Reviews

Basal-Edge-Bridged Square-Pyramidal Hexaruthenium Carbonyl Clusters: Synthesis, Structure, and Reactivity

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This paper reviews the current knowledge on the synthesis, structure, and reactivity of basal-edge-bridged square-pyramidal hexaruthenium carbonyl cluster complexes, covering the literature up to the end of 2007. These clusters are generally prepared at high temperature (>100 °C) through processes that involve a ligand-promoted condensation of two triruthenium clusters. All cluster complexes of this type contain a bridging ligand with an S-, C-, or N-donor fragment capping the four basal metal atoms of the pyramid. When the bridging ligand is bi- or polydentate, it is also bound to the edge-bridging metal atom. The reactivity of $[Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\kappa^2\text{-ampy})(\mu\text{-}CO)_2(CO)_{14}]$ (H_2ampy = 2-amino-6-methylpyridine) with various reagents has been recently investigated. Its reactions with unsaturated hydrocarbons (carbocycles, alkynes, diynes, alkenes) often involve multisite coordination and hydrogenation or dehydrogenation of the original reagents. The release of an $Ru(CO)_n$ fragment (the only one that is not bound to the bridging ampy ligand) or its exchange between hexanuclear species is also frequently observed. This leads to penta- and heptanuclear clusters as final products. The reactivity of $[Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\kappa^2\text{-ampy})(\mu\text{-}CO)_2(CO)_{14}]$ with other reagents (triphenylphosphine, hydrides, H_2ampy) and its thermolysis in solution are also surveyed.

Introduction

The last 30 years have witnessed a deep advance in the chemistry of ruthenium carbonyl cluster complexes. This intense research activity, which has provided thousands of such clusters, from very simple to very complicated (in terms of nuclearity, structure, and type and number of coordinated ligands), has shed light on many aspects related to metal−metal bonding, stability of particular metallic skeletons, cluster aggregation and degradation processes, CO-substitution reactions, interaction of metal atoms with ligands, transformation of coordinated ligands, and the use of metal clusters in catalytic reactions.[1–3]

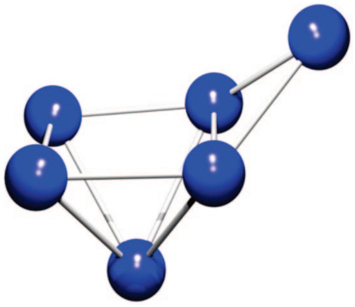

Figure 1. Basal-edge-bridged square-pyramidal (BEBSP) metallic skeleton.

In 2002, we unexpectedly obtained our first hexanuclear ruthenium carbonyl cluster with a basal-edge-bridged square-pyramidal (BEBSP) metallic skeleton (Figure 1).[4] After a literature search, we realized that there were no systematic methods to prepare such compounds from $[Ru_3(CO)_{12}]$ in high yield and that their reactivity was nearly unknown. In fact, the most recent and comprehensive review on medium- and high-nuclearity ruthenium and osmium metal carbonyl cluster complexes, which covers the scientific literature up to 2004,[5] mentions that, up to that date, only nine ruthenium clusters having a BEBSP metallic skeleton had been structurally characterized by X-ray diffraction methods, and four of them correspond to clusters reported by us in our first publication in this field, in 2003.[4] Since then, we have provided a significant number of compounds of this type, some of them prepared in

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(1) All reviews published up to 1988 on organo-transition-metal cluster chemistry are cited in: Bruce, M. I. In *The Chemistry of Metal Cluster Complexes*; Shriver, D. F., Kaesz, H. D., Adams, R. D., Eds.; VCH: New York, 1990; p 367.

(2) For important books on transition-metal clusters, see: (a) *The Chemistry of Metal Cluster Complexes*; Shriver, D. F., Kaesz, H. D., Adams, R. D., Eds.; VCH: New York, 1990. (b) *Metal Clusters in Chemistry*; Braunstein, P., Oro, L. A., Raithby, P. R., Eds.; Wiley-VCH: Weinheim, Germany, 1999. (c) Dyson, P. J.; McIndoe, J. S. *Transition Metal Carbonyl Cluster Chemistry*; Gordon & Breach: Amsterdam, 2000.

(3) Recent reviews on group 8 metal clusters are contained in: *Comprehensive Organometallic Chemistry III*; Crabtree, R. H., Mingos, D. M. P., Eds.; Elsevier: Amsterdam, 2007; Vol. 6. (Bruce, M. I., Ed.).

(4) Cabeza, J. A.; del Río, I.; García-Álvarez, P.; Riera, V.; Suárez, M.; García-Granda, S. *Dalton Trans.* **2003**, 2808.

(5) Humphrey, M. G.; Cifuentes, M. P. in *Comprehensive Organometallic Chemistry III*; Crabtree, R. H., Mingos, D. M. P., Eds.; Elsevier: Amsterdam, 2007; Vol. 6 (Bruce, M. I, Ed.), p. 973.

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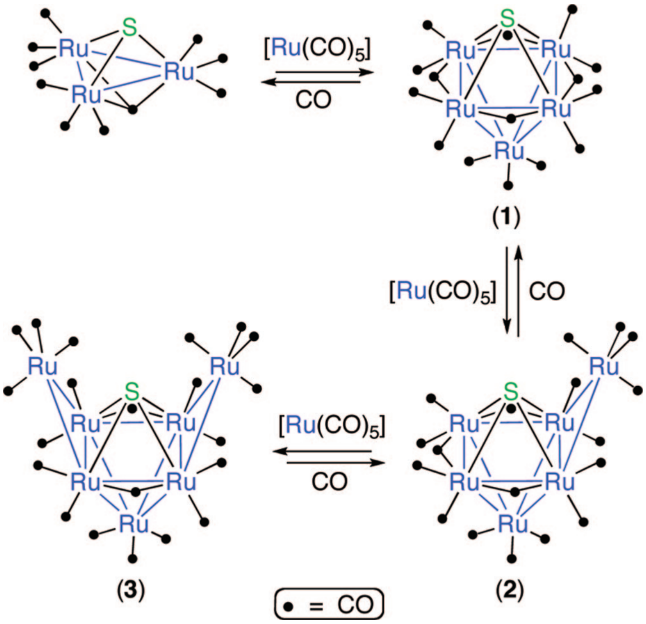
Scheme 1



high yield directly from $[Ru_3(CO)_{12}]$. The efficient synthesis of these compounds has allowed us to undertake a thorough study of their reactivity.

This paper reviews the current knowledge on the synthesis, structure, and reactivity of BEBSP hexaruthenium carbonyl cluster complexes. It covers the scientific literature up to the end of 2007.

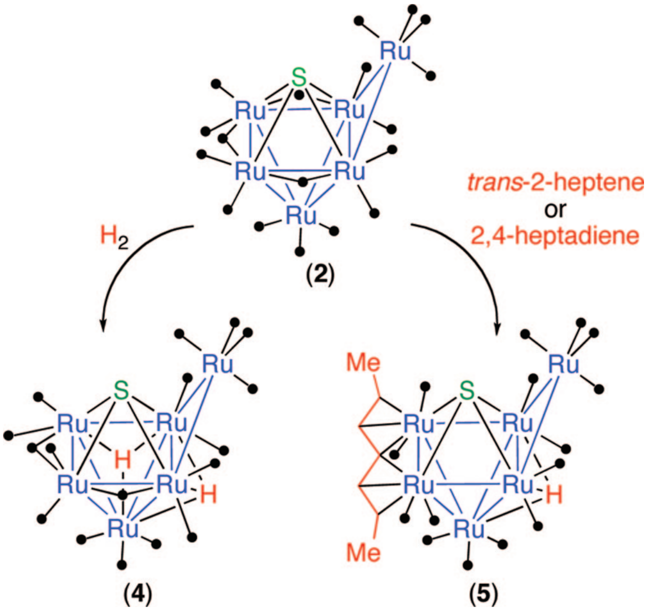
Syntheses and Structures of BEBSP Ruthenium Clusters

BEBSP Clusters with a μ_4-Sulfido Ligand. R. D. Adams' group reported in 1988 that the trinuclear sulfido cluster $[Ru_3(\mu_3\text{-}S)(\mu_3\text{-}CO)(CO)_9]$ can take up to 4 equiv of $[Ru(CO)_5]$ to give a separable mixture of the penta-, hexa-, and heptanuclear derivatives $[Ru_5(\mu_4\text{-}S)(\mu\text{-}CO)_4(CO)_{11}]$ (**1**), $[Ru_6(\mu_4\text{-}S)(\mu\text{-}CO)_3(CO)_{15}]$ (**2**), and $[Ru_7(\mu_4\text{-}S)(\mu\text{-}CO)_2(CO)_{19}]$ (**3**), respectively (Scheme 1). No tetranuclear species were detected. Under optimized conditions (1:10 cluster to $[Ru(CO)_5]$ ratio, heptane, reflux temperature, CO purge, 15 min), the BEBSP hexanuclear derivative **2** was obtained in 55% yield.

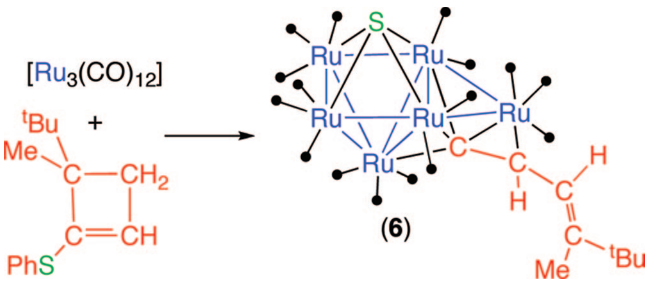
Compound **2** was the first hexaruthenium cluster with a BEBSP metallic skeleton to be reported.[6] It contains a sulfido ligand, which caps the 4 basal atoms of the pyramid, and 18 CO ligands, 3 of them bridging the basal edges that are not spanned by the $Ru(CO)_4$ fragment. The bonds to the apical Ru atom are 0.1−0.2 Å longer than those in the square base and those involving the edge-bridging Ru atom.

The metallic skeleton of **2** is retained in its reactions with hydrogen and *trans*-2-heptene (Scheme 2). The reaction with hydrogen (1 atm, 80 °C, 15 min) led to $[Ru_6(\mu_3\text{-}H)_2(\mu_4\text{-}S)(\mu\text{-}CO)_2(CO)_{15}]$ (**4**), which contains two face-capping hydrido ligands,[7] whereas that with *trans*-2-heptene (heptane, reflux temperature) gave a 7% yield of the dienyl derivative $[Ru_6(\mu_3\text{-}H)(\mu_4\text{-}S)(\mu\text{-}\eta^5\text{-}Me_2C_5H_5)(CO)_{15}]$ (**5**). A better yield of **5** (18%) was achieved when 2,4-heptadiene was used as the source of the dienyl ligand.[8]

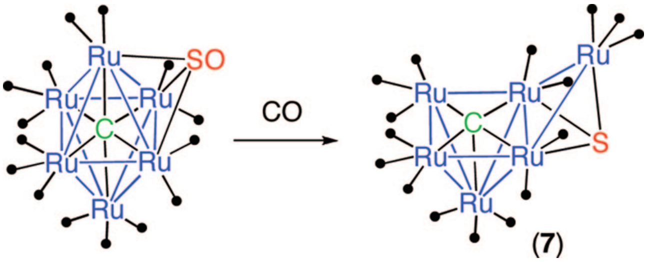
Scheme 2



Scheme 3



Scheme 4



In 1994, R. D. Adams' group isolated a new hexaruthenium sulfido cluster with a BEBSP metallic skeleton, $[Ru_6(\mu_4\text{-}S)\{\mu_4\text{-}\eta^2\text{-}CCHCHC(Me)^tBu\}(CO)_{16}]$ (**6**), though in very low yield (1%), from the reaction of $[Ru_3(CO)_{12}]$ with 4-*tert*-butyl-4-methyl-1-(phenylthio)cyclobutene in refluxing heptane (Scheme 3).[9] The opening of the cyclobutene ring and the cleavage of the S−C bonds are responsible for the formation of a sulfido and a vinylidene ligand, both bridging four metal atoms.

BEBSP Clusters with a Bridging Carbido Ligand. The BEBSP hexanuclear cluster $[Ru_6(\mu_5\text{-}C)(\mu_3\text{-}S)(CO)_{16}]$ (**7**) has been prepared by T. Chihara et al. in good yield (74%) from the octahedral carbido precursor $[Ru_6(\mu_6\text{-}C)(\mu_3\text{-}SO)(CO)_{15}]$ and CO at 70 °C. In this reaction, the reduction of the SO ligand

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(6) Adams, R. D.; Babin, J. E.; Tasi, M. *Organometallics* **1988**, *7*, 503.

(7) Adams, R. D.; Babin, J. E.; Tasi, M.; Wolfe, T. A. *New J. Chem.* **1988**, *12*, 481.

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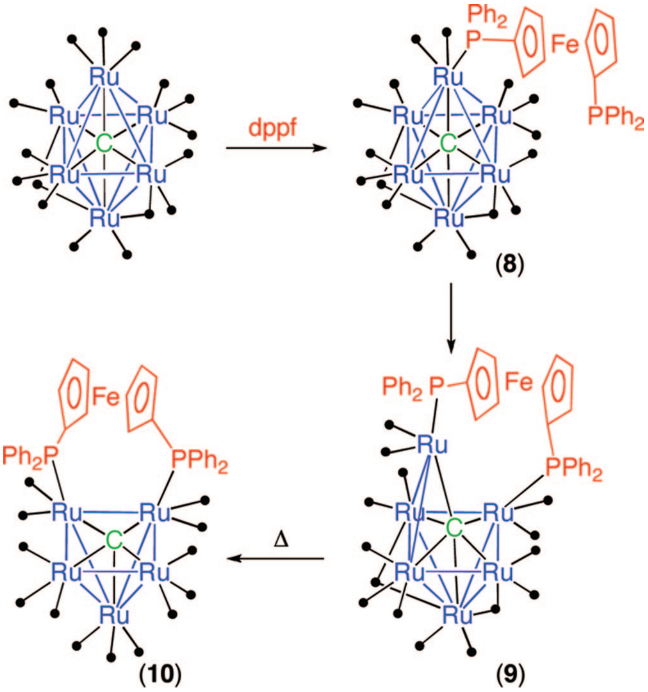
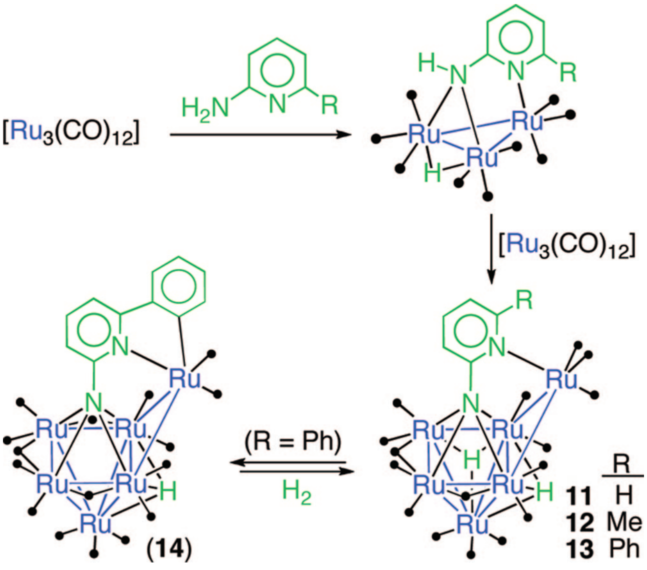
(9) Adams, R. D.; Qu, X.; Wu, W. *Organometallics* **1994**, *13*, 1272.

Scheme 5



Scheme 6



was accompanied by the addition of CO and cleavage of two Ru−Ru bonds (Scheme 4).[10]

B. F. G. Johnson's group has also reported a BEBSP hexaruthenium cluster derived from a carbido precursor. The reaction of $[Ru_6(\mu_6\text{-}C)(\mu\text{-}CO)_2(CO)_{15}]$ with 1,1′-bis(diphenylphoshino)ferrocene (dppf) in refluxing THF initially afforded the spectroscopically characterized monosubstituted derivative $[Ru_6(\mu_6\text{-}C)(\kappa^1\text{-dppf})(\mu\text{-}CO)_2(CO)_{14}]$ (**8**), which was slowly converted into the paramagnetic BEBSP cluster $[Ru_6(\mu_6\text{-}C)(\mu\text{-}\kappa^2\text{-dppf})(\mu\text{-}CO)_2(CO)_{13}]$ (**9**) (Scheme 5). Its magnetic moment is 35% of the moment expected for a spin triplet state. This is due to a weak antiferromagnetic coupling between the ferrocene fragment and the Ru_6 unit.[11] Further heating of complex **9** resulted in cluster degradation, to give the pentanuclear derivative $[Ru_5(\mu_5\text{-}C)(\mu\text{-}\kappa^2\text{-dppf})(CO)_{13}]$ (**10**).[12]

The molecular structure of compound **9** is curious, since its metallic core can also be considered to be a very distorted octahedron with two very long Ru−Ru distances, 3.171(1) and 3.450(1) Å, separating the P-bound apical Ru atom from two equatorial Ru atoms. All the remaining Ru−Ru distances are within the normal range. The carbido C atom is displaced 0.127(8) Å from the centroid of the four basal metal atoms of the pyramid toward the P-bound Ru atom.[11]

BEBSP Clusters with a μ_4-Imido Ligand. We have reported that treatment of $[Ru_3(CO)_{12}]$ with 0.5 equiv of 2-aminopyridine (H_2apyH) in refluxing xylene for 1 h allows the isolation of the BEBSP hexanuclear complex $[Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\kappa^2\text{-apyH})(\mu\text{-}CO)_2(CO)_{14}]$ (**11**) in 70% yield (Scheme 6).[4,13] Interestingly, the use of 2-amino-6-methylpyridine (H_2ampy) led to the analogous cluster $[Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\kappa^2\text{-ampy})(\mu\text{-}CO)_2(CO)_{14}]$ (**12**),[13] but the use of 2-amino-6-phenylpyridine (H_2apyPh) gave a mixture of products, from which the hexanuclear derivatives $[Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\kappa^2\text{-apyPh})(\mu\text{-}CO)_2(CO)_{14}]$ (**13**) and $[Ru_6(\mu_3\text{-}H)(\mu_5\text{-}\kappa^3\text{-apyC}_6H_4)(\mu\text{-}CO)_3(CO)_{13}]$ (**14**) were isolated in lower yields (Scheme 6).[14] By monitoring the reactions by IR spectroscopy and spot TLC, it was observed that the trinuclear amido-bridged derivatives $[Ru_3(\mu\text{-}H)(\mu_3\text{-}\kappa^2\text{-HapyR})(CO)_9]$[15] (R = H, Me, Ph) are intermediates in the formation of **11**−**13**.

The hexanuclear cyclometalated complex **14** seems to arise from more than one source, since the thermal transformation of **13** into **14** is rather inefficient, even after long reaction times. In addition, in the reaction of $[Ru_3(CO)_{12}]$ with H_2apyPh, complex **14** was formed after short reaction times in yields only a bit lower than those of **13**. Therefore, complex **14** may also be formed by condensation of $[Ru_3(CO)_{12}]$ with a trinuclear cyclometalated species that would arise from $[Ru_3(\mu\text{-}H)(\mu_3\text{-}\kappa^2\text{-HapyPh})(CO)_9]$ under the reaction conditions. Such an intermediate has been spectroscopically detected but has not been isolated.[14]

The structures of compounds **11**−**14** were determined by X-ray diffraction methods. They all have a BEBSP metallic skeleton. While the pyridine nitrogen atom of the bridging ligand is attached to the metal atom that spans the base of the square pyramid, the exocyclic nitrogen atom, an imido fragment, caps the metallic square, being ca. 0.06 Å closer to the metal atoms of the bridged edge than to the two remaining basal Ru atoms. The Ru−Ru distances between the apical metal atom and the four basal ruthenium atoms are 0.1−0.2 Å longer than the remaining Ru−Ru distances. While the phenyl ring of **13** is uncoordinated and perpendicular to the pyridine plane, that of complex **14** is cyclometalated and coplanar with the pyridine ring. Such an interaction induces a lengthening of the trans Ru−Ru distance, from 2.6841(6) Å in **13** to 2.9018(8) Å in **14**, as a consequence of the higher trans influence of the phenyl group with respect to that of the carbonyl ligand. While compound **14** has a face-capping hydride ligand, complexes **11**−**13** have two face-capping hydrides. All these clusters contain 16 CO ligands, but they differ in the number of bridging carbonyls, since **11**−**13** have 2 and **14** has 3 bridging CO

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(10) Chihara, T.; Wakatsuki, Y.; Tase, T.; Ogawa, H. *Chem. Commun.* **1999**, 279.

(11) Blake, A. J.; Harrison, A.; Johnson, B. F. G.; McInnes, E. J. L.; Parsons, S.; Shephard, D. S.; Yellowlees, L. J. *Organometallics* **1995**, *14*, 3160.

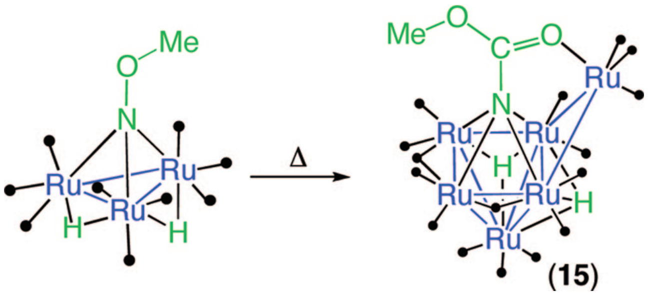
(12) Shephard, D. S.; Johnson, B. F. G.; Harrison, A.; Parsons, S.; Smidt, S. P.; Yellowlees, L. J.; Reed, D. *J. Organomet. Chem.* **1998**, *563*, 113.

(13) Cabeza, J. A.; del Río, I.; García-Álvarez, P.; Miguel, D.; Riera, V. *Inorg. Chem.* **2004**, *43*, 5450.

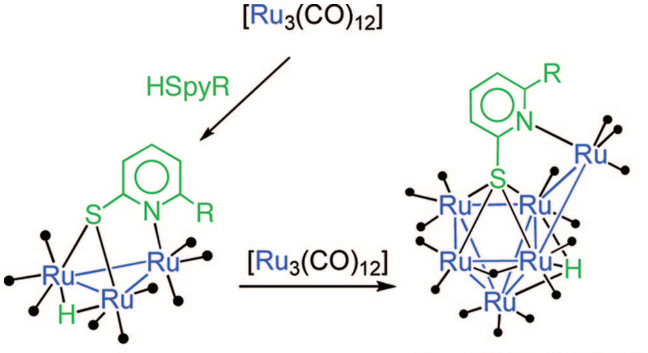
(14) Cabeza, J. A.; del Río, I.; Riera, V.; Suárez, M.; García-Granda, S. *Organometallics* **2004**, *23*, 1107.

(15) Cabeza, J. A. *Eur. J. Inorg. Chem.* **2002**, 1559.

Scheme 7



Scheme 8



R = H (**16**), Me (**17**)

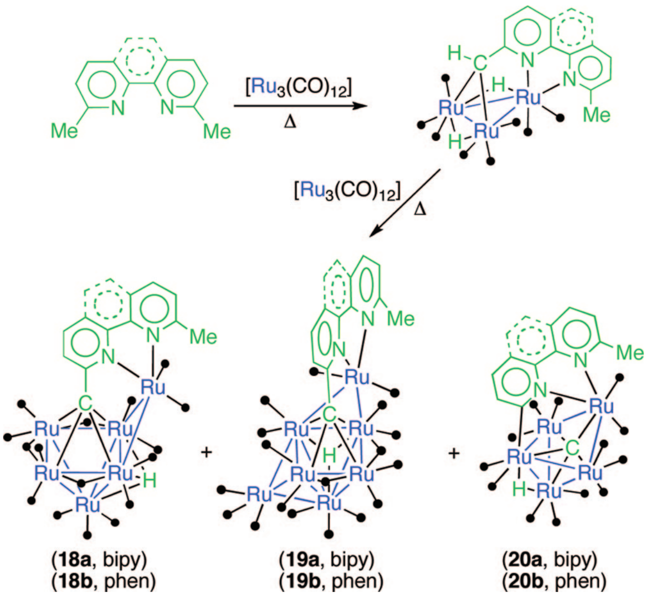
ligands. In both cases, these carbonyl ligands span the edges of the metallic square that are not bridged by hydride ligands.[13,14]

The efficient synthesis of compound **12** has allowed the development of its reactivity (vide infra). Although many of its derivatives also have a BSBSP metallic skeleton, their syntheses and structures are commented on below in the section devoted to the reactivity of compound **12**.

W. T. Wong's group has reported that the solid-state pyrolysis (140 °C, 2 h) of the trinuclear methoxyimido cluster $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-}NOMe)(CO)_9]$ affords a complicated mixture of products, from which the BEBSP cluster derivative $[Ru_6(\mu_3\text{-}H)_2\{\mu_5\text{-}\kappa^2\text{-}NC(O)OMe\}(\mu\text{-}CO)_2(CO)_{14}]$ (**15**) could be isolated in 5% yield (Scheme 7). Its molecular structure is entirely analogous to that of compounds **11**−**13**, but its bridging ligand is now a doubly deprotonated methyl carbamate, which arises from the insertion of a CO ligand into the N−O bond of the original methoxyimido ligand. The new imido-type ligand is coordinated through the nitrogen atom to the four basal Ru atoms and through the carbonyl oxygen to the edge-bridging Ru atom.[16]

BEBSP Clusters with a μ_4-Thiolato Ligand. The reaction of $[Ru_3(CO)_{12}]$ with 0.5 mol of 2-mercaptopyridine (HSpyH) in THF at reflux temperature lead to a mixture of products, from which the dark green BEBSP hexanuclear derivative $[Ru_6(\mu_3\text{-}H)(\mu_5\text{-}\kappa^2\text{-}SpyH)(\mu\text{-}CO)(CO)_{15}]$ (**16**) could be separated by chromatographic methods (38% yield) (Scheme 8).[17] The trinuclear thiolato cluster $[Ru_3(\mu\text{-}H)(\mu_3\text{-}\kappa^2\text{-}SpyH)(CO)_9]$[18,19] has been observed as a transient intermediate when the reaction is monitored by IR spectroscopy and spot TLC. In fact, complex **16** could also be prepared in comparable yield by heating $[Ru_3(CO)_{12}]$ and $[Ru_3(\mu\text{-}H)(\mu_3\text{-}\kappa^2\text{-}SpyH)(CO)_9]$ (1:1 mol ratio) in refluxing THF. The methylated derivative $[Ru_6(\mu_3\text{-}H)(\mu_5\text{-}\kappa^2\text{-}SpyMe)(\mu\text{-}CO)(CO)_{15}]$ (**17**) has been similarly obtained (28% yield) from 2-mercapto-6-methylpyridine (HSpyMe). The stepwise synthesis of compounds **16** and **17** is again an example of the sulfur-ligand-mediated condensation of trinuclear clusters. Although papers detailing other reactions of $[Ru_3(CO)_{12}]$ with HSpyH have been published,[18,19] none of them report the observation of a BEBSP hexanuclear product, because they all use HSpyH to $[Ru_3(CO)_{12}]$ mole ratios higher than that needed for the preparation of complex **16** (0.5).

Scheme 9



(**18a**, bipy)
(**18b**, phen)

(**19a**, bipy)
(**19b**, phen)

(**20a**, bipy)
(**20b**, phen)

The X-ray structure of compound **17** reveals a BEBSP metallic skeleton anchored to an SpyMe ligand in such a way that the four basal ruthenium atoms are attached to the thiolato S atom and the edge-bridging ruthenium atom is bound to the pyridine N atom. In contrast with the sulfido derivative **2**, which has no hydrides, and the imido derivatives **11**−**15**, which have two hydrides, the thiolate clusters **16** and **17** contain one hydride ligand capping a face of the pyramid. Their cluster shell is completed by 1 edge-bridging and 15 terminal CO ligands.[17]

BEBSP Clusters with a μ_4-Carbyne Ligand. We have reported that 6,6′-dimethyl-2,2′-bipyridine (Me_2bipy) and 2,9-dimethyl-1,10-phenanthroline (Me_2phen) react slowly with $[Ru_3(CO)_{12}]$ in refluxing THF to give the trinuclear derivatives $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-}\kappa^3\text{-}HCbipyMe)(CO)_8]$ and $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-}\kappa^3\text{-}HCphenMe)(CO)_8]$ in moderate yields (Scheme 9).[20,21] The successful preparation of the imido-bridged BEBSP clusters **11**−**13** by the thermal condensation of related trinuclear amido species with $[Ru_3(CO)_{12}]$ (Scheme 6) led us to attempt the condensation of $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-}\kappa^3\text{-}HCbipyMe)(CO)_8]$ and $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-}\kappa^3\text{-}HCphenMe)(CO)_8]$ with $[Ru_3(CO)_{12}]$, with the aim of preparing carbyne-bridged BEBSP hexanuclear derivatives.

The reactions of the trinuclear cluster $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-}\kappa^3\text{-}HCbipyMe)(CO)_8]$ with an equimolar amount of $[Ru_3(CO)_{12}]$ in chlorobenzene at reflux temperature afforded a mixture of the compounds $[Ru_6(\mu_3\text{-}H)(\mu_5\text{-}\kappa^3\text{-}CbipyMe)(\mu\text{-}CO)_3(CO)_{13}]$ (**18a**), $[Ru_7(\mu_3\text{-}H)(\mu_5\text{-}\kappa^3\text{-}CbipyMe)(\mu\text{-}CO)_2(CO)_{16}]$ (**19a**), and $[Ru_5(\mu\text{-}H)(\mu_5\text{-}C)(\mu\text{-}\kappa^3\text{-}bipyMe)(CO)_{13}]$ (**20a**), which could be separated by chromatographic techniques (Scheme 9). The

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(18) Andreu, P. L.; Cabeza, J. A.; Fernández-Colinas, J. M.; Riera, V. *J. Chem. Soc., Dalton Trans.* **1990**, 2927.

(19) Deeming, A. J.; Hardcastle, K. I.; Karim, M. *Inorg. Chem.* **1992**, *31*, 4792.

(20) Cabeza, J. A.; da Silva, I.; del Río, I.; Martínez-Méndez, L.; Miguel, D.; Riera, V. *Angew. Chem., Int. Ed.* **2004**, *43*, 3464.

(21) Cabeza, J. A.; del Río, I.; Martínez-Méndez, L.; Miguel, D. *Chem. Eur. J.* **2006**, *12*, 1529.

reaction starting from [Ru$_3$(μ-H)$_2$(μ_3-κ^3-HCphenMe)(CO)$_8$] gave [Ru$_6$(μ_3-H)(μ_5-κ^3-CphenMe)(μ-CO)$_3$(CO)$_{13}$] (**18b**), [Ru$_7$(μ_3-H)(μ_5-κ^3-CphenMe)(μ-CO)$_2$(CO)$_{16}$] (**19b**), and [Ru$_5$(μ-H)(μ_5-C)(μ-κ^3-phenMe)(CO)$_{13}$] (**20b**) (Scheme 9). The hexanuclear complex **18b** was formed in a very small amount and could not be obtained pure. These products could also prepared in analogous yields by treating [Ru$_3$(CO)$_{12}$] with Me$_2$bipy or Me$_2$phen, in a 2:1 ratio, in refluxing chlorobenzene.[20,21]

The structure of the hexanuclear compound **18a** was determined by X-ray diffraction. Its consists of a BEBSP metallic skeleton with the edge-bridging Ru atom chelated by both N atoms of the CbipyMe ligand and the metallic square capped by the carbyne-type C atom of the CbipyMe fragment. One face-capping hydride and 16 CO ligands (3 of them in bridging positions) complete the cluster shell.

The structures of the heptanuclear derivatives **19a**,**b** are very similar to those of **18a**,**b**, but an additional Ru atom now caps a triangular face of the square-pyramidal fragment of the metallic skeleton.

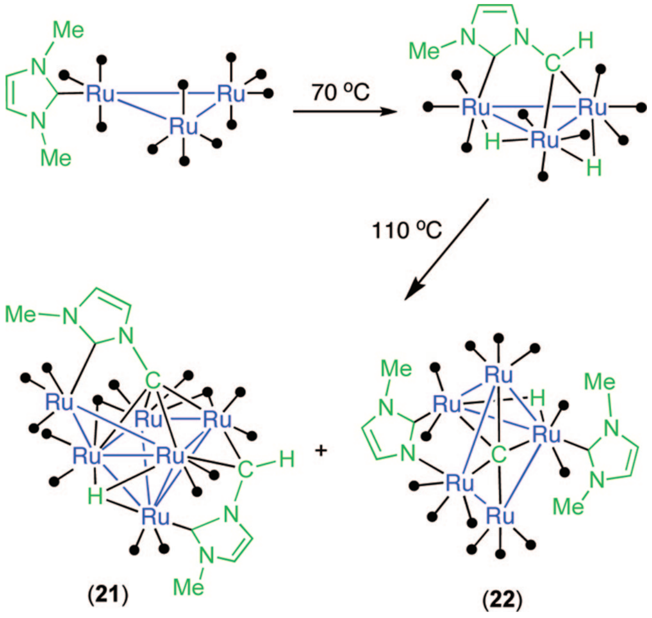
A very interesting feature of these compounds is that they contain a carbyne-type carbon atom that was originally bound to three hydrogen atoms in Me$_2$bipy or Me$_2$phen. The oxidative addition of all three C−H bonds of a C-bound methyl group has only been achieved one other time, very recently on an osmium cluster.[22]

The pentanuclear compounds **20a**,**b** contain a carbide ligand surrounded by five Ru atoms in a distorted-trigonal-bipyramidal environment (Scheme 9). Their cluster core only contains seven Ru−Ru bonds, because one equatorial Ru atom is only bonded to the axial Ru atoms, while the two remaining equatorial Ru atoms are bonded to each other and to both axial Ru atoms. The bipyMe (in **20a**) or phenMe (in **20b**) ligand chelates a Ru atom through both N atoms and is also attached to an additional Ru atom through the carbon atom that was originally bound to a methyl group. In both complexes, the cluster shell is completed by 13 terminal CO ligands and an edge-bridging hydride.[21,22] Although many transition-metal clusters containing carbide ligands have been reported, none of these ligands arise from a C-bound methyl group. It is also interesting to note that a few C−C bond activation reactions involving methyl groups have been reported,[23] but the metal-bound methyl groups of the products do not undergo further C−H bond activation processes.

Clearly, the trinuclear complexes [Ru$_3$(μ-H)$_2$(μ_3-κ^3-HCbipyMe)(CO)$_8$] and [Ru$_3$(μ-H)$_2$(μ_3-κ^3-HCphenMe)(CO)$_8$] are precursors to compounds **18a**,**b**. However, the hexanuclear complexes **18** are not intermediates in the synthesis of **19** and **20**, because the latter are not formed when complexes **18** are heated in refluxing chlorobenzene. Therefore, their formation should take place through the condensation of [Ru$_3$(μ-H)$_2$(μ_3-κ^3-HCbipyMe)(CO)$_8$] or [Ru$_3$(μ-H)$_2$(μ_3-κ^3-HCphenMe)(CO)$_8$] with [Ru$_n$(CO)$_m$] species (n = 1, 3), which are available in hot solutions of [Ru$_3$(CO)$_{12}$].

The thermolysis of the trinuclear cluster [Ru$_3$(Me$_2$Im)(CO)$_{11}$][24,25] (Me$_2$Im = 1,3-dimethylimidazol-2-ylidene) in THF at reflux temperature afforded [Ru$_3$(μ-H)$_2$(μ_3-κ^2-MeImCH)(CO)$_9$], which results from the intramolecular activation of two C−H bonds of an *N*-methyl group (Scheme 10).[25,26] The great basicity of the N-heterocyclic carbene (NHC) ligand Me$_2$Im probably is the driving force of this reaction. Longer reaction times or higher temperatures (refluxing toluene) transform [Ru$_3$(μ-H)$_2$(μ_3-κ^2-MeImCH)(CO)$_9$] into a ca. 1:1 mixture of the BEBSP cluster [Ru$_6$(μ_3-H)(μ_5-κ^2-MeImC)(μ_3-κ^2-MeImCH)(μ-CO)$_2$(CO)$_{13}$] (**21**) and the pentanuclear derivative [Ru$_5$(μ_5-C)(μ-H)(μ-κ^2-MeIm)(Me$_2$Im)(CO)$_{13}$] (**22**), which could be separated by chromatographic methods (Scheme 10).

Scheme 10



The BEBSP cluster **21** contains two NHC ligands. One has a carbyne-type C atom spanning the four basal metal atoms, whereas the carbene C atom 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 Ru atom through its carbene C atom and spans a basal edge through the C−H fragment. The cluster shell is completed by a triply bridging hydride and 15 CO ligands. Compound **21** arises from a thermally mediated condensation of two molecules of [Ru$_3$(μ-H)$_2$(μ_3-κ^2-MeImCH)(CO)$_9$], also involving the activation of the third C−H bond of an original *N*-methyl group. As far as we are aware, this is the only example of oxidative addition of all three C−H bonds of an *N*-methyl group.

The structure of compound **22** consists of a distorted-trigonal-bipyramidal arrangement of metal atoms surrounding an interstitial carbide ligand. The apical metal atoms are attached to the three equatorial Ru atoms, but one equatorial Ru atom is not bonded to the other two equatorial Ru atoms. An MeIm NHC ligand bridges two equatorial Ru atoms through its carbene C atom and one of its N atoms, while an additional NHC ligand, in this case an intact Me$_2$Im, is bonded to the remaining equatorial metal atom. The cluster shell is completed by an edge-bridging hydride and 13 terminal CO ligands. This structure is somewhat related to that of compounds **20a**,**b**. The intact Me$_2$Im

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[22] Cooke, C. E.; Jennings, M. C.; Pomeroy, R. K.; Clyburne, J. A. C. *Organometallics* **2007**, *26*, 6059.

[23] See, for example: (a) Gandelman, M.; Shimon, L. J. W.; Milstein, D. *Chem. Eur. J.* **2003**, *9*, 4295. (b) Gauvin, R. M.; Rozenberg, H.; Shimon, L. J. W.; Milstein, D. *Organometallics* **2001**, *20*, 1719. (c) Gandelman, M.; Vigalok, A.; Shimon, L. J. W.; Milstein, D. *Organometallics* **1997**, *16*, 3981. (d) Rybtchinski, B.; Oevers, S.; Montag, M.; Vigalok, A.; Rozenberg, H.; Martin, J. M. L.; Milstein, D. *J. Am. Chem. Soc.* **2001**, *123*, 9064. (e) Jazzar, R. F. R.; Macgregor, S. A.; Mahon, M. F.; Richards, S. P.; Whittlesey, M. K. *J. Am. Chem. Soc.* **2002**, *124*, 4944.

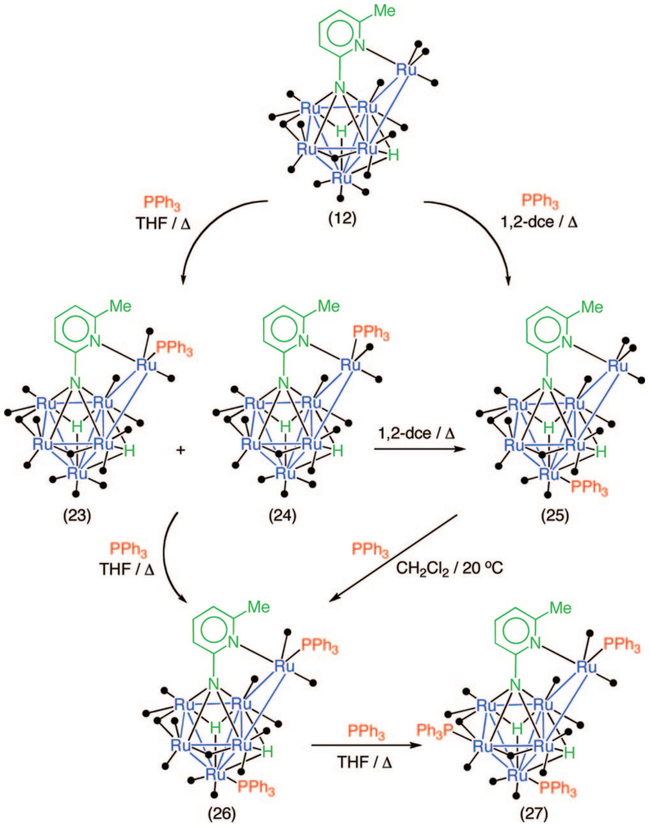
[24] Cabeza, J. A.; del Río, I.; Miguel, D.; Pérez-Carreño, E.; Sánchez-Vega, M. G. *Organometallics* **2008**, *27*, 211.

[25] Cabeza, J. A.; del Río, I.; Miguel, D.; Sánchez-Vega, M. G. *Chem. Commun.* **2005**, 3956.

[26] Cabeza, J. A.; del Río, I.; Miguel, D.; Pérez-Carreño, E.; Sánchez-Vega, M. G. *Dalton Trans.* **2008**, 1937.

[27] Cabeza, J. A.; del Río, I.; Miguel, D.; Sánchez-Vega, M. G. *Angew. Chem., Int. Ed.* **2008**, *47*, 1920.

Scheme 11



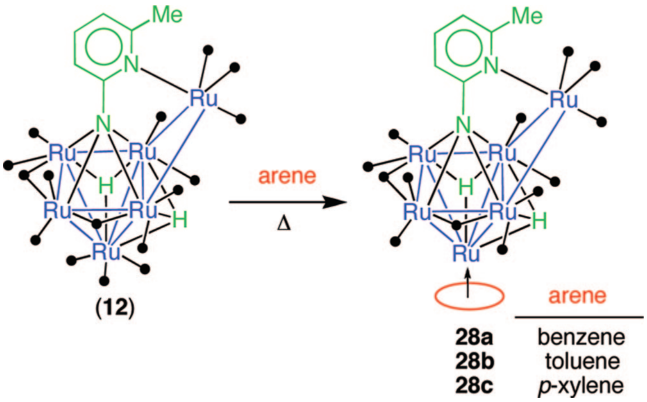
ligand of **22** confirms that, in these systems, the oxidative addition of C(sp^3)−H bonds can be reversed, as we had anticipated with trinuclear clusters.[25] Although a few C(sp^3)−N bond activation reactions have been reported,[28,29] including two recent reports involving NHCs,[29] the synthesis of compound **22** from [$Ru_3(Me_2Im)(CO)_{11}$] represents the only example of formation of a carbide ligand by activation of all bonds (three C−H and one C−N) of an N-bonded methyl group.

The structure of compound **22** led us to suppose that it might arise from the thermolysis of the carbyne cluster **21**. However, an independent experiment showed that **21** is stable in refluxing toluene. Therefore, although both clusters arise from [$Ru_3(\mu\text{-}H)_2(\mu_3\text{-}\kappa^2\text{-}MeImCH)(CO)_9$], they are formed by independent reaction pathways.

Reactivity of [$Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\kappa^2\text{-ampy})(\mu\text{-}CO)_2(CO)_{14}$] (12)

The successful preparation of the BEBSP cluster [$Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\kappa^2\text{-ampy})(\mu\text{-}CO)_2(CO)_{14}$] (**12**), in 77% yield from [$Ru_3(CO)_{12}$],[13] and the very few previous reports describing reactions of BEBSP hexaruthenium clusters (they all have been commented on above, along with the preparation and structure of the corresponding BEBSP clusters) led us to undertake a systematic study of the reactivity of compound **12**. An additional reason that prompted us to choose compound **12** as the starting material for reactivity studies (and not other compounds that can also be prepared in acceptable yields) was the presence of the methyl group on the pyridine ring, which facilitates the monitoring of the reactions by NMR spectroscopy without affecting the reactivity.

Scheme 12



Reactivity of 12 with Triphenylphosphine. The reactive sites of compound **12** in CO substitution reactions have been determined by studying its reactivity with triphenylphosphine (Scheme 11).[13] Two independent kinetically controlled monosubstitutions take place in refluxing THF on the edge-bridging metal atom, in positions cis to the pyridine nitrogen atom, leading to a mixture of two isomers of formula [$Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\kappa^2\text{-ampy})(\mu\text{-}CO)_2(CO)_{13}(PPh_3)$] (**23** and **24**). Upon heating in refluxing 1,2-dichloroethane, these monosubstituted isomers were transformed, via a dissociative pathway, into the product of thermodynamic control (**25**), which has the PPh_3 ligand on the apical Ru atom, cis to both hydride ligands. Therefore, the most labile CO ligands of **12** are those on the edge-bridging Ru atom, cis to the pyridine N atom (its substitution leads to compounds **23** and **24**), but the most stable monosubstituted product is complex **25**, which has the PPh_3 ligand on the apical Ru atom. The di- and trisubstituted derivatives [$Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\kappa^2\text{-ampy})(\mu\text{-}CO)_2(CO)_{12}(PPh_3)_2$] (**26**) and [$Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\kappa^2\text{-ampy})(\mu\text{-}CO)_2(CO)_{11}(PPh_3)_3$] (**27**) were formed in a stepwise fashion from **23**−**25** and PPh_3. Compound **26** has the PPh_3 ligands on the edge-bridging and apical Ru atoms, and compound **27** has an additional PPh_3 ligand on an unbridged basal Ru atom.

Reactivity of 12 with Cyclic Unsaturated Hydrocarbons. Monocyclic arenes reacted with cluster **12** at high temperatures (>110 °C) to give [$Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\kappa^2\text{-ampy})(\eta^6\text{-arene})(\mu\text{-}CO)_2(CO)_{11}$] (arene = benzene (**28a**), toluene (**28b**), *p*-xylene (**28c**)) in moderate to high yields. These complexes result from the substitution of the arene molecule for the three CO ligands of the apical Ru atom of **12** (Scheme 12).[30] The regioselectivity of these reactions is high in the sense that they only give one η^6-arene product. This is remarkable because, due to the low symmetry of compound **12**, several different reaction sites are potentially available and arenes can also coordinate in face-capping positions.[31] The high temperature required by these reactions suggests that the products are thermodynamically controlled. As noted above, studying the reactivity of **12** with phosphine ligands, we have determined that the activation of compound **12** implies the initial loss of a CO ligand from the Ru atom that is attached to the pyridine

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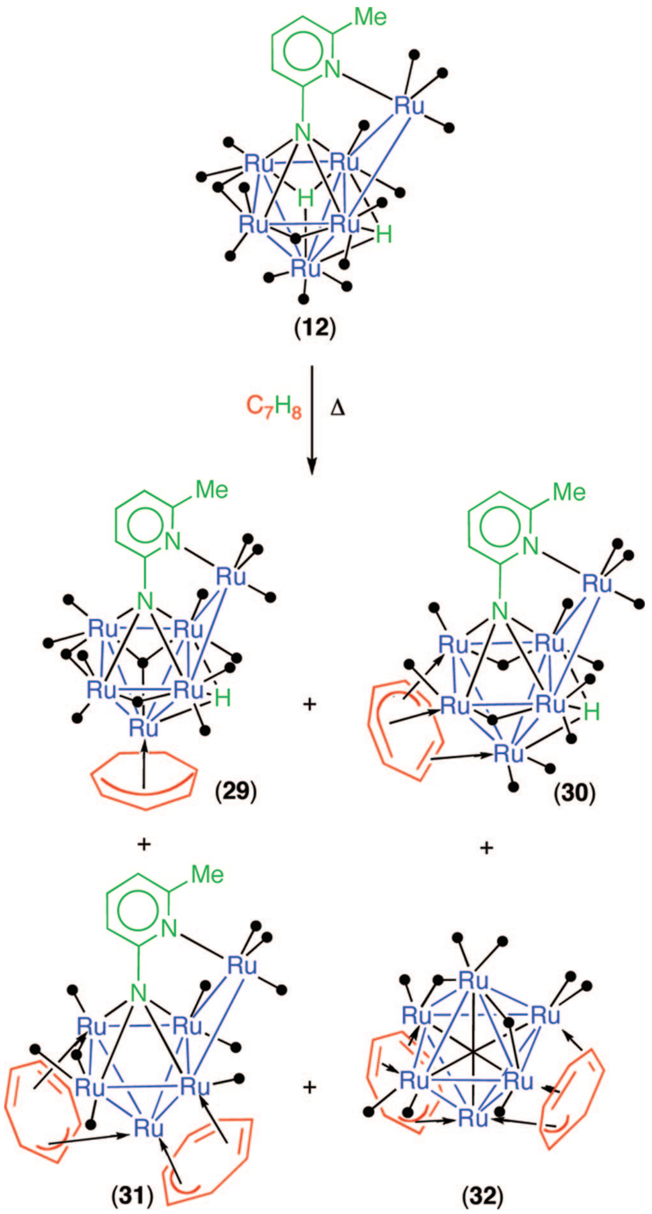
[28] For examples of C−N bond activation reactions, see: (a) Ozerovt, O. V.; Guo, C.; Papkov, V. A.; Foxman, B. M. *J. Am. Chem. Soc.* **2004**, *126*, 4792. (b) Ozerovt, O. V.; Guo, C.; Fan, L.; Foxman, B. M. *Organometallics* **2004**, *23*, 5573. (c) Torrent, M.; Musaev, D. G.; Morokuma, K. *Organometallics* **2000**, *19*, 4402.

[29] (a) Caddick, S.; Cloke, F. G. N.; Hitchcock, P. B. K.; Lewis, A. K. *Angew. Chem., Int. Ed.* **2004**, *43*, 5824. (b) Burling, S.; Powell, R. E.; Whittlesey, M. K.; Williams, J. M. J. *J. Am. Chem. Soc.* **2006**, *128*, 13702.

[30] Cabeza, J. A.; del Río, I.; García-Álvarez, P.; Miguel, D. *Organometallics* **2006**, *25*, 2683.

[31] For a review on η^6-arene clusters, see: Braga, D.; Dyson, P. J.; Grepioni, F.; Johnson, B. F. G. *Chem. Rev.* **1994**, *94*, 1585.

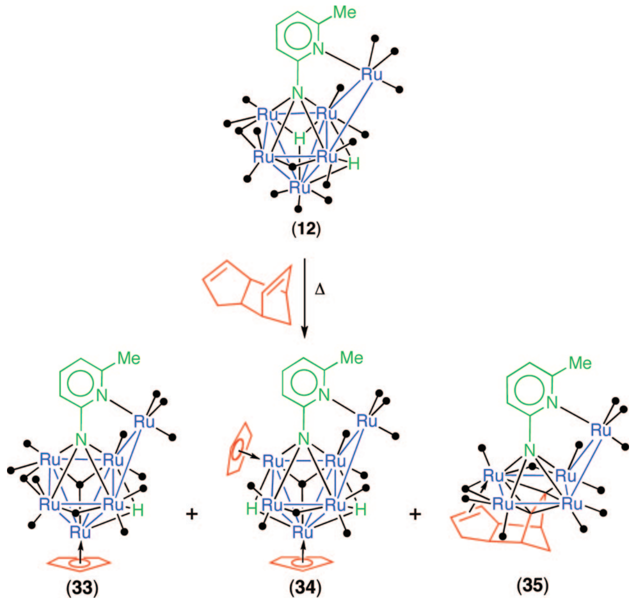
Scheme 13



fragment, but a subsequent thermally induced CO ligand rearrangement directs the substitution toward the apical Ru atom.[13] Experimental[31–33] and theoretical[33] studies have established that terminal η^6-arene clusters are thermodynamically more stable than face-capping η^6-arene clusters.

Cycloheptatriene reacted with complex **12** in chlorobenzene at reflux temperature (132 °C) to give a mixture of products, from which the hexanuclear cluster complexes [Ru$_6$(μ_3-H)(μ_5-κ^2-ampy)(η^5-C$_7$H$_9$)(μ_3-CO)(μ-CO)$_2$(CO)$_{11}$] (**29**), [Ru$_6$(μ_3-H)(μ_5-κ^2-ampy)(μ_3-η^7-C$_7$H$_7$)(μ-CO)$_2$(CO)$_{11}$] (**30**), [Ru$_6$(μ_5-κ^2-ampy)(μ-η^7-C$_7$H$_7$)$_2$(μ-CO)(CO)$_9$] (**31**), and [Ru$_6$(μ_6-C)(μ_3-η^7-C$_7$H$_7$)$_2$(μ-CO)$_2$(CO)$_8$] (**32**) have been isolated and characterized (Scheme 13). While compound **29** has a terminal η^5-cycloheptadienyl ligand, **30** contains a face-capping η^5:η^2-cycloheptatrienyl ligand, and **31** has two edge-bridging η^4:η^3-cycloheptatrienyl ligands. Compound **32**, a minor product of this reaction, contains an octahedral metallic skeleton with a μ_6-carbide and two face-capping η^3:η^2:η^2-cycloheptatrienyl ligands. It has been established that the thermolysis of complex **29** gives **30** and that complex **31** arises from the reaction of **30** with cycloheptatriene. In solution, the cycloheptatrienyl ligands of compounds **30**−**32** rotate freely, since the ^{1}H NMR spectra of these compounds display singlet resonances for the protons of their cycloheptatrienyl ligands, even at −80 °C. Therefore, the barriers to rotation of these ligands are very low, regardless of their edge-bridging or face-capping coordination mode. Only four reports have additionally described reactions of ruthenium clusters with cycloheptatriene.[34]

Scheme 14



The results noted above on reactions of compound **12** with arenes and cycloheptatriene led us to attempt the preparation of cyclopentadienyl derivatives of complex **12**. As the high temperatures (>110 °C) required for the activation of compound **12** are incompatible with the use of cyclopentadiene as reagent (bp 42 °C), we decided to use dicyclopentadiene (bp 170 °C) because this dimeric molecule gives the monomer at temperatures close to its boiling point. Treatment of compound **12** with dicyclopentadiene in chlorobenzene at reflux temperature afforded a mixture of compounds that could be separated by chromatographic methods. Three novel cluster derivatives, [Ru$_6$(μ_3-H)(μ_5-κ^2-ampy)(η^5-C$_5$H$_5$)(μ_3-CO)(μ-CO)$_2$(CO)$_{11}$] (**33**), [Ru$_6$(μ_3-H)$_2$(μ_5-κ^2-ampy)(η^5-C$_5$H$_5$)$_2$(μ_3-CO)(μ-CO)(CO)$_9$] (**34**), and [Ru$_5$(μ_5-κ^2-ampy)(μ_4-η^4-C$_{10}$H$_{10}$)(μ-CO)$_2$(CO)$_{10}$] (**35**), and the known binuclear complex [Ru$_2$(η^5-C$_5$H$_5$)$_2$(μ-CO)$_2$(CO)$_2$] were isolated and characterized (Scheme 14).[30] While compounds **33** and **34** retain the BEBSP hexanuclear skeleton and contain one and two terminal cyclopentadienyl ligands, respectively, the pentanuclear derivative **35** features a unique η^2:η^2-enyne ligand that is derived from the activation of two adjacent H−C(sp^2) bonds of dicyclopentadiene. The formation of the pentanuclear cluster **35** from **12** and dicyclopentadiene should be accompanied by the release of mononuclear species. This accounts for the observation of [Ru$_2$(η^5-C$_5$H$_5$)$_2$(μ-CO)$_2$(CO)$_2$] among the reaction products. To our knowledge, dicyclopentadiene has never been used to directly introduce cyclopentadienyl ligands into carbonyl metal clusters. Mono- and bis(cyclopentadienyl) ruthenium clusters have previously been prepared

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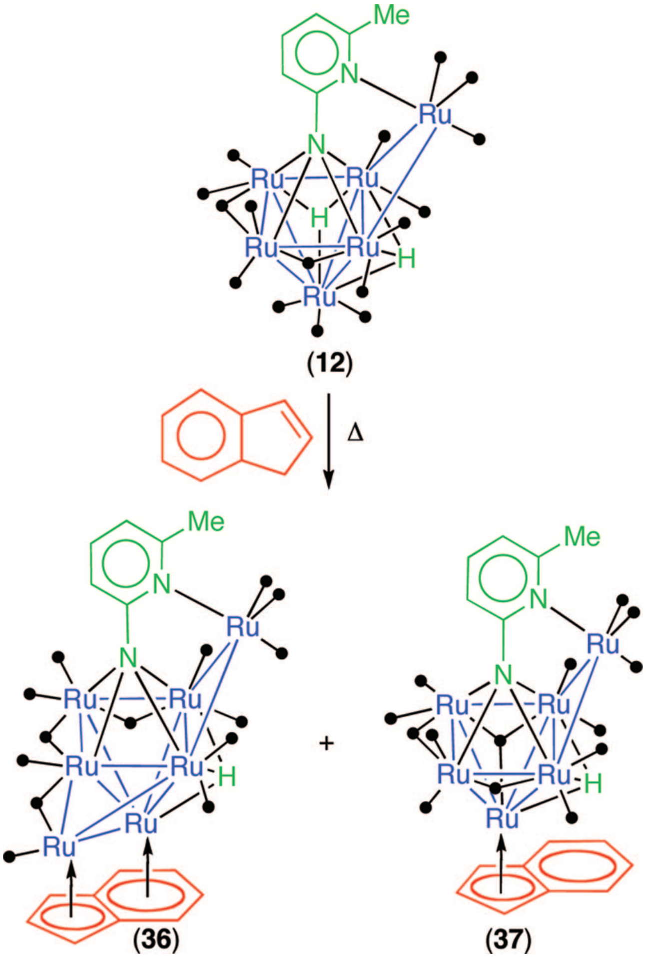
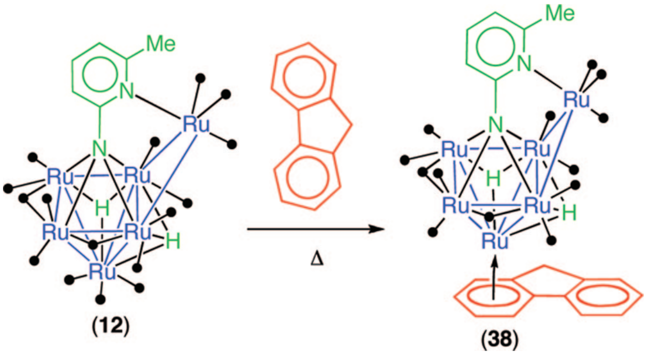
[32] (a) Braga, D.; Grepioni, F.; Sabatino, P.; Dyson, P. J.; Johnson, B. F. G.; Lewis, J.; Bailey, P. J.; Raithby, P. R.; Stalke, D. *J. Chem. Soc., Dalton Trans.* **1993**, 985. (b) Dyson, P. J.; Johnson, B. F. G.; Lewis, J.; Martinelli, M.; Braga, D.; Grepioni, F. *J. Am. Chem. Soc.* **1993**, *115*, 9062.

[33] Braga, D.; Dyson, P. J.; Grepioni, F.; Johnson, B. F. G.; Calhorda, M. J. *Inorg. Chem.* **1994**, *33*, 3218.

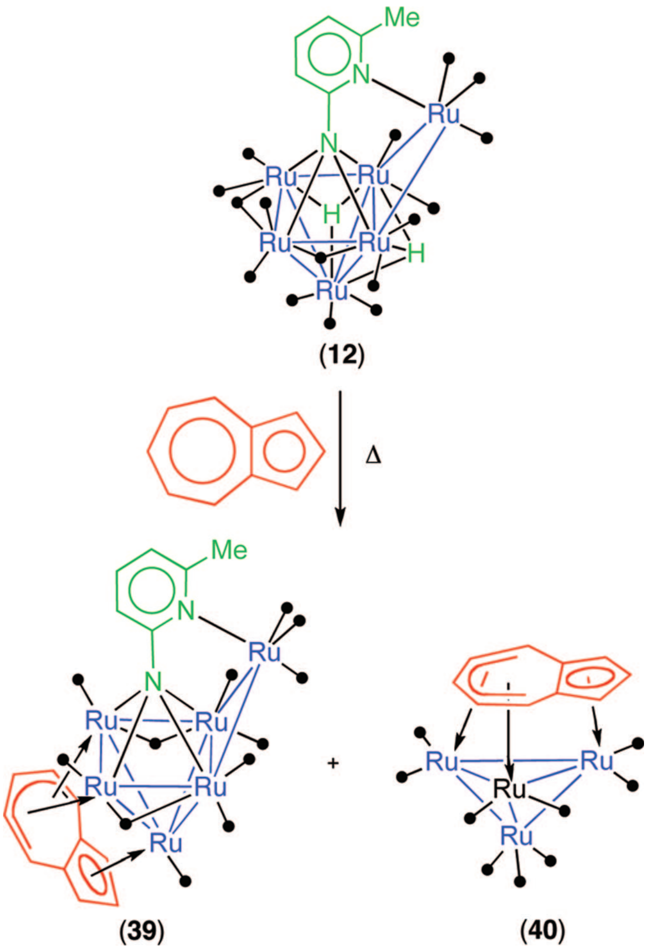
Scheme 15



Scheme 16



Scheme 17



via the reaction of $[Ru(\eta^5\text{-}C_5H_5)(MeCN)_3]^+$ with anionic precursors, such as $[Ru_5(\mu_5\text{-}C)(CO)_{14}]^{2-}$ and $[Ru_6(\mu_6\text{-}C)(CO)_{16}]^{2-}$.[35]

Compound **12** reacted with indene in refluxing chlorobenzene to give the heptanuclear cluster $[Ru_7(\mu_3\text{-}H)(\mu_5\text{-}\kappa^2\text{-ampy})(\mu\text{-}\eta^9\text{-}C_9H_7)(\mu\text{-}CO)_3(CO)_{11}]$ (**36**), the BEBSP hexanuclear cluster $[Ru_6(\mu_3\text{-}H)(\mu_5\text{-}\kappa^2\text{-ampy})(\eta^5\text{-}C_9H_7)(\mu_3\text{-}CO)(\mu\text{-}CO)_2(CO)_{11}]$ (**37**), and the known dimer $[Ru_2(\eta^5\text{-}C_9H_7)_2(\mu\text{-}CO)_2(CO)_2]$ (Scheme 15).[36] While the indenyl ligand of complex **36** is $\eta^5{:}\eta^6$ edge bridging, complex **37** has a terminal η^5-indenyl ligand.

The hexanuclear η^6-fluorene derivative $[Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\kappa^2\text{-ampy})(\eta^6\text{-}C_{13}H_{10})(\mu\text{-}CO)_2(CO)_{11}]$ (**38**) has been isolated in low yield (10%) from the reaction of compound **12** with an excess of fluorene in decane at reflux temperature (174 °C, 8 h) (Scheme 16).[36] Lower temperatures and/or shorter reaction times resulted in incomplete consumption of complex **12**. The low reactivity of fluorene may explain why no additional metal carbonyl clusters containing simple fluorene or fluorenyl ligands have been reported.

Azulene reacted with **12** in decane at reflux temperature to give $[Ru_6(\mu_5\text{-}\kappa^2\text{-ampy})(\mu_3\text{-}\eta^{10}\text{-}C_{10}H_8)(\mu\text{-}CO)_2(CO)_{10}]$ (**39**) and $[Ru_4(\mu_3\text{-}\eta^{10}\text{-}C_{10}H_8)(CO)_9]$ (**40**) (Scheme 17).[36] In both complexes, the azulene ligand is attached to 3 Ru atoms through its 10 C atoms. This face-capping coordination mode of azulene has also been observed in ruthenium clusters of lower nuclearity.[37]

Acenaphthylene reacted with cluster **12** in decane at reflux temperature to give a mixture of products that could be separated

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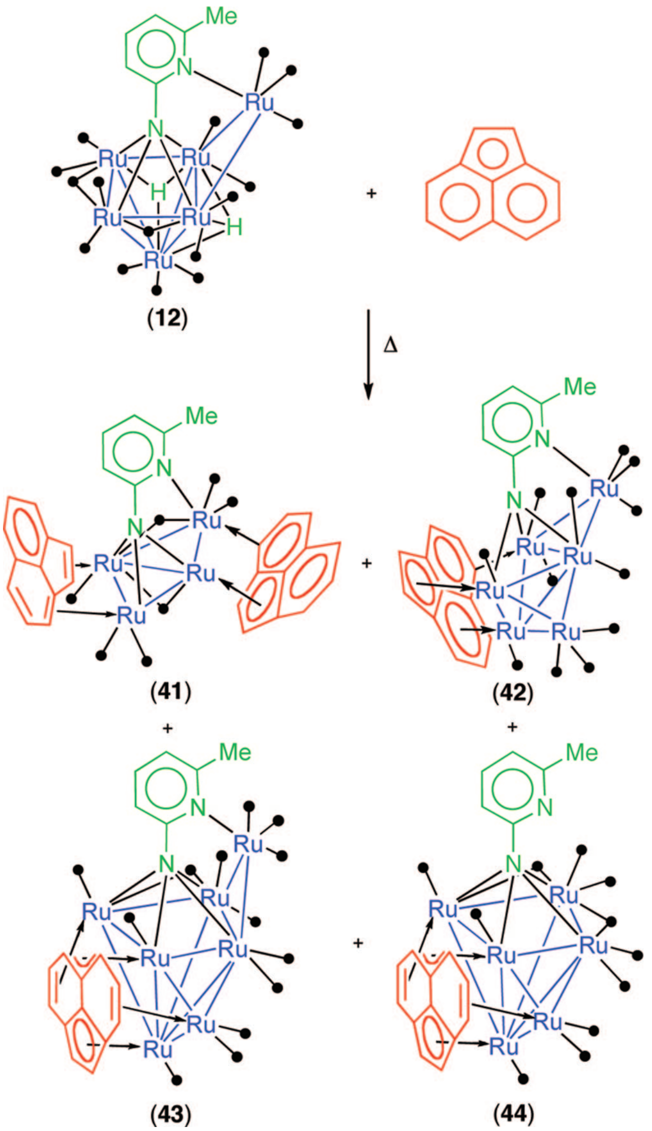
(34) (a) Bau, R.; Burt, J. C.; Knox, S. A. R.; Laine, R. M.; Phillips, R. P.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1973**, 726. (b) Braga, D.; Grepioni, F.; Scaccianoce, L.; Johnson, B. F. G. *J. Chem. Soc., Dalton Trans.* **1998**, 1321. (c) Braga, D.; Dyson, P. J.; Grepioni, F.; Johnson, B. F. G.; Martin, C. M.; Scaccianoce, L.; Steiner, A. *Chem. Commun* **1997**, 1259. (d) Cresswell, T. A.; Howard, J. A. K.; Kennedy, F. G.; Knox, S. A. R.; Wadepohl, H. *J. Chem. Soc., Dalton Trans.* **1981**, 2220.

(35) See, for example: Lewis, J.; Morewood, C. A.; Raithby, P. R.; Ramirez de Arellano, M. C. *J. Chem. Soc., Dalton Trans.* **1997**, 3335.

(36) Cabeza, J. A.; del Río, I.; Fernández-Colinas, J. M.; García-Álvarez, P.; Miguel, D. *Organometallics* **2007**, *26*, 1414.

(37) (a) Johnson, B. F. G.; Shephard, D. S.; Edwards, A. J.; Braga, D.; Parisini, E.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1995**, 3307. (b) Churchill, M. R.; Wormald, J. *Inorg. Chem.* **1973**, *21*, 191. (c) Nagashima, H.; Suzuki, A.; Nobata, M.; Aoki, K.; Itoh, K. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 2441. (d) Matsubara, K.; Ryu, K.; Maki, T.; Iura, T.; Nagashima, H. *Organometallics* **2002**, *21*, 3023. (e) Arce, A. J.; De Sanctis, Y.; Galarza, E.; Garland, M. T.; Gobetto, R.; Machado, R.; Manzur, J.; Russo, A.; Spodine, E.; Stchedroff, M. J. *Organometallics* **2001**, *20*, 359. (f) Churchill, M. R.; Gold, K.; Bird, P. H. *Inorg. Chem.* **1969**, *8*, 1956. (g) Wang, F.; Lai, Y. H.; Han, M. Y. *Org. Lett.* **2003**, *5*, 4791.

Scheme 18



by chromatographic methods. The following compounds were isolated and characterized: [$Ru_4(\mu_4-\kappa^2$-ampy)(μ-η^6-$C_{12}H_8$)(μ-η^4-$C_{12}H_8$)(μ-CO)$_2$(CO)$_5$] (**41**), [$Ru_6(\mu_4-\kappa^2$-ampy)(μ_3-η^{10}-$C_{12}H_8$)(CO)$_{12}$] (**42**), [$Ru_7(\mu_5-\kappa^2$-ampy)(μ_4-η^{12}-$C_{12}H_8$)(μ-CO)(CO)$_{12}$] (**43**), and [$Ru_6(\mu_4-\kappa^1$-ampy)(μ_4-η^{12}-$C_{12}H_8$)(μ-CO)$_2$(CO)$_9$] (**44**) (Scheme 18).[36] It is interesting to note that the BEBSP metallic framework of the starting material **12** is not retained in any of these products and only one, the heptanuclear derivative **43**, has the ampy ligand coordinated in the same way (μ_5-κ^2*N,N*) as in compound **12**. The hexanuclear complex **44** is the only example in which the pyridine N atom of the ampy ligand is not coordinated. The four different coordination modes displayed by the acenaphthylene ligand in these cluster compounds, μ-η^4 (**41**), μ-η^6 (**41**), μ_3-η^{10} (**42**), and μ_4-η^{12} (**43** and **44**), are also unique. A few reactions of acenaphthylene with ruthenium carbonyl clusters have been reported, but they only describe trinuclear products.[38]

Arenes and, particularly, polycyclic arenes have limited reactivity. Consequently, the reactions of cyclic and polycyclic unsaturated hydrocarbons with compound **12** have high activation energies. The high temperatures required by these reactions (110−174 °C) promote fragmentation processes that give clusters of lower nuclearity and Ru(CO)$_n$ fragments. Both may undergo decomposition (a black insoluble solid is formed in all reactions) or aggregation with other cluster species present in solution to give products of higher nuclearity. This explains the various metallic frameworks observed in the products isolated from these reactions and the low yields of some of them. High reaction temperatures also promote cluster decarbonylation processes. This accounts for the observation that, for polycyclic arenes, most of the reaction products contain the polycyclic hydrocarbon ligands attached through many carbon atoms to various metal atoms. In fact, the μ-indenyl ligand of **36**, the μ_3-azulenes of **39** and **40**, and the μ_4-acenaphthylenes of **43** and **44** are attached to the corresponding metal atoms through all of their carbon atoms. The coordination modes displayed by the ampy ligands in the acenaphthylene derivatives **41** (μ_4-κ^2*N,N*), **42** (μ_4-κ^2*N,N*), and **44** (μ_4-κ^1*N*), which are prepared in refluxing decane (174 °C), in addition to the formation of a black insoluble solid in these high-temperature reactions, indicate that, in contrast with previous observations in reactions of **12** performed at lower temperatures,[4,13,30] the ampy ligand is no longer efficient at maintaining its original coordination mode (μ_5-κ^2*N,N* in **12**) at temperatures as high as 174 °C.

Reactivity of 12 with Linear Alkenes. As noted above, cyclic dienes, such as cyclopentadiene and cycloheptatriene, are dehydrogenated by compound **12** to give η^5-cyclopentadienyl and η^7-cycloheptatrienyl ligands. Similarly, the reaction of compound **12** with cyclohexadiene gave the η^6-benzene derivative **28a**, though very slowly because the low boiling point of this diene prevents the use of a high reaction temperature.[39] The aromatization of the reacting alkene is believed to be an important component of the driving force of these reactions. These results prompted us to investigate the reactivity of compound **12** with linear alkenes, for which aromatization is not possible.

The isomeric heptanuclear octatrienyl derivatives [$Ru_7(\mu_3$-H)(μ_5-κ^2-ampy)(μ-η^3:η^4-MeC_7H_8)(μ-CO)$_3$(CO)$_{12}$] (**45a**) and [$Ru_7(\mu_3$-H)(μ_5-κ^2-ampy)(μ-η^3:η^4-C_7H_8Me)(μ-CO)$_3$(CO)$_{12}$] (**45b**) were synthesized by heating to reflux temperature a solution of **12** in 1-octene (Scheme 19). The products could be separated by preparative TLC.[40] The related trienyl derivatives [$Ru_7(\mu_3$-H)(μ_5-κ^2-ampy)(μ-η^3:η^4-MeC_7H_7Me)(μ-CO)$_3$(CO)$_{12}$] (**46a**), [$Ru_7(\mu_3$-H)(μ_5-κ^2-ampy)(μ-η^3:η^4-EtC_7H_8)(μ-CO)$_3$(CO)$_{12}$] (**46b**), [$Ru_7(\mu_3$-H)(μ_5-κ^2-ampy)(μ-η^3:η^4-C_7H_8Et)(μ-CO)$_3$(CO)$_{12}$] (**46c**), [$Ru_7(\mu_3$-H)(μ_5-κ^2-ampy)(μ-η^3:η^4-MeC_7H_7Et)(μ-CO)$_3$(CO)$_{12}$] (**47a**), and [$Ru_7(\mu_3$-H)(μ_5-κ^2-ampy)(μ-η^3:η^4-EtC_7H_7Me)(μ-CO)$_3$(CO)$_{12}$] (**47b**) were obtained from similar reactions using 1-nonene (**46a**−**c**) or 1-decene (**47a**,**b**) as solvents (Scheme 19).[40] The reaction times are strongly influenced by the reaction temperature (the solvent boiling point). A black insoluble residue, arising from the thermal decomposition of part of the starting material, is also formed in all cases. This decomposition provides the Ru(CO)$_n$ fragments necessary to obtain heptanuclear products from a hexanuclear precursor.

The structures of **45**−**47** differ only in the R^1 and R^2 groups attached to the ends of the trienyl fragment of each compound. They are reminiscent of the heptanuclear cluster [$Ru_7(\mu_3$-H)(μ_5-κ^2-ampy)(μ-η^9-C_9H_7)(μ-CO)$_3$(CO)$_{11}$] (**36**), which has an analo-

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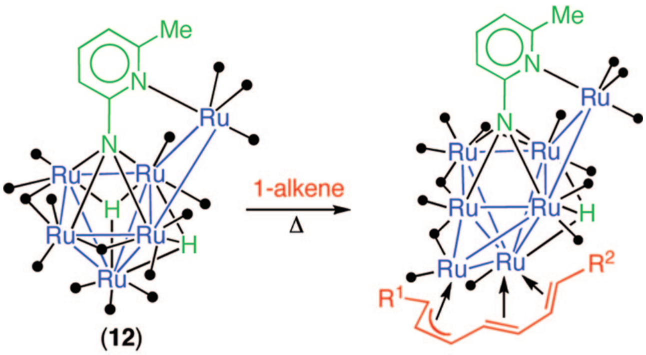
(38) (a) Nagashima, H.; Fukahori, T.; Aoki, K.; Itoh, K. *J. Am. Chem. Soc.* **1993**, *115*, 10430. (b) Nagashima, H.; Suzuki, A.; Iura, T.; Ryu, K.; Matsubara, K. *Organometallics* **2000**, *19*, 3579. (c) Nagashima, H.; Suzuki, A.; Kondo, H.; Nobata, M.; Aoki, K.; Itoh, K. *J. Organomet. Chem.* **1999**, *580*, 239. (d) Nagashima, H.; Suzuki, A.; Nobata, M.; Aoki, K.; Itoh, K. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 2231.

(39) Cabeza, J. A.; García-Álvarez, P. unpublished results (García-Álvarez, P. Ph.D. Thesis, Universidad de Oviedo, 2006).

(40) Cabeza, J. A.; del Río, I.; García-Álvarez, P.; Miguel, D. *Organometallics* **2007**, *26*, 2482.

Scheme 19



1-alkene	T (°C)	t (h)	products	yield (%)
1-octene	123	8	**45a**: R^1 = Me; R^2 = H	22
			45b: R^1 = H; R^2 = Me	8
1-nonene	146	4	**46a**: $R^1 = R^2$ = Me	38
			46b: R^1 = Et; R^2 = H	8
			46c: R^1 = H; R^2 = Et	6
1-decene	168	2	**47a**: R^1 = Me; R^2 = Et	25
			47b: R^1 = Et; R^2 = Me	25

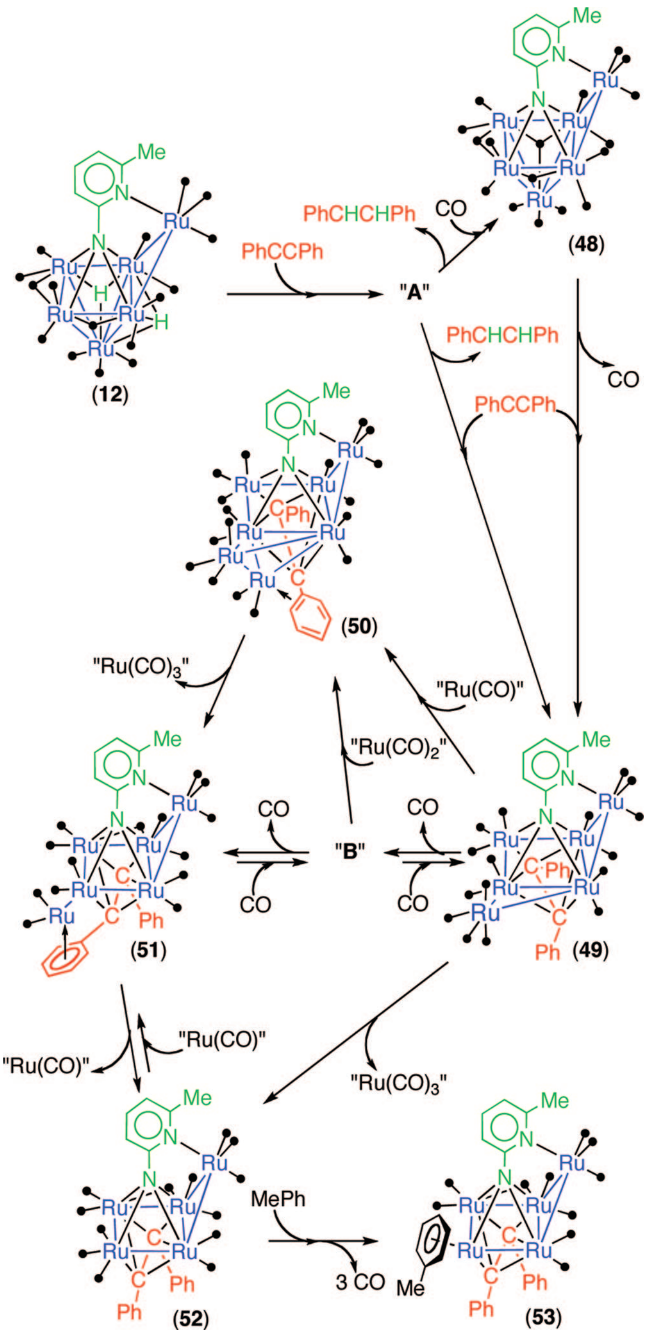
gous $Ru_7(\mu_3\text{-H})(\mu_5\text{-}\kappa^2\text{-ampy})$ fragment and an indenyl ligand coordinated to the same ruthenium atoms as the trienyl ligands of **45**−**47**. All the trienyl ligands have the same stereochemistry, being attached to the two Ru atoms that are not bonded to the ampy ligand through four and three carbon atoms (as η^4-butadiene and η^3-allyl fragments, respectively).

Considering that the reagents used are terminal alkenes and that the major products of the reactions with 1-nonene and 1-decene have internal trienyl ligands (R^1, $R^2 \neq$ H in Scheme 19), their synthesis (and probably the synthesis of the minor products as well) should involve not only the removal of five hydrogen atoms from the original alkene but also the exchange of at least one hydrogen atom between carbon atoms of the hydrocarbon chain. The high temperatures required by these processes and the relative abundance of the products of each reaction indicate that the compounds having internal trienyl ligands (such as **46a**) are thermodynamically more stable than those having terminal trienyl ligands (such as **46b**,**c**).

These results represent a unique example of the activation of five $C(sp^3)-H$ bonds of linear alkenes. Coupled to known data on metal complex promoted dehydrogenation of linear alkenes,[40] they allow us to conclude that to achieve extensive dehydrogenation reactions it is important that (a) the reactions should be carried out at high temperatures (>120 °C), (b) metal cluster complexes should be used as precursors, so that they allow the coordination of many unsaturated CC bonds, and (c) the clusters, precursors and products, should be thermally robust to prevent extensive decomposition at the working temperatures. This can only be achieved with clusters containing bridging ligands, such as the ampy ligand used in this work.

Reactivity of 12 with Alkynes. The reaction of compound **12** with 2 equiv of diphenylacetylene in toluene gave 1 equiv of *cis*-stilbene and mixtures of cluster compounds, the composition of which depends upon the reaction time and temperature. The following cluster compounds were isolated and characterized: $[Ru_6(\mu_5\text{-}\kappa^2\text{-ampy})(\mu_3\text{-CO})(\mu\text{-CO})_2(CO)_{14}]$ (**48**), $[Ru_6(\mu_5\text{-}\kappa^2\text{-ampy})(\mu_4\text{-}\eta^2\text{-PhCCPh})(CO)_{16}]$ (**49**), $[Ru_7(\mu_5\text{-}\kappa^2\text{-ampy})(\mu_5\text{-}\eta^4\text{-PhCCPh})(CO)_{17}]$ (**50**), $[Ru_6(\mu_5\text{-}\kappa^2\text{-ampy})(\mu_5\text{-}\eta^8\text{-PhCCPh})(\mu\text{-CO})(CO)_{13}]$ (**51**), $[Ru_5(\mu_5\text{-}\kappa^2\text{-ampy})(\mu_4\text{-}\eta^2\text{-PhCCPh})(\mu\text{-CO})(CO)_{12}]$ (**52**), and $[Ru_5(\mu_5\text{-}\kappa^2\text{-ampy})(\mu_4\text{-}\eta^2\text{-PhCCPh})(\eta^6\text{-PhMe})(\mu\text{-CO})(CO)_9]$ (**53**) (Scheme 20).[41] In all products, the nitrogen atoms of the ampy ligand are attached to five metal atoms, in the same way as in complex **12**. While complex **48** has no alkyne ligand and can be considered the result of a formal substitution of a CO ligand for the two hydrides of complex **12**, the remaining products have a diphenylacetylene ligand capping the four atoms of a metallic square through both C atoms of the original triple bond. This type of coordination of an alkyne ligand to four metal atoms has been previously observed on many occasions, including some tetra-,[42–44] penta-,[42,43] and hexaruthenium[45] complexes. Additionally, an

Scheme 20



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[41] Cabeza, J. A.; del Río, I.; García-Álvarez, P.; Miguel, D. *Organometallics* **2005**, *24*, 665.

[42] Adams, R. D.; Babin, J. E.; Tasi, M.; Wolfe, T. A. *Organometallics* **1987**, *6*, 2228.

[43] Ho, E. N. M.; Wong, W. T. *J. Chem. Soc., Dalton Trans.* **1998**, 4215.

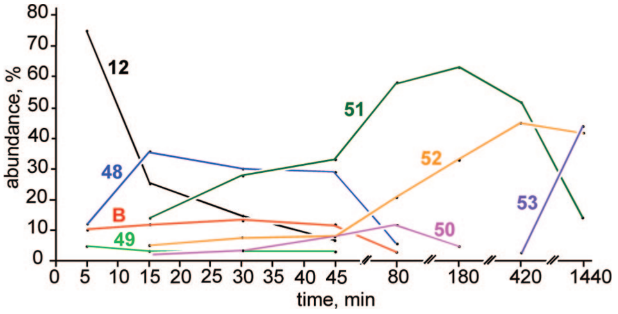


Figure 2. Evolution of the reaction of complex **12** with 2 equiv of Ph_2C_2 at 110 °C (monitored by ^1H NMR).

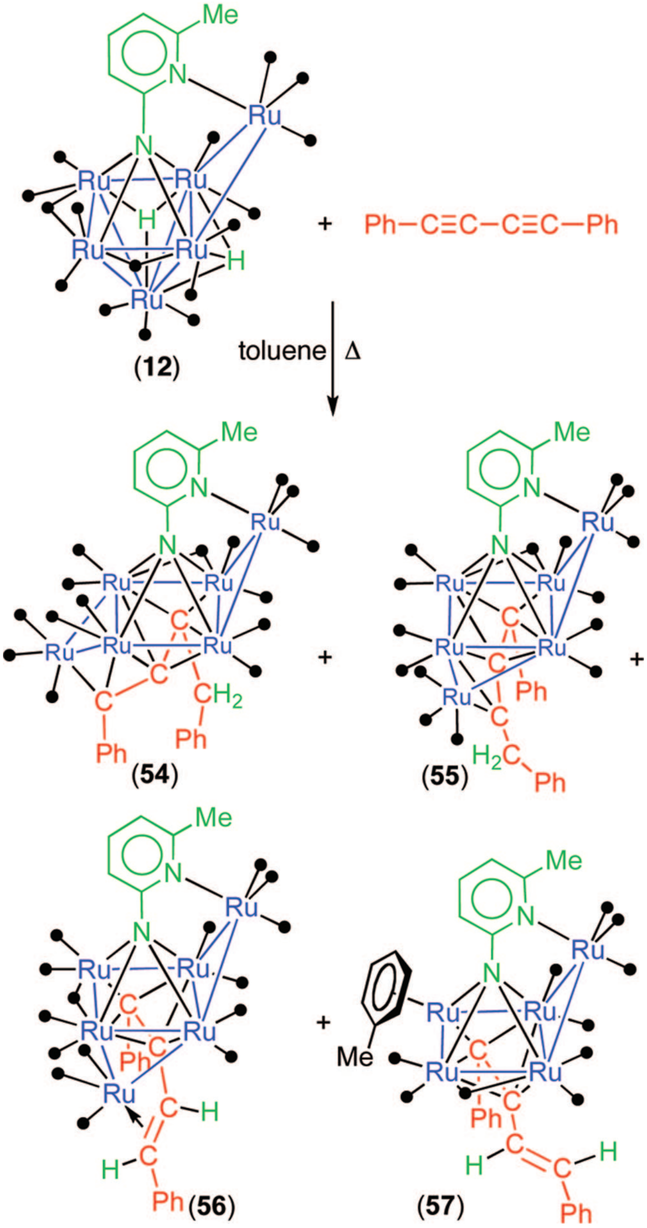
alkyne phenyl group of **50** is η^2-coordinated to a ruthenium atom, while an alkyne phenyl group of **51** is η^6-coordinated to a ruthenium atom. Although the coordination of arenes to ruthenium carbonyl clusters as η^6 ligands is now well established,[31] the coordination of diphenylacetylene as an η^8 ligand in compound **51** is unique.

Scheme 20 shows a reaction pathway that interconnects all these compounds. This scheme has been deduced with the help of results obtained by following (by ^1H NMR) the progress of the reaction of **12** with diphenylacetylene in toluene at 110 (Figure 2) and 80 °C and the thermolysis of compounds **49**−**52** in toluene at 110 °C.[41]

The reactions of compound **12** with diphenylbutadiyne also give mixtures of cluster compounds, the composition of which depends on the reaction time and temperature. The following products have been isolated and characterized working in toluene at temperatures between 50 and 110 °C: $[Ru_6(\mu_5\text{-}\kappa^2\text{-ampy})(\mu_5\text{-}\eta^3\text{-PhCCCCH}_2\text{Ph})(\mu\text{-CO})(CO)_{14}]$ (two isomers, **54** and **55**), $[Ru_6(\mu_5\text{-}\kappa^2\text{-ampy})(\mu_5\text{-}\eta^4\text{-}\textit{trans}\text{-PhCCCHCHPh})(\mu\text{-CO})(CO)_{14}]$ (**56**), and $[Ru_5(\mu_5\text{-}\kappa^2\text{-ampy})(\mu_4\text{-}\eta^2\text{-}\textit{trans}\text{-PhCCCHCHPh})(\eta^6\text{-PhMe})(\mu\text{-CO})(CO)_9]$ (**57**) (Scheme 21). The reaction pathway **12** + PhC_2C_2Ph → **54** → **55** → **56** → **57** has been established by studying the individual thermolysis of compounds **54**−**56** and reactions of **12** with diphenylbutadiyne at different reaction times and temperatures.[46]

In **54**−**57**, the ampy ligand is attached to five metal atoms through its nitrogen atoms in the same way as in complex **12**. As occurs for the aforementioned products derived from diphenylacetylene, compounds **54**−**57** do not have a BEBSP metallic skeleton, since they all have an alkyne CC fragment attached to the same four Ru atoms as the imido N atom. These compounds represent unusual examples of 1,1- and trans-1,2-additions of two hydrogen atoms to an internal CC triple bond, since **54** and **55** contain a hydrocarbon ligand that arises from the migration of the original hydrides of **12** onto a terminal carbon atom of the diyne C_4 chain and **56** and **57** contain a 1,4-diphenyl-*trans*-butenyne ligand. As far as we are aware, there is only one additional report describing the 1,1-hydrogenation of a diyne C≡C bond. That paper reports the synthesis of $[Ru_4(\mu_4\text{-RCH}_2C_3R)(CO)_{12}]$ (R = Me, $SiMe_3$, Ph) by reactions of $[Ru_4(\mu\text{-H})_4(CO)_{12}]$ with the corresponding diynes.[47] It is also interesting to note that metal complexes of conjugated *trans*-enynes are unprecedented.

Scheme 21



Miscellaneous Reactions of Compound 12. In contrast to many ligand-bridged ruthenium carbonyl clusters, including many clusters derived from 2-aminopyridines,[15] compound **12** cannot be protonated by strong acids, such as $[HOEt_2][BF_4]$ (CH_2Cl_2, 20 °C). It also does not react with dihydrogen (1 atm, 60 °C).[39] This indicates that the metal atoms of **12** hold little electron density. In contrast, compound **12** does react with strong bases, such as the hydride anion that arises from $[PPN][BH_4]$

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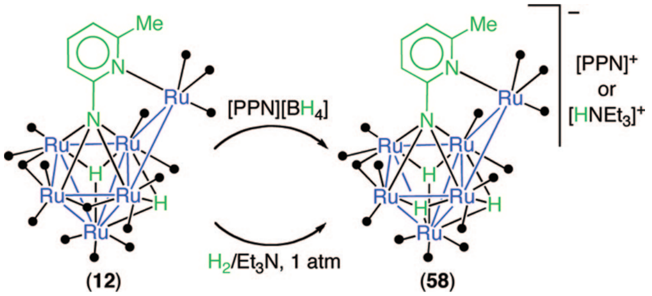
(44) See, for example: (a) Blohm, M. L.; Gladfelter, W. L. *Organometallics* **1986**, *5*, 1049. (b) Ho, E. N. M.; Wong, W. T. *J. Chem. Soc., Dalton Trans.* **1998**, 513. (c) Ho, E. N. M.; Lin, Z.; Wong, W. T. *Eur. J. Inorg. Chem.* **2001**, 1321. (d) Cabeza, J. A.; del Río, I.; García-Granda, S.; Moreno, M.; Riera, V.; Rosales-Hoz, M. J.; Suárez, M. *Eur. J. Inorg. Chem.* **2001**, 2899. (e) Corrigan, J. F.; Doherty, S.; Taylor, N. J.; Carty, A. J. *Organometallics* **1985**, *4*, 2066. (f) Corrigan, J. F.; Doherty, S.; Taylor, N. J.; Carty, A. J. *Organometallics* **1993**, *12*, 1365. (g) Jackson, P. F.; Johnson, B. F. G.; Lewis, J.; Raithby, P. *J. Chem. Soc., Chem. Commun.* **1980**, 1190. (h) Braga, D.; Grepioni, F.; Brown, D. B.; Johnson, B. F. G.; Calhorda, M. J. *Organometallics* **1996**, *15*, 5723. (i) Deeming, A. J.; Speel, D. M. *Organometallics* **1997**, *16*, 289. (j) Bruce, M. I.; Zaitseva, N. N.; Skelton, B. W.; White, A. H. *Dalton Trans.* **2002**, 3879. (k) Bruce, M. I.; Skelton, B. W.; White, A. H.; Zaitseva, N. N. *Aust. J. Chem.* **1999**, *52*, 681.

(45) Adams, R. D.; Babin, J. E.; Tasi, M.; Wolfe, T. A. *Polyhedron* **1988**, *7*, 1071.

(46) Cabeza, J. A.; del Río, I.; Fernández-Colinas, J. M.; García-Álvarez, P.; Miguel, D. *Organometallics* **2006**, *25*, 1492.

(47) Clarke, L. P.; Davies, J. E.; Raithby, P. R.; Shields, G. P. *Dalton Trans.* **2000**, 4527.

Scheme 22

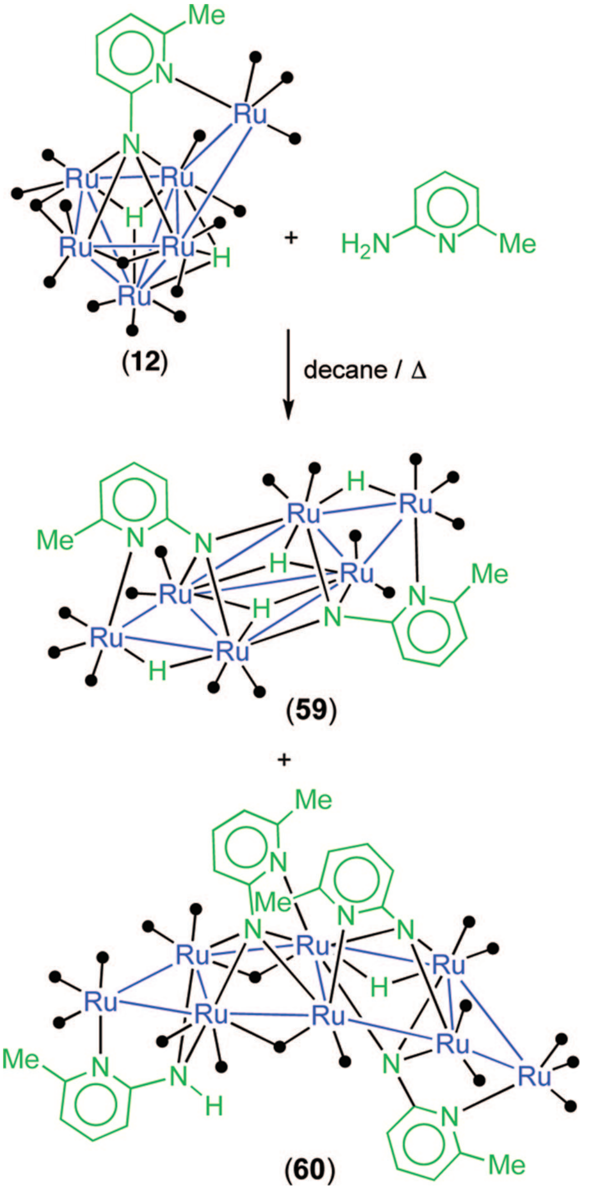


(CHCl$_2$, 20 °C)[4] or H$_2$/Et$_3$N (THF, 1 atm, 20 °C),[39] to give the anionic BEBSP derivative [Ru$_6$(μ_3-H)$_3$(μ_5-κ^2-ampy)(μ-CO)(CO)$_{14}$]$^-$ (**58**), which contains three face-capping hydrido ligands (Scheme 22).

Considering that the number of known ruthenium carbonyl cluster complexes of nuclearity greater than 5 that contain N-donor ligands is still small,[5] and having in mind the ability of ruthenium carbonyl clusters to undergo aggregation processes under appropriate thermal conditions, we decided to study the thermolysis of the hexanuclear BEBSP cluster **12** in the presence and in the absence of 2-amino-6-methylpyridine (H$_2$ampy), in an attempt to synthesize novel high-nuclearity ruthenium carbonyl clusters containing 2-imidopyridine ligands.

Compound **12** and 2-amino-6-methylpyridine reacted in decane at reflux temperature to give the hexanuclear ruthenium cluster [Ru$_6$(μ_3-H)$_2$(μ-H)$_2$(μ_4-κ^2-ampy)$_2$(CO)$_{14}$] (**59**) and the octanuclear [Ru$_8$(μ-H)(μ_4-κ^2-ampy)$_3$(μ_3-κ^2-Hampy)(μ-CO)$_2$(CO)$_{15}$] (**60**) (Scheme 23).[48] The metal atoms of these compounds are supported by imido (complex **59**) and/or amido ligands (complexes **59** and **60**) that are derived from the activation of both or one of the N−H bonds of the H$_2$ampy amino fragment. Both compounds contain at least one ampy ligand featuring an unusual coordination type: the imido N atom caps a triangle of metal atoms, while the pyridine N atom is attached to an additional metal atom. One of the ampy ligands of cluster **60** also displays a hitherto unique coordination type: it caps a distorted square of metal atoms through the imido N atom, while the pyridine N atom is attached to one of the atoms included in that square.

Scheme 23



The thermolysis of compound **12** in undecane at reflux temperature (196 °C) gave a dark greenish brown dichloromethane-soluble fraction and an insoluble black solid. A TLC separation of the soluble fraction allowed the isolation of the nonanuclear derivatives [Ru$_9$(μ-H)$_2$(μ_4-κ^2-ampy)$_4$(CO)$_{17}$] (**61**) and [Ru$_9$(μ_3-H)(μ-H)(μ_4-κ^2-ampy)$_3$(CO)$_{18}$] (**62**) (Scheme 24).[49] Both compounds have a similar metallic skeleton that can be described as an apex-to-apex bonded pentagonal bipyramid with two nonconsecutive equatorial edges spanned by two additional atoms. Such a unique metallic framework is supported by four (in **61**) or three (in **62**) μ_4-ampy ligands, each capping a face of the pentagonal bipyramid through the imido N atom, while being also attached to one of the edge-bridging Ru atoms through the pyridine N atom. The lack of the fourth ampy ligand in compound **62** not only reduces the symmetry of the cluster (ca. C_{2v} in **61**, C_1 in **62**) but also provokes a considerable distortion of the equatorial pentagon. Although triply bridging imido ligands are well-known in carbonyl metal cluster chemistry, the coordination mode displayed by the ampy ligands in complexes **61** and **62** is very rare for 2-imidopyridine ligands. In fact, only two previous reports have described such a coordination mode. One deals with the reactivity of compound **12** with 2-amino-6-methylpyridine, noted above,[48] and the other one describes the thermolysis of the trinuclear complex [Ru$_3$(μ-H)(μ_3-κ^2-Hampy)(CO)$_9$] in refluxing decane.[50]

Compound **62** does not react with H$_2$ampy in refluxing undecane to give **61**.[49] For this reason, in the thermolysis of complex **12**, these compounds should be formed by different reaction pathways by the aggregation of ampy-containing species. An additional remarkable feature of this reaction is that it makes clear that the bridging ampy ligands increase the thermal stability of the products which contain them. In fact, compounds **61** and **62** survive at temperatures as high as 196 °C. As the ampy to ruthenium ratio in **61** and **62** is greater than in the starting material **12**, the black solid also obtained as reaction product should arise from the decomposition, via thermal decarbonylation, of transient Ru$_n$(CO)$_m$ species released

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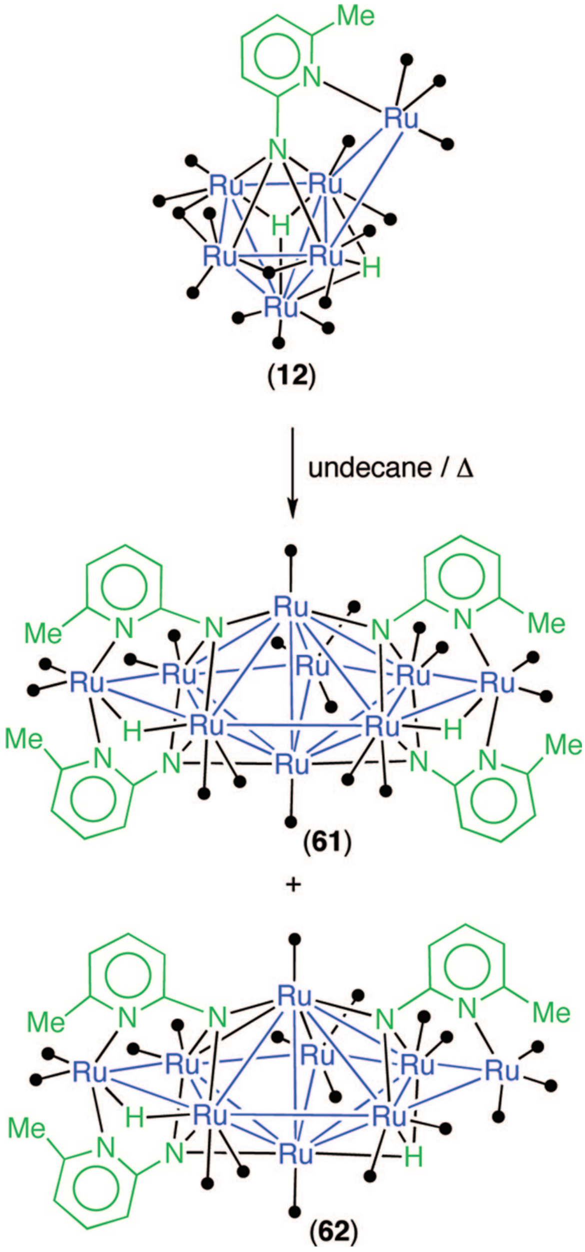
(48) Cabeza, J. A.; del Río, I.; García-Álvarez, P.; Miguel, D. *Can. J. Chem.* **2006**, *84*, 105.

(49) Cabeza, J. A.; del Río, I.; García-Álvarez, P.; Miguel, D. *Organometallics* **2006**, *25*, 5672.

(50) Cabeza, J. A.; del Río, I.; García-Álvarez, P.; Miguel, D. *Inorg. Chem.* **2006**, *45*, 6020.

Scheme 24



from **12** or from other ampy-containing species during the thermolysis reaction.

Conclusions and Outlook

All known BEBSP hexaruthenium clusters that are not derived from precursors with the same nuclearity have been prepared by condensation of clusters of lower nuclearity under thermal conditions. These conditions promote decarbonylation processes that lead to transient unsaturated species which are prone to condense and/or undergo oxidative addition processes to alleviate their unsaturation. Bridging ligands that can increase their metal connectivity are essential in the cluster precursors. In fact, all known BEBSP ruthenium clusters contain bridging S-donor (**2**, **4**−**6**, **16**, **17**), C-donor (**7**, **9**, **18**, **21**), or N-donor ligands (**11**−**15**) that span at least four metal atoms. When the bridging ligand is bi- or polydentate, it is also bound to the edge-bridging metal atom (**11**−**18**, **21**). These bridging ligands should also be very basic. Their strong basicity 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. These facts rationalize many reactions in which BEBSP ruthenium clusters are involved as products or reagents, in which decarbonylation and cluster condensation or fragmentation is often accompanied by processes that involve the multiple oxidative addition of very strong bonds, such as C(sp^3)−H, C(sp^3)−C, and C(sp^3)−N.

The high-yield preparation (77%) of the BEBSP cluster [$Ru_6(\mu_3\text{-}H)_2(\mu_5\text{-}\kappa^2\text{-ampy})(\mu\text{-}CO)_2(CO)_{14}$] (**12**) from [$Ru_3(CO)_{12}$] and 2-amino-6-methylpyridine has importantly contributed to increase the knowledge of the reactivity of BEBSP hexaruthenium clusters.

The substitution of triphenylphosphine for a CO in cluster **12** occurs, initially, on the edge-bridging Ru atom (**23**, **24**), but the thermodynamically stable product has the substituent on the apical Ru atom (**25**). Further CO substitution processes occur on the edge-bridging Ru atom (**26**) and on one of the basal Ru atoms (**27**).

With mono- and polycyclic hydrocarbon reagents, the coordination of the ligand is sometimes accompanied by hydrogenation (**29**) or dehydrogenation processes (**30**−**37**). In most of these reactions, the BEBSP metallic skeleton is retained and the ligands are attached to the apical Ru atom (arenes in **28**, cycloheptadienyl in **29**, cyclopentadienyl in **33**, indenyl in **37**, fluorene in **38**) and, in some instances, also to one (cycloheptatrienyl in **31**) or two of the basal Ru atoms (cycloheptatrienyl in **30**, azulene in **39**). In a few instances (indene, azulene, acenathphylene) some reaction products do not retain the metallic skeleton of the starting material. This is due to the high temperatures required by these reactions (174 °C), which facilitate decarbonylation processes and the cleavage of Ru−Ru bonds, and also to the particular preference of acenaphthylene to coordinate to four nearly coplanar Ru atoms (**43**, **44**).

The unprecedented activation of five C(sp^3)−H bonds of linear alkenes has been observed on studying reactions of compound **12** with linear 1-alkenes, which give cluster products that contain trienyl ligands (**45**−**47**).

Diphenylacetylene is hydrogenated by compound **12** to *cis*-stilbene. The resulting unsaturated cluster reacts with more alkyne to give a cascade of reactions that ends in the pentanuclear derivative **53**. Many intermediates of this process have been identified (**48**−**53**), and a reaction pathway has been proposed. Compound **12** reacts with diphenylbutadiyne to give products that arise from the unusual 1,1- (**54**, **55**) or *trans*-1,2-addition of dihydrogen to the diyne (**56**, **57**). All of the alkyne derivatives (**49**−**53**) and the diyne derivatives (**54**−**57**) do not have a BEBSP metallic skeleton. In all these cases, an alkyne CC fragment is coordinated to the four basal Ru atoms, replacing (**52**, **53**, **57**) or displacing it to a different position of the cluster (**49**−**51**, **54**−**56**).

The electrophilic character of compound **12** is demonstrated by its reactions with [PPN][BH_4] and H_2/Et_3N, which give the anionic trihydride **58**. New μ_4-κ^2 coordination modes of the ampy ligand have been observed in compounds **59**−**62**. While hexanuclear **59** and octanuclear **60** arise from the reaction of **12** with 2-amino-6-methylpyridine, compounds **61** and **62** are nonanuclear and arise from the thermolysis of **12** in refluxing undecane.[49] The doubly basal-edge-bridged pentagonal-bipyramidal metallic framework of clusters **61** and **62** is unique in cluster chemistry.

With the exception of the reactions with triphenylphosphine and hydrides, which are CO monosubstitutions and proceed at room temperature, the remaining reactions surveyed herein imply the substitution of more than one CO ligand and require high temperatures.

It is important to note the role played by the ampy ligand in the reactions of **12**, which acts as an anchor that helps prevent cluster fragmentation and increases the thermal stability of the products that contain it. Interestingly, the apical Ru atom of **12**, which is not attached to the ampy ligand, is frequently involved in processes that imply the exchange of $Ru(CO)_n$ fragments and that are responsible for the formation of penta- and/or heptanuclear products. It is also noticeable that the unique coordination modes (viz. μ_4-acenaphthylene) and the unique reactivity (viz. the 1,1-addition of dihydrogen to a 1,3-diyne or the multiple dehydrogenation of 1-alkenes) associated with some of the reactions discussed in this review are only possible in cluster chemistry.

Despite the amount of results described and discussed in this review, the synthesis and reactivity of BEBSP hexanuclear clusters is still at the beginning of its development. The future will bring new results in several directions: (a) the synthesis and reactivity of BEBSP hexaruthenium clusters containing other bridging ligands, particularly polydentate ones, (b) the synthesis and reactivity of BEBSP hexanuclear clusters of other transition metals, since to date they are only known for ruthenium, and (c) the applications of clusters of this type as catalyst precursors in homogeneously catalyzed reactions.

Acknowledgment. We wish to thank many co-workers, whose names are given in the references, for their important contribution to many of the results surveyed in this paper. Dr. I. del Río is thanked for his helpful comments on the paper. Continuous financial support from the European Union (FEDER grants), the Spanish Ministerio de Educación y Ciencia, and the Government of Principado de Asturias is gratefully acknowledged.

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