A Diolefin Diamide Rhodium(I) Complex and Its One-Electron Oxidation Resulting in a Two-Center, Three-Electron Rh–N Bond

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A Diolefin Diamide Rhodium(I) Complex and Its One-Electron Oxidation Resulting in a Two-Center, Three-Electron Rh–N Bond

Amos J. Rosenthal,[a] Matthias Vogt,[a] Bas de Bruin,*[b] and Hansjörg Grützmacher*[a,c]

A tetracoordinated diolefin diamide rhodium(I) complex **6** with the two amido and olefin groups in mutual *trans*-position and a butterfly structure has been prepared. This anionic complex undergoes a reversible one-electron oxidation at a remarkably negative potential ($E_{1/2} = -1.22$ V vs. Fc/Fc$^+$) to give a 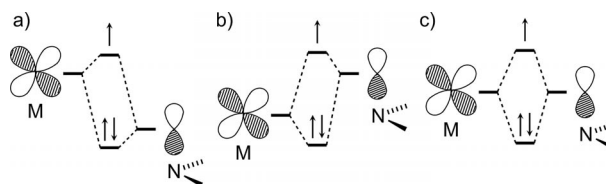stable, paramagnetic, tetracoordinated, planar Rh^I complex **7**. This complex was fully characterized, and all data indicate that this species is best described with an unprecedented two-center, three-electron Rh–N bond. DFT computations were performed to further elucidate the electronic structure, and the results fully agree with the two-center, three-electron Rh–N bond description.

Introduction

Metal complexes with coordinated cooperative radicals emerge as promising reagents in bond activation chemistry and catalysis.[1] Specifically, these redox non-innocent ligand metal complexes[2] find applications in catalytic oxidation reactions,[3] transfer and insertion reactions,[4] cyclization reactions and coupling reactions,[5] as well as hydrosilylation reactions.[6] The highly selective oxidation of primary alcohols to aldehydes mediated by galactose oxidase is a reference system. This process shows very high turnover frequencies (TOF up to 10^6 h^{-1}) and uses a copper complex with a coordinated tyrosine radical as C–H activating site.[7] Transition metal amide complexes, [M]–NR$_2$,[8] play a special role in the investigation of metal–ligand cooperativity, because in the reaction [M]–NR$_2$ + X–Y → [MX]–NYR$_2$ the newly formed strong N–Y bond facilitates the activation of an X–Y bond.[9] A redox reaction of a metal amide may occur at the metal center or at the amido ligand.[10] In the latter case, an aminyl radical complex is obtained in which the NR$_2$ radical may play the role of a cooperating ligand. Because amido groups coordinated to an electron-rich transition metal center with a d-electron configuration ≥ 6 create a "π-conflict" due to the antibonding N(pπ)–M(dπ) interaction,[11] it is generally assumed that late transition amides are unstable, which may hamper the investigation of their reactivity.[12,13]

Three electronic configurations may result from the oxidation of an electron-rich M–N bond (Scheme 1):[1f,1g,14] (a) The unpaired electron occupies a mainly metal-centered orbital. That is, the metal is oxidized and bound to an innocent amide ligand. This situation is frequently observed with electropositive metals especially from the fourth period (Ti to Co). (b) The odd electron resides in a ligand-centered orbital. That is, the oxidation process occurs at the non-innocent amide ligand, which leads to an aminyl radical complex. This situation is encountered with electronegative metals and/or amido ligands where the nitrogen center is incorporated in a larger delocalized π-system. (c) The oxidation results in a delocalized metallo amine radical with evenly distributed spin population on both the metal and

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Scheme 1. Three-electron N(pπ)–M(dπ) interaction leading to (a) a metal-centered radical (*innocent* ligand), (b) a ligand-centered radical (*non-innocent* ligand), or (c) a delocalized radical (*even* situation).

nitrogen center. This electronic configuration is expected for metal amides with strong covalent metal–nitrogen bonds.[1f,1g,15]

Results and Discussion

Stable aminyl radical complexes **1a,b**,[11a,11b] the stable diazadiene (dad) radical complexes **2a,b**,[16] and the persistent delocalized organometalloamine radical **3a,b** were characterized by EPR spectroscopy supported by DFT calculations (Scheme 2). We also isolated and structurally characterized anionic rhodium and iridium bis(amido) complexes **4a,b** with a d^8 valence electron configuration at the metal centers.[17] The remarkable stability of these compounds was attributed to the fact that in a rather rigid tetradentate ligand scaffold both amido groups are in mutual *cis*-positions but in *trans*-position to a π-electron-accepting olefin ligand. However, we did not succeed in the synthesis of stable paramagnetic complexes by oxidation of **4a,b**. Here we report that anionic bis(amido) complexes of rhodium(I) with olefin and amido groups in *trans*-positions are also stable, despite a more open ligand framework. Oxidation of such a complex leads to a stable radical complex, which we could isolate and fully characterize.
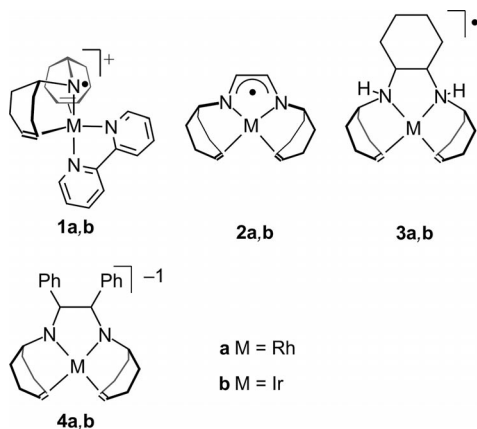
Scheme 2. Well characterized rhodium aminyl radical and amido complexes **1a,b**–**4a,b**.

Deep green complex **6** was obtained in good yield (78 %) by reacting the previously reported[18] dimeric complex [Rh$_2$(μ-Cl)$_2$(trop$_2$NH)$_2$] **5** with an excess amount of sodium hexamethyldisilazane {Na[N(SiMe$_3$)$_2$] (Scheme 3, trop = 5*H*-dibenzo[*a,d*]cyclohepten-5-yl). As expected, the ^{1}H NMR and ^{13}C{^{1}H} NMR resonances of the olefin moieties [^{1}H NMR: δ = 5.91, 7.01 ($^3J_{HH}$ = 11 Hz) ppm. ^{13}C{^{1}H} NMR: δ = 77.8 ($^1J_{CRh}$ = 16 Hz), 78.3 ($^1J_{CRh}$ = 7 Hz) ppm.] are shifted to higher frequencies when compared to those of *cis*-**4a,b** [^{1}H NMR: δ = 3.1, 4.0 ppm. ^{13}C{^{1}H} NMR: δ = 68, 73 ppm], which indicates smaller π-back-donation. Note that the nonequivalence of the olefin resonances indicates a butterfly-type structure, which is common for these types of 16-electron complexes.[18]
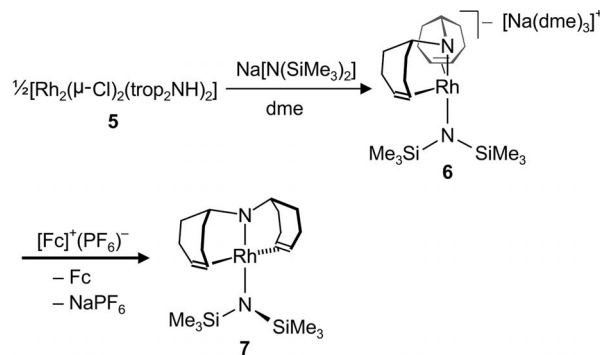
Scheme 3. Synthesis of anionic diamide complex **6** and its oxidation to paramagnetic complex **7** {[Fc]$^+$(PF$_6$)$^-$ = ferrocenium hexafluorophosphate, Fc = ferrocene, dme = dimethoxyethane}.

The cyclic voltammogram of **6** in tetrahydrofuran shows a reversible redox wave at a half-wave potential of $E_{1/2}$ = –1.22 V (vs. Fc/Fc$^+$). This potential is significantly more negative (about 100 mV) than that of **4a** ($E_{1/2}$ = –1.09 V).[17a] Neutral complex **7** was obtained by oxidation of **6** in diethyl ether using ferrocenium hexafluorophosphate (FcPF$_6$) as oxidant in quantitative yield as a paramagnetic red crystalline solid with μ_{eff} = 2.12 μ$_B$ (see Figure S3 in the Supporting Information).

The structures of **6** and **7** were determined with single-crystal X-ray diffraction techniques. The results are shown in Figures 1 and 2 for **6** and **7**, respectively. In accordance with the NMR spectroscopic data, anionic rhodate complex **6** adopts a butterfly-type geometry (with ct1–Rh1–ct2 139°, N1–Rh1–N2 170°; ct = centroid of the coordinated double
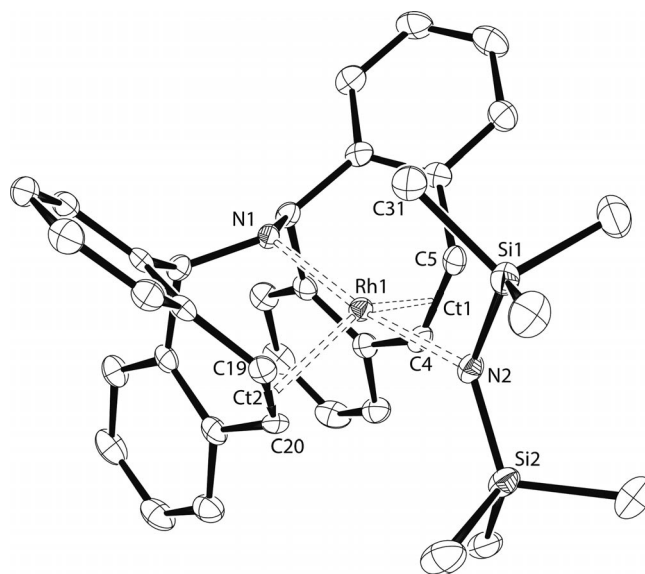

Figure 1. ORTEP plot of complex **6** (ellipsoids at 50 % probability). Hydrogen atoms and Na(dme)$_3$ counterion omitted for clarity. Selected bond lengths [pm] and angles [°]: Rh1–N1 203.80(16), Rh1–N2 215.34(16), Rh1–C4 211.0(2), Rh1–C5 212.3(2), Rh1–Ct1 199.3, Rh1–C19 214.1(2), Rh1–C20 212.7(2), Rh1–Ct2 201.3, C4–C5 142.0(3), C19–C20 141.6(3), Rh1–C31 292.2; N1–Rh1–N2 169.51(6), Ct1–Rh1–Ct2 139.47, Rh1–N2–Si1 103.38(8), Rh1–N2–Si2 129.26(9), ΣN1 342.7(4).
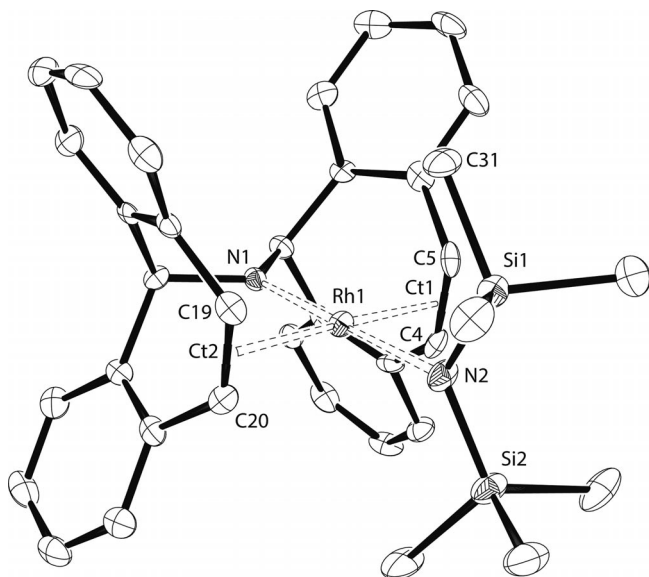
Figure 2. ORTEP plot of complex **7** (ellipsoids at 50% probability). Hydrogen atoms and one half *n*-hexane molecule omitted for clarity. Selected bond lengths [pm] and angles [°]: Rh1–N1 193.1(5), Rh1–N2 210.5(5), Rh1–C4 223.3(6), Rh1–C5 222.2(6), Rh1–Ct1 211.8, Rh1–C19 223.6(6), Rh1–C20 224.7(6), Rh1–Ct2 213.3, C4–C5 137.8(9), C19–C20 137.7(9), Rh1–C31 339.3; N1–Rh1–N2 179.5(2), Ct1–Rh1–Ct2 177.06, Rh1–N2–Si1 116.5(3), Rh1–N2–Si2 120.0(3), ΣN1 360.0(13).

bond). The Rh1–N1 bond (203.8 pm) is significantly shorter than the Rh–N2 bond (215.3 pm), which indicates a strong influence of the amide N1 atom of the tripodal trop$_2$N ligand on the planar N(SiMe$_3$)$_2$ group in *trans*-position, which is rotated to avoid steric interactions and an unfavorable 3-center-6π-electron 2p(N)–Rh(3d)–2p(N) interaction. The coordination sum of bond angles, ΣN1, around N1 is 343°. Upon oxidation to radical complex **7**, N1 resides in a planar coordination sphere, ΣN1 = 360°, and the complex adopts a planar structure (ct1–Rh1–ct2 177°, N1–Rh1–N2 180°). The Rh1–N1 bond in **7** contracts to 193 pm. The Rh1–N2 bond length (210.5 pm) in **7** is not shortened as much. As expected, the structural data indicate a weaker metal–ligand-π-back bonding in the neutral radical complex; that is, the Rh–ct distances in **7** are longer by about 12 pm while the C=C$_{olefin}$ bonds shorten from 142 pm in **6** to 138 pm in **7**.

The EPR spectra of complex **7** at 120 K (frozen solution) and 298 K were recorded in diethyl ether (Figure 3a, b). Simulation of the spectrum of **7** revealed rhombic **g**-tensors ($g_x = 2.147$, $g_y = 2.116$ and $g_z = 2.038$). The spin densities were assessed with computations: DFT at the bp86/TZP level gave Mulliken spin densities of 41.4% on Rh1, 46.6% on N1, and 5.5% on N2. Employing the b3-lyp/def-TZVP level yielded 40.5%, 55.9%, and 1.4% respectively (Table S1; for the numbering, see Figure 2). Both computa-
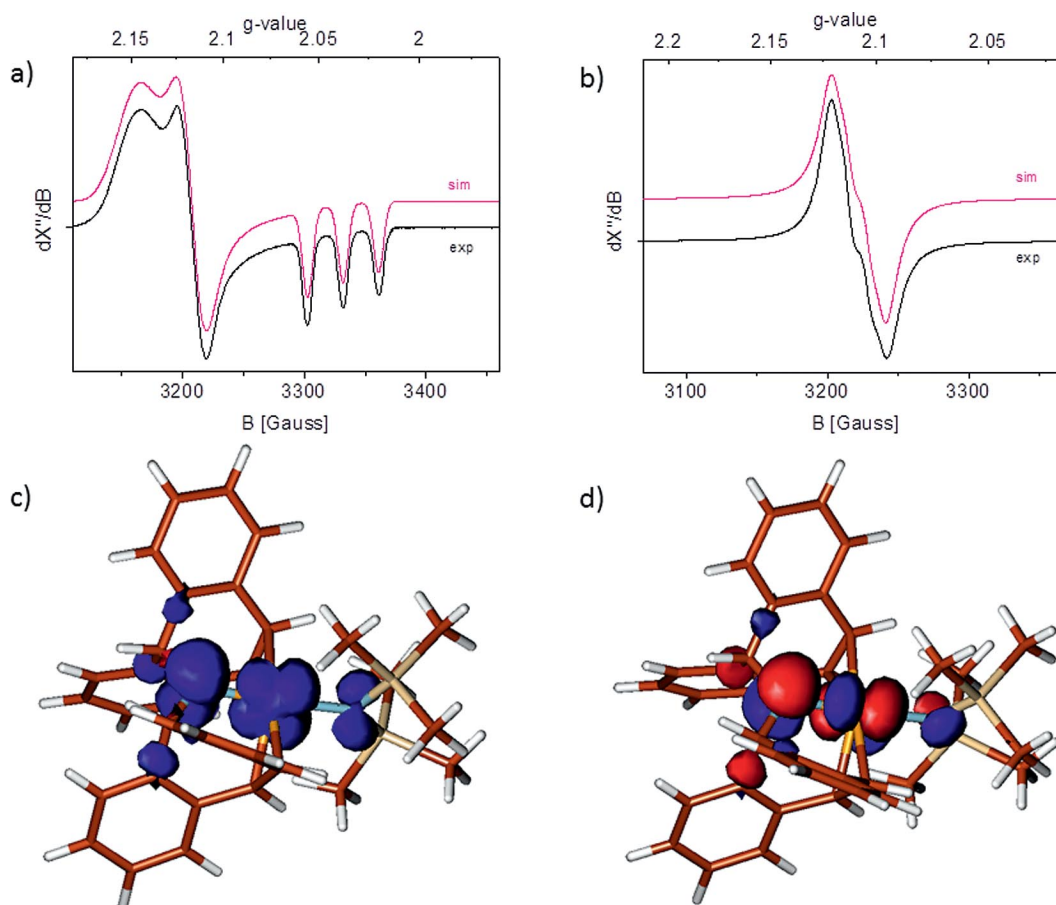

Figure 3. Experimental (black) and simulated (magenta) X-band EPR spectra of species **7** measured in (a) frozen solution at 120 K and (b) in solution at 298 K. (c) Spin density plot. (d) Singly occupied molecular orbital (SOMO).

tions are in good agreement with an even spin density distribution interaction between Rh1 and N1 with the unpaired electron residing in the π* orbital formed by the d_{xz} orbital of Rh1 and in the p_z orbital of N1 (Figure 3c, d). This bonding mode corresponds to model (c) in Scheme 1. An amidorhodium(II) complex (bonding mode a) or rhodium(I) aminyl radical species (bonding mode b) would carry the spin density either mainly on rhodium or nitrogen, respectively.

The comparison of the structural data showing a significant contraction of the Rh1–N1 bond length and the EPR data bolstered by DFT calculations indicate that the Rh–N interaction is best described as a two-center, three-electron bond, 2c-3e,[19] in which the unpaired electron is evenly distributed in an antibonding Rh(d)–N(p) π*-orbital.

While the previously reported aminyl radical complexes **1a,b** behave as nucleophilic aminyl radical complexes that react with hydrogen donors, complex **7** is remarkably stable and does not undergo H-abstraction reactions with substrates such as triphenylmethane, triphenylsilane, tributyltinhydride, 2,2,6,6-tetramethylpiperidin-1-ol, 2,6-di-*tert*-butyl-4-methylphenol, pinacolborane, or diphenylphosphane. Solutions of **7** can even be briefly handled in air without notable decomposition.

Conclusion

A well-defined example of a complex with a 2c-3e electron bond between Rh and N was synthesized by oxidation of anionic rhodium(I) bis(amido) complex **6**. The latter complex has a remarkable negative oxidation potential likely due to the *trans*-arrangement of the two electron donating amido groups ("push-push" configuration vs. a "push-pull" configuration in **4a,b**). As a consequence, paramagnetic complex **7** is remarkably stable against hydrogen donors relative to previous Rh^I aminyl complexes with a 10–20% higher spin density on the nitrogen center. With the present state of knowledge, it remains challenging to predict the reactivity of this type of radical complexes, which may depend on very subtle changes in the electronic structure of the ground state and/or the transition states for the H-abstraction reactions.

CCDC-800539 (for **6**) and -800180 (for **7**) 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.

Supporting Information (see footnote on the first page of this article): Experimental procedures, spectroscopic data, details of the X-ray structure determination of **6** and **7**, and DFT calculations for **7**.

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