Reactivity of a Triruthenium Cluster Complex Containing a μ_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 μ_3-Vinylidene and μ-Stannylene Derivatives

Javier A. Cabeza,*,† Ignacio del Río,† Santiago García-Granda,‡ Víctor Riera,† and Marta Suárez†

Departamento de Química Orgánica e Inorgánica, Instituto de Química Organometálica "Enrique Moles", Universidad de Oviedo-CSIC, E-33071 Oviedo, Spain, and Departamento de Química Física y Analítica, Universidad de Oviedo, E-33071 Oviedo, Spain

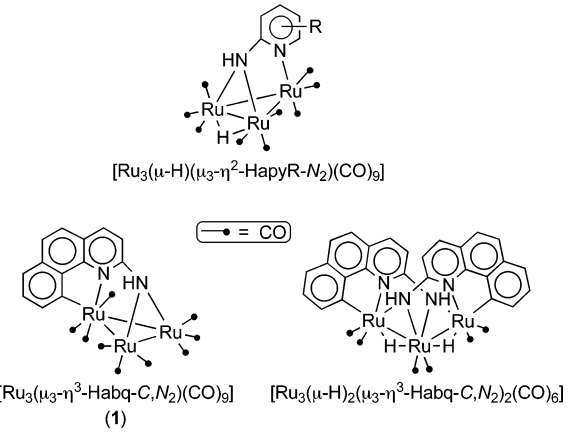
Received March 19, 2004

The reactivity of the triruthenium cluster complex $[Ru_3(\mu_3\text{-}\eta^3(C,N_2)\text{-Habq})(CO)_9]$ (**1**; H_2abqH = 2-amino-7,8-benzoquinoline) with alkynes, tetrafluoroboric acid, dihydrogen, and tertiary silanes and stannanes is reported. The compounds $[Ru_3(\mu_3\text{-}\eta^3(C,N_2)\text{-Habq})(\mu_3\text{-}\eta^2\text{-CCHR})(CO)_8]$ (R = Ph (**2**), *p*-tolyl (**3**), Bu (**4**), CMe_2OH (**5**), CPh_2OH (**6**), *c*-C_5H_8OH (**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 $[Ru_3(\mu_3\text{-}\eta^5(C_3,N_2)\text{-HabqCHCHCH}_2)(\mu\text{-CO})_2(CO)_6]$ (**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, $[Ru_3(\mu_3\text{-}\eta^3(C,N_2)\text{-Habq})(\mu_3\text{-}\eta^2\text{-CCHCH}_2\text{CCSiMe}_3)(CO)_8]$ (**9**) and $Ru_3(\mu_3\text{-}\eta^5\text{-}(C_3,N_2)\text{-HabqCHCHCH}_2)(\mu\text{-CO})_2(CO)_6]$ (**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 $[Ru_3(\mu_3\text{-}\eta^3(C,N_2)\text{-Habq})_2(\mu\text{-CO})(CO)_6]$ (**11**) and known alkyne-containing ruthenium compounds. Protonation of **1** with tetrafluoroboric acid gives the cationic hydride $[Ru_3(\mu\text{-H})(\mu_3\text{-}\eta^3(C,N_2)\text{-Habq})(CO)_9][BF_4]$ (**12**). Free H_2abqH and $[Ru_4(\mu\text{-H})_4(CO)_{12}]$ 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 $[Ru_3(\mu\text{-H})(\mu_3\text{-}\eta^3\text{-Habq-}C,N,N)(SnR_3)(CO)_8]$ (R = Ph (**13**), Bu (**14**)). These compounds slowly release HR at room temperature to render the derivatives $[Ru_3(\mu_3\text{-}\eta^3(C,N,N)\text{-Habq})(\mu\text{-SnR}_2)(\mu\text{-CO})(CO)_7]$ (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.[1,2] Most of these clusters are trinuclear and contain a face-capping HapyR ligand (H_2apyR = 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. $[Ru_3(\mu\text{-H})(\mu_3\text{-}\eta^2(N_2)\text{-HapyR})(CO)_9]$ (Chart 1). Some of these complexes have been recognized as catalytic precursors for the hydrogenation,[3,4] dimerization,[5] polymerization,[5] and hydroformylation[6] of selected alkynes.

Chart 1



2-Amino-7,8-benzoquinoline (H_2abqH) can be considered as a member of the 2-aminopyridine family. However, we have recently reported that its carbonyl cluster chemistry is quite different from that of "normal"

* To whom correspondence should be addressed. E-mail: jac@fq.uniovi.es. Fax: int + 34-985103446. Internet: http://www12.uniovi.es/investigacion/jac/.

† Universidad de Oviedo-CSIC.

‡ Universidad de Oviedo.

(1) For a recent review on the reactivity of triruthenium carbonyl clusters derived from 2-aminopyridines, see: Cabeza, J. A. *Eur. J. Inorg. Chem.* **2002**, 1559.

10.1021/om049797j CCC: $27.50
Publication on Web 06/02/2004

2-aminopyridines, because the coordination of the quinolinic N atom triggers the cyclometalation of the benzo ring, favoring the activation of the $C^{10}-H$ bond. Thus, the reactions of 2-amino-7,8-benzoquinoline with $[Ru_3(CO)_{10}(MeCN)_2]$ and $[Ru_3(CO)_{12}]$ lead to the cyclometalated derivatives $[Ru_3(\mu_3\text{-}\eta^3(C,N_2)\text{-Habq})(CO)_9]$ (**1**) and $[Ru_3(\mu\text{-H})_2(\mu_3\text{-}\eta^3(C,N_2)\text{-Habq})_2(CO)_6]$, 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]

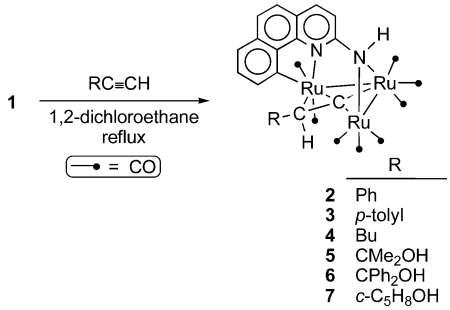
We now report our studies on the reactivity of complex **1**. These studies were prompted by the fact that complex **1** contains no hydride ligands and, therefore, its reactivity was expected to be very different from that of triruthenium monohydrido HapyR derivatives.[1,2]

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-ethynylcyclopentanol in 1,2-dichloroethane at reflux temperature to give the vinylidene derivatives $[Ru_3(\mu_3\text{-}\eta^3(C,N_2)\text{-Habq})(\mu_3\text{-}\eta^2\text{-CCHR})(CO)_8]$ (R = Ph (**2**), *p*-tolyl (**3**), Bu (**4**), CMe_2OH (**5**), CPh_2OH (**6**), *c*-C_5H_8OH (**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** (taken as a representative example) shows eight CO resonances, but only five peaks are observed in the spectra of all these compounds at room temperature (Figure 1). This indicates that, at room temperature, the carbonyl ligands are involved in a fluxional process. As far as the resonances associated with the Habq ligand are concerned, the $^{13}C\{^1H\}$ and ^1H NMR spectra of all these complexes are very similar.

Scheme 1



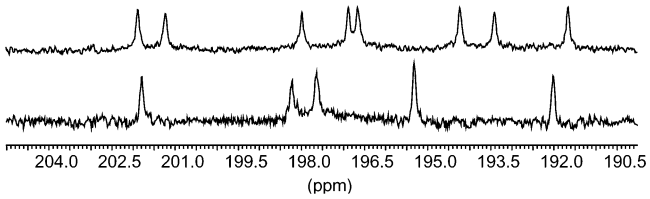


Figure 1. ^{13}C NMR spectra of a ^{13}CO-enriched sample of compound **5** at −80 °C (top) and 20 °C (bottom).

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

compd	$\delta(C_\alpha)$	$\delta(C_\beta)$	$\delta(C_\beta H)$
2	290.7	98.7	6.66
3	288.9	99.1	6.59
4	288.6	97.3	5.88
5	*a*	*a*	6.07
6	294.5	100.9	*a*
7	*a*	99.7	6.84

[a] Unobserved or overlapped with other resonances.

The presence of the vinylidene ligand in **2**−**7** was indicated by their $^{13}C\{^1H\}$ and ^1H NMR spectra (Table 1). The narrow ranges in which the ^{13}C and ^1H resonances of the atoms of the vinylidene fragment are observed also indicate that these compounds have the same structure. Other cluster complexes containing μ_3-vinylidene ligands display the ^{13}C and ^1H resonances of their vinylidene fragments in wider δ ranges: 305−200 for C_α, 150−65 for C_β, and 6.5−4.0 for $C_\beta H$.[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

(2) For relevant articles in the field, see: (a) Cabeza, J. A.; del Río, I.; García-Granda, S.; Riera, V.; Suárez, M. *Organometallics* **2002**, *21*, 2540. (b) Cabeza, J. A.; del Río, I.; García-Granda, S.; Lavigne, G.; Lugan, N.; Moreno, M.; Nombel, P.; Pérez-Priede, M.; Riera, V.; Rodríguez, A.; Suárez, M.; van der Maelen, J. F. *Chem. Eur. J.* **2001**, *7*, 2370. (c) Cabeza, J. A.; Riera, V.; Trivedi, R.; Grepioni, F. *Organometallics* **2000**, *19*, 2043. (d) Cabeza, J. A.; del Río, I.; Riera, V.; García-Granda, S.; Sanni, S. B. *Organometallics* **1997**, *16*, 1743. (e) Cabeza, J. A.; García-Granda, S.; Llamazares, A.; Riera, V.; van der Maelen, J. F. *Organometallics* **1993**, *12*, 2973. (f) Andreu, P. L.; Cabeza, J. A.; Pellinghelli, M. A.; Riera, V.; Tiripicchio, A. *Inorg. Chem.* **1991**, *30*, 4611. (g) Cabeza, J. A.; del Río, I.; García-Álvarez, P.; García-Granda, S.; Riera, V.; Suárez, M. *Dalton* **2003**, 2808. (h) Cabeza, J. A.; del Río, I.; Riera, V.; Suárez, M.; García-Granda, S. *Organometallics*, in press.

(3) Cabeza, J. A. In *Metal Clusters in Chemistry*; Braunstein, P., Oro, L. A., Raithby, P. R., Eds.; Wiley-VCH: Weinheim, Germany, 1999; p 715.

(4) For a review on alkyne hydrogenation mediated by 2-amidopyridine-bridged triruthenium carbonyl cluster complexes, see: Cabeza, J. A.; Fernández-Colinas, J. M.; Llamazares, A. *Synlett* **1995**, 579.

(5) Nombel, P.; Lugan, N.; Mulla, F.; Lavigne, G. *Organometallics* **1994**, *13*, 4673.

(6) Nombel, P.; Lugan, N.; Donnadieu, B.; Lavigne, G. *Organometallics* **1999**, *18*, 187.

(7) Cabeza, J. A.; del Río, I.; García-Granda, S.; Riera, V.; Suárez, M. *Organometallics* **2002**, *21*, 5055.

(8) (a) Patel, B. P.; Crabtree, R. H. *J. Am. Chem. Soc.* **1996**, *118*, 13105. (b) Lee, D.-H.; Patel, B. P.; Clot, E.; Eisenstein, O.; Crabtree, R. H. *Chem. Commun.* **1999**, 297. (c) Lee, D.-H.; Kwon, H. J.; Patel, B. P.; Liable-Sands, L. M.; Rheingold, A. L.; Crabtree, R. H. *Organometallics* **1999**, *18*, 1615. (d) Gruet, K.; Crabtree, R. H.; Lee, D.-H.; Liable-Sands, L. M.; Rheingold, A. L. *Organometallics* **2000**, *19*, 2228.

(9) For general reviews on metal complexes containing vinylidene ligands, see: (a) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197. (b) Bruce, M. I.; Swincer, A. G. *Adv. Organomet. Chem.* **1983**, *22*, 60.

(10) For relevant examples of μ_3-vinylidene ligands in ruthenium clusters, see: (a) Takao, T.; Takemori, T.; Moriya, M.; Suzuki, H. *Organometallics* **2002**, *21*, 5190. (b) Bruce, M. I.; Zaitseva, N. N.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1999**, 2777. (c) Adams, C. J.; Bruce, M. I.; Liddell, M. J.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1992**, 1314. (d) Adams, C. J.; Bruce, M. I.; Schulz, M.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1994**, *472*, 285. (e) Bruce, M. I.; Horn, E.; bin Shawkataly, O.; Snow, M. R. *J. Organomet. Chem.* **1985**, *280*, 289. (f) Dotsworth, R.; Dutton, T.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R. *Acta Crystallogr., Sect. C* **1989**, *45*, 707. (g) Fogg, D. E.; MacLaughlin, S. A.; Kwek, K.; Cherkas, A. A.; Taylor, N. J.; Carty, A. J. *J. Organomet. Chem.* **1988**, *352*, C17. (h) Sailor, M. J.; Brock, C. P.; Shriver, D. F. *J. Am. Chem. Soc.* **1987**, *109*, 6015. (i) Sailor, M. J.; Sabat, M.; Shriver, D. F. *Organometallics* **1988**, *7*, 728. (j) Connelly, N. G.; Forow, N. J.; Knox, S. A. R.; MacPherson, K. A.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1985**, 16.

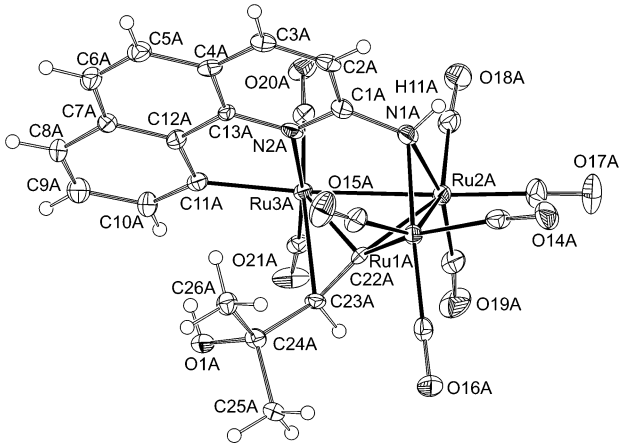


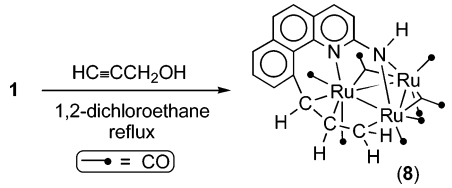
Figure 2. Molecular structure of one of the two crystallographically independent molecules of compound **5** found in the unit cell. Thermal ellipsoids are drawn at the 40% probability level. Both C and O atoms of the same carbonyl ligand bear the same number.

Table 2. Selected Interatomic Distances (Å) in Compounds 5, 8, 11, and 16

	5 (molecule A)	**8**	**11**	**16**
Ru(1)−Ru(2)	2.6721(6)	2.6698(4)	2.770(2)	2.691(2)
Ru(1)−Ru(3)	3.9367(6)	2.7571(4)	2.743(2)	2.839(2)
Ru(2)−Ru(3)	2.8204(6)	2.9210(4)	4.684(2)	2.884(2)
Ru(1)−Sn(1)				2.729(2)
Ru(3)−Sn(1)				2.637(2)
Ru(1)−N(1)	2.143(5)	2.145(3)	2.16(1)	2.18(1)
Ru(1)−N(3)			2.17(1)	
Ru(2)−N(1)	2.140(5)	2.155(3)		2.13(1)
Ru(2)−N(2)			2.14(1)	
Ru(2)−N(3)			2.16(1)	
Ru(3)−N(1)			2.15(1)	
Ru(3)−N(2)	2.116(5)	2.186(3)		2.12(1)
Ru(3)−N(4)			2.14(1)	
Ru(1)−C(22)	2.026(6)			
Ru(2)−C(11)			2.07(1)	
Ru(2)−C(22)	2.166(6)			
Ru(2)−C(24)		2.239(4)		
Ru(3)−C(11)	2.093(6)			2.13(2)
Ru(3)−C(22)	2.249(5)	2.170(4)		
Ru(3)−C(23)	2.359(5)	2.513(4)		
Ru(3)−C(33)			2.07(1)	
C(11)−C(22)		1.493(5)		
C(22)−C(23)	1.382(8)	1.440(6)		
C(23)−C(24)	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 3.9367(6) 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 **1**,[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 Ru_3 plane,[7] whereas the Habq ligand of **5** is leaning toward the open Ru−Ru edge, the angle between the Habq and Ru_3 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 π-mode to Ru(3A) through the atoms of its CC double bond, C(22A) and C(23A). The remaining substituents of C(23A) are

Scheme 2



a hydrogen atom and a CMe_2OH 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 μ_3-vinylidene ligands.[9−11] However, compounds **2**−**7** are unique in the sense that they are open clusters, since in all the previously known ruthenium carbonyl clusters containing μ_3-vinylidene ligands, such ligands cap closed metal triangles.[9,10]

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[11] and for some mononuclear derivatives.[9,12] The ruthenium carbonyl clusters containing μ_3-vinylidene ligands known so far are formed by reactions of previously coordinated ligands.[10]

The mechanism of isomerization of π-bound terminal alkynes into vinylidene ligands in mononuclear complexes has been extensively studied and discussed.[9,12] 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_α to the C_β 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 $[Ru_3(\mu\text{-H})(\mu_3\text{-}\eta^2\text{-CCR})(CO)_9]$[13] 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.[14] 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 $[Ru_3(\mu_3\text{-}\eta^5(C_3,N_2)\text{-HabqCHCHCH}_2)(\mu\text{-CO})_2(CO)_6]$ (**8**) (Scheme 2).

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

(11) Suades, J.; Mathieu, R. *J. Organomet. Chem.* **1986**, *312*, 335.

(12) For specific reviews on mononuclear vinylidene complexes, see: (a) Puerta, M. C.; Valerga, P. *Coord. Chem. Rev.* **1999**, *193*−*195*, 977. (b) Werner, H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1077. (c) Bruneau, C.; Dixneuf, P. H. *Acc. Chem. Res.* **1999**, *32*, 311.

(13) Deeming, A. J. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Shriver, D. F., Bruce, M. I., Eds.; Pergamon: Oxford, U.K., 1985; Vol. 7, p 772.

(14) For relevant reviews on allenylidene and related complexes, see: (a) Cadierno, V.; Gamasa, M. P.; Gimeno, J. *Eur. J. Inorg. Chem.* **2001**, 571. (b) Bruce, M. I. *Chem. Rev.* **1998**, *98*, 2797. (c) Gervasio, G.; King, P. J.; Marabello, D.; Sappa, E. *Inorg. Chim. Acta* **2003**, *215*, 244.

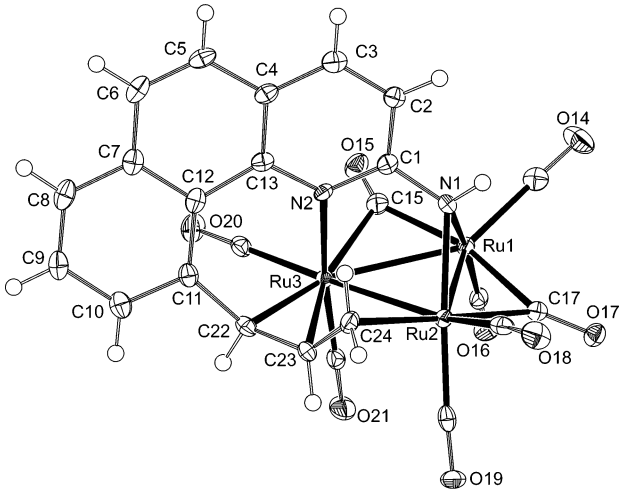


Figure 3. Molecular structure of compound **8**. Thermal ellipsoids are drawn at the 50% probability level. Both C and O atoms of the same carbonyl ligand bear the same number.

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 $CHCHCH_2$ fragment to the C^{10} 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 σ-bonded to Ru(2) through its terminal carbon atom C(24) and π-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 μ_3-$\eta^2(N_2)$ 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 π-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 $^{13}C\{^1H\}$ DEPT NMR spectra clearly show the presence of the Habq (7 *C*H and 6 *C*) and allyl (2 *C*H at 67.2 and 46.1 ppm and 1 CH_2 at 23.6 ppm) fragments of the novel $HabqCHCHCH_2$ ligand accompanied by six terminal and two bridging CO ligands. In contrast with the $^{13}C\{^1H\}$ 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 C^{10} 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 C*H*) and 2.71 (N*H*), the spectrum contains

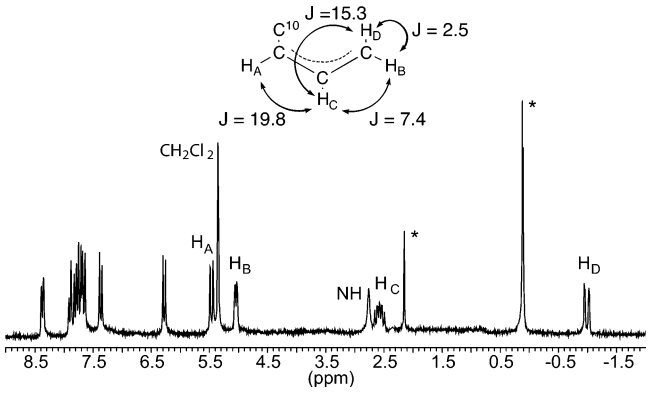
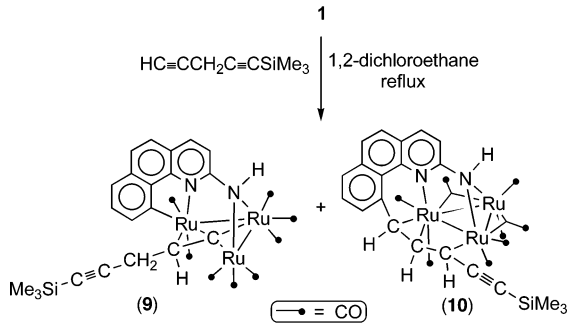


Figure 4. ^1H NMR spectrum of compound **8** (CD_2Cl_2, 20 °C, 300 MHz). The peaks marked with an asterisk are due to residual water and silicone grease.

Scheme 3



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 H_D, −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 chemistry 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]

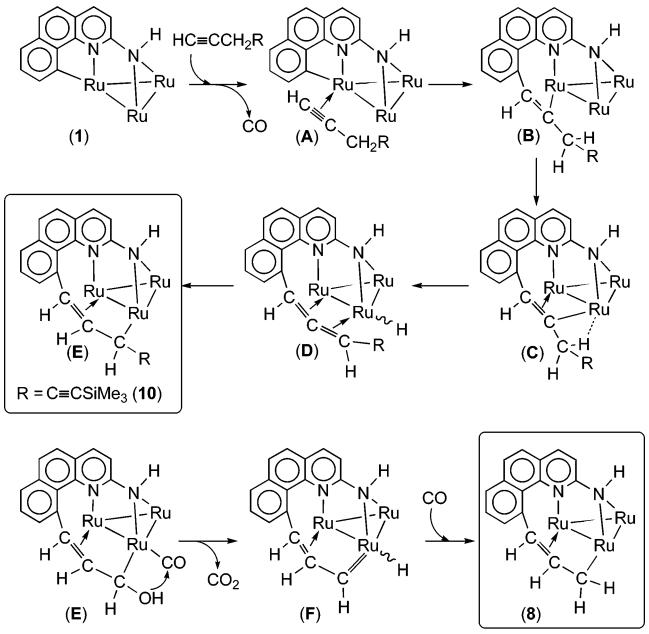
The reaction of complex **1** with 1-(trimethylsilyl)-penta-1,4-diyne led to a mixture of compounds from which the two major products [Ru_3(μ_3-η^3(*C*,N_2)-Habq)(μ_3-η^2-$CCHCH_2C{\equiv}CSiMe_3$)$(CO)_8$] (**9**) and [Ru_3(μ_3-η^5-(C_3,N_2)-HabqCHCHCHC≡$CSiMe_3$)(μ-CO)$_2(CO)_6$] (**10**) were separated by chromatographic methods (Scheme 3). Their IR and NMR spectroscopic data clearly indicate that **9** is a μ_3-η^2-vinylidene derivative analogous to compounds **2**−**7**, while **10** is structurally related to complex **8**. The chemical shift of the C^{10} carbon atom of

(15) See, for example: Cabeza, J. A.; del Río, I.; Grepioni, F.; Moreno, M.; Riera, V.; Suárez, M. *Organometallics* **2001**, *20*, 4190.

(16) For examples of triruthenium clusters containing η^3-allyl-type fragments, see: (a) Bruce, M. I.; Zaitseva, N. N.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1999**, 2777. (b) Rao, K. M.; Angelici, R. J.; Young, V. G. *Inorg. Chim. Acta* **1992**, *198*, 211. (c) Wong, W. Y.; Chan. S.; Wong, W. T. *J. Chem. Soc., Dalton Trans.* **1995**, 1497. (d) Cabeza, J. A.; da Silva, I.; del Río, I.; García-Granda, S.; Riera, V. *Inorg. Chim. Acta* **2003**, *347*, 107. (e) Beanan, L. R.; Keister, J. B. *Organometallics* **1985**, *4*, 1713. (f) Aime, S.; Milone, L.; Osella, D.; Valle, M. *J. Chem. Res., Synop.* **1978**, 77. (g) Castiglioni, M.; Milone, L.; Osella, D.; Valle, M. *Inorg. Chem.* **1976**, *15*, 396. (h) Gervasio, G.; Marabello, D.; King, P. J.; Sappa, E.; Secco, A. *J. Organomet. Chem.* **2003**, *671*, 137.

(17) It has been reported that the cluster [Ru_3(μ-H)(μ_3-η^3(C_3)-CHCHCH)$(CO)_9$] is formed from [$Ru_3(CO)_{12}$] and $Me_3SiC{\equiv}CCH_2OH$.[16h]

Scheme 4

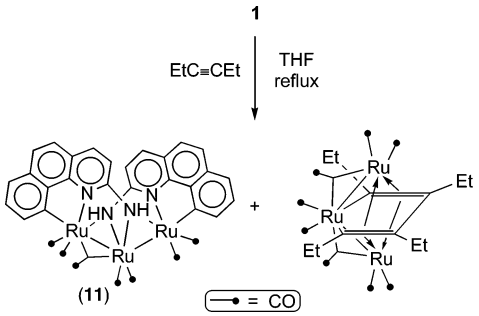


the Habq fragment of complex **10**, 128.8 ppm, suggests that this atom is not attached to ruthenium but to an organic fragment, as occurs in **8**. The coupling constants between the three protons of the allyl fragment of **10** and the fact that the proton resonance at negative chemical shift of complex **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_D in **8** (Figure 4): i.e. in an anti arrangement with respect to the central C*H* 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 η^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 alkyne reagent. Although the initial alkyne coordination to complex **1** might not take place on the Ru atom attached to the C-metalated fragment, the alkyne might end in that position after a fluxional process (intermediate **A**). This would be followed by a migratory insertion of the alkyne into the Ru−C^{10} bond to give the alkenyl intermediate (**B**). A subsequent rearrangement of this terminal alkenyl 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 hydroxycarbonyl 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**.

Scheme 5



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-butyn-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_3-η^3(*C*,N_2)-Habq)$_2$(μ-CO)(CO)$_6$] (**11**), a complex which contains two metalated Habq ligands and no fragments derived from the alkynes. The known complex [Ru_3(μ_3-η^4-EtC=CEtCEt=CEt)(μ-CO)$_2$-(CO)$_6$][16f] 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 cluster 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_3-η^3(*C*,N_2)-Habq)$_2$(CO)$_6$], which contains both Habq ligands in a similar arrangement.[7] However, while

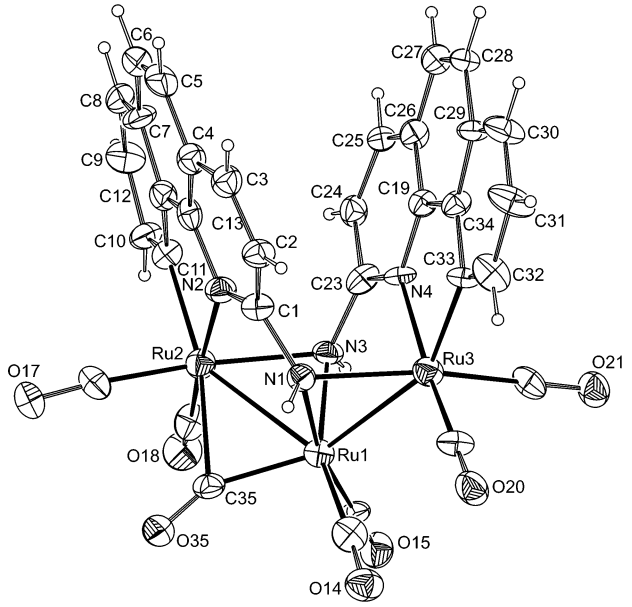


Figure 5. Molecular structure of compound **11**. Thermal ellipsoids are drawn at the 30% probability level. Both C and O atoms of the same carbonyl ligand bear the same number.

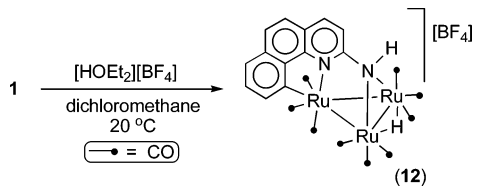
this latter complex has C_2 symmetry, complex **11** is asymmetric due to the presence of a unique bridging CO ligand.

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 carbonyls, in the range 2055−1940 cm^{-1}. However, its ^1H and DEPT ^{13}C 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 apparent C_2 symmetry on the NMR time scale. The activation energy of such a fluxional process should be very low, because ^1H and ^{13}C NMR spectra run at −80 °C are comparable with the aforementioned spectra taken at room temperature.

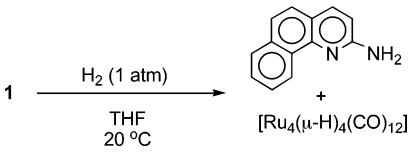
The way by which complex **11** is formed from **1** and internal alkynes is obscure. The isolation of [$Ru_3(\mu_3$-η^4-EtC═CEtCEt═CEt)(μ-CO)$_2$(CO)$_6$] from the mixture of products formed using 3-hexyne as reagent suggests that a rearrangement of the type 2 $Ru_3AB \rightarrow Ru_3AA + Ru_3BB$ (A = Habq; B = alkyne) may take place after **1** coordinates the alkyne. 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 diehtyl ether solution of tetrafluoroboric acid at room temperature led to the quantitative formation of the hydrido derivative [$Ru_3(\mu$-H)(μ_3-η^3(*C*,*N*$_2$)-Habq)(CO)$_9$]-[BF_4] (**12**). The cationic character of this complex was suggested by its IR spectrum, which shows the stretching ν_{CO} 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 $^{13}C\{^1H\}$ NMR

Scheme 6



Scheme 7



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_s symmetry.

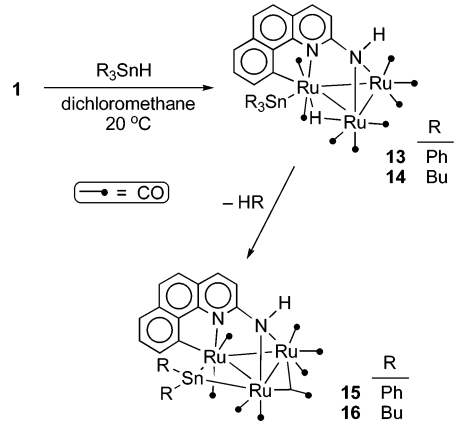
Complex **1** was quantitatively converted into a mixture of H_2abqH and [$Ru_4(\mu$-H)$_4$(CO)$_{12}$] when its solutions were treated with dihydrogen (1 atm) at room temperature (Scheme 7). This result was surprising, because the addition of dihydrogen to a coordinatively saturated 48-electron trinuclear 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 H_2abqH and [$Ru_4(\mu$-H)$_4$(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 (triphenylsilane, triethylsilane) 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 to give the stannyl hydrido derivatives [$Ru_3(\mu$-H)(μ_3-η^3(*C*,*N*$_2$)-Habq)(SnR$_3$)(CO)$_8$] (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 [$Ru_3(\mu_3$-η^3(*C*,*N*$_2$)-Habq)(μ-SnR$_2$)(μ-CO)(CO)$_7$] (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 ν_{CO} 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 ($J^{117}_{Sn-H} \approx J^{119}_{Sn-H}$ = 40.8 and 36.0 Hz, respectively) which indicate that the stannyl and the hydride ligands are in an approximately cis

Scheme 8



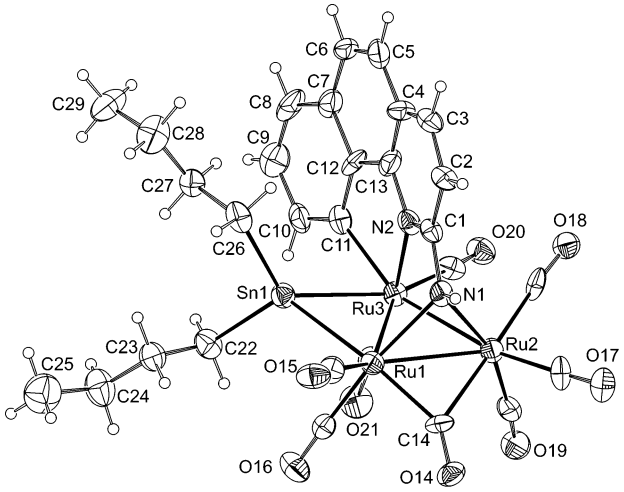


Figure 6. Molecular structure of compound **16**. Thermal ellipsoids are drawn at the 30% probability level. Both C and O atoms of the same carbonyl ligand bear the same number.

arrangement on the same metal atom.[18] No single crystals of compounds **13** and **14** suitable for X-ray diffraction studies could be obtained, due to their instability in solution. Therefore, the structure proposed for these complexes in Scheme 8, although supported by their analytical and spectroscopic data, could not be unambiguously established. Our proposal for the position of the stannyl ligand is based on the structure of derivatives **15** and **16** (vide infra) and on the fact that, in such a position, the stannyl ligand prevents a C_{benzo}–$H_{hydride}$ bond formation process (reductive elimination) that would lead to the decomposition of these products (vide supra).

Compounds **15** and **16** are also isostructural (similar ν_{CO} regions of their IR spectra). Complex **16** was characterized by X-ray diffraction methods (Figure 6). A selection of structural parameters is given in Table 2. The atom arrangement within the Ru_3(Habq) fragment is similar to that found in **1**.[7] The Ru(1)–Ru(3) 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_5,[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 $[Ru_2(\mu\text{-}SnMe_2)_2(SnMe_3)_2(CO)_6]$ 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.

(18) (a) Cabeza, J. A.; Llamazares, A.; Riera, V.; Triki, S.; Ouahab, L. *Organometallics* **1992**, *11*, 3334. (b) Cabeza, J. A.; Franco, R. J.; Llamazares, A.; Riera, V.; Bois, C.; Jeannin, Y. *Inorg. Chem.* **1993**, *32*, 4640. (c) Cabeza, J. A.; García-Granda, S.; Llamazares, A.; Riera, V.; van der Maelen, J. F. *Organometallics* **1993**, *12*, 157. (d) Cabeza, J. A.; Franco, R. J.; Riera, V. *Inorg. Chem.* **1994**, *33*, 5952. (e) Cabeza, J. A.; Franco, R. J.; Riera, V.; García-Granda, S.; van der Maelen, J. F. *Organometallics* **1995**, *14*, 3342. (f) Bois, C.; Cabeza, J. A.; Franco, R. J.; Riera, V.; Saborit, E. *J. Organomet. Chem.* **1998**, *564*, 201.

(19) (a) Cotton, J. D.; Knox, S. A. R.; Stone, F. G. A. *J. Chem. Soc. A* **1968**, 2758. (b) Burgess, K.; Guerin, C.; Johnson, B. F. G.; Lewis, J. *J. Organomet. Chem.* **1985**, *295*, C3. (c) Süss-Fink, G.; Ott, J.; Schmidkonz, B.; Guldner, J. *Chem. Ber.* **1982**, *115*, 2487.

(20) (a) Adams, R. D.; Captain, B.; Fu, W.; Smith, M. D. *Inorg. Chem.* **2002**, *41*, 2302. (b) Adams, R. D.; Captain, B.; Fu, W.; Smith, M. D. *Inorg. Chem.* **2002**, *41*, 5593.

(21) Adams, R. D.; Captain, B.; Fu, W. *J. Organomet. Chem.* **2003**, *671*, 158.

(22) Watkins, S. F. *J. Chem. Soc. A* **1969**, 1552.

(23) (a) Cardin, C. J.; Cardin, D. J.; Lawless, G. A.; Power, J. M.; Power, M. B.; Hursthouse, M. B. *J. Organomet. Chem.* **1987**, *325*, 203. (b) Cardin, C. J.; Cardin, D. J.; Convert, M. A.; Dauter, Z.; Fenske, D.; Devereux, M. M.; Power, M. B. *J. Chem. Soc., Dalton Trans.* **1996**, 1131.

Experimental Section

General Data. Solvents were dried over Na[Ph_2CO] (THF, diethyl ether, 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 and by spot TLC on silica gel. Compound **1** was prepared as described elsewhere.[7] ^{13}CO-enriched samples were prepared from ^{13}CO-enriched [$Ru_3(CO)_{12}$].[24] Instrumentation was as previously reported.[2a] Unless otherwise stated, NMR spectra were run at room temperature, using $SiMe_4$ as standard (δ 0). MS data (FAB ionization, positive ion) refer to the most abundant molecular ion isotopomer.

[Ru_3(μ_3-η^3(*C*,*N*$_2$)-Habq)(μ_3-η^2-CCHPh)(CO)$_8$] (2). A solution of compound **1** (50 mg, 0.067 mmol) and phenylacetylene (8 μL, 0.073 mmol) in 1,2-dichloroethane (20 mL) was stirred at reflux temperature for 10 min. The color changed from orange to dark orange. The solution was concentrated under reduced pressure to ca. 2 mL and placed onto silica gel TLC plates. After elution with dichloromethane/hexanes (1:2), the major band (yellow) afforded compound **2** upon extraction with dichloromethane and solvent removal (17 mg, 31%). Anal. Calcd for $C_{29}H_{14}N_2O_8Ru_3$ (fw 821.65): C, 42.39; H, 1.72; N, 3.41. Found: C, 42.61; H, 1.88; N, 3.33. FAB-MS (*m*/*z*): 823 [M^+]. IR (CH_2Cl_2): ν_{CO} 2079 (m), 2050 (s), 2020 (m), 2009 (m, sh), 1989 (m, br), 1960 (w, br) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 8.00 (d, J = 8.7, 1 H, bq), 7.98 (d, J = 7.5, 1 H, bq), 7.68 (d, J = 8.7, 1 H, bq), 7.54 (d, J = 8.7, 1 H, bq), 7.49 (d, J = 7.5, 1 H, bq), 7.35 (t, J = 7.5, 1 H, bq), 7.09 (d, J = 8.7, 1 H, bq), 6.84 (t, J = 7.6, 1 H, Ph), 6.68 (t, J = 7.6, 2 H, Ph), 6.66 (s, 1 H, CC*H*), 6.36 (d, J = 7.6, 2 H, Ph), 4.93 (s, br, 1 H, N*H*). ^{13}C{^{1}H} NMR, DEPT (CD_2Cl_2): δ 290.7 (*C*CH), 202.9, 199.5, 197.0, 195.8, 192.8 (COs), 169.3 (C_{bq}), 164.9 (C_{bq}), 151.8 (C_{bq}), 143.7 (C_{Ph}), 138.5 (C_{bq}), 137.5 (*C*H$_{bq}$), 135.8 (*C*H$_{bq}$), 135.2 (C_{bq}), 129.9 (*C*H$_{bq}$), 128.1 (2 *C*H$_{Ph}$), 127.8 (2 *C*H$_{Ph}$), 127.6 (*C*H$_{Ph}$), 126.6 (*C*H$_{bq}$), 123.3 (*C*H$_{bq}$), 122.0 (C_{bq}), 121.8 (*C*H$_{bq}$), 114.8 (*C*H$_{bq}$), 98.7 (C*C*H).

[Ru_3(μ_3-η^3(*C*,*N*$_2$)-Habq)(μ_3-η^2-CCH(*p*-tolyl))(CO)$_8$] (3). A solution of compound **1** (50 mg, 0.067 mmol) and *p*-tolylacetylene (9 μL, 0.071 mmol) in 1,2-dichloroethane (25 mL) was stirred at reflux temperature for 10 min. The color changed from orange to dark orange. The solvent was removed under reduced pressure to ca. 2 mL, and the resulting solution was placed onto silica gel TLC plates. After elution with dichloromethane/hexanes (1:1), the major band (yellow) afforded compound **3** upon extraction with dichloromethane and solvent removal (10 mg, 18%). Anal. Calcd for $C_{30}H_{16}N_2O_8Ru_3$ (fw 835.73): C, 43.12; H, 1.93; N, 3.35. Found: C, 43.43; H, 2.09; N, 3.22. FAB-MS (*m*/*z*): 837 [M^+]. IR (CH_2Cl_2): ν_{CO} 2078 (m), 2049 (s), 2020 (m), 2008 (m, sh), 1989 (m, br), 1960 (w, br) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 7.93 (d, J = 8.3, 2 H, bq), 7.62 (d, J = 8.7, 1 H, bq), 7.47 (d, J = 8.7, 1 H, bq), 7.46 (t, J = 8.7, 1 H, bq), 7.33 (d, J = 7.6, 1 H, bq), 7.01 (d, J = 7.6, 1 H, bq), 6.59 (s, 1H, CC*H*), 6.44 (d, J = 7.8, 2 H, *p*-tolyl), 6.19 (d, J = 7.8, 2 H, *p*-tolyl), 4.83 (s, br, 1 H, N*H*), 1.99 (s, 3 H, *p*-tolyl). ^{13}C{^{1}H} NMR, DEPT (CD_2Cl_2): δ 288.9 (*C*CH), 202.5, 199.0, 196.6, 195.3, 192.3 (COs), 168.9 (C_{bq}), 164.2 (C_{bq}), 151.3 (C_{bq}), 140.5 ($C_{p-tolyl}$), 138.0 (C_{bq}), 136.9 (*C*H$_{bq}$), 136.0 (C_{bq}), 135.3 (*C*H$_{bq}$), 134.6 ($C_{p-tolyl}$), 129.4 (*C*H$_{bq}$), 128.0 (2 *C*H$_{p-tolyl}$), 127.5 (2 *C*H$_{p-tolyl}$), 127.0 (*C*H$_{bq}$), 122.8 (*C*H$_{bq}$). 121.5 (C_{bq}), 121.3 (*C*H$_{bq}$), 114.2 (*C*H$_{bq}$), 99.1 (C*C*H), 20.8 (*C*H$_{3p-tolyl}$).

[Ru_3(μ_3-η^3(*C*,*N*$_2$)-Habq)(μ_3-η^2-CCHBu)(CO)$_8$] (4). A solution of compound **1** (60 mg, 0.080 mmol) and 1-hexyne (14 μL, 0.122 mmol) in 1,2-dichloroethane (20 mL) was stirred at reflux temperature for 8 min. The color changed from orange to dark orange. The solvent was removed under reduced pressure to ca. 2 mL and the residue set onto silica gel TLC plates. After elution with dichloromethane/hexanes (2:3), the major band (yellow) afforded compound **4** upon extraction with dichloromethane and solvent removal (19 mg, 30%). Anal. Calcd for $C_{27}H_{18}N_2O_8Ru_3$ (fw 801.66): C, 40.45; H, 2.26; N, 3.49. Found: C, 40.74; H, 2.32; N, 3.44. FAB-MS (*m*/*z*): 803 [M^+]. IR (CH_2Cl_2): ν_{CO} 2076 (m), 2047 (s), 2018 (m), 2004 (m), 1988 (m, br), 1960 (w, br) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 8.39 (dd, J = 5.2, 2.8, 1 H, bq), 7.90 (d, J = 8.8, 1 H, bq), 7.65 (d, J = 8.8, 1 H, bq), 7.61−7.59 (m, 2 H, bq), 7.46 (d, J = 8.7, 1 H, bq), 6.98 (d, J = 8.7, 1 H, bq), 5.88 (t, J = 5.6, 1 H, CC*H*), 4.80 (s, br, 1 H, N*H*), 1.78−1.66 (m, 1 H, C*H*$_2$), 1.48−1.38 (m, 2 H, C*H*$_2$), 1.29−1.00 (m, 3 H, C*H*$_2$), 0.67 (t, J = 7.4, 3 H, C*H*$_3$). ^{13}C{^{1}H} NMR, DEPT (CD_2Cl_2): δ 288.6 (*C*CH), 202.2, 198.8, 197.7, 195.9, 192.2 (COs), 168.9 (C_{bq}), 163.4 (C_{bq}), 151.1 (C_{bq}), 138.0 (C_{bq}), 136.6 (*C*H$_{bq}$), 136.3 (*C*H$_{bq}$), 134.8 (C_{bq}), 129.2 (*C*H$_{bq}$), 126.9 (*C*H$_{bq}$), 122.8 (*C*H$_{bq}$), 121.4 (*C*H$_{bq}$), 121.2 (C_{bq}), 114.0 (*C*H$_{bq}$), 97.3 (C*C*H), 42.0 (*C*H$_2$), 31.4 (*C*H$_2$), 22.4 (*C*H$_2$), 13.6 (*C*H$_3$).

[Ru_3(μ_3-η^3(*C*,*N*$_2$)-Habq)(μ_3-η^2-CCHCMe$_2$OH)(CO)$_8$] (5). A solution of compound **1** (70 mg, 0.094 mmol) and 2-methyl-3-butyn-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 $C_{26}H_{16}N_2O_9Ru_3$ (fw 803.64): C, 38.86; H, 2.01; N, 3.49. Found: C, 39.28; H, 2.14; N, 3.30. FAB-MS (*m*/*z*): 787 [M^+ − H_2O]. IR (CH_2Cl_2): ν_{CO} 2080 (m), 2051 (s), 2021 (m), 2003 (m, sh), 1992 (m, br), 1963 (w, br) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 8.51 (t, J = 4.0, 1 H, bq), 7.96 (d, J = 8.3, 1 H, bq), 7.70 (d, J = 8.8, 1 H, bq), 7.68−7.65 (m, 2 H, bq), 7.53 (d, J = 8.8, 1 H, bq), 7.05 (d, J = 8.3, 1 H, bq), 6.07 (s, 1 H, CC*H*), 4.88 (s, br, 1 H, N*H*), 1.31 (s, 3 H, C*H*$_3$), 0.66 (s, 3 H, C*H*$_3$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 20 °C, ^{13}CO-enriched sample, carbonyl data): δ 201.8, 198.2, 197.6, 195.3, 192.0. ^{13}C{^{1}H} NMR (CD_2Cl_2, −80 °C, ^{13}CO-enriched sample, carbonyl data): δ 201.8, 201.2, 197.9, 196.8, 196.6, 194.2, 193.4, 191.6.

[Ru_3(μ_3-η^3(*C*,*N*$_2$)-Habq)(μ_3-η^2-CCHCPh$_2$OH)(CO)$_8$] (6). A solution of compound **1** (60 mg, 0.080 mmol) and 1,1-diphenyl-2-propyn-1-ol (18 mg, 0.086 mmol) in 1,2-dichloroethane (20 mL) was stirred at reflux temperature for 45 min, whereupon 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 (1:1), the major band (yellow) afforded compound **6** upon extraction with dichloromethane and solvent removal (18 mg, 24%). Anal. Calcd for $C_{36}H_{20}N_2O_9Ru_3$ (fw 927.78): C, 46.61; H, 2.17; N, 3.02. Found: C, 46.69; H, 2.20; N, 3.00. FAB-MS (*m*/*z*): 929 [M^+]. IR (CH_2Cl_2): ν_{CO} 2082 (m), 2051 (s), 2021 (m), 2006 (m, sh), 1990 (m, br), 1965 (w, br) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 7.96 (d, J = 8.4, 1 H, bq), 7.75 (d, J = 8.9, 1 H, bq), 7.57−6.96 (m, 16 H), 4.84 (s, br, 1 H, N*H*), 0.52 (s, 1 H, O*H*). ^{13}C{^{1}H} NMR, DEPT (CD_2Cl_2): δ 294.5 (*C*CH), 202.0, 198.4, 195.7, 193.7, 192.1 (COs), 169.0 (C_{bq}), 158.3 (C_{bq}), 150.8 (C_{bq}), 148.9 (C_{Ph}), 148.8 (C_{Ph}), 137.9 (*C*H$_{bq}$), 137.6 (C_{bq}), 137.0 (*C*H$_{bq}$), 134.7 (C_{bq}), 129.6 (*C*H$_{bq}$), 128.6 (4 *C*H$_{Ph}$), 127.2 (*C*H$_{bq}$), 126.5 (2 *C*H$_{Ph}$), 125.3 (2 *C*H$_{Ph}$), 124.8 (2 *C*H$_{Ph}$), 123.0 (*C*H$_{bq}$), 121.6 (C_{bq}), 121.3 (*C*H$_{bq}$), 114.1 (*C*H$_{bq}$), 100.9 (C*C*H), 79.3 (*C*OH).

[Ru_3(μ_3-η^3(*C*,*N*$_2$)-Habq){μ_3-η^2-CCH(*c*-C$_5$H$_8$OH)}(CO)$_8$] (7). A solution of compound **1** (59 mg, 0.079 mmol) and 1-ethynylcyclopentanol (10 μL, 0.087 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. 2 mL of THF and placed onto silica gel TLC plates. After elution with dichloromethane/hexanes (2:3), the major band (yellow) af-

(24) Andreu, P. L.; Cabeza, J. A.; Miguel, D.; Riera, V.; Villa, M. A. *J. Chem. Soc., Dalton Trans.* **1991**, 533.

forded compound **7** upon extraction with dichloromethane and solvent removal (9 mg, 14%). Anal. Calcd for $C_{28}H_{18}N_2O_9Ru_3$ (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 [$M^+ - H_2O - CO$]. IR (CH_2Cl_2): ν_{CO} 2078 (m), 2049 (s), 2019 (m), 2006 (m, sh), 1992 (m, br), 1962 (w, sh) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 8.02 (t, J = 3.9, 1 H, bq), 7.93 (d, J = 8.7, 1 H, bq), 7.65 (d, J = 8.7, 1 H, bq), 7.57 (d, J = 3.9, 2 H, bq), 7.47 (d, J = 8.7, 1 H, bq), 7.04 (d, J = 8.7, 1 H, bq), 6.84 (s, 1 H, CC*H*), 5.93 (s, br, 1 H, O*H*), 4.84 (s, br, 1 H, N*H*), 2.15−2.05 (m, 3 H, CH_2), 1.71−1.62 (m, 1 H, CH_2), 1.29−1.20 (m, 2 H, CH_2), 0.31−0.21 (m, 1 H, CH_2), 0.03-(−0.05) (m, 1 H, CH_2). $^{13}C\{^1H\}$ NMR, DEPT (CD_2Cl_2, selected data): δ 169.0 (C_{bq}), 165.2 (C_{bq}), 150.9 (C_{bq}), 136.5 (C_{bq}), 135.5 (*C*H$_{bq}$), 133.5 (C_{bq}), 130.6 (*C*H$_{bq}$), 129.4 (*C*H$_{bq}$), 126.8 (*C*H$_{bq}$), 122.7 (*C*H$_{bq}$), 121.2 (*C*H$_{bq}$), 120.0 (C_{bq}), 114.1 (*C*H$_{bq}$), 99.7 (C*C*H), 59.6−58.6 (m, 4 *C*H$_2$).

[Ru$_3$(μ_3-η^5(*C*$_3$,*N*$_2$)-HabqCHCHCH$_2$)(μ-CO)$_2$(CO)$_6$] (8). A solution of compound **1** (50 mg, 0.067 mmol) and propargyl alcohol (5 μL, 0.091 mmol) in 1,2-dichloroethane (20 mL) was heated at reflux temperature for 30 min. The color changed to dark orange. The solvent was removed under reduced pressure, and the residue was redissolved in ca. 2 mL of dichloromethane and was placed onto silica gel TLC plates. After elution with dichloromethane/hexanes (1:1), the major band (yellow) gave compound **8** upon extraction with dichloromethane and solvent removal (8 mg, 16%). Anal. Calcd for $C_{24}H_{12}N_2O_8Ru_3$ (fw 759.58): C, 37.95; H, 1.59; N, 3.69. Found: C, 37.58; H, 1.47; N, 3.41. FAB-MS (*m*/*z*): 733 [$M^+ - CO$]. IR (CH_2Cl_2): ν_{CO} 2058 (s), 2021 (vs), 1986 (s), 1959 (w, sh), 1866 (w, br), 1811 (m, br) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 8.32 (d, br, J = 7.4, 1 H, bq), 7.84 (d, br, J = 7.4, 1 H, bq), 7.77 (t, J = 7.4, 1 H, bq), 7.68 (d, J = 8.4, 1 H, bq), 7.61 (d, J = 8.4, 1 H, bq), 7.32 (d, J = 8.4, 1 H, bq), 6.23 (d, J = 8.4, 1 H, bq), 5.41 (d, J = 10.8, 1 H, C*H*, allyl), 4.99 (dd, J = 7.4, 2.5, 1 H, CH_2, allyl), 2.71 (s, br, 1 H, N*H*), 2.52 (ddd, J = 15.3, 10.8, 7.4, 1 H, C*H*, allyl), −1.04 (dd, J = 15.3, 2.5, 1 H, CH_2, allyl). $^{13}C\{^1H\}$ NMR, DEPT (CD_2Cl_2): δ 253.3, 244.3, 198.5, 195.9, 195.8, 194.3, 192.1, 191.2 (COs), 169.0 (C_{bq}), 145.3 (C_{bq}), 140.2 (*C*H$_{bq}$), 137.6 (C_{bq}), 136.2 (C_{bq}), 130.9 (*C*H$_{bq}$), 129.0 (*C*H$_{bq}$), 128.4 (*C*H$_{bq}$), 127.7 (*C*H$_{bq}$), 127.4 (C_{bq}), 124.5 (*C*H$_{bq}$), 122.0 (C_{bq}), 113.9 (*C*H$_{bq}$), 67.2 (*C*H), 46.1 (*C*H), 23.6 (*C*H$_2$).

[Ru$_3$(μ_3-η^3(*C*,*N*$_2$)-Habq)(μ_3-η^2-CCHCH$_2$C≡CSiMe$_3$)-(CO)$_8$] (9) and [Ru$_3$(μ_3-η^5(*C*$_3$,*N*$_2$)-HabqCHCHCHC≡CSiMe$_3$)-(μ-CO)$_2$(CO)$_6$] (10). A solution of compound **1** (100 mg, 0.134 mmol) and 1-(trimethylsilyl)penta-1,4-diyne (25 μL, 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 several bands. The three major bands were worked up. The first band (orange) rendered the known complex [Ru$_3$(μ-H)$_2$(μ_3-η^3(*C*,*N*$_2$)-Habq)$_2$(CO)$_6$] upon extraction with dichloromethane and solvent removal (6 mg, 5%). The second band (yellow) afforded compound **9** upon extraction with dichloromethane and solvent removal (7 mg, 6%). The fifth band (yellow) gave compound **10** upon extraction with dichloromethane and solvent removal (13 mg, 11%). Data for **9** are as follows. Anal. Calcd for $C_{29}H_{20}N_2O_8Ru_3Si$ (fw 855.79): C, 40.70; H, 2.36; N, 3.27. Found: C, 41.02; H, 2.50; N, 3.20. FAB-MS (*m*/*z*): 857 [M^+]. IR (CH_2Cl_2): ν_{CO} 2080 (m), 2050 (s), 2021 (m), 2009 (m, sh), 1988 (m, br), 1962 (w, br) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 8.37 (dd, J = 4.8, 3.2, 1 H, bq), 7.92 (d, J = 8.3, 1 H, bq), 7.66 (d, J = 8.3, 1 H, bq), 7.64−7.61 (m, 2 H, bq), 7.47 (d, J = 8.7, 1 H, bq), 7.00 (d, J = 8.7, 1 H, bq), 5.81 (dd, J = 7.6, 4.8, 1 H, CC*H*), 4.85 (s, br, 1 H, N*H*), 2.25 (dd, J = 17.9, 4.8, 1 H, CH_2), 1.90 (dd, J = 17.9, 7.6, 1 H, CH_2), 0.12 (s, 9 H, Si*Me*$_3$). Data for **10** are as follows. Anal. Calcd for $C_{29}H_{20}N_2O_8Ru_3Si$ (fw = 855.79): C, 40.70; H, 2.36; N, 3.27. Found: C, 41.10; H, 2.54; N, 3.17. FAB-MS (*m*/*z*): 857 [M^+]. IR (CH_2Cl_2): ν_{CO} 2059 (s), 2025 (vs), 1989 (s), 1965 (w, sh), 1866 (w, br), 1812 (m, br) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 8.40 (d, br, J = 7.6, 1 H, bq), 7.91 (d, br, J = 7.6, 1 H, bq), 7.78 (t, J = 7.6, 1 H, bq), 7.72 (d, J = 8.7, 1 H, bq), 7.65 (d, J = 8.7, 1 H, bq), 7.36 (d, J = 8.3, 1 H, bq), 6.27 (d, J = 8.3, 1 H, bq), 6.19 (d, J = 8.7, 1 H, C*H*, allyl), 5.51 (d, J = 10.7, 1 H, C*H*, allyl), 2.84 (s, br, 1 H, N*H*), 1.89 (dd, J = 10.7, 8.7, 1 H, C*H*, allyl), −0.76 (s, 9 H, Si*Me*$_3$). $^{13}C\{^1H\}$ NMR, DEPT (CD_2Cl_2): δ 252.1, 243.0, 199.6, 197.2, 197.1, 195.4, 194.6, 193.8 (COs), 170.0 (C_{bq}), 147.1 (C_{bq}), 140.1 (*C*H$_{bq}$), 135.3 (C_{bq}), 134.9 (C_{bq}), 130.9 (*C*H$_{bq}$), 128.8 (C_{bq}), 128.2 (*C*H$_{bq}$), 128.1 (*C*H$_{bq}$), 127.2 (*C*H$_{bq}$), 124.0 (*C*H$_{bq}$), 121.6 (C_{bq}), 114.1 (*C*H$_{bq}$), 107.1 (*C*), 82.7 (*C*), 59.2 (*C*H), 45.1 (*C*H), 16.3 (*C*H), −0.9 (Si*Me*$_3$).

[Ru$_3$(μ_3-η^3(*C*,*N*$_2$)-Habq)$_2$(μ-CO)(CO)$_6$] (11). Method a. A THF solution (20 mL) of complex **1** (50 mg, 0.067 mmol) and 3-hexyne (9 μL, 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. The two major bands, first (yellow) and fifth (orange), led to [Ru$_3$(μ_3-η^4-EtC=CEtCEt=CEt)(μ-CO)$_2$(CO)$_6$] (8 mg) and compound **11** (9 mg, 30% based on Habq), respectively, after extraction with dichloromethane and solvent removal.

Method b. A THF solution (20 mL) of complex **1** (50 mg, 0.067 mmol) and diphenylacetylene (13 mg, 0.073 mmol) was heated at reflux temperature for 70 min. The solvent was evaporated under reduced pressure to ca. 3 mL, and the resulting solution was subjected to a TLC separation on silica gel, using dichloromethane/hexanes (1:2) as eluant. The major band (orange) led to compound **11** (7 mg, 24% based on Habq) after extraction with dichloromethane and solvent removal. Data for **11** are as follows. Anal. Calcd for $C_{33}H_{16}N_4O_7Ru_3$ (fw 883.71): C, 44.85; H, 1.82; N, 6.34. Found: C, 45.23; H, 1.91; N, 6.23. FAB-MS (*m*/*z*): 885 [M^+]. IR (CH_2Cl_2): ν_{CO} 2055 (s), 2027 (vs), 1997 (m), 1987 (m), 1963 (m), 1940 (w, sh), 1883 (w, br) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 8.30 (dd, J = 6.3, 1.7, 1 H), 7.61−7.56 (m, 2 H), 7.49 (d, J = 8.4, 1 H), 6.93 (d, J = 8.5, 1 H), 6.71 (d, J = 8.5, 1 H), 6.15 (d, J = 8.5, 1 H), 4.91 (s, br, 1 H, N*H*). $^{13}C\{^1H\}$ NMR, DEPT (CD_2Cl_2): δ 206.6, 200.3, 198.5 (COs), 164.6 (*C*), 163.9 (*C*), 150.3 (*C*), 138.7 (*C*), 136.4 (*C*H), 135.5 (*C*), 134.2 (*C*H), 128.3 (*C*H), 126.5 (*C*H), 122.4 (*C*H), 121.9 (*C*H), 121.4 (*C*), 119.2 (*C*H). Data for [Ru$_3$(μ_3-η^4-EtC=CEtCEt=CEt)(μ-CO)$_2$(CO)$_6$] are as follows. Anal. Calcd for $C_{20}H_{20}O_8Ru_3$ (fw = 691.59): C, 34.74; H, 2.91. Found: C, 34.56; H, 3.02. FAB-MS (*m*/*z*): 693 [M^+]. IR (CH_2Cl_2): ν_{CO} 2061 (m), 2020 (vs), 1996 (m), 1966 (m), 1867 (m, br), 1840 (m, br) cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.06 (q, J = 7.5, 2 H), 1.50 (m, 5 H), 0.51 (t, J = 7.5, 3 H).

[Ru$_3$(μ-H)(μ_3-η^3(*C*,*N*$_2$)-Habq)(CO)$_9$][BF$_4$] (12). Tetrafluoroboric acid (67 μL, 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%). Anal. Calcd for $C_{22}H_9BF_4N_2O_9Ru_3$ (fw 835.37): C, 31.63; H, 1.09; N, 3.35. Found: C, 31.93; H, 1.26; N, 3.26. FAB-MS (*m*/*z*): 750 [$M^+ - BF_4$]. IR (CH_2Cl_2): ν_{CO} 2127 (m), 2104 (vs), 2073 (vs), 2052 (s), 2000 (m, br), 1953 (w, br) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 8.31 (d, J = 8.8, 1 H), 8.26 (d, J = 7.2, 1 H), 7.99 (d, J = 8.0, 1 H), 7.89−7.82 (m, 2 H), 7.70 (t, J = 8.8, 2 H), 7.62 (s, br, 1 H, N*H*), −13.18 (s, 1 H, μ-H). $^{13}C\{^1H\}$ NMR, DEPT (CD_2Cl_2): δ 213.2 (2 CO), 194.6 (CO), 192.8 (2 CO), 186.3 (2 CO), 178.4 (2 CO), 174.2 (*C*), 151.9 (*C*), 150.4 (*C*), 140.7 (*C*H), 140.5 (*C*), 140.1 (*C*H), 135.6 (*C*), 132.0 (*C*H), 127.9 (*C*H), 125.0 (*C*H), 124.0 (*C*H), 123.8 (*C*), 113.5 (*C*H).

Reaction of Compound 1 with Hydrogen. Hydrogen was gently bubbled for 3.5 h through a solution of compound **1** (50 mg, 0.067 mmol) in THF (25 mL) at room temperature. The color changed from orange to tawny. IR monitoring showed the complete disappearance of the starting material. The solvent was removed under reduced pressure. The ^1H NMR

Table 3. Crystal, Measurement, and Refinement Data for the Compounds Studied by X-ray Diffraction Methods

	5	**8**·CH_2Cl_2	**11**	**16**·0.25C_6H_{14}
formula	$C_{16}H_{16}N_2O_9Ru_3$	$C_{25}H_{14}Cl_2N_2O_8Ru_3$	$C_{33}H_{16}N_4O_7Ru_3$	$C_{30.5}H_{29.5}N_2O_8Ru_3Sn$
formula wt	803.62	844.49	883.71	970.43
cryst syst	monoclinic	triclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P2_1/c$
a, Å	18.8779(4)	8.7066(3)	7.4346(10)	13.3400(10)
b, Å	17.1865(4)	9.4704(3)	20.515(3)	11.9377(7)
c, Å	17.8513(4)	16.0495(5)	19.854(3)	21.5467(14)
α, deg	90	78.350(2)	90	90
β, deg	113.396(1)	85.847(2)	100.515(8)	92.751(4)
γ, deg	90	85.284(3)	90	90
V, Å^3	5315.6(2)	1289.60(7)	2977.3(7)	3427.3(4)
Z	8	2	4	4
F(000)	3120	816	1720	1876
D_{calcd}, g cm^{-3}	2.008	2.175	1.971	1.881
radiation (λ, Å)	Cu Kα (1.541 80)	Cu Kα (1.541 80)	Cu Kα (1.541 80)	Cu Kα (1.541 80)
μ, mm^{-1}	14.137	16.442	12.669	16.647
cryst size, mm	0.18 × 0.15 × 0.15	0.20 × 0.15 × 0.10	0.18 × 0.03 × 0.03	0.25 × 0.10 × 0.05
temp, K	120(2)	120(2)	150(2)	120(2)
θ limits, deg	2.55−68.28	2.82−68.44	3.12−66.97	3.82−68.41
h, k, l	−22 to +20, −20 to 0, 0−21	0−10, −11 to +11, −19 to +19	0−8, 0−20, −22 to +20	0−15, 0−14, −25 to +25
no. of collected rflns	51 056	21 794	6398	11 974
no. of unique rflns	9735	4742	3914	6109
no. of rflns with $I > 2\sigma(I)$	8630	4639	1610	3181
abs cor	XABS2	XABS2	XABS2	SORTAV
max/min transmissn	0.125/0.115	0.193/0.098	0.725/0.105	0.430/0.175
no. of params/restraints	727/2	389/0	424/0	400/2
GOF on F^2	1.135	1.109	1.009	0.947
R1 (on F, $I > 2\sigma(I)$)	0.0407	0.0379	0.0630	0.0839
wR2 (on F^2, all data)	0.1600	0.1206	0.1563	0.2431
max/min $\Delta\rho$, e Å^{-3}	2.080/−1.122	1.648/−1.534	1.044/−1.012	2.043/−1.334

spectrum of the residue showed that it only contained H_2abqH and [$Ru_4(\mu\text{-H})_4(CO)_{12}$].

[$Ru_3(\mu\text{-H})(\mu_3\text{-}\eta^3(C,N_2)\text{-Habq})(SnPh_3)(CO)_8$] (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 × 10 mL) to give compound **13** as an orange solid (75 mg, 74%). Anal. Calcd for $C_{39}H_{24}N_2O_8Ru_3Sn$ (fw 1070.56): C, 43.76; H, 2.26; N, 2.62. Found: C, 44.01; H, 2.33; N, 2.51. IR (CH_2Cl_2): ν_{CO} 2084 (m), 2041 (s), 2022 (vs), 2011 (m, sh), 1964 (m, br) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 8.27 (d, J = 6.4, 1 H, bq), 7.99 (d, J = 8.9, 1 H, bq), 7.84−7.62 (m, 6 H, bq + Ph), 7.56 (d, J = 8.4, 1 H, bq), 7.54−7.20 (m, 12 H, Ph), 6.41 (d, J = 8.9, 1 H, bq), 4.04 (s, br, 1 H, N*H*), −12.74 (s, sat, J_{H-Sn} = 40.8, 1 H, μ-H).

[$Ru_3(\mu\text{-H})(\mu_3\text{-}\eta^3(C,N_2)\text{-Habq})(SnBu_3)(CO)_8$] (14). Tributyltin hydride (18 μL, 0.067 mmol) was added to a solution of compound **1** (50 mg, 0.067 mmol) in dichloromethane (20 mL). After 15 min, the solvent was removed under reduced pressure to give compound **14** as an orange oil. $C_{33}H_{36}N_2O_8Ru_3Sn$ (fw 1010.59). IR (CH_2Cl_2): ν_{CO} 2079 (m), 2036 (s), 2015 (vs), 2003 (m, sh), 1956 (m, br) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 8.25 (dd, J = 6.4, 1.0, 1 H, bq), 8.02 (d, J = 8.4, 1 H, bq), 7.82−7.71 (m, 3 H, bq), 7.56 (d, J = 8.9, 1 H, bq), 6.83 (d, J = 8.4, 1 H, bq), 4.33 (s, br, 1 H, N*H*), 1.73−0.61 (m, 27 H, 3 Bu), −12.82 (s, sat, J_{H-Sn} = 36.0, 1 H, μ-H).

[$Ru_3(\mu_3\text{-}\eta^3(C,N_2)\text{-Habq})(\mu\text{-SnPh}_2)(\mu\text{-CO})(CO)_7$] (15). A solution of compound **13** (50 mg, 0.047 mmol) in THF (15 mL) was heated at reflux temperature for 10 min. The color changed from orange to dark red. IR monitoring of the solution showed the quantitative formation of a new compound. The solvent was removed under reduced pressure to give compound **15** as a red solid. Anal. Calcd for $C_{33}H_{18}N_2O_8Ru_3Sn$ (fw 992.45): C, 33.94; H, 1.83; N, 2.82. Found: C, 33.66; H, 1.98; N, 2.70. FAB-MS (m/z): 937 [M^+ − 2 CO]. IR (CH_2Cl_2): ν_{CO} 2063 (m), 2019 (s, sh), 2010 (vs), 1991 (m, br), 1968 (m, br), 1948 (w, sh), 1848 (w, br) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 8.31 (d, J = 7.2, 1 H, bq), 7.88 (dd, J = 7.2, 2.0, 1 H, bq), 7.68 (d, J = 8.0, 1 H, Ph), 7.54−7.49 (m, 8 H, bq + Ph), 7.35 (d, J = 8.8, 1 H, bq), 7.05 (d, J = 8.8, 1 H, bq), 6.80 (td, J = 7.6, 1.2, 1 H, Ph), 6.72 (d, J = 8.4, 1 H, Ph), 6.60 (t, J = 7.6, 1 H, Ph), 5.69 (dd, J = 7.6, 1.2, 1 H, Ph), 4.26 (s, br, 1 H, N*H*).

[$Ru_3(\mu_3\text{-}\eta^3(C,N_2)\text{-Habq})(\mu\text{-SnBu}_2)(\mu\text{-CO})(CO)_7$] (16). A solution of compound **14** in THF (15 mL) was heated at reflux temperature for 20 min. The color changed from orange to dark red. The solvent was removed under reduced pressure, and the solid residue was extracted with hexanes (1 × 20 mL) to afford compound **16** as a red solid after solvent removal (37 mg, 58%). Anal. Calcd for $C_{29}H_{26}N_2O_8Ru_3Sn$ (fw 952.47): C, 36.57; H, 2.75; N, 2.94. Found: C, 36.70; H, 2.79; N, 2.88. FAB-MS (m/z): 841 [M^+ − 4 CO]. IR (CH_2Cl_2): ν_{CO} 2063 (m), 2018 (s, sh), 2008 (vs), 1980 (m, br), 1968 (m, br), 1945 (w, sh), 1843 (w, br) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 8.28 (d, J = 7.1, 1 H, bq), 7.94 (d, J = 8.3, 1 H, bq), 7.79 (d, J = 7.5, 1 H, bq), 7.69−7.57 (m, 3 H, bq), 6.78 (d, J = 8.3, 1 H, bq), 4.08 (s, br, 1 H, N*H*), 1.98−1.83 (m, 2 H, Bu), 1.44−1.31 (m, 3 H, Bu), 0.98−0.89 (m, 5 H, Bu), 0.40−0.38 (m, 6 H, Bu), −0.43- −0.64 (m, 2 H, Bu).

X-ray Structures of Compounds 5, 8·CH_2Cl_2, 11, and 16·0.25C_6H_{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 κ goniostat, using graphite-monochromated Cu Kα radiation. Data were reduced to F_o^2 values. Empirical absorption corrections were applied using XABS2[25] for **5**, **8**·CH_2Cl_2, and **11** or SORTAV[26] for **16**·0.25C_6H_{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 SHELXL-

(25) Parkin, S.; Moezzi, B.; Hope, H. *J. Appl. Crystallogr.* **1995**, *28*, 53.

(26) Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33.

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

97.[28] All non-H atoms were refined anisotropically. The NH hydrogen atoms of **5** and **11** and all nonaromatic hydrogen atoms of **8**·CH_2Cl_2 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**·$0.25C_6H_{14}$, 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.[29] The WINGX program system[30] was used throughout the structure determinations.

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

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**·CH_2Cl_2, **11**, and **16**·$0.25C_6H_{14}$. This material is available free of charge via the Internet at http://pubs.acs.org.

OM049797J

(29) Spek, A. L. The EUCLID Package. In *Computational Crystallography*; Sayre, D., Ed.; Clarendon Press: Oxford, U.K., 1982; p 528.
(30) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837.