



Syntheses, crystal structures and DFT studies of $[\text{Me}_3\text{EM}(\text{CO})_5]$ (E = Sb, Bi; M = Cr, W), *cis*- $[(\text{Me}_3\text{Sb})_2\text{Mo}(\text{CO})_4]$, and $[\text{}^t\text{Bu}_3\text{BiFe}(\text{CO})_4]$

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ABSTRACT

Syntheses of $[\text{Me}_3\text{SbM}(\text{CO})_5]$ [M = Cr (**1**), W (**2**)], $[\text{Me}_3\text{BiM}(\text{CO})_5]$ [M = Cr (**3**), W (**4**)], *cis*- $[(\text{Me}_3\text{Sb})_2\text{Mo}(\text{CO})_4]$ (**5**), $[\text{}^t\text{Bu}_3\text{BiFe}(\text{CO})_4]$ (**6**), crystal structures of **1–6** and DFT studies of **1–4** are reported.

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1. Introduction

In the family of trivalent pnictogen donors the antimony and more so the bismuth ligands have received less attention than their lighter congeners. In particular bismuthines have been considered as poor ligands, probably due to an inert character of the 6s lone pair of electrons at bismuth [1–4]. Nevertheless stable transition metal carbonyl complexes with bismuthine ligands were reported already decades ago, but only very few of them were fully characterized including crystal structure analyses [3]. In our precedent publication we reported the crystal structures of several metal (Cr, W, Mn) carbonyl complexes with the ligands ${}^t\text{Bu}_3\text{Sb}$ and ${}^t\text{Bu}_3\text{Bi}$ [5]. We have now included also the trimethyl pnictogen complexes $[\text{Me}_3\text{SbM}(\text{CO})_5]$ [M = Cr (**1**), W (**2**)], $[\text{Me}_3\text{BiM}(\text{CO})_5]$ [M = Cr (**3**), W (**4**)], *cis*- $[(\text{Me}_3\text{Sb})_2\text{Mo}(\text{CO})_4]$ (**5**), and $[\text{}^t\text{Bu}_3\text{BiFe}(\text{CO})_4]$ (**6**) in a comparative study of analogous Sb and Bi ligands and report here new syntheses and crystal structure analyses of **1–6** and DFT studies of **1–4**.

Syntheses of **1**, **2** [6] and **3** [7] were reported before. Other known transition metal carbonyl complexes with trimethylstibine or trimethylbismuthine ligands are $[\text{Me}_3\text{SbM}(\text{CO})_4]$ M = Fe [8], Ru [6], $[\text{Me}_3\text{SbMo}(\text{CO})_5]$ [6], $[(\text{Me}_3\text{Sb})_2\text{Fe}(\text{CO})_3]$ [8], $[\text{Me}_3\text{SbFe}(\text{CO})_3\text{-PPh}_3]$ [9], $[\text{CpFe}(\text{CO})_2\text{BiMe}_3]\text{BF}_4$ [10]. Also adducts of Me_3Sb with

antimony halides are known [11–13]. Crystal structures were reported for $[\text{Me}_3\text{SbFe}(\text{CO})_4]$ [14], $[\text{Me}_3\text{SbFe}(\text{CO})_3\text{PPh}_3]$ [9], whereas for **1**, **2**, and $[\text{Me}_3\text{SbMo}(\text{CO})_5]$ only Sb–M distances were published [6]. Related complexes with other triorganopnictogen ligands and with known crystal structures are $[\text{}^t\text{Bu}_3\text{SbFe}(\text{CO})_4]$ [15], $[\text{Ph}_3\text{SbM}(\text{CO})_5]$ M = Cr [16], Mo, W [17], $[\text{Ph}_3\text{BiM}(\text{CO})_5]$ M = Cr [16], Mo, W [18], and $[\text{CpFe}(\text{CO})_2\text{BiPh}_3]\text{BF}_4$ [10].

2. Results and discussion

The complexes **1–4** were prepared by substitution of tetrahydrofuran (thf) in reactions between Me_3Sb or Me_3Bi and $[\text{M}(\text{CO})_5(\text{thf})]$ (M = Cr, W). The substitution of piperidine in the reaction between Me_3Sb and *cis*- $[(\text{C}_5\text{H}_{11}\text{N})_2\text{Mo}(\text{CO})_4]$ gave **5**. The tetracarbonyl iron complex **6** was obtained from ${}^t\text{Bu}_3\text{Bi}$ and $\text{Fe}_2(\text{CO})_9$.

The complexes form as colourless (**1**), yellow (**2–5**), brown (**6**) crystalline solids. The antimony complexes **1**, **2**, **5** are air stable whereas the bismuth complexes **3**, **4**, **6** decompose in air. All complexes **1–6** are soluble in common organic solvents. ${}^1\text{H}$ and ${}^{13}\text{C}$ NMR spectra show the expected signals. In the infrared spectra the pattern of the CO stretching vibrations are typical for a C_{4v} local symmetry of the metalcarbonyl fragment in **1–4**. Electron impact mass spectra show molecular ions and characteristic fragments.

In order to get insight in the relative donor properties of trimethylstibine and trimethylbismuthine solutions of the bismuthine

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complexes **3** or **4** in tetrahydrofuran were reacted with solutions of Me_3Sb in diethyl ether at room temperature. After stirring for 12 h and working up the exchange was complete and crystalline samples of the stibine complexes **1** and **2** were obtained. The reverse reaction, i.e. substitution of trimethylstibine by trimethylbismuthine in **1** or **2** did not take place.

Complexes **1–6** were characterized by single crystal X-ray diffraction. All crystals are composed of molecular complexes with trigonal pyramidal ligands bonded through the Sb or Bi atom to the transition metal centres. Unusual intermolecular interactions were not observed. As a representative example the structure of **4** is shown in Fig. 1.

In **5** two trimethylstibine ligands occupy *cis* positions in an octahedral molybdenum carbonyl complex. The geometry of the iron complex **6** is trigonal bipyramidal with the *tert*-butylbismuthine ligand in the axial position. The structures of **5** and **6** are depicted in Figs. 2 and 3, respectively. Selected bond distances and angles of **1–6** are presented in Tables 1 and 2.

The values found for the coordinative bond lengths in **1**, Sb–Cr 2.6108(6) Å; **2**, Sb–W 2.7591(10) Å; **3**, Bi–Cr 2.701(2) Å; **4**, Bi–W 2.8374(8) Å; **5**, Sb–Mo av. 2.755 Å are very similar with the values

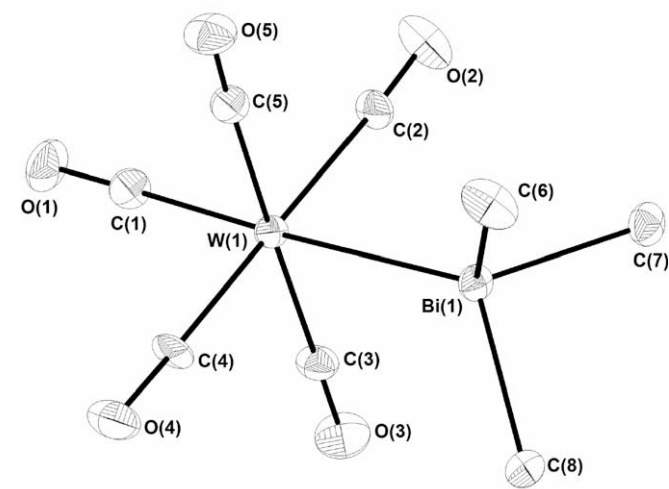


Fig. 1. Thermal ellipsoid (30%) representation of $[\text{Me}_3\text{BiW}(\text{CO})_5]$ (**4**). The hydrogen atoms were omitted for clarity.

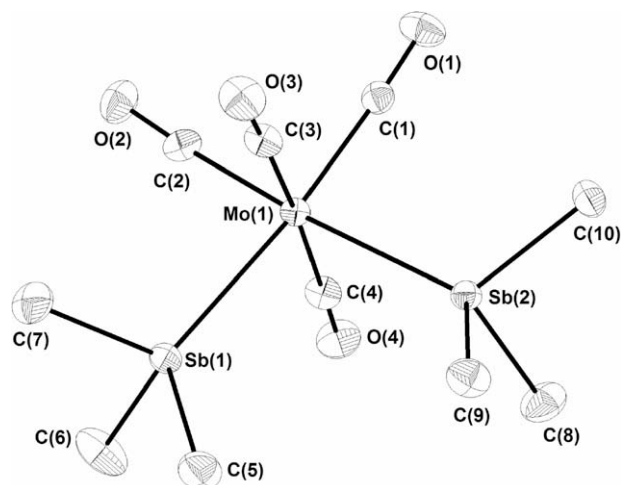


Fig. 2. Thermal ellipsoid (30%) representation of *cis*- $[(\text{Me}_3\text{Sb})_2\text{Mo}(\text{CO})_4]$ (**5**). The hydrogen atoms were omitted for clarity.

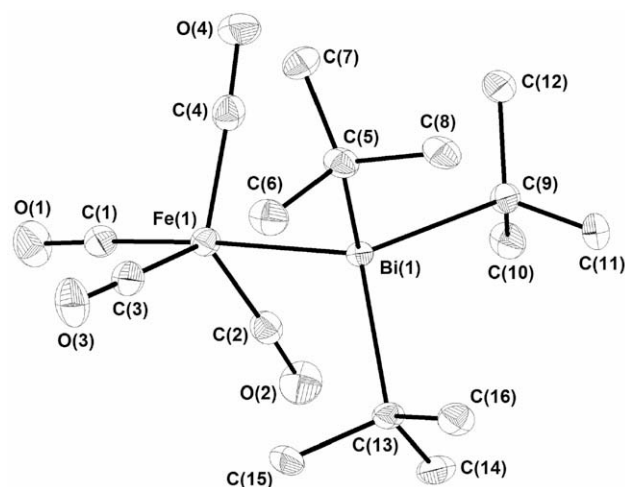


Fig. 3. Thermal ellipsoid (30%) representation of $[\text{tBu}_3\text{BiFe}(\text{CO})_4]$ (**6**). The hydrogen atoms were omitted for clarity.

reported by Takeda et al. for **1**, Sb–Cr 2.614(1) Å [6]; **5**, $[\text{Me}_3\text{SbMo}(\text{CO})_5]$, Sb–Mo 2.765(1) Å [6]; **2**, Sb–W 2.757(2) Å [6]. Similar bond lengths were also reported for $[\text{Ph}_3\text{EM}(\text{CO})_5]$ (E–M = Sb–Cr 2.6170(3), Sb–Mo 2.756(0), Sb–W 2.745(1), Bi–Cr 2.705(1), Bi–W 2.8294(5) Å) [16–18]. The coordinative bonds in $[\text{tBu}_3\text{EM}(\text{CO})_5]$ (E–M = Sb–Cr 2.7042(7), Bi–Cr 2.775(4), Bi–W 2.893(2) Å) are however significantly longer [5]. The comparison of analogous complexes with Sb and Bi ligands shows that the Bi–M (M = Cr, Mo, W) bonds are between 0.07 and 0.11 Å longer than the corresponding Sb–M bonds. This elongation approximately corresponds to the different covalent radii of antimony and bismuth (Sb 1.41 Å, Bi 1.50 Å). The structural data give no indication for unusual weak Bi–M (M = Cr, Mo, W) bonds.

Levason et al. reported that the coordination of Ph_3Sb to metal centres results in an increase of the C–Sb–C angles and a decrease of the C–Sb bond lengths [19,20]. Also for Ph_3Bi complexes an increase of the C–Bi–C bond angles by coordination from mean $93.9(1)^\circ$ to $99.1(9)^\circ$ was observed [19], but no relationship between the C–Bi–C angles and the Bi–C distances was found. The present results allow to extend these considerations to complexes with Me_3Sb and Me_3Bi as ligands.

The bond lengths and bond angles in **1–5** lie in the following ranges: Sb–C 2.122(4)–2.145(9) Å, Bi–C 2.208(12)–2.234(12) Å, C–Sb–C $97.3(4)$ – $102.5(4)^\circ$, C–Bi–C $97.0(7)$ – $100.6(7)^\circ$. For Me_3Sb and Me_3Bi gas phase structural data were reported with the bond parameters Sb–C 2.169 Å, Bi–C 2.266(4) Å, C–Sb–C = 94.2° and C–Bi–C = 97.1° [21,22]. The inspection of these data reveals that the trend for the decrease of the E–C bond lengths and the increase of the C–E–C bond angles on complexation of Me_3Sb and Me_3Bi is clearly evidenced for **1–5**.

In **6** the Bi–C bond lengths (2.314(5)–2.322(5) Å) are similar to the corresponding distances in $[\text{tBu}_3\text{BiM}(\text{CO})_5]$ (M = Cr, Mo) and $[\text{tBu}_3\text{BiM}(\text{CO})_2\text{Cp}^*]$ (2.314(5)–2.330(5) Å) [5]. The C–Bi–C bond angles in **6** ($106.1(2)$ – $106.8(2)^\circ$) and in $[\text{tBu}_3\text{BiM}(\text{CO})_5]$ (M = Cr, Mo) or $[\text{tBu}_3\text{BiMn}(\text{CO})_2\text{Cp}^*]$ C–Bi–C $103.93(13)$ – $106.6(3)^\circ$ [5] are in the same range. The Bi–Fe bond length in **6** (Bi–Fe 2.6269(9) Å) is longer than in $[\text{CpFe}(\text{CO})_2\text{BiPh}_3]\text{BF}_4$, Bi–Fe 2.570(1) Å [10]. The structure of **6** corresponds to other known complexes of $\text{Fe}(\text{CO})_4$ with respect to the axial position of the pnictogen ligand [14,15,23]. The coordinative bond in $[\text{tBu}_3\text{SbFe}(\text{CO})_4]$ Sb–Fe 2.547(1) Å [15] is 0.08 Å shorter than the corresponding bond in **6**. Again the comparison of structural data gives no hint for exceptionally poor ligand behaviour of $[\text{tBu}_3\text{Bi}]$ compared to the analogous antimony ligand.

Table 1
Measured and calculated bond lengths (Å) and bond angles (°) for **1–4**, **6**.

	(1) X-ray	(1) DFT	(2) X-ray	(2) DFT	(3) X-ray	(3) DFT	(4) X-ray	(4) DFT	(6) X-ray
C–O	1.147(5)	1.181	1.176(13)	1.185	1.149(16)	1.181	1.139(19)	1.185	1.139(8)
M–C	1.859(4)	1.850	1.984(11)	1.997	1.860(13)	1.847	1.977(15)	1.987	1.771(6)
E–M	2.6108(6)	2.666	2.7591(10)	2.826	2.701(2)	2.750	2.8374(8)	2.904	2.6269(9)
E–C	2.135(4)	2.151	2.124(11)	2.150	2.234(12)	2.224	2.236(16)	2.221	2.322(5)
	2.134(4)	2.151	2.133(10)	2.150	2.208(12)	2.224	2.225(14)	2.222	2.330(5)
	2.122(4)	2.151	2.145(9)	2.150	2.213(12)	2.223	2.252(16)	2.221	2.314(5)
C–E–C	100.47(17)	100.10	100.5(5)	100.03	99.4(6)	98.95	100.6(7)	99.14	106.8(2)
	99.95(17)	100.01	99.7(5)	100.22	99.4(6)	98.84	99.5(6)	99.10	106.7(2)
	101.88(16)	100.09	102.5(4)	100.14	99.8(5)	98.98	97.0(7)	99.17	106.1(2)

Table 2
Bond lengths (Å) and bond angles (°) for *cis*-[(Me₃Sb)₂Mo(CO)₄] (**5**).

	Molecule 1		Molecule 2	
	Sb(1)	Sb(2)	Sb(3)	Sb(4)
C ^a –O ^a	1.153(9)	1.153(9)	1.142(11)	1.143(9)
Mo–C ^a	1.986(7)	1.970(8)	1.966(8)	2.041(7)
Sb–Mo	2.7457(8)	2.7625(8)	2.7555(8)	2.7580(8)
Sb–C	2.138(9)	2.138(9)	2.120(7)	2.117(7)
	2.125(8)	2.127(8)	2.126(8)	2.124(8)
	2.132(8)	2.143(8)	2.133(8)	2.122(9)
C–Sb–C	99.7(4)	97.7(4)	97.8(4)	97.3(4)
	98.7(4)	99.0(4)	98.5(4)	99.4(4)
	97.7(4)	97.7(4)	100.4(4)	99.0(4)

^a Position *trans* to the antimony atom.

A theoretical study was carried out for a better understanding of the nature of the donor–acceptor bond in the series of complexes **1–4**. The theoretical calculations were carried out at DFT level using B3LYP functional [24], as included in the Gaussian software package [25], and the LANL2DZ basis set [26–28]. The basis set used for the pnictogen atoms was augmented with two polarization functions [29]. The bonding between the trimethylpnictogen ligand and the metal carbonyl fragment was studied using the charge decomposition analysis (CDA) [30]. With the ADF2007.01 software package the geometry optimizations, the frequency calculations, and the energy decomposition analysis were carried out using BLYP functional with the TZ2P basis set for H, C, O and the QZ4P basis set for Cr, Mo, W, Sb and Bi, as implemented [31–33]. A comparison of the calculated and the experimentally determined parameters is given as Supporting information, and the summary of CDA and EDA of **1–4** in Table 3.

Table 3
Charge decomposition analysis (CDA) and energy decomposition analysis (EDA) of the complexes **1–4**, and the EDA of Me₃PM(CO)₅, M = Cr, W (values taken from reference [34], and given for comparison^a).

	Me ₃ PCr(CO) ₅	Me ₃ PW(CO) ₅	1	2	3	4
CDA						
Donation (<i>d</i>)	–	–	0.375	0.508	0.342	0.482
Back-donation (<i>b</i>)	–	–	0.133	0.135	0.096	0.098
Repulsive polarization (<i>r</i>)	–	–	–0.220	–0.168	–0.180	–0.140
Residual (<i>s</i>)	–	–	–0.020	–0.017	–0.034	–0.036
Donation/back-donation ratio (<i>d/b</i>)	–	–	2.820	3.763	3.563	4.918
Bonding energy (kcal/mol)	–	–	–0.018	–0.018	–0.018	–0.018
EDA						
ΔE _{Pauli} (kcal/mol)	96.53	99.28	77.28	73.17	74.54	67.32
ΔE _{elstat} (kcal/mol)	–85.08	–94.85	–61.53	–64.04	–57.94	–57.97
	(60.7%)*	(65.1%)*	(57.85%)*	(63.83%)*	(56.60%)*	(62.22%)*
ΔE _{orb} (kcal/mol)	–55.11	50.80	–44.84	–36.29	–44.42	–35.20
	(39.3%)*	(34.9%)*	(42.15%)*	(36.17%)*	(43.40%)*	(37.78%)*
ΔE _{elstat} /ΔE _{orb} (kcal/mol)	–	–	1.37	1.76	1.30	1.65
ΔE (=–D _e) (eV)	–41.18	–43.82	–29.09	–27.15	–27.82	–25.85

^a The optimizations were carried out in Ref. [34] for Me₃PM(CO)₅, M = Cr, W using a different functional and a basis set than in the present work; * percentage of the total attractive interactions ΔE_{elstat} + ΔE_{orb}.

The calculated bond lengths are in very good agreement with the measured values. Large variations were found for the E–M and C–O_{trans} bond lengths. The calculated E–M bonds were found to be longer (2.07% in **1**, 2.37% in **2**, 1.78% in **3**, 2.29% in **4**) than the experimentally determined values. Similar differences between the measured and calculated bond lengths were reported before by Frenking et al. for the related complexes [X₃PM(CO)₅] M = Cr, Mo, W; X = H, Me, F, Cl [34]. They arise partly from the neglect of the crystal packing forces [34]. The calculated C–O_{trans} bond lengths are between 0.51% (**2**) and 3.72% (**4**) larger the experimentally determined values.

The small value of the repulsive polarization term of charge decomposition analysis [35,36], (CDA) indicates that the complexes **1–4** can be described with the Dewar–Chatt–Duncanson model [37]. The CDA shows that in all the complexes the donation term is dominant. It is larger for the tungsten complexes **2** and **4** than for the chromium complexes **1** and **3**, suggesting a better overlap between the orbitals of the transition metal and of the pnictogen containing ligand in the tungsten complexes. The back-donation term is slightly larger in the complexes of Me₃Sb than in those of Me₃Bi, leading to a larger donation/back-donation ratio (*d/b*) in the latter (see Supporting information). However, there are only small differences between the ligand properties of Me₃Sb and Me₃Bi in the complexes **1–4**.

Investigation of the coordinative bond between Me₃Sb and Me₃Bi and the M(CO)₅ fragments in terms of covalent vs. electrostatic contributions were carried out for **1–4** using energy decomposition analysis (EDA). These contributions, especially the latter, play an important role in the stability of metal carbonyl complexes [38,39]. This energy partitioning scheme and calculations on the related complexes Me₃PM(CO)₅, M = Cr, Mo, W were described before [34,39,40–42].

The largest contribution to the bonding energy (expressed in percents of the total bonding energy between the metacarbonyl and trimethylpnictogen fragment (**1**: 57.85%, **2**: 63.83%, **3**: 56.60%, **4**: 62.22%) is the electrostatic interaction. These findings are consistent with the analyses of the P–M bonds in $[\text{Me}_3\text{PM}(\text{CO})_5]$, M = Cr, Mo, W [34] where also electrostatic interactions are dominant. For the energy of the coordinative bonds very similar values were found (**1**: 29.09, **2**: 27.15, **3**: 27.82, **4**: 25.85 kcal/mol). These values are smaller than the bonding energy of the P–Cr coordinative bond in $[\text{Me}_3\text{PCr}(\text{CO})_5]$ (34.67 kcal/mol) calculated at the same theory level and with the same basis sets.

These findings confirm that the ligand properties of Me_3Sb and Me_3Bi ligands are comparable, the latter being only slightly weaker. Both Me_3Sb and Me_3Bi are weaker ligands than Me_3P , where the electrostatic interaction is much stronger. Nevertheless the complete ligand exchange between Me_3Sb and the bismuthine complexes **3** and **4** indicates that the formation of the stibine complex is favoured.

In the literature there are also cases where stable complexes were obtained with a Sb ligand but not with the analogous bismuthine. Reactivity studies of BiPh_3 and $\text{Ni}(\text{CO})_4$, $\text{Co}_2(\text{CO})_8$, $\text{Fe}_2(\text{CO})_9$ using conditions which successfully produce the corresponding SbPh_3 complexes led the formation of decomposition products [19].

3. Experimental

The operations were performed in inert atmosphere using dry solvents distilled under argon. The NMR spectra were recorded in C_6D_6 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 $\text{C}_6\text{D}_5\text{H}$ (^1H 7.15 ppm) and C_6D_6 (^{13}C 128.02 ppm). The infrared spectra were recorded as Nujol mull on a Perkin–Elmer Spectrum 1000 instrument. Mass spectra were recorded on Finnigan MAT 95 and MAT 8200 spectrometers. For the UV photolysis a Hanau TQ 150 mercury lamp was used. **1** (yield 32%, mp 76 °C), **2** (yield 55%, mp 86 °C) [6], and *cis*- $[(\text{C}_5\text{H}_{11}\text{N})_2\text{Mo}(\text{CO})_4]$ [43] were obtained by known methods.

3.1. Syntheses of $[\text{Me}_3\text{SbCr}(\text{CO})_5]$ (**1**)

(a) 2.5 g (6.8 mmol) $[\text{Cr}(\text{CO})_6]$ in 120 mL thf were photolysed for 3 h. Thereafter 1.0 g (6 mmol) Me_3Sb in diethylether were added and the solution was stirred 3 h. Removal of the solvents under reduced pressure and recrystallization from petroleum ether gave 1.55 g (72%) **1** (m.p. 74 °C). Single crystals suitable for X-ray crystallography were obtained by vacuum sublimation at 60 °C.

(b) 0.2 g (1.2 mmol) Me_3Sb in diethyl ether were added dropwise to 0.5 g (1.1 mmol) **3** in 50 mL thf. After stirring the solution at rt for 12 h the solvents were removed in vacuum. The remaining solid was extracted with *n*-hexane and the resulting yellow solution was filtered through a frit covered with kieselgur. Removal of the solvent in vacuum gave 0.7 g (92%) (**1**).

^1H NMR (C_6D_6): 0.48 (s, CH_3). ^{13}C NMR (C_6D_6): –3.24 (s, CH_3), 218.35 (s, –CO-*cis*), 223.60 (s, –CO-*trans*). MS (EI, 70 eV): 358 (37) $[\text{M}]^+$, 315 (9) $[\text{M}-\text{CO}-\text{Me}]^+$, 302 (9) $[\text{M}-2\text{CO}]^+$, 274 (11) $[\text{M}-3\text{CO}]^+$, 246 (38) $[\text{M}-4\text{CO}]^+$, 218 (100) $[\text{R}_3\text{SbCr}]^+$, 188 (13) $[\text{RSbCr}]^+$, 80 (14) $[\text{CrCO}]^+$, 52 (95) $[\text{Cr}]^+$, R = CH_3 . HRMS: Calc. 355.89487, Meas. 355.89605. IR (Nujol): $\nu(\text{CO})$ 2069, 1940; Lit. [6] 2069, 1947 cm^{-1} .

3.2. Syntheses of $[\text{Me}_3\text{SbW}(\text{CO})_5]$ (**2**)

(a) 2.1 g (6.0 mmol) $[\text{W}(\text{CO})_6]$ in 120 mL thf were photolysed for 3 h. Thereafter 1.0 g (6 mmol) Me_3Sb in diethylether were added

and the solution was stirred 2 h. Removal of the solvents under reduced pressure and recrystallization from petroleum ether gave 1.6 g (55%) **2** (m.p. 90 °C). Single crystals suitable for X-ray crystallography were obtained by vacuum sublimation at 60 °C.

(b) 0.3 g (1.1 mmol) Me_3Sb in diethylether were added dropwise to 0.9 g (1.5 mmol) **4** in 50 mL toluene. The mixture was stirred for 12 h at rt and the solvents were removed in vacuum. The remaining solid was extracted with *n*-hexane and filtered through a frit covered with kieselgur. After concentrating and cooling the solution to –10 °C 0.38 g (95%) crystals of **2** were obtained.

^1H NMR (C_6D_6): 0.55 (s, CH_3). ^{13}C NMR (C_6D_6): –2.81 (s, CH_3), 197.13 (s, –CO-*cis*), 199.70 (s, –CO-*trans*). MS (EI, 70 eV): 490 (77) $[\text{M}]^+$, 464 (65) $[\text{M}-\text{CO}]^+$, 433 (32) $[\text{M}-2\text{CO}]^+$, 405 (29) $[\text{M}-3\text{CO}]^+$, 378 (61) $[\text{M}-4\text{CO}]^+$, 350 (100) $[\text{M}-5\text{CO}]^+$, 333 (69) $[\text{M}-5\text{CO}-\text{R}]^+$, 318 (61) $[\text{M}-5\text{CO}-2\text{R}]^+$, 305 (20) $[\text{SbW}]^+$, 151 (6) $[\text{R}_2\text{Sb}]^+$, 121 (5) $[\text{Sb}]^+$, 28 (18) $[\text{CO}]^+$, R = CH_3 . HRMS Calc. 487.89705, Meas. 487.89819. IR (Nujol): $\nu(\text{CO})$ 2068, 1938, 1909; Lit. [6] 2068, 1938, 1901 cm^{-1} .

3.3. Synthesis of $[\text{Me}_3\text{BiCr}(\text{CO})_5]$ (**3**)

2.2 g (0.01 mol) $[\text{Cr}(\text{CO})_6]$ in 140 mL thf were photolysed for 2.5 h. Thereafter 2.54 g (10 mmol) Me_3Bi were added and the solution was stirred 6 h. Removal of the solvent under reduced pressure and recrystallization from petroleum ether at –28 °C gave 5.31 g (92%) **3** (m.p. 55 °C).

^1H NMR (C_6D_6): 1.11 (s, CH_3). ^{13}C (C_6D_6): –7.15 (s, CH_3), 218.18 (s, –CO-*cis*). MS (EI, 70 eV): 446 (7) $[\text{M}]^+$, 390 (2) $[\text{M}-2\text{CO}]^+$, 362 (3) $[\text{M}-3\text{CO}]^+$, 334 (5) $[\text{M}-4\text{CO}]^+$, 306 (7) $[\text{R}_3\text{BiCr}]^+$, 254 (53) $[\text{R}_3\text{Bi}]^+$, 239 (100) $[\text{R}_2\text{Bi}]^+$, 224 (70) $[\text{RBi}]^+$, 209 (87) $[\text{Bi}]^+$, 52 (22) $[\text{Cr}]^+$, R = CH_3 . IR (Nujol): $\nu(\text{CO})$ 1942, 2060 cm^{-1} .

3.4. Synthesis of $[\text{Me}_3\text{BiW}(\text{CO})_5]$ (**4**)

Analogous to the synthesis of **3** the reaction between photolysis product of 3.52 g (10 mmol) $[\text{W}(\text{CO})_6]$ and 2.54 g (10 mmol) was carried out and 3.21 g (72%) (**4**) (m.p. 78–80 °C) were obtained.

^1H NMR (C_6D_6): 1.16 (s, CH_3). ^{13}C NMR (C_6D_6): –7.20 (s, CH_3), 198.17 (s, –CO-*cis*). MS (EI, 70 eV): 578 (100) $[\text{M}]^+$, 563 (59) $[\text{M}-\text{R}]^+$, 533 (9) $[\text{M}-3\text{R}]^+$, 505 (40) $[\text{BiW}(\text{CO})_4]^+$, 477 (52) $[\text{BiW}(\text{CO})_3]^+$, 449 (81) $[\text{BiW}(\text{CO})_2]^+$, 421 (67) $[\text{BiW}(\text{CO})]^+$, 393 (32) $[\text{BiW}]^+$, 254 (23) $[\text{R}_3\text{Bi}]^+$, 239 (67) $[\text{R}_2\text{Bi}]^+$, 224 (34) $[\text{RBi}]^+$, 209 (82) $[\text{Bi}]^+$, R = CH_3 . IR (Nujol): $\nu(\text{CO})$ 1942, 2070 cm^{-1} .

3.5. Synthesis of *cis*- $[(\text{Me}_3\text{Sb})_2\text{Mo}(\text{CO})_4]$ (**5**)

0.43 g (2.57 mmol) Me_3Sb were added to 0.5 g (1.3 mmol) *cis*- $[(\text{C}_5\text{H}_{11}\text{N})_2\text{Mo}(\text{CO})_4]$ in toluene. After 1 h refluxing and 12 h stirring at room temperature the solvent was removed in vacuum and the remaining solid was extracted with petroleum ether. Crystallisation at –15 °C gave 0.52 g (72%) **5** (m.p. 87 °C).

^1H NMR (C_6D_6): 0.65 (s, CH_3). ^{13}C NMR (C_6D_6): –1.17 (s, CH_3), 211.445 (s, –CO-*cis*), 216.37 (s, –CO-*trans*). MS (EI, 70eV): 544 (86) $[\text{M}]^+$, 516 (69) $[\text{M}-\text{CO}]^+$, 486 (61) $[\text{M}-2\text{CO}]^+$, 430 (100) $[\text{M}-4\text{CO}]^+$, 383 (55) $[\text{MoSb}_2\text{R}_3]^+$, 367 (72) $[\text{MoSb}_2\text{R}_2]^+$, 247 (32) $[\text{R}_2\text{SbMo}]^+$, 232 (33) $[\text{RSbMo}]^+$, 151 (65) $[\text{R}_2\text{Sb}]^+$, 136 (20) $[\text{RSb}]^+$, 28 (14.7) $[\text{CO}]^+$, R = CH_3 . HRMS Calc. 535.83497, Meas. 535.83522. IR (Nujol): $\nu(\text{CO})$ 1901, 1912, 1925, 2018.

3.6. Synthesis of $[\text{Bu}_3\text{BiFe}(\text{CO})_4]$ (**6**)

To a solution of 2.0 g (5.26 mmol) $^t\text{Bu}_3\text{Bi}$ in 30 mL thf 1.92 g (5.3 mmol) $\text{Fe}_2(\text{CO})_9$ were added and the mixture was stirred at room temperature for 15 h. After filtration and removal of the solvent at reduced pressure a red oil remained. Crystallisation from hexane at –28 °C gave 1.17 g (40.6%) **6**.

Table 4
X-ray diffraction data and structure refinement details for **1–6**

Compound	1	2	3	4	5	6
Empirical formula	C ₈ H ₉ CrO ₅ Sb	C ₈ H ₉ O ₅ SbW	C ₈ H ₉ BiCrO ₅	C ₈ H ₉ BiO ₅ W	C ₁₀ H ₁₈ MoO ₄ Sb ₂	C ₁₆ H ₂₇ BiFeO ₄
Formula weight	358.90	490.75	446.13	577.98	541.68	548.21
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic
Space group	<i>P</i> 1 21 1	<i>P</i> 21	<i>P</i> 1 21 1	<i>P</i> 1 21 1	<i>P</i> 21 21 21	<i>P</i> 21 21 21
<i>a</i> (Å)	6.5688(11)	6.6472(12)	6.544(2)	6.6279(13)	10.1053(12)	10.155(2)
<i>b</i> (Å)	13.633(2)	13.872(4)	13.935(7)	14.138(3)	12.3624(17)	10.182(2)
<i>c</i> (Å)	6.8871(12)	6.9555(12)	6.868(3)	6.9490(14)	27.422(2)	19.166(4)
α (°)	90	90	90	90	90	90
β (°)	92.289(11)	91.718(14)	91.93(3)	91.49(3)	90	90
γ (°)	90	90	90	90	90	90
Volume (Å ³)	616.26(18)	641.1(2)	625.9(5)	650.9(2)	3425.7(7)	1981.8(7)
<i>Z</i>	2	2	2	2	8	4
<i>D</i> _{calc} (Mg/m ³)	1.934	2.542	2.367	2.949	2.101	1.837
Absorption coefficient (mm ⁻¹)	3.070	11.069	14.902	22.325	3.852	9.612
<i>F</i> (000)	344	444	408	508	2032	1056
Crystal size (mm ³)	0.50 × 0.40 × 0.30	0.80 × 0.40 × 0.30	0.80 × 0.30 × 0.15	0.40 × 0.30 × 0.20	0.60 × 0.40 × 0.30	0.40 × 0.30 × 0.20
θ Range for data collection (°)	2.96–27.49	2.93–27.52	2.92–27.51	2.88–26.02	2.50–27.50	2.13–26.09
Index ranges (<i>h</i> , <i>k</i> , <i>l</i>)	–2/8, \pm 17, \pm 8	–8/1, \pm 18, \pm 9	–2/8, \pm 18, \pm 8	\pm 8, \pm 17, \pm 8	–13/11, –16/12, –18/35	\pm 12, \pm 12, \pm 23
Reflections collected/unique [<i>R</i> _{int}]	3608/2834 [0.0202]	3728/2905 [0.0399]	3624/2840 [0.0577]	4470/2359 [0.0460]	5579/5231 [0.0160]	28157/3886 [0.0559]
Completeness to θ [θ] (%)	100.0 [27.49]	99.9 [27.52]	99.9 [27.51]	96.2 [26.02]	99.8 [27.50]	98.8 [26.09]
Maximum and minimum transmission	0.4594 and 0.3090	0.1360 and 0.0409	0.2134 and 0.0295	0.0945 and 0.0405	0.3911 and 0.2058	0.2494 and 0.1138
Data/restraints/parameters	2834/1/141	2905/1/140	2840/1/140	2359/1/140	5231/0/320	3886/0/209
Goodness-of-fit on <i>F</i> ²	1.111	1.112	1.046	1.080	1.064	1.200
Final <i>R</i> indices (<i>I</i> > 2 σ (<i>I</i>)) (<i>R</i> ₁ , <i>wR</i> ₂)	0.0197, 0.0516	0.0302, 0.0813	0.0454, 0.1116	0.0340, 0.0853	0.0302, 0.0766	0.0195, 0.0475
<i>R</i> indices (all data) (<i>R</i> ₁ , <i>wR</i> ₂)	0.0201, 0.0518	0.0302, 0.0814	0.0493, 0.1142	0.0349, 0.0872	0.0333, 0.0785	0.0227, 0.0580
Absolute structure parameter	0.16(3)	–0.012(10)	–0.034(15)	0.256(14)	–0.07(3)	0.111(7)
Extinction coefficient	0.0023(5)	0.0020(5)	0.0045(11)	–	0.00034(5)	–
Largest difference in peak and hole (e Å ⁻³)	0.393 and –0.298	1.158 and –1.167	3.021 and –2.541	2.165 and –2.555	0.946 and –1.225	0.753 and –1.206

¹H NMR (C₆D₆): 1.56 (s, CH₃). ¹³C NMR (C₆D₆): 32.78 (s, CH₃), 65.89 (s, CCH₃). MS (EI, 70 eV): 548 (29) [M]⁺, 520 (12) [M–CO]⁺, 491 (10) [M–2CO–H]⁺, 435 (3) [M–4CO–H]⁺, 379 (25) [R₃Bi–H]⁺, 320 (78) [R₂Bi–3H]⁺, 265 (57) [RBi–H]⁺, 57 (100) [R]⁺, R = ^tBu. IR (Nujol): ν (CO) 1925, 1957, 2032 cm⁻¹.

3.7. X-ray structure determination

Crystals suitable for X-ray diffraction of **1–6** were grown from concentrated petroleum ether (**3–5**) or hexane (**6**) solutions or by vacuum sublimation (**1**, **2**). Data were collected at 173(2) K on a Siemens P4 diffractometer using a 0.71073 Å Mo K α radiation and corrected for absorption effects using DIFABS [44]. The structures were solved by direct or Patterson methods [45,46]. Structure solutions and refinements were performed using WinGX software package [47]. The representations of the X-ray structures were created using the Diamond software package. Crystal data and structure refinement details for **1–6** are given in Table 4.

4. Concluding remarks

The crystal structures of **1–6** and DFT studies of **1–4** are reported. The crystallographic and the theoretical data indicate that Me₃Sb and Me₃Bi have similar ligand properties, and are able to form stable complexes with transition metalcarbonyl fragments. In the pnictogen transition metal bond an important role is played by the electrostatic interaction between the fragments.

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Appendix A. Supplementary material

CCDC 697290–697295 contain the supplementary crystallographic data for **1–6**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.11.022.

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