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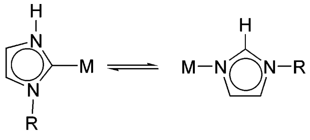
Ruthenium Induced C−N Bond Activation of an N-Heterocyclic Carbene: Isolation of C- and N-Bound Tautomers

Suzanne Burling, Mary F. Mahon, Rachael E. Powell, Michael K. Whittlesey,* and Jonathan M. J. Williams

Department of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, U.K.

Received August 2, 2006; E-mail: chsmkw@bath.ac.uk

N-Heterocyclic carbenes (NHCs) are now ubiquitous in organometallic chemistry, largely due to their exceptional ability to impact favorably in many catalytic processes.[1] However, there are now several examples illustrating that NHCs are not necessarily an inert class of ligands, being susceptible to C−H activation at the N-substituents[2] and reductive elimination.[3] Moreover, the precursor azolium salts are themselves subject to both normal (C2) and abnormal (C4/5) activation.[4] Crabtree and Eisenstein have recently discussed the possibility that C-bound imidazoles such as **1** could have some existence in metalloprotein chemistry, where only the N-bound tautomer **2** has so far been observed.[5]



1 **2**

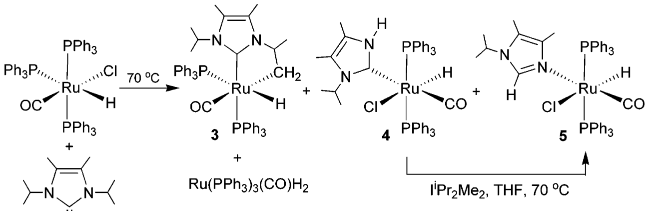
Only a single example of this tautomerism (for the parent species where R = H) has been reported and involved an acid induced transformation of **2** to **1**.[6] We now report the first example of C- to N-bound tautomerism in which an N-heterocyclic carbene is directly involved. Moreover, the C-bound 1-isopropyl-4,5-dimethylimidazol-2-ylidene complex (**4**, Scheme 1) is formed by a remarkable metal induced C−N bond activation reaction of an isopropyl substituted NHC precursor. Both **4** and the N-bound species **5** have been isolated and structurally characterized.[7]

Upon reaction of $Ru(PPh_3)_3(CO)HCl$ with 2 equiv of $I^iPr_2Me_2$ (1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene, Scheme 1) in THF at 70 °C for 16 h, a mixture of products was formed consisting of the C−H activated carbene complex $Ru(I^iPr_2Me_2)'(PPh_3)_2(CO)H$ **3**,[8] $Ru(PPh_3)_3(CO)H_2$, **4**, and **5** in a ratio of ca. 5:3.5:2:1, respectively.[9]

Multinuclear 1- and 2-D NMR experiments confirmed that **4** is the C-2 bound 1-isopropyl-4,5-dimethylimidazol-2-ylidene complex $Ru(C{-}I^iPrHMe_2)(PPh_3)_2(CO)HCl$, resulting from elimination of propene from one of the $N{-}^iPr$ groups. The ^1H NMR spectrum of **4** displayed a low-field singlet resonance at δ 9.73 for the N−H proton, which integrated in a 1:1:6:1 ratio with resonances at δ 5.43, 0.51, and −14.78 for the methine, methyl, and RuH groups, respectively. The formation of propene was also apparent in the proton NMR spectrum. Conclusive evidence for **4** being a carbene containing complex was provided by the appearance of a triplet C-2 resonance at δ 180.6 ($^2J_{CP} = 15.6$ Hz) in the $^{13}C\{^1H\}$ NMR spectrum. In contrast, complex **5** showed no such signal but displayed a singlet at δ 136.5 consistent with the presence of an imidazole C−H moiety.

Continued heating of the mixture for a total of 5 days (70 °C) resulted in complete conversion to **5**, which was shown by X-ray crystallography to be the tautomeric imidazole compound $Ru(N{-}I^iPrHMe_2)(PPh_3)_2(CO)HCl$ (Figure 1). Complex **4** was subsequently isolated by reaction of $Ru(PPh_3)_3(CO)HCl$ with $I^iPr_2Me_2$ under slower, lower temperature conditions (THF, 50 °C, 6 days) and similarly structurally characterized (Figure 1).

Scheme 1. Formation and Conversion of C- and N-Bound Tautomers **4** and **5**



While most of the metrics associated with the Ru-ancillary ligands vary little between the two structures, the expected widening of the N−C−N angle (103.91(15)° cf. 111.3(2)°) and contraction of the Ru−CO distance (1.884(2) Å cf. 1.844(3) Å) on going from **4** to **5** are most apparent. The proximity of H(1a) to Cl(1) in **4** and H(2) to Cl(1) in **5** (H(1a)···C(1) 2.41 Å, H(2)···Cl(1) 2.49 Å) suggest the presence of hydrogen-bonding interactions, which contribute to rationalizing the approximate coplanarity of the heterocyclic ring and the nonphosphine ligands in both structures. There was no evidence in either case for the presence of the conformers generated by a 180° rotation of the imidazole ring.

When the reaction of $Ru(PPh_3)_3(CO)HCl$ with $I^iPr_2Me_2$ was repeated but under 1 atm of H_2, none of complexes **3**, **4**, or **5** were formed. As H_2 often reverses the intramolecular C−H activation of NHC ligands,[8,10] this result implies that initial C−H cleavage plays a key role in the C−N activation reaction to afford **4**. In accord with this, when **3** was heated (16 h, 70 °C) with 1 equiv of an added "chloride source" (either $Ru(PPh_3)_3(CO)HCl$ or (PPN)-Cl), **4** and **5** were formed, along with some $Ru(PPh_3)_3(CO)H_2$.

The propensity of $I^iPr_2Me_2$ to undergo "direct" C−H activation[8] also appears to be important. In earlier work, we noted that IEt_2Me_2 (1,3-bis(ethyl)-4,5-dimethylimidazol-2-ylidene) is less prone to C−H cleavage than the isopropyl carbene, requiring the presence of a sacrificial alkene to accept the released H_2.[10] In accord with this lower reactivity, analogous C−N cleavage was not seen when IEt_2Me_2 was heated with $Ru(PPh_3)_3(CO)HCl$, with only the substitution product $Ru(IEt_2Me_2)(PPh_3)_2(CO)HCl$ **6** being observed. It is worth noting that the only other reported example of C−N activation of an NHC ligand, described by Cloke and Caddick following the reaction of I^tBu (1,3-bis-*tert*-butylimidazol-2-ylidene) with a low valent Ni precursor, also involves prior C−H activation, although, in this case, the two processes could be followed sequentially.[11]

To gain an insight into a possible mechanism for the conversion of **4** to **5**, a series of experiments was carried out on isolated samples of **4** and observations were made as follows:

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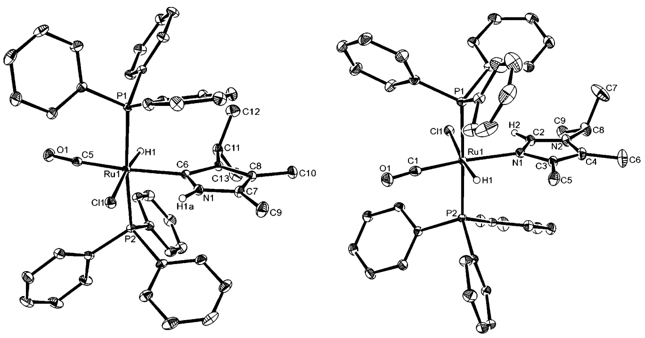

Figure 1. Molecular structures together with selected bond lengths (Å) and angles (deg) for (left) **4** (Ru(1)−C(6) 2.1282(18), Ru(1)−C(5) 1.884(2), N(1)−C(6) 1.346(2), N(2)−C(6) 1.366(2), N(1)−C(6)−N(2) 103.91(15)) and (right) **5** (Ru(1)−N(1) 2.1816(18), Ru(1)−C(1) 1.844(3), N(1)−C(2) 1.323(3), N(2)−C(2) 1.351(3), N(1)−C(2)−N(2) 111.3(2)). Ellipsoids are shown at 30% probability level.

(i) Heating **4** in the presence of 2 equiv of I^{i}Pr$_2$Me$_2$ (C_6D_6 or THF-d_8, 70 °C) affords complex **5** along with traces of Ru$(PPh_3)_3$(CO)H_2. The same transformation occurred upon heating with either I^{t}Bu or IEt$_2$Me$_2$, although the latter reaction was accompanied by formation of the simple substitution product **6**. Simply heating **4** alone in THF did not generate **5**.

(ii) Heating a 1:2 mixture of **4** + I^{i}Pr$_2$Me$_2$ side-by-side with a 1:2:5 solution of **4** + I^{i}Pr$_2$Me$_2$/PPh$_3$ (THF-d_8, 70 °C, 5 days) resulted in a 20% less conversion through to **5** in the latter reaction.

(iii) **5** was not formed upon heating **4** in the presence of 1,3-diisopropyl-4,5-dimethylimidazolium chloride, DBU, or a proton sponge.

We have attempted to prove that the N−H in **4** is the source of the C−H in **5** through N−H/N−D exchange using D_2O. However, these experiments proved inconclusive as not only partial H/D exchange was observed at nitrogen but also deuterium was incorporated into the Ru−H bond.

In summary, we have described a rare example of C−N bond activation of an NHC and the subsequent unprecedented transformation of the resultant C-2 bound carbene complex **4** to the N-1 bound product **5**. The need for free carbene in converting **4** to **5** is consistent with a base-catalyzed process. Our results provide experimental support to Crabtree and Eisenstein's computational study, which show that while C-binding is favored on moving to heavier metals, the presence of CO trans to the heterocycle stabilizes the N-bound form. This is the case with **4** and **5**.

This report of C−N cleavage and C-/N-tautomerism, alongside other recent examples detailing NHC insertion reactions,[12] illustrate new carbene degradation pathways which are of clear relevance to the catalysis and ionic liquid communities.

Acknowledgment. We thank the EPSRC for funding (S.B.) and Johnson Matthey plc for the loan of hydrated ruthenium trichloride.

Supporting Information Available: Spectroscopic data for compounds **3**−**6**, CIF files giving X-ray crystallographic data for **4** (CCDC code 616583) and **5** (CCDC code 616582). This material in available free of charge via the Internet at http://pubs.acs.org.

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JA065582K