# Reactivity of a 1-Azavinylidene-Bridged Triruthenium Carbonyl Cluster with Alkynes. Synthesis of Binuclear Derivatives Containing New C−H or C−N and C−C Bonds Formed by Alkyne Insertion into M−H or M−N and M−C Bonds†

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Treatment of the 1-azavinylidene cluster complex $[Ru_3(\mu\text{-}H)(\mu\text{-}N{=}CPh_2)(CO)_{10}]$ (**1**) with an excess of diphenylacetylene or 1-phenyl-1-propyne, in 1,2-dichloroethane at reflux temperature, gives the metallacyclic derivatives $[Ru_2\{\mu\text{-}PhC{=}CR{-}CPh{=}CR{-}N{=}CPh(C_6H_4)\}(\mu\text{-}CO)(CO)_4]$ (**2**, R = Ph; **3**, R = Me). These reactions represent the first examples of insertion of weakly electrophilic alkynes into metal−nitrogen bonds, since compounds **2** and **3** contain novel ligands that result from the orthometalation of a phenyl group of the original 1-azavinylidene ligand, the insertion of the corresponding alkyne molecule into a ruthenium−nitrogen bond, and the insertion of a second alkyne molecule into a ruthenium−carbon bond. At lower temperature (THF under reflux), the reactions of compound **1** with the same alkynes or with 3-hexyne, acetylene, phenylacetylene, *p*-tolylacetylene, or tertbutylacetylene proceed via cluster fragmentation and insertion of the corresponding alkyne into a ruthenium−hydrogen bond, resulting in the binuclear alkenyl derivatives $[Ru_2(\mu\text{-}R^1C{=}CHR^2)(\mu\text{-}N{=}CPh_2)(CO)_6]$ (**4**, $R^1 = R^2 = Ph$; **5**, $R^1 = Ph$, $R^2 = Me$; **6**, $R^1 = R^2 = Et$; **7**, $R^1 = R^2 = H$; **8**, $R^1 = Ph$, $R^2 = H$; **9**, $R^1 = p\text{-}MeC_6H_4$, $R^2 = H$; **10a**, $R^1 = {}^t\!Bu$, $R^2 = H$; **10b**, $R^1 = H$, $R^2 = {}^t\!Bu$). Compounds **10a** and **10b** were obtained as an unseparable mixture. Unlike **4** and **5**, which react further with the corresponding alkyne at higher temperature (1,2-dichloroethane under reflux) to give the corresponding metallacyclic derivatives **2** and **3**, compounds **6**−**10** do not give any metallacyclic derivative when treated with more alkyne at higher temperatures. The higher reactivity of **4** and **5**, as compared with that of **6**−**10**, seems to be associated with the nature of their alkenyl ligands, which are derived from internal alkynes containing at least one phenyl group. The molecular structures of compounds **2**, **3**, and **9** have been determined by X-ray diffraction methods.

## Introduction

Recently, we have described a high-yield synthesis of $[Ru_3(\mu\text{-}H)(\mu\text{-}N{=}CPh_2)(CO)_{10}]$ (**1**),[1] a compound that contains a bridging amido ligand derived from benzophenone imine, which can be regarded as a 1-azavinylidene ligand.[2] The interest in the synthesis and reactivity of late-transition-metal amido complexes has grown considerably in the last years as a consequence of the relative scarcity of such compounds[3−6] and of their potential use in carbon−nitrogen bond-forming reactions.[7−9]

In the field of carbon−nitrogen bond-forming reactions, we have briefly communicated the first insertion

† Dedicated to Prof. Peter M. Maitlis on his 65th birthday.

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(1) Andreu, P. L.; Cabeza, J. A.; del Río, I.; Riera, V.; Bois, C. *Organometallics* **1996**, *15*, 3004.

(2) See, for example: (a) Daniel, T.; Knaup, W.; Dziallas, M.; Werner, H. *Chem. Ber.* **1993**, *126*, 1981. (b) Esteruelas, M. A.; Lahoz, F. J.; Oliván, M.; Oñate, E.; Oro, L. A. *Organometallics* **1994**, *13*, 3315.

(3) For reviews on late-transition-metal amido complexes, see: (a) Fryzuk, M. D.; Montgomery, C. D. *Coord. Chem. Rev.* **1989**, *95*, 1. (b) Bryndza, H. E. *Chem. Rev.* **1988**, *88*, 1163.

(4) For reviews on bi- and polynuclear ruthenium complexes containing *N*-donor ligands, see: (a) Cabeza, J. A.; Fernández-Colinas, J. M. *Coord. Chem. Rev.* **1993**, *126*, 319. (b) Bruce, M. I.; Cifuentes, M. P.; Humphrey, M. G. *Polyhedron* **1991**, *10*, 277.

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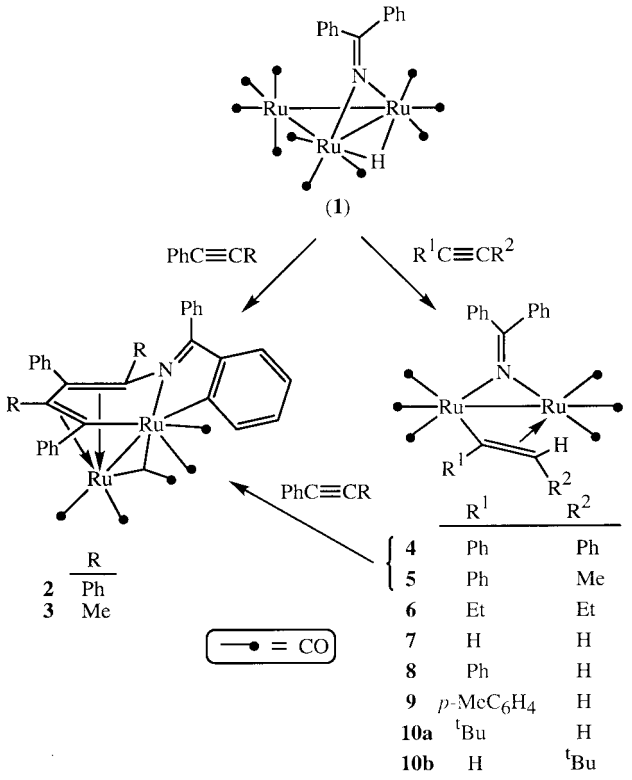
**Scheme 1**




of a nonactivated alkyne into a metal−nitrogen bond.[7] Such a process takes place in the thermal reaction of compound **1** with an excess of diphenylacetylene, which results in the formation of the binuclear metallacyclic derivative $[Ru_2\{\mu\text{-PhC=CPh-CPh=CPh-N=CPh-}(C_6H_4)\}(\mu\text{-CO})(CO)_4]$ (**2**). To date, the formation of carbon−nitrogen bonds via insertion of unsaturated molecules into the metal−nitrogen bonds of amido complexes has only been achieved with highly electrophilic substrates, such as dimethyl acetylenedicarboxylate, carbon monoxide, carbonyl sulfide, carbon dioxide, acrylonitrile, or phenyl isocyanate.[8,9] We now report full details of the synthesis and characterization of **2**, together with an insight into the mechanism of this reaction. We also report that this type of reaction can be extended to other internal alkynes containing one phenyl group, such as 1-phenyl-1-propyne, 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 metal−hydrogen bonds.

## Results and Discussion

Cluster **1** reacted with a excess of diphenylacetylene and 1-phenyl-1-propyne in 1,2-dichloroethane at reflux temperature to give, after chromatographic workups, the binuclear derivatives $[Ru_2\{\mu\text{-PhC=CR-CPh=CR-N=CPh}(C_6H_4)\}(\mu\text{-CO})(CO)_4]$ (**2**, R = Ph; **3**, R = Me) (Scheme 1). The best yields were obtained using at least 3 equiv of the alkyne. The microanalyses and mass spectra of compounds **2** and **3** were consistent with the given formulas. The similarity of their IR spectra in the carbonyl region suggested a similar arrangement of the ligands, but no further structural information could be drawn from their NMR spectra. Therefore, X-ray diffraction studies were carried out in order to determine their structures.

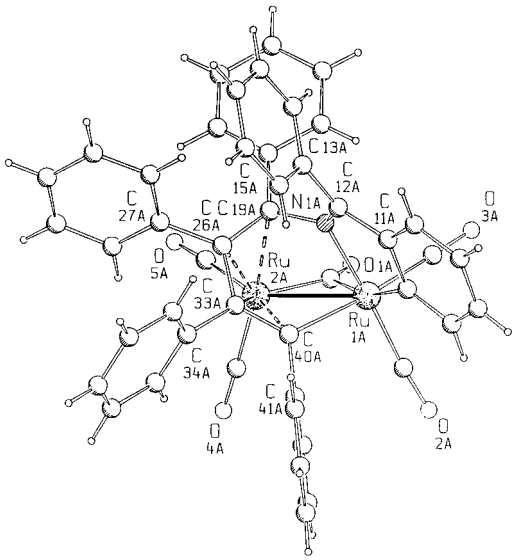



**Figure 1.** Molecular structure of compound **2**. Only one (molecule A) of the two independent molecules found in the asymmetric unit is shown.

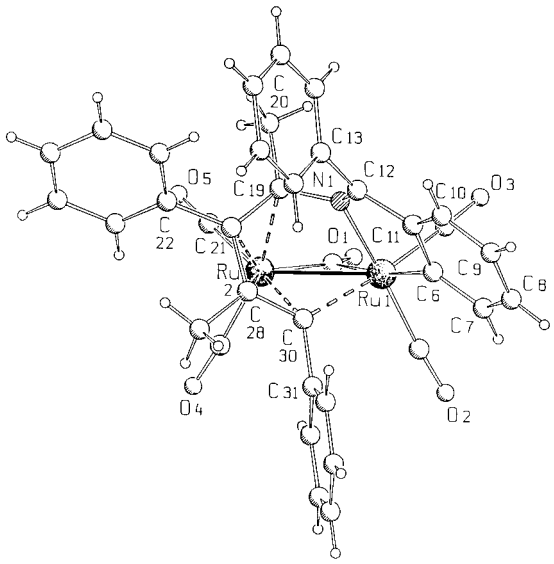



**Figure 2.** Molecular structure of compound **3**.

The molecular structures of **2** and **3** are depicted in Figures 1 and 2, respectively. The crystals of **2** contain two crystallographically independent but chemically equivalent molecules. A selection of bond distances and angles is given in Tables 1 and 2. The structures confirm the fragmentation of the starting material **1**, the insertion of two alkyne molecules (the first into a ruthenium−nitrogen bond and the second into a ruthenium−carbon bond), and the orthometalation of a phenyl ring of the original 1-azavinylidene group. In the case of **3**, the double insertion of the asymmetric alkyne 1-phenyl-1-propyne occurs regiospecifically, since only one of the four possible isomers is obtained. In each

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(8) Van der Lende, D. D.; Abboud, K. A.; Boncella, J. M. *Inorg. Chem.* **1995**, *34*, 5319.
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**Table 1. Selected Bond Lengths (Å) and Angles (deg) in Compound 2**

| | molecule A | molecule B |
|---|---|---|
| Ru(1)−Ru(2) | 2.764(1) | 2.770(1) |
| Ru(1)−N(1) | 2.049(3) | 2.049(3) |
| Ru(1)−C(1) | 2.313(5) | 2.265(4) |
| Ru(1)−C(2) | 1.897(5) | 1.902(5) |
| Ru(1)−C(3) | 1.910(6) | 1.925(5) |
| Ru(1)−C(6) | 2.066(4) | 2.076(4) |
| Ru(1)−C(40) | 2.141(5) | 2.123(4) |
| Ru(2)−C(1) | 2.001(6) | 2.012(5) |
| Ru(2)−C(4) | 1.896(5) | 1.895(5) |
| Ru(2)−C(5) | 1.898(5) | 1.890(5) |
| Ru(2)−C(19) | 2.319(4) | 2.310(4) |
| Ru(2)−C(26) | 2.218(4) | 2.226(4) |
| Ru(2)−C(33) | 2.316(5) | 2.330(4) |
| Ru(2)−C(40) | 2.153(4) | 2.254(4) |
| C(1)−O(1) | 1.143(6) | 1.151(5) |
| C(2)−O(2) | 1.133(6) | 1.125(6) |
| C(3)−O(3) | 1.140(7) | 1.123(6) |
| C(4)−O(4) | 1.133(6) | 1.127(6) |
| C(5)−O(5) | 1.123(7) | 1.142(5) |
| N(1)−C(12) | 1.297(5) | 1.295(5) |
| N(1)−C(19) | 1.449(5) | 1.451(4) |
| C(19)−C(26) | 1.420(6) | 1.435(5) |
| C(26)−C(33) | 1.463(6) | 1.456(5) |
| C(33)−C(40) | 1.421(6) | 1.417(5) |
| Ru(1)−C(1)−O(1) | 133.6(4) | 134.3(4) |
| Ru(2)−C(1)−O(1) | 146.9(5) | 145.2(4) |
| Ru(1)−N(1)−C(19) | 111.7(2) | 112.4(2) |
| N(1)−C(19)−C(26) | 114.2(4) | 113.8(3) |
| C(19)−C(26)−C(33) | 118.1(4) | 117.3(3) |
| C(26)−C(33)−C(40) | 121.0(4) | 121.9(3) |
| C(33)−C(40)−Ru(1) | 127.5(3) | 127.6(3) |

**Table 2. Selected Bond Lengths (Å) and Angles (deg) in Compound 3**

| | | | |
|---|---|---|---|
| Ru(1)−Ru(2) | 2.789(1) | Ru(2)−C(28) | 2.305(3) |
| Ru(1)−N(1) | 2.053(2) | Ru(2)−C(30) | 2.254(3) |
| Ru(1)−C(1) | 2.356(3) | C(1)−O(1) | 1.141(4) |
| Ru(1)−C(2) | 1.893(3) | C(2)−O(2) | 1.134(4) |
| Ru(1)−C(3) | 1.922(3) | C(3)−O(3) | 1.125(4) |
| Ru(1)−C(6) | 2.068(3) | C(4)−O(4) | 1.126(3) |
| Ru(1)−C(30) | 2.131(3) | C(5)−O(5) | 1.133(4) |
| Ru(2)−C(1) | 1.986(3) | N(1)−C(12) | 1.293(3) |
| Ru(2)−C(4) | 1.918(3) | N(1)−C(19) | 1.447(3) |
| Ru(2)−C(5) | 1.890(3) | C(19)−C(21) | 1.423(4) |
| Ru(2)−C(19) | 2.299(3) | C(21)−C(28) | 1.453(3) |
| Ru(2)−C(21) | 2.206(2) | C(28)−C(30) | 1.428(3) |
| Ru(1)−C(1)−O(1) | 130.1(2) | C(19)−C(21)−C(28) | 117.6(2) |
| Ru(2)−C(1)−O(1) | 150.5(3) | C(21)−C(28)−C(30) | 120.4(2) |
| Ru(1)−N(1)−C(19) | 110.4(2) | C(28)−C(30)−Ru(1) | 128.5(2) |
| N(1)−C(19)−C(21) | 115.6(2) | | |

complex, the new bridging ligand contributes 8 electrons to the electron count, being attached to Ru(1) through the nitrogen atom, the orthometalated phenyl ring, and the terminal carbon atom of the butadiene fragment (forming a cyclohexa-1-ruthena-2-aza-3,5-diene) and to Ru(2) through the four carbon atoms of the butadiene fragment. In both cases, the new butadiene fragments have the internal distances (C(26)−C(33) of **2** and C(21)−C(28) of **3**) slightly longer than the distances involving the two external carbon−carbon bonds, as found previously in other complexes containing $\eta^4$-butadiene fragments.[10,11a] There are also examples of complexes in which the central C−C bond of the $\eta^4$-butadiene fragment is shorter than the outer C−C bonds.[11] The Ru−Ru distances, 2.770(1) Å in **2** and 2.789(1) Å in **3**, are within the range found for other binuclear metal−metal-bonded ruthenium(I) complexes.[4a] The ligand shell is completed by four terminal and one semibridging carbonyl ligands. The complexes can also be described as formed by an $\eta^5$-cyclohexa-1-ruthena-2-aza-3,5-diene fragment attached to a tricarbonylruthenium(0) fragment. This ligand arrangement allows the assignment of formal oxidation states to the metal atoms: II for Ru(1) and 0 for Ru(2).

Previous examples of orthometalation of 2,2-diphenyl-1-azavinylidene[1] and benzophenone imine ligands[12] are known, but the results described above represent the first examples of insertion of weakly electrophilic alkynes into metal−nitrogen bonds. As commented in the Introduction, only highly electrophilic substrates have been previously inserted into such bonds,[8,9] as occurs in the formation of *trans*-[Ni(mes){$MeO_2CC$═C(NHPh)-$CO_2Me$}$(PMe_3)_2$] by reaction of dimethyl acetylenedicarboxylate with *trans*-[Ni(mes)(NHPh)$(PMe_3)_2$] (mes = mesityl),[8] which is the only previous example of insertion of an alkyne into a metal−nitrogen bond.

As IR monitoring of the reactions that lead to compounds **2** and **3** showed the presence of intermediate species at intermediate reaction times, these reactions were also carried out at lower temperatures in order to isolate and/or characterize reaction intermediates. Although no reactions were observed at room temperature between compound **1** and an excess of diphenylacetylene or 1-phenyl-1-propyne, the binuclear alkenyl derivatives [$Ru_2$($\mu$-PhC═CHR)($\mu$-N═$CPh_2$)$(CO)_6$] (**4**, R = Ph; **5**, R = Me) (Scheme 1) could be isolated in low yields from reactions carried out in THF at reflux temperature. The binuclear nature of **4** and **5** was confirmed by their microanalyses and mass spectra. Their IR spectra in the carbonyl region are similar to those of other binuclear hexacarbonylruthenium derivatives containing alkenyl and azavinylidene ligands (compounds **6**−**10**, see below). In the case of **4**, the alkenyl C−H fragment is clearly characterized by a singlet at $\delta$ 3.61 ppm in the $^1$H NMR spectrum and by a singlet at $\delta$ 88.5 ppm in the $^{13}C\{^1H\}$ NMR spectrum.[13] In the case of **5**, although two insertion isomers are possible, only that containing the methyl group in a geminal position to the hydrogen is obtained, since the C−H fragment is clearly characterized by a quartet ($J$ = 6.0 Hz) at $\delta$ 3.02 ppm in the $^1$H NMR spectrum and by a singlet at $\delta$ 82.5 ppm in the $^{13}C\{^1H\}$ NMR spectrum.

The participation of compounds **4** and **5** as intermediates in the synthesis of **2** and **3** from **1** and the corresponding alkynes was confirmed by checking the presence of their IR absorptions in the IR spectra of the

(10) See, for example; (a) Gemel, C.; Mereiter, K.; Schmid, R.; Kirchner, K. *Organometallics* **1997**, *16*, 2623 and references therein. (b) Meléndez, E.; Ilarraza, R.; Yap, G. P. A.; Rheingold, A. L. *J. Organomet. Chem.* **1996**, *522*, 1. (c) Chisholm, M. H.; Hoffman, D. M.; Northius, J. M.; Huffman, J. C. *Polyhedron* **1996**, *16*, 839.

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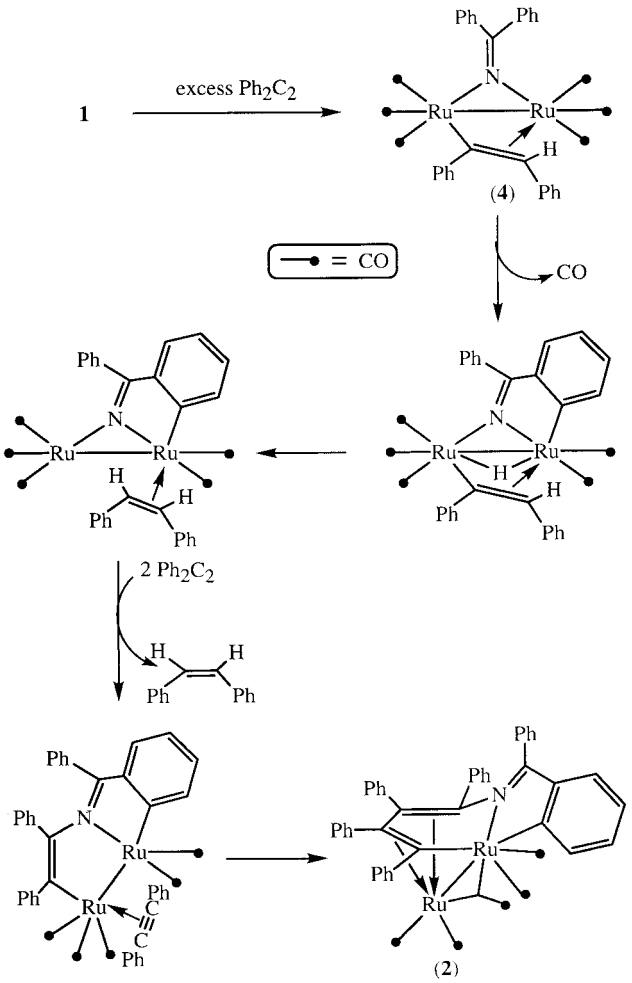
(13) For $^1$H and $^{13}C\{^1H\}$ NMR data of bridging alkenyl ligands in di-[13a] and triruthenium[13b] carbonyl complexes, see, for example: (a) Cabeza, J. A.; Fernández-Colinas, J. M.; Llamazares, A.; Riera, V. *Organometallics* **1992**, *11*, 4355. (b) Cabeza, J. A.; Fernández-Colinas, J. M.; Llamazares, A.; Riera, V.; García-Granda. S.; Van der Maelen, J. F. *Organometallics* **1994**, *13*, 4352.

**Scheme 2**




reacting solutions that finally led to **2** and **3**. Moreover, the treatement of **4** and **5** with an excess of the corresponding alkyne in 1,2-dichloroethane at reflux temperature led to the metallacyclic derivatives **2** and **3**, respectively. The presence of *cis*-stilbene and *cis*-1-phenyl-1-propene, respectively, in the reaction solutions was confirmed by gas chromatography.

All of these data shed some light on the mechanism of formation of **2** and **3** from complex **1**. As a representative example, Scheme 2 summarizes a possible reaction pathway for the synthesis of **2**. The trinuclear complex **1** would react first with the alkyne to give an unstable trinuclear alkenyl derivative which undergoes fragmentation to give the binuclear alkenyl intermediate **4**. Similar fragmentation processes have been previously observed in reactions of alkynes with ligand-bridged hydrido trinuclear clusters to give binuclear alkenyl-bridged derivatives.[13a,14] Under thermal conditions, the release of a CO ligand is accompanied by the orthometalation of a phenyl group of the diphenylazavinylidene ligand. This would lead to an unstable hydridoalkenyl derivative that would reductively eliminate *cis*-stilbene to give an unsaturated species. This species would react with the alkyne present in solution to give the metallacyclic derivative **2** via two consecutive insertion reactions, the first into a ruthenium−nitrogen bond and the second into a ruthenium−carbon bond.

To extend the results described above to other alkynes, the reactions of compound **1** with bis(trimethylsilyl)-acetylene, dimethyl acetylenedicarboxylate, 3-hexyne, and several terminal alkynes were studied. However, in none of these cases did we obtain products analogous to compounds **2** and **3**.

Complex **1** reacted with bis(trimethylsilyl)acetylene and dimethyl acetylenedicarboxylate in THF at reflux temperature to give mixtures of many products that we could not separate and identify. However, under comparable conditions, the reaction of **1** with 3-hexyne gave the binuclear alkenyl-bridged derivative $[Ru_2(\mu\text{-EtC}{=}CHEt)(\mu\text{-N}{=}CPh_2)(CO)_6]$ (**6**) in 43% yield. The structure proposed for compound **6** in Scheme 1 is based on its analytical and spectroscopic data. The binuclear formulation was indicated by its microanalysis (C, H, N) and mass spectrum, which shows the molecular ion and the successive loss of six CO ligands, while the presence of the bridging alkenyl ligand was confirmed by the $^{13}C\{^1H\}$ NMR spectrum, in which the resonances of alkenyl carbon atoms appear at $\delta$ 181.8 (*C*=CH) and 97.4 (C=*C*H) ppm.[13] The resonance of the alkenyl hydrogen atom could not be unambiguously assigned because of the coincidence of three different proton resonances (the alkenyl hydrogen and two methylene hydrogens) at very close chemical shifts (3.0−2.7 ppm).

When terminal alkynes were used, all of the reactions led to binuclear derivatives containing bridging alkenyl ligands (Scheme 1), regardless of the nature of the R group (hydrogen, alkyl, or aryl) attached to the alkyne fragment. Thus, treatment of compound **1** with acetylene (1 atm) in refluxing THF led to compound **7** (Scheme 1). The proton resonances of the alkenyl fragment of **7**, at $\delta$ 8.49 (dd, 13.9 and 9.9 Hz), 4.02 (d, 9.9 Hz), and 2.54 ppm (d, 13.9 Hz), can respectively, be assigned to protons $R^1$, $R^2$, and H (Scheme 1), confirming the bridging character of the ligand.[13]

Although the insertion of an asymmetric alkyne into a metal−hydrogen bond may take place in two different ways, and therefore may give rise to two isomeric products, the reactions of complex **1** with phenylacetylene and *p*-tolylacetylene gave only the alkenyl derivatives having the two hydrogen atoms in geminal positions, since their $^1H$ NMR spectra contain two uncoupled resonances at $\delta$ 3.88 and 2.11 ppm (**8**) and $\delta$ 3.88 and 2.08 ppm (**9**).

The structure of compound **9** was unambiguously determined by X-ray diffraction methods (Figure 3). A selection of bond distances and angles is given in Table 3. The complex consists of two $Ru(CO)_3$ fragments attached to two bridging ligands and connected to each other by a metal−metal bond, Ru(1)−Ru(2) = 2.716(1) Å. The alkenyl ligand is $\sigma$-attached to one ruthenium atom, Ru(2)−C(8) = 2.088(3) Å, and $\pi$-attached to the other metal atom, Ru(2)−C(6) = 1.959(4) Å, Ru(2)−C(8) = 2.088(3) Å. The C(7)−C(8) bond distance, 1.400(5) Å, is comparable to those found in other alkenyl-bridged complexes.[6c,13b,14] Despite the asymmetry imposed by the alkenyl ligand, the azavinylidene ligand spans the

(14) (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.

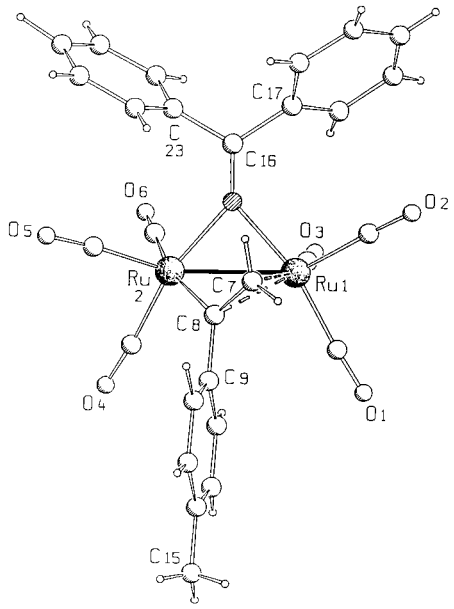



**Figure 3.** Molecular structure of compound **9**.

**Table 3. Selected Bond Lengths (Å) and Angles (deg) in Compound 9**

| | | | |
|---|---|---|---|
| Ru(1)−Ru(2) | 2.716(1) | Ru(2)−C(6) | 1.959(4) |
| Ru(1)−N(1) | 2.065(3) | Ru(2)−C(8) | 2.088(3) |
| Ru(1)−C(1) | 1.915(4) | C(1)−O(1) | 1.129(5) |
| Ru(1)−C(2) | 1.943(4) | C(2)−O(2) | 1.119(5) |
| Ru(1)−C(3) | 1.911(4) | C(3)−O(3) | 1.131(5) |
| Ru(1)−C(7) | 2.258(3) | C(4)−O(4) | 1.129(5) |
| Ru(1)−C(8) | 2.268(3) | C(5)−O(5) | 1.132(5) |
| Ru(2)−N(1) | 2.066(3) | C(6)−O(6) | 1.112(5) |
| Ru(2)−C(4) | 1.908(4) | C(7)−C(8) | 1.400(5) |
| Ru(2)−C(5) | 1.897(4) | N(1)−C(16) | 1.271(4) |
| Ru(1)−N(1)−C(16) | 139.2(3) | Ru(2)−C(8)−C(9) | 123.7(2) |
| Ru(2)−N(1)−C(16) | 138.1(2) | C(7)−C(8)−C(9) | 115.9(3) |
| Ru(1)−C(8)−C(9) | 123.0(2) | | |

Ru−Ru edge in a symmetrical manner, Ru(1)−N = 2.065(3) Å, Ru(2)−N = 2.066(3) Å.

In contrast to the results obtained from the reactions of **1** with phenylacetylene and *p*-tolylacetylene, the reaction of **1** with *tert*-butylacetylene gave a 1:2 mixture of the two isomers (**10a** and **10b**) that arise from the two possible insertion processes. These were easily distinguished by NMR spectroscopy, since **10a** shows the alkenyl protons as doublets at $\delta$ 4.18 and 1.83 ppm with a very small coupling constant ($J$ = 1.4 Hz), whereas **10b** shows the alkenyl protons as doublets at $\delta$ 8.16 and 3.48 ppm with a large coupling constant ($J$ = 13.9 Hz). We have found no reason that could unambiguously account for the different reactivity observed for *tert*-butylacetylene as compared to that found for phenylacetylene and *p*-tolylacetylene, although it might be related to the different electron-donating attributes of the alkyl and aryl fragments attached to the C≡CH moiety.

In all the reactions of compound **1** with alkynes the fate of the "third" Ru atom remains unknown. It seems clear that it is not lost as $[Ru_3(CO)_{12}]$, since this was not observed by IR or/and TLC, but we have no evidence to support the conclusion that it is lost as an alkyne−Ru(CO) complex, since although some orange-brown stuffs were always stuck on the chromatographic supports, all attempts to elute and characterize them were unsuccessful.

## Concluding Remarks

Although it is now clear that normal amido complexes have no tendency to insert alkynes into their metal−nitrogen bonds,[5] the results described herein suggest 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 resulting from the insertion of the alkyne into a Ru−N bond when the alkyne used is internal and contains at least one phenyl group. Otherwise, products resulting from the insertion of the alkyne into the Ru−H bond are formed. Although we cannot give an explanation for the different reactivities displayed by the alkynes used in this work, the findings we report here may have important implications for the synthesis of new organic compounds, since they represent the first examples of insertion of weakly electrophilic unsaturated substrates into metal−nitrogen bonds.

## Experimental Section

**General Data.** Solvents were dried over sodium diphenyl ketyl (diethyl ether, tetrahydrofuran, hydrocarbons) or $CaH_2$ (dichloromethane, 1,2-dichloroethane) 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.[1] The alkynes used were obtained from Aldrich and/or Farchan. Infrared spectra were recorded on a Perkin-Elmer FT 1720-X spectrophotometer, using 0.1-mm $CaF_2$ cells. $^1$H and $^{13}$C NMR spectra were run at room temperature with Bruker AC-200 and AC-300 instruments, using internal $SiMe_4$ as a standard ($\delta$ = 0 ppm). Fast atom bombardment (FAB) mass spectra were obtained on a Finnegan Mat-95 spectrometer, using nitrobenzyl alcohol as the matrix and cesium as the bombarding atoms. Microanalyses were obtained from the University of Oviedo Analytical Service.

**$[Ru_2\{\mu$-PhC=CPh−CPh=CPh−N=CPh$(C_6H_4)\}(\mu$-CO)$(CO)_4]$ (2).** A solution of **1** (165 mg, 0.216 mmol) and $Ph_2C_2$ (195 mg, 1.080 mmol) in 1,2-dichloroethane (20 mL) was stirred at reflux temperature for 4 h. The solvent was removed under reduced pressure, the residue was dissolved in toluene (2 mL), and this solution was separated by column chromatography (10 × 2 cm) on neutral alumina (activity I). Hexane−toluene (1:1) eluted an orange band, which gave compound **2** after solvent removal and crystallization from dichloromethane−pentane (86 mg, 58%). Anal. Calcd for $C_{46}H_{29}NO_5Ru_2$: C, 62.94; H, 3.32; N, 1.59. Found: C, 63.12; H, 3.41; N, 1.44. MS ($m/z$): 878 ($M^+$). IR (toluene): 2045 (s), 2019 (vs), 1984 (s), 1966 (m), 1869 (m) cm$^{-1}$. $^1$H NMR ($CDCl_3$): $\delta$ 7.6−6.5 (m, 27 H), 5.76 (d, 7.6 Hz, 1 H), 5.04 (d, 7.6 Hz, 1 H) ppm.

**$[Ru_2\{\mu$-PhC=CMe−CPh=CMe−N=CPh$(C_6H_4)\}(\mu$-CO)$(CO)_4]$ (3).** A solution of **1** (75 mg, 0.098 mmol) and 1-phenyl-1-propyne (0.15 mL) in 1,2-dichloroethane (15 mL) was stirred at reflux temperature for 8 h. The color changed from orange to brown. The solvent was removed under reduced pressure, the residue was dissolved in toluene (2 mL), and this solution was separated by column chromatography (10 × 2 cm) on neutral alumina (activity I). Hexane−toluene (1:1) eluted an orange band, which gave compound **3** after solvent removal and crystallization from toluene−pentane (30 mg, 41%). Anal. Calcd for $C_{36}H_{25}NO_5Ru_2$: C, 57.37; H, 3.34; N, 1.86. Found: C, 57.42; H, 3.47; N, 1.55. MS ($m/z$): 754 ($M^+$). IR (THF): 2043 (s), 2015 (vs), 1978 (s), 1962 (m), 1854 (w) cm$^{-1}$. $^1$H NMR ($CDCl_3$): $\delta$ 8.4−6.7 (m, 16 H), 6.67 (d, 8.1 Hz, 1 H), 6.41 (d, 7.8 Hz, 1 H), 5.51 (d, 7.8 Hz, 1 H), 1.84 (s, 3 H), 1.67 (s, 3 H) ppm.

**Table 4. Crystallographic and Refinement Data for Compounds 2, 3, and 9**

| | 2 | 3 | 9 |
|---|---|---|---|
| formula | $C_{46}H_{29}NO_5Ru_2$ | $C_{36}H_{25}NO_5Ru_2$ | $C_{28}H_{19}NO_6Ru_2$ |
| fw | 877.84 | 753.71 | 667.63 |
| cryst syst | triclinic | monoclinic | monoclinic |
| space group | $P\bar{1}$ | $P2_1/c$ | $C2c$ |
| $a$, Å | 13.539(4) | 17.833(8) | 22.070(6) |
| $b$, Å | 17.287(8) | 8.979(2) | 7.972(6) |
| $c$, Å | 17.918(5) | 20.426(8) | 31.688(8) |
| α, deg | 108.46(3) | 90 | 90 |
| $\beta$, deg | 98.10(2) | 110.39(3) | 104.80(2) |
| $\gamma$, deg | 101.42(3) | 90 | 90 |
| vol, Å$^3$ | 3805(2) | 3066(2) | 5390(5) |
| $Z$ | 4 | 4 | 8 |
| $F$(000) | 3520 | 1504 | 2488 |
| $D_{calcd}$, g/cm$^3$ | 3.066 | 1.633 | 1.557 |
| $\mu$, mm$^{-1}$ | 1.684 | 1.030 | 1.149 |
| radiation ($\lambda$, Å) | Mo Kα (0.710 69) | Mo Kα (0.710 69) | Mo Kα (0.710 69) |
| monochromator | graphite | graphite | graphite |
| cryst size, mm | 0.16 × 0.12 × 0.15 | 0.20 × 0.18 × 0.14 | 0.18 × 0.20 × 0.24 |
| temp | 293(2) | 293(2) | 293(2) |
| $\theta$ limits, deg | 3.0−25.0 | 3.0−25.0 | 3.0−27.0 |
| min/max $h$, $k$, $l$ | −16/15, −20/19, 0/19 | −21/19, 0/10, 0/24 | −28/27, 0/10, 0/40 |
| no. of reflns collected | 12 785 | 5921 | 6389 |
| no. of unique reflns | 12 322 | 5374 | 5850 |
| no. of reflns with $I > 2\sigma(I)$ | 10 388 | 4500 | 5373 |
| no. of parameters | 973 | 397 | 410 |
| GOF on $F^2$ | 1.146 | 1.007 | 0.867 |
| $R_1$ (on $F$, $I > 2\sigma(I)$) | 0.0372 | 0.0215 | 0.0290 |
| w$R_2$ (on $F^2$, all data) | 0.1127 | 0.0587 | 0.2389 |



**[Ru$_2$($\mu$-PhC=CHPh)($\mu$-N=CPh$_2$)(CO)$_6$] (4).** A solution of **1** (200 mg, 0.260 mmol) and diphenylacetylene (140 mg, 0.780 mmol) in THF (20 mL) was stirred at reflux temperature for 2.5 h. The color changed from orange to brown. The solvent was removed under reduced pressure, the residue was dissolved in toluene (2 mL), and this solution was separated by column chromatography (10 × 2 cm) on neutral alumina (activity I). Hexane eluted a yellow band which gave compound **4** after solvent removal (34 mg, 18%). Anal. Calcd for $C_{33}H_{21}NO_6Ru_2$: C, 54.32; H, 2.90; N, 1.92. Found: C, 54.41; H, 3.02; N, 1.81. MS ($m/z$): 730 (M$^+$). IR (THF): 2076 (m), 2052 (vs), 2000 (s), 1987 (m), 1978 (w) cm$^{-1}$. $^1$H NMR ($CD_2Cl_2$): $\delta$ 7.5−6.5 (m, 20 H), 3.61 (s, 1 H) ppm. Selected $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$): $\partial$ 202.2 (*C*O), 201.3 (br, 2 *C*O), 199.7 (*C*O), 195.9 (*C*O), 194.5 (*C*O), 181.6 (*C*=CH), 180.6 (N=*C*), 88.5 (C=*C*H) ppm. Further elution of the column with hexane−dichloromethane (1:1) gave an orange solution, which contained a small amount of compound **2** (IR identification).

**[Ru$_2$($\mu$-PhC=CHMe)($\mu$-N=CPh$_2$)(CO)$_6$] (5).** A solution of **1** (275 mg, 0.360 mmol) and 1-phenyl-1-propyne (0.1 mL) in THF (20 mL) was stirred at reflux temperature for 3.5 h. The color changed from orange to pale brown. The solvent was removed under reduced pressure, the residue was dissolved in toluene (2 mL), and this solution was separated by column chromatography (10 × 2 cm) on neutral alumina (activity I). Hexane eluted a yellow band, which gave compound **5** after solvent removal (24 mg, 10%). Anal. Calcd for $C_{28}H_{19}NO_6Ru_2$: C, 50.37; H, 2.87; N, 2.20. Found: C, 50.53; H, 2.98; N, 2.04. MS ($m/z$): 668 (M$^+$). IR (THF): 2074 (m), 2048 (vs), 1997 (s), 1978 (m), 1946 (w) cm$^{-1}$. $^1$H NMR ($CD_2Cl_2$): $\delta$ 7.5−7.0 (m, 15 H), 3.02 (q, 6.0 Hz, 1 H), 1.56 (d, 6.0 Hz, 3 H) ppm. Selected $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$): $\delta$ 201.8 (*C*O), 200.9 (*C*O), 200.1 (*C*O), 196.1 (*C*O), 195.8 (*C*O), 194.6 (*C*O), 183.6 (*C*=CH), 180.1 (N=*C*), 92.5 (C=*C*H), 22.0 (*C*H$_3$) ppm.

**[Ru$_2$($\mu$-EtC=CHEt)($\mu$-N=CPh$_2$)(CO)$_6$] (6).** A solution of **1** (100 mg, 0.130 mmol) and 3-hexyne (0.045 mL) in THF (30 mL) was stirred at reflux temperature for 5 h. The color changed from orange to brown. The solvent was removed under reduced pressure, the residue was dissolved in toluene (2 mL), and this solution was separated by column chromatography (10 × 2 cm) on neutral alumina (activity IV). Hexane eluted an orange band, which gave compound **6** after solvent removal (35 mg, 43%). Anal. Calcd for $C_{25}H_{21}NO_6Ru_2$: C, 47.39; H, 3.34; N, 2.21. Found: C, 47.43; H, 3.42; N, 2.15. MS ($m/z$): 634 (M$^+$). IR (THF): 2072 (m), 2045 (vs), 1994 (s), 1976 (m) cm$^{-1}$. $^1$H NMR ($CDCl_3$): $\delta$ 7.4−7.0 (m, 10 H), 3.0−2.7 (m, 3 H), 2.26 (m, 1 H), 1.90 (m, 1 H), 1.28 (t, 7.4 Hz, 3 H), 1.07 (7, 7.4 Hz, 3 H) ppm. Selected $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$): $\delta$ 201.9 (*C*O), 200.9 (br, 2 *C*O), 195.8 (*C*O), 194.7 (*C*O), 192.8 (br, *C*O), 181.8 (*C*=CH), 178.7 (N=*C*), 97.4 (C=*C*H), 41.2 (*C*H$_2$), 25.1 (*C*H$_2$), 18.4 (*C*H$_3$), 15.2 (*C*H$_3$) ppm.

**[Ru$_2$($\mu$-HC=CH$_2$)($\mu$-N=CPh$_2$)(CO)$_6$] (7).** Acetylene was bubbled through a refluxing solution of compound **1** (100 mg, 0.130 mmol) in THF (20 mL) for 3 h. The color changed from orange to brown. The solvent was removed under reduced pressure, the residue was dissolved in toluene (2 mL), and this solution was separated by column chromatography (15 × 2 cm) on neutral alumina (activity IV). Toluene eluted a brown-yellow band, which gave compound **7** after solvent removal (45 mg, 60%). Anal. Calcd for $C_{21}H_{13}NO_6Ru_2$: C, 43.68; H, 2.27; N, 2.43. Found: C, 43.81; H, 2.41; N, 2.36. MS ($m/z$): 578 (M$^+$). IR (THF): 2079 (m), 2052 (vs), 2003 (s), 1986 (m) cm$^{-1}$. $^1$H NMR ($CDCl_3$): $\delta$ 8.49 (dd, 13.9 and 9.9 Hz, 1 H), 7.5−7.0 (m, 10 H), 4.02 (d, 9.9 Hz, 1 H), 2.54 (d, 13.9 Hz, 1 H) ppm. Selected $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$): $\delta$ 200.5 (2 *C*O), 199.0 (*C*O), 194.6 (*C*O), 192.9 (*C*O), 192.6 (br, *C*O), 179.9 (N=*C*), 153.7 (*C*H=CH$_2$), 71.2 (CH=*C*H$_2$) ppm.

**[Ru$_2$($\mu$-PhC=CH$_2$)($\mu$-N=CPh$_2$)(CO)$_6$] (8).** A solution of complex **1** (75 mg, 0.098 mmol) and phenylacetylene (0.050 mL) in THF (20 mL) was stirred at reflux temperature for 3 h. The color changed from orange to brown. The solvent was removed under reduced pressure, and the residue was dissolved in dichloromethane (2 mL). This solution was separated by TLC (silica gel). Hexane−dichloromethane (1:1) eluted a yellow band, which gave compound **8** after solvent removal (45 mg, 70%). Anal. Calcd for $C_{27}H_{17}NO_6Ru_2$: C, 49.62; H, 2.62; N, 2.14. Found: C, 49.80; H, 2.71; N, 2.02. MS ($m/z$): 626 (M$^+$ − CO). IR (1,2-dichloroethane): 2079 (m), 2055 (vs), 2006 (s), 1994 (sh) cm$^{-1}$. $^1$H NMR ($CDCl_3$): $\delta$ 7.7−6.9 (m, 15 H), 3.88 (s, 1 H), 2.11 (s, 1 H) ppm.

**[Ru$_2$($\mu$-*p*-MeC$_6$H$_4$C=CH$_2$)($\mu$-N=CPh$_2$)(CO)$_6$] (9).** A solution of complex **1** (75 mg, 0.098 mmol) and *p*-tolylacetylene (0.050 mL) in THF (20 mL) was stirred at reflux temperature for 2 h. The color changed from orange to brown. The solvent

was removed under reduced pressure, the residue was dissolved in dichloromethane (2 mL), and this solution was separated by TLC (silica gel). Hexane eluted a yellow band, which gave compound **9** after solvent removal (50 mg, 57%). Anal. Calcd for $C_{28}H_{19}NO_6Ru_2$: C, 49.62; H, 2.62; N, 2.14. Found: C, 50.69; H, 2.97; N, 1.92. MS (*m*/*z*): 640 ($M^+ - CO$). IR (THF): 2077 (m), 2051 (vs), 2002 (s), 1988 (sh) $cm^{-1}$. $^1H$ NMR ($CDCl_3$): $\delta$ 7.7−6.7 (m, 14 H), 3.88 (s, 1 H), 2.30 (s, 3 H), 2.08 (s, 1 H) ppm. Selected $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$): $\delta$ 199.6 (*C*O), 198.9 (*C*O), 198.0 (*C*O), 193.0 (*C*O), 192.4 (*C*O), 191.1 (br, *C*O), 183.2 (N=*C*), 178.0 (*C*=$CH_2$), 65.5 (C=*C*$H_2$), 19.9 (*C*$H_3$) ppm.

**[$Ru_2$($\mu$-$^t$BuC=$CH_2$)($\mu$-N=C$Ph_2$)(CO)$_6$] (10a) and [$Ru_2$($\mu$-HC=CH$^t$Bu)($\mu$-N=C$Ph_2$)(CO)$_6$] (10b).** A solution of complex **1** (100 mg, 0.130 mmol) and *tert*-butylacetylene (0.070 mL) in THF (30 mL) was stirred at reflux temperature for 6 h. The color changed from orange to brown. The solvent was removed under reduced pressure, the residue was dissolved in toluene (2 mL), and this solution was separated by column chromatography on neutral alumina (activity IV). Hexane eluted a brown-yellow band, which gave a brown solid after solvent removal (30 mg, 36%). This solid consisted in a 1:2 mixture of the isomers **10a** and **10b** ($^1H$ NMR integration). Anal. Calcd for $C_{25}H_{21}NO_6Ru_2$: C, 47.39; H, 3.34; N, 2.21. Found: C, 47.58; H, 3.71; N, 2.03. IR (THF): 2076 (m), 2068 (sh), 2047 (vs), 2018 (sh), 1999 (s), 1979 (sh) $cm^{-1}$. Selected $^1H$ NMR data ($CDCl_3$) for isomer **10a**: $\delta$ 4.18 (d, 1.4 Hz, 1 H), 1.83 (d, 1.4 Hz, 1 H), 1.32 (s, 9 H) ppm. Selected $^1H$ NMR data ($CDCl_3$) for isomer **10b**: $\delta$ 8.16 (d, 13.9 Hz, 1 H), 3.48 (d, 13.9 Hz, 1 H), 1.06 (s, 9 H) ppm.

**Crystal Structure Characterization of Compounds 2, 3, and 9.** The X-ray diffraction data collections were carried out on a Nonius CAD-4 diffractometer. Crystal data and details of measurement for compounds **2**, **3**, and **9** are summarized in Table 4. SHELX86[15] and SHELXL92[16] were used for structure solution and refinement on $F^2$. Two independent molecules were found in the asymmetric unit of compound **2**. SCHAKAL92[17] was used for the graphical representation of the results.

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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 **2**, **3**, and **9** (31 pages). Ordering information is given on any current masthead page.

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