Rhodium Complexes

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Diamido Rhodates(1−)**

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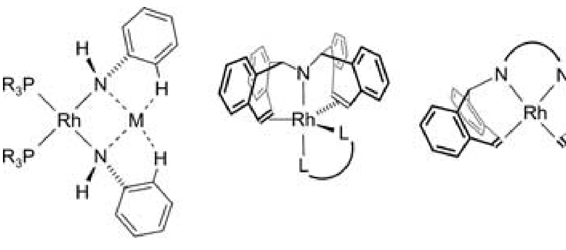
Dedicated to Professor Herbert W. Roesky
on the occasion of his 70th birthday

The M−N bond in late transition-metal amides[1] is susceptible to a number of useful synthetic transformations.[2] Some years ago, Brunet et al. reported the only known bis(amido)rhodium(I) complexes, which were characterized in rather complex equilibria in the reaction of $[Rh_nCl_m(PR_3)_l]$ compounds with anilide, MNHPh (M = Li, Na).[3] Based on NMR data, the structure **A** was proposed for $\{Li(solv)_x[Rh(NHPh)_2(PR_3)_2]\}$ (Scheme 1). In this intimate ion pair, which is only stable in the presence of an excess of anilide in solution, the NHPh groups are likely rotated such that they are orientated perpendicular to the central plane, and the lone pairs are involved in the complexation of the alkali-metal cation.



Scheme 1. The diamido rhodate(1−) **A** reported by Brunet et al. [3], and isolated 18-electron and 16-electron rhodium(I) amides **B** and **C**, respectively (L∩L = tropNH$_2$, bipy).

Previously, we reported the stable neutral rhodium(I) amides **B** and **C**, which were isolated and fully characterized (see Table 1 for pertinent data). The pentacoordinate 18-electron complex **B** adopts the expected trigonal-bipyramidal structure with the nitrogen atom in an apical position.[4,5] The $[Rh(trop_2N)(L\cap L)]$ amides **B** (trop$_2$N = bis(5*H*-dibenzo[*a,d*]cycloheptene-5-yl)amide; L∩L = tropNH$_2$, bipy) are reversibly oxidized at about −0.5 V (versus the ferrocenium/ferrocene, Fc$^+$/Fc, couple) to the aminyl radical complexes $[Rh(trop_2N)(L\cap L)]^{+\bullet}$. Their conjugated acids, $[Rh(trop_2NH)(L\cap L)]^+$, have p$K_a$ values of about 19 in DMSO.[5] In the neutral tetracoordinate 16-electron complex [Rh(trop$_2$dach−H)], **C**, the NR$_2$ group is approximately coplanar with the central plane, which leaves the amide nitrogen lone pair in a perpendicular position (trop$_2$dach = (*R*,*R*)-*N*,*N*′-bis(5*H*-dibenzo[*a,d*]cyclohepten-5-yl)-1,2-diaminocyclohexane; the "−H" indicates mono-deprotonation).[6] This complex is less readily oxidized (−0.34 V versus Fc$^+$/Fc) and the pK_a^{DMSO} of the conjugated acid $[Rh(trop_2dach)]^+$ (15.7) is significantly lower than in **B**. We now report the first stable and fully characterized diamido rhodates(1−) and some of their properties. Interestingly, we observe different aggregates between the countercation, $[M(solv)_n]^+$ (solv = solvent molecules), and the diamido rhodate(1−) anion.

For this purpose, we used the chiral tetrachelating amino olefin (*S*,*S*)-*N*,*N*′-bis(5*H*-dibenzo[*a,d*]cyclohepten-5-yl)-1,2-diphenyl-1,2-ethylenediamine ((*S*,*S*)-trop$_2$dpen = (*S*,*S*)-**1**)[6] as ligand (Scheme 2). The reaction of ligand (*S*,*S*)-**1** with $[Rh(cod)_2]OTf$ was straightforward and gave the orange-red complex (λ_{max} = 470 nm) (*S*,*S*)-**3**. When an orange solution of (*S*,*S*)-**3** in THF was treated with one equivalent of KO*t*Bu, the solution immediately turned red to furnish the amide (*S*,*S*)-**4** quantitatively. This compound was not isolated but was characterized by NMR and UV/Vis spectroscopy, which show that it is very similar to **C** (see Table 1 for selected data). Subsequently, (*S*,*S*)-**4** was further deprotonated under different reaction conditions: a) in THF, b) in the presence of three equivalents of [18]crown-6 (18C6), and c) in the presence of [2.2.2]cryptand (C222) (see Scheme 2). In case (a), an

Table 1: Selected structural and physical data of **B**, **C**, (*S*,*S*)-**3**, (*S*,*S*)-**4**, (*S*,*S*)-**5 hip**, (*S*,*S*)-**5 cip**, and (*S*,*S*)-**5 sip**. Σ° denotes the sum of bond angles around the nitrogen atom. $\delta(^{103}Rh)$ in ppm ([D$_8$]THF, 298 K).

	Rh−N1	Rh−N2	Σ°(N1)[a]	Σ°(N2)	pK_a^{DMSO}[b]	E°_{ox}[V][c]	λ_{max} [nm]	$\delta(^{103}Rh)$
B	2.05		340.0		19	−0.5	≈380	>1000
(*S*,*S*)-**3**	2.093(3)	2.083(3)	342.7(2)	339.8(3)		>0.6	470	897
C	1.962(2)	2.110(2)	351.1(2)	337.4(2)	15.7(2)	−0.34	516	736
(*S*,*S*)-**4**	–	–	–	–	–	–	506	702
(*S*,*S*)-**5 hip**	1.955(2)	2.030(2)	358.8(2)	340.0(2)		–	545	577
(*S*,*S*)-**5 cip**	1.964(4)	2.002(4)	355.7(4)	343.8(4)	21–23	−1.09	598	665[d]
(*S*,*S*)-**sip**	1.992(3)	1.976(3)	347.3(3)	350.9(3)			599	682

[a] N1 denotes the amido nitrogen center, N2 is NH in **C** and N-K in (*S*,*S*)-**5 hip**. [b] Data of the corresponding acids with the protonated ligand. [c] Potentials versus Fc$^+$/Fc in a THF/*n*Bu$_4$NPF$_6$ electrolyte at *T* = 20°C, scan rate 100 mV s^{-1}, Pt working electrode. [d] (*S*,*S*)-**5 sip** in [D$_6$]DMSO: $\delta(^{103}Rh)$ = 666 ppm.

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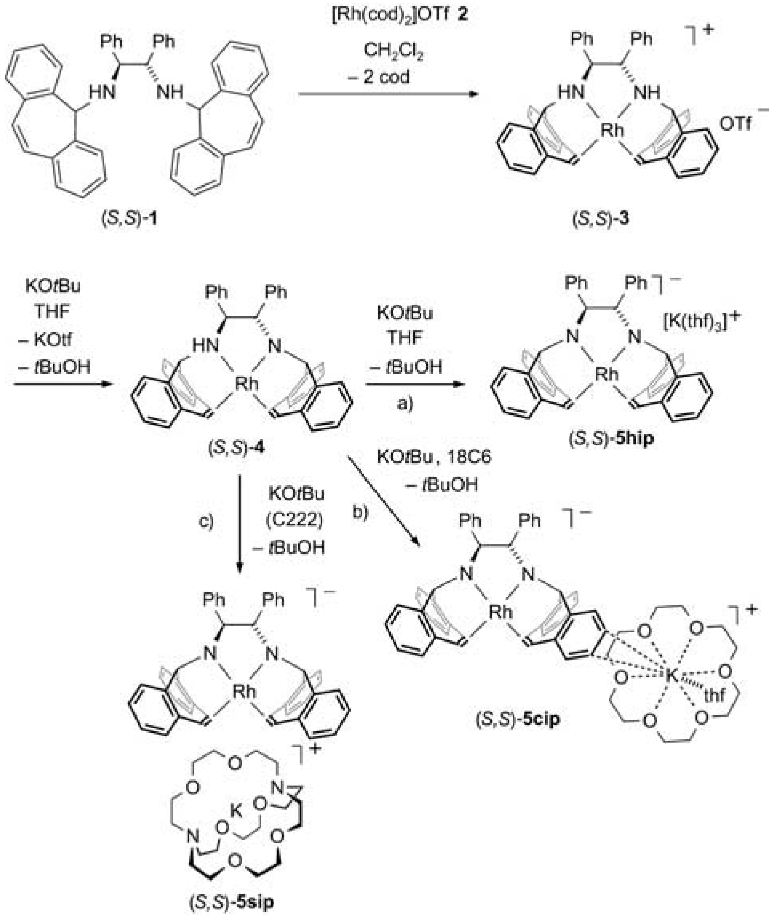

Scheme 2. Synthesis of the amidorhodium(I) complex (*S*,*S*)-**4**, and the various ion pairs (*S*,*S*)-**5 hip**, (*S*,*S*)-**5 cip**, and (*S*,*S*)-**5 sip**.

intensely deep red solution was obtained. In cases (b) and (c), deep green solutions were obtained. Double deprotonation of (*S*,*S*)-**3** in DMSO as solvent with two equivalents of KO*t*Bu also gave green solutions. The ^{1}H NMR spectra indicated in each case, that the doubly deprotonated diamido rhodate(1−), (*S*,*S*)-[Rh(trop$_2$dpen−2H)]$^-$ was obtained.

The products obtained under the conditions a)–c) in Scheme 2 were crystallized and the results of the X-ray diffraction studies are displayed in Figures 1–3, respectively.[7] From experiment (a), dark red crystals of the composition (*S*,*S*)-{K[Rh(trop$_2$dpen−2H)](thf)$_3$}, (*S*,*S*)-**5 hip**, precipitated (> 80 % yield) after the reaction mixture had been layered with *n*-hexane. From experiments (b) and (c), dark green needles of the composition (*S*,*S*)-{[K(18C6)(thf)][Rh(trop$_2$dpen−2H)]}·0.5 Et$_2$O, (*S*,*S*)-**5 cip**, and (*S*,*S*)-[K(C222)][Rh(trop$_2$dpen−2H)]·Et$_2$O·1.5 THF, (*S*,*S*)-**5 sip**, were obtained from solutions of the respective complexes in THF layered with Et$_2$O (≥ 80 % yield).

The structure of (*S*,*S*)-**5 hip** is best described as an electrostatically enforced host–guest complex,[8] in which the cationic [K(thf)$_3$]$^+$ fragment is embedded in the ligand framework of the anion (see Figure 1 b). The potassium ion has short contacts to the rhodium(I) atom, one amide nitrogen atom, one hydrogen atom in the ethylene bridge, and four carbon atoms of one of the adjacent benzo rings (see Figure 1 a). Such arene–potassium interactions were recently proposed to account for the performance of ruthenium(II) amides as hydrogenation catalysts.[9] Note that the coordination of the K$^+$ ion to N2 causes the Rh−N2 bond (2.030(2) Å) to be significantly longer and the N2 coordination sphere to be more pyramidal (sum of angles $\Sigma° = 340.0(2)°$) compared to N1 which binds at a remarkable short distance (1.955(2) Å) to Rh and resides in an almost planar coordination sphere ($\Sigma° = 358.8(2)°$).

In the crown-ether complex (*S*,*S*)-**5 cip**, the [K(18C6)(thf)]$^+$ and [Rh(trop$_2$dpen−2H)]$^-$ form a loose contact ion pair; the potassium ion binds at about 3.2 Å in an η^2-fashion to one benzo group from the outside of the anion (Figure 2). In the two crystallographically independent molecules in (*S*,*S*)-**5 cip** the slightly shorter Rh−N bond lengths (1.968(4) Å) correlate with a larger sum of bond angles $\Sigma°(\mathrm{N}) = 354.5°$ ($\Sigma°(\mathrm{N}) = 344.1°$ for the longer Rh−N distances, 1.994(4) Å; averaged data).

In [K(C222)][Rh(trop$_2$dpen−2H)]·Et$_2$O·1.5 THF, (*S*,*S*)-**5 sip** (Figure 3), the potassium ion has no direct contact to the anion and is encapsulated by the [2.2.2]cryptand. A "free" diamido rhodate(1−) ion is observed with short Rh−N distances (1.984(3) Å) and flattened coordination spheres at N1 and N2 ($\Sigma°(\mathrm{N}) = 349.1(3)°$) compared to the situation in (*S*,*S*)-**3** (R−N 2.09 Å, $\Sigma°(\mathrm{N}) = 341.2°$). Taking the average over all structures, the Rh−N distance to an amido nitrogen atom, NR$_2$, is about 5 % shorter than to an amino nitrogen atom, NR$_3$.

Figure 4 shows the UV/Vis spectra of the cationic complex (*S*,*S*)-**3**, the neutral rhodium amide (*S*,*S*)-**4**, the

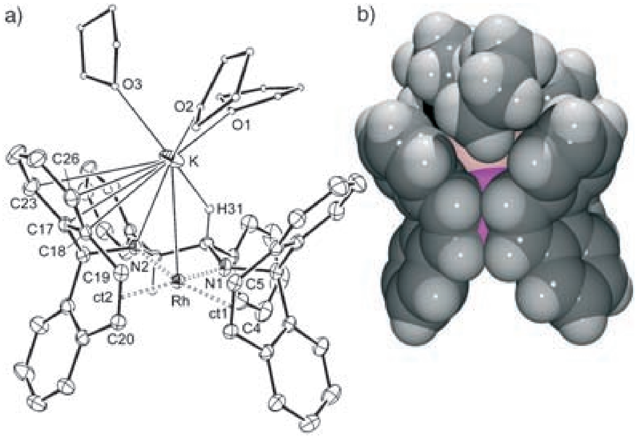

Figure 1. a) Structure of the complex (*S*,*S*)-**5 hip**. Thermal ellipsoids are drawn at 30 % probability; the three THF molecules are depicted as ball-and-stick models; hydrogen atoms apart from those in the ethylene bridge are omitted for clarity. Selected bond lengths [Å] and angles [°]: Rh−N1 1.955(2), Rh−N2 2.030(2), Rh−C4 2.141(3), Rh−C5 2.121(3), Rh−ct1 2.010(3), Rh−C19 2.126(3), Rh−C20 2.130(3), Rh−ct2 2.004(3), C4=C5$_{\mathrm{trop}}$ 1.418(4), C19=C20$_{\mathrm{trop}}$ 1.430(4), Rh−K 3.3596(9), K−N2 2.856(3), K−O1 2.727(3), K−O2 2.635(3), K−O3 2.736(4), K−C17 3.424(3), K−C18 3.387(3), K−C23 3.908(3), K−C26 3.797(3), K−H31 2.81; N1-Rh-N2 80.5(1), N1-Rh-ct1 90.8(1), N2-Rh-ct2 92.4(1), ct1-Rh-ct2 96.8(1); $\phi = 7.6°$; (ct = centroids of the C=C$_{\mathrm{trop}}$ units; ϕ is the intersection of the planes spanned by the rhodium atom, the N atom and ct of each bischelate ligand). b) Space-filling model of (*S*,*S*)-**5 hip**.

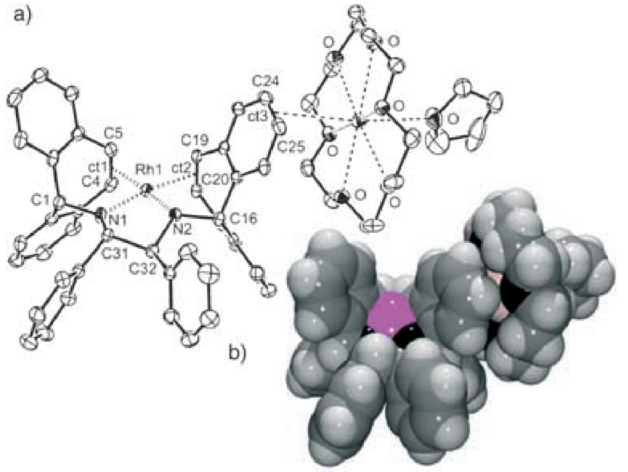

Figure 2. Structure of one of the two independent molecules in (*S*,*S*)-**5 cip**. a) A diethyl ether molecule in the crystal lattice and hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 30% probability. Selected bond lengths [Å] and angles [°] (data for the second molecule are given in italics): Rh1–N1 1.964(4), Rh1–N2 2.002(4), *Rh2–N3 1.986(4)*, *Rh2–N4 1.972(4)*, Rh1–C4 2.144(5), Rh1–C5 2.134(5), *Rh2–C53 2.156(5)*, *Rh2–C54 2.109(5)*, Rh1–C19 2.135(4), Rh1–C20 2.120(5), *Rh2–C68 2.159(5)*, *Rh2–C69 2.144(5)*, Rh1–ct1 2.022(5), Rh1–ct2 2.006(5), *Rh2–ct4 2.008(5)*, *Rh2–ct5 2.028(5)*, Rh1–ct3 3.164(6), *Rh2–ct6 3.217(6)*, $C4{=}C5_{trop}$ 1.397(8), $C19{=}C20_{trop}$ 1.416(8), *$C53{=}C54_{trop}$ 1.436(8)*, *$C68{=}C69_{trop}$ 1.439(8)*, K1–C24 3.179(6), *K2–C62 3.255(6)*, K1–$O_{(18C6)}$ 2.729(4)–2.861(4), *K2-$O_{(18C6)}$ 2.760(4)–2.833(4)*, N1-Rh1-N2 80.5(2), *N3-Rh2-N4 81.0(2)*, N2-Rh1-ct2 91.9(2), *N3-Rh2-ct4 91.9(2)*, N1-Rh1-ct1 90.5(2), *N4-Rh2-ct5 91.6(2)*, ct1-Rh1-ct2 97.4(2), *ct4-Rh2-ct5 97.8(2)*; $\phi = 6.4°$, *$\phi = 16.2°$*; (ct = centroids of C=C bonds; ϕ is the intersection of the planes spanned by the rhodium atom, the N atom and ct of each bischelate ligand). b) Space-filling model of (*S*,*S*)-**5 cip**.

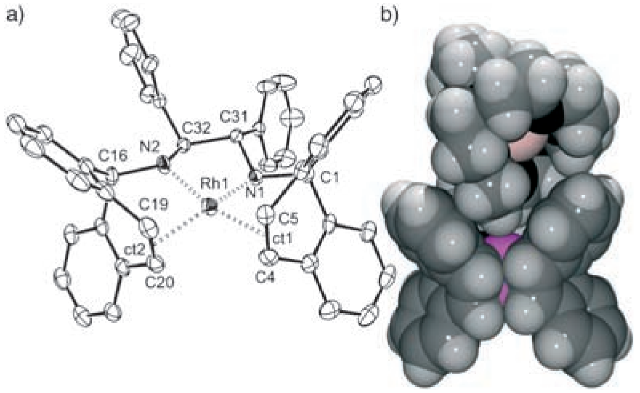

Figure 3. Structure of one of the two independent ion pairs in (*S*,*S*)-**5 sip**. a) Structure of the anion, hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 30% probability. Selected bond lengths [Å] and angles [°] (data for the second molecule are given in italics): Rh1–N1 1.992(3), Rh1–N2 1.976(3), *Rh2–N3 1.995(3)*, *Rh2–N4 1.970(3)*, Rh1–C4 2.145(4), Rh1–C5 2.110(4), *Rh2–C104 2.136(3)*, *Rh2–C105 2.113(4)*, Rh1–C19 2.161(4), Rh1–C20 2.114(4), *Rh2–C119 2.134(4)*, *Rh2–C120 2.119(4)*, Rh1–ct1 2.004(4), Rh1–ct2 2.014(4), *Rh2–ct3 2.001(4)*, *Rh2–ct4 2.004(4)*, $C4{=}C5_{trop}$ 1.429(6), $C19{=}C20_{trop}$ 1.434(6), *$C104{=}C105_{trop}$ 1.427(5)*, *$C119{=}C120_{trop}$ 1.422(5)*, N1-Rh1-N2 81.9(1), N1-Rh1-ct1 91.4(2), N2-Rh1-ct2 91.2(2), ct1-Rh1-ct2 97.9(2), *N3-Rh2-N4 82.0(1)*, *N3-Rh2-ct3 92.0(2)*, *N4-Rh2-ct4 91.3(2)*, *ct3-Rh2-ct4 97.3(2)*; $\phi = 16.6°$, *$\phi = 17.1°$*; (ct = centroids of the $C{=}C_{trop}$ units; ϕ is the intersection of the planes spanned by the rhodium atom, the N atom and ct of each bischelate ligand). b) Space-filling model of (*S*,*S*)-**5 sip**.

intimate ion pair (*S*,*S*)-**5 hip**, and the diamido rhodate(1−) salt (*S*,*S*)-**5 sip** in THF. Note the progressively red-shifted absorption λ_{max} in the series: (*S*,*S*)-**3**→(*S*,*S*)-**4** ($\Delta\lambda_{max} \approx 40$ nm), (*S*,*S*)-**4**→(*S*,*S*)-**5 hip** ($\Delta\lambda_{max} \approx 40$ nm), and (*S*,*S*)-**5 hip**→(*S*,*S*)-**5 sip** ($\Delta\lambda_{max} \approx 50$ nm).

We believe that the deep red color ($\lambda_{max} = 545$ nm) characterizes the host–guest ion pair (*S*,*S*)-**5 hip**. Furthermore we assume that (*S*,*S*)-**5 cip** and (*S*,*S*)-**5 sip** both dissociate in solution and the green color ($\lambda_{max} = 598$ nm) indicates the presence of the solvent separated "free" anion [Rh(trop$_2$-dpen−2H)]$^-$. ^{1}H NMR spectroscopy did not allow us to distinguish between both situations, but the ^{103}Rh NMR resonance signal of a red solution of (*S*,*S*)-**5 hip** is observed at $\delta = 580$ ppm, whereas the green solutions of (*S*,*S*)-**5 cip** and (*S*,*S*)-**5 sip** showed $\delta(^{103}\text{Rh}) \approx 670$ ppm (Table 1).

A cyclic voltammogram (Pt electrode, 0.1 M $n\text{Bu}_4\text{NPF}_6$/THF electrolyte at $T = 20\,°\text{C}$, scan rate 100 mV s^{-1}) of a green solution of (*S*,*S*)-**5** in DMSO shows a reversible redox wave for the process (1) at a remarkably low oxidation potential (−1.09 V, versus Fc$^+$/Fc):

$$[\text{Rh(trop}_2\text{dpen}{-}2\text{H)}]^- - e^- \rightarrow [\text{Rh(trop}_2\text{dpen}{-}2\text{H)}]^{\cdot} \qquad (1)$$

The relative differences between the pK_a values, redox potentials, E^{o}_{ox}, and UV/Vis absorptions in the complexes **B**, **C**, (*S*,*S*)-**3**, (*S*,*S*)-**4**, (*S*,*S*)-**5 hip**, and (*S*,*S*)-**5 sip** (Table 1) can be interpreted within the concept of filled/filled repulsions (FFR) elegantly developed by Caulton (see Figure 5).[10,11]

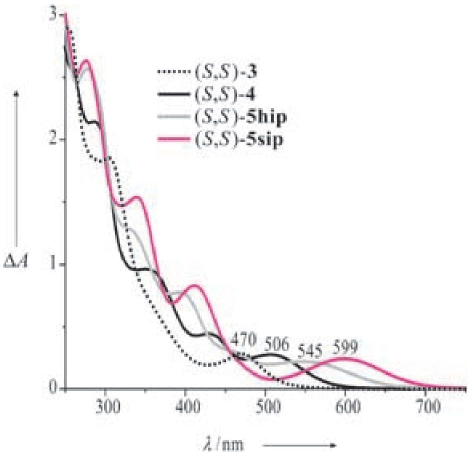

Figure 4. UV/Vis spectra of (*S*,*S*)-**3**, (*S*,*S*)-**4**, (*S*,*S*)-**5 hip**, and (*S*,*S*)-**5 sip** in solution in THF.

In a pentacoordinate 18-electron rhodium amide **I**, the lone pair at the amide nitrogen atom undergoes a strong and repulsive two-center–four-electron interaction with the occupied d_{xz} orbital at the metal center. This orbital is directed towards the filled p-type orbital at the nitrogen center and is

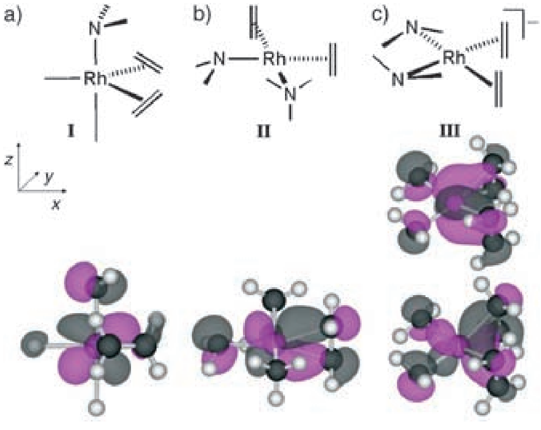

Figure 5. Schematic diagram showing the interaction of filled metal located and filled nitrogen located orbitals in a pentacoordinate 18-electron amido complex **I**, a tetracoordinate 16-electron amino amido complex **II**, and a bisamido complex **III** [filled/filled repulsion (FFR) model]. Only the energetically high-lying antibonding orbital interactions based on extended Hückel calculations are presented.

only slightly perturbed by the olefins which lie in the nodal plane (see Figure 5 a). In a tetracoordinate 16-electron amino amido complex **II**, the lone pair at N also suffers from a repulsive interaction (seen in the red shift of λ_{max} in (*S*,*S*)-**4** compared to that in (*S*,*S*)-**3**). However, less so because the filled d_{xz} and d_{yz} orbitals at the metal center are involved in M→L back-bonding into the π^*(C=C) orbitals and are polarized towards the coordinated olefins (see Figure 5 b). In that respect, the coordinated olefins contribute to the remarkable stability of late transition metal. Consequently, the strongly destabilized amide **I** is easy to oxidize and the NH function in its conjugated acid has a low acidity (large pK_a). On the other hand, the pK_a value of the NH function of a 16-electron amine complex such as (*S*,*S*)-**3**, which gives amide (*S*,*S*)-**4** upon deprotonation, is more acidic (by approximately four orders of magnitude). However, double deprotonation of a diamino complex to give a diamido complex **III** gives rise to two destabilizing interactions between the nitrogen lone pairs and the filled d_{xz} and d_{yz} orbitals at the metal center (see Figure 5 c). Consequently, λ_{max} is red-shifted to about 600 nm in compounds of type **III**. The facile oxidation of **III** can be taken as a further indication of this destabilization. The pK_a value of the NH function in the amine amide complex of type **II** falls in the region ($21 < pK_a^{DMSO} < 23$).[12] In the host–guest ion pairs, the destabilizing interaction is diminished (blue shift of λ_{max} ((*S*,*S*)-**5 sip**→(*S*,*S*)-**5 hip**) by about 50 nm) because of the interaction of the nitrogen lone pair with the potassium cation.

Caulton's FFR concept qualifies nicely as a model to interpret the results presented here with a set of structurally very closely related and rare dialkylamine/amide complexes. On the other hand, the fact that the NH functions in d^8 rhodium complexes are remarkably acidic[13] (note that the diamide (*S*,*S*)-**5** is even stable in presence of small amounts of methanol or water) and that the Rh–N bond shortens upon deprotonation must await a more deep-sighted (computational) analysis.

Experimental Section

General: Solvents were freshly distilled under argon from sodium/benzophenone (THF, Et_2O) or from sodium/diglyme/benzphenone (*n*-hexane). Air-sensitive compounds were stored and weighed in a glovebox (Braun MB 150 B-G system), and reactions on small scales were performed directly in the glovebox. NMR spectra were recorded on Bruker Avance 400 or 500 systems. The chemical shifts are given as δ values and were referenced against tetramethylsilane (TMS) for ^{1}H and ^{13}C. ^{103}Rh NMR spectra were calibrated with the frequency reference $\Xi = 3.16$ MHz. IR spectra were measured with the attenuated total reflection technique (ATR) on a Perkin-Elmer 2000 FT-IR spectrometer in the range from 4000 cm^{-1} to 600 cm^{-1} using a KBr beam splitter. The UV/Vis spectra were measured with a Perkin-Elmer UV/Vis/NIR Lambda 19 spectrometer in 0.5-cm quartz cuvettes.

(*S*,*S*)-{K[Rh(trop$_2$dpen−2H)](thf)$_3$} ((*S*,*S*)-**5 hip**): To an orange solution of (*S*,*S*)-[Rh(trop$_2$dpen)]SO$_3$CF$_3$ ((*S*,*S*)-**3**) (84 mg, 0.10 mmol) in THF (2 mL) was added KO*t*Bu (25 mg, 0.22 mmol). The color turned immediately to dark red and the solution was layered with *n*-hexane (10 mL). Dark red crystals of (*S*,*S*)-**5 hip** (80 mg, 0.84 mmol; 84 %) suitable for x-ray structure analysis grew overnight. M.p. > 130 °C (decomp); ^{1}H NMR (400.1 MHz, [D$_8$]THF): $\delta = 3.30$ (d, $^{3}J_{H,H} = 8.9$ Hz, 2H; CH$_{olefin}$), 3.91 (s, 2H; C*H*(Ph)(N)), 4.21 (d, $^{3}J_{H,H} = 8.9$ Hz, 2H; CH$_{olefin}$), 4.35 (s, 2H; CH$_{benzyl}$), 6.60–7.03 (m, 22H; CH$_{ar}$), 7.37–7.45 ppm (m, 4H; CH$_{ar}$); ^{13}C NMR (100.6 MHz, [D$_8$]THF): $\delta = 68.4$ (br, CH$_{olefin}$), 70.8 (CH$_{benzyl}$), 74.5 (d, $^{1}J_{Rh,C} = 13.0$ Hz; CH$_{olefin}$), 83.4 (*C*H(Ph)(N)), 123.6–129.0 (CH$_{ar}$), 141.1–148.2 ppm (C$_{quart}$); ^{103}Rh NMR (12.7 MHz, [D$_8$]THF): $\delta = 577$ (s); ATR-IR (neat): $\tilde{\nu} = 3061$ w, 2972 m, 2866 m, 1594 m, 1482 m, 1466 s, 1404 m, 1259 m, 1052 s, 1016 m, 896 m, 750 s, 699 s cm^{-1}; UV/Vis (THF): λ_{max} (ε) = 545 (2210), 339 (7760), 277 nm (25 680).

(*S*,*S*)-{[K([18]crown-6)(thf)][Rh(trop$_2$dpen)]} ((*S*,*S*)-**5 cip**): To an orange solution of (*S*,*S*)-[Rh(trop$_2$dpen)]SO$_3$CF$_3$ ((*S*,*S*)-**3**) (84 mg, 0.10 mmol) in THF (2 mL) was added KO*t*Bu (25 mg, 0.22 mmol) followed by [18]crown-6 (79 mg, 0.3 mmol). The resulting dark green solution was layered with Et$_2$O. Dark green crystals of (*S*,*S*)-**5 cip** (101 mg, 0.080 mmol; 80 %) grew overnight. M.p. > 155 °C (decomp); ^{1}H NMR (400.1 MHz, [D$_8$]THF): $\delta = 3.08$ (d, $^{3}J_{H,H} = 8.9$ Hz, 2H; CH$_{olefin}$), 3.53 (m, 24H; OC*H*$_2$C*H*$_2$O), 3.96 (s, 2H; C*H*(Ph)(N)), 3.99 (d, $^{3}J_{H,H} = 8.9$ Hz, 2H; CH$_{olefin}$), 4.27 (d, $^{3}J_{Rh,H} = 1.8$ Hz, 2H; CH$_{benzyl}$), 6.56–6.59 (m, 4H; CH$_{ar}$), 6.67–6.94 (m, 18H; CH$_{ar}$), 7.30 (d, $^{3}J_{H,H} = 7.4$ Hz, 2H; CH$_{ar}$), 7.35 ppm (d, $^{3}J_{H,H} = 7.4$ Hz, 2H; CH$_{ar}$); ^{13}C NMR (100.6 MHz, [D$_8$]THF): $\delta = 67.6$ (d, $^{1}J_{Rh,C} = 10.5$ Hz; CH$_{olefin}$), 70.5 (O*C*H$_2$*C*H$_2$O) 71.3 (CH$_{benzyl}$), 73.5 (d, $^{1}J_{Rh,H} = 12.8$ Hz, CH$_{olefin}$), 84.6 (*C*H(Ph)(N)), 122.4–129.7 (CH$_{ar}$), 142.3–148.6 ppm (C$_{quart}$); ^{103}Rh NMR (12.7 MHz, [D$_8$]THF): $\delta = 665$ ppm (s); ATR-IR (neat): $\tilde{\nu} =$ 2879 m, 1593 w, 1480 w, 1463 m, 1349 m, 1246 s, 1099 s, 960 m, 835 m cm^{-1}; UV/Vis (THF): λ_{max} (ε) = 598 (2420), 412 (8310), 339 (15 360), 275 nm (26 370).

(*S*,*S*)-{[K(C222)][Rh(trop$_2$dpen−2H)]} ((*S*,*S*)-**5 sip**): To an orange solution of (*S*,*S*)-[Rh(trop$_2$dpen)]SO$_3$CF$_3$ ((*S*,*S*)-**3**) (32 mg, 0.038 mmol) in THF (0.5 mL) was added KO*t*Bu (9 mg, 0.08 mmol, 2.1 equiv) followed by [2.2.2]cryptand (30 mg, 0.08 mmol, 2.1 equiv). The resulting dark green solution was layered with Et$_2$O (2.5 mL). Dark green crystals of (*S*,*S*)-**5 sip** (41 mg, 0.031 mmol; 80 %) grew overnight. M.p. > 210 °C (decomp); ^{1}H NMR (500.1 MHz, [D8]THF): $\delta = 2.55$- 2.57 (m, 12H; NC*H*$_2$CH$_2$O), 3.06 (d, $^{3}J_{H,H} = 9.0$ Hz, 2H; CH$_{olefin}$), 3.54–3.56 (m, 12H; NCH$_2$C*H*$_2$O), 3.60 (s, 12H; OC*H*$_2$C*H*$_2$O), 3.95 (d, $^{3}J_{H,H} = 9.0$ Hz, 2H; CH$_{olefin}$), 3.98 (s, 2H; C*H*(Ph)(N)), 4.27 (d, $^{3}J_{Rh,H} = 2.2$ Hz, 2H; CH$_{benzyl}$), 6.56–6.96 (m, 22H; CH$_{ar}$), 7.28–7.36 ppm (m, 4H; CH$_{ar}$); ^{13}C NMR (125.8 MHz, [D$_8$]THF): $\delta = 54.3$ (N*C*H$_2$CH$_2$O), 67.5 (d, $^{1}J_{Rh,C} = 10.0$ Hz; CH$_{olefin}$), 67.9 (NCH$_2$*C*H$_2$O), 70.7 (O*C*H$_2$*C*H$_2$O), 71.3 (CH$_{benzyl}$), 73.3 (d, $^{1}J_{Rh,H} = 12.7$ Hz; CH$_{olefin}$), 84.7 (*C*H(Ph)(N)), 122.2–129.8 (CH$_{ar}$), 142.8–149.7 ppm (C$_{quart}$); ^{103}Rh NMR (15.8 MHz, [D$_8$]THF): $\delta =$ 682 ppm (s); ATR-IR (neat): $\tilde{\nu} = 3055$ w, 2965 w, 2868 s, 1593 m, 1479 m, 1461 m, 1352 m, 1256 m, 1100 s, 946 m, 747 s, 700 m cm^{-1}; UV/

Vis (THF): λ_{max} (ε) = 599 (2160), 412 (8300), 339 (15750), 275 nm (23160).

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[7] Crystal structure of (*S*,*S*)-**5 hip**: Red, highly air-sensitive crystals were obtained from a THF solution which was layered with *n*-hexane at room temperature; $C_{56}H_{58}KN_2O_3Rh$, orthorhombic, space group *P*2(1)2(1)2(1); $a = 11.102(1)$, $b = 16.690(1)$, $c = 24.797(1)$ Å, $V = 4594.4(4)$ Å^3; $Z = 4$; $\rho_{calcd} = 1.372$ Mg m^{-3}; crystal dimensions 0.58 × 0.23 × 0.23 mm; diffractometer Bruker SMART Apex; Mo$_{K\alpha}$ radiation, 200 K, $2\Theta_{max} = 56.76°$; 48252 reflections, 11474 independent ($R_{int} = 0.0779$), direct methods; refinement against full matrix (versus F^2) with SHELXTL (ver. 6.12) and SHELXL-97, 568 parameters, 36 restraints, $R1 = 0.0434$ and w$R2$ (all data) = 0.0914, max./min. residual electron density 0.980/−0.706 e Å^{-3}. Crystal structure of (*S*,*S*)-**5 cip**: Dark green single crystals were obtained from a THF/Et$_2$O solution at room temperature; $C_{120}H_{132}K_2N_4O_{14}Rh_2 \cdot Et_2O$, monoclinic, space group *P*2(1); $a = 12.842(1)$, $b = 23.010(1)$, $c = 18.969(1)$ Å, $\beta = 101.780(1)°$; $V = 5487.1(5)$ Å^3; $Z = 2$; $\rho_{calcd} = 1.339$ Mg m^{-3}; crystal dimensions 0.60 × 0.32 × 0.30 mm; diffractometer Bruker SMART Apex; Mo$_{K\alpha}$ radiation, 200 K, $2\Theta_{max} = 52.74°$; 40465 reflections, 21957 independent ($R_{int} = 0.0285$), direct methods; empirical absorption correction SADABS (ver. 2.03); refinement against full matrix (versus F^2) with SHELXTL (ver. 6.12) and SHELXL-97, 1326 parameters, 1 restraint, $R1 = 0.0457$ and w$R2$ (all data) = 0.1124, max./min. residual electron density 0.775/−0.429 e Å^{-3}. Crystal structure of (*S*,*S*)-**5 sip**: Dark green single crystals were obtained from a THF solution which was layered with Et$_2$O at room temperature; $C_{124}H_{140}K_2N_8O_{12}Rh_2 \cdot 3\,THF \cdot 2\,Et_2O$, triclinic, space group *P*1; $a = 12.078(1)$, $b = 14.324(1)$, $c = 21.272(2)$ Å, $\alpha = 80.882(1)$, $\beta = 85.728(2)$, $\gamma = 68.406(1)°$; $V = 3378.1(5)$ Å^3; $Z = 1$; $\rho_{calcd} = 1.270$ Mg m^{-3}; crystal dimensions 0.54 × 0.48 × 0.47 mm; diffractometer Bruker SMART CCD1k; Mo$_{K\alpha}$ radiation, 200 K, $2\Theta_{max} = 56.50°$; 28372 reflections, 25863 independent, direct methods; empirical absorption correction SADABS (ver. 2.03); refinement against full matrix (versus F^2) with SHELXTL (ver. 6.12) and SHELXH-97, 1508 parameters, 22 restraints, $R1 = 0.0424$ and w$R2$ (all data) = 0.1106, max./min. residual electron density 0.660/−0.618 e Å^{-3}. For all reported x-ray crystal structures the non-hydrogen atoms were refined anisotropically. Only one carbon atom of a Et$_2$O solvent molecule in (*S*,*S*)-**5 sip** had to be refined using the ISOR restraint. The contribution of the hydrogen atoms, in their calculated position, was included in the refinement using a riding model. Upon convergence, the final Fourier difference map showed no significant peaks. CCDC-267206 ((*S*,*S*)-**5 hip**), CCDC-267207 ((*S*,*S*)-**5 cip**), and CCDC-272867 ((*S*,*S*)-**5 sip**) 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.

[8] Because the coordination sphere of the unsaturated $[K(thf)_3]^+$ fragment is completed by direct and close contacts within the cavity of the $[Rh(trop_2dpen{-}2H)]^-$ ion, we denote (*S*,*S*)-**5 hip** as a *h*ost–guest *i*on *p*air held together by electrostatic forces. Similarly, (*S*,*S*)-**5 cip** is considered as *c*ontact *i*on *p*air because the one open coordination site in the $[K(18C6)(thf)]^+$ ion is completed by one contact with the anion, however, outside of its cavity. The ion pair (*S*,*S*)-**5 sip** is denoted as a *s*eparated *i*on *p*air because of the lack of a direct contact between the potassium ion and the anion although the cryptand penetrates the anion in the solid state. For further definitions see, G. Boche, *Angew. Chem.* **1992**, *104*, 742; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 731, and references therein. For a review on ion pairing in organometallics see: A. Macchioni, *Chem. Rev.* **2005**, *105*, 2039.

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[12] The pK_a of (*S*,*S*)-**4** could not be determined exactly but was estimated by using indole (p$K_a^{dmso} = 20.95$) and benzamide (p$K_a^{dmso} = 23.35$) as reference substances. Green solutions of (*S*,*S*)-**5 sip** in DMSO react with a slight excess (≈ 10 %) of indole to give red (*S*,*S*)-**4**, which can be deprotonated with lithium benzamide to give back the green solution characteristic for the diamido rhodate(1−), (*S*,*S*)-**5 sip**.

[13] For rather basic amide complexes (p$K_a^{THF} > 22$) see: D. Rais, R. G. Bergman, *Chem. Eur. J.* **2004**, *10*, 3970; and references therein.