Reversible Intramolecular Alkyl C−H Bond Activation, Alcohol Dehydrogenation, and Trans−Cis Dihydride Isomerization in Ruthenium N-Heterocyclic Carbene Complexes

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Summary: Thermolysis of $Ru(IEt_2Me_2)(PPh_3)_2(CO)H_2$ *(*IEt_2Me_2 *= 1,3-bis(ethyl)-4,5-dimethylimidazol-2-ylidene) in the presence of* $CH_2{=}CHSiMe_3$ *results in C−H activation of an* $NCH_2CH_2{-}H$ *bond; the process can be reversed by* H_2 *or alcohols to give different isomers of the starting dihydride complex.*

It is now apparent that N-heterocyclic carbenes (NHCs) are not necessarily innocent, inert ligands that simply help to stabilize reactive and potentially catalytically useful metal complexes.[1] In a number of cases with late transition metals, NHCs have been found to undergo facile intramolecular C−H bond activation[2] and, in one case reported by us under more forcing conditions, C−C bond activation.[3] In all but two of these examples, N-substituted phenyl and mesityl groups are present. Herrmann[4] has reported the C−H bond cleavage of 1,3-bis(cyclohexyl)imidazol-2-ylidene (ICy) by $[(\eta^5\text{-}C_5Me_5)IrCl_2]_2$ (the direct activation product was not observed, since rapid β-hydrogen elimination afforded a 1-(2-cyclohexenyl)-3-cyclohexylimidazol-2-ylidene ligand in the ultimate product), while Nolan and co-workers have very recently described double C−H activation of 1,3-bis(*tert*-butyl)imidazol-2-ylidene (I^tBu) at rhodium.[5] We now describe an unexpected intramolecular C−H bond activation of the alkyl NHC IEt_2Me_2 (1,3-bis(ethyl)-4,5-dimethylimidazol-2-ylidene) in $Ru(IEt_2Me_2)(PPh_3)_2(CO)H_2$ (**1**), which generates a stable and fully characterized product resulting from $NCH_2CH_2{-}H$ activation. C−H cleavage is reversible, although the dihydride isomer which is formed depends on the hydrogen source employed.

The reaction of $Ru(PPh_3)_3(CO)H_2$ with a slight excess of IEt_2Me_2 at 70 °C for 20 h results in displacement of the PPh_3 ligand trans to Ru−H and formation of the monocarbene complex $Ru(IEt_2Me_2)(PPh_3)_2(CO)H_2$ (**1**), which was isolated as a colorless solid in 48% yield. The ^1H NMR spectrum of the complex in benzene-d_6 showed two doublet of triplet hydride resonances at δ −6.38 and −9.99, each coupled to two cis ^{31}P nuclei and the other inequivalent hydride. Two sets of ethyl signals are testimony to the fact that the carbene ligand does not rotate at room temperature. The equivalent nature of the phosphines was confirmed by the appearance of a singlet in the $^{31}P\{^1H\}$ NMR spectrum.[6] The geometry of **1** contrasts with that found for $Ru(IMes)(PPh_3)_2(CO)H_2$ (**2**; IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene), where the carbene is trans to one of the phosphine groups.[3] To confirm the geometry of **1**, the X-ray crystal structure was determined, as depicted in Figure 1.[7] Despite the disorder[7] in **1**, the crystal structure is unambiguous. Concentrating on the major disordered component (80% occupancy), it is clear that the geometry at ruthenium is distorted from regular octahedral with a trans P−Ru−P angle of 164.25(3)°. The Ru−C(carbene) bond distance (2.168(2) Å) is considerably longer than the value for Ru−IMes found in **2** (2.0956(17) Å). This presumably reflects both the longer M−C(alkyl NHC) versus M−C(aryl NHC) bond found by others[8] and the orientation of the IEt_2Me_2 ligand trans to hydride.

Treatment of **1** with $CH_2{=}CHSiMe_3$ at 50 °C results in alkene hydrogenation ($CH_3CH_2SiMe_3$ was detected

(1) See for example: (a) McGuinness, D. S.; Saendig, N.; Yates, B. F.; Cavell, K. J. *J. Am. Chem. Soc.* **2001**, *123*, 4029. (b) Danopoulos, A. A.; Tsoureas, N.; Green, J. C.; Hursthouse, M. B. *Chem. Commun.* **2003**, 756. (c) Dioumaev, V. K.; Szalda, D. J.; Hanson, J.; Franz, J. A.; Bullock, R. M. *Chem. Commun.* **2003**, 1670.

(2) (a) Hitchcock, P. B.; Lappert, M. F.; Pye, P. L. *J. Chem. Soc., Chem. Commun.* **1976**, 644. (b) Hitchcock, P. B.; Lappert, M. F.; Pye, P. L. *J. Chem. Soc., Chem. Commun.* **1977**, 196. (c) Hitchcock, P. B.; Lappert, M. F.; Pye, P. L.; Thomas, S. *J. Chem. Soc., Dalton Trans.* **1979**, 1929. (d) Hitchcock, P. B.; Lappert, M. F.; Terreros, P. *J. Organomet. Chem.* **1982**, *239*, C26. (e) Huang, J.; Stevens, E. D.; Nolan, S. P. *Organometallics* **2000**, *19*, 1194. (f) Danopoulos, A. A.; Winston, S.; Hursthouse, M. B. *Dalton* **2002**, 3090. (g) Trnka, T. M.; Morgan, J. P.; Sanford, M. S.; Wilhelm, T. E.; Scholl, M.; Choi, T.-L.; Deng, S.; Day, M. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **2003**, *125*, 2546. (h) Chilvers, M. J.; Jazzar, R. F. R.; Mahon, M. F.; Whittlesey, M. K. *Adv. Synth. Catal.* **2003**, *345*, 1111. (i) Giunta, D.; Hölscher, M.; Lehmann, C. W.; Mynott, R.; Wirtz, C.; Leitner, W. *Adv. Synth. Catal.* **2003**, *345*, 1139. (j) Abdur-Rashid, K.; Fedorkiw, T.; Lough, A. J.; Morris, R. H. *Organometallics* **2004**, *23*, 86.

(3) Jazzar, R. F. R.; Macgregor, S. A.; Mahon, M. F.; Richards, S. P.; Whittlesey, M. K. *J. Am. Chem. Soc.* **2002**, *124*, 4944.

(4) Prinz, M.; Grosche, M.; Herdtweck, E.; Herrmann, W. A. *Organometallics* **2000**, *19*, 1692.

(5) Dorta, R.; Stevens, E. D.; Nolan, S. P. *J. Am. Chem. Soc.* **2004**, *126*, 5054.

(6) See the Supporting Information for spectroscopic data.

(7) Crystal data for **1**: $C_{46}H_{48}N_2OP_2Ru$, M_r = 807.87, λ = 0.710 73 Å, monoclinic, space group *Cc*, a = 23.5760(2) Å, b = 9.9740(1) Å, c = 18.2220(2) Å, β = 113.239(1)°, T = 150 K, U = 3937.20(7) Å^3, Z = 4, D_c 1.363 Mg/m^3, μ = 0.517 mm^{-1}, $F(000)$ = 1680, crystal size 0.15 × 0.10 × 0.10 mm, 8871 unique reflections (R(int) = 0.0583), 7674 observed reflections ($I > 2\sigma(I)$), 8871/10/497 data/restraints/parameters, R1 = 0.0355 and wR2 = 0.0735 (observed data), R1 = 0.0470 and wR2 = 0.0773 (all data), maximum peak/hole 0.373 and −0.425 e Å^{-3}. Atoms Ru1, C1, and O1 exhibited 80:20 disorder with their primed labeled counterparts. The hydride ligand, H1, was located and refined at 1.6 Å from the metal centers. No attempt was made to locate the second hydride in this complex, due to the disorder present in the model. Crystallographic data have been deposited with the Cambridge Crystallograpic Database, CCDC No. 237882.

(8) Viciu, M. S.; Navarro, O.; Germaneau, R. F.; Kelly, R. A., III; Sommer, W.; Marion, N.; Stevens, E. D.; Cavallo, L.; Nolan, S. P. *Organometallics* **2004**, *23*, 1629.

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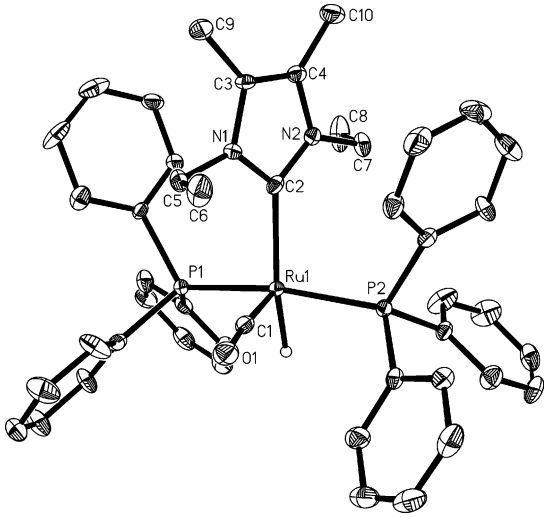


Figure 1. Molecular structure of the major component of **1** (thermal ellipsoids represented at 30% probability). Selected bond lengths (Å) and angles (deg): Ru(1)−C(2), 2.168(2); Ru(1)−C(1), 1.878(4); P(1)−Ru(1)−P(2), 164.25-(3); C(1)−Ru(1)−C(2), 99.85(17).

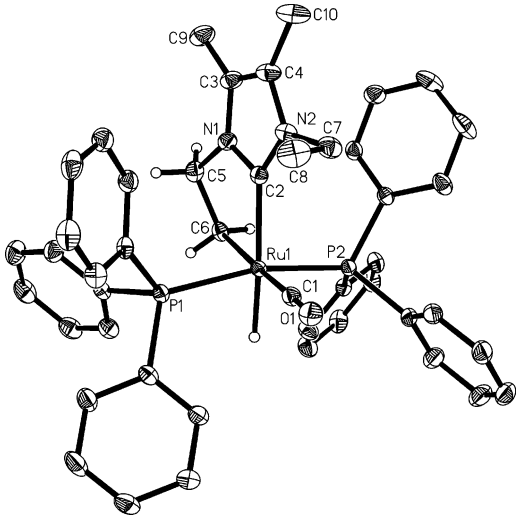
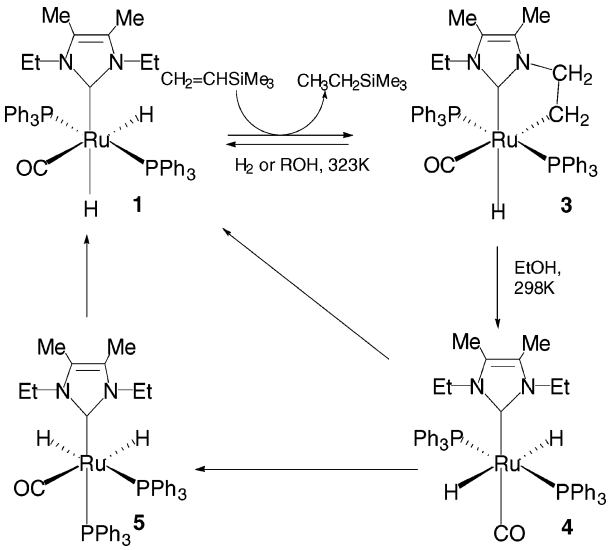


Figure 2. Molecular structure of **3** (thermal ellipsoids represented at 30% probability). Selected bond lengths (Å) and angles (deg): Ru(1)−C(2), 2.0893(18); Ru(1)−C(6), 2.2107(17); P(1)−Ru(1)−P(2), 164.789(17); C(5)−C(6)−Ru-(1), 109.95(11).

Scheme 1. Interconversion of Complexes 1, 3, 4, and 5



by NMR in quantitative yield) and affords Ru(IEt_2Me_2)′-(PPh_3)$_2$(CO)H (**3**), resulting from NCH_2CH_2−H bond activation (Scheme 1). Compelling evidence for the C−H cleavage reaction was provided by the ^{1}H NMR spectrum of **3**, which shows one hydride triplet (δ −7.01, $^2J_{HP}$ = 23.1 Hz), and the ^{13}C{^{1}H} NMR spectrum, which exhibited four distinct ethyl resonances, most tellingly a triplet at δ 8.3 ($^2J_{CP}$ = 11.0 Hz).[6] The X-ray crystal structure of **3** (Figure 2) displays clearly the metalated five-membered ring of the activated IEt_2Me_2 ligand, with a Ru−C bond length of 2.2107(17) Å and a Ru−C(6)−C(5) angle close to that expected for an unstrained sp^3-hybridized methylene group (109.95(11)°).[9]

Our results compare closely to those of Morris and co-workers, who recently reported that Ru(PPh_3)$_3$HCl reacts with 1,3-di-*tert*-butylimidazol-2-ylidene (I^tBu) in refluxing thf to give a highly reactive coordinatively unsaturated species postulated as Ru(I^tBu)(PPh_3)$_2$; while this could not be isolated, it was trapped by H_2 to give Ru(I^tBu)(PPh_3)$_2H_2$, which itself is stabilized through an agostic interaction with one of the NHC *tert*-butyl groups.[2j] Most pertinent is the fact that in neither the 14- nor the 16-electron species was there any evidence of NHC C−H activation. Given that the Morris system is more electron rich than ours, it is possible that the CO ligand in **1** and **3** plays a key role in allowing C−H activation to take place.

Unexpectedly, dissolution of **3** in ethanol at room temperature resulted in the rapid precipitation of **4**, the *trans*-dihydride isomer of Ru(IEt_2Me_2)(PPh_3)$_2$(CO)H_2. Although this complex displayed poor solubility in common NMR solvents (benzene-d_6, thf-d_8), it proved to be more soluble in pyridine-d_5, allowing assignment of the stereochemistry by 1- and 2-D multinuclear NMR.[6] Thus, **4** displayed a single triplet integrating to 2H in the hydride region of the proton spectrum (δ −4.90, $^2J_{HP}$ = 20.3 Hz) and a singlet in the ^{31}P{^{1}H} NMR spectrum. Due to the rapid isomerization of **4** in solution (see below), ^{13}C assignments for the carbene (δ 183.6) and carbonyl (δ 209.9) could only be made by a ^{13}C−^{1}H HMBC experiment. Stirring **3** with EtOD yielded an isotopic mixture of **4** with deuterium incorporated in one of the ethyl arms of the NHC and onto the metal to give the hydride deuteride complex. Complex **4** proved to be thermally unstable in solution and rapidly isomerized (in pyridine-d_5) to a mixture of **4**, **1**, and the all-cis isomer **5** after only 5 min at 323 K (1:1.2:1 ratio). After 40 min, **1** was essentially the only hydride species observable (Figure 3). The rate of

(9) Crystal data for **3**: $C_{46}H_{46}N_2OP_2Ru$, M_r = 805.86, λ = 0.710 73 Å, monoclinic, space group $P2_1/a$, a = 16.9680(1) Å, b = 10.5800(1) Å, c = 23.1530(2) Å, β = 109.720(1)°, T = 150 K, U = 3912.60(6) Å^3, Z = 4, D_c 1.368 Mg/m^3, μ = 0.520 mm^{-1}, F(000) = 1672, crystal size 0.15 × 0.15 × 0.10 mm, 8901 unique reflections (R(int) = 0.0497), 7511 observed reflections with $I > 2\sigma(I)$, 8901/5/479 data/restraints/parameters, R1 = 0.0276 and wR2 = 0.0629 (observed data), R1 = 0.0375 and wR2 = 0.0671 (all data), maximum peak/hole 0.356 and −0.642 e Å^{-3}. In the final least-squares cycles, atoms H1, H5A, H6A, and H6B were located and refined at fixed distances of 1.6 Å (H1−Ru1) and 0.89 Å (H−C) for the subsequent pairs, from the relevant parent atoms. Crystallographic data have been deposited with the Cambridge Crystallograpic Database, CCDC No. 237883.

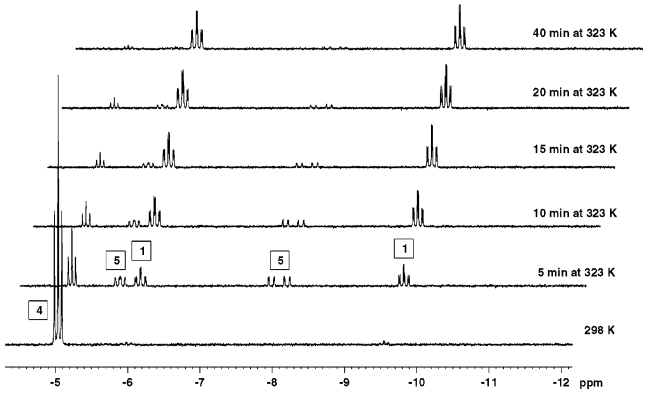


Figure 3. Hydride region of the ^{1}H NMR spectrum (400 MHz, pyridine-d_5) showing interconversion of **5**, **4**, and **1**.

isomerization was unaffected by the addition of 10 equiv of PPh_3 or by a change of solvent from pyridine to toluene.

Isolation of **4** only appears to be possible due to its rapid precipitation from solution at room temperature. When a sample of **3** in benzene-d_6/EtOH (**3**:EtOH = 1:100) was warmed to 323 K, only a mixture of **3** and **1** was observed (by ^{1}H NMR) with no evidence for either **4** or **5**.[10] Other benzene/alcohol solutions gave similar results, the rate of re-formation of **1** following the order ^{i}PrOH > EtOH > MeOH (^{t}BuOH gave no reaction). With MeOH or EtOH, we were unable to detect either acetaldehyde or formaldehyde as the expected products of the alcohol dehydrogenation reaction, although the appearance of a new doublet hydride resonance at δ −17.24 ($^2J_{HP}$ = 22.0 Hz) in the proton NMR spectrum suggested that aldehydes may undergo reaction with **1**. While additional experiments are in progress to identify the ruthenium-containing species that are formed, we note that addition of excess paraformaldehyde to a solution of **1** does indeed give the same hydride-containing species at δ −17.24.

In conclusion, we have described a rare case of intramolecular C−H bond activation of an alkyl-substituted N-heterocyclic carbene. The applications of this system in C−C bond-forming reactions will be reported in due course.[11]

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Supporting Information Available: Text giving synthesis and characterization data of compounds **1**, **3,** and **4** and X-ray crystallographic data for **1** and **3**, including tables of atomic coordinates, bond lengths and angles, anisotropic displacement parameters, hydrogen coordinates and U_{eq} values, and packing diagrams. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) Complex **3** also re-forms **1** in quantitative yield in benzene solution under 1 atm of H_2 at 323 K over a period of 12 h.

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