Reactivity of a Triruthenium Cluster Complex Containing a $\mu_3\eta^3(C,N_2)$ Ligand Derived from 2-Amino-7,8-benzoquinoline. Coupling of This Ligand with C$_3$ Fragments and Characterization of $\mu_3$-Vinylidene and $\mu$-Stannylene Derivatives

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Received March 19, 2004

The reactivity of the triruthenium cluster complex $[\text{Ru}_3(\mu_3\eta^3(C,N_2)-\text{Habq})(\text{CO})_9]$ (1; H$_2$abqH = 2-amino-7,8-benzoquinoline) with alkynes, tetrafluoroboric acid, dihydrogen, and tertiary silanes and stannanes is reported. The compounds $[\text{Ru}_3(\mu_3\eta^3(C,N_2)-\text{Habq})(\mu_3\eta^2\text{-CCHR})(\text{CO})_9]$ (R = Ph (2), p-tolyl (3), Bu (4), CMe$_2$OH (5), CPh$_2$OH (6), c-C$_7$H$_8$OH (7)), which contain a face-capping vinylidene ligand, have been prepared by treating complex 1 with the corresponding terminal alkynes. However, the reaction of complex 1 with propargyl alcohol leads to $[\text{Ru}_3(\mu_3\eta^3(C,N_2)-\text{HabqCHCHCH}_2)(\mu_3\text{-CO})(\text{CO})_9]$ (8), which bears a new ligand that contains an allylic C$_3$ fragment attached to the C$_{10}$ carbon atom of the original Habq ligand. Two compounds have been isolated from the reaction of complex 1 with 1-(trimethylsilyl)-penta-1,4-diyne, $[\text{Ru}_3(\mu_3\eta^3(C,N_2)-\text{Habq})(\mu_3\eta^2\text{-CCHCH}_2\text{CCSiMe}_3)(\text{CO})_9]$ (9) and $[\text{Ru}_3(\mu_3\eta^5\text{-}(C,N_2)_2\text{-HabqCHCHCH}_2)(\mu_3\text{-CO})(\text{CO})_9]$ (10). While compound 9 is a vinylidene derivative, analogous to 2–7, compound 10 contains an allylated Habq ligand analogous to 8. The reactions of 1 with internal alkynes lead to mixtures of $[\text{Ru}_3(\mu_3\eta^3(C,N_2)-\text{Habq})(\mu_3\text{-CO})(\text{CO})_9][\text{BF}_4]$ (12). Free H$_2$abqH and $[\text{Ru}_4(\mu_3\text{-H})(\text{CO})_9]$ are formed when complex 1 is treated with hydrogen (1 atm, 20 °C). At room temperature, complex 1 does not react with tertiary silanes but reacts with tertiary stannanes to give $[\text{Ru}_3(\mu_3\text{-H})(\mu_3\eta^3\text{-Habq-C$_7$H$_8$OH})]$ (R = Ph (13), Bu (14)). These compounds slowly release HR at room temperature to render the derivatives $[\text{Ru}_3(\mu_3\eta^3(C,N,N)_2\text{-Habq-C$_7$H$_8$O})]$ (R = Ph (15), Bu (16)), which contain a bridging stannylene ligand. All this reactivity is quite different from that known for neutral hydrido triruthenium carbonyl clusters containing face-capping N-heterocyclic ligands.

Introduction

The synthesis and reactivity of carbonylmetal clusters derived from 2-aminopyridines have been thoroughly studied. Most of these clusters are trinuclear and contain a face-capping HapyR ligand (H$_2$apyR = generic 2-aminopyridine) that results from the coordination of the pyridine N atom and the activation of an N–H bond to give a bridging amido fragment and a hydride ligand, e.g. $[\text{Ru}_3(\mu_3\eta^3(N_2)-\text{HapyR})(\text{CO})_9]$ (Chart 1). Some of these complexes have been recognized as catalytic precursors for the hydrogenation, dimerization, polymerization, and hydroformylation of selected alkynes.

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2-aminopyridines, because the coordination of the quinolinic N atom triggers the cyclometalation of the benzene ring, favoring the activation of the C10-H bond. Thus, the reactions of 2-amino-7,8-benzoquinoline with \([\text{Ru}(\text{CO})_2(\text{MeCN})_2]\) and \([\text{Ru}(\text{CO})_2]\) lead to the cyclometalated derivatives \([\text{Ru}(\mu_3-\text{η}^3(\text{C}_2\text{H}_4))\text{Habq})(\text{CO})_3]\) (1) and \([\text{Ru}(\mu_3-\text{η}^3(\text{C}_2\text{H}_4))\text{Habq})(\text{CO})_3]\), respectively (Chart 1), which represent the only polynuclear derivatives of this ligand reported to date.\(^7\) The cyclometalation of 2-amino-7,8-benzoquinoline has already been observed in a few iridium complexes, which are the only mononuclear transition-metal derivatives of this ligand known to date.\(^8\)

We now report our studies on the reactivity of complex 1. These studies were prompted by the fact that complex 1 contains no hydride ligands and, therefore, its reactivity was expected to be very different from that of triruthenium monohydrido HapyR derivatives.\(^1,2\)

**Results and Discussion**

**Reactions with Terminal Alkynes.** Complex 1 reacted with phenylacetylene, p-tolylacetylene, 1-hexyne, 2-methylbut-3-yn-2-ol, 1,1-diphenylprop-2-yn-1-ol, and 1-ethylcyclopentanol in 1,2-dichloroethane at reflux temperature to give the vinylidene derivatives \([\text{Ru}(\mu_3-\text{η}^3(\text{C}_2\text{H}_4))\text{Habq})(\text{CO})_3]\) (R = Ph (2), p-tolyl (3), Bu (4), CMe2OH (5), CPh2OH (6), c-CsH5OH (7)) (Scheme 1).

The trinuclear nature of these complexes was suggested by their microanalysis and mass spectra. Their IR spectra in the carbonyl region are very similar, indicating that they have a similar structure. At low temperature (−80 °C), the \(^{13}\)C NMR spectrum of a \(^{13}\)CO-enriched sample of compound 5 at \(−80 °C\) (top) and \(20 °C\) (bottom).

**Table 1. \(^{13}\)C and \(^1\)H NMR Spectroscopic Data for the Vinylidene Fragment of Compounds 2−7**

<table>
<thead>
<tr>
<th>compd</th>
<th>(\delta_c (\text{C}))</th>
<th>(\delta_c (\text{H}))</th>
<th>(\delta_c (\text{H}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>290.7</td>
<td>98.7</td>
<td>6.66</td>
</tr>
<tr>
<td>3</td>
<td>288.9</td>
<td>99.1</td>
<td>6.59</td>
</tr>
<tr>
<td>4</td>
<td>286.8</td>
<td>97.3</td>
<td>5.88</td>
</tr>
<tr>
<td>5</td>
<td>a</td>
<td>a</td>
<td>6.07</td>
</tr>
<tr>
<td>6</td>
<td>294.5</td>
<td>100.9</td>
<td>a</td>
</tr>
<tr>
<td>7</td>
<td>a</td>
<td>99.7</td>
<td>6.84</td>
</tr>
</tbody>
</table>

\(^{1}\) Unobserved or overlapped with other resonances.

![Figure 1](image)

**Figure 1.** \(^{13}\)C NMR spectra of a \(^{13}\)CO-enriched sample of compound 5 at \(−80 °C\) (top) and \(20 °C\) (bottom).

With the Habq ligand are concerned, the \(^{13}\)C-\(^1\)H and \(^1\)H NMR spectra of all these complexes are very similar.

The presence of the vinylidene ligand in 2–7 was indicated by their \(^{13}\)C-\(^1\)H and \(^1\)H NMR spectra (Table 1). The narrow ranges in which the \(^{13}\)C and \(^1\)H resonances of the atoms of the vinylidene fragment are observed also indicate that these compounds have the same structure. Other cluster complexes containing \(\mu_3\)-vinylidene ligands display the \(^{13}\)C and \(^1\)H resonances of their vinylidene fragments in wider \(\delta\) ranges: 305−200 for \(\text{C}_3\), 150−65 for \(\text{C}_4\), and 6.5−4.0 for \(\text{C}_4\) \(^{9,10}\).

Despite all these spectroscopic data, the precise attachment of the vinylidene ligands to these clusters could only be determined by X-ray diffraction methods. Figure 2 shows the molecular structure of molecule A, one of the two crystallographically independent, but...
Figure 2. Molecular structure of one of the two crystallographically independent molecules of compound 5 found in the unit cell. Thermal ellipsoids are drawn at the 40% probability level. Both C and O atoms of the same carbonyl ligand bear the same number.

| Table 2. Selected Interatomic Distances (Å) in Compounds 5, 8, 11, and 16 |
|-----------------|-------|-------|-------|
|                  | 5 (molecule A) | 8 | 11 | 16 |
| Ru(1)–Ru(2)     | 2.672(6)      | 2.6698(4) | 2.770(2) | 2.691(2) |
| Ru(1)–Ru(3)     | 3.936(7)      | 2.7571(4) | 2.743(2) | 2.839(2) |
| Ru(2)–Ru(3)     | 2.820(4)      | 2.9210(4) | 4.684(2) | 2.884(2) |
| Ru(1)–Sn(1)     | 2.686(4)      | 2.729(2)  | 2.637(2) |
| Ru(3)–Sn(1)     | 2.688(4)      | 2.717(2)  | 2.637(2) |
| Ru(1)–N(1)      | 2.143(5)      | 2.16(1)   | 1.218(1) |
| Ru(1)–N(3)      | 2.140(5)      | 2.16(1)   | 1.218(1) |
| Ru(2)–N(2)      | 2.140(5)      | 2.16(1)   | 1.218(1) |
| Ru(2)–N(3)      | 2.140(5)      | 2.16(1)   | 1.218(1) |
| Ru(3)–N(1)      | 2.116(5)      | 2.186(3)  | 2.12(1)  |
| Ru(3)–N(4)      | 2.026(6)      | 1.24(1)   | 2.10(1)  |
| Ru(2)–C(22)     | 2.166(6)      | 2.07(1)   |
| Ru(2)–C(24)     | 2.093(6)      | 2.239(4)  | 2.13(2)  |
| Ru(3)–C(22)     | 2.249(5)      | 2.170(4)  | 2.13(2)  |
| Ru(3)–C(23)     | 2.359(5)      | 2.513(4)  |
| Ru(3)–C(33)     | 1.493(5)      | 2.07(1)   |
| C(11)–C(22)     | 1.382(8)      | 1.440(6)  |
| C(22)–C(23)     | 1.530(8)      | 1.413(6)  |

chemically equivalent, molecules found in the unit cell of compound 5. A selection of interatomic distances is given in Table 2. The cluster consists of a triangular array of ruthenium atoms with only two metal–metal bonds, since the metals of the longest edge are separated by 3.936(7) Å, the Ru(1A)–Ru(2A)–Ru(3A) angle being 91.54(2)°. The Habq ligand maintains the same coordination mode as that found in 7, with the amido NH fragment spanning a closed edge of the metal triangle, Ru(1A)–Ru(2A). However, in 1, the plane defined by the atoms of the Habq ligand is perpendicular to the Ru3 plane, whereas the Habq ligand of 5 is leaning toward the open Ru–Ru edge, the angle between the Habq and Ru3 planes being 54.56(6)°. The vinylidene ligand caps the other face of the metal triangle, spanning the same metal triangle edge as the amido fragment of the Habq ligand, Ru(1A) and Ru(2A), through its terminal carbon atom C(22A), and also being attached in a α-mode to Ru(3A) through the atoms of its CC double bond, C(22A) and C(23A). The remaining substituents of C(23A) are a hydrogen atom and a CMe2OH group. The cluster shell is completed with eight terminal CO groups. Therefore, the electron count for this compound is 50, as expected for a trinuclear cluster with only two metal–metal bonds.

The type of coordination found for the vinylidene ligand of 5 has been previously observed for other metal clusters containing μ3-vinylidene ligands. However, compounds 2–7 are unique in the sense that they are open clusters, since in all the previously known ruthenium carbonyl clusters containing μ3-vinylidene ligands, such ligands cap closed metal triangles.

An additional novel feature of compounds 2–7 is that they are formed directly from terminal alkynes. Although unusual, this has been previously observed for cluster complexes of other metals and for some mononuclear derivatives. The ruthenium carbonyl clusters containing μ3-vinylidene ligands known so far are formed by reactions of previously coordinated ligands.

The mechanism of isomerization of α-bound terminal alkynes to vinylidene ligands in mononuclear complexes has been extensively studied and discussed. Although, to our knowledge, mechanistic studies of this kind with trinuclear clusters have not yet been reported, we think reasonable to propose that, in the synthesis of compounds 2–7, such a transformation should take place via a direct 1,2-hydrogen shift from the C(1) to the C(3) of the coordinated alkyne rather than through a hydride alkynyl intermediate. This is supported by the fact that a number of hydride alkynyl triruthenium clusters of the type [Ru3(μ-H)(μ3-η2-CCR)(CO)3] are known and their isomerization into vinylidene derivatives has not been observed.

The dehydration of 3-hydroxyvinylidenes frequently leads to allenylidene or 3-vinylvinylidene derivatives. However, all attempts to dehydrate compounds 5–7, either by treatment with strong acids or with activated silica and alumina, were unsuccessful.

An unprecedented reaction took place between complex 1 and propargyl alcohol. Under conditions similar to those used for the synthesis of compounds 2–7, this reaction led to [Ru3(μ-η2-C5H3N2)-HabqCHCHCH2]- (μ-CO)3(CO)3] 8 (Scheme 2).

The structure of compound 8 was determined by X-ray diffraction methods (Figure 3). A selection of structural

References:
parameters is given in Table 2. The cluster consists of a
closed triangular array of ruthenium atoms with the
metal atoms bridged by a ligand that results from the
coupling of a CHCHCH₂ fragment to the C₁₀ carbon
atom, C(11) in Figure 3, of the original Habq ligand.
This allyl fragment spans the longest edge of the metal
triangle, Ru(2)–Ru(3), through its three carbon atoms
in such a way that its coordination is best described as
being Ï–bonded to Ru(2) through its terminal carbon
atom C(24) and Ï–bonded to Ru(3) through C(22) and
C(23). This latter interaction is very asymmetric, since
the Ru(3)–C(22) distance is ca. 0.34 Å shorter than that
of Ru(3)–C(23). The rigidity, planarity, and, and μ₃-η²(Ν₂)
coordination of the Habq fragment to the metal triangle
forces the Ru(3)–C(22) and Ru(3)–C(23) distances to
be shorter and longer, respectively, than those of a
“normal” C–C fragment Ï–bonded to a Ru atom.¹⁵ On
the other hand, this attachment of the allyl and Habq
fragments also forces the Habq fragment to deviate from
perpendicularity with the metal triangle, the dihedral
angle between the two planes being 81.20(3)°. Two
bridging CO ligands span the Ru(1)–Ru(2) and Ru(1)–
Ru(3) edges. The cluster shell is completed with six
terminal CO ligands.

The spectroscopic data of compound 8 indicate
that its solid-state structure is maintained in solution. Thus,
its ¹³C{¹H} DEPT NMR spectra clearly show the presence
of the Habq (7 CH and 6 C) and allyl (2 CH at 67.2
and 46.1 ppm and 1 CH at 23.6 ppm) fragments of the
novel HabqCHCHCH₂ ligand accompanied by six terminal
and two bridging CO ligands. In contrast with the
¹³C{¹H} NMR spectra of compounds 1–7, the spectrum of 8
does not contain any signal in the range
158–165 ppm but shows a resonance at 127.4 ppm
which is missing in the spectra of 1–7. Therefore, these
resonances can now be assigned to the C₁₀ carbon atom
of the Habq fragment, which in 1–7 is attached to
a ruthenium atom, whereas in 8 it is attached to a
carbon atom. The ¹H NMR spectrum of 8 is shown in Figure 4.
In addition to the resonances of the Habq fragment, δ
8.4–6.2 (7 CH) and 2.71 (NH), the spectrum contains

![Figure 3](image)

**Figure 3.** Molecular structure of compound 8. Thermal ellipsoids are drawn at the 50% probability level. Both C
and O atoms of the same carbonyl ligand bear the same
number.

![Figure 4](image)

**Figure 4.** ¹H NMR spectrum of compound 8 (CD₂Cl₂, 20
°C, 300 MHz). The peaks marked with an asterisk are due to
residual water and silicone grease.

four resonances associated with the allyl protons, the
assignment of which (Figure 4) was confirmed by
selective proton-decoupled ¹H NMR experiments and by
comparing the observed coupling constants with those
of other allyl derivatives.¹⁶ It is interesting to note the
unusually low chemical shift of H₀, –1.04 ppm.

An intriguing feature of the reaction that leads to
complex 8 is that propargyl alcohol loses its oxygen atom
(only this atom). As noted above, dehydration processes
have often been observed in the organometallic chem-
istry of 3-hydroxy alkynes, including propargyl alcohol,¹⁴
but the loss of a single oxygen atom from these reagents,
as occurs during the formation of 8, is very rare.¹⁷

The reaction of complex 1 with 1-(trimethylsilyl)-
penta-1,4-diynne led to a mixture of compounds from
which the two major products [Ru₃(μ₃-η¹(C,N=C)-Habq)-
(μ₃-η²-CCHCH₂C≡CSiMe₃)(CO)₆] (9) and [Ru₃(μ₃-η³-
(C₃N₂)HabqCHCHCH≡CSiMe₃)(μ-CO)₂(CO)₆] (10)
were separated by chromatographic methods (Scheme 3).
Their IR and NMR spectroscopic data clearly indicate
that 9 is a μ₃-η²-vinylidene derivative analogous to
compounds 2–7, while 10 is structurally related to
complex 8. The chemical shift of the C₁₀ carbon atom of

¹¹ It has been reported that the cluster [Ru₂(μ-H)(μ₃-η¹(C≡
CCHCH(CH)CO)₆] is formed from [Ru₃(CO)₁₂] and Me₃SiC≡CCH₂OH.¹¹n

¹¹ For examples of triruthenium clusters containing ¹⁻allyl-type
fractions, see: (a) Bruce, M. I.; Zaitseva, N. N.; Skelton, B. W.; White,
D.; Valle, M. Inorg. Chem. 1976, 15, 396. (h) Gervasio, G.; Marabello,
the Habq fragment of complex 10, 128.8 ppm, suggests that this atom is not attached to ruthenium but to an organic fragment, as occurs in 8. The coupling constants between the three protons of the allyl fragment of 10 and the fact that the proton resonance at negative chemical shift of complex 8 is missing in the $^1$H NMR spectrum of 10 indicate that the C≡CSiMe$_3$ group of 10 is in the same position as H$_2$ in 8 (Figure 4): i.e. in an anti arrangement with respect to the central CH proton of the allyl fragment.

Compounds 8 and 10 are very interesting, not only because they represent the first C-functionalization of 2-amino-7,8-benzoquinoline with organic fragments but also because their allyl fragments span only two metal atoms. Although many triruthenium clusters containing allyl-type $\eta^3$-C$_3$ ligands are known, these clusters have such ligands capping the three metal atoms.$^{16}$

Scheme 4 shows a mechanistic proposal for the formation of compounds 8 and 10 from complex 1 and the corresponding allykene reagent. Although the initial alkyn coordination to complex 1 might not take place on the Ru atom attached to the C-metalated fragment, the allykene might end in that position after a fluxional process (intermediate A). This would be followed by a migratory insertion of the alkyn into the Ru-C$^{10}$ bond to give the alkynyl intermediate (B). A subsequent rearrangement of this terminal alkynyl group to a bridging position (C) would promote a C-H activation process on the methylene group that would lead to a hydride intermediate (D). The migration of this hydride from the metal to the central carbon atom of the C$_3$ group would lead to E. This species corresponds to complex 10 when R = C≡CSiMe$_3$, but it has not been detected for R = OH. To explain the absence of the propargyl oxygen atom in complex 8, we propose that the OH group of E would attack a carbonyl ligand to give an unstable hydroxy carbonyl species that would release CO$_2$ to give a hydride intermediate (F). A subsequent migration of the hydride to the terminal carbon atom of the C$_3$ fragment would end in complex 8.

This reaction pathway is reasonable, since it is based on common steps in organometallic chemistry (except for the transfer of the alcoholic OH group to the carbonyl ligand$^{17}$) and explains the formation of the observed products. However, the precise order by which the steps would take place does not necessarily have to be that proposed in Scheme 4. For example, the coupling of the Habq C$^{10}$ carbon atom with the C$_3$ fragment may occur before or after the step involving the C-H bond activation of the methylene group. The isolation of complex 10 suggests that, during the formation of 8, the loss of the oxygen atom would take place after the C=C bond forming and C-H bond activation steps.

The different reactivity observed for propargyl alcohol as compared with that found for the other propargylic alcohols used in this work (2-methyl-3-butyln-2-ol, 1,1-diphenyl-2-propyn-1-ol, and 1-ethynylcyclopentanol) is no doubt due to the fact that propargyl alcohol has a CH$_2$ group next to the terminal triple bond. However, we do not know the answers to questions such as (a) why 1-hexyne gives the vinylidene 4 instead of an allyl derivative analogous to 8 or (b) why propargyl alcohol does not give a vinylidene derivative.

Reactions with Internal Alkynes. The reactions of complex 1 with 3-hexyne and diphenylacetylene led to complex mixtures of products. In both cases, the major product was [Ru$_3$(µ-$\eta^3$(C$_3$N$_2$)-Habq)$_2$(µ-CO)(CO)$_6$] (11), a complex which contains two metalated Habq ligands and no fragments derived from the alkyne. The known complex [Ru$_3$(µ-$\eta^3$-EtC=CEt-CEt)(µ-CO)$_2$-(CO)$_6$]$^{18}$ was also isolated from the reaction of 1 with 3-hexyne (Scheme 5).

The structure of complex 11 was determined by X-ray diffraction methods (Figure 5). A selection of interatomic distances is collected in Table 2. The custer is an open 50-electron trinuclear species with a very long Ru–Ru edge; Ru(2)–Ru(3) = 4.684(2) Å. Two nearly parallel Habq ligands are attached to the three metal atoms in such a way that each Habq ligand spans a metal–metal bonded Ru–Ru edge through the N atom of the amido fragment and chelates the other Ru atom through both the quinoline N atom and the C atom of the cyclometalated ring. A CO ligand asymmetrically spans the Ru(1)–Ru(2) edge, the Ru(1)–C(35) and Ru(2)–C(35) distances being 1.93(2) and 2.36(2) Å, respectively. The cluster shell is completed with six terminal CO ligands (a pair attached to each Ru atom). Overall, this structure is reminiscent of that of the dihydride derivative [Ru$_3$(µ-H)$_2$(µ-$\eta^3$(C$_3$N$_2$)-Habq)$_2$(CO)$_6$], which contains both Habq ligands in a similar arrangement.$^7$ However, while
this latter complex has C2 symmetry, complex 11 is asymmetric due to the presence of a unique bridging CO ligand.

In solution, the IR spectrum of 11 clearly shows the absorption of the bridging CO ligand, at 1883 cm⁻¹, accompanying the bands due to the terminal carboxyls, in the range 2055–1940 cm⁻¹. However, its ¹H and DEPT ¹³C NMR spectra display only the resonances of one metalated Habq ligand. The latter spectrum also shows three peaks in the carbonyl region. These data indicate that, in solution, the CO ligands are involved in a fluxional process that confers the complex an asymmetric due to the presence of a unique bridging CO ligand.

The activation energy of such a fluxional process should be very low, because ¹H and ¹³C NMR spectra run at −80 °C are comparable with the aforementioned spectra taken at room temperature.

The way by which complex 11 is formed from 1 and internal alkynes is obscure. The isolation of [Ru₃(μ₃-η⁴-CEt)][BF₄] from the mixture of products formed using 3-hexyne as reagent suggests that a rearrangement of the type 2Ru₂AB → Ru₂AA + Ru₂BB (A = Habq; B = alkyn) may take place after 1 coordinates the alkyn. However, the reactions also give quite a few minor byproducts that contain no fragments derived from Habq and that remain uncharacterized.

**Protonation and Hydrogenation Reactions.**

Treatment of a dichloromethane solution of complex 1 with a dichetyl ether solution of tetrafluoroboric acid at room temperature led to the quantitative formation of the hydrido derivative [Ru₃(μ-H)(μ-η⁴-C₃N₄)-Habq][CO]₁₂[BF₄] (12). The cationic character of this complex was suggested by its IR spectrum, which shows the stretching νCO absorptions at wavenumbers higher than those of complex 1. The hydridic hydrogen atom resonates at −13.18 ppm in its ¹H NMR spectrum. The symmetric structure shown in Scheme 6 for this complex, in which the amido fragment and the hydride ligand span the same Ru–Ru edge, is supported by the ¹³C{¹H} NMR spectrum, which shows only five signals assignable to the CO ligands, with intensities 2:1:2:2:2, as expected for a nonacarbonyl derivative of C, symmetry.

Complex 1 was quantitatively converted into a mixture of H₂abqH and [Ru₄(μ-H)(CO)₁₂] when its solutions were treated with dihydrogen (1 atm) at room temperature (Scheme 7). This result was surprising, because the addition of dihydrogen to a coordinatively saturated 48-electron trinuclear carbonyl cluster is expected to have a high activation energy. In fact, to our knowledge, such reactions have never been reported to take place at room temperature. The instability of the putative dihydrido intermediate (it has not been detected) has to be associated with the fact that it should have a hydride ligand attached to the same Ru atom as the metalated benzo ring. This is required for a reductive elimination process that would lead to a non-C-metalated intermediate that, for steric reasons (there is no room for the new C–H fragment if the intermediate maintains both nitrogen atoms coordinated to the metal triangle), is readily transformed under dihydrogen into the mixture of H₂abqH and [Ru₄(μ-H)₃(CO)₁₂].

These arguments are consistent with the room-temperature stability observed for complex 12, in which the hydride ligand and the metalated benzo group are attached to different Ru atoms.

**Reactions with Tertiary Silanes and Stannanes.**

No reaction was observed between tertiary silanes (triaryl silane, triethyl silane) and complex 1 at room temperature. Complex mixtures of unidentified products were formed at higher temperature (refluxing 1,2-dichloroethane). However, triphenylstannane and tributylstannane did react with complex 1 at room temperature. The instability of the putative stannylhydrido derivatives [Ru₃(μ-H)(μ-η⁴-C₃N₄)-Habq][SnR₃][CO]₁₂ (R = Ph (13), Bu (14)). Both compounds were isolated as pure products but they slowly evolved at room temperature in solution (8–10 h) to give the stannylene derivatives [Ru₃(μ-H)(μ-η⁴-C₃N₄)-Habq][μ-SnR₃][μ-CO][CO]₁₂ (R = Ph (15), Bu (16)). This latter transformation occurred readily (5–10 min) in THF at reflux temperature (Scheme 8).

The IR spectra of compounds 13 and 14 suggest that they are isostructural (similar νCO regions). The hydride ligands of 13 and 14 resonate at −12.74 and −12.82 ppm, respectively, in their ¹H NMR spectra. Both signals show satellites (J₁¹¹Sn-⁻H ≈ J₁²¹Sn-⁻H = 40.8 and 36.0 Hz, respectively) which indicate that the stannyl and the hydride ligands are in an approximately dis
edge is symmetrically spanned by the tin atom of a dibutylstannylene fragment in such a way that the tin atom is approximately coplanar with the metal triangle. The coordination of the tin atom is approximately tetrahedral. The cluster shell is completed with one bridging and seven terminal CO groups.

The oxidative substitution of tertiary stannanes for carbonyl groups in triruthenium clusters has been reported on a few occasions.\(^{18,19}\) However, it is interesting to note that none of the previously reported reactions take place at room temperature. The mild conditions under which the reactions of complex 1 with tertiary stannanes take place have to be related to the presence of the Ru–C bond in the cluster, because analogous reactions with triruthenium carbonyl clusters derived from nonmetalated 2-aminopyridines require higher temperatures.\(^{18a}\)

The metal cluster mediated transformation of tertiary stannanes into bridging stannylene derivatives, although rare, has been reported for polynuclear Ru\(_6\),\(^{20}\) Ru\(_6\),\(^{21}\) and PtRu\(_5\)\(^{21}\) clusters. The mechanism of this transformation remains unknown, although the oxidative addition of a Sn–C bond to a metal atom seems to be involved in the process. The diruthenium derivative [Ru\(_2\)(μ-SnMe\(_2\))\(_2\)(SnMe\(_3\))(CO)\(_6\)] has been prepared from [Ru\(_3\)(CO)\(_{12}\)] and HSnMe\(_3\).\(^{19a,22}\) A few triruthenium compounds containing SnR\(_2\) bridging ligands are also known,\(^{23}\) but such compounds do not arise from the reactions of tertiary stannanes with the cluster precursors but from reactions with SnR\(_2\) reagents. This latter synthetic method is limited by the availability of the SnR\(_2\) reagents, which are only stable when they have very bulky R groups.\(^{23}\)

### Concluding Remarks

Reactivity studies on neutral non-hydridic triruthenium carbonyl clusters containing face-capping N-heterocyclic ligands, such as compound 1, have no precedent. As anticipated, the reactivity of complex 1 reported herein is quite different from that of its hydridic analogues\(^{1,2}\) and includes the following interesting achievements: (a) the preparation of triruthenium μ-3-vinylidene derivatives directly from terminal alkynes, (b) the modification of the Habq ligand by coupling its C\(^{10}\) carbon atom with an allyl fragment, (c) the room-temperature incorporation of tertiary stannanes into a triruthenium cluster, and (d) the facile transformation of the corresponding hydridostannyl products into derivatives containing bridging SnR\(_2\) ligands.

**General Data.** Solvents were dried over Na[Ph₂CO] (THF, diethyl ether, hydrocarbons), or CaH₂ (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 and by spot TLC on silica gel. Compound 1 was prepared as described elsewhere.¹ ¹³C-enriched samples were prepared from ¹³C-enriched [Ru₂(CO)₇]₂⁺. Instrumentation was as previously reported.¹² Unless otherwise indicated, NMR spectra were run at room temperature, using SiMe₄ as standard (δ 0). MS data (FAB ionization, positive ion) refer to the most abundant molecular ion isotopomer.

[Ru₂{(C₅H₅)₂Habq}²(C₂H₅)₂CH₂OH(CO)]₂ (5). A solution of compound 1 (70 mg, 0.094 mmol) and 2-methyl-3-butyl-2-ol (13 µL, 0.133 mmol) in 1,2-dichloroethane (20 mL) was stirred at reflux temperature for 45 min. The color changed from orange to tawny. The solvent was removed under reduced pressure and the residue redissolved in ca. 3 mL of THF and transferred onto silica gel TLC plates. After elution with dichloromethane/hexanes (4:1), the major band (yellow) afforded compound 5 upon extraction with dichloromethane and solvent removal (12 mg, 16%). Anal. Calcd for C₂₇H₁₈N₂O₉Ru₃: C, 40.45; H, 2.26; N, 3.49. Found: C, 40.74; H, 2.52; N, 3.44. FAB-MS (m/z): 803 [M⁺]. IR (CH₂Cl₂): νCO 2076 (m), 2047 (s), 2014 (m, 1H, CH₃), 1988 (m, br, 1H, CH₂), 1484–1383 (m, 2H, CH₂, 2-C), 129–1000 (m, 3H, CH₃), 0.67 (t, J = 7.4, 1H, CH₃). ¹³C(C₅H₅) NMR, DEPT (CD₂Cl₂): δ 38.8 (dd, J = 5.2, 2.8, 1H, bq), 7.90 (d, J = 8.8, 1H, bq), 7.61–7.59 (m, 2H, bq), 7.46 (d, J = 8.7, 1H, bq), 6.98 (d, J = 8.7, 1H, bq), 5.88 (t, J = 5.6, 1H, CCH), 4.80 (s, br, 1H, NH), 1.78–1.66 (m, 1H, CH₃), 1.48–1.38 (m, 2H, CH₂). ¹³C(C₆H₅) NMR, DEPT (CD₂Cl₂): δ 328.6 (CH₂), 202.2, 198.8, 197.7, 195.9, 192.2 (COs), 168.9 (C₉), 163.4 (C₈), 151.1 (C₇), 138.0 (C₆), 136.6 (C₅), 136.3 (CH₃), 134.8 (C₄), 129.2 (CH₂), 126.9 (CH₃), 122.8 (CH₃), 121.4 (CH₃), 121.2 (CH₄), 119.0 (CH₃), 97.3 (CCH), 42.0 (CH₃), 31.4 (CH₃), 22.4 (CH₃), 13.6 (CH₃).

**Experimental Section**

**Compound Preparation.** Solvents were dried over Na[Ph₂CO] (THF, diethyl ether, hydrocarbons), or CaH₂ (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 and by spot TLC on silica gel. Compound 1 was prepared as described elsewhere.¹ ¹³C-enriched samples were prepared from ¹³C-enriched [Ru₂(CO)₇]₂⁺. Instrumentation was as previously reported.¹² Unless otherwise indicated, NMR spectra were run at room temperature, using SiMe₄ as standard (δ 0). MS data (FAB ionization, positive ion) refer to the most abundant molecular ion isotopomer.

[Ru₂{(C₅H₅)₂Habq}²(C₂H₅)₂CH₂OH(CO)]₂ (5). A solution of compound 1 (70 mg, 0.094 mmol) and 2-methyl-3-butyl-2-ol (13 µL, 0.133 mmol) in 1,2-dichloroethane (20 mL) was stirred at reflux temperature for 45 min. The color changed from orange to tawny. The solvent was removed under reduced pressure and the residue redissolved in ca. 3 mL of THF and transferred onto silica gel TLC plates. After elution with dichloromethane/hexanes (4:1), the major band (yellow) afforded compound 5 upon extraction with dichloromethane and solvent removal (12 mg, 16%). Anal. Calcd for C₂₇H₁₈N₂O₉Ru₃: C, 40.45; H, 2.26; N, 3.49. Found: C, 40.74; H, 2.52; N, 3.44. FAB-MS (m/z): 803 [M⁺]. IR (CH₂Cl₂): νCO 2076 (m), 2047 (s), 2014 (m, 1H, CH₃), 1988 (m, br, 1H, CH₂), 1484–1383 (m, 2H, CH₂, 2-C), 129–1000 (m, 3H, CH₃), 0.67 (t, J = 7.4, 1H, CH₃). ¹³C(C₅H₅) NMR, DEPT (CD₂Cl₂): δ 38.8 (dd, J = 5.2, 2.8, 1H, bq), 7.90 (d, J = 8.8, 1H, bq), 7.61–7.59 (m, 2H, bq), 7.46 (d, J = 8.7, 1H, bq), 6.98 (d, J = 8.7, 1H, bq), 5.88 (t, J = 5.6, 1H, CCH), 4.80 (s, br, 1H, NH), 1.78–1.66 (m, 1H, CH₃), 1.48–1.38 (m, 2H, CH₂). ¹³C(C₆H₅) NMR, DEPT (CD₂Cl₂): δ 328.6 (CH₂), 202.2, 198.8, 197.7, 195.9, 192.2 (COs), 168.9 (C₉), 163.4 (C₈), 151.1 (C₇), 138.0 (C₆), 136.6 (C₅), 136.3 (CH₃), 134.8 (C₄), 129.2 (CH₂), 126.9 (CH₃), 122.8 (CH₃), 121.4 (CH₃), 121.2 (CH₄), 119.0 (CH₃), 97.3 (CCH), 42.0 (CH₃), 31.4 (CH₃), 22.4 (CH₃), 13.6 (CH₃).
Trithium Complexes with a μ$_{3}$-η$_{3}$-(C$_{2}$N$_{2}$) Ligand

Forced compound 7 upon extraction with dichloromethane and solvent removal (9 mg, 14%). Anal. Calcd for C$_{2}$H$_{2}$N$_{2}$O$_{2}$Ru$_{3}$(fw 829.67): C, 40.54; H, 2.19; N, 3.38. Found: C, 39.98; H, 2.02; N, 3.21. 

FAB-MS (m/z): 785 [M + H − CO − H$_2$O]$.^1$IR (CH$_2$Cl$_2$): 750 vs, 733 (COs), 164.6 (C$^1$H), 135.8 (C$^1$H), 133.5 (C$^1$H), 120.5, (CO$_{2}$SO$_3$), 101.3 (CO$_{2}$C), 91.5 (C$_{5}$H$_{11}$).$^1$H NMR (CD$_2$Cl$_2$): δ 8.33 (dd, J = 6.8, 1.7, 1 H), 7.61 (d, J = 4.8, 1 H, bq), 7.32 (J = 8.4, 1 H, bq), 6.23 (d, J = 8.4, 1 H, bq), 5.41 (J = 10.18, 1 H, allyl), 4.99 (dd, J = 7.4, 2.5, 1 H, CH$_2$, allyl), 2.71 (s, 1 H, NH), 2.52 (dd, J = 15.5, 10.8, 7.4, 1 H, allyl), −1.04 (dd, J = 15.3, 2.5, 1 H, CH$_2$, allyl), 75.0, 66.7, 61.5, 61.3, 50.9, 47.8, 45.1 (CO$_{2}$SO$_3$), 136.5 (CO$_{2}$SO$_3$), 135.5 (CH$_3$), 133.5 (CH$_3$), 130.6 (CHO$_2$), 129.4 (CHO$_2$), 126.8 (CHO$_2$), 122.7 (CH$_2$), 122.1 (CH$_2$), 120.0 (CH$_2$), 114.1 (CHO$_2$), 99.7 (C$^1$CH), 59.6–58.6 (m, 4 CH$_2$).

$[\text{Ru}_{3}(\mu_{3}-\eta_{3})(\text{C}_{2}\text{N}_{2})-\text{HabqCHCHCHC}_{2}\text{CH}-(\text{C}_{5}\text{Me}_{3})-(\text{CO})_{3}](9)$ and $[\text{Ru}_{3}(\mu_{3}-\eta_{3})(\text{C}_{2}\text{N}_{2})-\text{HabqCHCHCHC}_{2}\text{CH}-(\text{C}_{5}\text{Me}_{3})-(\mu_{3}-\eta_{3})(\text{CO})_{3}(\mu_{3}-\eta_{3})(\text{CO})_{3}](10)$. A solution of compound 1 (100 mg, 0.134 mmol) and 1-(trimethylsilyl)pentac-1,4-diyne (25 mL, 0.147 mmol) in 1,2-dichloroethane (20 mL) was stirred at reflux temperature for 1 h. The color changed from orange to dark brown. The solvent was removed under reduced pressure, and the residue was redissolved in ca. 2 mL of dichloromethane and placed onto silica gel TLC plates.

Elution with dichloromethane/hexanes (1:1) afforded 3 mmol (δ 8.32 (dd, J = 7.4, 1 H, bq), 7.84 (dd, J = 7.4, 1 H, bq), 7.77 (t, J = 7.4, 1 H, bq), 7.68 (d, J = 8.4, 1 H, bq), 7.32 (J = 8.4, 1 H, bq), 6.23 (d, J = 8.4, 1 H, bq), 5.41 (J = 10.18, 1 H, allyl), 4.99 (dd, J = 7.4, 2.5, 1 H, CH$_2$, allyl), 2.71 (s, 1 H, NH), 2.52 (dd, J = 15.5, 10.8, 7.4, 1 H, allyl), −1.04 (dd, J = 15.3, 2.5, 1 H, CH$_2$, allyl), 75.0, 66.7, 61.5, 61.3, 50.9, 47.8, 45.1 (CO$_{2}$SO$_3$), 136.5 (CO$_{2}$SO$_3$), 135.5 (CH$_3$), 133.5 (CH$_3$), 130.6 (CHO$_2$), 129.4 (CHO$_2$), 126.8 (CHO$_2$), 122.7 (CH$_2$), 122.1 (CH$_2$), 120.0 (CH$_2$), 114.1 (CHO$_2$), 99.7 (C$^1$CH), 59.6–58.6 (m, 4 CH$_2$).

$[\text{Ru}_{3}(\mu_{3}-\eta_{3})(\text{C}_{2}\text{N}_{2})-\text{Habq})(\mu_{3}-\eta_{3})(\text{C}_{2}\text{N}_{2})-\text{HabqCHCHCHC}_{2}\text{CH}-(\text{C}_{5}\text{Me}_{3})-(\mu_{3}-\eta_{3})(\text{CO})_{3}(\mu_{3}-\eta_{3})(\text{CO})_{3}](11)$. A THF solution (20 mL) of compound 1 (50 mg, 0.067 mmol) and 3-hexyne (9 mL, 0.075 mmol) was heated at reflux temperature for 4 h. The solvent was evaporated under reduced pressure to ca. 3 mL, and the resulting solution was separated by TLC on silica gel using dichloromethane/hexanes (1:2) as eluant.

$[\text{Ru}_{3}(\mu_{3}-\eta_{3})(\text{C}_{2}\text{N}_{2})-\text{Habq})(\mu_{3}-\eta_{3})(\text{C}_{2}\text{N}_{2})-\text{HabqCHCHCHC}_{2}\text{CH}-(\text{C}_{5}\text{Me}_{3})-(\mu_{3}-\eta_{3})(\text{CO})_{3}(\mu_{3}-\eta_{3})(\text{CO})_{3}](11)$ (9 mg, 30% based on Habq), respectively, after extraction with dichloromethane and solvent removal.

$[\text{Ru}_{4}(\mu_{3}-\eta_{3})(\text{C}_{2}\text{N}_{2})-\text{Habq})(\mu_{3}-\eta_{3})(\text{C}_{2}\text{N}_{2})-\text{HabqCHCHCHC}_{2}\text{CH}-(\text{C}_{5}\text{Me}_{3})-(\mu_{3}-\eta_{3})(\text{CO})_{3}(\mu_{3}-\eta_{3})(\text{CO})_{3}]_{3}][\text{BF}_4]_{2}(12)$. Tetrafluoroborate acid (67 mL, 54 wt % solution in diethyl ether, 0.498 mmol) was added to a solution of compound 1 (185 mg, 0.248 mmol) in dichloromethane (30 mL). The solution was stirred at room temperature for 1 h. The solvent was removed under reduced pressure, and the oily residue was washed with diethyl ether (2 × 5 mL) to give compound 12 as an orange solid (175 mg, 85%).

$[\text{Ru}_{2}(\mu_{3}-\eta_{3})(\text{C}_{2}\text{N}_{2})-\text{Habq})(\mu_{3}-\eta_{3})(\text{C}_{2}\text{N}_{2})-\text{HabqCHCHCHC}_{2}\text{CH}-(\text{C}_{5}\text{Me}_{3})-\text{H}_{2}(\mu_{3}-\eta_{3})(\text{CO})_{3}(\mu_{3}-\eta_{3})(\text{CO})_{3}](11)$.
Table 3. Crystal, Measurement, and Refinement Data for the Compounds Studied by X-ray Diffraction Methods

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<th>5</th>
<th>8-CH$_2$Cl$_2$</th>
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<th>16-0.25CaH$_{14}$</th>
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<tr>
<td>formula</td>
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<td>C$<em>{30}$H$</em>{24}$Cl$_2$N$_2$O$_2$Ru$_3$</td>
<td>C$<em>{30}$H$</em>{24}$N$_2$O$_2$Ru$_3$</td>
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<td>P2$_1$/c</td>
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<td>7.4346(10)</td>
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<td>9.4704(3)</td>
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<td>c, Å</td>
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<td>90</td>
</tr>
<tr>
<td>b, deg</td>
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<td>85.847(2)</td>
<td>100.515(8)</td>
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<td>12890.6(7)</td>
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<td>4</td>
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<td>150(2)</td>
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<td>$\theta$ limits, deg</td>
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<td>abs cor</td>
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<td>XAB2S</td>
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<td>1.648/−1.534</td>
<td>1.044/−1.012</td>
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</table>

The spectrum of the residue showed that it only contained H$_2$abqH and [Ru$_2$(μ-H)$_2$(CO)$_3$].

[Ru$_2$(μ-H)$_2$(C$_2$N$_2$)$_2$(bq)](SnPh$_3$)(CO)$_2$] (13). A solution of triphenyltin hydride (46 mg, 0.131 mmol) and compound 1 (70 mg, 0.094 mmol) in dichloromethane (20 mL) was stirred at room temperature for 90 min. The solvent was removed under reduced pressure, and the oily orange residue was washed with hexanes (2 x 10 mL) to give compound 13 as an orange solid (75 mg, 74%). Anal. Calcld for C$_{30}$H$_{30}$O$_2$Ru$_3$Sn (fw 1070.56): C, 43.76; H, 2.26; N, 6.26. Found: C, 44.01; H, 2.35; N, 2.51. IR (CH$_2$Cl$_2$): $\nu$ 3510 (m), 2063 (m), 2018 (s, sh), 2010 (vs), 1991 (m, br), 1968 (m, br).

[13] 1H NMR (CD$_2$Cl$_2$): $\delta$ 7.20 (m, 12 H, Ph), 7.62 (m, 6 H, bq), 7.94 (d, 1 H, Ph), 6.60 (t, 1 H, Ph), 7.69 (m, 8 H, bq), 7.54-7.49 (m, 8 H, bq + Ph), 7.35 (d, 1 H = 8.8, 1 H, Ph), 7.05 (d, 1 H = 8.8, 1 H, bq), 6.80 (td, 1 J = 7.6, 1.2, 1 H, Ph), 6.72 (d, 1 J = 8.4, 1 H, Ph), 6.60 (t, 1 J = 7.6, 1 H, Ph), 5.69 (dd, 1 J = 7.6, 1.2, 1 H, Ph), 4.26 (s, 1 H, NH).

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X-ray Structures of Compounds 5, 8-CH$_2$Cl$_2$, 11, and 16-0.25CaH$_{14}$. A selection of crystal, measurement, and refinement data is given in Table 3. Diffraction data were collected on a Nonius Kappa-CCD diffractometer equipped with a 95 mm CCD camera on a $\kappa$ goniostat, using graphite-monochromated Cu Kα radiation. Data were reduced to $F_2$ values. Empirical absorption corrections were applied using XAB2S for 5, 8-CH$_2$Cl$_2$, and 11 or SORTAV for 16-0.25CaH$_{14}$. The structures were solved by Patterson interpretation using the program DIRDIF-96.27 Isotropic and full-matrix anisotropic least-squares refinements were carried out using SHEXL-25.


All non-H atoms were refined anisotropically. The NH hydrogen atoms of 5 and 11 and all nonaromatic hydrogen atoms of 8-CH₃Cl₂ were located in the corresponding Fourier maps, and their thermal and positional parameters were refined. All the other hydrogen atom positions of the four compounds were geometrically calculated and refined riding on their parent atoms. Only three atoms of a disordered hexane solvent molecule were found in the asymmetric unit of 16-0.25C₆H₁₄, with occupancies of 0.5 each. The remaining three carbon atoms were symmetry generated. Only the carbon atoms of this solvent molecule were included in the final model. The molecular plots were made with the EUCLID program package. The WINGX program system was used throughout the structure determinations.

Acknowledgment. This work has been supported by the Spanish DGESIC (Grant PB98-1555 to J.A.C.), CICYT (Grants BQU2000-2019 to S.G.-G. and BQU2002-2623 to J.A.C.), and Principado de Asturias (Grant PR-01-GE-7 to V.R.).

Supporting Information Available: Crystallographic data as CIF files for 5, 8-CH₃Cl₂, 11, and 16-0.25C₆H₁₄. This material is available free of charge via the Internet at http://pubs.acs.org.