UvA-DARE (Digital Academic Repository)

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

Zhang, N.; Zhu, D.; Herbert, D.E.; van Leest, N.P.; de Bruin, B.; Budzelaar, P.H.M.

DOI

[10.1016/j.ica.2018.06.015](https://doi.org/10.1016/j.ica.2018.06.015)

Publication date

2018

Document Version

Final published version

Published in

Inorganica Chimica Acta

[Link to publication](#)

Citation for published version (APA):

Zhang, N., Zhu, D., Herbert, D. E., van Leest, N. P., de Bruin, B., & Budzelaar, P. H. M. (2018). Reactivity of Rhodium(II) amido/Rhodium(I) aminyl complexes. *Inorganica Chimica Acta*, 482, 709-716. <https://doi.org/10.1016/j.ica.2018.06.015>

General rights

It is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), other than for strictly personal, individual use, unless the work is under an open content license (like Creative Commons).

Disclaimer/Complaints regulations

If you believe that digital publication of certain material infringes any of your rights or (privacy) interests, please let the Library know, stating your reasons. In case of a legitimate complaint, the Library will make the material inaccessible and/or remove it from the website. Please Ask the Library: <https://uba.uva.nl/en/contact>, or a letter to: Library of the University of Amsterdam, Secretariat, Singel 425, 1012 WP Amsterdam, The Netherlands. You will be contacted as soon as possible.

Research paper

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

Nan Zhang^a, Di Zhu^b, David E. Herbert^a, Nicolaas P. van Leest^c, Bas de Bruin^c,
Peter H.M. Budzelaar^{a,d,*}

^a Department of Chemistry, University of Manitoba, 144 Dysart Road, Winnipeg, MB R3T 2N2, Canada

^b State Key Laboratory of Heavy Oil Processing, College of Science, China University of Petroleum, Beijing 102249, PR China

^c van't Hoff Institute for Molecular Sciences, University of Amsterdam, Science Park 904, 1098 XH Amsterdam, The Netherlands

^d Dipartimento di Scienze Chimiche, Università di Napoli Federico II, Via Cintia 4, 80126 Napoli, Italy

ARTICLE INFO

Keywords:

Aminyl
Hydrogen atom abstraction
N-C coupling
Radical
Nitrene

ABSTRACT

Reaction of the Rh(II) dimer $[\text{LRh}]_2(\mu\text{-Br})_2$ ($\text{L} = ([2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NCMe}]_2\text{CH})$) with the bulky amide $\text{LiNH}(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)$ leads to a monomeric Rh(II) amide with a T-shape N_3Rh arrangement and a pronounced agostic interaction. Reaction with the less bulky $\text{LiNH}(2,6\text{-Me}_2\text{C}_6\text{H}_3)$ results in benzylic C-H activation to a binuclear complex with a unique aza-xylylene bridging mode. With LiNHC_6H_5 we observe initial formation of $[\text{LRh}]_2(\mu\text{-NHPh})_2$ 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-amido 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 $^t\text{Bu}_2\text{O}_2$ as the terminal oxidant [4b].

We recently reported on the formation and characterization of the paramagnetic β -diiminate (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^{II} species with increased reactivity. We selected anilides as counterions since one could expect a degree of aminyl radical character for the products (c.f. Scheme 1) that might result in further interesting reactivity. Coordinated aniliny 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 ($\angle\text{N1RhN3} = 94.08(10)^\circ$, $\angle\text{N2RhN3} = 175.39(11)^\circ$) in which the methine hydrogen of an ^iPr group appears to occupy the fourth

* Corresponding author at: Dipartimento di Scienze Chimiche, Università di Napoli Federico II, Via Cintia 4, 80126 Napoli, Italy.

E-mail address: p.budzelaar@unina.it (P.H.M. Budzelaar).

<https://doi.org/10.1016/j.ica.2018.06.015>

Received 13 April 2018; Received in revised form 7 June 2018; Accepted 8 June 2018

Available online 22 June 2018

0020-1693/ © 2018 Elsevier B.V. All rights reserved.

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

Scheme 2. Generation of Rh amido/aminyll complexes.

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).

coordination site with an agostic interaction ($d(\text{Rh}-\text{H})$ 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 Rh^{III} 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)Rh^{II} 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 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)Rh^{II} 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 spectra showed the presence of several intermediate species. In the reaction with **2b**, cleanest 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 $\mu\text{-}\eta^4(\text{CCCC})\text{:}\eta^4(\text{CCCN})$ fashion (Fig. 3) [14]. There is precedent for benzyl-metallated *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 $\mu\text{-}\eta^4\text{:}\eta^4$ bridging *o*-xylylene ligand [17], with two diene-like ligand-metal interactions, and hence both Rh atoms are best viewed as Rh^I (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 κ^2 -chelate (aza-enediyl) manner with *sp*³ carbon and nitrogen atoms, so in this case the complex unambiguously contains Rh^{III}.

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 now bound to dimethylaniline migrates to the arene ring of the aza-xylylene 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 moreover sensitive to the choice of solvent(s). In C₆D₁₂ or in hexanes, one diamagnetic intermediate containing (according to ¹H NMR) C_s-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)Rh]₂(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 (N5–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 N,2′ *N*-C coupling of two anilide fragments. It bridges in a $\mu\text{-}\eta^4(\text{CCCC})\text{:}\kappa^2(\text{NN})$ fashion between two (BDI)Rh units, one containing Rh^I and one which appears to be in between Rh^I and Rh^{III} (see SI section 3.7). Several examples of this bridging mode have been reported [22], the most relevant one [22b] having a bis(amido)naphthalene unit bridging between Cp*Ru($\eta^4(\text{CCCC})$) and (Cp*)Ru(CN^tBu) ($\kappa^2(\text{NN})$) fragments.

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

Fig. 2. (A) EPR spectrum of **3a** in toluene glass (20 K). Parameters used for simulation: Majority species (70%), $g = [2.435\ 2.046\ 1.993]$, $W = [25\ 11\ 15]$; minority species (30%), $g = [2.250\ 2.087\ 2.008]$, $W = [30\ 20\ 15]$. (B) Calculated (TPSSH/def2-TZVP + ECP) spin density for the conformation of Fig. 1.

Fig. 3. X-ray structure of **4b**. All hydrogens except the NH and those of the activated methyl group omitted for clarity. Selected bond lengths (Å): Rh1–N5 2.166(6), Rh1–C71 2.269(6), Rh1–C72 2.137(6), Rh1–C77 2.138(7), Rh2–C73 2.218(6), Rh2–C74 2.116(7), Rh2–C75 2.134(7), Rh2–C76 2.363(7), N5–C71 1.327(9), C72–C77 1.387(10), C71–C72 1.454(10).

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 Rh^{II} anilide complexes with significant Rh^I aniliny radical character. The reactions we observe (HAA to **4b/5b**, N–C coupling to **6c**) are typical of aniliny 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.

Fig. 4. X-ray structure of **5b**. All hydrogens except the NH and those of the activated methyl group omitted for clarity. Selected bond lengths (Å): Rh1–N3 2.0748(19), Rh1–N4 2.0649(18), Rh1–C58 2.020(2), Li1–N3 2.077(4), Li1–N4 2.079(4).

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- d_8 , tetrahydrofuran, THF- d_8 , cyclohexane, and cyclohexane- d_{12} were distilled from sodium/benzophenone. $[\text{Rh}(\text{COE})_2\text{Cl}]_2$ 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 ^{13}C 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 ^{13}C chemical shifts (δ) were referenced to residual solvent signals (benzene- d_6 : δ 7.16 and 128.00; THF- d_8 : δ 3.58 and 67.21; cyclohexane- d_{12} : δ 1.38 and 26.43).

Scheme 3. Proposed paths leading to **4b** in hexane (top) and to **5b** in toluene (bottom).

Fig. 5. X-ray structure of **3c**. All hydrogens except NH omitted for clarity. Selected bond lengths (Å): Rh1–Rh2 2.5616(2), Rh1–N5 2.0409(17), Rh1–N6 2.0836(17), Rh2–N5 2.0609(17), Rh2–N6 2.0431(17).

Coupling constants J and linewidths at half-height ($W_{1/2}$) are given in Hz. COSY and HSQC spectra were also acquired to assist ^1H and ^{13}C assignments. $[(\text{BDI})\text{Rh}]_2(\mu\text{-Br})_2$ was prepared according to a published procedure [5].

4.2. $2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{NHLi}(\text{THF})$ (**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, $n\text{-BuLi}$ (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-

Fig. 6. X-ray structure of **6c**. All hydrogens except NH omitted for clarity. Selected bond lengths (Å): Rh1–C73 2.290(2), Rh1–C74 2.138(3), Rh1–C75 2.124(3), Rh1–C76 2.247(2), Rh2–N5 1.983(2), Rh2–N6 2.051(2), N5–C71 1.315(3), N6–C72 1.334(3), C71–C72 1.431(3).

diisopropylaniline, leaving 2.0 g of a white solid (59%).

^1H 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, CHMe_2), 3.00 (m, 4H, OCH_2), 2.87 (s, 1H, NH), 1.40 (d, 12H, J 7.1, CHMe_2), 1.05 (m, 4H, OCH_2CH_2).

4.3. $2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NHLi}$ (**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, $n\text{-BuLi}$ (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_6D_6 . ^1H NMR in $\text{THF-}d_8$ 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, $n\text{-BuLi}$ (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 $\text{THF-}d_8$ 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 ^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.

Scheme 4. Possible routes leading to **6c**. The “-H₂” steps could be straightforward elimination of H₂ or – more likely – H abstraction by aminyl radicals.

¹H NMR (benzene-*d*₆, 300 MHz), signals not assigned: δ 13.8 (W_{1/2} 290), 10.1 (W_{1/2} 57), 3.5 (W_{1/2} 340), 1.2 (W_{1/2} 44), –10.0 (W_{1/2} 1100).

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, *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 × *o*), 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'), 97.6 (d, *J*_{Rh} 3, 3' or 3), 90.6 (br, *c*), 80.6 (d, *J*_{Rh} 10, *b*), 76.4 (d, *J*_{Rh} 11, ?), 75.3 (d, *J*_{Rh} 8, *a*), (4 × 1 and 8 × *o-Me*), 12.2. (*e*). *d/f/g/h* not observed.

Anal. Calcd for C₅₀H₅₉N₅Rh₂ (935.85): C, 64.17; H, 6.35; N, 7.48. Found: C, 64.26; H, 6.45; N, 7.49.

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*), 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,

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*_{Rh} 4, half obscured by δ 4.98 3, *f*), 4.98 (1H, s, 3), 4.34 (1H, dd, *J* 10, *J*_{Rh} 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, NH₂Ar *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 $\sim 90\%$ according to ^1H 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.

^1H 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*/*o*), 134.8, 130.2 (2 $\times$ o), 129.3, 129.0, 127.1 (2 $\times$ *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 $\times$ 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 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 C_6D_{12} of crystallization were obtained as follows: Lithium anilide (**2c**: 3.5 mg) and **1** (5 mg) were dissolved in C_6D_{12} in an NMR tube and kept in a glove box. After standing for one month, the NMR cap was removed, allowing the C_6D_{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_6D_{12}), therefore elemental analysis was not attempted.

^1H NMR (cyclohexane- d_{12} , 300 MHz): δ 6.6–7.5 (m, Ar o/*m*/*p*), 6.21 (1H, br s, NH), 5.80 (1H, t, *J* 5, b), 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 $\times$ 1/*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 $\times$ 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, $\text{K}\alpha = 0.71073 \text{ \AA}$) 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 SHELXS 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. $(^{\text{Me}}\text{BDI})\text{RhNH-2,6-}^i\text{Pr}_2\text{C}_6\text{H}_3$ (**3a**)

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

4.10.2. $[(^{\text{Me}}\text{BDI})\text{Rh}]_2[\mu\text{-NHC}_6\text{H}_5]_2$ (**3c**)

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

4.10.3. $[(^{\text{Me}}\text{BDI})\text{Rh}][\mu\text{-}\eta^4\text{-1-NH-2-CH}_2\text{-6-Me-C}_6\text{H}_3\text{-}\eta^4][\text{Rh}(^{\text{Me}}\text{BDI})]$ (**4b**)

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

4.10.4. $(^{\text{Me}}\text{BDI})\text{Rh}[\mu\text{-NH-2-Me-6-CH}_2\text{-C}_6\text{H}_3][\mu\text{-NH-2,6-Me}_2\text{C}_6\text{H}_3]\text{Li}(\text{NH}_2\text{-2,6-Me}_2\text{C}_6\text{H}_3)_2$ (**5b**)

A yellow crystal fragment ($0.07 \times 0.15 \times 0.28 \text{ mm}$) was used. In excess of a sphere of X-ray diffraction data (222183 reflections) was collected to $2\theta = 55.8^{\circ}$ using 20 s per 1° frame. Data merging produced 49,265 ($R_{\text{int}} = 0.0697$) 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 $820 \text{ \AA}^3$).

4.10.5. $[(^{\text{Me}}\text{BDI})\text{Rh}][\mu\text{-}\eta^4\text{-1-NH-2-NPh-C}_6\text{H}_4\text{-}\eta^4][\text{Rh}(^{\text{Me}}\text{BDI})]$ (**6c**)

A black crystal fragment ($0.15 \times 0.19 \times 0.25 \text{ mm}$) was used. In excess of a sphere of X-ray diffraction data (186421 reflections) was collected to $2\theta = 66.3^{\circ}$ using 10 s per 1° frame. Data merging produced 40,033 ($R_{\text{int}} = 0.0311$) 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 voids than expected for two pentanes (95 vs 84 e in 495 Å³).

4.10.6. $[(^{\text{Me}}\text{BDI})\text{Rh}][\mu\text{-}\eta^4\text{-1-NH-2-NPh-C}_6\text{H}_4\text{-}\eta^4][\text{Rh}(^{\text{Me}}\text{BDI})]\text{-C}_6\text{D}_{12}$ ($6c\text{-C}_6\text{D}_{12}$)

A black (or dark brown) crystal fragment ($0.08 \times 0.08 \times 0.05$ mm) was used. In excess of a sphere of X-ray diffraction data (173,961 reflections) was collected to $2\theta = 61^\circ$ using 40 s per 1° frame. Data merging produced 61,439 ($R_{\text{int}} = 0.1257$) 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 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 (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/def2-TZVP level.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported in part by the National Science and Engineering Council (NSERC RGPIN-04766), by the National Natural Science Foundation of China (No. 21404118), and the Science Foundation of China University of Petroleum, Beijing (No. 2462013YJRC019).

Appendix A. Supplementary data

This includes ^1H and ^{13}C spectra, details of X-ray structure determinations, a comparison of geometric parameters diene/enediyl 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

- [1] A.I.O. Suarez, V. Lyaskovskyy, J.N.H. Reek, J.I. van der Vlugt, B. de Bruin, Complexes with nitrogen-centered radical ligands: classification, spectroscopic features, reactivity, and catalytic applications, *Angew. Chem., Int. Ed.* 52 (2013) 12510.
- [2] D. Sakic, H. Zipse, Radical stability as a guideline in C-H amination reactions, *Adv. Synth. Catal.* 358 (2016) 3983.
- [3] (a) A. Kochem, G. Gellon, N. Leconte, B. Baptiste, C. Philouze, O. Jarjayes, M. Orio, F. Thomas, Stable aniliny radicals coordinated to nickel: X-ray crystal structure and characterization, *Chem. Eur. J.* 19 (2013) 16707; (b) A.J. Rosenthal, M. Vogt, B. de Bruin, H. Grutzmacher, A diolefin diamide Rhodium(I) complex and its one-electron oxidation resulting in a two-center, three-electron Rh-N bond, *Eur. J. Inorg. Chem.* (2013) 5831; (c) T. Kikuchi, K. Kobayashi, K. Tsuge, S. Kitagawa, K. Tanaka, Asymmetric dimerization of aniline-ruthenium-dioxolene complex driven by stepwise PCET, *Dalton Trans.* 45 (2016) 14030; (d) R.E. Rodriguez-Lugo, B. de Bruin, M. Trincado, H. Grutzmacher, A stable aminyl radical coordinated to cobalt, *Chem. Eur. J.* 23 (2017) 6795.
- [4] (a) M.M. Melzer, S. Mossin, X. Dai, A.M. Bartell, P. Kapoor, K. Meyer, T.H. Warren, A. Three-Coordinate, Copper(II) amide from reductive cleavage of a nitrosamine, *Angew. Chem., Int. Ed.* 49 (2010) 904; (b) S. Wiese, Y.M. Badiei, R.T. Gephart, S. Mossin, M.S. Varonka, M.M. Melzer, K. Meyer, T.R. Cundari, T.H. Warren, Catalytic C-H Amination with unactivated Amines through Copper(II) amides, *Angew. Chem., Int. Ed.* 49 (2010) 8850.
- [5] D. Zhu, A.Z. Sharma, C.R. Wiebe, P.H.M. Budzelaar, Rhodium(II) dimers without metal-metal bonds, *Dalton Trans.* 44 (2015) 13460.
- [6] N.P. Mankad, W.E. Antholine, R.K. Szilagy, J.C. Peters, Three-coordinate Copper(I) amido and aminyl radical complexes, *J. Am. Chem. Soc.* 131 (2009) 3878.
- [7] (a) S. Samanta, S. Goswami, Regioselective knitting of aniline via ortho-C-N bond fusion using OsO₄ as a template, *J. Am. Chem. Soc.* 131 (2009) 924; (b) S. Chatterjee, P. Singh, J. Fiedler, R. Bakova, S. Zalis, W. Kaim, S. Goswami, Effect of metal exchange (Os vs. Ru) and co-ligand variation (Cl- vs. acac-) on the oxidation state distribution in complexes of an o-phenylenediamido(2(-))/o-quinonediimine redox system, *Dalton Trans.* (2009) 7778; (c) S. Samanta, S. Goswami, Tuning of the o-C-atom-N Bond-formation reactivity of aniline using Ruthenium(II) templates, *Inorg. Chem.* 50 (2011) 3171; (d) S.K. Roy, D. Sengupta, S.P. Rath, T. Saha, S. Samanta, S. Goswami, Role of mediator and effects of temperature on ortho-C-N bond fusion reactions of aniline using ruthenium templates: isolation and characterization of new ruthenium complexes of the in-situ-generated ligands, *Inorg. Chem.* 56 (2017) 4966.
- [8] Y. Wang, A. Olankitwanit, S. Rajca, A. Rajca, Intramolecular hydrogen atom transfer in aminyl radical at room temperature with large kinetic isotope effect, *J. Am. Chem. Soc.* 139 (2017) 7144.
- [9] (a) A.K. Singh, B.G. Levine, R.J. Staples, A.L. Odom, A 4-coordinate Ru(II) imido: unusual geometry, synthesis, and reactivity, *Chem. Commun.* 49 (2013) 10799; (b) R. Waterman, D.J. Mindiola, C.R. Clough, G.L. Hillhouse, Synthesis, structure, and reactivity of platinum compounds featuring terminal amido and phosphido ligands, *Inorg. Chim. Acta* 422 (2014) 57.
- [10] The third example shows two very different ipso-ortho bond lengths (1.35 and 1.48 Å) without an obvious explanation.
- [11] A.K. Burrell, A.J. Steedman, Synthesis, structure, and reactivity of ruthenium(II) terminal imido complexes, *Organometallics* 16 (1997) 1203.
- [12] (a) E. Morgan, D.F. MacLean, R. McDonald, L. Turculet, Rhodium and iridium amido complexes supported by silyl pincer ligation: ammonia N-H bond activation by a PSiP Ir complex, *J. Am. Chem. Soc.* 131 (2009) 14234; (b) S.A. Burgess, T. Bolano, T.B. Gunnoe, M. Sabat, W.H. Myers, Synthesis of Rh-III anilido, hydroxide, and methoxide complexes, *Eur. J. Inorg. Chem.* (2015) 1041.
- [13] D.A. Smith, D.E. Herbert, J.R. Walensky, O.V. Ozerov, Monomeric Rhodium(II) complexes supported by a Diarylamido/Bis(phosphine) PNP pincer ligand and their reactivity toward dihydrogen, *Organometallics* 32 (2013) 2050.
- [14] 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.
- [15] (a) E.R. King, G.T. Sazama, T.A. Betley, Co(III) imidos exhibiting spin crossover and C-H bond activation, *J. Am. Chem. Soc.* 134 (2012) 17858; (b) E.K. Huang, W.-M. Cheung, H.H.Y. Sung, I.D. Williams, W.-H. Leung, Reactions of a Ruthenium(VI) nitride with Rhodium(III) and Iridium(III) aryl complexes. Insertion of the Ru N Group into the Rh-C bonds of Trimesitylrhodium(III), *Organometallics* 32 (2013) 733; (c) R.R. Schrock, L.P.H. Lopez, J. Hafer, R. Singh, A. Sinha, P. Muller, Olefin metathesis reactions initiated by d(2) molybdenum or tungsten complexes, *Organometallics* 24 (2005) 5211.
- [16] R. Dorta, A. Togni, Facile and reversible O-H and C-H activation by a chiral Iridium (I) complex, *Organometallics* 17 (1998) 3423.
- [17] M.A. Bennett, M. Bown, L.Y. Goh, D.C.R. Hockless, T.R.B. Mitchell, Synthesis and Structure of Endo-Coordinated O-xylene complexes of zerovalent ruthenium and osmium, *M(ETA(4)-O-(CH₂)₂(C₆H₄)(PME(2)PH(3) (M = Ru, Os) and of a tri-carbonyliron adduct of the ruthenium complex, *Organometallics* 14 (1995) 1000.*

- [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 aminyl nitrogen that would do the abstraction.
- [21] P.H.M. Budzelaar, N.N.P. Moonen, R. de Gelder, J.M.M. Smits, A.W. Gal, Steric control over arene coordination to beta-diiminate rhodium(I) fragments, *Chem. Eur. J.* 6 (2000) 2740.
- [22] (a) N.A. Ketterer, H.J. Fan, K.J. Blackmore, X.F. Yang, J.W. Ziller, M.H. Baik, A.F. Heyduk, pi(radical)-pi(radical) bonding interactions generated by halogen oxidation of zirconium(IV) redox-active ligand complexes, *J. Am. Chem. Soc.* 130 (2008) 4364; (b) S. Takemoto, S. Oshio, T. Shiromoto, H. Matsuzaka, Dinuclear ruthenium(II) K-2-diamido/eta(6)-naphthalene complexes featuring a coordinatively unsaturated yet highly pi-basic (eta(5)-C5Me5)Ru diamide fragment, *Organometallics* 24 (2005) 801; (c) P.B. Hitchcock, Q.G. Huang, M.F. Lappert, X.H. Wei, M.S. Zhou, Synthesis and structures of some heterometallic (Li, Y)(2), (M-3, Ce) (M = Li or Na), (Li, Zr-2) and (Li, Zr)(4) oligomeric diamides derived from 1,2-bis(neopentylamino)benzene, *Dalton Trans.* 2991 (2006).
- [23] (a) M. Goswami, C. Rebreyend, B. de Bruin, Porphyrin Cobalt(III) "Nitrene Radical" reactivity; hydrogen atom transfer from ortho-YH substituents to the nitrene moiety of cobalt-bound aryl nitrene intermediates (Y = O, NH), *Molecules* 21 (2016); (b) D.E. Herbert, N.C. Lara, T. Agapie, Arene C-H amination at nickel in terphenyl-diphosphine complexes with labile metal-arene interactions, *Chem. Eur. J.* 19 (2013) 16453; (c) S. Wiese, J.L. McAfee, D.R. Pahls, C.L. McMullin, T.R. Cundari, T.H. Warren, C-H functionalization reactivity of a nickel-imide, *J. Am. Chem. Soc.* 134 (2012) 10114; (d) E. Kogut, H.L. Wiencko, L.B. Zhang, D.E. Cordeau, T.H. Warren, A terminal Ni (III)-imide with diverse reactivity pathways, *J. Am. Chem. Soc.* 127 (2005) 11248.
- [24] Bruker Bruker, Madison, Wisconsin, USA, 2016.
- [25] G. M. Sheldrick, University of Göttingen, Germany, 1996.
- [26] G.M. Sheldrick, Crystal structure refinement with SHELXL, *Acta Crystallogr., Sect. C Struct. Chem.* 71 (2015) 3.
- [27] A.L. Spek, Structure validation in chemical crystallography, *Acta Crystallogr., Sect. D: Biol. Crystallogr.* 65 (2009) 148.
- [28] A.L. Spek, Platon Squeeze: a tool for the calculation of the disordered solvent contribution to the calculated structure factors, *Acta Crystallogr., Sect. C Struct. Chem.* 71 (2015) 9.
- [29] F. Neese, W95EPR, QCPE Bulletin 1995, 15.
- [30] V6.3 ed., TURBOMOLE GmbH, since 2007, Karlsruhe, 2011, pp. a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH.
- [31] J.M. Tao, J.P. Perdew, V.N. Staroverov, G.E. Scuseria, Climbing the density functional ladder: nonempirical meta-generalized gradient approximation designed for molecules and solids, *Phys. Rev. Lett.* 91 (2003) 146401.
- [32] (a) F. Weigend, M. Haser, H. Patzelt, R. Ahlrichs, RI-MP2: optimized auxiliary basis sets and demonstration of efficiency, *Chem. Phys. Lett.* 294 (1998) 143; (b) F. Weigend, R. Ahlrichs, Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy, *Phys. Chem. Chem. Phys.* 7 (2005) 3297.
- [33] (a) R. Raucoles, T. de Bruin, P. Raybaud, C. Adamo, Theoretical unraveling of selective 1-butene oligomerization catalyzed by Iron-Bis(arylimino)pyridine, *Organometallics* 28 (2009) 5358; (b) S. Tobisch, T. Ziegler, Catalytic oligomerization of ethylene to higher linear alpha-olefins promoted by the cationic group 4 [(eta(5)-Cp-(CMe2-bridge)-Ph)M-II (ethylene)(2)](+) (M = Ti, Zr, Hf) active catalysts: A density functional investigation of the influence of the metal on the catalytic activity and selectivity, *J. Am. Chem. Soc.* 126 (2004) 9059.
- [34] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu, *J. Chem. Phys.* 132 (2010) 154104.
- [35] (a) C.F. Guerra, J.G. Snijders, G. te Velde, E.J. Baerends, Towards an order-N DFT method, *Theor. Chem. Acc.* 99 (1998) 391; (b) G. te Velde, E.J. Baerends, Numerical-integration for polyatomic systems, *J. Comput. Phys.* 99 (1992) 84; (c) L. Versluis, T. Ziegler, The determination of molecular-structures by density functional theory – the evaluation of analytical energy gradients by numerical-integration, *J. Chem. Phys.* 88 (1988) 322; (d) E.J. Baerends, D.E. Ellis, P. Ros, Self-consistent molecular Hartree-Fock-Slater calculations – I. The computational procedure, *Chem. Phys.* 2 (1973) 41.
- [36] (a) A.D. Becke, Density-functional thermochemistry. 3. The role of exact exchange, *J. Chem. Phys.* 98 (1993) 5648; (b) A.D. Becke, A new mixing of hartree-fock and local density-functional theories, *J. Chem. Phys.* 98 (1993) 1372; (c) C.T. Lee, W.T. Yang, R.G. Parr, Development of the colle-salvetti correlation-energy formula into a functional of the electron-density, *Phys. Rev. B* 37 (1988) 785.