C–H Activation

Coordinatively Unsaturated Cationic and Zwitterionic [Cp*Ru(κ^2-*P,N*)] Complexes: Ligand-Assisted Double-Geminal C–H Bond Activation and Reversible α-H Elimination at Ruthenium**

*Matthew A. Rankin, Robert McDonald,
Michael J. Ferguson, and Mark Stradiotto**

The catalytic cleavage and functionalization of an otherwise unactivated C–H bond within the ligand sphere of a coordinatively unsaturated transition-metal complex is developing into a practical synthetic methodology, despite the inherent difficulty associated with breaking such robust σ bonds.[1] In contrast, the activation of multiple C–H bonds on a single substrate has proven to be a significantly greater challenge; stoichiometric transformations of this type are still uncommon and examples in which this reactivity has been incorporated into useful catalytic cycles are few.[1,2] Given the central role that multiple C–H bond activation processes could play in the functionalization of hydrocarbons and other relatively unreactive molecules, we are targeting new classes

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[*] M. A. Rankin, Prof. Dr. M. Stradiotto
Department of Chemistry
Dalhousie University
Halifax, Nova Scotia B3H 4J3 (Canada)
Fax: (+1) 902-494-1310
E-mail: mark.stradiotto@dal.ca

Dr. R. McDonald, Dr. M. J. Ferguson
X-Ray Crystallography Laboratory
Department of Chemistry, University of Alberta
Edmonton, Alberta T6G 2G2 (Canada)

[**] Acknowledgment is made to the Natural Sciences and Engineering Research Council (NSERC) of Canada (including a Postgraduate Scholarship for M.A.R.), the Canada Foundation for Innovation, the Nova Scotia Research and Innovation Trust Fund, and Dalhousie University for their generous support of this work. We also thank Drs. B. Berno and M. Lumsden (Atlantic Region Magnetic Resonance Center, Dalhousie) for assistance in the acquisition of NMR spectroscopic data. Cp* = η^5-C_5Me_5.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

DOI: 10.1002/ange.200500528

of reactive transition-metal complexes that are designed to effect one or more C–H bond activation steps. On the basis of the propensity of late-transition-metal cations for C–H activation,[3] and the desirable reactivity characteristics commonly associated with P,N ligation,[4] one facet of our research targets coordinatively unsaturated cations supported by κ^2-*P,N*-ligated 1-P*i*Pr$_2$-2-NMe$_2$-indene (**1a**[H]) or 2-NMe$_2$-3-P*i*Pr$_2$-indene (**1b**[H]), as well as structurally related zwitterionic complexes that feature κ^2-*P,N*-ligated 2-NMe$_2$-3-P*i*Pr$_2$-indenide (**1**) in which the ten-π-electron indenide unit functions as a sequestered anionic charge reservoir.[5] We view these coordinatively unsaturated zwitterions as particularly attractive candidates for multiple C–H activation, since the anionic backbone in **1** is poised to accept a proton from a formally cationic metal center following an initial C–H bond activation step, thereby re-establishing coordinative unsaturation at the reactive metal center and enabling subsequent C–H activation processes. As part of this study, we identified the 16-electron cation [Cp*Ru(κ^2-*P,N*-**1b**[H])]$^+$ and the coordinatively unsaturated zwitterion [Cp*Ru(κ^2-*P,N*-**1**)] as important targets (Cp* = η^5-C$_5$Me$_5$); whereas 16-electron complexes of the type [Cp*RuL$_2$]$^+$X$^-$ (L = N- or P-donor fragments) have proven to be effective in the activation of C–H bonds, related P,N-ligated cations have yet to be isolated.[6,7] Herein, we report the preparation of a masked source of [Cp*Ru(κ^2-*P,N*-**1b**[H])]$^+$ that exhibits reversible C–H activation. We also report the facile isomerization of the putative zwitterion [Cp*Ru(κ^2-*P,N*-**1**)] to a [Cp*Ru(H)(κ^2-*P,C*)] hydridocarbene complex in an apparent double-geminal C–H bond activation process that is enabled by the proton-accepting ability of the indenide unit in **1**. Dynamic NMR spectroscopic and reactivity studies involving this hydridocarbene species provide compelling evidence for what appears to be the first documented interconversion of Ru(H)=CH and Ru–CH$_2$ fragments by reversible α-H elimination.

The addition of 0.25 equivalents of [(Cp*RuCl)$_4$] to **1a**[H] afforded **2a**, which was isolated in 92% yield (Scheme 1);[8] treatment of **2a** with NEt$_3$ resulted in a clean isomerization to **2b**. In the pursuit of the 16-electron cation [Cp*Ru(κ^2-*P,N*-**1b**[H])]$^+$ (**3**), complex **2b** was treated with Li(Et$_2$O)$_{2.5}$B(C$_6$F$_5$)$_4$. After 1.5 h, ^{31}P NMR spectroscopic analysis of the reaction mixture confirmed the consumption of **2b** ($\delta_{^{31}P}$ = 54.0 ppm) and the appearance of a single product ($\delta_{^{31}P}$ = 82.3 ppm), which was isolated in 83% yield as a pale-yellow solid. Elemental analysis data obtained from this solid were found to be consistent with **3**, but X-ray diffraction analysis allowed for the identification of this complex as the isomeric C–H activation product **4** (Figure 1),[8b,c] which exhibits interatomic distances in keeping with an aza-ruthenacyclopropane ring.[9] Notably, the ^{1}H and ^{13}C NMR spectra of **4** (300 K) in solution are not consistent with the rigid structure depicted in Figure 1.[8a] The effective mirror-plane symmetry, as well as the low-frequency and broadened ^{1}H NMR resonance of NMe$_2$ (δ = 0.95 ppm, $\Delta\nu_{1/2}$ = 20.3 Hz; cf. $\Delta\nu_{1/2}$ = 4.5 Hz for C$_5$Me$_5$ in **4**), suggest a reversible C–H oxidative addition process involving the NMe$_2$ unit of **4** in which the metalated and free N-C-H fragments exchange rapidly on the NMR timescale at 300 K.[10] On lowering the temperature from 300 to 178 K, the ^{1}H NMR spectra of **4** become increasingly complex and downfield signals attributable to non-metalated NMe groups emerge, thus suggesting a slowing of the aforementioned exchange process. However, neither low-frequency ^{1}H NMR signals attributable to Ru–H or agostic Ru-H-CH$_2$ units, nor new ^{31}P NMR resonances were detected over this temperature range. The apparent reversibility of the intramolecular C–H activation process leading to **4** suggests that this complex could serve as a masked source of

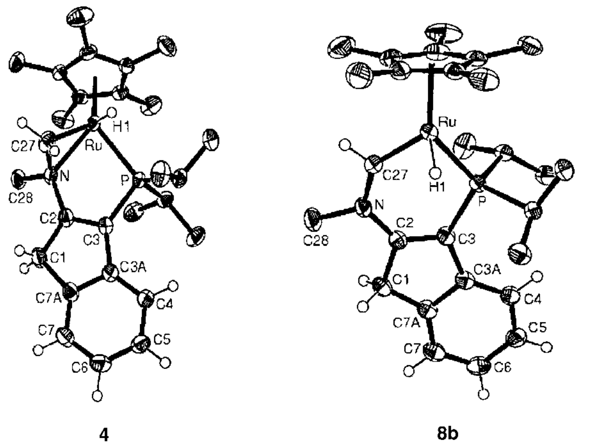
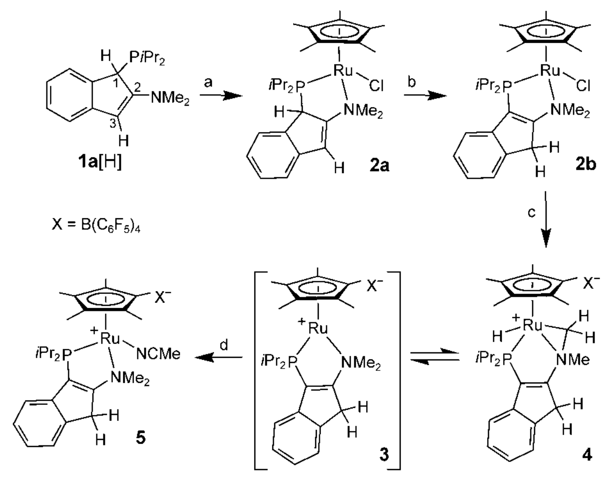


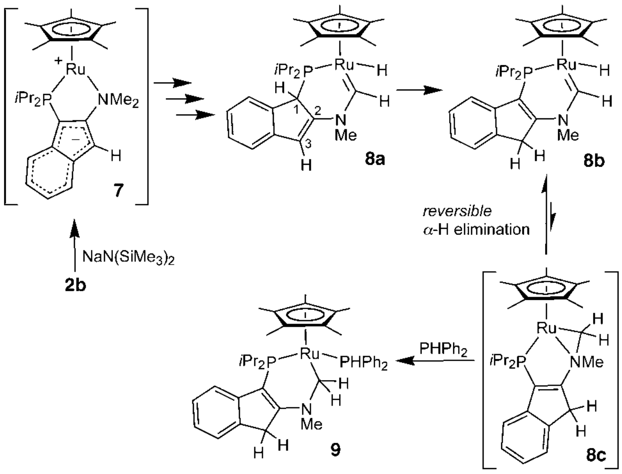
Figure 1. ORTEP diagrams for **4** and **8b** shown with 50% displacement ellipsoids; selected hydrogen atoms and the B(C$_6$F$_5$)$_4^-$ counteranion in **4** have been omitted for clarity. Selected bond lengths [Å] and angles [°]: **4**: Ru–P 2.3094(4), Ru–N 2.136(1), Ru–C27 2.071(2), P–C3 1.809(2), N–C2 1.441(2), N–C27 1.433(2), N–C28 1.484(2), C1–C2 1.503(2), C2–C3 1.336(2); P-Ru-N 82.26(4), Ru-P-C3 101.90(5), Ru-N-C27 67.67(9), Ru-N-C2 116.6(1), Ru-C27-N 72.55(9); **8b**: Ru–P 2.2374(7), Ru···N 3.05, Ru–C27 1.886(2), P–C3 1.812(2), N–C2 1.384(3), N–C27 1.374(3), N–C28 1.475(3), C1–C2 1.512(3), C2–C3 1.362(3); Ru-P-C3 112.74(9), C2-N-C27 123.5(2), C2-N-C28 117.1(2), C27-N-C28 119.4(2), N-C2-C3 129.3(2), P-C3-C2 122.7(2), Ru-C27-N 138.3(2).



Scheme 1. Synthesis and reactivity of the masked [Cp*Ru(κ^2-*P,N*)]$^+$ complex **4**. Reagents: a) 0.25 [(Cp*RuCl)$_4$]; b) NEt$_3$; c) Li(Et$_2$O)$_{2.5}$B(C$_6$F$_5$)$_4$; d) MeCN.

the coordinatively unsaturated target cation **3**. Indeed, treatment of **4** with CH_3CN cleanly yields **3**·CH_3CN (**5**),[11a] and as such we are currently assessing the intermolecular C–H bond activating abilities of **4**.

In an effort to prepare [Cp*Ru(κ^2-*P,N*-**1**)] (**7**), a zwitterionic analogue of **3**, compound **2b** was treated with NaN($SiMe_3$)$_2$ in toluene at ambient temperature (Scheme 2); ^{31}P NMR spectroscopic analysis of the reaction mixture after 24 hours indicated the clean conversion into a single product ($\delta_{31P} = 78.2$ ppm), which was isolated as an orange powder in 84% yield. Elemental analysis data for this powder were in keeping with **7**, but further characterization revealed this material to be the isomeric double-geminal C–H bond activation product **8b**. The identification of **8b** as a hydridocarbene complex was based in part on the observation of ^1H NMR signals at $\delta = 12.1$ and -12.4 ppm, as well as a ^{13}C NMR resonance at $\delta = 244.1$ ppm; the structure of **8b** was subsequently confirmed by X-ray diffraction analysis (Figure 1).[8b,d] The contracted Ru–C27 (1.886(2) Å) and N–C27 (1.374(3) Å) distances in **8b** are comparable to some other N-stabilized Ru=C fragments.[12b–d] These interatomic distances, the short N–C2 distance (1.384(3) Å; cf. N–C28 1.475(3) Å), and the planarity of the nitrogen center are all indicative of significant π-bonding interactions in **8b** extending from the Ru=C fragment through to the indene backbone.



Scheme 2. Synthesis and reactivity of the hydridocarbene complex **8b**.

In monitoring the progress of the reaction, the consumption of **2b** was confirmed after 20 minutes, with the ^{31}P NMR spectrum displaying new signals at $\delta = 67.8$ (possibly corresponding to **7**) and 112.6 ppm (**8a**; ratio ≈ 1:8). After 1 hour, only the resonance at $\delta = 112.6$ ppm was detected, and the features observed in the ^1H NMR spectrum allowed for the tentative assignment of **8a** as the allylic isomer of **8b**.[11b] Over the ensuing 23 hours, **8a** evolved into **8b** in the absence of detectable intermediates. These observations are consistent with the mechanism outlined in Scheme 2,[11c] in which the transiently formed zwitterion **7** undergoes an intramolecular C–H activation process to yield a zwitterionic relative of **4**.[11d] Regioselective proton transfer from ruthenium to the indenide ligand backbone regenerates a coordinatively unsaturated alkylruthenium complex that undergoes a second C–H activation step (α-H elimination) to yield **8a**, which isomerizes to **8b**.[13] The facile rearrangement of **7** to **8b** is remarkable, since double-geminal C–H bond activation to give a Ru=C complex is rare and invariably requires extended heating and loss of a small molecule to facilitate the reaction.[12]

In exploring the reactivity of **8b**, we observed that treatment with $PHPh_2$ provided **9**, a product that can be viewed as an adduct of a 16-electron alkylruthenium species; perhaps the most striking feature in the crystal structure of **9** is the elongated Ru–CH_2 distance (2.124(2) Å) relative to the Ru=C unit in **8b**.[8b,e] The formation of **9** provided indirect evidence of the dynamic interconversion of Ru(H)=CH and Ru–CH_2 fragments (as in **8b** and **8c**[11e]) by reversible α-H elimination. In contrast to the well-established reversibility of β-H eliminations, reversible α-H elimination is rare,[14] and to the best of our knowledge the latter process involving ruthenium has not been documented previously.

Data from 1D- and 2D-exchange spectroscopic (EXSY) ^1H NMR experiments provide definitive spectroscopic evidence for the operation of reversible α-H eliminations involving **8b**.[8a] In the case of ^1H EXSY experiments, irradiation of either the Ru(*H*)=CH or the Ru(H)=C*H* signal in **8b** results in significant positively-phased enhancement of the other resonance, indicating that these two sites are undergoing chemical exchange. Similarly, the ^1H-^1H EXSY spectrum of **8b** exhibits positively-phased off-diagonal exchange cross-peaks that connect the two Ru(*H*)=C*H* environments. The observation of reversible α-H elimination involving ruthenium is significant, as the interconversion of Ru=C and Ru–alkyl species by this mechanism may play a role in the transmutation of olefin metathesis and hydrogenation catalysts in situ.[15]

In conclusion, we have prepared and isolated a masked variant of the first coordinatively unsaturated [Cp*Ru(κ^2-*P,N*)]$^+$ complex, which has proven to be capable of *single* C–H bond activation. By comparison, the putative zwitterion **7** exhibits much more aggressive reactivity with C–H bonds to yield a hydridocarbene by way of a remarkably facile *double* C–H activation process that is enabled by the proton-accepting ability of the ancillary ligand **1**; moreover, an NMR investigation of this hydridocarbene has revealed a reversible α-H elimination process previously undocumented for ruthenium. We are currently developing more cyclometalation-resistant analogues of **7**, with the aim of exploiting the proton-accepting function of **1** in the establishment of new and synthetically useful intermolecular multiple C–H bond activation processes.

Received: February 11, 2005

Keywords: carbene ligands · C–H activation · α-elimination · ruthenium · zwitterions

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[8] a) The Supporting Information contains synthetic procedures and characterization data for all new compounds, NMR spectra for **4** at 300 K, EXSY NMR spectra for **8b**, and X-ray crystallographic details; b) CCDC-259456 (**4**), -259454 (**8b**), and -259455 (**9**·0.5 C_5H_{12}) contain the supplementary X-ray crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif; c) SG = space group, D/R/P = data/restraints/parameters; data for **4**: triclinic; SG = $P\bar{1}$; $a = 10.1928(7)$, $b = 15.617(1)$, $c = 16.321(1)$ Å; $\alpha = 79.3438(9)$, $\beta = 72.1948(9)$, $\gamma = 88.2354(9)°$; $V = 2430.0(3)$ Å^3; $Z = 2$; D/R/P = 9913/0/686; $R_1 = 0.0256$; $wR_2 = 0.0691$; d) data for **8b**: monoclinic; SG = $P2_1/c$; $a = 14.0492(5)$, $b = 16.1616(6)$, $c = 11.0248(4)$ Å; $\beta = 95.5325(7)°$; $V = 2491.6(2)$ Å^3; $Z = 4$; D/R/P = 5088/0/288; $R_1 = 0.0291$; $wR_2 = 0.0742$; e) selected X-ray crystallographic data for **9**·0.5 C_5H_{12} are provided in the Supporting Information.

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[11] a) The identity of **5** was confirmed by comparison with the BF_4^- analogue (**6**), which was prepared from **2b** and $AgBF_4$ in CH_3CN (see the Supporting Information); b) diagnostic ^{1}H NMR resonances for **8a**: $\delta = 12.01$ (br s, 1H; Ru=C-H), 5.83 (s, 1H; C3-H), 4.58 (d, $^2J_{\text{P,H}} = 13.7$ Hz, 1H; C1-H), −11.80 (d, $^2J_{\text{P,H}} = 38.5$ Hz, 1H; Ru-H); c) a detailed representation of this mechanistic proposal is provided in the Supporting Information; d) the viability of **7** as a reactive intermediate is supported by the observation that the related zwitterion $[(\eta^4\text{-cod})\text{Rh}(\kappa^2\text{-}P,N\text{-}\mathbf{1})]$[5] is an isolable species; e) the 18-electron intermediate **8c** is proposed by analogy with **4**; alternative 16-electron intermediates could also be invoked.

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