Easy activation of two C–H bonds of an *N*-heterocyclic carbene *N*-methyl group†

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The first trinuclear clusters containing NHC ligands are described; the compound [Ru₃(Me₂Im)(CO)₁₁] (Me₂Im = 1,3-dimethylimidazol-2-ylidene) is easily converted into [Ru₃(μ-H)₂(μ₃-MeImCH)(CO)₉] by a process involving the activation of two C–H bonds of a methyl group that is an example of degradation of a metal-coordinated NHC ligand under mild conditions.

In the last decade, *N*-heterocyclic carbenes (NHCs) have attracted increasing attention as ancillary ligands[1] because many of their metal complexes, particularly those of metals belonging to Groups 8–10 of the periodic table, have been revealed as excellent homogeneous catalysts for processes that are very useful in organic synthesis, most notably C–C coupling reactions and olefin metathesis.[2] Despite the widely diversified research activity in this area, which goes from early to late transition metals in low and high oxidation states,[1] no cluster complexes containing NHC ligands have hitherto been reported.

It is generally believed that NHCs are good ancillary ligands, *i.e.* strongly bound to the metal, inert to any external attack, and not susceptible to participate in rearrangements at the metal coordination sphere. In fact, these are key requirements for metal complex catalysts having NHCs.[2] However, recent reports have demonstrated that the NHC–metal bond is not always inert and that some bulky R groups attached to the NHC nitrogen atoms can be modified under certain reaction conditions.[3–5]

On the other hand, metal-promoted C–H bond activation is also a very active research area because of its great potential in organic synthesis.[6] C(sp³)–H bond activation processes by oxidative addition are among the most interesting reactions in this field.

The present communication reports the first examples of trinuclear cluster complexes containing NHC ligands and the observation of an easy activation of two C–H bonds of a methyl group attached to a nitrogen atom of an NHC ligand. Such a reaction represents an unprecedented degradation of an NHC ligand containing N-bonded methyl groups.

Deprotonation of 1,3-dimethylimidazolium iodide[7] by potassium *tert*-butoxide followed by addition of [Ru₃(CO)₁₂], at room temperature in THF solvent, led to the trinuclear NHC derivative [Ru₃(Me₂Im)(CO)₁₁] (**1**; Me₂Im = 1,3-dimethylimidazol-2-ylidene; Scheme 1).§

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† Electronic supplementary information (ESI) available: Experimental details for the synthesis of **1** and **2**. See http://dx.doi.org/10.1039/b506287j
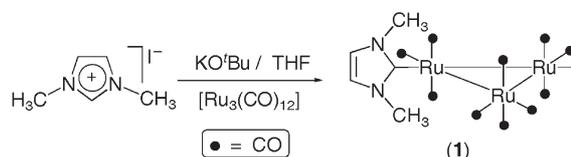
Scheme 1   Synthesis of compound **1**.

No simple di- or trisubstituted products were observed in reactions of [Ru₃(CO)₁₂] with an excess of the NHC ligand at higher temperatures. Although NHCs have often been compared with phosphine ligands,[1,2] it is noteworthy that the latter do not react with [Ru₃(CO)₁₂] at room temperature and that trisubstituted derivatives of the type [Ru₃(PR₃)₃(CO)₉] are the usual products at higher temperatures, because the second and third substitution processes have lower activation energies than the first substitution.[8]

The structure of compound **1** was determined by X-ray diffraction methods.¶Fig. 1 shows that the NHC ligand occupies an equatorial position. The structure resembles those of some phosphane-monosubstituted derivatives of [Ru₃(CO)₁₂].[9] The plane defined by the atoms of the NHC ligand forms an angle of 41.65(6)° with the Ru₃ plane, thus minimizing the steric interactions between the NHC methyl groups and the CO ligands that are attached to the same Ru atom.

The face-capped trinuclear derivative [Ru₃(μ-H)₂(μ₃-MeImCH)(CO)₉] (**2**) was prepared by heating to reflux a THF solution of complex **1**.§ Interestingly, this process was completely reversed when carbon monoxide was gently bubbled through a THF solution of **2** at room temperature (Scheme 2).
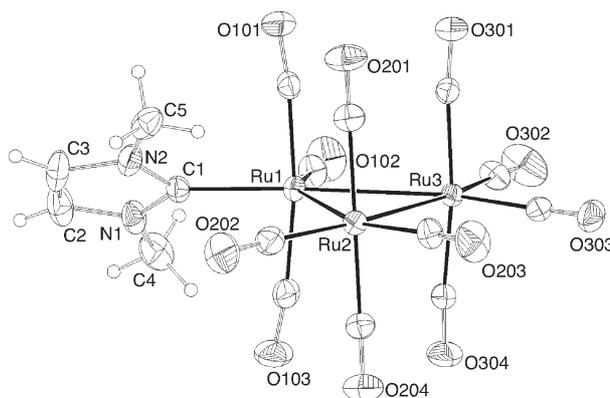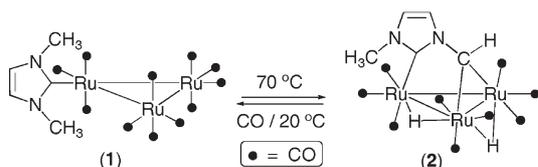

Fig. 1 Molecular structure of compound **1**. Selected bond distances (Å): Ru(1)–Ru(2) 2.917(2), Ru(1)–Ru(3) 2.884(2), Ru(2)–Ru(3) 2.887(2), Ru(1)–C(1) 2.115(4).

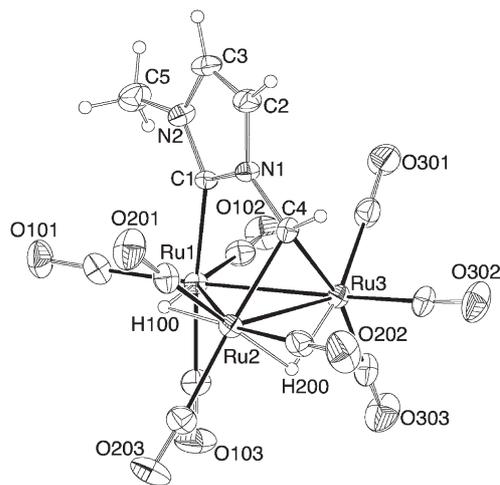**Scheme 2** Interconversion of compounds **1** and **2**.

Fig. 2 Molecular structure of compound **2**. Selected bond distances (Å): Ru(1)–Ru(2) 3.036(2), Ru(1)–Ru(3) 2.822(2), Ru(2)–Ru(3) 2.784(2), Ru(1)–C(1) 2.089(5), Ru(2)–C(4) 2.121(6), Ru(3)–C(4) 2.106(5), Ru(1)–H(100) 1.76(6), Ru(2)–H(100) 1.79(6), Ru(2)–H(200) 1.71(5), Ru(3)–H(200) 1.82(6).

The X-ray structure of **2** (Fig. 2)¶ shows that a bridging MeImCH ligand is attached to three ruthenium atoms in such a way that the CH fragment spans an Ru–Ru edge, while the carbene carbon atom is bound to the remaining ruthenium atom. Two Ru–Ru edges are also spanned by hydride ligands. The cluster shell is completed by nine terminal carbonyls. The compound is structurally related to $[Os_3(\mu\text{-}H)_2\{\mu_3\text{-}HCN(Me)CEt\}(CO)_9]$, which contains an aminocarbene ligand.[10]

Therefore, the transformation of **1** into complex **2** involves an uncommon oxidative addition of two C–H bonds of a nitrogen-bound methyl group to ruthenium.[11] The fact that this reaction can be reversed at room temperature, by exposing **2** to a low-pressure atmosphere of carbon monoxide, implies that both C–H bond activation steps should have small activation barriers.

We have recently reported that the reaction of $[Ru_3(CO)_{12}]$ with 6,6′-dimethyl-2,2′-bipyridine (Me_2bipy) gives $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-}MebipyCH)(CO)_9]$ *via* the double C–H activation of a carbon-bound methyl group.[12] However, in that case, the activated methyl group is attached to a carbon atom and the chelating ability of the Me_2bipy ligand is the driving force of the C–H activation process, since the chelation of this ligand induces the interaction of one of its methyl groups with the metal atoms. In agreement with this, no reaction at all was observed when $[Ru_3(CO)_{12}]$ was treated with an excess of 2,6-dimethylpyridine under similar conditions.[12] A related chelation-assisted approach, but with mononuclear complexes, has been used to activate C–H and C–C bonds of appropriate chelating ligands.[13] Interestingly, in the transformation described herein, the metalation of one of the Me_2Im ligand

methyl groups cannot be promoted by a previous chelation of the ligand. Therefore, the strong basicity of the NHC ligand has to be claimed as being responsible for the enhanced disposition of the cluster metal atoms to undergo the oxidative addition of $C(sp^3)$–H bonds.

The number of reports describing the double oxidative addition of nitrogen-bound methyl C–H bonds to metal fragments[10,11,14] is very small compared to those referring to carbon-bound methyl C–H bonds.[12,15] A few additional publications describing the oxidative addition of two metal-bound methyl C–H bonds to metal fragments have also been reported.[16]

In conclusion, we have described the first trinuclear clusters having NHC ligands and an unusual ruthenium-mediated activation of two C–H bonds of a nitrogen-bound methyl group. Such a double C–H bond cleavage process represents a rare example of degradation of a metal-coordinated NHC ligand under mild conditions and offers a reaction pathway that should be considered in future reactivity studies involving NHCs with *N*-methyl groups.

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