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Preliminary communication

The first examples of insertion of $SnCl_2$ into the Mn–Cl and Re–Cl bonds of octahedral complexes: X-ray structure of $[Mn(CO)_3(SnCl_3)(S_2CPCy_3)] \cdot CH_2Cl_2$

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Abstract

Compounds *fac*-$[M(CO)_3(S_2CPR_3)Cl]$ (M = Mn or Re; R = cyclohexyl or isopropyl) react with $SnCl_2$ in tetrahydrofuran (THF) within 30 min to give trichlorostannyl complexes *fac*-$[M(CO)_3(S_2CPR_3)(SnCl_3)]$, these being the first examples of a direct insertion of $SnCl_2$ into Mn–Cl or Re–Cl bonds of octahedral carbonyl complexes. The structure of the trichlorostannyl derivative of manganese (R = cyclohexyl) has been determined by X-ray diffraction. Several experimental facts suggest that the facile insertion of $SnCl_2$ in the starting *fac*-$[M(CO)_3(S_2CPR_3)Cl]$ complexes should be attributed to the presence of the S_2CPR_3 ligands.

The insertion of $SnCl_2$ into a transition metal–halogen bond is a well known reaction which has been extensively used to prepare M–$SnCl_3$ complexes of Groups 8–10 [1]. However, as far as we know, there is no report of such insertions in the otherwise well studied octahedral Mn^I and Re^I halogeno-carbonyl compounds. The only related report [2] refers to the insertion of $Sn(NR_2)_2$ (R = $SiMe_3$) into the Mn–Br bond of $[Mn(CO)_5Br]$. This is somewhat surprising, since carbonyl complexes of Mn and Re with a direct M–SnR_3 bond are among the first and better known examples of transition metal-tin heterodinuclear compounds [3–6]. Moreover, there are only a few examples of complexes $[L_5M(SnCl_3)]$, which were prepared by protolysis (with HCl) or halogenation (with Cl_2, or CCl_4) of the tin–carbon bonds of derivatives $[L_5M(SnR_3)]$ [1,3], but tin(II) halides have been reported to insert into the metal–metal bond of $[M_2(CO)_8(PPh_3)_2]$ (M = Mn or Re) [7]. We wish to report here a facile preparation of some new complexes of

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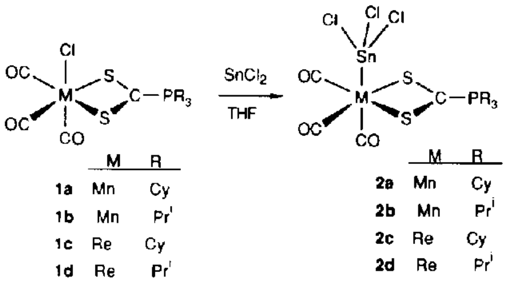

	M	R
1a	Mn	Cy
1b	Mn	Pr^i
1c	Re	Cy
1d	Re	Pr^i

	M	R
2a	Mn	Cy
2b	Mn	Pr^i
2c	Re	Cy
2d	Re	Pr^i

Scheme 1

formula *fac*-[$M(CO)_3(S_2CPR_3)(SnCl_3)$] by insertion of $SnCl_2$ into Mn–Cl and Re–Cl bonds.

A family of new chloro-derivatives *fac*-[$Mn(CO)_3(S_2CPR_3)(Cl)$] (**1a–d**, see Scheme 1), were prepared by thermal reaction of [$M(CO)_5Cl$] with S_2CPR_3, in a manner analogous to that described for the bromo-derivative *fac*-[$Mn(CO)_3(S_2CPCy_3)Br$] [8].

Compounds **1a–d** react with an excess of $SnCl_2$ in tetrahydrofuran (THF) solution at room temperature (approx. 30 min) to give virtually quantitative yields of the insertion products *fac*-[$M(CO)_3(S_2CPR_3)(SnCl_3)$] (**2a–d** in Scheme 1), which were isolated as purple-red crystalline solids, and characterized spectroscopically. An X-ray determination on a single-crystal of the derivative **2a**, confirmed the structure proposed in Scheme 1 (Fig. 1). The Mn atom lies in an octahedral environment, in which the main distortion from the ideal geometry is the small S(1)–Sn–S(2) angle of 72.9(1)°, this being a common feature in complexes with S_2CPR_3 chelate ligands, such as *fac*-[$Mn(CO)_3(S_2CPCy_3)_2$]ClO_4 [8] and *cis*-[$Mn(CO)_2(PEt_3)_2(S_2CPEt_3)$]$ClO_4$ [9]. The coordination around Sn is tetrahedral, the distances Sn–Mn [2.547(1) Å] and Sn–Cl [2.356(2), 2.369(3), and 2.371(2)], and the interbond angles being close to those found in [$Mn(CO)_5(SnCl_3)$] [10].

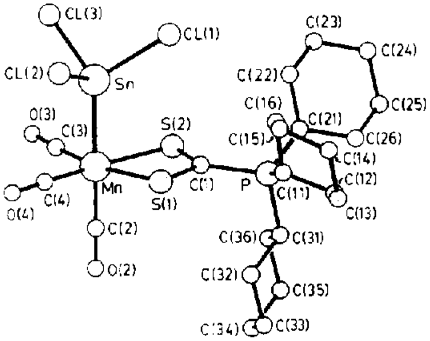

Fig. 1. Perspective view of the molecule of **2a**, showing the atom numbering. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Mn–Sn 2.547(1); Mn–S(1) 2.362(2); Mn–S(2) 2.348(3); Mn–C(2) 1.79(1); Mn–C(3) 1.794(9); Mn–C(4) 1.79(1); Sn–Cl(1) 2.356(2); Sn–Cl(2) 2.369(3); Sn–Cl(3) 2.371(2); C(1)–S(1) 1.676(8); C(1)–S(2) 1.663(7); C(1)–P 1.817(8); S(1)–Mn–Sn 84.6(1); S(2)–Mn–Sn 89.0(1); S(2)–Mn–S(1) 72.9(1); C(2)–Mn–Sn 175.8(3); C(3)–Mn–Sn 91.6(3); C(4)–Mn–Sn 87.6(3); C(3)–Mn–S(1) 168.6(3); C(4)–Mn–S(2) 170.1(3); angles C–Mn–C range from 89.4(5) to 93.1(4).

The facile insertion of $SnCl_2$ into the M–Cl bonds of **1a–d** contrasts sharply with the inertness of the metal–halogen bond of other substituted halidocarbonyl complexes of manganese and rhenium. Thus *fac*-[Mn(CO)$_3$(dppe)Cl] was stirred with an excess of $SnCl_2$ in THF for 48 h, without any reaction.

We have already reported [11] that the halide in *fac*-[Mn(CO)$_3$(S$_2$CPCy$_3$)Br] is very easily displaced by neutral ligands at room temperature, even in the absence of halide abstractors, suggesting a labilization of the M–X bond promoted by the S_2CPR_3 ligand. This does not occur in other complexes *fac*-[M(CO)$_3$(chelate)X] (M = Mn or Re; chel = diphosphines, phen, bipy, or diimines) and may help to rationalize the facile insertion of $SnCl_2$ into the M–Cl bonds of complexes **1a–b**.

Work is in progress to explore the insertion of Sn^{II} halides into Mn–X and Re–X bonds of other families of complexes.

Selected spectroscopic data

IR, ν(CO) (CH_2Cl_2 solutions) **1a**: 2024s, 1938s(br). **1b**: 2025s, 1942s, 1918m. **1c**: 2023s, 1924m, 1899m. **1d**: 2023s, 1925m, 1901m. **2a**: 2028s, 1955(sh), 1946s. **2b**: 2029s, 1955(sh), 1948s. **2c**: 2036s, 1943m. **2d**: 2037s, 1945m cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$ solutions, 121.5 MHz, δ, to high frequencies from external 85% H_3PO_4) **1a**: 21.83 (s). **1b**: 30.87 (s). **1c**: 35.69 (s). **1d**: 45.84 (s). **2a**: 25.11 (s, J(PSn) = 159 Hz). **2b**: 37.94 (s, J(PSn) = 160 Hz). **2c**: 38.51 (s, J(PSn) = 104 Hz). **2d**: 49.56 (s, J(PSn) = 105 Hz) ppm.

Crystal and refinement data for compound 1a

$C_{22}H_{33}Cl_3MnO_3PS_2Sn \cdot CH_2Cl_2$, M = 805.51, monoclinic, space group $P2_1/n$, $a = 9.981(2)$, $b = 18.256(2)$, $c = 19.195(4)$ Å, $\beta = 104.76(2)°$, $V = 3382(1)$ Å^3, $Z = 4$, $D_c = 1.58$ g cm^{-3}, $F(000)$ 1616, λ (Mo-K_α) 0.71073 Å, $\mu = 16.87$ cm^{-1}, 293 K. Dark red prismatic crystal (0.3 × 0.26 × 0.23 mm^3) grown by slow diffusion of Et_2O into a concentrated solution of the compound in CH_2Cl_2. Intensities were collected on an Enraf–Nonius CAD4 diffractometer, using the ω–2θ scan technique; 4225 reflections were measured in the range $0 \leq \theta \leq 25°$, 2484 with $I \geq 3\sigma(I)$ were used in the refinement. Sn and Mn atoms were located from a Patterson synthesis, and the remaining non-hydrogen atoms from DIRDIF [12]. An absorption correction was applied with DIFABS [13]. Full-matrix least-squares refinement was made with SHELX76 [14]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were geometrically positioned, and were given an overall isotropic temperature factor which was refined. Final $R = 0.039$ ($R_w = 0.041$). Total number of parameters was 326.

A complete list of atomic coordinates and bond lengths and angles has been deposited at the Cambridge Crystallographic Data Centre.

Acknowledgement

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