Full Articles

Formation of Pt—S—Mn groups in platinum triphenylphosphine complexes with cymanthrenylthiolate ligands

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Stepwise decarbonylation of the platinum complex with cymanthrenylthiolate ligands *cis*-$(Ph_3P)_2Pt[(SC_5H_4)Mn(CO)_3]_2$ (**1**) affords the *cis*-$(Ph_3P)_2Pt[(SC_5H_4)Mn(CO)_3]$-$[(SC_5H_4)Mn(CO)_2]$ (**2**) and *cis*-$(Ph_3P)_2Pt[(SC_5H_4)Mn(CO)_2]_2$ (**3**) complexes. The replacement of one carbonyl group at the manganese atom with the lone electron pair of sulfur is accompanied by the formation of a new Mn—S bond giving rise to an unusual norbornane-type core. Complexes **1—3** were characterized by elemental analysis and IR spectroscopy. The structures of complexes **1—3** were established by single-crystal X-ray diffraction.

Key words: heterometallic complexes, X-ray diffraction analysis, cyclopentadienyl complexes, metal carbonyls, metal chalcogenides, cymanthrene, manganese, platinum.

It is known that organomanganese chalcogenides can exist as unusual organometallic radicals, for examples, $CpMn(CO)_2SR$, where R = Ph [1] or C(O)Ph,[2] and formally biradical dichalcogenides $[CpMn(CO)_2]_2(\mu\text{-}X_2)$ (X = S [2] or Se [2,3]), which always contain sharply shortened Mn—X bonds.

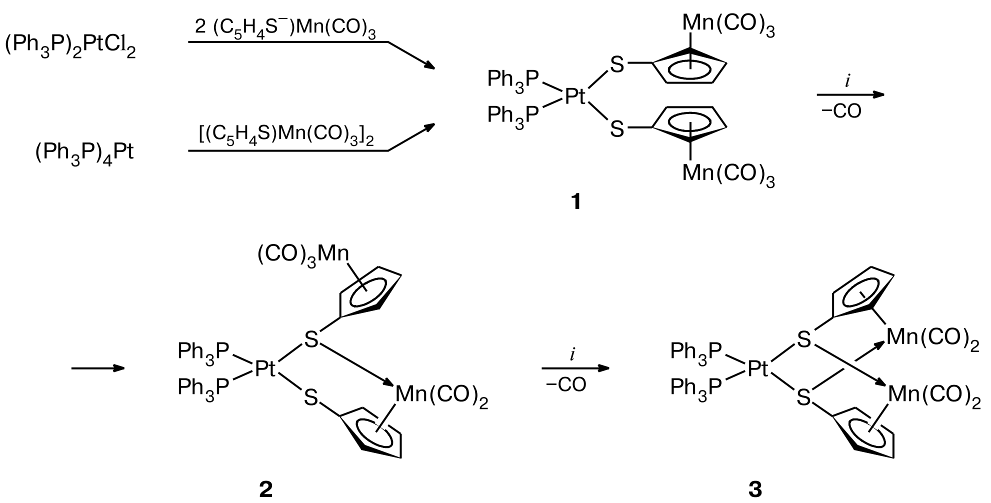
It was of interest to synthesize a platinum *cis*-triphenylphosphine complex containing the cymanthrenylthiolate ligands (cymanthrenyl is $C_5H_4Mn(CO)_3$), use this complex for generating radicals by replacing the carbonyl group at the manganese atom with SR groups, and study delocalization of lone electrons throughout the molecule by ESR spectroscopy. However, it was unexpectedly found that only intramolecular replacements of CO by the sulfur atoms of the cymanthrenylthiolate ligands occur giving rise to new sulfide-bridged heterometallic groups.

Results and Discussion

The starting platinum bis-triphenylphosphine complex with cymanthrenylthiolate ligands *cis*-$(Ph_3P)_2Pt[(SC_5H_4)Mn(CO)_3]_2$ (**1**) was prepared according to two procedures: 1) by the reaction of bis-triphenylphosphineplatinum dichloride with cymanthrenylthiolate anions and 2) by oxidative addition of dicymanthrenyl disulfide[4] to the Pt^0 tetraphosphine complex by analogy with the known insertion of the platinum atom at the S—S bond in organic disulfides[5,6] (Scheme 1).

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 7, pp. 1508—1512, July, 2005.

Scheme 1



i. Benzene, *h*ν, 20 °C.

Complex **1** was isolated as air-stable yellow crystals, which are readily soluble in chlorinated and aromatic hydrocarbons and poorly soluble in saturated hydrocarbons. The region of carbonyl stretching vibrations of the IR spectrum of complex **1** is analogous to that observed for dicymanthrenyl disulfide[4] (at 1995 and 1905 cm).

X-ray diffraction study demonstrated (Fig. 1, Tables 1 and 2) that the platinum atom is in a typical square-planar environment with a *cis* arrangement of two phosphorus atoms (Pt—P, 2.282(1) and 2.297(1) Å) and two sulfur atoms (Pt—S, 2.347(1) and 2.367(1) Å). The planes of the Cp ligands are parallel to each other and are almost perpendicular to the plane of the ligand environment of the platinum atoms. The $Mn(CO)_3$ groups are rotated with respect to each other. Nearly the same Pt—S distances (2.360(1) and 2.361(1) Å) and slightly elongated Pt—P distances (2.311(1) and 2.334(1) Å) are observed in the known *cis*-$(Ph_3P)_2Pt(2,4,6\text{-}C_6H_2{}^iPr_3S)_2$ complex containing the bulky thiolate groups.[7]

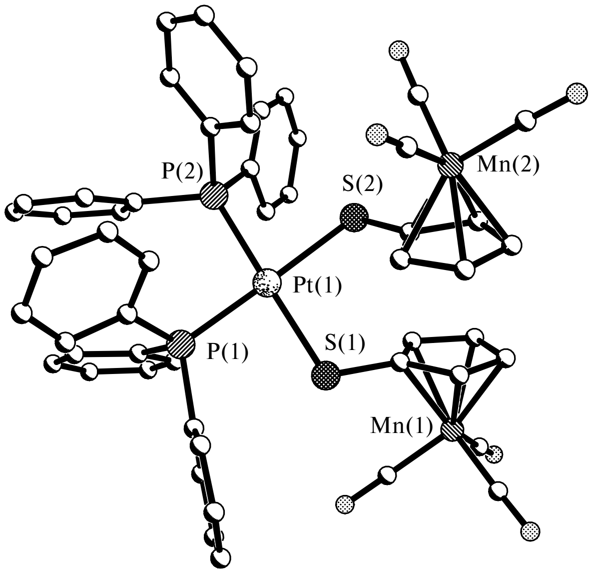


Fig. 1. Molecular structure of complex **1**.

An attempt to generate the radical from molecule **1** demonstrated that *tert*-butylmercaptane does not react with the latter even under photochemical conditions; instead, UV radiation causes the intramolecular replacement of one carbonyl group with the lone electron pair of the sulfur atom of the second thiolate group to give the monosubstituted *cis*-$(Ph_3P)_2Pt[(SC_5H_4)Mn(CO)_3][(SC_5H_4)Mn(CO)_2]$ complex (**2**). This compound was isolated as rick-red crystals, which are stable in air in the solid state, readily soluble in dichloromethane, moderately soluble in aromatic hydrocarbons, and poorly soluble in saturated hydrocarbons. The IR spectrum shows stretching vibrations of the tricarbonyl (ν(CO)/cm^{-1}: 2005 v.s and 1940 v.s) and dicarbonyl (ν(CO)/cm^{-1}: 1900 v.s and 1845 v.s) manganese-containing groups (the latter can be correlated with the analogous group in the $CpMn(CO)_2S(CH_3)_2$ complex,[2] whose IR spectrum shows bands at 1928 (v.s) and 1856 cm^{-1} (v.s)). X-ray diffraction study of compound **2** demonstrated (Fig. 2, see Tables 1 and 2) that the cyclopentadienylmanganesedicarbonyl group is twisted and the new Mn—S(2) bond (2.298(1) Å) is formed. The Pt(1)—S(2) bond in molecule **2** is slightly elongated (to 2.390(1) Å), but the square-planar geometry of the ligand environment of the platinum atom remains virtually unchanged.

The photochemical transformation of complex **1** is controlled by its concentration in a benzene solution,

Table 1. Crystallographic data for complexes **1—3**

Parameter	**1**	**2**	**3**
Molecular formula	$C_{52}H_{38}Mn_2O_6P_2PtS_2$	$C_{52}H_{40}Cl_2Mn_2O_5P_2PtS_2$	$C_{50}H_{38}Mn_2O_4P_2PtS_2$
Molecular weight	1189.85	1246.77	1133.83
Color of crystals	Yellow	Red	Dark-cherry
Diffractometer	«Bruker Smart CCD»	«Syntex»	«Syntex»
T/K	120	293(2)	120
Space group	P2(1)/c	P2(1)/n	P2(1)/c
a/Å	22.049(3)	13.585(3)	17.926(6)
b/Å	10.6972(15)	21.980(4)	12.002(3)
c/Å	21.409(3)	16.404(3)	20.577(6)
α/deg	90	90	90
β/deg	110.945(3)	102.37(3)	94.35(2)
γ/deg	90	90	90
V/Å^3	4715.9(12)	4784.7(17)	4414(2)
Z	4	4	4
F(000)	2352	2464	2240
ρ_{calc}/g cm^{-3}	1.676	1.731	1.706
Radiation, λ(Mo-Kα)/Å	0.71073	0.71073	0.71073
Linear absorption, μ/mm^{-1}	3.693	3.751	3.937
Scan mode	θ/2θ	θ/2θ	θ/2θ
Scan range/deg	1.92—28.08	2.19—27.07	1.97—24.05
Number of reflections			
measured	47610	10864	7165
independent	11375	10428	6916
with R_{int}	0.0694	0.0374	0.0857
with $I > 2\sigma(I)$	7640	7301	4933
Number of parameters	586	595	550
R_1	0.0407	0.0329	0.0348
wR_2	0.0805	0.0791	0.0814
GOOF	1.059	1.050	0.964
(ρ_{max}/ρ_{min})/e·Å^{-3}	2.918/−0.767	1.572/−3.049	2.366/−1.931

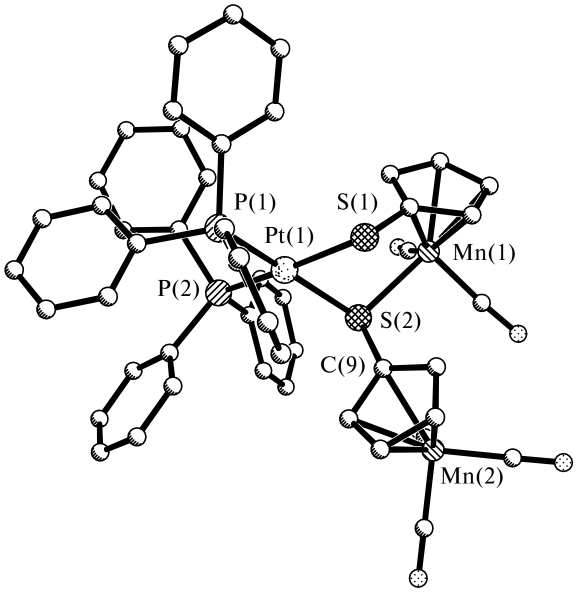


Fig. 2. Molecular structure of complex **2**.

because monosubstituted complex **2** is poorly soluble in benzene and precipitates at a high concentration, which hinders disubstitution. When the concentration of complex **1** is halved, UV irradiation of the solution afforded the *cis*-$(Ph_3P)_2Pt[(SC_5H_4)Mn(CO)_2]_2$ complex (**3**) as the major product. According to the elemental analysis data, the dark-cherry crystals of the later contain a benzene solvate molecule. In the IR spectrum of complex **3**, the CO stretching bands are shifted to lower frequencies (ν(CO)/cm^{-1}: 1880 v.s and 1825 v.s). Single crystals, which contained no solvate molecules, were grown from a chloroform solution covered with hexane. Single-crystal X-ray diffraction study of complex **1** (Fig. 3, see Tables 1 and 2) demonstrated that both manganesedicarbonyl groups are rotated toward each other, each group being involved in an Mn—S bond (2.310(2) and 2.315(2) Å). The geometry of the ligand environment of the platinum atom remains square-planar, but both Pt—S bonds are slightly elongated (to 2.369(2) and 2.399(2) Å), whereas the Pt—P bonds remain unchanged (2.313(2) and 2.289(2) Å). Noteworthy is the formation of the unusual norbornane-type core consisting of one platinum atom, two sulfur atoms, two carbon atoms of the Cp ligands bound to the sulfur atoms, and two manganese atoms.

Table 2. Bond lengths (*d*) and bond angles (ω) in molecules **1—3**

Parameter	1	2	3
Bond		*d*/Å	
Pt(1)—P(1)	2.2968(13)	2.2998(12)	2.3128(18)
Pt(1)—P(2)	2.2823(13)	2.2894(12)	2.2891(18)
Pt(1)—S(1)	2.3667(12)	2.3566(12)	2.3992(17)
Pt(1)—S(2)	2.3467(12)	2.3893(12)	2.3688(17)
Mn(1)—S(1)	—	—	2.310(2)
Mn(1)—S(2)	—	2.2987(14)	—
Mn(2)—S(2)	—	—	2.315(2)
Angle		ω/deg	
P(2)—Pt(1)—P(1)	96.74(4)	98.80(4)	97.20(6)
P(1)—Pt(1)—S(1)	82.71(4)	86.12(4)	89.00(6)
P(1)—Pt(1)—S(2)	171.87(4)	168.80(4)	168.76(6)
P(2)—Pt(1)—S(1)	176.75(4)	171.92(4)	173.64(6)
P(2)—Pt(1)—S(2)	85.70(4)	90.26(4)	90.75(6)
S(1)—Pt(1)—S(2)	—	85.65(4)	—
S(2)—Pt(1)—S(1)	95.29(4)	—	83.31(6)
C(1)—S(1)—Pt(1)	105.57(15)	97.94(15)	—
C(9)—S(2)—Pt(1)	108.96(16)	96.09(15)	—
C(9)—S(2)—Mn(1)	—	110.33(16)	—
Mn(1)—S(1)—Pt(1)	—	—	107.22(7)
Mn(1)—S(2)—Pt(1)	—	107.57(5)	—
Mn(2)—S(2)—Pt(1)	—	—	101.20(7)

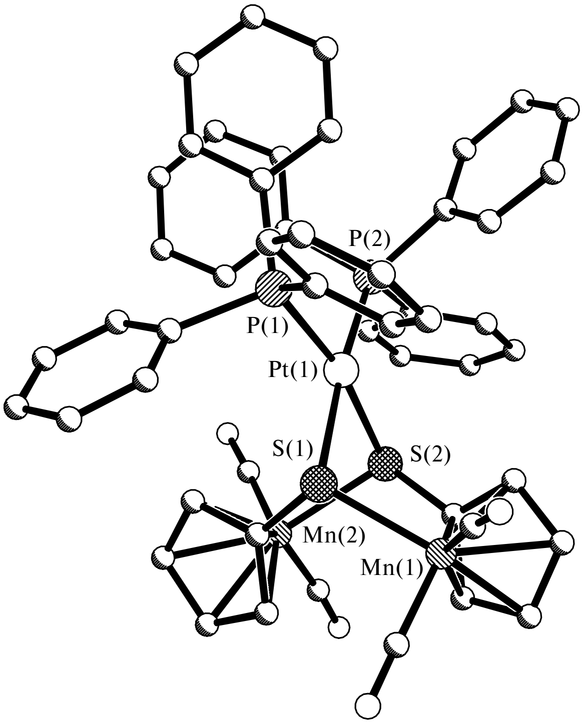


Fig. 3. Molecular structure of complex **3**.

Therefore, the stepwise insertion of the peripheral manganese atoms of cymanthrenyl substituents into the platinum manganese chalcogenide cluster provides a new promising approach to the directed synthesis of heterometallic clusters.

Experimental

All operations associated with the synthesis and isolation of the complexes were carried out under pure argon and in anhydrous solvents. Commercial $CpMn(CO)_3$ and $H_2PtCl_6 \cdot 6H_2O$ were used without additional purification. Dicymanthrenyl disulfide was synthesized according to a known procedure.[4] The $Pt(PPh_3)_4$ and *cis*-$(PPh_3)_2PtCl_2$ complexes were synthesized according to procedures published earlier.[8]

The IR spectra were recorded on a Specord IR 75 spectrophotometer in KBr pellets.

X-ray diffraction analysis. The crystallographic data, details of X-ray diffraction study, and characteristics of structure refinement of compounds **1—3** are given in Table 1. The structures were solved by direct methods and refined by the full-matrix least-squares method with anisotropic and isotropic thermal parameters for nonhydrogen and H atoms, respectively. The positions of the H atoms were calculated geometrically. A semiempirical absorption correction for crystals of **1** was applied based on equivalent reflections. All calculations were carried out with the use of the SHELXTL PLUS 5 program package. The principal geometric parameters of molecules **1—3** are given in Table 2. The atomic coordinates and thermal parameters were deposited with the Cambridge Structural Database.

cis*-Bis(triphenylphosphine)bis(cymanthrenylthiolate)platinum(II), $(Ph_3P)_2Pt[(SC_5H_4)Mn(CO)_3]_2$ (1).** ***A. A weighed sample of dicymanthrenyl disulfide (0.1 g, 0.21 mmol) was added to a bright yellow solution of $Pt(PPh_3)_4$ (0.3 g, 0.24 mmol) in benzene (40 mL). The reaction mixture was kept at room temperature for 20 h, after which the solvent was completely removed *in vacuo* using a water-jet pump. The resulting yellow-brown residue was dissolved in CH_2Cl_2 (10 mL), light petroleum (15 mL) was added to the solution, and the solution was concentrated to one-half of the initial volume *in vacuo*. The yellow crystals that precipitated upon storage of the solution at −18 °C for one day were separated by decantation, washed with light petroleum (5 mL), and dried *in vacuo*. The yield was 0.17 g (58%).

B. A solution of dicymanthrenyl disulfide (0.12 g, 0.25 mmol) in THF (30 mL) was stirred with a suspension of sodium metal (0.4 g, 17 mmol) for 2 h. The resulting solution was filtered off from excess sodium and added to $(PPh_3)_2PtCl_2$ (0.2 g, 0.25 mmol). The reaction mixture was stirred for 20 min, silica gel (2 g) was added, and the solvent was completely removed *in vacuo* using a water-jet pump. Compound **1** was isolated by column chromatography (10-cm column, SiO_2). The orange-yellow zone was eluted with a 1 : 1 light petroleum—CH_2Cl_2 mixture (50 mL). The eluate was concentrated to 5 mL. The yellow crystalline precipitate that formed upon storage of the solution at −18 °C for one day were separated by decantation, washed with light petroleum (5 mL), and dried *in vacuo*. The yield was 0.15 g (49%). Found (%): C, 52.80; H, 2.70; S, 5.40. $C_{52}H_{38}Mn_2O_6P_2PtS_2$. Calculated (%): C, 52.48; H, 3.22; S, 5.39. IR, ν/cm^{-1}: 3050 m.br, 1995 v.s, 1905 v.s, 1470 m, 1430 s, 1420 s, 1360 w, 1150 w, 1085 s, 1020 w, 995 w, 880 m, 820 w, 735 m, 690 s, 660 m, 620 s, 530 m, 520 s, 510 s.

Bis(triphenylphosphine)cymanthrenylthiolate(manganesedicarbonylcyclopentadienylthiolate)platinum(II), $(Ph_3P)_2Pt[(SC_5H_4)Mn(CO)_3][(SC_5H_4)Mn(CO)_2]$ (2). A bright yellow solution of complex **1** (0.46 g, 0.39 mmol) in benzene (30 mL) was irradiated with UV light (DRT-240 lamp) with stirring for 2.5 h using cooling with running water. The rick-red precipitate that formed was filtered off on a Buchner funnel, washed with light petroleum (10 mL), and dried in air. The yield was 0.07 g.

The mother liquor was concentrated to 20 mL. The crystals that precipitated upon storage of the solution at 5 °C for one day were separated by decantation, washed with light petroleum (5 mL), and dried *in vacuo*. The yield was 0.16 g. The combined product (total yield 0.23 g) was recrystallized from a CH_2Cl_2—toluene mixture to produce rick-red crystals of $(Ph_3P)_2Pt[(SC_5H_4)Mn(CO)_3][(SC_5H_4)Mn(CO)_2] \cdot CH_2Cl_2$ suitable for X-ray diffraction in a yield of 0.17 g. The yield was 35%. Found (%): C, 50.80; H, 3.25; S, 5.52. $C_{52}H_{40}Cl_2Mn_2O_5P_2PtS_2$. Calculated (%): C, 50.09; H, 3.23; S, 5.14. IR, ν/cm^{-1}: 3050 m.br, 2005 v.s, 1940 v.s, 1900 v.s, 1845 v.s, 1470 m, 1435 s, 1360 w, 1260 w, 1220 w, 1180 w, 1150 w, 1080 s, 1015 w, 990 w, 890 w, 825 w, 735 s, 685 s, 660 m, 630 m, 600 w, 530 m, 530 s, 520 m, 510 m, 495 w.

Bis(triphenylphosphine)bis(cyclopentadienylmanganesedicarbonylthiolate)platinum(II), $(Ph_3P)_2Pt[(SC_5H_4)Mn(CO)_2]_2$ (3). A bright yellow solution of complex **1** (0.2 g, 0.16 mmol) in benzene (30 mL) was irradiated with UV light (DRT-240 lamp) for 2 h using cooling with running water. The resulting cherry-colored solution was filtered through a layer of silica gel, light petroleum (15 mL) was added, and the solution was concentrated to 20 mL. The dark-cherry needle-like crystals that precipitated upon storage of the solution at 5 °C for one day were separated by decantation, washed with light petroleum (5 mL), and dried *in vacuo*. The yield of $(Ph_3P)_2Pt[(SC_5H_4)Mn(CO)_2]_2 \cdot C_6H_6$ was 0.14 g (77%). Found (%): C, 55.04; H, 4.18; S, 6.24. $C_{56}H_{46}Mn_2O_4P_2PtS_2$. Calculated (%): C, 55.50; H, 3.66; S, 5.29. IR, ν/cm^{-1}: 3050 m.br, 1880 v.s, 1825 v.s, 1475 w, 1430 m, 1360 v.w, 1080 m, 800 w, 730 m, 680 s, 650 m, 605 w, 530 w, 510 m.

Crystals suitable for X-ray diffraction were grown at the chloroform—hexane interface.

We thank K. A. Lyssenko (Center of X-ray Diffraction Studies, A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences) for help in establishing the structures of the complexes.

This study was financially supported by the Russian Foundation for Basic Research (Project No. 03-03-32730) and the Council on Grants of the President of the Russian Federation (State Program for Support of Young Scientists, Grant NSh-2243.2003.03).

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Received January 12, 2005;
in revised form March 31, 2005