Reactions of Conjugated Dienes with a Triruthenium Hydrido Carbonyl Cluster: Synthesis and Reactivity of Trinuclear Derivatives Having an Edge-Bridging Allyl Ligand

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The reactions of the hydrido triruthenium complex $[Ru_3(\mu\text{-H})(\mu_3\text{-}\kappa^2\text{-HNNMe}_2)(CO)_9]$ (**1**; H_2NNMe_2 = 1,1-dimethylhydrazine) with conjugated dienes give trinuclear derivatives that contain edge-bridging allyl ligands. The isolated allyl products are $[Ru_3(\mu\text{-}\kappa^3\text{-}C_8H_{13})(\mu_3\text{-}\kappa^2\text{-HNNMe}_2)(\mu\text{-CO})_2(CO)_6]$ (**2**) from 1,3-cyclooctadiene, $[Ru_3(\mu\text{-}\kappa^3\text{-}C_6H_9)(\mu_3\text{-}\kappa^2\text{-HNNMe}_2)(\mu\text{-CO})_2(CO)_6]$ (**4**) from 1,3-cyclohexadiene, and $[Ru_3(\mu\text{-}\kappa^3\text{-}C_4H_6OMe)(\mu_3\text{-}\kappa^2\text{-HNNMe}_2)(\mu\text{-CO})_2(CO)_6]$ (**5**) from *cis*-1-methoxybutadiene. While the cyclic structure of the allyl ligands of **2** and **4** forces these ligands to have an *anti-anti* arrangement, compound **5** contains an *anti*-MeO-*syn*-Me allyl ligand. This synthetic approach, which uses conjugated dienes as precursors to allyl ligands, represents an alternative to the use of alkynes having α-hydrogen atoms as precursors to allyl ligands, especially if the alkyne required to make a particular allyl ligand is unknown or difficult to obtain, as happens for cyclic alkynes. The cyclooctenyl derivative $[Ru_3(\mu\text{-}\kappa^2\text{-}C_8H_{13})(\mu_3\text{-}\kappa^2\text{-HNNMe}_2)(\mu\text{-CO})_2(CO)_6]$ (**3**) has also been obtained, as a minor product, from the reaction of **1** with 1,3-cyclooctadiene. A study of the reactivity of compound **2** has been performed. It undergoes protonation at the metal atoms to give the cationic derivative $[Ru_3(\mu\text{-H})(\mu\text{-}\kappa^3\text{-}C_8H_{13})(\mu_3\text{-}\kappa^2\text{-HNNMe}_2)(\mu\text{-CO})_2(CO)_6]^+$, which has an edge-bridging hydrido ligand and has been isolated as the $[BF_4]^-$ salt (**6**). Hydride addition to compound **2** occurs at the allyl ligand to give uncoordinated cyclooctene. Treatment of **2** with *tert*-butylisocyanide leads to the CO-substitution derivative $[Ru_3(\mu\text{-}\kappa^3\text{-}C_8H_{13})(\mu_3\text{-}\kappa^2\text{-HNNMe}_2)(^t\text{BuNC})(\mu\text{-CO})_2(CO)_5]$ (**7**), whereas its reaction with diphenylacetylene affords 1,3-cyclooctadiene and the 1,2-diphenylethenyl derivative $[Ru_3(\mu\text{-}\kappa^2\text{-PhCCHPh})(\mu_3\text{-}\kappa^2\text{-HNNMe}_2)(\mu\text{-CO})_2(CO)_6]$ (**8**). Some of these results have been rationalized with the help of DFT calculations.

Introduction

Recent studies have shown that the reactions of the hydrazido-bridged hydrido carbonyl triruthenium complex $[Ru_3(\mu\text{-H})(\mu_3\text{-}\kappa^2\text{-HNNMe}_2)(CO)_9]$[1] (**1**; H_2NNMe_2 = 1,1-dimethylhydrazine) with a variety of terminal and internal alkynes without α-hydrogen atoms give trinuclear alkenyl derivatives that have their alkenyl ligands in edge-bridging or face-capping positions.[2] The nature of the substituents of the alkyne reagent strongly affects the stability of each product and the selectivity of these reactions. However, when the alkyne reagents have α-hydrogen atoms, the products contain face-capping alkenyl (**A** and **B** in Scheme 1) and/or edge-bridging allyl ligands (**C** and **D** in Scheme 1), but never edge-bridging alkenyl ligands.[3] Again, the nature of the R substituents influences the regioselectivity of the reactions. In addition, DFT studies have shown that, for isomeric products, the allyl derivatives are thermodynamically more stable than their corresponding alkenyl isomers.[3]

Before the above commented works, triruthenium cluster complexes having organic allyl ligands ($R^1R^2CCR^3CR^4R^5$; R ≠ M) were very rare, the only precedents being $[Ru_3(\mu\text{-}\kappa^3\text{-}C_3H_5)(\mu_3\text{-}\kappa^2\text{-PPhCH}_2\text{PPh}_2)(CO)_8]$ and $[Ru_3(\mu_3\text{-}\kappa^5\text{-HabqCHCHCHR})(\mu\text{-CO})_2(CO)_6]$ (H_2abqH = 2-amino-7,8-benzoquinoline; R = H, C≡CSiMe$_3$), which also contain edge-bridging allyl ligands. The former was prepared by treating the anion $[Ru_3(\mu_3\text{-}\kappa^2\text{-PPhCH}_2\text{PPh}_2)(CO)_9]^-$ with allyl chloride,[4] whereas the H_2abqH-derived clusters were synthesized from $[Ru_3(\mu_3\text{-}\kappa^3\text{-Habq})(CO)_9]$ and propargyl alcohol or 1-trimethylsilyl-1,4-pentadiyne and contain the allyl fragment attached to a face-capping Habq group.[5] Quite a few cluster complexes containing 1,3-dimetalated allyl ligands ($MR^1CCR^2CR^3M$) are known. They have been prepared by treating nonhydridic ruthenium clusters with alkynes of the type $R^1CHR^2C{\equiv}CR^3$,[6] and also by inserting alkynes $R^1C{\equiv}CR^2$ into an Ru−CR^3 bond of complexes of the type $[Ru_3(\mu\text{-H})_3(\mu_3\text{-CR}^3)(CO)_9]$,[7] but these 1,3-dimetalated allyl ligands are attached to only one metal atom through a typical κ^3-allyl coordination. One penta-[8] and one hexaruthenium[9] cluster have been shown to contain edge-bridging allyl ligands.

Studying the reactivity of compound **1** with conjugated dienes, we have now found that these unsaturated reagents can also be

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(1) Jenke, T.; Stoeckli-Evans, H.; Süss-Fink, G. J. *Organomet. Chem.* **1990**, *391*, 395.

(2) Cabeza, J. A.; del Río, I.; Fernández-Colinas, J. M.; García-Granda, S.; Martínez-Méndez, L.; Pérez-Carreño, E. *Chem.−Eur. J.* **2004**, *10*, 6265.

(3) Cabeza, J. A.; del Río, I.; García-Granda, S.; Martínez-Méndez, L.; Pérez-Carreño, E. *Chem.–Eur. J.* **2005**, *11*, 6040.

(4) Bruce, M. I.; Williams, M. L. *J. Organomet. Chem.* **1985**, *288*, C55.

(5) Cabeza, J. A.; del Río, I.; García-Granda, S.; Riera, V.; Suárez, M. *Organometallics* **2004**, *23*, 3501.

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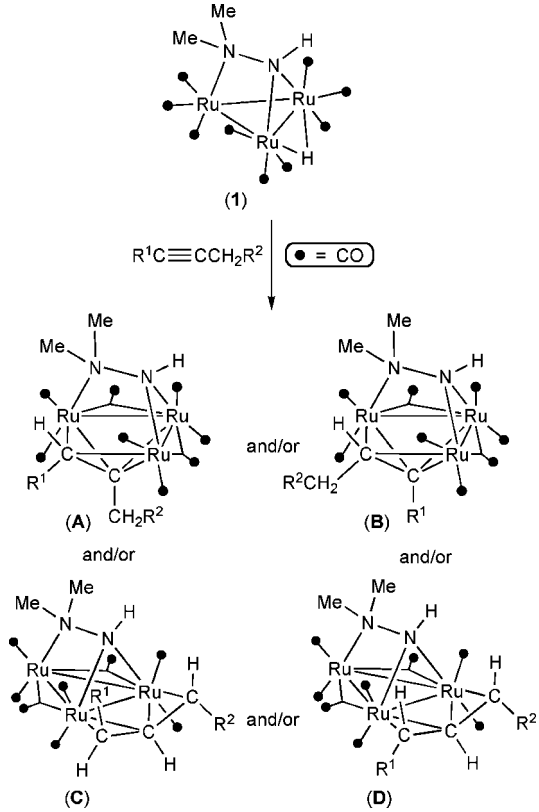
Scheme 1



used in cluster chemistry as precursors of allyl ligands and that this synthetic strategy can lead to allyl derivatives that cannot be prepared from alkyne precursors (e.g., clusters containing cyclic allyl ligands, for which the appropriate alkynes are unknown or of difficult availability).

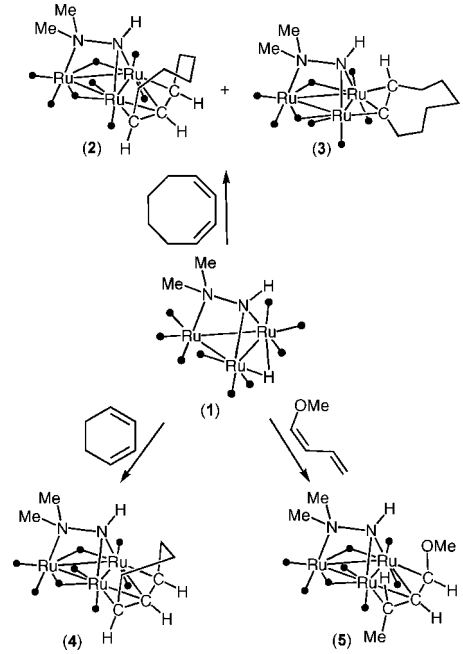
In this paper we also report the reactivity of the cluster $[Ru_3(\mu\text{-}\kappa^3\text{-}C_8H_{13})(\mu_3\text{-}\kappa^2\text{-}HNNMe_2)(\mu\text{-}CO)_2(CO)_6]$ (**2**), which contains a cycloocta-1,2,3-allyl ligand, with some representative reagents, such as $[HOEt_2][BF_4]$, $[PPN][BH_4]$, *tert*-butylisocyanide, and diphenylacetylene. This is the first time that reactions of triruthenium allyl clusters are reported.

X-ray diffraction, IR and NMR spectroscopy, and calculations of minimum-energy structures by DFT methods have been used to characterize the products. A comparison of the absolute energies of isomeric compounds (obtained by DFT calculations) has helped rationalize the experimental results.

Results and Discussion

Reactions of Compound 1 with Conjugated Dienes. Treatment of compound **1** with an excess of 1,3-cyclooctadiene in toluene at reflux temperature led to a 22:1 mixture of the

Scheme 2



isomeric μ-allyl and μ-alkenyl derivatives $[Ru_3(\mu\text{-}\kappa^3\text{-}C_8H_{13})(\mu_3\text{-}\kappa^2\text{-}HNNMe_2)(\mu\text{-}CO)_2(CO)_6]$ (**2**) and $[Ru_3(\mu\text{-}\kappa^2\text{-}C_8H_{13})(\mu_3\text{-}\kappa^2\text{-}HNNMe_2)(\mu\text{-}CO)_2(CO)_6]$ (**3**), respectively, which were separated by column chromatography (Scheme 2).

The μ-allyl clusters $[Ru_3(\mu\text{-}\kappa^3\text{-}C_6H_9)(\mu_3\text{-}\kappa^2\text{-}HNNMe_2)(\mu\text{-}CO)_2(CO)_6]$ (**4**) and $[Ru_3(\mu\text{-}\kappa^3\text{-}C_4H_6OMe)(\mu_3\text{-}\kappa^2\text{-}HNNMe_2)(\mu\text{-}CO)_2(CO)_6]$ (**5**) were similarly prepared from reactions of compound **1** with 1,3-cyclohexadiene and *cis*-1-methoxybutadiene, respectively (Scheme 2). In these cases, no alkenyl derivatives were observed as reactions products.

These reactions, which use conjugated dienes as precursors to allyl ligands, represent an important alternative to the use of alkynes having α-hydrogen atoms as precursors to allyl ligands,[3] particularly when the alkyne that would lead to the desired allyl ligand is unknown or difficult to obtain, as happens for cyclic alkynes.

The isolation of a small amount of the alkenyl cluster **3** in the reaction of **1** with 1,3-cyclooctadiene led us to consider the possibility that **3** might arise from the allyl cluster **2**. To check this, compound **2** was heated in toluene at reflux temperature. The only products that were observed since the beginning of the thermolysis were the hydride **1** (IR, ^{1}H NMR) and 1,3-cyclooctadiene (GC), accompanied by extensive decomposition. To avoid the decomposition of **2**, its thermolysis was also performed in the presence of an excess (4 equiv) of free 1,3-cyclooctadiene. In this case, compound **2** remained unchanged after 30 min in refluxing toluene. Similar results were obtained using the related allyl clusters **4** and **5** as starting materials. The cyclooctenyl cluster **3** was also heated in toluene at reflux temperature for 30 min, but no changes were observed. These data indicate that, in the reaction of **1** with 1,3-cyclooctadiene, the allyl cluster **2** and the alkenyl derivative **3** should be formed by independent reaction pathways. In other words, **2** is not a precursor of **3**, nor is the later a precursor of the former.

The fact that a cyclohexenyl cluster was not observed as a product in the reaction of **1** with 1,3-cyclohexadiene may be related to the smaller ring size of this diene, as compared with that of 1,3-cyclooctadiene, which may require strained high-energy transition states to give a cyclohexenyl cluster.

We have previously proposed that, for the reactions of compound **1** with alkynes having α-hydrogen atoms, the allyl

(6) (a) Evans, M.; Hursthouse, M.; Randall, E. W.; Rosenberg, E. *J. Chem. Soc., Chem. Commun.* **1972**, 545. (b) Castiglioni, M.; Milone, L.; Osella, D.; Vaglio, G. A.; Valle, M. *Inorg. Chem.* **1976**, *15*, 394. (c) Gervasio, G.; Osella, D.; Valle, M. *Inorg. Chem.* **1976**, *15*, 1176. (d) Rao, K. M.; Angelici, R. J.; Young, V. G. *Inorg. Chim. Acta* **1992**, *198*, 211. (e) Doherty, S.; Corrigan, J. F.; Carty, A. J.; Sappa, E. *Adv. Organomet. Chem.* **1995**, *37*, 39. (f) Bruce, M. I.; Zaitseva, N. N.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1999**, 2777. (g) Wong, W. Y.; Chan, S.; Wong, W. T. *J. Chem. Soc., Dalton Trans.* **1995**, 1497. (h) Gervasio, G.; Marabello, D.; King, P. J.; Sappa, E.; Secco, A. *J. Organomet. Chem.* **2003**, *671*, 385.

(7) (a) Beanan, L. R.; Rahman, Z. A.; Keister, J. B. *Organometallics* **1983**, *2*, 1062. (b) Beanan, L. R.; Keister, J. B. *Organometallics* **1985**, *4*, 1713. (c) Cabeza, J. A.; da Silva, I.; del Río, I.; García-Granda, S.; Riera, V. *Inorg. Chim. Acta* **2003**, *347*, 107.

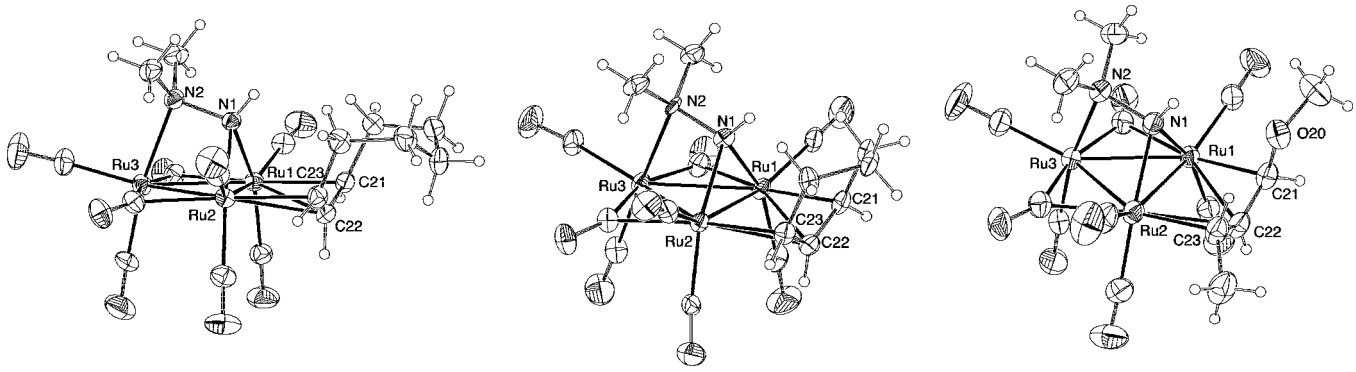


Figure 1. Molecular structures of the allyl clusters **2** (left), **4** (center), and **5** (right). Thermal ellipsoids are drawn at the 30% probability level.

Table 1. Selected Interatomic Distances (Å) in Compounds 2–5

	2	3	4	5
Ru(1)−Ru(2)	2.7490(5)	2.6884(9)	2.7422(8)	2.7689(4)
Ru(1)−Ru(3)	2.7555(5)	2.7902(10)	2.7623(8)	2.7476(4)
Ru(2)−Ru(3)	2.7331(5)	2.7682(10)	2.7806(8)	2.7562(4)
N(1)−Ru(1)	2.140(4)	2.110(6)	2.129(7)	2.124(3)
N(1)−Ru(2)	2.132(4)	2.143(6)	2.110(7)	2.130(3)
N(2)−Ru(3)	2.205(4)	2.203(6)	2.212(7)	2.215(3)
C(21)−Ru(1)	2.222(4)	2.306(6)	2.207(9)	2.181(4)
C(22)−Ru(1)	2.544(5)	2.228(7)	2.527(8)	2.570(4)
C(22)−Ru(2)	2.554(5)	2.100(8)	2.542(9)	2.493(4)
C(23)−Ru(2)	2.230(4)		2.193(9)	2.186(4)

products are formed via edge-bridging alkenyl intermediates, and we suggested a reaction pathway for such a transformation.[3] For the herein reported reactions of compound **1** with conjugated dienes, a reasonable reaction pathway that would lead to allyl derivatives can be proposed (it would involve, among other steps, coordination of the diene and CO elimination followed by transfer of the hydride to one of the terminal carbon atoms of the diene). However, we have been unable to envisage a reasonable reaction pathway to edge-bridging cycloalkenyl derivatives, such as **3**, without the intermediacy of edge-bridging allyl species. This has to be so because we have experimentally checked that the cycloallyl clusters **2** and **4** do not give cycloalkenyl derivatives when heated in refluxing toluene.

The structures of compounds **2**−**5** were determined by X-ray diffraction. A selection of interatomic distances is given in Table 1. For comparison purposes, a common atomic numbering scheme has been used.

The structures of the allyl derivatives **2**, **4**, and **5** (Figure 1) are closely related. In the three cases, the hydrazido group caps the metal triangle in the same way as that found previously in complex **1**[1] and in most of its derivatives.[2,3,10] The allyl ligand spans the same Ru−Ru edge as the amido fragment of the hydrazido group and is attached to Ru(1) through the carbon atoms C(21) and C(22) and to Ru(2) through C(22) and C(23), the distances from the central carbon atom C(22) to Ru(1) and Ru(2) being 0.39–0.31 Å longer than those from C(21) to Ru(1) and C(23) to Ru(2). The dihedral angle between the planes defined by the allyl C(21), C(22), and C(23) atoms and the Ru_3 triangle is 77.9(4)° in **2**, 83.6(5)° in **4**, and 91.0(4)° in **5**. The three compounds have eight CO ligands, two of which are

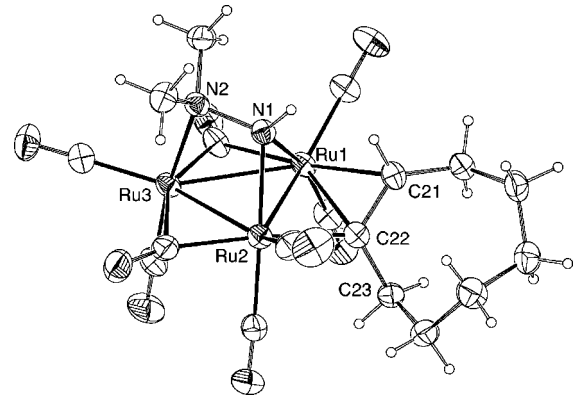


Figure 2. Structure of one of the two independent molecules of the alkenyl cluster **3** found in the asymmetric unit of $\mathbf{3}\cdot 0.25(C_6H_{14})$. Thermal ellipsoids are drawn at the 20% probability level.

bridging and six are terminal. The Ru−Ru distances, ranging from 2.73 to 2.78 Å, confirm the presence of Ru−Ru single bonds.[11] The most noticeable features of these compounds are associated with the arrangement of the substituents of their allyl fragment. While the cyclic character of the hydrocarbon ligands of **2** and **4** forces their allyl substituents to be in *anti* arrangements, the allyl ligand of compound **5** has an *anti*-methoxy group and a *syn*-methyl group. The oxygen atom of the methoxy group is hydrogen bonded to the hydrogen atom of the hydrazido NH group, O(20)···N(1) 2.933(4) Å, N(1)−H(1) 0.87(2) Å, and O(20)···H(1) 2.55(4) Å. A short contact is also observed between the methoxy O atom and the hydrogen atom of C(23), O(20)···C(23) 2.773(6) Å, C(23)−H(23) 0.99(5) Å, and O(20)···H(23) 2.35(4) Å. All previously known triruthenium allyl complexes, prepared from **1** and internal alkynes, have acyclic allyl ligands with substituents in *syn-syn* or *syn-anti* arrangements.[3] Therefore, the *anti-anti* arrangement of the allyl ligands of compounds **2** and **4** is unprecedented.

The X-ray structure of the alkenyl cluster **3**, depicted in Figure 2, has many features in common with the structures of the allyl clusters commented above (those associated with the bonding of the metal atoms with the capping hydrazido ligand and the carbonyl ligands). Instead of an allyl ligand, the cluster now has a cyclooctenyl ligand spanning the same Ru−Ru edge as the hydrazido NH fragment. This ligand is attached to Ru(1) through C(21) and C(22) and to Ru(2) through C(22) in an analogous manner with that found previously for other triru-

(8) Chihara, T.; Yamazaki, H. *J. Organomet. Chem.* **1992**, *428*, 169.
(9) Chihara, T.; Yamazaki, H. *J. Chem. Soc., Dalton Trans.* **1995**, 1369.
(10) (a) Cabeza, J. A.; del Río, I.; García-Granda, S.; Martínez-Méndez, L.; Riera, V. *J. Organomet. Chem.* **2002**, *663*, 227. (b) Cabeza, J. A.; del Río, I.; García-Granda, S.; Martínez-Méndez, L.; Riera, V. *Inorg. Chim. Acta* **2003**, *350*, 93. (c) Cabeza, J. A.; del Río, I.; García-Granda, S.; Martínez-Méndez, L.; Pérez-Carreño, E. *Organometallics* **2005**, *24*, 831.

(11) The Ru−Ru distances in $[Ru_3(CO)_{12}]$ are in the range 2.8595 to 2.8515 Å: Churchill, M. R.; Hollander, F. J.; Hutchinson, J. P. *Inorg. Chem.* **1977**, *16*, 2655.

thenium clusters having edge-bridging alkenyl ligands.[2,12–14] However, all these previous alkenyl clusters have been prepared from acyclic alkynes, and therefore they all have acyclic alkenyl ligands.

The ^{1}H NMR features of the allyl or alkenyl ligands **2**−**5** and the band patterns of the carbonyl stretching region of their IR spectra are comparable to those previously reported for other allyl[3] or alkenyl[2] (as applicable) derivatives of compound **1**.

Minimum-energy structure calculations (structure optimizations) were carried out by DFT methods at the B3LYP/LANL2DZ/6-31G(d,p) level. Calculations were performed on selected real molecules (products isolated in the present work) and on hypothetical ones with the aim of not only comparing their thermodynamic stability (important to rationalize the experimental results) but also to assign or confirm the structures of compounds for which no X-ray diffraction data were available. No simplified model compounds were used for the calculations. Calculated structures are assigned Roman numbers, irrespectively of whether they correspond to real (also designated with Arabic numbers) or hypothetical compounds. Computer-generated images of all these structures and their atomic coordinates are given as Supporting Information. In the cases where both experimental (X-ray diffraction) and theoretical (DFT calculations) structural data were obtained, the structural parameters given by both methods are practically identical. This fact validates the calculations.

Figure 3 shows the relative energies of the two families of isomeric allyl and alkenyl products formally derived from compound **1** and 1,3-cyclooctadiene or 1,3-cyclohexadiene. In both cases, the allyl derivatives (structures **I** and **III**) are more stable than the alkenyl derivatives (structures **II** and **IV**), but only by less than 1.7 kcal mol^{-1}. This contrasts with previous calculations on isomeric acyclic allyl and alkenyl derivatives of compound **1**, which showed that the edge-bridging alkenyl derivatives are 5–6 kcal mol^{-1} less stable than the most stable allyl isomer.[3] Figure 4, which compares the energies of isomeric products containing acyclic allyl or alkenyl ligands formally derived from compound **1** and 3-hexyne or 2,4-hexadiene, shows that, among the four possible allyl isomers, the structure **VIII**, which has both allyl substituents in *syn* positions, is the most stable, whereas structure **VII**, which has both allyl substituents in *anti* positions, is the least stable. As the cyclic nature of the allyl ligands of **2** and **4** forces their allyl substituents to be in *anti* arrangements, the data shown in Figure 4 explain why the differences between the energies of the cyclic allyl structures **I** and **III** and the cyclic alkenyl structures **II** and **IV** (Figure 3) are so small. Nevertheless, as the allyl derivatives **2** and **4** are the major/only products of the reactions of compound **1** with the studied cyclic dienes, it seems that these reactions are thermodynamically controlled because these products are the most stable ones.

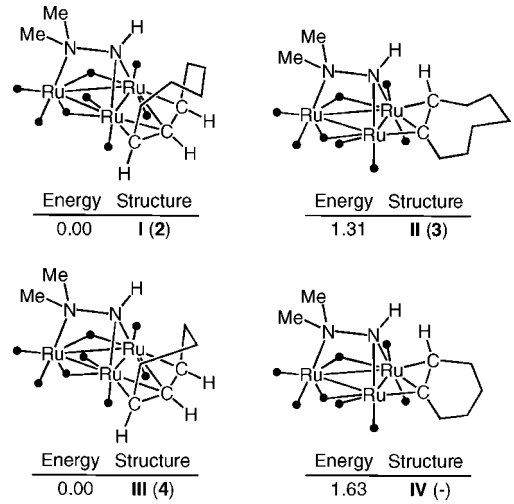


Figure 3. Relative energies (kcal mol^{-1}) of DFT-optimized structures of isomeric allyl and alkenyl products formally derived from compound **1** and 1,3-cyclooctadiene (top) or 1,3-cyclohexadiene (bottom). The energy of the most stable structure of each pair of isomers is assigned as 0.00 kcal mol^{-1}.

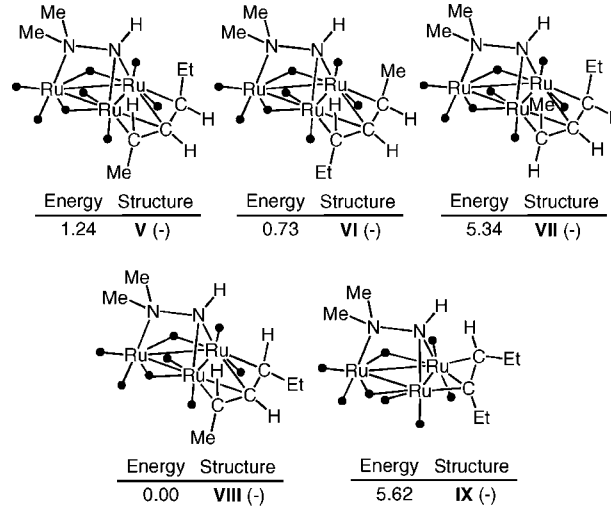


Figure 4. Relative energies (kcal mol^{-1}) of DFT-optimized structures of isomeric allyl and alkenyl products formally derived from compound **1** and 3-hexyne or 2,4-hexadiene (data taken from ref 3). The energy of the most stable structure is assigned as 0.00 kcal mol^{-1}.

Figure 5 shows the relative energies of isomeric allyl and alkenyl products formally derived from compound **1** and *cis*-1-methoxybutadiene. As for other isomeric derivatives of compound **1** having acyclic edge-bridging allyl or alkenyl ligands,[3] the most stable isomer is an allyl derivative (**5**, structure **X**). However, in this case, the allyl ligand of the most stable structure does not have both substituents in *syn* positions, as has been found for other acyclic allyl derivatives of compound **1**.[3] The fact that compound **5** has a *syn*-methyl group and an

(12) (a) Cabeza, J. A.; García-Granda, S.; Llamazares, A.; Riera, V.; Van der Maelen, J. F. *Organometallics* **1993**, *12*, 157. (b) Cabeza, J. A.; García-Granda, S.; Llamazares, A.; Riera, V.; Van der Maelen, J. F. *Organometallics* **1993**, *12*, 2973. (c) Briard, P.; Cabeza, J. A.; Llamazares, A.; Ouahab, L.; Riera, V. *Organometallics* **1993**, *12*, 1006. (d) Alvarez, S.; Briard, P.; Cabeza, J. A.; del Río, I.; Fernández-Colinas, J. M.; Mulla, F.; Ouahab, L.; Riera, V. *Organometallics* **1994**, *13*, 4360. (e) Cabeza, J. A.; Llamazares, A.; Riera, V.; Briard, P.; Ouahab, L. *J. Organomet. Chem.* **1994**, *480*, 205. (f) Cabeza, J. A.; Fernández-Colinas, J. M.; Llamazares, A.; Riera, V.; García-Granda, S.; Van der Maelen, J. F. *Organometallics* **1994**, *13*, 4352.

(13) (a) Lugan, N.; Laurent, F.; Lavigne, G.; Newcomb, T. P.; Liimatta, E. W.; Bonnet, J. J. *Organometallics* **1992**, *11*, 1351. (b) Nombel, P.; Lugan, N.; Mulla, F.; Lavigne, G. *Organometallics* **1994**, *13*, 4673. (c) Nombel, P.; Lugan, N.; Donnadieu, B.; Lavigne, G. *Organometallics* **1999**, *18*, 187.

(14) (a) Ferrand, V.; Merzweiler, K.; Rheinwald, G.; Stoeckli-Evans, H.; Süss-Fink, G. *J. Organomet. Chem.* **1997**, *549*, 263. (b) Ferrand, V.; Neels, A.; Stoeckli-Evans, H.; Süss-Fink, G. *Inorg. Chem. Commun.* **1999**, *2*, 561. (c) Ferrand, V.; Gambs, C.; Derrien, N.; Bolm, C.; Stoeckli-Evans, H.; Süss-Fink, G. *J. Organomet. Chem.* **1997**, *549*, 275.

(15) (a) See, for example: Andreu, P. L.; Cabeza, J. A.; Riera, V.; Bois, B.; Jeannin, Y. *J. Chem. Soc., Dalton Trans.* **1990**, 3347. (b) Cabeza, J. A.; del Río, I.; García-Granda, S.; Matínez-Méndez, L.; Riera, V. *Inorg. Chim. Acta* **2003**, *350*, 93. (c) Andreu, P. L.; Cabeza, J. A.; Pellinghelli, M. A.; Riera, V.; Tiripicchio, A. *Inorg. Chem.* **1991**, *30*, 4611. (d) Cabeza, J. A.; Fernández-Colinas, J. M.; Llamazares, A.; Riera, V.; García-Granda, S.; Van der Maelen, J. F. *Organometallics* **1994**, *13*, 4352.

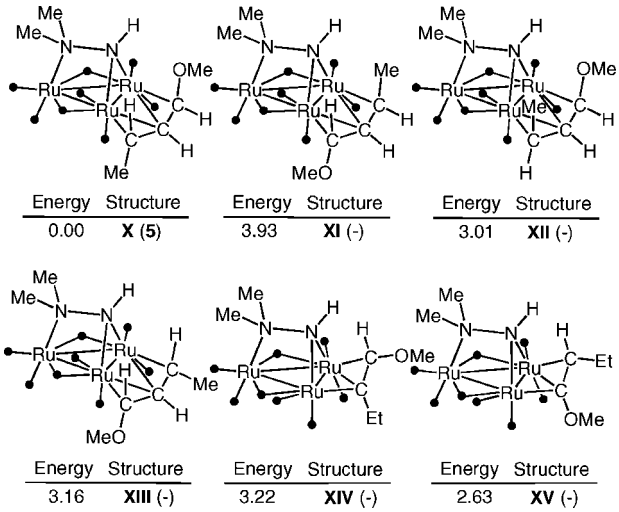


Figure 5. Relative energies (kcal mol^{-1}) of DFT-optimized structures of isomeric allyl and alkenyl products formally derived from compound **1** and *cis*-1-methoxybutadiene. The energy of the most stable structure is assigned as 0.00 kcal mol^{-1}.

anti-methoxy group can be explained taking into account that the *anti*-arrangement of the methoxy group favors the existence of a hydrogen-bonding interaction between the hydrazido NH group and the methoxy oxygen atom, which has indeed been experimentally observed by X-ray diffraction, and this interaction stabilizes this structure. In this case, the reaction is clearly thermodynamically controlled, because the obtained product (**5**, structure **X**) is at least 2.6 kcal mol^{-1} more stable than the other possible isomeric products (Figure 5).

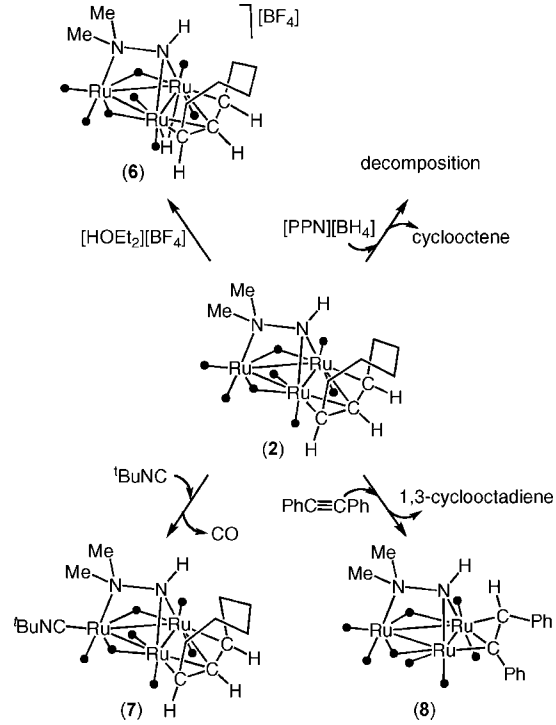
Reactivity of Compound 2. No reactions of edge-bridged allyl triruthenium clusters have been previously reported. This led us to undertake a study of the reactivity of one of the allyl clusters described above. We chose compound **2** for this study because it can be prepared in good yield and its symmetry reduces the number of possible isomeric reaction products. As representative reagents, we chose the proton (as an electrophile), the hydride (as a hard nucleophile), an isocyanide (as a soft nucleophile), and an alkyne (as an unsaturated reagent that could couple to the allyl ligand).

Complex **2** reacted immediately with an ethereal solution of tetrafluoroboric acid to give the ionic hydride $[Ru_3(\mu\text{-}H)(\mu\text{-}\kappa^3\text{-}C_8H_{13})(\mu_3\text{-}\kappa^2\text{-}HNNMe_2)(\mu\text{-}CO)_2(CO)_6][BF_4]$ (**6**; Scheme 3).

The IR spectrum of **6** shows the ν_{CO} absorptions at higher wave numbers than those of its precursor **2**, indicating an increase of the positive charge of the metal atoms. A medium-intensity band at 1858 cm^{-1} denotes that the bridging CO ligands of **2** are maintained in **6**. Its ^1H NMR spectrum confirms the presence of a hydride (δ −15.28) and of a symmetry plane that cuts the cation into two identical halves.

As no crystals of **6** suitable for X-ray diffraction could be obtained and as the above spectroscopic data are compatible with two alternative positions of the hydride ligand in the cation, namely, capping the ruthenium atoms or bridging the same Ru−Ru edge as the allyl ligand, these two possibilities were used as input models for two DFT structure optimizations. Both calculations converged to the same optimized structure, which is depicted in Figure 6. This figure shows that the cation has C_s symmetry, that the hydride H(1) spans the Ru(1)−Ru(1′) edge, H(1)−Ru(1) 1.828 Å, but it also interacts, although more weakly, with the Ru(2) atom, H(1)−Ru(2) 2.245 Å, and that the Ru−Ru and Ru−C_{allyl} distances are 0.2–0.1 Å longer than those of the starting material **2**.

Scheme 3



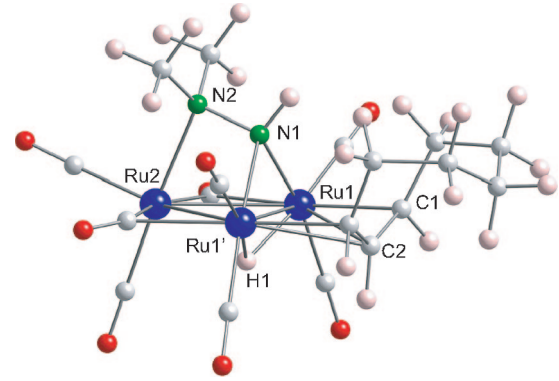


Figure 6. DFT-optimized structure of the cation of compound **6**. Selected interatomic distances (Å): Ru(1)−Ru(1′) 2.914, Ru(1)−Ru(2) 2.906, Ru(1)−N(1) 2.178, Ru(1)−C(1) 2.313, Ru(1)−C(2) 2.691, Ru(2)−N(2) 2.260, N(1)−N(2) 1.460, C(1)−C(2) 1.425, H(1)−Ru(1) 1.828, H(1)−Ru(2) 2.245.

The structural features of the cationic cluster of compound **6** can be easily rationalized having a look at the HOMO of compound **2** (Figure 7). This molecular orbital, which is mainly composed by orbitals of the metal atoms, has the maximum orbital concentration just in the place where the cationic cluster of **6** accommodates the hydride ligand. Therefore, the protonation of **2** is mainly controlled by its HOMO. This MO is bonding with respect to the Ru−Ru bonds and with respect to the Ru−C_{allyl} bonds. Consequently, as the protonation of **2** reduces the electron density of this MO, the cation of **6** has longer Ru−Ru and Ru−C_{allyl} distances than compound **2**.

As far as we are aware, the hydrides of all previously known cationic triruthenium hydrido carbonyl clusters arise from protonation of neutral precursors,[15] and curiously, most previously known cationic triruthenium hydrido carbonyl clusters are asymmetric, even those prepared from symmetric neutral clusters.[15a,b] However, the cation of **6** maintains the symmetry of its neutral precursor **2**. This is because, in the HOMO of **2**, the bonding interaction of the p−π orbital of the allyl fragment

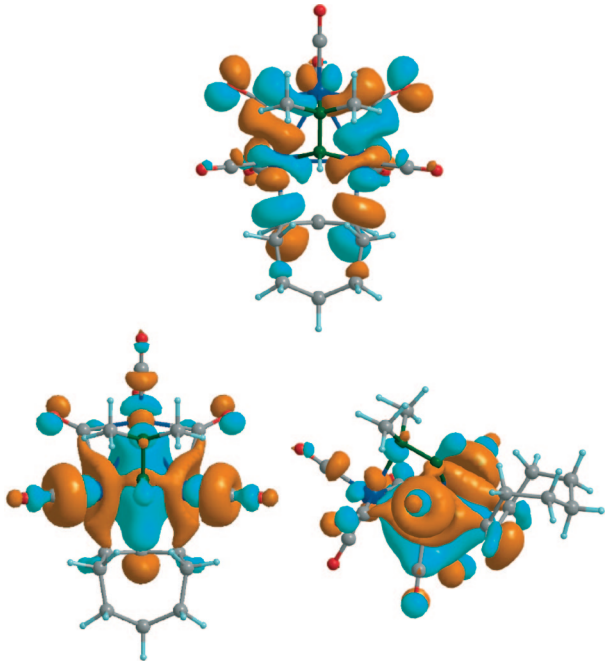


Figure 7. LUMO (top) and two views of the HOMO (bottom) of compound **2**.

central carbon atom with the metal orbitals makes the allyl-bridged Ru−Ru edge more electron rich than the other two Ru−Ru edges (Figure 7), thus favoring the protonation in that position.

Treatment of compound **2** with [PPN][BH_4] led to immediate cluster decomposition. A GC analysis of the resulting solution revealed the presence of cyclooctene. This fact indicates that the $[BH_4]^-$ anion acts in transferring a hydride to the allyl ligand of complex **2**. A look at the LUMO of compound **2** (Figure 7) suggests that it is this MO that controls this reaction, because it has an important contribution of the p−π orbitals of the terminal carbon atoms of the allyl fragment and the overlap of these orbitals with the orbitals of the metal atoms is antibonding. In addition, the intermetallic overlaps are also antibonding. Therefore, the addition of a hydride to complex **2** occurs on one of the terminal allyl C atoms and this results in the formation of cyclooctene and general cluster decomposition.

Compound **2** remained unchanged when it was treated with an excess of *tert*-butylisocyanide at room temperature. At higher temperature (refluxing THF), a slow reaction led to the substitution derivative $[Ru_3(\mu\text{-}\kappa^3\text{-}C_8H_{13})(\mu_3\text{-}\kappa^2\text{-}HNNMe_2)(^t\text{BuNC})(\mu\text{-}CO)_2(CO)_5]$ (**7**), among other minor unidentified products. Although this compound could not be characterized by X-ray diffraction methods, the structure proposed for this cluster in Scheme 3 is firmly supported by its ^{1}H NMR spectrum, which indicates that **7** also has C_s symmetry, and by the fact that the NMe_2 group of the face-capping hydrazido ligand is a strong *cis*-labilizing group.[15b] A similar behavior is expected for other soft two-electron donor reagents.

The reaction of cluster **2** with diphenylacetylene led to 1,3-cyclooctadiene and the known diphenylethenyl derivative $[Ru_3(\mu\text{-}\kappa^2\text{-}PhCCHPh)(\mu_3\text{-}\kappa^2\text{-}HNNMe_2)(\mu\text{-}CO)_2(CO)_6]$ (**8**; Scheme 3), among other minor uncharacterized products. The original synthesis of compound **8** involves the treatment of the hydride **1** with diphenylacetylene.[2] This result confirms that, upon heating, compound **2** evolves toward a hydrido diene trinuclear intermediate (see the thermolysis of compound **2**, above) that is able to react with the alkyne to give the final alkenyl product and the free diene. The low thermal stability of the allyl complex **2**, which easily releases 1,3-cyclooctadiene upon heating, suggests that other attempts to transform the allyl ligand of this cluster by coupling it to unsaturated reagents will probably be unsuccessful.

Concluding Remarks

This article describes the synthesis of allyl triruthenium clusters from hydrido triruthenium cluster complexes and conjugated dienes. This novel synthetic approach, which uses conjugated dienes as precursors to allyl ligands, represents a valuable alternative to the use of alkynes having α-hydrogen atoms as precursors to allyl ligands,[3] especially when the alkyne required to make a particular allyl ligand is unknown or difficult to obtain, as is the case of cyclic alkynes.

DFT calculations have shown that the allyl complexes are more stable than their alkenyl isomers. Although the *syn-syn* arrangement of the allyl 1,3-substituents is generally more stable than the *anti-syn* and the *anti-anti* arrangements, the presence of an intramolecular NH···OMe hydrogen bond interaction in compound **5** favors a *syn*-Me-*anti*-OMe arrangement of the substituents of its allyl ligand. The cyclic allyl ligands of **2** and **3** have an *anti-anti* arrangement.

Compound **2** underwent protonation at the metal atoms to give a cationic derivative (**6**) that has an edge-bridging hydrido ligand, whereas hydride addition to compound **2** occurred at the allyl ligand to give uncoordinated cyclooctene. The results of these reactions have been rationalized studying the HOMO and LUMO of compound **2**. Treatment of **2** with *tert*-butylisocyanide led to the symmetric CO-substitution derivative **7**.

The low thermal stability of the allyl complex **2**, which easily releases 1,3-cyclooctadiene upon heating, suggests that attempts to couple the allyl ligand of this cluster to unsaturated reagents will be unsuccessful. In fact, the reaction of **2** with diphenylacetylene afforded 1,3-cyclooctadiene and the 1,2-diphenylethenyl derivative **8**.

Experimental Section

General Data. Compound **1** was prepared by a published method.[1] The remaining reagents were purchased from commercial suppliers. Solvents were dried over sodium diphenyl ketyl (hydrocarbons, diethyl ether, THF) or CaH_2 (dichloromethane) and distilled under nitrogen before 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 spot TLC. IR spectra were recorded in solution on a Perkin-Elmer Paragon 1000 FT spectrophotometer. ^{1}H NMR spectra were run on a Bruker DPX-300 instrument, using the dichloromethane solvent resonance as internal standard (δ = 5.30). Microanalyses were obtained from the University of Oviedo Analytical Service. Mass spectra (ESI, FAB) were obtained from the University of Santiago de Compostela Mass Spectrometric Service; data given refer to the most abundant molecular ion isotopomer. GC analyses were performed on a Perkin-Elmer 8600 gas chromatograph, equipped with a 12-m AQ2 capillary column and a flame ionization detector.

$[Ru_3(\mu\text{-}\kappa^3\text{-}C_8H_{13})(\mu_3\text{-}\kappa^2\text{-}HNNMe_2)(\mu\text{-}CO)_2(CO)_6]$ (2) and $[Ru_3(\mu\text{-}\kappa^2\text{-}C_8H_{13})(\mu_3\text{-}\kappa^2\text{-}HNNMe_2)(\mu\text{-}CO)_2(CO)_6]$ (3). A toluene (20 mL) solution of compound **1** (50 mg, 0.081 mmol) and 1,3-cyclooctadiene (12.1 μL, 0.097 mmol) was stirred at reflux temperature for 2 h. The color changed from yellow to brown. The solvent was removed *in vacuo*, the residue was extracted into dichloromethane (2 × 1 mL), and the resulting solution was transferred onto a silica gel chromatographic column (10 × 3 cm) packed in

Table 2. Crystal, Measurement, and Refinement Data for the Compounds Studied by X-Ray Diffraction

	2	**3**·0.25(C_6H_{14})	**4**	**5**
formula	$C_{18}H_{20}N_2O_8Ru_3$	$C_{18}H_{20}N_2O_8Ru_3$ ·0.25(C_6H_{14})	$C_{16}H_{16}N_2O_8Ru_3$	$C_{15}H_{16}N_2O_9Ru_3$
formula wt	695.57	717.11	667.52	671.51
crystal syst	monoclinic	triclinic	orthorhombic	monoclinic
space group	$P2_1/c$	$P\bar{1}$	$P2_12_12_1$	$P2_1/c$
a, Å	16.8544(2)	13.993(2)	9.2887(1)	16.1234(2)
b, Å	10.9325(1)	14.883(3)	13.9925(1)	9.3005(1)
c, Å	13.4141(2)	16.361(3)	15.9506(2)	15.6395(2)
α, deg	90	63.08(2)	90	90
β, deg	108.679(1)	73.09(2)	90	113.828(2)
γ, deg	90	66.25(2)	90	90
V, Å^3	2341.50(5)	2756(1)	2073.13(4)	2145.33(6)
Z	4	4	4	4
F(000)	1352	1402	1288	1296
D_{calcd}, g cm^{-3}	1.973	1.728	2.139	2.079
μ (radiation), mm^{-1}	15.872 (Cu Kα)	13.504 (Cu Kα)	17.891 (Cu Kα)	17.329 (Cu Kα)
cryst size, mm	0.16 × 0.14 × 0.07	0.30 × 0.02 × 0.02	0.30 × 0.12 × 0.10	0.17 × 0.08 × 0.02
temp, K	293(2)	293(2)	293(2)	293(2)
θ limits, deg	2.77 to 74.59	3.06 to 74.15	4.20 to 70.22	3.00 to 73.93
min/max *h*	−21/20	−15/17	−7/11	−19/18
min/max *k*	−13/13	−17/18	−17/16	−10/9
min/max *l*	−16/15	−19/20	−18/18	−19/19
no. of collected rflns	47645	28358	6869	11985
no. of unique rflns	4523	10579	3613	4067
no. of reflns with $I > 2\sigma(I)$	3833	6806	3509	3439
no. of params/restraints	284/0	583/0	262/0	274/1
GOF on F^2	1.025	1.085	1.036	1.038
*R*1 (on *F*, $I > 2\sigma(I)$)	0.0451	0.0423	0.0514	0.0287
*wR*2 (on F^2, all data)	0.1365	0.1305	0.1395	0.0803
max/min Δ*ρ*, e Å^{-3}	0.832/−1.029	0.832/−1.029	0.938/−2.901	0.538/−0.804

hexane. Hexane−dichloromethane (3:1) eluted three yellow bands. The first band contained some unreacted starting material **1**. The second and third bands contained compounds **2** (50 mg, 88%) and **3** (2 mg, 4%), respectively. Data for **2**: Anal. Calcd for $C_{18}H_{20}N_2O_8Ru_3$ (697.84): C, 31.08; H, 2.90; N, 4.03. Found: C, 31.03; H, 2.87; N 3.99. (+)-ESI MS: *m/z* 697 $[M]^+$. IR (CH_2Cl_2): ν_{CO} 2057 (s), 1014 (vs), 1984 (s), 1963 (m), 1844 (w), 1799 (m). ^{1}H NMR (C_6D_6, 293 K): *δ* 3.63 (m, 2 H, 2 CH_2), 2.38 (m, 1 H, CH_2), 1.95 (m, 2 H, 2 CH_2), 1.72 (t, $J = 9.5$ Hz, 1 H, CH), 1.63 (m, 2 H, 2 CH_2) 1.44 (m, 1 H, CH_2), 1.16 (m, 2 H, 2 CH_2,), 1.02 (s, 6 H, 2 CH_3), 0.28 (s, 1 H, NH), −0.34 (m, 2 H, 2 CH). Data for **3**: Anal. Calcd for $C_{18}H_{20}N_2O_8Ru_3$ (697.84): C, 31.08; H, 2.90; N, 4.03. Found: C, 31.01; H, 2.87; N 4.00. (+)-ESI MS: *m/z* 697 $[M]^+$. IR (CH_2Cl_2): ν_{CO} 2059 (m), 2027 (vs), 2006 (vs), 1989 (w), 1974 (w), 1943 (m), 1796 (w). ^{1}H NMR (C_6D_6, 293 K): *δ* 3.37 (m, 1 H), 3.24 (s, 1 H, NH), 2.85 (m, 2 H), 2.76 (s, 3 H, CH_3), 2.57 (s, 3 H, CH_3), 2.46 (m, 1 H), 1.89 (m, 6 H) 1.25 (m, 3 H).

[Ru_3(*μ*-*κ*^{3}-C_6H_9)(*μ*$_3$-*κ*^{2}-HNNMe$_2$)(*μ*-CO)$_2$(CO)$_6$] (4). A toluene (30 mL) solution of compound **1** (200 mg, 0.325 mmol) and 1,3-cyclohexadiene (1 mL) was stirred at reflux temperature for 30 min. The color changed from yellow to dark brown. The solvent was removed *in vacuo*, the residue was extracted into dichloromethane (2 × 1 mL), and the resulting solution was transferred onto a silica gel chromatographic column (10 × 3 cm) packed in hexane. Hexane−dichloromethane (1:1) eluted a yellow band, which contained compound **4** (104 mg, 50%). Anal. Calcd for $C_{16}H_{16}N_2O_8Ru_3$ (669.80): C, 28.79; H, 2.42; N, 4.20. Found: C, 28,73; H, 2.40; N 4.16. (+)-ESI MS: *m/z* 669 $[M]^+$. IR (CH_2Cl_2): ν_{CO} 2057 (s), 2017 (vs), 1983 (s), 1965 (w), 1844 (w), 1799 (m). ^{1}H NMR ($CDCl_3$, 293 K): *δ* 4.76 (m, 2 H, 2 CH_2), 2.43 (m, 2 H, 2 CH_2), 1.98 (s, 6 H, 2 CH_3), 1.94 (m, 1 H, CH_2), 1.56 (m, 1 H, CH), 1.06 (m, 1 H, CH_2), 0.29 (s, 1 H, NH), −0.31 (m, 2 H, 2 CH).

[Ru_3(*μ*-*κ*^{3}-C_4H_6OMe)(*μ*$_3$-*κ*^{2}-HNNMe$_2$)(*μ*-CO)$_2$(CO)$_6$] (5). A toluene (20 mL) solution of compound **1** (50 mg, 0.081 mmol) and *cis*-1-methoxybutadiene (9.9 *μ*L, 0.975 mmol) was stirred at reflux temperature for 1.5 h. The color changed from yellow to brown. The solvent was removed *in vacuo*, the residue was extracted into dichloromethane (2 × 1 mL), and the resulting solution was transferred onto a silica gel chromatographic column (10 × 3 cm) packed in hexane. Hexane−dichloromethane (1:1) eluted two yellow bands. The first band contained some unreacted starting material **1**. The second band contained compound **5** (23 mg, 42%). Anal. Calcd for $C_{15}H_{16}N_2O_9Ru_3$ (673.80): C, 26.83; H, 2.40; N, 4.17. Found: C, 26.78; H, 2.35; N 4.14. (+)-ESI MS: *m/z* 645 $[M - CO]^+$. IR (CH_2Cl_2): ν_{CO} 2057 (s), 2017 (sh), 2009 (vs), 1985 (s), 1962 (m), 1848 (w), 1802 (m). ^{1}H NMR ($CDCl_3$, 293 K): *δ* 6.45 (m, 1 H, CH), 2.96 (s, 3 H, CH_3), 2.34 (s, 3 H, CH_3), 1.94 (s, 3 H, CH_3), 1.89 (s, 3 H, CH_3), 1.74 (m, 2 H, 2 CH), 0.78 (s, 1 H, NH).

[Ru_3(*μ*-H)(*μ*-*κ*^{3}-C_8H_{13})(*μ*$_3$-*κ*^{2}-HNNMe$_2$)(*μ*-CO)$_2$(CO)$_6$][BF_4] (6). An excess of [$HOEt_2$][BF_4] (seven drops from a Pasteur pipet of a 54% solution of HBF_4 in diethyl ether) was added to a solution of compound **2** (40 mg, 0.057 mmol) in dichloromethane (10 mL). A yellow solid precipitated. The solvent was removed *in vacuo*, and the residue was washed with diethyl ether (3 × 5 mL) to give compound **6** (42 mg, 93%). Anal. Calcd for $C_{18}H_{21}BF_4N_2O_8Ru_3$ (783.38): C, 27.60; H, 2.70; N, 3.58. Found: C, 27.54; H, 2.67; N 3.56. (+)-FAB MS: *m/z* 698 $[M - BF_4]^+$. IR (CH_2Cl_2): ν_{CO} 2096 (s), 2068 (vs), 2032 (s), 1903 (w, br), 1858 (m). ^{1}H NMR ($CDCl_3$, 293 K): *δ* 4.99 (m, 2 H, 2 CH_2), 2.51 (m, 1 H, CH_2), 2.40 (m, 2 H, CH + NH), 2.12 (m, 2 H, 2 CH_2), 1.97 (s, 6 H, 2 CH_3), 1.79 (m, 1 H, CH_2), 1.73 (m, 4 H), 0.72 (m, 2 H, 2 CH), −15.28 (s, 1 H, *μ*-H).

[Ru_3(*μ*-*κ*^{3}-C_8H_{13})(*μ*$_3$-*κ*^{2}-HNNMe$_2$)(^{t}BuNC)(*μ*-CO)$_2$(CO)$_5$] (7). A THF (30 mL) solution of compound **2** (50 mg, 0.072 mmol) and *tert*-butylisocyanide (16 mL, 0.144 mmol) was stirred at reflux temperature for 4 h. The color changed from yellow to brown. The solvent was removed *in vacuo*, the residue was extracted into dichloromethane (1 mL), and the resulting solution was supported on silica gel TLC plates. Hexane−diethyl ether (5:1) eluted several bands. The first and major band, yellow, was extracted with dichloromethane to afford compound **7** (16 mg, 30%). Anal. Calcd for $C_{22}H_{29}N_3O_7Ru_3$ (750.69): C, 35.20; H, 3.89; N, 5.60. Found: C, 35.16; H, 3.84; N 5.53. (+)-FAB MS: *m/z* 749 $[M]^+$. IR (CH_2Cl_2): ν_{CN} 2172 (m); ν_{CO} 1993 (vs), 1974 (sh), 1945 (s), 1840 (w), 1788 (m), 1799 (m). ^{1}H NMR ($CDCl_3$, 293 K): *δ* 4.06 (m, 2 H, 2 CH_2), 2.74 (m, 1 H, CH_2), 2.40 (t, $J = 9.2$ Hz, 1 H, CH), 2.22 (m, 2 H, 2 CH_2), 1.92 (s, 6 H, 2 CH_3), 1.61 (m, 2 H, 2 CH_2), 1.41

(m, 2 H, 2 CH_2), 1.09 (s, 9 H, ^{t}Bu), 0.88 (m, 1 H, CH_2), 0.80 (s, 1 H, NH), 0.15 (m, 2 H, 2 CH).

[$Ru_3(\mu$-κ^2-PhCCHPh)(μ_3-κ^2-HNNMe$_2$)(μ-CO)$_2$(CO)$_6$] (8). A THF (30 mL) solution of compound **2** (50 mg, 0.072 mmol) and diphenylacetylene (18 mg, 0.100 mmol) was stirred at reflux temperature for 15 min. The color changed from yellow to red. A GC analysis of the resulting solution conformed the presence of 1,3-cyclooctadiene. The solvent was removed *in vacuo*, the residue was extracted into dichloromethane (1 mL), and the resulting solution was supported on silica gel TLC plates. Hexane−dichloromethane (1:3) eluted several bands. The fourth and major band, red, was extracted with dichloromethane to afford compound **8** (19 mg, 30%). Its analytical and spectroscopic data matched those reported in the literature.[2]

Computational Details. All optimized structures were calculated by hybrid DFT, within the GAUSSIAN-03 program suite,[16] using the Becke's three-parameter hybrid exchange−correlation functional[17] and the B3LYP nonlocal gradient correction.[18] The LanL2DZ basis set, with relativistic effective core potentials, was used for the Ru atoms.[19] The basis set used for the remaining atoms was the standard 6-31G, with addition of (d,p)-polarization. Each structure was confirmed as an energy minimum by calculation of analytical frequencies. For each calculation, the input model molecule was based on one of the X-ray-determined structures reported in this article, conveniently modified, if necessary, by manually adding or removing the appropriate atoms.

X-Ray Diffraction Analyses. Diffraction data were collected on an Oxford Diffraction Xcalibur Nova single-crystal diffractometer, using Cu Kα radiation. Images were collected at a 60 mm crystal to detector distance, using the oscillation method, with 1° oscillation and variable exposure time per image. Data collection strategy was calculated with the program CrysAlisPro CCD.[20] Data reduction and cell refinement were performed with the program CrysAlisPro RED.[21] Empirical absorption corrections were applied using the SCALE3 ABSPACK algorithm as implemented in CrysAlisPro RED. Structures were solved by Patterson interpretation using the program DIRDIF-96.[22] Isotropic and full matrix anisotropic least-squares refinements were carried out using SHELXL-97.[23] All non-H atoms of all structures were refined anisotropically. Some hydrogen atoms were located in the corresponding Fourier maps and refined with restricted thermal and/or positional parameters. The remaining hydrogen atoms were set in calculated positions and refined riding on their parent atoms. Two independent but chemically equivalent cluster molecules of **3** and half-molecule of hexane were found in the asymmetric unit of **3**·0.25(C_6H_{14}). The molecular plots were made with the PLATON program package.[24] The WINGX program system[25] was used throughout the structure determinations. A selection of crystal, measurement, and refinement data is given in Table 2. CCDC deposition numbers: 667834 (**2**), 667835 (**3**), 667836 (**4**), and 667839 (**5**).

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Supporting Information Available: Images and atomic coordinates of the structures optimized by DFT methods, and crystallographic data in CIF format of the compounds studied by X-ray diffraction. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, E. R.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M.; Gonzalez, W. C.; Pople, J. A. *GAUSSIAN-03 (Revision C2)*; Gaussian Inc.: Wallingford, CT, 2004.

(17) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(18) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev., B* **1988**, *37*, 785.

(19) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.

(20) *CrysAlisPro CCD, version 1.171.31.7*; Oxford Diffraction Ltd.: Oxford, UK, 2006.

(21) *CrysAlisPro RED, version 1.171.31.7*; Oxford Diffraction Ltd.: Oxford, UK, 2006.

(22) Beurskens, P. T.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; García-Granda, S.; Gould, R. O.; Israël, R.; Smits, J. M. M. *The DIRDIF-96 Program System*; Crystallography Laboratory, University of Nijmegen: Nijmegen, The Netherlands, 1996.

(23) Sheldrick, G. M. *SHELXL97, version 97-2*; University of Göttingen: Göttingen, Germany, 1997.

(24) Spek, A. L. *PLATON: A Multipurpose Crystallographic Tool*; University of Utrecht: Utrecht, The Netherlands, 2003.

(25) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837.