

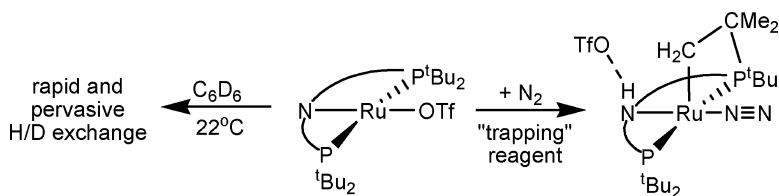
Communication

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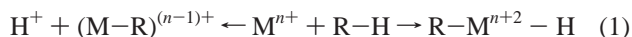
N₂ Provides Insight into the Mechanism of H–C(sp³) Bond Cleavage

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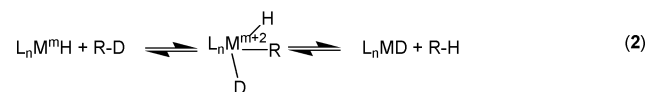
Execution of a difficult reaction like H–C(sp³) bond activation is facilitated by effecting substrate pre-coordination using a donor functionality in the substrate. This is evident in several recent synthetic organic reports^{1–3} and pervades the chemistry where a transition metal species cleaves C–H bonds of its own ancillary ligand.^{4–6} Here there are two variants (eq 1) of the H–C cleavage reaction by Mⁿ⁺: (i) full oxidative addition (producing an intermediate containing both hydride and CR₃ on Mⁿ⁺²) and (ii) C–H heterolysis, where a Brønsted base removes H as a proton so that oxidation to Mⁿ⁺² never mediates the reaction and the product has an unchanged oxidation state, Mⁿ⁺.



In practice, these mechanistic alternatives have been difficult to distinguish.^{7,8} We provide here an example which is mechanistically more revealing, especially when density functional theory (DFT) calculations supplement experiments.

Readily synthesized (PNP)Ru(OTf) **1** (PNP = κ^3 -N(SiMe₂CH₂P^t-Bu₂)₂) exhibits NMR spectra fully consistent with a planar, four-coordinate geometry and a triplet electronic ground state, as previously elucidated for (PNP)RuCl.⁹ The paramagnetically shifted ¹⁹F{¹H} NMR resonance for the triflate anion in **1** (shifted 56 ppm to –24 ppm) verifies that OTf occupies the fourth coordination site in C₆D₆. In C₆D₆, **1** shows remarkably facile exchange of all its ligand hydrogens with solvent deuterium. Within 20 min at 22 °C one sees growth of C₆D₅H and a dramatic decline in the intensities (¹H NMR) of ^tBu and SiCH₃ (90% at each), and CH₂ (10%). The H/D exchange occurs at an undiminished rate in the presence of 5 equiv of a hindered base (2,6-di-*tert*-butylpyridine) ruling out the possibility of catalysis by adventitious acid (HF or HOTf) derived from the synthesis of **1**. No H/D exchange is observed with (PNP)RuCl in C₆D₆, even after 24 h at 65 °C. The Ru to carbon distance for each of these hydrogens in ground state (PNP)RuCl is 3.7 Å (^tBu), 4.2 Å (SiCH₃), and 3.4 Å (CH₂); therefore, significant ligand distortion is required to bring each carbon within bonding distance of Ru (~2.1 Å).

Conventionally, H/D exchange of ligands in a metal complex with a deuterated reagent D–R requires at least one hydride on the metal and proceeds via oxidative addition (eq 2).^{10–13} While



oxidative addition to the Ru of **1** could be envisioned, deuteration of the PNP ligand carbons would require oxidative addition of that bond followed by a second 2-electron oxidation of the benzene C–D bond; participation by the implied Ru^{VI} seemed implausible.

Mechanistic insight into this facile H/D exchange was forthcoming from the unexpected reaction of 14-valence electron **1** with

N₂. The addition of N₂ (1 atm) to a yellow benzene solution of **1** at 22 °C results in an immediate color change to orange and the complete consumption of **1** to form a single diamagnetic product, **2**. Species **2** shows two inequivalent ³¹P nuclei (AX pattern, J_{AX} = 283 Hz, characteristic of trans phosphines). The ¹H NMR spectrum shows no hydride resonance and shows signals fully consistent with a product devoid of symmetry, where the phosphine donors are made inequivalent by metalation of one ^tBu group.

The X-ray diffraction structure of this product (Figure 1) reveals cleavage of one ^tBu C–H bond, with carbon bonded to Ru but the H bound to the PNP nitrogen. N₂ coordinates trans to the resulting amine, and the site trans to the Ru–C bond is unoccupied (with the closest approaching methyl group, C18, at 2.97 Å). Triflate has dissociated from Ru, but its oxygen hydrogen bonds to the amine proton (O···N = 3.11 Å). This is thus a net heterolytic splitting of the H–C(sp³) bond that leaves the metal oxidation state unaltered at +2. The above conclusions are supported by the observation of a linear Ru ← N≡N unit and a pyramidal nitrogen with a long (2.23 Å) Ru–N1 bond, consistent with an amine functionality. The N–H proton is assigned to a broadened, unit intensity ¹H NMR signal observed at +3.4 ppm. Surprisingly, the Ru–P distance in the strained four-membered ring is the shorter of the two Ru–P bonds.

Compound **2** shows a gradual decline in the intensity of all ¹H NMR signals (^tBu, SiMe, NH, CMe₂, and CH₂) under argon at 22 °C in C₆D₆, along with growth of the signal of C₆D₅H, but without formation of new products even after 5 days. This is consistent with a very low level (hence slow deuteration) conversion of **2** back to (PNP)Ru(OTf) by loss of N₂, although **2** does not detectably lose N₂ under vacuum (12 h) at 22 °C. The observations show that intramolecular scrambling of incorporated deuterium in **2** is faster than incorporation of D from C₆D₆ into **2**.

The calculated binding energy of N₂ to **1** (3 Scheme 1) is only 1.4 kcal/mol. How then can the weak ligand N₂ (weak σ -donation and weak π -acidity) “cause” cleavage of an alkyl C–H bond? As the H/D exchange does not require N₂, and because compound **2** shows a slower exchange rate, the role of N₂ here must be to trap an active intermediate and also to be in equilibrium with that species. This active species should also be formed via a unimolecular equilibrium with **1**.

DFT calculation of the energies of spectroscopically undetected C–H cleavage isomers **4** and **5** reveal that the Ru(II) species **5** is 18.0 kcal/mol more stable than **4**; i.e., the N–H isomer is significantly favored even without the hydrogen bonding present in **2**. Addition of N₂ to **1** in frozen *d*₈-toluene shows complete formation of **2** by –40 °C, but earlier, at –60 and –50 °C, one sees two equal-intensity ³¹P{¹H} NMR signals, the intensity changes of which track one ¹⁹F NMR signal (distinct from the ¹⁹F signal of **2**). These signals irreversibly decline at the same rate as the temperature is raised. The essential feature of this intermediate is that the two inequivalent phosphorus nuclei have a small J_{PP}

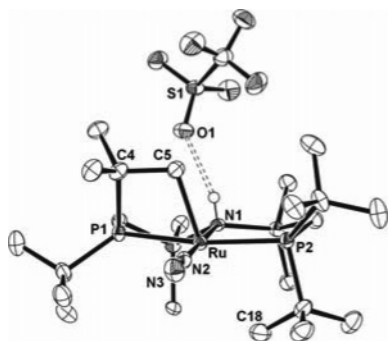
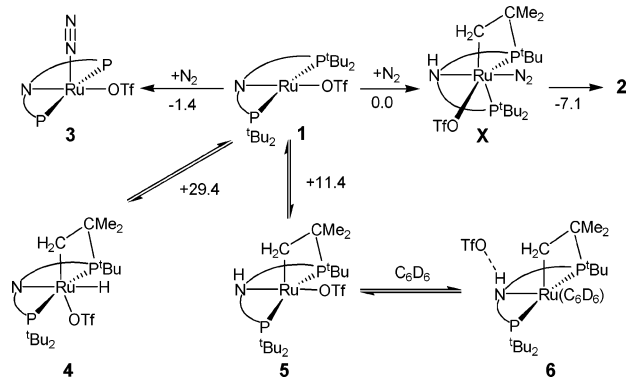


Figure 1. ORTEP drawing (50% probability ellipsoids) of **2** showing selected atom labeling. For clarity, all H's on carbon have been deleted. The hydrogen bonding between NH and the triflate oxygen is illustrated. Selected structural parameters: Ru–N2, 1.904(3) Å; Ru–C5, 2.109(4) Å; Ru–N1, 2.230(3) Å; Ru–P1, 2.338(1) Å; Ru–P2, 2.372(1) Å; N2–N3, 1.115(5) Å; N1···O1, 3.112(4) Å; P1–Ru–C5, 69.00(11)°; Ru–P1–C4, 87.24(12)°; Ru–N2–N3, 178.3(3)°; N1–Ru–N2, 179.38(12)°.

Scheme 1. Electronic Energies (kcal/mol relative to **1**) of a Number of Possible Ligand C–H Cleavage Isomers and N₂ Adducts of **1**



(<25 Hz) and therefore an unresolved splitting in the low-temperature ³¹P{¹H} NMR spectra. This is a product of 1,3 H migration, from C to N, consistent with no ¹H NMR hydride signal being seen at –60 and –50 °C. Calculations (DFT) of nine alternative candidate structures for this intermediate revealed that only **X** (Scheme 1) lies within 3 kcal/mol of the reagents, and also accommodates the observed unresolvably small *J*(PP′) by virtue of having the phosphorus nuclei not mutually trans ($\angle\text{P–Ru–P} = 117.8^\circ$ in **X**). Approximate facial PNP coordination is rendered energetically accessible by amide-to-amine conversion.¹⁴ This structure has the features of H and CH₂ being syn on the Ru–N bond but having triflate neither dissociated from Ru nor migrated to its hydrogen-bonding site. The activation energy for this migration, in a nonpolar (toluene) environment, is suggested to be the reason that intermediate **X** can be detected at –50 °C.

We propose that the H/D exchange takes place via species **6**, the Ru/benzene substructure of which is intentionally left vague in the scheme, based on currently available results. What the N₂ trapping and the DFT calculations do establish is the thermal accessibility of an unsaturated Ru^{II} species with a labile H (on N), which provides access to benzene for either a σ -bond metathesis or an oxidative addition reaction, to mix H and D in **6**. While we only isolate a species where the P^tBu C–H bond is cleaved, a previous report of the elimination of benzene from (PNP)₂YPh by abstraction of a chelate ring CH₂ hydrogen shows the accessibility of other PNP hydrogens.¹⁵

It is probably not mere coincidence that C–H cleavage reactivity (but not catalysis of exchange with C₆D₆) was reported for Ir in a not-low oxidation state, +3, and with a triflate ligand, via the

compound Cp*Ir(CH₃)(OTf)(PMe₃). Only the hydride Cp*Ir(H)–(OTf)(PMe₃) catalyzes H/D exchange, consistent with the generalization made above (eq 2).^{16–18} Since none of this reaction chemistry is observed for (PNP)RuCl, it is clearly dependent on multiple characteristics of triflate, including its anionic charge, its good leaving-group character, and its ability to hydrogen bond to the N–H proton of the product. It is also tempting to envision that N₂ is critical to spin pairing of the two unpaired electrons in **1** which have been suggested as the reason that these planar 14-electron species do not have agostic interactions; agostic interactions are attractive species on the path to C–H cleavage, especially heterolytic cleavage, since an agostic H would be expected to be Brønsted acidic (cf. the acidity of (η^2 -H₂)M). Finally, it is important to recognize that the active functional role played by the basic PNP amide nitrogen serves to change reaction thermodynamics, most notably by avoiding oxidation state +4 in **2**.^{19,20}

The small favorable energy for the overall reaction forming **2** is consistent with our initial surprise that a ligand as weak as N₂ could “trap” an intermediate involved in the H/D exchange of **1** and facilitate dissociative loss of OTf from **X** to produce **2**. Furthermore, compound **1** is a rare example of a non-hydride-containing transition metal complex that undergoes catalytic H/D exchange.

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Supporting Information Available: Full synthetic and spectroscopic details for all compounds; DFT-optimized geometries on all molecules discussed in the text crystallographic details (CIF) for compound **2**. This material is available free of charge at via the Internet at <http://pubs.acs.org>.

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