

## Synthesis and reactivity of $\text{SbCl}_2$ -bridged manganese dimetal compounds

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### Abstract

A low temperature reaction of  $\text{NaMn}(\text{CO})_5$ , initially with  $\text{SbCl}_3$  and then with  $\text{Cp}'(\text{CO})_2\text{MnTHF}$ , yielded the metallastibanes:  $[(\text{CO})_5\text{Mn}(\mu\text{-SbCl}_2)\text{Mn}(\text{CO})_2\text{Cp}']$  (**1**) and  $[\{(\text{CO})_5\text{Mn}\}_2(\mu_3\text{-SbCl})\text{Mn}(\text{CO})_2\text{Cp}']$  (**2**). Similarly  $\text{NaCr}(\text{CO})_3\text{Cp}$  reacted with  $\text{SbCl}_3$  and  $\text{Cp}'(\text{CO})_2\text{MnTHF}$  to yield  $[\text{Cp}(\text{CO})_3\text{Cr}(\mu\text{-SbCl}_2)\text{Mn}(\text{CO})_2\text{Cp}']$  (**3**). Complexes **1** and **3** reacted with 1,2-dimercaptoethane in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO) to afford the bimetallic chelate compounds  $[(\text{CO})_5\text{Mn}(\mu\text{-SbS}(\text{CH}_2)_2\text{S})\text{Mn}(\text{CO})_2\text{Cp}']$  (**4**) and  $[\text{Cp}(\text{CO})_3\text{Cr}(\mu\text{-SbS}(\text{CH}_2)_2\text{S})\text{Mn}(\text{CO})_2\text{Cp}']$  (**5**), respectively. A convenient high yield synthesis of **4** was found to be the reaction of  $\text{NaMn}(\text{CO})_5$  with first  $\text{ClSbS}(\text{CH}_2)_2\text{S}$  and then  $\text{Cp}'(\text{CO})_2\text{MnTHF}$ . The crystal structures of **1** and **4** were determined by X-ray crystallography.

### Introduction

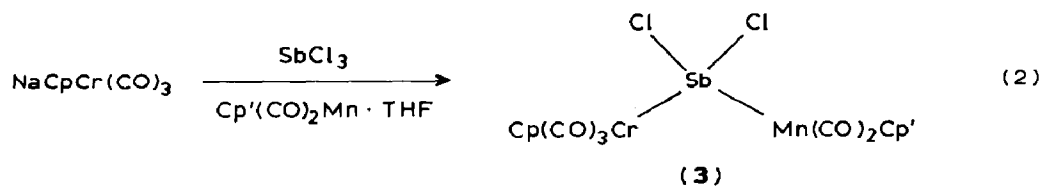
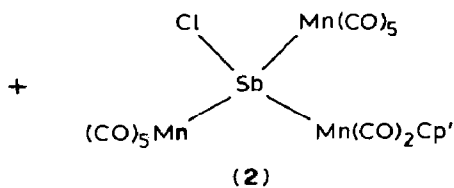
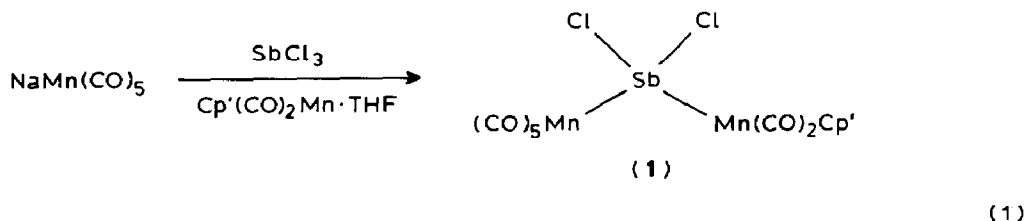
It has been shown, by the elegant work of Weiss that germanium is capable of entering the linearly coordinated bridge position in  $[\text{Cp}'(\text{CO})_2\text{Mn}]_2\text{Ge}$  ( $\text{Cp}' = \eta^5\text{-CH}_3\text{C}_5\text{H}_4$ ) [1]. This principle was later be expanded by Herrmann to include lead in the same bonding arrangement [2]. The isoelectronic principle indicates that in order to force a group 15 element like antimony into an analogous coordination environment, one would either have a positively charged species,  $[\text{L}_n\text{M}]_2\text{Sb}^+$  ( $\text{L}_n\text{M} = 16$ -electron fragment) or  $\text{L}_n\text{M}'\text{SbML}_n$  ( $\text{L}_n\text{M}' = 15$ -electron fragment). That this simple isoelectronic reasoning may, in fact be applied to unconventional bonding situations of antimony or tin, is demonstrated by the structural analogy between  $[(\text{CO})_5\text{W}]_3\text{Sn}$  ( $\text{W-W}$  bond closed  $\equiv 17$ -electron  $\text{W}$ ) [3] and  $[(\text{CO})_5\text{W}]_3\text{Sb}^-$  ( $\text{W-W}$  bond open  $\equiv 16$ -electron  $\text{W}$ ) [3], with both compounds containing trigonally planar coordinated main group centers. From the several attractive potential precursors of  $\text{L}_n\text{M}'\text{SbML}_n$  we chose to investigate the synthesis of  $\text{L}_n\text{M}''(\mu\text{-SbCl}_2)\text{Mn}(\text{CO})_2\text{Cp}'$  ( $\text{L}_n\text{M}'' = 17$ -electron fragment), which in principle, by reductive dehalogenation and decarbonylation of  $\text{L}_n\text{M}''$  such as  $\text{Mn}(\text{CO})_5$  or  $\text{Cp}(\text{CO})_3\text{M}$  ( $\text{M} = \text{Cr}$  or  $\text{Mo}$ ,  $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ) might yield the desired linear two-coordination for a bridging

antimony. While a number of  $\text{SbHal}_2$ -bridged dimetal compounds are known, most of the work in this field having been done by Malisch [4], no such compounds containing  $L_nM = \text{Cp}(\text{CO})_2\text{Mn}$  or its substituted derivatives were known; these fragments have shown an exceptional ability to stabilize unconventional coordination peripheries as amply demonstrated by the rich chemistry of  $[\text{Cp}(\text{CO})_2\text{Mn}]_2\text{XR}$  ( $X = \text{P, As, Sb, Bi}$ ;  $R = \text{univalent residue}$ ) [5].

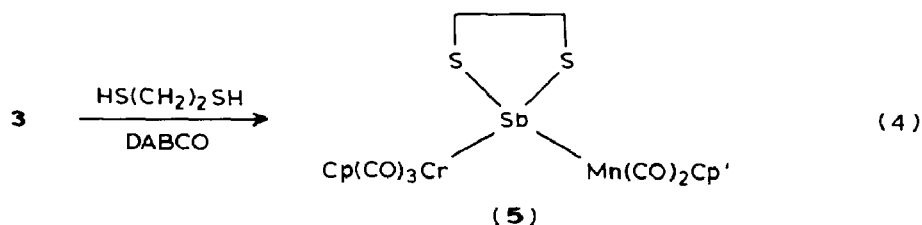
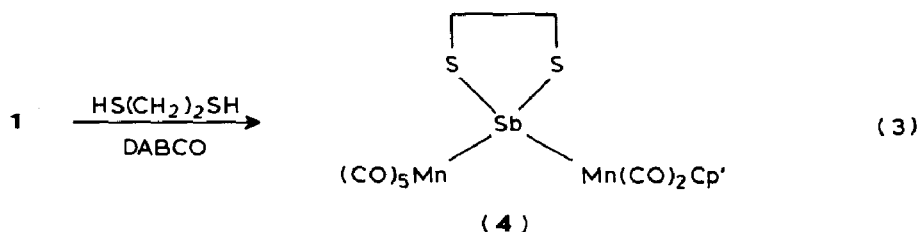
### Synthesis

In contrast to the existence of a number of stable dibromometallastibanes  $L_nM''\text{SbBr}_2$  [4], no dichloro analogues,  $L_nM''\text{SbCl}_2$ , have to the best of our knowledge been reported. Since in the syntheses of  $L_nM''\text{SbBr}_2$  a potential complication is the formation of dimetallastibanes  $[L_nM'']_2\text{SbBr}$  [4], we tried using the less reactive  $\text{SbCl}_2$  species instead of  $\text{SbBr}_2$  derivatives. At the same time we tried to stabilize the reactive  $L_nM''\text{SbCl}_2$  moiety by coordination to a  $\text{Cp}'(\text{CO})_2\text{Mn}$  fragment. Thus reaction of  $\text{NaMn}(\text{CO})_5$  with  $\text{SbCl}_3$  in the presence of  $\text{Cp}'(\text{CO})_2\text{MnTHF}$  [6] gave the desired  $\text{SbCl}_2$ -bridged compound **1**. As a side product the trinuclear compound **2** was formed (eq. 1). Both compounds are crystalline solids which are indefinitely stable at room temperature and which have been characterized by analytical and spectroscopic means, and in the case of **1**, by a single crystal X-ray crystallographic study (see below) [7\*].

The same procedure may be used with  $\text{NaCpCr}(\text{CO})_3$  as the starting material (eq. 2). The  $\text{SbCl}_2$ -bridged heterometallic compound **3** is obtained as a crystalline solid.

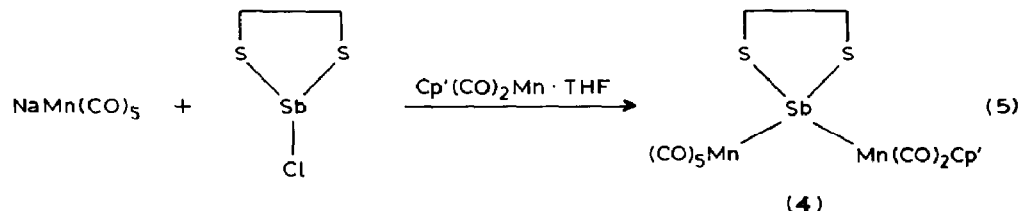


\* Reference number with asterisk indicates a note in the list of references.



Its stability in solution is markedly lower than that of **1** under similar conditions. It was, however, unequivocally characterized by its analytical and spectroscopic data.

Initial attempts to reductively eliminate chlorine from **1** or **3**, respectively, were unsuccessful, but we found that the chlorines are readily substituted by the chelating 1,2-dimercaptoethane (eq. 3 and 4). The substitution is a high yield process when 1,4-diazabicyclo[2.2.2]octane (DABCO) is present as the proton scavenger. A simpler route to compound **4** was found to be provided by the reaction of  $\text{ClSbS(CH}_2)_2\text{S}$  [8] with first  $\text{NaMn(CO)}_5$  and then  $\text{Cp}'(\text{CO})_2\text{Mn} \cdot \text{THF}$  (eq. 5) [6].



Compounds **4** and **5** are air stable crystalline solids, which have been characterized by analytical and spectroscopic means as well as in the case of **4** by an X-ray crystallographic structure determination [7\*].

#### *The solid state structures of compounds 1 and 4 [7\*]*

The structures are shown in Fig. 1. Selected bonding distances and angles are displayed in Table 1.

From an electron counting point of view, compounds **1** and **4** are isoelectronic with base adducts such as  $[\text{L}_n\text{M}]_2\text{Sb(R)} \leftarrow |\text{B}$  ( $|\text{B}$  = Lewis base) [9] and with the many well characterized phosphorus and arsenic homologues of such species [10,11]. This analogy is reflected in the large Mn–Sb–Mn angles of  $129.7^\circ$  in **1** and  $121.4^\circ$  in **4**; angles of this size are characteristic of the former compounds too [10]. In contrast to such “-inidene” derived species, **1** and **4** are definitely unsymmetrical. In each case the length of the Mn–Sb bond radiating from the 17-electron  $\text{Mn(CO)}_5$

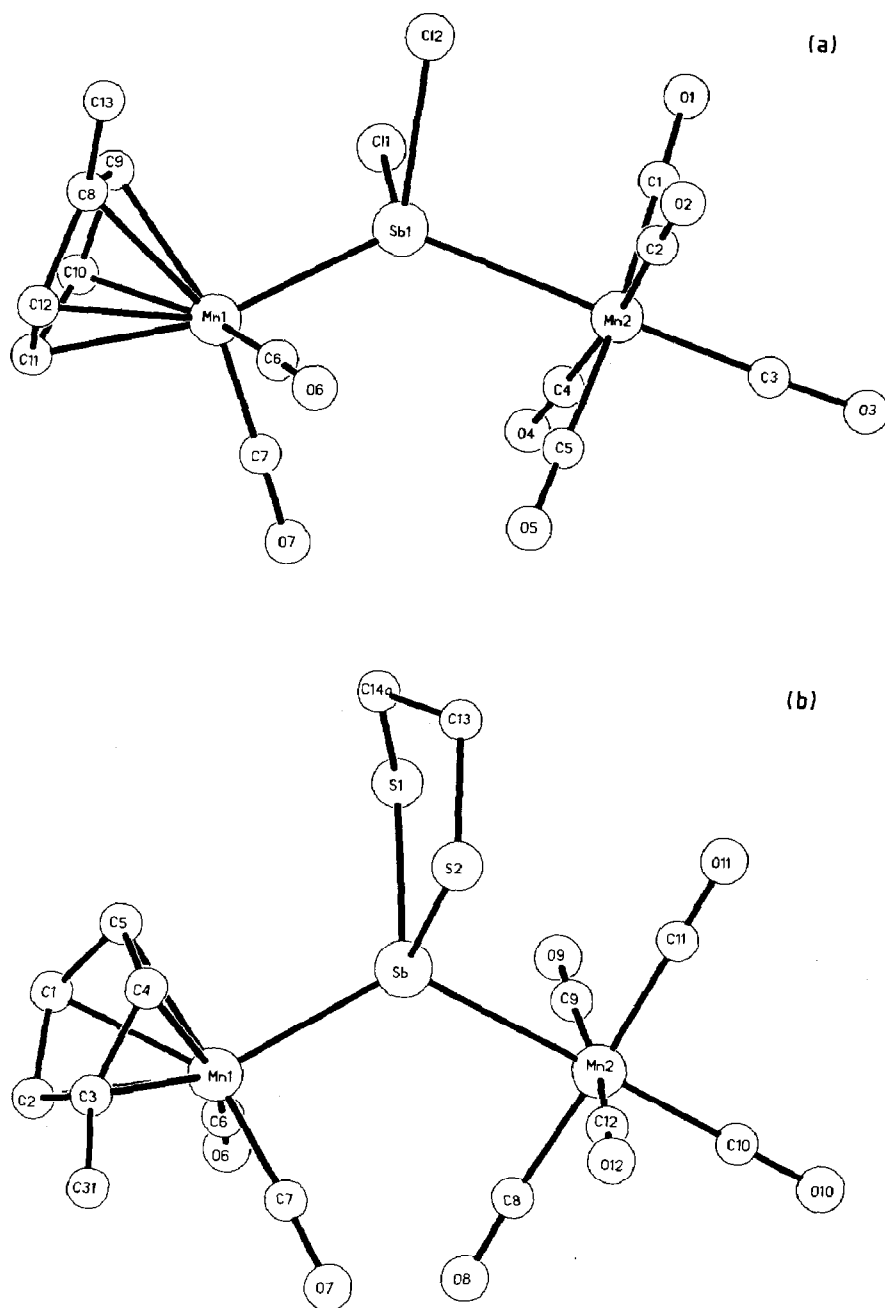


Fig. 1. The structures of **1** (a) and **4** (b).

fragment is some 20 pm longer than the bond between the 16-electron fragment,  $\text{Cp}'(\text{CO})_2\text{Mn}$ , and the bridging antimony ligand. While for formally similar bonding situations, such that in  $[(\text{CO})_5\text{Mn}(\mu\text{-As}(\text{CH}_3)_2)\text{Cr}(\text{CO})_5]$ , equal distances between 16- and 17-electron fragments and the bridging  $(\text{CH}_3)_2\text{As}$  moiety have been reported [12], there is a definite difference between what could be expected to be a covalent bond ( $\text{Sb-Mn}(\text{CO})_5$ ) and what might be termed a stibane-manganese

Table 1  
Selected bonding distances and angles for **1** and **4**

	<b>1</b>		<b>4</b>
<i>Bonding distances (pm)</i>			
Sb–Mn(1)	240.8(2)	Sb–Mn(1)	246.8(2)
Sb–Mn(2)	261.3(2)	Sb–Mn(2)	265.7(2)
Sb–Cl	238.7(3), 240.0(3)	Sb–S	244.9(3), 245.0(3)
Mn(1)–C(CO)	177.6(6), 178.8(5)	Mn(1)–C(CO)	175.5(6), 176.2(6)
Mn(2)–C(CO <sub>eq</sub> )	185.4(6)–186.5(6)	Mn(2)–C(CO <sub>eq</sub> )	184.9(6)–187.5(6)
Mn(2)–C(CO <sub>ax</sub> )	184.0(6)	Mn(2)–C(CO <sub>ax</sub> )	184.5(6)
<i>Bond angles (°)</i>			
Cl–Sb–Cl	92.0(1)	S–Sb–S	88.0(1)
Mn(1)–Sb–Mn(2)	129.7(1)	Mn(1)–Sb–Mn(2)	121.4(1)
<i>Torsion angles (°)</i>			
C(6)–Mn(1)–Sb–Mn(2)	56.0(1)	C(6)–Mn(1)–Sb–Mn(2)	55.1(1)
C(7)–Mn(1)–Sb–Mn(2)	37.2(1)	C(7)–Mn(1)–Sb–Mn(2)	37.5(1)

coordinative bond (Sb–Mn(1)). The observed, rotational orientation of the Cp'(CO)<sub>2</sub>Mn fragment relative to the MnSbMn plane, which is quite similar in both compounds **1** and **4** (see torsion angles, Table 1), might be taken to be a consequence of the orientation of the better Mn donor orbital in a way such as to maximize Mn(1)–stibane back bonding [13].

### Experimental

All reactions and manipulations were carried out under dinitrogen with dried and freshly distilled solvents. The silicagel (Merck 60, particle size 0.063–0.200 mm) used in the chromatographic separations was degassed under high vacuum and saturated with nitrogen before use.

IR-spectra: Perkin–Elmer 938G, m = medium, s = strong, w = weak. NMR-spectra: Bruker AC 200, S = singlet, M = multiplet. EI mass spectra: Varian Mat 312 (No EI mass spectra could be obtained for compounds **3** and **5** due to their decomposition under the measuring conditions employed.) X-Ray determination [7\*]: Measurement of intensity data: Syntex P3-diffractometer, Mo-K<sub>α</sub>, 71.069 pm, Graphite monochromator, ω-scan, Δω = 1° 2.8 ≤ ω ≤ 29.3°/min<sup>-1</sup>; 3° ≤ 2θ ≤ 52°. The structures were solved and refined using SHELXTL (G.M. Sheldrick, Göttingen, Revision 1984).

**1**: C<sub>13</sub>H<sub>7</sub>Cl<sub>2</sub>Mn<sub>2</sub>O<sub>7</sub>Sb *M* = 577.7; Space Group *P*2<sub>1</sub>/*c*; *a* 690.0(3), *b* 1327.8(4), *c* 2051.8(2) pm, β 97.7(2)°, *V* = 1863 × 10<sup>6</sup> pm<sup>3</sup>; *Z* = 4; *d*<sub>calc.</sub> 2.06 g cm<sup>-3</sup>; *T* 293 K; 2876 independent reflections (*I* ≥ 2σ); *R*<sub>1</sub> = 0.037, *R*<sub>2</sub> = 0.038.

**4**: C<sub>15</sub>H<sub>11</sub>Mn<sub>2</sub>O<sub>7</sub>S<sub>2</sub>Sb *M* = 599.0; Space Group *Pbca*; *a* 1188.1(2), *b* 2825.8(3), *c* 1202.2(2) pm, *V* = 4036 × 10<sup>6</sup> pm<sup>3</sup>; *Z* = 8; *d*<sub>calc.</sub> 1.97 g cm<sup>-3</sup>; *T* 293 K; 2658 independent reflections (*I* ≥ 2σ); *R*<sub>1</sub> = 0.034, *R*<sub>2</sub> = 0.035.

The atomic parameters are listed in Table 2.

### Reaction of NaMn(CO)<sub>5</sub> with first SbCl<sub>3</sub> and then Cp'(CO)<sub>2</sub>MnTHF

2.28 g (10.0 mmol) SbCl<sub>3</sub> was added to a cooled (–40 °C) solution of NaMn(CO)<sub>5</sub> [14] (2.60 g, 12 mmol) in 20 ml THF. After 3 h stirring at this temperature, the

Table 2

## Atomic coordinates for 1 and 4

ATOM	$x/a$	$y/b$	$z/c$
Sb(1)	0.27058(6)	0.23455(2)	0.14835(1)
Mn(1)	0.1599(1)	0.17208(6)	0.03958(3)
Mn(2)	0.3057(1)	0.14080(6)	0.26127(4)
Cl(1)	0.5881(3)	0.3080(1)	0.15398(8)
Cl(2)	0.1259(3)	0.3933(1)	0.17009(8)
O(1)	0.5163(7)	0.3246(3)	0.3185(2)
O(2)	-0.0719(7)	0.2278(3)	0.2899(2)
O(3)	0.3708(9)	0.0400(3)	0.3920(2)
O(4)	0.6709(6)	0.0560(3)	0.2193(2)
O(5)	0.0887(7)	-0.0336(3)	0.1940(2)
O(6)	-0.2133(7)	0.1021(3)	0.0758(2)
O(7)	0.3525(6)	-0.0219(3)	0.0726(2)
C(1)	0.4372(8)	0.2553(4)	0.2963(3)
C(2)	0.0707(9)	0.1957(4)	0.2787(3)
C(3)	0.3450(9)	0.0769(4)	0.3415(3)
C(4)	0.5342(8)	0.0888(4)	0.2364(3)
C(5)	0.1697(8)	0.0325(4)	0.2196(3)
C(6)	-0.0661(9)	0.1303(4)	0.0626(3)
C(7)	0.2782(8)	0.0542(4)	0.0599(2)
C(8)	0.0482(9)	0.2915(4)	-0.0256(3)
C(9)	0.2471(9)	0.3069(4)	-0.0036(3)
C(10)	0.350(1)	0.2251(5)	-0.0252(3)
C(11)	0.2155(9)	0.1605(5)	-0.0591(3)
C(12)	0.0339(9)	0.1987(5)	-0.0593(3)
C(13)	-0.117(1)	0.3616(6)	-0.0181(4)
Sb	0.28581(2)	0.11331(1)	0.04121(3)
Mn(1)	0.44718(6)	0.12589(3)	-0.08463(7)
Mn(2)	0.17689(5)	0.18569(3)	0.13241(7)
S(1)	0.1396(1)	0.05889(6)	-0.0240(2)
S(2)	0.3231(1)	0.05776(6)	0.1933(2)
C(1)	0.4831(5)	0.0789(2)	-0.2165(5)
C(2)	0.5800(5)	0.1068(2)	-0.1934(6)
C(3)	0.6162(4)	0.0982(2)	-0.0838(6)
C(31)	0.7189(4)	0.1183(2)	-0.0292(6)
C(4)	0.5415(4)	0.0650(2)	-0.0383(6)
C(5)	0.4600(5)	0.0525(2)	-0.1200(6)
C(6)	0.3675(4)	0.1628(2)	-0.1727(6)
O(6)	0.3181(3)	0.1883(2)	-0.2315(5)
C(7)	0.4963(4)	0.1740(2)	-0.0059(5)
O(7)	0.5340(3)	0.2062(2)	0.0436(4)
C(8)	0.2523(4)	0.2273(2)	0.0394(6)
O(8)	0.2961(3)	0.2550(2)	-0.0157(5)
C(9)	0.0668(4)	0.1771(2)	0.0225(6)
O(9)	-0.0002(4)	0.1717(2)	-0.0411(4)
C(10)	0.1064(4)	0.2355(2)	0.2029(5)
O(10)	0.0640(3)	0.2664(1)	0.2451(5)
C(11)	0.1042(4)	0.1415(2)	0.2204(5)
O(11)	0.0599(3)	0.1144(2)	0.2726(4)
C(12)	0.2946(4)	0.1859(2)	0.2331(6)
O(12)	0.3668(3)	0.1857(2)	0.2938(4)
C(13)	0.2199(5)	0.0128(2)	0.1642(7)
C(14A)	0.1891(9)	0.0056(4)	0.044(1)
C(14B)	0.142(1)	0.0168(6)	0.096(1)

orange solution was added to a pre-cooled ( $-20^{\circ}\text{C}$ ) solution of  $\text{Cp}'(\text{CO})_2\text{MnTHF}$  (prepared by UV-irradiation for 3 h of 3.05 g (14.0 mmol)  $\text{Cp}'(\text{CO})_3\text{Mn}$  in 150 ml THF [6]). After a further 1.5 h stirring at  $-25^{\circ}\text{C}$  the solvent was stripped off and the residue chromatographed ( $\text{SiO}_2$ ,  $-25^{\circ}\text{C}$ ). With pentane/toluene (4/1 to 1/3) a red zone (**1**) was eluted, followed by a green zone (**2**), which yielded after removal of solvent and recrystallization (n-pentane/ $\text{CH}_2\text{Cl}_2$ ,  $-30^{\circ}\text{C}$ ), dark-red crystals of **1** and dark-green crystals of **2**, respectively.

$[(\text{CO})_5\text{Mn}(\mu\text{-SbCl}_2)\text{Mn}(\text{CO})_2\text{Cp}']$  (**1**). (0.76 g, 13%), m.p.  $94\text{--}95^{\circ}\text{C}$  (dec.). Found: C, 27.06, H 1.26.  $\text{C}_{13}\text{H}_7\text{Cl}_2\text{Mn}_2\text{O}_7\text{Sb}$  (577.73) calc.: C, 27.02, H, 1.22%. IR (n-pentane): 2121m, 2043s, 2030m, 1947m  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR  $\delta(\text{CDCl}_3)$ : 1.96 (S, 3H), 4.5–4.7 (M, 4H). MS ( $m/z$  (fragment, ( $I_r$ )): 576 ( $M^+$ , 8), 541 ( $M^+ - \text{Cl}$ , 7), 520 ( $M^+ - 2\text{CO}$ , 10), 485 ( $M^+ - 2\text{CO} - \text{Cl}$ , 8), 429 ( $M^+ - 4\text{CO} - \text{Cl}$ , 65), 380 ( $M^+ - 7\text{CO}$ , 15), 366 ( $M^+ - 5\text{CO} - 2\text{Cl}$ , 7), 311 ( $\text{Cp}'(\text{CO})_2\text{MnSb}^+$ , 43), 213 ( $\text{Cp}'_2\text{Mn}^+$ , 7), 176 ( $\text{MnSb}^+$ , 18), 134 ( $\text{Cp}'\text{Mn}^+$ , 100), 79 ( $\text{Cp}'^+$ , 76), 55 ( $\text{Mn}^+$ , 100).

$[(\text{CO})_5\text{Mn}]_2(\mu_3\text{-SbCl})\text{Mn}(\text{CO})_2\text{Cp}'$ ] (**2**). (0.14 g, 2%), m.p.  $154\text{--}156^{\circ}\text{C}$  (dec.). Found: C, 29.30, H, 1.04.  $\text{C}_{18}\text{H}_7\text{ClMn}_3\text{O}_{12}\text{Sb}$  (737.27) calc.: C, 29.32, H, 0.96%. IR ( $\text{CH}_2\text{Cl}_2$ ): 2115w, 2092m, 2028s, 2001m, 1915w, 1861w  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR  $\delta(\text{CDCl}_3)$ : 1.91 (S, 3H), 4.5–4.7 (M, 4H). MS ( $m/z$  (fragment, ( $I_r$ )): 736 ( $M^+$ , 3) 680 ( $M^+ - 2\text{CO}$ , 3), 540 ( $M^+ - 7\text{CO}$ , 3), 511 ( $\text{Mn}_2(\text{CO})_{10}\text{Sb}^+$ , 6), 483 ( $\text{Mn}_2(\text{CO})_9\text{Sb}^+$ , 7), 455 ( $\text{Mn}_2(\text{CO})_8\text{Sb}^+$ , 5), 427 ( $\text{Mn}_2(\text{CO})_7\text{Sb}^+$ , 3), 399 ( $\text{Mn}_2(\text{CO})_6\text{Sb}^+$ , 12), 371 ( $\text{Mn}_2(\text{CO})_5\text{Sb}^+$ , 2), 343 ( $\text{Mn}_2(\text{CO})_4\text{Sb}^+$ , 3), 311 ( $\text{Cp}'(\text{CO})_2\text{MnSb}^+$ , 4), 213 ( $\text{Cp}'_2\text{Mn}^+$ , 9), 176 ( $\text{MnSb}^+$ , 2), 134 ( $\text{Cp}'\text{Mn}^+$ , 23), 79 ( $\text{Cp}'^+$ , 26), 55 ( $\text{Mn}^+$ , 100).

#### Synthesis of $[\text{Cp}(\text{CO})_3\text{Cr}(\mu\text{-SbCl}_2)\text{Mn}(\text{CO})_2\text{Cp}']$ (**3**)

Using 2.27 g (10.0 mmol)  $\text{SbCl}_3$  and 2.24 g (10.0 mmol)  $\text{NaCr}(\text{CO})_3\text{Cp}$  [15] and the procedure described above, **3** was eluted as a red zone by column chromatography ( $\text{SiO}_2$ ,  $-30^{\circ}\text{C}$ , n-pentane/ $\text{CH}_2\text{Cl}_2$  (4/1)). Recrystallization from n-pentane/ $\text{CH}_2\text{Cl}_2$  ( $-30^{\circ}\text{C}$ ) yielded **3** as dark-red needles.

$[\text{Cp}(\text{CO})_3\text{Cr}(\mu\text{-SbCl}_2)\text{Mn}(\text{CO})_2\text{Cp}']$  (**3**). (0.70 g, 12%), m.p.  $116\text{--}117^{\circ}\text{C}$  (dec.). Found: C, 33.03, H 2.13.  $\text{C}_{16}\text{H}_{12}\text{Cl}_2\text{CrMnSbO}_5$  (583.86) calc.: C, 32.92, H, 2.07%. IR ( $\text{CH}_2\text{Cl}_2$ ): 2026m, 1955s, 1885m  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR  $\delta(\text{CDCl}_3)$ : 1.94 (S, 3H), 4.5–4.7 (M, 4H), 5.25 (S, 5H).

#### Synthesis of $[(\text{CO})_5\text{Mn}(\mu\text{-SbS}(\text{CH}_2)_2\text{S})\text{Mn}(\text{CO})_2\text{Cp}']$ (**4**)

**Method A:** The reaction of  $[(\text{CO})_5\text{Mn}(\mu\text{-SbCl}_2)\text{Mn}(\text{CO})_2\text{Cp}']$  (**1**) with 1,2-dimercaptoethane. To a solution of 0.26 g (0.44 mmol) of **1** in 10 ml  $\text{CH}_2\text{Cl}_2$ , was added a solution of 0.12 g (1.30 mmol) 1,2-dimercaptoethane and 0.29 g (2.60 mmol) DABCO in 10 ml  $\text{CH}_2\text{Cl}_2$ . After 2 h stirring at  $25^{\circ}\text{C}$  the solvent was removed under high vacuum. n-Pentane (5 ml) and  $\text{CH}_2\text{Cl}_2$  (5 ml) were added to the orange residue upon which a colourless precipitate formed. The precipitate was filtered off, leaving an orange solution. Removal of solvent and recrystallization of the residual from pentane/ $\text{CH}_2\text{Cl}_2$  ( $-30^{\circ}\text{C}$ ) gave 0.22 g (83%) dark-orange needles of **4**.

**Method B:** The reaction of  $\text{NaMn}(\text{CO})_5$  with first  $\text{ClSbS}(\text{CH}_2)_2\text{S}$  and then  $[\text{Cp}'(\text{CO})_2\text{MnTHF}]$ . When 2.49 g (10.0 mmol)  $\text{ClSbS}(\text{CH}_2)_2\text{S}$  [8] and 2.17 g (10.0 mmol)  $\text{NaMn}(\text{CO})_5$  [14] were used in the procedure as described above for the synthesis of **1** and **3**, **4** was eluted as a wide dark-red band from a silicagel column (n-pentane/ $\text{CH}_2\text{Cl}_2$  (2/1);  $-30^{\circ}\text{C}$ ). **4** was obtained as dark-red crystals (2.82 g, 47%) after recrystallization from pentane/ $\text{CH}_2\text{Cl}_2$  at  $-30^{\circ}\text{C}$ .

$[(\text{CO})_5\text{Mn}(\mu\text{-}\overline{\text{SbS}(\text{CH}_2)_2\text{S}})\text{Mn}(\text{CO})_2\text{Cp}']$  (**4**). M.p. 122–124°C (dec.). Found: C, 30.06, H, 1.87.  $\text{C}_{15}\text{H}_{11}\text{Mn}_2\text{O}_7\text{S}_2\text{Sb}$  (599.00) calc.: C, 30.08, H, 1.85%. IR ( $\text{CH}_2\text{Cl}_2$ ): 2108m, 2023s, 1924m, 1867m  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR  $\delta((\text{CD}_3)_2\text{CO})$ : 1.91 (S, 3H), 3.41 (S, 4H), 4.4–4.6 (M, 4H);  $^{13}\text{C}$  NMR  $\delta((\text{CD}_3)_2\text{CO})$ : 99.1 (S, 1C), 82.2 (S, 2C), 81.8 (S, 2C), 42.9 (S, 2C), 14.0 (S, 1C). MS ( $m/z$  (fragment, ( $I_r$ )): 598 ( $M^+$ , 5), 542 ( $M^+ - 2\text{CO}$ , 2), 486 ( $M^+ - 4\text{CO}$ , 10), 458 ( $M^+ - 5\text{CO}$ , 2), 430 ( $M^+ - 6\text{CO}$ , 10), 402 ( $M^+ - 7\text{CO}$ , 71), 374 ( $M^+ - 7\text{CO} - \text{C}_2\text{H}_4$ , 96), 347 ( $\text{Cp}'(\text{CO})\text{MnSbS}_2^+$ , 16), 319 ( $\text{Cp}'\text{MnSbS}_2^+$ , 21), 268 ( $\text{Mn}(\text{CO})\text{SbS}_2^+$ , 5), 240 ( $\text{MnSbS}_2^+$ , 33), 134 ( $\text{Cp}'\text{Mn}^+$ , 24), 79 ( $\text{Cp}'^+$ , 54), 55 ( $\text{Mn}^+$ , 100).

#### Synthesis of $[\text{Cp}(\text{CO})_3\text{Cr}(\mu\text{-}\overline{\text{SbS}(\text{CH}_2)_2\text{S}})\text{Mn}(\text{CO})_2\text{Cp}']$ (**5**)

To a solution of 0.58 g (1.0 mmol) of **3** in 20 ml  $\text{CH}_2\text{Cl}_2$  was added a solution of 0.48 g, (3.9 mmol) 1,2-dimercaptoethane and 0.87 g (7.8 mmol) DABCO in 20 ml  $\text{CH}_2\text{Cl}_2$ . After 2 h stirring at 20°C and removal of solvent, 10 ml n-pentane and 10 ml of  $\text{CH}_2\text{Cl}_2$  were added to the residue. The colourless precipitate which formed was filtered off leaving an orange solution. Removal of the solvent and recrystallization of the residue (n-pentane/ $\text{CH}_2\text{Cl}_2$  (–30°C) gave red-brown crystals of **5**.

$[\text{Cp}(\text{CO})_3\text{Cr}(\mu\text{-}\overline{\text{SbS}(\text{CH}_2)_2\text{S}})\text{Mn}(\text{CO})_2\text{Cp}']$  (**5**): (0.53 g, 87%) m.p. 108–110°C. Found: C, 34.71, H, 2.74.  $\text{C}_{18}\text{H}_{16}\text{CrMnO}_5\text{S}_2\text{Sb}$  (605.13) calc.: C, 35.73, H, 2.66%. IR ( $\text{CH}_2\text{Cl}_2$ ): 2006m, 1933s, 1865m  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR  $\delta(\text{CDCl}_3)$ : 1.90 (S, 3H), 3.4 (M, 4H), 4.3–4.5 (M, 4H) 5.07 (S, 5H).

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