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


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

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1. Introduction

The last decade has seen a growing recognition of the diversity of reaction types realizable with aminyl radicals bound to transition metals [1]. The N–H bond is strong, so free aminyl radicals are capable of abstracting hydrogen atoms even from unactivated hydrocarbons. Coordination of the aminyl radical to a metal stabilizes it and hence lowers its H-abstracting 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 aminyl radicals [2], but the same idea – with suitable correction for metal stabilization – applies to coordinated radicals. Most reported aminyl 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–C coupling [6] and/or alternative reaction pathways. Anticipated that replacing the halides with bulkier “counterions” might result in formation of monomeric RhII species with increased reactivity.

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broad EPR spectra have been reported for the (PNP)RhII complexes with broad features and no resolved di
The EPR spectrum in toluene glass (Fig. 2A) showed the presence of two suggestive of a mainly metal-centered radical.

mentioned above [13]). These data are calculated by DFT for the conformation of the solid-state structure (similarly to Fig. 2); those for the majority species agree well with 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 (1.937(3) Å) even compared to known RhIII amido bonds slightly longer (≈ 1.42 vs ≈ 1.38 Å)[10,11]. The Rh-N bond is short (1.937(3) Å) even compared to known RhIII amido/aminyl complexes [9], with the two diene-like ligand-metal interactions, and hence both Rh atoms are best viewed as RhI (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 dimethylamidine [18]. The deprotonated anilide unit is bound to Rh in a c2-chelate (aza-enediyli) manner with sp2 carbon and nitrogen atoms, so in this case the complex unambiguously contains RhII.

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 aza-xylylene unit [19,20]. In hexanes, the (BDI)Rh fragment migrates to the solvent, eventually ending up as the known complex [(BDI)Rh]2(μ-toluene) [21]. Instead, intermediate A picks up a second equivalent of 2b and free dimethylamine 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 1H 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 μ-η4(CCCC):η(CCCN) fashion (Fig. 3) [14]. There is precedent for benzyl-metalated o-methyl-anilide 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 μ-η4⁻bridging o-xylene ligand [17], with two diene-like ligand-metal interactions, and hence both Rh atoms are best viewed as RhI (Section 3.7 of the SI compares relevant geometries).

2.3. Reaction of unsubstituted anilide

Anilide 2e is even less hindered than 2a/b and moreover has no benzylic hydrogens available for HAA. Monitoring the reaction of 1 with 2e by 1H NMR (see SI section 1), we observed a complicated series of reactions, which were moreover sensitive to the choice of solvent(s).

Instead, intermediate 4b eventually ending up as the known complex [(BDI)Rh]2(μ-toluene) [21]. Instead, intermediate A picks up a second equivalent of 2b and free dimethylamine to give 5b.

In C6D12 or in hexanes, one diamagnetic intermediate containing an aza-xylylene unit [19,20]. In hexanes, the (BDI)Rh fragment migrates to the solvent, eventually ending up as the known complex [(BDI)Rh]2(μ-toluene) [21]. Instead, intermediate A picks up a second equivalent of 2b and free dimethylamine to give 5b.

Fig. 1. X-ray structure of 3a. All hydrogens except NH and agostic methine H omitted for clarity. Selected bond lengths (Å): Rh1-N1 2.003(2), Rh1-N2 2.007(2), Rh1-N3 1.937(3), Rh1-H47 1.97(3), Rh1-C47 2.792(3), N3-C41 1.382(4).

Scheme 1. Formation of copper aminyl complexes [4].

Scheme 2. Generation of Rh amido/aminyl complexes.

Generation of Rh amido/aminyl complexes.

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 (1.937(3) Å) even compared to known RhIII amido 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)RhIII 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 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 (1.937(3) Å) even compared to known RhIII amido 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)RhIII complexes where the amido group is part of a pincer ligand framework [13]. These data are suggestive of a mainly metal-centered radical.

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2.3. Reaction of unsubstituted anilide

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In C6D12 or in hexanes, one diamagnetic intermediate containing (according to 1H NMR) C2-symmetric (BDI)Rh fragments appeared prominently in spectra recorded early in the reaction and could be isolated in fairly pure state. A crystal structure determination produced a dimeric structure [(BDI)Rh2(μ-NHPh)2] (3e) consistent with this symmetry (Fig. 5). Interestingly, and unlike the starting material 1, dimeric 3c has a Rh-Rh bond, as is clear from the short Rh-Rh distance of 2.5616(2) Å, the butterfly folding of the Rh2N2 ring (NS-Rh1-Rh2-N6 120.96(9)°) and the diamagnetic nature of the complex. The diamagnetic final product 6c also crystallized well. Its structure (Fig. 6) contains a bis(amido)arene unit formed through N2,C-N-C coupling of two anilide fragments. It bridges in a μ-η4(CCCC):η(NN) fashion between two (BDI)Rh units, one containing RhII and the other containing RhI (see SI section 3.7). Several examples of this bridging mode have been reported [22], the most relevant one [22b] having a bis(amido)napthalene unit bridging between Cp*Ru(η4(CCCC)) and (Cp*)Ru(CNBu)2 (η5(η5)NN) fragments.

Goswami and co-workers have reported several examples of N2,C-N-C coupling in the oxidation of aniline at Ru and Os centers [7], and proposed that this coupling happens between two anilines cis-coordinated to the same metal atom. A possible path leading to our product 6c (Scheme 4) starts with dimer 3c, the direct product of substitution of the bromides of 1 by anilides. C-N coupling might happen at this stage, e.g. through opening of one Rh-N bond of the Rh2N2 core, followed by re-aromatization through net loss of H2. Alternatively, and
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-d8, 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-d8: δ 7.16 and 128.00; THF-d8: δ 3.58 and 67.21; cyclohexane-d12 δ 1.38 and 26.43).
4.2. 2,6-iPr₂C₆H₃NHLi (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%).

1H NMR (benzene-d₆, 300 MHz): δ 7.12 (d, 2H, J 7.4, Ar m), 6.70 (t, 1H, J 7.4, Ar p), 3.25–3.38 (m, 2H, CHMe₂), 3.00 (m, 4H, OC₂H₂), 2.87 (s, 1H, NH), 1.40 (d, 12H, J 7.1, CHMe₂), 1.05 (m, 4H, OCH₂C₂H₅).

4.3. 2,6-Me₂C₆H₃NHLi (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 C₆D₆. 1H NMR in THF-d₈ 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. 1H NMR in THF-d₈ 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 [(BDI)Rh]₂(μ-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 1H 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 °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 (W½ 290), 10.1 (W½ 57), 3.5 (W½ 340), 1.2 (W½ 44), −10.0 (W½ 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 °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 °C. More solids were obtained, giving a combined yield of 36% based on [(BDI)Rh]₂(μ-Br)₂ used.

\(1\)H NMR (benzene-\(d_6\), 300 MHz), signals not assigned: \(\delta\) 13.8 (W½ 290), 10.1 (W½ 57), 3.5 (W½ 340), 1.2 (W½ 44), −10.0 (W½ 1100).

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 °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 \(^{13}\)C NMR spectroscopy or elemental analysis.

\(1\)H NMR (benzene-\(d_6\), 300 MHz): \(\delta\) 6.4–7.0 (m, Ar m/p), 4.98 (1H, dd J 10, Jab 4, half obscured by \(\delta\) 4.98 3, f), 4.98 (1H, s, 3), 4.34 (1H, dd, J 10, Jab 2, f), 2.79 (4H, br s, NH₂), 2.47, 2.34, 2.31, 1.97 (3H each, s, 4 × BDI/NHAr Me), 1.79 (12H, s, NH₂ Ar Me), 1.56, 1.55, 1.49, 1.43, 1.34 (3H each, s, 5 × BDI/NHAr Me), 0.79 (1H, s, NH), 0.48 (1H, s, NH).
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 a red solution. At this stage, a small amount of black X-ray quality crystals could be obtained by layering with hexane and cooling to −35 °C. Alternatively, the toluene was removed in vacuo and the residue was washed with cold hexane and dried, leaving 24 mg of 3c as a black powder (40% relative to the amount of 1 used). Purity was ∼90% according to 1H and 13C NMR (see the SI), and attempts at further purification resulted in partial conversion to 6c and other products, so we did not attempt EA.

1H NMR (benzene-d6, 300 MHz): δ 6.4–7.0 (m, Ar o/m/p), 5.38 (2H, s, 3), 4.59 (2H, br s, N), 2.32, 1.68, 1.63 (12H each, s, 1 and o-Me).

13C NMR (benzene-d6, 75 MHz): δ 159.8 (2/1), 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 one week at −35 °C, more solid was isolated by pipetting off the mother liquor. Combined yield: 11 mg, 15% (relative to the amount of 1 used); a crystal from this batch was used for single-crystal X-ray diffraction.

(b) In a separate experiment, X-ray quality crystals containing C6D12 of crystallization were obtained as follows: Lithium anilide (2c: 3.5 mg) and 1 (5 mg) were dissolved in C6D12 in an NMR tube and kept in a glove box. After standing for one month, the NMR cap was removed, allowing the C6D12 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 C6D12), therefore elemental analysis was not attempted.

1H NMR (cyclohexane-d12, 300 MHz): δ 6.6–7.5 (m, Ar o/m/p), 6.21 (1H, br s, N), 5.80 (1H, t, J, 5), 5.35 (1H, s, 3′/3′′), 5.00 (1H, t, J 5, c), 4.12 (1H, s, 3′/3′′), 2.59, 2.31, 2.08, 2.07, 2.00, 1.89 (3H each, s, 6 × 1/2-o-Me), 1.90 (1H, obscured by δ 1.89 Me, d), 1.83, 1.68, 1.55, 1.51, 1.42 (3H each, s, 5 × 1/o-Me), 1.17 (1H, d, J 6, a), 1.14 (3H, s, 1/o-Me).

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 MITiGen 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 F2. The structure was solved using XS (incorporated in SHELXTL) or SHELXS and refined using

4.10.1. (t-BuBD)Rh[N=2-iPrC6H3] (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. [(t-BuBD)Rh][μ-NHC6H5]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 (102,159 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. [(t-BuBD)Rh][μ-N=2-CH2=6-MeC6H3]-η4 (Rh[t-BuBD]) (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. [(t-BuBD)Rh][μ-N=2=6-CH2=C6H3][μ-N=2=6-MeC6H3]Li (NH2-2,6-Me2C6H3)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 (222,183 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 1H 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 Å2).

4.10.5. [(t-BuBD)Rh][μ-N=2=N-2-NPh-C6H4]=η4 (Rh[t-BuBD]) (6c)

A black crystal fragment (0.15 × 0.19 × 0.25 mm) was used. In excess of a sphere of X-ray diffraction data (186,421 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 1H 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 option [28] was used to handle electron density in the solvent spaces.

4.10.6. \((\text{C}_8\text{H}_{10}\text{BDI})\text{Rh}[\mu-\eta^1-\text{NH}-2\text{NPh}_{2}\text{C}_6\text{H}_4\eta^1]\)[(\text{C}_8\text{H}_{10}\text{BDI})_2\text{C}_6\text{H}_{12} (6c-C_6H_{12})]

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 = 0.12575) 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 psfsh functional [31], the def2-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 (entangy and entropy, 298 K, 1 bar) from the vibrational analysis (entropy scaled by 4.11. EPR study of 3a

There are no conflicts of interest.

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Appendix A. Supplementary data

This includes 1H and 13C spectra, details of X-ray structure determinations, a comparison of geometric parameters diene/ednely ligand fragments of complexes 4b, 5b and 6c, and an xyz archive of the optimized structures of 3a and 3a’. CCDC 1819936/1819938/1819939/1819941/1819942/1819943 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.
[18] Locations of hydrogens on aniline nitrogens based on calculations and diamagnetic nature of the complex.

[19] Alternatively, one aminyl group abstracts an N-bound proton from a second aminyl group, generating an imide which in turn activates an o-methyl group.

[20] 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.


