Syntheses and crystal structures of [$^tBu_3SbCr(CO)_5$], [$^tBu_3BiM(CO)_5$] (M = Cr, W), and [$^tBu_3BiMnCp'(CO)_2$] (Cp' = η^5-$C_5H_4CH_3$)

H.J. Breunig *, E. Lork, C.I. Raţ, R.P. Wagner

Institut für Anorganische und Physikalische Chemie, Universität Bremen, Fachbereich 2, Postfach 330 440, D-28334 Bremen, Germany

Abstract

Syntheses and crystal structures of [$^tBu_3SbCr(CO)_5$] (**1**), [$^tBu_3BiM(CO)_5$] [M = Cr (**2**), W (**3**)] and [$^tBu_3BiMnCp'(CO)_2$] (**4**) (Cp' = η^5-$C_5H_4CH_3$) are reported.
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Keywords: Antimony; Bismuth; Chromium; Tungsten; Manganese

1. Introduction

In the family of trivalent pnicogen donors the antimony and more so the bismuth ligands play the role of cinderellas [1–6]. Tertiary bismuthines R_3Bi are considered as particularly poor ligands, probably due to the inert character of the 6s electron pair at bismuth. However little is known in this field because only few stibine and bismuthine complexes have been thoroughly characterised. In our earlier work we had found that $^tBu_3Sb$ [7] and $^tBu_3Bi$ [8] form thermally stable transition metal carbonyl complexes, which at the time were characterised by infrared, Raman and ^1H NMR spectroscopy. We have now reinvestigated these compounds in order to achieve a full characterisation and report here the crystal structures, ^{13}C NMR and MS data of [$^tBu_3SbCr(CO)_5$] (**1**) and [$^tBu_3BiM(CO)_5$] [M = Cr (**2**), W (**3**)], the synthesis and structure of a novel complex, [$^tBu_3BiMnCp'(CO)_2$] (**4**), and spectroscopic data of $^tBu_3Sb$ and $^tBu_3Bi$. Related compounds with known crystal structures are [$^tBu_3SbFe(CO)_4$] [9], [$(Me_3Si)_3SbCr(CO)_5$] [10], [$Ph_3BiM(CO)_5$] (M = Cr [11], Mo, W [12,13]), [FeCp-$(CO)_2(Ph_3Bi)$][BF_4] [14] and [$Ph_2BiMn(CO)_5$] [15].

2. Results and discussion

The complexes **1**–**4** were prepared by ligand exchange reactions between $^tBu_3Sb$ or $^tBu_3Bi$ and [$M(CO)_5(thf)$] (M = Cr, W) [7,8] or [$MnCp'(CO)_2(thf)$] (thf = tetrahydrofuran). They are air sensitive, colourless or yellow solids, soluble in hydrocarbons. **1**–**3** are stable up to 130 °C. The manganese complex **4** is a red solid melting at 142 °C. The molecular structures of **1**–**3** are similar. As a representative example the structure of **3** is depicted in Fig. 1.

A molecular unit of [$^tBu_3BiMnCp'(CO)_2$] **4** is shown in Fig. 2.

Selected bond lengths and angles of **1**–**4** are given in Table 1.

The complexes **1**–**4** consist of trigonal pyramidal $^tBu_3E$ (E = Sb, Bi) ligands coordinated to square pyramidal $M(CO)_5$ units or to the Cp'Mn(CO)_2 group. The length of the coordinative Sb–Cr bond in **1** (2.7042(7) Å) is in the range of the corresponding values for related complexes, e.g. [$Cr(CO)_5(MeSbBr_2)$] 2.556(2) Å [16], [$Ph_3SbCr(CO)_5$] 2.6170(3) Å [11], [$(Me_3Si)_3SbCr(CO)_5$] 2.7167(8) Å [10]. The bismuth-transition metal coordinative bonds (Bi–Cr 2.775(4) Å in **2** and Bi–W 2.893(2) Å in **3** are slightly longer than in [$Ph_3BiCr(CO)_5$] (2.705(1) Å) or [$Ph_3BiW(CO)_5$] (2.8294(5) Å) [11,12]. The coordinative bond in **4** Bi–Mn 2.625(8) Å) is significantly shorter than the normal covalent

* Corresponding author. Tel.: +49 (0) 421 218 2266; fax: +49 (0) 421 218 4042.
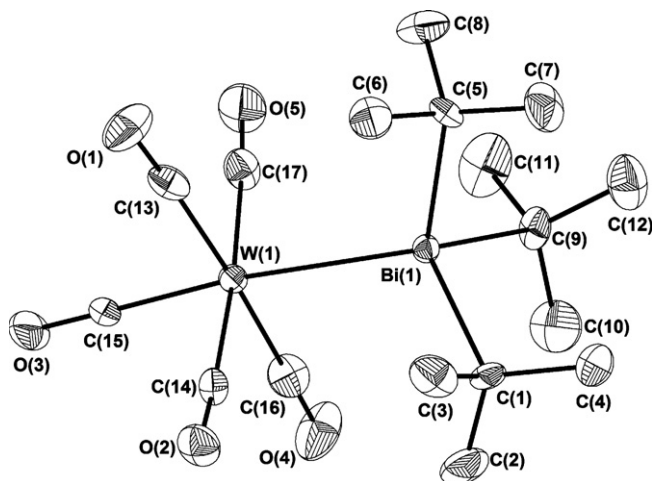 *E-mail address:* breunig@chemie.uni-bremen.de (H.J. Breunig).

Fig. 1. ORTEP like representation at 50 % probability of **3** showing the atomic numbering scheme. Hydrogen atoms were omitted for clarity.
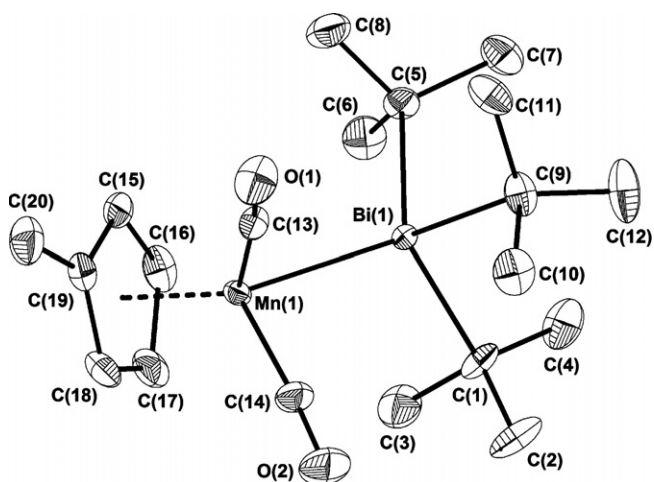

Fig. 2. ORTEP like representation at 50 % probability of **4** showing the atomic numbering scheme. Hydrogen atoms were omitted for clarity.

Table 1
Selected bond lengths (Å) and angles (°) for **1**–**4**

	E = Sb, M = Cr (**1**)	E = Bi, M = Cr (**2**)	E = Bi, M = W (**3**)	E = Bi, M = Mn (**4**)
E–C(1)	2.221(3)	2.326(5)	2.319(8)	2.315(5)
E–C(5)	2.223(3)	2.328(5)	2.317(9)	2.332(5)
E–C(9)	2.218(3)	2.337(5)	2.326(8)	2.311(5)
E–M(1)	2.7042(7)	2.775(4)	2.893(2)	2.625(8)
C(1)–E–C(5)	103.93(13)	105.12(2)	106.6(3)	104.12(2)
C(1)–E–C(9)	106.38(14)	104.6(2)	104.3(3)	104.4(2)
C(9)–E–C(5)	104.16(14)	103.9(2)	103.8(3)	104.3(2)
C(1)–E–M	113.59(9)	115.03(13)	114.4(2)	112.73(15)
C(5)–E–M	113.11(9)	115.13(13)	115.2(2)	117.73(13)
C(9)–E–M	114.64(10)	111.84(15)	111.4(2)	112.28(14)

Bi–Mn bond in Ph$_2$Bi–Mn(CO)$_5$ (2.842(2) Å) [15] or the Bi–Mn distances in {Cp′(CO)$_2$Mn}$_3$Bi$_2$ (2.897–2.950 Å), a complex with side-on coordination of the Bi$_2$ unit [17,18]. The environment of the Sb or Bi centres in the complexes **1**–**4** is

distorted tetrahedral with M–E–C (M = Cr, W, Mn; E = Sb, Bi) angles ranging between 111.4(2)° and 117.73(13)° and C–E–C angles between 103.8(3)° and 106.6(3)°. These values indicate that for the dative bonds from antimony or bismuth to the transition metal centre hybrid orbitals with considerable p orbital participation are used. In fact the mean C–Sb–C angles (**1**: 104.8(4)°) or mean C–Bi–C angles (**2**: 104.5(5)°, **3**: 104.9(3)°, **4**: 104.2(8)°) lie between 90°, the value expected for p^3 configuration at antimony and 109.5° for sp^3 hybridisation, closer to the latter. The tendency to widen the bond angles in pyramidal stibine, or bismuthine ligands through coordination is well documented, for instance for (Me$_3$Si)$_3$Sb (mean angle Si–Sb–Si 99.2°) and [(Me$_3$Si)$_3$SbCr(CO)$_5$] (mean Si–Sb–Si 103.6°) [10] or for Ph$_3$Bi (mean C–Bi–C 93.9° [13]) and [Ph$_3$BiM(CO)$_5$] (mean C–Bi–C M = Cr 102.6°, Mo 98.0°, W 98.9° [11–13].

In order to quantify the steric effects in **1**–**4** and in related complexes we have calculated the cone angle Θ, i.e. the apex angle of a cylindrical cone with origin in the transition metal atoms whose sides just touch the surfaces of the spheres defined by van der Waals radii of the outermost atoms of the ligands. The cone angle concept was originally applied by Tolman to nickel complexes with phosphine ligands with an fixed Ni–P distance of 2.28 Å and the cone angle $\Theta = 182°$ was determined for ^{t}Bu$_3$P [19]. For the heavier analogues the Θ values 183° (^{t}Bu$_3$As), 178° (^{t}Bu$_3$Sb), and 175° (^{t}Bu$_3$Bi) were reported [4]. We applied a variant of the method described by Mingos and Müller [20] for the determination of Tolman cone angles of phosphines from crystallographic parameters. Instead of a fixed transition metal pnicogen distance of 2.28 Å we used the experimentally determined bond lengths aiming at a more realistic representation of the sterical situation.

The geometric relationships are shown in Fig. 3. The distance, d, from the transition metal to the outermost hydrogen atom on each of the ^{t}Bu or Me$_3$Si groups of the stibine or bismuthine ligands was measured using the crystallographic data. The half angle θ_i was then calculated using the equation:

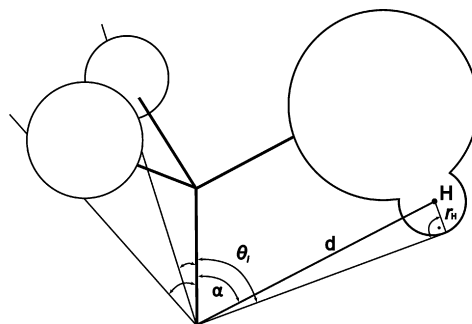$$\theta_i = \alpha + \frac{180}{\pi} \sin^{-1}\left(\frac{r_H}{d}\right)$$

Fig. 3. Geometrical definition of the cone angle Θ used for the calculation from crystallographic data.

Table 2

X-ray diffraction data and structure refinement for **1**–**4**

Compound	$1 \cdot 0.5CH_2Cl_2$	**2**	**3**	**4**
Empirical formula	$C_{17.5}H_{28}ClCrSbO_5$	$C_{17}H_{27}BiCrO_5$	$C_{17}H_{27}BiWO_5$	$C_{20}H_{34}BiMnO_2$
Formula weight	527.60	572.37	704.21	570.39
Crystal size (mm^3)	$0.6 \times 0.6 \times 0.5$	$0.6 \times 0.3 \times 0.2$	$0.6 \times 0.5 \times 0.3$	$0.6 \times 0.6 \times 0.5$
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	P 21/n	$P - 1$	$P - 1$	$P - 1$
a (Å)	9.039(18)	8.846(1)	8.831(3)	8.707(4)
b (Å)	15.895(3)	8.944(2)	9.033(3)	8.839(2)
c (Å)	15.483(3)	14.744(2)	14.793(3)	15.468(4)
α (°)	90.00	75.78(1)	76.19(2)	80.282(9)
β (°)	92.95(3)	85.72(1)	86.15(2)	79.08(2)
γ (°)	90.00	70.14(1)	70.36(4)	68.61(2)
Volume (Å)	2221.6(8)	1063.5(3)	1079.2(6)	1082.0(6)
Z	4	2	2	2
Absorption coefficient (mm^{-1})	1.847	8.793	13.487	8.713
$F(000)$	1060	552	652	556
θ range for data collections (°)	2.55–27.5	2.56–27.5	2.54–27.5	2.54–27.5
Index ranges (h, k, l)	−11/1, ±20, −19/20	−6/11, ±11, ±19	−8/11, ±11, ±19	±11, −10/11, −19/20
Reflections collected	10188	5863	5960	9954
Independent reflections/R_{int}	5097/ 0.0372	4836/0.022	4915/0.0419	4964/0.0304
Data with $I > 2\sigma(I)$	4395	4484	4274	4727
Goodness-of-fit (on F^2)[a]	1.076	1.014	1.045	1.104
Data/parameters/restraints	5097/ 1/244	4836/0/226	4915/0/226	4964/0/227
Final R indices $[I > 2\sigma(I)]$ (R_1, wR_2)[b]	0.0417, 0.1091	0.0294, 0.0702	0.0445, 0.1172	0.0335, 0.0866
R indices (all data) (R_1, wR_2)	0.0478, 0.1142	0.0331, 0.0722	0.0519, 0.1226	0.0356, 0.0877
Largest difference peak and hole (e Å^{-3})	1.912/−2.860	1.284/−1.799	2.427/−2.604	3.642/−1.597

[a] GooF $= S = \{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$.

[b] $R_1 = \Sigma\|F_o| - |F_c\|/\sum|F_o|; wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Table 3

Cone angles determined from the crystallographic data of **1**–**4**

Compound	(θ_i)	(Θ)
[^{t}Bu$_3$SbCr(CO)$_5$] (**1**)	72.4, 74.2, 75.1	147.8
[^{t}Bu$_3$BiCr(CO)$_5$] (**2**)	69.7, 70.8, 74.2	143.1
[^{t}Bu$_3$BiW(CO)$_5$] (**3**)	68.4, 70.1, 73.3	141.2
[^{t}Bu$_3$BiMnCp′(CO)$_2$] (**4**)	73.2, 75.8, 76.9	150.6
[^{t}Bu$_3$SbFe(CO)$_4$]	77.3, 77.4, 78.9	155.7

with the van der Waals radius of $r_H = 1.00$ Å for hydrogen. The procedure was repeated for the other groups and the crystallographic cone angle, Θ, was calculated from:

$$\Theta = \frac{2}{3} \sum_i \theta_i.$$

Values for the crystallographic cone angles are given in Table 2. For ^{t}Bu$_3$Bi and ^{t}Bu$_3$Sb they are considerably smaller than the previously reported Θ values, which were obtained without consideration of the experimentally determined bond lengths [4]. Despite the differences our data confirm the trend that sterical effects increase in the order ^{t}Bu$_3$Bi < ^{t}Bu$_3$Sb < ^{t}Bu$_3$P. The large Θ value for the bismuthine complex **4** results from the exceptionally short Bi–Mn bond length (Table 3).

3. Conclusion

Both, ^{t}Bu$_3$Sb and ^{t}Bu$_3$Bi are good donor ligands capable to form stable complexes with pentacarbonyl transition metal fragments in a similar way like the widely used triorgano phosphorus or arsenic ligands. The molecular structures of the stibine and bismuthine complexes are not exceptional. They correspond very well to known features of transition metal carbonyl complexes with triorgano pnicogen ligands. Considering the specific geometries and bonding properties of complexes with Sb or Bi ligands, applications as useful catalysts in addition to the well known catalytic active complexes with phosphine ligands can be envisaged.

4. Experimental

The operations were carried out in an argon atmosphere using dried solvents distilled under argon. ^{1}H and ^{13}C NMR spectra were recorded in C$_6$D$_6$ and CDCl$_3$ solutions at room temperature using a Bruker Avance DPX-200 spectrometer operating at 200.1 MHz, and 50.3 MHz respectively. The chemical shifts are reported in δ units (ppm) relative to the residual peak of the solvent C$_6$D$_5$H (^{1}H 7.15 ppm), CHCl$_3$ (^{1}H 7.26 ppm) and C$_6$D$_6$ (^{13}C 128.02 ppm). The infrared spectrum was recorded as Nujol mull on a Perkin–Elmer Spectrum 1000 instrument. Mass spectra were recorded on a Finnigan MAT 95 spectrometer for ^{t}Bu$_3$Sb and **1** and on a Finnigan MAT 8200 spectrometer for ^{t}Bu$_3$Bi, **2**, **3**, and **4**. For the UV photolysis a Hanau TQ 150 mercury lamp was used. [^{t}Bu$_3$SbCr(CO)$_5$] (**1**), [^{t}Bu$_3$BiM(CO)$_5$] [M = Cr (**2**), W (**3**)], were obtained by known reactions between ^{t}Bu$_3$Sb [7], ^{t}Bu$_3$Bi [8], and

[Cr(CO)$_5$(thf)] or [W(CO)$_5$(thf)] in thf [7,8]. Single crystals were obtained from petroleum ether/CH$_2$Cl$_2$ (**1**), petroleum ether (**2**, **3**) or *n*-hexane (**4**) solutions at −28 °C.

4.1. Spectroscopic data of $^tBu_3Sb$, $^tBu_3Bi$ and the complexes 1–3

$^tBu_3Sb$, ^1H NMR (C$_6$D$_6$): 1.30 (s, CH_3). ^{13}C NMR (C$_6$D$_6$): 32.33 (s, CH_3). MS (EI, 70 eV): 292 (5) [M]$^+$, 236 (5) [M−R]$^+$, 179 (10) [M−2R]$^+$, 57 (100) [R]$^+$, R = ^tBu.

$^tBu_3Bi$, ^1H NMR (C$_6$D$_6$): 1.79 (s, CH_3). ^{13}C NMR (C$_6$D$_6$): 32.39 (s, CH_3). MS (EI, 70 eV): 380 (5) [M]$^+$, 323 (4) [M−R]$^+$, 266 (4) [M−2R]$^+$, 209 (7) [Bi]$^+$, 57 (100) [R]$^+$, R = ^tBu.

[$^tBu_3SbCr(CO)_5$] (**1**), ^1H NMR (C$_6$D$_6$): 1.19 (s, CH_3). ^{13}C NMR (C$_6$D$_6$): 31.88 (s, CH_3), 38.11 (s, CMe_3), 204.76 (s, –CO-*cis*). MS (EI, 70 eV): 484 (18) [M]$^+$, 427 (8) [M−R]$^+$, 400 (10) [M−3CO]$^+$, 372 (18) [M−4CO]$^+$, 344 (93) [M−5CO]$^+$, 315 (13) [M−4CO−R]$^+$, 288 (21) [R$_2$SbCr]$^+$, 232 (34) [RSbCr]$^+$, 174 (13) [SbCr]$^+$, 108 (95) [Cr(CO)$_2$]$^+$, 57 (100) [R]$^+$, R = ^tBu.

[$^tBu_3BiCr(CO)_5$] (**2**) ^1H NMR (C$_6$D$_6$): 1.55 (s, CH_3). ^{13}C NMR (C$_6$D$_6$): 32.78 (s, CH_3), 49.49 (s, CMe_3), 210.22 (s, –CO-*cis*), 211.50 (s, –CO-*trans*). MS (EI, 70 eV): 572 (1) [M]$^+$, 515 (8) [M−R]$^+$, 459 (1) [M−R−2CO]$^+$, 373 (5) [R$_2$BiCr]$^+$, 318 (11) [RBiCr]$^+$, 261 (8) [BiCr]$^+$, 108 (8) [Cr(CO)$_2$]$^+$, 57 (100) [R]$^+$, R = ^tBu.

[$^tBu_3BiW(CO)_5$] (**3**) ^1H NMR (C$_6$D$_6$): 1.52 (s, CH_3), ^{13}C NMR (C$_6$D$_6$): 32.59 (s, CH_3), 48.57 (s, CMe_3), 199.78 (s, –CO-*cis*). MS (EI, 70 eV): 704 (1) [M]$^+$, 647 (7) [M−R]$^+$, 591 (2) [M−2R]$^+$, 533 (3) [M−3R]$^+$, 505 (7) [BiW(CO)$_4$]$^+$, 477 (4) [BiW(CO)$_3$]$^+$, 449 (3) [BiW(CO)$_2$]$^+$, 421 (1) [BiW(CO)]$^+$, 393 (3) [BiW]$^+$, 57 (100) [R]$^+$, R = ^tBu.

4.2. Synthesis of [$^tBu_3BiMnCp'(CO)_2$] (4)

A solution of 0.41 g (1.86 mmol) [MnCp'(CO)$_3$] in 120 ml thf was photolysed for 2 h and added under stirring to a solution of 0.71 g (1.86 mmol) $^tBu_3Bi$ in thf. Removal of the solvent at reduced pressure and recrystallisation from hexane at −28 °C gave 0.21 g (20%) **4** (mp 142 °C) ^1H NMR (C$_6$D$_6$): 1.59 (s, C(CH_3)$_3$), 1.78 (s, CH_3), 4.09, 4.49 (m, C$_5H_4$), ^{13}C NMR (C$_6$D$_6$): 13.97 (s, C(CH_3)$_3$), 32.63 (s, CH_3), 46.71 (s, CMe_3), 77.58 (s, CH), 78.07 (s, CH), 81.95 (s, CH), 82.07 (s, CH). MS (EI, 70 eV): 570 (2) [M]$^+$, 513 (7) [M−R]$^+$, 456 (2) [M−2R]$^+$, 399 (19) [M−3R]$^+$, 371 (3) [M−3R−CO]$^+$, 343 (9) [M$^+$−3R−2CO], 264 (13) [BiMn]$^+$, 209 (6) [Bi]$^+$, 190 (7) [MnCp'(CO)$_2$]$^+$, 134 (40) [MnCp']$^+$, 57 (100) [R]$^+$, R = ^tBu. IR (Nujol): v (CO) 1862, 1920 cm^{-1}.

4.3. X-ray structure determination

Crystals suitable for X-ray diffraction of **1–4** were obtained from petroleum ether solutions at −28 °C. Data were collected at 173(2) K on a Siemens P4 diffractometer using 0.71073 Å Mo Kα radiation and corrected for absorp-

tion effects using DIFABS [21]. The structures were solved by direct methods for **1** and by Patterson method for **2–4** [22]. Structure solutions and refinements (full-matrix least-squares on F^2, anisotropic displacement parameters and H atoms in calculated positions) were carried out using WINGX software package [23]. All the non-hydrogen atoms were treated anisotropically. Hydrogen atoms were included in idealized positions with isotropic thermal parameters set at 1.5 times that of the carbon atom to which they were attached for the methyl groups and at 1.2 times for the aromatic groups. Complex **1** contains a dichloromethane molecule with the middle of distance between the two chlorine atoms localized on the special position (1, 1/2, 1/2). The carbon atom can be located in two position reported to the weight centre of the Cl–Cl distance and was refined with an s.o.f of 0.5. The carbon chlorine distances were restrained to be equal. Crystallographic data are summarized in Table 2. The diagrams of the X-ray structures were created with the Diamond software package.

Acknowledgement

Appendix A. Supplementary material

CCDC 637240, 637241, 637242 and 637243 contain the supplementary crystallographic data for **1**, **2**, **3** and **4**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.04.009.

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