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C−C and C−H Bond Activation Reactions in N-Heterocyclic Carbene Complexes of Ruthenium

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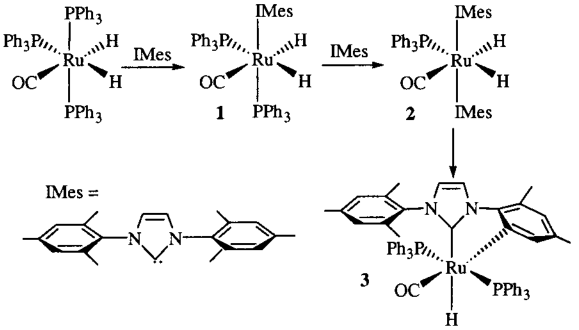
Carbon−carbon single bonds are among the most unreactive functional groups with respect to activation by transition metal complexes. Hence, a number of strategies have been adopted to enhance their reactivity, such as relief of ring strain or the attainment of aromaticity.[1] However, examples of metal insertion into unstrained C−C bonds are still rare. Milstein and co-workers have used phosphine-based substrates to "pre-coordinate" unstrained sp^2−sp^3 C−C bonds proximal to a reactive metal center for activation and have shown that C−C activation can be both kinetically and thermodynamically more favorable than the more common C−H activation, depending upon the choice of metal, ligand set, etc.[2] We report here the unprecedented activation of an unstrained C−C bond, as well as C−H bond cleavage, of the *N*-heterocyclic carbene (NHC) bis(1,3-(2,4,6-trimethylphenyl)imidazol-2-ylidene) (IMes) upon reaction with $Ru(PPh_3)_3(CO)H_2$. NHC ligands have been the subject of considerable interest in homogeneous catalysis where they have yielded highly active complexes for a range of processes, including metathesis polymerization and C−C coupling.[3] However, a number of recent reports have shown that NHC ligands can undergo degradation via activation or elimination reactions, which has important implications for their use in catalysis.[4]

Thermolysis of a benzene solution of $Ru(PPh_3)_3(CO)H_2$ with 3 equivalents of IMes at 80 °C for 14 days led to the sequential formation of $Ru(IMes)(PPh_3)_2(CO)H_2$ (**1**) and $Ru(IMes)_2(PPh_3)(CO)H_2$ (**2**). Continued heating at 110 °C for a further 2 days afforded the C−C insertion product **3** resulting from cleavage of an Ar−CH_3 bond (eq 1).[5] Complex **3** was isolated (96% yield) by crystallization from benzene/ethanol and characterized by multinuclear NMR spectroscopy. The Ru−H appears as a triplet at −6.99 ppm (J_{HP} = 28.4 Hz) in the ^1H NMR spectrum, demonstrating that the complex contains two mutually trans phosphine ligands. The proton NMR spectrum also exhibits four different methyl signals for the activated IMes ligand. In the $^{13}C\{^1H\}$ NMR spectrum, the ipso carbon of the aryl group gives rise to a triplet at 163.5 ppm (J_{CP} = 16.9 Hz); this was assigned unequivocally on the basis of ^{13}C PENDANT as well as $^{13}C-^1H$ HMQC and HMBC experiments.



(1)

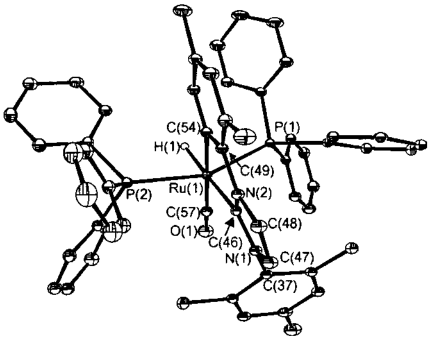


Figure 1. ORTEX drawing of **3** (thermal ellipsoids at the 30% level). Selected bond lengths (Å) and angles (deg): Ru(1)−C(46) 2.0746(12), Ru(1)−C(54) 2.1429(12), P(1)−Ru(1)−P(2) 156.010(12), C(46)−Ru(1)−C(54) 76.30(5).

The full molecular geometry of **3** was elucidated by X-ray crystallography (Figure 1). The structure clearly shows that the ruthenium atom has inserted into one of the ortho Ar−CH_3 bonds of the IMes ligand to give a new Ru−C bond (2.1429(12) Å) as an integral part of a five-membered metallacycle. The mesityl ring planes are approximately perpendicular to each other, presumably to minimize interaction with the phosphines. The attenuated P(1)−Ru−P(2) angle of only 156.0° is likely to be electronic in origin, as a similar distortion in related osmium hydrido−carbene complexes has been rationalized by enhanced π-back-donation to the cis carbene ligand.[6] While the precise mechanism surrounding the formation of **3** has yet to be established, a number of observations show that the pathway is not straightforward. In particular, when the reaction to give **3** was repeated in C_6D_6 and followed by ^1H and $^{31}P\{^1H\}$ NMR, extensive H/D exchange into both the hydride and the two PPh_3 ligands of the product was detected, in addition to the ortho positions of free PPh_3 in solution. We have determined that these exchange processes occur at different stages on the reaction pathway. Thus, conversion of **1** exclusively to **2** in C_6D_6 at 80 °C leads to no H/D exchange, while subsequent thermolysis of **2** at 100 °C affords a mixture of H/D exchanged **1**, **2**, **3**, and PPh_3. In contrast, reaction of **1**-D_2 with IMes at 80 °C in C_6D_6 gives **2**-H_2, **2**-HD, and exchanged PPh_3. These results suggest that PPh_3 activation is important in the conversion of **1** to **2**, and that solvent activation subsequently occurs at higher temperature. The conversion of **1** to **2** and ultimately to **3** requires the presence of free IMes, even though the C−C activation product only contains one carbene ligand. Thermolysis of **1** in C_6D_6 in the absence of

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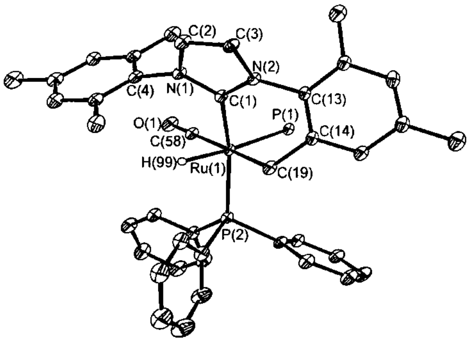
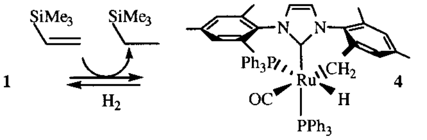


Figure 2. ORTEX drawing of **4** (thermal ellipsoids at the 30% level). Selected bond lengths (Å) and angles (deg): Ru(1)−C(1) 2.079(2), Ru(1)−C(19) 2.235(2), P(1)−Ru(1)−P(2) 102.10(2), Ru(1)−C(19)−C(14) 113.01(13). Phenyl rings on P(1) were omitted for clarity.

IMes yields only trace amounts of **3**, forming instead **1**-HD, **2**-H_2, **2**-HD, $Ru(PPh_3)_3(CO)H_2$, and $Ru(PPh_3)_3(CO)HD$.[7] At no stage in the formation of the C−C activated complex could we detect any signals arising from $ArCH_2$−H cleavage. However, this process does occur quantitatively upon addition of 1 equivalent of CH_2=$CHSiMe_3$ to a C_6D_6 solution of **1** at room temperature to yield **4** (eq 2).



(2)

The ^1H NMR spectrum of **4** contains two characteristic signals at δ 2.76 and 1.35 arising from the inequivalent protons of the Ru−CH_2Ar moiety. Selective $^1H-\{^{31}P\}$ experiments reveal that each proton couples to only one (and different) phosphine ligand. The hydride resonance appears as a doublet of doublets, with the magnitude of the coupling constants (J_{HP} = 102.4, 30.8 Hz) showing a trans and cis arrangement with respect to the two PPh_3 ligands.

The solid-state structure of **4** was established by X-ray crystallography (Figure 2) and shows a distorted octahedral geometry around ruthenium with a P(1)−Ru−P(2) angle of 102°. While **3** appears to be the thermodynamically favored product in this system, efforts to convert the C−H activated species **4** into the C−C complex **3** have been unsuccessful. Reaction of **4** with 1 atm of H_2 only leads to the reformation of **1** within 3 days at room temperature. To investigate these findings further, DFT calculations[8] have been carried out with (2-methylphenyl)imidazol-2-ylidene and PH_3 as model ligands (Figure 3). Computed metal−ligand distances in **5**, **6**, and **7** (models of **1**, **3**, and **4**, respectively) are generally in good agreement with the experimentally determined values, although the angles at the metal center (e.g. *cis*-P−Ru−P and *trans*-C_{IMes}−Ru−P) are underestimated as a consequence of using less sterically demanding ligands in the calculations. However the small *trans*-P−Ru−P angle in **3** (156.0°) is reproduced in **6** (159.4°) confirming that electronic factors are responsible for this distortion. The computed energies show that while **7** (+H_2) is 11.3 kcal/mol higher in energy than **5**, **6** (+CH_4) is 7.5 kcal/mol more stable than **5**. These results confirm that the C−C activation species is indeed the thermodynamically preferred reaction product. Moreover, the higher energy of the C−H activation product supports the idea that this species does not lie on the formation pathway of the C−C activated complex.

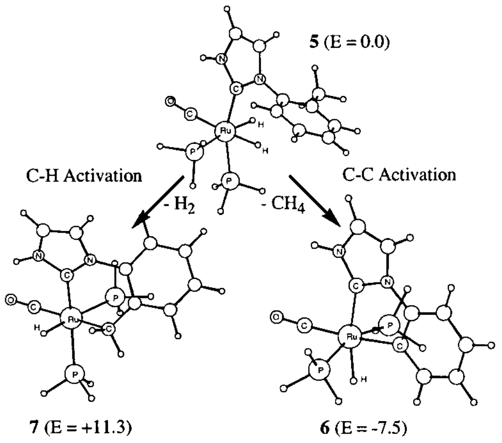


Figure 3. Computed structures and relative energies (kcal/mol) for **5**, **6** (C−C activation product) and **7** (C−H activation product).

In summary, direct insertion of a metal into an unstrained C−C bond of the *N*-heterocyclic carbene IMes has been demonstrated for the first time. This reaction is thermodynamically more favorable than insertion into a C−H bond, which is also reported. Our efforts are currently directed toward clarifying the mechanisms for both of these processes to show if similar reactivity can be extended to other NHC ligands.

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Supporting Information Available: Spectroscopic and X-ray crystallographic data for **3** and **4** and computed Cartesian coordinates of **5**−**7** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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