Electronic Structure

Electromeric Rhodium Radical Complexes**

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Dedicated to Professor Martin Quack

Electromers are species with significantly different electronic but only slightly different geometrical structures, whereby each species corresponds to a local minimum on the energy hypersurface.^[1a-c] Although they have been discussed several times in the literature, direct observation of "electroisomers"—the synonyms "redox isomers" or "valence isomers" are likewise used—is rare.^[2] Paramagnetic transition-metal complexes are ideally suited to the study of this phenomenon, and the localization of the spin on either the metal M[•](L) or the ligand M⁺(L^{-–}) can be characterized by EPR spectroscopy.^[3] We report herein a striking example in which two electromers of paramagnetic rhodium complexes coexist in a rapid equilibrium and the distortion of only one P–Rh–P angle results in a substantial redistribution of the spin density.

We previously reported paramagnetic $[M(tropp^{Ph})_2]^0$ complexes (Scheme 1; M = Rh, Ir),^[4a-d] which exist as rapidly exchanging *trans/cis* mixtures ($k_{isom} \approx 1 \times 10^4 \text{ s}^{-1}$) in solution. Both isomers have tetrahedrally distorted structures and their EPR spectra and consequently electronic structures are quite similar. They are best described as strongly delocalized organometallic radicals with less than 30% of the spin density localized on the metal centers.^[4e] We have now synthesized the rhodium complexes **5 a,b**, which likewise contain two olefin and two phosphane binding sites in mutual *trans* positions, but the constraints within the ligand system do not allow *trans* to *cis* isomerization.

The syntheses of the ligand trop₂PPh **2** and the deep red complexes $[Rh(trop_2PPh)(PPh_3)]^+A^-$ (**5a**: $A^- = PF_6^-$, **5b**: $A^- = BArF^-$) are straightforward and proceed with excellent

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Scheme 1. Synthesis of $trop_2PPh$ (2) and the Rh complexes 5a and 5b.

yields as shown in Scheme 1 (trop = 5H-dibenzo[a,d]-cyclohepten-5-yl). Exchange of the PF₆⁻ anion by the BArF⁻ anion (BArF⁻ = tetrakis[(3,5-trifluoromethyl)phenyl]borate)^[5]

enhances significantly the solubility of 5b (in diethyl ether, THF, or toluene). The structures of the ligand 2 and complex 5a are shown in Figure 1.^[6a,b] The rigid tripodal diolefin phosphane 2 is preorganized for binding a transition-metal ion in its cleft. Only a small rotation around the P-C_{trop} bonds is necessary to convert 2 into the conformation it adopts in 5a, explaining the high stability of this complex. As observed with the related amino ligand trop₂NH,^[7] **5a** shows a distorted "sawhorse" (SH) type structure (a trigonal bipyramid with one missing edge in the equatorial plane):^[8] the P1-Rh-P2 angle is 160.9° and the ct-Rh1-ct angle is 134.8° (ct = centroid of the coordinated C= C_{trop} bond). The NMR data for all these complexes indicate that C_s -symmetrical SH-type structures are retained in solution and that there are no significant cation anion interactions (³¹P nuclei in *trans* positions, inequivalent olefinic protons, superimposable data for 5a and 5b).

A cyclic voltammogram of **5a** in THF/1M $nBu_4N^+PF_6^$ shows two reversible waves at $E_1^\circ = -1.339$ V and $E_2^\circ =$



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Figure 1. A) ORTEP plot (at 30% ellipsoid probability) showing the structure of **2**. Only one of the two crystallographically independent molecules is shown. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] (bond length of the second molecule are given in italics): C4=C5 1.338(3), 1.339(3), C19=C20 1.340(3), 1.343(3), Σ° (C-P-C) 300.7(2), 301.3(2). B) ORTEP plot (at 30% ellipsoid probability) showing the structure of the cation of **5a**·2 CH₂Cl₂. The PF₆⁻ anion, the CH₂Cl₂ solvent molecules, and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Rh1–P1 2.231(1), Rh1–P2 2.359(1), Rh1–ct 2.099(3), Rh1–C4 2.194(3), Rh1–C5 2.233(3), C4=C5 1.405(4), Rh1–C22 3.712(5), Rh1–C28 2.905(4), P1-Rh1-P2 160.9(1), ct-Rh1-ct' 134.8(2), Rh1-P2-C22 124.9(3), Rh1-P2-C28 87.0(2), Σ° (C-P1-C) 314.7(8), Σ° (C-P2-C) 317.2(7).

-1.965 V (vs. ferrocenium/ferrocene) for the redox couples $[Rh(trop_2PPh)(PPh_3)]^+/[Rh(trop_2PPh)(PPh_3)]^0$ and $[Rh(trop_2PPh)(PPh_3)]^{-1}$, respectively.

Chemically, **5b** can be reduced by one electron with elemental sodium, sodium naphthalide, or $[CoCp_2]^{[9]}(Cp^* = 1,2,3,4,5$ -pentamethylcyclopentadienyl) in THF (Scheme 2). The EPR spectrum of the X band (T = 120 K) and W band (T = 20 K) of a frozen solution clearly supports two paramagnetic rhodium complexes **6L** and **6M** (Figure 2 A,B), which were fully characterized by high-resolution pulse EPR spectroscopy of the X, Q, and W bands (see the Supporting Information for details).^[10] In contrast to the *cis/trans*-[Rh-(tropp^{Ph})₂] complexes (Scheme 1), which are highly persistent









Scheme 2. Reduction of 5 b to give a mixture of 6 L and 6 M.

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Figure 2. A) X-band (9.5065 GHz) continuous wave (CW) EPR spectrum of a mixture of 6L[•] and 6M[•] measured at T = 120 K in a toluene/ THF mixture. The upper trace (black, bold) displays the experimental spectrum; the second trace (magenta) the simulated spectrum comprising 0.87 $\textbf{6L}\textbf{+}0.13~\textbf{6M}\textbf{\cdot}$. The lower traces show the simulated EPR spectra of the single components. B) W-band (94.2947 GHz) FIDdetected EPR spectrum measured at T = 20 K in a toluene/THF mixture. The g values of 6L were resolved at this microwave frequency. Isomer 6M[•] displays an axial spectrum with a resolved doublet from a large ³¹P hyperfine interaction. C) X-band (9.4793 GHz) CW EPR spectra of a mixture of **6L** and **6M** in THF recorded at T = 190-340 K. The simulated spectra describing the 6L'=6M' ratios are displayed in magenta. D) Van't Hoff plot, $\ln(K_{eq})$ vs. 1/T, for the ratio $K_{eq} = 6 M'/6L'$ from the simulation at each temperature in (C), used to evaluate the thermodynamic stabilities. E) Computed structure of 6L[•]. Selected bond lengths [Å] and angles [°]: P1-Rh 2.259, P2-Rh 2.397, Rh-ct1 2.114, Rh-ct2 2.106, P1-Rh-P2 165.5, ct1-Rh-ct2 134.5. F) Computed structure of 6M[•]. Selected bond lengths [Å] and angles [°]: P1-Rh 2.257, P2-Rh 2.444, Rh-ct1 2.097, Rh-ct2 2.094, P1-Rh-P2 122.0, ct1-Rh-ct2 131.2. G) Computed (b3-lyp, TZVP) spin density of 6L. H) Computed (b3-lyp, TZVP) spin density of 6M[.].

in solution, the radicals **6L** and **6M** react to give a mixture of diamagnetic products.^[11]

The EPR spectra of the X band of the deep brown solutions in the temperature range 190–340 K are shown in Figure 2 C. The changes in the spectra are fully reversible and indicate an equilibrium between two electronically different species that rapidly exchange on the EPR time scale (ca. 1 GHz).

The exchange process in solution is fast on the EPR time scale at all temperatures and only an averaged spectrum is observed. Lowering the temperature shifts the fast equilibrium $6L \rightleftharpoons 6M$ strongly towards 6L (the concentration of isomer 6L' is approximately 66% at 340 K and 88% at 190 K). However, the very different electronic structure and therefore markedly different g values and hyperfine couplings of 6L and 6M render the averaged spectrum very sensitive to its temperature-dependent ratio. This behaviour allowed us to evaluate the equilibrium constant $6 M'/6 L' = K_{eq}$ at each temperature T through spectral simulation. The relative thermodynamic stabilities were estimated through a Van't Hoff plot ($\ln K_{eq}$ vs. 1/T; Figure 2D). Accordingly, **6L** is more stable than **6M** by $\Delta H^{\circ} = (-1.2 \pm 1) \text{ kcal mol}^{-1}$ and $\Delta S^{\circ} =$ (3.9 ± 4) cal mol⁻¹ K⁻¹. In agreement with the experimentally observed fast exchange process, DFT computations based on smaller models of 6L[•] and 6M[•] (see the Supporting Information) reveal a small energy barrier (ca. 3 kcal mol^{-1}).^[12] Both species are detected in frozen solution upon rapid freezequenching with liquid nitrogen (i.e. under non-equilibrium conditions).

To gain insight into the electronic structures of $6L^{\cdot}$ and $6M^{\cdot}$, we performed DFT calculations with the complete molecule [Rh(trop₂PPh)(PPh₃)][•]. Table 1 lists the experimental and computed EPR data. Structure optimizations led to three stable species, which are close in energy. On the basis of comparison with the experimental data of $6L^{\cdot}$ and $6M^{\cdot}$, these

species are denoted as $6L'_{cal}$, $6L'_{cal}$, and $6M'_{cal}$, respectively. The most- and least-stable isomers $6L'_{cal}$ ($E_{rel} = 0.0 \text{ kJ mol}^{-1}$) and $6L'_{cal}$ ($E_{rel} = +2.1 \text{ kcal mol}^{-1}$), respectively, are rotamers obtained by rotation of the PPh₃ group (see the Supporting Information). Both have structures closely related to that of the cation of diamagnetic precursor **5a**.

The second most stable isomer $6M_{cal}$ is 2.0 kcalmol⁻¹ higher in energy than 6L'_{cal} and has a structure in which the P1-Rh-P2 angle closes from 165.5° to 122.0°. Concomitantly, the distance of Rh to the PPh₃ group becomes longer (Rh-P2 in 6L[•]_{cal}: 2.397 Å; in 6M[•]_{cal}: 2.444 Å). This result points to a shift of the electron density onto the metal on going from 6 L. to $6M^{\cdot}$ (see below). Structure $6M^{\cdot}_{cal}$ approaches the extreme case of a trigonal pyramid, in which the P-Rh-P angle would be 90°. This structural feature was recently observed for the bistropsilyl complex [Rh(trop₂SiMe)(PPh₃)] for which we assumed—because of the strong σ -electron donation of the silvl group—a strong contribution of the resonance form A (Scheme 2) and enhanced electron density at the metal center.^[13] A more detailed interpretation of the different electronic structures of 6L[•] and 6M[•] is given in the Supporting Information.

The computed EPR parameters of the lowest energy species $6L_{cal}$ fit best to the experimental values of the more stable major isomer 6L, whereas the computed data for the somewhat higher energy species $6M_{cal}$ are in good accord with the experimental values of the less abundant isomer 6M (Table 1). The experimental g_{iso} values of both isomers differ significantly from $g_e = 2.0023$ and indicate spin density at the metal center. In 6M, the larger anisotropy of the g tensor $(6L: \Delta g = 0.043; 6M: \Delta g = 0.101)$ shows that the spin density is higher at the Rh center. Note the large difference of the hyperfine couplings of the ³¹P nucleus of the trop₂PPh ligand in 6M ($A^{P}_{iso} = (602 \pm 5)$ MHz) and 6L: ($A^{P}_{iso} = (53 \pm 8)$ MHz), which demonstrate the very different electronic

Table 1: Experimental and DFT calculated (values in italics) g values, hyperfine coupling constants (A [MHz]), and spin densities ρ of compounds **6L**[•] and **6M**[•].^[a]

	6L [•] (major species detected in the experimental EPR spectra)					
exp calcd		$g_{11} = 2.063 \pm 1$ $g_{11} = 2.048$	$\begin{array}{c} g_{22} \!=\! 2.043 \!\pm\! 1 \\ g_{22} \!=\! 2.035 \end{array}$	$\begin{array}{c} g_{33} \!=\! 2.020 \pm \! 1 \\ g_{33} \!=\! 2.008 \end{array}$	$g_{iso} = 2.042 \pm 1$ $g_{iso} = 2.034$	
	ρ	A ₁₁	A ₂₂	A ₃₃	A _{iso}	
	-	22 ± 10	22 ± 10	115 ± 5	53	
	12.2%	22	27	70	40	
³¹ P2 exp	-	-56 ± 5	-50 ± 5	10 ± 15	-32	
calcd	9.0%	-7	-3	+ 24	+ 5	
¹⁰³ Rh exp	-	17 ± 5	-17 ± 10	-32 ± 2	-10	
calcd	32.8%	+2	-20	-39	-19	
	6M [•] (minor species detected in the experimental EPR spectra)					
	6 M • (min	or species detected	in the experimental	EPR spectra)		
exp. calcd	6 M * (min	$\frac{1}{g_{11}=2.100\pm1}$ $\frac{g_{11}=2.084}{g_{11}=2.084}$	in the experimental $g_{22} = 2.100 \pm 1$ $g_{22} = 2.078$	EPR spectra) $g_{33} = 1.999 \pm 1$ $g_{33} = 1.999$	$g_{iso} = 2.066 \pm 1$ $g_{iso} = 2.054$	
exp. calcd	6Μ' (min	$\frac{1}{g_{11} = 2.100 \pm 1}$ $\frac{g_{11} = 2.084}{g_{11} = 2.084}$	in the experimental $g_{22} = 2.100 \pm 1$ $g_{22} = 2.078$ A_{22}	EPR spectra) $g_{33} = 1.999 \pm 1$ $g_{33} = 1.999$ A_{33}	$g_{iso} = 2.066 \pm 1$ $g_{iso} = 2.054$ A_{iso}	
exp. calcd ³¹ P1 exp	6 Μ' (min ρ -	1000000000000000000000000000000000000	in the experimental $g_{22} = 2.100 \pm 1$ $g_{22} = 2.078$ A_{22} 575 ± 5	EPR spectra) $g_{33} = 1.999 \pm 1$ $g_{33} = 1.999$ A_{33} 655 ± 5	$g_{iso} = 2.066 \pm 1$ $g_{iso} = 2.054$ A_{iso} 602	
exp. calcd ³¹ P1 exp calcd	6 Μ' (min - 28.2%	$\frac{1}{g_{11} = 2.100 \pm 1}{g_{11} = 2.084}$ $\frac{A_{11}}{575 \pm 5}$ $\frac{457}{457}$	in the experimental $g_{22} = 2.100 \pm 1$ $g_{22} = 2.078$ A_{22} 575 ± 5 459	EPR spectra) $g_{33} = 1.999 \pm 1$ $g_{33} = 1.999$ A_{33} 655 ± 5 601	$g_{iso} = 2.066 \pm 1$ $g_{iso} = 2.054$ A_{iso} 602 506	
exp. calcd ³¹ P1 exp calcd ³¹ P2 exp	6 Μ' (min - 28.2%	$ \begin{array}{c} g_{11} = 2.100 \pm 1 \\ g_{11} = 2.084 \\ A_{11} \\ S75 \pm 5 \\ 457 \end{array} $	in the experimental $g_{22} = 2.100 \pm 1$ $g_{22} = 2.078$ A_{22} 575 ± 5 459 0 to -22	EPR spectra) $g_{33} = 1.999 \pm 1$ $g_{33} = 1.999$ A_{33} 655 ± 5 601	$g_{iso} = 2.066 \pm 1$ $g_{iso} = 2.054$ A_{iso} 602 506 -	
exp. calcd ³¹ P1 exp calcd ³¹ P2 exp calcd	6 Μ' (min - 28.2% - 3.1%	$ \begin{array}{c} \text{g}_{11} = 2.100 \pm 1 \\ \text{g}_{11} = 2.084 \\ \text{A}_{11} \\ \text{s}_{75} \pm 5 \\ \text{457} \\ \text{-35} \end{array} $	$\begin{array}{c} \text{in the experimental} \\ g_{22} = 2.100 \pm 1 \\ g_{22} = 2.078 \\ A_{22} \\ 575 \pm 5 \\ 459 \\ 0 \text{ to } -22 \\ -30 \end{array}$	EPR spectra) $g_{33} = 1.999 \pm 1$ $g_{33} = 1.999$ A_{33} 655 ± 5 601 -10	$g_{iso} = 2.066 \pm 1$ $g_{iso} = 2.054$ A_{iso} 602 50625	
exp. calcd ³¹ P1 exp calcd ³¹ P2 exp calcd ¹⁰³ Rh exp	6 M [•] (min - - 28.2% - 3.1% -	$ \begin{array}{c} \text{g}_{11} = 2.100 \pm 1 \\ \text{g}_{11} = 2.084 \\ \text{A}_{11} \\ \text{575} \pm 5 \\ \text{457} \\ \text{-35} \\ 24 \pm 2 \end{array} $	$\begin{array}{c} g_{22} = 2.100 \pm 1 \\ g_{22} = 2.078 \\ A_{22} \\ 575 \pm 5 \\ 459 \\ 0 \text{ to } -22 \\ -30 \\ 24 \pm 5 \end{array}$	EPR spectra) $g_{33} = 1.999 \pm 1$ $g_{33} = 1.999$ A_{33} 655 ± 5 601 -10 -38 ± 2	$g_{iso} = 2.066 \pm 1$ $g_{iso} = 2.054$ A_{iso} 602 506 $-$ -25 3	

structure of both electromers. Our DFT computations support this picture. In 6L'_{cal}, only 33% of the spin density is located at Rh, 12% at P1, and 9% at P2, with the residual spin density delocalized over the trop₂PPh and PPh₃ ligand. In 6M'cal, more than half of the spin density $[\rho(Rh) 58\%]$ is located at Rh. Another 28% resides on P1 and only 14% is delocalized over P2 $[\rho(P2) 3\%]$ and the hydrocarbon framework. Electromer 6L[•] is best described as a strongly delocalized organometallic radical, whereas 6M' should be considered as a metallo radical with a high localization of the spin density in the Rh-P1 bond.

In this report, we provide compelling evidence for the existence of interconverting and energetically almost degenerate organometallic electromers, which could be

[a] The signs of the experimental hyperfine couplings are assigned according to the DFT results.

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detected through the observation of the paramagnetic rhodium complex $[Rh(trop_2PPh)(PPh_3)]$ by EPR spectroscopy under ambient conditions. It remains to be explored how far the reactivity of the highly delocalized radical **6L** and the metalloradical **6M** can be distinguished.

Experimental Section

All manipulations were performed under an inert atmosphere of argon using standard Schlenk techniques. Selected analytical data are given below (see the Supporting Information for more details).

trop₂PPh (**2**): trop-Cl (8.20 g, 36 mmol) and phenylphosphane (1.9 mL, 17.3 mmol) were dissolved in toluene (100 mL). 1,4-Diazabicyclo[2.2.2]octane (dabco) (3.87 g, 34.5 mmol) dissolved in toluene (200 mL) was added dropwise under vigorous stirring. The mixture was heated at reflux for 2 h, and dabco hydrochloride was filtered off while the mixture was still hot. The mixture was reduced in volume to 30 mL under reduced pressure, and the product crystallized within 12 h to give 7.11 g (14.5 mmol, 84 %) of colorless microcrystals. ¹H NMR (300 MHz, CD₂Cl₂, 298 K): $\delta = 6.70$ (br d, ³*J*_{HH} = 11.7 Hz, 2H, H_{olefin}), 6.60 (br d, ³*J*_{HH} = 11.7 Hz, 2H, H_{olefin}), 4.53 ppm (br d, ²*J*_{PH} = 3.6 Hz, 2H, 2H_{berz}); ¹³C[¹H] NMR (75.5 MHz, CD₂Cl₂, 298 K): $\delta = 132.4$ (d, ⁴*J*_{PC} = 5.1 Hz, C_{olefin}), 131.7 (d, ⁴*J*_{PC} = 4.3 Hz, C_{olefin}), 55.6 ppm (d, *J*_{PC} = 26 Hz, C_{berz}); ³¹P[¹H] NMR (121.5 MHz, CD₂Cl₂, 23 °C): $\delta = -7.0$ ppm; m.p.: 218 ± 2 °C.

 $[Rh(PPh_3)(trop_2PPh)]PF_6$ (5a): $[Rh_2(\mu-Cl)_2(cod)_2]$ (105 mg, 0.212 mmol; cod = 1,5-cyclooctadiene) and $trop_2PPh$ (221 mg, 0.45 mmol) were dissolved in THF (15 mL). After several minutes, the solution changed color from yellow to orange and [Rh2(µ- $Cl_2(trop_2PPh)_2$]·1.5 THF started to precipitate. After 1 day at T =298 K, 271 mg (0.198 mmol, 94%) of the air stable product was collected as an orange microcrystalline powder. This product was dissolved in THF (40 mL) and heated at reflux for 12 h in the presence of PPh_3 (115 mg; 0.438 mmol) and $TIPF_6$ (210 mg; 0.601 mmol). Subsequently, the solvent was removed under reduced pressure, and the remaining red solid was treated with CH₂Cl₂ (150 mL). Insoluble material (TlCl) was filtered off over celite, and the filtrate was reduced in volume to 15 mL and layered with diethyl ether (50 mL) to give 400 mg (0.400 mmol, 100%) of 5a as air-stable red microcrystals. ¹H NMR (400 MHz, CD_2Cl_2 , 298 K): $\delta = 6.63$ (ddd, ${}^{3}J_{\rm HH} = 8.8 \text{ Hz}, {}^{3}J_{\rm PH} = 4.0 \text{ Hz}, {}^{3}J_{\rm PH} = 4.0 \text{ Hz}, 2 \text{ H}, \text{ H}_{\rm ol}$, 5.43 (ddd, ${}^{3}J_{\rm HH} =$ 8.8 Hz, ${}^{3}J_{HP} = 2.8$ Hz, ${}^{3}J_{HP} = 2.8$ Hz, 2H, H_{ol}), 5.31 ppm (dd, ${}^{2}J_{PH} =$ 14.6 Hz, ${}^{3}J_{RhH} = 7.6$ Hz, $2 H_{benz}$); ${}^{13}C{}^{1}H$ NMR (75.5 MHz, $CD_{2}Cl_{2}$, 298 K): $\delta = 90.3$ (d, ${}^{1}J_{RhC} = 10.8$ Hz, C_{ol}), 78.0 (d, ${}^{1}J_{RhC} = 4.8$ Hz, C_{ol}), 49.6 ppm (d, ${}^{1}J_{PC} = 15.9$ Hz, C_{benz}); ${}^{31}P{}^{1}H$ NMR (121.5 MHz, $CD_{2}Cl_{2}$, 23 °C): $\delta = 166.3 \text{ (dd, } {}^{1}J_{\text{RhP}} = 145.2 \text{ Hz}, {}^{2}J_{\text{PP}} = 327.6 \text{ Hz}, \text{trop}_{2}\text{PPh}), 24.4$ (dd, ${}^{1}J_{RhP} = 107.0 \text{ Hz}, {}^{2}J_{PP} = 327.6 \text{ Hz}, \text{ PPh}_{3}$), -144.06 ppm (sept, ${}^{1}J_{\rm PF} = 714.5$ Hz, PF₆). mp: 238 ± 2 °C (decomposition); for a description of the anion exchange leading to 5b see the Supporting Information.

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- [6] Crystal structure data: a) trop₂PPh (2): Colorless, air-sensitive single crystals of 2 were obtained by slow diffusion of hexane into a THF solution of **2**; $C_{36}H_{27}P$; triclinic; space group $P\overline{1}$; a =11.2327(5), b = 13.3384(6), c = 19.7300(9) Å, a = 106.945(1), $\beta =$ 99.145(1), $\gamma = 105.070(1)^{\circ}$; $V = 2640.9(2) \text{ Å}^3$; Z = 4; $\rho_{\text{calcd}} =$ 1.234 g cm⁻³; crystal dimensions $0.52 \times 0.47 \times 0.22$ mm³; diffractometer Bruker SMART Apex with CCD area detector; MoKa radiation (0.71073 Å), 298 K, $2\Theta_{max} = 54.20^{\circ}$; 11483 reflections, 7889 independent ($R_{int} = 0.0421$); direct methods; empirical absorption correction SADABS (ver. 2.03); refinement against full matrix (versus F^2) with SHELXTL (ver. 6.12) and SHELXL-97; 667 parameters, R1 = 0.0410 and wR2 (all data) = 0.1053, max./min. residual electron density 0.294/-0.221 e Å⁻³. All nonhydrogen atoms were refined anisotropically. The contribution of the hydrogen atoms, in their calculated positions, was included in the refinement using a riding model; b) [Rh(trop₂PPh)- (PPh_3)]PF₆·2 CH₂Cl₂ (**5a**): red single crystals were obtained by slow diffusion of hexane into a solution of 5a in CH₂Cl₂; $C_{56}H_{46}P_3Cl_4F_6Rh$; orthorhombic; space group *Pnma*; a =23.914(10), b = 12.033(8), c = 12.070(5) Å; V = 5205(4) Å³; Z =4; $\rho_{\text{calcd}} = 1.494 \text{ g cm}^{-3}$; crystal dimensions $0.42 \times 0.31 \times 0.29 \text{ mm}^{3}$; diffractometer Bruker SMART Apex with CCD area detector; Mo_{Kα} radiation (0.71073 Å), 298 K, 2Θ_{max} = 56.52°; 6504 reflec-

a) We refer to the definition given by G. N. Lewis and G. T. Seaborg who in 1939 defined the term "electromer" as two forms of a molecule with the atoms in the same, or nearly the same, relative position but with a difference in electronic distribution. G. N. Lewis, G. T. Seaborg, J. Am. Chem. Soc. 1939, 61, 1886; for recent work, see: b) T. Bally, A. Maltsev, F. Gerson, D. Frank, A.



tions, 5455 independent ($R_{int} = 0.0409$); direct methods; refinement against full matrix (versus F^2) with SHELXTL (ver. 6.12) and SHELXL-97; 337 parameters, R1 = 0.0486 and wR2 (all data) = 0.1406, max./min. residual electron density 1.207/ -0.678 e Å⁻³. All non-hydrogen atoms were refined anisotropically. The contribution of the hydrogen atoms, in their calculated positions, was included in the refinement using a riding model. CCDC 706734 (**2**) and 706733 (**5a**) 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.

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