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Synthesis and Structure of $[(CO)_4Mn\{(PPh_2)_2C{-}S_6{-}C(PPh_2)_2\}Mn(CO)_4]$: A Unique Tetraphosphinobis(methanide) Complex of Manganese(I) with a Hexasulfur Bridge

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*Summary: Nucleophilic degradation of cyclo-octasulfur by the diphosphinomethanide derivative $[Mn(CO)_4\{(PPh_2)_2CH\}]$ (**2**) yields $[(CO)_4Mn\{(PPh_2)_2C{-}S_6{-}C(PPh_2)_2\}Mn(CO)_4]$ (**3**), a complex containing the first example of a hexasulfur-bridged tetraphosphinobis(methanide) ligand. In the molecular structure of **3**, determined by a single-crystal X-ray structural analysis, the conformation of the C−S_6−C chain may be regarded as arising from an opened S_6 ring, with terminal groups attached in trans positions.*

During the past 2 decades, a lot of metal complexes containing diphosphinomethanide ligands have been prepared. Examples are known for a great amount of both transition and main group metals of the periodic table, and a variety of coordination modes have been described for these ligands.[1] With regard to the reactivity of coordinated diphosphinomethanides, much of the work has concentrated upon the synthesis of heterometallic species,[2] taking advantage of the ability of these groups to act as tridentate ligands through the two phosphorus atoms and the central carbon atom. However, it is surprising that, apart from the alkylation and acylation reactions,[3] very little is known about the reactivity of coordinated diphosphinomethanides with other non-metallic electrophilic agents. These reactions are of interest because they can lead to functionalization at the central carbon atom of the diphosphine giving access to an unexplored chemistry involving metal−assisted synthesis of more sophisticated diphosphines.

In relation with this, we have recently reported that the treatment of $[Mn(CO)_4\{(PPh_2)_2CH\}]$ (**2**) with halogens produces several coordinated C-halogenated diphosphine and diphosphinomethanide ligands of general formulas $(PPh_2)_2CH(X)$, $(PPh_2)_2CX_2$, and $[(PPh_2)_2CX]^-$ (X = Br, I).[4]

Now we have found that sulfurization of **2** with *cyclo*-octasulfur allows a S_6 bridge to be introduced between two molecules of **2**. Thus, in the treatment of a dichloromethane solution of **2** with sulfur at room temperature a mixture of $[Mn(CO)_4(dppm)]^+$ (**1**) and the new hexasulfur-linked tetraphosphinobis(methanide) complex $[(CO)_4Mn\{(PPh_2)_2C{-}S_6{-}C(PPh_2)_2\}Mn(CO)_4]$ (**3**) was formed in a ratio of approximately 2:1 (from ^{31}P NMR data) (see Scheme 1).[5] This ratio is essentially independent of the amount of sulfur added going from 2 to 20 equiv of S. This result can be tentatively explained assuming the formation in a first step of the intermediate $[(CO)_4Mn\{(PPh_2)_2C(H){-}S_6{-}C(H)(PPh_2)_2\}Mn(CO)_4]^{2+}(S_2)^{2-}$ (**4**(S_2)), arising from a nucleophilic degradation of S_8, for which the $P_2C(H)S_6(H)CP_2$ protons should have an enhanced acidic character, because of the electronegativity of sulfur, and could easily be transferred to **2** to give the final observed mixture. Supporting the proposed reaction pathway, the cationic complex **4** was prepared in a independent experiment by protonating **3** with HBF_4.[6] This process can be easily reversed by treatment of **4** with KOH. The analytical and spectroscopic data are in accordance with the

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(1) Selected articles: Karsch, H. H.; Appelt, A.; Riede, J.; Müller, G. *Organometallics* **1987**, *6*, 316. Karsch, H. H.; Deubelly, B.; Riede, J.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 673. Karsch, H. H.; Deubelly, B.; Riede, J.; Müller, G. *Ibid.* **1987**, *26*, 674. Balch, A. L.; Oram, D. E. *Inorg. Chem.* **1987**, *26*, 1906. Sharp, P. R.; Wen Ge, Y. *J. Am. Chem. Soc.* **1987**, *109*, 3797. Dawkins, G. M.; Green, M.; Jeffery, J. C.; Sambale, C.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1983**, 499. Karsch, H. H.; Appelt, A.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 823. Karsch, H. H.; Keller, U.; Gamper, S.; Müller, G. *Ibid.* **1990**, *29*, 295. Karsch, H. H.; Ferazin, G.; Steigelmann, O.; Kooijman, H.; Hiller, W. *Ibid.* **1993**, *32*, 1739. Karsch, H. H.; Graurogl, G.; Kawecki, M.; Bissinger, P.; Kumberger, O.; Schier, A.; Müller, G. *Organometallics* **1994**, *13*, 610. Karsch, H. H.; Ferazin, G.; Bissinger, P. *J. Chem. Soc., Chem. Commun.* **1994**, 505. Hao, S.; Song, J.; Aghabozorg, H.; Gambarotta, S. *Ibid.* **1994**, 157.

(2) Laguna, A.; Laguna, M. *J. Organomet. Chem.* **1990**, *394*, 743. Ruiz, J.; Riera, V.; Vivanco, M.; García-Granda, S.; García-Fernández, S. *Organometallics* **1992**, *11*, 4077. Ruiz, J.; Araúz, R.; Riera, V.; Vivanco, M.; García-Granda, S.; Pérez-Carreño, E. *J. Chem. Soc., Chem. Commun.* **1993**, *9*, 740. Fernández, E. J.; Gimeno, M. C.; Jones, P. G.; Laguna, A.; Laguna, M.; López-de-Luzuriaga, J. M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 87.

(3) Al-Jibori, S.; Shaw, B. L. *Inorg. Chim. Acta* **1983**, *74*, 235. Al-Jibori, S.; Hall, M.; Hutton, A. T.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1984**, 863.

(4) Ruiz, J.; Araúz, R.; Riera, V.; Vivanco, M.; García-Granda, S.; Menéndez-Velázquez, A. *Organometallics* **1994**, *13*, 4162.

(5) Preparation of **3**: A solution of $[Mn(CO)_4\{(Ph_2P)_2CH\}]$ (**2**) (200 mg, 0.36 mmol) in 25 mL of dichloromethane was added dropwise to 29 mg of S_8 (0.11 mmol) at room temperature with continuous stirring. When the addition was finished (about 15 min), two products were observed by infrared spectroscopy, namely, $[Mn(CO)_4\{(Ph_2P)_2CH_2\}]^+$ and **3**. The resultant yellow solution was evaporated to dryness and the remaining solid chromatographed through an alumina column (activity III, deactivated by appropriate addition of water under nitrogen to the commercial material). Elution with dichloromethane/hexane (1:2 v/v) gave the desired product (94 mg, 40% yield) as a yellow solid. Recrystallization of product by diffusion of hexane into dichloromethane gave yellow crystals suitable for X-ray diffraction studies. Anal. Calcd for $C_{58}H_{40}Mn_2O_8P_4S_6$: C, 53.96; H, 3.12. Found: C, 54.19; H, 3.34. Spectroscopic data for **3**: IR (CH_2Cl_2) ν(CO) 2074 (s), 2000 (sh), 1992 (s), 1968 (s) cm^{-1}; ^{31}P NMR (CD_2Cl_2) δ 24 ppm (s, broad).

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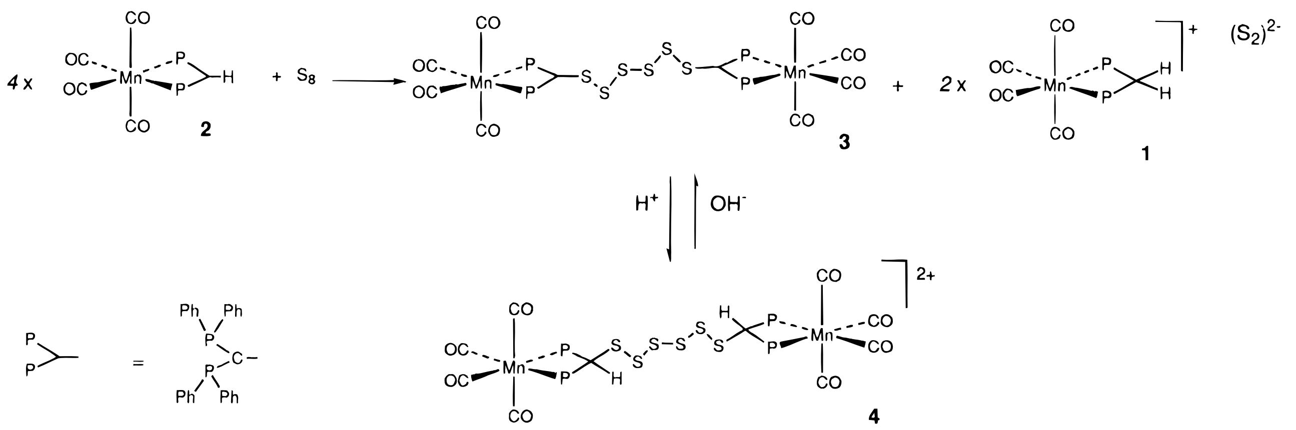
Scheme 1



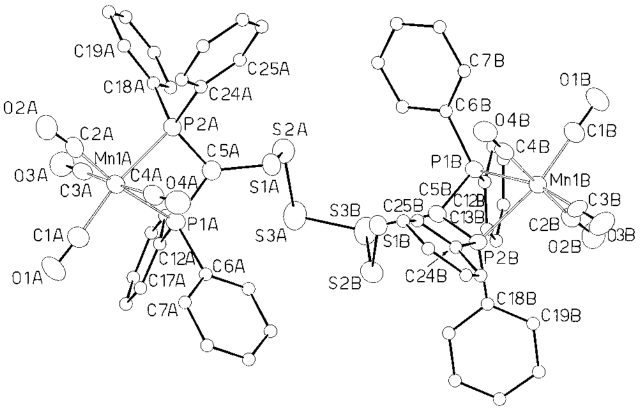


Figure 1. View of the molecular structure of the **3** together with the atomic numbering system. Selected bond distances (Å): S(1A)−S(2A) 2.113(4), S(2A)−S(3A) 2.054(5), S(3A)−S(3B) 2.054(4), S(2B)−S(3B) 2.053(4), S(1B)−S(2B) 2.113(4), S(1A)−C(5A) 1.718(8), S(1B)−C(5B) 1.717(7), P(1A)−C(5A) 1.760(8), P(2A)−C(5A) 1.750(9), Mn(1A)−P(1A) 2.347(3), Mn(1A)−P(2A) 2.339(2), P(1B)−C(5B) 1.758(8), P(2B)−C(5B) 1.761(8), Mn(1B)−P(1B) 2.339(3), Mn(1B)−P(2B) 2.355(3).

structure proposed for **4** in Scheme 1.[6] However, its ^{1}H NMR spectrum is rather puzzling because the P_2CH protons appear as an asymmetric quartet at about δ 6, as a consequence of the superposition of two triplets ($^2J_{PH} = 11$ Hz) of different intensity. This result can be explained by the presence of two isomers of **4**, which arise from the relative disposition of the S_6 chain with respect to the two P_2CH protons.

In order to gain light about the structural disposition of the S_6 bridge in the new ligands, the structure of **3** was fully elucidated by an X-ray diffraction analysis.[7] The complex, shown in Figure 1, has an approximate C_2 symmetry so that the two halves labeled as A and B are strictly comparable. The S_6 unit bridges two diphosphinomethanides in which each couple of P atoms chelates a Mn atom completing its octahedral coordination through four carbon atoms from terminal carbonyls. The torsion angles along the eight-membered $C-S_6-C$ chain are in the range 84.8(2)−93.8(2)°, the signs of the angles being $- - + - -$ or $+ + - + +$ for the two enantiomers present in the crystals. This conformation may be regarded as arising from an opened S_6 ring, with terminal groups attached in trans positions. The terminal S−S bond lengths are longer than the internal ones. There is a short separation between the S(1A) and S(1B) atoms of 3.506(3) Å. The conformation of the $C-S_6-C$ chain in **3** is similar to that found in the crystal structure of bis(piperidinothiocarbonyl)hexasulfane where, however, the short S···S contact was longer, 3.911(2) Å.[9]

To summarize this work, we have shown that the process of sulfurization of coordinated bis(diphenylphosphino)methanide provides access to a new class of hexasulfur-bridged tetraphosphine and tetraphosphinobis(methanide) ligands.

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Supporting Information Available: Tables giving crystal data, atomic coordinates and *U* values, anisotropic thermal parameters, and interatomic distances and angles for **3** (11 pages). Ordering information is given on any current masthead page.

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(6) Preparation of **4**$(BF_4)_2$: To a dichloromethane solution (20 mL) of **3** (150 g, 0.116 mmol) was added 48 mL (0.28 mmol) of tetrafluoroboric acid−diethyl ether complex (85%) at room temperature with continuous stirring. The solution changes instantaneously from yellow to colorless. The solvent was then evaporated to dryness, and the residue was washed three times with diethyl ether (3 × 5 mL). The product was recrystallized from Cl_2CH_2/hexane (0.14 g, 80% yield). Anal. Calcd for $C_{58}H_{42}B_2F_8Mn_2O_8P_4S_6$: C, 47.50; H, 2.89. Found: C, 47.28; H, 2.71. Spectroscopic data for **4**$(BF_4)_2$: IR (CH_2Cl_2) ν(CO) 2096 (s), 2037 (m), 2014 (vs) cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 6.01 ppm (t, $^2J_{PH} = 11$ Hz), δ 6.05 ppm (t, $^2J_{PH} = 11$ Hz); ^{31}P NMR (CD_2Cl_2) $\delta = 44$ ppm (s, broad). A broad signal was also observed when the spectrum was recorded at low temperature (−85 °C). The broadening of this signal is due to the quadrupolar moment effect on manganese (^{55}Mn, $I = {}^5/_2$).

(7) Crystal data for **3**: $C_{58}H_{40}Mn_2O_8P_4S_6$, $M = 1291.08$, triclinic, space group $P\bar{1}$, $a = 13.445(2)$ Å, $b = 14.052(3)$ Å, $c = 16.369(4)$ Å, $\alpha = 85.34(1)°$, $\beta = 73.50(1)°$, $\gamma = 89.28(1)°$, $V = 2955(1)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.451$ g cm^{-3}, niobium-filtered Mo Kα radiation, $\lambda = 0.710\,73$ Å, μ(Mo Kα) = 8.00 cm^{-1}. The intensity data were collected on a Siemens AED diffractometer, using the $\theta - 2\theta$ scan technique at room temperature. A standard reflection was measured after 50 reflections; no decay was observed during the data collection. A total of 10 384 unique reflections were measured (with θ in the range 3−25°), and 4030, having $I > 2\sigma(I)$, were used in the refinement. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares procedures, with anisotropic thermal parameters in the last cycles of refinement for all the non-hydrogen atoms, excepting for the carbons of the phenyl rings. The hydrogen atoms were introduced in calculated positions and refined "riding" on the corresponding carbon atoms (with isotropic thermal parameters). The SHELX-76 and SHELXS-86 systems of computer programs were used.[8] The *R* and R_w values were 0.0542 and 0.0622, respectively. Atomic coordinates, thermal parameters, and a complete list of bond distances and angles can be obtained from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 21 EW, U.K., on quoting the full journal citation.

(8) Sheldrick, G. M. SHELX-76. Program for Crystal Structure Determination, University of Cambridge, U.K., 1976. Sheldrick, G. M. SHELXS-86. Program for Crystal Structure Solution, Universität Göttingen, 1986.

(9) Foss, O.; Maartmann-Moe, K. *Acta Chem. Scand.* **1986**, *A40*, 664.