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Reactivity of Diynes with a 1-Azavinylidene-Bridged Triruthenium Carbonyl Cluster. Insertion Reactions of Diynes into Ru−H, Ru−C, and Ru−N Bonds

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The reactivity of the 1-azavinylidene cluster complex $[Ru_3(\mu\text{-}H)(\mu\text{-}N{=}CPh_2)(CO)_{10}]$ (**1**) with diynes has been studied. The nonconjugated diyne 1-trimethylsilyl-1,4-pentadiyne affords the binuclear ynenyl derivative $[Ru_2(\mu\text{-}N{=}CPh_2)(\mu\text{-}\eta^2\text{-}CH_2{=}CCH_2C{\equiv}CSiMe_3)(CO)_6]$ (**2**), which results from cluster fragmentation and from the insertion of the terminal alkyne fragment of the diyne into a Ru−H bond. The reactions of **1** with the internal conjugated diynes 1,6-diphenoxy-2,4-hexadiyne, 2,4-hexadiyne, and diphenylbutadiyne have allowed the isolation of the trinuclear derivatives $[Ru_3\{\mu\text{-}\eta^2\text{-}N{=}CPh(C_6H_4)\}(\mu_3\text{-}\eta^4\text{-}PhOCH_2CH{=}C{=}C{=}CHCH_2OPh)(CO)_8]$ (**3**), $[Ru_3\{\mu_3\text{-}\eta^4\text{-}N{=}CPh(C_6H_4)CH(Me)CH{=}C{=}CMe\}(CO)_9]$ (**4**), $[Ru_3\{\mu\text{-}\eta^2\text{-}N{=}CPh(C_6H_4)\}(\mu_3\text{-}\eta^4\text{-}PhCH{=}CHC{\equiv}CPh)(CO)_8]$ (**5**), and $[Ru_3\{\mu_3\text{-}\eta^4\text{-}PhCHCH{=}C(CPh)N{=}CPh(C_6H_4)\}(CO)_9]$ (**6**). The four compounds have been characterized by X-ray diffraction methods. They all arise from the orthometalation of a phenyl ring of the 1-azavinylidene ligand and from the transfer of two hydride ligands (the original plus that coming from the orthometalation) to the coordinated diyne. This hydrogenation process can proceed as a 1,4-addition to give a 1,2,3-triene fragment (as occurs in **3**) or as a 1,2-addition to give an enyne fragment (as occurs in **5**). In the cases of **4** and **6**, a 1,2-addition of hydrogen is accompanied by the insertion of the unsaturated hydrocarbon fragment into the Ru−C bond associated with the orthometalated ring (**4**, **6**) and into a Ru−N bond (**6**). The precise order by which these processes lead to the corresponding products has not been established. The reactions involved in the formation of compounds **2**−**6** represent excellent examples of insertion of diynes into M−H, M−C, and M−N bonds of metal clusters and have allowed the characterization of substituted 1-yn-3-enyl (in **2**), 1,2,3-triene (in **3**), 1,2-dienyl (in **4**), 1-en-3-yne (in **5**), and 2-(*N*-imido)-1,2,3-allyl-1-yl (in **6**) ligands.

Introduction

The past decade has been witness to an increasing interest in the synthesis and reactivity of late-transition-metal amido complexes as a consequence of the relative scarcity of such compounds[1−5] and of their potential use in C−N bond-forming reactions.[6−9]

In this field, we have recently described a high-yield synthesis of $[Ru_3(\mu\text{-}H)(\mu\text{-}N{=}CPh_2)(CO)_{10}]$ (**1**),[5] a compound that contains a bridging amido ligand derived from benzophenone imine, which can be regarded as a 1-azavinylidene ligand.[10] As part of a general study of the reactivity of compound **1**,[5−7,11] we have previously reported that the thermal reaction of **1** with an excess of diphenylacetylene results in the formation of the

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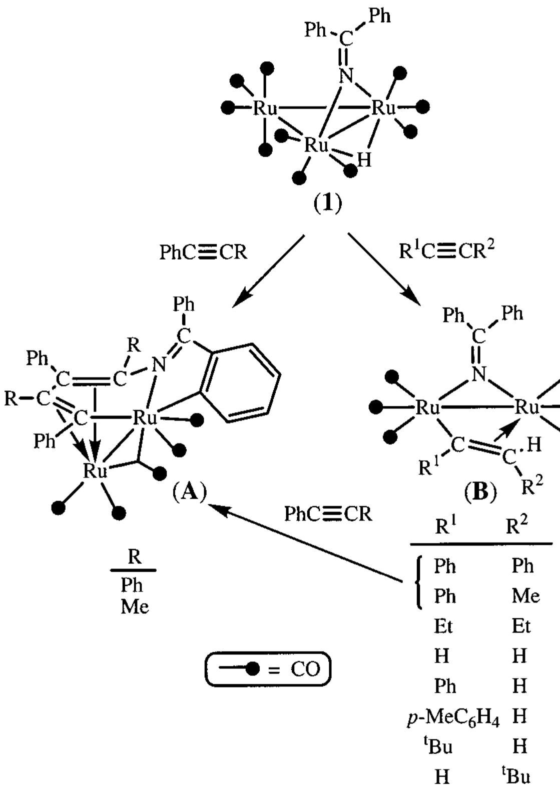
Scheme 1



R¹	R²
Ph	Ph
Ph	Me
Et	Et
H	H
Ph	H
p-MeC$_6$H$_4$	H
^{t}Bu	H
H	^{t}Bu

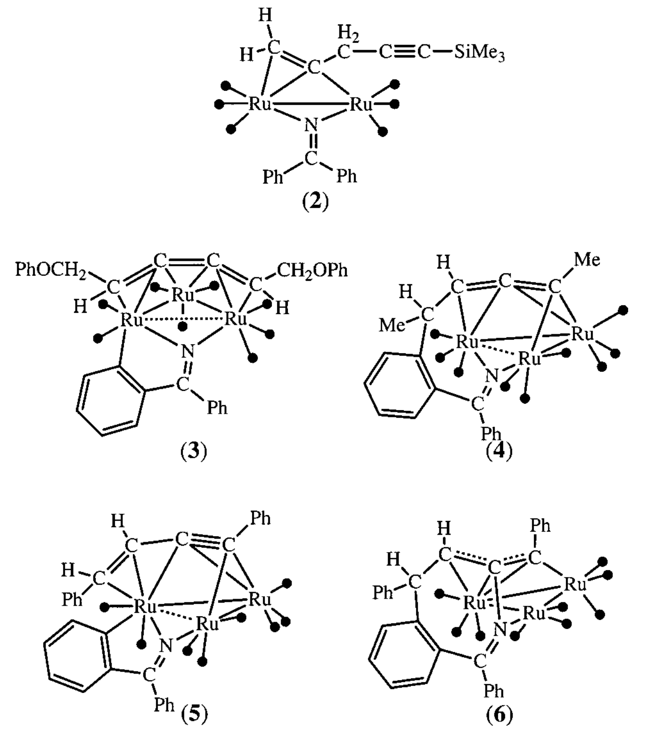
binuclear metallacyclic derivative $[Ru_2\{\mu\text{-}PhC{=}CPhCPh{=}CPhN{=}CPh(C_6H_4)\}(\mu\text{-}CO)(CO)_4]$ (**A**, R = Ph in Scheme 1).[6] We have also shown that this type of reaction can be extended to other internal alkynes containing one phenyl group, such as 1-phenyl-1-propyne (**A**, R = Me in Scheme 1), whereas the reactions of **1** with other types of alkynes lead only to binuclear derivatives containing alkenyl ligands that arise from the insertion of the alkynes into M−H bonds (**B** in Scheme 1).[7] To date, the formation of C−N bonds via insertion of unsaturated molecules into the M−N bonds of amido complexes is very uncommon, and it has only been achieved with highly electrophilic substrates, such as dimethyl acetylenedicarboxylate, carbon monoxide, carbonyl sulfide, carbon dioxide, acrylonitrile, or phenyl isocyanate.[8,9]

The results obtained from the reactions of compound **1** with alkynes,[7] summarized in Scheme 1, led us to investigate the reactivity of compound **1** with diynes, which were expected to be more reactive and, hence, to provide a richer derivative chemistry than that of simple alkynes. Moreover, very few reactions of ruthenium carbonyl cluster complexes with diynes have previously been described.[12] We now report that compound **1** reacts with 1-trimetilsilyl-1,4-pentadiyne, 1,6-diphenoxy-2,4-hexadiyne, 2,4-hexadiyne, and diphenylbutadiyne, under thermal conditions, to give products containing ligands that derive from insertion reactions of the diynes into Ru−H, Ru−C, and Ru−N bonds.

Results

Synthesis. The reactions of compound **1** with diynes were carried out in THF at reflux temperature, using an excess (2- to 3-fold) of the diyne. Heating was stopped when the IR spectra of the solutions no longer showed the bands of compound **1**. In all cases, qualitative TLC analysis of the resulting solutions indicated the presence of several products in addition to an uneluted residue. Chart 1 shows the schematic structures of the compounds $[Ru_2(\mu\text{-}N{=}CPh_2)(\mu\text{-}\eta^2\text{-}CH_2{=}CCH_2C{\equiv}CSiMe_3)(CO)_6]$ (**2**), $[Ru_3\{\mu\text{-}\eta^2\text{-}N{=}CPh(C_6H_4)\}(\mu_3\text{-}\eta^4\text{-}PhOCH_2CH{=}C{=}C{=}CHCH_2OPh)(CO)_8]$ (**3**), $[Ru_3\{\mu_3\text{-}\eta^4\text{-}N{=}CPh(C_6H_4)CH(Me)CH{=}C{=}CMe\}(CO)_9]$ (**4**), $[Ru_3\{\mu\text{-}\eta^2\text{-}N{=}CPh(C_6H_4)\}(\mu_3\text{-}\eta^4\text{-}PhCH{=}CHC{\equiv}CPh)(CO)_8]$ (**5**), and $[Ru_3\{\mu_3\text{-}\eta^4\text{-}PhCHCH{=}C(CPh)N{=}CPh(C_6H_4)\}(CO)_9]$ (**6**), which are the major products of the reactions of cluster **1** with 1-trimethylsilyl-1,4-pentadiyne (**2**), 1,6-diphenoxy-2,4-hexadiyne (**3**), 2,4-hexadiyne (**4**), and diphenylbutadiyne (**5** and **6**). They were separated by chromatographic workups from the corresponding reaction mixtures and were characterized as follows.

Chart 1



Characterization of Compound 2. The binuclear nature of this compound was indicated by its microanalysis and mass spectrum, which are consistent with the structure depicted in Chart 1. Its IR spectrum in the carbonyl region compares well with those known for the binuclear alkenyl derivatives shown in Scheme 1,[7] suggesting a similar arrangement of the ligands. Although there are four different possibilities for the

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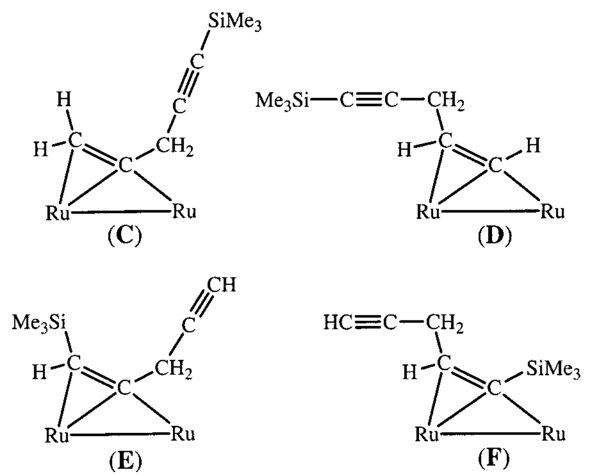
Chart 2



insertion of one of the alkyne fragments of 1-trimethylsilyl-1,4-pentadiyne into an M−H bond to give a binuclear ynenyl derivative (Chart 2), the ^{1}H NMR spectrum of **2** unambiguously confirms the absence of a terminal acetylenic hydrogen (structures **E** and **F**) and the presence of an alkenyl fragment which contains two geminal H atoms (structure **C**), since it shows two uncoupled resonances at δ 3.92 and 3.09 ppm, as expected for geminal vinyl hydrogens.[6] Moreover, the H atoms of the methylenic CH_2 fragment are observed as two doublets (they couple to each other), also ruling out the structures **D** and **F**, in which they should also couple to the corresponding vinyl hydrogen. Therefore, the structure shown in Chart 1 for compound **2** is strongly supported by its analytical and spectroscopic data.

Characterization of Compound 3. The trinuclear nature of this compound was revealed by its microanalytical and FAB-MS data. Its ^{1}H NMR spectum indicated (a) the possible orthometalation of a phenyl ring (several coupled resonances in the range 8.1−6.0 ppm), (b) the absence of hydride ligands, and (c) the addition of two hydrogen atoms to the original diyne framework (signals at 3.29 (t, 10.7 Hz) and 2.99 (t, 10.0 Hz) ppm). The multipliciy of these signals, in addition to selective homonuclear decoupling experiments, indicated that each of these hydrogen atoms is coupled to the hydrogens of a CH_2 group, being therefore attached to the carbon atom adjacent to the CH_2 group.

The structure of compound **3** was unambiguosly determined by X-ray diffraction methods (Chart 1, Figure 1a). A selection of bond distances is given in Table 1. The structure consists of an open triangle (V-shaped) of ruthenium atoms in which the longest (open) edge [3.502(1) Å] is spanned by the nitrogen atom of an orthometalated 2,2-diphenyl-1-azavinylidene ligand, which acts as a four-electron donor. A *cis*-1,6-diphenoxy-2,3,4-hexatriene ligand interacts with the three ruthenium atoms (Figure 1b) through the four C atoms involved in the cumulene moiety, in such a way that the central C═C double bond is parallel to the longest edge of the metallic triangle. Curiously, although the three C−C distances of the triene moiety are comparable, ranging from 1.372(9) to 1.40(1) Å, the Ru−C distances associated with the same carbon atoms range from 2.052(6) to 2.296(7) Å, the shortest ones corresponding to the bonds between the two central carbon atoms and the central ruthenium atom and the longest ones to the bonds between the two outer carbon atoms and the outer ruthenium atoms (Figure 1b). This ligand can be considered as a six-electron donor, since each C═C double bond is associated with a metal atom via a π-type interaction. The ligand shell of the cluster is completed by eight carbonyl ligands. Therefore, the electron count of this cluster is 50, compatible with the presence of only two metal−metal bonds between the three Ru atoms.[13]

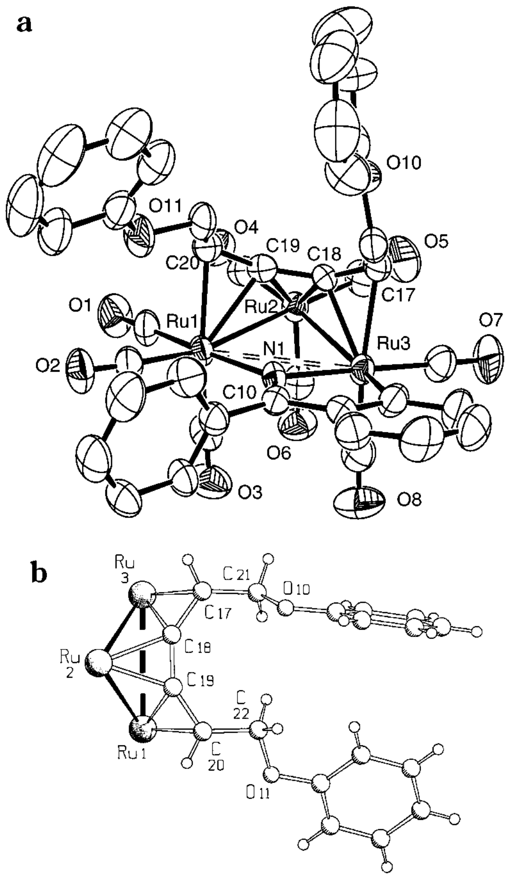


Figure 1. (a) Molecular structure of compound **3** (H atoms omitted for clarity). Thermal ellipsoids are drawn at 30% probability level. (b) Coordination of the *cis*-1,6-diphenoxy-2,3,4-hexatriene ligand to the metal triangle in compound **3** (all remaining atoms omitted for clarity).

Table 1. Selected Interatomic Distances (Å) in Compounds 3−6

	3	4	5	6
Ru(1)−Ru(2)	2.900(1)	2.812(1)	2.788(1)	2.758(1)
Ru(1)−Ru(3)	3.502(1)	3.381(1)	3.534(1)	2.825(2)
Ru(2)−Ru(3)	2.924(2)	2.819(1)	2.887(1)	2.830(1)
N(1)−Ru(1)	2.111(6)	2.107(6)	2.132(4)	2.12(1)
N(1)−Ru(3)	2.115(5)	2.166(6)	2.100(4)	
N(1)−C(10)	1.299(9)	1.263(10)	1.259(7)	1.33(1)
N(1)−C(19)				1.44(1)
C(12)−Ru(3)	2.063(8)		2.075(6)	
C(17)−Ru(3)	2.296(7)		2.380(5)	
C(18)−Ru(3)	2.154(7)	2.290(8)	2.224(5)	2.32(1)
C(19)−Ru(1)	2.224(7)			
C(19)−Ru(2)	2.052(6)	2.077(8)	2.062(5)	
C(19)−Ru(3)		2.296(8)	2.195(5)	2.21(1)
C(20)−Ru(1)	2.300(7)	2.086(8)	2.072(5)	
C(20)−Ru(2)		2.205(8)	2.251(5)	2.071(1)
C(20)−Ru(3)				2.19(1)
C(12)−C(17)		1.54(1)		1.53(2)
C(17)−C(18)	1.40(1)	1.53(1)	1.384(8)	1.51(1)
C(18)−C(19)	1.372(9)	1.40(1)	1.416(7)	1.38(1)
C(19)−C(20)	1.39(1)	1.37(1)	1.368(7)	1.43(1)

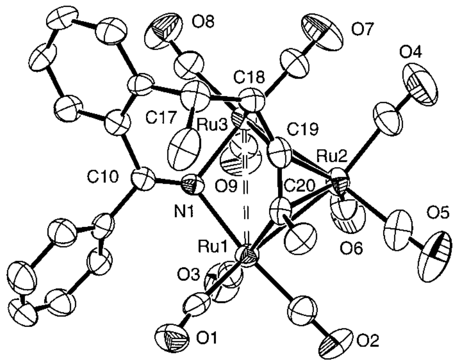


Figure 2. Molecular structure of compound **4** (H atoms omitted for clarity). Thermal ellipsoids are drawn at 30% probability level.

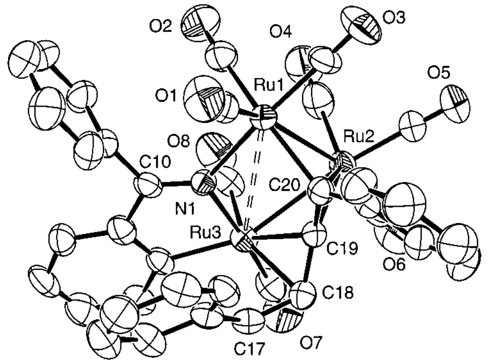


Figure 3. Molecular structure of compound **5** (H atoms omitted for clarity). Thermal ellipsoids are drawn at 30% probability level.

Characterization of Compound 4. The trinuclear nature of this compound was revealed by its microanalysis and mass spectrum. Its ^{1}H NMR spectum indicated (a) the possible orthosubstitution of a phenyl ring (a complex multiplet, in the range 7.5−7.1 ppm, accompanied by two doublets at 6.68 and 6.64 ppm), (b) the absence of hydride ligands, and (c) the addition of two hydrogen atoms to the original diyne framework (signals at 5.29 (d, 8.2 Hz) and 4.20 (dq, 8.2 and 7.7 Hz) ppm). The multipliciy and the coupling constants of these signals indicate that these hydrogen atoms couple to each other, but only one of them couples to a methyl group. Therefore, these hydrogen atoms are attached to the carbon atoms originally involved in one of the two triple bonds of 2,4-hexadiyne.

The structure of compound **4** was determined by X-ray diffraction methods (Chart 1, Figure 2). A selection of bond distances is given in Table 1. The structure consists of an open triangle (V-shaped) of ruthenium atoms in which the longest (open) edge [3.381(1) Å] is spanned by the nitrogen atom of a modified 2,2-diphenyl-1-azavinylidene ligand, which has one of the phenyl rings attached to the C^5 carbon atom of a hexa-2,3-diene-2,5-diyl fragment. This fragment interacts with the three ruthenium atoms through the three allenyl C atoms. While the C atoms of the two C=C bonds interact with two Ru atoms in a π-fashion, C(20) is also attached to the remaining Ru atom in a σ-fashion. The two C−C distances of the allenyl moiety are comparable [1.40(1) and 1.37(1) Å], while the Ru−C distances associated with these carbon atoms via π-type interactions range from 2.077(8) to 2.296(8) Å, the Ru(1)−C(20) distance (σ-type interaction) being 2.086(8) Å. Overall, the complete organic ligand contributes eight electrons to the cluster. The ligand shell of the molecule is completed by nine carbonyl ligands. Therefore, the electron count of this cluster is 50, compatible with the presence of only two metal−metal bonds between the three Ru atoms.[13]

Characterization of Compound 5. The trinuclear nature of this compound was again revealed by microanalysis and mass spectrometry. Its ^{1}H NMR spectum indicated (a) the possible orthometalation of a phenyl ring (several coupled resonances in the range 8.1−5.5 ppm), (b) the absence of hydride ligands, and (c) the addition of two hydrogen atoms to the original diyne framework (signals at 5.82 (d, 8.8 Hz) and 5.19 (d, 8.8 Hz) ppm). The multipliciy and the coupling constants of these signals indicate that these hydrogen atoms are located on adjacent carbon atoms.

The structure of compound **5** was determined by X-ray diffraction methods (Chart 1, Figure 3). A selection of bond distances is given in Table 1. The structure consists of an open triangle of ruthenium atoms in which the longest edge [3.533(1) Å] is spanned by the nitrogen atom of an orthometalated 2,2-diphenyl-1-azavinylidene ligand. A *cis*-1,4-diphenyl-3-buten-1-yne ligand interacts with the three Ru atoms through the four C atoms involved in the triple and double bonds, in such a way that the C atoms of the C≡C triple bond are parallel to the longest edge of the metallic triangle, interacting with the three metal atoms, as frequently observed for alkyne ligands in trinuclear metal clusters,[14,15] while the C atoms of the C=C double bond are attached to the same Ru atom as the metalated phenyl ring via a π-type interaction. As expected, the distances involving the C atoms of the four-electron donor C≡C [1.368(7) Å] and two-electron donor C=C [1.384(8) Å] moieties are similar and shorter than that of the C−C single bond [1.416(7) Å]; however, as a consequence of the distortion imposed by the fact that the alkene and alkyne fragments are rigidly attached to each other, the Ru−C distances associated with these C atoms (Table 1) differ substantially from those observed in normal ruthenium clusters containing μ_3-η^2-alkyne and η^2-alkene ligands.[14,15] The ligand shell of the molecule is completed by eight carbonyl ligands. Therefore, the electron count of this cluster is 50, compatible with the presence of only two metal−metal bonds between the three Ru atoms.[13]

Characterization of Compound 6. As occurred with compounds **3**−**5**, the trinuclear nature of compound **6** was again revealed by microanalysis and mass spectrometry. Its ^{1}H NMR spectum also indicated (a) the possible orthometalation or orthosubstitution of a phenyl ring (several resonances in the range 8.2−6.6 ppm), (b) the absence of hydride ligands, and (c) the addition of two hydrogen atoms to the original diyne

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[13] Mingos, D. M. P.; Wales, D. J. *Introduction to Cluster Chemistry*; Prentice Hall International: Englewood Cliffs, NJ, 1990.

[14] See, for example: (a) Sappa, E. *J. Cluster Sci.* **1994**, *5*, 211. (b) Deabate, S.; Giordano, R.; Sappa, E. *J. Cluster Sci.* **1997**, *8*, 407.

[15] Smith, A: K. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Vol. 7 (Shriver, D. F., Bruce, M. I., Eds.); Pergamon: Oxford, UK, 1995; p 747, and references therein.

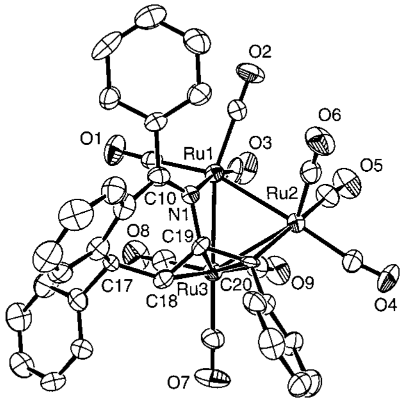

Figure 4. Molecular structure of compound **6** (H atoms omitted for clarity). Thermal ellipsoids are drawn at 30% probability level.

framework (signals at 3.62 (d, 10.2 Hz) and 3.48 (d, 10.2 Hz) ppm). The multipliciy and the coupling constants of these signals indicate that these hydrogen atoms are located on adjacent carbon atoms.

Again, an X-ray diffraction study was necessary to determine the structure of the compound (Chart 1, Figure 4). A selection of bond distances is given in Table 1. The structure consists of a nearly regular triangle of ruthenium atoms attached to an organic ligand which results from the coupling of the N atom and the metalated phenyl ring of an orthometalated 2,2-diphenyl-1-azavinylidene ligand with the C^2 and C^4 carbon atoms of an original *cis*-1,4-diphenyl-3-buten-1-yne ligand (which arises from the hydrogenation of diphenylbutadiyne). This ligand is attached to Ru(X) through the carbons C^1, C^2, and C^3, via a π-allyl-type interaction, to Ru(Y) through the N atom, and to Ru(Z) through C^1. The complete ligand contributes six electrons to the cluster. The ligand shell of the molecule is completed by nine carbonyl ligands. In this case, the electron count of this cluster is 48, compatible with the presence of three metal−metal bonds between the three Ru atoms.[13]

Discussion

Diynes can be divided into two groups (a) those that have the two triple C≡C bonds separated by carbon atoms and (b) those that have the two triple C≡C bonds in adjacent positions (conjugated). Both groups include diynes having one or both C≡C bonds in terminal or internal positions within the carbon chain. One of the diiynes used in this work, 1-trimethylsilyl-1,4-pentadiyne, belongs to the first group, while the remaining ones, 1,6-diphenoxy-2,4-hexadiyne, 2,4-hexadiyne, and diphenylbutadiyne, belong to the second group.

The above-described results involving 1-trimethylsilyl-1,4-pentadiyne indicate that the chemical behavior of nonconjugated diynes seems to be comparable to that of monoalkynes in their reactions with complex **1** (Scheme 1), since a binuclear ynenyl derivative, which results from the insertion of one of the two original alkyne functionalities into a Ru−H bond, has been isolated (Chart 1, compound **2**). Interestingly, the terminal alkyne fragment is preferred over the internal one. It has previously been determined that complex **1**[7] and many other ligand-bridged hydrido trinuclear clusters react easily with both internal and terminal alkynes to give binuclear alkenyl derivatives,[16] but no competitive reactions between these clusters and internal and terminal alkynes have been previously carried out. However, just one observation (only one nonconjugated alkyne has been studied) is not sufficient to unambiguously propose a pattern of behaviour for nonconjugated diynes.

The results obtained with 1,6-diphenoxy-2,4-hexadiyne, 2,4-hexadiyne and diphenylbutadiyne allow us to state that conjugated diynes behave quite differently from nonconjugated diynes in their reactions with compound **1**, since the characterized reaction products (Chart 1, compounds **3**−**6**), which are the major components of the corresponding reaction mixtures, are always trinuclear derivatives. In this case, the maintainance of the cluster nuclearity may be due to the proximity of the two C≡C triple bonds in the conjugated diynes, which allows their interacion with the three metal atoms of the cluster, thus preventing a subsequent cluster fragmentation.

Compounds **3**−**6** arise from multistep reaction pathways which involve not only the substitution of the corresponding diyne for carbonyl ligands and the orthometalation of a phenyl ring of the 2,2-diphenyl-1-azavinylidene ligand[17] but also a number of insertion processes of unsaturated hydrocarbon fragments into M−H, M−C, and M−N bonds, which deserve further comments.

Compounds **4**−**6** contain two hydrogen atoms attached to carbon atoms originally involved in C≡C triple bonds. These hydrogens (which correspond to the primitive hydride of **1** plus that coming from the orthometalation) must have been transferred from the metal to the diyne carbon atoms. In the case of complex **3**, this process leads to a 1,2,3-triene (1,4-addition of hydrogen), while in the case of **5**, an enyne is formed (1,2-addition of hydrogen). Although a 1,2-addition of hydrogen has evidently taken place during the course of formation of **4** and **6**, it is not clear whether the hydrogen transfer occurs before or after the coupling of the orthometalated 1-azavinylidene ligand to the corresponding unsaturated fragment.

As far as we are aware, the synthesis of 1,2,3-trienes has never been achieved by addition of dihydrogen to conjugated diynes. However, the isolation of compound **3** confirms that the 1,4-addition of hydrogen to a conjugated diyne is indeed possible *if it is carried out*

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(16) See, for example: (a) Boag, N. M.; Sieber, W. J.; Kampe, C. E.; Knobler, C. B.; Kaesz, H. D. *J. Organomet. Chem.* **1988**, *355*, 385. (b) Kaesz, H. D.; Xue, Z.; Chen. Y. J.; Knobler, C. B.; Sieber, W. J.; Boag, N. M. *Pure Appl. Chem.* **1988**, *60*, 1245. (c) Krone-Schmidt, W.; Sieber, W. J.; Knobler, C. B.; Kaesz, H. D. *J. Organomet. Chem.* **1990**, *394*, 433. (d) Xue, Z.; Sieber, W. J.; Knobler, C. B.; Kaesz, H. D. *J. Am. Chem. Soc.* **1990**, *112*, 1825. (e) Cabeza, J. A.; Fernández-Colinas, J. M.; Llamazares, A.; Riera, V. *Organometallics* **1992**, *11*, 4355.

(17) Previous examples of orthometalation of 2,2-diphenyl-1-azavinylidene[5−7] and benzophenone imine[17a−h] ligands are known. (a) Werner, H.; Daniel, T.; Braun, T.; Nürnberg, O. *J. Organomet. Chem.* **1993**, *462*, 309. (b) Bohanna, C.; Esteruelas, M. A.; López, A. M.; Oro, L. A. *J. Organomet. Chem.* **1996**, *526*, 73. (c) Daniel, T.; Müller, M.; Werner, H. *Inorg. Chem.* **1991**, *30*, 3118. (d) Daniel, T.; Werner, H. *Z. Naturforsch. B* **1992**, *47*, 1707. (e) Daniel, T.; Knaup, M.; Dziallas, M.; Werner, H. *Chem. Ber.* **1993**, *126*, 1981. (f) Werner, H.; Daniel, T.; Braun, T.; Nürnberg, O. *J. Organomet. Chem.* **1994**, *480*, 145. (g) Daniel, T.; Werner, H. *J. Chem. Soc., Dalton Trans.* **1994**, 221. (h) Esteruelas, M. A.; Lahoz, F. J.; López, A. M.; Oñate, E.; Oro, L. A. *Organometallics* **1995**, *14*, 2496. (i) Barea, G.; Esteruelas, M. A.; Lledós. A.; López, A. M.; Oñate, E.; Tolosa J. I. *Organometallics* **1998**, *17*, 4065. (h) Esteruelas, M. A.; Gutiérrez-Puebla, E.; López, A. M.; Oñate, E.; Tolosa J. I. *Organometallics* **2000**, *19*, 275.

on a metal cluster. Therefore, the preparation of 1,2,3-trienes by catalytic hydrogenation of conjugated diynes may be feasible if an appropriate metal cluster is used as catalyst precursor.

In compounds **4** and **6**, a new C−C bond has been formed, assembling the previously metalated phenyl ring with the terminal carbon atom of the original diyne. More interesting is the formation of a new C−N bond in compound **6**. As commented above, it has not been established whether these couplings occur before or after the hydrogenation of the original diyne. Insertion reactions of alkynes into M−C bonds are frequent in carbonyl ruthenium cluster chemistry.[15] However, insertion reactions into M−N bonds of amido complexes are very rare, being restricted to highly electrophilic unsaturated molecules, such as dimethyl acetylenedicarboxylate, carbon monoxide, carbonyl sulfide, carbon dioxide, or phenyl isocyanate.[8,9] Therefore, although normal amido complexes have no tendency to insert weakly electrophilic alkynes into their M−N bonds,[3] the results described herein support the suggestion that this is not always the case for 1-azavinylidene complexes. In fact, in the reactions of compound **1** with alkynes, we have observed products that result from the insertion of the alkyne into a Ru−N bond when the alkyne used is internal and contains at least one phenyl group (Scheme 1).[7]

Attempts to transform compounds **3**−**6** into other products under thermal conditions have failed. For example, attempts to make compound **6** or a compound of structure analogous to that of **4** by thermolysis of **5** and attempts to make a compound of structure analogous to that of **6** by thermolysis of **4** were unsuccessful. These results suggest that the C−N bond-forming step is not the final step in the mechanism that leads to complex **6**. Moreover, although **5** and **6** may come from a common reaction intermediate species, the pathways that lead from that intermediate to **5** and **6** are independent. These results also indicate that in the reactions that lead to compounds **3**−**6**, the thermodynamic stability of the reaction intermediates as well as the activation energies associated with their transformations are strongly affected by the nature of the substituents of the diyne ligand.

Concluding Remarks

In the present work, we have shown that, in their reaction with complex **1**, the chemical behavior of nonconjugated diynes seems comparable to that of monoalkynes, giving binuclear alkenyl derivatives, whereas conjugated diynes help maintain the cluster integrity, leading to trinuclear products.

The isolated compounds (**2**−**6**) contain new organic ligands that can be described as substituted 1-yn-3-enyl (in **2**), 1,2,3-triene (in **3**), 1,2-dienyl (in **4**), 1-en-3-yne (in **5**), and 2-(*N*-imido)-1,2,3-allyl-1-yl (in **6**) ligands. These ligands arise from a number of interesting chemical transformations that include carbonyl substitution, diyne coordination to the cluster framework, orthometalation of a phenyl ring of the original 2,2-diphenyl-1-azavinylidene ligand, hydrogenation of the unsaturated hydrocarbon fragment, and C−C and C−N bond-formation processes, representing excellent examples of insertion of diynes into M−H, M−C, and M−N bonds of metal clusters. Among these processes, the 1,4-addition of hydrogen to a conjugated diyne (occurred in **3**) and the C−N bond-forming reaction (occurred in **6**) are remarkable. The first one has never been observed previously, and it seems that it can only happen on polynuclear metal clusters. The C−N bond-forming process, occurring by insertion of a coordinated alkyne into a M−N bond, is very rare when a weakly electrophilic alkyne is involved.[7]

Experimental Section

General Data. Solvents were dried over sodium diphenyl ketyl (THF, hydrocarbons) or CaH_2 (dichloromethane) and distilled under nitrogen prior to use. The reactions were carried out under nitrogen, using Schlenk−vacuum line techniques, and were routinely monitored by solution IR spectroscopy (carbonyl stretching region) and by spot TLC (silica gel). Compound **1** was prepared as described previously.[5] The diynes used were obtained from Aldrich and/or Farchan. IR spectra were recorded in solution on a Perkin-Elmer FT 1720-X spectrophotometer, using 0.1 mm CaF_2 cells. ^1H NMR spectra were run at room temperature with Bruker AC-200 and AC-300 instruments, using internal $SiMe_4$ as standard ($\delta = 0$ ppm). FAB-MS were obtained from the University of Santiago de Compostela Mass Spectroscopic Service; data given refer to the most abundant molecular ion isotopomer. Microanalyses were obtained from the University of Oviedo Analytical Service.

$[Ru_2(\mu\text{-}N{=}CPh_2)(\mu\text{-}\eta^2\text{-}CH_2{=}CCH_2C{\equiv}CSiMe_3)(CO)_6]$ (2). A solution of **1** (250 mg, 0.327 mmol) and 1-trimethylsilyl-1,4-pentadiyne (127 μL, 0.982 mmol) in THF (20 mL) was stirred at reflux temperature for 85 min. The color changed from orange to red. The solvent was removed under reduced pressure, the residue was extracted into hexane (ca. 2 mL), and the extract was separated by column chromatography (10 × 2 cm) on neutral alumina (activity I). Hexane washed out the free diyne. Hexane−dichloromethane (2:1) eluted a yellow band, which gave compound **2** after solvent removal (87 mg, 38%). Anal. Found: C, 47.36; H, 3.48; N, 1.98. MS (*m*/*z*): 689 [M^+]. Calcd for $C_{27}H_{23}NO_6Ru_2Si$: C, 47.16; H, 3.37; N, 2.04. fw: 687.73. IR (hexane): ν(CO) 2080 (s), 2054 (vs), 2005 (vs), 1991 (s), 1986 (s), 1955 (sh) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 7.4−6.8 (m, 10 H), 3.92 (s, 1 H of vinyl CH_2), 3.89 (d, 17.9 Hz, 1 H of methylenic CH_2), 3.28 (d, 17.9 Hz, 1 H of methylenic CH_2), 3.09 (s, 1 H of vinyl CH_2), 0.09 (s, 9 H, $SiMe_3$) ppm.

$[Ru_3\{\mu\text{-}\eta^2\text{-}N{=}CPh(C_6H_4)\}(\mu_3\text{-}\eta^4\text{-}PhOCH_2CH{=}C{=}C{=}CHCH_2OPh)(CO)_8]$ (3). A solution of **1** (150 mg, 0.196 mmol) and 1,6-diphenoxy-2,4-hexadiyne (157 mg, 0.598 mmol) in THF (20 mL) was stirred at reflux temperature for 1.5 h. The color changed from orange to brown. The solvent was partially removed under reduced pressure, and the remaining solution (ca. 2 mL) was separated by TLC on silica gel. Hexane eluted free diyne and a small amount of starting material **1**. Multiple elution with hexane−dichloromethane (2:1) afforded several bands. The second and major band, yellow, was extracted with dichloromethane to give compound **3** after crystallization from dichloromethane−hexane (48 mg, 25%). Anal. Found: C, 48.39; H, 2.41; N, 1.54. MS (*m*/*z*): 972 [M^+]. Calcd for $C_{39}H_{25}NO_{10}Ru_3$: C, 48.25; H, 2.60; N, 1.44. fw: 970.87. IR (CH_2Cl_2): ν(CO) 2092 (s), 2059 (vs), 2043 (s), 1999 (m), 1985 (w), 1964 (w) cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.01 (d, 6.0 Hz, 1 H), 7.4−6.0 (m, 18 H), 5.09 (dd, 10.0 and 6.5 Hz, 1 H of CH_2), 4.75 (dd, 10.7 and 9.5 Hz, 1 H of CH_2), 4.70 (dd, 10.7 and 9.5 Hz, 1 H of CH_2), 3.80 (dd, 10.0 and 6.5 Hz, 1 H of CH_2), 3.29 (t, 10.7 Hz, 1 H, vinyl C*H*), 2.99 (t, 10.0 Hz, 1 H, vinyl C*H*) ppm.

$[Ru_3\{\mu_3\text{-}\eta^4\text{-}N{=}CPh(C_6H_4)CH(Me)CH{=}C{=}CMe\}(CO)_9]$ (4). A solution of **1** (200 mg, 0.262 mmol) and 2,4-hexadiyne (74 mg, 0.945 mmol) in THF (20 mL) was stirred at reflux temperature for 1.5 h. The orange color slightly darkened. The

Table 2. Crystal Data and Details of Measurement for Compounds 3−6

	3	**4**	**5**	**6**
formula	$C_{39}H_{25}NO_{10}Ru_3$	$C_{28}H_{17}NO_9Ru_3$	$C_{37}H_{21}NO_8Ru_3$	$C_{38}H_{21}NO_9Ru_3{\cdot}(CH_2Cl_2)_{x\ (x<1)}$
fw	970.81	814.64	910.76	949.40
cryst syst	monoclinic	orthorhombic	monoclinic	triclinic
space group	$P2_1/a$	$P2_12_12_1$	$P2_1/c$	$P\bar{1}$
a, Å	19.668(8)	10.106(4)	15.759(9)	12.445(3)
b, Å	9.327(8)	14.643(9)	10.818(6)	13.029(4)
c, Å	20.967(9)	18.880(9)	20.824(9)	13.946(5)
α, deg	90	90	90	76.20(3)
β, deg	106.42(3)	90	107.92(6)	72.28(2)
γ, deg	90	90	90	87.23(2)
vol, Å^3	3689(4)	2794(2)	3378(3)	2091.1(11)
Z	4	4	4	2
F(000)	1912	1584	1784	930
D_{calcd}, g/cm^3	1.748	1.937	1.791	1.508
μ, mm^{-1}	1.272	1.656	1.378	1.137
cryst size, mm	0.24 × 0.22 × 0.12	0.25 × 0.22 × 0.20	0.20 × 0.16 × 0.12	0.22 × 0.16 × 0.16
temp, K	293(2)	293(2)	293(2)	223(2)
θ limits, deg	3−25	3−25	3−25	3−23
min/max h, k, l	−23/22, 0/11, 0/24	0/12, 0/17, 0/22	−18/17, 0/12, 0/18	−13/13, −13/14, 0/12
no. of reflns collected	7057	2788	5772	5885
unique reflns	6420	2758	5306	5383
reflns with $I > 2\sigma(I)$	4925	2558	3456	3124
no. of params	442	370	448	433
GOF on F^2	0.955	1.369	0.929	0.921
R1 (on F, $I > 2\sigma(I)$)	0.0657	0.0367	0.0304	0.0538
wR2 (on F^2, all data)	0.1934	0.0985	0.0928	0.1672

solvent was partially evaporated under reduced pressure (to ca. 2 mL), and the remaining solution was separated by column chromatography (10 × 2 cm) on neutral alumina (activity I). Hexane washed out the free diyne and a small amount of compound **1**. Hexane−dichloromethane (5:1) eluted a yellow band, which gave compound **4** after solvent removal (36 mg, 17%). Anal. Found: C, 41.46; H, 2.10; N, 1.64. MS (*m*/*z*): 816 [M$^+$]. Calcd for $C_{28}H_{17}NO_9Ru_3$: C, 41.28; H, 2.10; N, 1.72. fw: 814.69. IR (CH_2Cl_2): ν(CO) 2078 (s), 2054 (s), 2029 (vs), 2009 (m), 1988 (w) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.5−7.1 (m, 7 H), 6.68 (d, 7.5 Hz, 1 H), 6.64 (d, 7.5 Hz, 1 H), 5.29 (d, 8.2 Hz, 1 H, vinyl C*H*), 4.20 (dq, 8.2 and 7.7 Hz, 1 H, alkyl C*H*), 2.97 (s, 3 H, Me), 1.72 (d, 7.7 Hz, 3 H, Me) ppm.

[Ru$_3${μ-η^2-N=CPh(C$_6$H$_4$)}(μ_3-η^4-PhCH=CHC≡CPh)(CO)$_8$] (5) and [Ru$_3${μ_3-η^4-PhCHCH=C(CPh)N=CPh(C$_6$H$_4$)}(CO)$_9$] (6). A solution of **1** (500 mg, 0.654 mmol) and diphenylbutadiyne (390 mg, 1.929 mmol) in THF (50 mL) was stirred at reflux temperature for 2.5 h. The color changed from orange to brown. The solvent was partially removed under reduced pressure, and the remaining solution (ca. 3 mL) was separated by TLC on silica gel. Hexane eluted free diyne and a small amount of starting material **1** (first band). Multiple elution with hexane−dichloromethane (10:1) afforded several bands. The second band, yellow, led to compound **5** after solvent removal (148 mg, 25%). The third band, orange, led to compound **6** after solvent removal (62 mg, 10%).

Analytical and Spectroscopic Data for Compound 5. Anal. Found: C, 48.20; H, 2.57; N, 1.48. MS (*m*/*z*): 912 [M$^+$]. Calcd for $C_{37}H_{21}NO_8Ru_3$: C, 48.79; H, 2.32; N, 1.54. fw: 910.82. IR (CH_2Cl_2): ν(CO) 2078 (s), 2048 (vs), 2029 (s), 2005 (m), 1986 (sh), 1964 (w) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 8.03 (d, 7.4 Hz, 1 H), 7.80 (d, 6.9 Hz, 1 H), 7.5−6.7 (m, 15 H), 6.19 (d, 7.8 Hz, 1 H), 5.82 (d, 8.8 Hz, 1 H, vinyl C*H*), 5.56 (d, 7.8 Hz, 1 H), 5.19 (d, 8.8 Hz, 1 H, vinyl C*H*) ppm.

Analytical and Spectroscopic Data for Compound 6. Anal. Found: C, 48.82; H, 2.31; N, 1.28. MS (*m*/*z*): 940 [M$^+$]. Calcd for $C_{38}H_{21}NO_9Ru_3$: C, 48.62; H, 2.25; N, 1.49. fw: 938.83. IR (CH_2Cl_2): ν(CO) 2068 (s), 2029 (vs), 1991 (m), 1978 (w) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 8.2−6.7 (m, 17 H), 6.83 (d, 7.4 Hz, 1 H), 6.61 (d, 7.4 Hz, 1 H), 3.62 (d, 10.2 Hz, 1 H, alkyl C*H*), 3.48 (d, 10.2 Hz, 1 H, allyl C*H*) ppm.

Crystal Structure Characterization of Compounds 3, 4, 5, and 6. X-ray diffraction data were collected on a NONIUS CAD-4 diffractometer equipped with a liquid nitrogen Oxford-Cryostream device. Crystal data and details of mesurements are summarized in Table 2. SHELXL97[18a] was used for structure solution and refinement based on F^2. SCHAKAL97[18b] was used for the graphical representation of the results. Common to all compounds: Mo Kα radiation, $\lambda = 0.71069$ Å, graphite monochromator, Ψ-scan absorption correction, all non-H atoms refined anisotropically. The H atoms were added in calculated positions and refined riding on their respective C atoms. The presence of disordered dichloromethane was detected in compound **6**, corresponding to less than one solvent molecule per formula unit.

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Supporting Information Available: ORTEP pictures and tables of bond distances and angles, fractional atomic coordinates, and anisotropic thermal parameters for compounds **3**−**6**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0005506

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[18] (a) Sheldrick, G. M. *SHELXL97, Program for Crystal Structure Determination*; University of Göttingen: Göttingen, Germany, 1997. (b) Keller, E. *SCHAKAL97, Graphical Representation of Molecular Models*; University of Freiburg: Freiburg, Germany, 1997.