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SUBSTITUTED CYCLOPENTADIENYL LIGANDS—10. INTRAMOLECULAR STERIC INTERACTIONS IN $[(\eta^5\text{-}C_5H_3(SiMe_3)_2)Mo(CO)_2(L)I]$

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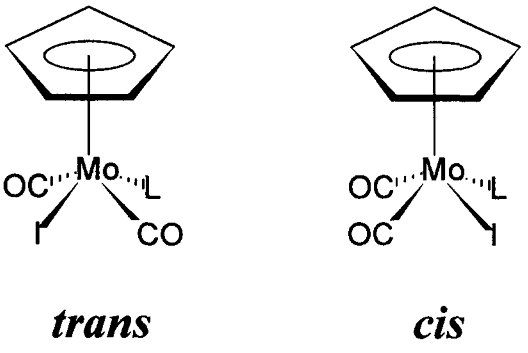
Abstract—Reaction of $C_5H_4(SiMe_3)_2$ with $Mo(CO)_6$ yielded $[(\eta^5\text{-}C_5H_3(SiMe_3)_2)Mo(CO)_3]_2$, which on addition of iodine gave $[(\eta^5\text{-}C_5H_3(SiMe_3)_2)Mo(CO)_3I]$. Carbonyl displacement by a range of ligands : [L = $P(OMe)_3$, $P(OPr^i)_3$, $P(O\text{-}o\text{-tol})_3$, PMe_3, PMe_2Ph, $PMePh_2$, PPh_3, $P(m\text{-tol})_3$] gave the new complexes $[(\eta^5\text{-}C_5H_3(SiMe_3)_2)Mo(CO)_2(L)I]$. For all L the *trans* isomer was the dominant, if not exclusive, isomer formed in the reaction. An NOE spectral analysis of $[(\eta^5\text{-}C_5H_3(SiMe_3)_2)Mo(CO)_2(L)I]$ [L = PMe_2Ph, $P(OMe)_3$] revealed that the L group resided on the sterically uncongested side of the cyclopentadienyl ligand and that the ligand did not access the congested side of the molecule. Quantification of this phenomenon [L = $P(OMe)_3$] was achieved by means of the vertex angle of overlap methodology. This methodology revealed a steric preference with the *trans* isomer (less congestion of CO than I with an $SiMe_3$ group) being the more stable isomer for L = $P(OMe)_3$. Copyright © 1996 Elsevier Science Ltd

Cyclopentadienyl complexes of molybdenum, $[(\eta^5\text{-}C_5H_5)Mo(CO)_2(L)R]$, are known to have seven-coordinate geometry with the cyclopentadienyl ligand occupying three coordination sites and the remaining four ligands pointing towards the corners of a square.[1] This arrangement gives rise to *cis* and *trans* isomers (Fig. 1), first detected by King for $[(\eta^5\text{-}C_5H_5)Mo(CO)_2(P(NMe_2)_3)I]$.[2] Later, solid-state structures of *trans*-$[(\eta^5\text{-}C_5H_5)Mo(CO)_2(PR_3)COR]$[3] and *cis*-$[(\eta^5\text{-}C_5H_5)Mo(CO)_2(PBu^n_3)I]$ were reported, which confirmed the geometries (Fig. 1).[4] Other molybdenum complexes of the type $[(\eta^5\text{-}C_5H_{5\text{-}}R_n)Mo(CO)_2LR']$ have since been synthesized, typically with L = group 15 donor ligands,[5] isonitrile[6,7] R = H, Me and R′ = hydride, alkyl or halogen.



trans *cis*

Fig. 1. *Cis* and *trans* isomers of $[(\eta^5\text{-}C_5H_5)Mo(CO)_2LI]$.

Faller and Anderson were the first to investigate the details of the *cis*/*trans* isomerization process in $[(\eta^5\text{-}C_5H_5)Mo(CO)_2(L)R]$ (L = phosphine or phosphite; R = H, D, CH_3, CH_2Ph, CH_2OCH_3, $CH_2S\text{-}CH_3Cl$, Br or I) complexes[1] and they showed that

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an intramolecular-non-dissociative process was operational. The energy differences between the two isomers were found to be small and the isomer equilibrium constant, $K = [cis]/[trans]$, dependent on solvent, L and R.[1] The *trends* in $\Delta G^{\ddagger}$ and $\Delta H^{\ddagger}$ were not found to be solvent dependent, suggesting the *cis/trans* ratio was influenced by *steric effects.* These workers noted qualitatively that a greater number of unfavourable interactions exist between L and R groups in the *cis* isomer than in the *trans* isomer and when the steric interactions became severe stability of the *trans* isomer became more favourable.[1]

Numerous synthetic strategies to achieve preferential synthesis of either the *cis* or *trans* isomers have been reported[8] and separation of the *cis* and *trans* isomers has been achieved by column chromatography.[9] Re-equilibration of isomers can be accomplished by refluxing the isomers in solvents. Interestingly, *cis/trans* isomerization of $[(\eta^5\text{-}C_5H_5)Mo(CO)_2(PBu^n)_3I]$ was achieved in the solid state.[3a]

A study of the influence of the R group on *cis/trans* isomer ratios in $[(\eta^5\text{-}C_5H_4R)Mo(CO)_2(L)I]$ (R = Me, Bu^t; L = phosphine, phosphite, isonitrile), has also been reported.[10] The authors found that an increase in the size of L produced a greater amount of *cis* isomer for both R = Me and Bu^t, in contrast to findings for complexes with R = H.[1] The isomer preference was rationalized in terms of steric effects associated with the substituent on the cyclopentadienyl ring, which were minimized when the L and I ligands were positioned away from the R group.

In this publication the influence of the $SiMe_3$ ring substituents in $[(\eta^5\text{-}C_5H_3(SiMe_3)_2)Mo(CO)_2(L)I]$ (L = phosphine, phosphite) complexes of the *cis/trans* isomer ratio has been studied. In particular an attempt to rationalize the isomer preference by quantification of the steric interactions of the ring system with the ligands attached to Mo in the *cis* and *trans* isomers, using the vertex angle of overlap methodology,[11] has been undertaken.

EXPERIMENTAL

All phosphine, phosphite and isonitrile ligands were obtained from available sources and used without further purification. Bis(trimethylsilyl) cyclopentadiene was synthesized from trimethylsilycyclopentadiene by literature procedures[12] and tris(trimethylsilyl)cyclopentadiene was obtained as a gift (Professor J. Okuda and Dr K. du Plooy, University of Marsburg, Germany). All operations were performed under nitrogen in a well-ventilated fume cupboard, using freshly distilled, dry, deoxygenated solvents. Column chromatography was performed using silica or activity V alumina with ethyl acetate/hexane as eluent, unless otherwise stated. All column separations were performed under nitrogen, with the required fractions being collected under nitrogen. IR spectra were recorded on a Bruker IFS 185 FTIR spectrometer in benzene. NMR spectra were recorded on a Bruker AC-200 spectrometer in C_6D_6 solutions.

Synthesis of $[(\eta^5\text{-}C_5H_3(SiMe_3)_2)Mo(CO)_3]_2$ *and* $[(\eta^5\text{-}C_5H_3(SiMe_3)_2)Mo(CO)_3I]$

(a) Molybdenum hexacarbonyl (11.34 g, 43.0 mmol) was added to a deoxygenated solution of diglyme : hexane (1 : 3, 100 cm^3) and heated under reflux, during which time the $Mo(CO)_6$ dissolved. Bis(trimethylsilyl)cyclopentadiene (13.02 g, 61.9 mmol) was added and the mixture heated (reflux) under nitrogen for 24 h. During this time the colour of the solution changed from light brown to bright red. The hexane was removed on a rotary evaporator and the product crystallised at *ca* −10°C. The dark red crystals, washed with pentane, yielded $[(\eta^5\text{-}C_5H_3(SiMe_3)_2)Mo(CO)_3]_2$. The dimer was dissolved in deoxygenated dichloromethane. A solution of iodine (12.64 g, 49.8 mmol) in dichloromethane was added and the cleavage of the dimer monitored by the disappearance of the band at 1965 cm^{-1} in the IR spectrum. On completion of the reaction the mixture was poured into an aqueous solution of sodium thiosulfate, the organic layer removed, the aqueous layer washed with CH_2Cl_2 and the combined organic layers dried ($MgSO_4$) and solvent removed *in vacuo.* This yielded a dark red powder identified as $[(\eta^5\text{-}C_5H_3(SiMe_3)_2)Mo(CO)_3I]$ by NMR spectroscopy (Table 1).

(b) Molybdenum hexacarbonyl (1.40 g, 5.32 mmol) was placed in deoxygenated hexane: diglyme (50 cm^3, 3 : 1), tris(trimethylsilyl) cyclopentadiene (1.02 g, 5.32 mmol) added and the reaction mixture heated under reflux. The reaction was monitored by TLC (hexane) and indicated the presence of only one new product. The solution was cooled and some solid residue separated by filtration through celite. The solvents were removed from the filtrate *in vacuo* to yield $[(\eta^5\text{-}C_5H_3(SiMe_3)_2)Mo(CO)_3]_2$, which was used without further purification. The molybdenum dimer was dissolved in CH_2Cl_2 (15 cm^3) and a dilute solution of iodine (1.25 mg, 5 mmol) in CH_2Cl_2 (100 cm^3) was added dropwise. The progress of the reaction was monitored by IR spectroscopy (by the disappearance of the peak at 1965 cm^{-1}). After completion of the reaction, the excess iodine was destroyed by reac-

Table 1. ^{1}H NMR data for *trans*-[(η^5-$C_5H_4SiMe_3$)$_2$Mo(CO)$_2$(L)I] complexes[a]

L	H(2)[b]	H(4),H(5)[c]	Si(CH$_3$)$_3$	L[d]	$J^e_{H(2),H(4)}$	$J^e_{P-H(2)}$	$J^e_{L,P}$
P(OMe)$_3$	5.84	4.72	0.37	3.26 (Me)	1.7	5.3	11.5
PMe$_3$	5.78	4.19	0.28	0.85 (Me)	1.7	6.1	9.3
PMe$_2$Ph	5.71	3.93	0.29	1.43 (Me)	1.7	6.2	9.0
P(OPr^i)$_3$	5.80	4.81	0.40	1.10 (CH$_3$) 4.61–4.39 (CH)	1.7	5.2	6.1
PPh$_2$Me	5.83	3.94			1.7	5.7	
P(O-*o*-tol)[f]$_3$	5.87	5.04	0.27	2.10 (Me)	1.7	5.7	
PPh$_3$	5.90	4.16	0.38		1.7	5.0	
P(*m*-tol)$_3$	5.87	4.25	0.39	1.99 (Me)	1.7	5.0	
CO	5.17[g]	5.01[h]	0.10				

[a] Recorded in C_6D_6 solution at 22°C, δ in ppm relative to TMS, J in Hz.
[b] Triplet.
[c] Doublet of doublets.
[d] Aromatic resonances not listed.
[e] Coupling constants, J, measured in Hz.
[f] *Ortho* protons 7.38, 7.35 ppm.
[g] Triplet.
[h] Doublet ($J_{H,H}$ = 1.7 Hz).

Table 2. IR and steric data for the [(η^5-C_5H_3(SiMe$_3$)$_2$)Mo(CO)$_2$(L)I] complexes[a]

L	ν_1 (cm^{-1})	ν_2 (cm^{-1})	Ω^b_s	θ (°)[c]
CO	2036.7	1955.7		
P(OMe)$_3$	1973.1	1897.8	0.225	107
PMe$_3$	1957	1879	0.267	118
PMe$_2$Ph			0.274	122
P(OPr^i)$_3$	1967.3	1888.2	0.319	130
PPh$_2$Me	1957.6	1882.4	0.266	136
P(O-*o*-tol)$_3$	1982.7	1913.3	0.357	141
PPh$_3$	1961.5	1886.3	0.286	145
P(*m*-tol)$_3$	1959.6	1884.4	0.331	148

[a] Recorded in C_6D_6.
[b] Solid angle, no units, see reference 16.
[c] Tolman cone angle, reference 15.

tion with aqueous sodium thiosulfate (2.0 g in 20 cm^3 H_2O). The organic layer was extracted with CH_2Cl_2 and the combined organic extracts dried ($MgSO_4$) and the solvent removed *in vacuo*. The product was purified by column chromatography (activity V alumina, 15% H_2O; hexane eluent). The solvent was removed *in vacuo* to yield [(η^5-C_5H_3(SiMe$_3$)$_2$)Mo(CO)$_3$I] (450 g, 0.901 mmol, 16.9%).

Synthesis of [(η^5-C_5H_3(SiMe$_3$)$_2$)Mo(CO)$_2$(L)I], L = PMe$_3$, P(OMe)$_3$, PMe$_2$Ph, P(OPr^i)$_3$, PPh$_2$Me, PPh$_3$, P(O-*o*-tol)$_3$ *and* P(*m*-tol)$_3$

The complex [(η^5-C_5H_3(SiMe$_3$)$_2$)Mo(CO)$_3$I] (98 mg, 0.221 mmol) was dissolved in deoxygenated benzene (10 cm^3). Ligand, L (0.240 mmol), and [(η^5-C_5H_5)Fe(CO)$_2$]$_2$ catalyst (10 mg) were added and the mixture heated under reflux. On completion of the reaction (as monitored by IR spectroscopy by the disappearance of the peak at 2040 cm^{-1}), the solvent was cooled and the reaction mixture filtered through celite. The benzene was removed *in vacuo* and the new compounds were purified by column chromatography (activity V alumina, ethyl acetate : hexane 1 : 4 eluent). The solvents were removed and the products [L = PMe$_3$, P(OMe)$_3$ and PPh$_3$] recrystallized from CH_2Cl_2 to yield the desired complexes (19–60%). This solution was heated under reflux for 4 h to equilibrate the isomers. The complexes were characterized by IR and NMR spectroscopy (Tables 1 and 2).

The vertex angle of overlap methodology

Consider two overlapping atoms, A and B, with centres situated at M and N (Fig. 2). The semi-vertex angle of atom A ($\angle$MOD) is given by α, the semi-vertex angle of atom B ($\angle$CON) by β and $\angle$MON by χ. The vertex angle of overlap is thus

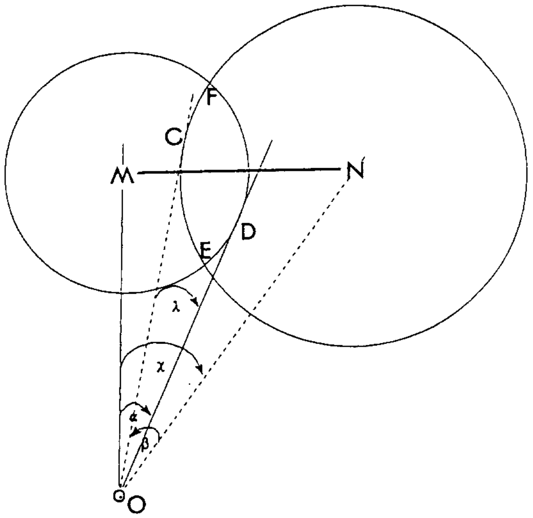

Fig. 2. Determination of the vertex angle of overlap for two spheres, A and B centred at M and N, respectively, attached to a common apex, O. λ, in radians, is a measure of the overlap of the spheres.

given by $\lambda = (\alpha+\beta)\text{-}\chi$. This linear angle ($\lambda$) gives a measure of overlap between the two atoms A and B. The overlap that is measured corresponds to $\angle$COD and relates to a maximum overlap as determined from apex O. The overlap does however vary from zero at E through a maximum and finally back to zero at F. This variation of overlap with distance from the apex provides a unique measure of atom overlap.

The algorithm to achieve measurement of λ has previously been developed for measuring total solid angles as a function of distance (radial profiles) and is readily applied to this measurement.[13] The plot of the variation of the vertex angle of overlap with distance is called the vertex angle profile.

Vertex angle of overlap radial profile calculations for $[(\eta^5\text{-}C_5H_3(SiMe_3)_2)Mo(CO)_2P(OMe_3)I]$

Radial profiles of the vertex angle of overlap (λ) were calculated for the molecule $[(\eta^5\text{-}C_5H_3(SiMe_3)_2)Mo(CO)_2P(OMe_3)I]$, which was based on the crystal structure of *trans*-$(\eta^5\text{-}C_5H_5)Mo(CO)_2P(OMe_3)I]$.[14] The trimethysilyl substituents of the cyclopentadienyl ring were added using average bond lengths, bond angles and torsion angles obtained from 37 crystal structures in the Cambridge Database (version 5.9 containing 140,268 structures), which contained the $\eta^5\text{-}C_5H_3(SiMe_3)_2$ fragment (65 fragments). The *cis* isomer was generated by interchanging the positions of the iodide and one carbonyl ligand. It was assumed that bond lengths, bond angles and torsion angles around the molybdenum atom would be unaffected by this change. It was further assumed that the $P(OMe)_3$ ligand conformation remained constant throughout the calculation.

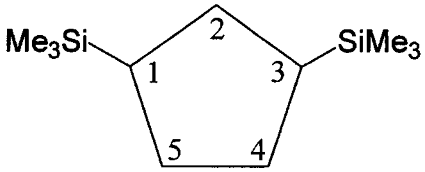

Fig. 3. Numbering scheme used for $[(\eta^5\text{-}C_5H_3(SiMe_3)_2)Mo(CO)_2LI]$. The ligand set (CO,L,I) is not shown.

Radial profiles of λ for both isomers of $[(\eta^5\text{-}C_5H_3(SiMe_3)_2)Mo(CO)_2P(OMe_3)I]$ were determined for the C(2)—Cen—Mo—P torsion angle set at 0, 90 and 180° (Figs 3 and 4). Only *non-bonded* overlap *between* the ligands was considered (i.e. overlap *within* ligands was subtracted out).

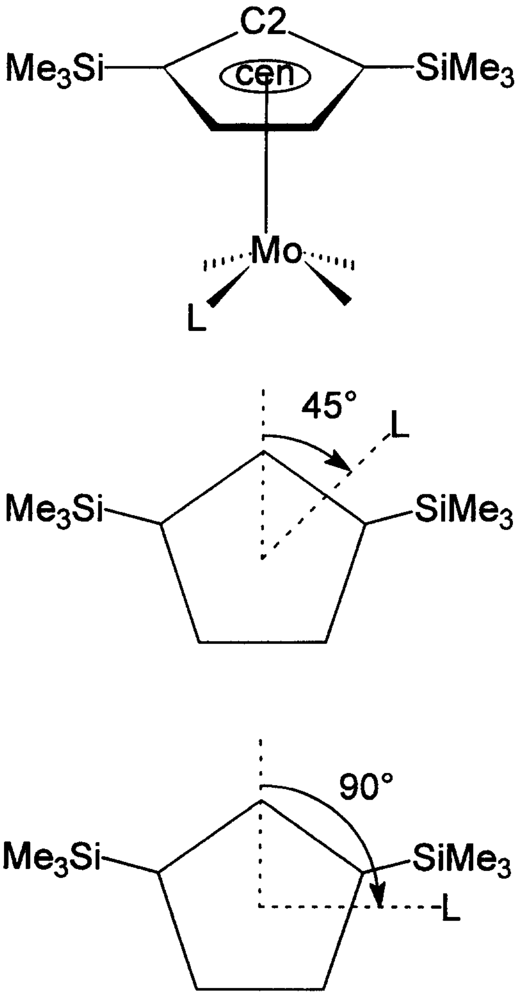

Fig. 4. (a) Numbering system used in the determination of the torsion angles in the new complexes. (b) Newman projection of conformer with L set at 45°C. (c) Newman projection of conformer with L set at 90°C.

Other sets of profiles were generated for the cases where the O(2)—Cen—Mo—P torsion angle was 45, 135, 225 and 315°.

RESULTS AND DISCUSSION

Synthesis

Reaction of bis(trimethylsilyl)cyclopentadiene[12] with molybdenum hexacarbonyl afforded $[(\eta^5\text{-}C_5H_3(SiMe_3)_2)Mo(CO)_3]_2$ smoothly. An alternative route to the synthesis of $[(\eta^5\text{-}C_5H_3(SiMe_3)_2)Mo(CO)_3]_2$ was achieved by heating tris(trimethylsilyl)cyclopentadiene with $Mo(CO)_6$. This gave the desired disubstituted ring product via loss of one trimethylsilyl substituent from the cyclopentadienyl ring slowly and free from contaminants.

Cleavage of the disilyl dimer with iodine gave $[(\eta^5\text{-}C_5H_3(SiMe_3)_2)Mo(CO)_3I]$. Substitution of a carbonyl ligand in $[(\eta^5\text{-}C_5H_3(SiMe_3)_2)Mo(CO)_3I]$ by a phosphine or phosphite proved facile in refluxing benzene in the presence of the $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ catalyst.[7,10]

^{1}H *NMR spectral characterization*

In all cases the ^{1}H NMR spectra of the new purified complexes showed the correct ratio of ligand (L) to cyclopentadienyl proton resonances. ^{1}H NMR and IR spectroscopies were used to determine the isomer composition of the $[(\eta^5\text{-}C_5H_3(SiMe_3)_2)Mo(CO)_2(L)I]$ complexes. The *trans* isomer is associated with a 1 : 2 intensity ratio of cyclopentadienyl proton resonances corresponding to protons H(2) and H(4)/H(5), respectively[12a] (Fig. 3 for numbering scheme). By comparison, the *cis* isomer is expected to give a 1 : 1 : 1 ratio of cyclopentadienyl proton resonances. The IR spectra of the dicarbonyl complexes show two ν(CO) resonances with intensity ratio consistent with a *trans* isomer.[15] Spectral data in Table 2 for the new $[(\eta^5\text{-}C_5H_3(SiMe_3)_2)Mo(CO)_2(L)I]$ complexes are found in Tables 1 (^{1}H NMR) and 2 (IR).

Rotational behaviour of the ligand set. We have previously used NOE spectroscopy to obtain information on the rotational behaviour of the ligand set (CO, L, I) relative to the cyclopentadienyl ring and the ring substituent in related cyclopentadienyl complexes.[16] An NOE spectral investigation was performed on the complex with L = $P(OMe)_3$ and the pertinent spectra are shown in Fig. 5. Irradiation of the methyl resonance of $P(OMe)_3$ [P, Fig. 5(b)] clearly reveals that the phosphite is found in the region of space close to protons H(4) and H(5) [Fig. 6: L = $P(OMe)_3$]. Similar results are found on irradiation of H(4)/H(5) [Fig. 5(c)]. No growth of the $P(OMe)_3$ resonance occurs on irradiation of H(2) (not shown). Similar results were observed for L = PMe_2Ph and are expected for all the other L groups with $\theta > \theta_{P(OMe)_3}$. The results are consistent with data obtained from a study of $[(\eta^5\text{-}C_5H_3(SiMe_3)_2)Fe(CO)(L)I]$ complexes.[12a]

As mentioned above, the new complexes were synthesized as the *trans* isomers, which could readily be identified by spectroscopic means. Since all the new complexes were purified by column chromatography, the possibility of one isomer decomposing preferentially on the column or isomerizing to the other isomer was considered. NMR spectra were thus recorded both before and after purification and no change in the isomer ratios was detected during the purification steps. Attempted equilibration of column isolated and *crystallized* materials was undertaken (refluxing benzene, 4 h) with no success. For example, refluxing the *trans* complex with L = PPh_3 in benzene in an NMR tube to achieve isomerization revealed partial decomposition to $[(\eta^5\text{-}C_5H_5(SiMe_3)_2)Mo(CO)_3I]$ and no *cis* isomer formation (benzene, 4 h). It is to be noted that NMR spectra for the complexes with L = PMe_3 and PMe_2Ph suggest small amounts of a *cis* isomer are present in solution, but no attempt was made to isolate and study these materials.

In previous work we have found that the differences between the positions of proton cyclopentadienyl resonances can give information about steric effects associated with the cyclopentadienyl ring substituent and the ligand set. A plot of $\Delta[H(2)-H(4,5)]$ versus θ[13] (Fig. 7; or Ω[17], not shown) indicates that steric effects associated with L do not affect the resonance separation.

Quantification of the steric interaction. Recently we described how the vertex angle of overlap could be used to quantify the overlap between spheres (atoms) attached to a common apex (metal).[11] This is described in the experimental section (see also Fig. 2). An attempt was made to rationalize the preference for the *trans* isomer of $[(\eta^5\text{-}C_5H_3(SiMe_3)_2)Mo(CO)_2(L)I]$ with L close to positions H(4) and H(5) using the vertex angle of overlap approach. The complex with L = $P(OMe)_3$, a small ligand, was chosen for study. In the steric analysis the conformer of $P(OMe_3)$, taken from the X-ray crystal structure of *trans*-$[(\eta^5\text{-}C_5H_5)Mo(CO)_2[(P(OMe_3)I]$, was used.[14] The steric interaction of a range of conformers for both the *cis* and *trans* isomers was then determined.

In the initial stages of the evaluation a single ligand L [L = CO,I,$P(OMe)_3$] was rotated around 360° relative to a "η^5-$(C_5H_3(SiMe_3)_2Mo)$" moiety

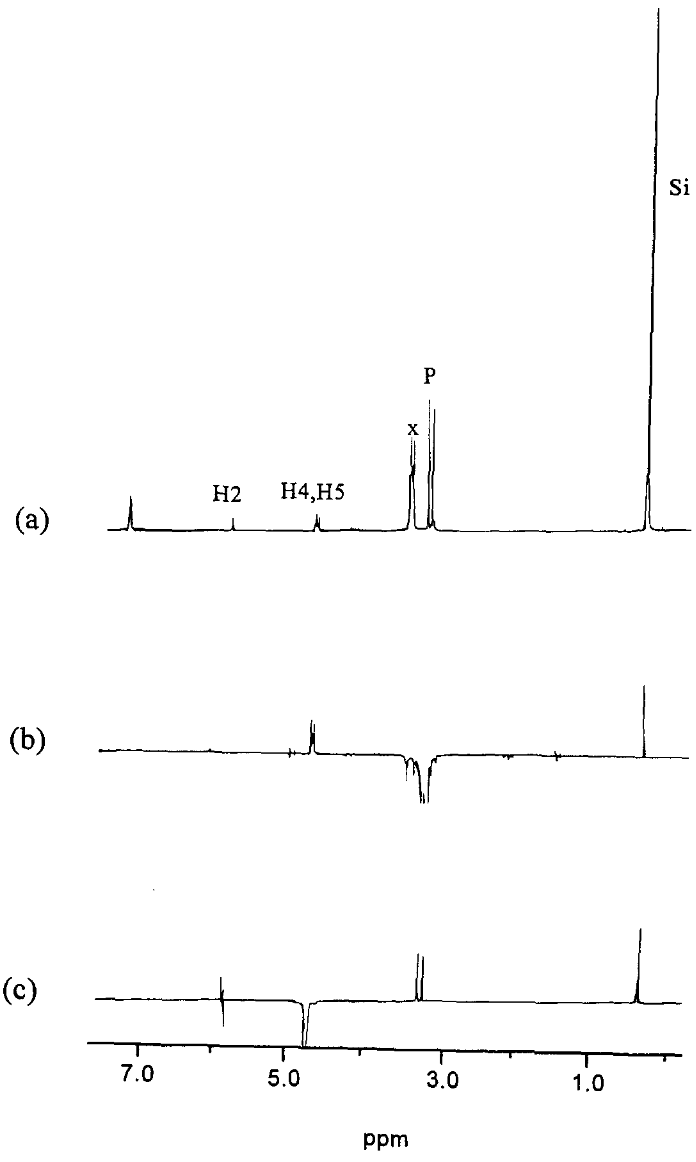

Fig. 5. NOE spectra for *trans*-[(η^5-$C_5H_3(SiMe_3)_2$)Mo$(CO)_2$P$(OMe)_3$I]: (a) Spectrum prior to irradiation where H(2), H(4) and H(5) correspond to the ring protons shown in Fig. 2, P corresponds to the P(OMe_3) protons and Si corresponds to the $SiMe_3$ protons (X = free ligand). (b) Irradiation of P$(OMe)_3$ protons. (c) Irradiation of H(4) and H(5).

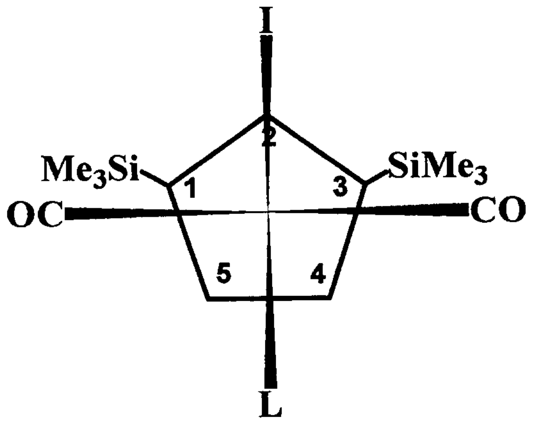

Fig. 6. Preferred conformer of *trans*-[(η^5-$C_5H_3(SiMe_3)_2$)$Mo(CO)_2(L)I$] as determined by NOE spectroscopy. The figure shows the Newman projection of the molecule down the Mo-ring centroid axis. The CO, L, I ligand set resides below the ring plane.

to obtain the maximum λ as a function of rotation angle. Figure 8 reveals that, as the ligands pass under the $SiMe_3$ group, steric interaction (overlap) is maximized. Furthermore, the degree (or size) of overlap varies with L; $P(OMe)_3 > I > CO$.[17a] The asymmetry in the curve for L = $P(OMe)_3$ reflects the asymmetry in the conformer used for this ligand. Finally, the rotational angle at which maximum overlap occurs is dependent on the ligand used.

In the actual *cis* and *trans* isomers steric interaction will involve all four ligands interacting with that ring and the analysis of this situation is described below.

Trans *isomer*. In [(η^5-C_5H_5)$Mo(CO)_2(L)I$] the ligands were arranged such that the angle C(2)—cen—Mo—L [Fig. 4(a)] was set at 45 [Fig. 4(b)] or 90° [Fig. 4(c)]. The different conformers thus generated are shown in Fig. 9. The maximum vertex angle of overlap, λ, was then measured (Table 3) for each of the conformers and pictorial representations of the vertex angle profiles (variation of λ with distance from the Mo atom) are shown in Figs 10(a) and (b). A spline fit to connect the maxima as rotation occurs through the full 360° is shown in Fig. 11. The sizes of the ligands follows the sequence $P(OMe)_3 > I > CO$.[13a,16]

A consideration of the data is revealing. The *trans*-90° data [Fig. 10(a)] shows a clear trend in which the overlap decreases (b) > (d) > (e), a sequence that can be correlated with the position of the largest ligand, $P(OMe)_3$. However, there are more subtle issues that are reflected in the data which reflect on both the size of the other ligands and the distance of the ligand from the ring and the $SiMe_3$ substituents.

The *shape* of the overlap curve [Fig. 10(a)] is

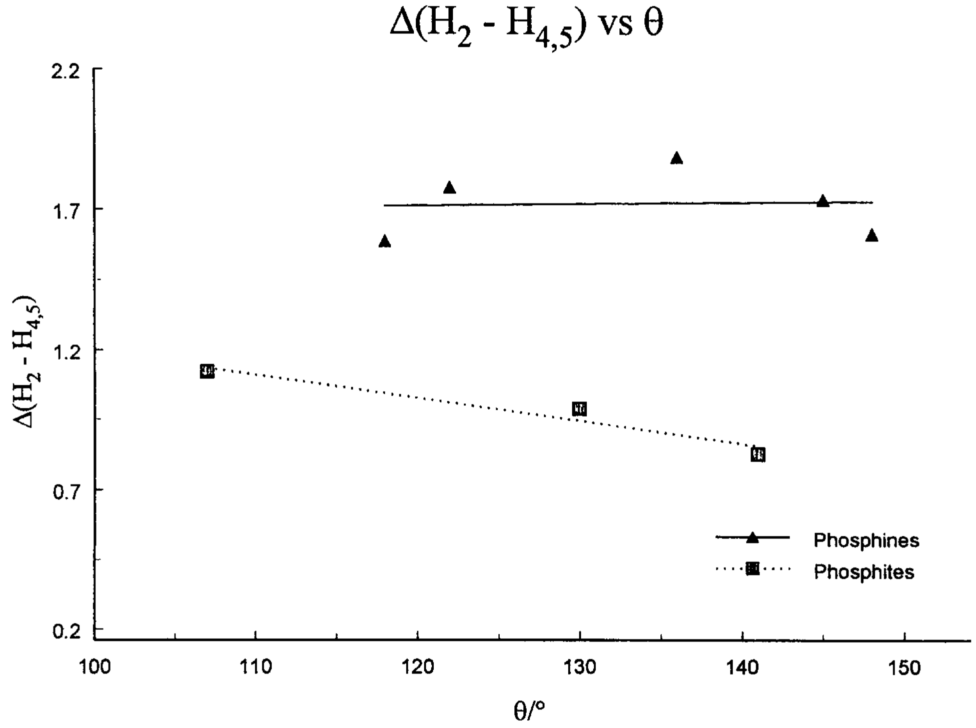

Fig. 7. Plot of Δ[H(2)-H(4),(5)] versus the Tolman cone angle,[15] θ, for the new complexes.

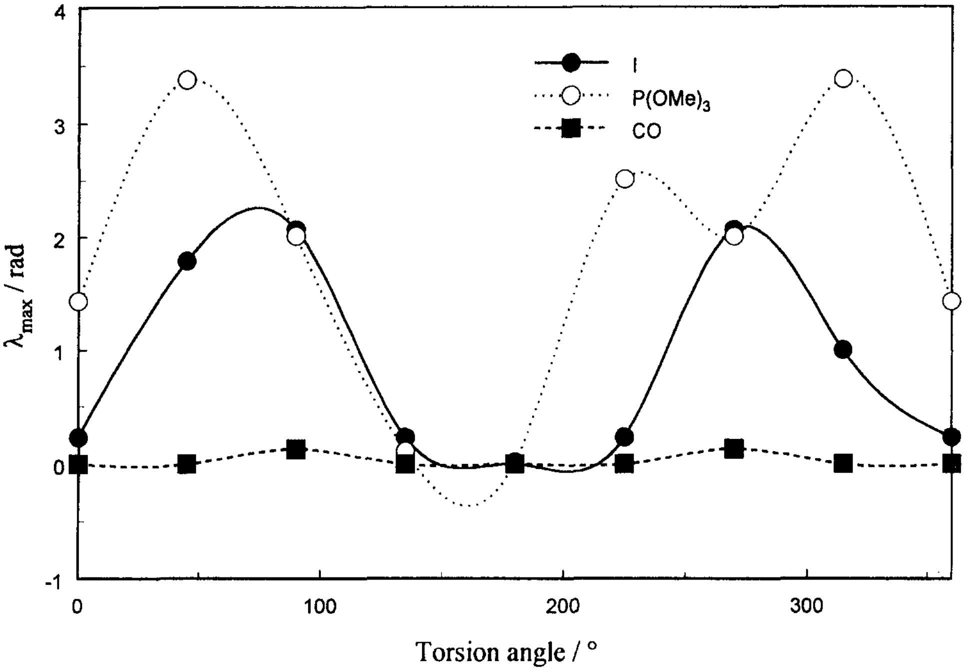

Fig. 8. Rotation of L around a "(η^5-$C_5H_3(SiMe_3)_2Mo$)" moiety [L = CO, I, P(OMe)$_3$].

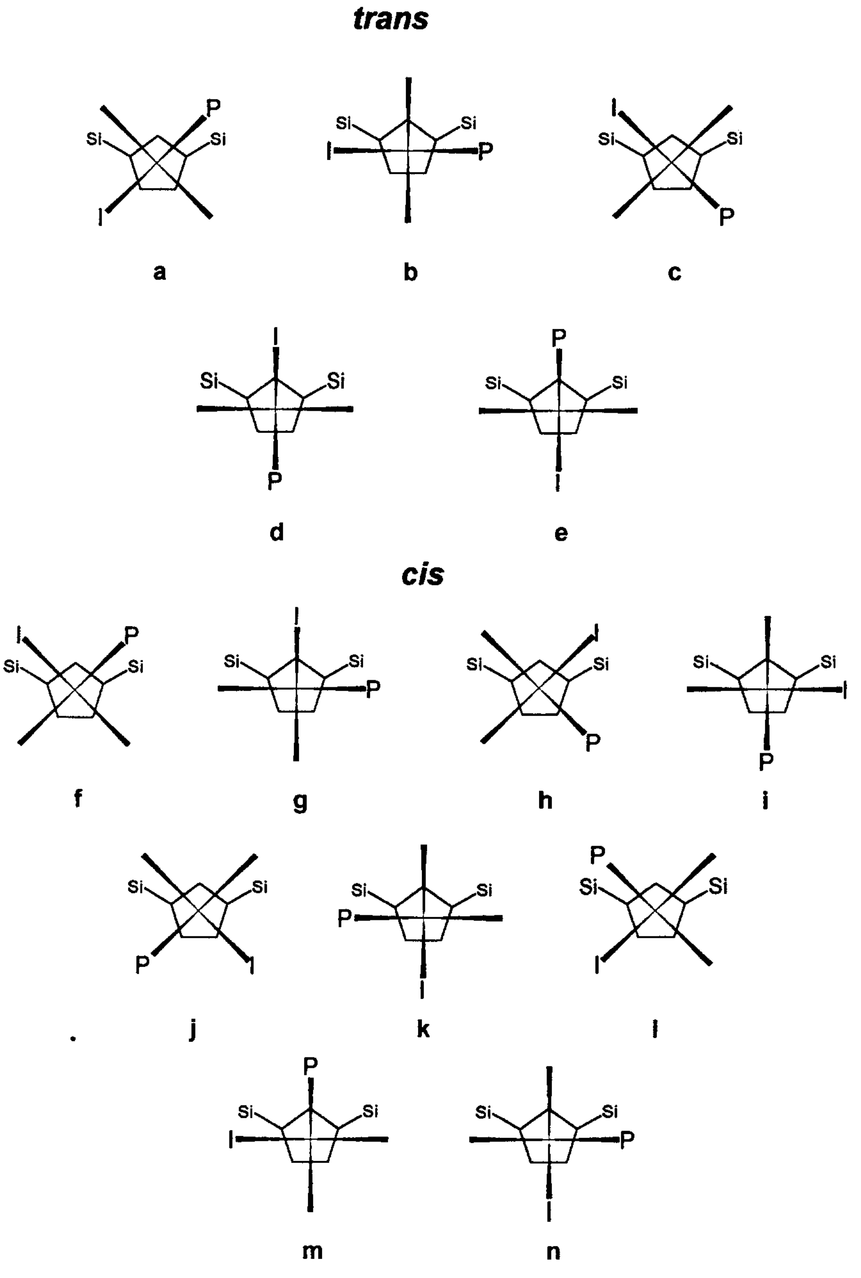

Fig. 9. Newman projection of possible *cis* and *trans* isomers corresponding to Figs 4(b) and (c).

Table 3. Vertex angle of overlap (λ) values for the different conformers

	Isomer[a]	$\lambda_{\max}$ (rad)[b]		Isomer[a]	$\lambda_{\max}$ (rad)[b]
trans	(a)	3.38	*cis*	(f)	3.52
	(b)	4.03		(g)	2.48
	(c)	1.34		(h)	1.59
	(d)	0.54		(i)	2.07
	(e)	1.63		(j)	2.73
				(k)	1.60
				(l)	3.52
				(m)	2.84
				(n)	2.68

[a] See Fig. 9.
[b] See Figs 10 and 12.

quite different for the three rotamers. In conformer (a), overlap of both I and $P(OMe)_3$ with the $SiMe_3$ groups occurs and is reflected by the area under the curve at distances of 1.5–3.0 and 3.0–5.5 Å, respectively (see below). In Fig. 10(a), conformer (b) shows little interaction of $SiMe_3$ with I (distance 1.5–3.0 Å), but significant overlap with $P(OMe)_3$ ($d > 2.5$ Å). Clearly conformer (c) [Fig. 10(a)] shows the smallest total overlap and corresponds to the conformer of lowest energy.

Also important is the data shown in Fig. 10(b). This data shows the difference in the overlap of the $P(OMe)_3$ group with $SiMe_3$, relative to the overlap of I with $SiMe_3$. Reflected in Fig. 10(b) is the recognition that the $P(OMe)_3$ interacts significantly with the $SiMe_3$ substituent at $d > 3$ Å, while the I interaction occurs for $d < 3$ Å. The overall conclusion is that steric effects can rationalize the experimental observations of a preferred conformer with the $P(OMe)_3$ group *trans* to position H(2).

Cis *isomer*. The conformers possible with settings at 45° [Fig. 4(b); of one of the two enantiomers] are shown in Fig. 9. The vertex angle profiles are shown in Table 3 and Figs 12(a) and (b), and the maxima are plotted in Fig. 11.

A seemingly more complex data set is reflected in Figs 12(a) and (b) for the *cis* isomers. However, analysis reveals the same details as described for the *trans* complexes. Thus, a comparison of the vertex angle of overlap radial profiles for the four conformers shown in Fig. 12(a) reveals that the conformers (f) and (l) (Fig. 9) have similar steric interactions, i.e. the position of the $P(OMe_3)$ and not I dominates the overlap picture. The difference between (h) and (j) is shown by the difference in the overlap at $d > 3$ Å. Clearly the choice of the $P(OMe)_3$ conformer is responsible for the difference (see below). However, the overall result is that isomers (h) and (j) show less overlap than isomers (f) and (l) and hence are the favoured conformers.

The four *cis* isomers, at 90°, give the expected results. Conformer (i) with the $P(OMe)_3$ *trans* to H(2) is expected to have the least overlap (see above). However, the interaction of I with $SiMe_3$, in isomer (i) leads to the increase in the size of the curve between 2 and 3 Å, relative to isomer (d). The conclusion is that in the *cis* isomer both the I and $P(OMe)_3$ ligands must be placed away from the $SiMe_3$ groups. Both conformers (h) and (j) would satisfy this criteria, but using the ligand conformers employed in this study, conformer (h) shows the lowest steric interaction.

Cis *versus* trans *isomer*. Comparison of the overlap data for the *cis* and *trans* isomers permits an assessment of the preferred isomer. This is most readily represented by the overlap data shown in diagrammatic form, Fig. 11. Clearly *cis* isomers, if formed, could access all conformers more readily than *trans* isomers. However, the *trans* isomer will be more stable and from a steric perspective conformer (d) (Fig. 9) is preferred. Thus, the isomer *and* the preferred conformer observed experimentally by NOE spectroscopy is predicted on purely steric grounds by the vertex angle of overlap methodology.

Our methodology does not presently permit minimization of the overlap for each conformer by adjustment of the methoxy group arrangement on the $P(OMe)_3$ ligand or the methyl group arrangement of the $SiMe_3$ group. This will affect $\lambda_{\max}$ for the different conformers [cf. conformers (k) and (n)], but will not affect the overall conclusions obtained from the approach.

CONCLUSION

Reaction of $[(\eta^5\text{-}C_5H_3(SiMe_3)_2)Mo(CO)_3I]$ with L gives the *trans*-$[(\eta^5\text{-}C_5H_3(SiMe_3)_2)Mo(CO)_2(L)I]$ isomers. NOE analysis of the complex when L = PMe_2Ph, or $P(OMe)_3$, reveals that neither of the ligands access the region close to H(2) in the molecule. This can be explained in terms of steric effects. The vertex angle of overlap methodology can rationalize the preferred orientation of the ring substituents relative to the ligand L in the ligand set as well as the lack of free rotation of the ligand set relative to the ring. The methodology can also provide some rationalization for the preference of the *trans* isomer over the *cis* isomers in these compounds.

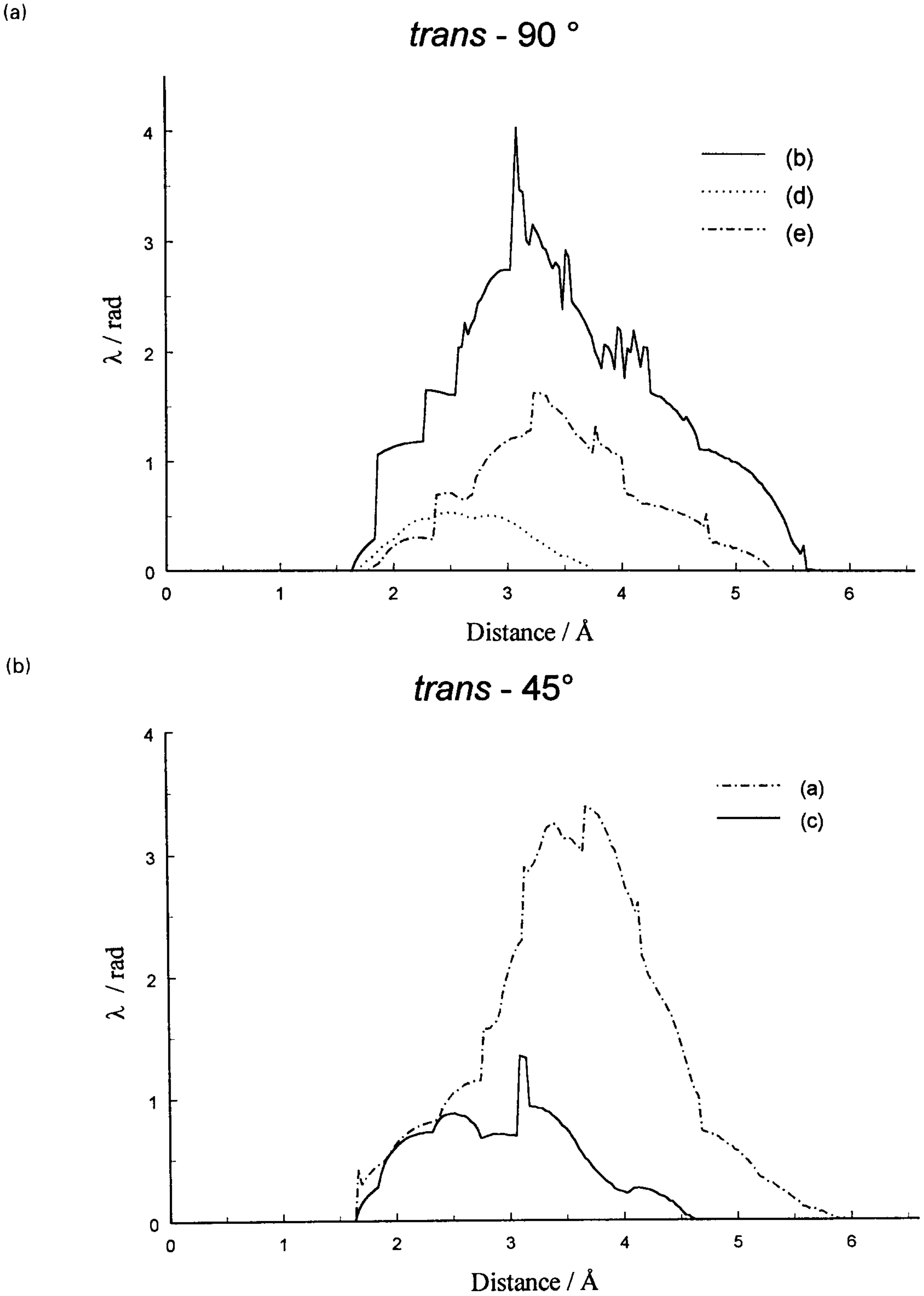

Fig. 10. Plot of λ against distances from the Mo atom for *trans*-[(η^5-C_5H_3($SiMe)_2$)Mo$(CO)_2$(P$(OMe)_3$)I]. (a) Torsion angle 45° [see Fig. 7(b)]; (b) torsion angle 90° [see Fig. 7(c)].

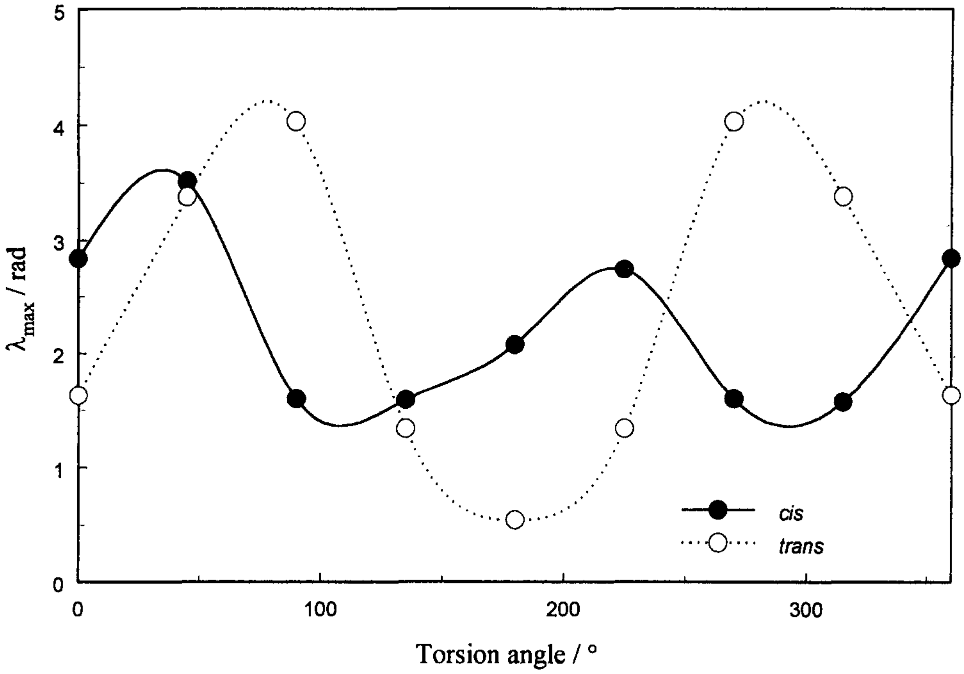

Fig. 11. Variation of λ_{max} with C(2)—Cen—Mo—P torsion angle (see Table 3).

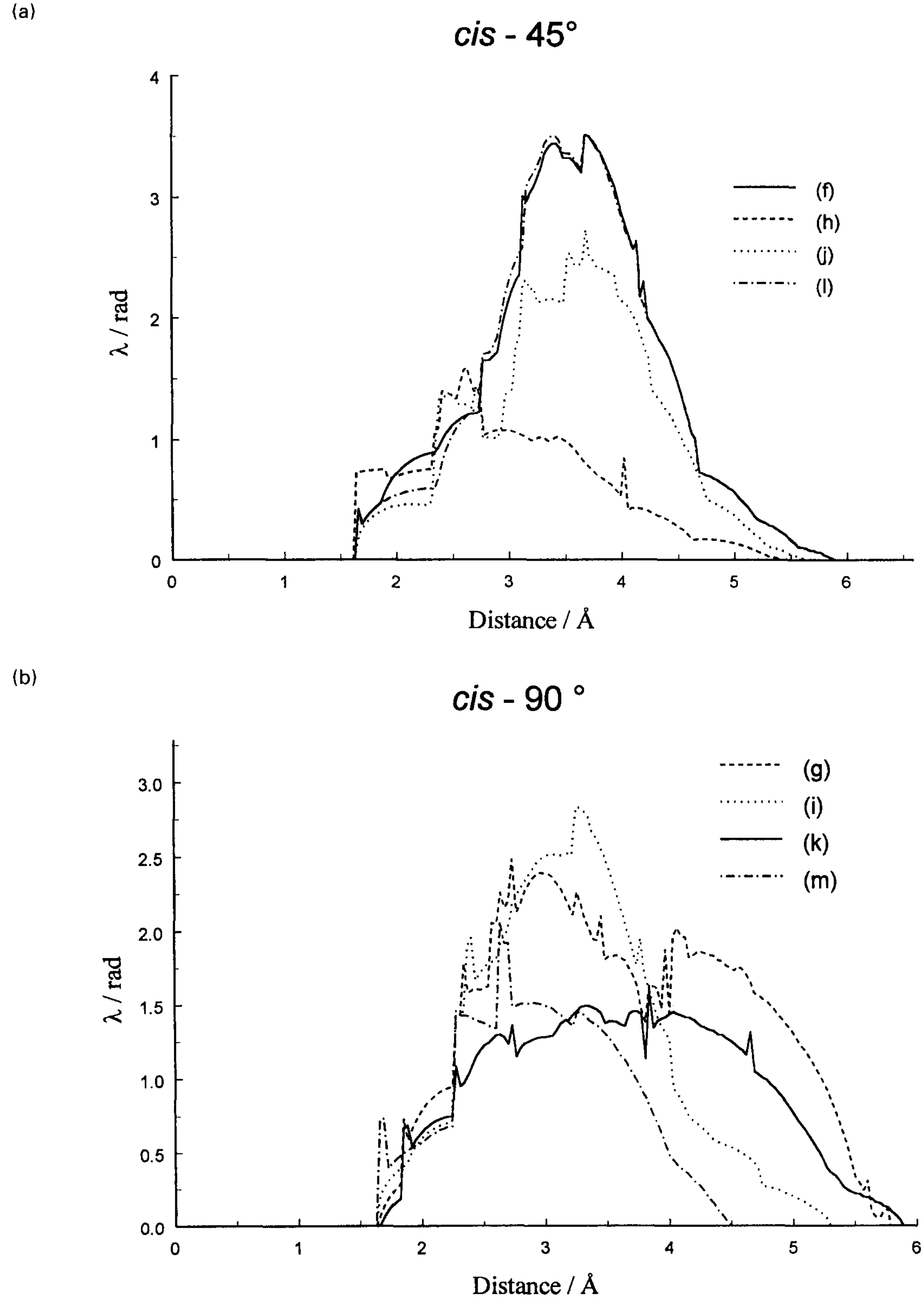

Fig. 12. Plot of λ, vertex angle of overlap, against distance from the Mo atom in *cis*-(η^5-C_5H_3(SiMe_3)$_2$)Mo(CO)$_2$(P(OMe)$_3$)I]. (a) Torsion angle 45° [see Fig. 4(b)]; (b) torsion angle 90° [see Fig. 4(c)].

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