Cluster Compounds

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The Subtle Art of Bimetallic Activation: Juggling Carbenes, Hydrocarbons, and Hydride Ligands Between Metals**

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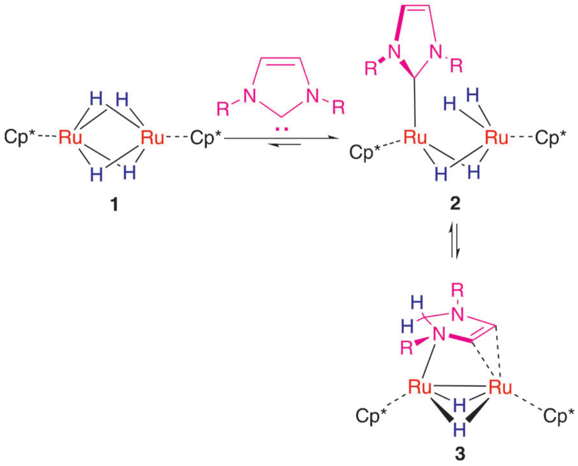
C–H activation · metathesis · N-heterocyclic carbenes · polyhydride clusters · ruthenium

In memory of Herbert D. Kaesz

Scientists freely undergoing curiosity-driven research are often regarded as poets: perhaps not necessarily needed in the modern chemistry world in the realm of sustainable development. Cluster chemists, who have too often been unduly categorized as such, may find an amusing reward (or revenge) in a growing number of novel observations, mainly from Beller and a few other groups.[1] These researchers have shown that cluster complexes as simple as $[Fe_3(CO)_{12}]$ are now back on stage as the best and simplest catalyst precursors (that is, the most useful sources of active unsaturated fragments) for a number of applied challenging organic reactions, the mechanisms of which are still unclear.

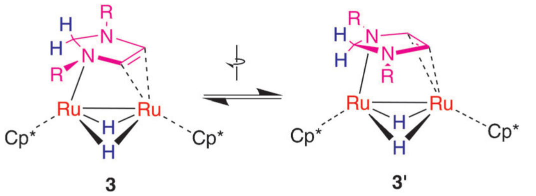
Independently, real and recurrent problems inherent to cluster catalysis, which have long been debated in authoritative monographs,[2] will be deliberately put aside here. The intrinsic beauty and instructive fundamental aspects of the chemistry of non-carbonyl polymetallic cyclopentadienyl ruthenium polyhydrides, which are currently being developed by Suzuki and his co-workers in Japan, will be the focus. With the growing emergence of nanosciences, such studies bring new hopes in cluster science and find a real utility in the modeling of chemical reactions that are prone to take place at the periphery of nanoparticles or at metal surfaces in heterogeneous systems.

In our first selected example (Scheme 1),[3] 1,3-di-*tert*-butylimidazol-2-ylidene, a representative N-heterocyclic carbene,[4] is engaged in a reversible addition–activation sequence with the binuclear ensemble **1**. Initial formation of the elusive hypothetical adduct **2**[5] is followed by multiple insertion of the carbene into Ru–H bonds to give the isolated species **3** in which the NHC has been hydrogenated to the corresponding imidazoline ligand. Such a heterocycle, acting as a four-electron donor, spans the metal edge in a side-on bridging position, where one of the two nitrogen atoms, and also the remote olefinic bond, are each engaged as donor sites. This phenomenon illustrates the multifunctionality of N-heterocyclic carbenes, which has only rarely been observed in non-cluster complexes.[6]



Scheme 1. Reversible insertion of an NHC into the Ru–H bonds of a binuclear ensemble.

Importantly, the geometrical situation found is **3** is not frozen, and a variable-temperature ^{1}H NMR investigation revealed an unusual fluxional behavior (Scheme 2) whereby the two nitrogen donors are alternately coordinated to the ruthenium center.



Scheme 2. Dynamic exchange process identified as a 1,3-migratory pendulum motion.

Even more surprising is the total reversibility of the double insertion of the carbenic carbon center into the Ru–H bonds (Scheme 1). Indeed, whereas the metal-mediated conversion of an imidazoline into the corresponding free imidazol-2-ylidene, requiring double C–H activation from an

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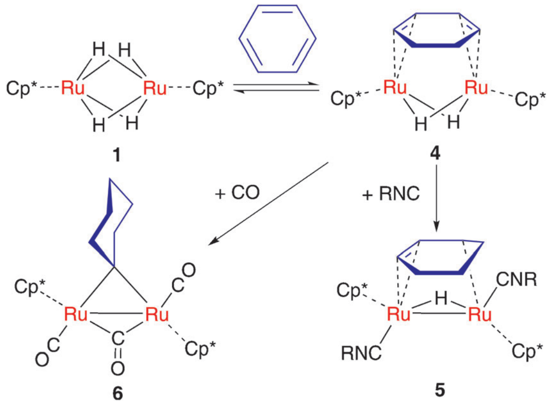
sp^3 carbon, is rarely observed in the case of mononuclear complexes,[7] it appears here as a facile low activation-energy pathway in which hydrogen-atom transfer between the carbon and the metal center are apparently facilitated by the second metal atom maintaining the heterocycle in an appropriate side-on position. This seems to indicate that a saturated NHC might be unable to undergo the same reaction.

In a recent report providing the first experimental evidence that N-heterocyclic carbenes are acting as efficient stabilizers for nanoparticles,[8] Philippot, Chaudret, and co-workers observed selective complexation of the most exposed atoms (apexes, edges) by the most bulky NHCs, followed by migration to the faces for the less bulky NHCs and accompanied by hydrogenation of the carbene center to an aliphatic carbon. This reaction might be rationalized in terms of the binuclear activation model proposed by Suzuki (Scheme 1).[3]

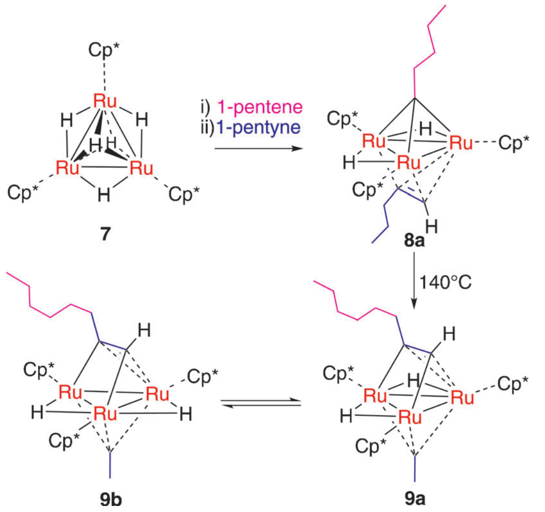
The parallel is even more convincing if we consider that the same binuclear ruthenium polyhydride **1** nicely models the partial hydrogenation of benzene,[9] a reaction also known to be catalyzed by colloidal ruthenium nanoparticles.[8]

This is illustrated in Scheme 3, where addition of benzene to **1** gives the μ-η^2:η^2-cyclohexadiene complex **4** in a reversible reaction. Interestingly, further hydrogen-atom transfer to the diene can be made to occur in a controlled manner by addition of appropriate donor ligands: while an excess of the isocyanide *t*BuNC gives mainly the μ-η^2-cyclohexenyl complex **5**, CO uptake instead promotes the formation of the μ-cyclohexylidene complex **6** in about 50% yield.

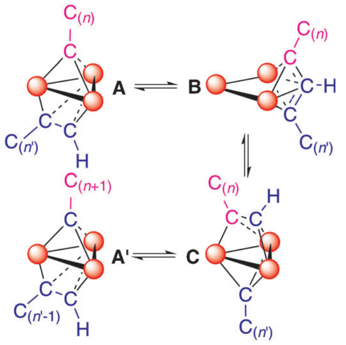


Scheme 3. Isolated complexes illustrating partial hydrogenation of benzene on a binuclear ensemble.

Certain transformations of unsaturated hydrocarbons onto the trinuclear pentahydride complex **7** are even more spectacular because they are selective and take full advantage of the flexibility of the cluster skeleton.[10] This is illustrated in Scheme 4: Complex **7** is prone to react sequentially with an olefin (1-pentene) and an alkyne (1-pentyne) in a self-organized manner at room temperature to give cleanly complex **8** (existing as a mixture of isomers **8a**,**b** differing in the position of hydrides).[10] The two ligands are each activated on a different cluster face (Scheme 4), as a μ_3-pentylidyne[11] (upper face), and a μ_3-pentyne (lower face). Upon thermal treatment, **8** generates an equilibrium mixture of **9a**,**b** in which the newly formed bridging ligands are respectively a μ_3-octyne (upper face) and a μ_3-ethylidyne (lower face), thereby revealing that a metathesis of the former hydrocarbon fragments has taken place. Such a reaction requires a perfectly organized stepwise exchange of three carbon atoms between the two faces of the cluster, through a repeated sequence whose intermediates (Scheme 5) were fully identified by a thorough NMR investigation. The proposed key intermediate **B** is an open cluster in which the terminal carbon of the cluster-bound alkyne couples with the alkylidyne carbon atom through the open edge of the cluster.



Scheme 4. Metathesis of hydrocarbon ligands on the face of cluster **7**: Recombination of two C_5 molecules into C_2 and C_8 fragments.



Scheme 5. Representation of one cycle of the selective redistribution of carbon chains involving face-to-face C–H group transfer (from **A** to **C**) through the open cluster **B** (hydrido ligands and Cp* groups omitted for clarity), followed by individual skeletal re-arrangements on the two faces (from **C** to **A′**).

In the final path, from **C** to **A′**, the individual hydrocarbon ligands undergo a fast skeletal re-arrangement on their respective cluster faces, probably involving the intermediacy of (unobserved) vinylidene groups.

Only a small part of the innovative work of Suzuki and co-workers has been highlighted here, and the reader is strongly encouraged to go to other relevant recent reports,[12] not only to see the parallels that can be drawn between C−H and N−H activation on polymetallic ensembles, but also how such reactions can be finely controlled by playing with hetero-metallic effects. The whole work is undoubtedly of high fundamental relevance and very important for the progress of knowledge, particularly in the context of nanosciences because it provides the most suitable molecular models for reactions that are susceptible to occur at the periphery of nanoparticles.

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