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Metal–ligand bonding in $\text{LM}(\text{CO})_5$ complexes ($\text{L} = \text{NMe}_3, \text{PMe}_3, \text{PCl}_3, \text{PBr}_3$ or AsMe_3 ; $\text{M} = \text{Cr}, \text{Mo}$ or W) from dielectric, electro-optic and spectroscopic evidence

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Abstract

A comparative study has been made of the electric dipole moments, optical polarisability anisotropies (from electric birefringence measurements), infrared carbonyl stretching frequencies and ^{13}C NMR spectral shifts of $\text{LM}(\text{CO})_5$ complexes where $\text{L} = \text{NMe}_3, \text{PMe}_3, \text{PCl}_3, \text{PBr}_3$ or AsMe_3 and $\text{M} = \text{Cr}, \text{Mo}$ or W . Analysis of the polarisability anisotropies of the complexes provides direct, experimentally based evidence indicating a substantial π -component in the phosphorus–metal and arsenic–metal bonding in $\text{P}(\text{As})\text{Me}_3\text{M}(\text{CO})_5$ within a highly polarisable $\text{P}(\text{As})\text{–M–}(\text{trans})\text{CO}$ delocalised π -electron system. The L–M π -bonding appears not to be significantly affected by change of L from PMe_3 to AsMe_3 or by change of M within the chromium triad. It is shown that π -bonding between the phosphorus and the metal and electron delocalisation along the $\text{P–M–}(\text{trans})\text{CO}$ linkage are enhanced by electronegative halogen substituents in the phosphine ligand. The conclusions reached are in general accord with results from interpretation of the infrared and ^{13}C NMR spectral and dipole moment data.

1. Introduction

A wide range of techniques has been applied to exploration of the steric and electronic factors that affect metal–phosphorus bonding in transition metal phosphine complexes. A substantial number of references to such work has been collated by Giering *et al.* [1] and by Pacchioni and Bagus [2]. Some assessment of ligand steric effects has been afforded by estimation of “cone angles”, as obtained by Tolman [3] by measuring the dimensions of space-filling models for the free ligands. Deeper insight into the steric effects of ligands and the steric forces that operate in metal–ligand bonding interactions for $\text{LCr}(\text{CO})_5$ complexes has been provided by Brown and his coworkers [4–6] using molecular mechanics methods; the ligands L have a phosphorus or arsenic donor atom. The fundamental problem of separating the electronic factor in M–P or M–As bonding into σ - and π -components remains,

however, a contentious issue, complicated by the generally accepted synergism between the two mechanisms.

In recent work Wang, Richmond and Schwartz [7] derived from a comparative NMR relaxation time analysis, the oxygen-17 quadrupole coupling constants of $\text{NMe}_3\text{W}(\text{CO})_5$, $\text{PMe}_3\text{W}(\text{CO})_5$ and $\text{P}(\text{OMe})_3\text{W}(\text{CO})_5$, and related them to the π^* orbital populations in each of the carbonyls. They found that in these complexes PMe_3 behaves more like $\text{P}(\text{OMe})_3$ than NMe_3 , and they concluded PMe_3 is “a substantially stronger π -electron acceptor than the π -neutral amine ligand”. The π -back-bonding in phosphine ligands is generally understood to refer to the donation of electron charge from filled metal d orbitals into empty 3d orbitals of phosphorus [8]. Alternative models of π -back-bonding have been suggested by Marynick [9] and by Pacchioni and Bagus [2] on the basis of *ab initio* calculations, in which P–R antibonding σ^* orbitals act as acceptor orbitals in coordinated PR_3 , an effect which is enhanced by a combination of the antibonding orbitals with phosphorus d functions. Such results are in conflict with other work in which alkylphosphines have

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been reported to have weak or negligible π -acceptor capacity [10–12] or even to act in some cases as π -electron donors [13].

An experimental approach, not previously applied to such systems, was suggested in 1986 by Aroney *et al.* [14]. They interpreted the experimentally derived molecular optical polarisability anisotropy of $\text{PMe}_3\text{Cr}(\text{CO})_5$, relative to that of $\text{NMe}_3\text{Cr}(\text{CO})_5$, to indicate a highly polarisable π -component in Cr–P bonding for this molecule. The procedure is based on earlier work by Le Fèvre *et al.* [15–17] who showed that π -electrons are more polarisable than the relatively tightly bound σ -electrons, and that π -electron systems are particularly polarisable along the π -bond axis or, in the case of extended π -systems, along the delocalisation pathway.

The work now described is an extension of the earlier preliminary study [14]. It involves the determination from experimental electric birefringences of the molecular anisotropic polarisabilities of the complexes $\text{LM}(\text{CO})_5$ ($\text{L} = \text{PMe}_3, \text{PCl}_3, \text{PBr}_3$ or AsMe_3 ; $\text{M} = \text{Cr}, \text{Mo}$ or W) and comparison with the polarisabilities of analogous amine $\text{M}(\text{CO})_5$ complexes that are stable enough to be examined by these techniques. Results of comparative studies of the electric dipole moments, infrared active carbonyl vibrational modes and ^{13}C NMR chemical shifts are also presented.

2. Experimental details

The phosphorus and arsenic complexes $\text{LM}(\text{CO})_5$ were prepared by photolysis of $\text{M}(\text{CO})_6$ in tetrahydrofuran followed by addition of a stoichiometric equivalent of the ligand L under nitrogen [18]. The mixture was stirred for 2 h at room temperature with the exclusion of light, and the solvent removed *in vacuo*. Purification of $\text{PMe}_3\text{M}(\text{CO})_5$ and $\text{AsMe}_3\text{M}(\text{CO})_5$ complexes was achieved by column chromatography on activated flash silica. This was carried out in air but protected from light. Elution with hexane produced two colourless fractions; the first ($R_f \sim 0.8$) contained the unchanged metal hexacarbonyl and the second ($R_f \sim 0.3$) the $\text{LM}(\text{CO})_5$ complex. Trace amounts of *cis*- $\text{L}_2\text{M}(\text{CO})_4$ were obtained by subsequent elution with benzene.

The complexes $\text{PCl}_3\text{Cr}(\text{CO})_5$ and $\text{PBr}_3\text{Cr}(\text{CO})_5$ were purified by vacuum sublimation from room temperature to 40°C for approximately 24 h away from light, followed by recrystallisation from hexane at *ca.* -78°C . The analogous tungsten complexes were purified in the same manner, with the additional step that metal hexacarbonyl was removed by fractional recrystallisation at 0°C . The product was further purified by column chromatography; elution with hexane produced initially the

$\text{LM}(\text{CO})_5$ complex ($R_f \sim 0.8$) followed by disubstituted products. The tungsten complexes were observed to be less stable than their chromium analogues, necessitating storage under nitrogen at *ca.* 5°C .

The $\text{NMe}_3\text{M}(\text{CO})_5$ complexes were prepared by reaction of trimethylamine *N*-oxide with metal hexacarbonyl in dichloromethane at room temperature under nitrogen [19]. A pure product was obtained by using a two-fold excess of NMe_3O in the reaction and by separation on a silica column eluting with hexane. The complexes were found to decompose rapidly on the column, so once all the hexacarbonyl had been removed dichloromethane was added to elute the monosubstituted compound. The $\text{NMe}_3\text{Mo}(\text{CO})_5$ proved to be relatively unstable. Melting points for all compounds agreed with literature values.

Solute electric dipole moments μ and electric birefringences, the latter expressed as molar Kerr constants ${}_mK$, were determined in dilute cyclohexane solution at 298 K and for sodium D-light (589 nm). Dielectric polarisations and refractivities were obtained from measurements of relative permittivity (100 kHz), density and refractive index. Birefringence was electrically induced by application of a strong, static electric field to bring about a partial dynamic orientational ordering of molecules. Plane polarised light passed through the medium, emerged elliptically polarised; the effect was measured using a birefringent plate as compensator. The experimental procedures, symbols, and treatment of data are more fully described in refs. 20 and 21.

Infrared spectra were recorded on a Digilab FTS 20/80 Fourier transform infrared spectrometer for cyclopentane solutions having solute concentrations between 1 and 5 mM. NMR spectra were recorded on a Bruker AC 200F Fourier transform NMR spectrometer at operating frequencies of 200.13 MHz (^1H) and 50.329 MHz (^{13}C); all chemical shifts were measured at room temperature in C_6D_{12} solution and were referenced against the solvent ($\text{C}_6\text{HD}_{11}\text{H}$ taken as $\delta = 1.38$ ppm for ^1H , and C_6D_{12} $\delta = 26.4$ ppm for ^{13}C).

3. Results and discussion

3.1. Infrared spectra

Infrared carbonyl absorptions corresponding to two A_1 and E vibrational modes (C_{4v} local symmetry) [22] are shown in Table 1. Vibrations of B_1 symmetry, formally infrared forbidden but sometimes observed for such molecules, were not apparent for the phosphorus or arsenic complexes.

The A_{1eq} frequencies show only small variations within the range of NMe_3 , PMe_3 and AsMe_3 complexes studied. The equatorial A_1 carbonyl stretching frequency follows the order $\text{Cr} < \text{W} \leq \text{Mo}$, a sequence

TABLE 1. Infrared carbonyl stretching frequencies (cm⁻¹) for LM(CO)₅ complexes in cyclopentane solution^a

Complex	A _{1eq}	A _{1ax}	E
NMe ₃ Cr(CO) ₅	2067	1917	1934
NMe ₃ Mo(CO) ₅	2074	1918	1936
NMe ₃ W(CO) ₅	2072	1918	1930
PMe ₃ Cr(CO) ₅	2063	1949	1941
PMe ₃ Mo(CO) ₅	2071	1952	1945
PMe ₃ W(CO) ₅	2071	1947	1937
PCl ₃ Cr(CO) ₅	2088	2000	1983
PCl ₃ W(CO) ₅	2094	1994	1980
PBr ₃ Cr(CO) ₅	2085	1998	1983
PBr ₃ W(CO) ₅	2092	1991	1981
AsMe ₃ Cr(CO) ₅	2063	1946	1940
AsMe ₃ Mo(CO) ₅	2072	1948	1948
AsMe ₃ W(CO) ₅	2071	1943	1939

^a Uncertainty is ±0.5 cm⁻¹.

previously reported for other complexes of these metals [23,24]. The $\nu(\text{CO})A_{1eq}$ frequencies of $\text{PX}_3\text{M}(\text{CO})_5$ (M = Cr or W; X = Cl or Br) are noticeably higher ($23 \pm 2 \text{ cm}^{-1}$) than for the corresponding $\text{PMe}_3\text{M}(\text{CO})_5$ compounds, indicating an overall electron drift from the equatorial carbonyls when coordinated PMe_3 is replaced by PX_3 . The $\nu(\text{CO})A_{1ax}$ values show greater variation with change of ligand L than the equatorial frequencies. Three distinct groupings are observed: at 1917–1918 cm⁻¹ for the NMe₃ complexes, at 1943–1952 cm⁻¹ for the PMe₃ and AsMe₃ complexes, and at 1991–2000 cm⁻¹ for the PX₃ complexes. The relative order of $\nu(\text{CO})A_{1ax}$ is consistent with the assumption of an M–P (or M–As) bond order greater than that for the σ -bonded M–N system in the LM(CO)₅ complexes, an effect especially evident in the $\text{PX}_3\text{M}(\text{CO})_5$ complexes.

3.2. ¹³C NMR spectra

The methyl carbon resonances in the $\text{EMe}_3\text{M}(\text{CO})_5$ complexes are increasingly shielded as E is changed

from nitrogen to phosphorus to arsenic, a sequence which Bodner *et al.* [26] have tried to correlate with the electronegativity and the atomic number of the donor atom E. From the data in Table 2 it is seen that the $\delta(^{13}\text{CO})$ values increase in the order $\text{NMe}_3 < \text{PMe}_3 \sim \text{AsMe}_3$ for a given metal M; for each complex $\delta(^{13}\text{CO})_{ax} > \delta(^{13}\text{CO})_{eq}$; and $\delta(^{13}\text{CO})$ decreases in the order $\text{Cr} > \text{Mo} > \text{W}$. The trends now found are generally in agreement with results for similar (though usually not identical) compounds that have been reported previously and discussed in terms of charge-donor abilities of the ligands L and CO in LM(CO)₅ and of the relative metal π -donor strength within the triad [27–29].

It is seen also that replacement of PMe_3 by PX_3 leads to upfield shifts in the carbonyl ¹³C resonances. The latter effect has been interpreted by Vincent *et al.* [30] to indicate a contraction of the phosphorus 3d orbitals under the influence of the electronegative halogen atoms. This results in an increase in the π -acceptor capacity of P and in turn a decrease in the metal–carbonyl π -bonding. The $^2J(^{13}\text{C}–\text{M}–^{31}\text{P})$ coupling constants agree reasonably with comparable values in refs. 25, 28 and 31 despite the change in solvent from CDCl₃. Large values of the through-metal couplings *trans* $^2J(^{13}\text{C}–\text{W}–^{31}\text{P})$ are observed for phosphorus trihalide complexes in accordance with that reported for $\text{PCl}_3\text{Mo}(\text{CO})_5$ by Bodner *et al.* [28].

3.3. Electric dipole moments

The dipole moments in column 2 of Table 3 are seen to vary over a wide range, depending mainly on the nature of the ligand L in LM(CO)₅. The complexes $\text{EMe}_3\text{M}(\text{CO})_5$ have μ values within the range 16.9–19.5 ($\times 10^{-30}$ Cm) while the phosphorus trihalide complexes have much lower moments, in the vicinity of 3×10^{-30} Cm. On a simple vector additivity model, replacement of PMe_3 in $\text{PMe}_3\text{Cr}(\text{CO})_5$ by PCl_3 results

TABLE 2. ¹³C NMR chemical shifts (ppm) and coupling constants (Hz) for LM(CO)₅ complexes in C₆D₁₂ solution^a

Complex	$\delta(^{13}\text{CH}_3)$	$^1J(^{13}\text{C}–^{31}\text{P})$	$\delta(^{13}\text{CO})_{eq}$	$^2J(^{13}\text{C}–\text{M}–^{31}\text{P}(\text{cis}))$	$\delta(^{13}\text{CO})_{ax}$	$^2J(^{13}\text{C}–\text{M}–^{31}\text{P}(\text{trans}))$	$^1J(^{13}\text{C}–^{183}\text{W}(\text{cis}))$
NMe ₃ Cr(CO) ₅	60.0s	–	214.2s	–	217.7s	–	–
NMe ₃ W(CO) ₅	61.8s	–	199.9s	–	200.2s	–	–
PMe ₃ Cr(CO) ₅	20.3d	25.2	217.6d	14.1	220.7d	8.6	–
PMe ₃ Mo(CO) ₅	21.0d	24.2	206.3d	9.5	209.5s ^b	20.1 ^b	–
PMe ₃ W(CO) ₅	21.6d	22.9	197.3d	5.6	199.1d	15.8	–
PCl ₃ Cr(CO) ₅	–	–	213.3d	16.6	217.7d	4.1	–
PCl ₃ W(CO) ₅	–	–	193.9d	9.0	197.0d	65.0	126.4
PBr ₃ Cr(CO) ₅	–	–	213.3d	14.2	218.1d	5.1	–
PBr ₃ W(CO) ₅	–	–	195.5d	7.6	196.8d	65.7	129.0
AsMe ₃ Cr(CO) ₅	14.4s	–	217.4s	–	221.6s	–	–
AsMe ₃ Mo(CO) ₅	15.3s	–	206.2s	–	210.2s	–	–
AsMe ₃ W(CO) ₅	15.6s	–	197.1s	–	199.1s	–	–

^a Signs of the coupling constants were not determined.^b The doublet was unresolved in our spectrum; Guns *et al.* [25] have reported $\delta(^{13}\text{CO})_{ax}$ as 210.7 ppm and $^2J(^{13}\text{C}–\text{Mo}–^{31}\text{P}(\text{trans}))$ as 20.1 Hz.

TABLE 3. Electric dipole moments, molar Kerr constants and molecular polarisability anisotropies of solutes at infinite dilution in cyclohexane at $T = 298$ K and $\lambda = 589$ nm^a

Solute	$10^{30}\mu$ ^{b,c} (Cm)	$10^{27}({}_mK)$ ^d (m ⁵ V ⁻² mol ⁻¹)	$10^{40}\Gamma$ ^e (Cm ² V ⁻¹)
NMe ₃ Cr(CO) ₅ ^f	16.9 ± 0.1	-1505 ± 15	-5.36 ± 0.05
NMe ₃ W(CO) ₅ ^f	19.5 ± 0.1	-2410 ± 35	-6.44 ± 0.09
PMe ₃ Cr(CO) ₅	16.9 ± 0.2	-58 ± 1	-0.21 ± 0.01
PMe ₃ Mo(CO) ₅	17.3 ± 0.1	-192 ± 6	-0.65 ± 0.02
PMe ₃ W(CO) ₅	17.7 ± 0.1	-218 ± 6	-0.70 ± 0.02
PCl ₃ Cr(CO) ₅	2.80 ± 0.33	15.4 ± 1.0	1.79 ± 0.11
PCl ₃ W(CO) ₅	2.80 ± 0.27	11.9 ± 0.7	1.41 ± 0.09
PBr ₃ Cr(CO) ₅	2.87 ± 0.20	18.8 ± 1.8	2.07 ± 0.20
PBr ₃ W(CO) ₅	3.20 ± 0.17	32.6 ± 0.8	2.85 ± 0.08
AsMe ₃ Cr(CO) ₅	17.0 ± 0.1	36.7 ± 2.2	0.12 ± 0.01
AsMe ₃ Mo(CO) ₅	17.4 ± 0.3	-121 ± 2	-0.40 ± 0.01
AsMe ₃ W(CO) ₅	17.9 ± 0.1	-131 ± 2	-0.41 ± 0.01
PCl ₃	3.04 ± 0.13	-7.7 ± 0.2	-0.87 ± 0.02
PBr ₃ ^g	2.2 ± 0.4	-	-

^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 Cm = 0.2998 × 10³⁰ D, 1 m⁵ V⁻² mol⁻¹ = 0.8988 × 10¹⁵ e.s.u. mol⁻¹, 1 Cm² V⁻¹ = 0.8988 × 10¹⁶ cm³.

^b Determined by the refractivity method on the basis that the molar distortion polarisation is equal to 1.05 times the molecular sodium D-line refractivity [21].

^c The dipole moments of PBr₃Cr(CO)₅ and PBr₃W(CO)₅ have earlier been reported as 2.90 ± 0.33 and 3.34 ± 0.33 (× 10⁻³⁰ Cm) respectively [32]; the other P and As complexes have not previously been studied. The moments of PCl₃ and PBr₃ are in agreement with μ values in ref. 33.

^d $({}_mK)$ designates the solute molar Kerr constant at infinite dilution.

^e Solution of the quadratic eqn. 1 results in an alternative Γ value for each of the compounds studied. For the NMe₃, PMe₃ and AsMe₃ complexes these solutions have no physical reality; for the phosphorus trihalide complexes they are highly unlikely [34].

^f Data from ref. 24.

^g Kerr constants could not be measured because PBr₃ solutions discharged in the Kerr cell.

in an estimated dipole moment for PCl₃Cr(CO)₅ in the region of 9.9×10^{-30} Cm. This is obtained as $\mu[\text{PMe}_3\text{Cr}(\text{CO})_5] - \mu(\text{PMe}_3) + \mu(\text{PCl}_3)$ and takes no account of possible electron charge rearrangements following such a ligand substitution. The dipole moment of PMe₃ is 3.97×10^{-30} Cm [35]; the assumption was made in the calculation that the dipole vector for this molecule is directed towards the P atom. If the sense of the PMe₃ dipole vector was reversed, then the predicted moment for PCl₃Cr(CO)₅ would be 17.8×10^{-30} Cm. In either case, the calculated dipole moment for PCl₃Cr(CO)₅ is of a higher order of magnitude than the experimental value. This is also found for the other three phosphorus trihalide complexes of this study. The results provide strong evidence for the withdrawal of electron charge from Cr(CO)₅ into the coordinated PCl₃ and PBr₃ ligands, a ground-state

effect directly attributable to the high electronegativity of the halogen atoms. This reinforces the conclusions from the IR and ¹³C NMR spectra and demonstrates the importance of the substituents on phosphorus for the π -acceptor capability of the phosphine ligand.

3.4. Molecular anisotropic polarisabilities

The experimental molar Kerr constants of column 3 in Table 3 show the acute sensitivity of the Kerr effect to both the molecular dipole moment and to the directional electronic properties. Particularly worthy of note is the large disparity in $_mK$ between the PMe₃ and AsMe₃ complexes and those of NMe₃, even though the dipole moments are not greatly different. For each of the molecules studied, the polarisability tensor is one of revolution with principal electron polarisabilities b_1 (along the molecular dipole axis) and $b_2 = b_3$ (mutually perpendicular to that axis). The molecular polarisability anisotropy Γ , defined as $(b_1 - b_2)$, is extracted from the experimental quantities using the Langevin–Born–Le Fèvre relation (eqn. 1) [15]:

$${}_mK = (N/405kT\epsilon_0) \left[({}_D P / {}_E P) \Gamma^2 + (kT)^{-1} \mu^2 \Gamma \right] \quad (1)$$

where $_D P$, $_E P$, N , k , T and ϵ_0 refer in turn to the molar distortion polarisation, the molar electron polarisation, Avogadro's number, the Boltzmann constant, the absolute temperature and the permittivity of a vacuum. The ratio $_D P / {}_E P$ is 1.09 for PCl₃ [36]; it was taken as 1.1 for the other compounds, which is a sufficiently good approximation for this work [37].

The molecular anisotropies Γ so derived are shown in column 4 of Table 3. An initial observation is that the six PMe₃ and AsMe₃ complexes studied have very low anisotropies, with small increases in $|\Gamma|$ going down the group from Cr to W. The NMe₃Cr(CO)₅ and NMe₃W(CO)₅ complexes (and for that matter the quinuclidineM(CO)₅ complexes for the triad) have large negative Γ values [24], indicating that for each of these the molecular polarisability b_1 along the dipole axis is much smaller than the polarisabilities b_2 and b_3 parallel to the plane of the four equatorial carbonyl groups. Replacement of coordinated NMe₃ in the complexes by PMe₃ or AsMe₃ results in a large augmentation of polarisability predominantly in the direction of the molecular L–M–(*trans*)CO axis, so that the complexes tend to become near optically isotropic. The differences in Γ between the P and As complexes and those of N are too great to be explained in terms of variations in the σ -characteristics of P(As)–M bonds relative to those of the corresponding N–M bonds. Nor can they be attributed to differences in the anisotropies of the NMe₃, PMe₃ and AsMe₃ groups; for the free

ligand molecules Γ is respectively -0.32 , -0.73 and -0.81 ($\times 10^{-40}$ Cm² V⁻¹) [35,38].

The experimental Γ values for the PMe₃ and AsMe₃ complexes are now compared with $\Gamma(\sigma)$ values predicted for a σ -bonded metal–phosphorus or metal–arsenic model. The procedure, based on segment polarisability additivity, is similar in principle to that applied to pyridine M(CO)₅ complexes [24]. For example, $\Gamma(\sigma)$ for PMe₃Cr(CO)₅ is predicted to be given to a reasonable approximation by $\Gamma(\text{exp.})\text{NMe}_3\text{Cr(CO)}_5 - \Gamma(\text{exp.})\text{NMe}_3 + \Gamma(\text{exp.})\text{PMe}_3$. The values $\Gamma(\sigma)$ so derived are compared with the experimental molecular anisotropies in Table 4.

For each of the six complexes $\Delta\Gamma$, defined as $\Gamma(\text{exp.}) - \Gamma(\sigma)$, is large and positive, with values ranging from $5.2 - 6.5$ ($\times 10^{-40}$ Cm² V⁻¹). The differences between the $\Delta\Gamma$ values are not significant since they are comparable with the expected uncertainties. The results show that in each case bonding interaction between PMe₃ (or AsMe₃) and M(CO)₅ fragments produces a molecular system with a greatly enhanced polarisability along the P(As)–M–(trans)CO axis, relative to a model in which the which the two “isolated” groupings are connected by a P(As)–M bond with purely σ -character.

Further analysis can be undertaken to evaluate the directional molecular polarisabilities. The sum Σb_i can be obtained from the molar electron polarisation using the Lorentz–Lorenz relation (eqn. 2) [15]. Thus, by using also $\Gamma(\text{exp.})$, it is easy to obtain the experimental b_i parameters shown in column 5 of Table 4. The $b_i(\sigma)$ values in column 6 were derived using the corresponding $\Gamma(\sigma)$ and are appropriate for a P(As)–M σ -bonded

model. Differences $\Delta b_i = b_i(\text{exp.}) - b_i(\sigma)$ are given in column 7.

$${}_E P = N(b_1 + 2b_2)/9\epsilon_0 \quad (2)$$

In each case, a strong polarisability enhancement is seen to occur along the molecular symmetry axis, with a concomitant fall in the transverse molecular polarisabilities. Such behaviour is classically characteristic of conjugated or delocalised π -electron systems, from the work of Le Fèvre *et al.* [15–17]. In this regard the present study provides strong evidence for π -character in the P–M and As–M bonds and for conjugative interactions along the P(As)–M–(trans)CO axis.

Finally, in Table 5 comparison is made between the anisotropic polarisabilities of complexes PMe₃M(CO)₅ and those of their phosphorus trihalide analogues. The experimental b_i values are given in column 2. Parameters designated $b_i(\text{calc.})$ for the PX₃ complexes in column 3 were obtained as $b_i(\text{exp.})\text{PMe}_3\text{M(CO)}_5 - b_i(\text{exp.})\text{PMe}_3 + b_i(\text{exp.})\text{PX}_3$, *i.e.* by making allowance for the intrinsic anisotropy difference between the PMe₃ and PX₃ groupings.

In all cases b_1 from experiment exceeds that predicted from segment additivity, while the experimental and calculated b_2 values are in reasonable agreement. The results clearly show enhanced polarisability along the molecular symmetry axis induced by the highly electronegative halogens bonded to phosphorus.

From this work, a consistent picture has emerged that embraces a range of LM(CO)₅ complexes. Analysis of the Kerr effect provides conclusions which are generally in accord with, and reinforce, results from the infrared and ¹³C NMR spectra and from electric

TABLE 4. Comparison of experimental molecular polarisability parameters for PMe₃M(CO)₅ and AsMe₃M(CO)₅ complexes with values predicted on the basis of a P–M or As–M σ -bonded model

Complex	$10^{40}\Gamma(\text{exp.})$ (Cm ² V ⁻¹)	$10^{40}\Gamma(\sigma)$ (Cm ² V ⁻¹)	$10^{40}\Delta\Gamma$ (Cm ² V ⁻¹)	$10^{40}b_i(\text{exp.})^a$ (Cm ² V ⁻¹)	$10^{40}b_i(\sigma)$ (Cm ² V ⁻¹)	$10^{40}\Delta b_i$ (Cm ² V ⁻¹)
PMe ₃ Cr(CO) ₅	-0.21	-5.8	5.6	$b_1 = 29.6$ $b_2 = 29.8$	25.8 31.6	$\Delta b_1 = 3.8$ $\Delta b_2 = -1.8$
PMe ₃ Mo(CO) ₅	-0.65	-5.8 ^b	5.2	$b_1 = 33.0$ $b_2 = 33.7$	29.6 35.4	$\Delta b_1 = 3.4$ $\Delta b_2 = -1.7$
PMe ₃ W(CO) ₅	-0.70	-6.8	6.1	$b_1 = 33.1$ $b_2 = 33.8$	29.1 35.9	$\Delta b_1 = 4.0$ $\Delta b_2 = -2.1$
AsMe ₃ Cr(CO) ₅	0.12	-5.9	6.0	$b_1 = 30.4$ $b_2 = 30.3$	26.4 32.3	$\Delta b_1 = 4.0$ $\Delta b_2 = -2.0$
AsMe ₃ Mo(CO) ₅	-0.40	-5.9 ^b	5.5	$b_1 = 32.0$ $b_2 = 32.4$	28.4 34.3	$\Delta b_1 = 3.6$ $\Delta b_2 = -1.9$
AsMe ₃ W(CO) ₅	-0.41	-6.9	6.5	$b_1 = 33.2$ $b_2 = 33.6$	28.9 35.8	$\Delta b_1 = 4.3$ $\Delta b_2 = -2.2$

^a Σb_i values were obtained from the following molar electron polarisations, given in sequence down the column from PMe₃Cr(CO)₅ to AsMe₃W(CO)₅: 67.4, 75.9, 76.1, 68.8, 73.2, and 75.9 (cm³) [34].

^b Since Kerr constant measurements could not be made for NMe₃Mo(CO)₅, estimates of $\Gamma(\sigma)$ for PMe₃Mo(CO)₅ and AsMe₃Mo(CO)₅ were based on experimental Γ values of the quinuclidineMo(CO)₅ complex and free quinuclidine from ref. 24.

TABLE 5. Anisotropic polarisabilities of complexes PX₃M(CO)₅ (X = Cl or Br) in relation to the PMe₃M(CO)₅ analogues

Complex	10 ⁴⁰ b _i (exp.) ^a (Cm ² V ⁻¹)	10 ⁴⁰ b _i (calc.) (Cm ² V ⁻¹)
PMe ₃ Cr(CO) ₅	b ₁ = 29.6 b ₂ = 29.8	–
PCl ₃ Cr(CO) ₅	b ₁ = 32.3 b ₂ = 30.5	29.9 30.3
PBr ₃ Cr(CO) ₅	b ₁ = 37.0 b ₂ = 34.9	32.8 ^b 34.3 ^b
PMe ₃ W(CO) ₅	b ₁ = 33.1 b ₂ = 33.8	–
PCl ₃ W(CO) ₅	b ₁ = 35.8 b ₂ = 34.4	33.4 34.3
PBr ₃ W(CO) ₅	b ₁ = 41.5 b ₂ = 38.7	36.3 ^b 38.3 ^b

^a Σb_i for the PX₃M(CO)₅ complexes were obtained from the following ϵ_P values: 70.5, 80.7, 79.0 and 89.9 (cm³) respectively, for PCl₃Cr(CO)₅, PBr₃Cr(CO)₅, PCl₃W(CO)₅ and PBr₃W(CO)₅ [34].

^b An approximate estimate of Γ PBr₃ was obtained as $-2(\times 10^{-40}$ Cm² V⁻¹) from Γ PCl₃ plus the difference in Γ between CHCl₃ and CHBr₃ [39]. The results are not sensitively dependent on this approximation. A one hundred percent error in this estimate of Γ PBr₃ affects b₁ (calc.) for each PX₃M(CO)₅ by $\pm 0.7(\times 10^{-40}$ Cm² V⁻¹) and b₂(calc.) by $\pm 0.4(\times 10^{-40}$ Cm² V⁻¹).

dipole moments. Direct evidence from experiment is presented to indicate a substantial π -component for phosphorus–metal and arsenic–metal bonding in P(As)Me₃M(CO)₅ within a highly polarisable P(As)–M–(trans)CO delocalised π -electron system. The L–M π -bonding, arising from overlaps between filled metal d orbitals and d or σ^* π -acceptor orbitals of L, appears not to be sensitively affected by change of L from PMe₃ to AsMe₃ or by change in M within the chromium triad. It is shown that π -bonding between phosphorus and metal and electron delocalisation along P–M–(trans)CO are enhanced by the presence of electronegative halogen substituents in the phosphine ligand.

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