Communication

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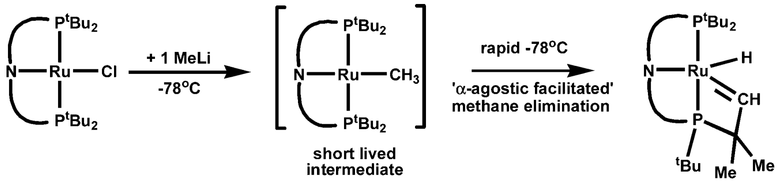

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COMMUNICATIONS

[(^{t}Bu$_2$PCH$_2$SiMe$_2$)$_2$N]RuCH$_3$: The Origin of Extremely Facile, Double H−C(sp^3) Activation Generating a "Hydrido-Carbene" Complex

Michael J. Ingleson, Xiaofan Yang, Maren Pink, and Kenneth G. Caulton*

Department of Chemistry and Molecular Structure Center, Indiana University, Bloomington, Indiana

Received May 6, 2005; E-mail: caulton@indiana.edu

The reactivity of the Ru(II) complex (PNP)RuCl (PNP = (^{t}Bu$_2$PCH$_2$SiMe$_2$)$_2$N$^-$) is of significant interest due to its formal 14-electron configuration, low-coordination number (4), and triplet ($S = 1$) ground state.[1] Recent work has demonstrated that despite the electron deficiency of the (PNP)RuCl moiety,[1,2] the Ru(II) center can act as a reducing agent, with halide for azide salt metathesis resulting in rapid metal oxidation and nitride formation (eq 1).[3] This seemingly paradoxical behavior can be attributed to the absence of any π acid ligands, the presence of the π basic amide, and the electron-rich nature of the two phosphine donors.

$$\text{(PNP)Ru}^{\text{(II)}}\text{Cl} \xrightarrow[-\text{TMSCl}]{+\text{TMSN}_3} \text{(PNP)Ru}^{\text{(IV)}}\text{N} + \text{N}_2 \qquad (1)$$

We are currently interested in extending our studies to examine the effects that installing a strong σ donor [X]$^-$ ligand has on the ground-state electronic configuration (triplet versus singlet), on molecular structure (planar versus "cis divacant" octahedral) and on subsequent reactivity of the four-coordinate (PNP)RuX. Herein we report preliminary experimental and theoretical findings for the methylation of (PNP)RuCl.

Treating (PNP)RuCl with a stoichiometric equivalent of MeLi at −78 °C in THF ultimately affords the hydrido−carbene complex **1** via the double intramolecular C−H activation of a single ^{t}Bu methyl group (Figure 1). Important NMR spectroscopic features (d_8-THF, 233 K) include the carbene =CH resonances at 13.7 ppm (^{1}H, d of d) and 276 ppm (^{13}C{^{1}H} s), a hydride signal as a "*pseudo*" triplet at −5.1 ppm along with the ^{31}P{^{1}H} spectrum exhibiting an AX pattern with a large $^2J_{PP}$ coupling of 338 Hz. Attempts to more fully characterize **1** were frustrated by its instability in solution above 273 K, resulting in intractable mixtures. The double activation of a single pendant CH$_3$ group of a pincer ligand by a Ru(II) center to generate a carbene complex has precedence (Figure 1 **(i)**), albeit requiring more severe conditions (boiling ^{t}BuOH in the presence of base) than for formation of **1**.[4] Furthermore, double C−H activation, leading to hydrido−carbenes, is well-known and has widespread literature precedent.[5−12]

The reaction proceeds via an observed red, transient complex which within minutes at −78 °C completely converts to **1**. We assign this intermediate as (PNP)RuMe, **A** (Scheme 1), but attempts at gaining any direct spectroscopic evidence have failed due to its short lifetime even at low temperatures. However, the immediate addition of benzonitrile successfully "traps" **A** as (PNP)Ru(PhCN)-Me, **2**. A mechanism to **1** can be proposed, involving stepwise C−H cleavage of a proximal CH$_3$ group, via an unobserved cyclometalated complex **B** (Scheme 1). To probe this facile reaction[13] and the relative energies of the spin isomers, DFT calculations (using the full PNP ligand) were undertaken.

For (PNP)RuMe, the triplet/singlet spin isomer energy difference is small (the triplet isomer is more stable by 3.4 kcal mol^{-1}), in contrast to the parent chloride complex ($\Delta E = 10.0$ kcal mol^{-1}). The singlet isomer (Figure 2) shows considerable deviation from planarity (N−Ru−CH$_3$ angles, singlet = 145° and triplet = 173.8°). Of particular note in the singlet structure is a 'tilted' methyl group due to one agostic Ru−H contact (2.15 Å to H84) and a number of close methyl C to ^{t}Bu proton distances (shortest at 2.75 Å). The calculated structure is approaching that previously found for the transition state of a concerted reductive elimination process,[14,15] where asymmetry in the M−CH$_3$ interaction enables a CH$_3$ valence orbital to have an improved orientation for forming a bonding interaction with a proximal group. In this case, the agostic interaction to H84 aligns the fourth CH$_3$ orbital away from Ru and more suitable for the exceptionally low barrier to H abstraction from ^{t}Bu; the view in Figure 2 is nearly down the C_3 axis of the agostic methyl on Ru. No methyl "canting" or α-agostic interactions are observed in the triplet state due to the necessary metal orbital now being singly occupied. With a triplet/singlet energy difference for (PNP)RuMe of only 3.4 kcal mol^{-1}, a low minimum energy crossing point between the potential energy surfaces of the two spin isomers would be expected.[16] This would lead to a kinetically competent concentration of singlet, "pre-organized" (with respect to CH$_4$ loss) (PNP)RuMe. The conversion of **A** to **B** is calculated to be essentially thermoneutral (i.e. less than ±2.0 kcal mol^{-1}) and entropically driven by irreversible CH$_4$ loss. This mechanism is supported by the formation of *perprotio* **1** and CD$_3$H on use of d_3-MeLi. At no point was there any spectroscopic indication for the formation of (PNP)Ru(=CH$_2$)(H), the product from the more conventional outcome of an *alpha* agostic interaction (namely C−H cleavage of the α-agostic bond). The calculated endoergic electronic energy for conversion to (PNP)Ru(=CH$_2$)(H) (+10.4 kcal mol^{-1}) shows that this C−H activation pathway is unfavorable; therefore, an undetected isomerization between **A** and (PNP)Ru(=CH$_2$)H is unlikely. The "thermoneutral" nature of the formation of **B** along with the orbital pre-organization in the singlet state of **A** could account for the absence of spin-blocking effects in the rapid formation of diamagnetic **1** on methylation of paramagnetic (PNP)-RuCl.

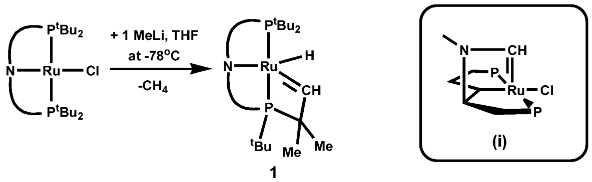

Figure 1. (Left) Formation of hydrido−carbene **1**, from (PNP)RuCl. (Right) Related ruthenium pincer carbene complex, **i**.

Analogous calculations performed for **B** produced a singlet ground state (3.0 kcal mol^{-1} below its triplet) and a geometry-optimized structure that is significantly closer to a "cis-divacant" octahedron (N−Ru−C angle of 114.8°) than that for singlet (PNP)-RuMe.[17] We attribute this to the constraints imposed by the asymmetrical four-membered metallacycle destabilizing the square planar conformer. An α-agostic interaction is also observed in **B**,

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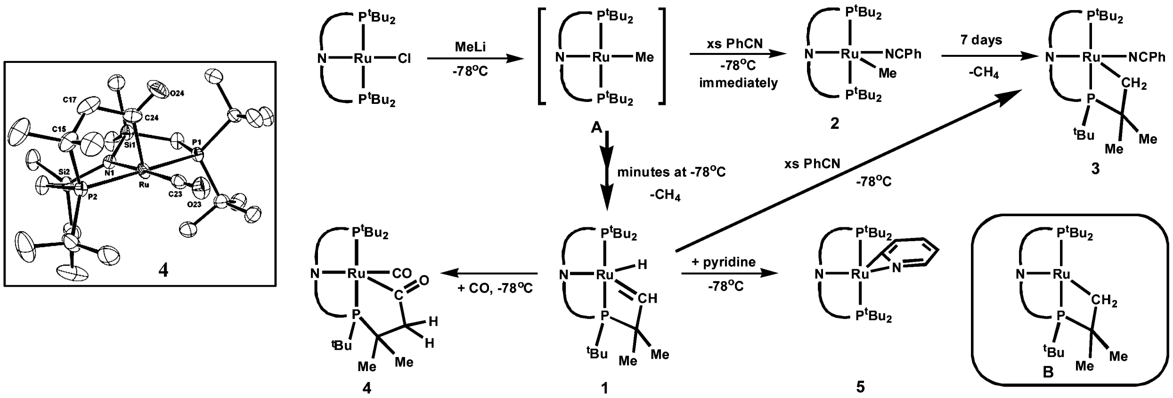
Scheme 1 Formation and Reactivity of the Hydrido−Carbene, **1**; Inset, ORTEP View of the Non-hydrogen Atoms of **4** (50% Probability Ellipsoids, Disorder in **4** Omitted for Clarity)[a]



[a] Selected bond lengths (Å) and angles (deg): Ru−N1, 2.129(2); Ru−C23, 1.881(4); Ru−C24, 2.075(5); C23−O23, 1.101(4); C24−O24, 1.190(6); N1−Ru−C24, 100.02; N1−Ru−C23 177.47(12); P1−Ru−P2, 173.25(3); Ru−C24−C17, 118.3(3).

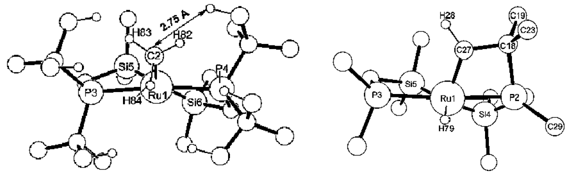


Figure 2. DFT geometry optimized structures (with Ru eclipsing the amide N in each case) of: (Left) Singlet (PNP)RuMe, selected bond lengths (Å) and angles (deg) Ru1−C2, 2.02; Ru−H84, 2.15; N7−Ru1−C2, 145.0. (Right) **1**, selected bond lengths (Å) and angles (deg): Ru1−C27, 1.84; H79−Ru1−N6 150.4; N6−Ru1−C27, 112.2; H79−Ru1−C27, 97.0.

which could facilitate the negligibly (3.4 kcal mol^{-1}) endothermic second C−H bond activation. The transformation of **B** to **1** results, apart from a reduction in the Ru−C bond length, in only minor geometrical changes in the metallacycle (in **A**, a Ru−C distance of 2.08 Å decreases to 1.84 Å in **1**, similar to that previously reported for structurally characterized **(i)**, Ru═C 1.868(4) Å).[4] The optimized geometry (Figure 2) for **1** is a distorted square-based pyramid with the hydride approximately trans to the amide nitrogen, in agreement with the observed chemical shift of the hydride in **1**. The facile formation of **1** from **A** is related to the behavior of [(Cy$_2$PCH$_2$SiMe$_2$)$_2$N]RuH$_3$ on dehydrogenation, that also undergoes multiple ligand sp^3 C−H activation, generating the allyl complex, [Cy$_2$PCH$_2$SiMe$_2$NSiMe$_2$CH$_2$PCy(C$_6$H$_8$)]Ru.[2]

Preliminary reactivity studies on **1** (Scheme 1) suggest that it can be viewed as a "resting state" for the four-coordinate cyclometalated alkyl complex **B**, with facile hydride migration from the metal center back to carbon occurring before any further reactivity. This has been previously termed "masking" and reduces the coordinative unsaturation at a metal center.[18] The addition of excess benzonitrile to a THF solution of **1** at −78 °C cleanly afforded the five-coordinate cyclometalated alkyl complex **3**. Alternatively, **2** slowly converts into **3** over the course of one week at 25 °C, with concomitant evolution of methane. Addition of CO to **1** at −78 °C yielded an insertion product, the acyl−carbonyl complex, **4**. An X-ray diffraction structure determination (Scheme 1) confirmed a square pyramidal structure with the acyl group in the axial position and the CO trans to the amide as expected to establish a stabilizing push/pull interaction. The structural features in **4** are unremarkable.[19,20] This supports the theoretical findings with initial C−H activation occurring at an axial ^{t}Bu leading to the calculated structure of **1**, with the carbene in the "*pseudo*" axial position (Figure 2). Addition of excess pyridine to **1** at −78 °C led, in time of mixing, to the green, diamagnetic η^2-pyridyl complex, (PNP)Ru(η^2-NC$_5$H$_4$) **5**, where C−H activation at the ortho position effected the opening of the metallacycle of **B**.

In summary, the unusually low barrier observed here for CH$_4$ loss is a consequence of the agostic interaction, which is in turn made possible by the high degree of unsaturation of (PNP)RuMe in its very low-lying singlet state. The "α-agostic-facilitated" CH$_4$ elimination mechanism (supported by the lack of any observed α-agostic C−D cleavage) suggests a different consequence in **A** of this interaction from that more often considered (and proposed here to connect **1** and **B**), the conversion to a hydrido−carbene.

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Supporting Information Available: Full synthetic and spectroscopic details for all compounds, along with crystallographic details (CIF) for compound **4**, together with DFT-optimized geometries on molecules described in the text (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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