

## ANISOTROPIC OPTICAL POLARISABILITIES OF THE COMPLEXES $\text{LCr}(\text{CO})_5$ (L = $\text{PMe}_3$ , $\text{NMe}_3$ or $\text{NH}_3$ ): A STUDY OF $\pi$ -BACK-BONDING

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### Summary

Dipole moments and electric birefringences are reported for the complexes  $\text{LCr}(\text{CO})_5$  where L is  $\text{PMe}_3$ ,  $\text{NMe}_3$  or  $\text{NH}_3$ . Comparison of the molecular optical polarisability anisotropies of  $\text{PMe}_3\text{Cr}(\text{CO})_5$  and  $\text{NMe}_3\text{Cr}(\text{CO})_5$  shows a large enhancement of polarisability specifically in the L-Cr-(*trans*)CO direction for the phosphorus compound; the polarisabilities perpendicular to the symmetry axis are closely similar for the two complexes. The results are interpreted as direct evidence for a highly deformable  $\pi$ -component in P-Cr bonding. This work presents a new experimental approach to the study of  $\pi$ -back-bonding.

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### Introduction

Metal to ligand  $\pi$ -bonding was originally invoked to account for the stability of complexes in which the metal is in a low formal oxidation state [1]. It was used to explain how negative charge, accumulated from ligand to metal  $\sigma$ -donation, could be delocalised away from the metal, and how strong overall bonds could be formed between metals and ligands of low basicity such as CO. The forward  $\sigma$ - and  $\pi$ -back-bonding were regarded as mutually reinforcing [2,3]. Though the concept has been widely applied, the reality and the extent of  $\pi$ -back-donation in metal-ligand bond formation remains a subject of great interest and controversy [1,2,4–13]. Many experimental techniques have been used to probe the validity or otherwise of back-donation, notably X-ray crystallographic determination of metal-ligand bond distances, dipole moments, vibrational, NMR and photoelectron spectroscopy; a substantive review is included in ref. 1. The investigations have given rise to conflicting results. Frequently experimental facts which have been interpreted as providing evidence for  $\pi$ -back-bonding, have subsequently been rationalised in a different or even opposite manner. Despite some deeper insight from recent theoretical [14–16] and photoelectron spectral [17,18] studies (which are generally consistent with the  $\pi$ -back-bonding scheme), current knowledge and understanding of metal-ligand  $\pi$ -charge transfer is limited and imperfect.

Ideally an experimental technique is needed which can probe the  $\pi$ -bonding system in comparative isolation from that of the  $\sigma$ -electrons. In this regard it was thought that a study of the directional optical polarisabilities of metal–ligand containing molecules might provide information relevant to this problem since it is known that in a multiple bonded system, electrons in  $\pi$ -molecular orbitals are more weakly bound and hence much more polarisable than electrons constrained in  $\sigma$ -bonds [19]. In this work, a comparative study is undertaken of the optical polarisabilities of the complexes  $\text{PMe}_3\text{Cr}(\text{CO})_5$ ,  $\text{NMe}_3\text{Cr}(\text{CO})_5$  and  $\text{NH}_3\text{Cr}(\text{CO})_5$ , derived from electric birefringence measurements [19,20], to explore whether such comparisons will reveal differences in electronic behaviour relatable to the  $\pi$ -acceptor potential of  $\text{PMe}_3$ .

## Experimental

The complexes  $\text{PMe}_3\text{Cr}(\text{CO})_5$  and  $\text{NMe}_3\text{Cr}(\text{CO})_5$  were synthesised via the intermediate  $\text{THFCr}(\text{CO})_5$  [21,22] which was prepared by the UV irradiation of a solution of  $\text{Cr}(\text{CO})_6$  in oxygen-free tetrahydrofuran (THF). Repeated sublimation gave melting points of 60 and 76°C, respectively, in agreement with literature values [22,23]. Cyclohexane was fractionated and stored over sodium; appropriate physical constants for the solvent are given in ref. 24.

Solute dipole moments  $\mu$  and electric birefringences, the latter expressed as molar Kerr constants  ${}_mK$ , were determined at 298 K and for light of 589 nm. The apparatus, techniques of measurement, symbols and analysis of data have been described before [20,24,25]. Oxygen was removed from the solvent by saturating it with dry nitrogen. The preparation and handling of solutions were carried out under dry, inert ( $\text{N}_2$ ) atmosphere. The results are summarised in Table 1 which also includes corresponding experimental quantities for  $\text{NH}_3\text{Cr}(\text{CO})_5$  in dioxane solution (quoted from ref. 26).  $^1\text{H}$  NMR spectra were recorded using a Bruker WM 400 NMR spectrometer; TMS was used as internal reference.

## Discussion

The electric dipole moments of the complexes  $\text{LCr}(\text{CO})_5$  decrease with different ligands L in the order:  $\text{NH}_3 > \text{NMe}_3 > \text{PMe}_3$ . Both  $\text{NH}_3$  and  $\text{NMe}_3$  function only as electron-donors so it is reasonable to expect that the dipole moment is directed from the ligand  $\text{NH}_3$  or  $\text{NMe}_3$ , towards the *trans*-CO group. According to the concept of  $\pi$ -back-bonding, replacement of one CO in  $\text{Cr}(\text{CO})_6$  by  $\text{NH}_3$  or  $\text{NMe}_3$  should result in the *trans*-CO accepting more electron density from the chromium atom [2] and this would enhance the overall moments of  $\text{NH}_3\text{Cr}(\text{CO})_5$  and  $\text{NMe}_3\text{Cr}(\text{CO})_5$ . The complex  $\text{PMe}_3\text{Cr}(\text{CO})_5$  has a dipole moment of  $16.1 \times 10^{-30}$  Cm which is slightly lower than the moment of  $16.9 \times 10^{-30}$  Cm found for  $\text{NMe}_3\text{Cr}(\text{CO})_5$ . Comparison with the dipole moments of borane complexes: 16.8, 15.6–16.0, and  $16.6 (\times 10^{-30})$  Cm for  $\text{NH}_3\text{BH}_3$ ,  $\text{NMe}_3\text{BH}_3$  and  $\text{PMe}_3\text{BH}_3$ , respectively [27], suggests that in  $\text{PMe}_3\text{Cr}(\text{CO})_5$  the electron drift from P towards *trans*-CO is less than expected for a  $\sigma$ -bonding model alone. The sense of the molecular dipole vector is verified by studying the solvent dependence of the  $^1\text{H}$  NMR chemical shifts:  $\delta(\text{C}_6\text{D}_{12})$  1.44 ppm and  $\delta(\text{C}_6\text{D}_6)$  0.72 ppm for  $\text{PMe}_3\text{Cr}(\text{CO})_5$ ;  $\delta(\text{C}_6\text{D}_{12})$  2.50 ppm and  $\delta(\text{C}_6\text{D}_6)$  1.65 ppm for  $\text{NMe}_3\text{Cr}(\text{CO})_5$ . In each case the

TABLE 1  
 MOLAR POLARISATIONS AND REFRACTIONS, DIPOLE MOMENTS AND MOLAR KERR CONSTANTS OF COMPLEXES  $\text{LCr}(\text{CO})_5$  ( $\text{L} = \text{PMe}_3, \text{NMe}_3$  or  $\text{NH}_3$ ) FROM MEASUREMENTS<sup>a</sup> IN SOLUTION AT  $T$  298 K AND  $\lambda$  589 nm

Solute	Solvent	$\alpha\epsilon_1$	$\beta$	$\gamma$	$\delta$	$\infty P_2$ ( $\text{cm}^3$ )	$R_D$ ( $\text{cm}^3$ )	$10^{30} \mu^{b,c}$ (Cm)	$10^{27} \infty(mK_2)^{c,d}$ ( $\text{m}^5 \text{V}^{-2} \text{mol}^{-1}$ )
$\text{PMe}_3\text{Cr}(\text{CO})_5$	cyclohexane	7.76	0.377	0.061	-8.8	554	70.8	$16.1 \pm 0.2$	$-48 \pm 4$
$\text{NMe}_3\text{Cr}(\text{CO})_5$	cyclohexane	9.08	0.355	0.053	-398	600	66.1	$16.9 \pm 0.1$	$-1505 \pm 15$
$\text{NH}_3\text{Cr}(\text{CO})_5^e$	dioxane	23.0	0.278	0.114	-943	834	54.6	$20.5 \pm 0.3$	$-2570 \pm 78$

<sup>a</sup> For each compound incremental changes in the relative permittivities, densities, refractive indices and Kerr constants ( $\Delta\epsilon$ ,  $\Delta d$ ,  $\Delta n$  and  $\Delta B$ , respectively) were measured for a range of solutions having solute weight fractions  $w_2$ . Coefficients  $\alpha\epsilon_1$ ,  $\beta$ ,  $\gamma$  and  $\delta$  were derived from the measured quantities using the relations:  $\alpha\epsilon_1 = \Sigma \Delta\epsilon / \Sigma w_2$ ;  $\beta = \Sigma \Delta d / d_1 \Sigma w_2$ ;  $\gamma = \Sigma \Delta n / n_1 \Sigma w_2$ ;  $\delta = \Sigma \Delta B / b_1 \Sigma w_2$ . The subscripts 1 and 2 refer in turn to the solvent and solute. <sup>b</sup> Dipole moments were derived on the basis that the molar distortion polarisation equals  $1.05 R_D$ . <sup>c</sup> Dipole moments and molar Kerr constants are given in SI units. The conversion factors from the electrostatic (c.g.s., e.s.u.) system are, respectively:  $1 \text{ Cm} = 0.2998 \times 10^{30} \text{ D}$ ,  $1 \text{ m}^5 \text{V}^{-2} \text{mol}^{-1} = 0.8988 \times 10^{15} \text{ e.s.u. mol}^{-1}$ . <sup>d</sup> The term  $\infty(mK_2)$  refers to the solute molar Kerr constant at infinite dilution. <sup>e</sup> Measured values for  $\text{NH}_3\text{Cr}(\text{CO})_5$  are quoted from ref. 26.

TABLE 2

MOLECULAR POLARISABILITY ANISOTROPIES  $10^{40}\Gamma$  ( $\text{Cm}^2 \text{V}^{-1}$ )<sup>a</sup> AND PRINCIPAL POLARISABILITIES  $10^{40}b_i$  ( $\text{Cm}^2 \text{V}^{-1}$ )<sup>a</sup> OF  $\text{PMe}_3\text{Cr}(\text{CO})_5$ ,  $\text{NMe}_3\text{Cr}(\text{CO})_5$ ,  $\text{NH}_3\text{Cr}(\text{CO})_5$ ,  $\text{Cr}(\text{CO})_6$ ,  $\text{PMe}_3$ ,  $\text{NMe}_3$  AND  $\text{NH}_3$

Solute	$\Gamma$	$b_1$	$b_2 = b_3$
$\text{PMe}_3\text{Cr}(\text{CO})_5$	$-0.2 \pm 0.1$	$29.5 \pm 0.1$	$29.7 \pm 0.1$
$\text{NMe}_3\text{Cr}(\text{CO})_5$	$-5.4 \pm 0.1$	$24.1 \pm 0.1$	$29.5 \pm 0.1$
$\text{NH}_3\text{Cr}(\text{CO})_5$	$-6.2 \pm 0.5$	$18.8 \pm 0.2$	$24.9 \pm 0.4$
$\text{Cr}(\text{CO})_6$ <sup>b</sup>	0	$22.7 \pm 0.3$	$22.7 \pm 0.3$
$\text{PMe}_3$ <sup>c</sup>	-0.7	10.3	11.0 <sub>5</sub>
$\text{NMe}_3$ <sup>d</sup>	$-0.32 \pm 0.05$	$8.31 \pm 0.03$	$8.63 \pm 0.02$
$\text{NH}_3$ <sup>d</sup>	$0.42 \pm 0.09$	$2.68 \pm 0.06$	$2.26 \pm 0.03$

<sup>a</sup> Expressed in SI units; the conversion factor to the c.g.s., e.s.u. system is:  $1 \text{ Cm}^2 \text{V}^{-1} = 0.8988 \times 10^{16} \text{ cm}^3$ . <sup>b</sup> Derived from the experimental  $R_D = 51.4 \pm 0.6 \text{ cm}^3$  [31]. <sup>c</sup> From ref. 32. <sup>d</sup> From ref. 33.

methyl proton resonances experience large upfield changes of chemical shift in the aromatic solvent:  $\Delta\delta$ , defined as  $\delta(\text{C}_6\text{D}_{12}) - \delta(\text{C}_6\text{D}_6)$ , is 0.72 ppm for  $\text{PMe}_3\text{Cr}(\text{CO})_5$  and 0.85 ppm for  $\text{NMe}_3\text{Cr}(\text{CO})_5$ . The benzene shielding results from statistically favoured stereospecific attractive interactions between the benzene  $\pi$ -electrons and the electrophilic methyl protons located near the positive end of the solute dipole [28,29].

The experimental molar Kerr constants, unlike the dipole moments, differ greatly between the complexes  $\text{NMe}_3\text{Cr}(\text{CO})_5$  and  $\text{PMe}_3\text{Cr}(\text{CO})_5$ . This reflects in most part a large difference in the molecular optical polarisability anisotropies  $\Gamma$  of the two compounds.  $\Gamma$  is defined as  $b_1 - b_2$ , i.e. the difference between the molecular polarisability in the direction of the dipole axis 1 and the polarisability perpendicular to that axis [19]. From symmetry it follows that  $b_2 = b_3$ .  $\Gamma$  can be obtained from the molar Kerr constant using the Le Fèvre modified Langevin-Born equation (eq. 1) [19,20].

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

The terms  ${}_D P$ ,  ${}_E P$ ,  $N$ ,  $k$ ,  $T$  and  $\epsilon_0$  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. In each case  ${}_E P$  was taken as  $0.95 R_D$ , and the ratio  ${}_D P / {}_E P$  as 1.1 [20,30]. Values of  $\Gamma$  for  $\text{PMe}_3\text{Cr}(\text{CO})_5$  and  $\text{NMe}_3\text{Cr}(\text{CO})_5$  are given in Table 2 together with the optical anisotropies of  $\text{NH}_3\text{Cr}(\text{CO})_5$ ,  $\text{Cr}(\text{CO})_6$ ,  $\text{NMe}_3$ ,  $\text{PMe}_3$  and  $\text{NH}_3$ , which are included for comparison. Principal optical polarisabilities are also listed (columns 3 and 4); these were derived using  $\Gamma$  and the Lorentz-Lorenz relation (eq. 2) [24].

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

The free ligands L (=  $\text{PMe}_3$ ,  $\text{NMe}_3$  and  $\text{NH}_3$ ) are near isotropically polarisable having small measured molecular polarisability anisotropies  $10^{40} \Gamma$  ( $\text{Cm}^2 \text{V}^{-1}$ ) of  $-0.7$ ,  $-0.32$  and  $0.42$ , respectively\*. When coordinated with  $\text{Cr}(\text{CO})_5$ , however,

\* The molecular  $\Gamma$  values for the free ligands L would include small anisotropy contributions from the P or N lone pair electrons; this does not detract from the subsequent interpretation.

the resulting complexes  $\text{LCr}(\text{CO})_5$  exhibit large differences in  $10^{40} \Gamma$  ( $\text{Cm}^2 \text{V}^{-1}$ ) between the amine complexes on the one hand ( $-5.4$  and  $-6.2$  for  $\text{L} = \text{NMe}_3$  and  $\text{NH}_3$ ) and the  $\text{PMe}_3$  complex on the other ( $-0.2$ ). The differences so found are too great to be explained by possible anisotropy variations between the  $\text{PMe}_3$ ,  $\text{NMe}_3$  or  $\text{NH}_3$  fragments.

It has been shown that the tying up of P or N lone pair electrons in bond formation in  $\text{OPMe}_3$ ,  $\text{ONMe}_3$  and  $\text{BH}_3\text{NMe}_3$  causes only small changes from the anisotropy of the molecules  $\text{PMe}_3$  or  $\text{NMe}_3$ :  $10^{40} \Gamma$  ( $\text{Cm}^2 \text{V}^{-1}$ ) is  $-0.2$ ,  $0.8$  and  $0.1$  for  $\text{OPMe}_3$ ,  $\text{ONMe}_3$  and  $\text{BH}_3\text{NMe}_3$  [32,34]. The reason for the gross disparity in  $\Gamma$  between the amine and phosphine complexes  $\text{LCr}(\text{CO})_5$  is primarily to be found in the interaction of the P or N containing ligand with the  $\text{Cr}(\text{CO})_5$  moiety.

The large negative  $\Gamma$  values for the amine complexes  $\text{NMe}_3\text{Cr}(\text{CO})_5$  and  $\text{NH}_3\text{Cr}(\text{CO})_5$  show that, in each case, the molecular polarisability along the dipole axis is substantially smaller than the polarisability within the plane of the four Cr-CO groups. This clearly suggests that the Cr-CO grouping is anisotropic and most polarisable along the bond direction. Further, it is possible, though it cannot be proved, that the polarisability would be enhanced along each *trans* OC-Cr-CO bond axis by electron delocalisation along that axis (according to the theory of  $\pi$ -back-bonding, carbonyl groups *trans* to each other share common metal orbitals in the formation of  $\pi$ -bonds and so the electrons can be expected to be extensively delocalised).

In contrast to the amine complexes,  $\text{PMe}_3\text{Cr}(\text{CO})_5$  is almost isotropically polarisable. The polarisability  $b_1$  for this complex is much greater than that of  $\text{NMe}_3\text{Cr}(\text{CO})_5$ , while the polarisabilities in the 2 and 3 directions for the two complexes are virtually the same. Thus we see that bonding between the  $\text{PMe}_3$  and  $\text{Cr}(\text{CO})_5$  fragments results in a very large enhancement of polarisability specifically along the P-Cr-(*trans*)CO axis, relative to that of the  $\text{NMe}_3$  analogue. This constitutes a fundamental difference in the electronic behaviour of these two complexes. Le Fèvre et al. [19,35-37] have shown that  $\pi$ -electrons are much more polarisable than the more tightly bound  $\sigma$ -electrons and that in delocalised electron systems, polarisability exaltations (corresponding to an enhanced degree of electron displacement in a perturbing field) will occur in the direction of the delocalisation pathway. The difference in  $b_1$  between the phosphorus and nitrogen complexes is too great to be explained by variation in the  $\sigma$ -characteristics of the L-Cr bond, especially since the dipole moments of the two complexes are closely similar. Rather the results are clearly indicative of a highly deformable  $\pi$ -component of the phosphorus-chromium bond within the P-Cr-(*trans*)CO system, arising from overlaps primarily between chromium  $d$  and phosphorus  $\pi$ -acceptor orbitals, the latter of  $d$  and possibly  $\sigma^*$  origin [15].

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