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Authors(s)	Krüger, Anneke, Neels, Antonia, Albrecht, Martin
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Rhodium-mediated activation of an alkane-type C–H bond ‡

Anneke Krüger,^a Antonia Neels^b and Martin Albrecht^{*a}

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Abnormal C4-bonding of N-heterocyclic carbenes effectively modulates the electron density at rhodium and allows for the selective cleavage of an unactivated C(sp³)–H bond, whereas no such intramolecular C–H bond breaking is observed when the carbene binds normally through the C2 carbon.

The functionalization of unactivated C–H bonds, especially in alkanes, constitutes one of the most challenging areas of catalysis and has major implications in various areas such as in organic (retro)synthesis or in utilizing fossil fuel feedstocks with greater efficiency.^{1,2} The absence of electronically active substituents in alkane substrates renders the C(sp³)–H bond particularly inert. Functionalization of alkanes has been achieved under heterogeneous conditions, though the required high temperatures are economically unattractive and typically preclude selective product formation.³ In recent years, powerful homogeneous catalysts have been developed for the functionalization of methane⁴ based on Shilov chemistry,⁵ and of alkanes,⁶ some with remarkable selectivities.^{6e}

Common to the most successful systems is the underlying mechanism, which involves oxidative addition of the C–H bond to an electron-rich transition center.⁷ Consequently, strong donor ligands tend to facilitate metal-mediated C–H bond activation. In search for strong donors, N-heterocyclic carbenes have emerged as a class of formally neutral ligands that are significantly more basic than the strongest trialkylphosphine donors, and indeed, modifications on Shilov's system using NHC ligands have successfully been accomplished.⁸ More recently, abnormal variations of NHCs have shown to substantially enhance the ligand donor properties,⁹ thus representing an attractive scaffold for metal-catalyzed functionalization of unactivated bonds.¹⁰ Here, we report on the successful application of this strategy for rhodium-mediated intramolecular activation of an alkane-type C–H bond. Such bond activation requires the abnormal bonding of the NHC ligand and was not observed in analogous normally bound NHC complexes, thus providing further evidence for the unique impact of abnormal carbene ligands.¹¹

The reaction of propylene-linked diimidazolium salts **1** and RhCl₃ in the presence of NaOAc induced multiple C–H bond activation (Scheme 1).‡ After anion metathesis using KI and subsequent column chromatography (SiO₂, CH₂Cl₂/acetone), the cyclometalated rhodium(III) complexes **3** comprising a facially C,C,C-tridentate coordinating ligand were obtained in good yields (**3a** 59%, **3b** 71%). While C4 bonding of the NHC ligand has been expected from previous studies on methylene-linked dicarbene ligands,¹² activation of the C_{alkyl}–H bond in the propylene linker is unprecedented and remarkable, given the mild (MeCN, 80 °C) and aerobic reaction conditions.

Scheme 1. Reagents and conditions: (i), RhCl₃, NaOAc, MeCN reflux, then KI; (ii) CH₂Cl₂ RT; (iii) MeCN, RT.

Figure 1. ORTEP representation of the cationic portion of **2a** (a; 50% probability) and of the dimeric complex **3a** (b; 30% probability).

Table 1. Selected bond lengths (Å) for **2a** and **3a**.

Bond	Complex 2a	Complex 3a
Rh(1)–C(1)	1.969(9)	1.958(16)
Rh(1)–C(7)	1.957(8)	1.968(17)
Rh(1)–C(5)	2.089(8)	2.066(12)
Rh(1)–I(1)	2.7929(8)	2.8104(13)
Rh(1)–I(2)	---	2.7890(13)
Rh(1)–I(3)	---	2.8145(13)

A crystal structure of **3a** confirmed the C–H bond activation (Figure 1, Table 1).‡ The two rhodium centers are crystallographically symmetry-related through a mirror plane and reside in a slightly distorted octahedral environment comprising the C,C,C-tridentate dicarbene ligand and three μ^2 -bridging iodide ligands. The Rh–C_{NHC} bond lengths are 1.968(17) Å and 1.957(17) Å and hence similar to the rhodium-carbene bond lengths in analogous bidentate NHC complexes (1.98 – 2.04 Å),^{12,13} yet they are significantly shorter than the Rh–C_{alkyl} bond (2.066(12) Å).

The dimeric structure of the tridentate complex can easily be cleaved in solution with a coordinating solvent such as acetonitrile, thus quantitatively affording the monomeric complexes **2** (Scheme 1). This monomeric complex is also

surmised to be the initially formed product in the cyclometalation reaction prior to column chromatography. Evidence for the monomeric structure of **2** was provided by X-ray crystallography (Figure 1, Table 1).[‡] While most bond lengths and angles of **2a** are similar to those of the dimeric complex **3a**, the Rh–C_{alkyl} bond length is slightly elongated (2.089(8) Å) and the carbene-rhodium-carbene bite angle decreased from 87.5(8)° in **3a** to 83.3(3)°. These geometrical changes suggests some flexibility of the tridentate ligand.

Further confirmation of the formed rhodium-alkyl bond was obtained by NMR analyses. Microanalytically pure samples of **2** showed consistently two sets of signals (ca. 2.5:1 ratio). In the major species the resonances of the carbene residue were broad, while ligand broadening comprised predominantly the propylene signals in the minor species.¹⁴ For example, the rhodium-bound alkyl carbon in complex **2a** appears in the ¹³C NMR spectrum as a doublet at 33.7 ppm (¹J_{RhC} = 28 Hz; major species) and as a broad signal at δ_C 39 (minor species). In contrast, the rhodium-bound carbene resonances were not resolved for the major species, yet they are distinguished as a well-resolved doublet at δ_C 144.6 (¹J_{RhC} = 46 Hz) in the minor complex. Based on the expected higher *trans* effect of iodide as compared to MeCN, a mutual *cis* arrangement of the iodide and the alkyl ligands has been tentatively assigned to the major species, and a *trans* configuration (*cf.* X-ray of **2a**) to the minor species. The nearly statistical distribution of the iodide ligand suggests a similar *trans* effect for the alkyl group and the abnormal carbene. In line with this model, the NMR spectrum of dimeric complex **3** reveals two sets of signals in approximate 1:2 ratio, attributed to isomers comprising the alkyl ligands in *syn* (*cf.* X-ray of **3a**) and *anti* eclipsed conformation, respectively. All signals are well-resolved, consistent with a rigid dimeric structure.

Obviously, the C–H bond activation process in the propylene linker of **1** benefits from a high degree of intramolecular preorganization. Related metal-mediated, intramolecular C_{alkyl}–H bond cleavage has been demonstrated previously in highly constrained systems.¹⁵ However, in the case reported here, the ligand system would have the flexibility to twist out and to avoid any constrained situation that may promote C–H activation. For example, no C–H bond activation has been detected when normal C2-bonding dicarbene were employed.^{13a} Thus, reaction of RhCl₃ and the diimidazolium salt **4** under similar reaction conditions as used for **2** gave complex **5** in moderate 21% yield (Scheme 2).[‡] The dicarbene ligand in complex **5** is only bidentate with the propylene bridge folded away from the metal coordination sphere. This configuration is the common motif in propylene-linked dicarbene complexes.¹⁶

Scheme 2. Reagents and conditions: (i), RhCl₃, NaOAc, MeCN reflux, then KBr

Apparently, only the abnormal bonding mode provides sufficient electron density to the rhodium center for inducing C–H bond activation. While rhodium(I) systems are known to oxidatively add C–H bonds,^{15c} low oxidation states are less likely involved in the current process due to the absence of reducing agents during C–H bond activation, and owing to the fact that the strongly donating abnormal carbene ligands stabilize high oxidation states.⁹ Instead we propose an electrophilic bond activation, which is facilitated by the presence of acetate as ligand to rhodium(III) as well as proton scavenger.¹⁷ Presumably, the bond activation may be further eased by increasing steric constraints in the carbene ligand similar to related phosphine chemistry.^{15a}

The Rh–C_{alkyl} bond in **2** is remarkably stable towards air, moisture, and temperature, presumably due to the rigid tridentate bonding, which minimizes the availability of β-hydrogens for elimination reactions. The complexes also seemed surprisingly stable towards acids. Upon treatment with H₃PO₄ or HOAc, no changes were observed and complex **2a** was recovered quantitatively. When using deuterated phosphoric acid, deuterium exchange of the heterocyclic C5-bound hydrogen atoms occurred instantaneously (**2a**–d₂, Scheme 3), indicated by the disappearance of the signal at δ_H 6.78 in the ¹H NMR spectrum and the appearance of a broad resonance at this frequency in the ²H NMR spectrum. Further support for the incorporation of two deuterium atoms and formation of **2a**–d₂ was provided by HR-MS. With deuterated acetic acid the reaction was slower and required several days for completion. Deuteration of the C5-position may proceed in analogy to the deuteration of free carbenes.¹⁸

Scheme 3. Deuterium incorporation into **2a**.

When complex **2a** was heated to 60 °C in the presence of an excess of D₃PO₄, D-incorporation at the metal-bound alkyl carbon was observed in addition to H/D exchange at C5, thus affording **2a**–d₃. This outcome cannot be rationalized by simple acidolysis of the Rh–C_{alkyl} bond. Instead, deuteration of the alkyl carbon may proceed via reversible cleavage of the Rh–C_{alkyl} bond and at least one of the Rh–C_{carbene} bonds, or via a strained alkylidene complex.^{15a} Reversible Rh–C_{alkyl} bond making and breaking under acidic conditions suggests that C_{alkyl}–H activation is a thermodynamically favored process that possibly occurs already under milder conditions.

No H/D exchange was observed when complex **2** was treated with D₂ (1 bar), even when gently heated to 60 °C. The thermodynamic stability of complex **2** along with the kinetic lability of the Rh–C_{alkyl} bond indicates a potential of these complexes for heterolytic bond cleavage across the Rh–C_{alkyl} bond. We therefore evaluated the activity of complex **2** in catalytic hydrogenations using cyclooctene as model substrate (Table 2, entries 1–4).

Table 2. Rhodium-catalyzed hydrogenation of cyclooctene.^a

entry	Rh-cat	<i>T</i> /°C	<i>P</i> /bar	<i>t</i> /h	conversion
1	2a	60	60	5	43%
2	2a	20	1	24	2%
3	2a	60	1	16	3%
4	2a	20	60	5	5%
5	6	60	60	1	>99%

^a General conditions: 1 mmol substrate, 1 mol% catalyst, 5 mL of EtOH, except for entry 5 (minimal amount of CH₂Cl₂ was used to dissolve the rhodium complex), conversions determined by GC.

Moderate activity of **2a** was observed at elevated temperatures and pressures. However, the catalytic performance was markedly increased in catalytic runs using the dicationic complex **6**, derived from AgBF₄-mediated abstraction of the iodides from **2** (entry 5). Possibly, the rise in activity originates from the enhanced availability of coordination sites for substrate binding at the metal center combined with the modulated electron density at rhodium in the dicationic species, which favors heterolytic H–H bond fission. Further studies towards the scope of the catalyst and its mode of action are currently in progress.

In conclusion, the activation of an electronically unactivated alkane-type C–H bond has been achieved by coordinating two abnormally bound NHC ligands to a rhodium center. The bond activation occurs under remarkably mild conditions (80 °C, no precautions towards air or moisture). No such activation was observed in analogous complexes comprising normally, C2-bound NHC ligands, indicating that C4-bound abnormal carbenes entail an electronic configuration at the metal center that allows for the activation of C–H bonds that are difficult to activate otherwise. Current work in our laboratories is directed towards extending this concept for devising processes that allow for intermolecular C–H bond activation.

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Notes and references

^a School of Chemistry and Chemical Biology, University College Dublin, Belfield, Dublin 4, Ireland. E-mail: martin.albrecht@ucd.ie; Fax: (+)353-17162501.

^b XRD Application Lab, CSEM, Rue Jaquet-Droz 1, CH-2002 Neuchâtel, Switzerland.

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[‡] Typical experimental procedure: The diimidazolium salt **1a** (450 mg, 1.0 mmol), hydrated RhCl₃ (263 mg, 1.0 mmol), and NaOAc (656 mg, 8.0 mmol) were stirred in refluxing acetonitrile (30 mL) for 16 hours. Potassium iodide (664 mg, 4.0 mmol) was added and stirring at reflux was continued for a further hour. The reaction mixture was cooled to room temperature and all volatiles were removed under reduced pressure.

The residue was purified by column chromatography (SiO₂; CH₂Cl₂/acetone, 5:2), thus affording **3a** as a light brown solid (380 mg, 59%). Notably, qualitatively similar results were obtained when salt metathesis was performed with KBr, yielding the bromide analogs of complexes **2** and **3**.

Crystal data for **2a**: C₂₁H₃₃I₂N₆Rh, *M* = 726.24, orthorhombic, *a* = 13.2142(12), *b* = 13.7680(13), *c* = 15.0238(10) Å, *U* = 2733.2(4) Å³, *T* = 173(2) K, space group Pca2₁, *Z* = 4, 18938 total reflections, 4629 unique (*R*_{int} = 0.0593), *R*₁ = 0.0374, *wR*₂ = 0.0846 for *I* > 2σ(*I*); for **3a**: C₄₀H₆₈I₄N₈Rh₂, *M* = 1374.44, orthorhombic, *a* = 15.2889(13), *b* = 15.9079(13), *c* = 20.8008(19) Å, *U* = 5059.1(8) Å³, *T* = 173(2) K, space group Pnma, *Z* = 4, 36742 total reflections, 5201 unique (*R*_{int} = 0.1149), *R*₁ = 0.0751, *wR*₂ = 0.1913 for *I* > 2σ(*I*).

§ HR-MS (ESI⁺): C₁₇H₂₅D₂IN₄ ([*M*–I–2MeCN]⁺) requires 519.046, found 519.04466.

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Rhodium-mediated activation of an alkane-type C–H bond

Anneke Krüger,^a Antonia Neels^b and Martin Albrecht^{*a}

Rhodium-mediated intramolecular activation of an electronically unactivated alkane-type C–H bond takes place when the metal center is coordinated by two abnormal carbene ligands, presumably as a direct consequence of the strong donor ability of this class of N-heterocyclic carbenes.

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