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The reaction of elemental sulfur with Rh(η^5-C_5H_4Z)(PPh_3)$_2$ (Z = H, CO_2Me). Formation of RhS_4, RhS_5, RhS_6, and $(RhS_2)_2$ catenated metallacycle complexes

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Abstract

The reaction of Rh(η^5-C_5H_5)(PPh_3)$_2$ with elemental sulfur, in addition to the previously reported Rh(η^5-C_5H_5)(PPh_3)S_5 (**1**), affords the novel complexes formulated as Rh(C_5H_5)(PPh_3)S_6 (**2**) and Rh(C_5H_5)(PPh_3)S_4 (**3**). Complexes **2** and **3** in solution convert spontaneously into **1** at room temperature. A similar reaction of Rh(η^5-$C_5H_4CO_2Me$)(PPh_3)$_2$ with elemental sulfur yields the complexes, Rh(η^5-$C_5H_4CO_2Me$)(PPh_3)S_x ($x = 2$, 4, and 5). X-ray diffraction studies reveal that **1**, **2**, and Rh($C_5H_4CO_2Me$)(PPh_3)S_4 (**5**) have chelated polysulfido ligands.

In recent years there has been an increasing interest in transition-metal complexes that have polysulfur ligands. Coordinated polysulfido ligands exhibit an exceptionally rich structural chemistry [1]. Synthetic and structural studies on such complexes are relevant in respect of their possible application in industrial [2] and mineralogical [3] processes. In particular, ruthenium and rhodium sulfides are expected to be efficient catalysts for hydrodesulfurization of fossil fuels [2a].

The most notable of the published methods for introducing polysulfido ligands is the reaction of elemental sulfur, S_8, with low valent metal complexes. Many mono- and di-nuclear transition-metal sulfido complexes, often containing cyclic catenated sulfur chelates of various ring sizes, have been prepared by this procedure, viz.: $Cp_2Cr_2(\mu$-$S_2)(CO)_4$ (Cp = η^5-C_5H_5) [4], [Ir($Ph_2PCH_2CH_2PPh_2$)(η^2-S_2)]Cl [5], [Cp*Co(S_2)]$_2$ (Cp* = η^5-C_5Me_5) [6], $Cp^*_2Ti(S_3)$ [7], [Cp*Ru(CO)(S_3)]$_2$ [8], $Cp_2M(S_4)$ (M = Mo, W) [9], $(PPh_3)_2M(S_4)$ (M = Pd, Pt) [10], [Cp*Rh(S_4)]$_2$(CO) [6],

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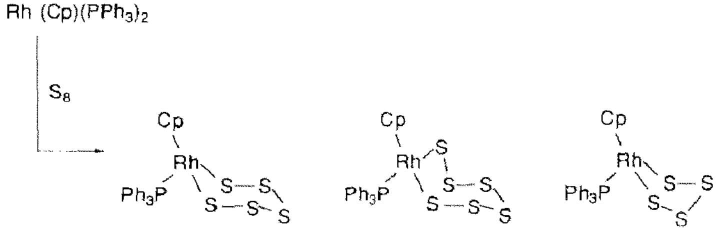
$Cp_2Re_2(CO)_2(\mu$-$S_3)(\mu$-$S_2)$ [11], $Cp_2Ti(S_5)$ [12], $Cp_2^*Zr(S_5)$ [13], $(Me_2dtc)_3Os(S_5)$ [14], and $(PMe_3)_3Os(S_7)$ [15].

In our previous report on the reactivity of $Rh(\eta^5$-$C_5H_5)(PPh_3)_2$, we described the reaction with elemental sulfur at 70 °C which gives a stable complex formulated as $Rh(\eta^5$-$C_5H_5)(PPh_3)S_5$ (**1**) [16]. Later a cobalt analog of **1** having a polysulfido chelate in chair conformation was prepared and structurally characterized by Werner et al. [17]. Upon reinvestigation of our previous reaction, $Rh(\eta^5$-$C_5H_5)(PPh_3)_2$ with S_8, we found that two more complexes are obtained when the reaction is carried out at ambient temperature. A similar reaction that of S_8 with the complex having a substituted cyclopentadienyl ligand—$Rh(\eta^5$-$C_5H_4CO_2Me)(PPh_3)_2$—has also been examined. Our findings, as reported here, demonstrate that rhodium is able to trap various sulfur fragments and that the change in the rhodium induced by an auxiliary ligand can determine the polysulfur ligands in their size and coordination modes.

Results and discussion

The reaction of $Rh(\eta^5$-$C_5H_5)(PPh_3)_2$ with an excess amount of elemental sulfur was carried out in benzene solution at room temperature. Subsequent column chromatography on alumina afforded three fractions. The first, a brown fraction, gave the known complex, $Rh(\eta^5$-$C_5H_5)(PPh_3)S_5$ (**1**) [16], the second fraction, also brown in color, yielded dark crystals of the composition $Rh(C_5H_5)(PPh_3)S_6$ (**2**). The third band, a dark-purple eluate, gave dark powder of composition $Rh(C_5H_5)(PPh_3)S_4$ (**3**). The crystal structures of **1** and **2** were determined by X-ray diffraction: our efforts to obtain single crystals of **3** were unsuccessful but its analog, containing a substituted-cyclopentadienyl ligand, did give crystals suitable for X-ray diffraction (vide infra). Furthermore, molecular weight measurement of **3** in benzene was consistent with the monomeric structure (calcd. 559; found 556) shown in equation 1.

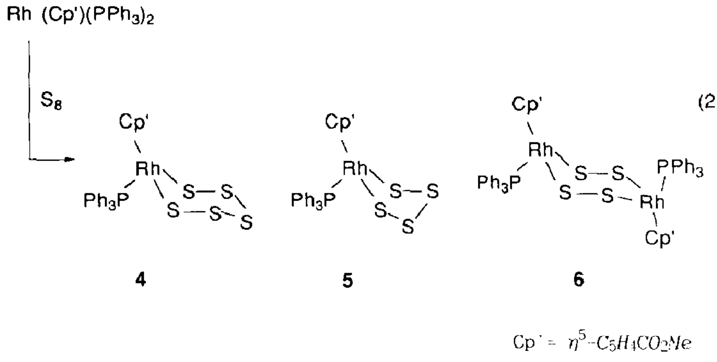
$Rh(\eta^5$-$C_5H_4CO_2Me)(PPh_3)_2$, prepared in situ, was allowed to react in benzene with elemental sulfur; work-up of the mixture and column chromatography as described, gave three complexes: $Rh(C_5H_4CO_2Me)(PPh_3)S_5$ (**4**), $Rh(C_5H_4CO_2Me)(PPh_3)S_4$ (**5**), and $Rh(C_5H_4CO_2Me)(PPh_3)S_2$ (**6**). **4** and **5** are dark-brown crystals but **6** remains a brown powder. The molecular weight of **6** measured in benzene indicates that it is a dimer (calcd. 1104; found 1056) whose structure is assigned as



1 **2** **3**

(1)

Cp = η^5-C_5H_5



shown in equation 2. The dimeric structure of **6** is also supported by the relevant molecular ion peak in its mass spectrum.

Single crystals of **5**, as well as those of complexes **1** and **2**, have been subjected to X-ray diffraction. Figure 1 depicts the perspective view and numbering schemes of these complexes. The atomic co-ordinates are listed in Table 1 and important bond lengths and angles are given in Table 2.

The chair conformation of the chelated S_5 ligand in **1** is similar to those found in $(C_5H_5)_2MS_5$ (M = Ti, V) [12,18], $(S_5)Fe_2(S_2)S_5^{2-}$ [19], $(S_6)Mn(S_5)$ [20], $(S_5)FeMS_4^{2-}$ (M = Mo, W) [21], $(C_5H_5)Co(S_5)(PMe_3)$ [17], and $Pt(S_5)_3$ [21]. Examples of hexasulfido ligands coordinated to a single metal atom are scarce; $M(S_6)_2^{2-}$ (M = Hg [22], Zn [23]), and $(S_6)Mn(S_5)^{2-}$ [20], in which the S_6 chelate ring is in a crown or a twisted-chair conformation whereas $Ag_2(S_6)_2^{2-}$ adopts a chair conformation [23]. The RhS_6 unit in **2** displays an almost perfect chair conformation.

The overall geometries of **1** and **2** are essentially identical except that the "back" of the metallocycle "chair" is a triangular in **1** and square in **2**. The square "back" of **2** is almost planar; the deviations from best plane are Rh 0.005, S(1) 0.111(3), S(2) 0.074(2), and S(6) − 0.039(1) Å. The "seats" of the chairs in **1** and **2** are flat since the largest deviation from the planarity is 0.011(2) Å in **1** and 0.015(2) Å in **2**. The lean-back angle, i.e. the angle between the "back" and the "seat"' in **1** is 116.4° and coincides with that of **2**. Some of the bond angles differ significantly between the two metallocycle frames. Thus the S(1)–Rh–S(6) angle of 102.1(1)° is 10° larger than the corresponding angle in **1**: Rh–S(1)–S(2) in the RhS_6 ring, 119.4(2)°, is about 12–14° larger than any other binding angles of sulfur atoms in **1** and **2**.

Two conformations of the MS_4 metallocycle are usually observed. The half-chair conformation, which is found in Cp_2MoS_4 [24], Cp_2WS_4 [25], $Zn(S_4)_2^{2-}$ and $Ni(S_4)_2^{2-}$ complexes [20], is characterized by equidistant central S atoms from and on the opposite side of the plane that contains the metal and the two coordinated S atoms. In the envelope conformation, which is found in the complexes $[SMo(S_4)_2]^{2-}$ and $[Mo_2S_{10}]^{2-}$ [26], the central S atoms lie both above and to one side of the plane defined by the metal and the two coordinated S atoms. In **5** Rh–S(1)–S(2)–S(4) forms a good plane, the largest deviation being 0.054 Å, and S(3) is tipped away from this plane toward the Cp ring by 1.150 Å. Such a conformation of a S_4 ligand has also been observed in the $(PPh_3)_2PtS_4$ complex [27]. Although alternation in S–S bond lengths are observed in other S_4 complexes, no such tendency has been noted in the Pt complex [27] or in the Rh complex **5**.

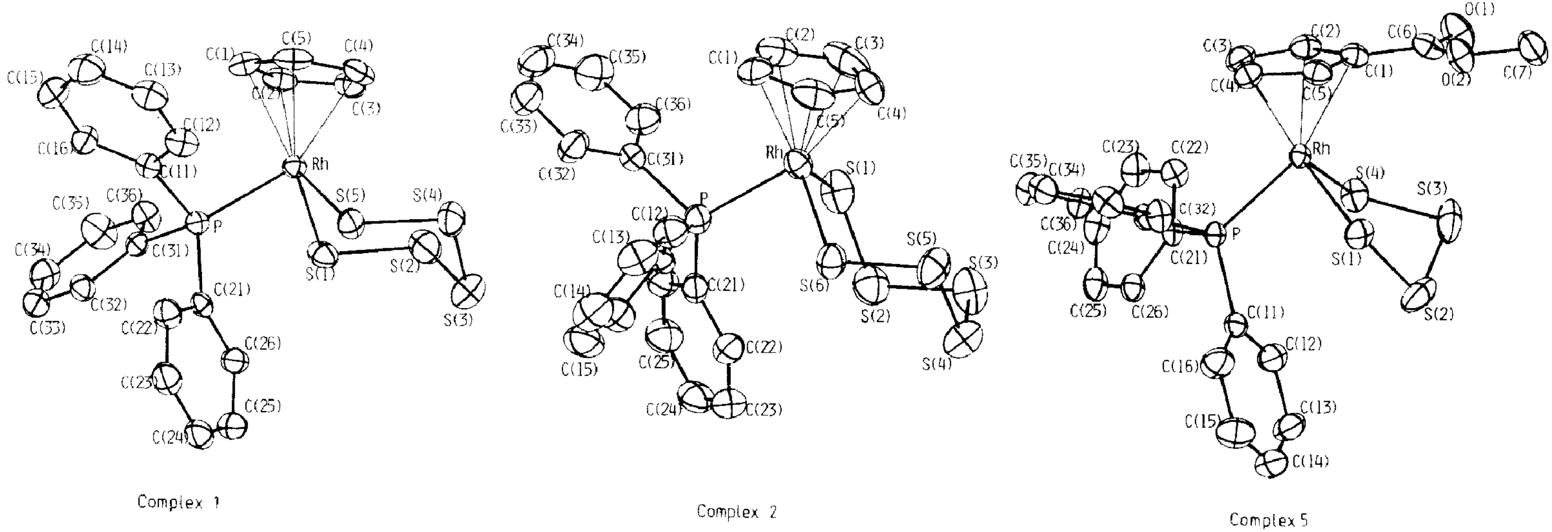


Fig. 1. Molecular structures of complexes **1**, **2**, and **5** with atomic numbering schemes.

Table 1

Atomic co-ordinates ($\times 10^4$) for **1**, **2**, and **5** (estimated standard deviations are in parentheses)

Complex 1

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Rh	3723(1)	2695(1)	6001(1)	C(14)	1938(9)	207(6)	7410(11)
S(1)	5081(2)	3217(1)	4666(2)	C(15)	2133(8)	165(5)	6028(11)
S(2)	5178(3)	4154(1)	5384(3)	C(16)	2906(7)	597(4)	5425(9)
S(3)	6138(3)	4117(2)	7123(4)	C(21)	5850(6)	1441(4)	6170(7)
S(4)	5042(2)	3698(1)	8455(3)	C(22)	6009(8)	866(5)	6930(9)
S(5)	4911(2)	2735(1)	7921(2)	C(23)	7113(8)	664(5)	7320(10)
P	4440(2)	1675(1)	5523(2)	C(24)	8040(8)	1036(5)	6916(10)
C(1)	1929(7)	2402(5)	5579(10)	C(25)	7882(8)	1607(5)	6146(10)
C(2)	2171(7)	2969(5)	4797(9)	C(26)	6786(7)	1821(4)	5779(8)
C(3)	2452(7)	3493(5)	5696(9)	C(31)	4540(6)	1449(4)	3749(7)
C(4)	2367(7)	3265(5)	7016(9)	C(32)	5135(7)	883(4)	3385(8)
C(5)	2050(7)	2584(5)	6975(9)	C(33)	5189(7)	700(5)	2034(8)
C(11)	3494(6)	1056(4)	6213(8)	C(34)	4647(8)	1083(5)	1059(9)
C(12)	3292(7)	1092(5)	7600(8)	C(35)	4055(9)	1647(6)	1414(10)
C(13)	2529(8)	667(5)	8181(10)	C(36)	4010(8)	1840(5)	2766(9)

Complex 2

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Rh	722(1)	2126(1)	1901(1)	C(14)	2632(4)	1896(14)	5919(12)
S(1)	580(1)	1350(3)	−480(3)	C(15)	2740(4)	1058(13)	4845(13)
S(2)	1049(1)	1865(3)	−1916(3)	C(16)	2359(4)	691(11)	3784(12)
S(3)	838(1)	3712(4)	−2664(4)	C(21)	1700(3)	−1(9)	954(10)
S(4)	1338(1)	4930(4)	−1569(4)	C(22)	2020(4)	866(10)	331(11)
S(5)	1094(1)	5208(3)	437(4)	C(23)	2292(4)	445(12)	−809(12)
S(6)	1365(1)	3689(3)	1709(3)	C(24)	2236(4)	−842(12)	−1317(11)
P	1362(1)	649(3)	2453(3)	C(25)	1915(4)	−1669(11)	−668(12)
C(1)	353(4)	1914(12)	3959(11)	C(26)	1651(4)	−1268(10)	453(11)
C(2)	45(4)	1333(11)	2858(13)	C(31)	1120(3)	−788(9)	3353(10)
C(3)	−126(4)	2280(16)	1850(13)	C(32)	1303(4)	−1150(10)	4748(11)
C(4)	86(4)	3451(11)	2281(14)	C(33)	1097(4)	−2226(12)	5376(12)
C(5)	388(4)	3247(11)	3591(12)	C(34)	722(4)	−2965(11)	4632(13)
C(11)	1878(3)	1224(9)	3747(11)	C(35)	544(4)	−2620(11)	3237(13)
C(12)	1781(4)	2103(11)	4820(11)	C(36)	735(4)	−1504(11)	2615(11)
C(13)	2154(4)	2439(12)	5898(12)				

Complex 5

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Rh	2714(1)	5922(1)	7297(1)	C(13)	2250(5)	9530(4)	10669(5)
S(1)	3441(1)	5721(1)	9867(1)	C(14)	3337(6)	9620(4)	11654(5)
S(2)	2018(1)	6450(1)	10710(1)	C(15)	4409(5)	9143(5)	11370(5)
S(3)	587(1)	5946(1)	9167(2)	C(16)	4419(4)	8532(4)	10100(5)
S(4)	727(1)	6748(1)	7369(1)	C(21)	2247(3)	8670(3)	5997(4)
P	3232(1)	7649(1)	7395(1)	C(22)	1527(4)	8327(3)	4701(4)
O(1)	647(3)	3566(3)	6653(4)	C(23)	901(4)	9113(4)	3584(5)
O(2)	2431(3)	2866(2)	8252(3)	C(24)	951(4)	10231(4)	3784(5)
C(1)	2449(3)	4190(3)	6561(4)	C(25)	1647(4)	10582(3)	5088(5)
C(2)	1981(4)	4953(3)	5325(4)	C(26)	2302(4)	8908(3)	6189(4)
C(3)	2965(4)	5385(4)	5115(5)	C(31)	4728(3)	7538(3)	7055(4)
C(4)	4046(4)	4914(4)	6219(5)	C(32)	5726(4)	6822(3)	7958(5)
C(5)	3729(4)	4174(3)	7093(5)	C(33)	6878(4)	6696(3)	7729(5)
C(6)	1728(4)	3537(3)	7122(4)	C(34)	7040(4)	7279(4)	6603(5)
C(7)	1825(5)	2179(4)	8901(6)	C(35)	6053(4)	7971(4)	5681(5)
C(11)	3323(4)	8425(3)	9091(4)	C(36)	4900(4)	8108(3)	5912(4)
C(12)	2236(4)	8928(4)	9395(5)				

Table 2

Selected bond distances (Å) and angles (°) for **1**, **2**, and **5** with standard deviations in parentheses

Complex 1			
Rh–S(1)	2.359(2)	S(1)–Rh–S(5)	92.09(6)
Rh–S(5)	2.351(2)	Rh–S(1)–S(2)	104.9(1)
S(1)–S(2)	2.022(3)	S(1)–S(2)–S(3)	106.9(1)
S(2)–S(3)	2.053(4)	S(2)–S(3)–S(4)	102.4(1)
S(3)–S(4)	2.058(4)	S(3)–S(4)–S(5)	105.9(1)
S(4)–S(5)	2.020(3)	S(4)–S(5)–Rh	106.9(1)
Rh–P	2.284(2)	P–Rh–S(1)	91.66(6)
Rh–C(1)	2.225(6)	P–Rh–S(5)	89.03(6)
Rh–C(2)	2.232(6)		
Rh–C(3)	2.212(7)		
Rh–C(4)	2.220(7)		
Rh–C(5)	2.229(6)		
C(1)–C(2)	1.405(10)		
C(2)–C(3)	1.400(10)		
C(3)–C(4)	1.370(10)		
C(4)–C(5)	1.420(11)		
C(5)–C(1)	1.417(10)		
Complex 2			
Rh–S(1)	2.335(3)	S(1)–Rh–S(6)	102.1(1)
Rh–S(6)	2.345(3)	Rh–S(1)–S(2)	119.4(2)
S(1)–S(2)	1.970(5)	S(1)–S(2)–S(3)	107.6(2)
S(2)–S(3)	2.065(5)	S(2)–S(3)–S(4)	104.7(2)
S(3)–S(4)	2.011(5)	S(3)–S(4)–S(5)	107.2(2)
S(4)–S(5)	2.040(5)	S(4)–S(5)–S(6)	107.3(2)
S(5)–S(6)	2.031(4)	S(5)–S(6)–Rh	110.4(2)
Rh–P	2.281(3)	P–Rh–S(1)	92.0(1)
Rh–C(1)	2.229(11)	P–Rh–S(6)	86.7(1)
Rh–C(2)	2.219(11)		
Rh–C(3)	2.234(11)		
Rh–C(4)	2.207(12)		
Rh–C(5)	2.189(11)		
C(1)–C(2)	1.374(15)		
C(2)–C(3)	1.387(18)		
C(3)–C(4)	1.361(19)		
C(4)–C(5)	1.398(16)		
C(5)–C(1)	1.407(16)		
Complex 5			
Rh–S(1)	2.354(1)	S(1)–Rh–S(4)	93.06(5)
Rh–S(4)	2.350(1)	Rh–S(1)–S(2)	107.0(1)
S(1)–S(2)	2.067(2)	S(1)–S(2)–S(3)	99.4(1)
S(2)–S(3)	2.057(2)	S(2)–S(3)–S(4)	98.3(1)
S(3)–S(4)	2.053(2)	S(3)–S(4)–Rh	101.2(1)
Rh–P	2.276(1)	P–Rh–S(1)	90.91(5)
Rh–C(1)	2.239(4)	P–Rh–S(4)	90.25(4)
Rh–C(2)	2.223(4)		
Rh–C(3)	2.229(5)		
Rh–C(4)	2.237(5)		
Rh–C(5)	2.253(4)		
C(1)–C(2)	1.436(5)		
C(2)–C(3)	1.404(7)		
C(3)–C(4)	1.427(6)		
C(4)–C(5)	1.405(7)		
C(5)–C(1)	1.423(6)		

That the Rh–S_5 ring is thermodynamically more stable than the Rh–S_6 metallocycle was demonstrated by the spontaneous and quantitative transformation of **2** into **1** at room temperature. Thus in dichloromethane, complex **2** gradually changes into **1**. The conversion was followed by monitoring the C_5H_5 signals of the two species, δ 5.30 for **2** and 5.42 for **1**. The half life of **2** was found to be about 6 days.

Complex **3** also changes into **1** in solution. When **3** was recrystallized from dichloromethane/hexane, and the supernatant solution was evaporated, the remaining brown powder was found to be almost pure **1** on the basis of its NMR spectrum. Since the conversion of **3** into **1** in benzene was cleaner but much slower than in chloroform or dichloromethane, the conversion in C_6D_6 was followed by NMR spectroscopy in C_6D_6 with toluene as internal standard: it took 12 hours at 45 °C for the two peaks due to **1** (doublet at δ 5.02) and **3** (doublet at 4.82) became equal in intensities, after 32 hours—at completion the conversion to **1** was ca. 50%, which means that half of the Rh-containing species had decomposed. Since the process is unaffected by the addition of elemental sulfur, the ring expansion of the sulfur chelate appears to involve bimolecular disproportionation of the Rh–S_4 rings. In contrast, the analogous complex, **5**, is stable.

Experimental

All reactions and the chromatography were carried out under argon. Proton NMR spectra were recorded on a JEOL GX-400 spectrometer in $CDCl_3$.

Reaction of $Rh(\eta^5\text{-}C_5H_5)(PPh_3)_2$ with elemental sulfur

A mixture of $Rh(\eta^5\text{-}C_5H_5)(PPh_3)_2 \cdot C_6H_6$ (200 mg, 0.29 mmol), triphenylphosphine (152 mg, 0.54 mmol), and elemental sulfur (80 mg, 0.3 mmol) in benzene (50 ml) was stirred at room temperature overnight. The reaction mixture was concentrated to ca. 10 ml and chromatographed on alumina. Three bands separate. The first, a brown band, was eluted with benzene/dichloromethane (1/1) and gave complex **1** on evaporation of the solvent (30 mg). It was contaminated with triphenylphosphine sulfide but recrystallization gives **1** pure. The second band was also a brown fraction, that was eluted by dichloromethane shortly after the first band. Concentration of the solvent and the addition of hexane yielded brown crystals of **2** (11 mg); decomp. 145–150 °C. ^1H NMR: δ 5.28 (d, 5H, Cp, $J(\text{Rh–H}) = 1.8$ Hz); 7.1–7.6 (broad m, 15H, Ph). Analysis. Found: C, 44.78; H, 3.20; S, 30.33. $C_{23}H_{20}PS_6Rh$ calcd.: C, 44.37; H, 3.24; S, 30.89%.

The third, a purple band was eluted with dichloromethane/THF (10/1). Evaporation of the solvent and recrystallization of the residue from dichloromethane-hexane gave **3** as a dark-purple powder (10 mg). ^1H NMR: δ 5.34 (dd, 5H, Cp, $J_{(\text{Rh-H})} = 1.9$, $J_{(\text{P-H})} = 0.4$ Hz); 7.0–7.6 (broad m, 15H, Ph). Analysis. Found: C, 49.43; H, 3.57; S, 22.86. $C_{46}H_{40}P_2S_8Rh_2$ calcd.: C, 49.46; H, 3.61; S, 22.96%.

Reaction of $[Rh(\eta^5\text{-}C_5H_4CO_2Me)(PPh_3)_2]$ with sulfur

To a suspension of $Rh(PPh_3)_3Cl$ (3.6 g, 3.9 mmol) in benzene (60 ml) was added a THF solution (5 ml) containing $(C_5H_4CO_2Me)Na$ (5 mmol) [28] and the mixture was stirred overnight. The brown solution was chromatographed on alumina and a dark brown band was eluted with dichloromethane. After the solvent was evaporated under reduced pressure, elemental sulfur (1.4 g) in benzene (40 ml) was added and the mixture was stirred for 4 hours. The solution was concentrated and chromatographed on alumina (deactivated beforehand with 10 wt% of water). The first, a dark greenish-brown band was eluted with dichloromethane/benzene (1/1), the second, a purple band was eluted with dichloromethane, and the third, a brown band was eluted with dichloromethane. Each fraction was concentrated and hexane was added to give crystals of **4** (932 mg), **5** (55 mg), and **6** (165 mg), respectively. Complex **4**: brown crystals, m.p. 171–175°C. ^{1}H NMR: δ 3.87 (s, 3H, CO$_2$Me); 5.42 (m, 2H, C$_5$H$_2$); 5.71 (q, 2H, C$_5$H$_2$, J(Rh–H) $\approx$ J(H–H) $\approx$ 2.2 Hz); 7.3–7.6 (m, 15H, Ph). Analysis. Found: C, 46.08; H, 3.39; S, 23.68. $C_{25}H_{22}O_2PS_5Rh$ calcd.: C, 46.29; H, 3.42; S, 24.71%. Complex **5**: black crystals, m.p. 147–148°C. ^{1}H NMR: δ 3.78 (s, 3H, CO$_2$Me); 4.98 (t, 2H, C$_5$H$_2$, J(H–H) = 2.2 Hz); 6.17 (q, 2H, C$_5$H$_2$, J(Rh–H) $\approx$ J(H–H) $\approx$ 1.6 Hz); 7.3–7.7 (m, 15H, Ph). Analysis. Found: C, 48.49; H, 3.59. $C_{25}H_{22}O_2PS_4Rh$ calcd.: C, 48.70; H, 3.60%. Complex **6**: brown powder, m.p. 200–201°C. ^{1}H NMR: δ 3.67 (s, 3H, CO$_2$Me); 5.00 (broad-s, 5H, C$_5$H$_4$); 7.2–7.6 (m, 15H, Ph). Analysis. Found: C, 54.25; H, 4.02; S, 10.83. $C_{25}H_{22}O_2PS_2Rh$ calcd.: C, 54.35; H, 4.01; S, 11.61%.

Table 3

Crystal data and refinement information of **1**, **2**, and **5**

	1	**2**	**5**
Formula	$C_{23}H_{20}PRhS_5$	$C_{23}H_{20}PRhS_6$	$C_{25}H_{22}O_2PRhS_4$
M	590.6	622.5	616.5
Crystal dimensions, mm	0.37×0.24×0.16	0.32×0.12×0.05	0.35×0.16×0.10
Space group	monoclinic, $P2_1/n$	monoclinic, $P2_1/a$	triclinic, $P\bar{1}$
a, Å	11.829(2)	26.335(5)	11.578(3)
b, Å	20.245(4)	10.203(2)	12.127(2)
c, Å	9.954(2)	9.245(2)	9.491(3)
α, deg			92.04(2)
β, deg	91.13(1)	95.56(2)	106.12(3)
γ, deg			79.22(2)
V, Å^3	2383.3(7)	2472.3(8)	1257.3(6)
Z	4	4	2
ρ(calcd), g cm^{-3}	1.65	1.67	1.63
μ, cm^{-1}	12.0	12.4	10.7
Radiation (λ, Å)	graphite-monochromated Mo-K_α (0.7107)		
Diffractometer	Rigaku AFC-5		
Scan speed, deg min^{-1}	constant, 3.6		
2θ scan limits, deg	$2 < 2\theta < 55$		
Scan method	ω-2θ		
Standard reflections	3 std/150 rflns (var. < 2%)		
Data collection	$\pm h$, $+k$, $+l$	$+h$, $+k$, $\pm l$	$\pm h$, $\pm k$, $+l$
Unique data	5963	6125	6135
Unique data	3619	2725	4133
R, %	4.67	6.39	3.49
R_w, ($w = 1/\sigma(F)$), %	4.47	5.33	2.98
Number of parameters	352	361	387
GOF	4.9	5.4	1.67
$\Delta(\rho)_{max}$, eÅ^{-3}	1.1	1.3	0.6

X-ray structure determination

The crystal data and refinement information are summarized in Table 3. The structures were solved by a direct method which revealed the positions of Rh and some of the S atoms. The remaining non-hydrogen atoms and the methyl hydrogens of complex **5** were located from subsequent difference Fourier syntheses. The hydrogen atoms of the phenyl and cyclopentadienyl rings were placed at calculated positions. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined with isotropic thermal parameters, by block-diagonal least squares. Anomalous dispersion corrections [29] for Rh were included in the refinement. Neutral-atom scattering factors were taken from ref. 30. Tables of anisotropic temperature factors, hydrogen atom coordinates, and structure factors are available from the authors.

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