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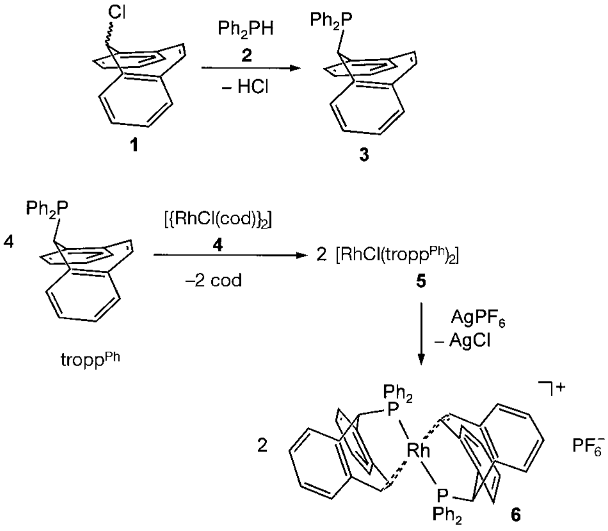
[21] All reactions contain a 3′-^{32}P-end-labeled (15000 cpm) *Eco*RI/*Hin*dIII restriction fragment of the plasmid pJT-LTR, 10 mM Tris · HCl, 10 mM KCl, 10 mM $MgCl_2$, and 5 mM $CaCl_2$ (pH 7.0, 24 °C). The plasmid pJT-LTR was prepared by ligating an insert having the sequence 5′-CCGGTAACCAGAGAGACCCAGTACAGGCAA-AAAGCAGCTGCTTATATGCAGCATCTGAGGGACGCCACTCCCCAGTCCCGCCCAGGCCACGCCTCCCTGGAAAGTCCCCAGCGGAAAGTCCCTTGTAGAAAGCTCGATGTCAGCAGTCTTTGTAGTACTCCGGATGCAGCTCTCGGGCCACGTGATGAAATGCTAGGCGGCTGTCAATCGA-3′ to the large *Ava*I/*Sal*I fragment of pUC19.

A Monomeric d^9-Rhodium(0) Complex**

Hartmut Schönberg, Souad Boulmaâz, Michael Wörle, Lorenz Liesum, Arthur Schweiger,* and Hansjörg Grützmacher*

Complexes with rhodium centers in low formal oxidation states (0 or −1) are rare. They have been described as relatively short-lived intermediates in electrochemical reactions,[1] as polynuclear clusters,[2] or as complexes with strong π-acceptor ligands (such as $[Rh(CO)_4]^-$,[2] $[Rh(PF_3)_4]^{-[3]}$).[4] As far as we are aware, the isolation of a paramagnetic, monomeric d^9-rhodium(0) compound has not yet been achieved. We report here a new ligand that allows the easy synthesis and reversible transformation of rhodium complexes with formal oxidation states +1, 0, and −1. 5-Chloro-5*H*-dibenzo[*a*,*d*]cycloheptene (**1**)[5] reacts with diphenylphosphane (**2**) to form (5*H*-dibenzo[*a*,*d*]cycloheptene-5-yl)diphenylphosphane (**3**) ("dibenzo-tropylidenyldiphenylphosphane", tropp^{Ph}) in good yield. In contrast to the synthesis of simple cycloheptatrienylphosphanes,[6] only one isomer of **3** is obtained: the Ph_2P group is in the axial position of the seven-membered ring[7] (Scheme 1).



Scheme 1. Synthesis of the rhodium(I) complexes **5** and **6**.

Reaction of four equivalents of **3** with $[\{RhCl(cod)\}_2]$ (**4**) (cod = cyclooctadiene) leads in almost quantitative yield to the intense yellow rhodium(I) complex $[RhCl(tropp^{Ph})_2]$ (**5**).

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The chloride atom in **5** can be abstracted with $AgPF_6$, and the complex salt $[Rh(tropp^{Ph})_2]^+PF_6^-$ (**6**) is obtained. X-ray crystal structure analysis shows that the d^8-rhodium(I) center lies on a center of inversion and has square-planar coordination geometry, as expected.[8] Both **5** and **6** can be electrochemically reduced in a CH_3CN/nBu_4NPF_6 electrolyte in reversible one-electron transfer steps, to generate, initially, the rhodium(0) complex **7** ($E^1_{1/2} = -1.003$ V), and subsequently the rhodium(−I) complex **8** ($E^2_{1/2} = -1.189$ V) (Figure 1). The reduction potentials are significantly shifted to more anodic potentials when compared to previously reported values [1b–g, 2] (−1.3 to −2.1 V vs. Ag/0.1M Ag^+). Reaction of **5** or **6** with sodium metal in THF also generates the deep green d^9-complex $[Rh(tropp^{Ph})_2]$ (**7**) or the red d^{10}-complex $[Na(thf_6)][Rh(tropp^{Ph})_2]$ (**8**) (Scheme 2).

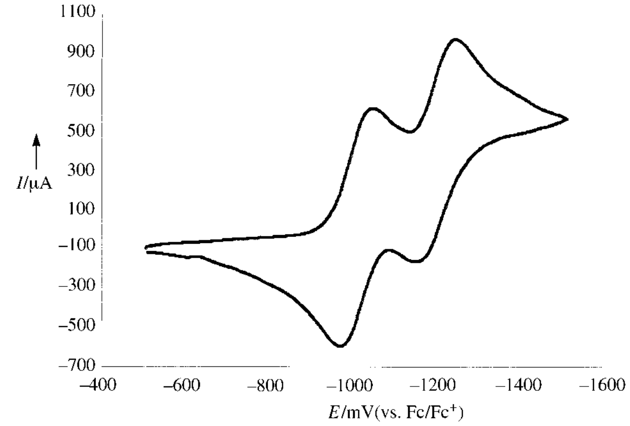
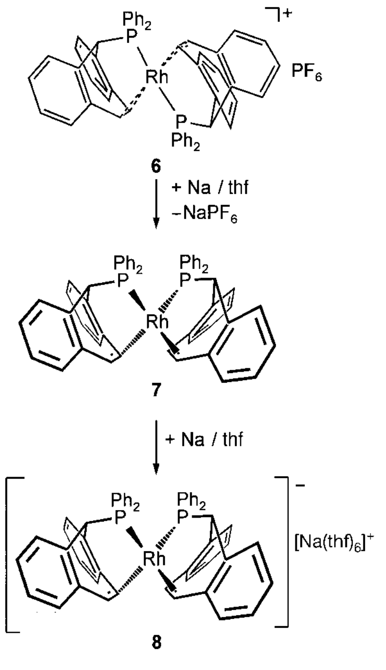


Figure 1. Cyclovoltammogram of **7**. Scan rate 30 mV s−1, Pt/nBu_4PF_6, CH_3CN/Ag.



Scheme 2. Synthesis of the rhodium(0) complex **7** and the rhodium(−I) complex **8**.

The rhodium(0) compound **7** can also be prepared by a comproportionation reaction of the rhodium(I) complex **5** with **8**. The complex **7** is only slightly soluble in THF and hydrocarbons. Both complexes, **7** and **8**, are very air sensitive. Magnetic measurements of **7** gave an effective magnetic moment of 1.73 μ_B, as expected for one unpaired electron. The structures of **7** and **8** were determined by single-crystal X-ray structure analysis; the structure of **7** is shown in Figure 2.[9]

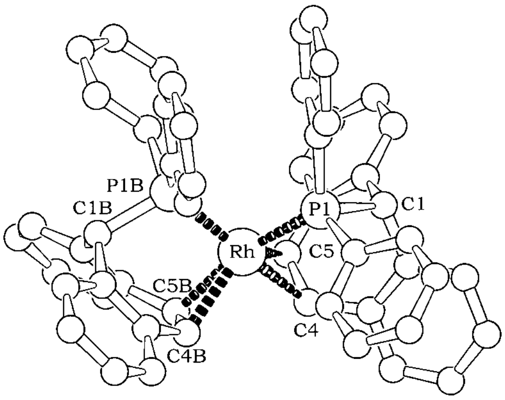


Figure 2. Structure of **7** in the crystal. Selected bond lengths [Å] and angles [°]: Rh1–P1 2.273(2), Rh–P1B 2.267(2), Rh1–C4 2.270(7), Rh1–C5 2.208(7), Rh1–C4B 2.216(7), Rh1–C5B 2.202(7), C4–C5 1.410(10), C4B–C5B 1.426(9), P1–C1 1.898(7), P1B–C1B 1.891(8); P1-Rh1-P1B 98.41(7), C4-Rh1-C4B 93.1(3), C5-Rh1-C5B 86.9(3), P1-Rh-C4 91.5(2), P1-Rh1-C5 91.1(2), P1B-Rh-C4B 87.1(2), P1B-Rh1-C5B 93.4(2).

The average Rh–P (2.270(2) Å) and Rh–C distances (2.224(7) Å) show no significant deviations from known values. The d^9-rhodium(0) center in **7** has a nonplanar coordination in the crystal. The φ angle, defined by the planes running through the phosphorus and rhodium center as well as the middle of the coordinated C=C bond, is about 43°. The phosphorus atoms have *cis* positions in this coordination sphere, which has an intermediate geometry between tetrahedral and square planar. The structure of the rhodanate anion in **8** (Rh–P 2.251(1) Å, Rh–C 2.159(4) Å, $\varphi = 52°$) with formal d^{10} valence electron configuration at the metal center differs only slightly from the structure of the radical in **7**. The coordination polyhedron around the rhodium center in **8** is a little more distorted towards tetrahedral coordination ($\varphi = 52°$). By means of EPR spectroscopy, a slightly distorted tetrahedral structure (D_{2d} symmetry) has been proposed for $[Rh(CO)_4]$,[1a] while a more square-planar structure was suggested for $[Rh\{P(OiPr)_3\}_4]$[1b] and $[Rh(cod)_2]$.[1g]

Figure 3 shows the X-band CW-EPR spectrum of the Rh^0 complex **7** in THF at room temperature. The triplet structure is caused by isotropic coupling ($a_{iso} = 2.46$ mT (69.5 MHz)) with two equivalent phosphorus centers. Further magnetically relevant nuclei were detected by means of pulsed electron-nucleus-double-resonance spectroscopy (Davies-ENDOR)[10] in a frozen solution at 30 K (Figure 4). In addition to the proton peaks between 11 and 18 MHz with hyperfine couplings (HFC) of up to 7 MHz, a doublet at 9 MHz with a splitting of 0.9 MHz is observed. This splitting is in agreement with the double Zeeman frequency of the rhodium nucleus. The assignment of this ENDOR line to rhodium with a HFC

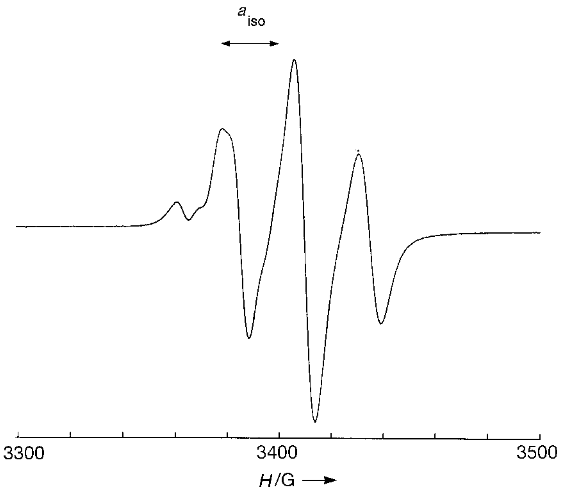


Figure 3. CW-ESR spectrum of **7** in THF at 295 K showing a hyperfine coupling constant a_{iso} of 69.5 MHz and an isotropic g factor of 2.0195.

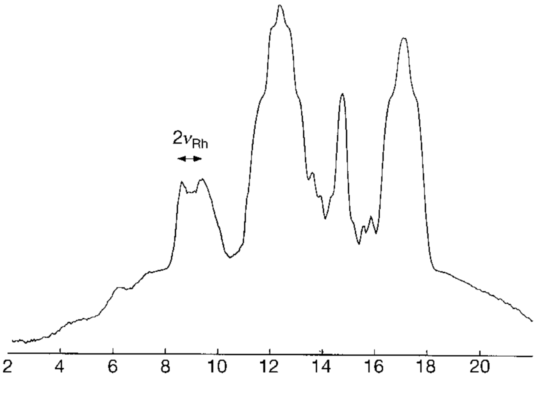


Figure 4. Davies-ENDOR spectrum of **7** at 30 K.

of 18 MHz was verified by two-dimensional pulse methods.[11] A spin density of less than 1% in the s orbital of the phosphorus atom can be estimated from the isotropic ^{31}P HFC.[12] The proton hyperfine couplings lie within the range expected for complexes in which the unpaired electron is localized at the transition metal center.[13]

Experimental Section

3: A solution of **1** (5.5 g, 24.3 mmol) in toluene (50 mL) was slowly added to a solution of **2** (4.5 g, 24.3 mmol) in toluene (50 mL) at room temperature. After stirring for 1 h at room temperature, the reaction mixture was refluxed for 15 h. The solvent was distilled off under vacuum, and the colorless residue was recrystallized from acetonitrile to afford 8.77 g (96%) **3** as colorless crystals. ^1H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS): $\delta = 4.84$ (d, $^2J_{P,H} = 6.1$ Hz, 1H, CHP), 7.07 (s, 2H, CH=CH); ^{31}P NMR ($CDCl_3$, 81 MHz): $\delta = -14.9$ (s).

5: **3** (3 g, 7.96 mmol) and **4** (0.98 g, 1.99 mmol) were dissolved in toluene (50 mL). The resulting deep red solution was stirred for 2 h at room temperature. After some time, **5** crystallized to give fine bright yellow needles 3.5 g (98.6%). ^1H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS): $\delta = 5.19$ (s, 1H, CHP), 4.68 (s, 2H, CH=CH); ^{31}P NMR ($CDCl_3$, 81 MHz): $\delta = 79.9$ (d, $J_{P,Rh} = 75.5$ Hz); ^{103}Rh NMR ($CDCl_3$, 12.8 MHz): $\delta = 440$ (br.); UV/Vis: $\lambda_{max} = 277$ nm ($\varepsilon = 8.8 \times 10^3$ m^{2}mol^{-1}).

7: Sodium (13 mg, 0.56 mmol) was added to a solution of **5** (500 mg, 0.56 mmol) in THF (10 mL), and the reaction mixture was stirred for 30 h at room temperature. A deep green solution and some precipitate were formed. The residue was filtered off and washed several times with THF until only colorless NaCl remained. The combined THF extracts were concentrated to 5 mL and were layered with n-hexane (2 mL). Compound **7** crystallized as green black crystals (476 mg, 99%). ^{31}P NMR ([D$_8$]THF, 81 MHz): $\delta = 81.3$ ($\Delta\tilde{\nu}_{1/2} \approx 3600$ Hz); UV/Vis: $\lambda_{max} = 645$ nm ($\varepsilon = 1.0 \times 10^3$ m^{2}mol^{-1}).

8: Sodium (6 mg, 1.12 mmol) was added to a solution of **5** (500 mg, 0.56 mmol) in THF (10 mL), and the mixture was stirred for 48 h at room temperature. A deep red solution with some precipitate was formed. The residue was filtered off and extracted several times with THF until only colorless NaCl remained. The THF solution was reduced to 3 mL and layered with n-hexane (5 mL). Compound **8** crystallized as deep red crystals (larger crystals have a metallic golden luster) (727 mg, 99%). ^1H NMR ([D$_8$]THF, 300 MHz, 25 °C, TMS): $\delta = 4.32$ (d, $J_{H,P} = 9.48$ Hz, 2H; CHP), 4.15 (m, 2H, CH=CH), 2.81 (m, 2H, CH=CH); ^{31}P NMR ([D$_8$]THF, 81 MHz): $\delta = 87.7$ (d, $J_{P,Rh} = 183$ Hz); ^{103}Rh NMR ([D$_8$]THF, 12.8 MHz): $\delta = -496$ (t, $J_{Rh,P} = 179.6$ Hz); UV/Vis: $\lambda_{max} = 491$ nm ($\varepsilon = 16.0 \times 10^3$ m^{2}mol^{-1}).

7 from reaction of **5** with **8**: Compounds **5** (500 mg, 0.561 mmol) and **8** (735 mg, 0.561 mmol) were dissolved in THF (15 mL) and stirred 2 h at room temperature. The resulting deep green solution was separated from the precipitate. The latter was treated as before and the combined THF extracts were reduced to 10 mL and layered with n-hexane (5 mL). Compound **7** crystallized as green-black crystals (950 mg, 99%).

Compounds **3**, **5** and **7** gave satisfactory elemental analyses after careful drying in vacuum. No correct elemental analysis, however, could be obtained for **8**, which rapidly loses solvent molecules.

Cyclovoltammetry and EPR measurements: The electrochemical investigations were performed on an apparatus designed by Heinze et al.[14] Working electrode: planar platinum electrode (approx. surface area 0.785 mm^2); reference electrode: silver; counterelectrode: platinum wire; acetonitrile as solvent. At the end of each measurement, ferrocene was added as internal standard for calibration (+0.352 V vs. Ag/AgCl).

In order to determine the ^{103}Rh HFC, Davies-ENDOR experiments were performed on a frozen solution at various field positions. The measured ^{103}Rh HFC was found to be almost orientation independent.

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[9] **7**: triclinic, space group $P\bar{1}$; $a = 11.294(7)$, $b = 13.009(9)$, $c = 18.967(12)$ Å, $\alpha = 94.770(2)$, $\beta = 98.823(1)$, $\gamma = 112.285(2)°$; $V = 2518(3) \times 10^{-6}$ pm^3; $Z = 2$, Mo$_{K\alpha}$ radiation, $2\Theta_{max} = 46.5°$, 8247 reflections, 6294 independent ($R_{int.} = 0.0412$), direct methods; refinement against full matrix (versus F^2) with SHELXTL (Version 5.0), $R_1 = 0.065$, $wR_2 = 0.1258$ (based on F^2) for 626 parameters and 4213 reflections with $I > 2\sigma(I)$. **8**: orthorhombic, space group $Pcca$ (No. 54); $a = 23.853(2)$, $b = 12.709(1)$, $c = 23.874(2)$ Å, $V = 7237.3(10) \times 10^{-6}$ pm^3, $Z = 4$, Mo$_{K\alpha}$ radiation, $2\Theta_{max} = 41.2°$, 27343 reflections, 3815 independent ($R_{int.} = 0.0880$), direct methods, refinement against full matrix (versus F^2) using SHELXL96, $R_1 = 0.046$, $wR_2 = 0.1252$ (based on F^2) for 448 parameter and 3815 reflections with $I > 2\sigma(I)$. All non-hydrogen atoms in **7** and **8** were refined with anisotropic, hydrogen atoms at calculated positions with common isotropic parameters (riding model). In addition to the complex **7**, a THF molecule, and additional electron density were localized, probably due to the presence of further disordered solvent molecules corresponding to about six C atoms. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-100707 and CCDC-101085. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Novel Bonding of Iodine: Crystal Structure of HIS_2O_8**

Martin Jansen* and Ralph Müller

Dedicated to Professor Achim Müller on the occasion of his 60th birthday

Ternary oxides of nonmetals are either ionic crystals with complex cations and anions or polymeric networks with oxygen as bridging atom, depending on the extent to which oxide ions are transferred from the acidic binary oxide to the more basic oxide. The polymeric networks are usually regarded as mixed anhydrides of oxoacids of the corresponding nonmetals, and their constitutions can be described in terms of known oxo anions as structural increments. The title compound contains the structural increment IO_2, for which neither the corresponding free acid nor the corresponding free anion is known.

The system $IO_x/SO_3/H_2O$ is very complex and only rudimentarily understood.[1] The difficulty in isolating pure crystalline phases is attibuted to their polymeric nature and thermal instability. By carefully controlling the reaction conditions, especially the duration of crystallization, compounds of this system can be prepared reproducibly in amounts of up to one gram.[2] The essential role of crystallization time is due mainly to changes in the composition of the reaction mixture during the crystallization of the product phases, and less to kinetic control of product formation. The title compound crystallizes from concentrated solutions of iodic acid in oleum under conditions similar to those described for the synthesis of $(IO_2)_2S_2O_7$ (see Experimental Section).

The composition of the title compound, including its hydrogen content, was confirmed by a single-crystal structure determination and by vibrational spectroscopy (Table 1).[3]

Table 1. IR and Raman data for HIS_2O_8 [cm^{-1}].

IR	433(w)	455(w)	573(s)	613(w)	643(w)	738(w)	851(m)
	886(m)	1008(m)	1069(s)	1231(s)	1293(s)	2479(w)	2603(w)
	2895(m)						
Raman	102(s)	139(w)	162(w)	188(m)	205(m)	240(w)	278(s)
	305(s)	457(w)	513(m)	578(w)	639(vs)	744(m)	813(w)
	870(m)	899(m)	928(w)	1001(w)	1090(m)	1149(w)	1308(w)

The constitution of the trinuclear unit $I(SO_4)(HSO_4)$ can be understood as the condensation product of one unit of sulfuric acid and one unit of hydrogensulfate with the protonated form of the hypothetical iodic(III) acid $H_2IO_2^+$. The result is a zwitterion with a positive formal charge on the iodine center and a negative charge on the the nonprotonated sulfate group (Figure 1). The S–O distances and angles have a wide range of values, but their mean values lie in the range expected for sulfates and hydrogensulfates. Both intramolecular I–O distances correspond to single-bond lengths, and the environment of the iodine(III) center can be described as ψ^2 tetrahedral.[4]

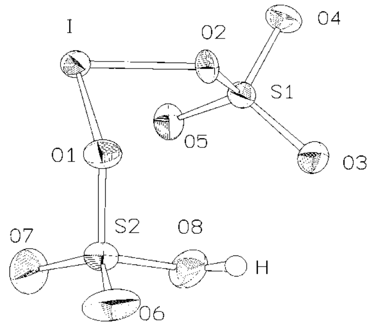

Figure 1. Structure of the trinuclear unit $I(SO_4)(HSO_4)$. Selected bond lengths [pm] (50% probability ellipsoids): I–O1 198.1(6), I–O2 197.0(6), S1–O2 158.5(6), S1–O3 145.3(7), S1–O4 147.2(7), S1–O5 140.7(7), S2–O1 157.9(6), S2–O6 140.9(9), S2–O7 139.2(8), S2–O8 151.9(8), O8–H 81.0(102).

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