

# Quantification of steric interactions in phosphine ligands from single crystal X-ray diffraction data. Crystal structures of $(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Mo}(\text{CO})_2(\text{PR}_3)\text{I}$ ( $\text{R}_3 = \text{PhMe}_2, \text{PhEt}_2, \text{Et}_3$ )

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## Abstract

Distorted square pyramidal complexes of molybdenum  $(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Mo}(\text{CO})_2(\text{PR}_3)\text{I}$  ( $\text{R}_3 = \text{PhMe}_2$  (**2a**);  $\text{PhEt}_2$  (**3a**) and  $\text{Et}_3$  (**4a**)) have been synthesized and the structures of the *lateral (cis)* isomers have been determined by X-ray diffraction. The cone ( $\theta$ ) and solid ( $\Omega$ ) angles as well as the angular profiles of the phosphine ligands in the complexes have been computed using the program STERIC. Values for the crystallographic cone and solid angles calculated for **2a**, **3a** and **4a** are  $\theta$  ( $129^\circ$ ,  $135^\circ$  and  $139^\circ$ ) and  $\Omega$  (2.73, 2.99 and 2.93 sr), respectively. A search of the Cambridge Structural Database (CSD) was made for piano stool, 5- and 6-coordinate complexes containing the title phosphine ligands. Results from this study show a wide range of sizes for each of the ligands and even the seemingly simple  $\text{PPhMe}_2$  ligand exhibited a wide range of values for the cone ( $113\text{--}137^\circ$ ) and solid (2.49–3.07 sr) angles. These observations have been rationalized and related to the possible group conformations from the crystallographic data.

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**Keywords:** Piano-stool molybdenum complexes; Phosphine ligands; CSD search; Steric interactions

## 1. Introduction

The need to predict the relative reactivity of organic ligands and metal fragments has been the driving force behind the application of theoretical models and physical probes in chemistry and catalysis. In this respect, the study of steric effects is important since the numerous sizes and conformations of ligands and organic groups play a role in determining the rate and course of chemical transformations [1,2]. In organometallic chemistry the Tolman cone angle ( $\theta$ ) [3], the solid angle ( $\Omega$ ) [4,5] and the Brown  $E_R$  [6] values have been used. The Tolman cone angle in particular, is widely accepted and freely quoted as the standard for gauging steric interactions and often compared with values obtained by techniques using ligand repulsive ener-

gies [6], ab initio calculations [2], molecular mechanics [7] and X-ray crystallographic structures [8]. The Tolman concept [3] has the advantage of being easy to use and understand.

Over the years deviations from  $\theta$  have been recorded [9] and adjustments to the Tolman values have been proposed and documented for flexible ligands capable of assuming multiple conformations such as phosphites and  $\text{PEt}_3$  [10]. It is such perceived shortcomings of  $\theta$  that led to the development of alternative quantification techniques such as  $\Omega$  [11] and the introduction of ligand profiles [12] that takes into account the actual shape and conformation of a ligand. Simply defined  $\theta$  is cylindrically symmetrical and rigid, while  $\Omega$  is best visualized as the area of the “shadow” cast by a ligand on the inside of a unit sphere (Fig. 1).

Furthermore, it has been shown that phosphine ligands show a variable degree of intermeshing especially in

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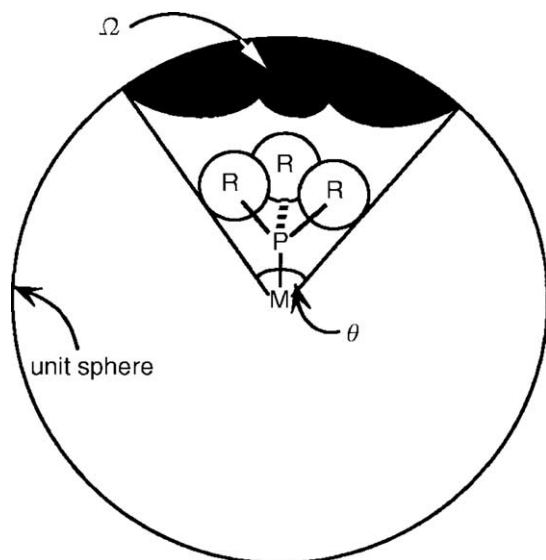


Fig. 1. The relationships between the cone ( $\theta$ ) and the solid ( $\Omega$ ) angles.

crowded environments [13]. The combination of a ligand's ability to assume a variable conformation depending on the space and environment available and its compressibility potential has led to a large spread in the calculated values of  $\theta$  [14–16].

In earlier studies, we [14] and others [15,16] have attempted to evaluate the effects of the ligand environment on a series of ligands. In this manuscript, a continuation on the evaluation of environmental interactions of a metal–ligand set on a series of ligands of different flexibility/compressibility is presented. Here we report a study of the synthesis and characterization by spectroscopic and single crystal X-ray crystallography of some four-legged piano stool complexes of molybdenum containing three commonly encountered tertiary phosphine ligands  $\text{PPhMe}_2$ ,  $\text{PPhEt}_2$ ,  $\text{PEt}_3$  that potentially have a varying degree of flexibility and steric bulk. Also, a CSD search was conducted on these same three ligands. Computations of  $\theta$ ,  $\Omega$ , and the radial profiles of the ligands from the crystallographic data were performed on the three new complexes and the data compared with similar structures reported in the literature as documented in the CSD.

## 2. Results and discussion

The title compounds **2**, **3**, and **4** were obtained in relatively low to moderate yields, due generally to material loss on the long column required for isomer separation and isolation. In general the *lateral* (*cis*) isomers that elute first are obtained in higher yields when compared to the *diagonal* (*trans*) isomers. The pure isomers were initially characterized by IR and NMR spectroscopy, and product composition confirmed by elemental analysis or X-ray crystallography. Detailed spectroscopic and analytical data are presented in the supplementary material (see Table S1).

### 2.1. Molecular structure

The IR stretching frequencies for the CO ligands in these complexes all occur within a narrow band at  $1955(3)$  and  $1870(2) \text{ cm}^{-1}$  and there is no clear distinction between the two isomers with respect to peak positions. A characteristic feature that clearly distinguishes the two isomers is the relative intensity of the two carbonyl absorption bands. In all the *diagonal* isomers the symmetric CO absorption band located at higher wave number is usually weaker in intensity, while the reverse is true for all the *lateral* isomers [17].

The Cp region of the  $^1\text{H}$  NMR spectra readily differentiates and can be used to quantify the two isomers of complexes **2**, **3** and **4**. Thus, the *lat* isomer shows four resonances for the non-equivalent protons and two resonances (further downfield) for each pair of the two equivalent protons in the *diag* isomer. The phosphine ligands exhibited characteristic  $^1\text{H}$  resonances typical of the respective Me, Et or Ph components of the ligands. All the complexes crystallized only as the *lat* isomer. Further characterization of the *diag* isomers was achieved by elemental analysis (see Supplementary Table S1).

### 2.2. Crystallography

The crystal structures of the three *lateral* isomers **2a**, **3a** and **4a** have been determined and the crystallographic data and selected bond lengths and angles are presented in Tables 1 and 2. In addition, Figs. 2–4, respectively, represent the ORTEP diagrams showing the atom numbering scheme of the crystal structures.

The bond lengths and angles are within limits recorded for piano-stool complexes having similar ligand arrangements around molybdenum as listed in Table 4. The crystallographically measured Mo–P and P–C bond lengths for all the three complexes are within very narrow margins of 2.49–2.51 and 1.82–1.83 Å, respectively, hence comparison of data from the steric calculations are not influenced by variations in bond lengths between complexes containing different ligand moieties. The program STERIC utilises atomic coordinates from diffraction data for calculating the steric parameters, hence the calculated variation in  $\theta$  and  $\Omega$  between the three ligands may be observed from the differences in corresponding bond angles, atomic coordinates and equivalent isotropic displacement parameters in **2a**, **3a** and **4a**. In order to make the calculations the program reads the parameters in the form of \*.cif, \*.res or \*.ins files. For **2a**, **3a** and **4a** the calculated values of  $\theta$  ( $129^\circ$ ,  $135^\circ$  and  $139^\circ$ , respectively) and  $\Omega$  (2.73, 2.99 and 2.93 sr, respectively) correspond well with their observed crystallographic configurations (see ORTEP diagrams) in relation to the various conformations available that rationalises the wide spread in  $\theta$  and  $\Omega$  values observed from the CSD data (see later).

Table 1  
Crystal data and structure refinement data for compounds **2a**, **3a** and **4a**

	<b>2a</b>	<b>3a</b>	<b>4a</b>
Identification code	<b>2a</b>	<b>3a</b>	<b>4a</b>
Empirical formula	C <sub>16</sub> H <sub>18</sub> IMoO <sub>2</sub> P	C <sub>18</sub> H <sub>22</sub> IMoO <sub>2</sub> P	C <sub>14</sub> H <sub>22</sub> I MoO <sub>2</sub> P
Formula weight	496.11	524.17	476.13
Temperature (K)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71069
Crystal system, space group	Orthorhombic, <i>P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub></i>	Monoclinic, <i>C2/c</i>	Monoclinic, <i>P2<sub>1</sub>/n</i>
Unit cell dimensions			
<i>a</i> (Å)	7.9752(8)	34.466(4)	7.5828(9)
<i>b</i> (Å)	11.7571(12)	7.5872(10)	16.0537(18)
<i>c</i> (Å)	19.172(2)	15.4454(19)	14.4459(16)
$\beta$ (°)	–	96.501(2)	95.272(2)
Volume (Å <sup>3</sup> )	1797.6(3)	4013.0(9)	1751.1(3)
<i>Z</i> , calculated density (mg/m <sup>3</sup> )	4, 1.833	8, 1.735	4, 1.806
Absorption coefficient (mm <sup>-1</sup> )	2.537	2.278	2.599
<i>F</i> (000)	960	2048	928
Crystal size (mm)	0.42 × 0.38 × 0.17	0.26 × 0.10 × 0.08	0.32 × 0.24 × 0.14
$\theta$ range for data collection (°)	2.03–28.30	2.38–25.00	1.90–28.27
Limiting indices	–10 ≤ <i>h</i> ≤ 10, –14 ≤ <i>k</i> ≤ 15, –23 ≤ <i>l</i> ≤ 25	–40 ≤ <i>h</i> ≤ 40, –9 ≤ <i>k</i> ≤ 9, –18 ≤ <i>l</i> ≤ 12	–10 ≤ <i>h</i> ≤ 10, –21 ≤ <i>k</i> ≤ 11, –19 ≤ <i>l</i> ≤ 19
Reflections collected/unique ( <i>R</i> <sub>int</sub> )	12,579/4447 (0.0185)	10,566/3523 (0.0296)	11,990/4319 (0.0204)
Completeness to $\theta = 25.00$ (%)	99.9	99.8	99.5
Maximum and minimum transmission	0.6723 and 0.4155	0.8388 and 0.5889	0.7123 and 0.4901
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>	Full-matrix least-squares on <i>F</i> <sup>2</sup>	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data/restraints/parameters	4447/0/194	3523/1/208	4319/0/173
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.033	1.027	1.015
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0230, <i>wR</i> <sub>2</sub> = 0.0539	<i>R</i> <sub>1</sub> = 0.0314, <i>wR</i> <sub>2</sub> = 0.0716	<i>R</i> <sub>1</sub> = 0.0322, <i>wR</i> <sub>2</sub> = 0.0679
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0246, <i>wR</i> <sub>2</sub> = 0.0547	<i>R</i> <sub>1</sub> = 0.0464, <i>wR</i> <sub>2</sub> = 0.0764	<i>R</i> <sub>1</sub> = 0.0429, <i>wR</i> <sub>2</sub> = 0.0720
Largest difference in peak and hole (e Å <sup>-3</sup> )	1.032 and –1.136	0.769 and –0.832	1.469 and –1.118

Table 2  
Selected bond lengths (Å) and angles (°) for **2a**, **3a**, and **4a**

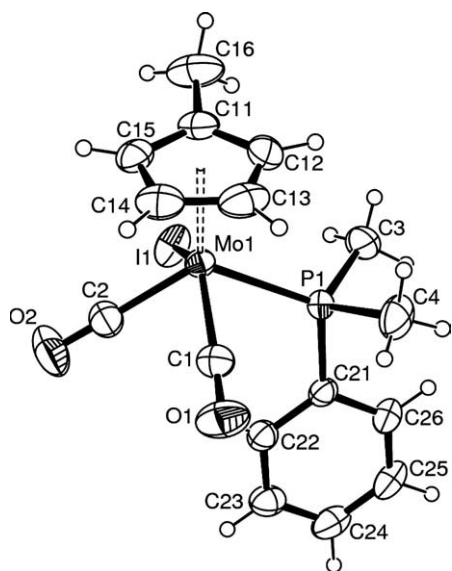
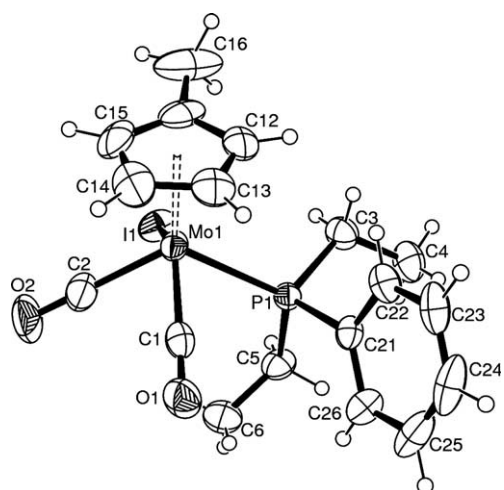
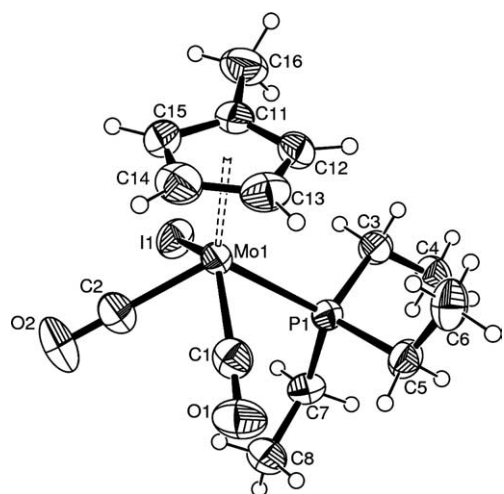
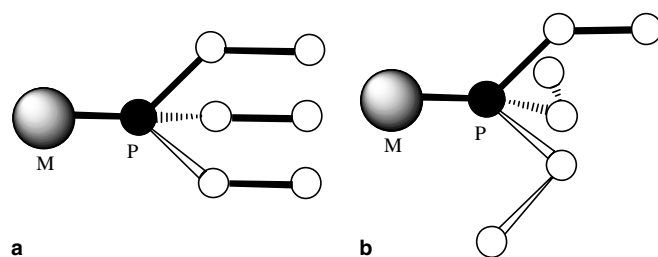
<b>2a</b>		<b>3a</b>		<b>4a</b>	
Mo–P1	2.494(8)	Mo–P1	2.507(1)	Mo–P1	2.511(1)
P1–C3	1.823(4)	P1–C3	1.840(4)	P1–C3	1.832(3)
P1–C4	1.826(4)	P1–C5	1.834(4)	P1–C5	1.835(4)
P1–C21	1.834(3)	P1–C21	1.828(4)	P1–C7	1.831(4)
Mo–P1–C3	117.29(15)	Mo–P1–C3	115.01(14)	Mo–P1–C3	113.37(13)
Mo–P1–C4	111.30(16)	Mo–P1–C5	117.86(14)	Mo–P1–C5	115.79(14)
Mo–P1–C21	119.00(11)	Mo–P1–C21	112.40(13)	Mo–P1–C7	117.73(14)

### 2.3. Quantification of steric parameters

Calculations of the cone ( $\theta_c$ ) and solid ( $\Omega_c$ ) angles for **2a**, **3a**, and **4a** were based on the atomic coordinates obtained from the crystallographic data. The actual ligand conformations observed in the crystal structures were used to correlate ligand steric parameters and radial profiles. Also, it appears that the choice of the crystallographic value of the M–P bond distance is not critical in the analysis. For example, after statistically evaluating thousands of complexes from the CSD, Mingos and Müller [18] have concluded that the distance of 2.28 Å employed for earlier calculations is smaller than the mean crystallographic M–P bond distance for all the complexes studied [2.32(9) Å] (see also Table 4).

The cone angle increases with ligand chain length (cf. PPhMe<sub>2</sub> and PPhEt<sub>2</sub>). The trend (PPhMe<sub>2</sub> < PPhEt<sub>2</sub>

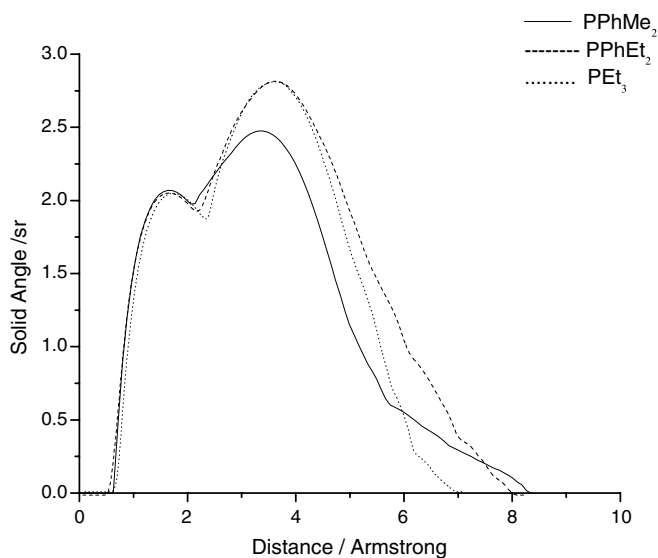
< PEt<sub>3</sub>) in the value of  $\theta_c$  can be accounted for by considering the ligand conformation and the lack of a rigid group (e.g., phenyl) that imposes constraints on free rotation around the P–C bond for the PEt<sub>3</sub> ligand. Ernst and co-workers have previously shown that the conformer (Fig. 5(a)) in which the three arms of the PEt<sub>3</sub> ligand are in a C<sub>3v</sub> conformation (used to compute the Tolman cone angles) is an idealized non-existent specie. This is due to the repulsive van der Waals forces that will build up between adjacent members. They revised the Tolman cone angle values to match the crystallographically observed species (Fig. 5(b)), which is the sterically more demanding bent-back conformer/or variants thereof. Hence a value of  $\theta = 137^\circ$  has been determined for the PEt<sub>3</sub> ligand taking into consideration its true conformation, which is similar to the crystallographically determined data here ( $\theta_c = 139^\circ$ ) [19].

Fig. 2. ORTEP diagram of **2a** showing the atomic numbering scheme.Fig. 3. ORTEP diagram of **3a** showing the atomic numbering scheme.Fig. 4. ORTEP diagram of **4a** showing the atomic numbering scheme.Fig. 5. (a) Idealized extreme conformation adopted by Tolman; (b) crystallographic conformation of the  $\text{PET}_3$  ligand.

Results of calculations on the two steric measures  $\theta_c$  and  $\Omega_c$ , selected for this study are presented in Table 3. The quantification of the variations in solid angle, and the cone angle with distance from the metal, i.e., the solid angle radial profile (Fig. 6), and the cone angle radial profile (Fig. 7), respectively, are presented. The solid angle radial profiles for **2a**, **3a**, and **4a** all show two maxima at ca. 1.7 Å and at 3.6 Å, then drops off to zero beyond 8 Å in the order  $\text{PPhMe}_2 < \text{PET}_3 < \text{PPhEt}_2$ . A similar plot for the cone angle radial profiles has resulted in comparable

Table 3  
Calculation of steric parameters from single crystal and CSD data

Parameter	$\text{PPhMe}_2$	$\text{PPhEt}_2$	$\text{PET}_3$
Crystallographic cone angle $\theta_c$ (°)	129	135	139
Tolman cone angle $\theta$ (°) <sup>a</sup>	122	136	132
Number of data points from CSD	63	17	39
Mean CSD cone angle (°)	122	134	140
Range of CSD cone angle (°)	113–137	126–140	129–156
Crystallographic solid angle $\Omega_c$ (sr)	2.73	2.99	2.93
Mean CSD solid angle $\Omega$ (sr)	2.74	2.97	3.06
Range of CSD solid angle $\Omega$ (sr)	2.49–3.07	2.80–3.11	2.79–3.50

<sup>a</sup> Ref. [3].Fig. 6. Solid angle radial profile of the ligands  $\text{PPhMe}_2$ ,  $\text{PPhEt}_2$  and  $\text{PET}_3$  in **2a**, **3a** and **4a**.

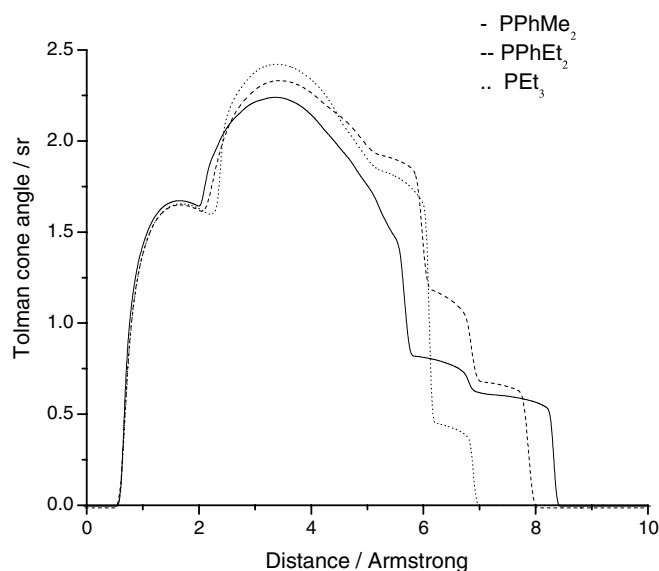


Fig. 7. Tolman cone angle radial profile of the ligands PPhMe<sub>2</sub>, PPhEt<sub>2</sub> and PET<sub>3</sub> in **2a**, **3a** and **4a**.

profiles (very close total curve area) for all the three ligands confirming its insensitivity to conformational changes. It is interesting to note that the observed difference between the calculated solid angles  $\Omega_c$  and the maxima ( $\Omega_{\max}$ ) from the solid angle radial profile further indicates a lack of symmetry in the shapes of the ligands (implying that they cannot be treated as symmetrical cones), since it has been shown that  $\Omega_c = \Omega_{\max}$  for cylindrical cones [11].

In general, the crystallographically calculated steric parameters ( $\Omega_c$  and  $\Theta_c$ ) are larger than Tolman's (by about 7°; researchers have even proposed an addition of 10° to the cone angles) [19a]. Our calculated values are within the range of values published by Ernst and co-workers [19] as a revision to Tolman's original data.

#### 2.4. Statistical analysis of CSD data

The variations in calculated cone  $\Theta_c$  and solid angles  $\Omega_c$  for a range of metal complexes containing the three title ligands are presented in Table 3, and summarized in the form of histograms (see Supplementary material Figs. S1–S3). A large spread in  $\Theta_c$  data from the CSD has already been demonstrated for phosphine [14] and phosphite ligands [15]. For each ligand the high and low values are given in Table 4. It is expected that in addition to the degrees of conformational freedom possible for the ligand, two other factors can play a role in determining  $\Theta_c$  and  $\Omega_c$  and the amount of deviation from the mean. These factors are the central metal (its relative position in the periodic table) and the degree of coordination (congestion) around it [15]. For the same ligand environment, complexes of early transition metals have smaller cone and solid angles compared to those of late transition metals and the cone and solid angle values increase moving across a transition series. The chromium complex **15** illustrates a case of ligand overcrowding (3 CO and 3 PET<sub>3</sub> ligands) around a relatively small metal (Cr) centre, yielding the smallest  $\Theta_c$  and  $\Omega_c$  values for the PET<sub>3</sub> ligand. On the other extreme **16** with a 3-legged piano stool ligand arrangement around a relatively large Ru metal allows for the only PET<sub>3</sub> ligand to move freely thereby generating high  $\Theta_c$  and  $\Omega_c$  angles of 156° and 3.41 sr, respectively. The PET<sub>3</sub> ligand is flexible and has a high degree of conformational freedom (see Fig. 5(a) and (b)).

Interestingly even for the PPhMe<sub>2</sub> ligand which theoretically may at a first approximation seem uni-conformational a large spread in  $\Theta_c$  and  $\Omega_c$  values are observed. It seems that the bulky phenyl group has a relatively variable degree of freedom and is capable of assuming varied conformations depending on the size of the central metal and degree of metal coordination. This becomes evident by

Table 4

The  $\Theta_c$  and  $\Omega_c$  data and references to some piano stool complexes containing the phosphine ligands PPhMe<sub>2</sub>, PPhEt<sub>2</sub> and PET<sub>3</sub> from the CSD highlighted in the text

No.	CSD Refcode	Complex	$\Theta_c$ (°)	$\Omega_c$ (sr)	M–P (Å)	Ref.
	Ligand	PPhMe <sub>2</sub>				
5	LAMXOM	( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> )Mo(Cl) <sub>3</sub> (PPhMe <sub>2</sub> ) <sub>2</sub> · (CH <sub>2</sub> ) <sub>4</sub> O	113	2.49	2.55	[20]
6	TOWSED	( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> )MoCl(PPhMe <sub>2</sub> ) <sub>3</sub>	113	2.49	2.50	[21]
7	JISBIW	( $\eta^5$ -C <sub>5</sub> Me <sub>5</sub> )RhBrPh(PPhMe <sub>2</sub> )	137	3.1	2.27	[22]
8	ROMHIK	( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> )MoH <sub>3</sub> (PPhMe <sub>2</sub> ) <sub>2</sub>	119	2.71	2.41	[23]
9	QEMVIN	( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> )RuCl(PPhMe <sub>2</sub> ) <sub>2</sub>	125	2.92	2.28	[24]
10	JUFCAO	( $\eta^2$ -C <sub>2</sub> H <sub>2</sub> )( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> )Ru <sup>+</sup> (PPhMe <sub>2</sub> ) <sub>2</sub> · BF <sub>4</sub> <sup>-</sup>	132	2.98	2.30	[25]
	Ligand	PPhEt <sub>2</sub>				
11	OCEPRE01	Re(O)Cl <sub>3</sub> (PPhEt <sub>2</sub> ) <sub>2</sub>	126	2.96	2.48	[26]
12	TCEPRH	Rh(Cl) <sub>3</sub> (PPhEt <sub>2</sub> ) <sub>3</sub>	140	3.10	2.32	[27]
13	GILNAQ	( $\eta^5$ -C <sub>5</sub> H <sub>7</sub> )RuCl(PPhEt <sub>2</sub> ) <sub>2</sub>	134	3.09	2.32	[28]
14	HEPRUP	( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> )Mo(CO) <sub>2</sub> I(PPhEt <sub>2</sub> )	135	2.99	2.51	[29]
	Ligand	PET <sub>3</sub>				
15	ETPHCR	Cr(CO) <sub>3</sub> (PET <sub>3</sub> ) <sub>3</sub>	129	2.79	2.43	[30]
16	IKELAL	[ $\eta^6$ -C <sub>6</sub> H <sub>4</sub> (C <sub>4</sub> H <sub>8</sub> OH)]RuCl <sub>2</sub> PET <sub>3</sub>	156	3.41	2.35	[31]
17	ZUWSOZ	( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> )MoCl <sub>2</sub> (PET <sub>3</sub> ) <sub>2</sub>	137	2.89	2.52	[32]
18	YIXDIS	( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> )RuCl(PET <sub>3</sub> ) <sub>2</sub>	144	3.19	2.29	[33]



comparing structures **8**, **9** and **10** (Table 4). The 3 complexes are structurally similar and all are variants of the piano stool arrangement with slight chemical modifications. An analysis of the two extreme points in the data range reveals that the PPhMe<sub>2</sub> ligands in these complexes exist in the conformations depicted as **A** and **B** in Figs. 8 and 9, respectively. In conformer **A** the phenyl group of the PPhMe<sub>2</sub> ligand is on a plane parallel to the plane of the methyl groups while in conformer **B** its plane is perpendicular to the plane of the methyl groups, with the consequence that ligand steric parameters (cone and solid angles) are lowest in the former conformation and highest in the latter. These are the extreme points for which cone angles of 113° and 137° were calculated corresponding to solid angles of 2.55 and 3.07 sr, respectively. Therefore, the unexpected wide spread in the CSD data for the PPhMe<sub>2</sub> ligand is due to the ability of the phenyl group to twist on its plane and also tilt with respect to the methyl groups between the two extreme conformations in order to be accommodated within the lattice space available in a given crystal volume. It is also this flexibility that leads to situations where 2 or more ligands of the same moiety in the same complex can each exist in a unique conformation

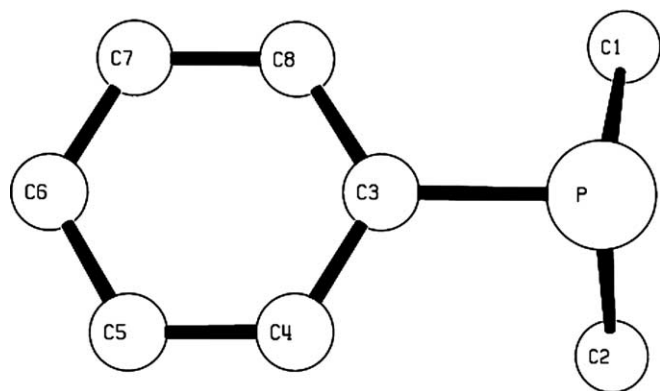


Fig. 8. Conformer **A**: Phenyl group on parallel plane to the plane of methyl groups in the PPhMe<sub>2</sub> ligand. Steric parameters are lowest in this conformation.

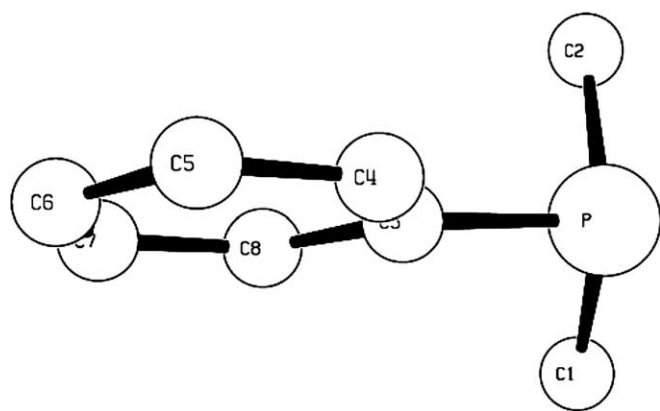


Fig. 9. Conformer **B**: Phenyl group on plane perpendicular to the plane of methyl groups in the PPhMe<sub>2</sub> ligand. Steric parameters are highest in this conformation.

(for e.g., cf. the 2 PPhMe<sub>2</sub> ligands in OCEPRE01 or the 3 PPhMe<sub>2</sub> ligands in TCEPRH) [26,27]. The spread in the CSD data points of complexes bearing the PPhEt<sub>2</sub> ligand is due to a combination of the factors discussed above, i.e., the flexibility of the ethyl groups coupled to the ability of the phenyl group to exist in conformations that tilt towards **A** or **B** depending on the degree of congestion (or freedom) in the crystal lattice.

From Table 4, it seems the substituent on the cyclopentadienyl moiety has little effect in influencing the values of  $\Theta_c$  and  $\Omega_c$  (cf. complex **2a** with **7**, **3a** with **14**, and **4a** with **18**). The data obtained is consistent with the crystallographic configuration of the Cp ring as lying at the apex position of the pseudo seven-coordinate stool and the group has little interaction with the rest of the ligands and hence substitution on the ring has little effect on the steric requirements of the phosphine ligands attached to the central metal. As noted above the position of the metal in the periodic table, has the most influence on the steric requirement. The trend in the crystallographically determined cone and solid angles can be summarized as follows: moving across a period or down a group of the periodic table, ligand species of the same kind increase in the size of calculated  $\Theta_c$  and  $\Omega_c$  [15].

### 3. Conclusion

The X-ray crystal structures of  $(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Mo}(\text{CO})_2\text{-}(\text{PR}_3)\text{I}$  ( $\text{R}_3 = \text{PhMe}_2, \text{PhEt}_2, \text{Et}_3$ ) have been determined and the cone and solid angles for the coordinated phosphines computed from the data. The metal fragment  $(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Mo}(\text{CO})_2\text{I}$  attached to the  $\text{PR}_3$  ligands provides a common 'hole' with which to evaluate the size of the  $\text{PR}_3$  ligands. These values were compared with data obtained from a CSD search.

The CSD search revealed that the three ligands each gave a wide range of steric values ( $\Theta_c$  and  $\Omega_c$ ) with two cone angles larger (PPhMe<sub>2</sub>, PEt<sub>3</sub>) and one similar (PPhEt<sub>2</sub>) to the original Tolman values. All three values are *typical* average values when compared to the average CSD values computed. This suggests that while the PPhMe<sub>2</sub> and PEt<sub>3</sub> ligands show expected (larger) values than the Tolman values (due to the method of measurement) the PPhEt<sub>2</sub> ligand *fortuitously* shows the same value as measured by Tolman. This arises from the ligand conformations measured (one Et group bent towards the metal, and the phenyl ring in the plane of an Et C–C bond). The implication is that a simple correction to modify the Tolman values to increase the ligand size (e.g., cone angle) to more correctly represent the actual ligand conformation is not possible and that corrections must be done on a ligand to ligand basis.

### 4. Experimental

All operations involving the handling of air sensitive materials were carried out under dry nitrogen using

standard Schlenk techniques or a glove box. Solvents were dried by conventional methods and distilled under nitrogen prior to use.  $\text{Mo}(\text{CO})_6$  and the three phosphines  $\text{PR}_3$  ( $\text{R}_3 = \text{Me}_2\text{Ph}$ ,  $\text{Et}_2\text{Ph}$ ,  $\text{Et}_3$ ) were used as supplied (Strem Chemicals). Trimethylamine *N*-oxide dihydrate (Aldrich) was used as received. Solution IR spectra were recorded ( $\text{CH}_2\text{Cl}_2$ ) on a Bruker Vector FTIR spectrometer in KBr cells.  $^1\text{H}$  NMR spectra were recorded ( $\text{CDCl}_3$ ) at 300 MHz on a Bruker AC 300 spectrometer. Elemental analyses were conducted at the Institute for Soil, Climate and Water, CSIR, Pretoria.

Crystallographic data were collected on a Bruker SMART 1K CCD area detector diffractometer with graphite monochromated  $\text{Mo K}\alpha$  radiation (50 kV, 30 mA). The collection method involved  $\omega$ -scans of width  $0.3^\circ$ . Numerical data pertaining to the experimental measurement and details of the structure analyses are given in Table 1. Data reduction was carried out using the program SAINT+ [34] and data were corrected for absorption using the program SADABS [34]. The structures were solved by standard Patterson procedures and refined by least-squares methods based on  $F^2$ . The SHELX-97 [35] suite of programs as incorporated into WINGX [36] were used for all crystallographic computations. In the final stages of refinement hydrogen atoms were geometrically fixed and allowed to ride on the respective parent atoms.

#### 4.1. Synthesis of $(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Mo}(\text{CO})_3\text{I}$ (**1**)

The starting material **1** was prepared by the adaptation of a standard procedure [37]. A dimethoxyethane suspension of  $\text{Mo}(\text{CO})_6$  and  $\text{C}_5\text{H}_5\text{Me}$  was refluxed for 24 h, cooled to room temperature and iodine was added to the solution with continued stirring. After 3 h the solvent was removed in vacuo. Extraction with hexane afforded the title compound as red needles. IR  $\nu_{\text{CO}}$  ( $\text{cm}^{-1}$ ): 2039 (s), 1961 (s).  $^1\text{H}$  NMR (ppm): 5.22–5.24 (t, 2H, CpMe), 5.11–5.14 (t, 2H, CpMe), 2.12 (s, 3H, CpMe).

#### 4.2. Synthesis of $(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Mo}(\text{CO})_2(\text{PR}_3)\text{I}$ ( $\text{R}_3 = \text{PhMe}_2, \text{PhEt}_2, \text{Et}_3$ )

All the compounds were prepared via a common route. Typically the reaction of **1** with a 5–10-fold excess of ligand  $\text{PPhMe}_2$  and trimethylamine *N*-oxide in dichloromethane at room temperature afforded **2** as a mixture of the *lat* (**a**, *cis*) and *diag* (**b**, *trans*) isomers. Isomer separation was achieved by dissolving the crude material in  $\text{CH}_2\text{Cl}_2$  followed by mixing with a small quantity of silica gel. The yellow powder remaining after solvent removal was chromatographed on a column of silica ( $2 \times 60$  cm), eluting with 1:1 toluene/hexane mix solvent.

#### 4.3. CSD data retrieval and steric parameter calculations

The information utilized for the statistical analysis was retrieved from the January 2004 updated edition of the

CSD using the search and retrieval program CONQUEST 1.6, Version 5.25 [38]. A search string for any single-bonded transition metal to tertiary phosphine ligands  $\text{PR}_3$  ( $\text{R}_3 = \text{Me}_2\text{Ph}$ ,  $\text{Et}_2\text{Ph}$ ,  $\text{Et}_3$ ) was used. The CSD program Mercury was used to manually screen the entries based on the following criteria: (a) 3D atomic coordinates of the ligand must include all the hydrogens and be of sufficient quality ( $R \leq 0.07$ ); (b) ligand arrangement around the metal should be piano stool or 5- & 6-coordinated non-cyclopentadienyl based ligand systems, hence, metal clusters, bimetallic compounds, solvated and ionic compounds were excluded. The coordinates of all compounds satisfying the above conditions were saved for input to the in-house program STERIC which performs steric parameter calculations running on a Pentium 450 PC operating on a RED HAT LINUX program as earlier described [9,14]. The program was based on the following covalent and van der Waals radii ( $\text{\AA}$ ): Mo (1.30, 1.30); P (1.10, 1.85); C (0.77, 1.70); and H (0.37, 1.20). Mean crystallographic bond lengths ( $\text{\AA}$ ) from the crystal structures are: Mo–P (2.49,  $\text{PPhMe}_2$  ligand); Mo–P (2.51,  $\text{PPhEt}_2$  and  $\text{PEt}_3$  ligands); P–C (1.83); C–H (0.96, alkyl); C–H (0.93, aromatic).

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#### Appendix A. Supplementary data

Spectroscopic and elemental analysis data (Table S1) for the title complexes and histograms (Figs. S1–S3) showing the spread in data from the CSD are available. Also, crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 281979, 281980 and 281981 for compounds **2a**, **3a**, and **4a**, respectively. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ UK; fax: +44 1223 336 033, e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2005.10.032](https://doi.org/10.1016/j.jorganchem.2005.10.032).

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