C–H/C–C Activation

Activation of All Bonds of a Methyl Group Attached to an Organic Fragment**

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Activation of C–H[1] and C–C[2] bonds promoted by transition-metal complexes has increasingly attracted the attention of researchers over the last two decades. The use of these processes in chemoselective organic synthesis[1–3] with atom economy[4] is the final goal of this intense research activity. In the case of sp^3 carbon atoms, examples of C–H bond activation by oxidative addition processes in solution are still scarce,[1,3] and the number of processes in which C–C bonds are activated is even smaller.[2,3] Therefore, the search

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[**] This work has been supported by the Spanish MCyT (projects BQU2002-02623 to J.A.C. and BQU2002-03414 to D.M.) and the Government of Principado de Asturias (project PR01-GE-7 to V.R.).

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

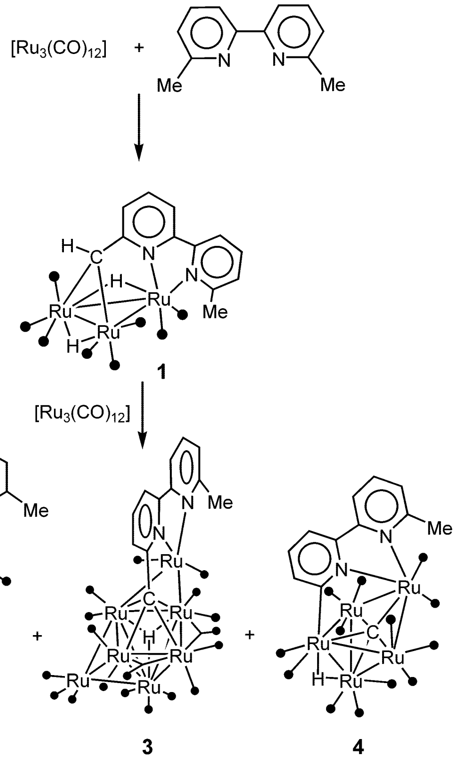
DOI: 10.1002/ange.200454066

for new systems capable of activating C–H and C–C bonds involving sp^3 carbon atoms under mild conditions and understanding the factors that control such processes are currently highly active research fields.

During our study of the reactivity of transition metal carbonyl compounds with 2-aminopyridines in solution we discovered that $[Ru_3(CO)_{12}]$ can promote the oxidative addition of both N–H bonds of the amino group and transform it into a μ_4-imido fragment.[5] Such an uncommon reaction prompted us to attempt the activation of the methyl C–H bonds of a series of 2-methylpyridines under analogous conditions.

We now report the transformation of an organic methyl group into bridging methylene, carbyne, and carbide ligands by using $[Ru_3(CO)_{12}]$ as the transition metal complex promoter and 6,6′-dimethyl-2,2′-bipyridine (Me_2bipy) as the organic precursor.

The trinuclear cluster $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-}HCbipyMe)(CO)_8]$ (**1**) was prepared by treating $[Ru_3(CO)_{12}]$ with 2.5 equivalents of Me_2bipy in THF at reflux temperature (Scheme 1). Its X-ray structure (Figure 1) shows that a bridging HCbipyMe ligand is attached to three ruthenium atoms in such a way that the CH fragment spans an Ru–Ru edge and the bipy fragment chelates the remaining Ru atom. The cluster shell is completed by eight terminal CO ligands and two edge-bridging hydride ligands.[6]



Scheme 1. Synthesis of **1**–**4** from $[Ru_3(CO)_{12}]$ and 6,6′-dimethyl-2,2′-bipyridine. ● = CO.

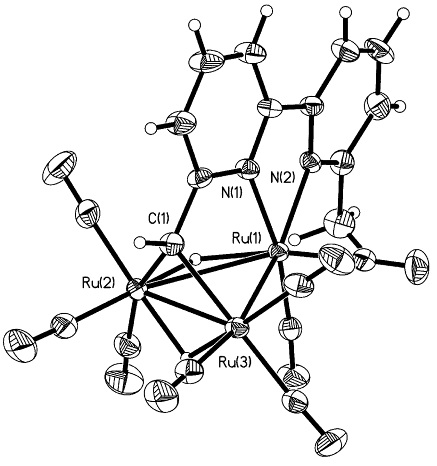


Figure 1. Molecular structure of **1**.

The reaction of $[Ru_3(CO)_{12}]$ with bipy has been reported to give $[Ru_3(bipy)(\mu\text{-}CO)_2(CO)_8]$, in which the bipy ligand chelates a ruthenium atom.[7] Careful inspection of its X-ray structure reveals that such a structure would not be possible for Me_2bipy, because there is not enough room to accommodate the methyl groups without their interacting with the carbonyl ligands. Thus, in the reaction of $[Ru_3(CO)_{12}]$ with Me_2bipy, chelation of the ligand should be accompanied by the release of at least three CO ligands. The unsaturation of the thus-formed intermediate (46e) would promote the activation of a methyl C–H bond. However, such a monohydrido nonacarbonyl intermediate has not been observed, probably because it is thermodynamically less stable than **1**, which arises from a double C–H activation process. As no reaction was observed between 2,6-dimethylpyridine and $[Ru_3(CO)_{12}]$ in refluxing chlorobenzene, it is clear that the chelating ability of Me_2bipy is probably the driving force for the metalation of one of its methyl groups. A related chelation-assisted approach, but with mononuclear complexes, was used to activate methyl C–H and C–C bonds of appropriate bidentate ligands.[8] There are very few published reports describing the oxidative addition of two C–H bonds of a methyl group to a metal fragment, and none of them deals with organic methyl groups, but with methyl groups already attached to metal atoms.[9] The activation of both methylene C–H bonds of a metal-bound ethyl group has also been reported.[10]

The compounds $[Ru_6(\mu_3\text{-}H)(\mu_5\text{-}CbipyMe)(\mu\text{-}CO)_3(CO)_{13}]$ (**2**), $[Ru_7(\mu_3\text{-}H)(\mu_5\text{-}CbipyMe)(\mu\text{-}CO)_2(CO)_{16}]$ (**3**), and $[Ru_5(\mu\text{-}H)(\mu_5\text{-}C)(\mu\text{-}bipyMe)(CO)_{13}]$ (**4**; Scheme 1) were prepared by heating equimolar amounts of **1** and $[Ru_3(CO)_{12}]$ in chlorobenzene under reflux. In addition, these clusters were also obtained in similar yields when $[Ru_3(CO)_{12}]$ was treated with Me_2bipy in a 2:1 ratio in refluxing chlorobenzene. Their structures were determined by single-crystal X-ray diffraction.[6]

Compounds **2** and **3** contain a carbyne-type carbon atom that was originally bound to three hydrogen atoms in Me_2bipy. The structure of hexanuclear **2** (Figure 2a) is comparable to that of $[Ru_6(\mu\text{-}H)_3(\mu_5\text{-}NpyC_6H_4)(\mu\text{-}CO)_3(CO)_{13}]$,[5] in which the ligand $NpyC_6H_4$ is attached to the metal skeleton in the same way as the CbipyMe ligand in **2**, but with exchanged positions of an N and a C atom. The structure of heptanuclear cluster **3** (Figure 2b) is reminiscent

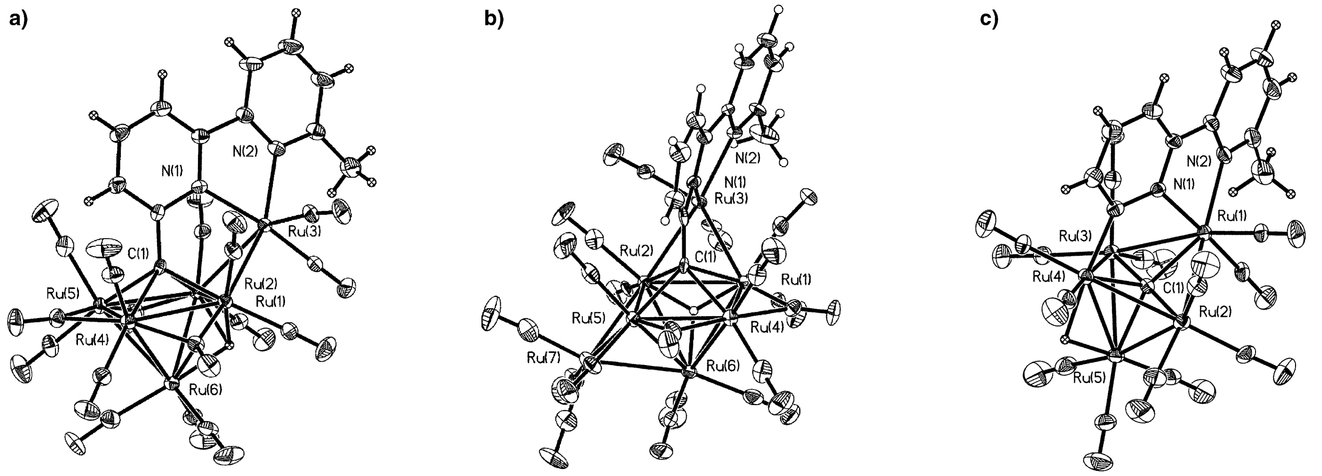


Figure 2. Molecular structures of **2** (a), **3** (b), and **4** (c).

of that of **2**, but now an additional Ru atom caps a triangular face of the square-pyramidal fragment of the metal skeleton.

Activation of the three C–H bonds of a metal-bound methyl group has been reported.[11] However, to our knowledge, the oxidative addition of all three C–H bonds of an organic methyl group is unprecedented. Carbyne ligands bridging four metal atoms are also scarce,[9a,b,12] and none of them arose from an organic methyl group.

The structure of **4** (Figure 2c) clearly shows the presence of a carbide ligand surrounded by five Ru atoms in a distorted trigonal-bipyramidal environment and a bipyMe ligand attached to a Ru atom through both N atoms and to another Ru atom through the carbon atom which was originally bound to the activated methyl group. The cluster shell is completed by 13 CO ligands and a bridging hydride ligand. Many transition-metal clusters containing carbide ligands have been reported, but no such ligands arose from an organic methyl group. A few C–C bond-activation reactions involving methyl groups have been reported,[2,8,13] but the products contain methyl groups that do not undergo further C–H activation.

Clearly **1** is an intermediate in the synthesis of **2**–**4**. We have checked that the hexanuclear complex **2** is not transformed into a mixture of **3** and **4** when it is heated in refluxing chlorobenzene. Therefore, the formation of **2**–**4** should take place through the condensation of compound **1** with $[Ru_n(CO)_m]$ ($n=1$, 3) species, which are available in hot solutions of $[Ru_3(CO)_{12}]$.

In conclusion, we have described the ruthenium-cluster-mediated transformation of an organic methyl group into a carbide ligand. Such a process involves the unprecedented activation of all bonds (three C–H and one C–C) associated with the carbon atom of an organic methyl group. In addition, **1**–**3** are unique examples of activation of two and three C–H bonds of an organic methyl group.

Received: February 22, 2004 [Z54066]

Keywords: C–C activation · C–H activation · cluster compounds · N ligands · ruthenium

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[6] Data for **1**: $C_{20}H_{12}N_2O_8Ru_3$, $M_r=711.53$, crystal dimensions $0.19\times0.10\times0.05$ mm, triclinic, space group $P\bar{1}$, $a=8.159(1)$, $b=10.953(2)$, $c=13.132(2)$ Å, $\alpha=91.752(3)$, $\beta=98.785(3)$, $\gamma=95.719(3)°$, $V=1152.8(3)$ Å^3, $Z=2$, $\rho_{calcd}=2.050\ g\,cm^{-3}$, $F(000)=684$, $\mu=1.988\ mm^{-1}$, 3293 independent reflections, $R_1=0.0269$, $wR_2=0.0514$ (all data). Data for **2**: $C_{28}H_{10}N_2O_{16}Ru_6$, $M_r=1236.80$, crystal dimensions $0.14\times0.12\times0.08$ mm, monoclinic, space group $P2_1/c$, $a=10.306(3)$, $b=30.631(8)$, $c=10.826(3)$ Å, $\beta=94.188(4)$, $V=3409(1)$ Å^3, $Z=4$, $\rho_{calcd}=2.410\ g\,cm^{-3}$, $F(000)=2336$, $\mu=2.667\ mm^{-1}$, 4811 independent reflections, $R_1=0.0304$, $wR_2=0.0656$ (all data). Data for **3**: $C_{30}H_{10}N_2O_{18}Ru_7$, $M_r=1393.89$, crystal dimensions $0.24\times0.21\times0.11$ mm, orthorhombic, space group $Pna2_1$, $a=30.505(12)$, $b=11.815(5)$, $c=10.394(4)$ Å, $V=3746(3)$ Å^3, $Z=4$, $\rho_{calcd}=2.472\ g\,cm^{-3}$, $F(000)=2624$, $\mu=2.825\ mm^{-1}$, 4152

independent reflections, $R_1 = 0.0315$, $wR_2 = 0.0650$ (all data). Data for **4**: $C_{25}H_{10}N_2O_{13}Ru_5$, $M_r = 1051.70$, crystal dimensions $0.19 \times 0.12 \times 0.06$ mm, triclinic, space group $P\bar{1}$, $a = 10.282(2)$, $b = 10.895(2)$, $c = 13.508(2)$ Å, $\alpha = 89.939(3)$, $\beta = 89.194(3)$, $\gamma = 89.532(3)°$, $V = 1513.0(4)$ Å^3, $Z = 2$, $\rho_{calcd} = 2.309$ g cm^{-3}, $F(000) = 996$, $\mu = 2.506$ mm^{-1}, 4268 independent reflections, $R_1 = 0.0293$, $wR_2 = 0.0763$ (all data). CCDC-231373 (**1**), CCDC-231374 (**2**), CCDC-231375 (**3**), and CCDC-231376 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.uk).

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