

Reactions of $K_2[Fe(CO)_3(PPh_3)]$: Reductive Sb–Sb Coupling with Ph_2SbCl To Form *trans*- $[Fe(CO)_3(PPh_3)(Sb_2Ph_4)]$ and Salt Metathesis with Me_3SbCl_2 To Yield *trans*- $[Fe(CO)_3(PPh_3)(SbMe_3)]$

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Dedicated to Professor Dr. Hubert Schmidbaur on the occasion of his 70th birthday

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In contrast to the ferrate $K_2[Fe(CO)_4]$, the phosphane-substituted ferrate $K_2[Fe(CO)_3(PPh_3)]$ (**1**) reacts with the stibane derivative Ph_2SbCl by metal-assisted reductive Sb–Sb coupling to give the distibane complex *trans*- $[Fe(CO)_3(PPh_3)(Sb_2Ph_4)]$ (**3**). The distibane ligand in **3** is terminally η^1 -coordinated *trans* to the phosphane ligand. However, the stiborane derivative Me_3SbCl_2 reacts with **1** in a metathetical substitui-

tion reaction to form the monostibane complex *trans*- $[Fe(CO)_3(PPh_3)(SbMe_3)]$ (**5**). Both compounds have been characterized by spectroscopic (IR, NMR, MS), analytical (C, H) and X-ray diffraction analyses.

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Introduction

Molecules containing transition metal–phosphorus frameworks are among the most frequently reported in coordination and cluster chemistry. The most common examples show terminal metal– PR_3 , $-PR_2$ - and $-PR$ - modular systems, as well as their metal-bridging analogs.^[1] Simple diphosphanes of the type $R_2X-X-PR_2$ ($X = CH_2$, NH , O) considerably increase the potential variety and applicability of these compounds. While the analogous arsane and diarsane homologues exist in great numbers with similar structural motifs, analogous examples of antimony and bismuth species are much less common.^[2,3] Weaker σ -donor and π -acceptor interactions in antimony and bismuth compounds may be a reason for this. Therefore, only monostibane and methyldiene-bridged distibane complexes ($X = CH_2$) obtained by substitution reactions, as in the case of phosphorus and arsenic compounds, have been structurally characterized. Mixed bispentelane complexes with Sb participation are not, to the best of our knowledge, known.

We report here the synthesis and structural characterization of the distibane ligand Sb_2Ph_4 bound to iron; it is produced by a metal-assisted reductive Sb–Sb coupling reaction in the presence of a coordinated phosphane ligand (PPh_3). Thus, we have successfully synthesized the first η^1 - (Sb_2Ph_4) -coordinated complex as well as a very rare ex-

ample of a mixed bispentelane complex. We also report the synthesis of a second mixed bispentelane complex by the metathetical reaction of $K_2[Fe(CO)_3(PPh_3)]$ with Me_3SbCl_2 .

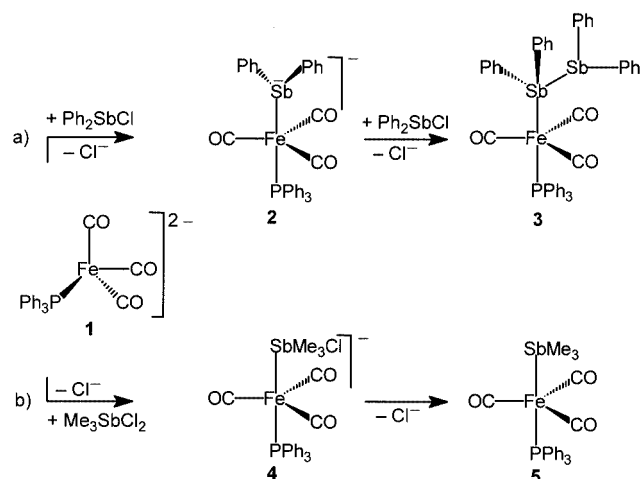
Results and Discussion

One synthetic route to pentelane complexes of iron(0) is the catalytic reaction of $Fe(CO)_5$ with the pentelanes ER_3 ($E = P, As, Sb$).^[4–6] A similar route is the reaction of $Na_2[Fe(CO)_4]$ with one equivalent of Ph_2ECl ($E = P, As$), which gives first the monosubstituted ferrate $Na[Fe(CO)_4(EPh_2)]$ and then, upon reaction with a second equivalent of Ph_2ECl , the neutral dipentelane complex $[Fe(CO)_4(E_2Ph_4)]$ by E–E coupling.^[7] Thus, mixed phosphanylarsane complexes can be obtained. Attempts to form distibane complexes of iron(0) have thus far been unsuccessful. Similarly, the reaction of the phosphane-substituted ferrate $K_2[Fe(CO)_3(PPh_3)]$ (**1**) with two equivalents of Ph_2SbCl proceeds with elimination of KCl to yield the first η^1 -coordinated tetraphenyldistibane ligand by ferrate-assisted reductive Sb–Sb coupling of two Ph_2SbCl molecules. The resulting complex, *trans*- $[Fe(CO)_3(PPh_3)(Sb_2Ph_4)]$ (**3**), was structurally characterized by X-ray analysis.

The first mononuclear distibane complexes of the type $[M(CO)_5(Sb_2R_4)]$ ($M = Cr, W$; $R = CH_3, C_2H_5, C_6H_5$) were synthesized by photochemically induced substitution of $M(CO)_6$ (in THF) with the intact distibanes, but were only spectroscopically characterized.^[8] The analogous diphosphane complexes, however, have already been synthesized and structurally characterized by Vahrenkamp et al.^[9,10]

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In our case, the distibane molecule is synthesized from monostibane derivatives bound to a metal by template-control and is incorporated as an η^1 -bound ligand *trans* to the PPh_3 ligand (see a in Scheme 1). Attempts to obtain mixed bispentelane complexes of the type $\text{R}_3\text{EFe}(\text{CO})_3\text{E}'\text{R}_3$ were previously unsuccessful because of symmetrization reactions.



Scheme 1. Synthesis of **3** and **5**

The reductive Sb–Sb coupling reaction of **1** is similar to the Wurtz reaction and proceeds by two steps: electrophilic attack on the iron(II-) center of **1** by the first stibane (Sb^{3+}), followed by elimination of KCl . The monoanionic stibane complex **2**, with the negative charge located mainly on antimony, may be formed as an intermediate. As a result, the electrophilic attack of the second stibane occurs at the coordinated antimony, and leads to the formation of a neutral tetraphenyldistibane complex, **3**, with one $\text{Fe}(0)$ and two Sb^{II} centers, and thus the formal redox reaction is completed.

The energy (1883 cm^{-1}) of the single $\nu(\text{CO})$ absorption in the IR spectrum of **3** (E' symmetry) is similar to the single $\nu(\text{CO})$ absorption of the symmetrical species *trans*- $[\text{Fe}(\text{CO})_3(\text{PPh}_3)_2]$ (1886 cm^{-1}).^[11] The signal in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **3** is found at $\delta = 86.4$ ppm. The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra show only the multiplets due to the phenyl protons ($\delta = 7.26\text{--}7.59$ ppm) and phenyl-C atoms ($\delta = 126\text{--}131$ ppm), in addition to one signal for the CO ligand ($\delta = 212$ ppm).

If the ferrate **1** is treated with an excess of the stiborane derivative Me_3SbCl_2 no coupling reaction occurs; instead, a simple salt-metathesis reaction results in the formation of the novel mixed-dipentelane complex *trans*- $[\text{Fe}(\text{CO})_3(\text{PPh}_3)(\text{SbMe}_3)]$ (**5**). As in the case of **3**, the formation of **5** can also occur via the intermediate **4**, which is formed by an electrophilic attack of Me_3SbCl^+ on the nucleophilic ferrate dianion (Scheme 1b).

The spectroscopic data of **5** (IR: $\nu(\text{CO}) = 1877\text{ cm}^{-1}$; $^{31}\text{P}\{^1\text{H}\}$ NMR: $\delta = 85.5$ ppm) are similar to those of **3**, except for the methyl-group signals in the NMR spectra (^1H NMR: $\delta = 1.31$ ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR: $\delta = 40.1$ ppm).

Comparison of **3** and **5** is best achieved by single-crystal X-ray diffraction analysis.^[12] Relevant bond lengths and angles are tabulated in the legends of the corresponding figures. As expected, the Fe center is trigonal-bipyramidally configured with the phosphane and distibane ligands in *trans*-axial positions. The Fe1-P1 and Fe1-Sb1 bond lengths are $2.188(2)$ and $2.457(1)$ Å, respectively, and the P1-Fe1-Sb1 bond angle of $177.99(6)^\circ$ indicates a nearly linear P1-Fe-Sb1 arrangement (Figure 1). The three CO ligands surround the central iron in a trigonal planar grouping with the sum of angles at $\text{Fe}(1)$ being exactly 360° . As Figure 2 shows, the Sb_2Ph_4 ligand exists in the gauche conformation, and differs by approximately 4° from the *trans* conformation. The Sb1-Sb2 bond length of 2.828 Å is slightly shorter than that of the free stibane Sb_2Ph_4 (2.844 Å).^[13] The Sb-C_{Ph} bond lengths around the two Sb centers are quite different. The bonds to Sb1 are $2.130(6)$ and $2.132(7)$ Å, whereas bonds to Sb2 are distinctly longer [$2.138(9)$ and $2.145(7)$ Å], although both pairs are shorter than those in free tetraphenyldistibane (2.16 and 2.18 Å). Both Sb centers show a strongly distorted tetrahedral configuration. The steric demand of the nonbonding Sb2 MO

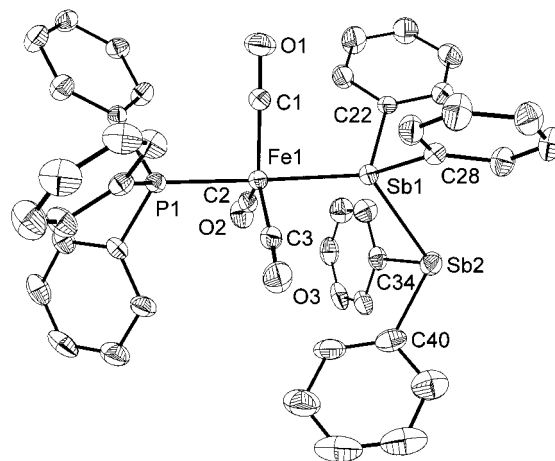


Figure 1. Molecular structure of **3** in the solid state; selected bond lengths (Å) and angles ($^\circ$): Fe1-P1 $2.188(2)$, Fe1-Sb1 $2.457(1)$, Sb1-Sb2 $2.828(7)$, Fe1-C1 $1.752(7)$, Fe1-C2 $1.758(7)$, Fe1-C3 $1.776(8)$, Sb1-C22 $2.130(6)$, Sb1-C28 $2.132(7)$, Sb2-C40 $2.138(9)$, Sb2-C34 $2.145(7)$; P1-Fe1-Sb1 $177.99(6)$, Fe1-Sb1-Sb2 $125.62(3)$, C1-Fe1-C2 $119.6(3)$, C1-Fe1-C3 $118.3(3)$, C2-Fe1-C3 $122.1(3)$, C22-Sb1-C28 $100.5(2)$, C22-Sb1-Sb2 $98.6(2)$, C22-Sb1-Fe1 $113.7(2)$, C28-Sb1-Fe1 $114.5(2)$, C28-Sb1-Sb2 $100.0(2)$, C40-Sb2-C34 $98.4(3)$, C40-Sb2-Sb1 $94.9(2)$, C34-Sb2-Sb1 $98.1(2)$

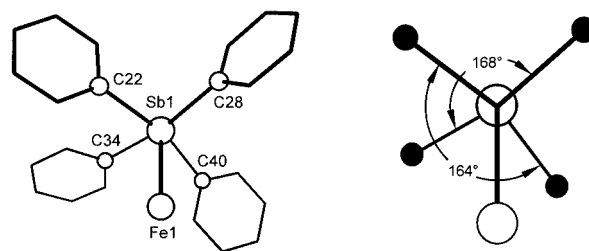


Figure 2. Conformation of the Sb_2Ph_4 ligand in **3** [Newman projection along the Sb1-Sb2 axis with dihedral angles ($^\circ$)]

leads to an 11–14° reduction of the bond angles compared to those of coordinated SbI. In the same fashion, the Fe(CO)₃(PPh₃) group bound to SbI forces a greater deformation from an ideal tetrahedral configuration about SbI, with the FeI–SbI–Sb2 angle of 126° differing most of all.

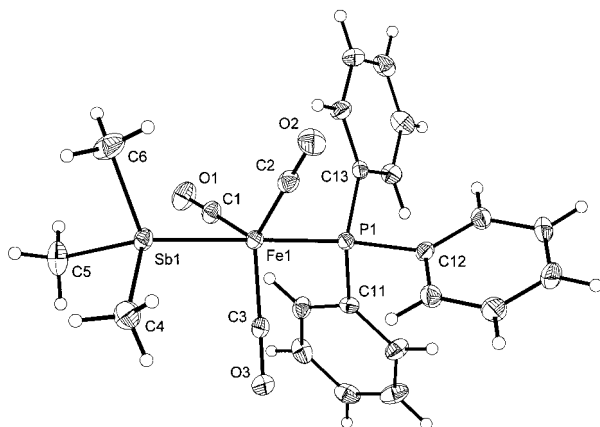


Figure 3. Molecular structure of **5** in the solid state; selected bond lengths (Å) and angles (°): FeI–P1 2.199(1), FeI–Sb1 2.463(6), FeI–C1 1.769(5), FeI–C2 1.778(5), FeI–C3 1.778(4), Sb1–C4 2.094(5), Sb1–C5 2.118(5), Sb1–C6 2.114(5), P1–C_{Ph} 1.835(4); P1–FeI–Sb1 177.56(4), C1–FeI–C2 121.8(2), C1–FeI–C3 119.5(2), C2–FeI–C3 118.4(2), C4–Sb1–FeI 116.62(15), C5–Sb1–FeI 117.54(15), C6–Sb1–FeI 118.46(16), C_{Ph}–P1–FeI ca. 115.7, C_{Ph}–FeI–C5 ca. 102.6

The molecular structure of **5** (Figure 3) is similar to that of **3**; the analogous bond lengths and angles at the central iron are practically identical. The Newman projection of **5** shows the almost perfectly staggered conformation of the Me, CO, and Ph substituents along the SbI–FeI–P1 axis (Figure 4).

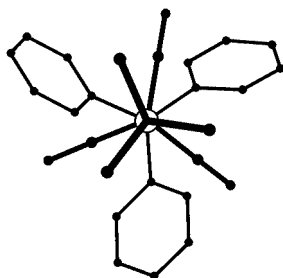


Figure 4. Newman projection of **5** along the SbI–FeI–P1 axis

Our new reductive Sb–Sb coupling reaction of two molecules of Ph₂SbCl to give the η¹-ligand Sb₂Ph₄ in **3** is explained by the presence of [Fe(CO)₃(PPh₃)]^{2–} (**1**) (as suitable reducing agent) and by the activating and at the same time stabilizing effect of the complex fragment Fe(CO)₃(PPh₃). The *trans*-directing influence of PPh₃ may also play a positive role in the formation of the mixed dipentelane complex **3**. An analogous effect is also found in the reaction of **1** with the stiborane Me₃SbCl₂ to give **5**. However, in the case of the nonsubstituted ferrate Na₂[Fe(CO)₄], the corresponding Sb–Sb coupling reaction

and distibane formation, as well as Fe–Sb bond formation, are not possible. When the monoanionic metalates [CpM(CO)_n][–] (M = Fe, *n* = 2; M = Mo, W, *n* = 3) are reacted with Me₂SbBr, for example, a simple salt-metathesis reaction to form the metallostibanes [{Cp(CO)_nM}SbMe₂] is observed.^[14] An Sb–Sb coupling reaction similar to the Wurtz reaction was recently reported in the reaction of Ph₂SbI with the metals Sm or Y in THF.^[15] Further investigations with respect to the general application of this simple and elegant synthesis using other substituted phosphanes (PR₃ where R ≠ Ph) or coupling different pentelanes [e.g. Sb–E (E = P, As)] are in progress.

Experimental Section

All operations were carried out under an Argon atmosphere with complete exclusion of oxygen and moisture (Schlenk techniques). Solvents were dried and then saturated with argon. The following instruments were used for the spectroscopic and analytical measurements: IR: Nicolet 520 FT-IR spectrometer. ³¹P NMR: Jeol 6SX

Table 1. X-ray structure analysis of **3** and **5**^[12]

	3	5
Empirical formula	C ₄₅ H ₃₅ FeO ₃ Sb ₂	C ₂₄ H ₂₄ FeO ₃ PSb
Molecular weight (g mol ^{–1})	1038.98	569.024
Crystal size (mm)	0.37 × 0.33 × 0.10	0.34 × 0.23 × 0.14
Crystal color, habit	yellow-brown	red-brown prism
Crystal system	monoclinic	orthorhombic
Space group	<i>P</i> 2 ₁ / <i>c</i> (No. 14)	Pbca
<i>a</i> (Å)	12.999(2)	10.897(1)
<i>b</i> (Å)	10.462(2)	16.6396(1)
<i>c</i> (Å)	32.805(4)	26.7645(2)
<i>a</i> (°)	90	90
<i>β</i> (°)	98.274(2)	90
<i>γ</i> (°)	90	90
Volume (Å ³)	4412.5(12)	4853.30(6)
<i>Z</i>	4	8
Density calcd. (g cm ^{–3})	1.564	1.558
Absorption coefficient (mm ^{–1})	1.736	1.798
<i>F</i> (000)	2056	
Index ranges	–14 ≤ <i>h</i> ≤ 0 –11 ≤ <i>k</i> ≤ 0 –37 ≤ <i>l</i> ≤ 37	–14 ≤ <i>h</i> ≤ 11 –21 ≤ <i>k</i> ≤ 21 –34 ≤ <i>l</i> ≤ 34
<i>θ</i> Range (°)	2.51–23.98	1.52–27.49
Reflections collected	7221	70393
Independent reflections	6885	5563
Observed reflections	5081	3959
Parameter/restraints	525/42	274/0
<i>R</i> ₁ / <i>wR</i> ₂ (all data)	0.0745/0.1077	0.0747/0.1418
<i>R</i> ₁ / <i>wR</i> ₂ (final)	0.0467/0.0928	0.0402/0.1004
GOOF	1.133	1.173
Min./max. ρ _c (e Å ^{–3})	0.7242/0.9995	–1.184/1.404
Temperature (K)	293(2)	200(2)
Diffractometer	ENRAF	Nonius
	Nonius CAD-4	Kappa CCD
Radiation	Mo- <i>K</i> _α , λ = 0.71073	Mo- <i>K</i> _α , λ = 0.71073
Scan type	ω-scan	area detection
Solution	SHELXS 86	SIR 97, direct methods
Refinement	SHELXL-93	SHELXL-97

270 (85% H_3PO_4 as standard). X-ray analysis: ENRAF-Nonius CAD 4-diffractometer and Nonius Kappa CCD-diffractometer. Elemental analysis: Elementar vario EL (W. C. Heraeus). Melting Point: Büchi-510 (m.p. were not corrected).

Synthesis of 3: $K_2[Fe(CO)_3(PPh_3)]$ (**1**; 124 mg, 0.259 mmol) and Ph_2SbCl (353 mg, 0.518 mmol) were dissolved in 10 mL of THF, upon which the solution immediately turned deep red. After stirring for 2 h and filtering, the solvent was distilled off in vacuo to yield a viscous brownish oil. Repeated recrystallization from CH_2Cl_2/n -hexane resulted in a microcrystalline solid, which was dried in vacuo. Yield: 154 mg (63%), orange brown crystals, m.p. 137 °C. IR (KBr): $\nu(CO) = 1883\text{ cm}^{-1}$. ^{13}C NMR ($[D_6]acetone$): $\delta = 126\text{--}131$ (Ph), 212 (CO) ppm. $^{31}P\{^1H\}$ NMR: $\delta = 86.4$ ppm. $C_{46}H_{37}FeO_3PSb_2$ (954.09): calcd. C 57.9, H 3.9; found C 57.9, H 3.8.

Synthesis of 5: $K_2[Fe(CO)_3(PPh_3)]$ (**1**; 275 mg, 0.573 mmol) was dissolved in 20 mL of THF containing Me_3SbCl_2 (136 mg, 0.573 mmol). The color of the solution changed to red, and a fine, light-colored precipitate of KCl formed. After stirring for 2 h and careful decantation, the solvent was distilled off in vacuo. The red-brown residue was recrystallized several times to give analytically pure **5**. Yield: 179 mg (55%), red-brown crystals, m.p. 121 °C. IR (KBr): $\nu(CO) = 1877\text{ cm}^{-1}$. 1H NMR ($[D_6]acetone$): $\delta = 1.31$ (s, 9 H, Me), 7.22–7.63 (m, 15 H, Ph) ppm. $^{13}C\{^1H\}$ NMR ($[D_6]acetone$): $\delta = 40.1$ (s, Me), 126–131 (m, Ph), 209 (s, CO) ppm. $^{31}P\{^1H\}$ NMR ($[D_6]acetone$): $\delta = 85.5$ ppm. $C_{24}H_{24}FeO_3PSb$ (567.99): calcd. C 50.7, H 4.3; found C 51.6, H 3.7.

[1] C. A. McAuliffe, W. Levason, *Phosphine, Arsine and Stibine Complexes of the Transition Elements*, Elsevier **1979**.

- [2] N. R. Champness, W. Levason, *Coord. Chem. Rev.* **1994**, *133*, 115–217.
[3] H. J. Breunig, I. Ghesner, *Adv. Organomet. Chem.* **2003**, *95*–131.
[4] M. O. Albers, E. Singleton, N. J. Coville, *Inorg. Synth.* **1990**, *28*, 168–173.
[5] M. O. Albers, N. J. Coville, T. V. Ashworth, E. Singleton, *J. Organomet. Chem.* **1981**, *217*, 385–390.
[6] M. O. Albers, N. J. Coville, E. Singleton, *J. Organomet. Chem.* **1982**, *232*, 261–266.
[7] J. P. Collmann, R. G. Komoto, W. O. Siegl, *J. Am. Chem. Soc.* **1973**, *95*, 2389–2390.
[8] H. J. Breunig, W. Fichtner, *Z. Anorg. Allg. Chem.* **1979**, *454*, 167–174.
[9] M. Brockhaus, F. Staudacher, H. Vahrenkamp, *Chem. Ber.* **1972**, *105*, 3716–3725.
[10] L. Staudacher, H. Vahrenkamp, *Chem. Ber.* **1976**, *109*, 218–228.
[11] A. F. Clifford, A. K. Mukherjee, *Inorg. Synth.* **1966**, *8*, 185–189.
[12] CCDC-246697 (for **3**) and -246325 (for **5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
[13] G. Becker, H. Freudenkamp, C. Witthauer, *Z. Anorg. Allg. Chem.* **1982**, *492*, 37–51.
[14] W. Malisch, P. Panster, *J. Organomet. Chem.* **1974**, *76*, C7–C10.
[15] E. A. Fedorova, O. A. Trokhaeva, G. S. Kalinina, M. W. Bochkarev, G. A. Razuvaev, *Metallorg. Khim.* **1988**, *1*, 397–399.
[16] Organikum, VEB Deutscher Verlag der Wissenschaften, Berlin, **1988**.
[17] J. E. Ellis, Y.-S. Chen, *Organometallics* **1989**, *8*, 1350–1361.
[18] M. Nunn, D. B. Sowerby, D. M. Wesolek, *J. Organomet. Chem.* **1983**, *251*, C45–C46.

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