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Research paper

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

Nan Zhang, Di Zhu, David E. Herbert, Nicolaas P. van Leest, Bas de Bruin, Peter H.M. Budzelaar

A B S T R A C T

Reaction of the Rh(II) dimer [LRh]_2(μ-Br)_2 (L = [(2,6-Me_2C_6H_3NCMe)_2CH] with the bulky amide LiNH(2,6-Pr_2C_6H_5) leads to a monomeric Rh(II) amide with a T-shape N,Rh arrangement and a pronounced agostic interaction. Reaction with the less bulky LiNH(2,6-Me_2C_6H_5) results in benzyl C-H activation to a binuclear complex with a unique aza-xylylene bridging mode. With LiNHPh we observe initial formation of [LRh]_2(μ-NHPh)_2 followed by N,C2 coupling of two anilines. These reactions can be explained based on aminyl 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 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-amiido complexes [3]. However, several copper complexes with significant radical character have been generated by simple metathesis from Cu(II) halides and lithium amides (Scheme 1) [4]. The NHAd complex is particularly interesting because it catalyzes amination of C–H bonds using Bu_3O_2 as the terminal oxidant [4b].

We recently reported on the formation and characterization of the paramagnetic β-diminate (BDI) rhodium bromide complex 1 and its iodide analog, which were found to contain paramagnetic Rh(II) 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 Rh(III) species with increased reactivity. We selected anilides as counterions since one could expect a degree of aminyl 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′ [7] N-C coupling) 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-diisopropylanilide

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 (κN1RhN3 = 94.08(10)°, κN2RhN3 = 175.39(11)°) in which the methane 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 (1.937(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 the toluene glass (Fig. 2A) showed the presence of two different species in an approximately 70:30 ratio. Both have rhombic spectra with broad features and no resolved fine structure (similarly broad EPR spectra have been reported for the (PNP)RhII complexes mentioned above [13]). g values were obtained by simulation (legend to Fig. 2); those for the majority species agree well with g values calculated by DFT for the conformation of the solid-state structure (g = [2.381 2.016 1.948]). These calculations suggest a mostly metal-centered radical with significant spin density (Fig. 2B) on the nitrogen atom (Rh 55%, N 23%). At this point it is not clear whether the minority species is an alternative conformation (see the SI for further discussion of this possibility), a solvento complex, or associated with the easy decomposition of 3a in solution.

2.2. Reaction of 2,6-dimethylanilide

With less bulky anilides (2b, 2c), complexes analogous to 3a could not be isolated. Initial 1H NMR 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(CCCN):η4(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 μ-η1,η1 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).

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 κ2-chelate (aza-enediy) 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-xylene unit [19,20]. In hexanes, the (BDI)Rh fragment migrates to the arene ring of the aza-xylene unit to form 4b. In toluene, the same (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 dimethylaniline to give 5b.

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 1H NMR (see SI section 1), we observed a complicated series of reactions, which were more sensitive to the choice of solvent(s). In C6D12 or in hexanes, one diamagnetic intermediate containing (ac-3c) fragment 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(3c)] 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-Nb 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 N,2η coupling of two anilide fragments. It bridges in a μ-η1,η1 fashion between two (BDI)Rh units, one containing RhI and one which appears to be in a κ2-chelate (aza-enediy) manner with sp2 carbon and nitrogen atoms, so in this case the complex unambiguously contains RhII. Goswami and co-workers have reported several examples of N,2′ 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-d6: δ 7.16 and 128.00; THF-d8: δ 3.58 and 67.21; cyclohexane-d12 δ 1.38 and 26.43).
Coupling constants $J$ and linewidths at half-height (W½) are given in Hz. COSY and HSQC spectra were also acquired to assist 1H and 13C assignments. [(BDI)Rh]$_2$(μ-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): 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, CH$_2$Me$_2$), 3.00 (m, 4H, OCH$_2$C$_6$H$_4$), 2.87 (s, 1H, NH), 1.40 (d, 12H, $J$ 7.1, CHMe$_2$), 1.05 (m, 4H, OCH$_2$C$_6$H$_4$).

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 [(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. Wasing 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 $-35$ °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: δ 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.

1H NMR (THF-d$_8$, 300 MHz): δ 6.69–7.12 (12H, m, Ar m/p), 6.40 (1H, d, J 4.5, c), 5.12, 4.82 (1H each, s, 3 and 3′), 4.04 (1H, dd, J 6.0 and 4.5, b), 2.32 (6H, s, 2×Me), 2.3 (1H, obscured by δ 2.32 Me groups, a), 2.19, 2.12, 1.98, 1.93, 1.91, 1.80, 1.50 (3H each, s, Me), 1.48 (6H, s, 2×Me), 1.43 (3H, s, Me), −0.67 (3H, s, e), NH and f not observed.

13C NMR (THF-d$_8$, 75 MHz): δ 158.1, 157.5, 156.8 (d, JRh 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, JRh 3, 3 or 3′), 97.6 (d, JRh 3, 3′ or 3), 90.6 (br, c), 80.6 (d, JRh 10, b), 76.4 (d, JRh 11, ?), 75.3 (d, JRh 8, a), (4×1 and 8×a-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 °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 13C NMR spectroscopy or elemental analysis.

1H NMR (benzene-d$_6$, 300 MHz): δ 6.4–7.0 (m, Ar m/p), 4.98 (1H, dd, J 10, J$_{ab}$ 4, half obscured by δ 4.98 3, f), 4.98 (1H, s, 3), 4.34 (1H, dd, J 10, J$_{ab}$ 2, f), 2.79 (4H, br s, NH$_2$), 2.47, 2.34, 2.31, 1.97 (3H each, s, 4×BDI/NHArMe), 1.79 (12H, s, NH$_2$ArMe), 1.56, 1.55, 1.49, 1.43, 1.34 (3H each, s, 5×BDI/NHArMe), 0.79 (1H, s, NH), 0.48 (1H, s, NH).

Scheme 4. Possible routes leading to 6c. The "H$_2$" steps could be straightforward elimination of H$_2$ or – more likely – H abstraction by aminyl radicals.
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, NH), 2.32, 1.68, 1.63 (12H each, s, 1 and o-Me).

13C NMR (benzene-d6, 75 MHz): δ 159.8 (2i), 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 50 °C. After two weeks, a black crystalline solid had deposited. The mother liquid was pipetted off and concentrated. After another 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.

(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.

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 MHTGen 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 SHEXLTL or SHELXS and refined using SHEXL [26]. No obvious missed symmetry was reported by PLATON [27]. Hydrgen atoms were placed 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. (MeBDI)Rh[NH-2,6-Me2C6H3]2 (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. (MeBDI)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 (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. (MeBDI)Rh[(μ-η4-1-NH-2-CH2-6-Me-C6H3)]2 (4a)

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. (MeBDI)Rh[μ-NH-2-6-Me-C6H3][μ-NH-2,6-Me2C6H3]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 (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 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 Å3).

4.10.5. (MeBDI)Rh[μ-η4-1-NH-2-NPh-C6H4-η4] (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
cell-unit 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 voids than expected for two pentanes (95 vs 84 in 495 Å³).

4.10.6. (1HBDI)Rh[μ-η1−1-NH-2-NPh-C6H4η1]([Rh(1HBDI)]CpD12 (6c-C6D12)

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 W5EPR 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 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 (enthalpy and entropy, 298 K, 1 bar) from the vibrational analysis at this level.

Conflicts of interest

There are no conflicts to declare.

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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/endiyli 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.

References

[10] The third example shows two very different ipso-ortho bond lengths (1.35 and 1.48 Å) without an obvious explanation.
[13] The presence of a hydrogen atom at the anilide N is inferred from (a) the diamagnetic nature of the complex; (b) the better agreement between calculated and observed structure if the H is included; (c) successful free refinement of the H atom position. However, the NH resonance could not be located in the 1H NMR spectrum.


