

CAS Registry numbers:

2a, 114095-85-1; **2b**, 114095-86-2; **2c**, 114095-87-3; **3b**, 114130-39-1; **3c**, 114130-40-4; **4**, 114095-88-4; C₆H₆, 71-43-2; C₂(CH₃)₂, 503-17-3; C₂[Si(CH₃)₃]₂, 14630-40-1; Co, 7440-48-4; toluene, 108-88-3; hexamethylbenzene, 87-85-4; acetonitrile, 75-05-8.

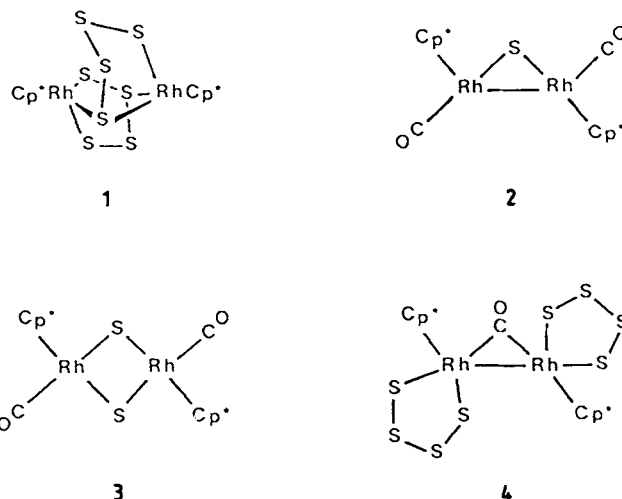
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- [5] a) Space group $P2_12_12_1$, $a = 5.975(5)$, $b = 8.67(1)$, $c = 17.32(2)$ Å, $V = 897$ Å³, $Z = 4$. 789 observed reflections ($I \geq \sigma_i$). Two-circle diffractometer, MoK α radiation, ω -scan, rapid decomposition of the crystals during the measurement. Co and butyne C-atoms anisotropic, the disordered benzene ligand was refined with two rigid C₆H₆ rings (C-C 1.395, C-H 0.95 Å) with anisotropic temperature factors for the C atoms, $R = 0.046$. b) Further details of the crystal structure are available on request from the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2 (FRG), on quoting the depository number CSD-52910, the names of the authors, and the journal citation.
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- [10] Space group $P2_1/c$, $a = 17.504(8)$, $b = 16.581(6)$, $c = 18.130(7)$ Å, $\beta = 115.70(3)^\circ$, $V = 4741$ Å³, $Z = 8$, 3315 observed reflections ($I \geq \sigma_i$). Four-circle diffractometer, MoK α radiation, ω -scan. Co and C atoms anisotropic, the toluene rings as rigid rings (C-C 1.425, C-H 0.95 Å), H-atoms with common isotropic temperature factor for each ring, $R = 0.058$ [5b].
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Synthesis and Structure of [(C₅Me₅)₂Rh₂S₈], a Dirhodium Complex with Unusual Polysulfide Bridge

By Henri Brunner, Norbert Janietz, Walter Meier, Bernd Nuber, Joachim Wachter,* and Manfred L. Ziegler

Chalcogen-rich transition-metal complexes of the type L₂M₂X_n (L = any substituted cyclopentadienyl ligand; X = S, Se; n ≥ 4) are currently attracting interest because of their structural variability and versatile chemistry, both of which are strongly influenced by the nature of the metal.^[1,2] The reaction of chalcogens with dimeric cyclopentadienylmetal complexes containing metal-metal multiple bonds has proven useful as a general synthetic route for such compounds. The chalcogen chains and rings undergo degradation thereby to mono- or diatomic moieties. Complexes with polysulfide ligands have been postulated as intermediates,^[3] but only seldom has it been possible to detect them.^[4] We now report on the synthesis and structure of the rhodium dinuclear complex [Cp*₂Rh₂S₈] **1** (Cp* = η⁵-C₅Me₅), which contains two unusually coordinated S₄ bridges.

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The diamagnetic, red-brown complex **1** is obtainable in ca. 62% yield from [Cp*₂Rh₂(CO)₂] and sulfur (Rh : S 1 : 4, tetrahydrofuran, room temperature). Its composition is confirmed by elemental analysis; the field desorption mass spectrum, however, contains only the molecular ion less one sulfur atom. Contrary to expectation the ¹H-NMR spectrum^[5] indicates a non-symmetrical structure for the compound. An X-ray structure analysis^[6] on a single crystal of **1** (from toluene or CH₂Cl₂) confirms the non-equivalence of the Cp* rings (Fig. 1). The structure is characterized by two RhS₄ chelate rings, which are coupled to each other in such a way that they give the puckered Rh₂S₃ core (envelope conformation) of the molecule. Each S₄ ligand functions as 4e donor. As a consequence of this behavior the length of the S-S bonds varies from 2.032(3) to 2.106(3) Å. The bond angles fall in three ranges: The S-Rh-S angles lie between 78.2(1) and 94.0(1)°, while the other angles in the chelate ring, with exception of Rh1-S1-Rh2 (114.5(1)°) range from 100.1(1) to 109.2(1)°. The "real" chelate angles S1-Rh-S6 and S3-Rh2-S7 are both 94.0(1)°. Both RhS₄ rings have a slightly distorted envelope conformation. Their tips S3 and S4 are 3.539 Å from each other; this could possibly make them suitable for the

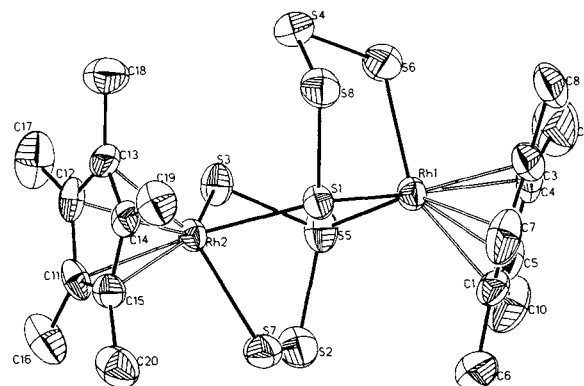


Fig. 1. Crystal structure of **1** (ORTEP). Selected bond lengths [Å] and angles [°]: Rh1-S1 2.384(2), Rh1-S5 2.327(2), Rh1-S6 2.384(2), Rh1-C(Cp*1)_{mean} 2.197(9), Rh2-S1 2.373(2), Rh2-S3 2.324(2), Rh2-S7 2.407(2), Rh2-C(Cp*2)_{mean} 2.196(9), S1-S8 2.103(3), S2-S5 2.106(3), S2-S7 2.043(3), S3-S5 2.032(3), S4-S6 2.057(3), S4-S8 2.040(3), Rh1...Rh2 3.999, S1...S5 3.372, S3...S4 3.539; S1-Rh1-S5 91.4(1), S1-Rh1-S6 94.0(1), S5-Rh1-S6 88.3(1), S1-Rh2-S3 91.3(1), S1-Rh2-S7 78.2(1), S3-Rh2-S7 94.0(1), Rh1-S1-Rh2 114.5(1), Rh1-S1-S8 100.1(1), S5-S2-S7 101.5(1), S6-S4-S8 101.7(1), Rh1-S5-S2 108.8(1), Rh1-S5-S3 109.2(1), S2-S5-S3 100.2(1), Rh1-S6-S4 107.4(1), S1-S8-S4 100.7(1).

bidentate coordination of unsaturated complex fragments. To our knowledge the only other bridge-forming S_4 ligands are found in copper(I) polysulfide clusters, in which two copper centers are each bridged by a terminal member of the S_4 chain.^[3]

The formation of **1** proceeds via several intermediates. When the dark blue solution of $[Cp^*_2Rh_2(CO)_2]$ in THF is allowed to react with $1/8 S_8$ at room temperature, the color changes to brown within 15 minutes, and the red-violet **2** can be isolated in 46% yield by column chromatography (Al_2O_3 , toluene).^[5] The Rh_2S three-membered ring in **2** can be expanded to a four-membered ring by addition of a further S atom. However, there is only IR spectroscopic proof available (ν_{CO} frequency at 2015 cm^{-1}) for the existence of the resulting complex **3**. The Se complex analogous to **3**, on the other hand, can be isolated.^[7]

When, however, the reaction of $[Cp^*_2Rh_2(CO)_2]$ with sulfur is carried out at -25°C instead of at room temperature, about equal amounts of **1** and **4** can be isolated. The symmetrical compound^[5] **4** may contain two RhS_4 chelate rings linked together by a Rh-Rh bond and a μ -CO group.^[8] **4** slowly transforms into **1** in solution. The structural changes on going from **3** to **4** are indicated by weak ν_{CO} frequencies temporarily occurring at 1785 and 1980 cm^{-1} , which were observed between -80 and -60°C . Unfortunately, these absorptions disappear in favor of those of **1** and **4** at higher temperatures, so that they cannot be assigned to specific structures. However, it cannot be ruled out that the monosulfide bridges in **2** and **3** are substitution-labile towards larger sulfur units, e.g. S_4^{2-} . An indication in this direction is that the Se analogues of **2** and **3** can be converted into **1** with S_8 .^[7]

Although rhodium sulfides are of interest as hydrodesulfurization catalysts,^[9] **1** is only the third structurally characterized rhodium polychalcogenide complex, after $[Cp^*_2Rh_2Se_3]^{10}$ and $[Rh(S_2)_3]^{3-}$.^[11] From the relatively high number of S-S bonds, a considerable reaction potential can be expected for **1**. Consistent with this prediction three irreversible oxidation waves were found at $E_{1/2} = +0.53$, $+1.38$ and 1.60 V in a cyclic voltammetric experiment (CH_2Cl_2 , standard calomel electrode).

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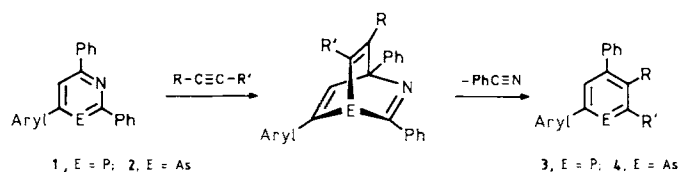
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- [5] $^1\text{H-NMR}$ (60 MHz, $CDCl_3$): $\delta = 1.68$, 1.85 (**1**), 1.93 (**2**), 1.86 (**4**). IR (KBr): $\nu_{CO} = 1955$ (**2**), 1811 (**4**) cm^{-1} . All the compounds gave correct elemental analyses (C, H, S) and were characterized by field desorption mass spectrometry.
- [6] **1**: Space group $P2_1/c$, $a = 14.195(7)$, $b = 12.833(8)$, $c = 17.202(6)\text{ Å}$, $\beta = 103.30(4)^\circ$, $V = 3049.54\text{ Å}^3$, $Z = 4$. AED-II diffractometer ($MoK\alpha$), $3 < 2\theta < 65^\circ$, 4220 measured reflections with $I > 2.5\sigma(I)$, Patterson and Fourier methods, anisotropic refinement to $R_w = 0.042$. Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2 (FRG), on quoting the depository number CSD-52930, the names of the authors, and the journal citation.
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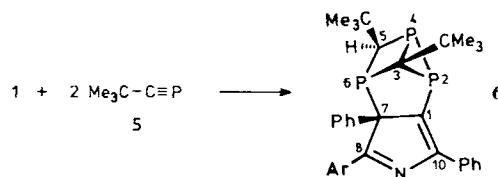
Reaction of 1,3-Azaarsinines with 2-*tert*-Butyl-1-phosphaethyne—2,9,10-Tri-*tert*-butyl-4,6-diphenyl-1,3,8-triphospharsatetracyclo[4.4.0.0^{2,8}.0^{3,7}]deca-4,9-diene

By Gottfried Märkl,* Stefan Dietl, Manfred L. Ziegler, and Bernd Nuber

The 1,3-azaphosphinines **1**^[1] and 1,3-azaarsinines **2**^[2] recently described by us undergo Diels-Alder reactions with a large variety of alkyne-dienophiles;^[1,3,4] the bicycles initially formed rearomatize with elimination of benzonitrile to give the corresponding—in particular also functionally substituted—phosphinines **3**^[1,3] and arsinines **4**.^[4]



We have already reported on the fully unexpected reaction of the azaphosphinines **1** with the heteroalkyne *tert*-butyl-1-phosphaethyne **5** in the molar ratio 1 : 2; the tetracycles **6** are formed.^[5]



We have now been able to show that the 1,3-azaarsinines **2** behave differently again toward **5**. Reaction with **5** in toluene at 120°C in a Carius tube (48 h) furnishes (after treatment of the residue with ethyl acetate) a colorless, crystalline compound **7a**, m.p. $204\text{--}207^\circ\text{C}$ (from ethyl acetate), which according to an elemental analysis and its mass spectrum is a product formed from **2a** and **5** (in the molar ratio 1 : 3) with elimination of benzonitrile (Table 1). According to analytical and spectroscopic findings, **2b** reacts analogously to give **7b** (Table 1).

Both the $^1\text{H-NMR}$ spectrum, which shows three *tert*-butyl signals, and the $^{31}\text{P-NMR}$ spectrum, with three signals, are consistent with the unsymmetric structure of **7a**. The X-ray structure analysis shows that **7a** has a tetracyclic skeletal framework other than that in **6** and that all P

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