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PREPARATION AND X-RAY CRYSTAL STRUCTURE OF THE ANION $[Sn_2Co_5Cl_2(CO)_{19}]^-$ AS THE BIS[TRIS(1-PYRAZOLYL)BORATE]-COBALT(III), $Co[HB(pz)_3]_2^+$, SALT

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Summary

Interaction of the tris(pyrazolyl)borate anion, $HB(pz)_3^-$ with $ClSn[Co(CO)_4]_3$ gives as a major product the novel anion $[Sn_2Co_5Cl_2(CO)_{19}]^-$ with $Co[HB(pz)_3]^+$ as the counterion. An X-ray crystal structure analysis (monoclinic, *C2/c*, *a* 27.325, *b* 9.516, *c* 23.316 Å, *β* 113.51°, $Z = 4$, $R = 0.043$ for 2839 reflections with $I > 2.5\sigma(I)$) shows the anion to have two $ClSn[Co(CO)_4]_2$ groups *trans* to one another about a planar $Co(CO)_3$ fragment, while the cation contains Co^{III} octahedrally coordinated by the two tridentate tris(pyrazolyl)borate ligands.

Introduction

The closed tetrahedral cluster unit MCo_3 is well established for the Main Group IV elements M = C, Si and Ge in a variety of compounds of the type $RMCo_3(CO)_9$ [1–6]. For tin no similar cluster has been characterised; open species such as $XSn[Co(CO)_4]_3$ [7] or $Sn[Co(CO)_4]_4$ [8] are known, but attempts to condense these by elimination of CO and formation of Co-Co bonds have been unsuccessful. This can be rationalised in terms of the size of the Group IV atom. Thus the smaller C, Si and Ge members can be accommodated within the closed cluster, whereas the larger Sn atom would involve unrealistically long Co–Co bonds, or excessively acute Co–Sn–Co angles in the same type of compound. Using reasonable estimates for Sn–Co and Co–Co bonds a Co–Sn–Co angle of ca. 64° would result for a $SnCo_3$ cluster, compared with values of ca. 70° for the Ge and Si analogues. Schmid concluded in an extensive survey that only atoms with a covalent radius of < 1.30 Å can fit into a closed MCo_3 tetrahedron [9]; hence germanium (*r* 1.22 Å) forms such clusters but tin (*r* 1.41 Å) does not. These figures are appropriate only for four-coordinate tin. It seemed reasonable to suppose that a six-coordinate tin atom might be incorporated into a cluster since the preferred bond angles about an sp^3d^2 atom are naturally smaller than those for sp^3 hybridisation. Support for this

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supposition comes from the observation that the $SnCo_2$ triangle incorporating four-coordinate tin in (μ-Me_2Sn)(μ-CO)$Co_2(CO)_6$ is "exceedingly unstable" [10] whereas the same unit involving six-coordinate tin in [μ-$(acac)_2Sn$](μ-CO)$Co_2(CO)_6$ is quite robust [11].

Herein we report the results of an initial attempt to generate a $SnCo_3$ cluster unit by reaction of $ClSn[Co(CO)_4]_3$ with the tridentate, mono-negative ligand $[HB(pz)_3]^-$ (pz = 1-pyrazolyl, 1-$N_2C_3H_3$), and the structure of the unexpected product.

Experimental

General

All reactions were performed under nitrogen in standard Schlenk equipment. Infrared spectra were recorded on a Perkin–Elmer Model 180 spectrometer. $Co_2(CO)_8$ (Pressure Chemicals) and $SnCl_4$ were commercial samples while $K[HB(pz)_3]$ [12] was a generous gift from Professor M.I. Bruce. $ClSn[Co(CO)_4]_3$ was prepared using the method of Patmore and Graham [7].

Reaction of $ClSn[Co(CO)_4)]_3$ with $K[HB(pz)_3]$

A solution of $ClSn[Co(CO)_4]_3$ (1.33 g, 2 mmol) in tetrahydrofuran was treated with a tetrahydrofuran solution of $K[HB(pz)_3]$ (0.50 g, 2 mmol). After 30 minutes at room temperature a red solution had formed with prominent carbonyl bands at 2090(m), 2081(m) and 2008(s) cm^{-1}. The mixture was evaporated under vacuum and the residue dissolved in CH_2Cl_2. Petroleum spirit (40–60° fraction) was layered onto the filtered solution which was stored at −30°C for a week. Intensely coloured crystals (which redissolved in CH_2Cl_2 to give a mauve solution) were deposited (0.53 g, 35%), and identified as $[\{HB(pz)_3\}_2Co][Sn_2Co_5Cl_2(CO)_{19}]$ by X-ray crystallography. ν(CO) (CH_2Cl_2) 2078(s), 2070(s), 2064(s), 2001(vs,br), 1934(m,br) cm^{-1}. The presence of Co, Sn and Cl in the sample was confirmed by electron-probe analysis.

Crystal structure of $[\{HB(pz)_3\}_2Co][Sn_2Co_5Cl_2(CO)_{19}]$

Well formed prisms were obtained from CH_2Cl_2/petroleum spirit. Preliminary precession photography indicated monoclinic symmetry with systematic absence appropriate for either *Cc* or *C2/c*, the latter being shown as correct by the full analysis. A suitable crystal was sealed in a glass capillary and mounted on an Enraf–Nonius CAD4 diffractometer with Zr filtered Mo-K_α X-rays. Lattice parameters were obtained using 25 high-angle reflections.

Crystal data. $C_{37}H_{20}B_2Cl_2Co_6N_{12}O_{19}Sn_2$, $M = 1620.15$, Monoclinic, space group *C2/c*, *a* 27.325(4), *b* 9.516(1), *c* 23.316(8) Å, β 113.51(2)°, *U* 5559.3 Å^3, D_c 1.93 g cm^{-3}, $Z = 4$. $F(000) = 3136$, $\bar{\mu}$(Mo-K_α) 28.7 cm^{-1}, λ(Mo-K_α) 0.7107 Å.

A total of 3576 unique reflections in the range $0 < 2\theta < 46°$ were collected by ω-scans. After correction for Lorentz, polarisation, crystal decomposition (3%) and absorption (by a series of ϕ-scans) effects the 2839 reflections for which $I > 2.5\sigma(I)$ were used in all calculations.

The structure was solved by direct methods (MULTAN) [13] to give the positions of the Sn and Co atoms. Subsequent refinement-difference map cycles revealed all other non-hydrogen atoms. In the final cycles of least-squares refinement the Sn, Co and Cl atoms were assigned anisotropic temperature factors, other non-hydrogen atoms were given isotropic temperature parameters while hydrogen atoms were

TABLE 1

FINAL POSITIONAL PARAMETERS FOR $[Co\{HB(pz)_3\}_2][Sn_2Co_5Cl_2(CO)_{19}]$

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
Sn(1)	0.7056(1)	0.0218(1)	0.3257(1)	O(31)	0.8451(3)	−0.0115(8)	0.5765(4)
Co(1)	0.75	0.0239(2)	0.25	O(32)	0.8446(3)	−0.1514(8)	0.4073(3)
Co(2)	0.6318(1)	0.2200(1)	0.3072(1)	O(33)	0.7751(2)	0.3101(7)	0.4366(3)
Co(3)	0.7714(1)	0.0049(1)	0.4455(1)	O(34)	0.6888(3)	−0.1460(8)	0.4699(3)
Cl(1)	0.6529(1)	−0.1900(3)	0.3094(1)	Co(6)	0.0	0.0	0.0
C(11)	0.8037(3)	0.1143(9)	0.3048(4)	B(81)	0.0208(3)	0.123(1)	0.1289(5)
C(12)	0.75	−0.162(1)	0.25	N(811)	0.0690(2)	0.0273(7)	0.0668(3)
O(11)	0.8404(3)	0.1730(7)	0.3415(3)	N(812)	0.0730(2)	0.0826(7)	0.1223(3)
O(12)	0.75	−0.282(1)	0.25	C(811)	0.1185(3)	−0.0050(8)	0.0733(4)
C(21)	0.6341(3)	0.1717(9)	0.3808(4)	C(812)	0.1540(3)	0.0299(9)	0.1335(4)
C(22)	0.5861(4)	0.355(1)	0.2964(5)	C(813)	0.1249(3)	0.0844(9)	0.1625(4)
C(23)	0.5937(4)	0.120(1)	0.2420(5)	N(821)	−0.0258(2)	−0.0760(7)	0.0585(3)
C(24)	0.6812(3)	0.330(1)	0.3000(4)	N(822)	−0.0134(2)	−0.0108(7)	0.1147(3)
O(21)	0.6339(2)	0.1475(7)	0.4298(3)	C(821)	−0.0541(3)	−0.1896(9)	0.0582(4)
O(22)	0.5573(3)	0.4518(9)	0.2918(4)	C(822)	−0.0609(3)	−0.200(1)	0.1135(4)
O(23)	0.5653(3)	0.0556(9)	0.1989(4)	C(823)	−0.0348(3)	−0.087(1)	0.1478(4)
O(24)	0.7119(3)	0.4048(8)	0.2952(3)	N(831)	−0.0210(2)	0.1839(7)	0.0152(3)
C(31)	0.8149(4)	−0.004(1)	0.5248(4)	N(832)	−0.0083(2)	0.2264(7)	0.0756(3)
C(32)	0.8126(4)	−0.094(1)	0.4185(4)	C(831)	−0.0464(3)	0.2885(9)	−0.0219(4)
C(33)	0.7727(3)	0.189(1)	0.4390(4)	C(832)	−0.0507(3)	0.401(1)	0.0135(4)
C(34)	0.7196(4)	−0.086(1)	0.4578(4)	C(833)	−0.0269(3)	0.359(1)	0.0733(4)

TABLE 2

SELECTED BOND LENGTHS AND ANGLES FOR $[Co\{HB(pz)_3\}_2][Sn_2Co_5Cl_2(CO)_{19}]$

Bond lengths (Å)

Co(1)–Sn(1)	2.508(1)	B–N(2)[a]	1.537(9)
Co(2)–Sn(1)	2.668(1)	N(1)–N(2)[a]	1.365(8)
Co(3)–Sn(1)	2.656(1)	N(1)–C(1)[a]	1.327(9)
Sn(1)–Cl(1)	2.418(2)	N(2)–C(3)[a]	1.352(9)
Co(6)–N(811)	1.926(6)	C(1)–C(2)[a]	1.386(9)
Co(6)–N(821)	1.911(6)	C(2)–C(3)[a]	1.347(9)
Co(6)–N(831)	1.918(6)		

All Co–C bonds are in the range 1.74(1)–1.77(1) Å

All C–O bonds are in the range 1.14(1)–1.18(1) Å

Bond angles (degrees)

Co(2)–Sn(1)–Co(1)	115.3(1)	N(831)–Co(6)–N(811)	89.8(2)
Co(3)–Sn(1)–Co(1)	115.3(1)	N(831)–Co(6)–N(821)	89.5(3)
Co(3)–Sn(1)–Co(2)	111.3(1)	N(2)–B–N(2)[a]	106.3(7)
Co(1)–Sn(1)–Cl(1)	108.7(1)	Co(6)–N(1)–N(2)[a]	119.6(5)
Co(2)–Sn(1)–Cl(1)	101.5(1)	Co(6)–N(1)–C(1)[a]	133.1(6)
Co(3)–Sn(1)–Cl(1)	103.0(1)	N(1)–N(2)–B[a]	118.4(7)
Sn(1)–Co(1)–Sn(1)	179.1(1)	C(1)–N(1)–N(2)[a]	107.2(6)
Sn(1)–Co(1)–C(11)	89.5(3)	C(3)–N(2)–B[a]	133.4(7)
Sn(1)–Co(1)–C(12)	89.5(0)	C(3)–N(2)–N(1)[a]	108.1(6)
C(11)–Co(1)–C(12)	119.6(3)	C(2)–C(1)–N(1)[a]	109.7(7)
Sn–Co–Ceq[a]	84.8(3)	C(1)–C(2)–C(3)[a]	105.7(8)
Sn–Co–Cax[a]	178.2(3)	C(2)–C(3)–N(2)[a]	109.2(8)
N(821)–Co(6)–N(811)	89.7(2)		

[a] Averaged over all corresponding distances or angles in the ions

included in their calculated positions with a common fixed temperature factor. Refinement converged at $R = 0.043$, $R_w = 0.042$ where $w = 1.0[\sigma^2(F) + 0.00011 F^2]^{-1}$. A final difference map showed no residual electron density. Calculations were performed using the SHELX76 system [14].

Final positional parameters are given in Table 1, while selected bond lengths and angles are listed in Table 2. Lists of structure factors, thermal parameters and calculated hydrogen positions are available from the authors.

Results and discussions

The reaction of $ClSn[Co(CO)_4]_3$ with $K[HB(pz)_3]$ did not proceed by the expected route (eq. 1). Instead a more complicated sequence occurred to give a salt

$$K[HB(pz)_3] + ClSn[Co(CO)_4]_3 \not\rightarrow [HB(pz)_3SnCo_3(CO)_9] + KCl \qquad (1)$$

containing a $[Sn_2Co_5Cl_2(CO)_{19}]^-$ anion with $Co[HB(pz)_3]_2^+$ as gegenion. Presumably attack by the $HB(pz)_3^-$ ligand occurs, not at the Sn–Cl bond, but at a $Co(CO)_4$ group, eq. 2. The $\{ClSn[Co(CO)_4]_2\}^-$ fragment, which is of the form X_3Sn^- and is isoelectronic with X_3Sb, then displaces a *trans* CO ligand of a $Co(CO)_4$ moiety on

$$ClSn[Co(CO)_4]_3 + [HB(pz)_3]^- \rightarrow \{ClSn[Co(CO)_4]_2\}^- + \text{“}[HB(pz)_3]Co(CO)_n\text{”} \qquad (2)$$

$$\{ClSn[Co(CO)_4]_2\}^- + ClSn[Co(CO)_4]_3 \rightarrow [Sn_2Co_5Cl_2(CO)_{19}]^- + CO \qquad (3)$$

another molecule of the starting complex to generate the anion, eq. 3. The "$[HB(pz)_3]Co(CO)_n$" reacts with a further $[HB(pz)_3]^-$ to ultimately give the cation, although it is perhaps surprising that under these conditions it is $Co[HB(pz)_3]_2^+$ that forms rather than the stable Co^{II} analogue [15,16]. The overall process is more complicated the the above conjecture would indicate, since the isolated product is not the first formed species as evidenced by the colour change and different infrared spectrum which develop during the crystallisation step. Nevertheless the changes are quite specific since the yields of the isolated product are reasonable.

The crystal structure of $[Co[HB(pz)_3]_2][Sn_2Co_5Cl_2(CO)_{19}]$ consists of discrete cations and anions, which are illustrated in Fig. 1 and 2, respectively. Both species lie on crystallographic symmetry elements, the Co atom of the cation on an inversion centre while the anion is on a two-fold rotation axis coincident with the Co(1)–C(12)–O(12) vector.

The anion consists of two $Sn(Cl)(Co(CO)_4)_2$ groups bonded *trans* to one another about the planar $Co(CO)_3$ unit. Within these groups the $Co(CO)_4$ moieties have the normal trigonal bipyramidal geometry, and are bonded to the Sn atoms by relatively long bonds (Sn–Co(av) 2.662 Å) compared with those of $ClSn[Co(CO)_4]_3$ or $BrSn[Co(CO)_4]_3$ which average 2.60 Å [17,18]. The Sn–Cl bond, 2.418 Å, is also slightly longer than is usually found [19]. In contrast, the bond between Sn(1) and the central Co(1) atom, at 2.508 Å, is over 0.15 Å shorter than the other Sn–Co bonds in the molecule and is remarkably short compared with bond lengths found for $R_3Sn–Co(CO)_4$ systems. This apparent shortening arises because the tin atoms in the anion are not opposite CO ligands which have a strong *trans* influence. Analogous examples of this behaviour include the shortening of the Si–Mn vector of

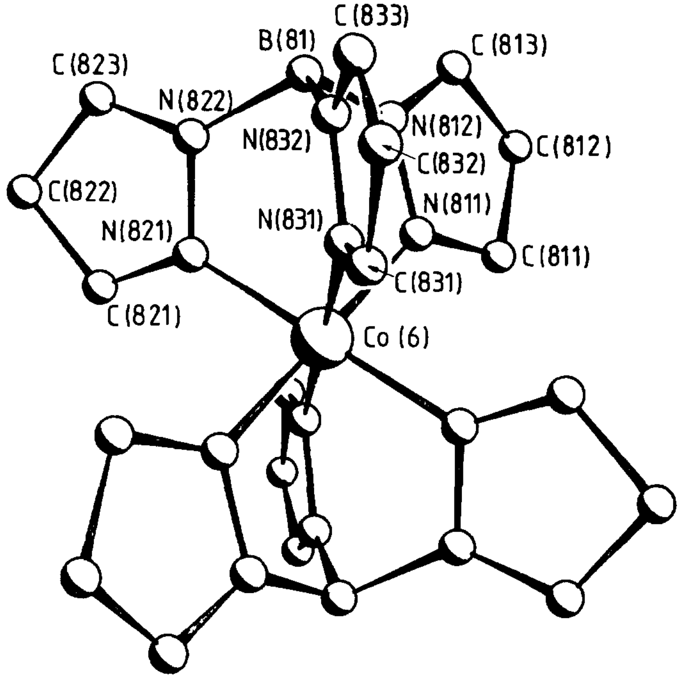

Fig. 1. The structure of the Co[HB(pz)$_3$]$_2$$^+$ cation showing atom labelling scheme.

Me$_3$SiMn(CO)$_5$ on replacing the *trans* CO by the stronger σ-donor and weaker π-acceptor ligand PPh$_3$ [21]. Similarly, the central Ge–Co bonds of [{(CO)$_9$Co$_3$Ge}$_2$Co(CO)$_3$]$^-$ at 2.288 Å are much shorter than the ca. 2.4 Å usually found [5]. A further relevant example is the short Sn–Co bond of 2.498 Å in Cl$_2$Sn[Co(CO)$_3$(nbd)]$_2$ (nbd = η^4-norbornadiene) which is *trans* to a η^2-olefin bond [22]. Although for all these examples the shortening could be explained in terms of d_π–d_π bonding between the cobalt and tin atoms this is probably insignificant; in fact the observation of a short Sn–Co bond *trans* to another Sn–Co bond argues against the Sn acting as a π-acceptor. A more likely explanation for the short bonds relates to the stronger σ-donor properties of a X$_3$Sn$^-$ ligand compared to those of CO.

The relative orientations of the carbonyl groups and the chlorine atom with respect to the other parts of the anion are consistent with minimisation of steric interactions with no other apparent constraints. The opening out of the Co–Sn–Co angles around the tin atom to ca. 114° with corresponding Cl–Sn–Co angles of ca. 104° can be partly attributed to greater steric interactions between adjacent Co(CO)$_n$ groups than those involving the smaller Cl substituent, and partly to the tendency for the electronegative Cl atom to bond to a hybrid orbital of greater *p* character than those used for bonding to the electropositive Co(CO)$_4$ groups (cf. Bents rule) [20].

The crystallographically centro-symmetric cation Co[HB(pz)$_3$]$_2$$^+$, Fig. 1, is of interest. There have been extensive studies on analogous Co^{II} and other M^{II} species [12], but to the best of our knowledge the Co^{III} (and other M^{III}) derivatives are

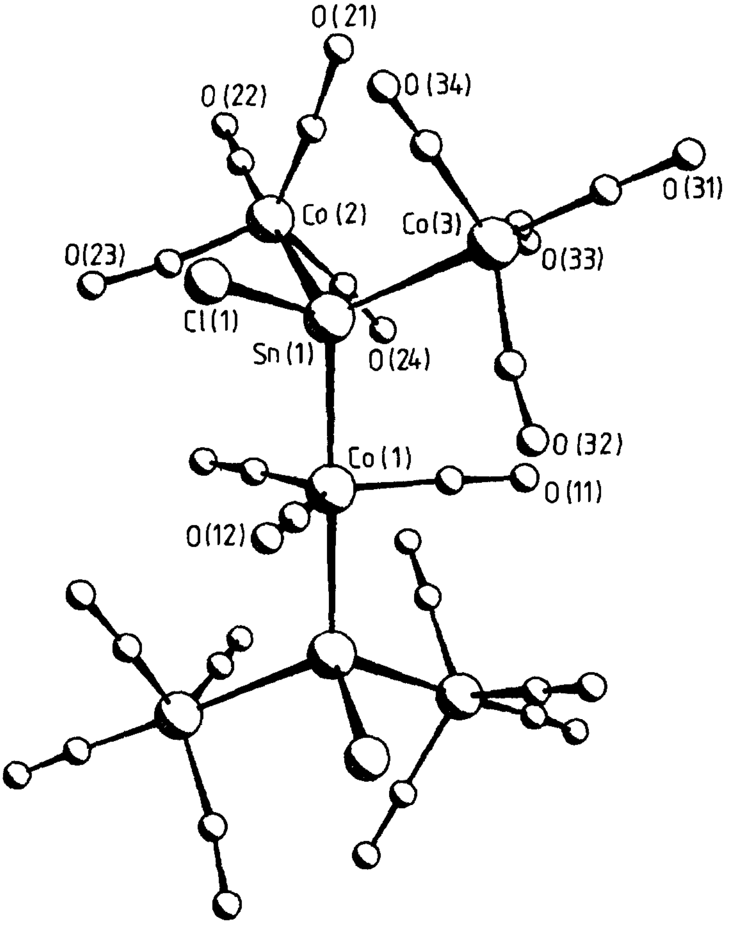

Fig. 2. The structure of the $[Sn_2Co_5Cl_2(CO)_{19}]^-$ anion; the Co(1)-C(12)-O(12) vector is a crystallographic two-fold rotation axis.

unrecorded in the literature. The only previous mention seems to be a comment that the neutral $Co[HB(pz)_3]_2$ undergoes a one-electron oxidation in acetonitrile at $\epsilon_{1/2}$ -0.09 V versus a standard calomel electrode [23].

The structure of the neutral $Co[HB(pz)_3]_2$ has been published [16] so a comparison between the corresponding Co^{II} and Co^{III} species can be made. The most obvious difference is the much shorter Co–N distance in the Co^{III} complex (av. 1.918 Å) compared with that in the Co^{II} analogue (av. 2.129 Å) reflecting the decrease in the cobalt covalent radius with increasing oxidation state. The coordination sphere is more regular in the Co^{III} example with all N–Co–N angles within 0.5° of 90° whereas for Co^{II} there is a significant trigonal elongation along the B–Co–B vector to give N–Co–N angles of ca. 85°.

Finally, we note that the $Co[HB(pz)_3]_2^+$ may have a useful application as a counterion in the crystallisation of large anions, as an alternative to the more commonly used $(Ph_3P)_2N^+$, Ph_4As^+, R_4N^+ etc.

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References

1 B. Penfold and B.H. Robinson, Acc. Chem. Res., 6 (1973) 73.

2 G. Schmid, V. Batzel and G. Etzrodt, J. Organomet. Chem., 112 (1976) 345.

3 R. Boese and G. Schmid, J. Chem. Soc., Chem. Commun., (1979) 349; G. Schmid and G. Etzrodt, J. Organomet. Chem., 137 (1977) 367; R.F. Gerlach, B.W.L. Graham and K.M. Mackay, ibid., 182 (1979) 285.

4 G. Etzrodt and G. Schmid, J. Organomet. Chem., 169 (1979) 259.

5 D.N. Duffy, K.M. Mackay, B.K. Nicholson and R.A. Thomson, J. Chem. Soc. Dalton Trans., (1982) 1029.

6 R.A. Croft, D.N. Duffy and B.K. Nicholson, J. Chem. Soc. Dalton Trans., (1982) 1023.

7 D.J. Patmore and W.A.G. Graham, Inorg. Chem., 5 (1966) 2222.

8 D.J. Patmore and W.A.G. Graham, Inorg. Chem., 7 (1968) 771; G. Schmid and G. Etzrodt, J. Organomet. Chem., 131 (1977) 477.

9 G. Schmid, Angew. Chem. Int. Ed. Engl., 17 (1978) 392.

10 K. Triplett and M.D. Curtis, Inorg. Chem., 15 (1976) 431.

11 R.D. Hall and D. Hall, J. Organomet. Chem., 56 (1973) 209; D.J. Patmore and W.A.G. Graham, Inorg. Chem., 6 (1967) 1879.

12 S. Trofimenko, Acc. Chem. Res., 4 (1971) 17; Chem. Rev., 72 (1972) 497; Adv. Chem. Ser., 150 (1976) 289.

13 P. Main, S.E. Hull, L. Lessinger, G. Germain, J.P. Declercq and M.M. Woolfson, MULTAN 78, University of York, 1978.

14 G. Sheldrick, SHELX76, University of Cambridge, 1976.

15 S. Trofimenko, J. Am. Chem. Soc., 89 (1967) 3148.

16 M.R. Churchill, K. Gold and C.E. Maw, Inorg. Chem., 9 (1970) 1597.

17 R.D. Ball and D. Hall, J. Organomet. Chem., 52 (1973) 293.

18 B.P. Birynkov, E.A. Kikhtenkova, Y.T. Struchkov, K.N. Anisimov, N.E. Kolobova and V.I. Khandozhko, J. Organomet. Chem., 27 (1971) 337.

19 J.A. Zubieta and J.J. Zuckerman, Prog. Inorg. Chem., 24 (1978) 251.

20 K.M. Mackay and B.K. Nicholson, Ch. 43 in G. Wilkinson, F.G.A. Stone and E. Abel, (Eds.), Comprehensive Organometallic Chemistry, Pergamon, Oxford, 1982.

21 M.C. Couldwell and J. Simpson, J. Chem. Soc., Dalton Trans., (1976) 714.

22 F.P. Boer and J.J. Flynn, J. Am. Chem. Soc., 93 (1971) 6495.

23 S. Trofimenko, J. Am. Chem. Soc., 89 (1967) 3170.