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Heterometallic Derivatives of Dicarbonylcyclopentadienylrhenium Disulfide Containing Chromium Pentacarbonyl and Bis(triphenylphosphine)platinum

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Abstract—The reaction of Cp'Re(CO)$_2$THF (Cp' = C$_5$H$_4$Me), THF is tetrahydrofuran) with sulfur affords Cp'Re(CO)$_2$S$_2$(**I**) and [Cp'Re(CO)$_2$]$_2$S (**II**). The synthesized compounds are isolated chromatographically and characterized by X-ray diffraction analysis. The adduct Cp'Re(CO)$_2$S$_2$Cr(CO)$_5$ (**III**) is synthesized by the reaction of compound **I** with Cr(CO)$_5$(THF). The adduct CpRe(CO)$_2$S$_2$Cr(CO)$_5$ (**IV**) is obtained similarly from known CpRe(CO)$_2$S$_2$ and Cr(CO)$_5$(THF). The reaction of compound **I** with (PPh$_3$)$_2$Pt(C$_2$Ph$_2$) results in the removal of Ph$_2$C$_2$ and one sulfur atom to form Cp'Re(CO)$_2$SPt(PPh$_3$)$_2$ (**V**). The structures of compounds **I–V** are determined by X-ray diffraction analysis (CIF files CCDC nos. 984554 (**I**), 984555 (**II**), 984556 (**III**), 984557 (**IV**), and 984558 (**V**)). Compound **I** contains the three-membered cycle ReS$_2$ with the ordinary S–S bond (2.044(4) Å) and shortened Re–S bonds (average 2.434(3) Å). The three-membered cycle Re$_2$S containing the ordinary Re–Re bond (2.932(1) Å) and shortened Re–S bonds (2.371(1) Å) is observed in compound **II**. In compounds **III** and **IV**, the formation of the ordinary S–Cr(CO)$_5$ bond (2.406(1) Å) with one of the sulfur atoms almost does not change the geometry of the ReS$_2$ fragment. The thermal decomposition of compound **III** proceeds with the elimination of six CO ligands in the range 110–160°C and then with the loss of CO and Cp' in the range 160–430°C and the formation of the inorganic residue ReCrS$_2$. Compound **V** contains the triangular framework ReSPt with the ordinary Pt–Re bond (2.7882(3) Å) and substantially shortened bonds Re–S (2.3984(9) Å) and Pt–S (2.2724(8) Å). It is assumed that compounds **II** and **V** can be presented as products of the π-coordination of the double bonds in Cp'(CO)$_2$Re=S with the Cp'Re(CO)$_2$ or Pt(PPh$_3$)$_2$ groups, respectively.

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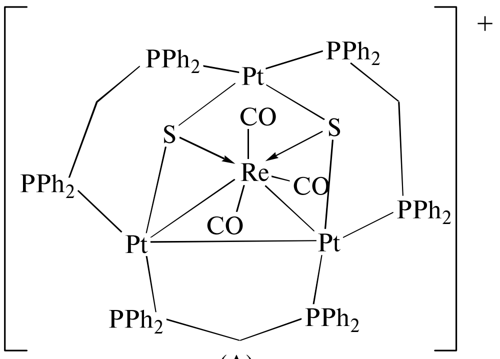
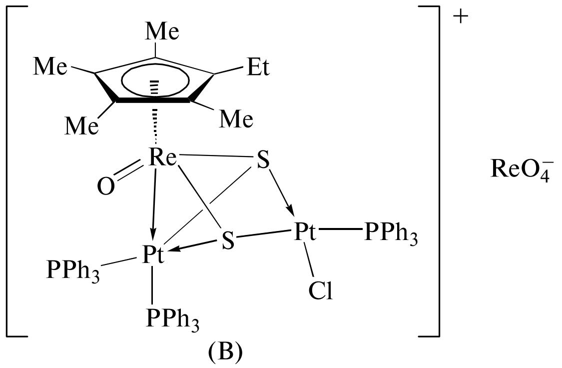
INTRODUCTION

The commercial heterogeneous Pt–Re catalysts for hydrocarbon reforming are known. In industry they are sulfurized to decrease alkane hydrogenolysis and favor dehydrocyclization and isomerization reactions with an increase in the octane number of the fuel [1]. These sulfurization reactions were simulated by the treatment of the heterometallic cluster [Pt$_3${Re(CO)$_3$}(μ-Dppm)$_3$]$^+$ (Dppm is bis(diphenylphosphinomethane)) with propenesulfide to form the cationic cluster [Pt$_3${Re(CO)$_3$}(μ^3-S)$_2$(μ-Dppm)$_3$]$^+$ (**A**) containing only very weak bonds in the RePt$_2$ triangle formed due to the two-electron three-center interaction [2]. The reaction of Cp''ReCl$_2$S$_3$ (Cp'' = C$_5$Me$_4$Et) with Pt(PPh$_3$)$_3$ in the presence of air afforded the cluster [Cp''ReO(μ-S)$_2$Pt$_2$(PPh$_3$)$_3$Cl]$^+$ReO$_4^-$ (**B**) in which Re(V) forms an elongated donor–acceptor bond (2.9557(4) Å) with one of two Pt(II) atoms that are not directly bonded (3.0961(4) Å) [3].

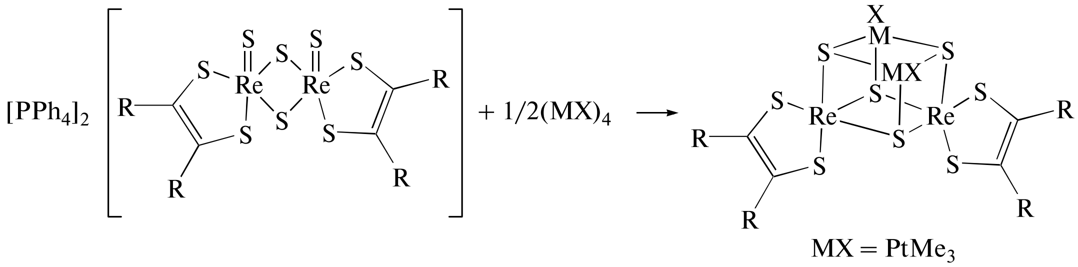


(A)

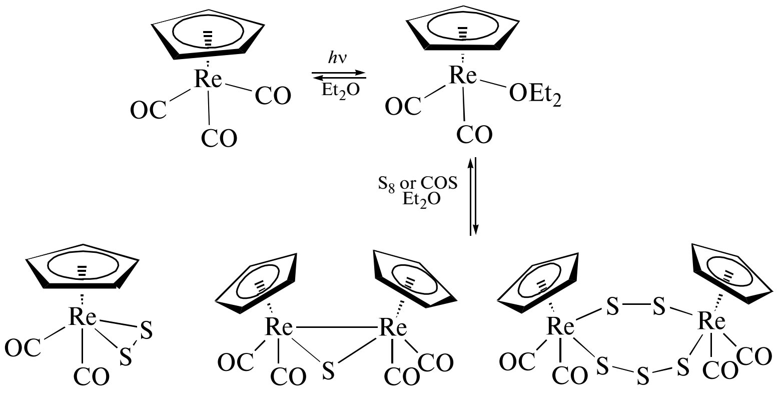


(B)

In addition, the rhenium–platinum–sulfide clusters were synthesized from the binuclear rhenium sulfide complexes [4, 5] by the reaction:



At the same time, the rhenium disulfide complexes can be useful for the synthesis of heterometallic clusters as the starting reactants. These complexes are obtained by the reactions of photochemically activated tricarbonylcyclopentadienylrhenium with sulfur or COS [6].



For example, the complex $Cp^*Re(CO)_2S_2Mn(CO)_2Cp$ was earlier synthesized from $Cp^*Re(CO)_2S_2$ ($Cp^* = Me_5C_5$) with the assumed terminal coordination of the manganese atom to one of the sulfur atoms; however, X-ray diffraction data for its structure were lacking [7]. We studied the synthesis of heterometallic derivatives $Cp'Re(CO)_2S_2$ ($Cp' = CH_3C_5H_4$) containing the chromium and platinum atoms. The choice of the methylcyclopentadienyl complex expected lower temperatures of thermal decomposition because of the elimination of the five-membered ring in the form of fulvene, which has previously been shown as an example for the comparative thermal decomposition of $[LFe(CO)_2]_2Sn(TePh)_2$, where L = Cp or Cp' [8].

EXPERIMENTAL

All reactions were carried out in the standard Schlenk apparatus under an argon atmosphere using dehydrated solvents. The reaction course was monitored by the data of IR spectroscopy. IR spectra were recorded on a Bruker Alpha FT-IR spectrometer. Absorption spectra were detected on a SPECORD UV VIS instrument. ^1H, $^{13}C\{H\}$, and $^{31}P\{H\}$ NMR spectra were measured on a Bruker AV 400 spectrometer with the working frequencies 400.13, 100.61, and 162.0 MHz, respectively, and internal stabilization for deuterium at room temperature (298 K). The ^1H and ^{13}C chemical shifts were presented relatively to tetramethylsilane, and the ^{31}P chemical shifts were given relatively to 85% H_3PO_4 used as an external standard.

Signals in the proton and carbon resonance spectra were assigned using the 2D heteronuclear multiple quantum correlation experiment (^{13}C, ^1H HMQC).

Deuterated solvents were dried over molecular sieves 4 Å. Samples for NMR experiments were prepared in an argon atmosphere using the standard Schlenk technique.

Elemental analyses were carried out on a Carlo-Erba CHNS analyzer. The thermal decomposition was studied on a NETZSCH TG 209 F1 instrument.

X-ray diffraction analyses for compounds I–V were carried out on a Bruker APEX II CCD diffractometer. An absorption correction was applied by the method of multiple measurements of equivalent reflections using the SADABS program [9]. Structures **I–V** were determined by a direct method and refined by least squares for F^2 in the anisotropic approximation for non-hydrogen atoms using the SHELXTL program package [10]. The positions of hydrogen atoms were calculated geometrically. The unit cell of the structure

Table 1. Crystallographic data and refinement parameters for structures **I–V**

Parameter	Value				
	I	**II**	**III**	**IV**	**V**
FW	385.46	674.73	577.51	563.48	1073.03
Radiation (λ , Å)	MoK_α (0.71073)				
Recording temperature, K	296(2)	150(2)	173(2)	150(2)	150(2)
Space group	$P2_1/n$	$C2/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a, Å	8.534(11)	8.8410(9)	7.1819(4)	6.9963(3)	11.855(1)
b, Å	21.46(3)	12.008(1)	9.8922(5)	10.0721(4)	12.074(1)
c, Å	10.915(13)	16.035(2)	12.1439(7)	11.5335(5)	15.279(1)
α, deg	90	90	95.057(1)	87.5340(10)	75.501(1)
β, deg	92.07(3)	103.439(1)	91.5060(1)	88.4690(10)	80.568(1)
γ, deg	90	90	102.508(1)	77.1730(10)	65.780(1)
V, Å^3	1998(4)	1655.7(3)	838.09(8)	791.60(6)	1926.4(3)
Z	8	4	2	2	2
ρ_{calcd}, g/cm^{-3}	2.563	2.707	2.288	2.364	1.850
μ, mm^{-1}	12.545	14.751	8.144	8.619	6.940
F(000)	1424	1232	544	528	1032
Scan range θ, deg	1.9–29.0	2.61–30.47	2.58–29.00	1.77–30.56	2.09–29.00
Scan type	ω				
Independent reflections (N_1)	5317 (R_{int} = 0.0484)	2504 (R_{int} = 0.0370)	4435 (R_{int} = 0.0359)	4798 (R_{int} = 0.0297)	10219 (R_{int} = 0.0417)
Reflections with $I > 2\sigma(I)$ (N_2)	4942	2359	4183	4590	7980
Number of refined parameters	227	106	218	208	460
Goodness-of-fit (F^2)	0.950	1.107	1.034	1.081	0.915
R_1 for N_2	0.0333	0.0325	0.0185	0.0223	0.0227
wR_2 for N_1	0.1155	0.0875	0.0416	0.0577	0.0501
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	2.006/–4.848	3.984/–4.500	1.516/–1.141	1.414/–1.956	1.149 /–0.831

of complex **I** contains two independent molecules, and the methylcyclopentadienyl ligand of one of them is disordered over two positions with site occupancies 0.66 : 0.34. The coordinates of the disordered atoms were refined in the isotropic approximation. The refinements for complexes **II** and **III** were carried out taking into account the extinction by the formula $Fc^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$. The coefficient x was refined as 0.0023(2) and 0.0010(2) in structures **II** and **III**, respectively. The crystallographic data and refinement parameters for structures **I–V** are presented in Table 1. Selected bond lengths and bond angles in structures **I–V** are listed in the figure captions to Figs. 1–5.

The coordinates of atoms and other parameters for structures **I–V** were deposited with the Cambridge Crystallographic Data Centre (CCDC 984554 (**I**), 984555 (**II**), 984556 (**III**), 984557 (**IV**), and 984558 (**V**), respectively; http://www.ccdc.cam.ac.uk/data_request/cif).

Synthesis of Cp'Re(CO)$_3$. A solution (2.5 mL) of $C_5H_5CH_3$ in THF (0.35 mL of $C_5H_5CH_3$, 0.38 mmol) was added to a suspension of NaH (0.283 g, 1.08 mmol) in THF (2 mL). The reaction mixture was stirred for 30 min. The pink solution that formed was added dropwise to Re(CO)$_5$Br (1.542 g) in THF (10 mL). The obtained suspension was stirred until the complete dissolution of Re(CO)$_5$Br, and the mixture was refluxed for 1 h until the gas stopped to evolve. The reaction mixture was evaporated to dryness, extracted with hexane, and purified on a column with silica gel. The eluate was evaporated to 10 mL and kept at –20°C for 24 h. Colorless crystals that formed were separated by decantation, washed with cooled pentane (5 mL), and dried in vacuo. The yield was 0.60 g (46%).

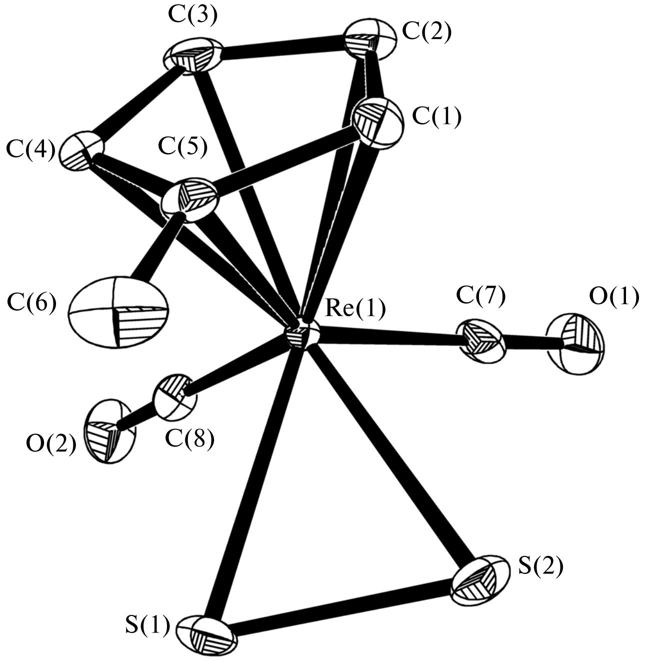


Fig. 1. Molecular structure of compound **I**. One of two independent molecules is shown. Selected bond lengths and angles: Re(1)–S(2) 2.433(3), Re(1)–S(2) 2.436(3), S(1)–S(2) 2.044(4) Å and S(1)Re(1)S(2) 49.6(1)°, C(7)Re(1)S(2) 83.5(2)°, C(8)Re(1)S(2) 81.7(2)°, C(7)Re(1)C(8) 81.9(3)°.

IR (KBr), ν, cm^{-1}: 3111 v.w, 2934 v.w, 2020 v.s, 1915 v.s, 1475 w, 1454 w, 1388 v.w, 1375 w, 1114 w, 1062 v.w, 1040 v.w, 1024 v.w, 923 v.w, 877 v.w, 830 w, 597 m, 510 m.

Syntheses of Cp'Re(CO)$_2$S$_2$ (I) and [Cp'Re(CO)$_2$]$_2$S (II). A solution of Cp'Re(CO)$_3$ (0.275 g, 0.785 mmol) in THF (50 mL) was UV-irradiated (DRT-240 mercury lamp) for 1.5 h on cooling with running water and passing an Ar current. The obtained brown solution was added with S_8 (0.208 g, 0.813 mmol), and the mixture was stirred for 40 min. The red-brown reaction mixture was evaporated to dryness, and the residue was dissolved in CH_2Cl_2 (15 mL). The solution was deposited on a chromatographic column (silica gel, 7 cm), and yellow, red-brown, and light green zones were eluted with CH_2Cl_2. The red-brown solution was evaporated to half a volume, heptane (10 mL) was added, and the solution was evaporated to the beginning of crystallization and kept at –20°C for 24 h. Red-brown crystals of compound **I** that formed were separated by decantation, washed with heptane (2 × 3 mL), and dried in vacuo. The yield was 87 mg (29%).

IR (KBr), ν, cm^{-1}: 3074 w, 2923 w, 2005 s, 1997 s, 1935 s, 1927 s, 1483 w, 1371 w, 1114 w, 1063 v.w, 1028 w, 865 m, 611 v.w, 597 w, 531 m, 508 w, 493 w, 471 w; IR (C_6H_6), ν, cm^{-1}: 2012 s, 1942 s. ^{1}H NMR (C_6H_6), δ, ppm: (m, A_2B_2, $\delta_A = 4.54$, $\delta_B = 4.56$, $J_{AB} = 1.95$ Hz, $J_{A\text{-}CH_3} = 0.4$ Hz, $C_5\mathbf{H}_4CH_3$), 1.32 (s, CH_3). $^{13}C\{H\}$ NMR C_6D_6; δ, ppm: 201.8 (Re($\mathbf{C}$O)$_2$), 92.4, 84.4 ($\mathbf{C}_5H_4CH_3$), 12.2 ($\mathbf{C}H_3$).

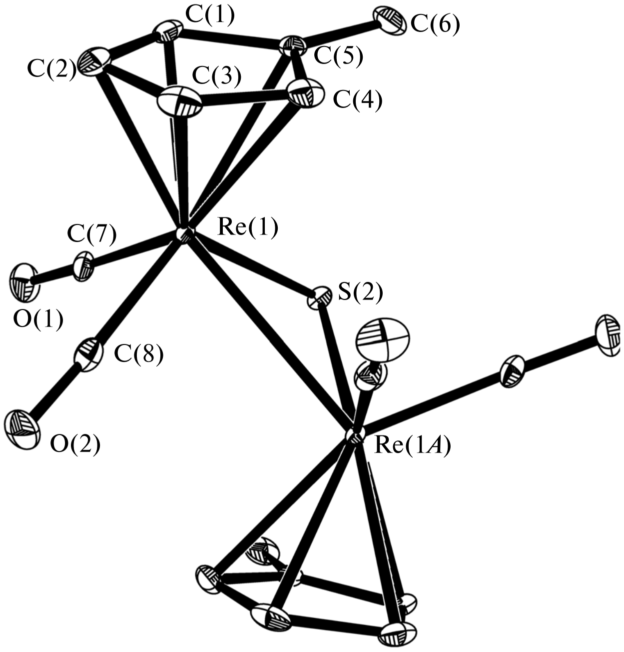


Fig. 2. Molecular structure of compound **II**. Selected bond lengths and angles: Re(1)–Re(1*A*) 2.932(1), Re(1)–S(1) 2.371(1) Å and Re(1)S(1)Re(1*A*) 76.38(5)°, S(1)Re(1)Re(1*A*) 51.81(2)°.

For $C_8H_7O_2S_2Re$ ($M = 385.47$)

anal. calcd., %:	C, 24.93;	H, 1.83;	S, 16.64.
Found, %:	C, 25.14;	H, 2.32;	S, 17.28.

The light green fraction was evaporated to half a volume, and heptane (10 mL) was added. The solution was evaporated to the beginning of crystallization and kept at –20°C for 24 h. The formed light green crystals of compound **II** were separated by decantation, washed with heptane (2 × 3 mL), and dried in vacuo.

IR (KBr), ν, cm^{-1}: 3107 v.w, 2920 v.w, 1947 s, 1876 s, 1483 w, 1446 v.w, 1113 v.w, 1024 w, 929 v.w, 899 v.w, 849 w, 606 w, 557 w, 521 w, 501 w, 483 w, 459 w.

For $C_{16}H_{14}O_4SRe_2$ ($M = 674.76$)

anal. calcd., %:	C, 28.48;	H, 2.1;	S, 4.75.
Found, %:	C, 28.63;	H, 2.6;	S, 5.36.

Synthesis of Cp'Re(CO)$_2$S$_2$Cr(CO)$_5$ (III). A solution of $Cr(CO)_6$ (0.048 g, 0.214 mmol) in THF (25 mL) was UV-irradiated (DRT-240 mercury lamp) for 1 h on cooling with running water and passing an Ar current. The obtained yellow solution was added with Cp'Re(CO)$_2$S$_2$ (0.08 g, 0.204 mmol). The red solution was evaporated to dryness, and the residue

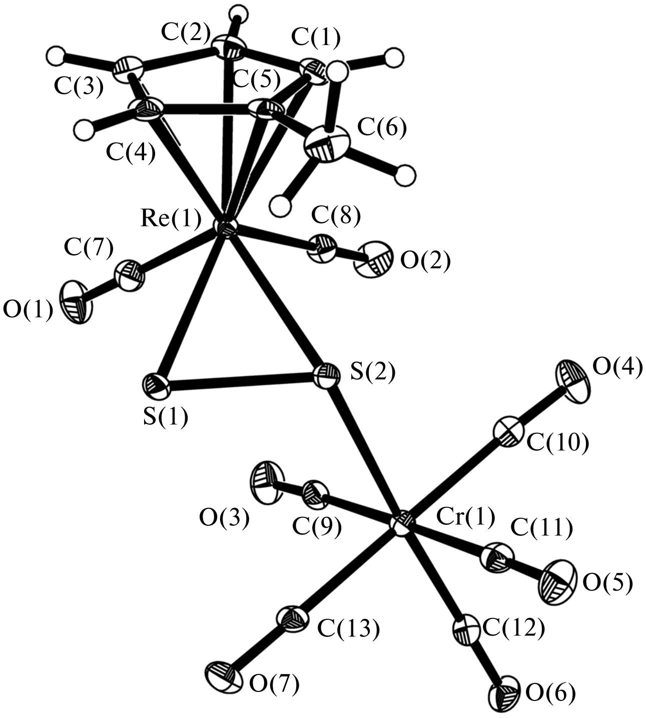


Fig. 3. Molecular structure of compound **III**. Selected bond lengths and angles: Re(1)–S(1) 2.4260(7), Re(1)–S(2) 2.4355(6), S(1)–S(2) 2.0377(8), Cr(1)–S(2) 2.4153(7) Å and S(1)Re(1)S(2) 49.56(2)°, C(7)Re(1)S(1) 82.54(9)°, C(8)Re(1)S(2) 85.54(8)°, C(8)Re(1)C(7) 81.3(1)°.

was dissolved in CH_2Cl_2 (12 mL) and filtered. Hexane (6 mL) was added, and the solution was evaporated to one-third of the volume. The formed red oil was triturated with hexane, the solution was separated by decantation, and the orange powder was dried in vacuo. The yield was 0.067 g (57%).

IR (KBr), ν, cm^{-1}: 3120 v.w, 3099 v.w, 2928 w, 2065 m, 2014 s, 1987 m, 1965 s, 1928 v.s, 1889 s, 1735 w, 1484 v.w, 1451 w, 1397 v.w, 1384 v.w, 1370 v.w, 1161 v.w, 1114 w, 1063 v.w, 1048 v.w, 1030 w, 865 w, 665 m, 650 m, 616 v.w, 597 v.w, 546 w, 528 w, 494 w, 466 w, 445 w. ^1H NMR (C_6D_6) δ, ppm: 4.33, 4.23, 4.20, 4.19 (m, $C_5\mathbf{H}_4CH_3$), 1.04 (s., $C\mathbf{H}_3$). $^{13}C\{H\}$ NMR (C_6D_6) δ, ppm: 221.46, 216.91 (s., $Cr(CO)_5$), 202.23, 196.71 (c., $Re(\mathbf{C}O)_2$), 115.5 (s., $\mathbf{C}CH_3$), 85.2, 84.2, 92.0, 93.9 (s, $\mathbf{C}_5H_4CH_3$), (s., 11.80 $\mathbf{C}H_3$).

For $C_{13}H_7O_7S_2CrRe$ (M = 577.52)

anal. calcd., %:	C, 27.04;	H, 1.22;	S, 11.10.
Found, %:	C, 27.05;	H, 2.11;	S, 11.78.

The crystals suitable for X-ray diffraction analysis were obtained by recrystallization from a CH_2Cl_2–hexane mixture at –20°C.

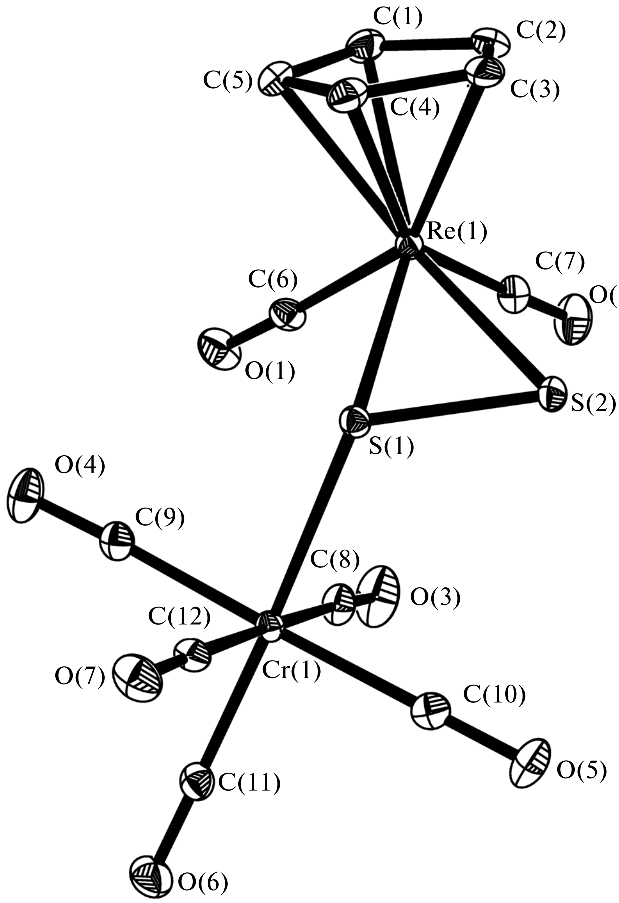


Fig. 4. Molecular structure of compound **IV**. Selected bond lengths and angles: Re(1)–S(2) 2.430(1), Re(1)–S(1) 2.437(1), S(1)–S(2) 2.042(1), Cr(1)–S(1) 2.406(1) Å and S(1)Re(1)S(2) 49.60(2)°, C(7)Re(1)S(2) 81.14(9)°, C(6)Re(1)S(1) 87.13(9)°, C(6)Re(1)C(7) 81.5(1)°.

Synthesis of $CpRe(CO)_2S_2Cr(CO)_5$ (IV).. Complex **IV** was synthesized by analogy to the synthesis of complex **III** from $Cr(CO)_6$ (0.029 g, 0.129 mmol) and $CpRe(CO)_2S_2$ (0.048 g, 0.129 mmol). The yield of red-brown crystals was 0.039 g (28%).

IR (KBr), ν, cm^{-1}: 3113 w, 3083 w, 2066 m, 2016 s, 1967 s, 1929 v.s, 1894 v.s, 1419 m, 1354 v.w, 1114 v.w, 1058 v.w, 1008 w, 938 v.w, 879 v.w, 851 w, 835 w, 665 m, 650 m, 599 w, 546 w, 531 w, 493 w, 466 w, 446 w.

Synthesis of $Cp'Re(CO)_2SPt(PPh_3)_2$ (V). A green solution of $Cp'Re(CO)_2S_2$ (0.086 g, 0.223 mmol) in C_6H_6 (20 mL) was added with $(PPh_3)_2Pt(C_2Ph_2)$ (0.215 g, 0.224 mmol), and the mixture was stirred for 100 min. The obtained red-brown solution was evaporated to dryness. The red-orange resin was triturated with hexane (14 mL) until a solid was formed. The solid was separated, dissolved in CH_2Cl_2, and precipitated with heptane. The brown-orange powder (presumably $Cp'Re(CO)_2S_2Pt(PPh_3)_2$) was obtained.

IR (KBr), ν, cm^{-1}: 3053 v.w, 2923 w, 2853 w, 2361 w, 2342 w, 1983 w, 1944 m, 1906 m, 1840 m, 1480 w, 1435 m, 1311 v.w, 1261 v.w, 1183 v.w, 1158 v.w, 1096 w, 1028 v.w, 745 w, 694 m, 542 m, 523 m, 513 m.

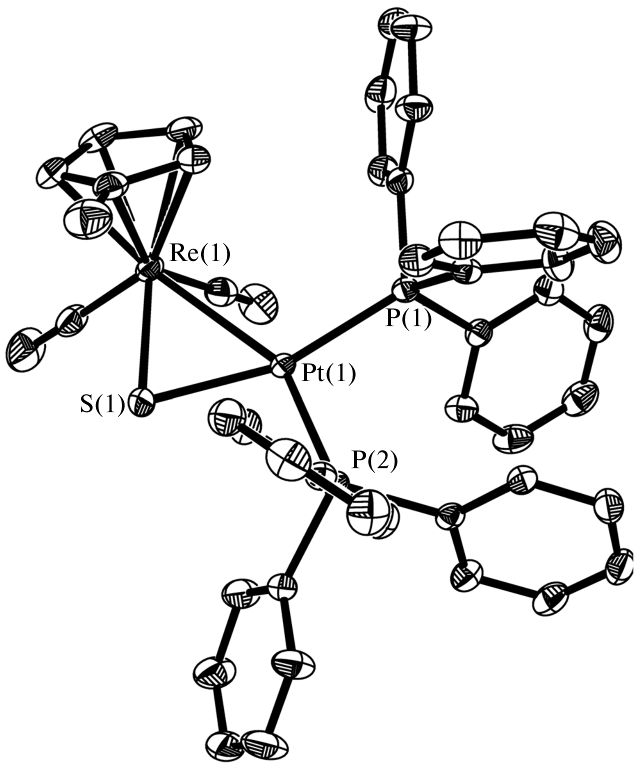


Fig. 5. Molecular structure of compound **V**. Selected bond lengths and angles: Pt(1)–Re(1) 2.7882(3), Pt(1)–S(1) 2.2724(8), Re(1)–S(1) 2.3984(9), Pt(1)–P(1) 2.2867(8), Pt(1)–P(2) 2.2738(8) Å and S(1)Pt(1)Re(1) 55.46(2)°, S(1)Re(1)Pt(1) 51.30(2)°, Pt(1)S(1)Re(1) 73.25(2)°, P(2)Pt(1)P(1) 100.26(3)°.

The isolated powder was dissolved in benzene (12 mL). Heptane (3.5 mL) was added to the filtered solution, and the mixture was concentrated to the beginning of the formation of a finely crystalline orange-brown precipitate. After the mixture was kept at room temperature for 3 weeks, the precipitate turned dark green with an admixture of a yellow-green touch. The precipitate was separated and dissolved in CH_2Cl_2 (30 mL). The resulting bright green solution was filtered and, after addition of heptane (10 mL), concentrated until crystallization began. The green crystals of V that precipitated from the solution exposed to –20°C were separated by decantation, washed with hexane (2 × 5 mL), and dried in vacuo. The yield was 17.6 mg (7%).

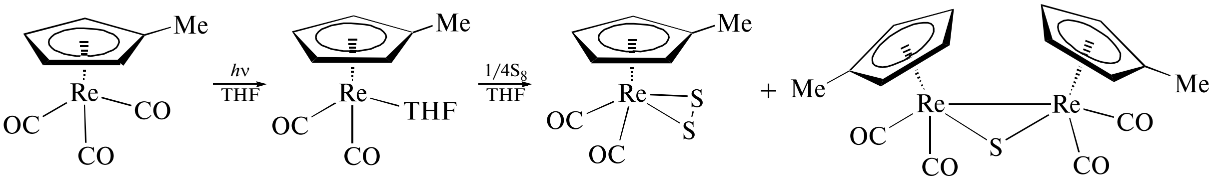
IR (KBr), ν, cm^{-1}: 3053 w, 1941 v.s, 1860 v.s, 1586 v.w, 1481 w, 1435 m, 1259 v.w, 1187 v.w, 1157 v.w, 1094 m, 1027 w, 999 w, 906 w, 824 w, 747 m, 698 m, 611 v.w, 560 v.w, 539 m, 522 m, 498 m, 482 w, 445 v.w. ^{1}H NMR (CD_2Cl_2), δ, ppm: 4.98, 4.10 (s.br, $C_5\mathbf{H}_4CH_3$), (s. 1.84 $C\mathbf{H}_3$), 7.6–7.0 (m, $6C_6H_5$). $^{31}P\{H\}$ NMR (CD_2Cl_2), δ, ppm: 32.4 (d, $^2J_{P-P}$ = 16.0 Hz, $^1J_{Pt-P}$ = 3524 Hz), 24.9 (d, $^2J_{P-P}$ = 16.0 Hz, $^1J_{Pt-P}$ = 3897 Hz).

For $C_{44}H_{37}O_2P_2PtReS$ (*M* = 1073)

anal. calcd., %:	C, 49.25;	H, 3.48;	S, 2.99.
Found, %:	C, 48,27;	H, 3.70;	S, 3.52.

RESULTS AND DISCUSSION

The procedure for the preparation of $CpRe(CO)_2S_2$ and $Cp^*Re(CO)_2S_2$ [6, 7] was used for the synthesis of their methylcyclopentadienyl analog **I**. In this case, binuclear rhenium complex **II** was formed along with compound **I**.



(I) **(II)**

Table 2. Comparative structural data for $LRe(CO)_2S_2$ (L = Cp, Cp*, Cp' (**I**))

Parameter	$CpRe(CO)_2S_2$	$Cp^*Re(CO)_2S_2$	**I**
Re–S, Å	2.40(2)	2.419(3), 2.421(3)	2.433(3), 2.436(3)
S–S, Å	1.96(5)	2.023(6)	2.044(4)
SReS, deg	48.9(2)	49.4(1)	49.6(1)

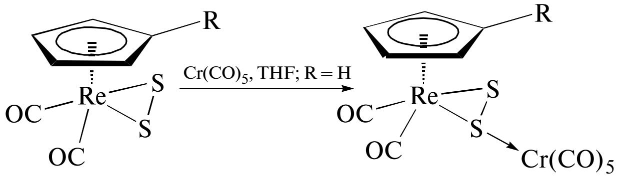
Solutions of $Cp'Re(CO)_2S_2$ do not absorb the red light and partially transmit the green light (bands at 19300 cm^{-1} in CH_2Cl_2 or 19660 cm^{-1} in $C_6H_5CH_3$). This results in dichroism: as the concentration increases, the color of the solution changes from green to red. In more polar CH_2Cl_2, the absorption band broadening weakens the green light transmission and the transition to the red color occurs in significantly lower concentrations.

According to the X-ray diffraction data, the bond lengths and bond angles in structure **I** (Fig. 1) do not almost differ from those found for the known analogs $CpRe(CO)_2S_2$ and $Cp^*Re(CO)_2S_2$ (Table 2).

The presence of two independent molecules **I** in the unit cell, probably, explains four peaks in the region of CO stretching vibrations in the IR spectrum of solid **I**, whereas the IR spectra of the solutions exhibit only two bands of CO stretching vibrations.

According to the X-ray diffraction data, in binuclear complex **II** having only one sulfide bridge (Fig. 2), the Re–S bonds (2.371(1) Å) are noticeably shortened compared to similar bonds in compound **I**, which seems natural if compound **II** is considered as a π-coordination of the $Cp'Re(CO)_2$ fragment with complex $Cp'(CO)_2Re{=}S$.

The reactions of the photochemically generated complex $Cr(CO)_5THF$ with the rhenium disulfide complexes $(C_5H_4R)Re(CO)_2S_2$ (R = Me, H) afforded new heterometallic complexes **III** and **IV** (Figs. 3, 4).



R = H (**IV**), Me (**III**)

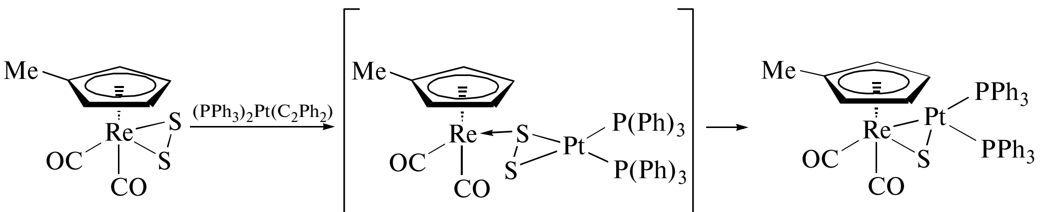
The addition of the $Cr(CO)_5$ fragment occurs without substantial changes in the geometry of the ReS_2 framework: only an insignificant shortening of all bonds is observed (within 0.01 Å) compared to the initial complex.

The thermal decomposition of compound **III** was studied by differential scanning calorimetry and thermogravimetry:

$$(CH_3C_5H_4)Re(CO)_2S_2Cr(CO)_5 \xrightarrow[100-160^\circ C]{-6CO} (CH_3C_5H_4)ReS_2Cr(CO) \xrightarrow[160-430^\circ C]{-CO,\ -CH_3C_5H_4} ReS_2Cr.$$

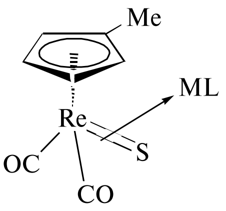
The complex is thermally stable below 110°C, and the stage decomposition starts with the further temperature increase. The first stage (110–160°C) occurs with a significant energy absorption, and ions $[CO]^+$ and $[C]^+$ are observed in the mass spectrum of the gas phase at this stage, which corresponds by the mass loss to the removal of six CO molecules. At the second stage (160–430°C), CO continues to eliminate, but ions $[C_5H_4CH_3]^+$, $[C_5H_4CH_2]^+$, $[C_5H_5]^+$, $[C_5H_3]^+$, $[C_4H_4]^+$, and $[C_4H_2]^+$ corresponding to the elimination and fragmentation of methylcyclopentadiene and fulvene are also detected. The solid residue corresponds to the inorganic composition ReS_2Cr.

The reaction of compound **I** with the zero-valence complex $(PPh_3)_2Pt(C_2Ph_2)$ in benzene gives an unstable orange-brown intermediate. According to the IR spectral data of this intermediate, the CO absorption bands shift to the low-frequency region to 1906 and 1840 cm^{-1} compared to 2012 and 1942 cm^{-1} in the starting compound **I**. A similar shift has recently been observed for the formation of $[CpMn(CO)_2]_2S_2Pt(PPh_3)_2$ from $(CpMn(CO)_2)_2S_2$ [11]. However, an attempt to crystallize the obtained compound from a CH_2Cl_2–hexane mixture led, probably, to its partial desulfurization to form new complex **V** and unidentified products.



(**V**)

According to the X-ray diffraction data (Fig. 5), complex **V** contains the triangular framework ReSPt including the ordinary covalent bond Pt(I)–Re(III) 2.7882(3) Å, being by 0.2 Å shorter than the aforementioned donor–acceptor bond Re(V) → Pt(II) in the mentioned above cationic complex $[Cp''ReO(\mu\text{-}S)_2Pt_2(PPh_3)_3Cl]^+$ [3]. The Re–S bond in compound **V** (2.3984(9) Å) is by 0.04 Å shorter than that in compound **I**, which, as in the case of complex **II**, can be explained under the assumption of the π-coordination of the $Pt(PPh_3)_2$ fragment to complex $Cp'(CO)_2Re{=}S$ according to the following type:



ML = $CpRe(CO)_2$, $Pt(PPh_3)_2$

The ^1H NMR spectrum of complex **V** exhibits only two signals of protons of the methylcyclopentadienyl ring, one of which is strongly broadened. The further broadening is observed on cooling to 0°C. This can be due to the dynamic process resulting in the racemization of the chiral center on the Re atom. A similar but slower process has earlier been detected for complex $Cp'Cr(CO)_2(SBu)Pt(PPh_3)_2$ using ^1H EXSY spectroscopy, and the exchange of the triphenylphosphine ligands within the molecule was also observed. The latter manifested itself as the appearance in the spectrum of the corresponding cross peaks from the *ortho*-protons of two different phosphines [12]. In the ^1H NMR spectrum of complex **V**, the signals of the *ortho*-protons of the phenyl rings are not resolved, but the spectrum in the phenyl region remains unchanged from 0 to 25°C.

Thus, the $Cp'Re(CO)_2$ fragment can form heterometallic complexes due to the addition of $Cr(CO)_5$ to one sulfur atom of the disulfide bridge or due to the π-coordination of $Pt(PPh_3)_2$ with the double bond in $Cp'(CO)_2Re{=}S$.

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