

Journal of Molecular Structure 326 (1994) 81-91

Journal of MOLECULAR STRUCTURE

Conformational studies of $EPh_3M(CO)_5$ complexes (E = P, As or Sb; M = Cr, Mo or W)¹

M.S. Davies, G.W. Allen, M.J. Aroney*, T.W. Hambley, R.K. Pierens

Department of Inorganic Chemistry, The University of Sydney, Sydney NSW, 2006, Australia

Received 21 March 1994

Abstract

Studies are reported of the electro-optical Kerr effect, electric dipole moments and IR carbonyl stretching frequencies of the nine EPh₃(CO)₅ complexes (E = P, As or Sb and M = Cr, Mo or W). The experimental results are applied in conjunction with molecular mechanics calculations and data from X-ray crystal structure analysis, to explore the stereostructural preferences of the EPh₃M(CO)₅ molecules with regard to orientations about the M-E bond and phenyl group rotations about $E-C_{ar}$. Evidence is drawn together and compared for EPh₃M(CO)₅ in the solution and solid states and as isolated molecules. It is found that for all states, phenyl ring dispositions of like helicity are favoured for the coordinated EPh₃ ligands in these complexes.

1. Introduction

This work is part of a continuing programme of study of the steric and electronic factors that affect metal-ligand interactions in mixed-ligand metal carbonyls [1-5]. Complexes $EPh_3M(CO)_5$ are examined (E = P, As or Sb; M = Cr, Mo or W) primarily to determine the stereochemical characteristics of the coordinated EPh_3 group with regard to orientations about the M-E bond and phenyl group rotations about $E-C_{ar}$.

Steric properties of ligands are important since they often influence the course of metalcentred reactions in complexes [6]. Solid-state configurations can be determined with precision by X-ray structure analysis while molecular mechanics calculations will often yield information on the relative conformational energies of isolated, flexible molecules. However, conformational preferences in solution, the state in which a great number of important chemical reactions occur, are much more difficult to access.

Measurements of the electro-optical Kerr effect (electric birefringence) of the EPh₃M(CO)₅ complexes are reported in a dilute cyclohexane environment and these are interpreted together with experimental dipole moments and IR carbonyl stretching frequencies, to obtain information on the preferred solute conformations. Application of molecular mechanics calculations to such systems is also explored. Comparisons are made with the solid-state structures of EPh₃M(CO)₅ [5,7–10].

¹ Dedicated to Professor Dr. Wolfgang Lüttke of the University of Göttingen, a distinguished colleague and friend, on the occasion of his 75th birthday.

^{*} Corresponding author.

^{0022-2860/94/\$07.00 © 1994} Elsevier Science B.V. All rights reserved SSDI 0022-2860(94)08333-D

2. Experimental

All reactions were performed under nitrogen using standard Schlenk techniques. Tetrahydrofuran (THF) and cyclohexane were distilled from sodium benzophenone ketyl and stored on sodium.

The complexes $EPh_3M(CO)_5$ were synthesised by photolysis of $M(CO)_6$ in THF; the ligand EPh_3 was added to the solution of $[M(CO)_5THF]$ to give $EPh_3M(CO)_5$ in high yield [11,12]. The solvent was removed in vacuo and the residue vacuum sublimed (60°C, 1 mmHg) to remove unreacted $M(CO)_6$. Any residual EPh_3 was removed by rinsing with cold hexane. The solid was dissolved in acetone and reprecipitated with water and filtered. This was followed by column chromatography on activated silica (Keiselgel 60, mesh 30–70). The product in each case was eluted with hexane and recrystallised from that solvent. Melting points and carbonyl IR spectra agreed well with those of the literature [13–16].

Solute dipole moments μ and electric birefringences, the latter expressed as molar Kerr constants $_{m}K$, were determined in cyclohexane solution at 298 K and 589 nm. The apparatus, techniques of measurement and treatment of data are described in Refs. 17 and 18. Infrared spectra were recorded in cyclopentane using a Digilab FTS 20/ 80 Fourier transform IR spectrometer. The experimental results are given in Tables 1 and 2. Molecular mechanics calculations were performed using the MOMEC-87 program which has been described previously [19,20].

3. Results and discussion

3.1. Infrared spectra

The EPh₃M(CO)₅ complexes have IR carbonyl absorptions corresponding to two A₁, one B₁ and one E vibrational modes in C_{4v} local symmetry [21–23]. The B₁ band is formally IR forbidden in strict C_{4v} symmetry, but is observed as a very weak band for these complexes. Various activation mechanisms have been proposed for this band [24–29] though it is widely believed to result from symmetry lowering because of ligand asymmetry and steric bulk. The experimental IR data are given in Table 1; the carbonyl IR band positions of the analogous $EMe_3M(CO)_5$ complexes are included for comparison. The B₁ band was not observed for the latter complexes in cyclopentane but did appear in spectra that were recorded in tetrahydrofuran [4]. The B₁ frequencies for all the LM(CO)₅ complexes are taken from Raman spectra in cyclopentane [30].

The carbonyl frequencies of the listed complexes are in close agreement throughout. The results indicate that the electron distributions within the $M(CO)_5$ moiety for the analogous $EMe_3M(CO)_5$ and $EPh_3M(CO)_5$ complexes are very similar.

3.2. Molecular mechanics

Initial investigation of the conformational preferences of EPh₃M(CO)₅ molecules was undertaken using molecular mechanics (MM) calculations. The primary aim was to characterise the EPh₃ geometry through determination of the torsion angles φ (M-E-C_{ar}-C_{ar}) for phenyl rotations about each E-C_{ar} bond axis and rotations ω (C_{eq}-M-E-C_{ar}) about the M-E bond showing the disposition of EPh₃ with respect to the M(CO)₄ plane (see Fig. 1).

Input coordinates for complexes¹ were orthogonalised positions of atoms determined from their X-ray crystal structures [5,7–10]. Force constants for the various bond stretch, bend, torsion and out-of-plane deformations were taken from literature sources $[31-39]^2$. Stretching force constants for CO were derived from ν (CO) using the Cotton-Kraihanzel method [26]. Default bond angles about E were taken to be tetrahedral. The calculations were simplified by fixing the metal and the five carbonyl carbon atoms at their crystallographically determined positions. The coordinated

¹ The input data for AsPh₃Cr(CO)₅ and SbPh₃Cr(CO)₅ were the coordinates for the analogous molybdenum complexes, adjusted to take account of changes in E-M bond distances. The phenyl carbon positions for these chromium complexes were provided by A.J. Carty (personal communication); however the hydrogen positions were not included.

² Details of the bond stretch and valence deformation force constants are supplied in a supplementary publication, deposited with B.L.L.D. as SUP 26497.

٥	2
ð	э

	Aleq	Alax	D 1	E	
PPh ₃ Cr(CO) ₅	2064	1948	1982	1944	
PMe ₃ Cr(CO) ₅ ^d	2063	1949	1973	1941	
AsPh ₃ Cr(CO) ₅	2065	1946	1983	1946	
$AsMe_3Cr(CO)_5^d$	2063	1946	1976	1940	
SbPh ₃ Cr(CO) ₅	2062	1951	1982	1946	
PPh ₃ Mo(CO) ₅	2073	1951	1989	1951	
PMe ₃ Mo(CO) ₅ ^d	2071	1952	1981	1945	
AsPh ₃ Mo(CO) ₅	2074	1952	1989	1952	
AsMe ₃ Mo(CO) ₅ ^d	2072	1948	1983	1948	
SbPh ₃ Mo(CO) ₅	2074	1954	1990	1954	
PPh ₃ W(CO) ₅	2072	1951	1980	1942	
PMe ₃ W(CO) ₅ ^d	2071	1947	1972	1937	
AsPh ₃ W(CO) ₅	2073	1944	1981	1944	
$AsMe_3W(CO)_5^d$	2071	1943	1975	1939	
SbPh ₃ W(CO) ₅	2073	1947	1981	1947	

Table 1 Infrared carbonyl stretching frequencies (cm^{-1}) for LM(CO)₆ complexes in cyclopentane solution^{a,b}

^a Uncertainty $\pm 0.5 \,\mathrm{cm}^{-1}$.

^b Same frequency is indicated where the A_{lax} and E bands closely overlap and are not resolved.

^c The B₁ band was not observed for EMe₃M(CO)₅ and was a very weak band for EPh₃M(CO)₅; the values used are from Raman data in the same solvent.

^d From Ref. 3.

 EPh_3 was then allowed to adapt to an energyminimised geometry. Energy minimisation was continued until the shifts of all atoms were less than 0.001 Å.

An M-E stretching force constant of $1.25 \times 10^2 \text{ N m}^{-1}$ was employed for all complexes, based on normal coordinate studies on Ph₃M(CO)₅ (M = Cr, Mo and W) by Jeanne et al. [32] and $PMe_3Ni(CO)_3$ by Bigorgne et al. [40]. A force constant of this magnitude necessitated the use of strain-free bond lengths approximately 0.1 Å lower than that determined experimentally by X-ray crystallography. The exact value used was determined by trial and error until this bond distance in the energy-minimised structure was equal to the bond length from X-ray crystallography.

Table 2

Electric dipole moments, molar Kerr constants and molecular refractivities of EPh₃M(CO)₅ complexes in cyclohexane solution at T = 298 K and $\lambda = 589$ nm^a

Solute	$R_{\rm D}$ (cm ³)	$10^{30} \mu^{b}$ (C m)	$10^{27} {}_{\rm m}K$ (m ⁵ V ⁻² mol ⁻¹)	
	()	()	(
PPh ₃ Cr(CO) ₅	137 ± 1	17.2 ± 0.2	-867 ± 17	
PPh ₃ Mo(CO) ₅	144 ± 1	18.0 ± 0.3	-1052 ± 34	
PPh ₃ W(CO) ₅	145 ± 3	18.0 ± 0.2	-1061 ± 18	
AsPh ₃ Cr(CO) ₅	138 ± 1	18.3 ± 0.2	-894 ± 13	
AsPh ₃ Mo(CO) ₅	145 ± 2	18.0 ± 0.4	-978 ± 9	
AsPh ₃ W(CO) ₅	146 ± 2	18.6 ± 0.2	-977 ± 16	
SbPh ₃ Cr(CO) ₅	142 ± 1	18.0 ± 0.2	-147 ± 1	
SbPh ₃ Mo(CO) ₅	147 ± 2	16.7 ± 0.1	-65 ± 4	
SbPh ₃ W(CO) ₅	149 ± 3	17.9 ± 0.1	-72 ± 2	

^a Dipole moments and molar Kerr constants are expressed in SI units. The conversion factors from the electrostatic (c.g.s., e.s.u.) system are, respectively: $1 \text{ Cm} = 0.2998 \times 10^{30} \text{ D}$; $1 \text{ m}^5 \text{ V}^{-2} \text{ mol}^{-1} = 0.8988 \times 10^{15} \text{ e.s.u. mol}^{-1}$.

^b Dipole moments were derived on the basis that the molar distortion polarisation equals 1.05 $R_{\rm D}$.



Fig. 1. Illustration of torsion angles φ and ω for EPh₃M(CO)₅ molecules.

Care was taken to avoid local energy minima [33]. One method used to achieve this was to fix the three $M-P-C_{ar}-C_{ar}$ torsions at equal angles and to vary them synchronously from 30° to 70°. Outside this range serious steric intramolecular interactions occur. For conformers such as these and, as well, for a variety of unsymmetrical forms (different φ values) chosen randomly as input coordinates, energy minimisation was undertaken. The results were monitored to determine the minimumenergy form.

The energy profiles determined through the range of equal phenyl rotations φ of $0-90^{\circ}$ for PPh₃Cr(CO)₅ and SbPh₃W(CO)₅ are shown in Fig. 2. Similar plots were obtained for the other seven EPh₃M(CO)₅ complexes. An analogous procedure with correlated cog-like rotation of the three phenyl rings was used by Davies et al. [41] in an investigation of the triphenylphosphine conformation in [CpFe(CO)(PPh₃)COCH₃] and by Brock and Ibers in a study of free PPh₃ [42]. A marked decrease is found in the energy profile and the potential well is broadened as the M-E bond becomes longer, reflecting increased rotational freedom within the EPh₃ ligand.

The disposition of EPh_3 with respect to the nearly planar $M(CO)_4$ grouping is reflected by the

 $C_{eq}-M-E-C_{ar}$ torsion angle ω . An angle of 0° indicates $E-C_{ar}$ and equatorial M-CO are eclipsed, while an angle of 45° indicates that the plane M-E-C_{ar} bisects the angle between vicinal equatorial M-CO groups. The crystal structures of the nine EPh₃M(CO)₅ complexes display one angle ω very close to 45°; the ω values of the other two $E-C_{ar}$ bonds are approximately 15° relative to an equatorial M-CO group [5]. The energy-minimised structures of these compounds are found to have ω values of approximately 40°, 20° and 10°.

Global minima discerned from the calculations for the EPh₃M(CO)₅ series correspond to conformational forms with $\varphi_1 = 66-67^\circ$, $\varphi_2 = 45-54^\circ$, and $\varphi_3 = 59-62^\circ$. The coordinated EPh₃ in each case has a somewhat irregular propeller structure. The irregularity could arise from symmetry mismatch between the trigonal $E(C_{ar})_3$ and the near square planar $M(CO)_4$ moieties. For each EPh₃M(CO)₅, the global minimum differs in energy by less than 2kJmol⁻¹ from the minimum of the broad potential well associated with symmetric propeller structures of the EPh₃ ligands. Such small differences indicate that there is no well-defined preferred conformation for the free $EPh_3M(CO)_5$ molecules. In view of this, further MM structural analysis appears not to be warranted.

Though the MM treatment does not yield precise stereostructural information for the $EPh_3M(CO)_5$ molecules, it does show that a multitude of low-energy conformational forms are possible and that the EPh_3 ligand in the minimum-energy conformers is effectively propeller shaped.

3.3. Dipole moments and molar Kerr constants

The electric dipole moments of the EPh₃M(CO)₅ complexes, listed in column 3 of Table 2, are in good agreement with previous literature values [43-46]. It is seen that the μ values are not much affected by variation of E or M within the series studied. They range from 17.2×10^{-30} to 18.6×10^{-30} C m apart from that of SbPh₃Mo(CO)₅ which is marginally lower at 16.7×10^{-30} C m. The PMe₃M(CO)₅ and AsMe₃M(CO)₅ complexes have dipole moments in the range 16.9×10^{-30} - 17.9×10^{-30} C m [3], which are close to those of



Fig. 2. Energy profile for synchronised rotations φ from 0° to 90°: - - -, PPh₃Cr(CO)₅, ----, SbPh₃W(CO)₅.

the triphenyl analogues. It appears that exchange of EMe₃ by EPh₃ in these complexes has relatively little effect on the electron charge distribution of the central $EC_3M(CO)_5$ moiety. This accords with the results earlier obtained from comparisons of the IR spectral data.

Unlike the dipole moments and the carbonyl IR spectra, the electric birefringences of these complexes are very sensitive to replacement of methyl substituents in EMe₃M(CO)₅ by phenyl groups. The experimental $_{m}K$ (×10⁻²⁷ m⁵ V⁻² mol⁻¹) values reported for EMe₃M(CO)₅ are -58 (P, Cr), -192 (P, Mo), -218 (P, W), 36.7 (As, Cr), -121 (As, Mo) and -131 (As, W) [3]. The large differences between these values and the molar Kerr constants of the corresponding EPh₃M(CO)₅ complexes result from the sensitivity of this physical property to the various possible rotational dispositions of the highly anisotropic phenyl substituent groups relative to the molecular dipole vector [47].

According to the Langevin-Born treatment,

modified by Le Fèvre [17,48], the molar Kerr constant is related to the molecular dipole vector μ and the polarisability tensor **b** by the following relation:

$$\begin{split} {}_{m}K &= (N_{A}/810kT\epsilon_{0})\{({}_{D}P/{}_{E}P)[(b_{xx} - b_{yy})^{2} \\ &+ (b_{yy} - b_{zz})^{2} + (b_{zz} - b_{xx})^{2} \\ &+ 6(b_{xy}^{2} + b_{xz}^{2} + b_{yz}^{2})] \\ &+ (kT)^{-1}[\mu_{x}^{2}(2b_{xx} - b_{yy} - b_{zz}) \\ &+ \mu_{y}^{2}(2b_{yy} - b_{xx} - b_{zz}) + \mu_{z}^{2}(2b_{zz} - b_{xx} - b_{yy}) \\ &+ 6(b_{xy}\mu_{x}\mu_{y} + b_{xz}\mu_{x}\mu_{z} + b_{yz}\mu_{y}\mu_{z})]\} \end{split}$$
(1)

where b_{xx} , b_{yy} , b_{zz} , b_{xy} , b_{xz} and b_{yz} are the elements of the matrix defining the molecular polarisability tensor with reference to molecule-fixed orthogonal axes X, Y and Z; μ_x , μ_y and μ_z are the resolved parts of the permanent electric dipole moment vector along X, Y and Z; $_DP$, $_EP$, N_A , k, T and ϵ_0 refer, in turn, to the molar distortion polarisation, the molar electron polarisation, Avagadro's number, the Boltzmann constant, the absolute temperature and the permittivity of a vacuum. For a specific geometry of the molecule, the elements of the molecular polarisability tensor can be determined according to the valence optical scheme of segment polarisability additivity [47,48]. Group anisotropic polarisabilities required for such calculations are obtainable from the molecular tensor components of EMe₃M(CO)₅ complexes (listed in Table 4 of Ref. 3) and of the phenyl and C-H groups given in Refs. 47 and 50. It is worth noting that, where comparisons can be made, the C-E-C angles are virtually the same in the $EPh_3M(CO)_5$ and $EMe_3M(CO)_5$ complexes; e.g. 102.6°, 102.6°, 102.9° and 102.7° for PPh₃Cr(CO)₅, PMe₃Cr(CO)₅, PPh₃W(CO)₅ and PMe₃W(CO)₅, respectively [5,7,8,38,49]. Polarisability anisotropies of the antimony complexes have not been determined; they were taken as zero in close analogy with the phosphorus and arsenic complexes which are near isotropically polarisable [3].

Using the procedure described in Ref. 48, molar Kerr constants were calculated for possible conformational forms of PPh₃Cr(CO)₅. This molecule was studied as a test model since it is reasonably believed that because of the smaller size in comparison to the rest of the series, rotationally induced strain energy effects would be more pronounced and preferred conformational geometries better defined. Molar Kerr constants were calculated at 10° increments for both equal and unequal ring rotations over the ranges $\varphi_1 = 0-90^\circ$, $\varphi_2 =$ $0-180^\circ$ and $\varphi_3 = 0-180^\circ$. The resultant array of



Fig. 3. The $_{\rm m}K$ (calc.) function for phenyl rotations φ_2, φ_3 of PPh₃Cr(CO)₅ when φ_1 is fixed at 50°.

Table 3 Combinations $\varphi_1, \varphi_2, \varphi_3$ for which ${}_{m}K(\text{calc.})$ equals ${}_{m}K(\text{obs.})$

	0	10	20	30	40	50	60	70	80	90
0							89/91	68/112	62/118	59/121
10							79/101	66/114	60/120	58/122
20							69/111	59/121	54/126	52/128
30						72/108	59/121	49/131	46/134	44/136
40					73/107	59/121	49/131	42/138	37/143	35/145
50				72/108	59/121	49/131	39/141	31/149	25/155	23/157
60	89/91	97/101	69/111	59/121	49/131	39/141	31/149	19/161	7/171	
70	68/112	66/114	59/121	51/129	42/138	31/149	19/161	,	,	
80	62/118	60/120	54/126	46/134	37/143	25/155	7/171			
90	59/121	58/122	52/128	44/136	35/145	23/157				
100	62/118	60/120	54/126	46/134	37/143	25/155	7/171			
110	68/112	66/114	59/121	51/129	42/138	31/149	19/161			
120	89/91	97/101	69/111	59/121	49/131	39/141	31/149	19/161	7/171	
130	,	,	,	72/108	59/121	49/131	39/141	31/149	25/155	23/157
140				,	73/107	59/121	49/131	42/138	37/143	35/145
150					,	72/108	59/121	49/131	46/134	44/136
160						,	69/111	59/121	54/126	52/128
170							79/101	66/114	60/120	58/122
180							89/91	68/112	62/118	59/121

 $_{\rm m}K({\rm calc.})$ values is very large and as such has not been reproduced here. Graphical representation of one set of results is depicted as Fig. 3; in this φ_1 is arbitrarily fixed at 50° and the dependence of mK(calc.) on φ_2 , φ_3 is shown. Table 3 lists combinations of $\varphi_1, \varphi_2, \varphi_3$ which give concordance between the experimental and computed molar Kerr constants. Molecular mechanics was applied to calculate strain energies for the geometric models so specified. It was found that the range of such conformational possibilities having strain energies in the order of kT (Boltzmann constant \times absolute temperature) per mole relative to groundstate geometry, is still very large and this approach does not lead to a clear specification of preferred conformations. The results from this approach generally indicate that conformations with phenyl ring rotations of similar helicity in the coordinated PPh₃ fragment are lower in energy and much more abundant than rotamer forms having mixed helical arrangements of phenyl rings.

Pertinent to this study is evidence from X-ray crystal structure determinations recently collated for all nine $EPh_3M(CO)_5$ complexes [5]. The solid-state configurations are stereostructurally similar across the series. The phenyl groups were

found to have different torsion angles φ_1, φ_2 and φ_3 in each structure (see Table 4), but the deviations from the symmetric propeller C_3 symmetry for the coordinated EPh₃ are not great.

Molar Kerr constants were calculated for the solid-state molecular geometry of each of the $EPh_3M(CO)_5$ complexes and these are shown in

Table 4

Torsion angles φ (M-E-C_{ar}-C_{ar}) for the X-ray crystal structures of EPh₃M(CO)₅

Compound	<i>φ</i> 1	φ2	φ3
PPh ₃ Cr(CO) ₅ "	51.4	52.3	48.3
PPh3Mo(CO)5 ^b	47.0	56.0	44.5
PPh ₃ W(CO) ₅ ^c	44.0	51.0	54.0
AsPh ₃ Cr(CO) ₅ ^d	50.0	45.6	52.3
AsPh ₃ Mo(CO) ₅ ^c	50.4	41.6	51.9
AsPh ₃ W(CO) ₅ ^c	49.0	42.4	52.0
SbPh ₃ Cr(CO) ₅ ^d	44.9	52.4	40.9
SbPh3Mo(CO)5 °	45.6	52.1	36.2
SbPh ₃ W(CO) ₅ ^c	45.2	52.7	36.9
J /J			

^a From Refs. 7 and 8.

^b From Ref. 10.

^c From Ref. 5.

^d A.J. Carty, personal communication 1993; structural data for the phenyl ring carbon atoms were not included in the original paper [9] or the Cambridge data file. Table 5

Comparison of the molar Kerr constants calculated for the X-ray crystal structures of EPh₃M(CO)₅ complexes with the experimental solute values

Compound	$10^{27} {}_{m}K$ (solute) (m ⁵ V ⁻² mol ⁻¹)	$10^{27} {}_{\rm m}K$ (crystal structure) (m ⁵ V ⁻² mol ⁻¹)	
PPh ₃ Cr(CO) ₅	-867	983	
PPh ₃ Mo(CO) ₅	-1052	-1090	
PPh ₃ W(CO) ₅	-1061		
AsPh ₃ Cr(CO) ₅	-894	-826	
AsPh ₃ Mo(CO) ₅	978	-846	
AsPh ₃ W(CO) ₅	-977	-874	
SbPh ₃ Cr(CO) ₅	-147	-473	
SbPh ₃ Mo(CO) ₅	-65	-284	
SbPh ₃ W(CO) ₅	-72	-365	



Fig. 4. Variation of the calculated $_{\rm m}K(\varphi)$ with the Cr-P-C_{ar}-C_{ar} torsion angle φ in PPh₃Cr(CO)₅.

Table 5 together with the experimental solute ${}_{\rm m}K$ values. The agreement is surprisingly good for the six phosphorus and arsenic compounds. This means that the ${}_{\rm m}K$ from experiment for each of the solutes is close to that predicted for the near symmetric propeller structure found in the crystal. The agreement is not quite as good with the antimony compounds possibly because of greater rotational freedom of the phenyl groups about the longer $C_{\rm ar}$ -Sb bonds. Similar calculations for the minimum-energy MM conformation of EPh₃M (CO)₅ yielded ${}_{\rm m}K$ (calc.) values of -1771 (P, Cr), -1984 (P, Mo), -1953 (P, W), -2003 (As, Cr), -2062 (As, Mo), -2230 (As, W), -2114 (Sb, Cr), -1797 (Sb, Mo) and -2211 (Sb, W) (all $\times 10^{-27}$ m⁵ V⁻² mol⁻¹).

For the solution state, information on the conformations of $EPh_3M(CO)_5$ was drawn from the experimental solute Kerr constants. These were interpreted, in each case, in terms of an effective or ensemble average conformation φ (solute). _mK values were calculated for geometric forms of each $EPh_3M(CO)_5$ molecule with equal rotations φ of like helicity for the EPh₃ propeller. Such conformational behaviour is in concordance (approximately) with the X-ray structures for the complexes and with correlated librational motion minimising inter-ring steric repulsions within EPh₃. In addition, following from the Onsager reaction field model [51], the EPh₃M(CO)₅ molecule within a solvent cavity would tend to a more spherical, compact structure than for the free molecule [52,53]. Such considerations are in agreement with theoretical and experimental studies [41,54-57] which indicate an equilibrium propeller type conformation for coordinated PPh₃ in molecules in the gas or solution states¹ and with the results of Bye et al. [59] and Garner and Orpen [6] who came to similar conclusions for crystal-state structures.

The plot of ${}_{\rm m}K$ (calc.) with torsion angle φ for PPh₃Cr(CO)₅, shown in Fig. 4, illustrates the acute response of the Kerr constant to variations in the molecular geometry. Agreement between calculation and experiment is found when $\varphi = 49^{\circ}$. Trial computations were also made to test the effect of including polarisability exaltations Δb , i.e. polarisability correction terms to

Table (6
---------	---

Comparison of average φ values for EPh₃M(CO)₅ complexes in the solution and solid states

Compound	$\varphi(\text{solute})^{a}$ (deg)	φ (crystal structure) (deg)
PPh ₃ Cr(CO) ₅	49	50.7
PPh ₃ Mo(CO) ₅	48	49.2
PPh ₃ W(CO) ₅	49	49.7
AsPh ₃ Cr(CO) ₅	49	49.3
AsPh ₃ Mo(CO) ₅	49	48.0
AsPh ₃ W(CO) ₅	49	47.8
SbPh ₃ Cr(CO) ₅	42.5	46.1
SbPh ₃ Mo(CO) ₅	42	44.6
SbPh ₃ W(CO) ₅	42	44.9

^a Estimated uncertainty of $\pm 2^{\circ}$ throughout.

account for possible electronic interactions between the phenyl and $M(CO)_5$ groups (see pp. 64 and 65 of Ref. 48). Such terms must be small from the IR spectral and dipole moment evidence presented earlier.² The results in Fig. 4 show that φ deduced above is not significantly affected by such factors. The experimental molar Kerr constants for the other EPh₃M(CO)₅ complexes were similarly analysed.

The $\varphi(\text{solute})$ values thus determined for the effective solute conformations of EPh₃M(CO)₅ molecules are shown in column 2 of Table 6. They are seen to be in remarkably good agreement with the analogous average torsion angles φ (crystal structure) for the solid-state configurations (column 3). For each set of data, φ tends to decrease with change of E from P to Sb. It may be that with elongation of the E-M and E-C_{ar} bonds and with decreasing C_{ar}-E-C_{ar} angles [5,9], the inter-ring repulsions assume increasing importance relative to repulsions between the phenyl and equatorial CO groups.

¹ Loss of propeller symmetry can occur where other particularly bulky ligands impose strong steric constraints on the PPh₃ moiety [55,58].

² An exaltation of 1.3×10^{-40} C m² V⁻¹ was used in the calculations, equivalent to a molecular refractivity exaltation of 1 cm³ (589 nm); $\Delta_E P = 0.95 \quad \Delta R_D = N_A \Delta b / 9\epsilon_0$ from Ref. 47. According to Le Fèvre [48], this exaltation would be directed along an axis of electromeric shift, i.e. along E–M or alternatively along each C_{ar}-E. The conversion factor from the electrostatic (c.g.s., e.s.u.) system for polarisability is: $1 \text{ Cm}^2 \text{ V}^{-1} = 0.8988 \times 10^{16} \text{ cm}^3$.

4. Conclusion

In summary, the techniques of electric birefringence and molecular mechanics have been applied, in conjunction with data from X-ray crystal structure analyses, to probe the stereostructural preferences of EPh₃M(CO)₅ molecules with regard to phenyl ring rotations and EPh₃ orientations relative to M(CO)₅. Evidence is brought together and compared for the EPh₃M(CO)₅ molecules in the solid, solution and (effective) gas states. It is found that for all states, propeller geometry is favoured for the coordinated EPh₃ ligands.

5. References

- M.J. Aroney, M.K. Cooper, R.K. Pierens and S.J. Pratten, J. Organomet. Chem., 309 (1986) 293.
- [2] M.J. Aroney, R.M. Clarkson, T.W. Hambley and R.K. Pierens, J. Organomet. Chem., 426 (1992) 331.
- [3] M.S. Davies, R.K. Pierens and M.J. Aroney, J. Organomet. Chem., 458 (1993) 141.
- [4] M.J. Aroney, M.S. Davies, T.W. Hambley and R.K. Pierens, J. Chem. Soc., Dalton Trans., (1994) 91.
- [5] M.J. Aroney, I.E. Buys, M.S. Davies and T.W. Hambley, J. Chem. Soc., Dalton Trans., in press.
- [6] S.E. Garner and A.G. Orpen, J. Chem. Soc., Dalton Trans., (1993) 533.
- [7] H.J. Plastas, J.M. Stewart and S.O. Grim, J. Am. Chem. Soc., 91 (1969) 4326.
- [8] H.J. Plastas, J.M. Stewart and S.O. Grim, Inorg. Chem., 12 (1973) 265.
- [9] A.J. Carty, N.J. Taylor, A.W. Coleman and M.F. Lappert, J. Chem. Soc., Chem. Commun., (1979) 639.
- [10] F.A. Cotton, D.J. Darensbourg and W.H. Ilsley, Inorg. Chem., 20 (1981) 578.
- [11] W. Strohmeier, Angew. Chem., Int. Ed. Engl., 3 (1964) 730.
- [12] W. Strohmeier and F.J. Muller, Chem. Ber., 102 (1969) 3608.
- [13] R.A. Brown and G.R. Dobson, Inorg. Chim. Acta, 6 (1972) 65.
- [14] E. Vincent, L. Verdonck and G.P. Van der Kelen, J. Mol. Struct., 69 (1980) 33.
- [15] R. Poilblanc and M. Bigorgne, Bull. Soc. Chim. Fr., (1962) 1301.
- [16] R.J. Angelici and M.D. Malone, Inorg. Chem., 6 (1967) 1731.
- [17] C.G. Le Fèvre and R.J.W. Le Fèvre, in A. Weissberger

(Ed.), Techniques of Chemistry, Vol. 1, Part IIIC, Wiley-Interscience, New York, 1972.

- [18] R.J.W. Le Fèvre, Dipole Moments, Methuen, London, 1953.
- [19] T.W. Hambley, MOMEC-87, A Program for Strain Energy Minimisation, The University of Sydney, 1987.
- [20] G.W. Allen, M.J. Aroney and T.W. Hambley, J. Mol. Struct., 216 (1990) 227.
- [21] L.E. Orgel, Inorg. Chem., 1 (1962) 25.
- [22] D.M. Adams, Metal-Ligand and Related Vibrations, Edward Arnold, London, 1967, pp. 97-109.
- [23] R.E. Dessy and L. Wieczorek, J. Am. Chem. Soc., 91 (1969) 4963.
- [24] D.J. Darensbourg and T.L. Brown, Inorg. Chem., 7 (1968) 959.
- [25] T.L. Brown and D.J. Darensbourg, Inorg. Chem., 6 (1967) 971.
- [26] F.A. Cotton and C.S. Kraihanzel, J. Am. Chem. Soc., 84 (1962) 4432.
- [27] S.F.A. Kettle and I. Paul, Inorg. Chim. Acta, 2 (1968) 15.
- [28] J.R. Miller, Inorg. Chim. Acta, 2 (1968) 421.
- [29] D.N. Kariuki and S.F.A. Kettle, J. Raman Spectrosc., 6 (1977) 319.
- [30] M.S. Davies, unpublished results, 1993.
- [31] J.C.A. Boeyens, F.A. Cotton and S. Han, Inorg. Chem., 24 (1985) 1750.
- [32] C. Jeanne, R. Pince and R. Poilblanc, Spectrochim. Acta, Part A, 31 (1975) 819.
- [33] G.R. Brubaker and D.W. Johnson, Coord. Chem. Rev., 53 (1984) 1.
- [34] N. Redouane, F. Vila, F. Chalier, G. Gronchi and P. Tordo, Phosphorus, Sulfur and Silicon, 77 (1993) 101.
- [35] J.P. Bowen and N.L. Allinger, J. Org. Chem., 52 (1987) 2937.
- [36] J.D. Andose and K. Mislow, J. Am. Chem. Soc., 96 (1974) 2168.
- [37] G. Bouquet and M. Bigorgne, Spectrochim. Acta, Part A, 23 (1967) 1231.
- [38] K.J. Lee and T.L. Brown, Inorg. Chem., 31 (1992) 289.
- [39] W. Schneider, W. Thiel and A. Komornicki, J. Phys. Chem., 92 (1988) 5611.
- [40] M. Bigorgne, A. Loutellier and M. Pankowski, J. Organomet. Chem., 23 (1970) 201.
- [41] S.G. Davies, A.E. Derome and J.P. McNally, J. Am. Chem. Soc., 113 (1991) 2854.
- [42] C. Pratt Brock and J.A. Ibers, Acta Crystallogr., Sect B, 29 (1973) 2426.
- [43] C. Barbeau and J. Turcotte, Can. J. Chem., 48 (1970) 3583.
- [44] C. Barbeau, L. Ricard and J. Turcotte, Can. J. Chem., 48 (1970) 1698.

- [45] C. Barbeau and J. Turcotte, Can. J. Chem., 54 (1976) 1612.
- [46] W. Strohmeier and H. Hellmann, Ber. Bunsenges. Phys. Chem., 68 (1964) 481.
- [47] M.J. Aroney, Angew. Chem., Int. Ed. Engl., 16 (1977) 663.
- [48] R.J.W. Le Fèvre, in V. Gold (Ed.), Advances in Physical Organic Chemistry, Vol. 3, Academic Press, London, 1965, p. 1.
- [49] F.A. Cotton, D.J. Darensbourg and B.W.S. Kolthammer, Inorg. Chem., 20 (1981) 4440.
- [50] M.J. Aroney and S.J. Pratten, J. Chem. Soc., Faraday Trans. 1, 80 (1984) 1201.
- [51] L. Onsager, J. Am. Chem. Soc., 58 (1936) 1486.
- [52] T. Halicioglu and O. Sinanoglu, Ann. N.Y. Acad. Sci., 158 (1969) 308.

- [53] D.L. Beveridge, M.M. Kelly and R.J. Radna, J. Am. Chem. Soc., 96 (1974) 3769.
- [54] S.C. Mackie and M.C. Baird, Organometallics, 11 (1992) 3712.
- [55] J. Polowin, S.C. Mackie and M.C. Baird, Organometallics 11 (1992) 3724.
- [56] E.E. Wille, D.S. Stephenson, P. Capriel and G. Binsch, J. Am. Chem. Soc., 104 (1982) 405.
- [57] D. Gust and K. Mislow, J. Am. Chem. Soc., 95 (1973) 1535.
- [58] J.A. Chudek, G. Hunter, R.L. MacKay, P. Kremminger, K. Schlögl and W. Weissensteiner, J. Chem. Soc., Dalton Trans., (1990) 2001.
- [59] E. Bye, W.B. Schweizer and J.D. Dunitz, J. Am. Chem. Soc., 104 (1982) 5893.

۱