C–C Bond Activation

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Breaking News: Tungsten Cleaves Aromatic C–C Bonds**

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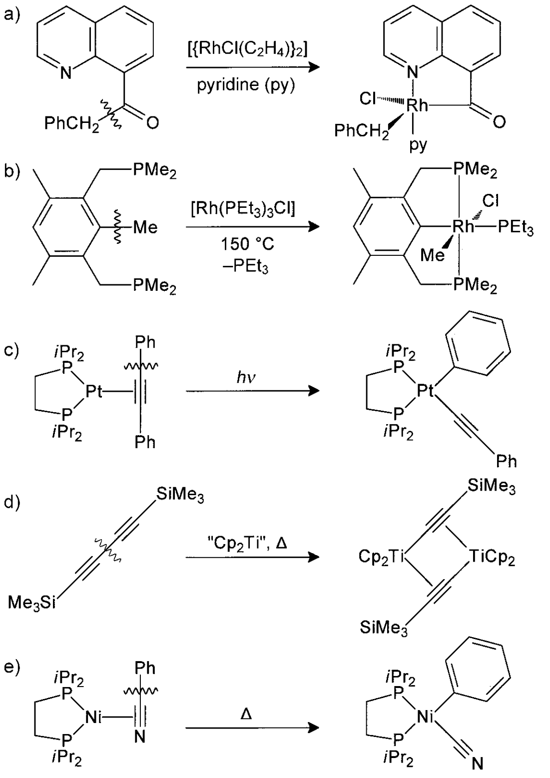
C–C activation · C–H activation · isocyanides · oxidative addition · tungsten

Dedicated to Professor Uwe Rosenthal on the occasion of his 60th birthday

The efficient processing and refinement of aliphatic or aromatic hydrocarbons from petroleum feedstock into value-added organic compounds by *selective* C–H and/or C–C bond activation still represent major challenges for organometallic chemists; this is because the bonds to be broken are thermodynamically strong and kinetically inert.[1] Nevertheless, C–H bond activation in the coordination sphere of a metal complex to form the corresponding metal–carbon and metal–hydrogen bonds has witnessed tremendous progress during the last decades,[2,3] whereas examples of C–C bond activation in solution by insertion of a transition metal are relatively scarce.[4] In general, thermodynamic and kinetic factors favor C–H over C–C activation: 1) upon oxidative addition, metal–hydrogen and/or metal–carbon bonds are formed, with the latter being significantly less stable,[5] 2) C–H bonds are generally more accessible than C–C bonds, and 3) the higher degree of C–C bond directionality (sp^x-sp^x) compared to that of C–H (sp^x-s) contributes to higher kinetic barriers. Accordingly, an additional thermodynamic driving force, such as strain relief or aromatization, is normally required for C–C activation to occur.[4,6] Milestones in this area were reported by Suggs and Jun and by Milstein and coworkers in 1984 and 1993,[7,8] respectively. In these studies, nonstrained and unactivated C–C single bonds were shown to undergo metal insertion, provided that the process is intramolecular and molecular design ensures that the C–C bond to be activated is positioned in close proximity to the central transition metal (Scheme 1 a,b). Later, the research groups of Jones, Rosenthal, and others have shown that C–C single bonds in alkynes and diynes can be broken without the prerequisite of a constrained ligand design (Scheme 1 c,d).[9,10] The related cleavage of C–CN bonds in nitriles by oxidative addition and metal insertion was also reported a number of years ago (Scheme 1 e),[11] and this reaction plays a key role in catalytic inter- and intramolecular carbocyanation reactions.[12]



Scheme 1. Selected examples of stoichiometric C–C bond cleavage by metal insertion; the bonds to be broken are marked with a wavy line.

In this context, the recent report by Sattler and Parkin constitutes a significant advancement in this area, because no assistance by other groups is required and the broken aromatic C–C bond in quinoxaline (benzopyrazine) is substantially stronger than a typical aliphatic C–C bond (Scheme 2).[13] Similar N-heterocyclic aromatic molecules are ubiquitous in nature, for example, in fossil fuels. Notably, emerging fossil fuel sources such as heavy oils, tar sands, shale oil, and coal suffer from lower H/C ratios and higher heteroatom contents, and therefore, a more in-depth understanding of how to activate these heteroaromatic compounds is indispensable for better utilization of resources (e.g. hydrogen) and for the minimization of environmental effects of fuel production and burning.

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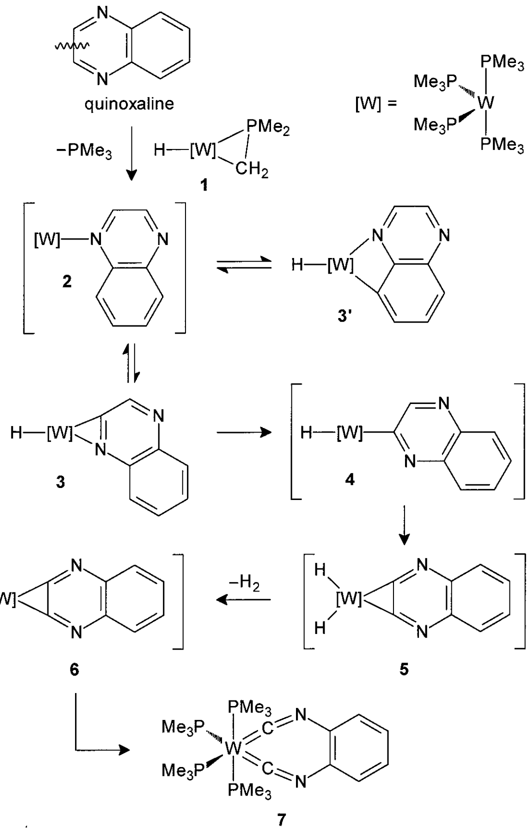

Scheme 2. Proposed mechanism for the formation of an *o*-phenylene diisocyanide complex from quinoxaline; the same reactivity was observed for 6-methyl- and 6,7-dimethylquinoxaline.[13]

In previous work, Parkin and co-workers reported a molybdenum-based complex, $[Mo(PMe_3)_6]$, that interacts with quinoxaline to form a simple molybdenum–quinoxaline π-complex —although this is an interesting observation, no bond activation occurred.[14] In the present work, the authors turned their attention to tungsten, the heavier congener of molybdenum, which is more potent with respect to bond breaking, as already indicated by the stronger tendency to form the cyclometalated tungsten(II) complex $[W(\eta^2\text{-}CH_2PMe_2)(PMe_3)_4]$ (**1**).[15] By reductive elimination and PMe_3 substitution, complex **1** was able to provide the 14-valence-electron $[W(PMe_3)_4]$ complex fragment upon reaction with quinoxaline, which—through serendipity—inserted unexpectedly into the C−C bond located between the two nitrogen atoms in the quinoxaline heterocycle and formed a structurally unprecedented diisocyanide complex **7** as the final product (Scheme 2).[13]

Although additional mechanistic and computational studies are still required to explain how this remarkable C−C bond activation process occurs in detail, the authors propose an intriguing pathway (Scheme 2). The first step involves a reversible C−H bond activation at two different positions proximal to the nitrogen atoms to show the formation of isomers **3** and **3′** during an early reaction state. However, only isomer **3** initiates the series of events leading to the breaking of an even more unreactive C−C bond. Next, the tungsten atom inserts itself into the C−H bond of the second carbon atom, in a β-hydrogen elimination reaction to form the benzyne intermediate **5**. Complex **5** then reductively eliminates the two hydrogen atoms that were initially attached to the carbon atoms, thus generating a molecule of dihydrogen and complex **6**. The feasibility of a benzyne-based pathway and therefore of the unobserved intermediates **5** and **6** relies on a previous report on a structurally similar ruthenium benzyne complex $[(\eta^2\text{-}C_6H_4)Ru(PMe_3)_4]$.[16] The considerable steric strain in **6** is relieved upon breaking the C−C bond, and the final product **7** is formed.

Complex **7** is one of the few examples, in which chelating isocyanide ligands are observed.[17] Isocyanide ligands usually adopt a linear M-C-N-R moiety and therefore 1,2-phenylene diisocyanide $[o\text{-}(CN)_2C_6H_4]$ usually acts as a bridging ligand.[18] The observed severe bending of the C-N-C bond angle in **7** is indicative of considerable metal-to-ligand π back-bonding and a strong contribution from the M=C=NR mesomeric form,[19] which is further confirmed by IR and NMR spectroscopy. These metal–isocyanide fragments in **7** are thermodynamically stable and provide the majority of the driving force for this unusual C−C addition process. Unfortunately, the same thermodynamic stability of **7** renders this complex unreactive, and therefore, it will probably be difficult to incorporate this transformation into a productive catalytic cycle.

In conclusion Sattler and Parkin[13] not only present an intriguing example of an "unassisted" C−C bond activation, but also provide important new structural motifs to show how nitrogen-containing heterocycles may bind to the surface of hydrodenitrogenation catalysts. Overall, this reaction demonstrates how inexpensive and abundant metals can be employed to activate strong bonds and the proposed unusual mechanism may inspire new innovative routes to a more general cleavage of C−C bonds, followed by suitable functionalization to generate value-added organic compounds.

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