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Heterometallic Cluster $[CpMn(CO)_2]_2S_2Ni(Dppe)$ Containing the Binuclear Manganese Disulfide Complex as a Ligand

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Abstract—A reaction of the disulfide complex $[CpMn(CO)_2]_2S_2$ with the Ni(0) diphosphine acetylene complex, $(Dppe)Ni(C_2Ph_2)$ (**I**), yielded the heterometallic complex $[CpMn(CO)_2]_2S_2Ni(Dppe)$ (**II**). An X-ray diffraction study revealed lateral coordination of the disulfide group to the Ni atom in complex **II**, which results in lengthening of both the S–S and Mn–S bonds against those in the starting complex. However, the Mn–S and Ni–S bonds are still much shorter than the sums of the covalent radii of the corresponding atoms.

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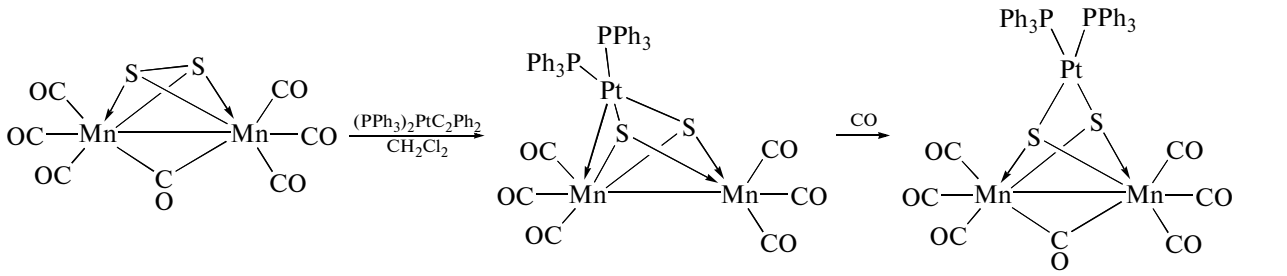
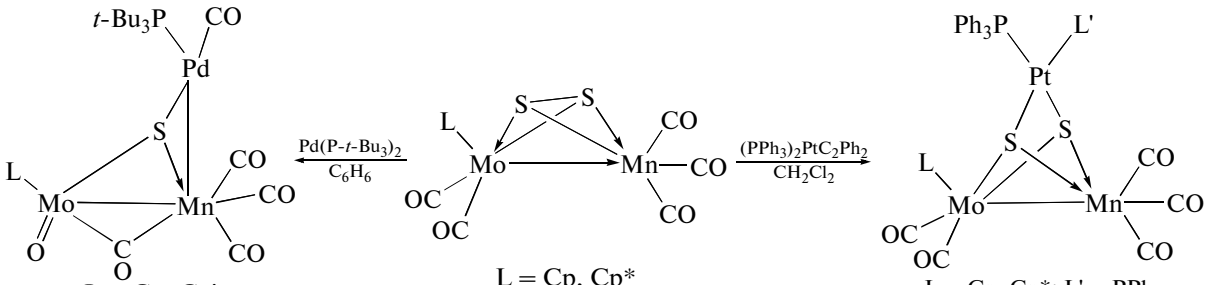
Complexes of low-valence transition metals can be inserted into chalcogen–chalcogen bonds [1, 2] (e.g., in iron hexacarbonyl dichalcogenides, $Fe_2(CO)_6E_2$, where E = S [3] or Se [4]) to give heterometallic clusters $(PPh_3)_2M(\mu_3\text{-}E)_2Fe_2(CO)_6$ (M = Pt or Pd). Analogous insertion of platinum into the S–S bond of the dimanganese complex $[Mn_2(CO)_7(\mu\text{-}S_2)]$ yields new clusters $[Mn_2(CO)_6Pt(PPh_3)_2(\mu_3\text{-}S)_2]$ and $[Mn_2(CO)_6(\mu\text{-}CO)Pt(PPh_3)_2(\mu_3\text{-}S)_2]$ [5, 6]:



The heterometallic Mn-Mo dichalcogenide $[LMoMn(CO)_5(\mu\text{-}E_2)]$ (L = Cp and Cp*; E = S and Se) reacts similarly, producing the trimetallic clusters $[LMoMn(CO)_5Pt(PPh_3)_2(\mu_3\text{-}E)_2]$ or $[Cp^*MoMn(CO)_6Pt(PPh_3)(\mu_3\text{-}S)_2]$, respectively. However, an analogous reaction with $Pd(PBu^t_3)_2$ gives the trimetallic thiooxo cluster $[LMo(O)Mn(CO)_4(\mu\text{-}CO)Pd(PBu^t_3)(\mu_3\text{-}S)]$ [7]:



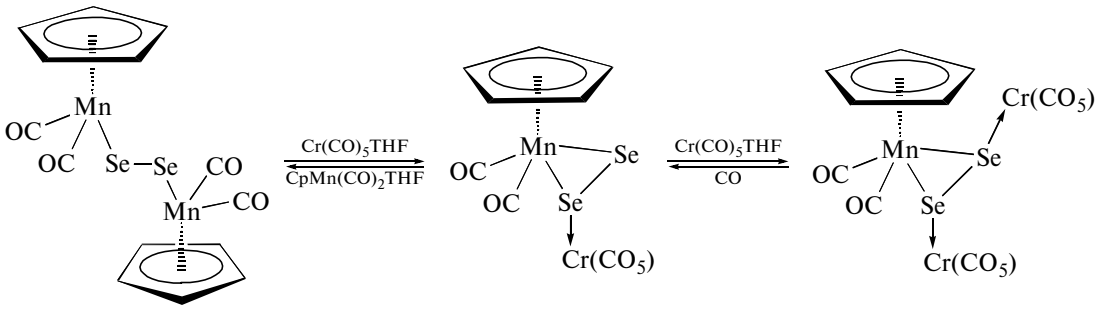
L = Cp, Cp'

L = Cp, Cp*

L = Cp, Cp*; L' = PPh_3

L = Cp*, L' = PPh_3, CO

Unlike the aforementioned μ,η²-dichalcogenide complexes, the complexes μ,η¹-[CpMn(CO)$_2$]$_2$(E$_2$) (E = S [8] or Se [9]) contain a system of conjugated bonds Mn–E–E–Mn, where the Mn–E bonds (on average, 2.16 and 2.29 Å) are substantially shorter than the sums of the covalent radii of the corresponding atoms (2.44 and 2.59 Å for E = S and Se, respectively [10]); the same is true for the E–E bonds (S–S, 2.001 Å; Se–Se, 2.305 Å; the covalent radii of the S and Se atoms are 2.10 and 2.40 Å, respectively [10]). Their reactions with complexes of low-valence metals (e.g., with carbonyl complexes M(CO)$_5$THF) involve transmetalation through the loss of one CpMn(CO)$_2$ group; however, the E–E bond is retained to give the complexes CpMn(CO)$_2$(E$_2$)M(CO)$_5$ and CpMn(CO)$_2$(E$_2$)[M(CO)$_5$]$_2$ (E = S, M = Cr or W; E = Se, M = Cr) containing the triangular framework MnE$_2$ [11]:



We found it interesting to carry out a similar reaction with the Ni(0) diphosphine acetylene complex, (Dppe)Ni(C$_2$Ph$_2$) (**I**).

EXPERIMENTAL

All reactions and all manipulations for isolation of reaction products were carried out under argon in dehydrated solvents. The starting complex [CpMn(CO)$_2$]$_2$S$_2$ was prepared as described in [9]. IR spectra were recorded on a Specord 75IR spectrophotometer in KBr pellets. Elemental analysis was performed on a CHNS analyzer (Carlo Erba) at the Collective Use Center of the Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences.

Synthesis of complex I. Pulverized zinc (0.552 g, 8.4 mmol) was activated with 2 M HCl (25 mL) for 5 min, washed with distilled water (3 × 20 mL) and THF (3 × 10 mL). Then Dppe (1.67 g, 4.2 mmol) and diphenylacetylene (0.75 g, 4.2 mmol) in THF (40 mL) were added to the activated zinc. After the ligands dissolved completely, a suspension of NiCl$_2$ · 6H$_2$O (1.0 g, 4.2 mmol) in THF (10 mL) was added. The reaction mixture was stirred at room temperature for 1 h, whereupon the excess of zinc was filtered off. The resulting orange-yellow solution was diluted with ethanol (20 mL), concentrated to 1/3 of the initial volume, and kept at −20°C for 24 h. The yellow crystals of complex **I** that formed were separated by decanting, washed with methanol (10 mL) and diethyl ether (2 × 10 mL), and dried in vacuo. The yield of complex **I** was 1.28 g (48%). The crystals obtained are suitable for X-ray diffraction.

For $C_{40}H_{34}P_2Ni$ (M = 635)		
anal. calcd. (%):	C, 75.62;	H, 5.39.
Found (%):	C, 76.13;	H, 5.58.

Synthesis of [CpMn(CO)$_2$]$_2$S$_2$Ni(Dppe) · CH$_2$Cl$_2$ (II · CH$_2$Cl$_2$). The complex [CpMn(CO)$_2$]$_2$S$_2$ (0.15 g, 0.36 mmol) in benzene (20 mL) was added to complex **I** (0.26 g, 0.41 mmol); the resulting suspension was stirred for 10 min. The resulting black-green solution was evaporated to dryness in vacuo. The residue was washed with hexane (15 mL) and the product was extracted with CH$_2$Cl$_2$ (15 mL). The extract was diluted with hexane (2 mL), concentrated by half, and kept at −20°C for 72 h. The black-violet crystals of complex **II** · CH$_2$Cl$_2$ that formed were separated by decanting, washed with hexane (2 × 5 mL), and dried in vacuo. The yield was 0.18 g (52%). The crystals obtained are suitable for X-ray diffraction.

IR (KBr, ν, cm^{-1}): 1895 s, 1840 s, 1425 m, 1085 m, 875 w, 810 vw, 725 m, 680 m, 590 m, 525 m.

For $C_{40}H_{34}O_4P_2S_2Mn_2Ni \cdot CH_2Cl_2$ (M = 958)			
anal. calcd. (%):	C, 51.39;	H, 3.79;	S, 6.69.
Found (%):	C, 51.56;	H, 3.71;	S, 6.93.

X-ray diffraction analysis. Crystallographic parameters and the data collection and refinement statistics for structures **I** and **II** are given in table. The crystal of complex **II** used for X-ray diffraction proved to be a twin. Unit cell determination with the CELL_NOW program [12] revealed the presence of two components of the twin crystal that make with each other an angle of 180° about the axis *x*. Data were processed

Crystallographic parameters and the data collection and refinement statistics for structures **I** and **II**

Parameter	Value	
	I	**II**
M	635.32	958.25
Diffractometer	Bruker APEX II CCD	
Radiation (λ, Å)	MoK_α (0.71073)	
Temperature, K	173(2)	173(2)
Space group	$P\bar{1}$	$P\bar{1}$
a, Å	10.6931(8)	11.272(1)
b, Å	16.751(1)	16.311(2)
c, Å	18.732(1)	23.334(2)
α, deg	79.464(1)	109.417(2)
β, deg	74.342(1)	97.277(2)
γ, deg	88.186(1)	90.557(2)
V, Å^3	3175.7(4)	4007.2(6)
Z	4	4
ρ_{calcd}, g/cm^{-3}	1.329	1.588
μ, mm^{-1}	0.74	1.445
F(000)	1328	1952
θ scan range, deg	1.83–25.07	0.93–28.10
Scan mode	ω	
Number of independent reflections (N_1)	11236 ($R_{int} = 0.0149$)	18934 ($R_{int} = 0.0765$)
Number of reflections with $I > 2\sigma(I)$ (N_2)	6789	11401
Number of parameters refined	775	964
GOOF (F^2)	0.938	1.045
R_1 for N_2	0.0483	0.0574
wR_2 for N_1	0.1169	0.1620
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	0.408/–0.315	0.775/–0.631

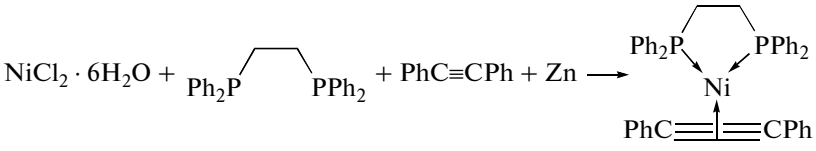
and the unit cell parameters were refined with the SAINT program [13], with allowance for the presence of two components of the twin crystal for complex **II**. An absorption correction was applied by multiple measurements of equivalent reflections with the SADABS [14] (for complex **I**) and TWINABS programs [15] (for **II**). Structures **I** and **II** were solved by direct methods and refined by the least-squares

method on F^2 in the anisotropic approximation for non-hydrogen atoms (isotropically for the carbon atoms of the disordered cyclopentadienyl rings in **II**) with the SHELXTL program package [16]. The H atoms were located geometrically. Selected bond lengths and bond angles in structures **I** and **II** are given in the captions to Figs. 1 and 2.

The atomic coordinates and other parameters of structures **I** and **II** have been deposited with the Cambridge Crystallographic Data Centre (nos. 854060 (**I**) and 854061 (**II**); http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

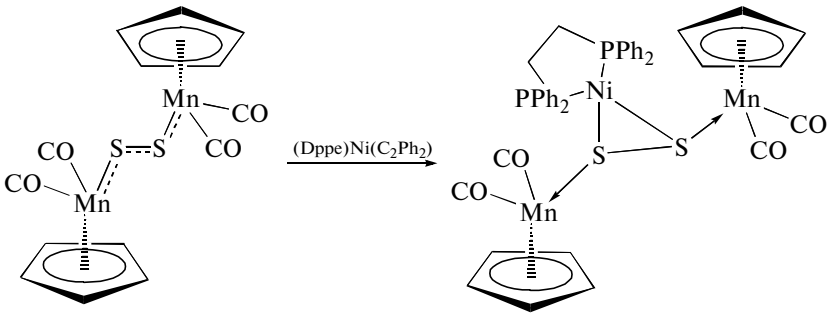
The starting Ni complex **I** was prepared from nickel chloride and appropriate ligands by reduction with pulverized zinc in THF and crystallized from THF–ethanol to give bright yellow crystals:



Complex **I** is unstable in air as well as in an inert atmosphere at room temperature in both solutions and the solid state. Earlier, related complexes (*iso*-$Pr_2PCH_2CH_2P$*iso*-Pr_2)Ni(PhC≡CPh) [17] and $(PPh_3)_2$Ni(PhC≡CPh) [18] have been obtained by reduction of appropriate nickel phosphine halide complexes with amalgamated sodium in the presence of diphenylacetylene.

Structure **I** was determined by X-ray diffraction. The C≡C bond of coordinated diphenylacetylene, which is nearly parallel to the NiP_2 plane, is lengthened to 1.292 Å compared to that in its free molecule (1.21 Å). The angles C≡C–C_{Ph} are diminished from 180° to 146.5(3)° and 144.6(3)°, which is typical of the four-electron-donating coordination of ethynes. The Ni–C distances are 1.878(3) and 1.889(3) Å. The structure of the coordinated acetylene is virtually the same as in the known analog, (*iso*-$Pr_2PCH_2CH_2P$*iso*-Pr_2)Ni(PhC≡CPh): C–C, 1.29 Å; Ni–C, 1.88 Å (average); C≡C–C–Ph, 146.4° (average) [19].

When complex **I** is treated with $[CpMn(CO)_2]_2S_2$ at room temperature, the acetylene fragment is replaced by the dimanganese disulfide fragment, giving rise to heterometallic complex **II**.



The bands due to the CO stretching vibrations (1895 and 1840 cm^{-1}) are shifted to the lower frequencies compared to those for the starting Mn complex (1930 and 1900 cm^{-1}). This can be attributed to an increased electron density on the fragment Mn_2S_2 because of the oxidation of Ni(0) into Ni(II).

The structure of the solvate **II** · CH_2Cl_2 was determined by X-ray diffraction. Its unit cell comprises two crystallographically independent molecules that differ by the conformation of the phenyl rings of the diphosphine ligand and, to a lesser degree, by the conformation of the fragments $CpMn(CO)_2$ with respect to the chelate ring NiS_2. The ligand environment of the Ni(II) atom is nearly planar: the angle between the P_2Ni and NiS_2 is 11.3(1)° or 11.33(9)°. The Ni–S bonds (2.174 and 2.181 Å) are substantially shorter than the sum of the covalent radii of these atoms (2.29 Å) [10]. A similar shortening has been noted for known Ni complexes containing the disulfide ligand that is not coordinated to other metal atoms. The examples are $S_2NiN_2C(Ph(iso\text{-}Pr)_2CH_3)_2$ (2.163 and 2.166 Å) [20] and $S_2Ni((iso\text{-}Pr_2P)_2C_{10}H_6)$ (2.204(3) and 2.185(3) Å) [21]. The coordination of nickel weakens the multiple bonds in the system MnSSMn and, consequently, lengthens the Mn–S (2.262(2)–2.265 Å) and S–S bonds (2.094(2)–2.097(2) Å) compared to those in the starting Mn complex (Mn–S, 2.166 Å; S–S, 2.006 Å). However, the Mn–S bond

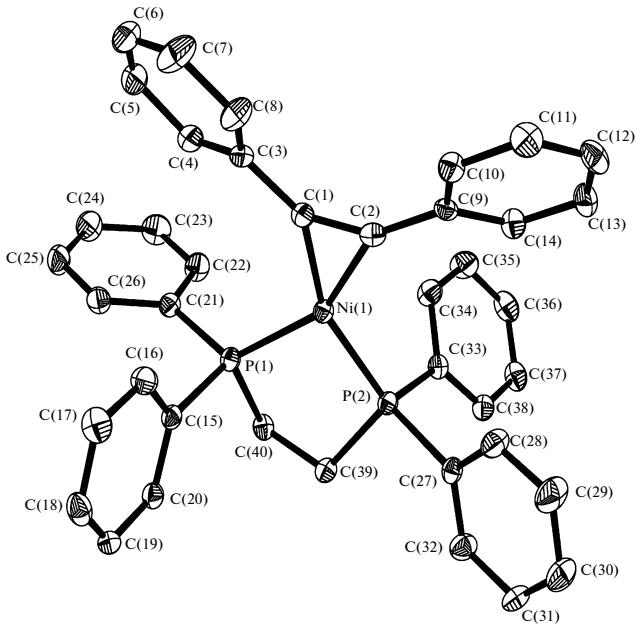


Fig. 1. Molecular structure of complex **I**. Selected bond lengths and bond angles: Ni(1)–C(1), 1.878(3) Å; Ni(1)–C(2), 1.889(3) Å; Ni(1)–P(1), 2.147(1) Å; Ni(1)–P(2), 2.156(1) Å; C(1)–C(2), 1.292(5) Å; C(1)–C(3), 1.465(5) Å; C(2)–C(9), 1.454(5) Å; P(1)Ni(1)P(2), 90.48(4)°; C(2)C(1)C(3), 146.5(3)°; C(1)C(2)C(9), 144.6(3)° (these data relate to one of two crystallographically independent molecules).

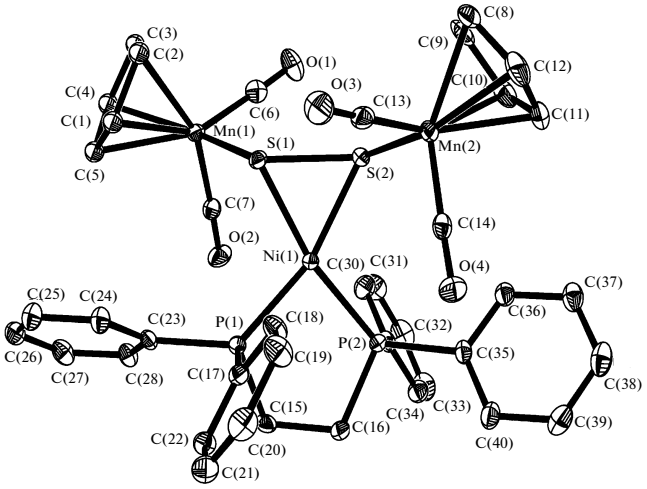


Fig. 2. Molecular structure of complex **II**. Selected bond lengths and bond angles: Ni(1)–P(1), 2.163(2) Å; Ni(1)–P(2), 2.178(2) Å; Ni(1)–S(1), 2.174(1) Å; Ni(1)–S(2), 2.181(2) Å; Mn(1)–S(2), 2.262(2) Å; Mn(2)–S(2), 2.265(2) Å; S(1)–S(2), 2.094(2) Å; P(1)Ni(1)P(2), 89.06(6)°; S(1)Ni(1)S(2), 57.49(5)°; S(2)S(1)Mn(1), 117.09(7)°; S(1)S(2)Mn(2), 114.28(8)° (these data relate to one of two crystallographically independent molecules; the solvate CH_2Cl_2 molecules are omitted).

lengths are still shorter than the sum of the covalent radii of Mn and S (2.44 Å) [10].

ACKNOWLEDGMENTS

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