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Syntheses, structures and DFT study of [W(CO)$_5$(Ph$_2$SbX)] X = Cl, Br, I

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Abstract

The complexes [W(CO)$_5$(Ph$_2$SbX)], X = Cl (**1**), Br (**2**) and I (**3**) were prepared by reaction of [W(CO)$_5$(tetrahydrofuran)] with Ph$_2$SbX. The structures of **1**–**3** were studied by X-ray diffraction. In the crystals there are weak contacts between the oxygen atoms of the CO ligands and antimony atoms of neighbouring molecules. DFT calculations were carried out for **1** using gradient corrected functional B3LYP. The bonding between Ph$_2$SbCl and the W(CO)$_5$ fragment in **1** was analysed using charge decomposition analysis.
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1. Introduction

Pentacarbonyl metal complexes with diorganoantimony halide ligands of the type [M(CO)$_5$(R$_2$SbX)] possess a functional group at antimony and hence they can be useful as antimony reagents with protection by the metal carbonyl fragment. The inspection of their crystal structures and theoretical calculations allow to study the effect of coordination on the geometry of the R$_2$SbX unit. Several complexes of this type have been synthesised [1–5]; none of them was studied by X-ray diffraction. We chose the series [W(CO)$_5$(Ph$_2$SbX)], X = Cl (**1**), Br (**2**) and I (**3**) for an inspection of the crystal structures and selected **1** for a study at the DFT level. The synthesis and characterisation of **1** [1] and the crystal structures of the free ligands Ph$_2$SbX (X = Cl [6], Br [7], I [8]) were reported before.

2. Results and discussion

[W(CO)$_5$(Ph$_2$SbCl)] (**1**) was prepared by the exchange reaction between [W(CO)$_5$(THF)] (THF = tetrahydrofuran) and diphenylantimony chloride as described by Wieber and Graf [1]. An analogous procedure led to [W(CO)$_5$(Ph$_2$SbX)] [X = Br (**2**), I (**3**)]. Yellow green (**1**) or yellow (**2**, **3**) single crystals were obtained by cooling solutions in petroleum ether. The crystals are air stable and well soluble in organic solvents. Also thermally **1**–**3** are relatively stable. They melt without decomposition above 80 °C but become slowly brown after further heating of the liquids. The structures of **1**–**3** were determined by single crystal X-ray diffraction. The molecules are composed of pyramidal Ph$_2$SbX units coordinated through the antimony atoms to tetragonal pyramidal W(CO)$_5$ fragments. The phenyl groups adopt a propeller like arrangement. As a representative example the structure of **3** is depicted in Fig. 1. Relevant bond lengths and bond angles of **1**–**3** and of the non-coordinated diphenylantimony halides are listed in Table 2.

The Sb–W bonds in **1**: 2.7184(10), **2**: 2.7243(8), **3**: 2.7256(7) Å are slightly shorter than the corresponding

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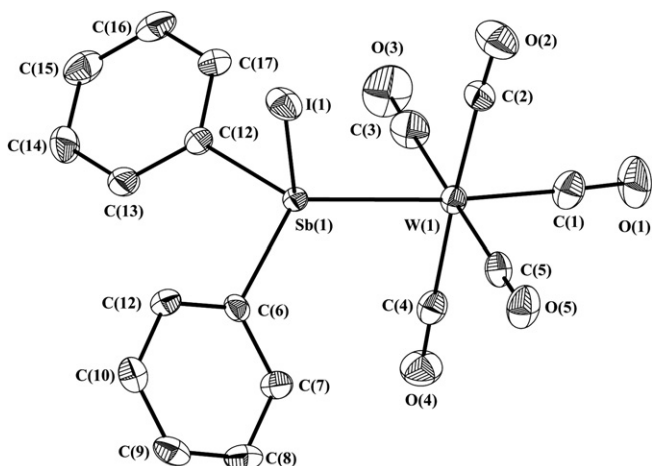*E-mail address:* breunig@chemie.uni-bremen.de (H.J. Breunig).

Fig. 1. ORTEP style representation at 50% probability and the numbering scheme of [W(CO)$_5$(Ph$_2$SbI)] (**3**).

bonds in [W(CO)$_5$(Ph$_3$Sb)] 2.745(1) Å [9], [{W(CO)$_5$}$_n$-{(Ph$_2$Sb)$_2$CH$_2$}], $n = 1$; 2.743(1), $n = 2$; 2.756(2) Å [10], or [{W(CO)$_5$}$_2$(Ph$_2$Sb$_2$)] 2.749(1) Å [11]. The values for the W–C bond lengths in **1–3** range from 1.989(8) to 2.056(6) Å. The W–C bonds *trans* to the Ph$_2$SbX ligands are in average 3% (0.048 Å in **1**, 0.047 Å in **2** and 0.044 Å in **3**) shorter than those in *cis* positions. The C–O bond lengths lie between 1.114(8) and 1.154(11) Å close to the values encountered in related complexes [9–11]. The Sb–C and the Sb–halogen bonds are a little shorter in the complexes than in the free ligands. A remarkable result of the coordination is the widening of the C–Sb–C and C–Sb–X bond angles. The sum of the bond angles, i. e. C–Sb–C and C–Sb–X at antimony is between 8° and 11° larger in the complexes **1–3** than in the free ligands.

Interesting differences emerge also when the packing of **1–3** in the crystal is inspected. Crystals of **1** contain pairs of molecules (Fig. 2), with contact distances of 3.451(8) Å
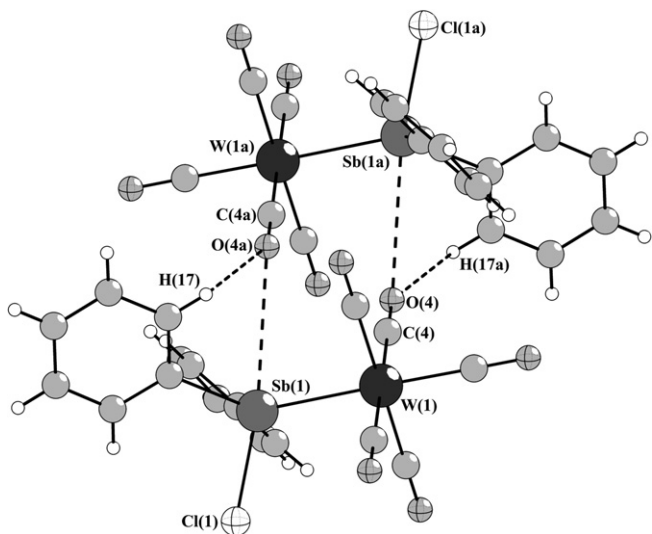

Fig. 2. Dimeric association of [W(CO)$_5$(Ph$_2$SbCl)] (**1**).

between oxygen atoms of carbonyl groups and antimony atoms of the neighbouring molecules. These distances are close to the sum of van der Waals radii of antimony and oxygen [∑$_{rvdW}$(Sb, O) 3.52 Å] [12]. Although it appears that the intermolecular Sb···O contacts are very weak it is remarkable that the oxygen atoms of the neighbouring molecules occupy positions *trans* to the Sb–Cl bonds (Cl–Sb···O 172.39(14)°). This pattern is typical for Lewis-acid–base interactions between diorgano antimony halides and donor molecules [13]. In an analogous manner also the dimeric association of **1** in the crystal may result from a very weak intermolecular Lewis-acid–base interaction, which leads to the bridging coordination of the CO molecule between tungsten and antimony. The interaction M–CO···M′ in **1** leads to an elongation of the C–O bond. In fact the bond length of the CO group involved in the intermolecular interaction with 1.154 Å is the longest encountered in **1–3**. Examples of complexes with a CO group coordinated to a second metal centre are well known [14,15]. Bridging CO groups between a transition metal and a p block elements were reported in the structures of [{η-C$_5$H$_5$W(CO)$_3$(AlMe$_2$)}$_2$] (C–O 1.18(3), CO···Al 1.793(18) Å) [16] and [Co(Ph$_3$P)$_2$(CO)$_3$BEt$_3$] (C–O 1.157(4), CO···B 1.601(5) Å) [17]. In crystals of **1** there are also weak intermolecular contacts between the oxygen atom of the bridging CO group and the *ortho* hydrogen atoms of the closest phenyl ring. The contact distance (H···O 2.641 Å) is close to the sum of van der Waals radii of the respective elements [∑$_{vdW}$(H, O) ca. 2.72 Å].

Weak intermolecular Sb···O contacts [3.368(5) Å] exist also in crystals of **2**. The Br–Sb···O angle of 156.58(9)° indicates a considerable deviation from an ideal *trans* arrangement. Through the Sb···O interactions the molecules of **2** are arranged to infinite chains. Between the chains there are weak contacts (H···O 2.64 Å) connecting the oxygen atoms of carbonyl groups and *para*-hydrogen atoms of phenyl groups. A section of two chains in the crystals of **2** is shown in Fig. 3.

Also the molecules of **3** are arranged in infinite chains through weak intermolecular interactions between antimony and oxygen atoms of carbonyl groups. The shortest Sb···O distance is 3.548(6) Å, right at the van der Waals limit. The angle I–Sb···O is 155.65(11)°. Besides the weak interactions listed above the molecular units are connected through a net of interactions between the hydrogen atoms of the phenyl groups and the oxygen atoms of the carbonyl groups.

For a better understanding of the coordinative bonding in **1** theoretical studies using DFT, NBO and CDA methods were carried out. The DFT and NBO calculations were performed for the free ligand, Ph$_2$SbCl and for the complex **1**. In particular, we wanted to explain the experimentally observed increase in the sum of bond angles at antimony in the Ph$_2$SbCl unit as a result of the complexation. The calculated geometrical parameters are in good agreement with the experimental data. The bond lengths and bond angles are listed in Table 1. The former
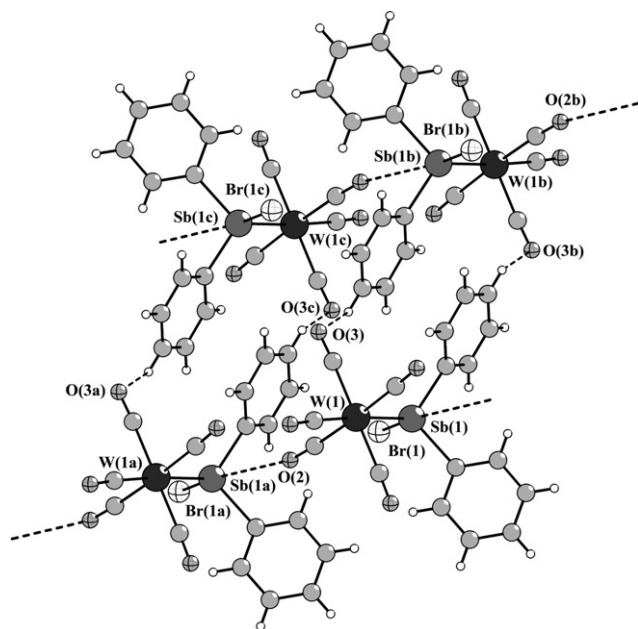
Fig. 3. Supramolecular assembly of [W(CO)$_5$(Ph$_2$SbBr)] (2) in the crystal.

are slightly longer than the experimental values [18]. HOMO-3 represents the sigma bonding between antimony and the tungsten pentacarbonyl unit. The largest contribution to HOMO and HOMO-1 comes from the orbitals d_{xz}, respectively, d_{xy} of tungsten. Nevertheless both orbitals feature also some electron density delocalisation from tungsten toward antimony representing the π back bonding where antibonding Sb–Cl and Sb–C orbitals are involved.

The natural bonding orbital (NBO) [19,20] analysis reveals that the contributions of the atomic orbitals of antimony to the lone pair in Ph$_2$SbCl are 74.22% s and 25.78% p. The corresponding values for the contribution of antimony orbitals to the W–Sb bond in 1 are 16.91% s and 83.05% p. These data show that the configuration at antimony changes from close to p^3 with the lone pair having mainly s character towards a close to sp^3 hybridisation. This change leads to the experimentally observed widening of the bond angles at antimony and to a strengthening of the dative bond between antimony and tungsten.

A quantitative description of the bonding in 1 in terms of donation, back donation and repulsion can be drawn using the charge decomposition analysis scheme (CDA) [21,22]. The method is based on the model of Dewar–Chatt–Duncanson of the synergistic metal–ligand bonding [22,23]. Good descriptions of the technical details regarding CDA application and examples of the usage on metal carbonyls can be found in the literature [22,24,25].

The CDA of 1 confirms the donor–acceptor nature of the interaction between the Ph$_2$SbCl and W(CO)$_5$ moieties, through the low value of the residual term Δ(−0.018). Although CDA does not provide any information about

Table 1
Measured and calculated bond lengths (Å) and angles (°) in Ph$_2$SbX and [W(CO)$_5$(Ph$_2$SbX)], X = Cl (1), Br (2), I (3)

	Ph$_2$SbCl (X-ray) [6]	Ph$_2$SbCl (calc.)	1 (X-ray)	1 (calc.)	(1)$_2$ (calc.)	Ph$_2$SbBr (X-ray) [7]	2 (X-ray)	Ph$_2$SbI (X-ray) [8]	3 (X-ray)
W(1)–C(1)			1.989(8)	2.016	2.012		2.001(6)		1.999(7)
C(1)–O(1)			1.154(11)	1.156	1.158		1.129(8)		1.140(10)
Sb(1)–W(1)			2.7184(10)	2.779	2.791		2.7243(8)		2.7256(7)
Sb(1)–X(1)	2.409(1)	2.437	2.362(2)	2.414	2.417	2.553(1)	2.5115(10)	2.771(1)	2.7181(8)
Sb(1)–C(6)	2.136(3)	2.160	2.117(7)	2.138	2.138	2.143(8)	2.120(5)	2.136(6)	2.120(6)
Sb(1)–C(12)	2.144(3)	2.162	2.122(7)	2.143	2.141	2.150(7)	2.106(5)	2.139(6)	2.113(6)
W(1)–Sb(1)–X(1)			109.40(6)	114.29	110.65		112.81(3)		112.34(2)
C(6)–Sb(1)–C(12)	98.6(1)	97.41	100.5(3)	100.83	101.42	98.5(3)	104.1(2)	98.7(2)	104.0(2)
C(6)–Sb(1)–X(1)	94.6(1)	96.32	98.2(2)	98.06	97.66	95.3(8)	97.32(15)	93.6(2)	96.16(17)
C(12)–Sb(1)–X(1)	93.1(1)	96.61	97.2(2)	97.75	97.49	93.5(2)	96.56(15)	95.8(2)	98.21(18)
Σ^a	286.3	290.3	295.9	296.3	296.6	287.3	298.0	290.0	298.4
Δ^b			9.6	10.0	6.3		10.7		8.4

a Σ = sum of the bond angles at antimony in the Ph$_2$SbX unit.
b Δ = Σ ([W(CO)$_5$(Ph$_2$SbX)])–Σ(Ph$_2$SbX); calc. = DFT geometry optimization using B3LYP and 6-31(d,p) basis set for H, C and O; LANL2DZdp for Sb; LANL2DZ for W.
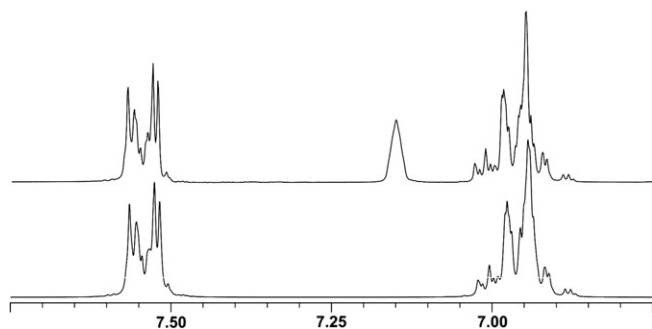
Fig. 4. Simulated (down) and experimental in C_6D_6 (up) spectra of **2**. The additional signal (δ, 7.15 ppm) in the experimental spectrum is the residual peak of C_6D_5H.

the contributions to the bond energy between the ligand and the metal centre it is a measurement for the changes of the electronic structure [24]. Both donation and back donation terms have positive values, 0.379 and 0.211, respectively.

In an attempt to understand also the nature of the intermolecular interaction between antimony and oxygen from **1** we have optimized the molecular geometry of the dimer (1_2). The DFT calculation was made at the same level of theory and using the same basis sets as for the monomer. The geometrical parameters are listed in the column 5 of Table 1. The Sb···O distances are overestimated at the B3LYP level of theory, the calculated values for the dimer being 3.765 and 3.764 Å [18]. These theoretical values are 0.314, respectively, 0.313 Å larger than the experimental ones. Another source of error is the neglect of packing forces in the crystal. The calculated Bond Dissociation Energy (BDE) of one Sb···O interaction in (1_2) is 18.719 kJ mol^{-1}. This value suggests a very weak interaction compared to a Sb–O single bond where the BDE is 434.3 kJ mol^{-1} [26]. The Mulliken charges in the optimized structure of the dimer are 0.774 for antimony, and −0.273 for the oxygen atom of the neighbouring molecule. This result suggests an electrostatic contribution to the weak Sb···O Lewis acid base interaction.

The complexes **1–3** were characterised also by ^{1}H- and ^{13}C NMR spectroscopy. The ^{1}H NMR spectra show two multiplet signals. The NMR parameters were determined

by iterative simulation using the MestReC software package and compared with the experimental spectra. The calculated values of the chemical shifts and of the coupling constants obtained are listed in Table 2 (see Fig. 4).

The complexation leads to a shielding of the *ortho* protons with an increment of 0.1 ppm and a deshielding of the *meta* and *para* protons of the phenyl groups with 0.4 ppm in all complexes compared to the analogous values from the free ligands. The coupling constants of the complexes **1–3** and the free ligands are very similar.

3. Conclusion

The high stability and the easy syntheses of the complexes **1–3** open perspectives for various applications. With the antimony halogen bond the complexes possess functional groups for further synthetic reactions of the coordinated ligands avoiding scrambling reactions which occur frequently in the chemistry of free diphenylantimony(III) halides. The comparison of the geometrical parameters of the diphenylantimony halide moieties in crystals of the free ligands and in the complexes **1–3** together with DFT calculations reveal that major effects of the complexation are the widening of the bond angles at antimony allowing a strengthening of the bond to the tungsten centres and an increase of intermolecular contacts.

4. Experimental and computational

All experiments were performed in an argon atmosphere using modified Schlenck techniques in carefully dried solvents. Ph_2SbCl [6] and Ph_2SbI [8] were prepared as described. ^{1}H and ^{13}C 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 solvent C_6D_5H (^{1}H 7.15 ppm) and C_6D_6 (^{13}C 128.02 ppm). Infrared spectra were recorded as Nujol mulls on a Perkin–Elmer Spectrum 1000 instrument. Mass spectra were recorded on a Finnigan MAT 95 spectrometer for **3** and on a Finnigan MAT 8200 spectrometer for **1**, **2**. The C, H elemental analysis for **2** and **3** were made by Mikroanalytisches Labor Beller–Matthies, Göttingen, Germany.

Density functional theory calculations were performed using Gaussian 98 Revision A.7 software package [27]. Geometry optimizations were made using the gradient corrected functional B3LYP [28]. The basis sets used were: 6-31 G(d,p) for hydrogen, carbon and oxygen atoms [29], LANL2DZ for chlorine and tungsten [30,31], and LANL2DZ with two polarization functions for antimony [31,32]. The energy minima were confirmed by frequency calculations.

For charge decomposition analysis the program CDA 2.1 was used [21]. The relative orbital contributions were taken from the NBO analysis performed by Gaussian, using the partitioning scheme of Weinhold [19,20].

Table 2
^{1}H Chemical shifts (δ, ppm) and coupling constants (J, Hz) of Ph_2SbX, X = Cl, Br, I [8] and **1–3**

	Ph_2SbCl	**1**	Ph_2SbBr	**2**	Ph_2SbI	**3**
δ 2, 6	7.662	7.510	7.686	7.540	7.728	7.560
δ 3, 5	7.458	6.980	7.436	6.970	7.394	6.938
δ 4	7.416	6.930	7.396	6.925	7.360	6.889
$^3J_{2,3}$, $^3J_{5,6}$	7.61	7.64	7.51	7.64	7.64	7.64
$^4J_{2,4}$, $^4J_{4,6}$	1.24	1.30	1.28	1.30	1.30	1.30
$^5J_{2,5}$, $^5J_{3,6}$	0.56	0.54	0.64	0.54	0.54	0.54
$^4J_{2,6}$	1.37	1.37	1.47	1.37	1.37	1.37
$^3J_{3,4}$, $^3J_{4,5}$	7.50	7.50	7.48	7.50	7.50	7.50
$^4J_{3,5}$	1.57	1.44	1.44	1.44	1.44	1.44

4.1. Synthesis of Ph₂SbBr

To a solution of 3.11 g (10 mmol) Ph_2SbCl in ethanol was added 3.09 g (30 mmol) NaBr. The reaction mixture is stirred for 16 h at room temperature. The solvent was removed under vacuum and the solid product was extracted with benzene. After the removal of the benzene a green yellow oil which crystallizes at 7 °C remained. Yield: 2.74 g (76.95%). ¹H NMR: δ 6.95–7.09 ppm (m, 6H, $-C_6H_5$-$m + p$), 7.44–7.50 ppm (m, 4H, $-C_6H_5$-o) [8].

4.2. Syntheses of [W(CO)₅(Ph₂SbX)], X = Cl (1), Br (2), I (3)

To solutions of [W(CO)₅(THF)] in 120 ml THF, prepared from 1.76 g (5 mmol) W(CO)₆, photolyzed for 2.5 h, 5 mmol of the respective diphenylantimony halide (1.56 g Ph_2SbCl, 1.78 g Ph_2SbBr, 2.01 g Ph_2SbI) were added. The reaction mixtures were stirred for 16 h at room temperature and the solvent was removed at reduced pressure. Recrystallization of the remaining solid from petroleum ether at 7 °C afforded crystals of 1–3.

1: yield 1.89 g (59.4%, lit.: 60% [1]), m.p.: 83–85 °C, lit. 65 °C [1]. ¹H NMR: δ 6.87–7.01 ppm (m, 6H, $-C_6H_5$-$m + p$), 7.50–7.55 ppm (m, 4H, $-C_6H_5$-o). ¹³C-{¹H} NMR: δ 129.96 ppm (s, $-C_6H_5$-p), 131.66 ppm (s, $-C_6H_5$-m), 133.20 ppm (s, $-C_6H_5$-o), 139.08 ppm (s, $-C_6H_5$-i), 194.96 ppm (s, $-CO$-$trans$), 197.13 ppm (s, $-CO$-cis). MS (EI, 70 eV): 28 (46.83) [CO]⁺, 77 (27.52) [Ph]⁺, 154 (100) [Ph₂]⁺, 198 (9.50) [SbPh]⁺, 235 (4.83) [PhSbCl]⁺, 275 (24.24) [Ph₂Sb]⁺, 310 (4.58) [Ph₂SbCl]⁺, 418 (26.64) [W(PhSbCl)]⁺, 459 (5.94) [W(Ph₂Sb)]⁺, 494 (12.12) [M−5CO]⁺, 524 (3.60) [M−4CO]⁺, 580 (10.63) [M−2CO]⁺, 636 (9.97) [M]⁺. IR (nujol, 25 °C, cm⁻¹): 1954 (E), 2078 (A₁).

2: yield: 1.31 g (38.6%), m.p.: 82–83 °C. ¹H NMR: δ 6.88–7.03 ppm (m, 6H, $-C_6H_5$-$m + p$), 7.51–7.57 ppm (m, 4H, $-C_6H_5$-o). ¹³C-{¹H} NMR: δ 129.91 ppm (s, $-C_6H_5$-p), 131.54 ppm (s, $-C_6H_5$-m), 133.58 ppm (s, $-C_6H_5$-o), 136.77 ppm (s, $-C_6H_5$-i), 195.35 ppm (s, $-CO$-$trans$), 197.27 ppm (s, $-CO$-cis). MS (EI, 70 eV): 28 (13.37) [CO]⁺, 77 (21.19) [Ph]⁺, 154 (100) [Ph₂]⁺, 198 (9.54) [PhSb]⁺, 275 (54.33) [Ph₂Sb]⁺, 341 (10.65) [WPh₂]⁺, 462 (50.33) [W(SbPh₂)]⁺, 540 (23.72) [M−5CO]⁺, 568 (10.39) [M−4CO]⁺, 624 (26.72) [M−2CO]⁺, 680 (22.21) [M]⁺. IR (nujol, 25 °C, cm⁻¹): 1955 (E), 2077 (A₁). Anal. Calc. for C₁₇H₁₀O₅BrSbW (679.76): C, 30.04; H, 1.48. Found: C, 30.08; H, 1.51%.

3: yield: 3.23 g (89.0%), m.p.: 107–108 °C. ¹H NMR: δ 6.84–6.99 ppm (m, 6H, $-C_6H_5$-$m + p$), 7.52–7.58 ppm (m, 4H, $-C_6H_5$-o). ¹³C-{¹H} NMR: δ 129.80 ppm (s, $-C_6H_5$-$para$), 131.32 ppm (s, $-C_6H_5$-m), 132.48 ppm (s, $-C_6H_5$-o), 134.26 ppm (s, $-C_6H_5$-i), 196.14 ppm (s, $-CO$-$trans$), 197.62 ppm (s, $-CO$-cis). MS (EI, 70 eV): 77 (19.30) [Ph]⁺, 154 (100) [Ph₂]⁺, 198 (23.24) [SbPh]⁺, 248 (12.91) [SbI]⁺, 275 (42.85) [Ph₂Sb]⁺, 402 (10.42) [Ph₂SbI]⁺, 459 (12.69) [W(Ph₂Sb)]⁺, 510 (7.13) [W(PhSbI)]⁺, 586

(3.60) [M−5CO]⁺, 614 (0.86) [M−4CO]⁺, 670 (4.86) [M−2CO]⁺, 728 (8.47) [M]⁺. IR (nujol, 25 °C, cm⁻¹): 1953 (E), 2077 (A₁). Anal. Calc. for C₁₇H₁₀O₅ISbW (726.75): C, 28.10; H, 1.39. Found: C, 28.22; H, 1.61%.

4.3. X-ray structure determination

Crystals suitable for X-ray diffraction of **1**, **2** and **3** were obtained from petroleum ether solutions at 7 °C. Cell refinement gave constants corresponding to the triclinic crystal system for all three structures. Data were collected at 173(2) K on a Siemens P4 diffractometer using 0.71073 Å Mo Kα radiation and corrected for absorption

Table 3
X-ray diffraction data and structure refinement for **1–3**

Compound	1	2	3
Empirical formula	C₁₇H₁₀O₅ClSbW	C₁₇H₁₀O₅BrSbW	C₁₇H₁₀O₅ISbW
Formula weight	635.30	679.76	726.75
Crystal size (mm³)	$0.7 \times 0.5 \times 0.2$	$0.6 \times 0.5 \times 0.4$	$0.7 \times 0.6 \times 0.2$
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	8.981(3)	7.026(3)	7.228(2)
b (Å)	9.264(3)	9.784(3)	9.757(5)
c (Å)	12.215(3)	13.783(4)	13.876(3)
α (°)	107.60(2)	83.58(2)	82.47(2)
β (°)	104.25(1)	88.84(2)	87.65(1)
γ (°)	91.03(1)	87.83(3)	86.94(2)
Volume (Å)	934.2(5)	940.7(6)	968.2(6)
Z	2	2	2
Absorption coefficient (mm⁻¹)	7.763	9.691	8.947
$F(000)$	588	624	660
θ range for data collections (°)	2.35–27.50	2.70–27.49	2.73–27.50
Index ranges (h, k, l)	±11, ±11, ±15	−8/+9, ±12, ±17	±9, ±12, ±18
Reflections collected	8608	5444	9013
Independent reflections/R_{int}	4239/0.0244	4309/0.0305	4439/0.0237
Data with $I > 2\sigma(I)$	4064	4112	4319
Goodness-of-fit (on F^2)[a]	1.105	1.169	1.179
Data/parameters/restraints	4239/227/0	4309/227/0	4439/227/0
Final R indices [$I > 2\sigma(I)$] (R_1, wR_2)[b]	0.0527, 0.1513	0.0330, 0.0898	0.0348, 0.0991
R indices (all data) (R_1, wR_2)	0.0539, 0.1531	0.0345, 0.0907	0.0356, 0.0996
Largest difference peak and hole (e Å⁻³)	3.731, −4.343	2.967, −1.413	2.723, −2.1

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

effects using DIFABS [33]. The structures were solved by Patterson method [34]. 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 [35]. All the non-hydrogen atoms were treated anisotropically. Hydrogen atoms were included in idealized positions with isotropic thermal parameters set at 1.2 times that of the carbon atom to which they were attached. Crystallographic data are summarized in Table 3. The diagrams of the X-ray structures were created with the Diamond software package.

Acknowledgements

Appendix A. Supplementary material

CCDC 631375, 631376, 631377, contain the supplementary crystallographic data for **1**, **2** and **3**. These data can be obtained free of charge via www.ccdc.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.

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