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Syntheses, crystal structures and DFT studies of $[Me_3EM(CO)_5]$ (E = Sb, Bi; M = Cr, W), *cis*-$[(Me_3Sb)_2Mo(CO)_4]$, and $[^tBu_3BiFe(CO)_4]$

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ABSTRACT

Syntheses of $[Me_3SbM(CO)_5]$ [M = Cr (**1**), W (**2**)] , $[Me_3BiM(CO)_5]$ [M = Cr (**3**), W (**4**)], *cis*-$[(Me_3Sb)_2Mo(CO)_4]$ (**5**), $[^tBu_3BiFe(CO)_4]$ (**6**), crystal structures of **1–6** and DFT studies of **1**–**4** are reported.

1. Introduction

In the family of trivalent pnicogen 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 $^tBu_3Sb$ and $^tBu_3Bi$ [5]. We have now included also the trimethyl pnicogen complexes $[Me_3SbM(CO)_5]$ [M = Cr (**1**), W (**2**)], $[Me_3BiM(CO)_5]$ [M = Cr (**3**), W (**4**)], [*cis*-$[(Me_3Sb)_2Mo(CO)_4]$ (**5**), and $[^tBu_3BiFe(CO)_4]$ (**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 $[Me_3SbM(CO)_4]$ M = Fe [8], Ru [6], $[Me_3SbMo(CO)_5]$ [6], $[(Me_3Sb)_2Fe(CO)_3]$ [8], $[Me_3SbFe(CO)_3PPh_3]$ [9], $[CpFe(CO)_2BiMe_3)]BF_4$ [10]. Also adducts of Me_3Sb with antimony halides are known [11–13]. Crystal structures were reported for $[Me_3SbFe(CO)_4]$ [14], $[Me_3SbFe(CO)_3PPh_3]$ [9], whereas for **1**, **2**, and $[Me_3SbMo(CO)_5]$ only Sb–M distances were published [6]. Related complexes with other triorganopnicogen ligands and with known crystal structures are $[^tBu_3SbFe(CO)_4]$ [15], $[Ph_3SbM(CO)_5]$ M = Cr [16], Mo, W [17], $[Ph_3BiM(CO)_5]$ M = Cr [16], Mo, W [18], and $[CpFe(CO)_2BiPh_3)]BF_4$ [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 $[M(CO)_5(thf)]$ (M = Cr, W). The substitution of piperidine in the reaction between Me_3Sb and *cis*-$[(C_5H_{11}N)_2Mo(CO)_4]$ gave **5**. The tetracarbonyl iron complex **6** was obtained from $^tBu_3Bi$ and $Fe_2(CO)_9$.

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. ^1H and ^{13}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 reported by Takeda et al. for **1**, Sb–Cr 2.614(1) Å [6]; **5**, $[Me_3SbMo(CO)_5]$, Sb–Mo 2.765(1) Å [6]; **2**, Sb–W 2.757(2) Å [6]. Similar bond lengths were also reported for $[Ph_3EM(CO)_5]$ (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 $[{}^tBu_3EM(CO)_5]$ (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.

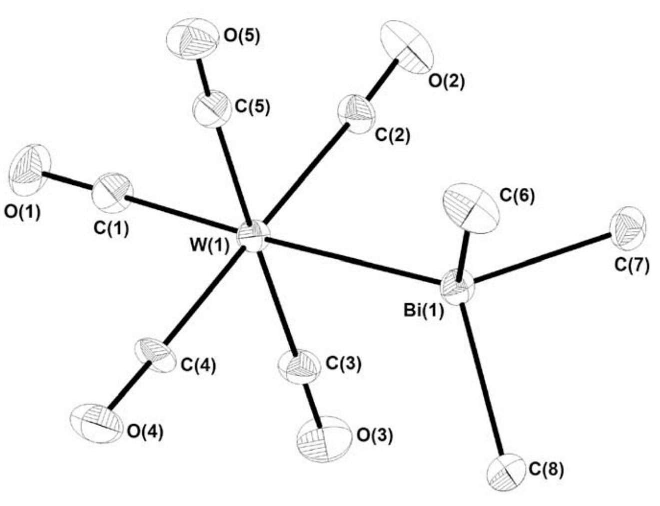

Fig. 1. Thermal ellipsoid (30%) representation of $[Me_3BiW(CO)_5]$ (**4**). The hydrogen atoms were omitted for clarity.

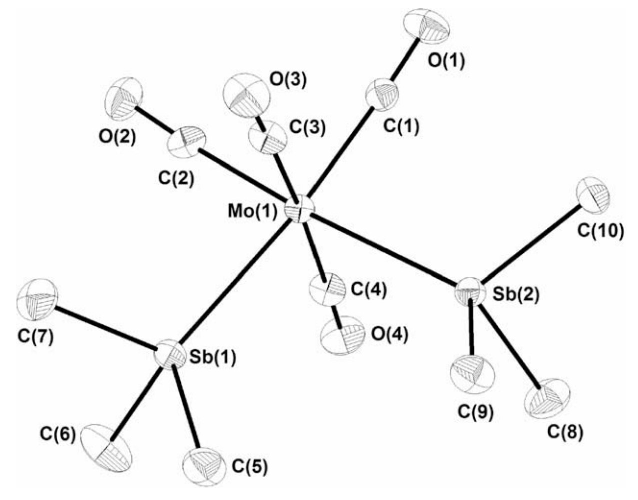

Fig. 2. Thermal ellipsoid (30%) representation of *cis*-$[(Me_3Sb)_2Mo(CO)_4]$ (**5**). The hydrogen atoms were omitted for clarity.

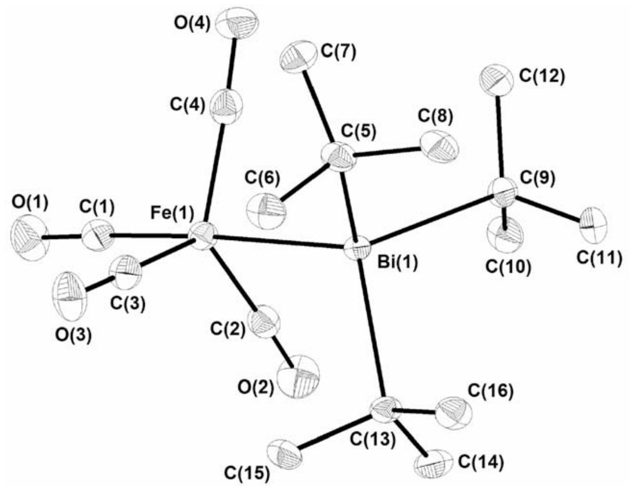

Fig. 3. Thermal ellipsoid (30%) representation of $[{}^tBu_3BiFe(CO)_4]$ (**6**). The hydrogen atoms were omitted for clarity.

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)° to 99.1(9)° 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)°, C–Bi–C 97.0(7)–100.6(7)°. 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 $[{}^tBu_3BiM(CO)_5]$ (M = Cr, Mo) and $[{}^tBu_3BiM(CO)_2Cp']$ (2.314(5)–2.330(5) Å) [5]. The C–Bi–C bond angles in **6** (106.1(2)–106.8(2)°) and in $[{}^tBu_3BiM(CO)_5]$ (M = Cr, Mo) or $[{}^tBu_3BiMn(CO)_2Cp']$ C–Bi–C 103.93(13)–106.6(3)° [5] are in the same range. The Bi–Fe bond length in **6** (Bi–Fe 2.6269(9) Å) is longer than in $[CpFe(CO)_2BiPh_3]BF_4$, Bi–Fe 2.570(1) Å [10]. The structure of **6** corresponds to other known complexes of $Fe(CO)_4$ with respect to the axial position of the pnicogen ligand [14,15,23]. The coordinative bond in $[{}^tBu_3SbFe(CO)_4]$ 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 ${}^tBu_3Bi$ compared to the analogous antimony ligand.