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Activation of an Alkyl C−H Bond Geminal to an Agostic Interaction: An Unusual Mode of Base-Induced C−H Activation

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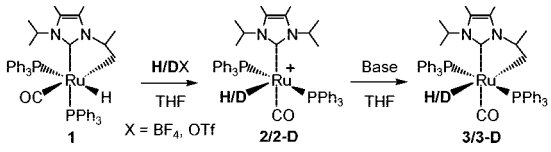
Agostic complexes are widely recognized in transition metal chemistry and are often postulated as transient intermediates on the pathway to C−H activation.[1] C−H bond cleavage may proceed via oxidative addition, σ-bond metathesis, or electrophilic activation.[2] In the last case, interaction with an electron-deficient metal center is thought to confer enhanced acidity on the agostic C−H bond and heterolytic cleavage can occur, often facilitated by an external base.[3] Herein, we report the base-induced C−H activation of an agostic Ru−N-heterocyclic carbene (NHC) complex which, contrary to expectation, proceeds not at the metal-bound C−H agostic but rather at a C−H bond geminal to the agostic interaction.



(1)

Addition of 1.9 equiv of either HBF_4 or HOTf to a THF solution of the previously reported[4] C−H activated complex $Ru(I^iPr_2Me_2)'(PPh_3)_2(CO)H$, **1**, resulted in the facile formation of the BF_4^- and OTf^- salts of the cationic monohydride complex $[Ru(I^iPr_2Me_2)(PPh_3)_2(CO)H]^+$ (**2**, eq 1).[5] An X-ray crystal structure determination of the BF_4^- salt (Figure 1) revealed a distorted octahedral geometry with trans PPh_3 groups and an agostic interaction occupying the sixth coordination site involving the metal and a C−H bond of one of the N−^{i}Pr methyl groups on the carbene. The agostic Ru−C distance (Ru(1)···C(7), 2.825(7) Å) is more than 0.75 Å shorter than the next nearest interaction with an isopropyl carbon (Ru(1)···C(10), 3.591(5) Å), with both the Ru(1)···H(7B) distance (2.05(1) Å) and Ru(1)···H(7B)−C(7) angle (134.8(4)°) in the expected range by comparison to literature precedent.[6] Evidence for the agostic interaction in solution was provided by ^{1}H−^{13}C HMBC spectroscopy, which showed a correlation between the Ru−H signal and one of the two ^{13}C methyl resonances (see Supporting Information, SI). The ^{1}H NMR spectrum proved uninformative as the two sets of ^{i}Pr methyl and methine signals seen at 298 K simply broadened upon cooling to 195 K.

Deprotonation of **2** by strong bases ($I^iPr_2Me_2$, KO^{t}Bu, or $KN(SiMe_3)_2$) led to C−H activation to give **3**, an isomer of **1** with trans PPh_3 ligands (see Figure 1 for the X-ray crystal structure). To assess the mechanism of C−H activation we prepared the Ru-deuteride, **2-D**, by reaction of **1** with DOTf.[7] Deprotonation of **2-D** with $KN(SiMe_3)_2$ gave exclusively **3-D**, indicating that C−H activation in **2-D** does not involve deprotonation of the metal center but rather removal of a proton exclusively from one of the ^{i}Pr arms.

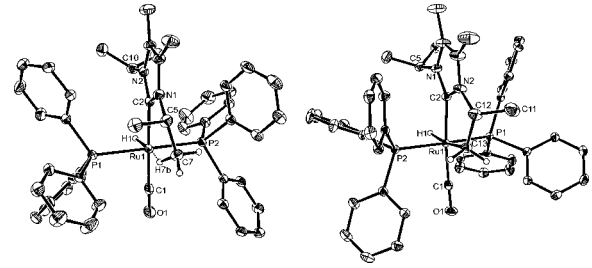


Figure 1. Molecular structures for **2** and **3**. Selected bond lengths (Å) and angles (deg) for (left) **2** Ru(1)−C(2) 2.101(5), Ru(1)−P(1) 2.3661(13), Ru(1)−P(2) 2.3781(12), C(1)−Ru(1)−C(2) 178.4(2) and (right) **3** Ru(1)−C(2) 2.085(2), Ru(1)−C(13) 2.230(3), Ru(1)−P(1) 2.3166(7), Ru(1)−P(2) 2.3302(7), C(2)−Ru(1)−C(13) 77.40(10). Ellipsoids are at the 30% probability level. Solvent, minor disordered components, and hydrogens not involved in coordination are omitted for clarity.

Density functional theory (DFT) calculations[8] have been employed to investigate the mechanism of formation of **3** from **2**. Initial studies focused on a model system comprising $[Ru(I^iPrMe)(PMe_3)_2(CO)H]^+$ (**2′**) and IMe_2 as the external base.[5] Our choice of an NHC as the base was motivated by our interest in the role that these species may play in forming C−H activated complexes in a wide range of TM-NHC systems.[4,9] The Ru−ligand distances within **2′.IMe$_2$** show good agreement with the experimental structural data for **2** (see Figure 2a). In particular, the short Ru···H1 contact (2.01 Å) and elongated C1−H1 bond (1.14 Å) are consistent with an agostic interaction. A close contact to the external IMe_2 molecule is seen, but this actually involves the C1−H2 bond (C2···H2 = 2.40 Å) and *not* the agostic C1−H1 bond. A lengthening of the C1−H2 distance to 1.12 Å is also computed, suggestive of a weakening of this bond. Indeed a reaction profile varying the C2···H2 distance led to the location of a transition state (**TS(2′−3′).IMe$_2$**, E = +12.7 kcal/mol) featuring significant C1···H2 bond elongation (1.64 Å), a shorter C2···H2 distance (1.27 Å), and a shorter Ru···C1 distance (2.63 Å). Interestingly, the original agostic interaction appears reduced on the basis of a longer Ru···H1 distance (2.13 Å) and a shorter C1−H1 bond (1.12 Å). Characterization of **TS (2′−3′).IMe$_2$** showed it leads directly to product **3′.IMe$_2$**, where the IMe_2H^+ imidazolium cation (omitted in Figure 2) is loosely associated with the carbonyl oxygen (O···H2 = 1.97 Å).

In contrast, reaction profiles for the approach of the external IMe_2 toward the agostic hydrogen (H1) did not lead to deprotonation. Instead IMe_2 remains a spectator, and deliberate elongation of the C1−H1 bond only led to oxidative addition ($\Delta E^‡$ = +19.6 kcal/mol) without inducing any approach of the base. The resulting seven-coordinate Ru(IV) intermediate, **4′.IMe$_2$** (E = +18.9 kcal/mol, Figure 2b) can then be deprotonated by IMe_2 to generate

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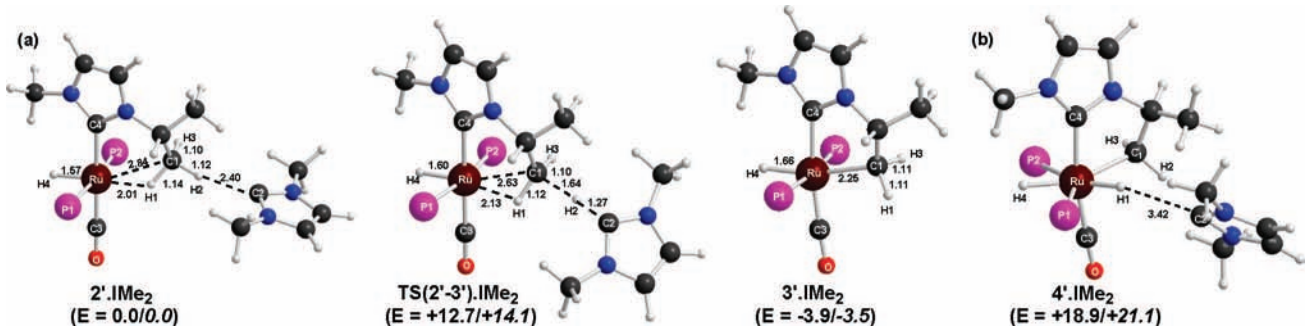

Figure 2. Stationary points for C−H activation in **2′.IMe$_2$** to give **3′.IMe$_2$**: (a) base-assisted process; (b) the oxidative addition intermediate **4′.IMe$_2$**. Selected distances (Å) and relative energies (kcal/mol) are indicated, with computed free energies in italics. PMe_3 substituents and, in **3′.IMe$_2$**, the imidazolium ion are omitted for clarity.

3′.IMe$_2$, although this involves an even higher transition state at +22.5 kcal/mol (see SI).

The easier deprotonation of the C1−H2 bond that is geminal to agostic C1−H1 can be rationalized by computed natural atomic charges. For **2′** (i.e., in the absence of IMe_2) the agostic proton, H1, in fact displays a much lower positive charge (+0.226) than either H2 (+0.295) or H3 (+0.268). This is accentuated in **2′.IMe$_2$** (H1: +0.218; H2: +0.313; H3: +0.251). Thus in **2′** H2 is already the most acidic hydrogen, and this is only enhanced by the approach of a base. This pattern has in fact been noted before in a benzylic Rh pincer complex, where a higher positive charge for a hydrogen atom geminal to an agostic C−H bond was also computed. In that case, however, no reaction with external base was observed experimentally.[10]

Further calculations on **2′** showed that, unsurprisingly, a stronger external base[11] facilitates C−H activation (IMe_4: $\Delta E^{\ddagger} = 10.6$ kcal/mol; $I^iPr_2Me_2$: $\Delta E^{\ddagger} = 9.2$ kcal/mol).[5] Computation of the full experimental system (i.e., **2** plus $I^iPr_2Me_2$) showed that including the full PPh_3 ligands increased the barrier to 11.8 kcal/mol, presumably due to steric effects that impede approach of the base.[12] Despite this, the computed barrier for the full system is consistent with it being readily surmountable at room temperature. In contrast, weaker external bases entail much higher barriers (e.g., NMe_3: $\Delta E^{\ddagger} = +25.4$ kcal/mol), while with H_2O no equivalent C−H activation process could be defined.

In summary, we have demonstrated facile deprotonation of a nonagostic alkyl C−H bond to give a C−H activation product. Our results contrast with examples in the literature where base-assisted intramolecular electrophilic activation involves agostic C−H bonds. In many cases an internal base is employed (e.g., acetate) which is geometrically predisposed to target the agostic bond.[13] Assistance by external base has been modeled elsewhere, for example, in the intermolecular activation of CH_4 in the Catalytica process.[14] In that case a σ-CH_4 complex was formed and subsequent C−H activation was reported only for the bond directly interacting with the metal center. The present computational studies indicate that the base-induced cleavage of a nonagostic C−H bond is possible and indeed preferable to cleavage of an agostic C−H bond, despite the perception that the latter should be more acidic. This insight adds a further mode of C−H activation to what is already a mechanistically rich and diverse area.

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Note Added after ASAP Publication. This paper was published ASAP on March 12, 2009 with typographical errors in References (2) and (3). The corrected version was published ASAP on March 17, 2009.

Supporting Information Available: Spectroscopic data for **2** and **3**, NMR spectra of **2**, X-ray crystallographic files (CIF format) for **2** (CCDC 718933) and **3** (CCDC 718934). Computed Cartesian coordinates and energies; full ref 8. This material in available free of charge via the Internet at http://pubs.acs.org.

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(5) NHC abbreviations: $I^iPr_2Me_2$ = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene, I^iPrMe = 1-isopropyl-3-methylimidazol-2-ylidene, IMe_2 = 1,3-dimethylimidazol-2-ylidene, IMe_4 = 1,3,4,5-tetramethylimidazol-2-ylidene.

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