Research Reactivity of Rhodium(II) amido/Rhodium(I) aminyl complexes

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ABSTRACT

Reaction of the Rh(II) dimer [LRh][μ-Br]2 (L = ([2,6-Me2C6H3NCMe]2CH) with the bulky amide LiNH(2,6-Pr2C6H3) leads to a monomeric Rh(II) amide with a T-shape bond arrangement and a pronounced agostic interaction. Reaction with the less bulky LiNH(2,6-Me2C6H3) results in benzyl C-H activation to a binuclear complex with a unique aza-xylylene bridging mode. With LiNHPh2, we observe initial formation of [LRh][μ-NHPh]2 followed by N,C2' coupling of two anilines. These reactions can be explained based on aminal radical character of the Rh(II) amides (supported by EPR evidence) and/or involvement of nitrene intermediates.

1. Introduction

The last decade has seen a growing recognition of the diversity of reaction types realizable with aminal radicals bound to transition metals [1]. The N−H bond is strong, so free aminal radicals are capable of abstracting hydrogen atoms even from unactivated hydrocarbons. Coordination of the aminal radical to a metal stabilizes it and hence lowers its H-abstraction power, potentially leading to higher selectivity and/or alternative reaction pathways. Šakić and Zipse recently emphasized the importance of N−H/C−H bond strengths in tuning reactivity of free aminal radicals [2], but the same idea – with suitable correction for metal stabilization – applies to coordinated radicals. Most reported aminal complexes have been prepared via (electro) chemical oxidation of regular metal-amido complexes [3]. However, several copper complexes with significant radical character have been generated by simple metathesis from CuII halides and lithium amides (Scheme 1) [4]. The NHAd complex is particularly interesting because it catalyzes amination of C−H bonds using Bu4NO2 as the terminal oxidant [4b].

We recently reported on the formation and characterization of the paramagnetic β-diaminate (BDI) rhodium bromide complex 1 and its iodide analog, which were found to contain paramagnetic RhIII centers without metal-metal bonds [5]. While the complexes are air- and moisture-sensitive, they did not display particularly high reactivity, possibly because dimer formation reduces coordinative unsaturation and results in steric shielding of the Rh centers. Accordingly, we anticipated that replacing the halides with bulkier “counterions” might result in formation of monomeric RhII species with increased reactivity. We selected anilides as counterions since one could expect a degree of aminal radical character for the products (cf. Scheme 1) that might result in further interesting reactivity. Coordinated anilinyl radicals have been reported to undergo various couplings (4,4'-C-C coupling [6], N,4'-[3c] and N,2'-N,C2 coupling [7] as well as hydrogen atom abstraction (HAA) reactions [4b,6,8].

In the present work, we report on the reactions of dimeric complex 1 with lithium anilides 2a−2c (Scheme 2). An amido/aminyl complex (3a−3c) (or its dimer) is probably generated in all cases, but the eventual fate of the product depends crucially on the steric properties of the anilide used.

2. Results and discussion

2.1. Reaction of 2,6-diisopropylaniline

Addition of anilide 2a to a green solution of 1 in toluene results in an immediate colour change to deep blue. The 1H NMR spectrum of the mixture shows broad peaks and unusual shifts characteristic of paramagnetic compounds, as well as a smaller amount of a diamagnetic impurity. Salt removal and crystallization gave dark blue crystals of 3a. The X-ray structure (Fig. 1) shows a monomeric T-shape complex (\(\angle N1RbN3 = 94.08(10)°, \angle N2RbN3 = 175.39(11)°\)) in which the methine hydrogen of an Pr group appears to occupy the fourth
coordination site with an agostic interaction (d(Rh-H) 1.97(3) Å). Bond lengths within the (BDI)Rh fragment are similar to those of dimeric precursor complex 1 [5], and bond lengths within the anilide ring are similar to those in two of the three reported “innocent” platinum metal-NHdipp complexes [9], with the two ipso-ortho bonds slightly longer than the remaining ring bonds (≈1.42 vs 1.38 Å) [10,11]. The Rh-N (anilide) bond is short (1.93(3) Å) even compared to known RhIII anilide complexes (2.05–2.07 Å [12]) but falls within the narrow range of 1.93–1.97 Å reported for a series of (PNP)RhII complexes where the amido group is part of a pincer ligand framework [13]. These data are suggestive of a mainly metal-centered radical.

Complex 3a is reactive, and decomposes in solution within hours. The EPR spectrum in toluene glass (Fig. 2A) showed the presence of several intermediate species. In the reaction with 2b, clearest results were obtained in hexanes at room temperature. A very dark, diamagnetic complex (4b) could be isolated in fair yield. NMR spectra were complicated; X-ray diffraction revealed a benzyl-deprotonated anilide ligand bridging between two (BDI)Rh fragments in an \( \mu-\eta^1(\text{CCCC})\eta(\text{CCCN}) \) fashion (Fig. 3) [14]. There is precedent for benzyl metallated o-methylanilide ligands, formed mostly [15] but not exclusively [16] via imido intermediates, but the coordination mode of this ligand in 4b is surprising and as far as we know unprecedented. It can be regarded as the aza analog of a \( \mu-\eta^1 \) bridging o-xylylene ligand [17], with two diene-like ligand-metal interactions, and hence both Rh atoms are best viewed as RhIII (Section 3.7 of the SI compares relevant geometries).

If the same reaction is performed in toluene instead of hexanes, it is faster but also less clean; yellow crystals of 5b could be isolated. The structure (Fig. 4) contains only a single (BDI)Rh fragment bound to a deprotonated anilide, but this is now associated with a unit of 2b and two molecules of Li-bound dimethylaniline [18]. The deprotonated anilide unit is bound to Rh in a \( \kappa^2 \)-chelate (aza-enediyli) manner with sp\(^3\) carbon and nitrogen atoms, so in this case the complex unambiguously contains RhIII.

We can only speculate about the mechanism of formation of 4b/5b (Scheme 3). Presumably, one molecule of 3b abstracts a hydrogen atom from a second one, generating intermediate A containing an azaxylylene unit [19,20]. In hexanes, the (BDI)Rh fragment migrates to the solvent, eventually ending up as the known complex [(BDI)Rh]_2(\( \mu \)-toluene) [21]. Instead, intermediate A picks up a second equivalent of 2b and free dimethylaniline to give 5b.

### 2.2. Reaction of 2,6-dimethylanilide

With less bulky anilides (2b, 2c), complexes analogous to 3a could not be isolated. Initial \(^1\)H spectra showed the presence of several intermediate species. In the reaction with 2b, clearest results were obtained in hexanes at room temperature. A very dark, diamagnetic complex (4b) could be isolated in fair yield. NMR spectra were complicated; X-ray diffraction revealed a benzyl-deprotonated anilide ligand bridging between two (BDI)Rh fragments in an \( \mu-\eta^1(\text{CCCC})\eta(\text{CCCN}) \) fashion (Fig. 3) [14]. There is precedent for benzyl metallated o-methylanilide ligands, formed mostly [15] but not exclusively [16] via imido intermediates, but the coordination mode of this ligand in 4b is surprising and as far as we know unprecedented. It can be regarded as the aza analog of a \( \mu-\eta^1 \) bridging o-xylylene ligand [17], with two diene-like ligand-metal interactions, and hence both Rh atoms are best viewed as RhIII (Section 3.7 of the SI compares relevant geometries).

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### 2.3. Reaction of unsubstituted anilide

Anilide 2c is even less hindered than 2a/b and moreover has no benzylic hydrogens available for HAA. Monitoring the reaction of 1 with 2c by \(^1\)H NMR (see SI section 1), we observed a complicated series of reactions, which were moreover sensitive to the choice of solvent(s). In \( \text{C}_6\text{D}_{12} \) or in hexanes, one diamagnetic intermediate containing (\( \kappa^2 \)-chelate (aza-enediyli) manner with sp\(^3\) carbon and nitrogen atoms, so in this case the complex unambiguously contains RhIII.

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Perhaps more likely, aminyl complex 3c first disproportionates into amine and nitrene complexes (H abstraction from one aminyl radical by a second one), and the resulting nitrene complex then undergoes N-C coupling to form the final product [23].

### 3. Conclusions

In summary, complexes 3a–c, easily generated from 1 and Li anilides, are best viewed as RhII anilide complexes with significant RhI anilinyl radical character. The reactions we observe (HAA to 4b/5b, N-C coupling to 6c) are typical of anilinyl radical species, but the selectivity we also observe suggests that coordination has for a large part quenched the reactivity associated with such radicals. We found no indications for attack at the para position of coordinated anilides, even though this is often a site of reactivity for C-C or N-C coupling [3c]. The selective N-C2′ coupling observed with Ru/Os [7] and now also with Rh illustrates that coordination to a metal centre can be used for tuning not just of reactivity but also of selectivity.

### 4. Experimental

#### 4.1. General

All experiments were carried out in a nitrogen-filled dry-box or under an argon atmosphere using standard Schlenk techniques. Hexane, pentane, toluene, toluene-d₈, tetrahydrofuran, THF-d₆, cyclohexane, and cyclohexane-d₁₂ were distilled from sodium/benzophenone. [Rh(COE)₂Cl]₂ was purchased from Strem Chemicals and used as received. Aniline, 2,6-dimethylaniline, 2,6-diisopropylaniline and n-butyllithium (1.6 M in hexanes) were purchased from Sigma-Aldrich and used as received.

¹H and ¹³C NMR spectra were recorded on Bruker Avance 300 MHz and Bruker Avance 500 MHz spectrometers at room temperature. All chemical shifts (δ) are reported in ppm. ¹H and ¹³C chemical shifts (δ) were referenced to residual solvent signals (benzene-d₆: δ 7.16 and 128.00; THF-d₆: δ 3.58 and 67.21; cyclohexane-d₁₂ δ 1.38 and 26.43).
Coupling constants \( J \) and linewidths at half-height \( (W_{\text{½}}) \) are given in Hz. COSY and HSQC spectra were also acquired to assist \( ^{1}H \) and \( ^{13}C \) assignments. \((\text{BDI})\text{Rh})_{2}(\mu-\text{Br})_{2}\) was prepared according to a published procedure \([5]\).

4.2. 2,6-iPr\(_{2}\)C\(_{6}\)H\(_{3}\)NHLi(THF) (2a)

Under an argon atmosphere, 2,6-diisopropylaniline (2.5 mL, 0.0133 mol) was added into a Schlenk tube and dissolved in 15 mL dry THF. At high stirring speed, \( n\)-BuLi (1.6 M in hexane, 8.3 mL, 0.0133 mol) was added dropwise. After 30 min at room temperature, all solvents were evaporated to dryness. The resulting white solid was washed with dry hexane twice to remove possible unreacted 2,6-diisopropylaniline, leaving 2.0 g of a white solid (59%).

\(^{1}H\) NMR (benzene-\(d_{6}\), 300 MHz): \( \delta \) 7.12 (d, 2H, \( J \) 7.4, Ar \( m \)), 6.70 (t, 1H, \( J \) 7.4, Ar \( p \)), 3.25–3.38 (m, 2H, CH\(_{3}\)Me\(_{2}\)), 3.00 (m, 4H, OC\(_{2}\)H\(_{2}\)), 2.87 (s, 1H, NH), 1.40 (d, 12H, \( J \) 7.1, CH\(_{3}\)Me\(_{2}\)), 1.05 (m, 4H, OCH\(_{2}\)C\(_{2}\)H\(_{5}\)).

4.3. 2,6-Me\(_{2}\)C\(_{6}\)H\(_{3}\)NHLi (2b)

Under an argon atmosphere, 2,6-dimethylaniline (1.0 mL, 0.0081 mol) was placed in a Schlenk tube and dissolved in 10 mL dry THF. At high stirring speed, \( n\)-BuLi (1.6 M in hexane, 5.0 mL, 0.0081 mol) was added dropwise. After 30 min at room temperature, all solvents were evaporated in vacuo. The resulting white solid was washed with dry hexane twice to remove possible unreacted 2,6-dimethylaniline, leaving 0.61 g (36%) of a white solid which did not dissolve in C\(_{6}\)D\(_{6}\). \(^{1}H\) NMR in THF-\(d_{8}\) revealed the absence of coordinated THF in the product. The anilide was used without further characterization.

4.4. PhNHLi (2c)

Under an argon atmosphere, aniline (1.0 mL, 0.011 mol) was placed in a Schlenk tube and dissolved in 10 mL dry THF. At high stirring speed, \( n\)-BuLi (1.6 M in hexane, 6.9 mL, 0.011 mol) was added dropwise. After 30 min at room temperature, all solvents were evaporated in vacuo. The resulting white solid was washed with dry hexane twice to remove possible unreacted aniline, leaving 0.88 g (81%) of a white solid. \(^{1}H\) NMR in THF-\(d_{8}\) revealed the absence of coordinated THF in the product. The anilide was used without further characterization.

4.5. Formation of 3a

A solution/suspension of lithium 2,6-diisopropylanilide(THF) (2a: 30 mg, 0.117 mmol) in 1 mL toluene was added dropwise to a solution of \((\text{BDI})\text{Rh})_{2}(\mu-\text{Br})_{2}\) (1: 45 mg, 0.042 mmol, 2.8 eq.) in toluene (1 mL) at room temperature. Solvents were removed in vacuo immediately. Washing with 1 mL of cold hexane left 45 mg of a blue powder which according to \(^{1}H\) NMR was reasonably pure 3a (see Fig. S4), yield 64% based on the amount of 1 used. Attempts at further purification always resulted in partial decomposition, so we did not attempt elemental analysis. Extraction of the solid with hexane and cooling to \(-35^\circ\text{C}\) produced a small amount of blue crystals after weeks. One of the crystals was further analyzed by single-crystal X-ray diffraction.
1H NMR (benzene-\(d_6\), 300 MHz), signals not assigned: \(\delta\) 13.8 (W\(\frac{1}{2}\) 290), 10.1 (W\(\frac{1}{2}\) 57), 3.5 (W\(\frac{1}{2}\) 340), 1.2 (W\(\frac{1}{2}\) 44), −10.0 (W\(\frac{1}{2}\) 1100).

4.6. Formation of 4b in hexane

Complex 1 (63.3 mg, 0.059 mmol) was weighed into a small vial and dissolved in 10 mL hexane, and the resulting dark green solution was transferred into a Schlenk tube. Lithium 2,6-dimethylanilide (2b: 30.1 mg, 0.24 mmol, 4.0 eq.) was weighed and washed into the same Schlenk tube using 15 mL of hexane. After stirring at room temperature for 16 h, all solvents were evaporated to dryness in vacuo. To the residue was added 5 mL toluene. The suspension was centrifuged and the liquid was transferred into another Schlenk tube. After all solvents were evaporated to dryness in vacuo, the residue was dissolved in 1 mL toluene and layered with 1 mL hexane and stored at \(-35^\circ\text{C}\) for 2 days. A crystalline solid was isolated by pipetting off the mother liquor. The mother liquor was further concentrated and layered with more hexane at \(-35^\circ\text{C}\). More solids were obtained, giving a combined yield of 36% based on [(BDI)Rh](\(\mu\)-Br)

^{1}H NMR (benzene-\(d_6\), 300 MHz): \(\delta\) 6.69–7.12 (12H, m, Ar), 6.40 (1H, d, \(J\ 4.5, c\)), 5.12, 4.82 (1H each, s, 3 and 3\(^{\prime}\)), 4.04 (1H, dd, \(J\ 6.0\) and 4.5,

1H NMR (THF-\(d_8\), 300 MHz): \(\delta\) 6.69–7.12 (12H, m, Ar), 6.40 (1H, d, \(J\ 4.5, c\)), 5.12, 4.82 (1H each, s, 3 and 3\(^{\prime}\)), 4.04 (1H, dd, \(J\ 6.0\) and 4.5,

13C NMR (THF-\(d_8\), 75 MHz): \(\delta\) 158.1, 157.5, 156.8 (d, \(J\) Rh 1), 155.3, 155.1, 154.5, 154.1, 154.0 (4 × 2 and 4 × i), 133.8, 133.6, 132.7, 132.3, 131.2, 130.8, 130.7, 130.6 (8 × a), 129.4, 129.0, 128.7, 128.4, 128.2, 2 × 127.9, 127.4 (8 × m), 125.3, 124.7, 124.5, 123.9 (4 × p), 99.3 (d, \(J\) Rh 3, 3 or 3\(^{\prime}\)), 97.6 (d, \(J\) Rh 3, 3\(^{\prime}\) or 3\(^{\prime}\) or 3\(^{\prime}\)), 90.6 (br, c), 80.6 (d, \(J\) Rh 10, b), 76.4 (d, \(J\) Rh 11, f), 75.3 (d, \(J\) Rh 8, a), (4 × 1 and 8 × o-Me), 12.2.

4.7. Formation of 5b in toluene

A solution/suspension of lithium 2,6-dimethylanilide (21.9 mg, 0.17 mmol) in 0.4 mL toluene was added to a solution of 1 (45 mg, 0.042 mmol) in toluene (0.5 mL). Addition of a few drops of THF produced a clear solution. Solvents were removed in vacuo immediately, and the residue was extracted with hexane. After standing in hexane at room temperature overnight, solvent was removed in vacuo. Pentane with 5 drops of toluene was added and cooling to \(-35^\circ\text{C}\) produced a few yellow crystals overnight. The mother liquor was removed and the solid was dried. One of the crystals was used for single-crystal X-ray diffraction. We were not successful in generating enough of a pure sample for \(^{13}\text{C}\) NMR spectroscopy or elemental analysis.

\begin{align*}
\text{Anal. Calcd for C}_{50}\text{H}_{59}\text{N}_{5}\text{Rh}_{2} (935.85): C, 64.17; H, 6.35; N, 7.48.} \\
\text{Found: C, 64.26; H, 6.45; N, 7.49.}
\end{align*}
4.8. Formation of 3c

A solution/suspension of lithium anilide (2c: 46.9 mg, 0.47 mmol) in 10 mL hexane was added to a solution of 1 (67 mg, 0.06 mmol) in hexane (10 mL). The mixture was stirred at room temperature for 18.5 h. Solvents were removed in vacuo, the residue was extracted with toluene, and solids were removed by centrifugation, leaving 24 mg of 3c as a black powder (40% relative to the amount of 1 used). Purity was ~90% according to $^1$H and $^{13}$C NMR (see the SI), and attempts at further purification resulted in partial conversion to 6c and other products, so we did not attempt EA.

$^1$H NMR (benzene-$d_6$, 300 MHz): δ 6.4−7.0 (m, Ar o/m/p), 5.38 (2H, s, 3), 4.59 (2H, br s, NH), 2.32, 1.68, 1.63 (12H each, s, 1 and o-Me).

$^{13}$C NMR (benzene-$d_6$, 75 MHz): δ 159.8 (2/i), 154.9 (Ph i), 153.2 (i/2), 134.8, 130.2 (2 × o), 129.3, 129.0, 127.1 (2 × m and Ph m), 125.9 (Ph o), 124.9 (p), 122.1 (Ph p), 98.0 (3), 23.1, 20.6, 19.1 (1 and 2 × o-Me).

4.9. Formation of 6c

(a) A solution/suspension of lithium anilide (2c: 48 mg, 0.48 mmol) in 10 mL hexane was added to a solution of 1 (75 mg, 0.07 mmol) in hexane (10 mL). The mixture was stirred at room temperature for 50 min. Solvents were removed in vacuo, and the residue was extracted with pentane. After centrifugation, the dark blue solution was cooled to −35 °C. After two weeks, a black crystalline solid had deposited. The mother liquid was pipetted off and further concentrated. After another week at −35 °C, more solid was isolated by pipetting off the mother liquor. Combined yield: 11 mg, 15% (relative to the amount of the excess of a sphere of X-ray di). Purity was completely gone and small crystals had formed inside the tube, one of which was used for X-ray powder diffraction. Alternatively, the toluene was removed in vacuo and the residue was washed with cold hexane and dried, leaving 24 mg of 6c as a black powder (40% relative to the amount of 1 used). Purity was ~90% according to $^1$H and $^{13}$C NMR (see the SI), and attempts at further purification resulted in partial conversion to 6c and other products, so we did not attempt EA.

(b) In a separate experiment, X-ray quality crystals containing C$_8$D$_{12}$ of crystallization were obtained as follows: Lithium anilide (2c: 3.5 mg) and 1 (5 mg) were dissolved in C$_8$D$_{12}$ in an NMR tube and kept in a glove box. After standing for one month, the NMR cap was removed, allowing the C$_8$D$_{12}$ to slowly evaporate. After two weeks, the solvent was completely gone and small crystals had formed inside the tube, one of which was used for X-ray diffraction.

This compound always crystallized with loosely bound solvent in the lattice, as was also evident from the two X-ray structure determinations (with pentane and with C$_8$D$_{12}$), therefore elemental analysis was not attempted.

4.10. X-ray structure determinations

A multi-faceted crystal of suitable size and quality was selected from a representative sample of crystals of the same habit using an optical microscope and mounted onto a MFTiGen loop. X-ray data were obtained on a Bruker D8 QUEST ECO CMOS diffractometer (Mo sealed X-ray tube, Ka = 0.71073 Å) at 150 K. All diffractometer manipulations, including data collection, integration and scaling were carried out using the Bruker APEX3 software suite [24]. An absorption correction was applied using SADABS [25]. The space group was determined on the basis of systematic absences and intensity statistics and the structure was solved by direct methods and refined by full-matrix least squares on $F^2$. The structure was solved using XS (incorporated in SHELXTL or SHELXL and refined using SHELXL [26]. No obvious missed symmetry was reported by PLATON [27]. Hydrogens were put at calculated positions and refined in riding mode, except H(N-Rh), which were freely refined. The following contains details specific to individual determinations; results are summarized in Table S1, and Figures showing the resulting structures together with the adopted numbering schemes are presented in the Supporting Information.

4.10.1. $^{(^{6}^bBDI)RhNH-2,6-iPr_{2}C_{6}H_{3}}$(3a)

A blue crystal fragment (0.05 × 0.11 × 0.13 mm) was used. In excess of a sphere of X-ray diffraction data (114,385 reflections) was collected to 2θ = 61.0° using 20 s per 1° frame. Data merging produced 35,778 (Rint = 0.0619) reflections covering the Ewald hemisphere. The unit-cell parameters were obtained by least-squares refinement on 9559 reflections.

4.10.2. $^{(^{6}^bBDI)Rh}_{2}[$μ-NHC$_6$H$_5$]$_{2}$(3c)

A black crystal fragment (0.13 × 0.067 × 0.030 mm) was used. In excess of a sphere of X-ray diffraction data (102159 reflections) was collected to 2θ = 69.9° using 40 s per 0.5° frame. Data merging produced 42,733 (Rint = 0.0427) reflections covering the Ewald hemisphere. The unit-cell parameters were obtained by least-squares refinement on 9991 reflections.

4.10.3. $^{(^{6}^bBDI)Rh}[$μ-η$^{1}$-1-NH-2,6-C$_6$H$_3$-η$^{4}$]$^{4}$][Rh($^{6}^b$BDI)] (4b)

A brown crystal fragment (0.10 × 0.05 × 0.04 mm) was used. In excess of a sphere of X-ray diffraction data (109,154 reflections) was collected to 2θ = 57.4° using 30 s per 1° frame. Data merging produced 39,719 reflections (Rint = 0.1091) covering the Ewald hemisphere. The unit-cell parameters were obtained by least-squares refinement on 14,598 reflections.

4.10.4. $^{(^{6}^bBDI)Rh}[$μ-η$^{4}$-1-NH-2,6-C$_6$H$_3$-η$^{4}$]$^{4}$][Li(NH$_2$-2,6-C$_6$H$_3$)$_2$] (5b)

A yellow crystal fragment (0.07 × 0.15 × 0.28 mm) was used. In excess of a sphere of X-ray diffraction data (222183 reflections) was collected to 2θ = 55.8° using 20 s per 1° frame. Data merging produced 49,265 (Rint = 0.0697) reflections covering the Ewald hemisphere. The unit-cell parameters were obtained by least-squares refinement on 9693 reflections. PLATON reported the presence of four voids in the unit cell each corresponding in size to a pentane molecule (the solvent used for crystallization). Pentane was also visible in the $^1$H NMR spectrum. However, attempts to refine a solvent model were unsuccessful and indicated a high degree of disorder. Therefore, the PLATON SQUEEZE option [28] was used to handle electron density in the solvent spaces. PLATON reported a slightly higher number of electrons in the solvent voids than expected for four pentanes (183 vs 168 e in 820 Å$^3$).

4.10.5. $^{(^{6}^bBDI)Rh}[$μ-η$^{4}$-1-NH-2-NPh-C$_6$H$_4$-η$^{4}$]$^{4}$][Rh($^{6}^b$BDI)] (6c)

A black crystal fragment (0.15 × 0.19 × 0.25 mm) was used. In excess of a sphere of X-ray diffraction data (186421 reflections) was collected to 2θ = 66.3° using 10 s per 1° frame. Data merging produced 40,033 (Rint = 0.0311) reflections covering the Ewald hemisphere. The
unit-cell parameters were obtained by least-squares refinement on 9921 reflections. PLATON reported the presence of two voids in the unit cell each corresponding in size to a pentane molecule (the solvent used for crystallization). Pentane was also visible in the 1 H NMR spectrum. However, attempts to refine a solvent model were unsuccessful and indicated a high degree of disorder. Therefore, the PLATON SQUEEZE option [28] was used to handle electron density in the solvent spaces. PLATON reported a slightly higher number of electrons in the solvent spaces.

\[40.16. \ (\text{I}-4\text{mm})\text{R}h\{\mu-\text{η}^1-\text{NH}-2\text{-NPh-C}_6\text{H}_4\text{η}^1\}\text{(I}-4\text{mm})\text{R}h\text{-C}_2\text{D}_2\ (6\text{c}-6\text{c},6\text{c})\]

A black (or dark brown) crystal fragment (0.08 × 0.08 × 0.05 mm) was used. In excess of a sphere of X-ray diffraction data (173,961 reflections) was collected to 2θ = 61° using 40 s per 1° frame. Data merging produced 61,439 (Rint = 0.1257) reflections covering the Ewald hemisphere. The unit-cell parameters were obtained by least-squares refinement on 17,273 reflections.

4.11. EPR study of 3a

Experimental X-band EPR spectra were recorded at 20 K on a Bruker EMX spectrometer equipped with a Bruker temperature control cryostat system coupled to a He liquefier, using a frozen solution (glass) of complex 3a in toluene. The spectrum was simulated by iteration of the anisotropic g values and line widths using the EPR simulation program W95EPR developed by Prof. Dr. Frank Neese [29].

4.12. Computational study of 3a

The geometry of 3a was optimized starting from the X-ray structure using Turbomole [30], the tpssh functional [31], the de2-TZVP basis set [32] and on Rh the corresponding small-core ECP. A vibrational analysis at this level produced no imaginary frequencies, confirming that the structure was a local minimum. A final free energy was obtained by combining this energy with thermal corrections (enthalpy and entropy, 298 K, 1 bar) from the vibrational analysis (entropy scaled by 0.67 to account for reduced freedom in solution [33]) and a correction for dispersion (DFTD3, ‘zero’ damping) [34].

EPR parameters for 3a and isomer 3a’ (see SI) were calculated with ADF [35] using spin-unrestricted spin-orbit density functional theory (collinear approach for the hyperfine couplings) at the B3LYP level [36] and the ZORA TZ2P basis set as included in ADF, using the geometries of 3a and 3a’ as optimized with Turbomole at the tpssh/de2-TZVP level.

Conflicts of interest

There are no conflicts to declare.

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Appendix A. Supplementary data

This includes 1 H and 13 C spectra, details of X-ray structure determinations, a comparison of geometric parameters diene/enediyli ligand fragments of complexes 4b, 5b and 6c, and an xyz archive of the optimized structures of 3a and 3a’. CCDC 1819936/1819938/1819939/1819942/1819943 contain the supplementary crystallographic data for this paper. These data are provided free of charge by the Cambridge Crystallographic Data Centre. Supplementary data associated with this article can be found in the online version, at https://doi.org/10.1016/j.ica.2018.06.015.

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The benzylic positions of the anilide ligand in 3a should be even more susceptible to H atom abstraction than those in 3b. We therefore attribute the non-observation of such a reaction in 3a to the much higher steric shielding in this complex of the anilinyl nitrogen that would do the abstraction.

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Locations of hydrogens on aniline nitrogens based on calculations and diamagnetic shielding re

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