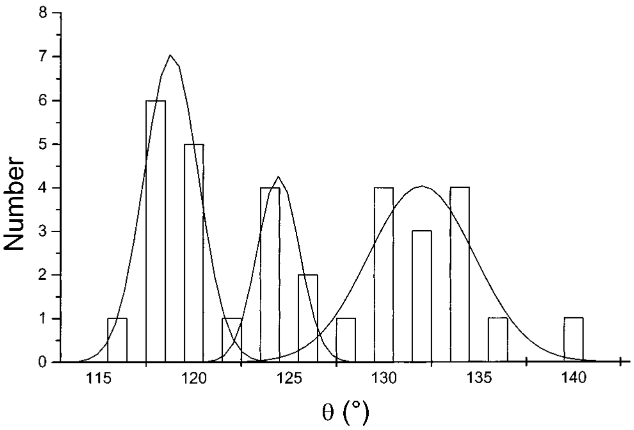

Figure 4. Histogram showing the spread of cone angle values determined from data in the CSD for the $P(OEt)_3$ ligand. Gaussian curves are shown to fit the data.

Solid angles were calculated for the same phosphite ligand fragments retrieved from the CSD. In this case, due to the complexity of the calculation, each individual phosphite fragment was retrieved from the database, and the solid angle calculated as before.[27,28] Calculated solid angle values for the phosphite ligands are listed in Table 1. The solid angle data for these ligands showed trends similar to the cone angle data; the results of the calculations for the $P(OMe)_3$ ligand are shown in Figure 5, while those of $P(OEt)_3$ and $P(O^iPr)_3$ are shown in the Supporting Information.

Implications for Quantitative Analysis. Given that the cone angle data reported above suggest that more than one value could be reasonably used for the alkyl phosphite ligands, the question arises as to which values should be used for these ligands. For instance, an upward revision of 10° from the Tolman cone angle values for the $P(OMe)_3$ and $P(OEt)_3$ ligands, based on molecular mechanics calculations, has been suggested.[19,29] This result corresponds to a conformation close to that of **B**, but this ignores the larger accessible cone angles. Despite our results above, a single value, applicable to as many data sets as possible, would be preferred. One possibility would be to use the average of our crystal-

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(20) Lagadec, A.; Misterkiewicz, B.; Patin, H.; Mousser, A.; Marouille, J.-Y. L. *J. Organomet. Chem.* **1986**, *315*, 201–210.

(21) Darchen, A.; Lhadi, E. K.; Grandjean, D.; Mousser, A.; Patin, H. *J. Organomet. Chem.* **1988**, *342*, C15–C19.

(22) Zhou, Z.; Jablonski, C.; Bridson, J. *Organometallics* **1994**, *13*, 781–794.

(23) Treichel, P. M.; Crane, R. A.; Haller, K. J. *Polyhedron* **1990**, *9*, 1893–1899.

(24) Albertin, G.; Antoniutti, S.; Bacchi, A.; Barbera, D.; Bordignon, E.; Pelizzi, G.; Ugo, P. *Inorg. Chem.* **1998**, *37*, 5602–5610.

(25) Bruce, M. I.; Liddell, M. J.; Tiekink, E. R. T.; Nicholson, B. K.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1991**, *410*, 211–229.

(26) Ogo, S.; Suzuki, T.; Isobe, K. *Inorg. Chem.* **1995**, *34*, 1304–1305.

(27) White, D.; Taverner, B. C.; Leach, P. G. L.; Coville, N. J. *J. Comput. Chem.* **1993**, *36*, 1042.

(28) Taverner, B. C. *J. Comput. Chem.* **1996**, *17*, 1612–1623.

(29) Poë, A. J.; Farrar, D. H.; Zheng, Y. *J. Am. Chem. Soc.* **1992**, *114*, 5146–5152.

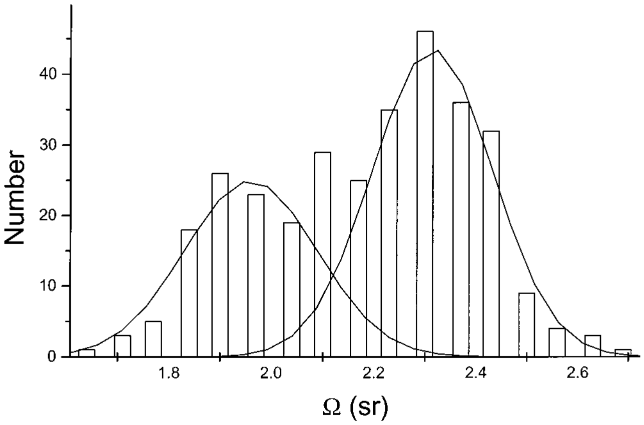

Figure 5. Histogram showing the spread of solid angle values determined from data in the CSD for the $P(OMe)_3$ ligand. Gaussian curves are shown to fit the data.

lographic cone angles for further calculations, which is roughly equivalent to using a weighted average cone angle.[30,31] However, it is possible that this particular value may not be applicable to all systems and further data will be needed to evaluate this suggestion.

To test the applicability of the various sets of steric data, we have applied these steric data to the isoequilibrium behavior arising from the temperature dependence of $E°/T$ values for the $Fe(\eta^5\text{-}C_5H_5)(L)(CO)(COMe)^+/Fe(\eta^5\text{-}C_5H_5)(L)(CO)(COMe)^0$ couple. As mentioned above, without the addition of new ligand parameters,[10] the QALE model is unable to quantify the isoequilibrium behavior arising from the temperature dependence of $E°/T$ values for the $Fe(\eta^5\text{-}C_5H_5)(L)(CO)(COMe)^+/Fe(\eta^5\text{-}C_5H_5)(L)(CO)(COMe)^0$ couple for phosphite ligands, whereas the aryl and alkyl phosphines are readily modeled.[9] The feature of this isoequilibrium system is that it tests families of ligands, whose parameters need to be internally consistent to model the system adequately and thus avoid the problem of changing individual parameters based on the lack of fit to one set of data,[12,13] while not considering the effect of changing parameters on the fit to other data sets.[19]

In addition to the Tolman cone angle and average crystallographic cone angle values (see above), we have also used values that may be typical of this system. The $P(OMe)_3$ ligand conformation in an iron complex similar to that used in the isoequilibrium study, $[Fe(\eta^5\text{-}C_5H_4Me)(CO)(P(OMe)_3)I]$,[32] is of type **C**, producing a cone angle of 130°. We anticipate that the space available to the phosphite ligands in this series of complexes would be similar,[11] and thus the $P(OEt)_3$ ligand would have a similar conformation to that of the $P(OMe)_3$ ligand. The cone angle for this conformation of the $P(OEt)_3$ ligand is 132° (see above).

Table 2. R^2 Values for Fitting E/T at Each Temperature for Each Steric Parameter

temperature (K)	θ^a	$\theta_{av}{}^b$	$\theta_C{}^c$	$\Omega_C{}^d$
229	0.984	0.984	0.988	0.988
252	0.979	0.979	0.984	0.984
264	0.984	0.985	0.989	0.989
273	0.984	0.984	0.988	0.988
293	0.982	0.982	0.986	0.986

[a] Tolman cone angle. [b] Average crystallographic cone angle. [c] Cone angle based on conformation **C**. [d] Solid angle based on conformation **C**.

Table 3. Results of Linear Regression Analysis (R^2) of $\Delta H°$, $\Delta S°$, $E°$, and χ for the Different Steric Parameters, θ, θ_C, θ_C, and Ω_C

	θ^a	$\theta_{av}{}^b$	$\theta_C{}^c$	$\Omega_C{}^d$
$\Delta H°$	0.8145	0.8063	0.9559	0.9979
$\Delta S°$	0.7552	0.5599	0.7862	0.9069
$E°$	0.7475	0.7383	0.9171	0.9853
χ	0.6434	0.6336	0.8366	0.9320

[a] Tolman cone angle. [b] Average crystallographic cone angle. [c] Cone angle based on conformation **C**. [d] Solid angle based on conformation **C**.

We have thus examined four sets of steric data in modeling the isoequilibrium behavior of this system: the Tolman cone angle (θ), the average crystallographic cone angle (θ_{av}), and the cone (θ_C) and solid angles (Ω_C) determined for ligand conformations of type **C**, which we believe to be applicable to this system. To be considered suitable descriptors of the system, three criteria must be met for these sets of steric parameters. First, there should be a good fit of the experimental E/T data at each temperature to the steric parameters.[9] When χ_i is used as the electronic parameter, as previously, all four sets of steric parameters give excellent results (Table 2). Second, the parameters should reproduce the isoequilibrium behavior for the family of phosphite ligands.[9] This requirement is also met by all sets of steric parameters, as shown in Figure 6, where each steric parameter is able to reproduce the experimental isoequilibrium point. Third, the parameters for a single family of ligands, viz., alkyl phosphite ligands, must be linearly related.[9] In this case, clear differences between the sets of steric parameters emerge. The Tolman cone angle (θ) and the average crystallographic cone angle (θ_{av}) are both poorly related to the thermodynamic parameters (Table 3). There is however a very good linear fit between the thermodynamic parameters and the cone angles for conformation **C** (θ_C), while the solid angles based on this conformation (Ω_C) give an excellent fit to the data. Thus, as we have previously suggested,[11] steric parameters for phosphite ligands whose conformations are particular to the system under consideration seem to give the best results.

From these and previous results,[11] it appears that the alkyl phosphites, in particular, are “steric chameleons”, adapting to their environment, and thus are not always amenable to quantitative interpretations. Thus, there is a danger in using parameters for these ligands in quantitative analyses, especially when far-reaching conclusions are drawn from the results of such analyses.[19,29,33−35]

It is to be further noted that the problems of ligand conformational flexibility are not restricted to the phosphite ligands. It has been previously observed that for bulky ligands such as P^tBu_2Me, P^iPr_3, and PCy_3 the steric and electronic effects of ligands can be interrelated and that the shape of a ligand can be more important than the size as measured by cone or solid angles.[36]

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(30) DeSanto, J. T.; Mosbo, J. A.; Storhoff, B. N.; Bock, P. L.; Bloss, R. E. *Inorg. Chem.* **1980**, *19*, 3086−3092.

(31) Chin, M.; Durst, G. L.; Head, S. R.; Bock, P. L.; Mosbo, J. A. *J. Organomet. Chem.* **1994**, *470*, 73−85.

(32) Johnston, P.; Denner, L.; Marais, C. F.; Boeyens, J. C. A.; Coville, N. J. *J. Crystallogr. Spectrosc. Res.* **1988**, *18*, 403−428.

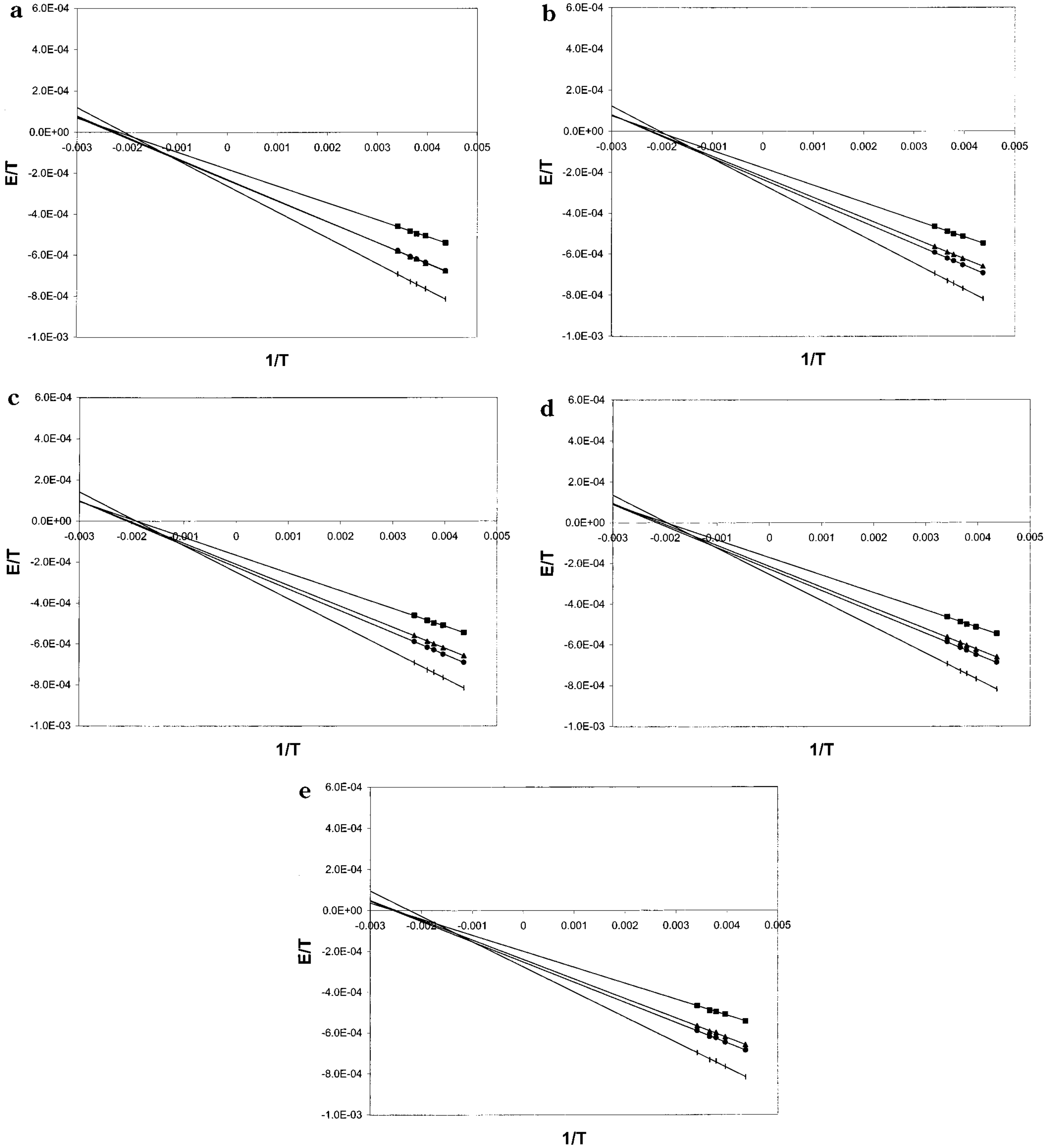

Figure 6. Isoequilibrium behavior of the [Fe(η^5-C_5H_5)(L)(CO)(COMe)]$^+$/[Fe(η^5-C_5H_5)(L)(CO)(COMe)]^0 couple. Steric data for P(OBu)$_3$ is estimated from P(OEt)$_3$ as previously:[39] (a) experimental results;[9] (b) results predicted using the original Tolman cone angles;[9] (c) results predicted using the average crystallographic cone angles; (d) results predicted using the cone angles determined for conformation **C**; (e) results predicted using the solid angles determined for conformation **C**: (■) P(OMe)$_3$, (▲) P(OEt)$_3$, (●) P(OBu)$_3$, (+) (O^{i}Pr)$_3$.

Experimental Section

The information used to calculate cone and solid angles was retrieved from the Cambridge Structural Database, version 5.18. To be considered suitable for use in the calculations, the retrieved ligand needed to have atomic coordinate data available in the CSD and a structure free of errors and be sufficiently precise (crystallographic *R* factor ≤ 0.75). The C−H distances were normalized to 0.96 Å, and a dummy atom X was placed at a distance 2.28 Å from the phosphorus atom along the M−P vector.

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(33) Neubrand, A.; Poë, A. J. *Organometallics* **1995**, *14*, 3249−3258.

(34) Hudson, R. H. E.; Poë, A. J. *Organometallics* **1995**, *14*, 3238−3248.

(35) Farrar, D. H.; Poë, A. J.; Zheng, Y. *J. Am. Chem. Soc.* **1994**, *116*, 6, 6252−6261.

(36) Li, C.; Ogasawara, M.; Nolan, S. P.; Caulton, K. G. *Organometallics* **1996**, *15*, 4900−4903.

For cone angle calculations, an experimental procedure similar to that previously reported was used.[16] The angles P−X−H (α) and P−X−O (β) and the distances XH (x) and XO (y) for every hydrogen and oxygen atom in the phosphite were determined and saved in a summary file. The algorithm discussed above was used to calculate cone angles, using the CPK van der Waals radii for hydrogen and oxygen.

For the solid angle calculations, the coordinates of each ligand fragment only were retrieved from the database. The solid angles were calculated for each fragment by literature procedures[27,28] using the program Steric[37] on a Pentium 450 PC operating on Red Hat Linux. The Bondi data set[38] was used for atomic radii, in accordance with previous work.

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Supporting Information Available: Histograms used for the analysis of the steric data for the $P(OEt)_3$ (Ω) and $P(O^iPr)_3$ (θ and Ω) ligands and equations for the linear regression analyses in Tables 2 and 3. This information is available free of charge via the Internet at http://pubs.acs.org.

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(37) Taverner, B. C. *Steric*, 1.12B; Available on the Internet at http://www.gh.wits.ac.za.

(38) Bondi, A. *J. Phys. Chem*. **1964**, *68*, 441−451.

(39) Rahman, M. M.; Liu, H. Y.; Prock, A.; Giering, W. P. *Organometallics* **1987**, *6*, 650−658.