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# *Communications to the Editor*

## β- and γ-Dehydrogenation of N$^i$Pr$_2$ in the Formation of the Azaallyl (Cp*Ru)$_2$($^i$PrNC$_3$H$_5$)(μ-H)

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The reactivity of CpRuL$_n$X compounds increases as *n* decreases.[1-6] The extreme case of *no* neutral donor ligands yields compounds (e.g., (Cp*RuOR)$_2$[7] and [Cp*Ru(H)$_2$]$_2$[8]) which display impressive abilities for reaction with aryl and vinyl C–H bonds. We report here the outcome of an attempt to create a related unsaturated species by replacement of halide by amide in [Cp*Ru($\mu_3$-Cl)]$_4$.[9]

Reaction of LiN$^i$Pr$_2$ with [Cp*Ru($\mu_3$-Cl)]$_4$ (N:Ru = 1:1) in THF occurs within 0.5 h at ambient temperature. After extraction with pentane, one product is isolated (74% yield) which can be further purified by sublimation (8 × 10$^{-5}$ Torr at 90 °C). Proton (and $^{13}$C) NMR studies[10] clearly reveal two inequivalent Cp* rings and *one* $^i$Pr group with diastereotopic methyls. Additionally, $^1$H NMR signals at 2.05 (s, 3H), 0.24 (d, *J* = 5.1 Hz, 1H), and –2.77 (d of d, *J* = 5.1 Hz, 3.3 Hz, 1H) ppm indicate that the second isopropyl group has been fundamentally transformed by the metal center. Only five hydrogens remain on this *C*$_3$ fragment. The resonance at –2.77 ppm also shows coupling[11] to a bridging[12] hydride (–6.09 ppm, d, *J* = 3.3 Hz, 1H). The proton-coupled $^{13}$C NMR spectrum shows, for the dehydrogenated isopropyl group, one methyl, one methylene, and one quaternary carbon (eq 1). The CH$_2$ group has an unusual upfield carbon chemical shift (3.5 ppm) and bears the hydrogens at 0.24 and –2.77 ppm; these have $^1J_{C-H}$ values of 155 and 143 Hz, respectively. These data indicate that the *C*$_3$ fragment is in fact an isopropenyl group and suggest that one of the methylene C–H bonds is involved in an agostic interaction.

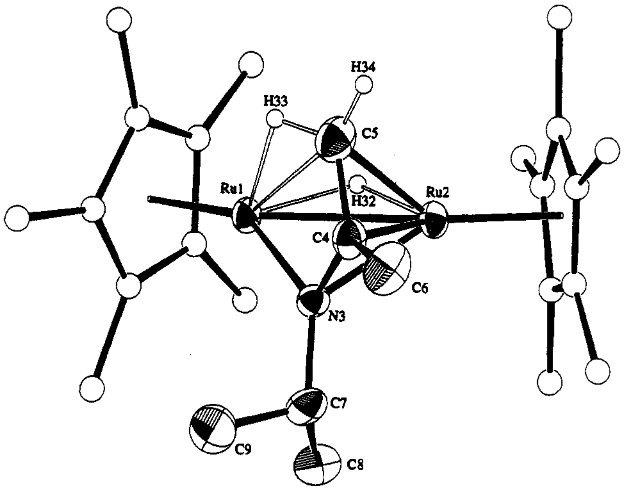
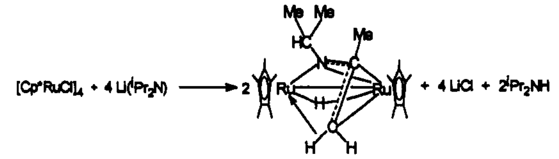
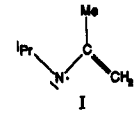


**Figure 1.** ORTEP drawing of (Cp*Ru)$_2$(H)($^i$PrNC$_3$H$_5$), showing selected atom labeling. Only selected hydrogens are shown. Selected structural parameters (bonds in angstroms, angles in degrees): Ru–Ru, 2.743(1); Ru(1)–N(3), 2.124(4); Ru(2)–N(3), 2.161(4); Ru(2)–C(4), 2.107(6); Ru(2)–C(5), 2.192(7); Ru(1)–C(5), 2.622(7); N(3)–C(4), 1.385(7); C(4)–C(5), 1.418(9); Ru(1)–H(32), 1.70(7); Ru(2)–H(32), 1.76(7); Ru(1)–H(32)–Ru(2), 105(3); Ru(1)–N(3)–Ru(2), 79.60(15); Ru(1)–C(5)–Ru(2), 68.81(18).



(1)

A single-crystal X-ray structure determination[13] (Figure 1) revealed a bridging nitrogen, one of whose substituents is indeed an isopropenyl group. Alternatively, this ligand can be considered as an azaallyl (**I**). In fact, the bond lengths of N(3)–C(4) (1.385(7) Å) and C(4)–C(5) (1.418(9) Å) fall in the range between single and double bonds.[14] While the nitrogen is bound equally to both metals, the two vinylic carbons are bound to Ru(2). There is one $\mu_2$-hydride ligand. The compound is thus formally Ru$_2$$^{II}$, and the Ru–Ru separation is 2.743(1) Å. To this point, Ru(1) is unsaturated in comparison to Ru(2), but this deficiency is alleviated by an agostic interaction[15] from H(33) to Ru(1) (Ru(1)–H(33) = 2.24(7) Å).[16] The agostic interaction is the cause of the unusual chemical shifts of H(33) and C(5).



**I**

Reaction 1 is thus not simply a β-hydrogen migration (which would generate the imine[17] ligand $^i$PrN=CMe$_2$); it also involves the loss of a γ-hydrogen.[18] The other key point is that the product incorporates only one of the two amide groups (per Ru$_2$ unit)

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(9) Reaction with NaNHPh proceeds to give *cis*-[Cp*Ru($\mu$-NHPh)]$_2$. See: Blake, R. E.; Heyn, R. H.; Tilley, T. D. *Polyhedron* **1992**, *11*, 709.

(10) Spectroscopic data are as follows. $^1$H NMR (C$_6$D$_6$, 300 MHz, 25 °C): δ 2.62 (sept, *J* = 6.6 Hz, 1H, CH), 2.05 (s, 3H, NC*Me*), 1.89 (s, 15H, C$_5$*Me*$_5$), 1.81 (s, 15H, C$_5$*Me*$_5$), 1.63 (d, *J* = 6.6 Hz, 3H, CH*Me*Me), 0.64 (d, *J* = 6.6 Hz, 3H, CHMe*Me*), 0.24 (d, *J* = 5.1 Hz, 1H, C*H*H$_{agostic}$), –2.77 (d of d, *J* = 5.1 Hz, *J* = 3.3 Hz, 1H, H$_{agostic}$), –6.09 (d, J = 3.3 Hz, 1H, Ru-*H*-Ru). $^{13}$C NMR (C$_6$D$_6$, 125 MHz, 25 °C): δ 97.96 (s, N*C*(Me)CH$_2$), 86.50 (mult, *C*$_5$Me$_5$), 76.67 (mult, *C*$_5$Me$_5$), 53.10 (d of sept, $^1J_{CH}$ = 132.9 Hz, $^2J_{CH}$ = 3.5 Hz, *C*HMe$_2$), 26.73 (q of d of q, $^1J_{CH}$ = 125.8 Hz, $^2J_{CH}$ = 4.9 Hz, $^3J_{CH}$ = 1.6 Hz, CHCH$_3$*C*H$_3$), 19.75 (q of t, $^1J_{CH}$ = 125.8 Hz, $^3J_{CH}$ = 2.0 Hz, NC*C*H$_3$), 13.02 (q, *J* = 125.8 Hz, C$_5$(*C*H$_3$)$_5$), 11.87 (q, *J* = 125.8 Hz, C$_5$(*C*H$_3$)$_5$), 3.46 (d of d of mult, $^1J_{CH}$ = 155.1 Hz, $^1J_{CHagostic}$ = 142.6 Hz, *C*H$_2$).

(11) All assignments of $^1$H–$^1$H coupling were confirmed by selective homonuclear decoupling experiments.

(12) There is no evidence for Ru–H stretching vibrations in the 1700–2200-cm$^{-1}$ region of the infrared spectrum.

(13) Crystallographic data (–90 °C): *a* = 10.939(1) Å, *b* = 15.242(2) Å, *c* = 8.422(1) Å, α = 101.78(1)°, β = 109.75(1)°, γ = 83.58(1)° with *Z* = 2 in space group P$\bar{1}$. *R*(*F*) = 0.0370. There is evidence for some disorder of the Cp* carbons on Ru(2).

(14) For comparison with an azaallyl in a similar bonding mode, see: Polm, L. H.; van Koten, G.; Vrieze, K.; Stan, C.; van Tunnen, W. C. J. *J. Chem. Soc., Chem. Commun.* **1983**, 1177.

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employed in the reaction. By following the progress of eq 1 by $^{1}$H NMR in THF-$d_8$, we observed the production of HN$^{i}$Pr$_2$. This establishes the fate of the remaining $^{i}$Pr$_2$N moiety[19] and one of the two aliphatic hydrogens (the other presumably being the $\mu_2$-hydride). We suggest that steric constraints frustrate the formation of [Cp*Ru(N$^{i}$Pr$_2$)]$_2$,[9] and the metals therefore achieve saturation by dismantling one N$^{i}$Pr$_2$ ligand. Thus, both $\beta$- and $\gamma$-hydrogen abstractions occur, along with deprotonation of the metal(s) by N$^{i}$Pr$_2$ (free or coordinated). The ability of ruthenium to doubly dehydrogenate the pendant isopropyl fragment at 25 °C reveals the high reactivity that can be developed by maintaining a phosphine-free environment. It is also essential that we have replaced chloride ligands (which make the metal saturated in [Cp*Ru($\mu_3$-Cl)]$_4$) with ligands which cannot be $\mu_3$ and thus leave the metal unsaturated.

Metal attack on an amide $\beta$-hydrogen is established to be the origin of carbidic carbon incorporation during CVD production of thin films from Ti(NR$_2$)$_4$ precursors.[20] The present solution study is relevant to the beginning step in such fragmentation of a pendant alkyl group. Such reactivity is also an element of hydrodenitrogenation chemistry.[21]

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**Supplementary Material Available:** Tables of positional parameters and all bond lengths and angles for (Cp*Ru)$_2$($^{i}$PrNC$_3$H$_5$)(H); stereodrawings with atoms labeled (5 pages). Ordering information is given on any current masthead page.

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