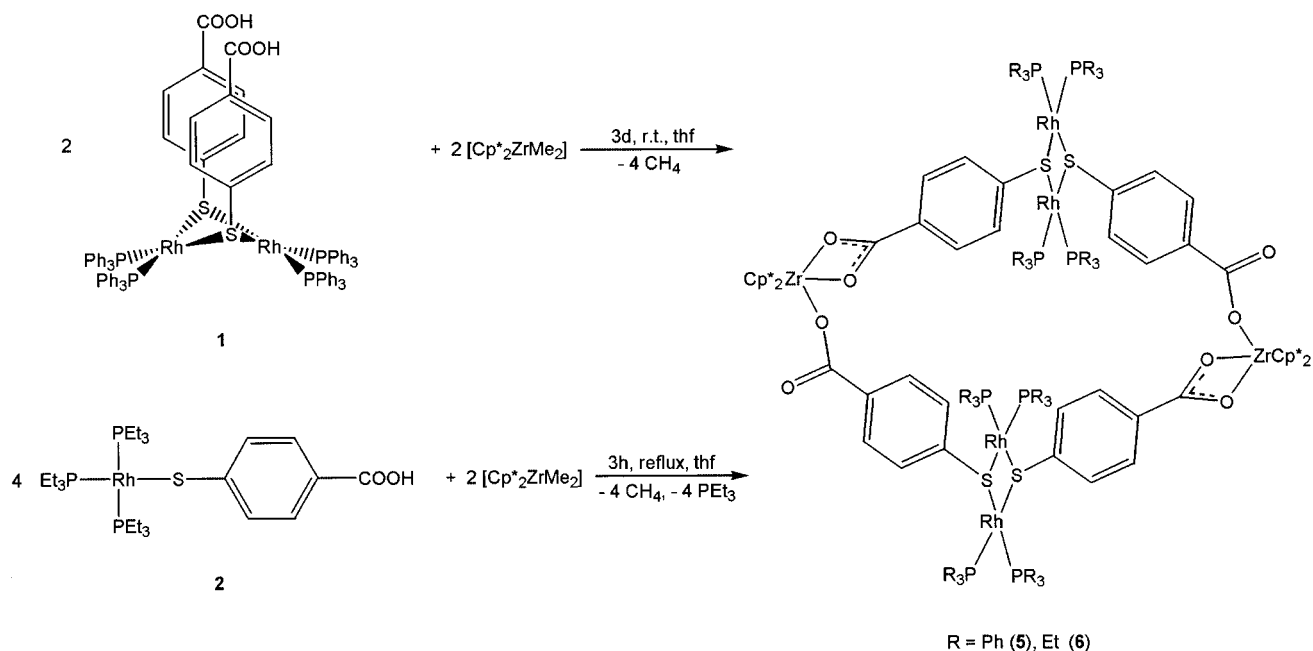


Scheme 1.

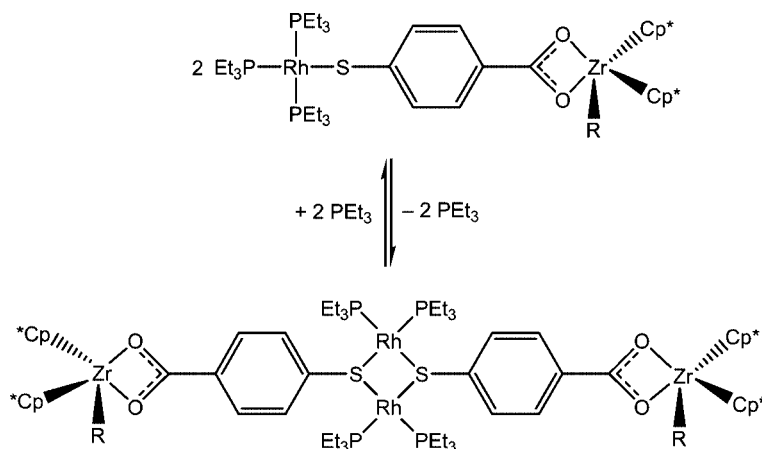


Scheme 2.

vated temperatures. In contrast, **1** readily reacts with the zirconocene derivative even at room temperature with elimination of 2 equiv. of methane (Scheme 2). Purification of the highly air- and moisture-sensitive complexes was facilitated by the fact that only methane was produced as byproduct.

Mono(carboxylato)zirconocene Complexes

As shown previously, **2** dimerises in solution with phosphane dissociation (Scheme 3). To stabilise the monomeric form, an excess of triethylphosphane must be used. Complex **2** reacts with 1 equiv. of $[\text{Cp}^*_2\text{ZrMe}_2]$ in the presence

Scheme 3. $\text{R} = \text{Me}$ (**3**) or OH (**4**).

of an excess of PEt_3 to yield $[\text{Cp}^*_2\text{Zr}(\text{Me})\{\mu\text{-O}_2\text{CC}_6\text{H}_4\text{S}\}\text{Rh}(\text{PEt}_3)_3]$ (**3**) exclusively. Complex **3** could be isolated as orange crystals; the molecular structure in the solid state is shown in Figure 1.

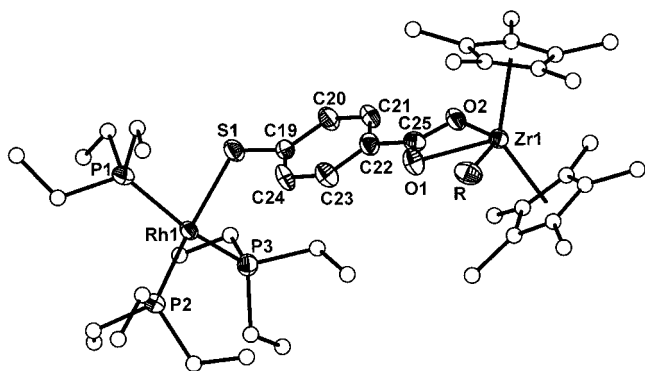


Figure 1. View of the molecular structure of $[\text{Cp}^*_2\text{Zr}(\text{Me})\{\mu\text{-O}_2\text{CC}_6\text{H}_4\text{S}\}\text{Rh}(\text{PEt}_3)_3]$ (**3**) ($\text{R} = \text{Me}$) and $[\text{Cp}^*_2\text{Zr}(\text{OH})\{\mu\text{-O}_2\text{CC}_6\text{H}_4\text{S}\}\text{Rh}(\text{PEt}_3)_3]$ (**4**) ($\text{R} = \text{OH}$). Hydrogen atoms are omitted for clarity. Thermal ellipsoid level 50%. The atoms not shown as ellipsoids are the carbon atoms of the coligands. Selected bond lengths [pm] and bond angles [$^\circ$] for **3**: Zr1–O1 230.3(4), Zr1–O2 227.1(4), Zr1–C46 226.9(8), O1–C25 126.3(8), O2–C25 126.9(7), Rh1–S1 241.4(2), Rh1–P1 230.5(2), Rh1–P2 224.7(2), Rh1–P3 232.7(2); O1–Zr1–O2 56.6(2), O1–Zr1–C46 73.8(3), O1–C25–O2 117.9(6), S1–Rh1–P1 82.93(6), S1–Rh1–P2 166.98(7), S1–Rh1–P3 83.94(6), P1–Rh1–P2 96.76(6), P2–Rh1–P3 101.05(6), P1–Rh1–P3 153.70(7), Rh1–S1–C19 104.8(2). Selected bond lengths [pm] and bond angles [$^\circ$] for **4**: Zr1–O1 229.5(5), Zr1–O2 228.6(5), Zr1–O3 207.8(6), O1–C25 128(1), O2–C25 124.8(9), Rh1–S1 241.4(2), Rh1–P1 231.0(2), Rh1–P2 225.0(3), Rh1–P3 232.6(3); O1–Zr1–O2 56.4(2), O1–Zr1–O3 76.8(2), O1–C25–O2 117.6(8), S1–Rh1–P1 83.06(9), S1–Rh1–P2 167.39(9), S1–Rh1–P3 84.25(9), P1–Rh1–P2 96.39(9), P2–Rh1–P3 100.64(9), P3–Rh1–P1 154.79(9), Rh1–S1–C19 106.2(3).

Complex **3** crystallises in the monoclinic space group $P2_1/c$ with four molecules per unit cell. The rhodium atom is coordinated by three triethylphosphane and one thiolato ligand in a tetrahedrally distorted square-planar fashion [S1–Rh1–P2 166.98(7) $^\circ$, P1–Rh1–P3 153.70(7) $^\circ$]. The carboxylato group coordinates in a bidentate mode, resulting in the zirconium atom being an 18-valence-electron species. The two oxygen atoms, the carbon atom of the methyl group and the zirconium atom are coplanar. The plane defined by Zr1, O1 and O2 forms an angle of 9.12 $^\circ$ with the plane of the aromatic ring. The bond lengths C25–O1 [126.3(8) pm] and C25–O2 [126.9(7) pm] as well as Zr1–O1 [230.3(4) pm] and Zr1–O2 [227.1(4) pm] are similar, and this indicates delocalisation of the lone pair of electrons. This is supported by the IR spectrum (KBr), which shows symmetric and asymmetric COO vibrations at 1561 and at 1420 cm^{-1} instead of discrete C=O and C–O vibrations.

By treating a solution of **3** with 1 equiv. of water, the methyl group can be exchanged selectively with an OH group to form $[\text{Cp}^*_2\text{Zr}(\text{OH})\{\mu\text{-O}_2\text{CC}_6\text{H}_4\text{S}\}\text{Rh}(\text{PEt}_3)_3]$ (**4**), a rare example of a terminal hydroxo complex of a zirconocene. Stabilisation by the sterically bulky Cp^* ligands prevents dimerisation with formation of oxo bridges, which

usually occurs with elimination of water,^[15] as first described by Hillhouse et al.^[16] and Bortolin et al.^[17] Complex **4** is the first heteroleptic carboxylato hydroxo complex structurally characterised by X-ray crystallography. Pellny et al. reported the NMR spectroscopic observation of the compounds $[\text{Cp}^*_2\text{Zr}(\text{OH})\{\text{OOC}-\text{C}(\text{SiMe}_3)=\text{CHPh}\}]$ and $[\text{Cp}^*_2\text{Zr}(\text{OH})\{\text{OOC}-\text{CPh}=\text{CH}(\text{SiMe}_3)\}]$, but could not isolate them.^[18] Yellow needle-like crystals of **4** were structurally characterised by X-ray crystallography. Complex **4** crystallises isotypic to **3** (Figure 1).

The short Zr–O bond length of 207.8 pm corresponds to those in other structurally characterised compounds of this kind.^[17,19] The O3 $\cdots$ O1 distance of 272.1 pm seems to indicate the presence of a hydrogen bond between them. As the C46 $\cdots$ O1 distance in **3** is also only 274.6 pm, it appears that the two atoms are forced into close proximity due to the high steric demand of the Cp^* rings. The steric crowding is also apparent from the deviation of the methyl groups from the C₅ ring plane where the two rings are in close proximity.

The OH stretching vibration (3658 cm^{-1}) has very low intensity but could be observed in the IR spectra of a KBr pellet and of a single crystal. The intensities of OH vibrations reported in the literature also differ.^[19a,19b]

In the ^1H NMR spectrum, the signals of the protons of the aromatic ring of the 4-thiolatobenzoate ligand (AA'BB' spin system) are broader than the other signals. This indicates hindered rotation of the $\text{SC}_6\text{H}_4\text{COOZr}(\text{R})\text{Cp}^*_2$ group ($\text{R} = \text{Me}, \text{OH}$) and prevents simulation of the spectra to determine the coupling constants. As can be observed with the help of ^{31}P NMR spectroscopy, **3** and **4** dimerise in solution with dissociation of 1 equiv. of PEt_3 per rhodium atom, as already described for **2** (Scheme 3). The equilibrium can be shifted towards the monomer by adding an excess of triethylphosphane.

Bis(carboxylato)zirconocene Complexes

Treatment of **1** with $[\text{Cp}^*_2\text{ZrMe}_2]$ in a 1:1 ratio as well as of **2** with $[\text{Cp}^*_2\text{ZrMe}_2]$ in a 2:1 ratio results in the formation of compounds of the type $[(\text{Cp}^*_2\text{Zr}\{\mu\text{-O}_2\text{CC}_6\text{H}_4\text{S}\}\text{Rh}(\text{PR}_3)_2)_2]$ [$\text{R} = \text{Ph}$ (**5**), $\text{R} = \text{Et}$ (**6**)]. In the solid state both compounds reveal a nearly identical molecular structure, that is, a 32-membered macrocycle containing two dimeric $\text{Rh}_2(\text{SR})_2$ units, as observed in metalloligand **1**, which are deprotonated and bridged by two zirconocene groups (Scheme 2).

Both compounds crystallise in the triclinic space group $P\bar{1}$, and one molecule in the unit cell is located on a crystallographic centre of inversion (Figures 2 and 3). Co-crystallisation of 12 molecules of thf (two of them disordered) for **5** and one molecule of diethyl ether for **6** is observed per unit cell.

The typical bonding mode for zirconocene bis(carboxylato) complexes^[20,24–26] is also observed in **5** and **6**: one carboxylato ligand coordinates in a bidentate fashion and the other in a monodentate one. All coordinating oxygen atoms are coplanar with the zirconium atom. In contrast to **3** and

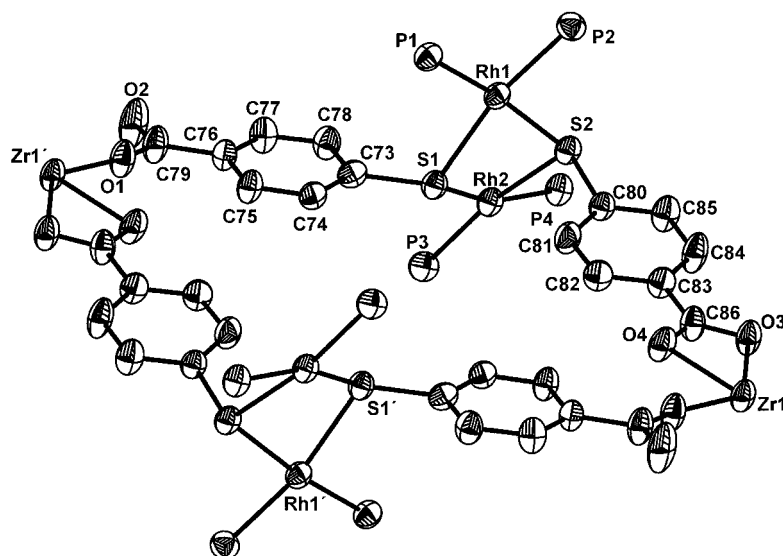


Figure 2. View of the molecular structure of $[(\text{Cp}^*_2\text{Zr}\{(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{S})\text{Rh}(\text{PPh}_3)_2\}_2)_2]$ (**5**). Thermal ellipsoid level 50%. Hydrogen atoms and the carbon atoms of the coligands and thf molecules are omitted for clarity. Selected bond lengths [pm] and bond angles $^\circ$: Zr1–O1 207.1(2), Zr1–O3 232.2(2), Zr1–O4 223.9(2), Rh1–S1 244.12(9), Rh1–S2 237.73(9), Rh1–P1 228.0(1), Rh1–P2 224.3(1), Rh2–S1 236.72(9), Rh2–S2 239.41(9), Rh2–P3 224.8(1), Rh2–P4 226.6(1), C79–O1 129.9(4), C79–O2 122.4(4), C86–O3 126.9(4), C86–O4 127.5(4); O3–Zr1–O4 56.94(8), S1–Rh1–S2 78.76(3), P1–Rh1–S1 96.64(3), P1–Rh1–P2 94.36(4), S1–Rh2–S2 79.91(3), P3–Rh2–S1 99.75(3), P3–Rh2–P4 98.13(4), (S1–Rh1–S2)/(S1–Rh2–S2) 146.46(5).

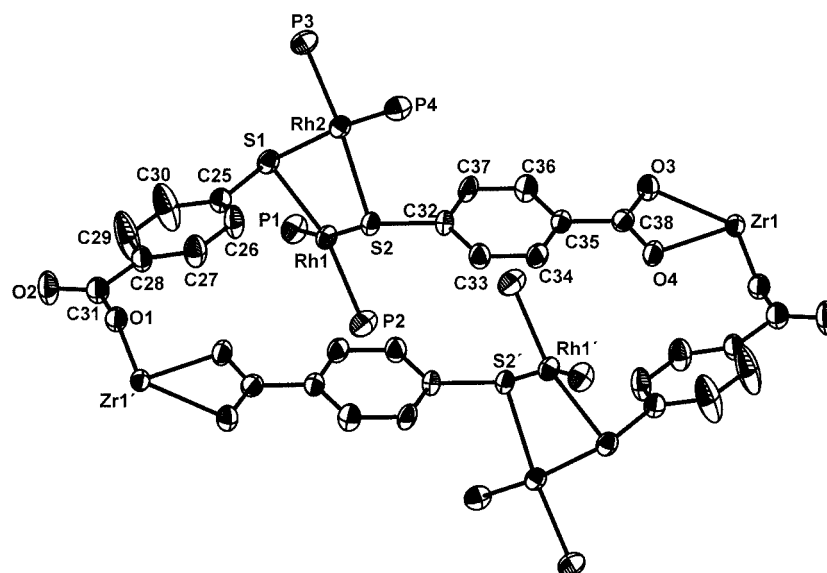


Figure 3. View of the molecular structure of $[(\text{Cp}^*_2\text{Zr}\{(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{S})\text{Rh}(\text{PET}_3)_2\}_2)_2]$ (**6**). Thermal ellipsoid level 50%. Diethyl ether, hydrogen atoms and the carbon atoms of the coligands are omitted for clarity. Selected bond lengths [pm] and bond angles $^\circ$: Zr1–O1 206.9(3), Zr1–O3 236.1(3), Zr1–O4 222.2(3), Rh1–S1 239.8(1), Rh1–S2 241.3(1), Rh1–P1 224.3(1), Rh1–P2 226.5(1), Rh2–S1 240.6(1), Rh2–S2 242.2(1), Rh2–P3 224.5(1), Rh2–P4 224.5(1), C31–O1 131.2(5), C31–O2 121.9(5), C38–O3 126.3(5), C38–O4 127.6(5); O3–Zr1–O4 56.6(2), S1–Rh1–S2 81.47(4), P1–Rh1–S1 85.33(4), P1–Rh1–P2 102.08(5), S1–Rh2–S2 81.47(4), P3–Rh2–S1 93.40(4), P3–Rh2–P4 97.69(5), (S1–Rh1–S2)/(S1–Rh2–S2) 145.50(5).

4, the Zr–O bond lengths of the bidentate ligand differ by 8 pm (**5**) and 14 pm (**6**) and are thus indicative of the strain imposed by the macrocycle. This is also supported by the IR spectrum (KBr), in which the COO vibration is observed at 1633 cm^{-1} (**5**) and 1635 cm^{-1} (**6**), which are in between the values for a C=O bond [1678 cm^{-1} for $\text{HSC}_6\text{H}_4(\text{C}=\text{O})$ -

OH] and a symmetric vibration of the COO group as expected for unstrained molecules {e.g. 1561 cm^{-1} for $[\text{Cp}^*_2\text{Zr}(\text{Me})\{(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{S})\text{Rh}(\text{PET}_3)_3\}]$ (**3**) and $[\text{Cp}^*_2\text{Zr}(\text{OH})\{(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{S})\text{Rh}(\text{PET}_3)_3\}]$ (**4**)}. The position of the asymmetric COO vibration could not be identified because of overlap with other bands.

In both compounds, the Rh_2S_2 ring is puckered and shows an *anti* conformation. The angle between the S–Rh–S planes is 147° for **5** and 146° for **6**. The only considerable difference is that in **5** the thiolato ligands occupy the *exo* position of the Rh_2S_2 ring, and the *endo* position in **6**. This has a crucial influence on the size and shape of the macrocyclic cavity (Figure 4). For **5** the cavity is rhombohedral with internal edges of 470 and 331 pm, while in **6**, because

of the different conformation of the Rh_2S_2 ring and the different orientation of the arylene bridges, the cavity is divided into two smaller cavities with dimensions of 87×380 pm.

The cavity is shielded by coligands, as shown exemplarily for **6** in Figure 5. Thus, the solvent molecules are not located inside the cavity. Figure 5 also shows that the 32-membered rings are almost planar, with the exception of

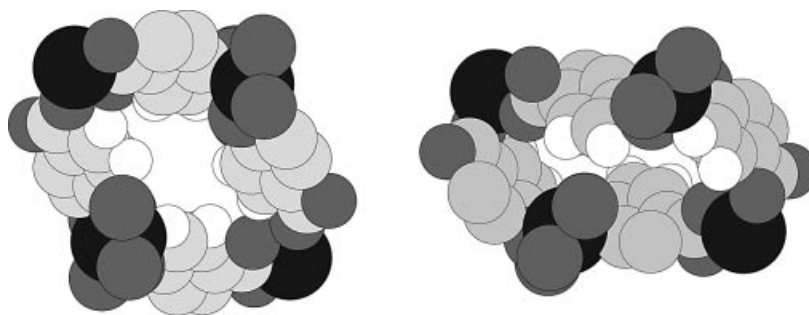


Figure 4. Space-filling model of the macrocycles **5** (left) and **6** (right). The carbon atoms of the coligands and those hydrogen atoms that do not influence the size of the cavities are omitted for clarity. The metal atoms are black, the heteroatoms (oxygen, sulfur and phosphorus) grey, the carbon atoms light grey and the hydrogen atoms white.

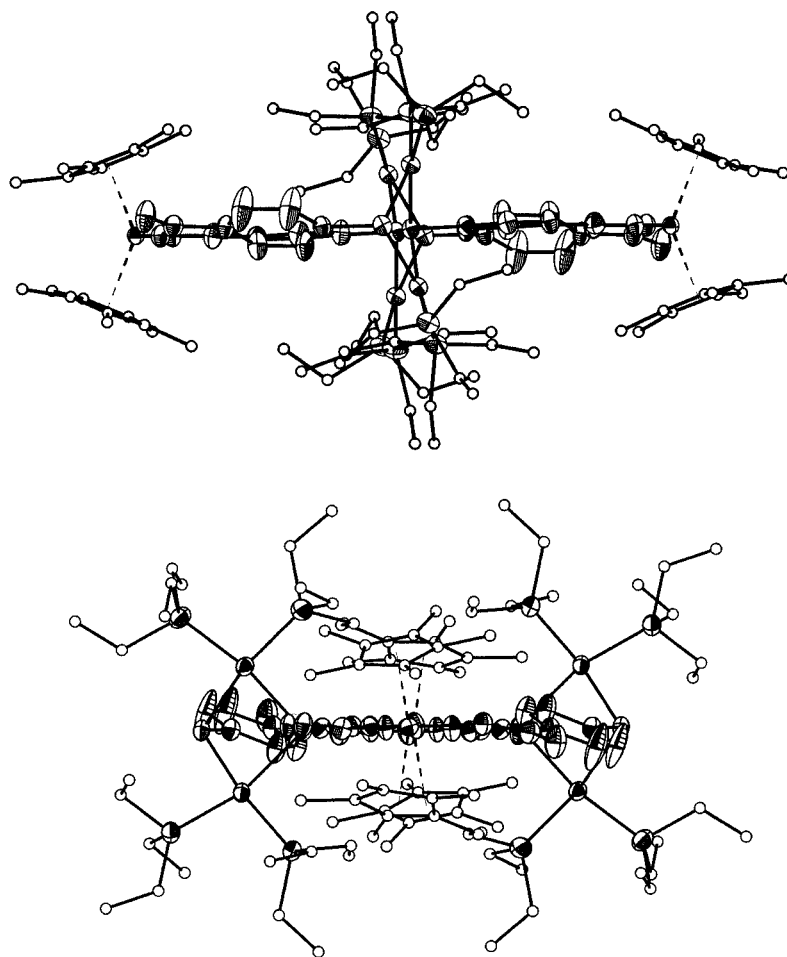


Figure 5. View of the molecular structure of $[(\text{Cp}^*_2\text{Zr}\{(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{S})\text{Rh}(\text{PEt}_3)_2\}_2)_2]$ (**6**). Thermal ellipsoid level 50%. Hydrogen atoms and Et_2O have been omitted for clarity. The atoms not shown as ellipsoids are the carbon atoms of the coligands. Top: View along the axis through the Rh_2S_2 rings. Bottom: View along the axis through the zirconocene groups.

the aromatic rings of two of the bridging thiolatobenzoato ligands.

The solubility of **5** and **6** in common organic solvents (*n*-hexane, toluene, thf, Et₂O, CH₃CN, dmf and dmsO) is very low. A sufficient concentration for ³¹P{¹H} NMR studies was achieved solely for **5** in thf. At room temperature, a very broad signal is observed at $\delta = 38$ ppm, which splits into two broad doublets ($\delta = 37.7$ ppm, $^1J_{\text{P-Rh}} = 153$ Hz, PPh₃ of isomer 1, and 38.4 ppm, $^1J_{\text{P-Rh}} = 149$ Hz, PPh₃ of isomer 2) on cooling the sample to -100 °C. Considering that fluxional behaviour of zirconocene bis(carboxylato) complexes in solution is known from the literature^[12b] (one of the ligands coordinates alternately in a mono- or bidentate fashion) and that dynamic behaviour, that is exchange between different conformers of the Rh₂S₂ ring, could be observed for **1**,^[13] one could consider different isomers in solution. However, because of solvent restrictions, the sample could not be cooled down sufficiently to achieve fine splitting and to gain deeper insights into the species present in solution.

Comparison of the Spectroscopic and Electrochemical Properties of **2** and **3**

Information about the change in electron density at the rhodium atom after introduction of the second metal centre can be obtained by comparing the spectroscopic and electrochemical properties of the monometallic complex [Rh(SC₆H₄COOH)(PEt₃)₃] (**2**)^[13] and the corresponding heterometallic complex [Cp*₂Zr(Me){(μ-O₂CC₆H₄S)-Rh(PEt₃)₃}] (**3**). For this purpose, the ³¹P NMR chemical shifts of the phosphorus nuclei of the phosphane ligands, the oxidation potentials (Table 1) and the wavelengths of the S–Rh charge-transfer bands of **2** and **3** (Figure 6) were compared.

Table 1. Anodic peak potentials vs. SCE, ³¹P NMR shifts of the phosphorus nucleus *trans* (δ_{trans}) and *cis* (δ_{cis}) to the thiolato ligand and the lowest energy UV/Vis absorption bands.

Compound	E_{pa} [V]	δ_{trans} [ppm]	δ_{cis} [ppm]	λ_{max} [nm]
2	1.28	26.7	12.1	337
3	1.32	28.4	13.5	358

After introduction of the zirconium atom as the second metal centre, the ³¹P chemical shifts of the phosphorus nuclei *cis* and *trans* to the thiolato ligand are shifted to lower field by 1.4 and 1.7 ppm, respectively. This indicates a weak electron-withdrawing character of the Lewis-acidic zirconium atom. This is also shown by a 40-mV shift of the oxidation potential of **3** compared to **2**. The oxidation is irreversible, as known for other rhodium(I) complexes.^[21] The observation of a small cathodic peak at -0.72 V in both cases proposes a following chemical reaction and the reduction of its reaction product.

The DFT calculations were carried out for the model compounds [Rh(SC₆H₄COOH)(PMe₃)₃] (for **2**) and

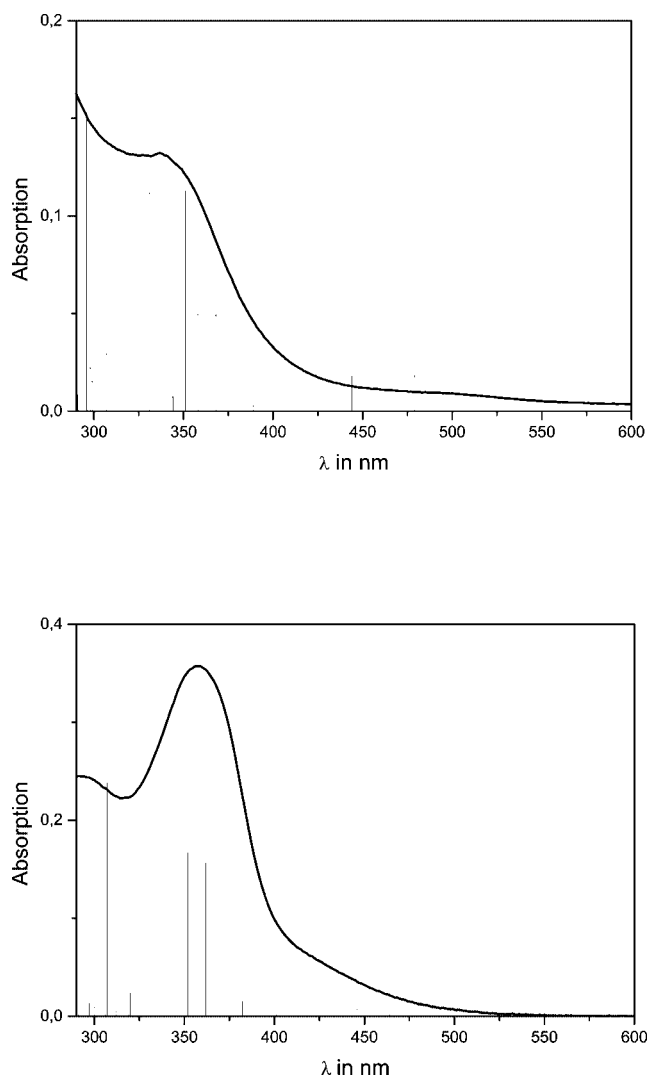


Figure 6. Comparison of the observed UV/Vis spectra of **2** (top) and **3** (bottom) in thf with the calculated transitions (line spectra).

[Cp₂ZrCH₃{(μ-O₂CC₆H₄S)Rh(PMe₃)₃}] (for **3**; Cp = C₅H₅). According to these calculations for both model compounds, the highest occupied molecular orbitals (HOMO) have both sulfur lone pair and rhodium d character. The HOMO itself is mainly sulfur-centred with some rhodium contribution. The lowest unoccupied molecular orbitals (LUMO) correspond to the σ* orbitals of the almost square-planar coordination sphere of the rhodium(I) centre.

The UV/Vis spectra of **2** and **3** are dominated by one broad band at 337 nm for **2** and 358 nm for **3**. TD-DFT studies show that for both model compounds this band can be assigned to several HOMO-to-LUMO excitations (Figure 6). Cp→Zr charge transfer processes, usually reported for the UV/Vis spectra of zirconocene complexes,^[22] seem to play no role for **3**. They are calculated to be of too high energy and too low oscillator strength to be observable in the spectrum.

Conclusions

While $[\text{Cp}^*_2\text{ZrMe}_2]$ reacts with $[\text{Rh}(\text{SC}_6\text{H}_4\text{COOH})(\text{PET}_3)_3]$ to give selectively either the 1:1 or the 2:4 product, $[\text{Cp}^*_2\text{Zr}(\text{Me})\{\mu\text{-OCC}_6\text{H}_4\text{S}\}\text{Rh}(\text{PET}_3)_3]$ (**3**) or $[(\text{Cp}^*_2\text{Zr}\{\mu\text{-O}_2\text{CC}_6\text{H}_4\text{S}\}\text{Rh}(\text{PET}_3)_2)_2]$ (**6**), the reaction with $[\{\text{Rh}(\mu\text{-SC}_6\text{H}_4\text{COO})(\text{PPh}_3)_2\}_2]$ (more labile phosphane ligands) gives exclusively the 2:4 product, $[(\text{Cp}^*_2\text{Zr}\{\mu\text{-O}_2\text{CC}_6\text{H}_4\text{S}\}\text{Rh}(\text{PPh}_3)_2)_2]$ (**5**).

Complex **3** reacts with 1 equiv. of water to yield $[\text{Cp}^*_2\text{Zr}(\text{OH})\{\mu\text{-OCC}_6\text{H}_4\text{S}\}\text{Rh}(\text{PET}_3)_3]$ (**4**), a rare example of a terminal hydroxo complex of a zirconocene. Complexes **3** and **4** are isotopic in the solid state. The introduction of the Lewis-acidic zirconium atom in **3** has a weak electron-withdrawing effect on the rhodium centre.

The hexanuclear complexes **5** and **6** consist of 32-membered metallacycles in which two zirconocene groups bridge two $\{\text{Rh}(\text{SC}_6\text{H}_4\text{COO})(\text{PR}_3)_2\}_2$ units [$\text{R} = \text{Ph}$ (**5**), Et (**6**)]. The main structural difference in **5** and **6** is the presence of two different isomers, in which the bridging thiolato ligands occupy either the *exo* or the *endo* position of the Rh_2S_2 ring, which has, however, a significant influence on the size of the macrocyclic cavity.

Experimental Section

General Remarks: All reactions were performed under nitrogen using standard Schlenk techniques. Solvents were dried with the appropriate drying agents and distilled under nitrogen. $\text{K}(\text{Hmba})$ ($\text{H}_2\text{mba} = 4\text{-mercaptobenzoic acid}$),^[13] $[\text{RhCl}(\text{PPh}_3)_3]$,^[23] $[\text{RhCl}(\text{PET}_3)_3]$ ^[24] and $[\text{Cp}^*_2\text{ZrMe}_2]$ ^[25] were prepared according to literature procedures. Complexes **1** and **2** were prepared in situ; their synthesis and spectroscopic data are given in ref.^[13] NMR spectra were recorded with a Bruker AVANCE DRX 400 (^1H NMR 400.13 MHz, ^{13}C NMR 100.3 MHz, ^{31}P NMR 161.97 MHz); $\text{Si}(\text{CH}_3)_4$ was used as internal standard in the ^1H NMR spectra. All heteronuclei spectra were referenced to $\text{Si}(\text{CH}_3)_4$ with the Ξ scale.^[26] NMR spectra of **3** and **4** were measured in the presence of excess PET_3 . IR spectra were recorded with an FTIR spectrometer Perkin–Elmer Spektrum 2000 (KBr) in the range of 350–4000 cm^{-1} ; a single crystal of **4** was measured with a Perkin–Elmer AutoImage microscope system with a diamond cell. The elemental composition was determined with a Hereaus CHN–O–S Analyzer. The melting points were determined in sealed capillaries (under nitrogen) using a Gallenkamp apparatus and are uncorrected. Cyclovoltammetry experiments were performed in an airtight three-electrode cell attached to a Schlenk line. The working electrode was a platinum disc electrode (diameter 2 mm), the counter electrode a platinum sheet and a silver wire was used as pseudoreference electrode. The working electrode was polished on alumina according to standard procedures. The measurements were performed in 5×10^{-3} M solutions of the substances in thf containing 0.1 mol of $[\text{nBu}_4\text{N}]\text{BF}_4$ per L. The potentials were referenced to the ferrocene/ferrocenium redox couple ($E_{1/2} = 0.54$ V vs. saturated calomel electrode). UV/Vis spectra were recorded with a Perkin–Elmer UV/Vis/NIR spectrometer Lambda 900.

(Methyl-1 κC)bis(pentamethylcyclopentadienyl-1 $\kappa^5\text{C}$)(μ -4-thiolatobenzoato-1 $\kappa^2\text{O}$:2 κS)tris(triethylphosphane-2 κP)zirconiumrhodium (3**):** Complex **2** was prepared in situ by adding a solution of $[\text{RhCl}(\text{PET}_3)_3]$ (243 mg, 0.5 mmol) and PET_3 (1 mL) in thf (15 mL) to a suspension of $\text{K}(\text{Hmba})$ (100 mg, 0.5 mmol) in thf (10 mL) at

0 °C. The suspension was warmed to room temperature over 1 h and was then stirred for 16 h. The red solution was filtered and added to a solution of $[\text{Cp}^*_2\text{ZrMe}_2]$ (194 mg, 0.5 mmol) in thf (5 mL). After stirring at room temperature overnight, the solvent was removed in vacuo and the resulting red solid was washed with cold diethyl ether (2 mL) and cold *n*-hexane (2 mL). Recrystallisation from *n*-hexane/ PET_3 gave 380 mg (77%) of orange needles. M.p. 175–180 °C (dec.). $\text{C}_{46}\text{H}_{82}\text{O}_2\text{P}_3\text{RhSZr}$ (986.26): calcd. C 56.02, H 8.38; found C 55.75, H 8.45. ^1H NMR ($[\text{D}_8]\text{thf}$): $\delta = -0.26$ (s, 3 H, ZrCH_3), 1.20, 1.38, 1.94 [each m, 45 H, $\text{P}(\text{C}_2\text{H}_5)_3$], 1.94 [s, 30 H, $\text{C}_5(\text{CH}_3)_5$], 7.59 [m, 2 H, A part of the AA'BB' spin system, H^1 in $\text{O}_2\text{CC}_6\text{H}_4\text{S}$ (for numbering, see Scheme 1)], 8.04 (m, 2 H, B part of the AA'BB' spin system, H^2 in $\text{O}_2\text{CC}_6\text{H}_4\text{S}$) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR ($[\text{D}_8]\text{thf}$): $\delta = 1.7$ (ZrCH_3), 9.5 [$2 \times \text{P}(\text{CH}_2\text{CH}_3)_3$][†], 10.0 [$\text{P}(\text{CH}_2\text{CH}_3)_3$], 11.6 [$\text{C}_5(\text{CH}_3)_5$], 18.8 [$2 \times \text{P}(\text{CH}_2\text{CH}_3)_3$][†], 22.7 [d, $^1J_{\text{C,P}} = 34.6$ Hz, $\text{P}(\text{CH}_2\text{CH}_3)_3$], 118.1 [$\text{C}_5(\text{CH}_3)_5$], 123.8 (SC), 127.9 (C^1 in $\text{O}_2\text{CC}_6\text{H}_4\text{S}$), 132.7 (C^2 in $\text{O}_2\text{CC}_6\text{H}_4\text{S}$), 164.6 (CCO_2), 181.6 (CCO_2) ppm ([†]coupling constants $J_{\text{A-X}}$, $J_{\text{A'-X}}$ and $J_{\text{M-X}}$ of the AA'MX spin system could not be simulated because of low resolution). $^{31}\text{P}\{^1\text{H}\}$ NMR ($[\text{D}_8]\text{thf}$): $\delta = 13.5$ [dd, $^1J_{\text{P-Rh}} = 137.4$ Hz, $^2J_{\text{P-P}} = 38.6$ Hz, 2 P, $\text{P}(\text{C}_2\text{H}_5)_3$], 28.4 [dt, $^1J_{\text{P-Rh}} = 160.4$, $^2J_{\text{P-P}} = 38.6$ Hz, 1 P, $\text{P}(\text{C}_2\text{H}_5)_3$] ppm. IR (KBr): $\tilde{\nu} = 2960$ s, 2908 s, 2890 m, 1583 s, 1561 w, 1494 m, 1420 s (sh), 1377 m, 1290 w, 1262 w (sh), 1168 w, 1078 m (sh), 1030 s (sh), 869 m, 847 w, 806 w (br), 775 m, 763 m, 732 w, 703 m, 677 w, 617 w, 552 m, 481 cm^{-1} .

(Hydroxo-1 κO)bis(pentamethylcyclopentadienyl-1 $\kappa^5\text{C}$)(μ -4-thiolatobenzoato-1 $\kappa^2\text{O}$:2 κS)tris(triethylphosphane-2 κP)zirconiumrhodium (4**):** Complex **3** was prepared as described above from $[\text{RhCl}(\text{PET}_3)_3]$ (162 mg, 0.33 mmol), PET_3 (1 mL), $\text{K}(\text{Hmba})$ (67 mg, 0.35 mmol) and $[\text{Cp}^*_2\text{ZrMe}_2]$ (129 mg, 0.33 mmol). The resulting red solid was dissolved in *n*-hexane (5 mL) which contained H_2O (6 μL , 0.33 mmol) and PET_3 (1 mL). The solution was refluxed for 15 min and the solvent evaporated in vacuo until the solution became slightly cloudy. Light orange crystals (209 mg, 64%) were obtained at room temperature from this mixture. $\text{C}_{45}\text{H}_{80}\text{O}_3\text{P}_3\text{RhSZr}$ (988.19): calcd. C 54.69, H 8.16; found C 54.39, H 8.32. ^1H NMR (C_6D_6): $\delta = 1.20$, 1.39, 1.88 [each m, 45 H, $\text{P}(\text{C}_2\text{H}_5)_3$], 1.91 [s, 30 H, $\text{C}_5(\text{CH}_3)_5$], 3.47 [s (br), 1 H, ZrOH], 7.45 (m, 2 H, A part of the AA'BB' spin system, H^1 in $\text{O}_2\text{CC}_6\text{H}_4\text{S}$), 8.10 (m, 2 H, B part of the AA'BB' spin system, H^2 in $\text{O}_2\text{CC}_6\text{H}_4\text{S}$) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): $\delta = 9.0$ [$2 \times \text{P}(\text{CH}_2\text{CH}_3)_3$][†], 10.8 [$\text{P}(\text{CH}_2\text{CH}_3)_3$], 11.9 [$\text{C}_5(\text{CH}_3)_5$], 17.6 [$2 \times \text{P}(\text{CH}_2\text{CH}_3)_3$][†], 21.4 [d, $^1J_{\text{C-P}} = 34.5$ Hz, $\text{P}(\text{CH}_2\text{CH}_3)_3$], 118.7 [$\text{C}_5(\text{CH}_3)_5$], 123.8 (SC, overlapped by solvent signal), 124.5 (C^1 in $\text{O}_2\text{CC}_6\text{H}_4\text{S}$), 131.8 (C^2 in $\text{O}_2\text{CC}_6\text{H}_4\text{S}$), 163.3 (CCO_2), 180.5 (CCO_2) ppm ([†]coupling constants $J_{\text{A-X}}$, $J_{\text{A'-X}}$ and $J_{\text{M-X}}$ of the AA'MX spin system could not be simulated because of low resolution). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): $\delta = 14.2$ [dd, $^1J_{\text{P-Rh}} = 136.6$ Hz, $^2J_{\text{P-P}} = 38.6$ Hz, 2 P, $\text{P}(\text{C}_2\text{H}_5)_3$], 28.4 [dt, $^1J_{\text{P-Rh}} = 162.5$ Hz, $^2J_{\text{P-P}} = 38.4$ Hz, 1 P, $\text{P}(\text{C}_2\text{H}_5)_3$] ppm. IR (KBr): $\tilde{\nu} = 3658$ w, 2960 m, 2924 m, 2908 m, 2874 m, 1583 m, 1561 m, 1494 m, 1420 s (sh), 1377 w, 1306 w (br), 1260 w (br), 1169 w, 1078 m (sh), 1030 m (sh), 869 m, 848 w, 805 w (br), 775 m, 763 m, 733 w, 702 w, 616 w, 552 w (sh) cm^{-1} .

Bis[bis(pentamethylcyclopentadienyl-1 $\kappa^5\text{C}$)(μ -4-thiolatobenzoato-1 $\kappa^2\text{O}$:2 κS)bis(triphenylphosphane-2 κP)zirconiumdirhodium] (5**):** A solution of $[\text{RhCl}(\text{PPh}_3)_3]$ (167 mg, 0.18 mmol) in thf (50 mL) was added to a suspension of $\text{K}(\text{Hmba})$ (27 mg, 0.18 mmol) in thf (50 mL). The mixture was heated to 50 °C for 4 h. The resulting orange solution was filtered and added to a solution of $[\text{Cp}^*_2\text{ZrMe}_2]$ (35.2 mg, 0.09 mmol) in thf (5 mL). After standing at room temperature for 3 d (stirring resulted in the precipitation of impure product), the solvent was removed in vacuo and the brown residue was washed with cold thf (0.5 mL) and *n*-hexane (2 mL).

Table 2. Crystallographic data for **3**, **4**, **5**·12thf and **6**·Et₂O.

	3	4	5 ·12thf	6 ·Et ₂ O
Empirical formula	C ₄₆ H ₈₂ O ₂ P ₃ RhSZr	C ₄₅ H ₈₀ O ₃ P ₃ RhSZr	C ₂₆₀ H ₂₉₂ O ₂₀ P ₈ Rh ₄ S ₄ Zr ₂	C ₁₂₀ H ₂₀₆ O ₉ P ₈ Rh ₄ S ₄ Zr ₂
<i>M_r</i>	986.22	988.19	4707.02	2762.93
<i>T</i> [K]	213(2)	213(2)	243(2)	213(2)
<i>λ</i> [pm]	71.073	71.073	71.073	71.073
Crystal system	monoclinic	monoclinic	triclinic	triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 1̄	<i>P</i> 1̄
<i>a</i> [pm]	931.91(8)	932.52(6)	1732.7(1)	1418.35(9)
<i>b</i> [pm]	3155.1(3)	3160.6(2)	1854.2(1)	1564.7(1)
<i>c</i> [pm]	1706.3(1)	1695.1(2)	2044.1(1)	1822.6(1)
<i>α</i> [°]	90	90	86.354(1)	66.950(1)
<i>β</i> [°]	90.833(1)	90.083(9)	76.425(1)	86.797(1)
<i>γ</i> [°]	90	90	67.987(1)	67.515(1)
<i>V</i> [nm ³]	5.0163(7)	4.9961(7)	5.9161(7)	3.4180(4)
<i>Z</i>	4	4	1	1
<i>ρ</i> _{calcd.} [g cm ^{−3}]	1.306	1.314	1.321	1.342
<i>μ</i> [mm ^{−1}]	0.707	0.712	0.509	0.822
<i>F</i> (000)	2080	2080	2456	1442
Crystal size [mm]	0.60 × 0.10 × 0.08	0.20 × 0.10 × 0.05	0.60 × 0.30 × 0.30	0.30 × 0.30 × 0.05
<i>θ</i> range [°]	1.76–26.39	1.76–24.10	1.83–28.40	1.54–28.32
<i>h</i> , <i>k</i> , <i>l</i> collected	−11 ≤ <i>h</i> ≤ 11 −38 ≤ <i>k</i> ≤ 39 −21 ≤ <i>l</i> ≤ 21	−10 ≤ <i>h</i> ≤ 9 −36 ≤ <i>k</i> ≤ 36 −16 ≤ <i>l</i> ≤ 19	−21 ≤ <i>h</i> ≤ 22 −24 ≤ <i>k</i> ≤ 16 −26 ≤ <i>l</i> ≤ 24	−18 ≤ <i>h</i> ≤ 18 −20 ≤ <i>k</i> ≤ 20 −22 ≤ <i>l</i> ≤ 24
Measured reflections	36561	19408	37232	24670
Unique reflections	10148	7733	27376	12941
Restraints/parameters	0/518	0/507	352/1347	7/682
<i>Gof</i> (all data)	1.582	0.597	0.935	1.093
Final <i>R</i> indices	<i>R</i> ₁ = 0.0931	<i>R</i> ₁ = 0.0470	<i>R</i> ₁ = 0.0479	<i>R</i> ₁ = 0.0499
[<i>I</i> > 2σ(<i>I</i>)]	<i>wR</i> ₂ = 0.1391	<i>wR</i> ₂ = 0.1004	<i>wR</i> ₂ = 0.1065	<i>wR</i> ₂ = 0.0978
<i>R</i> indices	<i>R</i> ₁ = 0.1010	<i>R</i> ₁ = 0.1237	<i>R</i> ₁ = 0.1011	<i>R</i> ₁ = 0.0716
(all data)	<i>wR</i> ₂ = 0.1410	<i>wR</i> ₂ = 0.1126	<i>wR</i> ₂ = 0.1248	<i>wR</i> ₂ = 0.1046
Δ <i>ρ</i> (max/min) [e Å ^{−3}]	0.795/−1.229	1.044/−0.576	1.184/−0.664	0.853/−0.379

Recrystallisation from thf gave 146 mg (42%) of red crystals. M.p. 198–202 °C (dec.). C₂₁₂H₁₉₆O₈P₈Rh₄S₄Zr₂ (3842.04): calcd. C 66.27, H 5.14; found C 65.85, H 5.32. ¹H NMR ([D₈]thf, *T* = 300 K): δ = 1.73–1.78 (br., 60 H, C₃Me₅), 7.00–8.00 [br., 136 H, P(C₆H₅)₃ + O₂CC₆H₄S] ppm. ³¹P{¹H} NMR ([D₈]thf): *T* = 300 K: δ ≈ 38 (br. d, PPh₃); *T* = 173 K: 37.7 (br. d, ¹J_{P-Rh} = 153 Hz, PPh₃ of isomer 1), 38.4 (br. d, ¹J_{P-Rh} = 149 Hz, PPh₃ of isomer 2) ppm. IR (KBr): ν̄ = 3050 m, 3000 w, 1633 m, 1585 m, 1495 m, 1481 m, 1432 s, 1380 w, 1306 s, 1262 m, 1170 w, 1135 w, 1091 m (sh), 1027 m, 1016 m, 872 w, 848 w, 805 w, 775 w, 740 m, 694 s, 619 w, 534 m, 522 s, 492 w, 458 w, 437 w cm^{−1}.

Bis[bis(pentamethylcyclopentadienyl-1κ⁵C)(μ-4-thiolatobenzoato-1κ²O:2κS)bis(triethylphosphane-2κP)zirconiumdirhodium] (6): [RhCl(PET₃)₃] (162 mg, 0.33 mmol) was dissolved in thf (7 mL) and added to a suspension of K(Hmba) (67 mg, 0.35 mmol) in thf (7 mL) at 0 °C. The suspension was warmed to room temperature over 1 h and then stirred for 16 h. The red solution was filtered, treated with a solution of [Cp*₂ZrMe₂] (65 mg, 0.17 mmol) in thf (5 mL) and heated to reflux for 3 h. After cooling, the solvent was reduced to half its volume. Vapour diffusion with diethyl ether yielded dark red crystals (170 mg, 37%), which were washed with *n*-hexane and dried in vacuo. M.p. 239–242 °C (dec.). C₁₁₆H₁₉₆O₈P₈Rh₄S₄Zr₂ (2688.97): calcd. C 51.81, H 7.35; found C 51.28, H 7.69. IR (KBr): ν̄ = 2958, 2908, 2873, 1635, 1585, 1494, 1429, 1392, 1379, 1301, 1261, 1169, 1136, 1094, 1032, 873, 848, 807, 766, 730, 702, 658, 622, 549, 515, 480, 413 cm^{−1}.

X-ray Crystallography: X-ray data were collected with a Siemens CCD Smart diffractometer for **3**, **5** and **6**, and with a Stoe IPDS1 for **4** using graphite-monochromated Mo-*K*_α radiation (λ = 0.71073 Å). Absorption correction was performed with the pro-

gram SADABS^[27] for **3**, **5** and **6**, and numerically for **4**. Structure solution and refinement were performed with WinGX,^[28] SHELXS-97 and SHELXL-97.^[29] All non-hydrogen atoms were refined anisotropically; most hydrogen atoms were refined in calculated positions. Visualisation was carried out with the program DIAMOND. The crystallographic data are summarised in Table 2. CCDC-609917 (for **3**), -609918 (for **4**), -609915 (for **5**) and -609916 (for **6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

DFT Calculations: The calculations were carried out with the Gaussian03 program package^[30] using B3LYP^[31] hybrid functionals. For the metal atoms, effective core potentials were used;^[32] the outer core electrons were considered explicitly. For the coordinating atoms, the standard 6-31g(d) basis set was used.^[33] The calculations of the ultraviolet spectra were performed with time-dependent density functional theory based on the optimised ground-state structure for **2** and on the experimental structure for **3**.

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