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Article

Insertion of a Bis(phosphine)platinum Group into the S–S Bond of $Mn_2(CO)_7(\mu\text{-}S_2)$

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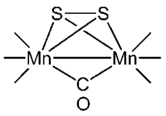
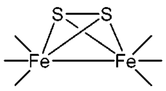
The reaction of $Mn_2(CO)_7(\mu\text{-}S_2)$, **1**, with $Pt(PPh_3)_2(PhC_2Ph)$ yielded the new complex, $Mn_2(CO)_6Pt(PPh_3)_2(\mu_3\text{-}S)_2$, **3**, by loss of CO and insertion of a $Pt(PPh_3)_2$ group into the S–S bond of **1**. Complex **3** was characterized crystallographically and was found to consist of an open Mn_2Pt cluster with one Mn–Mn bond, 2.8154(14) Å, one Mn–Pt bond, 2.9109(10) Å, and two triply bridging sulfido ligands. Compound **3** reacts with CO to form adduct $Mn_2(CO)_6(\mu\text{-}CO)Pt(PPh_3)_2(\mu_3\text{-}S)_2$, **4**. Compound **4** also contains an open Mn_2Pt cluster with two triply bridging sulfido ligands but has only one metal–metal bond, Mn–Mn = 2.638(2) Å. Under nitrogen, compound **4** readily loses CO and reverts back to **3**.

Introduction

We have recently reported the new manganese disulfide $Mn_2(CO)_7(\mu\text{-}S_2)$, **1**, obtained from the reaction of $Mn_2(CO)_9(NCMe)$ with thiirane.[1] Compound **1** is related to the well-known diiron disulfide, $Fe_2(CO)_6(\mu\text{-}S_2)$,[2] **2**, that was first reported by Hieber in 1958. Compound **2** has been extensively investigated over the years.[3−14]

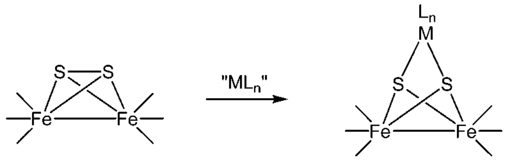


1



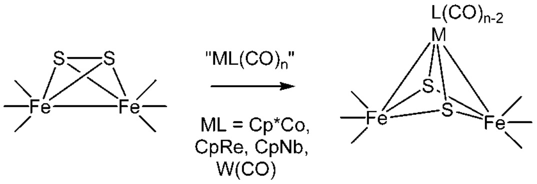
2

Most reactions of $Fe_2(CO)_6(\mu\text{-}S_2)$ with metal complexes occur at the disulfide group with insertion of a metal grouping into the S−S bond. For example, the reaction of **2** with certain low-valent palladium and platinum complexes yields the complexes $Fe_2(CO)_6Pd(PPh_3)_2(\mu_3\text{-}S)_2$ and $Fe_2(CO)_6Pt(PPh_3)_2(\mu_3\text{-}S)_2$ by insertion of the metal into a S−S bond of **2** (eq 1).[10−14]



(1)

By contrast, the reactions of **2** with $C_5Me_5Co(CO)_2$, $C_5H_5Re(CO)_3$, $C_5H_5Nb(CO)_4$, and $W(CO)_6$ yield products formed by insertion of a metal fragment into the S−S bond with formation of two new metal−metal bonds and cleavage of the Fe−Fe bond (eq 2).[11−13]



(2)

For comparison, we have now investigated the reaction of **1**

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10.1021/ic0110023 CCC: $22.00

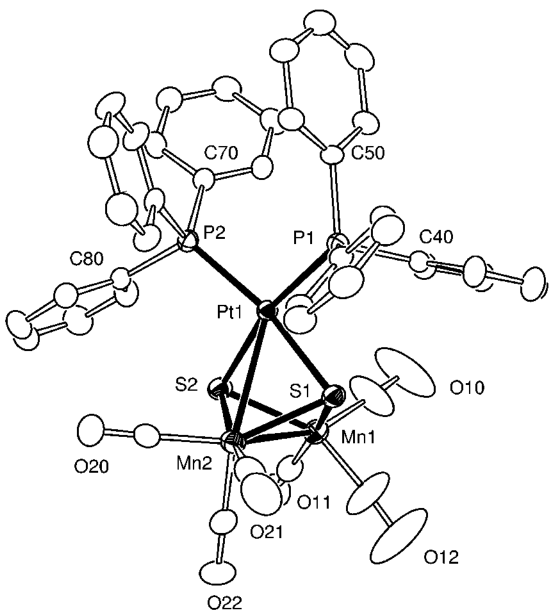

Figure 1. ORTEP diagram of $Mn_2(CO)_6Pt(PPh_3)_2(\mu_3\text{-}S)_2$, **3**, showing 30% probability thermal ellipsoids. Selected interatomic distances (Å) are Mn(1)−Mn(2) = 2.8154(14), Mn(1)−S(1) = 2.2821(19), Mn(1)−S(2) = 2.273(2), Mn(2)−S(1) = 2.2818(19), Mn(2)−S(2) = 2.291(2), Mn(2)−Pt(1) = 2.9109(10), Pt(1)−S(1) = 2.3443(16), Pt(1)−S(2) = 2.3333(15), Mn(1)···Pt(1) = 3.1608(10).

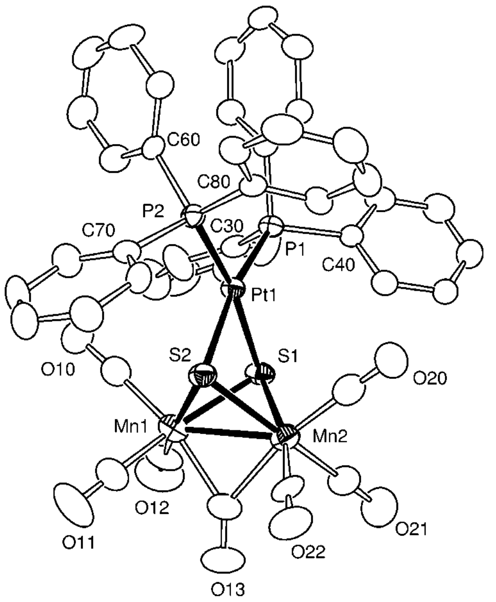

Figure 2. ORTEP diagram of $Mn_2(CO)_7Pt(PPh_3)_2(\mu_3\text{-}S)_2$, **4**, showing 30% probability thermal ellipsoids. Selected interatomic distances (Å) are Mn(1)−Mn(2) = 2.638(2), Mn(1)−S(1) = 2.336(3), Mn(1)−S(2) = 2.338(3), Mn(2)−S(1) = 2.340(3), Mn(2)−S(2) = 2.317(3), Pt(1)−S(1) = 2.346(2), Pt(1)−S(2) = 2.355(3), Mn(1)−C(13) = 2.037(14), Mn(2)−C(13) = 2.112(13), Mn(1)···Pt(1) = 3.3293(18), Mn(2)···Pt(1) = 3.3906(19).

with $Pt(PPh_3)_2(PhC_2Ph)$. The results of these studies are reported here.

Results

The reaction of **1** with $Pt(PPh_3)_2(PhC_2Ph)$ in CH_2Cl_2 produced the new green compound $Mn_2(CO)_6Pt(PPh_3)_2(\mu_3\text{-}S)_2$, **3**, in 38% yield in 3 h at 25 °C. Compound **3** was isolated by TLC by using a hexane/CH_2Cl_2 solvent mixture. The infrared spectrum of compound **3** shows three absorptions in the CO region that can be attributed to terminal CO ligands. The ^1H NMR spectrum exhibits multiple resonances at $\delta = 7.4-7.0$ that can be assigned to the phenyl group of the phosphine ligand. The $^{31}P\{^1H\}$ NMR spectrum of compound **3** exhibits a single resonance at 14.24 ppm with ^{195}Pt satellites ($J_{Pt-P} = 4316$ Hz). Details of the structure of **3** were established by a single-crystal X-ray diffraction analysis, and an ORTEP diagram of its molecular structure is shown in Figure 1. The structure of **3** contains an open $PtMn_2$ cluster with one Mn−Mn bond (2.8154(14) Å) and one Pt−Mn bond, Mn(2)−Pt(1) = 2.9109(10) Å. The Mn(1)−Pt(1) distance of 3.1608(1) Å is believed to be nonbonding. The Mn−Mn distance is considerably longer than that observed in $Mn_2(CO)_7(\mu\text{-}S_2)$, 2.6745(5) Å,[1] but is significantly shorter than that in $Mn_2(CO)_{10}$, 2.8950(6)[15a] and 2.9038(6) Å,[15b] which contains no bridging ligands. There are two triply bridging sulfido ligands. The four Mn−S bond distances, 2.273(2)−2.291(2) Å, are similar to those found for other sulfidomanganese carbonyl compounds.[1]

Solutions of **3** quickly turn red when purged with CO at 25 °C. Upon slow evaporation of the solvent by using a purge of CO, red crystals of new compound $Mn_2(CO)_6(\mu\text{-}CO)Pt(PPh_3)_2(\mu_3\text{-}S)_2$, **4**, can be obtained in 28% yield. Compound **4** was characterized by a combination of IR, ^1H NMR, ^{31}P NMR, and single-crystal X-ray diffraction analysis. The infrared spectrum of compound **4** shows a shoulder peak at 1876 cm^{-1} that is attributed to a bridging carbonyl ligand. Its $^{31}P\{^1H\}$ NMR spectrum exhibits a single resonance at 18.98 ppm with ^{195}Pt satellites ($J_{Pt-P} = 3526$ Hz). Details of the structure of **4** were established by a single-crystal X-ray diffraction analysis, and its molecular structure is shown in Figure 2. The structure of **4** also consists of an open $PtMn_2$ cluster, but there is only one metal−metal bond, Mn−Mn = 2.638(2) Å. The Mn−Mn distance is shorter than that in **3**. This may be due to the presence of the carbonyl ligand that bridges the Mn−Mn bond. Both Pt−Mn distances are long and nonbonding in length: Mn(1)···Pt(1) = 3.3293(18) Å, and Mn(2)···Pt(1) = 3.3906(19) Å. These values are very similar to the nonbonding Fe···Pt distances, av = 3.358 Å, found for $Fe_2(CO)_6Pt(PPh_3)_2(\mu_3\text{-}S)_2$.[11] As in **3**, there are two triply bridging sulfido ligands, but the Mn−S distances in **4** are slightly longer than those in **3**. The Pt−S distances are similar to those in **3**. The bridging carbonyl ligand in **4**, C(13)−O(13), is slightly asymmetrical, Mn(1)−C(13) = 2.037(14) Å, and Mn(2)−C(13) = 2.112(13) Å. Interestingly, the bridging CO ligand in **1** is also slightly asymmetrical in character, Mn(1)−C = 2.033(3) Å and Mn(2)−C = 2.084(3) Å. There is no particular reason for this, other than possible crystal packing effects. The coordination about each manganese atom in **4** is approximately octahedral. Under a nitrogen atmosphere, compound **4** readily loses CO in solution and reverts back into compound **3**.

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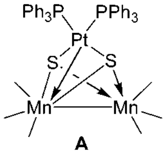
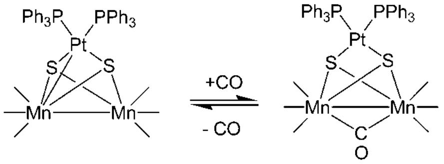
Discussion

The reaction of **1** with $Pt(PPh_3)_2(PhC_2Ph)$ proceeds by the loss of PhC_2Ph from the platinum reagent and the addition and insertion of a bis(phosphine)platinum grouping into the S−S bond of **1**. Concomitantly, there is a loss of one CO ligand from the manganese atoms and the formation of a Pt−Mn bond. Through the formation of the Pt−Mn bond, both manganese atoms are able to achieve 18 electron configurations. There are various ways that one can count the electrons in this compound; one of these is represented in the structure **A** shown here.



A

Note: the sulfido ligands in **A** are counted as neutral four-electron donors, the Pt−Mn bond is a heteropolar Pt to Mn donor, and the platinum atom has a 16-electron configuration. Interestingly, compound **3** readily reacts with CO at 1 atm/25 °C to form the adduct **4** by cleavage of the Pt−Mn bond. Interestingly, the reaction is readily reversible, eq 3. In fact, compound **4** can be isolated in pure form only when kept under an atmosphere of CO. Spectroscopically, the reaction appears to be quantitative in both directions, but the isolated yield of **4** is low because of its instability.



The facile addition and elimination of CO to metal carbonyl cluster complexes with concomitant breaking and making of metal−metal bonds has been observed previously.[16] While there are similarities in the insertion of bis(phosphine)-platinum grouping into the S−S bond of **1** and **2**, the facile loss of CO to yield **3** is quite different from that of the related iron compounds.

Experimental Section

General Data. All reactions were performed under a nitrogen atmosphere. Reagent grade solvents were dried by the standard procedures and were freshly distilled prior to use. Infrared spectra were recorded on a Nicolet 5DXBO FTIR spectrophotometer. ^1H NMR data were recorded on a Varian Inova 300 spectrometer operating at 300 MHz, and ^{31}P NMR data were recorded on a Varian Inova 400 spectrometer operating at 400 MHz. Elemental analyses were performed by Desert Analytics (Tucson, AZ). $Mn_2(CO)_7(\mu\text{-}S_2)$[1] and $Pt(PPh_3)_2(PhC_2Ph)$[17] were prepared according to published procedures. Product separations were performed by TLC in air on Analtech 0.25 and 0.5 mm silica gel 60 Å F_{254} glass plates.

Table 1. Crystallographic Data for Compounds **3** and **4**

	3	4
empirical formula	$Mn_2(CO)_6Pt(PPh_3)_2$-$(\mu_3\text{-}S)_2$	$Mn_2(CO)_7Pt(PPh_3)_2$-$(\mu_3\text{-}S)_2\cdot(1/2)C_6H_{14}$
fw	1061.69	1132.79
lattice params		
a (Å)	11.0995(7)	12.3163(17)
b (Å)	16.7179(10)	13.968(2)
c (Å)	21.9289(12)	15.052(2)
α (deg)	90	66.559(3)
β (deg)	99.1490(10)	75.851(3)
γ (deg)	90	72.623(3)
V (Å^3)	4017.8(4)	2243.8(6)
space group	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
Z	4	2
no. obsd ($I > 2\sigma(I)$)	5924	5171
no. params	496	521
GOF	0.949	1.004
max shift in final cycle	0.003	0.001
residuals: R1; wR2	0.0449; 0.0834	0.0540; 0.1019

Synthesis of $Mn_2(CO)_6Pt(PPh_3)_2(\mu_3\text{-}S)_2$, 3. A 54.7 mg amount (0.14 mmol) of **1** and a 131 mg amount of $Pt(PPh_3)_2(PhC_2Ph)$ (0.14 mmol) were dissolved in 50 mL of distilled CH_2Cl_2 in a 100 mL three-neck round-bottom (r. b.) flask equipped with a stir bar and a nitrogen inlet. This solution was stirred at 25 °C for 3 h. The volatiles were removed in vacuo, and the product was separated by TLC using hexane/CH_2Cl_2 (3/2) solvent mixture as an eluent. 59.2 mg (38% yield) of green $Mn_2(CO)_6Pt(PPh_3)_2(\mu_3\text{-}S)_2$, **3**, was obtained. Spectral data for **3**: IR ν_{CO} (cm^{-1} in CH_2Cl_2) 2021(s), 1987(vs), 1934(br). ^1H NMR (δ in CD_2Cl_2) 7.4−7.0 (m, 30H). ^{31}P NMR (δ in CD_2Cl_2) 14.23. Anal. Calcd: C(%), 47.51; H(%), 2.85. Found: C, 46.59; H, 2.70.

Synthesis of $Mn_2(CO)_7Pt(PPh_3)_2(\mu_3\text{-}S)_2$ (4). A 5.0 mg (0.053 mmol) amount of $Mn_2(CO)_6Pt(PPh_3)_2(\mu_3\text{-}S)_2$, **3**, was dissolved in 0.5 mL CH_2Cl_2 and added to 0.5 mL hexane. At 25 °C, CO gas was bubbled through the solution through a hypodermic needle. There was an immediate color change from dark green to red. The solvent was evaporated under a slow CO stream to yield needle-shaped red crystals: 1.5 mg (28% yield) of $Mn_2(CO)_7Pt(PPh_3)_2$-$(\mu_3\text{-}S)_2\cdot 0.5C_6H_{14}$, **4**. Spectral data for **4**: IR ν_{CO} (cm^{-1} in CH_2Cl_2) 2045(s), 2007(vs), 1944(br), 1875(sh). ^1H NMR (δ in CD_2Cl_2) 7.4−7.0 (m, 30H). ^{31}P NMR (δ in CD_2Cl_2) 18.98.

Crystallographic Analyses. A dark green crystal of **3** was grown by slow evaporation of the solvent from a hexane/CH_2Cl_2 solution of the complex at −17 °C. A red-brown crystal of **4** was grown by slow evaporation of the solvent from a hexane/CH_2Cl_2 solution of the complex under a slow CO stream at room temperature. The crystals used in data collections were glued onto the end of thin glass fibers. X-ray intensity data for **3** and **4** were measured at 293 K on a Bruker SMART APEX CCD-based diffractometer using Mo Kα radiation (λ = 0.71073 Å). The unit cells were initially determined on the basis of reflections collected from a set of three orthogonal scans. Crystal data, data collection parameters, and results of the analyses are listed in Table 1. The raw intensity data frames were integrated with the SAINT+ program which also applied corrections for Lorentz and polarization effects.[18] Final unit cell parameters are based on the least-squares refinement of all reflections with $I > 5(\sigma)I$ from the data sets. For each analysis, an empirical absorption correction based on the multiple measurement of equivalent reflections was applied using the program SADABS.[19]

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Compound **3** crystallized in the monoclinic crystal system. Systematic absences in the intensity data were consistent with the space group $P2_1/c$, which was confirmed by successful solution and refinement of the structure. Compound **4** crystallized in the triclinic system. The space group $P\bar{1}$ was assumed and confirmed by successful solution and refinement of the structure. In each structure, all heavy atoms were readily located. Subsequently, all non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atom positions were calculated assuming idealized geometries and refined using a riding model. Both structures were solved by a combination of direct methods and difference Fourier synthesis and refined on F^2 by full-matrix least-squares using all data. All calculations were performed with the SHELXTL software package by using neutral atom scattering factors.[19]

Acknowledgment. This research was supported by a Grant from the National Science Foundation, CHE-9909017.

Supporting Information Available: Tables of final atomic coordinates, bond distances and angles, and anisotropic thermal parameters are available for the structural analyses of **3** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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