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Platinum and Rhenium Phosphine Carbonyl Thiolate Complexes

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Abstract—The heterometallic complex $(CO)_3(PPh_3)Re(\mu\text{-}SPr)Pt(PPh_3)(CO)$ (**I**) was formed in the reaction of $Re_2(\mu\text{-}SPr)_2(CO)_8$ with $(PPh_3)_2Pt(C_2Ph_2)$, together with $(CO)_3(PPh_3)Re(\mu\text{-}SPr)_2Re(CO)_4$ (**II**), which was also prepared by an alternative synthesis. Compounds **I** and **II** were characterized by X-ray diffraction. In **I**, the Re–Pt single bond, 2.7414(5) Å, is supplemented by a thiolate bridge with shortened bonds: Pt–S (2.336(2) Å) and Re–S (2.449(2) Å). The Re–P (2.469(2) Å) and Pt–P (2.329(2) Å) bonds are also shortened. Complex **II** resulting from replacement of one CO group in the starting rhenium complex by triphenylphosphine has no M–M bond, and the Re–S and Re–P bond lengths (2.511(2)–2.527(2) and 2.517(3) Å) are close to the length of single bonds. It is assumed that the platinum atom in **I** is attached to the formally double bond Re $\rightleftharpoons$ SPr arising upon dissociation of $Re_2(\mu\text{-}SPr)_2(CO)_8$.

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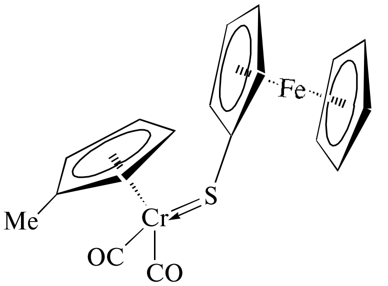
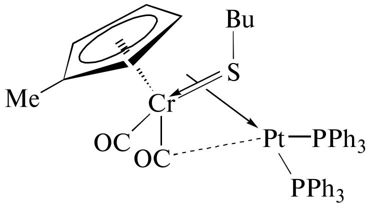
INTRODUCTION

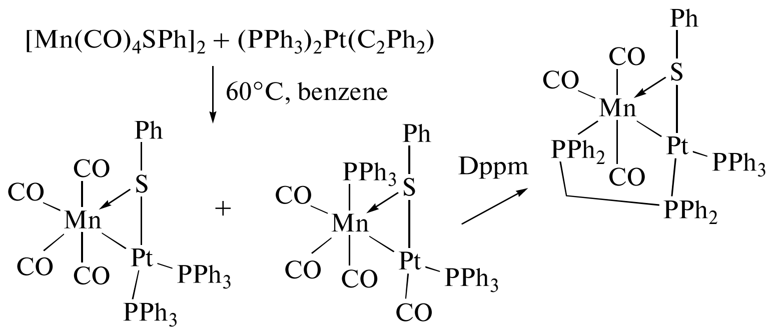
Mononuclear chalcogenate metal complexes can function as monodentate ligands with respect to atoms of other transition metals, as in $(\pi\text{-}C_4Me_4)Co(CO)_2TePh \cdot W(CO)_5$ [1], or as bidentate chelating ligands, as in platinum complexes with $Cp_2Ti(SR)_2$ (R = Me, Ph) [2]. Also, there are numerous chalcogenate-bridged homonuclear complexes $[LM(\mu\text{-}ER)]_2$ [3], which can dissociate to monomers containing LM $\Leftarrow$ ER double bonds similar to the short Cr $\Leftarrow$ S bond (2.136(1) Å) that we found in chromium cylopentadienyl-dicarbonyl-ferrocenylthiolate, $Cp'Cr(CO)_2SFc$, where Cp' = $CH_3C_5H_4$, Fc = C_5H_4FeCp [4].





Recently we showed that $[Cp'Cr(CO)_2(\mu\text{-}SBu)]_2$ having bridging Cr–S single bonds (2.4107(4)–2.4311(4) Å) reacts with the platinum complex $(PPh_3)_2Pt(PhC{\equiv}CPh)$, which easily loses the diphenylacetylene ligand, to give the complex $Cp'(CO)_2(\mu\text{-}SBu)CrPt(PPh_3)_2$ containing a direct Cr–Pt bond (2.7538(15) Å) and Cr–S (2.274(3) Å) and Pt–S (2.294(2) Å) bonds, which are noticeably shortened compared to the sum of the covalent radii (SCR) [5]. It was assumed that this compound can be regarded as a sort of zerovalent platinum π-complex with a Cr $\Leftarrow$ SPh double bond [6].

The $[Mn(CO)_4(SPh)]_2$ molecule dissociates in a similar way when reacts with $(PPh_3)_2Pt(C_2Ph_2)$.



Here, in addition to the heterometallic $(CO)_4Mn(\mu\text{-}SPh)Pt(PPh_3)_2$ complex having the direct Mn–Pt bond (2.6946(3) Å) and shortened Pt–S (2.3129(5) Å) and Mn–S (2.2900(6) Å) bonds, the isomeric $(CO)_3(PPh_3)Mn(\mu\text{-}SPh)Pt(PPh_3)(CO)$ complex is formed in which one phosphine ligand at the platinum atom and the CO molecule at manganese have exchanged places. This has little effect on the bond lengths (Mn–Pt, 2.633(1); Pt–S, 2.332(2); Mn–S, 2.291(2) Å), as in the case of replacement of triphenylphosphine molecules at manganese and platinum by a bridging Dppm molecule (Mn–Pt, 2.623(1); Pt–S, 2.341(2); Mn–S, 2.292(2) Å) [7].

It appeared pertinent to study the behavior in this reaction of $[(CO)_4Re(SPr)]_2$, which is distinguished by the presence of a heavier and a more basic metal atom (rhenium) and alkyl substituent instead of the aryl in the thiolate group.

EXPERIMENTAL

All reactions and operations for product isolation were carried out under argon in anhydrous solvents. The initial complex $(PPh_3)_2Pt(C_2Ph_2)$ was prepared by a reported procedure [8], and the complex $Re_2(\mu\text{-}SPr)_2(CO)_8$ was obtained by analogy with $Re_2(\mu\text{-}SMe)_2(CO)_8$ [9]. The IR spectra were measured on a SPECORD 75 IR spectrophotometer for KBr pellets. Elemental analysis was carried out at the collective use center of the Kurnakov Institute of General and Inorganic Chemistry using a Carlo Erba CHNS analyzer.

Synthesis of $(CO)_3(PPh_3)Re(\mu\text{-}SPr)Pt(PPh_3)(CO)$ (I). A solution of $(PPh_3)_2Pt(C_2Ph_2)$ (229 mg, 0.25 mmol) and $Re_2(SPr)_2(CO)_8$ (91 mg, 0.12 mmol) in toluene (15 mL) was heated at 40°C for 6 h. The red-brown reaction mixture was concentrated to dryness, and the residue was washed with heptane (2 × 10 mL) and extracted with benzene (15 mL). Heptane (5 mL) was added to the benzene extract and the mixture was concentrated to half the initial volume. The precipitated non-identified dark brown solid was separated by decantation. On keeping the mother liquor for a week at 10°C, light yellow crystals were formed. The crystals were washed with heptane and dried in vacuum. Yield 29 mg (5.5%).

IR (KBr; ν(CO), cm^{-1}): 1990 vs, 1965 s, 1890 vs, 1855 s.

For $C_{43}H_{37}O_4P_2SRePt$ ($M = 1093$)

anal. calcd., %:	C, 47.25;	H, 3.41.
Found, %:	C, 47.97;	H, 3.61.

Synthesis of $(CO)_3(PPh_3)Re(\mu\text{-}SPr)_2Re(CO)_4$ (II). A solution of $Re_2(\mu\text{-}SPr)_2(CO)_8$ (30 mg, 0.04 mmol) and PPh_3 (11 mg, 0.04 mmol) in toluene (10 mL) was heated to reflux for 5 min. The solvent was removed in a water-jet pump vacuum, and the resulting yellow-orange oil was dissolved in hexane (5 mL). The light yellow crystals that precipitated on keeping the solution at –30°C for a week were separated by decantation and dried in vacuum. Yield 16 mg (41%).

IR (KBr; ν, cm^{-1}): 2090 vs, 2005 vs, 1970 vs, 1925 vs, 1895 vs, 1860 vs, 1545 w, 1430 w, 1170 w, 740 m, 680 w, 615 w, 580 m, 520 s.

For $C_{31}H_{29}O_7PS_2Re_2$ ($M = 981$)

anal. calcd., %:	C, 37.95;	H, 2.98.
Found, %:	C, 38.22;	H, 3.17.

Simultaneous synthesis of I and II with chromatographic separation. A solution of $(PPh_3)_2Pt(C_2Ph_2)$ (194 mg, 0.22 mmol) and $Re_2(\mu\text{-}SPr)_2(CO)_8$ (162 mg, 0.22 mmol) in toluene (20 mL) was stirred at 60°C for 4 h. The red-brown reaction mixture was evaporated to dryness, and the residue was washed with heptane (3 × 10 mL) and dissolved in benzene (10 mL). Heptane (12 mL) was added to the resulting red solution and the mixture was chromatographed on a silica gel column (10 × 2 cm, elution with heptane). The pale yellow band was washed out by a 2 : 1 benzene–heptane mixture (30 mL) and the orange band was washed out with benzene (30 mL).

The pale yellow eluate was concentrated to dryness and the residue was dissolved in heptane (3 mL). The pale yellow crystals of **II** that precipitated on keeping the solution for 24 h at room temperature were suitable for X-ray diffraction. Yield 12 mg (5.6%).

The orange solution was concentrated to dryness and the residue was dissolved in cyclohexane (2 mL).

Crystal data and structure refinement parameters of **I** and **II**

Parameter	Value	
	I	**II**
M	1093.02	981.03
Diffractometer	Bruker APEX II CCD	
Radiation (λ, Å)	MoK_α (0.71073)	
Measurement temperature, K	150(2)	296(2)
Space group	$P\bar{1}$	$P2_1/c$
a, Å	9.653(1)	11.884(3)
b, Å	10.285(1)	12.277(3)
c, Å	23.215(2)	23.861(6)
α, deg	78.358(2)	90
β, deg	83.754(2)	98.886(5)
γ, deg	82.191(2)	90
V, Å^3	2228.5(4)	3439.4(14)
Z	2	4
ρ_{calcd}, g/cm^{-3}	1.629	1.895
μ, mm^{-1}	6.004	7.243
F(000)	1052	1872
Scaning range, θ, deg	0.90–30.54	1.73–24.89
Type of scanning	ω	
The number of independent reflections (N_1)	13447 (R_{int} = 0.0545)	5945 (R_{int} = 0.0445)
The number of reflections with $I > 2\sigma(I)$ (N_2)	8375	5214
The number of refined parameters	468	387
GOOF (F^2)	0.958	1.121
R_1 for N_2	0.0494	0.0467
wR_2 for N_1	0.1181	0.1281
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	1.768/–1.701	1.159/–0.869

The unidentified red-orange crystals that precipitated on keeping the solution for 2 days at 10°C were separated by decantation. The solution was further kept for 10°C for a week and the precipitated light yellow intergrown crystals of **I** were separated by decantation, washed with cold hexane (–10°C), and dried in vacuum. Yield 4 mg (1.6%). The crystals of $(CO)_3(PPh_3)Re(SPr)Pt(PPh_3)(CO) \cdot C_6H_6$ were prepared by slow diffusion of heptane into a benzene solution of the complex.

X-ray diffraction. The crystallographic data and structure refinement parameters of **I** and **II** are summarized in the table. The absorption corrections were applied by multiple measurement of equivalent reflections by the SADABS program [10]. The structures of **I** and **II** were determined by the direct method and refined by the least-squares method on F^2 in the anisotropic approximation for non-hydrogen atoms (except for the carbon atoms of the disordered propyl groups) using the SHELXTL program package [11].

The H atom positions were calculated geometrically. Selected bond lengths and bond angles in structures **I** and **II** are given in the captions to Fig. 1 and Fig. 2. The structure of complex **I** has a highly disordered benzene solvent molecule. The structure of **I** without the benzene molecules was refined by using the "squeeze" procedure of the PLATON program package [12].

The atom coordinates and other structure parameters of **I** and **II** are deposited with the Cambridge Crystallogtaphic Data Centre (no. 941914 (**I**), 941913 (**II**); http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

The reaction of $Re_2(\mu\text{-}SPr)_2(CO)_8$ with $(PPh_3)_2Pt(C_2Ph_2)$ is accompanied by dissociation of the initial dimer and by π-coordination of the platinum atom to the arising Re $\Leftarrow$ SPr double bond to give light yellow crystals of the heterometallic complex **I**, an analogue of one of the isomers of the corre-

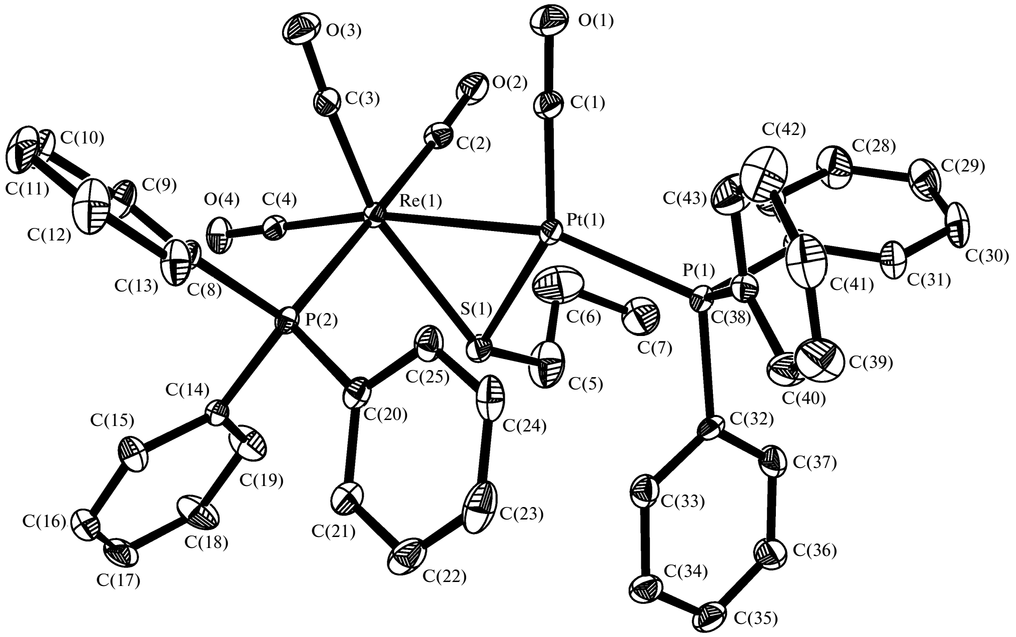


Fig. 1. Molecular structure of complex **I**. Selected bond lengths and angles: Pt(1)–P(1) 2.328(2), Pt(1)–S(1) 2.337(2), Pt(1)–Re(1) 2.7416(4), Re(1)–S(1) 2.447(2), Re(1)–P(2) 2.468(2), S(1)–C(5) 1.792(9) Å и Pt(1)S(1)Re(1) 69.90(5)°.

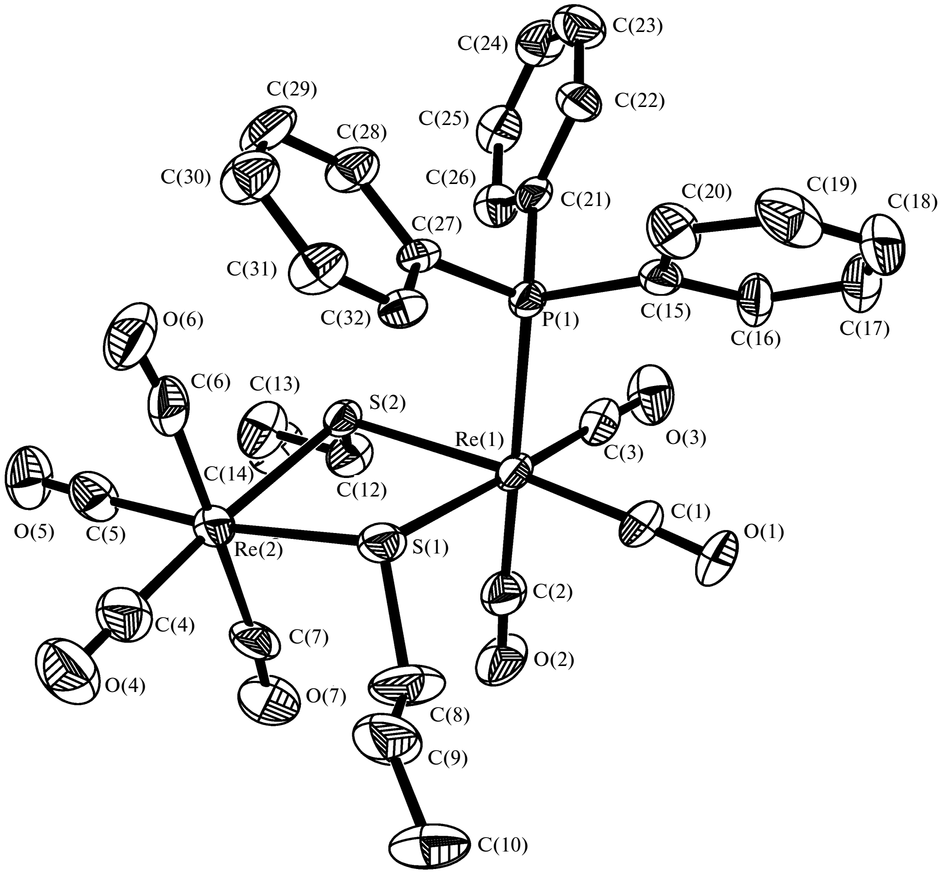
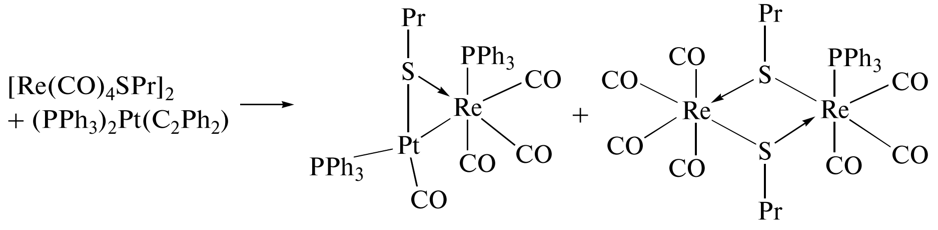


Fig. 2. Molecular structure of complex **II**. Selected bond lengths and angles: Re(1)–S(2) 2.512(2), Re(1)–P(1) 2.518(3), Re(1)–S(1) 2.527(3), Re(2)–S(1) 2.510(3), Re(2)–S(2) 2.519(3) Å и Re(2)S(1)Re(1) 98.8(1)°, Re(1)S(2)Re(2) 99.01(9)°.

sponding manganese complex [7]. According to X-ray diffraction data (table, Fig. 1), **I** contains a single Re–Pt bond (2.7416(4) Å) supplemented by the thiolate bridge in which the Pt–S (2.337(2) Å) and Re–S (2.447(2) Å) bonds are substantially shortened as compared with the sum of the covalent radii (SCR) (2.41 and 2.56 Å, respectively [5]). The Re–P (2.469(2) Å) and Pt–P (2.329(2) Å) bonds are also shortened with respect to the SCR (2.58 and 2.43 Å respectively [5]), probably, due to the dative interaction of the lone electron pair of rhenium with vacant *d*-orbitals of phosphorus. It is worth noting that the absence, in the reaction mixture, of the isomer of complex **I** containing two triphenylphosphine molecules at the platinum atom is in line with the formation, in the beginning of the reaction, of the binuclear rhenium phosphine complex **II** resulting from the exchange of one CO molecule at one of the rhenium atoms with the triphenylphosphine molecule at the platinum atom. Compound **II** is easily prepared by alternative synthesis (on treatment of the initial rhenium thiolate dimer with the proper triphenylphosphine). The structure of **II** was unambiguously determined by X-ray diffraction (table, Fig. 2). It is of interest that in **II**, not only the formally single Re–S bonds are elongated (to 2.512(2)–2.527(2) Å) but also the Re–P bond (2.517(3) Å) is elongated as compared with **I**.



(I) **(II)**

Apparently, dissociation of the binuclear thiolate-bridged rhenium complex into two monomers is facilitated by fast exchange of one triphenylphosphine molecule at platinum with the carbon monoxide molecule at rhenium. The more electron-donating rhenium phosphine-thiolate-tricarbonyl thus formed ensures stronger binding to the more electron-withdrawing phosphine-carbonyl-platinum fragment.

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