**Rhodium Redox Chemistry** 

## Stereochemical Control of the Redox Potential of Tetracoordinate Rhodium Complexes\*\*

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Dedicated to Professor Helmut Werner on the occasion of his 70th birthday

Understanding the factors which control the redox potential of transition-metal complexes is of fundamental importance for the design of functionality. In classical experiments, the redox potential of Cu<sup>II[1]</sup> or Ni<sup>II</sup> complexes<sup>[2]</sup> was shifted substantially to less negative values (i.e. anodic  $|E_A^{\circ}| < |E^{\circ}|$  in Scheme 1) by enforcing tetrahedral structures on the



**Scheme 1.** Schematic representation of approaches for the stereochemical control over transition-metal-complex redox potentials. Left: Destabilization of the oxidized form  $|E_{\rm A}^0| < |E^0|$ ; right: destabilization of the reduced form  $|E_{\rm B}^0| > |E^0|$ .

usually planar  $M^{II}$  complexes which are destabilized by the torsion energy  $E_t^{ox}$ . Tetrahedral structures are preferred for the reduced  $M^1$  complexes. To our knowledge, this concept has not been systematically applied to complexes of the transition metals from the fifth and sixth periods. For such an investigation the redox couple of tetracoordinate  $d^8 Rh^1/d^9 Rh^0$  complexes are ideally suited because 16-valence-electron-configured  $d^8$  rhodium(t) complexes strongly favor

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Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author. planar structures while the reduced 17-valence-electronconfigured d<sup>9</sup>rhodium(**0**) complexes prefer a distorted tetrahedral form.<sup>[2]</sup>

Longato et al.<sup>[3]</sup> and our group<sup>[4]</sup> have prepared strongly tetrahedrally distorted tetracoordinate 16-electron rhodium complexes, such as  $[Rh(dppf)_2]^+$  ( $\varphi = 49.7^\circ$ ; dppf = 1,1'-bis-(diphenylphosphanyl)ferrocene) and  $[Rh(^{Me}tropp^{Ph})_2]^+$  (tropp<sup>Ph</sup> = 5-diphenylphosphanyl-5*H*-dibenzo[*a,d*]cycloheptene;  $\varphi = 42.0^\circ$ ; where  $\varphi$  is the intersection of the planes spanned by the rhodium atom and the two donor atoms of each bischelate ligand) but a significant anodic shift of the reduction potentials was not observed.<sup>[5]</sup> The EPR spectra of these rhodium(0) complexes clearly show that the unpaired electron is predominantly located at the metal center.<sup>[3,6]</sup>

We therefore thought of another experiment allowing the control the redox potential. A destabilization of the structure of the reduced species in a redox couple by the energy  $E_t^{\text{red}}$  should lead to a cathodic shift of the reduction potential, that is,  $|E_B^0| > |E^0|$  (Scheme 1; right). For this experiment we used the stereoisomers of a ligand system; one enforcing an unfavorable coordination sphere for the reduced metal complex, and the other one allowing the coordination sphere to adapt to the more favorable geometry on reduction of the metal center. Structure models indicated, that the diastereomers of the tetrachelating bis(tropp) ligand **4** may fulfill these requirements. This approach allows a direct comparison of the stereochemical influence on the redox potential while electronic influences (i.e. different donor/ acceptor properties) are minimized.

The synthesis of **4** is presented in Scheme 2. Treating 1,3bis(diphenylphosphanyl)propane (**1**) with finely divided lithium in THF leads to cleavage of one P–Ph bond in each PPh<sub>2</sub> group and after hydrolysis furnished **2** as a mixture of



**Scheme 2.** Syntheses of the stereoisomers of the bis(tropp) ligands 4 and the corresponding rhodium(i)/(**0**) complexes **6** and **7**.

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isomers.<sup>[7]</sup> Reaction with 5-chloro-5*H*-dibenzo[*a*,*d*]cycloheptene (trop-Cl, **3**) gives after alkaline work-up the desired bis(tropp) compounds *R*,*S*-**4** (*meso*-**4**) and the racemic mixture *R*,*R*-/*S*,*S*-**4** (*rac*-**4** in the following) in satisfactory yield ( $\approx$  70%). The diastereomers, *meso*-**4** and *rac*-**4**, could not be separated and were treated with [Rh(cod)<sub>2</sub>]<sup>+</sup>CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> (COD = cyclooctadiene) to yield almost quantitatively the corresponding mixture of diastereomeric rhodium(t) complexes *meso*-**6** and *rac*-**6** as a microcrystalline red powder. Pure *rac*-**6** crystallizes from an approximately 0.02 M solution in THF, while the other diastereomer, *meso*-**6**, is obtained by layering the mother liquor with *n*-hexane (contaminated with about 10% *rac*-**6**).

The structures of *rac*-**6** and *meso*-**6** were determined by X-ray structure analyses (Figure 1 a and b and Table 1).<sup>[8]</sup>



Figure 1. Structures of the cation in *meso-***6** (a), the *R*,*R*-configured cation in *rac-***6** (b), the *R*,*R*-configured enantiomer in *rac-***7** (c).

As planned, the coordination sphere in the *rac*-**6** cation is significantly distorted towards a tetrahedral geometry ( $\varphi \approx 30^{\circ}$ ). The six-membered Rh-P-(CH<sub>2</sub>)<sub>3</sub>-P ring has a twist conformation. In the *meso*-**6** cation, however, this ring adopts the expected chair conformation with the two phenyl groups at P1 and P2 in the axial positions and the sterically demanding dibenzo[*a,d*]cycloheptenyl (trop) units in the equatorial positions. This arrangement permits a metal coordination sphere which is closer to square planar ( $\varphi \approx 19^{\circ}$ ).<sup>[9]</sup>

In the cyclic voltammogram of pure *rac*-**6** in THF/0.1M  $[nBu_4N]^+PF_6^-$  only two reversible redox waves are observed  $(E_{1/2}^1 = -1.11 \text{ V}; E_{1/2}^2 = -1.42 \text{ V} \text{ (Figure 2 a)).}$ 



**Figure 2.** Cyclic voltammograms of a) pure *rac*-**6**, b) a mixture of *rac*-**6** and *meso*-**6**; 0.1  $\times$  [*n*Bu<sub>4</sub>N]<sup>+</sup>PF<sub>6</sub><sup>-</sup>, THF, *T*=298 K, Pt working electrode, versus Ag/AgCl, scan rate=100 mVs<sup>-1</sup>.

A mixture of *rac*-**6** with *meso*-**6** in THF shows a cyclic voltammogram with four separated redox waves (Figure 2b). Clearly, *rac*-**6** is much easier to reduce than *meso*-**6** (*rac*-**6**:  $E_{1/2}^1 = -1.12 \text{ V}$ ,  $E_{1/2}^2 = -1.44 \text{ V}$ ; *meso*-**6**:  $E_{1/2}^1 = -1.36 \text{ V}$ ,  $E_{1/2}^2 = -1.72 \text{ V}$ ). The same features and almost identical redox potentials are obtained in a cyclic voltammogram taken in CH<sub>2</sub>Cl<sub>2</sub>, which shows that solvent effects are not responsible for the different redox potentials. The slight cathodic shift of  $E_{1/2}^1$  by about 100 mV observed for *rac*-**6** in comparison to [Rh(tropp<sup>Ph</sup>)<sub>2</sub>]<sup>+</sup> (see Scheme 1) is probably caused by replacing one P-phenyl group in the tropp<sup>Ph</sup> ligand by the alkyl chain in the bis(tropp) ligand.<sup>[10]</sup>

On a preparative scale, *rac*-6 can be reduced to give pure rac-[Rh{bis(tropp)}]<sup>0</sup> (*rac*-7) with sodium or sodium naph-

Compound	Rh-P [Å]	Rh-Ct [Å] <sup>[a]</sup>	C=C <sub>trop</sub> [Å]	P1-Rh-P2 [°]	P1-Rh-Ct1 [°]	P2-Rh-Ct2 [°] <sup>[a]</sup>	Ct-Rh-Ct [°] <sup>[a]</sup>	$\varphi \ [^{o}]^{[b]}$
meso- <b>6</b>	2.242	2.199	1.373	87.1	89.9	90.3	94.5	18.6
rac- <b>6</b>	2.240	2.182	1.383	86.3	91.4	90.9	97.5	26.8
rac- <b>6</b> ′ <sup>[c]</sup>	2.209	2.203	1.395	88.0	91.6	91.5	98.1	32.9
rac- <b>7</b>	2.231	2.084	1.413	88.9	92.0	92.0	102.7	42.7

Table 1: Selected structural data for meso-6, rac-6, and rac-7.

[a] Ct is the center of the coordinated C=C<sub>trop</sub> bond. [b]  $\varphi$  is the angle between the planes P1-Rh-Ct1 and P2-Rh-Ct2 and is a measure of the tetrahedral distortion. [c] Crystals of *rac*-**6** contain two independent molecules (one molecule of each enantiomer) per asymmetric unit.

thalenide,  $[Na^+(naph)^{-}]$  in THF. Alternatively, the neutral paramagnetic complexes *rac-7/meso-7* are obtained by a comproportion reaction of *rac-6/meso-6* with the fully reduced 18-valence-electron sodium rhodates  $[Na(thf)_n]^+$ -*rac/meso-*[Rh{bis(tropp)}]<sup>-</sup> (*rac-8/meso-8*).

The result of an X-ray structure analysis<sup>[8]</sup> for *rac*-**7**, which is only the third example of the still rare mononuclear rhodium(**0**) complexes, is shown in Figure 1 c. As previously observed,<sup>[3,5]</sup> the Rh–Ct bonds (Ct = midpoint of the coordinated C=C bond) is shorter and the coordinated C=C<sub>trop</sub> bond slightly longer in *rac*-**7** than in *rac*-**6**. The twist conformation of the central six-membered chelate ring is retained, however, the distortion towards a tetrahedron is more pronounced ( $\varphi \approx$ 43°) in *rac*-**7** and equals the one observed in *cis*-[Rh(tropp<sup>Ph</sup>)<sub>2</sub>]<sup>0</sup> ( $\varphi \approx$  43°).<sup>[5]</sup>

Crystals of the other diastereomer *meso-7* suitable for an X-ray analysis could not be obtained. However, information concerning the structure of *meso-7* were obtained from continuous wave (CW) X-band EPR spectra in a THF solution. The EPR spectrum of pure *rac-7* (Figure 3 a) consists



**Figure 3.** CW X-band EPR spectrum of a) pure *rac-***7**, b) a mixture of *meso-***7** and *rac-***7** in THF, c) the simulated spectrum of *rac-***7**, d) and the simulated spectrum of *meso-***7**. Experimental conditions: room temperature, modulation frequency 100 kHz, modulation amplitude 0.05 mT, microwave frequency 9.76 GHz.

of a triplet (intensity ratio 1:2:1, and g = 2.0208) with a <sup>31</sup>P hyperfine coupling of  $A_{iso} = 84$  MHz corresponding to two equivalent phosphorus nuclei as seen in the solid state structure.

Subtraction of the spectrum of *rac*-**7** from a spectrum of the *rac*-**7**/*meso*-**7** mixture (Figure 3b) allows the EPR parameters for *meso*-**7** to be determined (Figure 3c, d).<sup>[11]</sup> In contrast to *rac*-**7**, the *meso*-diastereomer has a lower symmetry and the hyperfine couplings with two inequivalent phosphorus nuclei lead to the observation of a doublet of

doublets with g=2.0137,  $A_{iso}^1=81.8$  MHz and  $A_{iso}^2=51.4$  MHz. A straightforward explanation for this observation is that the d<sup>9</sup> valence-electron *meso-7* radical is unable to adapt to the preferred tetrahedral structure because of the rigid chair conformation of the central Rh-P-(CH<sub>2</sub>)<sub>3</sub>-P chelate ring. As a consequence, one Rh–P bond elongates which also lowers the energy of the SOMO.<sup>[12]</sup> However, this stabilization is less effective than the distortion towards a tetrahedron and as a net result, a significant cathodic shift for the potential of the [*meso-7*]<sup>+</sup>/[*meso-7*]<sup>0</sup> redox couple is observed.

While it seems to be difficult to influence the redox couples of tetracoordinate  $d^8M/d^9M$  centers (M = Rh, Ir, Pt) using the classical approach for the 4th period metals, that is, destabilizing the oxidized form ( $d^8$  complex) by distortion towards a tetrahedron, the experiments reported herein (in combination with preliminary results for M = Ir and Pt)<sup>[13]</sup> show that the redox potentials of late-transition-metal complexes can be controlled effectively by destabilization of the reduced complex ( $d^9$  complex) by enforcing a more planar structure.

## **Experimental Section**

In the following, short descriptions of the syntheses and selected NMR resonances of diagnostic value are given. <sup>1</sup>H and <sup>13</sup>C NMR spectra are referenced relative to TMS, <sup>31</sup>P NMR spectra to H<sub>3</sub>PO<sub>4</sub>, and <sup>103</sup>Rh NMR spectra to  $\Xi$ =3.16 MHz. For full details, see the Supporting Information.

rac-4/meso-4: A solution of 2 (1 g, 3.8 mmol) in toluene (50 mL) was added to a solution of 3 (1.74 g, 7.6 mmol) in toluene (50 mL). After stirring for 2 h at RT, an aqueous solution of K<sub>2</sub>CO<sub>3</sub> (40 mL; 1M) was added and the reaction mixture was stirred for 14 h at RT, and then heated under reflux until the organic phase became yellow. The organic layer was separated, the solvent was removed under vacuum, and the residue was recrystallized from ethanol (30 mL) to afford 1.6 g (66%) of a 1:1 mixture of meso-4/rac-4 as a white airsensitive solid. M.p. (mixture): 162-166°C. Only some of the NMR signals of the rac-4/meso-4 mixture and could be assigned to one isomer: <sup>1</sup>H NMR (500.2 MHz,  $C_6D_6$ , 298 K):  $\delta = 6.92$  (2d, 4H, =CH), 6.86 (2d, 4H, =CH), 4.09 (d, 2H,  ${}^{2}J_{PH}$  = 5.7 Hz, CHP(*rac*)), 4.08 (d, 2H,  ${}^{2}J_{PH} = 5.7$  Hz, CHP(meso)), 1.89 (m, 2H, PCHH-CH<sub>2</sub>-CHHP(rac)), 1.80 (m, 2H, PCHH-CH2-CHHP(meso)), 1.40 (2m, 4H, PCHH-CH<sub>2</sub>-CHHP(meso+rac)), 1.23 (2 m, 3H, PCH<sub>2</sub>-CH<sub>2</sub>- $CH_2P(meso + rac)$ ), 0.97 ppm (m, 1H,  $PCH_2-CHH-CH_2P(meso)$ ); <sup>13</sup>C NMR (125.7 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K):  $\delta = 130.4$  (2d,  $J_{PC} = 1.4$  Hz, = CH), 130.1 (2d,  $J_{P,C} = 1.4$  Hz, =CH), 60.8 (2d,  ${}^{1}J_{P,C} = 19.4$  Hz, CHP), 29.3–28.9 (4d,  ${}^{1}J_{P,C} = 19.4$  Hz, PCH<sub>2</sub>), 23.5 ppm (2t,  ${}^{1}J_{P,C} = 19.6$  Hz,  ${}^{1}J_{PC} = 18.8 \text{ Hz}, \text{ PCH}_{2}\text{-}CH_{2}\text{-}CH_{2}\text{P}); {}^{31}\text{P NMR} (202.5 \text{ MHz}, \text{ CDCl}_{3},$ 298 K):  $\delta = -22.6$  (s, *rac*), -22.8 ppm (s, *meso*).

*rac*-6/*meso*-6: The phosphanes *rac*-4/*meso*-4 (137 mg, 0.2 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) were treated with a solution of [Rh(cod)<sub>2</sub>]OTf (**5**; 100 mg, 0.2 mmol; Tf = CF<sub>3</sub>SO<sub>2</sub>) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL). After stirring for 20 min, the solution was concentrated to 20% of its volume and hexane was added to afford *rac*-6 and *meso*-6 as an orange-red air stable microcrystalline powder (164 mg, 92%). The diastereomers were separated by fractional crystallization from THF; *rac*-6 crystallized first from a 0.02 M solution and *meso*-6 crystallized after addition of *n*-hexane to the mother liquor in about 90% purity. *rac*-6: M.p. > 250 °C. <sup>1</sup>H NMR (400.1 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K):  $\delta$  = 7.31 (m, 4H, =CH), 5.09 (m, 2H, CHP), 2.36 (m, 2H, PCHH-CH<sub>2</sub>-CH*I*P), 1.83 (m, 2H, PCH*H*-CH<sub>2</sub>-C*H*HP), 0.82 ppm (m, 2H, PCH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>P); <sup>13</sup>C NMR (100.7 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K):  $\delta$  = 103.3 (m, <sup>2</sup>*J*<sub>PC</sub> = <sup>5</sup>.1 Hz, <sup>1</sup>*J*<sub>Rh,C</sub> = 6.3 Hz, =CH), 92.4 (m, <sup>2</sup>*J*<sub>PC</sub> + <sup>2</sup>*J*<sub>P,C</sub> = 10.8 Hz, <sup>1</sup>*J*<sub>Rh,C</sub> = 5.0 Hz, =CH), 52.9 (m, <sup>1</sup>*J*<sub>PC</sub> + <sup>3</sup>*J*<sub>PC</sub> = 18.1 Hz, CHP), 17.3 (m, PCH<sub>2</sub>-

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CH<sub>2</sub>-CH<sub>2</sub>P), 16.0 ppm (m,  ${}^{1}J_{PC} + {}^{3}J_{PC} = 38.7$  Hz, PCH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>P);  ${}^{31}$ P NMR (162.0 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta = 80.3$  ppm (d,  ${}^{1}J_{Rh,P} = 170$  Hz);  ${}^{103}$ Rh (12.7 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta = -330$  ppm (t); meso-6: M.p. > 250 °C.  ${}^{1}$ H NMR (400.13 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K):  $\delta = 6.70$  (m, 2 H, =CH), 6.57 (m, 2 H, =CH), 4.72 (m, 2 H, CHP), 2.50 (m, 2 H, PCHH-CH<sub>2</sub>-CHHP), 2.19 (m, 1 H, PCH<sub>2</sub>-CHH-CH<sub>2</sub>P), 1.86 (m, 2 H, PCHH-CH<sub>2</sub>-CHHP), 0.89 ppm (m, 1 H, PCH<sub>2</sub>-CHH-CH<sub>2</sub>P);  ${}^{13}$ C NMR (100.7 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K):  $\delta = 84.6$  (m,  ${}^{2}J_{PC} + {}^{2}J_{P,C} = 10.0$  Hz, =CH), 79.3 (m,  ${}^{2}J_{PC} + {}^{2}J_{P',C} = 13.7$  Hz, =CH), 51.2 (m,  ${}^{1}J_{PC} + {}^{3}J_{P,C} = 24.4$  Hz,  ${}^{2}J_{PC} =$ 9.0 Hz, CHP), 21.2 (m,  ${}^{2}J_{PC} + {}^{4}J_{P',C} = 37.2$  Hz, PCH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>P), 20.5 ppm (m, PCH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>P);  ${}^{31}$ P NMR (162.0 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K):  $\delta = 72.0$  ppm (d,  ${}^{1}J_{Rh,P} = 163$  Hz);  ${}^{103}$ Rh NMR (12.7 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K):  $\delta = -576$  ppm (t).

rac-8/meso-8: Sodium (3 mg, 0.13 mmol) was added to a suspension of the complexes rac-6 and meso-6 (50 mg, 0.056 mmol) in THF (5 mL). The reaction mixture was sonicated for 12 h at 25 °C, and subsequently the resulting deep red reaction mixture was filtered. The filtrate was evaporated to dryness and washed several times with hexane leading to a deep red highly air-sensitive powder (45 mg, 67%). rac-8: <sup>1</sup>H NMR (400.1 MHz,  $[D_8]$ THF, 298 K):  $\delta = 4.35$  (m, 2H, CHP), 4.20 (m, 2H, =CH), 2.83 (m, 2H, =CH), 1.40 (m, 2H, PCHH-CH<sub>2</sub>-CHHP), 1.01 (m, 2H, PCH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>P), 0.81 ppm (m, 2H, PCHH-CH<sub>2</sub>-CHHP); <sup>13</sup>C NMR (100.7 MHz, [D<sub>8</sub>]THF, 298 K):  $\delta = 57.2$  (m, CHP), 53.7 (m, =CH), 40.3 (d,  ${}^{2}J_{P,C}$  or  ${}^{2}J_{Rh,C} = 11.1$  Hz, = CH), 25.6 (m, PCH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>P), 21.5 ppm (m, PCH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>P); <sup>31</sup>P NMR (121.5 MHz, [D<sub>8</sub>]THF, 298 K):  $\delta = 81.1$  ppm (d, <sup>1</sup>J<sub>PRh</sub> = 179 Hz); <sup>103</sup>Rh NMR (12.7 MHz, [D<sub>8</sub>]THF, 298 K):  $\delta = -681$  ppm (t). meso-8: <sup>31</sup>P NMR (121.5 MHz, [D<sub>8</sub>]THF, 298 K):  $\delta = 88.1$  ppm (br)

*rac*-**7**: A solution of sodium-naphthalenide in THF (0.056 M, 0.056 mmol, 1 mL) was added to a suspension of *rac*-**6** (50 mg, 0.056 mmol) in THF (2 mL). The deep green solution was filtered. After removing the solvent from the filtrate under reduced pressure, a deep green highly air-sensitive powder was obtained, which was washed several times with hexane (40 mg, 93 %). EPR (THF, 298 K):  $g_{\rm iso} = 2.017$  [t,  $A_{\rm iso}$  (<sup>31</sup>P) = 84 MHz].

*rac-7/meso-7*: A 1:1 mixture of the compounds *rac-8* and *meso-8* (29 mg, 0.024 mmol) were mixed in THF (2 mL) with a 1:1 mixture of *rac-6* and *meso-6* (20 mg, 0.022 mmol). An immediate color change from red to deep green was observed. After removing the solvent under reduced pressure, the product was isolated as highly airsensitive deep green powder (40 mg, 93%). *meso-7*: EPR (THF, 298 K):  $g_{iso} = 2.0145$  [dd,  $A_{iso}^{1}$  (<sup>31</sup>P) = 81.8 MHz,  $A_{iso}^{2}$  (<sup>31</sup>P) = 51.4 MHz].

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- [8] rac-6·CH<sub>2</sub>Cl<sub>2</sub>: C<sub>93</sub>H<sub>78</sub>Cl<sub>2</sub>F<sub>6</sub>O<sub>6</sub>P<sub>4</sub>Rh<sub>2</sub>S<sub>2</sub>; monoclinic; P2(1); a =1334.0(5), b = 1830.2(7), c = 1793.5(7) pm,  $\beta = 104.191(8)$ ; V =4.25(1) nm<sup>3</sup>, Z = 2,  $\rho_{calcd} = 1.463 \text{ mg m}^{-3}$ , crystal dimensions:  $0.15 \times 0.15 \times 0.20$  mm, diffractometer Siemens CCD 1k area detector;  $Mo_{K\alpha}$  radiation, 293 K, measurement range: 3.14 <  $2\Theta < 56.56^{\circ}$ , 20789 independent reflections, 43894 reflections  $F > 4\sigma(F)$ ,  $\mu = 0.644$  mm<sup>-1</sup>; direct methods; refinement against full matrix (versus  $F^2$ ) with SHELXTL (Rel. 5.1) and SHELXL-97; 1036 parameters, R1 = 0.0568 and wR2 (all data) = 0.1094, max/min residual electron density:  $916/-429 \text{ e} \text{ nm}^{-3}$ . meso-6:  $C_{53}H_{46}F_{3}O_{3}P_{2}RhS$ ; monoclinic; P2(1); a = 1109.6(1), b =1841.8(1),  $c = 1189.2(1) \text{ pm}, \beta = 111.523(6)^\circ, V = 2.2609(3) \text{ nm}^3$ , Z=2,  $\rho_{\text{calcd}}=1.447 \text{ mg m}^{-3}$ , crystal dimensions:  $0.12 \times 0.11 \times$ 0.10 mm, diffractometer Stoe IPDS II image plate system,  $Mo_{K\alpha}$  radiation, 293 K, measured range:  $3.94 < 2\Theta < 55.72^{\circ}$ , 9377 independent reflections, 15169 reflections  $F > 4\sigma(F)$ ,  $\mu =$ 0.55 mm<sup>-1</sup>; direct methods; refinement against full matrix (versus  $F^2$ ) with SHELXTL (Rel. 5.1) and SHELXL-97; 567 parameters; R1 = 0.0403 and wR2 (all data) = 0.0888, max/min residual electron density: 426/-460 enm<sup>-3</sup>. rac-7.2 THF:  $C_{53}H_{54}O_2P_2Rh$ ; monoclinic; P21/n; a = 1318.9(2), b = 1889.8(3),  $c = 1807.5(3) \text{ pm}, \quad \beta = 109.857(4); \quad V = 4.237(1) \text{ nm}^3, \quad Z = 4,$  $\rho_{\text{calcd}} = 1.392 \text{ mg m}^{-3}$ , crystal dimensions:  $0.08 \times 0.14 \times 0.27 \text{ mm}$ , diffractometer Bruker AXS SMART APEX with CCD area detector;  $Mo_{K\alpha}$  radiation, 180 K, phase transition at temperatures beyond 180 K, measurement range:  $3.22 < 2\Theta < 56.58^{\circ}$ , 10510 independent reflections, 31246 reflections  $F > 4\sigma(F)$ ,  $\mu =$ 0.521 mm<sup>-1</sup>; direct methods; refinement against full matrix (versus  $F^2$ ) with SHELXTL (Rel. 5.1) and SHELXL-97; 523 parameters, R1 = 0.0570 and wR2 (all data) = 0.1396, max/min residual electron density: 916/-625 enm<sup>-3</sup>. CCDC-229384 (rac-6·CH<sub>2</sub>Cl<sub>2</sub>), CCDC-229383 (meso-6), CCDC-229385 rac-7·2 THF contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam. ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK: fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).
- [9] Alternatively, the distortion can be described by the deviation of Ct from the plane running through the P-Rh-P plane: *meso-6*: 25.1 pm (Ct1), -66.3 pm (Ct2); *rac-6*: 81.5 and 78.7 pm (Ct1), -95.4 and -68.2 pm; *rac-7*: 100.2 pm (Ct1), -115.3 pm (Ct2).
- [10] The redox potentials of the P-bis(cyclohexyl) substituted complex  $[\text{Rh}(\text{tropp}^{\text{cyc}})_2]^{+i0-1}$  are at  $E_{1/2}^1 = -1.19 \text{ V}$  and  $E_{1/2}^2 = -1.53 \text{ V}$ ; S. Deblon, Dissertation, ETH Zürich, **2000**, No. 13920.
- [11] The EPR parameters were obtained by calculating the experimental spectra (least-squares-fittings using EasySpin, see: http://www.esr.ethz.ch).
- [12] A correlation of  $A_{iso}$ <sup>(3)</sup>P) with Rh–P separations has been clearly established in [Rh(dppf)<sub>2</sub>]<sup>0[3]</sup> where the Rh–P bond lengths show a linear inverse correlation with the hyperfine couplings.
- [13] Experiments with the corresponding diastereomers of [M{bis-(tropp)}] with M=Ir or Pt show the same behavior as reported here for M=Rh; C. Laporte, Dissertation, ETH Zürich, 2003, No. 15137.