Carbene Heterocycles

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From an *N*-Methyl N-Heterocyclic Carbene to Carbyne and Carbide Ligands via Multiple C−H and C−N Bond Activations[**]

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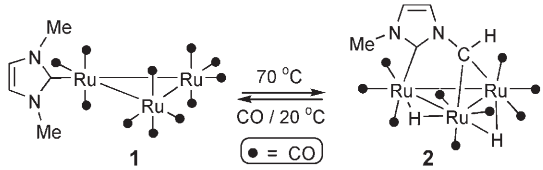
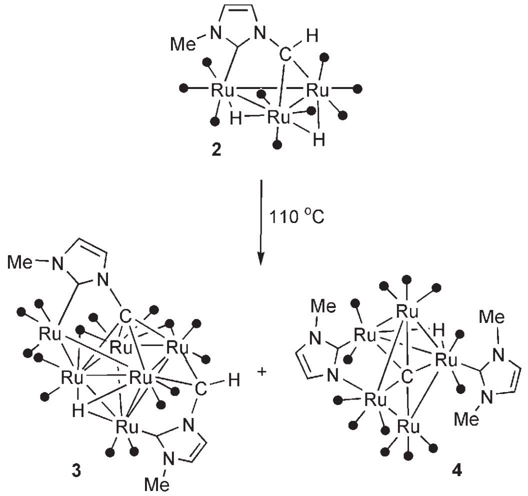
Ruthenium complexes containing N-heterocyclic carbene (NHC) ligands, and particularly 1,3-disubstituted imidazol-2-ylidenes, are among the most active catalysts for important organic reactions, such as olefin metathesis[1–3] and various C−C bond-forming processes.[3] However, recent reports have shown that the N–R arms of some NHC–ruthenium complexes may be involved in intramolecular C−H,[4–7] C−C,[6] and/or C−N[7] bond-activation reactions. Some NHC ligand degradation processes have important implications in catalyst activation[5a] or deactivation.[1,8] In fact, a ruthenium complex with an *N*-alkyl-metalated NHC ligand has been shown to be a more efficient catalyst than the nonmetalated precursor for a tandem oxidation/Wittig/reduction reaction that gives C−C bonds from alcohols.[5a] On the contrary, the deactivation of the second and third generations of Grubbs alkene metathesis catalysts occurs through intramolecular C−H bond-activation processes.[1] Therefore, the design of new NHC–ruthenium complexes, the study of their thermal intramolecular transformations, and the understanding of the factors that control such processes are currently relevant themes of research.

The interest in combining ruthenium complexes with NHC ligands and the absence of reports describing the reactivity of triruthenium clusters with NHCs[9] led us to study the reactivity of [Ru$_3$(CO)$_{12}$] with NHCs.[10] We previously reported the synthesis of the trinuclear derivative [Ru$_3$(Me$_2$Im)(CO)$_{11}$] (**1**; Me$_2$Im = 1,3-dimethylimidazol-2-ylidene) and its transformation into [Ru$_3$(μ-H)$_2$(MeImCH)(CO)$_9$] (**2**) through a process that involves the unusual reversible cleavage of two C−H bonds of an *N*-methyl group (Scheme 1).[4]



Scheme 1. Reversible activation of two C−H bonds of Me$_2$Im.

We have now discovered that an *N*-methyl group of Me$_2$Im can not only be transformed into a bridging methylene group (complex **2**), but also into bridging carbyne and carbide ligands. The thermolysis of compound **2** in toluene at reflux temperature led to an approximately 1:1 mixture of [Ru$_6$(μ_3-H)(μ_5-MeImC)(μ_3-MeImCH)(μ-CO)$_2$(CO)$_{13}$] (**3**) and [Ru$_5$(μ_5-C)(μ-H)(μ-MeIm)(Me$_2$Im)(CO)$_{13}$] (**4**), which were separated by chromatographic methods (Scheme 2).



Scheme 2. Synthesis of the carbyne and carbide complexes **3** and **4**.

The X-ray structure of the hexanuclear compound **3** is shown in Figure 1.[11] Its metal skeleton can be described as a basal-edge-bridged square pyramid. It contains two NHC ligands. One has a carbyne-type carbon atom C1, which spans the four basal metal atoms, whereas the carbene carbon atom C2 is attached to the edge-bridging Ru atom. The remaining NHC ligand caps a triangular face of the pyramid, as it is attached to the apical Ru6 atom through the carbene C atom and spans the Ru2–Ru5 edge through the C3–H fragment. The cluster shell is completed by a triply bridging hydride and 15 CO ligands. This structure is related to those of [Ru$_6$(μ_3-H)$_2$(μ_5-ampy)(μ-CO)$_2$(CO)$_{14}$] (H$_2$ampy = 2-amino-6-methylpyridine), which contains a quadruply bridging nitrene ligand,[12] and [Ru$_6$(μ_3-H)(μ_5-MebipyC)(μ-CO)$_3$(CO)$_{13}$] (Mebipy = 6,6′-dimethyl-2,2′-bipyridine), which contains a chelating Mebipy ligand attached to a quadruply bridging carbyne fragment.[13]

There is no doubt that compound **3** arises from a thermally mediated condensation of two molecules of **2**,

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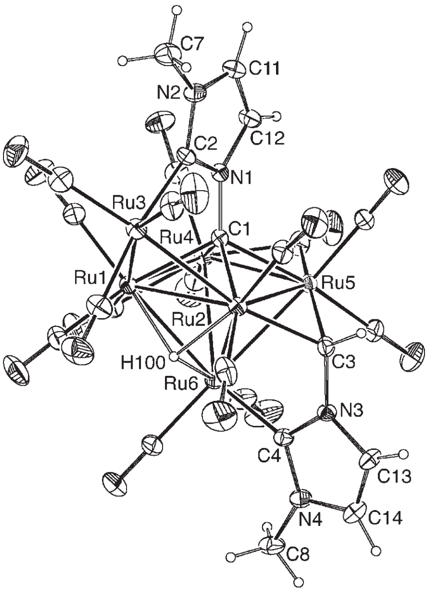

Figure 1. Molecular structure of the carbyne cluster **3** (ellipsoids set at 30% probability). Selected bond lengths [Å]: Ru1–C1 2.161(7), Ru2–C1 2.127(7), Ru2–C3 2.099(7), Ru3–C2 2.110(8), Ru4–C1 2.186(7), Ru5–C1 2.185(7), Ru5–C3 2.130(8), Ru6–C4 2.035(8).

also involving the activation of the third C–H bond of an original *N*-methyl group. Although there are precedents for the activation of all three C–H bonds of a *C*-methyl group,[13,14] to our knowledge the oxidative addition of all three C–H bonds of an *N*-methyl group has not been reported before. Carbyne ligands bridging four metal atoms are also scarce.[15]

The structure of compound **4** (Figure 2) consists of a distorted trigonal bipyramidal arrangement of metal atoms surrounding an interstitial carbide ligand C1. The apical Ru3 and Ru5 metal atoms are attached to the three equatorial Ru atoms, but the equatorial atom Ru1 is not bonded to the other two equatorial Ru atoms. An MeIm NHC ligand is attached to Ru2 through the carbene C2 atom and to Ru1 through the N1 atom. An additional NHC ligand, in this case intact Me_2Im, is bonded to the Ru4 atom. The cluster shell is completed by a hydride, which spans the Ru2–Ru4 edge, and 13 terminal CO ligands. This structure is somewhat related to that of $[Ru_5(\mu_5\text{-}C)(\mu\text{-}H)(\mu\text{-}Mebipy)(CO)_{13}]$.[13]

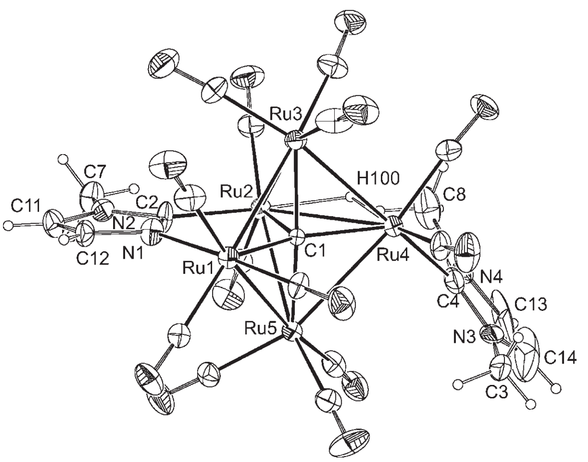

Figure 2. Molecular structure of the carbide cluster **4** (ellipsoids set at 30% probability). Selected bond lengths [Å]: Ru1–N1 2.12(2), Ru1–C1 2.09(2), Ru2–C1 2.09(2), Ru2–C2 2.07(2), Ru3–C1 1.99(2), Ru4–C1 2.07(2), Ru4–C4 2.15(3), Ru5–C1 1.97(2).

In compound **4**, the presence of the N-bound MeIm ligand suggested that the carbide C atom arises from the cleavage of a C–N bond. Nevertheless, to make sure that this carbide does not arise from a CO ligand, as frequently occurs for carbide-containing carbonyl ruthenium clusters,[16] we also studied the thermolysis of a ^{13}CO-enriched sample of compound **2**. A $^{13}C\{^1H\}$ NMR spectrum of the carbide derivative obtained in this reaction[17] indicated that the only ^{13}C-enriched C atoms of this product were those of the CO ligands. Therefore, the carbide C atom of **4** does not arise from a CO ligand but from the cleavage of a C–N bond.

On the other hand, the intact Me_2Im ligand of **4** confirms that, in these systems, the oxidative addition of $C(sp^3)$–H bonds can be reversed, as we had anticipated with trinuclear clusters.[4] To date, many articles describing transition-metal clusters containing carbide ligands have been published, but, to our knowledge, only two report the transformation of organic methyl groups into carbides through C–C bond activation.[13] Additionally, although a few $C(sp^3)$–N bond-activation reactions have been reported,[7,18,19] including two recent reports involving NHCs,[7,18] the activation of all bonds (three C–H and one C–N) of an N-bonded methyl group is unprecedented.

The structure of compound **4** led us to suppose that it might arise from the thermolysis of the carbyne cluster **3**. However, an independent experiment showed that **3** is stable in refluxing toluene. Therefore, although both clusters arise from compound **2**, they should be formed by independent reaction pathways.

The thermally induced decarbonylation of ruthenium carbonyl clusters generally leads to transient unsaturated species that are prone to condense and/or undergo oxidative addition processes to alleviate their unsaturation.[12,13] The very strong basicity of NHCs increases the electron density of the metal atoms to which they are attached, and this enhances the tendency of these metals to become involved in oxidative addition processes. A combination of these two factors (unsaturated and electron-rich metals) rationalizes the results reported herein, in which cluster condensation is accompanied by processes that involve the multiple oxidative addition of very strong bonds, such as $C(sp^3)$–H and $C(sp^3)$–N.

The overall transformation of an *N*-methyl group of Me_2Im into a carbyne and finally into a carbide ligand are unprecedented not only in the chemistry of NHCs, but also for *N*-methyl groups of organic molecules. In addition to being relevant to the field of NHC ligand degradation, these results are also of interest to the currently important fields of $C(sp^3)$–H and $C(sp^3)$–N bond activation. As anticipated by Whittlesey et al., ruthenium clusters can be used to generate a remarkable range of products when reacted with NHCs.[10b]

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[11] Data for **3**·CH_2Cl_2: $C_{24}H_{12}N_4O_{15}Ru_6{\cdot}CH_2Cl_2$, $M_r = 1299.73$, crystal dimensions $0.21 \times 0.20 \times 0.07$ mm, triclinic, space group $P\bar{1}$, $a = 10.653(6)$, $b = 11.238(6)$, $c = 16.363(9)$ Å, $\alpha = 80.910(10)$, $\beta = 74.523(9)$, $\gamma = 78.891(10)°$, $V = 1840.6(17)$ Å^3, $Z = 2$, $\rho_{calcd} = 2.345$ g cm^{-3}, $F(000) = 1232$, $\mu = 2.615$ mm^{-1}, 5288 independent reflections, $R_1 = 0.0407$, $wR_2 = 0.1109$ (all data). Data for **4**: $C_{23}H_{14}N_4O_{13}Ru_5$, $M_r = 1059.73$, crystal dimensions $0.12 \times 0.10 \times 0.02$ mm, triclinic, space group $P\bar{1}$, $a = 9.6546(3)$, $b = 17.0975(5)$, $c = 20.3049(8)$ Å, $\alpha = 109.641(2)$, $\beta = 94.075(3)$, $\gamma = 91.866(2)°$, $V = 3143.04(18)$ Å^3, $Z = 4$, $\rho_{calcd} = 2.240$ g cm^{-3}, $F(000) = 2016$, $\mu = 19.627$ mm^{-1}, 11 388 independent reflections, $R_1 = 0.0968$, $wR_2 = 0.3477$ (all data).
CCDC-662883 (**3**·CH_2Cl_2) and CCDC-662884 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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