

Synthesis, structure and reactivity of highly functionalized arsan-yl- and stibanyl-diazomethanes

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Dedicated to Professor François Mathey on the occasion of his 60th birthday

Abstract

Reaction of the ferriphosphane and ferriarsane $[\text{Cp}^*(\text{CO})_2\text{FeE}(\text{SiMe}_3)\{\text{C}(\text{OSiMe}_3)=\text{CPh}_2\}]$ (**2a**, E = P; **2b**, E = As) with an equimolar amount of hexachloroethane proceeded smoothly to afford the chlorinated derivatives $[\text{Cp}^*(\text{CO})_2\text{FeE}(\text{Cl})\{\text{C}(\text{OSiMe}_3)=\text{CPh}_2\}]$ (**3a**, E = P; **3b**, E = As). Only **3b** could be converted into the pnictogen functionalized diazoalkane $[\text{Cp}^*(\text{CO})_2\text{FeAs}\{\text{C}(\text{N}_2)\text{SiMe}_3\}\{\text{C}(\text{OSiMe}_3)=\text{CPh}_2\}]$ (**4b**) by treatment with $\text{LiC}(\text{N}_2)\text{SiMe}_3$. Upon gentle heating or irradiation, compound **4b** as well as its antimony analogue **4c** proved to be inert towards N_2 -extrusion. Diazoalkane **4c** and dialkyl acetylenedicarboxylates underwent [3 + 2] cycloadditions with the result of the (1-pyrazolyl)stibanes **9c** and **9d**. This process involved a sigmatropic migration of the antimony fragment from carbon to nitrogen. The novel products were characterized by elemental analyses and spectra (IR, ^1H -, ^{13}C -, ^{29}Si -, ^{31}P -NMR). In addition the diazoalkanes **4b** and **4c** as well as the (1-pyrazolyl)stibane **9d** were subjected to single crystal X-ray structure determinations. © 2002 Published by Elsevier Science B.V.

Keywords: Iron complexes; Arsenic; Antimony; Diazoalkanes

1. Introduction

Metallo-disilyl-pnictanes of the type $[(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2\text{Fe-E}(\text{SiMe}_3)_2]$ (**1a**: E = P [1]; **1b**: E = As [2]; **1c**: E = Sb [3]) are versatile reagents for the generation of metallophospha- and metalloarsaalkenes [4,5], metallo-diphosphenes [6], metalloarsaphosphenes [6] and metallo-diarsenes [6] (Scheme 1). The treatment of metallo-disilylstibanes with carboxylic acid chlorides did not furnish the expected metallo-stibaalkenes but has led only to their precursors, the respective metallo-silyl-acyl-stibanes [3].

With diphenylketene compounds **1a–c** reacted analogously to yield η^1 -phosphaallyl-, η^1 -arsaallyl- and η^1 -stibaallyliron complexes of the type $[(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2\text{Fe-E}(\text{SiMe}_3)\text{C}(\text{OSiMe}_3)=\text{CPh}_2]$ (E = P (**2a**), As (**2b**), Sb (**2c**)) [7] (Scheme 1). Compound **2c** was smoothly converted into the chlorostibaallyl iron com-

plex **3c** (Scheme 2) by treatment with an equimolar amount of hexachloroethane [8]. The synthesis of diazoalkane **4c** was envisaged to provide an appropriate precursor for a highly reactive silyl-stibanyl carbene **5c**, which could possibly be stabilized by rearrangement to afford metallo-stibaalkenes **6c** or **7c** or by intramolecular [2 + 1] cycloaddition to give a stiba-bicyclobutane derivative **8c** [8].

Unexpectedly, however, the stibanyldiazoalkane proved to be inert towards N_2 -extrusion under the conditions employed.

In view of the rich chemistry of phosphanyldiazoalkanes performed by the groups of Bertrand [9,10] and Regitz [11] we envisaged the synthesis of phosphanyl- and arsanyldiazoalkanes analogous to **4c**.

2. Results and discussion

In situ generated **2a** was allowed to combine with an equimolar amount of hexachloroethane in *n*-pentane at room temperature. Product **3a** separated from the

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filtered reaction mixture as an air- and moisture-sensitive orange solid in 85% yield. Analogously, orange **3b** was prepared in 79% yield from equimolar quantities of **2b** and hexachloroethane (Scheme 3).

Compounds **3a** and **3b** seemed to be suitable candidates for the preparation of phosphanyl- and arsanyl-functionalized diazomethanes. The metallated arsanyl(silyl)diazomethane **4b** was smoothly generated as red-brown air- and moisture-sensitive crystals, when **3b** was allowed to react with freshly prepared $\text{LiC}(\text{N}_2)\text{-SiMe}_3$ in diethyl ether at -50°C (74% yield). The phosphorus analogue **3a** however, turned out to be completely inert towards the organolithium reagent (Scheme 4).

In view of Bertrand and Regitz's successful preparations of a series of phosphanyl(silyl)diazomethanes via reaction of organophosphorus halides with $\text{LiC}(\text{N}_2)\text{-SiMe}_3$ [10,11], our result is surprising.

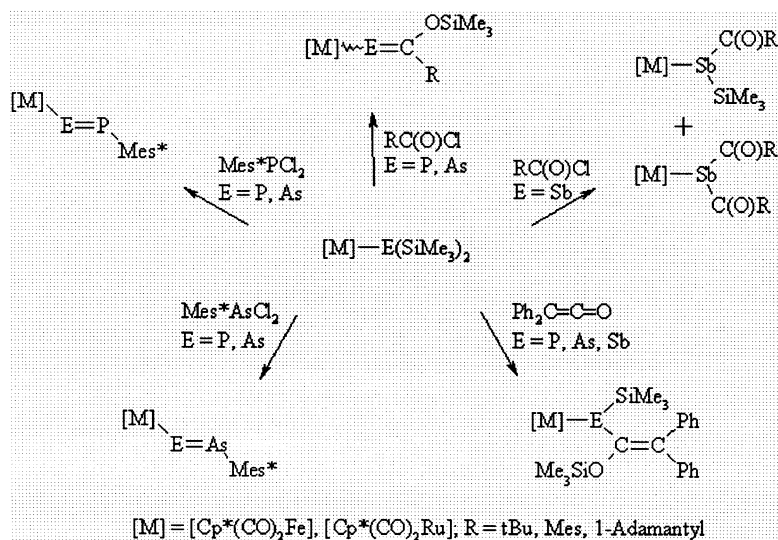
All attempts to cleave dinitrogen from molecule **4b** (heat, UV-irradiation, Cu^{2+} -catalysis) failed. Compound **4b** is not the first diazoalkane featuring arsanyl substituents. $\text{Me}_3\text{Si}(\text{Me}_2\text{As})\text{CN}_2$ was previously prepared by combining $\text{Me}_3\text{SiCHN}_2$ and $\text{Me}_2\text{AsNMe}_2$ in the presence of Me_3SnCl [12]. Similarly, reaction of $\text{Me}_2\text{AsNMe}_2$, CH_2N_2 and Me_3SnCl in various molecular ratios gave rise to the formation of $(\text{Me}_2\text{As})_2\text{CN}_2$ [13] and $\text{Me}_2\text{AsCHN}_2$ [14]. Derivative $\text{Me}_2\text{AsC}(\text{N}_2)\text{-CO}_2\text{Et}$ resulted from $\text{Me}_2\text{AsNMe}_2$ and ethyl diazoacetate [13]. Diazo compounds are valuable synthetic reagents. The 1,3-dipolar cycloaddition to alkynes and phosphalkynes represents an important access to pyrazoles [15] and 1,2,4-diazaphospholes [16]. The antimony-substituted diazoalkane **4c** was subjected to reaction with stoichiometric amounts of dimethyl acetylenedicarboxylate and diethyl acetylenedicarboxy-

late in *n*-pentane solution at 0°C . From the filtered and concentrated reaction mixtures the cycloadducts **9c** and **9d** were isolated as orange crystalline solids by crystallization at -4°C (yield: 88 and 83%) (Scheme 5).

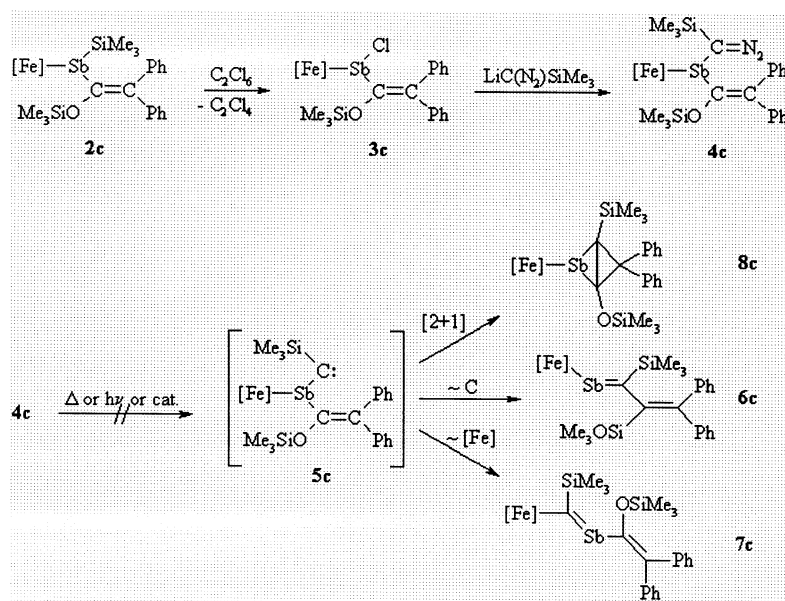
The initially generated cycloadduct **A** could not be detected spectroscopically. It rapidly underwent a sigmatropic 1,3-migration of the stibanyl group onto a nitrogen atom to yield the observed products **9c,d**. Obviously, this reaction proceeded chemo- and regioselectively. No products of a 1,5-sigmatropic stibanyl shift could be observed, and moreover there were no indications of any sigmatropic silyl shifts instead.

The corresponding arsanyldiazomethane **4b** did not react with the acetylenedicarboxylic esters. Previously, in contrast to $\text{Me}_2\text{SbC}(\text{N}_2)\text{CO}_2\text{Et}$, no reaction was observed between organoarsenic diazoalkanes [$(\text{Me}_2\text{AsCHN}_2)$, $(\text{Me}_2\text{As})_2\text{CN}_2$ and $\text{Me}_2\text{AsC}(\text{N}_2)\text{CO}_2\text{Et}$] and $\text{MeO}_2\text{C-C}\equiv\text{C-CO}_2\text{Me}$ [17]. Phosphino-substituted (silyl)diazomethanes $\text{R}_2\text{PC}(\text{SiMe}_3)\text{N}_2$ also did not react with acetylenedicarboxylates but smoothly underwent [3 + 2]-cycloadditions with phosphalkynes [11]. In our hands no cycloadditions could be achieved with **4b** and **4c** and dipolarophiles such as fumarodinitrile, fumarates, acrolein, di-*tert*-butyl acetylenedicarboxylate, ethyl propiolate, methyl propiolate and $\text{tBuC}\equiv\text{P}$.

The IR spectra of the products **3a,b**, **4b** and **9c,d** are dominated by two intense bands for the symmetric and antisymmetric carbonyl stretching vibrations of the $[\text{Fe}(\text{CO})_2]$ building block. The bathochromic shift of the bands of **2a** [$\nu(\text{CO})$ 1985, 1934 cm^{-1}] and **2b** [$\nu(\text{CO})$ 1980, 1930 cm^{-1}] with respect to those of **3a** [$\nu(\text{CO})$ 2003, 1951 cm^{-1}] and **3b** [$\nu(\text{CO})$ 2000, 1948 cm^{-1}] is due to the decreased σ -donor/ π -acceptor capacity of the chlorinated phosphanyl and arsanyl ligands. The transfer of electron density by the diazomethyl-arsanyl



Scheme 1.



ligand onto the $[\text{Fe}(\text{CO})_2]$ fragment in **4b** [$\nu(\text{CO})$ 1980, 1937 cm^{-1}] is comparable to the situation in diazomethyl-stibanyl complex **4c** [$\nu(\text{CO})$ 1979, 1934 cm^{-1}], whereas the ligating properties of the (pyrazolyl)stibanyl ligands in **9c,d** [$\nu(\text{CO})$ 1996, 1942 and 1995, 1943 cm^{-1}] compare with the stibanyl ligand in **3c** [$\nu(\text{CO})$ 1993, 1939 cm^{-1}] [8].

In the $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra of the chloro derivatives **3a–c** resonances at $\delta = 214.1$ – 216.5 are assigned to the carbonyl ligands. Due to an increased σ -donor/ π -acceptor ratio of the ligands in **4b** and **4c** these absorptions are slightly shifted to low field ($\delta = 216.3$ – 217.4). The carbonyl ligands in the pyrazolyl-stibanyl derivatives **9c,d** ($\delta = 214.0$ – 215.2) are deshielded with respect to the precursor **4c**. The α -carbon atoms of the alkenyl substituents at the pnictogene atoms in **3a–c** resonate at $\delta = 163.4$ – 164.6 . In **3a** a $^1J_{\text{PC}}$ coupling of 75.9 Hz was observed. These signals are considerably deshielded with respect to the precursors **2a–c** ($\delta = 147.1$ – 158.0) which reflects the electron withdrawing effect of the chlorine in comparison with the Me_3Si group. In the diazoalkane derivatives **4b** and **4c** singlets at $\delta = 163.2$ and 158.8 are attributed to these carbon atoms. The carbon atom of the CN_2 moiety of **4b** is tentatively assigned to a singlet at $\delta = 20.8$, which is close to the respective resonances in $\text{Me}_3\text{Ge}(\text{Me}_2\text{As})\text{CN}_2$ ($\delta = 20.6$), CH_2N_2 ($\delta = 23.1$), $\text{Me}_2\text{AsCHN}_2$ ($\delta = 24.1$) or $(\text{Me}_2\text{As})_2\text{CN}_2$ ($\delta = 24.7$) [18]. A characteristic feature in the IR spectra of the diazoalkane **4b** is the strong $\nu(\text{NN})$ band at $\tilde{\nu} = 2025 \text{ cm}^{-1}$, which compares well with the corresponding band of **4c** ($\tilde{\nu} = 2016 \text{ cm}^{-1}$), $\text{Me}_3\text{Ge}(\text{Me}_2\text{As})\text{CN}_2$ ($\tilde{\nu} = 2020 \text{ cm}^{-1}$) and $(\text{Me}_3\text{Si})(\text{Me}_2\text{Sb})\text{CN}_2$ ($\tilde{\nu} = 2020 \text{ cm}^{-1}$) [12]. For the precursor $\text{Me}_3\text{SiCHN}_2$ the band for the $\text{N}=\text{N}$ stretching vibration was observed at 2065 cm^{-1} [12].

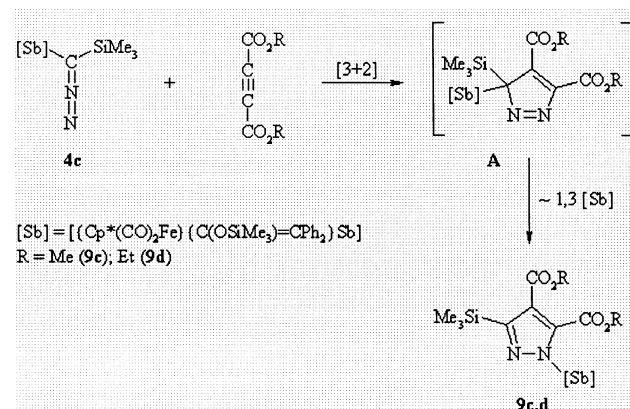
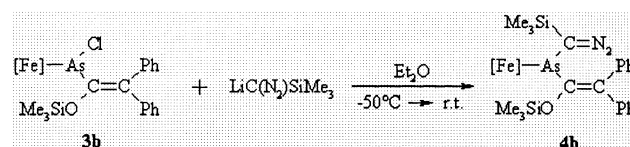
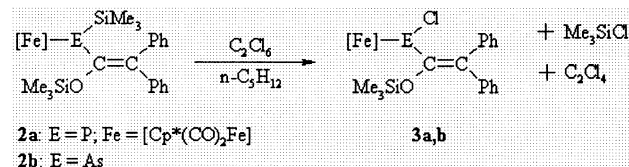


Table 1
Crystallographic data for compounds **4b**, **4c** and **9d**

Complex	4b	4c	9d
Empirical formula	C ₃₃ H ₄₃ AsFeN ₂ O ₃ Si ₂	C ₃₃ H ₄₃ FeN ₂ O ₃ SbSi ₂	C ₄₁ H ₅₃ FeN ₂ O ₇ SbSi ₂
<i>M_r</i>	702.64	749.47	913.63
Crystal habit	Orange rhombs	Orange prisms	Orange rhombs
Crystal size (mm)	0.30 × 0.27 × 0.24	0.20 × 0.20 × 0.30	0.21 × 0.17 × 0.07
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>
Unit cell dimensions			
<i>a</i> (Å)	11.2440(1)	17.407(4)	15.1780(1)
<i>b</i> (Å)	11.7800(1)	12.883(3)	17.5330(1)
<i>c</i> (Å)	13.3380(1)	16.737(4)	16.8650(1)
α (°)	87.0290(3)	90	90
β (°)	76.8880(3)	108.721(5)	92.3780(3)
γ (°)	88.1770(3)	90	90
<i>V</i> (Å ³)	1717.94(2)	3554.8(16)	4484.18(5)
<i>Z</i>	2	4	4
<i>D</i> _{calc} (g cm ^{−3})	1.358	1.400	1.362
μ (mm ^{−1})	1.499	1.268	1.026
<i>F</i> (000)	732	1536	1896
<i>T</i> (K)	100(2)	223(2)	100(2)
2 θ _{max}	60.0	56.8	60.0
Reflections collected	19 567	22 656	25 752
Unique reflections	9995 [<i>R</i> _{int} = 0.0143]	8421 [<i>R</i> _{int} = 0.0491]	13080 [<i>R</i> _{int} = 0.0189]
Reflections with <i>I</i> > 2 σ (<i>I</i>)	8879		10 927
Parameters	390	390	496
Final <i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)]	0.0231	0.0370	0.0280
<i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0542 (8879)	0.0740	0.0651 (10927)
<i>R</i> ₁ (all data)	0.0288	0.0805	0.0391
<i>R</i> ₂ (all data)	0.0563	0.0877	0.0701
Remarks			Disorder of Cp* ring on 3 positions (62:23:15) Disorder of C41 on 2 positions (51:49)

2.1. X-ray structure analyses of **4b**, **4c** and **9d**

For a full characterization of the novel arsanyl- and stibanyl-diazoalkanes X-ray structural analyses of compounds **4b** and **4c** were performed. Single crystals (orange rhombs) of the diazoalkanes were grown from *n*-pentane at −4 °C. Crystal data are given in Table 1 and selected bonding parameters in Tables 2 and 3. Compound **4b** (Fig. 1) has the shape of a three-legged piano stool with two legs represented by nearly linear carbonyl ligands [Fe(1)–C(11)–O(1), 173.6(16)°; Fe(1)–C(12)–O(2), 173.6(1)°]. The most interesting feature of the molecule is the diazomethyl–arsanyl ligand with a trigonal–pyramidal geometry at arsenic (sum of angles 309.26°). In the related arsanyl iron complex **2b** it amounts to 317.4° [7]. The iron–arsenic bond length of 2.4333(2) Å is close to the values measured in **2b** [2.448(1) Å] and [Cp(CO)₂Fe–As(Ph)–As(Ph)–Fe(CO)₂Cp] [2.450(2) Å] [19]. The As–Fe bond falls in the range between 2.257(2), 2.276(2), 2.359(2) Å in **10** [20] and 2.469(6), 2.472(5) Å found in **11** [21] and thus has to be regarded as single bond. The single bond length As(1)–C(17) of 1.977(1) Å compares well with that of 1.985(3) Å in **2c**. The arsenic atom is also linked to the trigonal planar carbon atom C(13) (sum of

angles 359.8°). The bond lengths C(13)–N(1) [1.293(2) Å] and N(1)–N(2) [1.145(1) Å] closely resemble the corresponding distances in [(ⁱPr₂N)₂P]₂CN₂ [1.28(1) and 1.15(1) Å] and are in the range of those usually ob-

Table 2
Selected bond lengths (Å) and angles (°) of **4b**

Bond lengths			
As(1)–C(17)	1.9773(11)	Fe(1)–C(1)	2.1501(11)
As(1)–C(13)	1.9780(11)	Si(1)–C(13)	1.8652(12)
As(1)–Fe(1)	2.43327(19)	Si(2)–O(3)	1.6737(8)
)			
Fe(1)–C(12)	1.7590(12)	O(1)–C(11)	1.1484(15)
Fe(1)–C(11)	1.7655(12)	O(2)–C(12)	1.1493(15)
Fe(1)–C(4)	2.1135(11)	O(3)–C(17)	1.3711(13)
Fe(1)–C(5)	2.1164(11)	N(1)–N(2)	1.1445(14)
Fe(1)–C(2)	2.1174(11)	N(1)–C(13)	1.2928(15)
Fe(1)–C(3)	2.1213(11)		
Bond angles			
C(17)–As(1)–C(13)	100.19(5)	O(1)–C(11)–Fe(1)	173.63(10)
C(17)–As(1)–Fe(1)	101.99(3)	O(2)–C(12)–Fe(1)	173.60(11)
C(13)–As(1)–Fe(1)	107.08(3)	N(1)–C(13)–Si(1)	117.33(8)
C(12)–Fe(1)–C(11)	91.30(6)	N(1)–C(13)–As(1)	120.20(8)
C(17)–O(3)–Si(2)	130.04(7)	Si(1)–C(13)–As(1)	122.28(8)
N(2)–N(1)–C(13)	179.13(13)	C(21)–C(17)–O(3)	123.15(10)
As(1)–Fe(1)–C(11)	92.83(4)	C(21)–C(17)–As(1)	118.60(8)
As(1)–Fe(1)–C(12)	92.62(4)	O(3)–C(17)–As(1)	117.52(8)

Table 3
Selected bond lengths (Å) and angles (°) of **4c**

Bond lengths			
Fe(1)–C(1)	2.115(3)	O(1)–C(11)	1.167(4)
Fe(1)–C(2)	2.124(4)	O(2)–C(12)	1.148(4)
Fe(1)–C(3)	2.094(4)	N(1)–C(13)	1.284(4)
Fe(1)–C(4)	2.094(3)	Si(1)–C(13)	1.859(4)
Fe(1)–C(5)	2.139(3)	Sb(1)–C(13)	2.176(3)
Fe(1)–C(11)	1.739(4)	Sb(1)–C(20)	2.185(3)
Fe(1)–C(12)	1.761(4)	O(3)–C(20)	1.379(3)
Fe(1)–Sb(1)	2.5773(8)	C(20)–C(21)	1.340(4)
N(1)–N(2)	1.147(4)	O(3)–Si(2)	1.666(2)
Bond angles			
O(1)–C(11)–Fe(1)	176.4(3)	C(20)–C(21)–C(28)	124.2(3)
O(2)–C(12)–Fe(1)	173.2(3)	C(22)–C(21)–C(28)	113.6(2)
N(1)–C(13)–Si(1)	117.2(2)	C(11)–Fe(1)–C(12)	93.03(16)
N(1)–C(13)–Sb(1)	119.8(2)	C(11)–Fe(1)–Sb(1)	86.91(12)
Si(1)–C(13)–Sb(1)	122.06(16)	C(12)–Fe(1)–Sb(1)	94.29(11)
C(21)–C(20)–O(3)	122.0(3)	C(20)–O(3)–Si(2)	125.95(19)
C(21)–C(20)–Sb(1)	119.6(2)	C(13)–Sb(1)–C(20)	98.84(11)
O(3)–C(20)–Sb(1)	117.96(19)	C(13)–Sb(1)–Fe(1)	105.90(9)
C(20)–C(21)–C(22)	122.1(3)	C(20)–Sb(1)–Fe(1)	102.20(8)

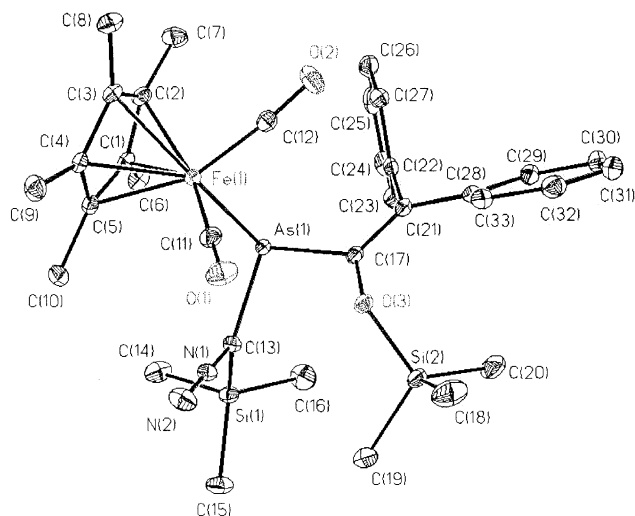
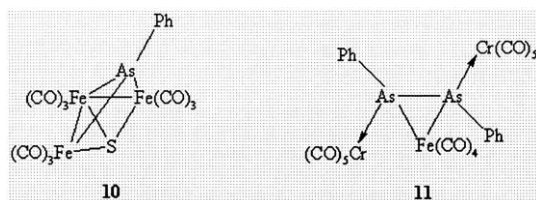


Fig. 1. Molecular structure of **4b** in the crystal.



Scheme 6.

served for diazoalkanes, namely 1.28–1.32 and 1.12–1.15 Å, respectively [22]. The valence angle at N(1) is 179.1(1)°. The bonding parameters within the 2,2-diphenyl-1-trimethylsiloxyvinyl unit are as expected and mainly compare well with those in precursor **2c**. One exception concerns the angle C(17)–O(3)–Si(2) of 130.0(1)° which is less obtuse than that in **2c** [139.5(2)°].

The torsion angle C(21)–C(17)–As(1)–Fe(1) is -94.5° and shows that the lone pair at the As atom and the π -system of the C=C-bond avoid each other. The π -system of the linear C(13)–N(1)–N(2) unit also deviates from the As lone pair [torsion angles N(1)–C(13)–As(1)–Fe(1) = -30.1° and N(1)–C(13)–As(1)–C(17) = 75.9°] (Scheme 6).

The geometry of the diazomethyl–stibanyl complex **4c** closely resembles that of its arsenic analogue (Fig. 2). A trigonal–pyramidal antimony atom (sum of angles 306.94°) is linked to the iron atom via a single bond of 2.577(1) Å. The pyramidalization of the Sb atom is between that of **3c** (sum of angles 298.6°) and **2c** (sum of angles 310.6°), which may to some degree reflect the steric congestion of the substituents $\text{Cl} < \text{C}(\text{SiMe}_3)_2 < \text{SiMe}_3$. The Fe–Sb bond length is also among those in **3c** [2.539(1) Å] and **2c** [2.617(2) Å]. The single bond lengths Sb(1)–C(13) of 2.176(3) Å and Sb(1)–C(20) [2.185(3) Å] compare with those in **3c** [2.176(3) Å] and **2c** [2.203(2) Å] and clearly exceed the sum of the covalence radii of 2.16 Å for Sb (1.41 Å) and C (0.75 Å). Bonding parameters within the dia-

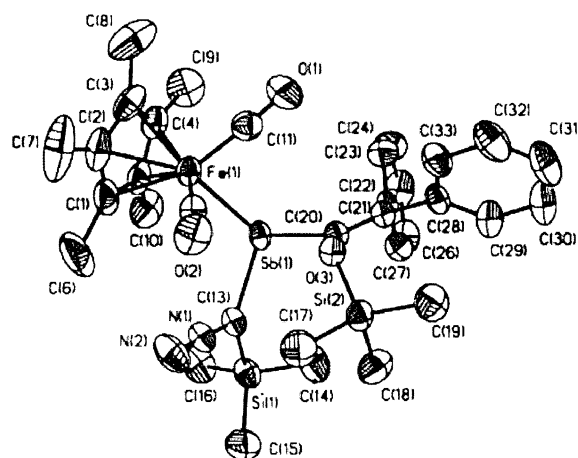


Fig. 2. Molecular structure of **4c** in the crystal.

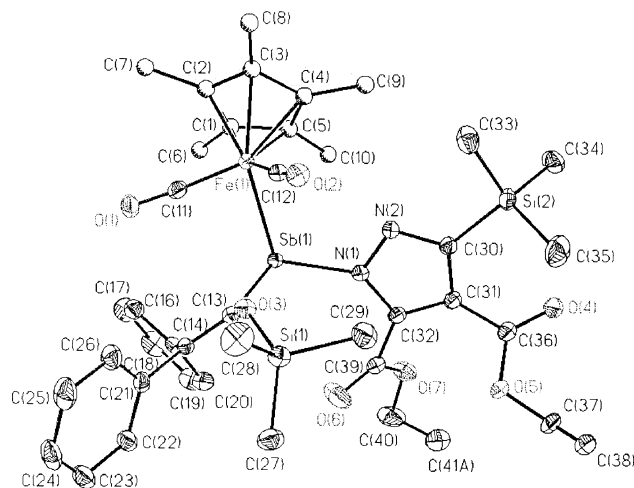


Fig. 3. Molecular structure of **9d** in the crystal.

Table 4
Selected bond lengths (Å) and angles (°) of **9d**

<i>Bond lengths</i>			
Sb(1)–C(13)	2.1581(16)	O(1)–C(11)	1.153(2)
Sb(1)–N(1)	2.1585(14)	O(2)–C(12)	1.146(2)
Sb(1)–Fe(1)	2.5303(2)	O(3)–C(13)	1.3698(19)
Fe(1)–C(11)	1.7542(17)	O(4)–C(36)	1.206(2)
Fe(1)–C(12)	1.7717(17)	O(5)–C(36)	1.340(2)
C(30)–C(31)	1.420(2)	O(6)–C(39)	1.204(2)
C(31)–C(32)	1.383(2)	O(7)–C(39)	1.330(2)
C(31)–C(36)	1.471(2)	N(1)–C(32)	1.362(2)
C(32)–C(39)	1.482(2)	N(1)–N(2)	1.3669(18)
C(13)–C(14)	1.341(2)	N(2)–C(30)	1.352(2)
Si(2)–C(30)	1.8817(17)		
<i>Bond angles</i>			
C(13)–Sb(1)–N(1)	94.77(6)	N(1)–C(32)–C(31)	108.04(14)
C(13)–Sb(1)–Fe(1)	98.65(4)	N(1)–C(32)–C(39)	121.20(14)
N(1)–Sb(1)–Fe(1)	102.72(4)	C(31)–C(32)–C(39)	130.75(15)
C(11)–Fe(1)–C(12)	93.45(8)	O(4)–C(36)–O(5)	124.00(16)
C(13)–O(3)–Si(2)	134.01(10)	O(4)–C(36)–C(31)	123.57(16)
C(36)–O(5)–C(37)	116.34(14)	O(5)–C(36)–C(31)	112.43(14)
C(39)–O(7)–C(40)	117.73(14)	O(6)–C(39)–O(7)	125.44(17)
C(32)–N(1)–N(2)	110.04(13)	O(6)–C(39)–C(32)	123.75(17)
C(32)–N(1)–Sb(1)	125.78(11)	O(7)–C(39)–C(32)	110.78(14)
N(2)–N(1)–Sb(1)	121.92(10)	O(1)–C(11)–Fe(1)	176.19(15)
C(30)–N(2)–N(1)	107.18(13)	O(2)–C(12)–Fe(1)	173.29(15)
N(2)–C(30)–C(31)	109.10(14)	C(14)–C(13)–O(3)	123.32(14)
N(2)–C(30)–Si(2)	119.87(12)	C(14)–C(13)–Sb(1)	118.56(11)
C(31)–C(30)–Si(2)	130.69(12)	O(3)–C(13)–Sb(1)	117.16(10)
C(32)–C(31)–C(30)	105.63(14)	C(13)–C(14)–C(21)	124.75(15)
C(32)–C(31)–C(36)	129.08(15)	C(13)–C(14)–C(15)	119.29(14)
C(30)–C(31)–C(36)	125.28(15)	C(21)–C(14)–C(15)	115.93(13)

zomethylsilyl group of **4c** [C(13)–N(1) = 1.284(4) and N(1)–N(2) = 1.147(4) Å] and within the diphenyl(trimethylsiloxy)vinyl substituent are as expected. In comparison to **4b** [130.0(1)°], the angle C(20)–O(3)–Si(2) in **4c** of 126.0(2)° is slightly more compressed and thus is identical with that in **3c**. The torsion angles C(21)–C(20)–Sb(1)–Fe(1) [–119.7(2)°], N(1)–C(13)–Sb(1)–Fe(1) [–21.5(3)°] and N(1)–C(13)–Sb(1)–C(20) [84.0(3)°] indicate that again the lone pair at the pnictogen atom deviates from the adjacent π -systems.

An X-ray crystal structure of the cycloadducts **9c** or **9d** was necessary to unambiguously determine the substitution pattern of the pyrazolyl ring and thus the identity of the migrated group (trimethylsilyl or stibanyl). Single crystals of **9d** (orange rhombs) were grown from *n*-pentane at –20 °C. The molecule (Fig. 3, Table 4) is regarded as a stibane with three chemically different substituents which are ligated to a trigonal–pyramidal antimony atom (sum of angles 296.1°) via single bonds. The bond length Fe(1)–Sb(1) of 2.5303(2) Å is markedly shorter than in the diazoalkane **4c** [2.577(1) Å] but compares well to the corresponding distance in the chlorostibane **3c** [2.5391(7) Å]. The bond Sb(1)–C(13) of 2.1518(2) Å is slightly shortened with respect to those in precursors **4c** [2.176(3) Å] and **3c** [2.176(3) Å]. The most interesting feature of the

molecule concerns the pyrazolyl–antimony moiety. The planar heterocycle (sum of angles 540.0°) and the pnictogen atom are connected by the single bond Sb(1)–N(1) of 2.159(1) Å. This bond length is longer than the sum of the covalent radii of 2.11 Å (Sb 1.41; N 0.70 Å) [23] and may be compared with the shorter Sb–N distances in [SbCl₂(NSiMe₃)₂CPh] (2.123(2) Å) [24] and ClSb[PhC(NSiMe₃)₂]₂ (2.169(3) Å) [25]. The trimethylsilyl group is bonded to the carbon atom C(30) of the ring [Si(2)–C(30) = 1.882(2) Å] which clearly indicates that the silyl group of the diazoalkane **4c** remained its location during the [3 + 2] cycloaddition and that the stibanyl group underwent a 1,3 sigmatropic shift from the initial adduct to yield the final product. The bonding parameters within the pyrazolyl moiety are as expected with the two carboethoxy groups at C(31) and C(32) twisted out of the ring plane (interplanar angles: 28.0 and 50.7°). The same holds for the bonding parameters within the [Cp*(CO)₂Fe] building block and within the diphenyl(trimethylsiloxy)vinyl substituent. One exception concerns the valence angle Si(2)–O(3)–C(13) of 134.01(10)° which clearly exceeds those in the chlorostibane **3c** [126.0(2)°] and the diazoalkane precursor **4c** [126.0(2)°].

3. Conclusion

It has been demonstrated that the metalloarsane and the metallostibane [Cp*(CO)₂FeE(Cl){C(OSiMe₃)=CPh₂}] (E = As: **3b**; Sb: **3c**) can smoothly be converted into the corresponding pnictogen-substituted diazoalkanes by treatment with LiC(N₂)SiMe₃. In contrast to this, the analogous metallophosphane [Cp*(CO)₂FeP(Cl){C(OSiMe₃)=CPh₂}] appeared to be inert towards the organolithium reagent. Only the antimony-functionalized diazoalkane underwent a [3 + 2] cycloaddition to dimethyl- and diethyl acetylenedicarboxylates to afford *N*-stibanylpyrazoles **9c** and **9d**, which involved a 1,3 sigmatropic stibanyl shift from the initial [3 + 2] adduct to the final product.

4. Experimental

4.1. General comments

All procedures were carried out using standard Schlenk techniques under a nitrogen atmosphere. All solvents were dried by common methods and freshly distilled prior to use. The compounds [Cp*(CO)₂FeE(SiMe₃)₂] (E = P [1], E = As [2]), [Cp*(CO)₂Fe–Sb{C(SiMe₃)N₂}{C(OSiMe₃)=CPh₂}] [8] (**4c**) and LiC(N₂)SiMe₃ [26] were prepared according to literature methods. Hexachloroethane, HC(N₂)SiMe₃, diethyl acetylenedicarboxylate and dimethyl acetylene-

dicarboxylate were purchased commercially. NMR spectra were recorded in C_6D_6 on a Bruker Avance DRX 500 (1H , ^{13}C , ^{29}Si , ^{31}P) spectrometer using $SiMe_4$ or 85% H_3PO_4 as external standard. IR spectra were recorded on Bruker FTIR IFS66 and FTIR Vector 22 instruments.

4.2. $[Cp^*(CO)_2FeP(Cl)\{C(OSiMe_3)=CPh_2\}]$ (**3a**)

A solution of diphenylketene (0.68 g, 3.5 mmol) in 10 ml of *n*-pentane was added dropwise to a chilled solution ($-50^\circ C$) of $[Cp^*(CO)_2FeP(SiMe_3)_2]$ (1.48 g, 3.5 mmol) in 25 ml of *n*-pentane. Warming up to ambient temperature was followed by the addition of solid hexachloroethane (0.83 g, 3.5 mmol) and the resulting mixture was stirred for 18 h. It was concentrated to ca. 10 ml, filtered, and the filtercake was dried in vacuo to give **3a** as an air- and moisture-sensitive orange solid (1.73 g, 85% yield). Anal. Found: C, 59.68; H, 5.92. Calc. for $C_{29}H_{34}ClFeO_3PSi$: C, 59.96; H, 5.90%. IR (KBr) $\nu(CO)$ 2003 s, 1951 s; $\delta(SiMe_3)$ 1256 s; $\rho(SiMe_3)$ 861 $m\ cm^{-1}$. 1H -NMR: $\delta = 0.27$ (s, 9H, $SiCH_3$), 1.33 (s, 15H, C_5CH_3), 6.93–6.96 (m, 1H, Ph-H), 7.04–7.13 (m, 5H, Ph-H), 7.45 (d, $^3J_{HH} = 6.9$ Hz, 2H, Ph-H), 7.53 (d, $^3J_{HH} = 7.6$ Hz, 2H, Ph-H). $^{13}C\{^1H\}$ -NMR: $\delta = 1.2$ (s, $SiCH_3$), 8.9 (d, $^3J_{PC} = 7.0$ Hz, C_5CH_3), 97.1 (s, C_5CH_3), 126.7 (s, Ph-C), 126.8 (s, Ph-C), 128.1 (s, Ph-C), 129.3 (d, $^2J_{PC} = 39.1$ Hz, CPh_2), 131.1 (s, Ph-C), 131.35 (s, Ph-C), 131.40 (s, Ph-C), 141.9 (d, $^3J_{PC} = 4.6$ Hz, Ph-C1), 143.0 (d, $^3J_{PC} = 11.5$ Hz, Ph-C1), 163.4 (d, $^1J_{PC} = 75.9$ Hz, P-C=C), 216.2 (s, $FeCO$), 216.4 (d, $^3J_{PC} = 5.7$ Hz, $FeCO$). ^{29}Si -NMR: $\delta = 19.8$ (s, OSi). $^{31}P\{^1H\}$ -NMR: $\delta = 264.5$ (s, $FePCl$).

4.3. $[Cp^*(CO)_2FeAs(Cl)\{C(OSiMe_3)=CPh_2\}]$ (**3b**)

Analogously product **3b** was obtained as an air- and moisture-sensitive solid (2.38 g, 79%) from the reaction of 2.26 g (4.8 mmol) of $[Cp^*(CO)_2FeAs(SiMe_3)_2]$ with diphenylketene (0.94 g, 4.8 mmol) and treatment of the resulting mixture with hexachloroethane (1.14 g, 4.8 mmol). Anal. Found: C, 55.40; H, 5.47. Calc. for $C_{29}H_{34}AsClFeO_3Si$: C, 55.74; H, 5.48%. IR (KBr) $\nu(CO)$ 2000 s, 1948 s; $\delta(SiMe_3)$ 1255 m; $\rho(SiMe_3)$ 859 $m\ cm^{-1}$. 1H -NMR: $\delta = 0.29$ (s, 9H, $SiCH_3$), 1.34 (s, 15H, C_5CH_3), 6.95–7.54 (m, 10H, Ph-H). $^{13}C\{^1H\}$ -NMR: $\delta = 1.3$ (s, $SiCH_3$), 9.0 (s, C_5CH_3), 96.3 (s, C_5CH_3), 126.8 (s, Ph-C), 127.2 (s, Ph-C), 129.3 (s, CPh_2), 130.9 (s, Ph-C), 131.6 (s, Ph-C), 141.5 (s, Ph-C1), 142.0 (s, Ph-C1), 164.6 (s, As-C=C), 215.6 (s, $FeCO$), 216.5 (s, $FeCO$). ^{29}Si -NMR: $\delta = 20.5$ (OSi).

4.4. $[Cp^*(CO)_2FeAs\{C(N_2)SiMe_3\}\{C(OSiMe_3)=CPh_2\}]$ (**4b**)

A freshly prepared solution of $LiC(N_2)SiMe_3$ (from

0.52 ml of a 2 M solution of $HC(N_2)SiMe_3$ and 0.65 ml of a 1.6 M solution of methylolithium) in 10 ml of Et_2O was added dropwise to the chilled solution ($-50^\circ C$) of **3b** (0.65 g, 1.04 mmol) in Et_2O (25 ml). The reaction mixture was warmed up to room temperature and then freed from volatile components in vacuo. The residue was triturated with *n*-pentane (15 ml) and filtered. The filtrate was stored at $-4^\circ C$ to afford **4b** as red-brown air- and moisture-sensitive crystals (0.54 g, 74% yield). Anal. Found: C, 56.64, H, 6.01; N, 4.00. Calc. for $C_{33}H_{43}AsFeN_2O_3Si_2$: C, 56.41; H, 6.17; N, 3.99%. IR (KBr): $\nu(NN)$ 2025 s; $\nu(CO)$ 1980 s, 1937 s; $\delta(SiMe_3)$ 1245 m; $\rho(SiMe_3)$ 846 $m\ cm^{-1}$. 1H -NMR: $\delta = 0.21$ (s, 9H, $OSiCH_3$), 0.39 (s, 9H, $CSiCH_3$), 1.42 (s, 15H, C_5CH_3), 6.93 (t, $^3J_{HH} = 7.5$ Hz, 2H, Ph-H), 7.07–7.18 (m, 4H, Ph-H), 7.46–7.49 (m, 4H, Ph-H). $^{13}C\{^1H\}$ -NMR: $\delta = -0.1$ (s, $CSiCH_3$), 1.0 (s, $OSiCH_3$), 9.1 (s, C_5CH_3), 20.8 (s, CN_2), 95.3 (s, C_5CH_3), 126.3 (s, Ph-C), 126.6 (s, Ph-C), 128.7 (s, CPh_2), 131.2 (s, Ph-C), 132.2 (s, Ph-C), 142.2 (s, Ph-C1), 144.0 (s, Ph-C1), 163.2 (s, As-C=C), 217.3 (s, $FeCO$), 217.4 (s, $FeCO$). ^{29}Si -NMR: $\delta = 1.0$ ($CSiMe_3$), 17.9 ($OSiMe_3$).

4.5. $[Cp^*(CO)_2FeSb\{\overline{NN=C(SiMe_3)C(CO_2Me)=C-(CO_2Me)}\}\{C(OSiMe_3)=CPh_2\}]$ (**9c**)

A sample of dimethyl acetylenedicarboxylate (0.13 g, 0.95 mmol) was added to the chilled solution ($0^\circ C$) of **4c** (0.71 g, 0.95 mmol) in 30 ml of *n*-pentane. The mixture was stirred at $0^\circ C$, then warmed up to ambient temperature and concentrated to ca. 10 ml. It was filtered, and the filtercake was dried in vacuo to afford product **9c** as an orange moisture- and air-sensitive solid (0.75 g, 88% yield). Anal. Found: C, 52.32; H, 5.67; N, 3.13. Calc. for $C_{39}H_{49}FeN_2O_7SbSi_2$: C, 52.54; H, 5.54; N, 3.14%. IR (KBr): $\nu(CO)$ 1996 s, 1942 s; $\nu(CO_{ester})$ 1709 s; $\delta(SiMe_3)$ 1246 m; $\rho(SiMe_3)$ 847 $m\ cm^{-1}$. 1H -NMR: $\delta = -0.14$ (s, 9H, $CSiCH_3$), 0.65 (s, 9H, $OSiCH_3$), 1.32 (s, 15H, C_5CH_3), 3.48 (s, 3H, CO_2CH_3), 3.77 (s, 3H, CO_2CH_3), 6.92–7.21 (m, 6H, Ph-H), 7.53 (d, $^3J_{HH} = 7.5$ Hz, 2H, Ph-H), 7.78 (d, $^3J_{HH} = 7.5$ Hz, 2H, Ph-H). $^{13}C\{^1H\}$ -NMR: $\delta = -0.7$ (s, $CSiCH_3$), 0.2 (s, $OSiCH_3$), 9.1 (s, C_5CH_3), 50.7 (s, CO_2CH_3), 52.1 (s, CO_2CH_3), 95.1 (s, C_5CH_3), 121.2 (s, Ar-C), 126.5 (s, Ar-C), 127.3 (s, CPh_2), 130.7 (s, Ar-C), 132.4 (s, Ar-C), 133.8 (s, Ar-C), 141.5 (s, Ar-C), 141.9 (s, Ar-C), 146.0 (s, Ar-C), 156.7 (s, Ar-C), 163.9 (s, Sb-C=C), 164.3 (s, CO_2CH_3), 164.4 (s, CO_2CH_3), 214.0 (s, $FeCO$), 214.9 (s, $FeCO$). ^{29}Si -NMR: $\delta = -7.6$ ($CSiMe_3$), 19.5 ($OSiMe_3$).

4.6. $[Cp^*(CO)_2FeSb\{\overline{NN=C(SiMe_3)C(CO_2Et)=C-(CO_2Et)}\}\{C(OSiMe_3)=CPh_2\}]$ (**9d**)

Analogously, 0.99 g (83% yield) of orange solid **9d** were synthesized from 0.97 g (1.3 mmol) of **4c** and 0.22

g (1.3 mmol) of diethyl acetylenedicarboxylate. Anal. Found: C, 53.32; H, 5.90; N, 3.05. Calc. for $C_{41}H_{53}FeN_2O_7SbSi_2$: C, 53.55; H, 5.81; N, 3.05%. IR (KBr): $\nu(\text{CO})$ 1995 s, 1943 s; $\nu(\text{CO}_{\text{ester}})$ 1702 s; $\delta(\text{SiMe}_3)$ 1249 m; $\rho(\text{SiMe}_3)$ 849 m cm^{-1} . $^1\text{H-NMR}$: $\delta = -0.12$ (s, 9H, CSiCH_3), 0.69 (s, 9H, OSiCH_3), 1.02 (t, $^3J_{\text{HH}} = 7.6$ Hz, 3H, CH_2CH_3), 1.23 (t, $^3J_{\text{HH}} = 7.6$ Hz, 3H, CH_2CH_3), 1.33 (s, 15H, C_5CH_3), 4.10 (q, $^3J_{\text{HH}} = 7.6$ Hz, 2H, CH_2CH_3), 4.42 (m, 2H, CH_2CH_3), 6.93 (t, $^3J_{\text{HH}} = 7.5$ Hz, 1H, Ph-H), 7.06–7.14 (m, 3H, Ph-H), 7.23 (t, $^3J_{\text{HH}} = 7.5$ Hz, 2H, Ph-H), 7.55 (d, $^3J_{\text{HH}} = 7.5$ Hz, 2H, Ph-H), 7.83 (d, $^3J_{\text{HH}} = 7.5$ Hz, 2H, Ph-H). $^{13}\text{C}\{^1\text{H}\}$ -NMR: $\delta = -0.4$ (s, CSiCH_3), 0.5 (s, OSiCH_3), 9.3 (s, C_5CH_3), 14.3 (s, CH_2CH_3), 60.1 (s, CH_2CH_3), 61.5 (s, CH_2CH_3), 95.2 (s, C_5CH_3), 121.6 (s, Ar-C), 126.7 (s, Ar-C), 127.5 (s, CPh_2), 127.9 (s, Ar-C), 131.0 (s, Ar-C), 132.7 (s, Ar-C), 134.1 (s, Ar-C), 141.8 (s, Ar-C), 142.2 (s, Ar-C), 146.5 (s, Ar-C), 156.7 (s, Ar-C), 164.26 (s, $\text{CO}_2\text{CH}_2\text{CH}_3$), 164.30 (s, $\text{CO}_2\text{CH}_2\text{CH}_3$), 164.4 (s, Sb-C=C), 214.3 (s, FeCO), 215.2 (s, FeCO). $^{29}\text{Si-NMR}$: $\delta = -7.6$ (CSiMe_3), 19.6 (OSiMe_3).

5. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 164513, 164151 and 164514 for **4b**, **4c** and **9d**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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