

Alkylation and metalation of binuclear anions containing a novel tricyclohexylphosphonioethanetrithiolate ligand $S(SR)C=C(PCy_3)S$

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Abstract

The reaction of homobinuclear rhenium–rhenium complex $[Re_2(CO)_6(\mu-S_2CPCy_3)]$ (**1c**) with $Li[BHEt_3]$ in THF produces anionic **2c** which reacts with CS_2 affording a new anion **3c**, through desulfurization and CS insertion, in a fashion parallel to that of the previously known Mn–Mn and Mn–Re analogues. Anions **3a–3c** undergo allylation and metallation to give neutral products **4a–4k**. The structures of $[MnRe(CO)_6(\mu-H)\{\mu-S(SSnBu_3^+)C=C(PCy_3)S\}]$ (**4d**) and $[MnRe(CO)_6(\mu-H)\{\mu-S(SC_3H_5)C=C(PCy_3)S\}]$ (**4h**) have been determined by X-ray diffraction revealing the $(OC)_3Mn-Re(CO)_3$ core unit bridged by hydride and the novel *S*-tributylstannyl-, or (*S*-allyl)-(tricyclohexylphosphonio)ethanetrithiolate ligands.

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1. Introduction

Metal assisted formation and breaking of C–S bonds is of current interest in many fields, from organic synthesis [1] to catalytic hydrodesulfurization (HDS) [2], and the study of the coordination of *S*-donor ligands to homo-, and heterobimetallic systems is relevant to gain knowledge of some biological systems such as metalloenzymes [3].

At the same time phosphine-carbon disulfide adducts, S_2CPR_3 , are very versatile ligands that exhibit a variety of coordination modes to transition metal centers being able to formally donate from 2 to $8e^-$ to a metal (or metals) [4]. We have found recently that binuclear complexes containing S_2CPR_3 bridges, undergo C–S splitting upon reduction followed by protonation, a process which models the hydrogenolysis of thiophene [5,6]. In previous papers, we have shown that bimetallic complexes **1** (Scheme 1) undergo hydride addition at the

metal–metal bond, to afford anionic complexes **2** [7]. Addition of CS_2 produces novel anionic species **3**, containing the (tricyclohexylphosphonio)ethanetrithiolate ligand $S(S)C=C(PCy_3)S$ [8]. This results from a pathway which involves formally the desulfurization of CS_2 , metal–carbon bond cleavage and insertion into the S_2CPCy_3 ligand on the anionic **2**, with formation of a carbon–carbon double bond. Monitoring by NMR by using ^{13}C -enriched CS_2 suggested that the insertion of CS occurred into one of the C–S bonds of S_2CPCy_3 , and not into the C–P bond.

In the present paper, we report the extension of this chemistry to dirhenium complexes, and the synthesis and characterization of a series of neutral homo- and heterobinuclear compounds containing the novel trialkylphosphoniotrithiocarboxylate ligand, $S(SR)C=C(PCy_3)S$, in which the R group can be a metal–ligand fragment or an active allyl or propargyl group.

2. Results and discussion

As previously observed for their Mn–Mn and Mn–Re congeners [8], dirhenium complex **1c** undergoes addition

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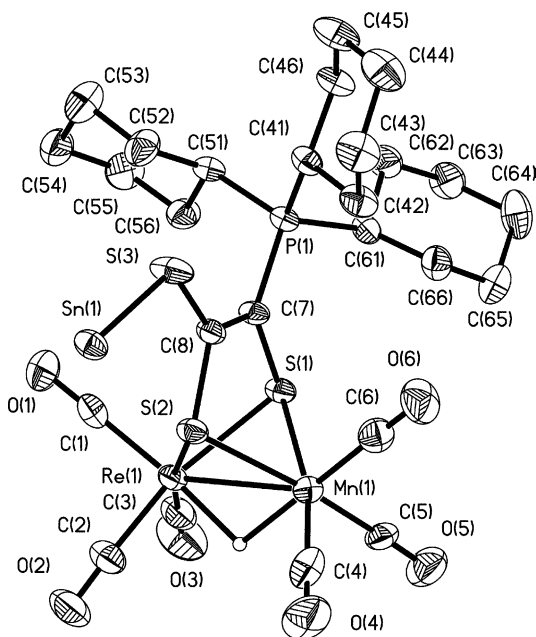


Fig. 1. Perspective view of compound **4d** showing the atom numbering. The butyl groups on the tin atom have been omitted for clarity.

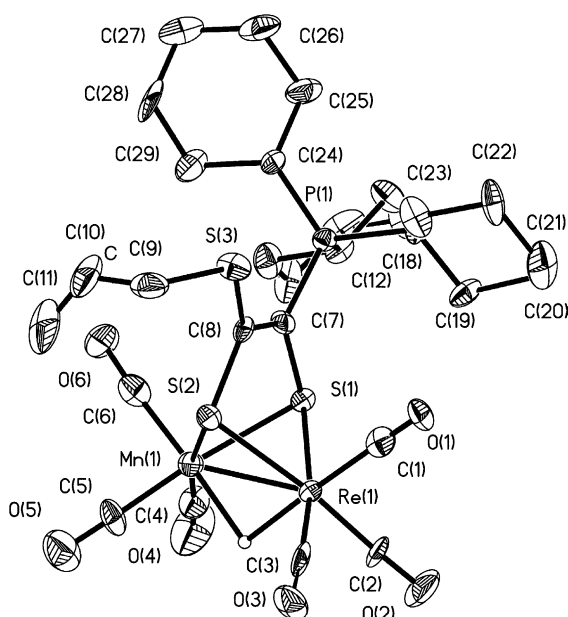


Fig. 2. Perspective view of compound **4h** showing the atom numbering.

strongly supported by the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra. The signals of C(7) and C(8) appear as doublets due to the coupling to ^{31}P . Thus, the carbon bonded to both sulfur atoms appears in the region $\delta = 183\text{--}193$ ppm [$^2J(\text{P}\text{--}\text{C})$ from 7 to 11 Hz], while the carbon bonded to phosphorus is observed in the range $\delta = 114\text{--}128$ ppm [$^1J(\text{P}\text{--}\text{C})$ from 66 to 74 Hz].

The Mn–Re distances of 2.786(1) Å for **4d**, and 2.781(1) Å for **4h**, are consistent with the existence of a metal–metal bond. The bridging hydride ligands have

been located for both structures in difference maps. For **4d**, the hydride was fully refined (coordinates and isotropic thermal parameter) while in the case of **4h** both the position and the thermal parameter had to be fixed during the refinement. In the two structures, the bridging hydride is placed in a fairly symmetrical position spanning the Mn–Re bond. The plane of the ethenetriolate ligand is placed perpendicular at the middle point of the Mn–Re vector. Therefore the two $\text{M}(\text{CO})_3$ fragments are symmetrically placed at both sides of the plane. Since the size of both $\text{M}(\text{CO})_3$ fragments is similar, there is no significant difference in the packing forces upon changing the orientation of the Mn–Re vector. On these grounds it is not surprising that the positions of Mn and Re are disordered in both structures leading to refined occupancy factors of about 59/41 (i.e., close to randomly distributed) for both structures.

In conclusion, we have shown that the anions **3** can be used to prepare neutral derivatives which incorporate a wide range of substituents, from metal–ligand fragments to activated allyl or propargyl groups. This opens the way to further studies, and some more work is now being done to attempt the polymerization of the allyl and propargyl derivatives, aiming to prepare metal containing polymers.

3. Experimental

3.1. Materials and general methods

All operations were performed under an atmosphere of dry argon using Schlenk and vacuum techniques. All solvents were dried by standard methods and distilled prior to use. Elemental analyses were determined on a Yanaco CHN Corder MT-3 elemental analyzer. IR spectra were recorded on a Bruker Equinox 55 spectrometer in THF solution. NMR spectra were measured on a Bruker AC-200 spectrometer in CDCl_3 solution with TMS as internal standard. $[\text{MM}'(\text{CO})_6(\mu\text{-S}_2\text{CPCy}_3)]$ [9] and R_3SnX [10], were synthesized by literature procedures.

3.2. $\text{Li}[\text{Re}_2(\text{CO})_6(\mu\text{-H})(\mu\text{-S}_2\text{C}=\text{C}(\text{S})\text{PCy}_3)]$ (**3c**) in THF solution

Compound **1c** (0.1 mmol, 0.090 g) and $\text{Li}[\text{BHET}_3]$ (molar ratio 1:2) were made to react in THF (20 ml) for 4h at 0 °C to obtain a solution of anion **2a**. Water (0.1 ml) and CS_2 (0.9 ml, excess) were then added, and the solution was stirred for 2h affording the THF solution of anion **3c** to be used in subsequent reactions. IR (THF), $\nu(\text{CO})$: 2016 m, 1992 s, 1901 vs, cm^{-1} . ^{31}P NMR (acetone- d_6): $\delta = 32.42$. ^1H NMR (acetone- d_6): $\delta = 1.27\text{--}2.12$ (m, 33H, PCy_3), -8.91 (s, 1H, $\mu\text{-H}$).

Table 1
Crystal data and refinement details for **4d** and **4h**

	4d	4h
Empirical formula	C ₃₈ H ₆₁ MnO ₆ PREs ₃ Sn	C ₂₉ H ₃₈ MnO ₆ PREs ₃ .CH ₂ Cl ₂
Formula weight	1100.85	935.81
Crystal system	Monoclinic	Triclinic
Space group	<i>Cc</i>	<i>P</i>
<i>a</i> (Å)	20.880(2)	10.892(5)
<i>b</i> (Å)	10.774(1)	11.161(5)
<i>c</i> (Å)	20.917(2)	17.133(8)
α (°)	90	103.724(8)
β (°)	91.356(2)	99.538(10)
γ (°)	90	106.532(8)
<i>V</i> (Å ³)	4704(1)	1878(2)
<i>Z</i>	4	2
<i>D</i> _{calc} (g cm ⁻³)	1.554	1.655
<i>F</i> (000)	2200	930
λ (Mo K α) (Å)	0.71073	0.71073
Crystal size (mm)	0.22 × 0.10 × 0.08	0.25 × 0.20 × 0.15
μ (Mo K α) (mm ⁻¹)	3.563	3.946
Collection range (°)	1.95 ≤ θ ≤ 23.36	2 ≤ θ ≤ 25.03
Absorption correction	SADABS	SADABS
Corr. factors (min, max)	1.000, 0.652	1.000, 0.745
Reflections collected	14 737	7694
Independent reflections	6730	6491
Reflections observed, <i>I</i> > 2 σ (<i>I</i>)	5950	2418
GOF on <i>F</i> ²	1.060	0.840
Number of parameters	464	402
<i>R</i> , <i>wR</i> 2 (all)	0.0429, 0.1129	0.0626, 0.0954

Table 2
Selected bond lengths (Å) and angles (°) for compound **4d**

Re(1)–Mn(1)	2.786(1)	Re(1)–S(1)	2.433(3)
Re(1)–S(2)	2.460(3)	Mn(1)–S(1)	2.421(3)
Mn(1)–S(2)	2.424(3)	Sn(1)–C(21)	2.122(11)
Sn(1)–C(31)	2.147(15)	Sn(1)–C(11)	2.156(13)
Sn(1)–S(3)	2.480(3)	S(2)–C(8)	1.798(9)
S(1)–C(7)	1.802(9)	S(3)–C(8)	1.726(10)
C(7)–C(8)	1.367(13)	P(1)–C(7)	1.788(9)
C(2)–Re(1)–S(1)	164.8(4)	C(3)–Re(1)–S(2)	168.7(4)
S(1)–Re(1)–S(2)	75.35(8)	C(4)–Mn(1)–S(1)	167.9(4)
C(5)–Mn(1)–S(2)	166.1(4)	C(8)–C(7)–P(1)	125.8(7)
C(8)–C(7)–S(1)	116.4(7)	P(1)–C(7)–S(1)	117.8(5)
C(7)–C(8)–S(3)	127.7(7)	C(7)–C(8)–S(2)	117.1(7)
S(3)–C(8)–S(2)	115.2(6)		

3.3. [Mn₂(CO)₆(μ -H) { μ -S(SSnBu₃)C=C(PCy₃)S}] (4a)

To a solution of anion **3a** [8] was added Bu₃SnCl (0.33 g, 1.0 mmol), and the mixture was stirred for 2 h. The solvents were evaporated in vacuo, and the residue was taken up in CH₂Cl₂/hexane (V/V, 1:1) and filtered through alumina (activity III). The yellow band was collected and evaporated in vacuo to obtain compound **4a** (0.069 g) as a yellow, microcrystalline solid. Overall yield was 71%, based on starting compound **1a**. Anal. Calc. for: C₃₈H₆₁Mn₂O₆PS₃Sn: C, 47.07; H, 6.34. Found: C, 47.49; H, 6.42%. IR (THF), ν (CO): 2021 s, 1995 vs, 1929 s. ³¹P NMR (CD₂Cl₂): δ = 32.70. ¹H

Table 3
Selected bond lengths (Å) and angles (°) for compound **4h**

Re(1)–Mn(1)	2.781(1)	Re(1)–S(2)	2.430(3)
Re(1)–S(1)	2.439(3)	Mn(1)–S(1)	2.414(3)
Mn(1)–S(2)	2.424(4)	P(1)–C(7)	1.842(11)
S(1)–C(7)	1.782(12)	S(2)–C(8)	1.784(11)
S(3)–C(8)	1.711(12)	S(3)–C(9)	1.768(14)
C(9)–C(10)	1.50(2)	C(10)–C(11)	1.30(2)
C(2)–Re(1)–S(2)	169.2(5)	C(3)–Re(1)–S(1)	171.1(4)
C(5)–Mn(1)–S(1)	169.9(4)	C(4)–Mn(1)–S(2)	169.8(5)
C(8)–C(7)–S(1)	119.1(9)	C(8)–C(7)–P(1)	127.2(10)
S(1)–C(7)–P(1)	113.5(6)	C(7)–C(8)–S(3)	126.3(9)
C(7)–C(8)–S(2)	115.3(9)	S(3)–C(8)–S(2)	117.9(6)
C(10)–C(9)–S(3)	115.2(13)	C(11)–C(10)–C(9)	127(2)

NMR (CDCl₃): δ = 2.95 – 0.92 (m, 60H, Bu and Cy), –8.59(s, 1H, μ -H). ¹³C NMR (CD₂Cl₂): δ = 223.12, 222.06, 221.76 (Mn–CO); 189.32, 114.35 (P–C=C); 32.71, 27.14, 26.78, 25.92 (C₆H₁₁); 13.54, 17.98, 25.26, 28.52 (Bu).

3.4. [Mn₂(CO)₆(μ -H) { μ -S(SSnPh₃)C=C(PCy₃)S}] (4b)

Compound **4b** was prepared as described above for compound **4a**, from a solution of **3a** (0.1 mmol) and Ph₃SnCl (1.0 mmol). The workup was as described for **4a** to afford compound **4b**. Yield: 0.078 g, 75%. Anal. Calcd. for C₄₄H₅₇Mn₂O₆PS₃Sn: C, 50.97; H, 5.53.

Found: C, 50.97; H, 5.05%. IR (THF), $\nu(\text{CO})$: 2022 s, 1995 vs, 1929 s, cm^{-1} . ^{31}P NMR (CD_2Cl_2): $\delta = 33.16$. ^1H NMR (CD_2Cl_2): $\delta = 7.63$ – 7.28 (m, 15H, Ph), 2.91–1.30 (m, 33H, Cy), -8.72 (s, 1H, $\mu\text{-H}$). ^{13}C NMR (CD_2Cl_2): $\delta = 223.82$, 222.41, 221.46 (Mn–CO), 185.90 (P–C=CS), 117.07 (P–C=CS); 139.45, 136.92, 130.17, 129.37 (Ph); 33.21, 27.80, 27.46, 25.84 (C_6H_{11}).

3.5. $[\text{Mn}_2(\text{CO})_6(\mu\text{-H})\{\mu\text{-S}(\text{SCH}_2\text{CH}=\text{CH}_2)\text{C}=\text{C}(\text{PCy}_3)\text{S}\}]$ (**4c**)

Compound **4c** was prepared as described above for compound **4a**, from a solution of **3a** (0.1 mmol) and allyl bromide (1.0 mmol). The workup was as described for **4a** to afford compound **4c**. Yield: 0.041 g, 56%. Anal. Calc. for $\text{C}_{29}\text{H}_{39}\text{Mn}_2\text{O}_6\text{PS}_3$: C, 48.33; H, 5.45. Found: C, 48.38; H, 5.12%. IR (THF), $\nu(\text{CO})$: 2022 s, 1996 vs, 1926 s, 1910(sh), 1898 s. ^{31}P NMR (CD_2Cl_2): $\delta = 36.39$; ^1H NMR (CD_2Cl_2): $\delta = 5.87$ [m, 1H, $\text{CH}=\text{CH}_2$], 5.37 [d(16), 1H, *trans*- $\text{C}=\text{CH}_2$], 5.22 [d(10), 1H, *cis*- $\text{C}=\text{CH}_2$], 3.90 [d(9), 2H, $\text{CH}_2\text{CH}=\text{CH}_2$], 3.16 [m, 3H, *CH* of Cy], 1.92–1.37 [m, 30H, CH_2 of Cy], -8.42 [s, 1H, $\mu\text{-H}$]. ^{13}C NMR (CD_2Cl_2): 223.82, 223.31, 222.39 (Mn–CO), 187.38 [d(7), P–C=CS], 125.72 [d(66), P–C=CS], 133.58 and 120.04 ($\text{CH}=\text{CH}_2$), 40.28 (SCH_2), 33.36 [d(41), C^1 of Cy], 27.92 [d(3), $\text{C}^{2,6}$ of Cy], 27.65 [d(13), $\text{C}^{3,5}$ of Cy], 26.07 [C^4 of Cy].

3.6. $[\text{MnRe}(\text{CO})_6(\mu\text{-H})\{\mu\text{-S}(\text{SSnBu}_3)\text{C}=\text{C}(\text{PCy}_3)\text{S}\}]$ (**4d**)

Compound **4b** was prepared as described above for compound **4a**, from a solution of **3a** (0.1 mmol) and Bu_3SnCl (0.33 g, 1.0 mmol). The workup was as described for **4a** to afford compound **4d**. Yield: 0.084 g, 76%. Anal. Calc. for $\text{C}_{38}\text{H}_{61}\text{MnO}_6\text{PReS}_3\text{Sn}$: C, 41.46; H, 5.58. Found: C, 41.97; H, 5.62%. IR (THF), $\nu(\text{CO})$: 2026 s, 2000 vs, 1926 s, 1914 s, 1900 m. ^{31}P NMR (CD_2Cl_2): $\delta = 28.20$; ^1H NMR (CD_2Cl_2): $\delta = 2.08$ – 1.00 (m, 60H, Bu and Cy), -7.30 (s, 1H, $\mu\text{-H}$). ^{13}C NMR (CD_2Cl_2): $\delta = 223.65$, 222.35, 218.41 (Mn–CO), 197.07, 196.51, 193.22 (Re–CO), 186.55 (P–C=C–S), 115.31 (P–C=CS); 33.58, 27.80, 27.21, 25.72 (C_6H_{11}), 29.24, 27.54, 18.49, 13.95 (Bu).

3.7. $[\text{MnRe}(\text{CO})_6(\mu\text{-H})\{\mu\text{-S}(\text{SSnPh}_3)\text{C}=\text{C}(\text{PCy}_3)\text{S}\}]$ (**4e**)

Compound **4e** was prepared as described above for compound **4d**, from a solution of **3b** (0.1 mmol) and Ph_3SnCl (1.0 mmol). The workup was as described for **4d** to afford compound **4e**. Yield: 0.095 g, 81%. Anal. Calc. for $\text{C}_{44}\text{H}_{57}\text{MnO}_6\text{PReS}_3\text{Sn}$: C, 48.88; H, 4.59. Found: C, 48.30; H, 4.56. IR (THF), $\nu(\text{CO})$: 2027 m, 2001 vs, 1931 s, 1915 s, 1900 s. ^{31}P NMR (CD_2Cl_2): $\delta = 33.68$; ^1H NMR (CD_2Cl_2): $\delta = 7.46$ – 7.63 (m, 15H,

Ph), 1.27–2.98 (m, 33H, Cy), -10.00 (s, 1H, $\mu\text{-H}$). ^{13}C NMR (CD_2Cl_2): $\delta = 223.22$, 222.09, 218.00 (Mn–CO), 197.38, 196.44, 197.38 (Re–CO), 182.44 (P–C=CS), 118.09 (P–C=CS), 138.45, 136.62, 131.17, 129.75 (Ph), 33.32, 27.90, 27.49, 25.84 (Cy).

3.8. $[\text{MnRe}(\text{CO})_6(\mu\text{-H})\{\mu\text{-S}(\text{SSnCy}_3)\text{C}=\text{C}(\text{PCy}_3)\text{S}\}]$ (**4f**)

Compound **4f** was prepared as described above for compound **4**, from a solution of **3b** and Cy_3SnCl (1.0 mmol). The workup was as described for **4d** to afford compound **4f**. Yield: 0.065 g, 55%. Anal. Calc. for $\text{C}_{44}\text{H}_{67}\text{MnO}_6\text{PReS}_3\text{Sn}$: C, 44.74; H, 5.72. Found: C, 44.79; H, 5.76%. IR (KBr), $\nu(\text{CO})$: 2023 s, 1995 vs, 1908 (br). ^{31}P NMR (CDCl_3): $\delta = 33.78$; ^1H NMR (CDCl_3): $\delta = 2.90$ – 1.10 (m, 66H, Cy), -7.85 (s, 1H, $\mu\text{-H}$).

3.9. $[\text{MnRe}(\text{CO})_6(\mu\text{-H})\{\mu\text{-S}(\text{SAuPPh}_3)\text{C}=\text{C}(\text{PCy}_3)\text{S}\}]$ (**4g**)

Compound **4g** was prepared as described above for compound **4a**, from a solution of **3b** (0.1 mmol) and Ph_3PAuCl (1.0 mmol). The workup was as described for **4d** to afford compound **4g**. Yield: 0.088 g, 69%. Anal. Calc. for $\text{C}_{44}\text{H}_{49}\text{AuMnO}_6\text{P}_2\text{ReS}_3$: C, 41.61, H, 3.89. Found: C, 41.47; H, 3.77. IR (THF), $\nu(\text{CO})$: 2022 m, 1996 vs, 1922 s, 1910 s, 1890 (sh). ^{31}P NMR (CD_2Cl_2): $\delta = 37.13$ (PPh₃), 35.17 (PCy₃). ^1H NMR (CD_2Cl_2): $\delta = 7.59$ – 7.66 (m, 15H, Ph), 3.25 (m, 3H, *CH* of Cy), 2.90–1.28 (30H, CH_2 of Cy), -8.47 (s, 1H, $\mu\text{-H}$). ^{13}C NMR (CD_2Cl_2): 223.58, 221.93, 218.71 (Mn–CO), 198.12, 197.73, 193.52 (Re–CO), 192.57 [d(10), P–C=CS], 134.90 [d(14), $\text{C}^{2,6}$ of Ph], 132.95 [d(3), C^4 of Ph], 130.38 [d(12), $\text{C}^{3,5}$ of Ph], 130.07 [d(59), C^1 of Ph], 115.06 [d(74), P–C=CS], 33.75 [d(43), C^1 of Cy], 28.16 [d(4), $\text{C}^{2,6}$ of Cy], 27.76 [d(13), $\text{C}^{3,5}$ of Cy], 26.18 [C^4 of Cy].

3.10. $[\text{MnRe}(\text{CO})_6(\mu\text{-H})\{\mu\text{-S}(\text{SC}_3\text{H}_5)\text{C}=\text{C}(\text{PCy}_3)\text{S}\}]$ (**4h**)

Compound **4h** was prepared as described above for compound **4a**, from a solution of **3b** (0.1 mmol) and allyl bromide (1 ml, excess). Yield 0.047 g, 52%. Block-shaped single crystals suitable for X-ray diffraction were grown from CH_2Cl_2 /hexane (*V/V* = 1:5) at -20 °C. Anal. Calc. for $\text{C}_{29}\text{H}_{39}\text{MnO}_6\text{RePS}_3$: C, 40.89; H, 4.61. Found: C, 40.84; H, 4.05%. UV–Vis(CHCl_3): $\lambda_{\text{max}} = 262$, 242 nm. IR (THF), $\nu(\text{CO})$: 2025 m, 1990 vs, 1926 s, 1916 s, 1904 s, cm^{-1} . ^{31}P NMR (CDCl_3): $\delta = 33.78$; ^1H NMR (CDCl_3): $\delta = 5.90$ – 5.75 [m, 1H, $\text{CH}=\text{CH}_2$], 5.35–5.18 [m, 2H, $\text{C}=\text{CH}_2$], 3.71 [d(9), 2H, $\text{CH}_2\text{CH}=\text{CH}_2$], 2.98 [m, 3H, *CH* of Cy], 1.86–1.37 [m, 30H, CH_2 of Cy], -7.62 [s, 1H, $\mu\text{-H}$]. ^{13}C NMR (CDCl_3): 223.05, 222.03, 218.61 (Mn–CO); 196.71, 196.39, 192.54 (Re–CO), 185.10 (P–C=CS), 120.50

(PC=CS), 132.14 (CH₂CH=CH₂), 120.59 (CH₂CH=CH₂), 40.14 (S-CH₂CH=CH₂), 33.38, 27.70, 27.23, 24.18 (C₆H₁₁).

3.11. [MnRe(CO)₆(μ-H){μ-S(SCH₂C≡CH)C=C(PCy₃)-S}] (**4i**)

Compound **4i** was prepared as described above for compound **4a**, from a solution of **3b** (0.1 mmol) and ClCH₂C≡CH (1.0 mmol). Yield: 0.066 g, 78%. Anal. Calc. for C₂₉H₃₇MnO₆PrReS₃: C, 40.98; H, 4.39. Found: C, 40.70; H, 4.46%. IR (THF), ν(CO): 2026 m, 2000 vs, 1925 s, 1917 (sh), 1906 s. ³¹P NMR (CD₂Cl₂): δ = 34.33. ¹H NMR (CD₂Cl₂): 2.91 (m, 3H, CH of Cy), 3.92 [d(3), 2H, CHC=CH₂], 2.40 [t(3), 1H, CHC=CH₂], 2.01–1.34 (m, 30H, CH₂ of Cy), -7.53(s, 1H, μ-H). ¹³C NMR(CD₂Cl₂): δ = 222.30, 218.21, 207.48 (Mn-CO), 196.44, 196.11, 192.21 (Re-CO), 183.20 [d(8), P-C=CS], 126.90 [d(66), PC=CS], 77.28 and 74.16 (C≡CH), 32.80 [d(42), C¹ of Cy], 27.43 [s(br), C^{2,6} of Cy], 27.15 [d(13), C^{3,5} of Cy], 25.37 [C⁴ of Cy], 24.92 (SCH₂C≡).

3.12. [Re₂(CO)₆(μ-H){μ-S(SMe)C=C(PCy₃)S}] (**4j**)

To the solution of anion **3c** (prepared from 0.1 mmol compound **1c** as described above) was added excess methyl iodide, and the mixture was stirred for 2h. The workup was as described for **4a**, to afford **4j** as a yellow microcrystalline solid. Yield 0.062 g, 65%, (based on starting compound **1c**). Anal. Calc. for C₂₇H₃₇O₆PrRe₂S₃: C, 33.38; H, 3.90. Found: C, 33.65; H, 3.82%. IR (THF), ν(CO): 2029 s, 2004 vs, 1919 s, 1911 s. ³¹P NMR (CD₂Cl₂): δ = 34.30. ¹H NMR (CD₂Cl₂): 2.52 (s, 3H, SCH₃), 2.42–1.20 (m, 33H, Cy), -7.71(s, 1H, μ-H); ¹³C NMR (CD₂Cl₂): 195.26, 189.15 (Re-CO), 184.32 [d(9), P-C=CS], 125.17 [d(67), PC=CS], 33.53 [d(41), C¹ of Cy], 28.13 [d(2), C^{2,6} of Cy], 27.72 [d(12), C^{3,5} of Cy], 25.97 [C⁴ of Cy], 19.99 (SCH₃).

3.13. [Re₂(CO)₆(μ-H){μ-S(SCH₂C≡CH)C=C(P-Cy₃)-S}] (**4k**)

Compound **4k** was prepared as described above from a solution of **3c** (0.1 mmol) and ClCH₂C≡CH (1 ml, excess). Yield: 0.067 g, 68%. Anal. Calc. for C₂₉H₃₇O₆PrRe₂S₃: C, 35.50; H, 3.80. Found: C, 35.21; H, 3.70%. IR (THF), ν(CO): 2029 m, 2005 vs, 1917 s. ³¹P NMR (CD₂Cl₂): δ = 34.73. ¹H NMR (CD₂Cl₂): δ = 4.10 [d(3), SCH₂C≡], 3.39 (m, 3H, CH of Cy), 2.97 [t(3), 1H, C≡CH], 2.12–1.45 (m, 30H, CH₂ of Cy), -7.95(s, 1H, μ-H). ¹³C NMR(CD₂Cl₂): δ = 195.45, 189.11 (Re-CO), 181.30 [d(7), P-C=CS], 128.39 [d(64), PC=CS], 77.49 and 75.71 (C≡CH), 33.21 [d(41), C¹ of Cy], 28.03 [d(3), C^{2,6} of Cy], 27.66 [d(13), C^{3,5} of Cy], 26.03 [C⁴ of Cy], 25.44 (SCH₂C≡).

3.14. X-ray crystallography

Crystals suitable for diffraction studies were grown by slow diffusion of hexane into dichloromethane solutions of **4d** and **4h** at -20 °C. Data for were collected on a Bruker Smart 1000 CCD diffractometer (graphite-monochromatized Mo Kα radiation, λ = 0.71073 Å). Raw frame data were integrated with SAINT [11]. The structures were solved by direct methods with SHELXTL [12]. A semi-empirical absorption correction was applied with SADABS [13]. Crystallographic data and experimental details for both structures are summarized in Table 1.

4. Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 220315 (compound **4d**) and 220316 (compound **4h**). Copies of the data may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or [www: http://www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk)).

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References

- [1] T. Kondo, T. Mitsudo, Chem. Rev. 100 (2000) 3205.
- [2] (a) C. Bianchini, A. Meli, Acc. Chem. Res. 31 (1998) 109; (b) K.E. Janak, J.M. Tanski, D.G. Churchill, G. Parkin, J. Am. Chem. Soc. 124 (2002) 4182; (c) D.A. Vasic, W.D. Jones, Organometallics 16 (1997) 1912; (d) P.J. Lim, V.C. Cook, C.J. Doonan, C.G. Young, E.R.T. Tiekink, Organometallics 19 (2000) 5643.
- [3] (a) E.J. Lyon, I.P. Georgakaki, J.H. Reibenspies, M.Y. Darensbourg, Angew. Chem. Int. Ed. 38 (1999) 3178; (b) V.E. Kaasjager, R.K. Henderson, E. Bowman, M. Lutz, A.L. Spek, J. Reedijk, Angew. Chem. Int. Ed. 37 (1998) 1668.
- [4] A. Galindo, D. Miguel, J. Pérez, Coord. Chem. Rev. 193–195 (1999) 643.
- [5] J. Li, D. Miguel, M.D. Morales, V. Riera, S. García-Granda, Organometallics 17 (1998) 3448.
- [6] D. Miguel, J. Li, D. Morales, V. Riera, S. García-Granda, Organometallics 20 (2001) 3063.
- [7] B. Alvarez, S. García-Granda, Y. Jeannin, D. Miguel, J.A. Miguel, V. Riera, Organometallics 10 (1991) 3005.

- [8] B. Alvarez, S. García-Granda, J. Li, D. Miguel, V. Riera, *Organometallics* 13 (1994) 16.
- [9] (a) Mn–Mn: D. Miguel, V. Riera, J.A. Miguel, M. Gómez, X. Soláns, *Organometallics* 10 (1991) 1683;
(b) Mn–Re: B. Alvarez, D. Miguel, V. Riera, J.A. Miguel, S. García-Granda, *Organometallics* 10 (1991) 384;
(c) Re–Re: B. Alvarez, J. Li, D. Miguel, M.D. Morales, V. Riera, S. García-Granda, *Chem. Ber.* 130 (1997) 1507.
- [10] R.L. Ingham, S.D. Rosenberg, H. Gilman, *Chem. Rev.* 60(1960)459.
- [11] SAINT+. SAX area detector integration program. Version 6.02. Bruker AXS, Madison, WI, 1999.
- [12] G.M. Sheldrick, *SHELXL*, An Integrated System for Solving, Refining, and Displaying Crystal Structures from diffraction Data. Version 5.1, Bruker AXS, Madison, WI, 1999.
- [13] G.M. Sheldrick, *SADABS*, Empirical Absorption Correction Program, University of Göttingen, Göttingen, Germany, 1977.