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FULL PAPER

Synthesis, structure and reactivity of highly functionalized η^1-stibaallyliron complexes $[(OC)_2(\eta^5\text{-}C_5Me_5)Fe–Sb(Cl)\text{-}C(OSiMe_3)=CPhR]$ (R = Ph, Me or *c*-C_6H_{11})

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Insertion of one equivalent of methyl(phenyl)ketene or cyclohexyl(phenyl)ketene into the Sb–Si bond of $[FeCp^*(CO)_2\{Sb(SiMe_3)_2\}]$ afforded η^1-stibaallyliron complexes $[(OC)_2(\eta^5\text{-}C_5Me_5)Fe–Sb(SiMe_3)C(OSiMe_3)=CR^1Ph]$ (R^1 = *c*-C_6H_{11} or Me). The remaining Sb–Si bond was readily cleaved by C_2Cl_6 to give complexes $[(OC)_2Cp^*Fe–Sb(Cl)C(OSiMe_3)=CR^1Ph]$. Treatment of the latter where R^1 = Ph with $LiSb(SiMe_3)_2\cdot 2.8$thf, LiC≡CPh, or $LiC(N_2)SiMe_3$ resulted in the formation of compounds $[(OC)_2Cp^*Fe–Sb(R)C(OSiMe_3)=CPh_2]$ [R = $Sb(SiMe_3)_2$, C≡CPh or $C(N_2)SiMe_3$]. The new compounds were characterized by elemental analyses and spectra (IR, ^{1}H, ^{13}C, ^{29}Si NMR). The molecular structure of $[(OC)_2Cp^*Fe–Sb(Cl)C(OSiMe_3)=CPh_2]$ was elucidated by a single crystal X-ray diffraction analysis.

Introduction

Transition metal phosphanyl complexes L_nMPX_2 with functional groups X (X = H[1], halide[2] or $SiMe_3$[3]) have been the subject of considerable research effort, in part because of their involvement as precursors in the syntheses of organoelement compounds with low co-ordinate phosphorus (phosphaalkenes,[4] diphosphenes[5]) or interesting metal-functionalized homo- and hetero-cycles.[6] Corresponding metalloarsanes L_nMAsX_2 (here particularly those where X = Me_3Si) have also been considered, albeit to a much lesser extent.[3a,7] In contrast to this, our knowledge on the chemistry of complexes with functionalized stibanido ligands $[L_nMSb(X)(Y)]$ is still scarce. First examples such as $[FeCp(CO)_2(SbBr_2)]$[8] and $[MCp(CO)_3(SbBr_2)]$[8] (M = Mo or W) have been studied by Malisch and Panster in the 1970s. Characteristic features of their reactivity are the replacement of one or two halogen atoms by transition metalates as well as their propensity to act as a two-electron donor towards 16 electron fragments through the antimony lone pair.[8–10] In complexes such as $[(OC)_5Mn(\mu\text{-}SbCl_2)MnCp'(CO)_2]$ (Cp′ = C_5H_4Me) and $[(OC)_3CpCrSbCl_2\text{-}MnCp'(CO)_2]$ it was possible to substitute both Cl atoms by a chelating ethane 1,2-dithiolato bridge in the presence of a base.[10] The reaction between $SbCl_3$ and one equivalent of $K[Co(CO)_3\{P(OR)_3\}]$ (R = Ph or Me) afforded the complexes $[Co(CO)_2(SbCl_2)\{P(OR)_3\}_2]$ which were characterized by X-ray crystallography.[11]

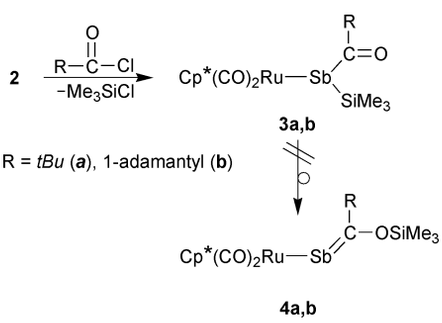
A different approach was utilized for the synthesis of $[Fe(1,3\text{-}Bu^t_2C_5H_3)(CO)_2(SbCl_2)]$. The complex resulted from the chlorination of $[Fe(1,3\text{-}Bu^t_2C_5H_3)(CO)_2\{Sb(SiMe_3)_2\}]$ with 2 equivalents of hexachloroethane.[12]

Compounds $[MCp^*(CO)_2\{Sb(SiMe_3)_2\}]$ (Me = Fe **1** or Ru **2**) were generated by treatment of the bromo complexes with $LiSb(SiMe_3)_2\cdot xD$ (*x*D = 2.8 thf or dme), eqn. (1), and proved

$$Cp^*(CO)_2M{-}Br + LiSb(SiMe_3)_2 \cdot x\ thf \xrightarrow[-\ LiBr]{-\ x\ thf} Cp^*(CO)_2M{-}Sb(SiMe_3)_2 \quad (1)$$

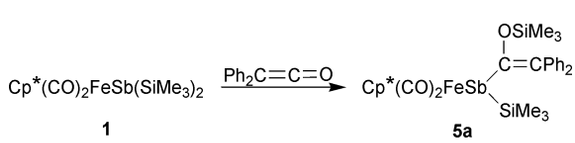
1 (M = Fe)
2 (M = Ru)

to be valuable precursors for a series of chemical transformations.[13] Reaction of **2** with pivaloyl chloride or adamantoyl chloride afforded the corresponding pivaloyl(silyl)stibanido and adamantoyl(silyl)stibanido complexes, eqn. (2). In contrast



(2)

to their phosphorus and arsenic analogues the anticipated 1,3-silyl migration to yield metallostibaalkenes did not occur.[13] To the best of our knowledge, metal-free acyclic stibaalkenes with localized Sb=C bonds are rare and confined to the compounds $[RC(OSiMe_3)=Sb–]_2$ (R = Mes or Mes*) and Mes*C(O)SbC(Mes*)OH[14] (Mes = 2,4,6-$Me_3C_6H_2$, Mes* = 2,4,6-$Bu^t_3C_6H_2$). One molar equivalent of diphenylketene reacted with **1** to give the crystalline adduct **5a**, eqn. (3). All attempts to extrude



(3)

hexamethyldisiloxane from **5a** with formation of a metallostibaallene or a dimer thereof failed.[15]

Obviously, the chemistry of silylated metallostibanes does not just mirror the organometallic chemistry of phosphorus and arsenic, and therefore we decided to study the chemistry of functionalized metallostibanes in more detail.

Results and discussion

Having prepared the alkenylstibanido complex (or η^1-stibaallyl complex) **5a** we were interested in the influence of the

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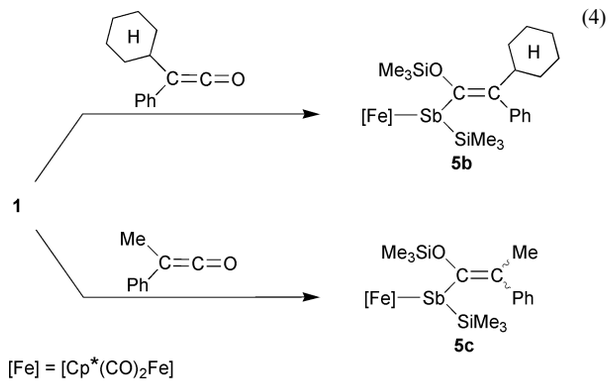
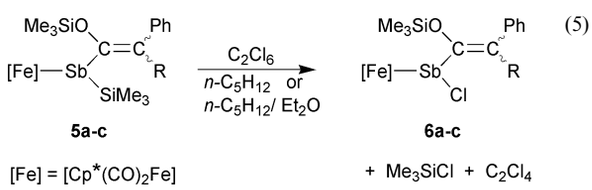
substitution pattern at the ketene component upon the course of the reaction and the reactivity of the products. The reaction of **1** with an equimolar amount of cyclohexylphenylketene in *n*-pentane in the temperature range −50 to 20 °C afforded **5b**, eqn. (4). The pure compound was obtained by crystallization



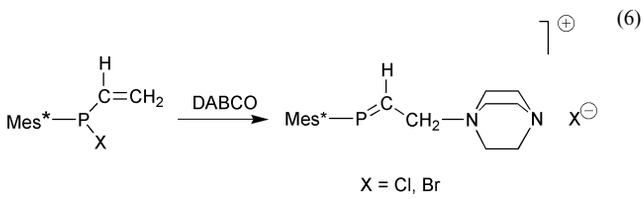
from *n*-pentane as a dark red microcrystalline solid (76% yield). The air and moisture sensitive metallostibane is well soluble in saturated hydrocarbons, arenes and ethers. In an inert gas atmosphere **5b** is stable at room temperature.

Treatment of complex **1** with Me(Ph)C=C=O under analogous conditions led to the formation of thermolabile **5c**, which is formed as a mixture of isomers. The metallostibane could not be isolated. It decomposed within a few hours to an intractable material. The employment of ether solvents and modified reaction conditions was without success. The stability of alkenyl functionalized metallostibanes could be improved considerably by exchange of the antimony-bound silyl group by chlorine. *In situ* generated **5a** was allowed to combine with an equimolar amount of hexachloroethane in *n*-pentane at room temperature. Product **6a** separated as an orange precipitate, which was collected after 12 h by filtration, eqn. (5). Crystallization from

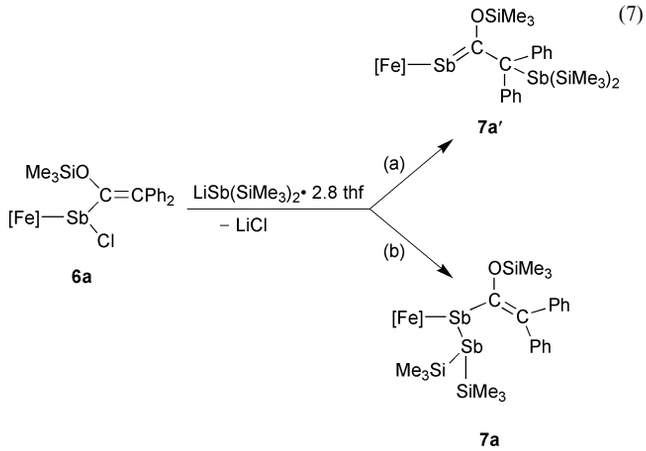


toluene at −30 °C afforded orange rhombs, suitable for an X-ray structural analysis. Analogously, orange **6b** was prepared in 72% yield from equimolar quantities of **1** and cyclohexyl(phenyl)ketene. The synthesis of **6c** was achieved from *in situ* prepared **5c** in a mixture of *n*-pentane and diethyl ether. Analytically pure samples of **6b** and **6c** were obtained by crystallization from *n*-pentane at −20 or 0 °C, respectively. The presence of a reactive antimony–chlorine bond in the molecule renders **6a–6c** valuable as starting materials for further chemical transformations.

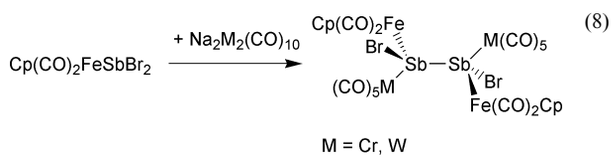
In a brief communication Mercier and Mathey described the addition of a nitrogen base to the β-carbon atom of a vinyl(chloro)phosphane with generation of a cationic phosphaalkene,[16] eqn. (6). Bulky nucleophiles such as LiSb-



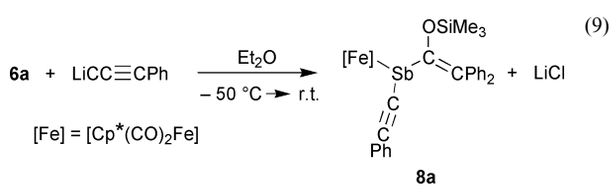
$(SiMe_3)_2$·2.8thf could also attack the β-carbon atom of the C=C-bond in compound **6a**, giving rise to the formation of a metallostibaalkene (path a). The alternative attack at the antimony centre would lead to a metallodistibane (path b), eqn. (7). Reaction of **6a** with an equimolar amount of LiSb-



$(SiMe_3)_2$·2.8thf[17] in *n*-pentane in the temperature range −50 to 20 °C yielded the dark red microcrystalline ferriodistibane **7a** (54%). There was no evidence for the anticipated metallostibaalkene **7a′**. To the best of our knowledge **7a** is the first distibane which is functionalized by only one transition metal. The only other transition metal substituted distibanes were synthesized previously by reductive coupling of a [$FeCp(CO)_2$-$(SbBr_2)$],[18] eqn. (8).

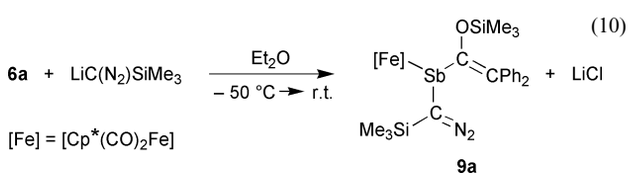


The alkenyl(alkynyl)metallostibane **8a** was formed in moderate yield upon combination of compound **6a** with freshly prepared lithium phenylacetylide in diethyl ether, eqn. (9). The

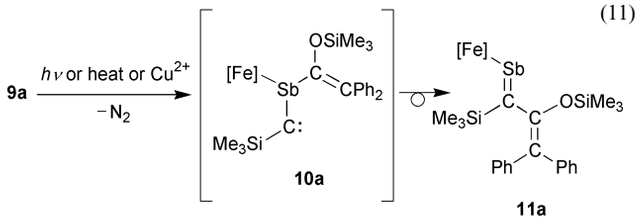


red microcrystalline solid was crystallized from *n*-pentane at −20 °C.

The metal-functionalized stibanyl(silyl)diazoalkane **9a** resulted from treatment of compound **6a** with freshly prepared $LiC(N_2)SiMe_3$ as a dark red solid in 90% yield, eqn. (10). All



attempts to cleave dinitrogen from molecule **9a** (heat, UV irradiation, Cu^{2+} catalysis) failed. It is conceivable that the hypothetical carbene **10a** could undergo rearrangement to give metallostibaalkene **11a**, eqn. (11). Compound **9a** is not the first diazoalkane exhibiting stibanyl substituents. Previously $Me_3Si(Me_2Sb)CN_2$ was synthesized from $Me_3SiCH(N_2)$ and Me_2SbNMe_2.[19] Analogously, $Me_2SbC(N_2)CO_2Et$,[20] $Me_2SbC(N_2)C(O)Ph$,[20] $(Me_2Sb)_2CN_2$[20] and $(Me_2As)(Me_2Sb)CN_2$[21] were obtained.



(11)

Products **5a**–**5c**, **6a**–**6c**, **7a**, **8a** and **9a** can be regarded as stibanes, in which the Group 15 atom is asymmetrically ligated by the transition metal, an alkenyl unit and a third substituent varying from Me_3Si (**5a–5c**) *via* Cl (**6a–6c**) and $Sb(SiMe_3)_2$ (**7a**) to an phenylalkynyl and a diazoalkyl function. The IR spectra of the compounds are dominated by two intense bands for the symmetric and antisymmetric carbonyl stretching vibrations of the $[Fe(CO)_2]$ building block. The bathochromic shift of the bands of **5a** (1969, 1917 cm^{-1}) and **5b** (1970, 1914 cm^{-1}) with respect to those in **6a–6c** (1990–1995 and 1939–1946 cm^{-1}) is due to the decreased σ-donor/π-acceptor capacity of the chlorinated stibanido ligands. The transfer of electron density by the distibanido ligand onto the $[Fe(CO_2)]$ fragment in **7a** [ν(CO) 1969, 1920 cm^{-1}] is comparable to the situation in **5a–5c**, whereas the ligating properties of the alkynyl stibanido group in **8a** [ν(CO) 1990, 1945 cm^{-1}] compare with the stibanido ligands in **6**. This trend is also reflected in the ^{13}C-{^1H} NMR resonances of the carbonyl ligands at δ 218.9–219.9, whereas for **6a–6c** the carbonyl resonances are observed at δ 214.1–215.9. The similarity of the ^{13}C-{^1H} NMR shifts of the alkenyl groups in **5a** [δ 138.9 (CPh_2); 147.1 (SbC)] and **7a** [δ 135.4; 148.2] is indicative of comparable structural features in the compounds and clearly excludes the presence of the metallostibaalkene structure **7a′**. In the latter compound the ^{13}C resonance for the Sb=C unit would be expected at δ >200. Compound **5c** is formed as a 1 : 1 mixture of geometric isomers as is obvious from two singlets for the allylic methyl groups at δ 2.14 and 2.36. Also the protons of the $OSiMe_3$ units give rise to two discrete singlets at δ 0.12 and 0.16. In contrast to this, only one isomer was isolated for **5b**, which is presumably due to the bulky cyclohexyl ring. Owing to steric reasons we postulate that the cyclohexyl ring and the stibanido group are oriented in *trans* disposition at the C=C bond. The same stereochemistry is present in **6b**. Such an arrangement would explain the deshielding of the protons of the $OSiMe_3$ group in **5b** (δ 0.48) and **6b** (δ 0.63) as compared to **5a** (δ 0.43) and **6a** (δ 0.31) where the silyl protons experience the magnetic anisotropy of the vicinal phenyl ring.

A characteristic feature of the IR spectrum of diazoalkane **9a** is the strong ν(NN) band at 2016 cm^{-1}. This absorption compares well with the corresponding band of $(Me_3Si)(Me_2Sb)CN_2$ at 2020 cm^{-1}.[19] For the precursor $Me_3SiC(N_2)H$ the band for the N=N stretching vibration was observed at 2065 cm^{-1}.[19] The carbon atom of the diazoalkane unit could not be detected in the ^{13}C-{^1H} NMR spectrum of **9a**.

X-Ray structural analysis of compound 6a

For a full characterization an X-ray structural analysis of compound **6a** was performed. Single crystals (orange rhombs) of the compound were grown from toluene at −30 °C. Crystal data are given in Table 2 and selected bonding parameters in Table 1. **6a** (Fig. 1) exhibits a three-legged piano stool with two legs represented by nearly linear carbonyl ligands [Fe–C(11)–O(1) 175.6(3); Fe–C(12)–O(2) 176.0(3)°]. The most interesting feature of the molecule is the η^1-stibaallyl ligand with a trigonal-pyramidal geometry at antimony (sum of angles 298.6°). In precursor **5a** the pyramidalisation of the Sb atom was less pronounced (sum of angles 310.6°). The lone pair at the Sb atom is oriented towards the Cp* ligand. The iron–antimony bond length [2.539(1) Å] is markedly shorter than in **5a** [2.617(2) Å] or **1** [2.6219(11) Å] but close to the value measured in $[Fe(1,3\text{-}Bu^t_2C_5H_3)(CO)_2(SbCl_2)]$ [2.508(2)].[12] The Sb–Cl distance in **6a** of 2.429(1) Å is comparable with the situation in the latter compound where lengths of 2.451(4) and 2.399(4) Å were found.[12] The single bond length Sb–C(13) of 2.176(3) Å compares well with that in **5a** [2.203(2) Å][15] and related bond distances in $[RuCp^*(CO)_2\{Sb(SiMe_3)[C(O)\text{-}Bu^t]\}]$ [2.245(7) Å].[13]

The bond lengths clearly exceed the sum of the covalence radii of 2.16 Å for Sb (1.41 Å) and C (0.75 Å). Significantly shorter Sb–C distances are measured in $[Fe(CO)_4(SbPh)_3]$[22] [2.122(3)–2.128(3) Å] and in $[Ru(CO)_4(SbPh)_3]$ [2.130(4)–2.135(4) Å].[23] The bonding parameters within the 2,2-diphenyl-1-trimethylsiloxyvinyl unit are identical within the threefold standard deviation with those in **5a**. One single exception concerns the angle C(13)–O(3)–C(27) [126.0(2)°] in **6a**, which is less obtuse than in **5a** [132.79(16)°]. The torsion angle Fe(1)–Sb(1)–C(13)–C(14) is −103.7°, and shows that the lone pair at the Sb atom and the π system of the C=C bond avoid each other.

Table 1 Selected bond lengths (Å) and angles (°) for complex **6a**

Sb(1)–C(13)	2.176(3)	Sb(1)–Cl(1)	2.4286(12)
Sb(1)–Fe(1)	2.5391(7)	Fe(1)–C(12)	1.757(4)
Fe(1)–C(11)	1.760(4)	Si(1)–O(3)	1.673(3)
O(1)–C(11)	1.149(4)	O(2)–C(12)	1.146(5)
O(3)–C(13)	1.378(4)	C(13)–C(14)	1.333(4)
C(14)–C(21)	1.482(4)	C(14)–C(15)	1.502(5)
C(13)–Sb(1)–Cl(1)	96.48(10)	C(13)–Sb(1)–Fe(1)	100.78(9)
Cl(1)–Sb(1)–Fe(1)	101.35(3)	C(12)–Fe(1)–C(11)	93.19(19)
C(12)–Fe(1)–Sb(1)	90.09(13)	C(11)–Fe(1)–Sb(1)	90.40(12)
C(13)–O(3)–Si(1)	126.0(2)	O(1)–C(11)–Fe(1)	175.6(3)
O(2)–C(12)–Fe(1)	176.0(3)	C(14)–C(13)–O(3)	123.4(3)
C(14)–C(13)–Sb(1)	117.2(2)	O(3)–C(13)–Sb(1)	118.5(2)
C(13)–C(14)–C(21)	124.9(3)	C(13)–C(14)–C(15)	118.9(3)
C(21)–C(14)–C(15)	116.2(3)		

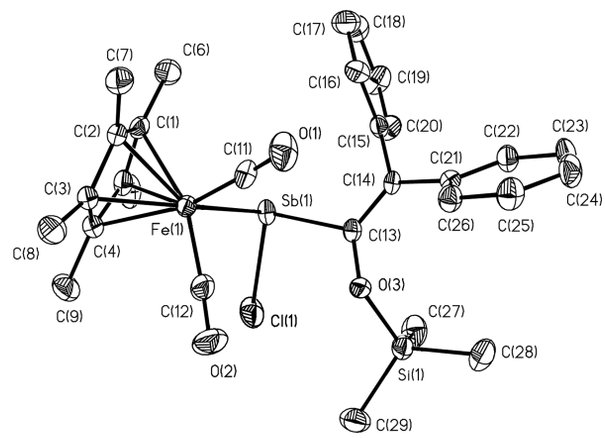


Fig. 1 Molecular structure of $[FeCp^*(CO)_2\{SbC(OSiMe_3)=CPh_2\}Cl]$ **6a** (showing 50% probability ellipsoids; hydrogen atoms are omitted for clarity).

Conclusion

It has been demonstrated that the metallostibane $[FeCp^*(CO)_2\{Sb(SiMe_3)_2\}]$ **1** is a precursor for a series of chemical transformations. Ketenes are readily inserted in one of the Sb–Si bonds to give η^1-stibaallyliron complexes **5a–5c**. The cleavage of hexamethyldisiloxane from these products to afford ferriostibaallenes or oligomers thereof, however, failed. The remaining Sb–Si bond in **5a–5c** was smoothly cleaved by hexachloroethane, resulting in formation of the chlorostibanido complexes **6a–6c**. Replacement of the chloride in **6a** by nucleophiles such as $[Sb(SiMe_3)_2]^-$, phenylacetylide or $[C(N_2)SiMe_3]^-$

furnished the metallodistibane **7a**, the alkenyl(alkynyl)-stibanido complex **8a**, and the metallated diazoalkane derivative **9a**. The presence of a variety of functional groups in **7a**, **8a** and **9a** promises a rich chemistry of these molecules.

Experimental

General procedures

All manipulations were performed under an atmosphere of dry argon using standard Schlenk techniques. All solvents were dried by common methods and freshly distilled prior to use. The compounds $[FeCp^*(CO)_2\{Sb(SiMe_3)_2\}]$ **1**,[13] $[FeCp^*(CO)_2\{Sb[C(OSiMe_3)=CPh_2](SiMe_3)\}]$ **5a**,[15] $Ph_2C=C=O$,[24] $Ph(Me)C=C=O$,[25] $Ph(c\text{-}C_6H_{11})C=C=O$,[25] $LiSb(SiMe_3)_2\cdot 2.8$ thf[17] and $LiC(N_2)SiMe_3$[26] were prepared according to literature methods. Phenylacetylene and $HC(N_2)SiMe_3$ were purchased commercially. NMR spectra were recorded in C_6D_6 on a Bruker AM Avance DRX 500 (^1H, ^{13}C, ^{29}Si) spectrometer using $SiMe_4$ as external standard, IR spectra on Bruker FT-IR IFS66 and FT-IR Vector22 instruments.

Preparations

$[FeCp^*(CO)_2\{Sb[C(OSiMe_3)=C(c\text{-}C_6H_{11})Ph](SiMe_3)\}]$ 5b. A stirred solution of compound **1** (1.28 g, 2.50 mmol) in *n*-pentane (30 ml) was chilled to −50 °C and a solution of $Ph(c\text{-}C_6H_{11})C=C=O$ (0.50 g, 2.50 mmol) in 20 ml of *n*-pentane added dropwise. The mixture was warmed and stirred for 8 h at ambient temperature. Volatile components were removed *in vacuo*, and the residue was extracted with 20 ml of *n*-pentane. It was filtered and the filtrate stored overnight at 0 °C, whereupon dark red crystalline **5b** separated, yield 1.36 g (76%) (Found: C, 53.64; H, 6.88; $C_{32}H_{50}FeO_3SbSi_2$ requires C, 53.72; H, 6.90%). ^1H NMR: δ 0.48 (s, 9H, $OSiMe_3$), 0.64 (s, 9H, $SbSiMe_3$), 0.86–1.85 (m, 11H, $c\text{-}C_6H_{11}$), 1.44 (s, 15H, C_5Me_5) and 7.21–7.24 (m, 5H, Ph). $^{13}C\text{-}\{^1H\}$ NMR: δ 2.2 [s, $OSi(CH_3)_3$], 3.8 [s, $SbSi(CH_3)_3$], 9.9 [$C_5(CH_3)_5$], 26.3 (s), 27.1 (s), 27.4 (s), 32.0 (s), 32.6 (s), 38.9 (s) ($c\text{-}C_6H_{11}$), 94.2 [s, $C_5(CH_3)_5$], 126.4 (s, C=*C*Ph), 132.8 (s), 141.0 (s), 141.8 (s, Ph), 143.4 (s, Sb*C*=C), 218.9 (s, FeCO) and 219.8 (s, FeCO). $^{29}Si\text{-}\{^1H\}$ NMR: δ −5.3 (s, SbSi) and 11.8 (s, OSi). IR (KBr, cm^{-1}): $\tilde{\nu}$(CO) 1970vs, 1914vs; $\delta(SiMe_3)$ 1250s, 1241s; $\rho(SiMe_3)$ 842s.

$[FeCp^*(CO)_2\{Sb[C(OSiMe_3)=C(Me)Ph](SiMe_3)\}]$ 5c. Crude **5c** was prepared analogously from compound **1** (0.47 g, 0.9 mmol) and Ph(Me)C=C=O (0.12 g, 0.9 mmol) in a mixture of 30 ml of *n*-pentane and 20 ml of diethyl ether in the temperature range between −50 and +20 °C. Owing to its thermolability the crude product, which was formed as a 1 : 1 mixture of isomers, could not be purified further, and characterization was limited to ^1H NMR spectroscopy and derivatization (see below). ^1H NMR : δ 0.12 (s) and 0.16 (s, 9H, $OSiMe_3$), 0.69 (s, 18H, $SbSiMe_3$), 1.58 (s, 30H, C_5Me_5), 2.14 (s) and 2.36 (s, 3H, C=CMe), 6.98–7.53 (m, 10H, Ph).

$[FeCp^*(CO)_2\{Sb[C(OSiMe_3)=CPh_2]Cl\}]$ 6a. A solution of compound **5a**, prepared from 0.91 g (1.8 mmol) of **1** and 0.34 g (1.8 mmol) of $Ph_2C=C=O$ in 45 ml of *n*-pentane as described before, was treated at 20 °C with 0.42 g (1.8 mmol) of solid hexachloroethane. Stirring was continued for 12 h before the solid orange precipitate was filtered off. The filter-cake was washed (3 × 10 ml *n*-pentane) and dried *in vacuo*. The crude product was crystallized from toluene (4 ml) at −30 °C to give **6a** as orange rhombs (1.06 g, 88% yield) (Found: C, 51.51; H, 4.81. $C_{29}H_{34}ClFeO_3SbSi$ requires C, 51.85; H, 5.10%). ^1H NMR: δ 0.31 (s, 9H, $SiMe_3$), 1.35 (s, 15H, C_5Me_5) and 7.05–7.54 (m, 10H, Ph). $^{13}C\text{-}\{^1H\}$ NMR: δ 1.3 [s, $Si(CH_3)_3$], 9.4 [s, $C_5(CH_3)_5$], 95.5 [s, $C_5(CH_3)_5$], 126.8 (s, C=*C*Ph), 130.7 (s), 132.1 (s), 134.6 (s), 141.4 (s), 141.9 (s, Ph), 164.3 (s, Sb*C*=C), 214.1 (s, FeCO) and 215.3 (s, FeCO). $^{29}Si\text{-}\{^1H\}$ NMR: δ 19.8 (s). IR (KBr, cm^{-1}): $\tilde{\nu}$(CO) 1993vs, 1939vs; $\delta(SiMe_3)$ 1249s; $\rho(SiMe_3)$ 847s.

$[FeCp^*(CO)_2\{Sb[C(OSiMe_3)=C(c\text{-}C_6H_{11})Ph]Cl\}]$ 6b. A solution of compound **5b** (0.40 g, 0.6 mmol) in *n*-pentane (20 ml) was treated at 20 °C with solid hexachloroethane (0.13 g, 0.6 mmol), and the mixture stirred for 3 h. Volatile components were removed *in vacuo*, and the residue was dissolved in 15 ml of *n*-pentane. It was filtered and the filtrate stored at −20 °C to afford **6b** as an orange solid (0.29 g, 72% yield) (Found: C, 52.27; H, 6.24. $C_{29}H_{40}ClFeO_3SbSi$ requires C, 51.39; H, 5.59%). ^1H NMR: δ 0.63 (s, 9H, $OSiMe_3$), 0.85–3.23 (m, 11H, $c\text{-}C_6H_{11}$), 1.38 (s, 15H, C_5Me_5) and 7.04–7.30 (m, 5H, Ph). $^{13}C\text{-}\{^1H\}$ NMR: δ 1.8 [$OSi(CH_3)_3$], 9.5 [$C_5(CH_3)_5$], 26.2 (s), 26.6 (s), 27.0 (s), 31.1 (s), 32.0 (s), 38.8 (s, $c\text{-}C_6H_{11}$), 95.4 [s, $C_5(CH_3)_5$], 127.1 (s, C=*C*Ph), 129.0 (s), 131.4 (s), 133.1 (s), 138.7 (s), 139.3 (s), 158.4 (s, Sb*C*=C), 214.1 (s, FeCO) and 215.9 (s, FeCO). $^{29}Si\text{-}\{^1H\}$ NMR: δ 18.1 (s). IR (KBr, cm^{-1}): $\tilde{\nu}$(CO) 1990vs, 1946vs; $\delta(SiMe_3)$ 1248s; $\rho(SiMe_3)$ 844s.

$[FeCp^*(CO)_2\{Sb[C(OSiMe_3)=C(Me)Ph]Cl\}]$ 6c. A solution of compound **5c** was freshly prepared from 0.62 g (1.2 mmol) of **1** and 0.16 g (1.2 mmol) of Ph(Me)C=C=O as described before. Solid hexachloroethane (0.16 g, 1.2 mmol) was added at room temperature and the mixture stirred for 14 h. After removal of volatiles the residue was dissolved in 20 ml of *n*-pentane and filtered. The filtrate was stored overnight at 0 °C. Product **6c** separated as orange crystals. Yield: 0.31 g (42%) (Found: C, 46.95; H, 5.07. $C_{24}H_{32}ClFeO_3SbSi$ requires C, 47.28; H, 5.29%). ^1H NMR: δ 0.16 (s, 9H, $OSiMe_3$), 1.47 (s, 15H, C_5Me_5), 2.11 (s, 3H, C=CMe), 7.01 (t, $^3J_{H,H} = 7.3$, 1H, *p*-H of Ph), 7.15–7.17 (m, 2H, *m*-H of Ph) and 7.46 (d,d, $^3J_{H,H} = 7.3$, $^4J_{H,H} = 1.1$ Hz, 2H, *o*-H of Ph); $^{13}C\text{-}\{^1H\}$ NMR: δ 1.1 [s, $OSi(CH_3)_3$], 9.5 [s, $C_5(CH_3)_5$], 22.3 (s, C=C*C*H_3), 95.7 [s, $C_5(CH_3)_5$], 126.7 (s, C=*C*CH_3), 128.5 (s), 129.6 (s), 143.1 (s, Ph), 157.0 (s, Sb*C*=C), 214.0 (s, FeCO) and 214.6 (FeCO). $^{29}Si\text{-}\{^1H\}$ NMR: δ 18.0 (s). IR (KBr, cm^{-1}): $\tilde{\nu}$(CO) 1995vs, 1944vs; $\delta(SiMe_3)$ 1248s; $\rho(SiMe_3)$ 839s.

$[FeCp^*(CO)_2\{Sb[C(OSiMe_3)=CPh_2][Sb(SiMe_3)_2]\}]$ 7a. A solution of 0.18 g (0.4 mmol) of $LiSb(SiMe_3)_2\cdot 2.8$ thf in 30 ml of *n*-pentane was slowly added at −50 °C to a well stirred solution of 0.26 g (0.4 mmol) of compound **6a** in *n*-pentane. It was warmed to ambient temperature and stirred for 5 h. Filtration and crystallization at −30 °C afforded 0.20 g (54% yield) of dark red **7a** (Found: C, 46.56; H, 5.53. $C_{35}H_{52}FeO_3Sb_2Si_3$ requires C, 46.48; H, 5.80%). ^1H NMR: δ 0.22 (s, 9H, $OSiMe_3$), 0.70 (s, br, 18H, $SbSiMe_3$), 1.49 (s, 15H, C_5Me_5), 6.96 (t, $^3J_{H,H} = 6.9$, *p*-H of Ph), 7.09 (t, $^3J_{H,H} = 7.5$, 1H, *p*-H of Ph), 7.12–7.18 (m, 4H, *m*-H of Ph), 7.44 (d, $^3J_{H,H} = 6.9$, 2H, *o*-H of Ph) and 7.51 (d, $^3J_{H,H} = 7.5$ Hz, 2H, *o*-H of Ph). $^{13}C\text{-}\{^1H\}$ NMR: δ 2.1 [s, $OSi(CH_3)_3$], 5.7 [s, $SbSi(CH_3)_3$], 9.9 [s, $C_5(CH_3)_5$], 94.7 [s, $C_5(CH_3)_5$], 126.4 (s), 127.0 (s), 131.1 (s), 131.8 (s, Ph), 135.4 (s, C=*C*Ph), 141.6 (s, Ph), 145.7 (s, Ph), 148.2 (s, Sb*C*=C), 219.0 (s, FeCO) and 219.1 (s, FeCO). $^{29}Si\text{-}\{^1H\}$ NMR: δ 15.8 (s). IR (KBr, cm^{-1}): $\tilde{\nu}$(CO) 1969vs, 1920vs; $\delta(SiMe_3)$ 1248s, 1238 (s); $\rho(SiMe_3)$ 848s.

$[FeCp^*(CO)_2\{Sb[C(OSiMe_3)=CPh_2](C\equiv CPh)\}]$ 8a. A freshly prepared solution of LiC≡CPh (0.10 g, 0.8 mmol) (from HC≡CPh and MeLi in 15 ml of diethyl ether) was slowly added to a chilled solution (−50 °C) of compound **6a** (0.45 g, 0.7 mmol) in 30 ml of diethyl ether. It was warmed to ambient temperature and stirring continued for 12 h. Solvent was removed and the residue stirred with 15 ml of *n*-pentane. Filtration and storage of the filtrate at −20 °C afforded 0.19 g (37%) of **8a** as a red microcrystalline solid (Found: C, 60.20; H, 5.53. $C_{37}H_{39}FeO_3SbSi$ requires C, 60.27; H, 5.33%). ^1H NMR: δ 0.28 (s, 9H, $OSiMe_3$), 1.44 (s, 15H, C_5Me_5) and 6.96–7.65 (m, 15H, Ph). $^{13}C\text{-}\{^1H\}$ NMR: δ 1.2 [s, $OSi(CH_3)_3$], 9.5

Table 2 Crystallographic data for compound **6a**

Empirical formula	$C_{29}H_{34}ClFeO_3SbSi$
M_r	671.70
T/K	173
Space group	$P2_1/n$
Crystal system	Monoclinic
a/Å	8.565(2)
b/Å	17.591(3)
c/Å	20.285(4)
β/°	99.87(2)
V/Å^3	3011.0(11)
Z	4
μ(Mo-Kα)/mm^{-1}	1.534
Reflections collected	9302
Independent reflections	8766
Reflections with $I > 2\sigma(I)$/parameters	6167/333
Final $R1$, $wR2$ ($I > 2\sigma(I)$)	0.0465, 0.0820
(all data)	0.0807, 0.0929

[s, $C_5(CH_3)_5$], 84.7 (S, C≡*C*Sb), 94.3 [s, $C_5(CH_3)_5$], 112.9 (s, C≡*C*Ph), 125.7 (s, C=*C*Ph$_2$), 126.6 (s), 127.3 (s), 131.1 (s), 131.9 (s), 132.6 (s), 137.4(s), 141.7 (s), 143.8 (s, Ph), 156.4 (s, Sb*C*=C), 216.7 (s, FeCO) and 216.9 (s, FeCO). ^{29}Si-{^{1}H} NMR: δ 18.0 (s). IR (KBr, cm^{-1}): $\tilde{\nu}$(CO) 1990vs, 1945vs; δ(SiMe$_3$) 1247s; ρ(SiMe$_3$) 844s.

[FeCp*(CO)$_2${Sb[C(OSiMe$_3$)=CPh$_2$][CN$_2$(SiMe$_3$)]}] 9a. A freshly prepared solution of 1.9 mmol LiC(N$_2$)(SiMe$_3$) (obtained from HC(N$_2$)(SiMe$_3$) and *n*-butyllithium in 10 ml of diethyl ether) was added dropwise to a chilled solution (−50 °C) of compound **6a** (1.25 g, 1.9 mmol) in 30 ml of diethyl ether. The mixture was warmed to room temperature and stirred for 2 h. It was evaporated to dryness and the residue extracted into 20 ml of *n*-hexane. Filtration and removal of solvent led to dark red solid **9a** (1.29 g, 90% yield) (Found: C, 52.60; H, 5.86; N, 3.58. $C_{33}H_{43}FeN_2O_3SbSi_2$ requires C, 52.88; H, 5.78; N, 3.74%). ^{1}H NMR: δ 0.22 (s, 9H, OSiMe$_3$), 0.41 (s, 9H, CSiMe$_3$), 1.46 (s, 15H, C$_5$Me$_5$) and 6.88–7.50 (m, 10H, Ph). ^{13}C-{^{1}H} NMR: δ 0.2 [s, OSi(CH$_3$)$_3$], 0.9 [s, CSi(*C*H$_3$)$_3$], 9.5 [s, C(*C*H$_3$)$_5$], 94.7 [s, *C*$_5$(CH$_3$)$_5$], 126.5 (s), 127.2 (s), 131.2 (s), 132.5 (s, Ph), 135.3 (s, C=*C*Ph), 141.9 (s, Ph), 144.1 (s, Ph), 158.8 (s, Sb*C*=C), 216.3 (s, FeCO) and 216.6 (s, FeCO). ^{29}Si-{^{1}H} NMR: δ 2.5 (s, CSiMe$_3$) and 18.2 (s, OSiMe$_3$). IR (KBr, cm^{-1}): $\tilde{\nu}$(N$_2$) 2016vs; $\tilde{\nu}$(CO) 1979vs, 1934vs; δ(SiMe$_3$) 1248s; ρ(SiMe$_3$) 859s.

Crystal structure determination

Data for compound **6a** were collected on a Siemens P3 diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71073). A semi-empirical absorption correction using ψ scans was applied. Crystallographic programs used for structure solution and refinement were SHELXTL PLUS[27] and SHELXL 97.[28] The structure was solved by direct methods and refined by full-matrix least squares on F^2 of all unique reflections with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were included at calculated positions with U(H) = 1.2 U_{eq} for aromatic groups, U(H) = 1.5 U_{eq} for CH$_3$ groups. Crystal data are listed in Table 2.

CCDC reference number 186/2232.

See http://www.rsc.org/suppdata/dt/b0/b007366k/ for crystallographic files in .cif format.

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