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**

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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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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

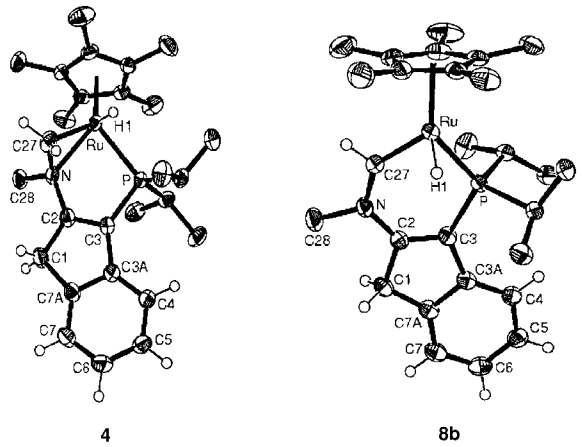
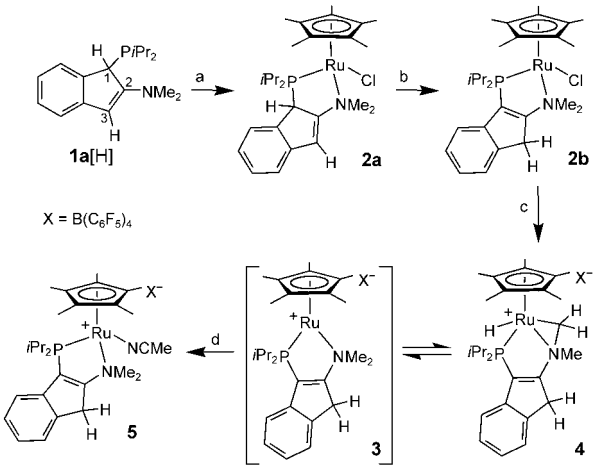


Figure 1. ORTEP diagrams for **4** and **8b** shown with 50% displacement ellipsoids; selected hydrogen atoms and the B(C$_6$F$_5$)$_4^-$ counteranion in **4** have been omitted for clarity. Selected bond lengths [Å] and angles [°]: **4**: Ru–P 2.3094(4), Ru–N 2.136(1), Ru–C27 2.071(2), P–C3 1.809(2), 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).

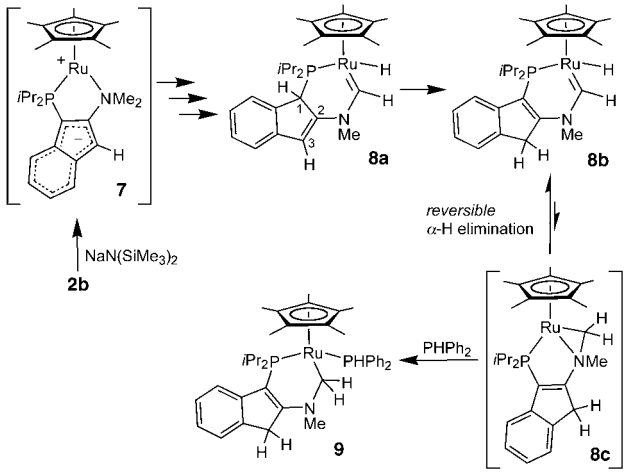


Scheme 1. Synthesis and reactivity of the masked [Cp*Ru(κ^2-*P,N*)]$^+$ complex **4**. Reagents: a) 0.25 [(Cp*RuCl)$_4$]; b) NEt$_3$; c) Li(Et$_2$O)$_{2.5}$B(C$_6$F$_5$)$_4$; d) MeCN.

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

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);



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

^{31}P NMR spectroscopic analysis of the reaction mixture after 24 hours indicated the clean conversion into a single product ($\delta_{^{31}P} = 78.2$ 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.

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.

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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; α = 79.3438(9), β = 72.1948(9), γ = 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; β = 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**: δ = 12.01 (br s, 1H; Ru=C-H), 5.83 (s, 1H; C3-H), 4.58 (d, $^2J_{P,H}$ = 13.7 Hz, 1H; C1-H), −11.80 (d, $^2J_{P,H}$ = 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 [(η^4-cod)Rh(κ^2-*P*,*N*-**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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