Desulfurization and C—C Coupling in the Reaction of the Anions $[MnM(CO)_6(\mu\text{-}H)(\mu\text{-}S_2CPCy_3)]^-$ (M = Mn, Re) with Carbon Disulfide. X-ray Structure of $[Li(THF)_3][Mn_2(CO)_6(\mu\text{-}H)\{\mu\text{-}S(S)C{=}C(PCy_3)S\}]$

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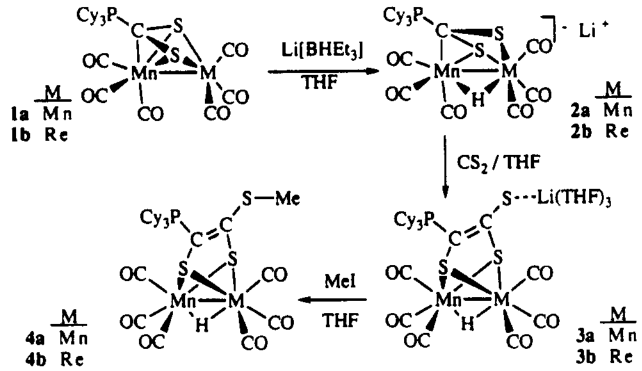
Summary: The anions $[MnM(CO)_6(\mu\text{-}H)(\mu\text{-}S_2CPCy_3)]^-$ (M = Mn, Re) react with CS_2 to afford the new anionic species $[MnM(CO)_6(\mu\text{-}H)\{\mu\text{-}S(S)C{=}C(PCy_3)S\}]^-$, containing the new (tricyclohexylphosphonio)ethenetrithiolate ligand $S(S)C{=}C(PCy_3)S$. This results from a complex pathway which involves formally the desulfurization of CS_2 and the insertion of CS into a C—S bond of the S_2CPCy_3 ligand on the parent anion, with formation of a carbon–carbon double bond.

The activation of CS_2 and the chemistry of transition-metal complexes with sulfur ligands are topics of continuing interest in several fields.[2] Particularly, metal dithiolene complexes have received much attention due to their unusual properties and their practical applications.[3] Herein we report that binuclear hydridocarbonylmetal anions which contain S_2CPR_3 ligands react with carbon disulfide to afford anionic or neutral (after reaction with MeI) complexes in which the new species (*trialkylphosphonio)ethenetrithiolate*, $S(S)C{=}C(PR_3)S$, or its methyl derivative, $S(MeS)C{=}C(PR_3)S$, are produced through a process which involves desulfurization of CS_2 and carbon–carbon coupling.

We have recently shown that the complexes $[Mn_2(CO)_6(\mu\text{-}S_2CPR_3)]$ (**1a**) undergo hydride attack at the metal–metal bond, producing anionic complexes (**2a** in Scheme 1) which can be alkylated at one of the sulfur atoms, to afford neutral hydrido compounds which contain phosphoniodithioformate esters as bridging ligands.[4] The heteronuclear compound $[MnRe(CO)_6(\mu\text{-}S_2CPCy_3)]$ (**1b**)[5] behaves similarly, giving the anion **2b**, which can be crystallized as the tetraethylammonium salt. An X-ray analysis has confirmed the structure proposed[4] for the dimanganese analogue.

Anions **2a,b** react with excess CS_2 to give new anionic complexes with the formula $[Li(THF)_3][MnM(CO)_6(\mu\text{-}H)\{\mu\text{-}S(S)C{=}C(PCy_3)S\}]$ (M = Mn, **3a**; M = Re, **3b**), which can be isolated as red crystals from THF/hexane mixtures.[6] From an X-ray determination,[7] the solid-state structure of compound **3a** can be described as a strongly associated ion pair, closer to a covalent molecule[8] than to a saltlike species (Figure 1). The lithium atom lies in a distorted-tetrahedral environment, surrounded by three oxygen atoms of the THF ligands (average Li—O distance 1.96(2) Å) and by a sulfur atom (S(3)—Li = 2.41(1) Å). The anionic part of the molecule can be described as consisting of a $(OC)_3Mn—Mn(CO)_3$ unit bridged, on opposite sides, by a hydride and the new ligand $S(S)C{=}C(PCy_3)S$, which is formulated as (tricyclohexylphosphonio)ethenetrithiolate on the basis of the C—C and C—S distances (see caption

Scheme 1[a]



[a] **2a,b** and **3a,b** are defined as being the anionic parts of the salts.

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(6) 1 (0.15 mmol) and $Li[BHEt_3]$ (molar ratio 1:4) were made to react in THF at 0 °C to obtain a solution of **2** (4 h for **2a**, 2 h for **2b**). Water (0.1 mL) and CS_2 (1 mL, excess) were then added, and the solution was stirred for 2 h. After filtration, addition of hexane and slow concentration in vacuo gave complexes **3** as red microcrystals (isolated yield 55–65%).

(7) Crystal Data for **3a**: $C_{38}H_{58}LiMn_2O_9PS_3$, M_r = 902.84, triclinic, space group $P\bar{1}$, a = 10.817(2) Å, b = 11.546(2) Å, c = 20.075(3) Å, α = 75.80(1)°, β = 74.79(1)°, γ = 75.22(2)°, V = 2296.0(7) Å^3, D_c = 1.30 g cm^{-3}, Z = 2, $F(000)$ = 948, $\lambda(Mo\ K\alpha)$ = 0.710 73 Å, $\mu(Mo\ K\alpha)$ = 7 .34 cm^{-1}, room temperature, yellow prismatic crystal (0.2 × 0.17 × 0.17 mm), 8323 reflections measured ($1 \le \theta \le 25°$), 3057 used in refinement ($I \ge 3\sigma(I)$), heavy atoms located from a Patterson synthesis, remaining non-H atoms from DIRDIF.[14] Full-matrix least-squares refinement was carried out with SHELX76.[15] After isotropic refinement, a semiempirical absorption correction was applied with DIFABS[16] (maximum 1.173, minimum 0.723). All non-H atoms were refined anisotropically. The bridging hydride was found from a Fourier-difference map and refined with a fixed isotropic temperature factor of 0.08 Å^2. The remaining H atoms in the anion were geometrically positioned, with an overall isotropic temperature factor which was refined. The hydrogen atoms of THF ligands were geometrically positioned with a common isotropic temperature factor which was fixed to 0.12 Å^2. The final cycles of refinement were conducted with the weighting scheme $[\sigma^2(F) + 0.0002F^2]^{-1}$: number of parameters 492, final R 0.046 (R_w 0.043).

(8) Conductivity measurements indicate that **3a** behaves as a 1:1 electrolyte in acetone. This suggests that the Li—S interaction is cleaved in solution.

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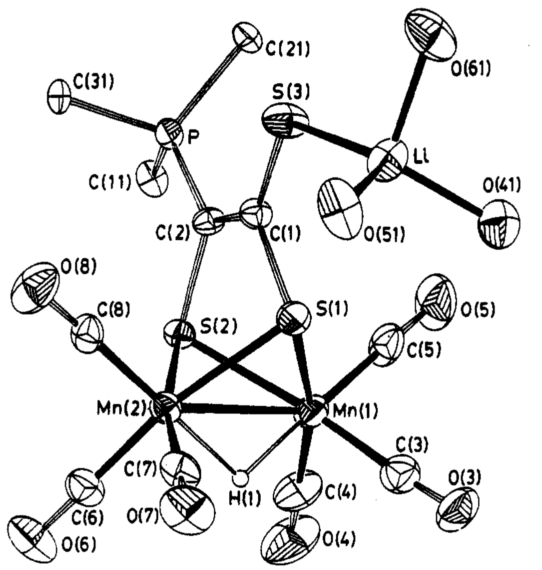

Figure 1. Perspective view (EUCLID package)[17] of [Li(THF)$_3$][Mn$_2$(CO)$_6$(μ-H){μ-S(S)C=C(PCy$_3$)S}] ([Li(THF)$_3$]-**3a**) showing the atom numbering. Methylene groups of cyclohexyl and THF rings have been omitted for clarity. Selected bond distances (Å) and angles (deg): Mn(1)–Mn(2) = 2.651(2), Mn(1)–S(1) = 2.340(2), Mn(1)–S(2) = 2.324(2), Mn(2)–S(1) = 2.336(2), Mn(2)–S(2) = 2.342(2), C(1)–C(2) = 1.336(8), C(1)–S(1) = 1.810(6), C(1)–S(3) = 1.720(7), C(2)–S(2) = 1.807(6), S(3)–Li = 2.41(1); S(2)–Mn(1)–S(1) = 77.6(1), S(2)–Mn(2)–S(1) = 77.4(1), S(1)–C(1)–C(2) = 115.5(5), S(3)–C(1)–C(2) = 130.7(5), S(2)–C(2)–C(1) = 116.3(5), P–C(2)–C(1) = 127.3(5), S(1)–C(1)–S(3) = 113.7(4), P–C(2)–S(2) = 116.3(4); Mn–C(carbonyl) distances range from 1.773(9) to 1.806(9); C(carbonyl)–Mn–C(carbonyl) angles range from 89.9(4) to 95.6(4).

to Figure 1). The grouping S$_2$C=C(S)P forms a fairly planar arrangement, and the two Mn(CO)$_3$ fragments are symmetrically placed at both sides of the plane of the ligand.

Anions **3a,b** readily react with methyl iodide, affording the neutral derivatives **4a,b**.[9] Their analytical and spectroscopic data[10] are consistent with the structure proposed in Scheme 1, the entering methyl group being attached to the sulfur atom not bonded to the metals. The signals of the central carbons of the trithiolate ligand in the ^{13}C{^{1}H} NMR spectra of **4a,b** appear in the region expected for ethylenic carbons and can be easily assigned on the basis of the values of the P—C coupling constants.[10] The overall process leading to the formation of the S(S)C=C(PCy$_3$)S ligand in the reaction of **2a,b** with CS$_2$ involves (formally) the desulfurization of CS$_2$ and the insertion of the resulting CS fragment into a C—S or into the C—P bond of the coordinated S$_2$CPR$_3$ ligand in the starting anion **2**, with formation of a carbon—carbon double bond. To obtain additional information, the anion **2a** was made to react with CS$_2$ enriched in ^{13}C (50%), and the resulting anion **3a*** was methylated to obtain the derivative **4a***. Its ^{13}C{^{1}H} NMR spectrum showed an increase of the signal corresponding to the carbon bonded to two sulfur atoms and no significant increase of the signal of the carbon bonded to phosphorus, thus supporting the pathway which involves the formal insertion of thiocarbonyl into a C—S (and not into the P—C) bond of **2a**. This, however, should be taken as an overall, simplified description of a very complex mechanism which, most probably, proceeds through several steps with ionic intermediates. In fact, ^{31}P NMR monitoring of the reaction of **2b** (NEt$_4$ salt) with CS$_2$ shows the formation of, at least, three intermediates which are sequentially transformed to give the final product. Some work is now in progress, in an attempt to gather more information about the mechanism of the reaction.

In spite of the wide variety of organic synthetic reactions in which carbon disulfide has been used to produce carbon–carbon and carbon–heteroatom bonds,[11] we have found no report of the preparation of phosphonioethenetrithiolate either as a free species or as a group coordinated to metals. The closest precedent for the trithiolate ligand in **3a** can be found in a few reported examples of ethenetetrathiolate ligands formed through dimerization of CS$_2$[12] and in one example of diarylethenedithiolate formed through dimerization of thioacyl ligands.[13]

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Supplementary Material Available: Tables of positional and thermal parameters and bond lengths and angles for the structure of **3a** (6 pages). Ordering information is given on any current masthead page.

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(9) To a solution of anion **3** (ca. 0.1 mmol, prepared as in ref 6) was added CH$_3$I (1 mL, excess), and the mixture was stirred for 1 h. Solvents were evaporated in vacuo, and the residue was taken up in CH$_2$Cl$_2$/hexane (1:1) and filtered through alumina (activity III). Slow concentration of the filtrate yielded microcrystals of the neutral derivatives **4** (isolated yields 50–65% based on starting **1**).

(10) Selected spectroscopic data are as follows. IR spectra (cm^{-1}) are taken from THF solutions. ^{31}P{^{1}H} (121.5 MHz), ^{1}H (300 MHz), and ^{13}C{^{1}H} NMR (75.5 MHz) are taken from acetone-d_6 solutions. **2b**: ν(CO) 1993 s, 1959 s, 1880 vs, 1845 m; ^{1}H NMR δ –11.36 (s, 1H, μ-*H*). Anal. Calcd for C$_{33}$H$_{54}$MnO$_6$PReS$_2$: C, 44.19; H, 6.07; N, 1.56. Found: C, 43.90; H, 6.15; N, 1.63. **3a**: ν(CO) 2006 m, 1977 s, 1900 vs; ^{31}P{^{1}H} NMR δ 32.21; ^{1}H NMR δ –9.84 (s, 1H, μ-*H*). **3b**: ν(CO) 2012 m, 1986 s, 1903 vs; ^{31}P{^{1}H} NMR δ 32.40; ^{1}H NMR δ –9.10 (s, 1H, μ-*H*). **4a**: ν(CO) 2023 s, 1995 vs, 1921 (sh); ^{1}H NMR δ 2.56 (s, 3H, SC*H*$_3$), –8.21 (s, 1H, μ-*H*); ^{31}P{^{1}H} NMR δ 33.69; ^{13}C{^{1}H} NMR δ 189.3 (d (9 Hz), P—C=*C*), 128.9 [d (61 Hz), P—*C*=C), 19.8 (s, S*C*H$_3$). Anal. Calcd for C$_{27}$H$_{37}$Mn$_2$O$_6$PS$_3$: C, 46.69; H, 5.37. Found: C, 46.31; H, 5.43. **4b**: ν(CO) 2027 s, 2001 vs, 1915 (sh); ^{1}H NMR δ 2.57 (s, 3H, SC*H*$_3$), –7.73 (s, 1H, μ-*H*); ^{31}P{^{1}H} NMR δ 34.43; ^{13}C{^{1}H} NMR δ 186.2 (d (9 Hz), P—C=*C*), 124.7 (d (67 Hz), P—*C*=C), 19.8 (s, S*C*H$_3$). Anal. Calcd for C$_{27}$H$_{37}$MnO$_6$PReS$_3$: C, 39.27; H, 4.51. Found: C, 39.57; H, 5.51.

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