

# Carbon–Sulfur Bond Cleavage of S<sub>2</sub>CPR<sub>3</sub> Ligands in Dinuclear Complexes Promoted by Reduction and Protonation

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Complexes [Mn<sub>2</sub>(CO)<sub>6</sub>(μ-S<sub>2</sub>CPR<sub>3</sub>)] (R = Cy (**1a**), Pr<sup>i</sup> (**1b**)) are reduced with Na[Hg] in THF to afford the anions [Mn<sub>2</sub>(CO)<sub>6</sub>(μ-S<sub>2</sub>CPR<sub>3</sub>)]<sup>2-</sup> (**2a,b**), which give neutral unstable [Mn<sub>2</sub>(CO)<sub>6</sub>(μ-SH){μ-SC(H)PR<sub>3</sub>}(NH<sub>3</sub>)] (**3a,b**) upon protonation with excess NH<sub>4</sub>PF<sub>6</sub>. The NH<sub>3</sub> ligand of **3a,b** is readily replaced by PET<sub>3</sub> to obtain [Mn<sub>2</sub>(CO)<sub>6</sub>(μ-SH){μ-SC(H)PR<sub>3</sub>}(PET<sub>3</sub>)] (**5a,b**) as stable crystalline solids, which have been isolated and characterized. The same reduction/protonation sequence when applied to the dirhenium analogue [Re<sub>2</sub>(CO)<sub>6</sub>(μ-S<sub>2</sub>CPCy<sub>3</sub>)] (**1c**) affords stable crystalline [Re<sub>2</sub>(CO)<sub>6</sub>(μ-SH){μ-SC(H)PCy<sub>3</sub>}(NH<sub>3</sub>)] (**6**). An X-ray determination revealed that **6** contains one bridging SH<sup>-</sup> and the novel ligand Cy<sub>3</sub>PC(H)S<sup>-</sup> which is bonded as μ<sub>2</sub>-η<sup>1</sup>(S);η<sup>2</sup>(C,S), donating 5e to the metals. Both bridging ligands are produced from the cleavage of one C–S bond of the starting S<sub>2</sub>CPR<sub>3</sub> during the reduction/protonation process, which can be regarded globally as hydrogenolysis of the C–S bond. Additionally, the Re–Re bond is also cleaved during the process. As their dimanganese analogues, **6** undergo easy substitution of NH<sub>3</sub> by PET<sub>3</sub> to give [Re<sub>2</sub>(CO)<sub>6</sub>(μ-SH){μ-SC(H)PCy<sub>3</sub>}(PET<sub>3</sub>)] (**7**). Comparison of the spectroscopic data indicate that both series of compounds are isostructural, with the only difference being the higher stability of the dirhenium complexes when compared to those of dimanganese.

## Introduction

The cleavage of carbon–sulfur bonds are of primary importance in the process of hydrodesulfurization of crude oils (HDS).<sup>1</sup> It is well-known that, in this process, compounds containing carbon–sulfur multiple bonds, such as thiophene and its derivatives, are more difficult to desulfurate than compounds which contain C–S with a bond of order 1, such as thiols or thioethers. In practice, the HDS process requires the use of heterogeneous catalysts which contain molybdenum and other transition-metal oxides and sulfides. This has stimulated many studies of the coordination of thiophenes to transition metals, both on surfaces<sup>2a–c</sup> and in molecular

complexes,<sup>2c,d</sup> and the cleavage of C–S bonds of thiophene has been attained within the coordination sphere of the metal.<sup>3</sup>

We have been interested in recent years in the chemistry of mono- and dinuclear carbonyl complexes containing S<sub>2</sub>CPR<sub>3</sub> ligands. These compounds display a wide range of reactions depending on the bonding mode of the ligands. Thus, mononuclear complexes containing the ligands as a η<sup>2</sup>(S,S') chelate<sup>4</sup> undergo hydride addition to the central carbon;<sup>5</sup> while those in which the ligands are bonded as η<sup>3</sup>(S,C,S') pseudoallyl

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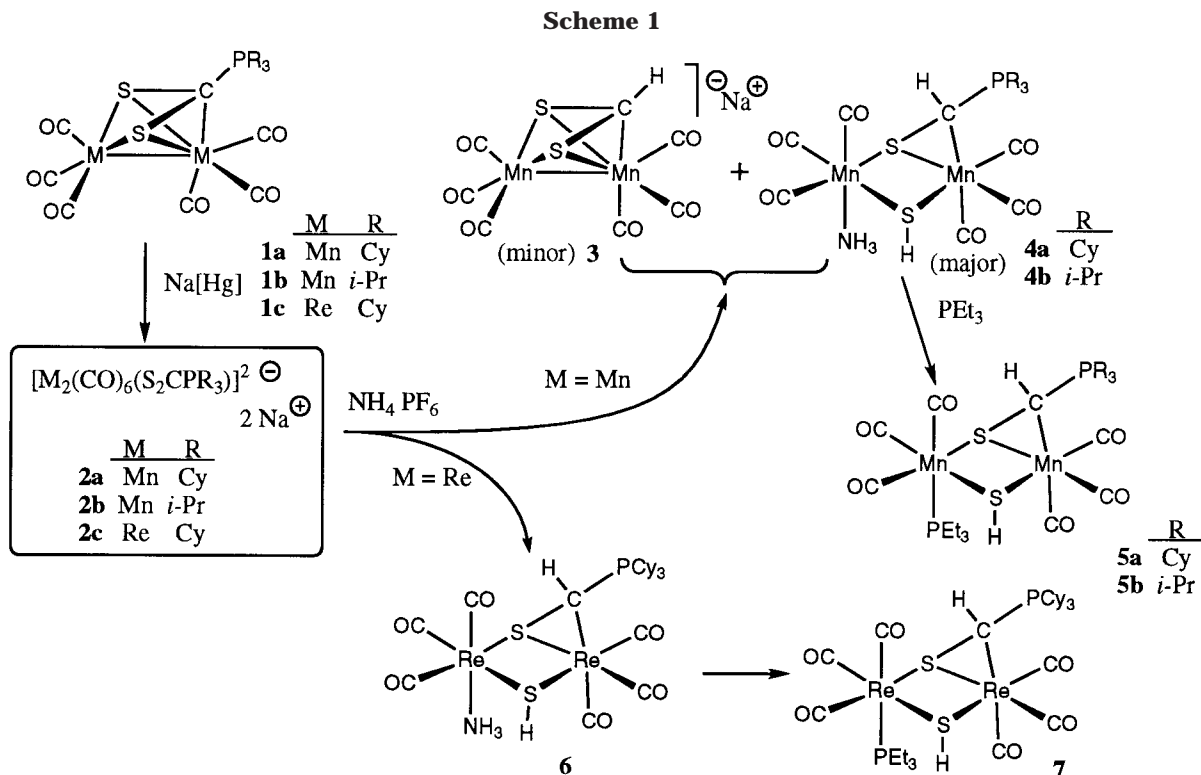
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are able to add electrophiles to one of the sulfur atoms.<sup>6</sup> In binuclear complexes containing  $\eta^2(S,S); \eta^3(S,C,S)$  and halogen bridges,<sup>7</sup> it is possible to create a metal–metal bond by reduction with sodium amalgam, affording anions capable of undergoing addition of electrophiles to the metals.<sup>8</sup> Finally, dinuclear complexes containing  $\eta^2(S,S); \eta^3(S,C,S)$  bridges spanning a direct metal-to-metal bond<sup>9</sup> undergo hydride addition on the M–M bond to afford hydrido-bridged carbonylmetalate anions.<sup>10</sup> Subsequent addition of alkyl halides leads to neutral complexes containing trialkylphosphoniodithioesters, while the reaction with CS<sub>2</sub> produces anionic complexes containing trialkylphosphonioethene-trithiolate bridges formed through desulfurization and C–C coupling.<sup>11</sup>

As an extension of these studies, we have found that the reduction of S<sub>2</sub>CPR<sub>3</sub> complexes containing metal–metal bonds, followed by protonation, affords stable neutral species containing new ligands produced through cleavage of one C–S bond, thus splitting the starting S<sub>2</sub>CPR<sub>3</sub> ligand into two parts which remain both as bridging ligands in the final complex: one hydrogeno-

sulfido SH<sup>−</sup> and one *trialkylphosphoniothiolate*ylide R<sub>3</sub>PC(H)S<sup>−</sup> attached as  $\eta^2(C,S)$ . Thus, the two-electron reduction, followed by addition of two protons, can be viewed globally as a formal hydrogenolysis of the C–S bond.

## Results and Discussion

When [Mn<sub>2</sub>(CO)<sub>6</sub>( $\mu$ -S<sub>2</sub>CPR<sub>3</sub>)] (**1a,b** in Scheme 1) was treated with excess 1% sodium amalgam in THF at 0 °C, the IR spectra of the solutions, in the  $\nu(\text{CO})$  region, showed the quick disappearance of the bands of the starting compounds while a new set of bands, shifted to lower frequencies, developed over a period of 15 min. The low position of the new bands suggests the formation of anionic species **2a,b** (see Scheme 1).

Unfortunately, all attempts to isolate and characterize them as Na<sup>+</sup> or NET<sub>4</sub><sup>+</sup> salts led to extensive decomposition. It was not possible, therefore, to propose a reasonable structure for these anions on the sole basis of the IR spectra in solution. Aiming to obtain neutral, isolable species, we attempted the protonation of the anions under several conditions. When freshly prepared solutions of the anions of **2a,b** were transferred over solid NH<sub>4</sub>PF<sub>6</sub> at low temperature (−78 °C), an instantaneous reaction was detected by IR monitoring to afford a mixture of compounds. The minor compound was readily identified by spectroscopic methods to be the dithioformate complex [Mn<sub>2</sub>(CO)<sub>6</sub>( $\mu$ -S<sub>2</sub>CH)]<sup>−</sup> (**3**), which had been previously isolated and structurally characterized by our group.<sup>10</sup> The major compounds, **4a,b** in Scheme 1, have been formulated as [Mn<sub>2</sub>(CO)<sub>6</sub>( $\mu$ -SH){ $\mu$ -SC(H)PR<sub>3</sub>}(NH<sub>3</sub>)] by their IR spectra in solution, which correspond to that of the dirhenium analogue **6**, which will be described below. Unfortunately, the dimanganese complexes **4a,b** decompose quickly in solution and did not resist the necessary workup to

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**Table 1. Crystal Data and Refinement Details for  $[\text{Re}_2(\text{CO})_6(\mu\text{-SH})\{\mu\text{-SC(H)PCy}_3\}(\text{NH}_3)]\cdot\text{THF}$  (**6**)**

formula	$\text{C}_{29}\text{H}_{46}\text{NO}_7\text{PRe}_2\text{S}_2$
fw	988.16
cryst syst	monoclinic
space group	$P2_1/c$
<i>a</i> , Å	10.111(2)
<i>b</i> , Å	22.531(4)
<i>c</i> , Å	15.896(4)
$\beta$ , deg	102.65(3)
<i>V</i> , Å <sup>3</sup>	3533(1)
<i>Z</i>	4
<i>T</i> , K	293(2)
$\rho_{\text{calc}}$ , g cm <sup>-3</sup>	1.86
<i>F</i> (000)	1920
$\lambda$ (Mo K $\alpha$ ), Å	0.710 73
cryst size, mm; color	0.35 × 0.15 × 0.15, pale yellow
$\mu$ , cm <sup>-1</sup>	7.051
method of collection	$\omega/2\theta$ scan
scan range, deg	0 ≤ $\theta$ ≤ 25
no. of reflns measd	6562
no. of reflns obsd, $I \geq 2\sigma(I)$	4064
no. of params	393
goodness of fit	0.977
residuals <i>R</i> (observed)	0.036
w <i>R</i> 2 (all)	0.090

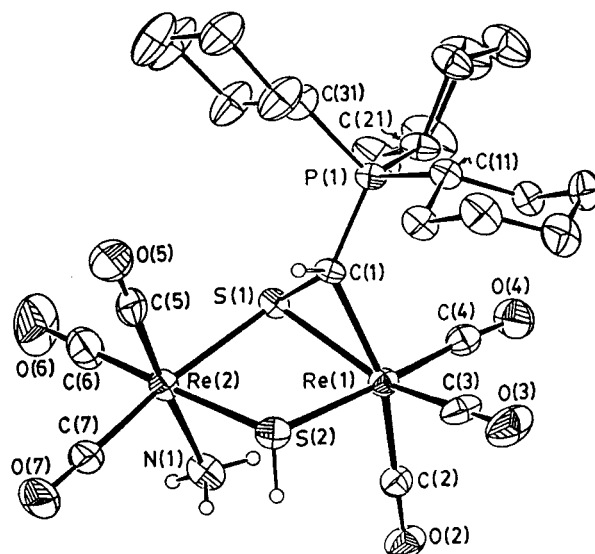
isolate them. After extensive decomposition, only minor amounts (5–10%) of the starting **1a,b** complexes were recovered. Nevertheless, the solutions of complexes **4a,b** can be used to obtain stable derivatives by replacing  $\text{NH}_3$  with phosphines. Thus, treatment of solutions of **4a,b** with 1 mol equiv of  $\text{PET}_3$  affords derivatives  $[\text{Mn}_2(\text{CO})_6(\mu\text{-SH})\{\mu\text{-SC(H)PR}_3\}(\text{PET}_3)]$  (**5a,b**) in good yield. The structures depicted for **5a,b** in Scheme 1 are supported by the comparison of their analytical and spectroscopic data (see Experimental Section) with those obtained for the dirhenium derivatives described below.

In contrast with the instability of dimanganese complexes **4a,b**, the reduction of the recently prepared  $[\text{Re}_2(\text{CO})_6(\mu\text{-S}_2\text{CPCy}_3)]$  (**1c**)<sup>12</sup> with sodium amalgam, followed by protonation with excess  $\text{NH}_4\text{PF}_6$ , cleanly affords a new complex **6**, which could be isolated and characterized by analytical and spectroscopic methods. Additionally, the structure of **6** was determined by X-ray crystallography. As with the dimanganese complexes **4a,b**, the  $\text{NH}_3$  ligand of **6** can be easily replaced by  $\text{PET}_3$  to give  $[\text{Re}_2(\text{CO})_6(\mu\text{-SH})\{\text{SC(H)PCy}_3\}(\text{PET}_3)]$  (**7**). Analytical and spectroscopic data indicate that **7** has essentially the same structure as **6** and support the structures proposed for the dimanganese derivatives with  $\text{NH}_3$  (**4a,b**) and  $\text{PET}_3$  (**5a,b**).

Relevant crystal data and refinement details for the structure of **6** are in Table 1, and selected bond distances and angles are listed in Table 2.

As can be seen in Figure 1, the molecule of **6** consists of two  $\text{Re}(\text{CO})_3$  fragments which are held together by two bridges: one of them is the well-known hydrogenosulfido  $\text{HS}^-$  and the other is the novel ligand *tricyclohexylphosphonothiolateylide*  $\text{Cy}_3\text{PC(H)S}^-$ , which is bonded to one rhenium through the sulfur atom [ $\text{S}(1)\text{-Re}(2) = 2.504(2)$  Å] and to the other rhenium both through the sulfur [ $\text{S}(1)\text{-Re}(1) = 2.496(2)$  Å] and through the carbon [ $\text{C}(1)\text{-Re}(1) = 2.194(8)$  Å].

There is only one precedent for this ligand, bonded in a  $\eta^2(\text{C},\text{S})$  fashion in the mononuclear complex  $[\text{3-}\{\eta^2\text{-}$

**Figure 1.** Perspective view (EUCLID Package)<sup>17</sup> of the molecule of  $[\text{Re}_2(\text{CO})_6(\mu\text{-SH})\{\mu\text{-SC(H)PCy}_3\}(\text{NH}_3)]$  (**6**), showing the atom-numbering scheme.**Table 2. Selected Bond Lengths (Å) and Angles (deg) for  $[\text{Re}_2(\text{CO})_6(\mu\text{-SH})\{\mu\text{-SC(H)PCy}_3\}(\text{NH}_3)]$  (**6**)**

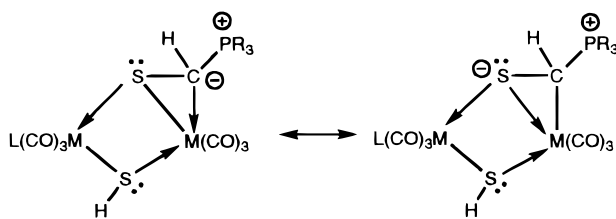
$\text{Re}(1)\text{-C}(3)$	1.887(10)	$\text{Re}(1)\text{-C}(4)$	1.903(10)
$\text{Re}(1)\text{-C}(2)$	1.903(8)	$\text{Re}(1)\text{-C}(1)$	2.187(7)
$\text{Re}(1)\text{-S}(1)$	2.496(2)	$\text{Re}(1)\text{-S}(2)$	2.548(2)
$\text{Re}(2)\text{-C}(5)$	1.881(11)	$\text{Re}(2)\text{-C}(6)$	1.899(12)
$\text{Re}(2)\text{-C}(7)$	1.920(9)	$\text{Re}(2)\text{-N}(1)$	2.234(7)
$\text{Re}(2)\text{-S}(1)$	2.505(2)	$\text{Re}(2)\text{-S}(2)$	2.522(2)
$\text{P}(1)\text{-C}(1)$	1.782(7)	$\text{S}(1)\text{-C}(1)$	1.821(7)
$\text{C}(2)\text{-O}(2)$	1.154(9)	$\text{C}(3)\text{-O}(3)$	1.168(11)
$\text{C}(4)\text{-O}(4)$	1.136(10)	$\text{C}(5)\text{-O}(5)$	1.165(11)
$\text{C}(6)\text{-O}(6)$	1.155(13)	$\text{C}(7)\text{-O}(7)$	1.137(10)
$\text{C}(3)\text{-Re}(1)\text{-C}(4)$	89.2(4)	$\text{C}(3)\text{-Re}(1)\text{-C}(2)$	88.6(3)
$\text{C}(4)\text{-Re}(1)\text{-C}(2)$	89.7(3)	$\text{C}(3)\text{-Re}(1)\text{-C}(1)$	110.3(3)
$\text{C}(4)\text{-Re}(1)\text{-C}(1)$	97.9(3)	$\text{C}(2)\text{-Re}(1)\text{-C}(1)$	159.6(3)
$\text{C}(3)\text{-Re}(1)\text{-S}(1)$	155.1(2)	$\text{C}(4)\text{-Re}(1)\text{-S}(1)$	97.9(3)
$\text{C}(2)\text{-Re}(1)\text{-S}(1)$	115.2(2)	$\text{C}(1)\text{-Re}(1)\text{-S}(1)$	45.16(18)
$\text{C}(3)\text{-Re}(1)\text{-S}(2)$	93.2(3)	$\text{C}(4)\text{-Re}(1)\text{-S}(2)$	177.3(3)
$\text{C}(2)\text{-Re}(1)\text{-S}(2)$	91.7(3)	$\text{C}(1)\text{-Re}(1)\text{-S}(2)$	80.02(19)
$\text{S}(1)\text{-Re}(1)\text{-S}(2)$	79.41(7)	$\text{C}(5)\text{-Re}(2)\text{-C}(6)$	87.5(5)
$\text{C}(5)\text{-Re}(2)\text{-C}(7)$	90.2(4)	$\text{C}(6)\text{-Re}(2)\text{-C}(7)$	88.9(5)
$\text{C}(5)\text{-Re}(2)\text{-N}(1)$	176.6(3)	$\text{C}(6)\text{-Re}(2)\text{-N}(1)$	92.6(5)
$\text{C}(7)\text{-Re}(2)\text{-N}(1)$	93.2(3)	$\text{C}(5)\text{-Re}(2)\text{-S}(1)$	93.7(3)
$\text{C}(6)\text{-Re}(2)\text{-S}(1)$	97.3(3)	$\text{C}(7)\text{-Re}(2)\text{-S}(1)$	172.8(3)
$\text{N}(1)\text{-Re}(2)\text{-S}(1)$	82.92(19)	$\text{C}(5)\text{-Re}(2)\text{-S}(2)$	94.5(3)
$\text{C}(6)\text{-Re}(2)\text{-S}(2)$	176.5(4)	$\text{C}(7)\text{-Re}(2)\text{-S}(2)$	93.9(3)
$\text{N}(1)\text{-Re}(2)\text{-S}(2)$	85.2(2)	$\text{S}(1)\text{-Re}(2)\text{-S}(2)$	79.75(7)
$\text{Re}(2)\text{-S}(2)\text{-Re}(1)$	96.70(8)	$\text{C}(1)\text{-P}(1)\text{-C}(31)$	112.7(4)
$\text{C}(1)\text{-P}(1)\text{-C}(11)$	106.7(4)	$\text{C}(31)\text{-P}(1)\text{-C}(11)$	105.6(4)
$\text{C}(1)\text{-P}(1)\text{-C}(21)$	114.6(3)	$\text{C}(1)\text{-S}(1)\text{-Re}(1)$	58.4(2)
$\text{C}(1)\text{-S}(1)\text{-Re}(2)$	106.7(2)	$\text{Re}(1)\text{-S}(1)\text{-Re}(2)$	98.49(7)
$\text{P}(1)\text{-C}(1)\text{-S}(1)$	119.5(4)	$\text{P}(1)\text{-C}(1)\text{-Re}(1)$	129.6(4)
$\text{S}(1)\text{-C}(1)\text{-Re}(1)$	76.5(2)	$\text{O}(2)\text{-C}(2)\text{-Re}(1)$	178.6(7)
$\text{O}(3)\text{-C}(3)\text{-Re}(1)$	179.6(8)	$\text{O}(4)\text{-C}(4)\text{-Re}(1)$	176.7(8)
$\text{O}(5)\text{-C}(5)\text{-Re}(2)$	179.2(9)	$\text{O}(6)\text{-C}(6)\text{-Re}(2)$	178.3(12)
$\text{O}(7)\text{-C}(7)\text{-Re}(2)$	177.9(9)		

$\text{SC(H)PPh}_3\}\text{-3-(PPh}_3\text{-}closo\text{-3,1,2-RhC}_2\text{B}_9\text{H}_{11})]$ , generated by attack of  $\text{PPh}_3$  on a coordinated dithioformate.<sup>13</sup> Complex **6** constitutes, therefore, the first example of  $\text{R}_3\text{PC(H)S}^-$  acting as a bridging ligand. The intermetallic distance in **6** (3.788(1) Å) is too long to permit any significant interaction between the two Re atoms (cf.  $\text{Re-Re}$  2.975(1) Å in the starting **1c**). The central Re-

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Scheme 2



(1)–S(1)–Re(2)–S(2) is not planar, adopting an envelope conformation which is folded by an angle of  $23.31^\circ$  with respect to the S(1)⋯S(2) line. The geometry around Re(1) can be described as octahedral by assuming that the phosphonothiolateylide ligand occupies two coordination positions. Nevertheless, there is a severe distortion of the geometry due to the angle S(1)–Re(1)–C(1) of  $45.16(18)^\circ$ , which deviates greatly from the value of  $90^\circ$  required for the ideal octahedral geometry. Around Re(2), the three carbonyl groups in a *facial* disposition, the two sulfurs, and one ammonia ligand complete a fairly regular octahedral disposition, with values of interligand angles ranging from  $79.75(7)^\circ$  to  $97.3(3)^\circ$ . Since there is no direct metal–metal bond, and assuming that the  $SH^-$  bridge donates  $3e$ , the electron counting in **6** requires the phosphonothiolateylide to donate five electrons to complete  $18e$  around each metal, as outlined in Scheme 2. In this fashion, the new ligand supports a net charge of  $1^-$ , i.e.,  $1^-$  in the sulfur,  $1^-$  in the carbon, and  $1^+$  in the phosphorus. This, together with the negative charge of  $SH^-$ , leads to the assignment of a formal oxidation number (+1) to each Re atom.

By comparing **6** with the precursor **1b**, it is apparent that the reduction/protonation sequence of reactions produces the cleavage of the Re–Re and one C–S bonds and the addition of hydrogen atoms to the split sulfur and to the central carbon of the phosphonothiolate ligand. Due to the high reactivity of the anions **2**, we have not been able to obtain spectroscopic data apart from their IR spectra in solution. Therefore, it is not possible to propose, on safe grounds, a sensible structure for these carbonyl anions. In view of the structure of the final compounds, it is reasonable to question in which of the two steps of the process the cleavage of the bond has occurred. A tentative mechanism is outlined in Scheme 3, supported by additional indirect data.

We have previously found that hydride addition to the starting complexes **1a,b** occurs at the metal–metal bond to produce the carbonyl anions  $[Mn_2(CO)_6(\mu-H)(\mu-S_2-CPCy_3)]^-$  (**D** in Scheme 3) without cleavage of the Mn–Mn bond.<sup>10</sup> This suggests that the LUMO of the substrate **1** lies mainly on the metals. On the other hand, it is well-known that reduction of binuclear species with  $Na[Hg]$  usually produces cleavage of the M–M bond. In the present case, this would lead to an intermediate (**A** in Scheme 3) with the charges centered on the metals. An intramolecular oxidative addition of one C–S bond to one of the metal atoms in **A** would produce the cleavage of the C–S bond, leading to intermediate **B** with the charges now centered on the two atoms of the split bond: C and S. Subsequent protonation of these atoms forms the ligands  $SH^-$  and  $R_3PC(H)S^-$  of the final compounds. Consistent with the

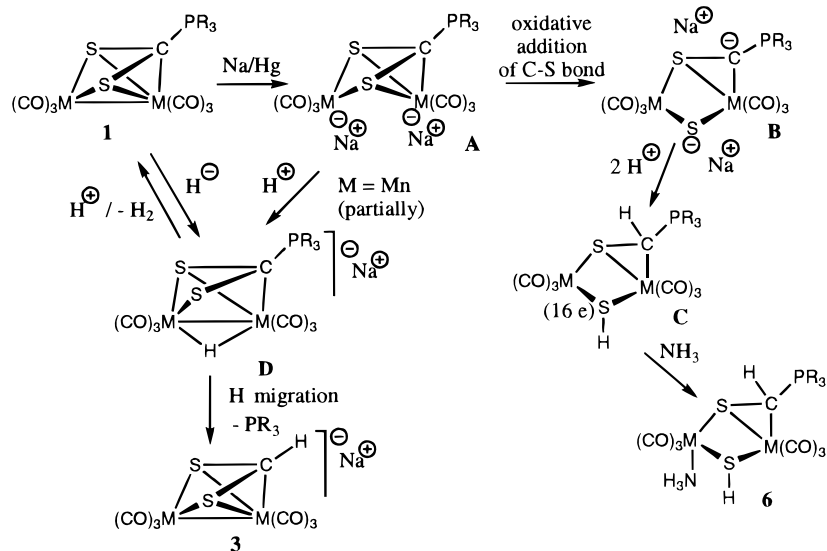
electron counting discussed above, in the protonated intermediate **C** one of the metals possesses only 16e and, thus, requires the coordination of an additional ligand, in this case one molecule of the ammonia liberated (2 mol equiv) in the protonation. It has been mentioned above that in the case of the dimanganese complexes, some amount of the starting complex **1a,b** is found at the end of the reaction. This could result from a partial oxidation of intermediate **A** by the protons. Addition of one proton to intermediate **A** would produce the previously known hydrido carbonyl anion **D**.<sup>10</sup> While it has not been possible to detect this intermediate in the protonation of the anions, there is some indirect evidence which support this hypothesis. Spectroscopically pure hydridocarbonyl anion **D** can be prepared in THF solution by addition of  $Li[BHET_3]$  to **1a** at  $0^\circ C$ . When this solution was transferred over excess  $NH_4PF_6$ , the starting material **1a** was produced instantaneously in high yield. Additionally, it was known previously<sup>10</sup> that **D** rearranges spontaneously, with loss of  $PR_3$ , to give the dithioformate complex anion  $[Mn_2(CO)_6(\mu-S_2CH)]^-$  (**3**), which has also been found in the reduction/protonation of the dimanganese complexes.

The transformation of complexes **1** into their derivatives containing  $R_3PC(H)S^-$  and  $SH^-$  bridges involves the addition of  $2e$  in the reduction and  $2H^+$  in the protonation. Therefore, it can be regarded as hydrogenolysis of a C=S bond  $\pi$ -coordinated to a Mn or Re atom.

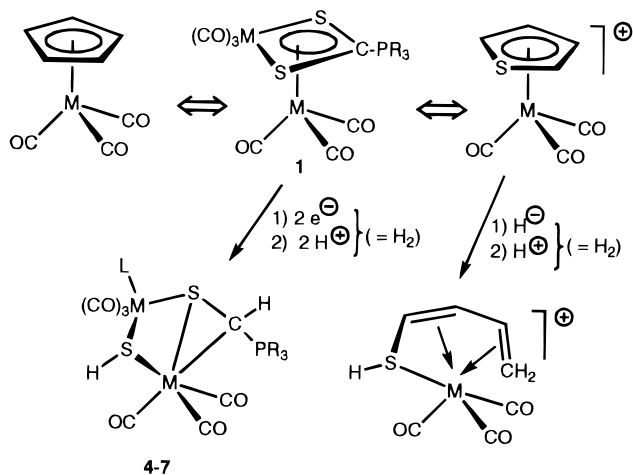
We have previously shown that complexes **1** could be viewed as consisting of a manganadithiabutene ring coordinated to a  $M(CO)_3$  fragment, with structural and electronic features similar to those found in the well-known cymantrene-like derivatives  $[M(\eta^5-C_5H_5)(CO)_3]$ .<sup>9b</sup> Pursuing this analogy one step further, the similarity can be extended to isoelectronic  $[M(\eta^5\text{-thiophene})(CO)_3]^+$ , as shown in Scheme 4. In fact, the close relationship of the fragments “ $CpML_n^{z+}$ ” and “(thiophene) $ML_n^{(z+1)+}$ ” has been supported by the results of Fenske–Hall MO calculations.<sup>2e</sup> In this way, the process described here may serve as a model for the hydrogenolysis of a  $\eta^5$ -coordinated thiophene. However, the analogy is not limited to the structural or bonding features, but it extends to some aspects of the reactivity. It has been shown that the reduction of cationic complexes of Rh and Ir is often followed by the opening of the thiophene ring to afford a metallathiabenzene.<sup>3f,k</sup> Calculations of the Fenske–Hall type show that this is produced through an oxidative addition of a C–S bond to the metal atom, such as the transformation from **A** to **B** proposed in Scheme 3.<sup>2e</sup> Quite understandably, the calculations also suggest that the metal center should be more electron rich to promote the oxidative addition. This is the case for the carbonyl anion **A**, and it can be taken as additional support for the pathway proposed in Scheme 3.

Apart from their interest as models for the ring opening of thiophene and related molecules, compounds **4–7** represent the first examples of compounds containing the new bridging ligand  $Cy_3PC(H)S^-$ . Additionally, complexes **4–7** and their very reactive, anionic precursors **2** described here open new and unexpected synthetic pathways which are currently being studied.

Scheme 3



Scheme 4



### Experimental Section

All reactions were carried out in dry solvents under a nitrogen atmosphere. Details of the instrumentation and experimental procedures have been given elsewhere.<sup>7b</sup> Literature procedures for the preparation of the starting materials are quoted in each case. Ligands and other reagents were purchased and used without purification unless otherwise stated.

**Na<sub>2</sub>[Mn<sub>2</sub>(CO)<sub>6</sub>(μ-S<sub>2</sub>CPCy<sub>3</sub>)] (2a) in THF Solution.** [Mn<sub>2</sub>(CO)<sub>6</sub>(μ-S<sub>2</sub>CPCy<sub>3</sub>)] (**1a**) (0.10 g, 0.15 mmol) was dissolved in THF (20 mL), and the solution was cooled in an ice bath. Freshly prepared sodium amalgam (1% w/w, 10 g, excess) was then added, and the mixture was stirred for 15 min, when the IR spectrum of the solution showed that all starting **1a** had been consumed. The mixture was decanted, and the solution was filtered through a cannula over the appropriate reagent to obtain the protonated derivatives. IR (THF): ν(CO) 1987m, 1946vs, 1917m, 1877vs, cm<sup>-1</sup>.

**Na<sub>2</sub>[Mn<sub>2</sub>(CO)<sub>6</sub>(μ-S<sub>2</sub>CPPr<sup>t</sup><sub>3</sub>)] (2b) in THF Solution.** The procedure was similar to that described above for the preparation of **2a**, starting from [Mn<sub>2</sub>(CO)<sub>6</sub>(μ-S<sub>2</sub>CPPr<sup>t</sup><sub>3</sub>)] (**1b**) (0.12 g, 0.23 mmol) and sodium amalgam (1% w/w, 10 g, excess) in THF (10 mL). The reaction was complete in 15 min, and the solution was similarly filtered through a cannula to be used in subsequent reactions. IR (THF): ν(CO) 1987m, 1947vs, 1917m, 1877vs, cm<sup>-1</sup>.

**Na<sub>2</sub>[Re<sub>2</sub>(CO)<sub>6</sub>(μ-S<sub>2</sub>CPCy<sub>3</sub>)] (2c) in THF Solution.** The procedure was similar to that described above for the prepara-

tion of **2a**, starting from [Re<sub>2</sub>(CO)<sub>6</sub>(μ-S<sub>2</sub>CPCy<sub>3</sub>)] (**1c**) (0.13 g, 0.15 mmol) and sodium amalgam (1% w/w, 10 g, excess) in THF (10 mL). The reaction required 4 h to reach completion. The reaction was filtered as described above, to be used in the preparation of derivative **6**. IR (THF): ν(CO) 1985m, 1966vs, 1868vs, 1846s, cm<sup>-1</sup>.

**[Mn<sub>2</sub>(CO)<sub>6</sub>(μ-SH){μ-SC(H)PCy<sub>3</sub>}(NH<sub>3</sub>)] (4a).** A solution of **2a** (0.15 mmol) in THF (20 mL), prepared as described above, was cooled to -78 °C and transferred through a cannula into a Schlenk flask containing NH<sub>4</sub>PF<sub>6</sub> (0.065 g, 4 mmol). The reaction was clean and instantaneous, according to IR monitoring, to give **4a** together with some of the dithioformate complex anion **3** (10–20%). Attempts at isolation led to extensive decomposition of **4a** to give only small amounts of starting **1a** (5–10%). However, the solution of **4a** was used successfully to prepare the PET<sub>3</sub> derivative **5a** (see below). IR (THF): ν(CO) 2009m, 1975vs, 1907s, 1882s, 1864m, cm<sup>-1</sup>.

**[Mn<sub>2</sub>(CO)<sub>6</sub>(μ-SH){μ-SC(H)PPr<sup>t</sup><sub>3</sub>}(NH<sub>3</sub>)] (4b).** A solution of **2b** (0.23 mmol) in THF (10 mL), prepared as described above, was cooled to -78 °C and transferred through a cannula into a Schlenk flask containing NH<sub>4</sub>PF<sub>6</sub> (0.065 g, 4 mmol). Similarly to **4a**, compound **4b** could not be isolated and was used in solution to prepare the derivative **5b** (see below). IR (THF): ν(CO) 2009m, 1975vs, 1908s, 1883s, 1864m, cm<sup>-1</sup>.

**[Mn<sub>2</sub>(CO)<sub>6</sub>(μ-SH){μ-SC(H)PCy<sub>3</sub>}(PET<sub>3</sub>)] (5a).** To a cooled (-78 °C) solution of **4a** (0.15 mmol) in THF (20 mL), prepared as described above, was added PET<sub>3</sub> (19 μL, 0.15 mmol). The mixture was stirred for 20 min, and the solvent was evaporated in vacuo. The residue, containing **5a** together with minor amounts (10–20%) of the dithioformate anionic complex **3** (sodium salt), was dissolved in a CH<sub>2</sub>Cl<sub>2</sub>/hexane mixture (1:3, v:v) and filtered through a short column (2.5 × 10 cm) of alumina (activation degree III). Under these conditions, complex **3** remained adsorbed on the column. The filtrate containing **5a** was evaporated in vacuo, and the concentrated solution was placed overnight in a refrigerator (-20 °C) to afford compound **5a** as a yellow microcrystalline solid. Yield: 0.052 g, 50.5% (with respect to starting [Mn<sub>2</sub>(CO)<sub>6</sub>(μ-S<sub>2</sub>CPCy<sub>3</sub>)]). Anal. Calcd for C<sub>31</sub>H<sub>50</sub>Mn<sub>2</sub>O<sub>6</sub>P<sub>2</sub>S<sub>2</sub>: C, 49.34; H, 6.68. Found: C, 49.31; H, 6.93. IR (THF): ν(CO) 2002m, 1976vs, 1912m, 1902s, 1882m, 1866m, cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 3.29 [s(br), 1H, SC(H)P], 2.44–0.84 [m, 48 H, Cy, Et], -3.29 [d (16), 1H, SH]. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 40.5 [s, SCP], 37.0 [s, PET<sub>3</sub>]. <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>): 229.2, 227.4, 223.4 [MnCO], 35.4 [d (43), C<sup>1</sup> of Cy], 31.3 [dd(41 and 5), SC(H)P], 28.8 and 28.2 [2 × s, C<sup>2</sup> and C<sup>6</sup> of Cy], 27.8 [d(11)] and 27.5 [d(11) (C<sup>3</sup> and C<sup>5</sup> of Cy)], 26.6 (s, C<sup>4</sup> of Cy), 17.8 [d(22), CH<sub>2</sub> of Et], 8.8 (s, CH<sub>3</sub> of Et).

**[Mn<sub>2</sub>(CO)<sub>6</sub>(μ-SH){μ-SC(H)PPr<sup>i</sup><sub>3</sub>}(PET<sub>3</sub>)] (5b).** Compound **5b** was prepared as described above for **5a**, from a solution of **4b** (ca. 0.23 mmol) and PET<sub>3</sub> (31 μL, 0.23 mmol) in THF (20 mL). The workup was as described for **5a**, affording **5b** as yellow-orange microcrystals. Yield: 0.051 g, 41%. Anal. Calcd for C<sub>22</sub>H<sub>38</sub>Mn<sub>2</sub>O<sub>6</sub>P<sub>2</sub>S<sub>2</sub>: C, 41.65; H, 6.04. Found: C, 41.34; H, 6.36. IR (THF): ν(CO) 2003s, 1977vs, 1914m, 1902m, 1884m, 1867m, cm<sup>-1</sup>. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 3.32 [s(br), 1H, SC(H)P], 2.41 [m, 3 H, CH of Pr<sup>i</sup>], 1.55 [m, 24H, CH<sub>3</sub> of Pr<sup>i</sup> and CH<sub>2</sub> of Et], 1.22 [m, 9H, CH<sub>3</sub> of Et], -2.29 [s(br), 1H, SH]. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 49.9 [s, SCP], 36.9 [s, PET<sub>3</sub>]. <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>): 227.9, 226.8, 226.7 [MnCO], 28.2 [dd(43 and 6), SC(H)P], 24.5 [d(45), CH of Pr<sup>i</sup>], 18.2 [d(33), CH<sub>3</sub> of Pr<sup>i</sup>], 17.1 [d(22), CH<sub>2</sub> of Et], 8.2 (s, CH<sub>3</sub> of Et).

**[Re<sub>2</sub>(CO)<sub>6</sub>(μ-SH){μ-SC(H)PCy<sub>3</sub>}(NH<sub>3</sub>)] (6).** A solution of **2c** (0.15 mmol) in THF (10 mL), prepared as described above, was cooled to -78 °C and transferred through a cannula into a Schlenk flask containing NH<sub>4</sub>PF<sub>6</sub> (0.065 g, 4 mmol) at 0 °C. The mixture was stirred for 2 h, until the complete disappearance of the bands of the anion **2c**. The solvent was evaporated in vacuo, the solid residue was extracted with a THF/hexane (1:1) mixture, and the extracts were filtered through alumina (activation degree III). Evaporation of the solvent in vacuo gave a yellow solid, which was recrystallized from THF/hexane to obtain **6** as yellow crystals. Yield: 0.09 g, 65%. Anal. Calcd for C<sub>25</sub>H<sub>38</sub>NO<sub>6</sub>Pre<sub>2</sub>S<sub>2</sub>·THF: C, 35.25; H, 4.69; N, 1.42. Found: C, 35.41; H, 4.82; N, 1.35. IR (THF): ν(CO) 2015m, 1988vs, 1892vs, 1865m, cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 3.61 (THF), 3.10 [s, 3H, NH<sub>3</sub>], 2.30–1.29 [m, 36H, THF, SC(H)P, and Cy], -1.13 [s(br), 1H, SH]. <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 36.5 [s, SCP]. <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>): 202.4, 199.1, 197.2, 196.5, 192.9, 192.5 [ReCO], 68.0 (s, THF), 34.7 [d(43), C<sup>1</sup> of Cy], 28.5 [d(3)] and 28.1 [d(2) [C<sup>2</sup> and C<sup>6</sup> of Cy]], 27.7 [d(11)] and 27.1 [d(11) (C<sup>3</sup> and C<sup>5</sup> of Cy)], 26.4 (s, C<sup>4</sup> of Cy), 21.6 [d(35), SC(H)P].

**X-ray Diffraction Study of 6.** Crystals were grown by slow diffusion of hexane into a concentrated solution of **6** in THF at -20 °C. Relevant crystallographic details are given in Table 1. Unit cell parameters were determined from the least-squares refinement of a set of 25 centered reflections in the range 15° < θ < 18°. Three reflections were measured every 1 h as orientation and intensity control. Significant decay was not observed. The structure was solved by Patterson methods, phase expansion, and subsequent Fourier maps with DIRDIF.<sup>14</sup> Full-matrix least-squares refinement was made with SHELX-93.<sup>15</sup> After isotropic refinement, an ab-

sorption correction was applied with DIFABS.<sup>16</sup> All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were geometrically positioned, with a common isotropic temperature factor which was refined. The perspective drawing in Figure 1 was made with PLATON.<sup>17</sup>

**[Re<sub>2</sub>(CO)<sub>6</sub>(μ-SH){μ-SC(H)PCy<sub>3</sub>}(PET<sub>3</sub>)] (7).** To solution of **6** (0.1 g, 0.1 mmol) in THF (15 mL) at 0 °C was added PET<sub>3</sub> (16 μL, 0.1 mmol), and the mixture was stirred for 10 min. The solvent was evaporated in vacuo, the residue was extracted with CH<sub>2</sub>Cl<sub>2</sub>/hexane (2/1, v/v, 4 × 15 mL), and the collected extracts were filtered through a short column of alumina (2.5 × 5 cm, activation degree III). Slow concentration in vacuo afforded **7** as a creamy-white microcrystalline solid. Yield: 0.07 g, 71%. Anal. Calcd for C<sub>31</sub>H<sub>50</sub>O<sub>6</sub>P<sub>2</sub>Re<sub>2</sub>S<sub>2</sub>: C, 36.60; H, 4.95. Found: C, 36.87; H, 5.06. IR (THF): ν(CO) 2013m, 1990vs, 1914s, 1897s, 1884s, 1868m, cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 2.43 [s, 1H, SC(H)P], 2.33–2.18 [m, 9H, CH of Cy and CH<sub>2</sub> of Et], 2.13–1.26 [m, 30H, CH<sub>2</sub> of Cy], 1.18 [m, 9H, CH<sub>3</sub> of Et], -0.96 [s(br), 1H, SH]. <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 36.3 [d(3.5), SCP], 0.7 [d(3.5), PET<sub>3</sub>]. <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>): 200.6 [s, ReCO], 200.5 [s, 2 × ReCO], 196.6 [s, ReCO], 195.2 [d(59), ReCO], 192.9 [dd (46 and 8), ReCO], 34.3 [d(43), C<sup>1</sup> of Cy], 27.6 [d(4)] and 27.5 [d(4) [C<sup>2</sup> and C<sup>6</sup> of Cy]], 27.0 [d(12)] and 26.5 [d(12) (C<sup>3</sup> and C<sup>5</sup> of Cy)], 25.7 (s, C<sup>4</sup> of Cy), 24.1 [dd-(35 and 5), SC(H)P], 16.6 [d(28), CH<sub>2</sub> of PET<sub>3</sub>], 8.0 [d(2.5), CH<sub>3</sub> of PET<sub>3</sub>].

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**Supporting Information Available:** Complete tables of atomic coordinates, anisotropic thermal parameters, bond lengths and angles, torsion angles, and least squares planes for the structure of **6** (8 pages). Ordering information is given on any current masthead page. A list of structure factor amplitudes is available from the authors.

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