The Chromium–Heavy Group 5 Donor Bond: a Comparison of Structural Changes within the Series $[\mathrm{Cr(CO)_5(XPh_3)}]$ (X = P, As, Sb, or Bi) *via* Their *X*-Ray Crystal Structures

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Summary Accurate *X*-ray data for $[\mathrm{Cr(CO)_5(XPh_3)}]$ (X = As, Sb, or Bi) when compared with data for $[\mathrm{Cr(CO)_5PPh_3}]$ show significant variations in C–X–C and Cr–X–C bond angles as well as in Cr–X distances consistent with increasing *s*-orbital participation in Cr–X bonding down the series $\mathrm{X = P \leqslant X = As < X = Sb < X = Bi}$.

The degree to which $ns\sigma$ and $nd\pi$ ligand orbitals contribute to the ground-state description of the M–X bond (X = P, As, Sb, or Bi) has been one of the most controversial aspects of transition metal–heavy group 5 ligand chemistry.[1–4] Two major lines of experimental evidence cited by proponents of the π-bonding hypothesis in support of significant $\mathrm{M}d\pi$–$\mathrm{P}d\pi$ bonding are: (a) ^{31}P–M (*e.g.*, M = ^{183}W or ^{195}Pt) n.m.r. coupling constants vary inversely with ligand basicity, the poorer σ-donor, better π-acceptor ligands giving the highest *J* values;[2] (b) M–P bond lengths are shorter for $\mathrm{P(OR)_3}$ than $\mathrm{PR_3}$ {*e.g.*, Cr–P 2·422(1) Å in $[\mathrm{Cr(CO)_5PPh_3}]$ *vs.* 2·309(1) Å in $[\mathrm{Cr(CO)_5P(OPh)_3}]$}.[1,5] However observation (a) may be due to the tendency (Bent's rule) for *s*-orbital character to accumulate in the phosphorus donor orbital as the electronegativity of the substituents on phosphorus increases[3,4] and there is now evidence that a difference of 0·02—0·04 Å between metal–phosphine and metal–phosphite bond lengths may be due to an intrinsic σ effect independent of metal oxidation state.[6] We now report accurate *X*-ray data for $[\mathrm{Cr(CO)_5(XPh_3)}]$ (X = As, Sb, or Bi) for comparison with $[\mathrm{Cr(CO)_5PPh_3}]$. The results are pertinent not only to *s*-orbital participation in chromium–group 5 ligand bonding but also to structural features of transition metal–heavy atom donor co-ordination chemistry in general.

The compounds $[\mathrm{Cr(CO)_5(XPh_3)}]$ (X = P, As, Sb, or Bi) are isomorphous.† Single-crystal intensity data were collected on a Syntex $P2_1$ automatic diffractometer. Structures were refined by full-matrix least-squares methods.‡ Structural parameters of interest are in the Table and compared with data for $[\mathrm{Cr(CO)_5PPh_3}]$. The most striking features are the decrease in C–X–C (av.) bond angles from 102·6° for X = P to 98·7° for X = Bi and the parallel increase in Cr–X–C angles [av. 115·6° (X = P) to 118·9°

Table. Bond lengths (Å) and angles (°) for $[\mathrm{Cr(CO)_5(XPh_3)}]$ (X = P, As, Sb, or Bi).

	X = P[a]	X = As	X = Sb	X = Bi
Bond lengths				
Cr–X	2·422(1)	2·4972(5)	2·6170(3)	2·705(1)
Cr–C (*trans* X)	1·845(4)	1·859(3)	1·865(3)	1·86(1)
av. Cr–C (*cis* X)	1·880	1·897	1·899	1·905
C–O (*trans* X)	1·154(5)	1·147(4)	1·136(4)	1·14(1)
av. C–O (*cis* X)	1·147	1·139	1·140	1·133
X–C(11)[b]	1·828(4)	1·947(3)	2·132(2)	2·222(9)
X–C(21)[b]	1·834(4)	1·947(3)	2·130(3)	2·212(9)
X–C(31)[b]	1·821(3)	1·947(3)	2·136(2)	2·215(8)
av. X–C	1·828	1·947	2·133	2·216
Bond angles				
X–Cr–C(*trans* X)	174·3(1)	174·7(1)	175·0(0)	175·7(3)
Cr–X–C(11)[b]	116·6(1)	117·3(0)	117·9(0)	118·5(2)
Cr–X–C(21)[b]	112·2(1)	112·9(1)	114·1(0)	114·6(2)
Cr–X–C(31)[b]	118·1(1)	119·7(0)	121·8(0)	123·6(2)
av. Cr–X–C	115·6	116·6	117·9	118·9
C(11)–X–C(21)	102·6(2)	101·6(1)	99·3(0)	97·8(3)
C(11)–X–C(31)	101·8(2)	100·5(1)	98·4(0)	97·0(3)
C(21)–X–C(31)	103·4(2)	102·2(1)	101·8(0)	101·2(3)
av. C–X–C	102·6	101·4	99·2	98·7

[a] Ref. 7. [b] C(11), C(21), and C(31) are the carbon atoms attached to X.

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† Triclinic, space group $P\bar{1}$, $Z = 2$. The structure of $[\mathrm{Cr(CO)_5PPh_3}]$ has been described (ref. 7). Cell constants for X = As, Sb, and Bi are as follows: X = As, a = 9·7872(7), b = 12·0900(10), c = 9·5419(10) Å; α = 90·422(8), β = 95·370(7), γ = 74·032(6)°; X = Sb, a = 9·8773(10), b = 12·2953(14), c = 9·5385(10) Å; α = 88·136(9), β = 94·231(9), γ = 74·477(9)°; X = Bi, a = 9·8174(14), b = 12·4932(17), c = 9·5158(13) Å, α = 86·580(11), β = 93·434(11), γ = 76·003(11)°.

‡ X = As, R = 0·030 for 3461 observed reflections [Mo-K_α; $I \geqslant 3\sigma(I)$]; X = Sb, R = 0·025 for 4920 observed reflections; X = Bi, R = 0·042 for 3197 observed reflections.

(X = Bi)]. In the free ligands C–X–C angles are 103° (av.) (PPh_3)[8] and 94° (av.) ($BiPh_3$).[9]§ If, as expected, C–X–C angles reflect orbital contributions, it seems clear that the Cr–Bi bond has greater *s*-character than the Cr–P or Cr–As bonds. Also the lone-pair orbital of $BiPh_3$ has more *s*-character than the Bi orbital used in Cr–Bi bonding. An analysis of the Cr–X and X–C distances provides compelling evidence for an *increase* in Cr–X bond order in parallel with increasing *s*-character in the ligand–metal bond. Thus, subtraction of the tetrahedral covalent radii for P (1·10), As (1·18), Sb (1·36), and Bi (1·46 Å) from the X–C distances (Table) yields values of 0·73, 0·77, 0·77, and 0·76 Å, respectively, which compare with the standard C(sp^2) radius of 0·73 Å.[1] In contrast the same procedure applied to the Cr–X distances yields differences of 1·322, 1·317, 1·257, and 1·245 Å, respectively. While the significance of these individual differences is debatable, the trend (a decrease of 0·077 Å from X = P to X = Bi), considered together with the C–X bond length data, is meaningful. These observations are not compatible with π-bonding arguments since, *a priori*, Cr–X $d\pi$–$d\pi$ bonding should be maximised at X = P where there is optimum matching of *d*-orbital energies and sizes. In the context of *s*-orbital involvement in the Cr–X bonds it is interesting that the Cr–CO (*trans* to X) bond distances suggest an increase in structural *trans*-influence down the series $PPh_3 < AsPh_3 < SbPh_3 \sim BiPh_3$.

Finally we point out that our observations and interpretation of C–X–C bond angle variations for $[Cr(CO)_5XPh_3]$ may have general significance in heavy-atom donor chemistry. Thus the C–Ge–C bond angle {102·8(2)° in $[Cr(CO)_5(Ge\{CH(SiMe_3)_2\}_2)]$} is intermediate between the corresponding angles in $[Cr(CO)_5(carbene)]$ (108—114°) and $[Cr(CO)_5(Sn\{CH(SiMe_3)_2\}_2)]$ (98·2°).[10] *X*-Ray studies of neutral group 6 complexes $[Cr(CO)_5L]$ (L = Me_2S, Me_2Se, or Me_2Te) are in progress to confirm the generality of these structural trends.

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§ In $As(4\text{-}MeC_6H_4)_3$ (J. Trotter, *Canad. J. Chem.*, 1963, **41**, 14) the angle is 102°. No comparable data are available for $SbPh_3$.

The atomic co-ordinates for these three structures are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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