DOI: 10.1002/chem.200500813

Ruthenium-Cluster-Mediated Activation of All Bonds of a Methyl Group of 6,6′-Dimethyl-2,2′-bipyridine and 2,9-Dimethyl-1,10-phenanthroline: Transformation of the Latter into a 2-Alkenyl-9-methyl-1,10-phenanthroline Ligand

Javier A. Cabeza,*[a] Ignacio del Río,[a] Lorena Martínez-Méndez,[a] and Daniel Miguel[b]

Abstract: The treatment of $[Ru_3(CO)_{12}]$ with 6,6′-dimethyl-2,2′-bipyridine (Me_2bipy) or 2,9-dimethyl-1,10-phenanthroline (Me_2phen) in THF at reflux temperature gives the trinuclear dihydride complexes $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-}L^1)(CO)_8]$ (L^1 = HCbipyMe **1a**, HCphenMe **1b**), which result from the activation of two C–H bonds of a methyl group. The hexa-, hepta-, and pentanuclear derivatives $[Ru_6(\mu_3\text{-}H)(\mu_5\text{-}L^2)(\mu\text{-}CO)_3(CO)_{13}]$ (L^2 = CbipyMe **2a**, CphenMe **2b**), $[Ru_7(\mu_3\text{-}H)(\mu_5\text{-}L^2)(\mu\text{-}CO)_2(CO)_{16}]$ (L^2 = CbipyMe **3a**, CphenMe **3b**), and $[Ru_5(\mu\text{-}H)(\mu_5\text{-}C)(\mu\text{-}L^3)(CO)_{13}]$ (L^3 = bipyMe **4a**, phenMe **4b**) can also be obtained by treating **1a** and **1b** with $[Ru_3(CO)_{12}]$. Compounds **2a** and **2b** have a basal edge-bridged square-pyramidal metallic skeleton with a carbyne-type C atom capping the four Ru atoms of the pyramid base. The structures of **3a** and **3b** are similar to those of **2a** and **2b**, respectively, but an additional Ru atom now caps a triangular face of the square-pyramidal fragment of the metallic skeleton. The most interesting feature of **2a**, **2b**, **3a**, and **3b** is that their carbyne-type C atoms were originally bound to three hydrogen atoms in Me_2bipy or Me_2phen and, therefore, they arise from the unprecedented activation of all three C–H bonds of C-bound methyl groups. The pentanuclear compounds **4a** and **4b** contain a carbide ligand surrounded by five Ru atoms in a distorted trigonal-bipyramidal environment. They are the products of a series of processes that includes the activation of all bonds (three C–H and one C–C) of organic methyl groups, and are the first examples of complexes having carbide ligands that arise from C-bonded methyl groups. The alkenyl derivatives $[Ru_5(\mu_5\text{-}C)(\mu\text{-}p\text{-}MeC_6H_4CHCHphenMe)(CO)_{13}]$ (**5b**), $[Ru_5(\mu\text{-}H)(\mu_5\text{-}C)(\mu\text{-}p\text{-}MeC_6H_4CHCHphenMe)(p\text{-}tolC_2)(CO)_{12}]$ (**6b**), and $[Ru_5(\mu\text{-}H)(\mu_5\text{-}C)(\mu\text{-}PhCHCHphenMe)(PhC_2)(CO)_{12}]$ (**7b**) have been obtained by treating **4b** with *p*-tolyl- and phenylacetylene, respectively. Their heterocyclic ligands contain an alkenyl fragment in the position that was originally occupied by a methyl group. Therefore, these complexes are the result of the formal substitution of an alkenyl group for a methyl group of 2,9-dimethyl-1,10-phenanthroline.

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

Introduction

The activation of C–H[1] and C–C[2] bonds promoted by transition-metal complexes has increasingly attracted the attention of researches over the last two decades. The use of these processes in chemoselective organic synthesis[1–3] is the final goal of such an intense research activity. However, the applied aspects of these reactions are not the only area of interest. When sp^3 carbon atoms are involved, the known examples of C–H bond activation by oxidative addition processes in solution are fewer than those known for $C(sp^2)$–H bonds,[1,3] and the number of processes in which $C(sp^3)$–C bonds are activated is even smaller.[2,3] Therefore, the search for new systems capable of activating $C(sp^3)$–H and $C(sp^3)$–C bonds under mild conditions and the understanding of the factors that control such processes are currently highly active research fields.

It has been reported that C–H and C–C bonds of molecules in which these bonds are in the proximity of a coordin-

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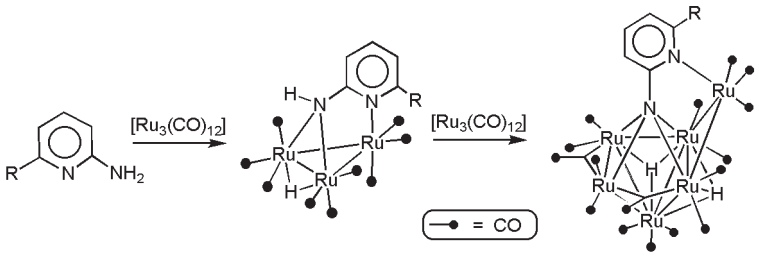
able heteroatom or functional group are, in general, more easily cleaved than bonds that are far apart from these groups.[1–4] These processes have been named "chelation-assisted" bond activations[3a,4] because their driving force is the formation of a stable metallacycle after the bond cleavage.

In a related chelation-assisted approach, we have observed that $[Ru_3(CO)_{12}]$ can promote the oxidative addition of both N–H bonds of the amino group of 2-aminopyridines, transforming it into a μ_4-imido fragment (Scheme 1).[5,6]



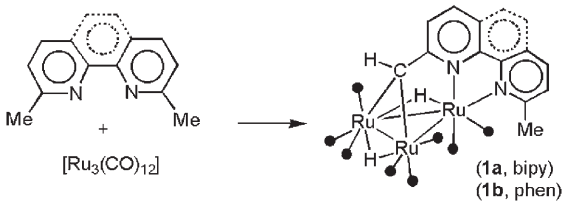
Scheme 1. Reactivity of 2-aminopyridines with $[Ru_3(CO)_{12}]$.

Such an uncommon reaction prompted us to attempt the activation of methyl C–H bonds of a series of 2-methyl-*N*-heterocycles under the same conditions as those used for the reactions with 2-aminopyridines.

We now report that simple 2-methylpyridines fail to react with $[Ru_3(CO)_{12}]$ in a similar manner to 2-aminopyridines. However, with substrates with two coordinable heteroatoms, one of which is close to the bond to be activated, that are therefore capable of forming at least two metallacycles after the bond cleavage, we have managed to transform an organic methyl group, that is, a methyl group attached to a C atom of an organic fragment, into bridging methylene-type, carbine, and carbide groups. Such processes imply the activation of two $C(sp^3)$–H bonds, three $C(sp^3)$–H bonds, and the $C(sp^3)$–C bond plus the three $C(sp^3)$–H bonds, respectively, of an organic methyl group.[7] We also report that the metalated heterocyclic ligand left after the C–Me bond cleavage can be functionalized with alkenyl fragments at the C atom that was originally attached to the methyl group.

Results and Discussion

No reaction at all was observed when $[Ru_3(CO)_{12}]$ was treated with 2,6-dimethylpyridine (2.5:1 mol ratio) in THF or chlorobenzene at reflux temperature for 2 h. However, 6,6′-dimethyl-2,2′-bipyridine (Me_2bipy) and 2,9-dimethyl-1,10-phenanthroline (Me_2phen) reacted slowly with $[Ru_3(CO)_{12}]$ in refluxing THF to give the trinuclear derivatives $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-}HCbipyMe)(CO)_8]$ (**1a**) and $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-}HCphenMe)(CO)_8]$ (**1b**), respectively, in moderate yields (Scheme 2). Both N-donor ligands were used in excess to accelerate the consumption of $[Ru_3(CO)_{12}]$ and to minimize the formation of polynuclear by-products (see below).



Scheme 2. Synthesis of **1a** and **1b**.

Higher reaction temperatures resulted in lower yields of these compounds.

The trinuclear nature of these complexes was inferred from their FAB mass spectra, which contain the corresponding molecular ion. The activation of two C–H bonds of a methyl group was indicated by their ^{1}H NMR spectra, which, in addition to the aromatic proton resonances, contain signals assignable to two hydrides (mutually coupled), one CH, and only one methyl group.

The molecular structure of **1a** was confirmed by X-ray diffraction. A selection of interatomic distances is given in Table 1. 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 com-

Table 1. Selected interatomic distances [Å] in compound **1a**.

Ru1–Ru2	2.9654(7)	Ru1–Ru3	2.7466(6)
Ru2–Ru3	2.7916(7)	Ru1–N1	2.099(4)
Ru1–N2	2.253(4)	Ru2–C1	2.157(5)
Ru3–C1	2.133(5)		

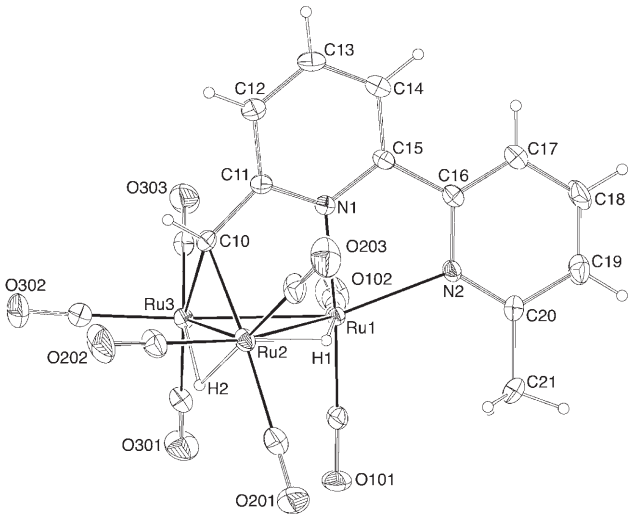


Figure 1. Molecular structure of **1a**.

pleted by eight terminal CO ligands and two edge-bridging hydrides.

It has been reported that the reactions of $[Ru_3(CO)_{12}]$ with 2,2′-bipyridine (H_2bipy) and 1,10-phenanthroline (H_2phen) give $[Ru_3(H_2bipy)(\mu\text{-}CO)_2(CO)_8]$[8] and $[Ru_3(H_2phen)(\mu\text{-}CO)_2(CO)_8]$,[9] respectively, in which the H_2bipy and H_2phen ligands chelate a ruthenium atom. A careful inspection of the X-ray structure of the H_2bipy derivative (Figure 2) reveals that a similar structure would not be possible for Me_2bipy or Me_2phen because there is not enough room to accommodate the methyl groups without their interacting with the carbonyl ligands.

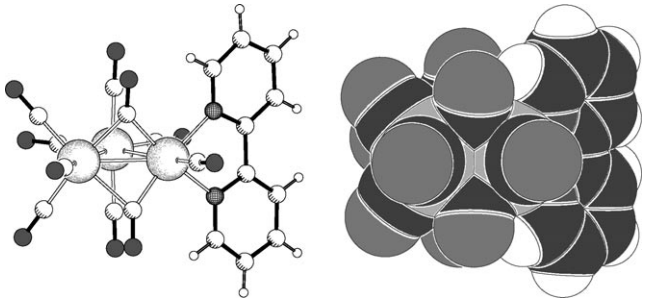


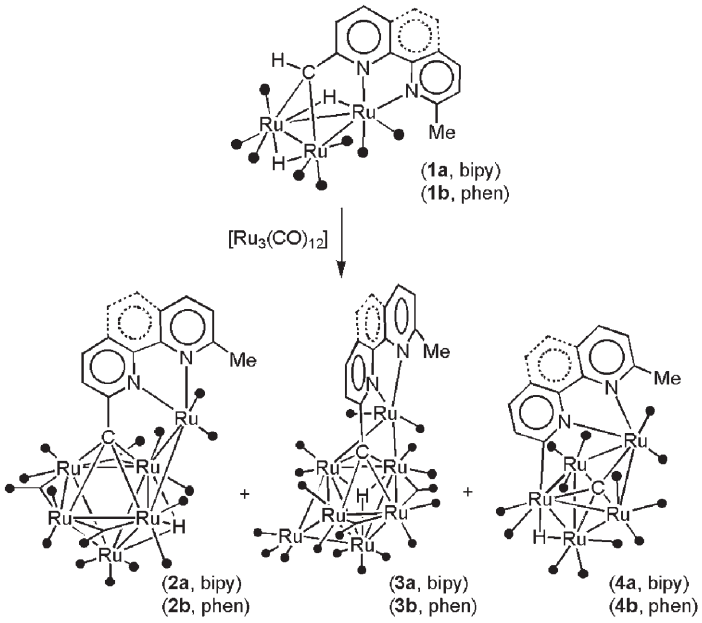
Figure 2. Ball-and-stick and space-filling views of $[Ru_3(H_2bipy)(\mu\text{-}CO)_2(CO)_8]$.

Thus, in the reaction of $[Ru_3(CO)_{12}]$ with Me_2bipy (or Me_2phen), the chelation of this ligand should be accompanied by the release of at least three CO ligands. This is in accordance with the observation that the reaction is slow and requires thermal activation. The unsaturation of the 46-electron intermediate thus-formed and the proximity of one methyl group to the metal atoms 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 complex **1a**, which arises from a double C–H bond activation.

As no reaction was observed between 2,6-dimethylpyridine and $[Ru_3(CO)_{12}]$ under analogous conditions, it is clear that the chelating ability of Me_2bipy and Me_2phen is the driving force for the metalation of one of their methyl groups. A related chelation-assisted approach, in which two metallacycles are formed after the bond activation step, has been used to activate methyl C–H and C–C bonds of appropriate bidentate ligands with mononuclear complexes.[10]

Previous reports describing the oxidative addition of two C–H bonds of a C-bonded methyl group to a metallic fragment are scarce[11] and, as far as we are aware, only one corresponds to a ruthenium cluster.[11a] Some examples of double C–H activation of methyl groups attached to metal[12] or nitrogen[13] atoms are known.

The reaction of **1a** with an equimolar amount of $[Ru_3(CO)_{12}]$ in chlorobenzene at reflux temperature afforded a mixture of the compounds $[Ru_6(\mu_3\text{-}H)(\mu_5\text{-}CbipyMe)(\mu\text{-}CO)_3(CO)_{13}]$ (**2a**), $[Ru_7(\mu_3\text{-}H)(\mu_5\text{-}CbipyMe)(\mu\text{-}CO)_2(CO)_{16}]$ (**3a**), and $[Ru_5(\mu\text{-}H)(\mu_5\text{-}C)(\mu\text{-}bipyMe)(CO)_{13}]$ (**4a**), which were separated by chromatographic techniques (Scheme 3). An analogous reaction starting from **1b** gave $[Ru_6(\mu_3\text{-}H)(\mu_5\text{-}CphenMe)(\mu\text{-}CO)_3(CO)_{13}]$ (**2b**), $[Ru_7(\mu_3\text{-}H)(\mu_5\text{-}CphenMe)(\mu\text{-}CO)_2(CO)_{16}]$ (**3b**), and $[Ru_5(\mu\text{-}H)(\mu_5\text{-}C)(\mu\text{-}phenMe)(CO)_{13}]$ (**4b**) (Scheme 3). The hexanuclear complex **2b** was formed in a very small amount and could not be obtained pure (it was always contaminated by some **3b**). These products could also be prepared in analogous yields by treating $[Ru_3(CO)_{12}]$ with Me_2bipy or Me_2phen, in a 2:1 ratio, in refluxing chlorobenzene.



Scheme 3. Synthesis of **2a,b**, **3a,b**, and **4a,b**.

The IR spectra of the Me_2bipy-derived compounds are similar to those of the Me_2phen-derived complexes, thereby indicating analogous structures. However, the analytical and spectroscopic data of these products were insufficient to assign their structures. These were determined by X-ray diffraction.

The structure of the hexanuclear compound **2a** is shown in Figure 3. A selection of bond lengths is collected in Table 2. It consists of a basal edge-bridged square-pyramidal metallic skeleton with the edge-bridging Ru3 atom chelated by both N atoms of the CbipyMe ligand and the metallic square capped by the carbyne-type C1 atom of the CbipyMe fragment. One face-capping hydride and 16 CO ligands (three of them in bridging positions) complete the cluster shell. Overall, this structure is related to those of $[Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}NpyMe)(\mu\text{-}CO)_2(CO)_{14}]$,[5] $[Ru_6(\mu_3\text{-}H)(\mu_5\text{-}NpyC_6H_4)(\mu\text{-}CO)_3(CO)_{13}]$,[6] $[Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}NCO_2Me)(\mu\text{-}CO)_2(CO)_{14}]$,[14] and $[Ru_6(\mu_4\text{-}S)(\mu\text{-}CO)_3(CO)_{15}]$,[15] although these compounds have μ_4-imido or μ_4-sulfido ligands instead of a μ_4-carbyne.

The structures of the heptanuclear derivatives **3a** and **3b** are shown in Figure 4. Table 3 contains a selection of inter-

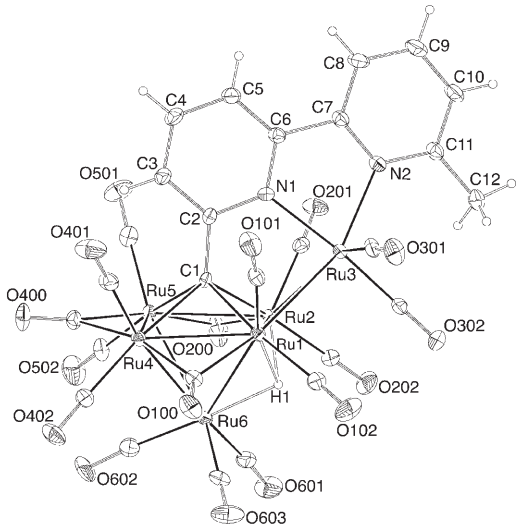


Figure 3. Molecular structure of **2a**.

Table 2. Selected interatomic distances [Å] in compound **2a**.

Ru1−Ru2	2.8438(8)	Ru1−Ru3	2.8550(9)
Ru1−Ru4	2.7311(8)	Ru1−Ru6	2.9686(9)
Ru2−Ru3	2.7798(8)	Ru2−Ru5	2.7469(8)
Ru2−Ru6	2.8859(8)	Ru4−Ru5	2.7596(9)
Ru4−Ru6	2.8599(9)	Ru5−Ru6	2.9116(9)
Ru3−N1	2.126(5)	Ru3−N2	2.208(5)
Ru1−C1	2.168(5)	Ru2−C1	2.229(6)
Ru4−C1	2.266(5)	Ru5−C1	2.223(6)

Table 3. Selected interatomic distances [Å] in compounds **3a** and **3b**.

	3a	**3b**
Ru1−Ru2	2.7719(15)	2.7468(9)
Ru1−Ru3	2.7819(13)	2.8103(8)
Ru1−Ru4	2.7347(14)	2.7315(9)
Ru1−Ru6	2.9367(15)	2.9796(11)
Ru2−Ru3	2.8176(15)	2.8008(10)
Ru2−Ru5	2.7317(15)	2.7377(9)
Ru2−Ru6	2.8682(14)	2.8412(8)
Ru2−Ru7	2.7326(15)	2.7033(10)
Ru4−Ru5	2.7256(16)	2.7085(9)
Ru4−Ru6	2.9161(17)	2.9069(9)
Ru5−Ru6	2.8384(16)	2.8344(9)
Ru5−Ru7	2.7279(17)	2.7283(10)
Ru6−Ru7	2.8635(17)	2.8852(10)
Ru3−N1	2.091(9)	2.096(4)
Ru3−N2	2.180(9)	2.201(5)
Ru1−C1	2.231(11)	2.213(5)
Ru2−C1	2.133(12)	2.127(5)
Ru4−C1	2.244(10)	2.237(5)
Ru5−C1	2.191(10)	2.187(5)

atomic distances. Both structures are very similar to that of **2a**, but an additional Ru atom now caps a triangular face of the square-pyramidal fragment of the metallic skeleton.

The most interesting feature of compounds **2a**, **2b**, **3a**, and **3b** is that they contain a carbyne-type carbon atom that was originally bound to three hydrogen atoms in Me_2bipy or Me_2phen. The activation of the three C–H bonds of a metal-bound methyl group has been reported.[16] However, to the best of 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,[12a,b,17] and none of them arises from an organic methyl group.

The structures of the pentanuclear compounds **4a** and **4b** are very similar. Table 4 contains a comparative selection of interatomic distances. Figure 5 shows, for both complexes, the presence of a carbide ligand, C1, surrounded by five Ru atoms in a distorted trigonal-bipyramidal environment. The cluster core of **4a** and **4b** only contains seven Ru–Ru bonds because the equatorial Ru1 atom is only bonded to the axial Ru2 and Ru3 atoms, while the equatorial Ru4 and Ru5

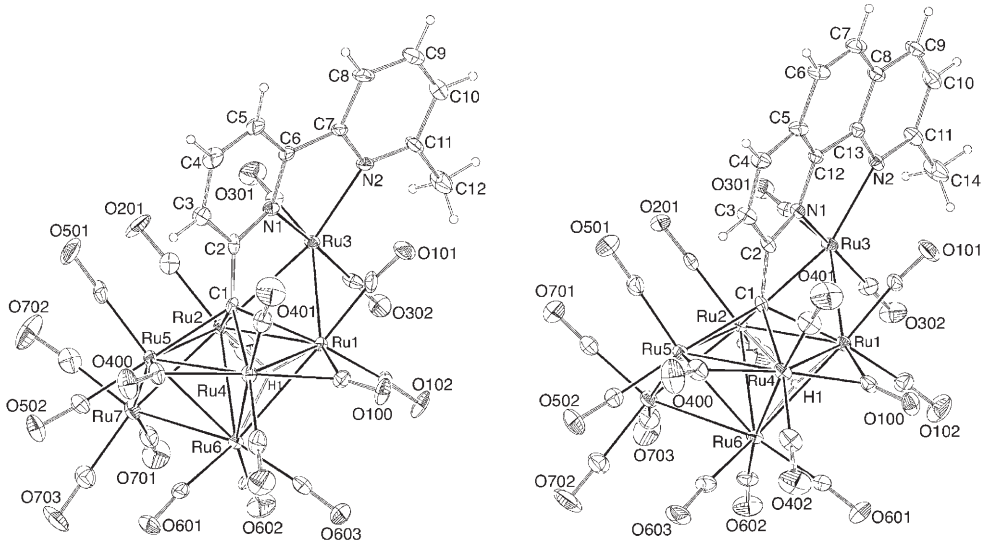


Figure 4. Molecular structures of **3a** (left) and **3b** (right).

Table 4. Selected interatomic distances [Å] in compounds **4a** and **4b**.

	4a	**4b**
Ru1–Ru2	2.8645(7)	2.8750(10)
Ru1–Ru3	2.8933(6)	2.8887(10)
Ru2–Ru4	2.8096(7)	2.7892(11)
Ru2–Ru5	2.8798(7)	2.8745(10)
Ru3–Ru4	2.8552(7)	2.8469(9)
Ru3–Ru5	2.8586(7)	2.8576(10)
Ru4–Ru5	2.8840(7)	2.8835(10)
Ru1–N1	2.098(4)	2.106(6)
Ru1–N2	2.173(4)	2.168(6)
Ru1–C1	2.056(5)	2.042(6)
Ru2–C1	2.004(5)	2.006(7)
Ru3–C1	1.961(5)	1.964(7)
Ru4–C1	2.035(5)	2.042(6)
Ru5–C1	2.104(5)	2.102(7)
Ru4–C2	2.056(5)	2.066(7)

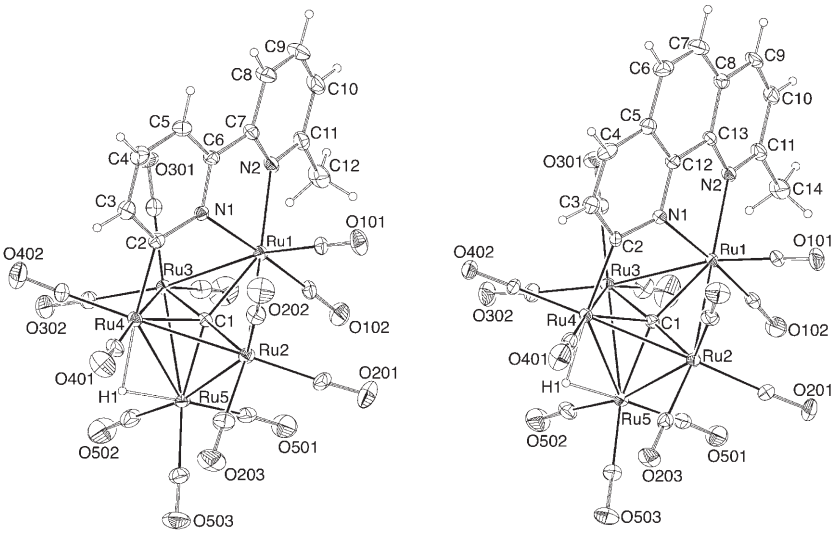


Figure 5. Molecular structures of **4a** (left) and **4b** (right).

atoms are bonded to each other and to both axial Ru atoms. The bipyMe (in **4a**) or phenMe (in **4b**) ligands chelate a Ru atom through both N atoms and are also bonded to an additional Ru atom through the carbon atom, C2, that was originally bound to a methyl group. In both complexes, the cluster shell is completed by 13 terminal CO ligands and a bridging hydride that spans the Ru4–Ru5 edge.

Many transition metal clusters containing carbide ligands have been reported, but none of these ligands arises from an organic methyl group. It is also interesting to note that a few C–C bond activation reactions involving methyl groups have been reported,[2,10,18] but the metal-bound methyl groups of the products do not undergo further C–H bond activation processes.

It is clear that compounds **1** (**a** or **b**) are precursors to compounds **2**–**4** (**a** or **b**, respectively). However, complex **2a** was not transformed into a mixture of **3a** and **4a** when it was heated in refluxing chlorobenzene. Therefore, as the hexanuclear complexes **2** are not intermediates in the synthesis of **3** and **4**, the formation of the latter should take place through the condensation of compound **1** with $[Ru_n(CO)_m]$ species ($n=1$, 3) that are available in hot solutions of $[Ru_3(CO)_{12}]$.

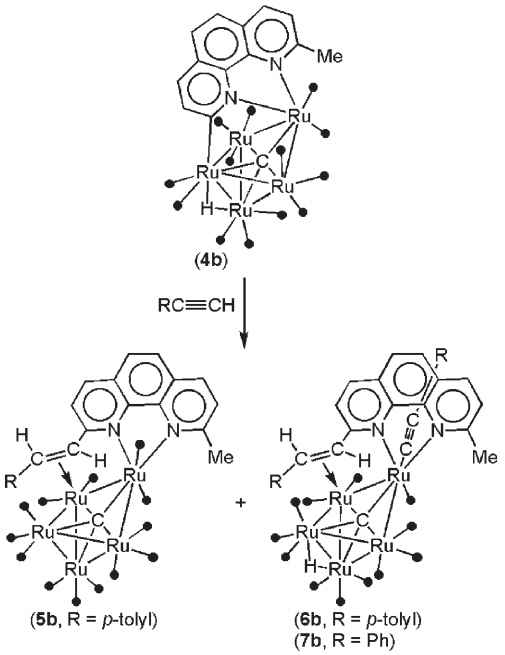
The fact that the pentanuclear compounds **4a** and **4b** contain C-metalated N-heterocyclic ligands prompted us to study their reactions with alkynes as such reactions could lead to cluster complexes containing novel ligands having an unsaturated group (alkenyl or alkynyl) in the same position as that originally occupied by one of the methyl groups of Me_2bipy or Me_2phen. In addition, these reactions could also lead to products arising from carbide–alkenyl or carbide–alkynyl coupling processes.

As no significant differences had so far been observed in the structure and reactivity of the Me_2bipy- and Me_2phen-derived complexes **1**–**4**, we decided to use **4b** as a representative starting material for these reactions because we had accumulated a large amount of this complex compared with what we had of **4a**.

Only untractable decomposition products were obtained when **4b** was treated with diphenylacetylene in toluene at reflux temperature (>2 h), and no reaction was observed under milder conditions or with shorter reaction times. However, the treatment of **4b** with *p*-tolylacetylene in toluene at reflux temperature afforded a mixture of compounds from which complexes $[Ru_5(\mu_5\text{-}C)(\mu\text{-}p\text{-}MeC_6H_4CHCHphenMe)(CO)_{13}]$ (**5b**) and $[Ru_5(\mu\text{-}H)(\mu_5\text{-}C)(\mu\text{-}p\text{-}MeC_6H_4CHCHphenMe)(p\text{-}tolC_2)(CO)_{12}]$ (**6b**) could be separated by chromatographic methods in 29 and 34% yield, respectively (Scheme 4). Under similar conditions, the reaction of **4b** with phenylacetylene also gave an analogous mixture of compounds (^{1}H NMR and TLC monitoring), but $[Ru_5(\mu\text{-}H)(\mu_5\text{-}C)(\mu\text{-}PhCHCHphenMe)(PhC_2)(CO)_{12}]$ (**7b**) was the only product (35% yield) that could be efficiently separated (Scheme 4).

The microanalyses and mass spectra of **5b**, **6b**, and **7b** confirmed their formulation and molecular weight. Their ^{1}H NMR spectra show the presence of *trans* alkenyl fragments in all three compounds and the absence (in **5b**) or the presence of one hydride ligand (in **6b** and **7b**), but give no additional structural information. The CO-stretching regions of the IR spectra of **6b** and **7b** are nearly identical, thus indicating that both compounds have similar structures.

The molecular structure of compound **5b** was determined by X-ray diffraction (Figure 6). A selection of interatomic distances is collected in Table 5. The metal core of **5b** is similar to that of its predecessor **4b** and it also maintains the μ_5-carbide carbon atom. The novel feature of this complex is



Scheme 4. Reactivity of **4b** with *p*-tolyl- and phenylacetylene.

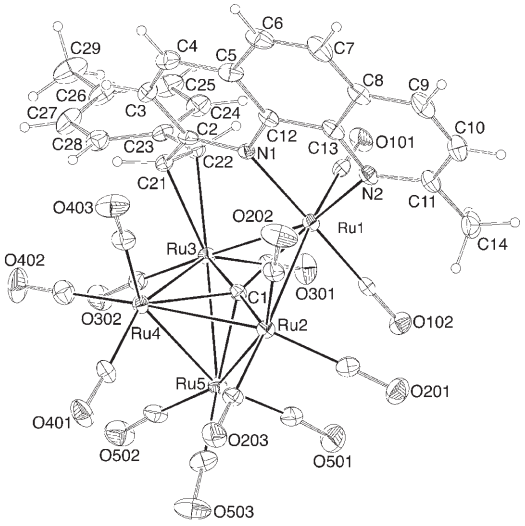


Figure 6. Molecular structure of **5b**.

Table 5. Selected interatomic distances [Å] in compound **5b**.

Ru1–Ru2	2.9480(12)	Ru1–Ru3	2.8420(12)
Ru2–Ru4	2.8533(12)	Ru2–Ru5	2.8923(11)
Ru3–Ru4	2.9017(12)	Ru3–Ru5	2.8735(12)
Ru4–Ru5	2.7067(13)	Ru1–N1	2.123(7)
Ru1–N2	2.169(7)	Ru1–C1	2.101(9)
Ru2–C1	1.968(9)	Ru3–C1	1.963(9)
Ru4–C1	2.138(9)	Ru5–C1	2.111(9)
Ru3–C21	2.223(10)	Ru3–C22	2.276(9)

that it contains the novel ligand (*E*)-1-(9-methyl-1,10-phenanthro-2-yl)-2-(*p*-tolyl)ethene. This ligand is coordinated to Ru3 through both C atoms of its olefin moiety while it chelates the adjacent metal atom Ru1 through the N atoms of its heterocyclic fragment. As in **4b**, 13 terminal CO ligands complete the cluster shell.

Many attempts to get crystals of compounds **6b** and **7b** suitable for X-ray diffraction analysis were carried out but, unfortunately, only poor-quality crystals of **7b**·H_2O were obtained. Nevertheless, one of those crystals was studied by X-ray diffraction. Although the results are not accurate (many non-metal atoms were found to be nonpositive definite after anisotropic refinement),[19] they unambiguously reveal the atom connectivity (Figure 7). The position of the hydride

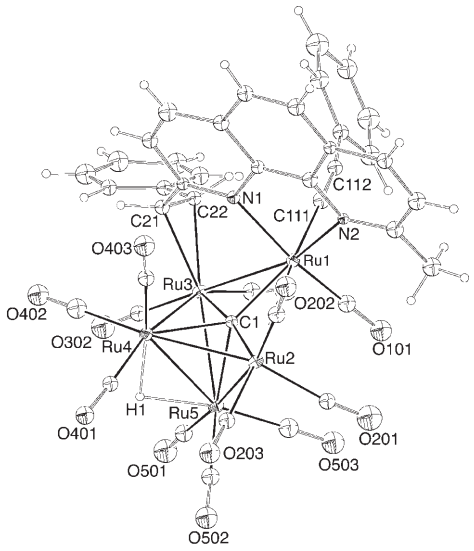


Figure 7. Molecular structure of **7b**.

ligand was calculated with XHYDEX.[20] In **7b**, one of the CO ligands on Ru1 of the phenyl analog of **5b** has been replaced by an alkynyl ligand and a hydride now spans the Ru4–Ru5 edge. Therefore, complex **7b** can be described as the result of the formal substitution of a CO ligand of the phenyl analogue of **5b** by two one-electron ligands—hydride and alkynyl—that arise from the oxidative addition of the terminal alkyne C–H bond.

A reasonable reaction pathway that would account for the formation of **5b**, **6b**, and **7b** is as follows. As **4b** is a coordinatively saturated 76-electron species, it most probably needs to release a CO ligand to allow the coordination of the incoming alkyne reagent. This should be the slowest step of the whole reaction pathway because the reaction requires strong thermal activation (reflux in toluene); **4b** disappears very slowly as the reaction progresses (IR monitoring). A migratory insertion of the coordinated alkyne into a hydride–ruthenium bond would give a metal-bound alkenyl fragment which, through a reductive coupling with the C-metalated heterocycle, would subsequently render an intermediate with the same organic ligand as **5b** (or its phenyl analog), but with only 12 CO ligands. This species could alleviate its unsaturation by either taking a CO from solution to give **5b** (or its phenyl analog), reacting with more alkyne

to give **6b** (or **7b**), or undergoing decomposition. The observation of **5b**, **6b**, and some other minor by-products in the reaction of **4b** with *p*-tolylacetylene suggests that these three possibilities occur at similar rates. The fact that we have not isolated the phenyl analog of **5b** from the reaction of **4b** with phenylacetylene does not necessarily imply that such a complex is not formed as a product. It most probably is formed in a small amount and we simply have been unable to separate it from the decomposition products. The use of **4b**-to-alkyne ratios lower than two only increased the amount of decomposition products.

Therefore, in the reactions of **4b** with terminal alkynes, the first incoming alkyne is transformed into an alkenyl ligand that ends up coupled to the heterocyclic fragment and not to the carbide carbon atom. Space-filling diagrams of the molecular structure of **4b** demonstrate that the carbide is very well protected from external attack by the metal atoms and also by some CO ligands.

Conclusion

We have described the ruthenium cluster-mediated transformation of organic methyl groups into carbide ligands (compounds **4a** and **4b**). Such reactions involve 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, compounds **2** and **3** (**a** and **b**) are unique examples of the activation of three C–H bonds of C-bonded methyl groups.

We have demonstrated that the proximity of a methyl group to a coordinating atom of a ligand is not the only requisite necessary to accomplish various bond-activation processes associated with such a methyl group. There are two additional requirements: one is that the ligand should be a chelate (the energy released on its coordination compensates the high activation energy of the bond-cleavage process), and the other requirement is the use of a polymetallic complex, since the possibility to have the methyl group of a ligand in close proximity to a metal atom of a complex (and thus being susceptible to undergo a C–H or a C–C bond activation) is much greater for polynuclear than for mononuclear complexes.

We have also been able to attach alkenyl fragments to the C^2 carbon atom of the heterocyclic ligand of complex **4b** and, hence, to transform 2,9-dimethyl-1,10-phenanthroline into 2-alkenyl-9-methyl-1,10-phenanthroline ligands.

Experimental Section

General: Solvents were dried over Na/Ph_2CO (THF, diethyl ether, hydrocarbons), CaH_2 (dichloromethane), or molecular sieves (chlorobenzene) and distilled under nitrogen prior to use. The reactions were carried out under nitrogen, using Schlenk/vacuum line techniques, and were routinely monitored by solution IR spectroscopy (carbonyl stretching region) and by spot TLC on silica gel. All reagents were purchased as analytically pure samples. IR: Perkin–Elmer FT Paragon 1000X. NMR: Bruker AV-400 and DPX-300, room temperature, TMS as internal standard ($\delta=0$ ppm). Microanalyses: Perkin–Elmer 2400. MS: VG Autospec double-focusing mass spectrometer operating in the FAB+ mode; ions were produced with a standard Cs^+ gun at about 30 kV; 3-nitrobenzyl alcohol (NBA) was used as matrix; data given refer to the most abundant molecular ion isotopomer.

$[Ru_3(\mu\text{-}H)_2(\mu_3\text{-}HCbipyMe)(CO)_8]$ (1a): A solution of $[Ru_3(CO)_{12}]$ (300 mg, 0.469 mmol) and 6,6′-dimethyl-2,2′-bipyridine (216 mg, 1.173 mmol) in THF (30 mL) was stirred at reflux temperature for 5.5 h. The color changed from orange to black. The solvent was then removed under reduced pressure and the residue dissolved in dichloromethane (2 mL). This solution was separated by column chromatography (15× 2 cm) on silica gel. Hexane/dichloromethane (3:1) eluted some unreacted $[Ru_3(CO)_{12}]$ and a major band (orange), which gave compound **1a** after solvent removal (108 mg, 32%). ^1H NMR (CD_2Cl_2): $\delta=7.8$–6.6 (m, 6H; C*H* bipy), 5.46 (s, 1H; CH), 2.77 (s, 3H; Me), −12.42 (d, $J=3.2$ Hz, 1H; μ-H), −13.72 ppm (d, $J=3.2$ Hz, 1H; μ-H); IR (CH_2Cl_2): $\nu(CO)=2088$ (m), 2049 (s), 2014 (s), 1990 (m), 1980 (m, sh), 1962 (w), 1928 cm^{-1} (w); FAB-MS: *m/z*: 712 $[M]^+$; elemental analysis (%) calcd for $C_{20}H_{12}N_2O_8Ru_3$ (711.53): C 33.76, H 1.70, N 3.94; found: C 33.82, H 1.75, N 3.86.

$[Ru_3(\mu\text{-}H)_2(\mu_3\text{-}HCphenMe)(CO)_8]$ (1b): A solution of $[Ru_3(CO)_{12}]$ (100 mg, 0.057 mmol) and 2,9-dimethyl-1,10-phenanthroline (65 mg, 0.312 mmol) in THF (30 mL) was stirred at reflux temperature for 75 min. The color changed from orange to dark brown. The solvent was removed under reduced pressure and the residue dissolved in dichloromethane (2 mL). This solution was supported on preparative silica gel TLC plates. Hexane/dichloromethane (2:1) eluted several bands. The major band (second, orange) gave compound **1b** upon extraction with dichloromethane and solvent removal (29 mg, 25%). A dark residue remained uneluted in the baseline of the TLC plates. ^1H NMR ($CDCl_3$): $\delta=8.13$ (d, $J=8.2$ Hz, 1H; C*H* phen), 7.76 (d, $J=8.2$ Hz, 1H; C*H* phen), 7.55 (m, 4H; 4 C*H* phen), 5.36 (s, 1H; CH), 2.97 (s, 3H; Me), −12.21 (d, $J=3.9$ Hz, 1H; μ-H), −13.39 ppm (d, $J=3.9$ Hz, 1H; μ-H); IR (CH_2Cl_2): $\nu(CO)=2089$ (m), 2050 (s), 2017 (s), 1991 (m), 1980 (m, sh), 1963 (w), 1928 cm^{-1} (w); FAB-MS: *m/z*: 737 $[M]^+$; elemental analysis (%) calcd for $C_{22}H_{12}N_2O_8Ru_3$ (735.54): C 35.92, H 1.64, N 3.81; found: C 36.10, H 1.73, N 3.71.

$[Ru_6(\mu_3\text{-}H)(\mu_5\text{-}CbipyMe)(\mu\text{-}CO)_3(CO)_{13}]$ (2a), $[Ru_7(\mu_3\text{-}H)(\mu_5\text{-}CbipyMe)(\mu\text{-}CO)_2(CO)_{16}]$ (3a) and $[Ru_5(\mu\text{-}H)(\mu_5\text{-}C)(\mu\text{-}bipyMe)(CO)_{13}]$ (4a): A solution of $[Ru_3(CO)_{12}]$ (100 mg, 0.156 mmol) and 6,6′-dimethyl-2,2′-bipyridine (14 mg, 0.078 mmol) in chlorobenzene (10 mL) was stirred at reflux temperature for 5 h. The color changed from orange to very dark green. The solvent was then removed under reduced pressure and the residue was dissolved in dichloromethane (2 mL) and applied onto silica gel TLC plates. Hexane/dichloromethane (3:2) eluted five bands. The first band (yellow) contained a small amount of a mixture of $[Ru_3(CO)_{12}]$ and $[Ru_4H_4(CO)_{12}]$. The second (orange) contained a trace amount of compound **1a**. The third (yellow), fourth (dark green), and fifth (dark green) bands afforded compounds **4a** (19 mg, 23%), **3a** (18 mg, 17%), and **2a** (13 mg, 14%), respectively, after extraction with dichloromethane and solvent removal. A dark residue remained uneluted in the baseline of the TLC plates.

*Data for **2a**:* ^1H NMR (CD_2Cl_2): $\delta=7.9$–5.9 (m, 6H; CH bipy), 3.05 (s, 3H; Me), −14.37 ppm (s, 1H; μ-H); IR (CH_2Cl_2): $\nu(CO)=2079$ (m), 2042 (vs), 2016 (w), 2000 (m), 1935 (w, br), 1850 (w), 1824 cm^{-1} (m); FAB-MS: *m/z*: 1237 $[M]^+$; elemental analysis (%) calcd for $C_{28}H_{10}N_2O_{16}Ru_6$ (1236.8) : C 27.19, H 0.81, N 2.26; found: C 27.25, H 0.93, N 2.18.

*Data for **3a**:* ^1H NMR (CD_2Cl_2): $\delta=7.9$–5.9 (m, 6H; C*H* bipy), 3.12 (s, 3H; Me), −15.46 ppm (s, 1H; μ-H); IR (CH_2Cl_2): $\nu(CO)=2084$ (m), 2052 (s), 2034 (vs), 2013 (m), 1971 (w), 1947 (w), 1849 (w), 1817 cm^{-1} (w); FAB-MS: *m/z*: 1394 $[M]^+$; elemental analysis (%) calcd for $C_{30}H_{10}N_2O_{18}Ru_7$ (1393.89): C 25.85, H 0.72, N 2.01; found: C 25.93, H 0.80, N 1.95.

*Data for **4a**:* ^1H NMR (CD_2Cl_2): $\delta=7.9$–7.0 (m, 6H; C*H* bipy), 2.96 (s, 3H; Me), −21.31 ppm (s, 1H; μ-H); IR (CH_2Cl_2): $\nu(CO)=2085$ (m), 2046 (s), 2041 (s), 2029 (s), 2006 (w), 1989 (m), 1970 (w, sh), 1943 cm^{-1}

(w); FAB-MS: *m/z*: 1052 $[M]^+$; elemental analysis (%) calcd for $C_{25}H_{10}N_2O_{13}Ru_5$ (1051.70): C 28.55, H 0.96, N 2.66; found: C 28.61, H 1.03, N 2.57.

$[Ru_6(\mu_3\text{-}H)(\mu_5\text{-}CphenMe)(\mu\text{-}CO)_3(CO)_{13}]$ (2b), $[Ru_7(\mu_3\text{-}H)(\mu_5\text{-}CphenMe)(\mu\text{-}CO)_2(CO)_{16}]$ (3b), and $[Ru_5(\mu\text{-}H)(\mu_5\text{-}C)(\mu\text{-}phenMe)(CO)_{13}]$ (4b): A solution of $[Ru_3(CO)_{12}]$ (300 mg, 0.471 mmol) and 2,9-dimethyl-1,10-phenanthroline (60 mg, 0.276 mmol) in chlorobenzene (10 mL) was stirred at reflux temperature for 5 h. The color changed from orange to very dark green. The solvent was then removed under reduced pressure and the residue was dissolved in THF (5 mL) and supported on silica gel (ca. 5 g) by evaporation under vacuum. This material was placed on top of a silica gel chromatographic column (15×3 cm) packed in hexane. Hexane eluted trace amounts of $[Ru_3(CO)_{12}]$ and $[Ru_4H_4(CO)_{12}]$. Hexane/dichloromethane (5:1) eluted a small amount of **1b** followed by a yellow band, which afforded compound **4b** upon solvent removal (32 mg, 11%), and a red band containing a trace amount of an unidentified product. Hexane/dichloromethane (3:2) eluted a dark green band that contained a 1:8 mixture of compounds **2b** and **3b**. Recrystallization of this mixture from dichloromethane/hexane afforded pure **3b** (43 mg, 11%). A dark residue remained uneluted in the baseline of the TLC plates.

*Data for **2b**:* ^{1}H NMR ($CDCl_3$, mixture with **3b**): δ = 3.25 (s, 3H; Me), −14.34 ppm (s, 1H; μ-H); the resonances of the phen protons overlap with those of complex **3b**.

*Data for **3b**:* ^{1}H NMR ($CDCl_3$): δ = 8.35 (d, J = 8.2 Hz, 1H; C*H* phen), 7.83 (d, J = 8.2 Hz, 1H, C*H* phen), 7.81 (d, J = 8.6 Hz, 1H; C*H* phen), 7.71 (m, 2H; 2 C*H* phen), 6.22 (d, J = 8.6 Hz, 1H; C*H* phen), 3.32 (s, 3H; Me), −15.57 ppm (s, 1H; μ-H); IR (CH_2Cl_2): ν(CO) = 2084 (m), 2052 (s), 2034 (vs), 2014 (m), 1970 (w), 1944 (w), 1845 (w), 1817 cm^{-1} (w); FAB-MS: *m/z*: 1418 $[M]^+$; elemental analysis (%) calcd for $C_{32}H_{10}N_2O_{18}Ru_7$ (1417.9): C 27.11, H 0.71, N 1.98; found: C 27.01, H 0.75, N 2.03.

*Data for **4b**:* ^{1}H NMR (CD_2Cl_2): δ = 8.39 (d, J = 8.2 Hz, 1H; C*H* phen), 7.75 (d, J = 3.7 Hz, 1H; C*H* phen), 7.72 (d, J = 3.7 Hz, 1H; C*H* phen), 7.65 (m, 2H, 2 C*H* phen), 7.45 (d, J = 8.2 Hz, 1H; C*H* phen), 3.16 (s, 3H; Me), −21.28 ppm (s, 1H; μ-H); IR (CH_2Cl_2): ν(CO) = 2085 (m), 2046 (s), 2041 (s), 2029 (s), 2006 (w), 1989 (m), 1969 (w, sh), 1945 cm^{-1} (w); FAB-MS: *m/z*: 1076 $[M]^+$; elemental analysis (%) calcd for $C_{27}H_{10}N_2O_{13}Ru_5$ (1075.7): C 30.15, H 0.94, N 2.60; found: C 30.20, H 0.95, N 2.55.

$[Ru_5(\mu_5\text{-}C)(\mu\text{-}p\text{-}MeC_6H_4CHCHphenMe)(CO)_{13}]$ (5b) and $[Ru_5(\mu\text{-}H)(\mu_5\text{-}C)(\mu\text{-}p\text{-}MeC_6H_4CHCHphenMe)(p\text{-}tolC_2)(CO)_{12}]$ (6b): A toluene solution (20 mL) of **4b** (25 mg, 0.023 mmol) and *p*-tolylacetylene (6 μL, 0.050 mmol) was stirred at reflux temperature for 75 min. The color changed from yellow to brown. The solvent was then removed under reduced pressure, the residue was dissolved in dichloromethane (2 mL), and the resulting solution was supported onto preparative silica gel TLC plates. Repeated elution of the plates with hexane/dichloromethane (3:2) allowed the separation of several bands. The two major bands, fourth and fifth in order of elution, both orange, were worked up to afford compounds **5b** (8 mg, 29%) and **6b** (7 mg, 24%), respectively.

*Data for **5b**:* ^{1}H NMR ($CDCl_3$): δ = 8.44 (d, J = 8.3 Hz, 1H; C*H* phen), 8.21 (d, J = 8.7 Hz, 1H, C*H* phen), 7.92 (d, J = 8.3 Hz, 1H; C*H* phen), 7.84 (m, 3H; C*H* phen + *p*-tolyl), 7.45 (d, J = 7.8 Hz, 2H; C*H* *p*-tolyl), 7.21 (m, 2H; C*H* phen), 5.91 (d, J = 11.4 Hz, 1H; C*H* alkenyl), 5.84 (d, J = 11.4 Hz, 1H; C*H* alkenyl), 3.32 (s, 3H; Me), 2.39 ppm (s, 3H; Me); IR (CH_2Cl_2): ν(CO) = 2064 (m), 2030 (vs), 2024 (s, sh), 2005 (m), 1972 (w, br), 1956 cm^{-1} (w, sh); FAB-MS: *m/z*: 1192 $[M]^+$; elemental analysis (%) calcd for $C_{36}H_{18}N_2O_{13}Ru_5$ (1191.9): C 36.28, H 1.52, N 2.35; found: C 36.33, H 1.73, N 2.23.

*Data for **6b**:* ^{1}H NMR ($CDCl_3$): δ = 8.27 (d, J = 8.3 Hz, 1H; C*H* phen), 8.12 (d, J = 8.3 Hz, 1H; C*H* phen), 7.88 (d, J = 12.0 Hz, 1H; C*H* alkenyl), 7.79 (m, 6H, C*H* phen + *p*-tolyl), 7.47 (d, J = 7.9 Hz, 2H; C*H* *p*-tolyl), 7.19 (d, J = 7.9 Hz, 1H; C*H* phen), 7.07 (d, J = 8.3 Hz, 1H; C*H* phen), 6.90 (d, J = 7.9 Hz, 2H; C*H* *p*-tolyl), 6.07 (d, J = 12.0 Hz, 1H; C*H* alkenyl), 3.27 (s, 3H; Me), 2.37 (s, 3H; Me), 2.23 (s, 3H; Me), −21.48 ppm (s, 1H; μ-H); IR (CH_2Cl_2): ν(CO) = 2081 (s), 2055 (s), 2034 (s), 2016 (m), 1992 (w, sh), 1978 (w), 1966 cm^{-1} (w); FAB-MS: *m/z*: 1281 $[M]^+$; elemental analysis (%) calcd for $C_{44}H_{26}N_2O_{12}Ru_5$ (1280.1): C 41.29, H 2.05, N 2.19; found: C 41.37, H 2.16, N 2.05.

$[Ru_5(\mu\text{-}H)(\mu_5\text{-}C)(\mu\text{-}PhCHCHphenMe)(PhC_2)(CO)_{12}]$ (7b): A toluene solution (20 mL) of **4b** (25 mg, 0.023 mmol) and phenylacetylene (6 μL, 0.053 mmol) was stirred at reflux temperature for 60 min. The color changed from yellow to brown. The solvent was then removed under reduced pressure, the residue was dissolved in dichloromethane (2 mL), and the resulting solution was supported onto preparative silica gel TLC

Table 6. Selected crystal, measurement, and refinement data for compounds **1a**, **2a**, **3a**, and **3b**

	1a	**2a**	**3a**	**3b**
formula	$C_{20}H_{12}N_2O_8Ru_3$	$C_{28}H_{10}N_2O_{16}Ru_6$	$C_{30}H_{10}N_2O_{18}Ru_7$	$C_{32}H_{10}N_2O_{18}Ru_7$
formula weight	711.53	1236.80	1393.89	1417.91
color	orange	black	black	black
crystal system	triclinic	monoclinic	orthorhombic	monoclinic
space group	$P\bar{1}$	$P2_1/c$	$Pna2_1$	$P2_1/n$
a [Å]	8.1592(14)	10.306(3)	30.505(12)	17.406(5)
b [Å]	10.9528(19)	30.631(8)	11.815(5)	11.007(4)
c [Å]	13.132(2)	10.826(3)	10.394(4)	20.420(6)
α [°]	91.752(3)	90	90	90
β [°]	98.785(3)	94.188(4)	90	101.140(6)
γ [°]	95.719(3)	90	90	90
V [Å^3]	1152.8(3)	3408.6(15)	3746(3)	3838(2)
Z	2	4	4	4
F(000)	684	2336	2624	2672
ρ_{calcd} [g cm^{-3}]	2.050	2.410	2.472	2.454
radiation (λ, Å)	$Mo_{K\alpha}$, 0.71073	$Mo_{K\alpha}$, 0.71073	$Mo_{K\alpha}$, 0.71073	$Mo_{K\alpha}$, 0.71073
μ [mm^{-1}]	1.988	2.667	2.825	2.759
crystal size [mm]	0.05×0.10×0.19	0.08×0.12×0.14	0.11×0.21×0.24	0.06×0.13×0.22
temperature [K]	299(2)	293(2)	293(2)	296(2)
θ limits [°]	1.57 to 23.28	1.33 to 23.28	1.34 to 23.33	1.41 to 23.28
min./max. h, k, l	−9/9, −12/12, −14/14	−11/10, −30/33, −11/11	-33/33, −13/13, −6/11	−15/19, −12/12, −21/22
collected reflns.	7401	14898	16343	16669
unique reflns.	3293	4811	4152	5508
reflns. with $I>2\sigma(I)$	2614	3975	3977	4468
absorption correction	SADABS	SADABS	SADABS	SADABS
parameters/restraints	311/0	475/0	520/1	538/0
GOF on F^2	1.016	1.011	1.110	1.029
R_1 (on F, $I>2\sigma(I)$)	0.0269	0.0304	0.0315	0.0285
wR_2 (on F^2, all data)	0.0540	0.0656	0.0650	0.0721
max./min. $\Delta\rho$ [e Å^{-3}]	0.490 and −0.371	0.595 and −0.549	0.752 and −0.642	0.629 and −0.616

Table 7. Selected crystal, measurement, and refinement data for compounds **4a**, **4b**·CH_2Cl_2, and **5b**·H_2O·0.5(C_6H_{14}).

	4a	**4b**·CH_2Cl_2	**5b**·H_2O·0.5(C_6H_{14})
formula	$C_{25}H_{10}N_2O_{13}Ru_5$	$C_{27}H_{10}N_2O_{13}Ru_5{\cdot}CH_2Cl_2$	$C_{36}H_{18}N_2O_{13}Ru_5{\cdot}H_2O{\cdot}0.5(C_6H_{14})$
formula weight	1051.70	1160.65	1252.98
color	yellow	yellow	red
crystal system	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a [Å]	10.2820(16)	12.975(4)	11.588(3)
b [Å]	10.8950(16)	12.596(4)	12.322(3)
c [Å]	13.508(2)	21.621(6)	15.818(4)
α [°]	89.939(3)	90	106.282(5)
β [°]	89.194(3)	102.307(5)	105.529(4)
γ [°]	89.532(3)	90	90.351(5)
V [Å^3]	1513.0(4)	3452.7(16)	2080.7(9)
Z	2	4	2
F(000)	996	2208	1214
ρ_{calcd} [g cm^{-3}]	2.309	2.233	2.000
radiation (λ, Å)	$Mo_{K\alpha}$, 0.71073	$Mo_{K\alpha}$, 0.71073	$Mo_{K\alpha}$, 0.71073
μ [mm^{-1}]	2.506	2.357	1.842
crystal size [mm]	0.06×0.12×0.19	0.23×0.29×0.37	0.03×0.09×0.15
temperature [K]	293(2)	293(2)	296(2)
θ limits [°]	1.87 to 23.29	1.61 to 23.29	1.40 to 23.29
min./max. h, k, l	−11/11, −9/12, −15/14	−14/13, −14/13, −24/21	−12/9, −11/13, −17/17
collected reflns.	6685	15022	9498
unique reflns.	4268	4943	5913
reflns. with $I>2\sigma(I)$	3609	4483	3999
absorption correction	SADABS	SADABS	SADABS
parameters/restraints	412/0	453/0	547/2
GOF on F^2	0.978	1.184	0.943
R_1 (on F, $I>2\sigma(I)$)	0.0293	0.0378	0.0441
wR_2 (on F^2, all data)	0.0763	0.0940	0.1194
max./min. $\Delta\rho$ [e Å^{-3}]	0.695 and −1.046	1.087 and −1.173	2.323 and −0.538

plates. A major band was separated from several minor bands by eluting the plates several times with hexane/dichloromethane/acetone (8:1:1). Work-up the major band afforded compound **7b** as an orange solid (10 mg, 35%). ^{1}H NMR ($CDCl_3$): δ = 8.34 (d, J = 8.1 Hz, 1H; C*H* phen), 8.19 (d, J = 8.1 Hz, 1H; C*H* phen), 7.83 (m, 3H, C*H* phen + Ph), 7.57 (d, J = 7.1 Hz, 2H; C*H* Ph), 7.18 (m, 10H, CH phen + Ph + alkenyl), 6.13 (d, J = 11.5 Hz, 1H; C*H* alkenyl), 3.41 (s, 3H; Me), −21.46 ppm (s, 1H; μ-H); IR (CH_2Cl_2): ν(CO) = 2081 (s), 2055 (s), 2033 (s), 2019 (m), 1993 (w, sh), 1968 cm^{-1} (w, br); FAB-MS: m/z: 1253 $[M]^+$; elemental analysis (%) calcd for $C_{42}H_{22}N_2O_{12}Ru_5$ (1252.0): C 40.29, H 1.77, N 2.24; found: C 40.36, H 1.92, N 2.16.

X-ray diffraction studies on 1a, 2a, 3a, 3b, 4a, 4b·CH_2Cl_2, and 5b·H_2O·0.5(C_6H_{14}): Intensity measurements were made with a Bruker AXS SMART 1000 diffractometer with graphite-monochromated $Mo_{K\alpha}$ X-radiation and a CCD area detector. Selected crystallographic data can be found in Tables 6 and 7. Raw frame data were integrated with the SAINT+[21] program. The structures were solved by direct methods with SHELXTL.[22] A semi-empirical absorption correction was applied with the program SADABS.[23] All non-hydrogen atoms were refined anisotropically. The hydride ligands of all compounds and the hydrogen atom of the bridging CH fragment of **1a** were located in difference maps and were fully refined (both coordinates and isotropic thermal parameters). The remaining hydrogen atoms were set in calculated positions and refined as riding atoms. Refinements were made with SHELXTL,[22] and molecular plots were produced with the PLATON program package.[24] CCDC-231373 (**1a**), CCDC-231374 (**2a**), CCDC-231375 (**3a**), CCDC-277942 (**3b**), CCDC-231376 (**4a**), CCDC-277943 (**4b**·CH_2Cl_2), and CCDC-277944 (**5b**·H_2O·0.5(C_6H_{14})) 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.

Acknowledgements

This work was supported by the Spanish MCyT (projects BQU2002-02623 and BQU2003-03414) and the Government of the Principado de Asturias (project PR01-GE7).

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Received: July 14, 2005
Published online: November 22, 2005

