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Syntheses and Structures of Distibene Complexes of Tungsten and Titanium: $[W(CO)_5\{(2,6\text{-}Mes_2C_6H_3)_2Sb_2\}]$ (Mes = $2,4,6\text{-}Me_3C_6H_2$) and $[Cp_2Ti\{(2,6\text{-}Mes_2C_6H_3)_2Sb_2)\}]$

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Exposure of $[W(CO)_5(2,6\text{-}Mes_2C_6H_3SbH_2)]$ (**1**) in toluene to day light leads to the distibene complex $[W(CO)_5\{(2,6\text{-}Mes_2C_6H_3)_2Sb_2\}]$ (**2**). $[Cp_2Ti\{(2,6\text{-}Mes_2C_6H_3)_2Sb_2\}]$ (**3**) is obtained by reaction of $[Cp_2Ti\{(Me_3Si)_2C_2\}]$ with $2,6\text{-}Mes_2C_6H_3SbH_2$. The structures of **2** and **3** were determined by single-crystal X-ray diffraction, and DFT calculations were carried out on Me_2Sb_2, $[W(CO)_5(Me_2Sb_2)]$ (**2a**), and $[Cp_2Ti(Me_2Sb_2)]$ (**3a**).

Introduction

The coordination chemistry of stable distibenes R_2Sb_2[1−3] has not been studied before, and little is also known about complexes with stable diphosphene ligands.[4] Recently, the first complex of a stable dibismuthene, i.e., $[Cp_2Zr\{(2,6\text{-}Mes_2C_6H_3)_2Bi_2)\}]$, was reported.[5] Known distibene complexes[6−10] contain R_2Sb_2 ligands that exist only in the coordination sphere of a transition-metal complex. In the absence of a transition-metal complex fragment the corresponding cyclo-oligomers $(RSb)_n$[11−15] are stable. The distibene complexes can be obtained by elimination of hydrogen from complexes containing $RSbH_2$ as ligands or by other methods.[6−10] Related examples of group 4 metallocene complexes of other p block organoelement fragments have been reported before.[16−21] Well-characterized complexes with antimony−titanium bonds are rare.[22]

We report here the synthesis and characterization of $[W(CO)_5(2,6\text{-}Mes_2C_6H_3SbH_2)]$ (**1**), $[W(CO)_5\{(2,6\text{-}Mes_2C_6H_3)_2Sb_2\}]$ (**2**), and $[Cp_2Ti\{(2,6\text{-}Mes_2C_6H_3)_2Sb_2\}]$ (**3**) as well as DFT calculations on the model compounds Me_2Sb_2, $[W(CO)_5(Me_2Sb_2)]$ (**2a**), and $[Cp_2Ti(Me_2Sb_2)]$ (**3a**). **2** and **3** are the first complexes of the stable distibene $(2,6\text{-}Mes_2C_6H_3)_2Sb_2$.[2] **3** is among the first titanium complexes with antimony ligands.

Results and Discussions

The stibine complex **1** was obtained in a reaction between $2,6\text{-}Mes_2C_6H_3SbH_2$[23] and $[W(CO)_5(thf)]$ (thf = tetrahydrofuran) in thf after separation of the initially obtained dark green product mixture by column chromatography. **1** is a colorless, air- and light-sensitive solid that is very soluble in organic solvents. Exposing solutions of **1** in toluene to day light for several days leads to decomposition of **1** with formation of **2** and $2,6\text{-}Mes_2C_6H_4$. A small crop of air-stable, red crystals of **2** was obtained from solutions of **1** in benzene. **2** is thermally stable up to the melting point of 224 °C. **2** is also formed by direct ligand exchange between $(2,6\text{-}Mes_2C_6H_3)_2Sb_2$ and $[W(CO)_5(thf)]$ in tetrahydrofuran, but the yield is very low. The titanocene distibene complex $[Cp_2Ti\{(2,6\text{-}Mes_2C_6H_3)_2Sb_2\}]$ (**3**) is produced in the reaction of $2,6\text{-}Mes_2C_6H_3SbH_2$ and $[Cp_2Ti\{(Me_3Si)_2C_2\}]$[24] in benzene in day light. **3** is a green air-sensitive solid melting at 240−242 °C with decomposition. The solubility of **2** and **3**

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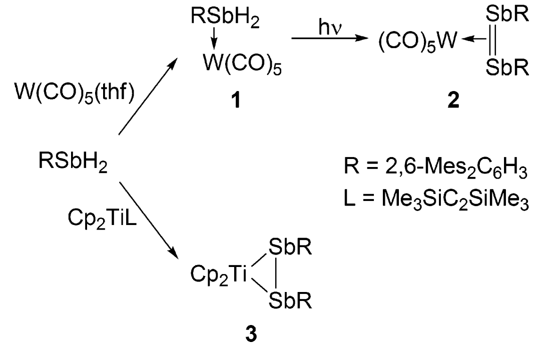
Scheme 1



in aromatic solvents is higher than in hexane or petroleum ether. Direct ligand exchange between $(2,6\text{-Mes}_2C_6H_3)_2Sb_2$ and $[Cp_2Ti\{(Me_3Si)_2C_2\}]$ giving **3** was not observed in deuterated benzene at 25 °C in sealed NMR tubes. An overview of the reactions leading to **1**−**3** is given in Scheme 1.

Compounds **1**−**3** were characterized by spectroscopic methods. The composition was confirmed by elemental analysis for **2** and high-resolution mass spectrometry for **3**. The ^1H and ^{13}C NMR spectra of **1**−**3** contain the characteristic signals of the dimesitylphenyl groups. In the HMBC spectra of **1** long-range coupling at three bonds between the carbon atoms of the cis CO groups and the SbH_2 units is observed. The signal for the SbH_2 protons in **1** appears at 3.04 ppm, shielded respective to the value found in the free ligand (2.81 ppm).[23] By contrast complexation of $(Me_3Si)_2CHSbH_2$ (SbH_2 2.12 ppm) has the opposite effect on the SbH_2 protons ($[W(CO)_5\{(Me_3Si)_2CHSbH_2\}]$ 2.09 ppm).[7,25] In the ^1H NMR spectrum of **1** there are two signals in a ratio of 2:1 of the ortho and para methyl groups, respectively, indicating equivalence of the mesityl groups in the terphenyl substituent. However, in the spectra of **2** and **3** there are six signals equal in intensity for the methyl groups, revealing that rotation of the mesityl groups around the Mes−C bonds is hindered by the $W(CO)_5$ or Cp_2Ti moieties. It is likely that rotation of the whole terphenyl groups around the Sb−C bond is restricted also. ^1H NMR spectra of **2** in C_6D_6 at 55 °C are identical to the room-temperature spectra. In solution the hydrogen atoms and carbon atoms of the cyclopentadienyl rings of **3** are equivalent, and singlet signals appear in the NMR spectra. Assignment of the signals was made using 2D NMR spectra and is provided as Supporting Information.

Infrared spectra of **1** and **2** are in the region of the CO valence vibration show the typical pattern for $W(CO)_5$ groups with local C_{4v} symmetry. Mass spectra of **1**−**3** contain characteristic fragments. Molecular ions were observed for **1** in the CI spectra and for **2** and **3** in the EI spectra.

The crystal structures of **2** and **3** were determined by X-ray diffraction on single crystals obtained from benzene. Both compounds crystallize in the $P\bar{1}$ space group with two molecules per unit cell and **3** as a solvate with 1.5 benzene molecules. The center of one of the benzene molecules has the coordinates 0, 1/2, 1/2. The molecular structures of **2** and **3** are depicted in Figures 1 and 2; selected bond lengths and angles of **2**, **3**, and $(2,6\text{-Mes}_2C_6H_3)_2Sb_2$ are presented in Table 1. The structures of **2** and **3** contain central Sb_2M triangles with the aryl groups on antimony in trans positions. Inspection of the Sb−Sb, Sb−W, and Sb−Ti distances however leads to different descriptions of the interactions between the R_2Sb_2 units and the transition-metal complex fragments: the structure of **2** corresponds to a distibene complex, whereas **3** is better described as a Sb_2Ti heterocycle.

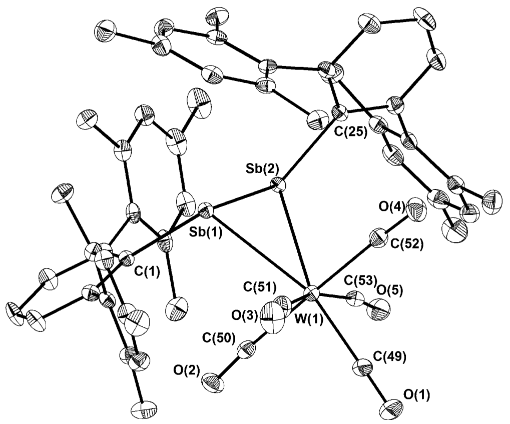


Figure 1. Thermal ellipsoid (40%) representation of $[W(CO)_5\{(2,6\text{-Mes}_2C_6H_3)_2Sb_2\}]$ (**2**). The hydrogen atoms were omitted for clarity.

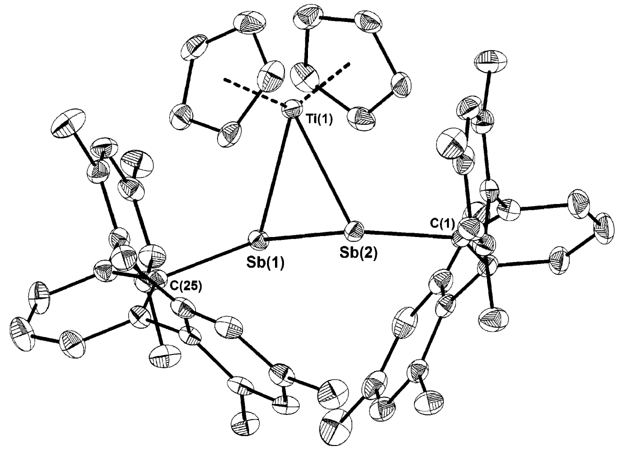


Figure 2. Thermal ellipsoid (40%) representation of $[Cp_2Ti\{(2,6\text{-Mes}_2C_6H_3)_2Sb_2\}]$ (**3**). The hydrogen atoms were omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) of 2, 3, and R_2Sb_2[2] [a]

	2	3	R_2Sb_2[2]
Sb(1)−Sb(2)	2.7358(6)	2.8642(6)	2.6558(5)
M−Sb(1)	2.9726(5)	2.8402(8)	
M−Sb(2)	2.9828(5)	2.8487(9)	
C_i−Sb(1)	2.204(4)	2.208(4)	2.169(4)
C_i−Sb(2)	2.197(4)	2.203(4)	2.169(4)
Sb(1)−Sb(2)−C_i	103.2(1)	109.9(1)	94.1(1)
C_i−Sb(1)−Sb(2)	103.3(1)	110.9(1)	94.1(1)
Sb(1)−M−Sb(2)	54.694(12)	60.461(18)	
C_i−Sb(1)−Sb(2)−C_i	162.3(2)	155.1(2)	180

[a] M = W (**2**), Ti (**3**); R = $2,6\text{-Mes}_2C_6H_3$.

The Sb−Sb bonds in **2** (2.7358(6) Å) and **3** (2.8642(6) Å) are longer than the double bond in $(2,6\text{-Mes}_2C_6H_3)_2Sb_2$ (2.6558(5) Å).[2] For **2** the value lies in the range of the slightly elongated double-bond lengths found for known distibene complexes, e.g., $R_2Sb_2Fe(CO)_4$, R = $(Me_3Si)_2CH$ (2.774(1) Å);[6] $R_2Sb_2W(CO)_5$, R = $(Me_3Si)_2CH$ (2.7413(9) Å);[7] $R_2Sb_2Pt(PEt_3)_2$, R = $^tBuC(O)$ (2.7551(12) Å).[8] In **3** the bond length is close to typical values for Sb−Sb single bonds in distibines (Me_4Sb_2 2.862(2) Å,[26] Ph_4Sb_2 2.844(1) Å,[27] Mes_4Sb_2 2.8481(9) Å[28]) or a tellu-

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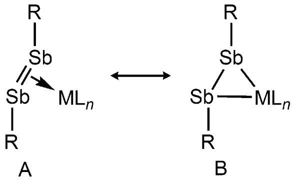
Scheme 2



radistibirane (2.8833(6) Å).[29] The Sb−W distances in **2** (2.9726(5); 2.9828(5) Å) are much longer than the sum of covalent radii ($\Sigma_{\text{r cov.}}$(Sb,W) = 2.71 Å).[30] They are similar to the analogous values in $R_2Sb_2W(CO)_5$, R = $(Me_3Si)_2CH$ (Sb−W 2.9495(11) and 2.9912(11) Å).[7] In contrast, the Sb−Ti distances (2.8402(8) and 2.8487(9) Å) in **3** are slightly larger than Sb−Ti single bonds ($\Sigma_{\text{r cov.}}$(Sb,Ti) = 2.73 Å).[30] The bond angles at the transition metal are larger in **3** (Sb−Ti−Sb 60.461(18)°) than in **2** (Sb−W−Sb 54.694(12)°). The structures of **2** and **3** can be described by two mesomeric forms (A and B) as shown in Scheme 2. Considering the MSb_2 core parameters the limit structure A better describes the bonding situation for **2**, whereas for **3**, B has the largest contribution.

Not only the Sb−Sb distances but also the arrangement of the aryl groups in the $(2,6\text{-}Mes_2C_6H_3)_2Sb_2$ units in complexes **2** and **3** differ considerably from the structure of the free distibene. The values of the torsion angles C_i−Sb−Sb−C_i are smaller (**2**, 162.3(2)°; **3**, 155.1(2)°) than the ideal 180° found in R_2Sb_2.[2] The C−Sb−Sb angles (**2**, 103.1(1)° and 103.3(1)°; **3**, 109.9(1)° and 110.9(1)°) are larger in the complexes than in the free ligand (94.1(1)°).[2] These changes indicate transition from a close to p^3 configuration at antimony in the free ligand to a close to sp^3 hybridization in the complexes as observed for other pnicogen complexes.[31]

The arrangement of the aryl groups leads to close contacts between the Sb atoms and the ring carbon atoms of the mesityl groups with Sb···C distances between 3.1 and 3.7 Å. Similar distances were found in the π complexes between arenes and $SbCl_3$ ($C_6H_6 \cdot SbCl_3$, 3.3−3.7 Å;[32] 1,2,4,5-$(CH_3)_4C_6H_2 \cdot SbCl_3$, 3.2−3.6 Å;[33] $(C_2H_5)_6C_6 \cdot SbCl_3$, 3.2−3.3 Å[34]). Graphical representations of the Sb···C interactions are provided in the Supporting Information.

The geometrical parameters of the $W(CO)_5$ group in **2** and of the Cp_2Ti unit in **3** are unspectacular.

For understanding the changes induced by coordination in the electronic structure of the distibine ligands a theoretical study was performed on Me_2Sb_2, $[W(CO)_5(Sb_2Me_2)]$ (**2a**), and $[Cp_2Ti(Sb_2Me_2)]$ (**3a**) as models for $(2,6\text{-}Mes_2C_6H_3)_2Sb_2$, **2**, and **3**. Related studies on dibismuthene complexes were reported before.[5] The structural parameters obtained for Me_2Sb_2, **2a**, and **3a** are close to the experimental values and in the range of those found in similar theoretical studies.[35,36] A summary of the structural parameters obtained is presented in the Supporting Information. The calculated energy required for separation of the R_2Sb_2 unit from the transition-metal moiety is 19.77 kcal/mol larger for **3a** than for **2a**, indicating relatively stronger bonding between the diantimony and metallocene units.

Table 2. Charge Decomposition Analysis (CDA) of 2a and 3a[a]

	d	b	r	s	d/b
2a	0.544	0.337	−0.441	0.009	1.61
3a	0.415	0.058	−0.303	0.403	7.15

[a] Donation = *d*, back-donation = *b*, repulsive polarization = *r*, residual = *s*, donation back-donation ratio = *d*/*b*.

The bonding between distibene ligands and the transition-metal complex fragments in **2a** and **3a** can be described in terms of the Dewar−Chatt−Duncanson model with synergic donation and back-donation between the π and π^* orbitals of the distibene and molecular orbitals of $W(CO)_5$ or Cp_2Ti units with mainly d character. In **2a** the donation of electrons from the π orbital of the distibene ligand to empty orbitals of the $W(CO)_5$ unit contributes more to the bonding than the back-donation into the π^* orbital of the distibene. In **3a** the cyclopentadienyl groups increase the electron density at the titanium atom, affording a larger amount of electron density available for back-donation to the antibonding orbitals of the antimony−antimony double bond. This produces a pronounced decrease of the bond order between the antimony atoms. In **2a** tungsten is bonded to five CO groups, ligands well known for their good π acceptor properties. Thus, in this case there is a poorer back-donation from tungsten to the π^* orbitals of the distibene ligand due to the competition of CO groups.

Complexes **2a** and **3a** were also studied using the charge decomposition analysis (CDA) method of Frenking et al.,[37−40] a direct application of the Dewar−Chatt−Duncanson model[41] for olefin complexes. The CDA terms are listed in Table 2. CDA revealed a significantly larger residual term for **3a** than for **2a** and a surprisingly small value for the back-donation in **3a**. These findings indicate that the Dewar−Chatt−Duncanson model is more appropriate for the tungsten complex **2a** than for the titanocene complex **3a**, where probably an important covalent contribution to the Sb−Ti bonds is present. Therefore, an alternative description of **3a** as a $TiSb_2$ heterocycle with single bonds between all ring atoms is more appropriate. This description is also supported by the experimentally found bond lengths in the crystal structure of **3**.

Experimental Section

General Comments. The reactions and manipulations of the compounds were performed under an atmosphere of argon. All solvents were dried and freshly distilled prior to use. For synthesis of $[W(CO)_5(thf)]$ a TQ 150 mercury lamp from Hanau Co. was used.

The NMR spectra were recorded on Bruker AVANCE DPX-200 and AVANCE NB-360 spectrometers. ^1H and ^{13}C chemical shifts are reported in δ units (ppm) relative to the residual peak of solvent ($CHCl_3$, ^1H, 7.26 ppm; $CDCl_3$, ^{13}C, 77.0 ppm; C_6D_5H, ^1H, 7.15 ppm; C_6D_6, ^{13}C, 128.02 ppm). C-DEPT, H,H-COSY, H,C-HSQC, and H,C-HMBC experiments, used for assignment of the signals, were recorded using standard pulse sequences provided by

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Table 3. Crystal Data and Structure Refinement for 2 and 3

	2	**3**·1.5 C_6D_6
empirical formula	$C_{53}H_{50}O_5Sb_2W$	$C_{67}H_{60}D_9Sb_2Ti$
fw	1194.28	1174.63
cryst syst	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a (Å)	11.575(2)	11.2720(10)
b (Å)	13.026(2)	12.836(2)
c (Å)	17.558(2)	20.263(2)
α (deg)	78.000(10)	97.060(10)
β (deg)	82.340(10)	93.690(10)
γ (deg)	64.950(10)	109.120(10)
vol. (Å^3)	2342.8(6)	2731.9(6)
Z	2	2
calcd density (Mg/m^3)	1.693	1.417
abs coeff (mm^{-1})	3.640	1.165
F(000)	1168	1190
cryst color	orange	green
cryst size (mm)	0.50 × 0.30 × 0.15	0.50 × 0.30 × 0.15
θ range for data collection (deg)	2.53−27.50	2.64−27.50
limiting indices (*h*, *k*, *l*)	±14, −15/16, ±22	−14/2, −15/16, ±26
reflns collected/unique [*R*(int)]	12 499/10 717 [0.0237]	14 678/12 549 [0.0274]
completeness to $\theta = 27.5$ (%)	99.7	99.7
max and min transmission	0.6112 and 0.2633	0.8446 and 0.5935
data/restraints/params	10 717/0/563	12 549/0/643
goodness-of-fit on F^2	1.051	0.976
Final *R* indices ($I > 2\sigma(I)$) (R1, wR2)	0.0341, 0.0740	0.0431, 0.0880
R indices (all data) (R1, wR2)	0.0451, 0.0780	0.0735, 0.0983
extinction coefficient	0.00068(9)	
largest diff. peak and hole (e Å^{-3})	1.541 and −1.027	0.571 and −0.652

Bruker BioSpin. Analysis of the data was carried out with MestReC software package.[42]

Mass spectra were recorded on a Finnigan MAT 8200 (CI) and Finnigan MAT 95 (EI, HRMS). Analysis of the data and calculation of the isotopic patterns were made using the MASPECII software package.[43]

IR spectra were recorded from Nujol mulls on a Perkin-Elmer FT-IR SPEKTRUM 1000 spectrometer. The spectra were analyzed using the KnowItAll software package.[44]

The elemental analysis of **2** was performed at Mikroanalytisches Labor Beller, Göttingen, Germany.

[W(CO)$_5$(2,6-Mes$_2$C$_6$H$_3$SbH$_2$)] (1). A solution of 3.22 g (9.1 mmol) of $W(CO)_6$ in 120 mL of THF was photolyzed in a UV lamp for 3 h and then added to 1.99 g (4.5 mmol) of 2,6-$Mes_2C_6H_3$-SbH_2. The reaction mixture was stirred for 16 h, and the solvent was removed in vacuum. The black green product was dissolved in toluene and filtered. The solution was concentrated. Separation on a chromatography column (14 × 2.2 cm Al_2O_3 activity level 2) using toluene as the mobile phase gave, first, a yellow-orange (70 mL) fraction and, second, a dark orange-red fraction (100 mL). The first fraction contained DmpH and **1**. The second fraction contained pure **1**. Solvent removal from the second fraction under reduced pressure afforded 0.69 g (20%) of **1**. ^{1}H NMR (200.1 MHz, C_6D_6): δ 2.01 (s, 12H; *o*-CH_3), 2.16 (s, 6H; *p*-CH_3), 3.04 (s, 1H; Sb*H*), 6.81 (d, 2H; *m*-C$_6$*H*$_3$, $^3J_{HH} = 7.2$ Hz), 6.86 (s, 4H; *m*-Mes), 7.11 (t, 1H; *p*-C$_6$*H*$_3$, $^3J_{HH} = 7.2$ Hz). ^{13}C NMR (90.3 MHz, C_6D_6): δ 21.4 (*o*-*C*H$_3$), 21.5 (*p*-*C*H$_3$), 127.9 (*i*-*C*$_6$H$_3$), 128.6 (*m*-*C*$_6$H$_3$), 129.9 (*m*-Mes), 135.5 (*o*-Mes), 138.6 (*p*-Mes), 139.9 (*i*-Mes), 149.5 (*o*-*C*$_6$H$_3$), 196.1 (*cis*-*C*O), 198.0 (*trans*-*C*O). MS (CI, positive, NH$_3$) *m/z* (relative intensity %): 759 (6.05) [M +H]$^+$, 434 (34.36) [RSb]$^+$ (R = 2,6-Mes$_2$C$_6$H$_3$), 314 (100) [R +H]$^+$. IR (nujol, cm^{-1}): ν (CO) 1943.5 (E), 2075.5 (A$_1$).

[W(CO)$_5${(2,6-Mes$_2$C$_6$H$_3$)$_2$Sb$_2$}] (2). A solution of 0.69 g (0.9 mmol) of **1** in 20 mL of toluene and 20 mL of petroleum ether was exposed in a glass tube to day light for 4 weeks. The solvent was removed under reduced pressure, and the remaining brown solid was washed with diethyl ether and dissolved in benzene. Slow evaporation of the solvent at ambient temperatures gave 8.0 mg (15%) of **2** as red crystals. Mp: 224−226 °C. ^{1}H NMR (360.1 MHz, CDCl$_3$): δ 1.80, 1.93, 2.09, 2.10 (s, 24H; *o*-C*H*$_3$), 2.40, 2.47 (s, 12H; *p*-C*H*$_3$), 6.70, 6.83 (d, 4H; *m*-C$_6$*H*$_3$, $^3J_{HH} = 7.5$ Hz), 6.80, 6.94, 6.95, 6.98 (s, 8H; *m*-Mes), 7.07 (t, 2H; *p*-C$_6$*H*$_3$ $^3J_{HH} = 7.5$ Hz). ^{13}C NMR (90.3 MHz, CDCl$_3$): δ 20.4, 21.1, 22.1, 22.2 (*o*-*C*H$_3$), 21.1, 21.7 (*p*-*C*H$_3$), 127.9 (*p*-*C*$_6$H$_3$), 128.2, 129.0 (*m*-*C*$_6$H$_3$), 128.1, 129.1, 129.5, 129.6 (*m*-Mes), 135.8, 136.28, 136.33, 136.8 (*o*-Mes), 137.10, 137.13 (*p*-Mes), 140.4 (*i*-*C*$_6$H$_3$), 140.5, 142.1 (*i*-Mes), 147.5, 149.0 (*o*-*C*$_6$H$_3$), 203 (*cis*-CO); the resonance for the *trans*-CO group could not be observed. (EI, 70 eV) *m/z* (relative intensity %): 1190 (0.16) [M]$^+$, 1106 (2.55) [M -3CO]$^+$, 1050 (0.85) [M -5CO]$^+$, 868 (60.44) [R$_2$Sb$_2$]$^+$ (R = 2,6-Mes$_2$C$_6$H$_3$), 434 (15.37) [RSb]$^+$, 314 (40.36) [R +H]$^+$. IR (nujol, 25 °C, cm^{-1}): 1953 (E), 2063.5 (A$_1$). Anal. Calcd: C, 53.30; H, 4.22. Found: C, 53.28; H, 4.30.

[Cp$_2$Ti{(2,6-Mes$_2$C$_6$H$_3$)$_2$Sb$_2$}] (3). A 0.2 g (0.6 mmol) amount of [Cp$_2$Ti{(Me$_3$Si)$_2$C$_2$}] was added to a solution of 0.57 g (1.3 mmol) of 2,6-Mes$_2$C$_6$H$_3$SbH$_2$ in benzene at room temperature. After 1 h of stirring the solvent was removed under reduced pressure and the residue was washed with 20 mL of hexane (for removal of the (Me$_3$Si)$_2$C$_2$), and after drying 0.51 g (35%) of **3**, as a green solid, was obtained. Crystals suitable for X-ray diffraction were grown from solutions of the **3** in C$_6$D$_6$ in sealed NMR tubes. Mp: 240−242 °C (decomp.). ^{1}H NMR (360.1 MHz, C$_6$D$_6$): δ 1.13, 1.69, 1.73, 3.84 (s, 24H; *o*-C*H*$_3$), 2.27 (s, 12H; *p*-C*H*$_3$), 6.28 (s, 10H; Cp), 6.02, 6.50, 6.57, 7.22 (s, 8H; *m*-Mes), 6.77, 7.41 (m, 4H; *m*-C$_6$*H*$_3$), 7.17 (m, 2H; *p*-C$_6$*H*$_3$). ^{13}C NMR (90.3 MHz, C$_6$D$_6$): δ 21.2 (*p*-*C*H$_3$), 19.4, 21.8, 23.5 (*o*-*C*H$_3$), 115.8 (Cp), 127.2 (*p*-*C*$_6$H$_3$), 126.6, 129.3 (*m*-*C*$_6$H$_3$), 126.4, 127.8, 129.0, 129,6 (*m*-Mes), 134.0, 137.2, 135.7, 138.5 (*o*-Mes), 136.1 (*p*-Mes), 139.5, 143.2 (*i*-Mes), 146.1, 150.9 (*o*-*C*$_6$H$_3$), 142.9 (*i*-*C*$_6$H$_3$). (EI, 70 eV) *m/z* (relative intensity %): 1043 (0.31) [M -H]$^+$, 867 (100) [R$_2$Sb$_2$ -H]$^+$ (R = 2,6-Mes$_2$C$_6$H$_3$), 434 (49.75) [RSb]$^+$, 314 (40.27) [R + H]$^+$, 178 (31.29) [Cp$_2$Ti]$^+$. HRMS (EI, 70 eV) *m/z*: Calcd for [M]$^+$ C$_{58}$H$_{60}$-Sb$_2$Ti, 1048.22549; found, 1048.22549.

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[42] *MestrReC*, version 4.9.9.6; Mestrelab Research: Santiago de Compostela, A Coruña, Spain, 2006.

[43] *MASPEC II^{32} Data System*, version 3.1a; Mass Spectrometry Services Ltd.: Manchester, England, 2000.

[44] *KnowItAll Informatics System*, version 5.007; Bio-Rad Laboratories, Inc.: Philadelphia, PA, 2004.

X-ray Crystallographic Studies. Crystals of **2** and **3** were obtained in sealed NMR tubes from deuterated benzene solutions. Crystals were mounted with KelF oil on a fiber glass and placed under a nitrogen stream on a Siemens P4 four-circle diffractometer using Mo Kα radiation, $\lambda = 0.71073$ Å, graphite monochromated. The structures were solved using Patterson methods and refined using full-matrix least-squares on F^2.[45] For solution and refinement SHELXL-97 was used,[46] as included in the WinGX software package.[47,48] Absorption corrections were done with the DIFABS software as included in the WinGX software package.[47,48] All non-hydrogen atoms were treated anisotropically. Hydrogen atoms were included in riding positions with isotropic thermal parameters set at 1.2 times the carbon atoms directly attached for aromatic hydrogen atoms and 1.5 for hydrogen atoms of the methyl groups. The ring centroids and angles were calculated using the PLATON software,[49,50] according to the description of Cremer.[51] Representation of the crystallographic data was carried out using the Diamond software package.[52] A summary of the crystal data and structure refinement for **2** and **3** is included in Table 3.

Theoretical Studies. Geometry optimizations on Me_2Sb_2, **2a**, and **3a** were carried out with the Gaussian 98 software[53] at the DFT theory level using gradient-corrected functional B3LYP[54] and ECP basis set LANL2DZ[55−57] augmented with two polarization functions[58] on antimony. The energy minima of the geometries were confirmed by the frequency calculations. Charge decomposition analyses were performed with CDA 2.1.[37] The source code was obtained from http://www.uni-marburg.de/fb15/ag-frenking/cda and compiled on a PC running SUSE 9.2. ChemCraft software[59] was used for visualization of the outputs and representation of the Kohn−Sham molecular orbitals.

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Supporting Information Available: Crystallographic data in CIF data format; crystallograpic data, coordinates of the optimized structures, summary of the calculations, frontier molecular orbitals of **2a** and **3a**, CDA of **2a** and **3a**, assignment of the NMR signals for 2,6-$Mes_2C_6H_3SbH_2$ and **1**−**3**, ^{1}H NMR spectra of **1** and **2**, and HMBC spectrum of **1**; complete ref 53. This material is available free of charge via the Internet at http://pubs.acs.org. The CIF files are also available online from the Cambridge Crystallographic Data Centre (CCDC Nos. 652787 (**2**), 652788 (**3**)).

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