

## Synthesis and Reaction of $[\text{MnRe}(\text{CO})_6(\mu\text{-SH})(\mu\text{-SC}(\text{H})\text{PPr}^i_3)(\text{PPh}_3)]$

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**Abstract:** The synthesis, the crystal structure and the reaction of the hetero-binuclear complex  $[\text{MnRe}(\text{CO})_6(\mu\text{-SH})(\mu\text{-SC}(\text{H})\text{PPr}^i_3)(\text{PPh}_3)]$  are reported. The results of single crystal X-ray structure analysis showed that the fragments  $\text{Mn}(\text{CO})_3$  and  $\text{Re}(\text{CO})_3$  were bridged by SH and  $\text{SC}(\text{H})\text{PPr}^i_3$ . The title complexes can react with  $\text{Bu}^n\text{Li}$  and  $\text{RX}$  forming complexes  $\text{MnRe}(\text{CO})_6(\mu\text{-SR})(\mu\text{-SC}(\text{H})\text{PPr}^i_3)(\text{PPh}_3)$  ( $\text{R} = \text{Me}, \text{CH}_2\text{CH}=\text{CH}_2, \text{SnBu}_3^n$ ).

**Keywords:** Hetero-binuclear complexes, synthesis, reaction, crystal structure.

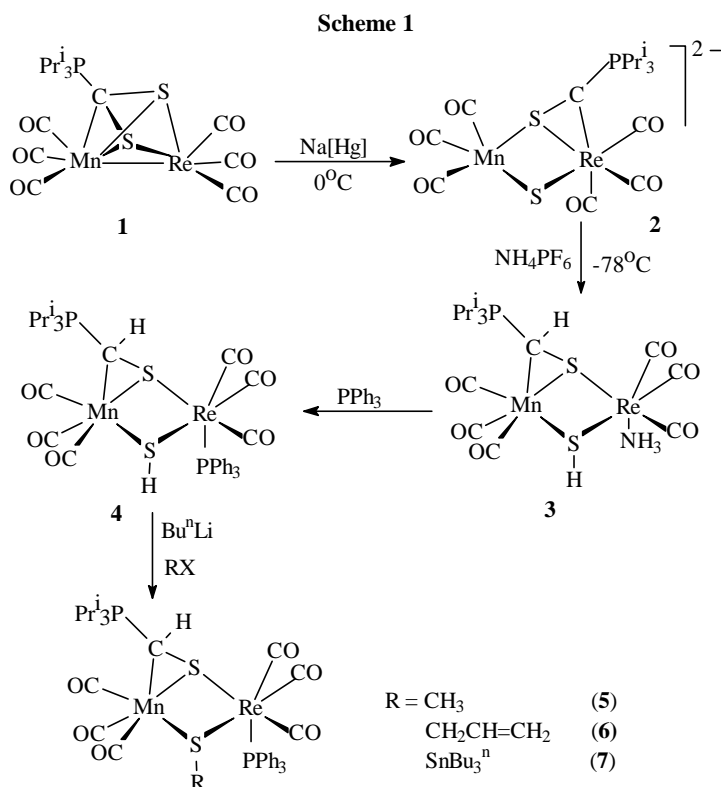
In recent years the chemistry of mono- or hetero-binuclear complexes containing metal-S(C) bonding modes is a very active field of research. Many useful applications of this kind of complexes have been exploited, such as industrial catalytic hydrodesulfurization (HDS)<sup>1,2</sup> and transition metals mediated organic synthesis<sup>3-5</sup>. In this paper we report that the reduction and subsequent protonation of hetero-binuclear complex  $[\text{MnRe}(\text{CO})_6(\mu\text{-S}_2\text{CPr}^i_3)]$  occur with cleavage of metal-metal bond and one S-C bond of the ligand  $\text{S}_2\text{CPr}^i_3$ . The two resulting fragments of the ligand: SH and  $\text{SC}(\text{H})\text{PPr}^i_3$  bridge between the metal groups. In addition, the reactions with  $\text{Bu}^n\text{Li}$  and  $\text{RX}$  ( $\text{R} = \text{Me}, \text{CH}_2\text{CH}=\text{CH}_2, \text{SnBu}_3^n$ ) of the title complex are studied (see **Scheme 1**).

### Experimental

All reactions were carried out in dry solvent under nitrogen atmosphere. The starting complex **1**  $[\text{MnRe}(\text{CO})_6(\mu\text{-S}_2\text{CPr}^i_3)]^6$  (0.12 g, 0.18 mmol) was dissolved in THF (20 mL) at 0°C. Freshly prepared sodium amalgam (1% w/w, 10 g, excess) was added, and the mixture was stirred for half an hour to prepare the dianion  $\text{Na}_2[\text{MnRe}(\text{CO})_6(\mu\text{-S}_2\text{CPr}^i_3)]$ . The solution of the dianion was transferred through a cannula into a Schlenk flask containing  $\text{NH}_4\text{PF}_6$  (0.059 g, 0.36 mmol) at -78°C. Subsequently, the mixture was warmed to 35-40°C for 20 min. to obtain complex **3**. The solvent was evaporated *in vacuo*. And the residue was dissolved in  $\text{CH}_2\text{Cl}_2$  (20 mL). To the above solution  $\text{PPh}_3$  (0.18 g, 0.68 mmol) was added. The mixture was stirred for another 30 min. After the solvent was evaporated *in vacuo* the residue was extracted with  $\text{CH}_2\text{Cl}_2$ /petroleum ether (1/1 v/v) and the collected extracts were filtered through a column of alumina (activity

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degree III). Slow concentration *in vacuo* afforded the title complex **4** as yellow microcrystalline solid. Block-shaped single crystals suitable for X-ray diffraction were recrystallized from  $\text{CH}_2\text{Cl}_2$ /petroleum ether ( $V/V = 1:5$ ) at  $-20^\circ\text{C}$ .



To the solution of **4** in THF (20 mL)  $\text{Bu}^n\text{Li}$  (0.15 mL, 2.5 mol/L, excess) was added at  $-78^\circ\text{C}$ . The color of the solution changed from yellow to red. Then the corresponding  $\text{RX}$  (excess) was added. Following this, the reaction mixture was allowed to warm slowly to room temperature. After the solvent was evaporated *in vacuo* the residue was treated as compound **4** to obtain compounds **5-7**. The corresponding yield and the elemental analysis data of complexes **4-7** were listed in **Table 1**.

**Table 1** The yield and the elemental analysis data of complexes **4-7**

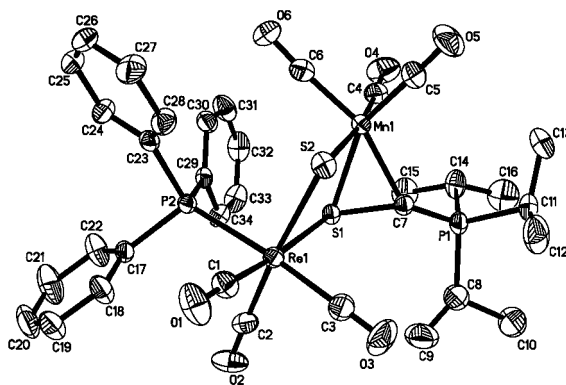
Entry	Yield (%)	Elemental Analysis		
		C (calcd.)	H (calcd.)	Formula
<b>4</b>	51.5	44.90 (44.93)	4.12 (4.07)	$\text{C}_{34}\text{H}_{37}\text{MnO}_6\text{P}_2\text{ReS}_2$
<b>5</b>	27.0	45.57(45.59)	4.36(4.37)	$\text{C}_{35}\text{H}_{39}\text{MnO}_6\text{P}_2\text{ReS}_2$
<b>6</b>	21.1	46.60(46.79)	4.49(4.47)	$\text{C}_{37}\text{H}_{41}\text{MnO}_6\text{P}_2\text{ReS}_2$
<b>7</b>	25.9	46.05(46.07)	5.35(5.39)	$\text{C}_{46}\text{H}_{63}\text{MnO}_6\text{P}_2\text{ReS}_2\text{Sn}$

## Results and Discussion

The molecular structure of the title complex is showed in **Figure 1**. The single crystal structure was determined on a BRUCKER SMART 1000 diffract-meter ( $T = 293\text{K}$ ) with graphite monochromated  $\text{MoK}\alpha$  ( $\lambda = 0.71073\text{\AA}$ ). The important crystal data were as follows:  $\text{C}_{34}\text{H}_{37}\text{MnO}_6\text{P}_2\text{ReS}_2$ , monoclinic, space group  $P_2(1)/n$ ,  $a = 10.355(3)\text{\AA}$ ,  $b = 12.766(7)\text{\AA}$ ,  $c = 15.844(5)\text{\AA}$ ,  $\beta = 92.969^\circ$ ,  $\alpha = \gamma = 90^\circ$ ,  $V = 3723.4(19)\text{\AA}^3$ ,  $Z = 4$ ,  $D_c = 1.621\text{ Mg/m}^3$ ,  $\mu = 3.826\text{ mm}^{-1}$ ,  $F(000) = 1804$ ,  $R1 = 0.0260$ ,  $wR2 = 0.0542$ .

The fragments  $\text{Mn}(\text{CO})_3$  and  $\text{Re}(\text{CO})_3$  of the title molecule **4** are held together by  $\text{SC}(\text{H})\text{PPr}^i_3$  and  $\text{SH}$  bridges. The intermetallic distance in complex **4** ( $3.724\text{\AA}$ ) is too long to permit any significant interaction between Mn and Re atoms ( $\text{Mn-Re } 2.830\text{\AA}$ , in the starting complex **1**). The group  $\text{SC}(\text{H})\text{PPr}^i_3$  coordinates to Mn through S and C atoms [ $\text{Mn}(1)\text{-C}(7) 2.111(5)\text{\AA}$ ;  $\text{Mn}(1)\text{-S}(1) 2.362(15)\text{\AA}$ ] and to Re through S atom [ $\text{Re}(1)\text{-S}(1) 2.518(3)\text{\AA}$ ]. The distances between metals and SH are  $2.547\text{\AA}$  [ $\text{Re}(1)\text{-S}(2)$ ] and  $2.454(14)\text{\AA}$  [ $\text{Mn}(1)\text{-S}(2)$ ], respectively. The entering ligand  $\text{PPh}_3$  is now bonded to rhenium instead of manganese [ $\text{Re}(1)\text{-P}(2) 2.5028(14)\text{\AA}$ ]. The  $\text{PPh}_3$  and  $\text{Pr}_3^i\text{P}$  are on the both sides of the plane consisting of Mn, Re and S(1) or S(2). The geometries around both Mn(1) and Re(1) can be described as distorted octahedral, the axial bond angles are  $171.99(17)^\circ$  [ $\text{C}(4)\text{-Mn}(1)\text{-S}(2)$ ] and  $175.66(17)^\circ$  [ $\text{C}(3)\text{-Re}(1)\text{-P}(2)$ ], respectively.

**Figure 1** Molecular structure of the title complex



The title complex can react with a base such as  $\text{Bu}^n\text{Li}$  (excess) to obtain the anion  $[\text{MnRe}(\text{CO})_6(\mu\text{-S})(\mu\text{-SC}(\text{H})\text{PPr}^i_3)(\text{PPh}_3)]\text{Li}^+$ . That means the proton on bridged SH is somewhat acidic. This anion cannot be separated but can be followed by IR under the nitrogen atmosphere.

Then the anion can easily react with different alkyl halides or trialkyltin halides. Their analytical and spectroscopic data are consistent with the structures proposed in **Scheme 1**, the entering R group being attached to the bridging sulfur atom not bonded to the metals. The neutral alkylation or metalation products (complexes **5-7**) are stable in solid state, however they decompose slowly in solution.

**Acknowledgment**

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**References and Note**

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