Organometallics 1993, 12, 2973–2979

Incorporation of Silanes and Diphenylacetylene into Face-Bridged Triruthenium Carbonyl Clusters. Attempted Hydrosilylation of Diphenylacetylene

Javier A. Cabeza,*[1a] Santiago García-Granda,[1b] Angela Llamazares,[1a]
Víctor Riera,[1a] and Juan F. Van der Maelen[1b]

Departamento de Química Organometálica and Departamento de Química Física y Analítica, Universidad de Oviedo, 33071 Oviedo, Spain

Received February 23, 1993

Although the cluster complexes $[Ru_3(\mu\text{-H})(\mu_3,\eta^2\text{-ampy})(CO)_9]$ and $[Ru_3(\mu\text{-H})(\mu_3,\eta^2\text{-ampy})(CO)_8(PPh_3)]$ (Hampy = 2-amino-6-methylpyridine) react with silanes and diphenylacetylene to form compounds in which SiR_3 and diphenylalkenyl groups coexist in the ligand shell of triruthenium clusters, they do not promote the hydrosilylation of diphenylacetylene because, in all cases, the products have the SiR_3 and diphenylalkenyl ligands attached to different ruthenium atoms. The new compounds $[Ru_3(\mu\text{-H})_2(\mu_3,\eta^2\text{-ampy})\{Si(OMe)_3\}(CO)_8]$, $[Ru_3(\mu\text{-H})(\mu_3,\eta^2\text{-ampy})(SiR_3)_2(CO)_8]$ (R = Et, OMe), $[Ru_3(\mu_3,\eta^2\text{-ampy})\{\mu,\eta^1{:}\eta^2\text{-PhC}{=}C(H)Ph\}(SiR_3)(CO)_7]$ (R = Et, OMe), $[Ru_3(\mu_3,\eta^2\text{-ampy})\{\mu,\eta^1{:}\eta^2\text{-PhC}{=}C(H)Ph\}(CO)_7(PPh_3)]$, and $[Ru_3(\mu\text{-H})(\mu_3,\eta^2\text{-ampy})\{\mu,\eta^1{:}\eta^2\text{-PhC}{=}C(H)Ph\}(SiEt_3)(CO)_6(PPh_3)]$ have been isolated and characterized by analytical and spectroscopic (IR, NMR) methods; the last complex has also been studied by X-ray diffraction methods: $C_{50}H_{49}N_2O_6PRu_3Si$, monoclinic, space group $P2_1/n$, $a = 10.731(5)$ Å, $b = 28.577(7)$ Å, $c = 15.729(7)$ Å, $\beta = 91.47(3)°$, $V = 4822(3)$ Å^3, $Z = 4$, $R = 0.034$, $R_w = 0.031$ for 3810 reflections and 685 variables.

Introduction

Transition-metal carbonyl clusters are effective catalyst precursors for many transformations of organic substrates.[2] However, despite the current interest in hydrosilylation reactions,[3] the application of metal carbonyl cluster complexes as catalyst precursors for such reactions remains nearly unexplored.[2–7] In fact, as far as ruthenium carbonyl clusters are concerned, the compounds $[Ru_3(CO)_{12}]$ and $[Ru_3(\mu\text{-H})(CO)_{11}]^-$ are the only ones which have been studied in silylation reactions.[5,6]

In previous papers, we reported that the face-bridged cluster complex $[Ru_3(\mu\text{-H})(\mu_3,\eta^2\text{-ampy})(CO)_9]$[8] (1) (Hampy = 2-amino-6-methylpyridine) is an efficient catalyst precursor for the homogeneous hydrogenation of unsaturated organic substrates under mild conditions,[9] and that 1 and its phosphine-substituted derivatives $[Ru_3(\mu\text{-H})(\mu_3,\eta^2\text{-ampy})(CO)_{9-n}(PPh_3)_n]$[10] ($n = 1, 2$) react readily with triethylsilane to give the hydridosilyl derivatives $[Ru_3(\mu\text{-H})_2(\mu_3,\eta^2\text{-ampy})(SiEt_3)(CO)_{8-n}(PPh_3)_n]$ ($n = 0$–2).[11] Also from previous work, we knew that complex 1 reacts with diphenylacetylene to give the $\mu,\eta^1{:}\eta^2$-alkenyl derivative $[Ru_3(\mu_3,\eta^2\text{-ampy})\{\mu,\eta^1{:}\eta^2\text{-PhC}{=}C(H)Ph\}(CO)_8]$ (2).[9,12] All these data prompted us to attempt the hydrosilylation of diphenylacetylene under homogeneous conditions using complex 1 as a catalyst precursor.

We now report that complex 1 and its phosphine-substituted derivative $[Ru_3(\mu\text{-H})(\mu_3,\eta^2\text{-ampy})(CO)_8(PPh_3)]$ react with diphenylacetylene and hydrosilanes to give compounds in which SiR_3 and diphenylalkenyl groups coexist in the ligand shell of triruthenium clusters; however, they do not promote the hydrosilylation of diphenylacetylene because the arrangement of the ligands in the clusters does not favor the reductive elimination of the silylated organic fragment.

We initially used triethylsilane as the silylating reagent, but in order to know whether or not the obtained results could be extended to other silanes, we also carried out the reactions using trimethoxysilane.

Results

Attempted Catalytic Hydrosilylation of Diphenylacetylene. No hydrosilylated diphenylacetylene was produced when triethylsilane (or trimethoxysilane), diphenylacetylene, and complex 1 (100:75:1 mole ratio) were

---

(1) (a) Departamento de Química Organometálica. (b) Departamento de Química Física y Analítica.

(2) Gladfelter, W. L.; Roesselet, K. J. In *The Chemistry of Metal Cluster Complexes*; Shriver, D. F., Kaesz, H. D., Adams, R. D., Eds.; VCH Publishers: New York, 1990; Chapter 7.

(3) See, for example: (a) *Comprehensive Handbook on Hydrosilylation*; Marciniec, B., Ed.; Pergamon Press: Oxford, England, 1992. (b) Ojima, I. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley and Sons: New York, 1989; Chapter 25. (c) Speier, J. L. *Adv. Organomet. Chem.* **1979**, *17*, 407. (d) Noels, A. F.; Hubert, A. J. In *Industrial Applications of Homogeneous Catalysis*; Mortreux, A., Petit, F., Eds.; D. Reidel: Boston, MA, 1988; Chapter 3.1.3.

(4) (a) Ojima, I.; Donovan, R. J.; Clos, N. *Organometallics* **1991**, *10*, 2606 and references cited therein. (b) Matsuda, I.; Ogiso, A.; Sato, S.; Izumi, Y. *J. Am. Chem. Soc.* **1989**, *111*, 2332. (c) Ojima, I.; Ingallina, P.; Donovan, R. J.; Clos, N. *Organometallics* **1991**, *10*, 38.

(5) (a) Seki, Y.; Takeshita, K.; Kawamoto, K.; Murai, S.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 928. (b) Ojima, I.; Fuchikami, T.; Yatabe, M. *J. Organomet. Chem.* **1984**, *260*, 335.

(6) (a) Süss-Fink, G.; Reiner, J. *J. Mol. Catal.* **1982**, *16*, 231. (b) Süss-Fink, G. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 73. (c) Süss-Fink, G.; Reiner, J. *J. Organomet. Chem.* **1981**, *221*, C36.

(7) Adams, R. D.; Cortopassi, J. E.; Pompeo, M. P. *Organometallics* **1992**, *11*, 1.

(8) Andreu, P. L.; Cabeza, J. A.; Riera, V.; Jeannin, Y.; Miguel, D. *J. Chem. Soc., Dalton Trans.* **1990**, 2201.

(9) Cabeza, J. A.; Fernández-Colinas, J. M.; Llamazares, A.; Riera, V. *J. Mol. Catal.* **1992**, *71*, L7.

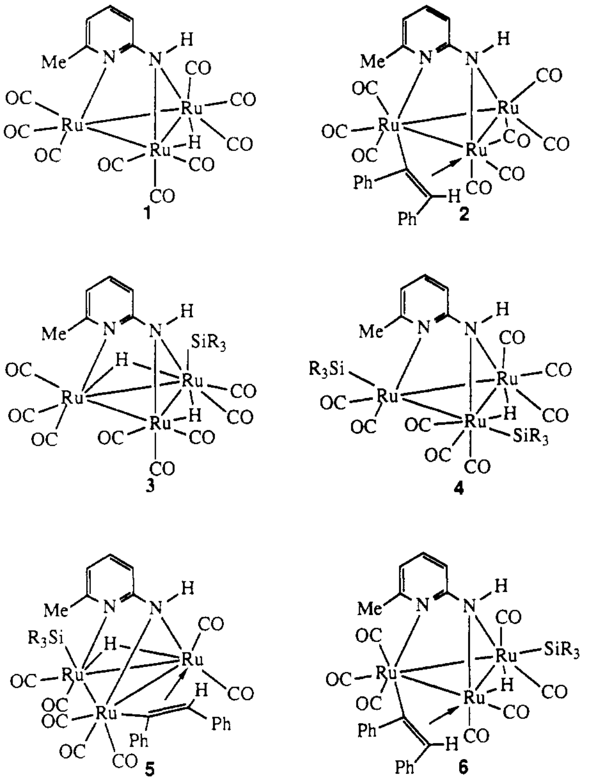
(10) (a) Andreu, P. L.; Cabeza, J. A.; Riera, V.; Bois, C.; Jeannin, Y. *J. Chem. Soc., Dalton Trans.* **1990**, 3347. (b) Andreu, P. L.; Cabeza, J. A.; Pellinghelli, M. A.; Riera, V.; Tiripicchio, A. *Inorg. Chem.* **1991**, *30*, 4611.

(11) Cabeza, J. A.; Llamazares, A.; Riera, V.; Triki, S.; Ouahab, L. *Organometallics* **1992**, *11*, 3334.

(12) Lugan, N.; Laurent, F.; Lavigne, G.; Newcomb, T. P.; Liimatta, E. W.; Bonnet, J.-J. *Organometallics* **1992**, *11*, 1351.

0276-7333/93/2312-2973$04.00/0

Chart I[a]



[a] R = Et (**a**), OMe (**b**).

allowed to react in toluene at 80 °C for 1 h.[13] Analogous results were obtained using the phosphine-substituted cluster [$Ru_3(\mu$-H)(μ_3,η^2-ampy)$(CO)_8(PPh_3)$] as the catalyst precursor.

Noncatalytic Reactions. The silanes $HSiEt_3$ and $HSi(OMe)_3$ behaved similarly in their reactions with the alkenyl complex [$Ru_3(\mu_3,\eta^2$-ampy){$\mu,\eta^1:\eta^2$-PhC=C(H)Ph}$(CO)_8$] (**2**) (see Chart I to identify the structures of the compounds which do not contain phosphine ligands), giving analogous mixtures of products (eqs 1 and 2). The reactions were carried out in THF, at room temperature, using a large excess of silane.

$$\mathbf{2} + HSiEt_3 \rightarrow \mathbf{3a}\ (36\%) + \mathbf{4a}\ (46\%) + \mathbf{5a}\ (18\%) \quad (1)$$

$$\mathbf{2} + HSi(OMe)_3 \rightarrow \mathbf{3b}\ (6\%) + \mathbf{4b}\ (75\%) + \mathbf{5b}\ (19\%) \quad (2)$$

On the other hand, it was observed that the behavior of the silyl derivatives [$Ru_3(\mu$-H$)_2(\mu_3,\eta^2$-ampy)$(SiR_3)(CO)_8$] (R = Et (**3a**), OMe (**3b**)) in their reactions with diphenylacetylene was quite different. Thus, the reaction of **3a** with diphenylacetylene proceeded at room temperature, rendering the alkenyl complex **2** when the reaction was carried out in THF (eq 3) or a mixture of products when the solvent was toluene (eq 4).

$$\mathbf{3a} + Ph_2C_2 \rightarrow \mathbf{2}\ (100\%) + HSiEt_3 \quad (3)$$

$$\mathbf{3a} + Ph_2C_2 \rightarrow \mathbf{2}\ (35\%) + \mathbf{4a}\ (49\%) + \mathbf{5a}\ (16\%) \quad (4)$$

Chart II

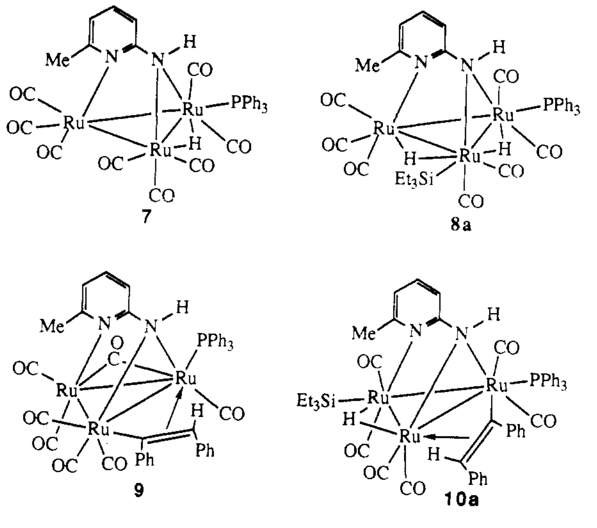


Table I. Carbonyl Stretching Absorptions

compd	ν(CO),[a] cm^{-1}
3b[b]	2083 (s), 2050 (s), 2029 (s), 2002 (s), 1984 (m), 1966 (m)
4a[c]	2069 (m), 2023 (s), 1995 (m), 1987 (m, sh), 1982 (w), 1965 (m), 1947 (w)
4b[b]	2075 (m), 2032 (s), 1997 (m), 1984 (m), 1971 (m), 1948 (w)
5a[c]	2063 (m), 2030 (s), 2009 (s), 1978 (m), 1944 (w)
5b[b]	2060 (m), 2026 (s), 2010 (s), 1998 (m, sh), 1976 (m), 1966 (m, sh), 1945 (w)
6b[b]	2057 (m), 2026 (s), 2015 (s), 1990 (m), 1976 (m), 1953 (w)
9[b]	2032 (m), 2000 (s), 1977 (m), 1963 (m), 1932 (s), 1912 (m), 1794 (w)
10a[b]	2022 (m), 1999 (s), 1973 (w), 1956 (m), 1942 (m), 1920 (w)

[a] Abbreviations are as follows: s = strong, m = medium, w = weak, sh = shoulder. [b] In THF. [c] In pentane.

However, no reaction was observed when **3b** was treated with diphenylacetylene in THF at room temperature, but a mixture of two products resulted at reflux temperature (eq 5).

$$\mathbf{3b} + Ph_2C_2 \rightarrow \mathbf{5b}\ (20\%) + \mathbf{6b}\ (80\%) \quad (5)$$

In all cases the mixtures were separated by chromatographic methods. The product ratios shown in eqs 1–5 were estimated by integrating the ^1H NMR spectra of the reaction mixtures prior to the chromatographic separations.

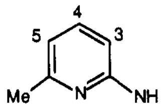
It was previously known[11] that the phosphine-substituted cluster [$Ru_3(\mu$-H)(μ_3,η^2-ampy)$(CO)_8(PPh_3)$] (**7**) (see Chart II to identify the structures of the compounds containing PPh_3) reacts with $HSiEt_3$ to give the silyl derivative [$Ru_3(\mu$-H$)_2(\mu_3,\eta^2$-ampy)$(SiEt_3)(CO)_7(PPh_3)$] (**8a**); however, the reactivity of **7** with diphenylacetylene needed yet to be determined. We have now found that the alkenyl complex [$Ru_3(\mu_3,\eta^2$-ampy){$\mu,\eta^1:\eta^2$-PhC=C(H)Ph}$(CO)_7(PPh_3)$] (**9**) is the only product of the reaction of complex **7** with diphenylacetylene.

Complex **8a** reacted with diphenylacetylene in refluxing 1,2-dichloroethane to give a mixture of products (complexes **7**, **9**, and **10a** were observed in the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture) from which the alkenylsilyl derivative [$Ru_3(\mu$-H)(μ_3,η^2-ampy){$\mu,\eta^1:\eta^2$-PhC=C(H)Ph}$(SiEt_3)(CO)_6(PPh_3)$] (**10a**) was separated and isolated in 32% yield. On the other hand, compound **10a**

---

[13] Small amounts of *cis*- and *trans*-stilbene, Si_2R_6, and some unidentified products could be detected by GC-MS. The metal-mediated dehydrogenation of silanes has been reported. See for example: Harrod, J. F.; Yun, S. S. *Organometallics* **1987**, *6*, 1381.

Table II. Selected ^1H NMR Data[a]



compd	H^5	H^4	H^3	NH	Me	μ-H	SiR_3	$CH_{alkenyl}$
3b	5.67 (d)	6.24 (t)	6.55 (d)	5.20 (s)	1.96 (s)	−9.76 (s), −12.16 (s)	3.71 (s)	
4a	5.85 (d)	6.40 (t)	5.84 (d)	3.78 (s)	2.10 (s)	−11.18 (s)	0.96 (m)	
4b	5.97 (d)	6.37 (t)	5.83 (d)	4.86 (s)	2.10 (s)	−11.41 (s)	3.59 (s), 3.38 (s)	
5a	5.99 (d)	6.42 (t)	5.24 (d)	2.78 (s)	2.62 (s)	−11.49 (s)	1.00 (m)	3.84 (s)
5b	6.06 (d)	6.39 (t)	5.22 (d)	*b*	2.91 (s)	−11.30 (s)	3.54 (s)	3.92 (s)
6b	5.93 (d)	6.49 (t)	5.83 (d)	5.80 (s)	1.99 (s)	−11.22 (s)	3.74 (s)	4.39 (s)
9	5.90 (d)	6.43 (t)	5.47 (d)	6.21 (d)[c]	2.66 (s)			3.10 (d)[d]
10a	6.01 (d)	6.51 (t)	5.50 (d)	2.76 (s)	2.71 (s)	−11.39 (d)[e]	0.95 (m)	4.27 (s)

[a] General information and conditions: spectra recorded in C_6D_6, at 300 MHz, 25 °C; chemical shifts (δ, ppm) relative to internal $SiMe_4$; multiplicities (s = singlet, d = doublet, t = triplet, m = multiplet) in parentheses; coupling constants J_{H-H} for H^5, H^4, and H^3 are *ca.* 7.4 Hz in all cases. The ^1H resonances of the phenyl fragments, although confirming their presence in the clusters, are uninformative multiplets. [b] Unobserved. [c] J_{H-P} = 5.5 Hz. [d] J_{H-P} = 3.0 Hz. [e] J_{H-P} = 2.3 Hz.

Table III. Selected ^{13}C NMR Data[a]

compd	CO	ampy	Et or OMe	$CH_{alkenyl}$
3b[b]	202.4 (d) [21.9], 201.6, 199.2 (d) [3.1], 196.9 (d) [7.0], 196.4 (d) [15.8], 194.2 (d) [5.5], 189.6 (d) [6.3], 182.7	180.2, 160.2, 139.3, 119.8, 111.5, 30.2	50.4	
4a[c]	207.4, 207.0, 206.8, 204.5 (d) [18.0], 200.6, 199.1, 189.8 (d) [23.0], 189.6	175.8, 158.5, 136.6, 117.5, 109.4, 28.7	11.6, 8.9, 7.7, 7.6	
4b[d]	205.0 (d) [17.0], 202.5, 201.9, 199.1 (d) [9.5], 198.7, 198.4, 189.8, 187.1	177.5, 158.8, 137.5, 118.4, 110.0, 31.1	49.5, 49.2	
5a[c]	204.7, 202.2, 201.9, 197.6 (d) [11.9], 195.2, 194.5, 193.4	173.7, 159.7, 137.5, 117.8, 110.2, 29.4	10.7, 7.7	79.2
5b[d]	203.4, 202.7, 200.8, 196.4 (d) [12.5], 195.9, 195.2, 194.1	173.5, 161.5, 138.1, 118.5, 110.4, 29.3	49.1	79.2
6b[b]	207.1, 203.7, 202.7 (d) [2.4], 200.7, 196.1, 195.4, 194.2 (d) [9.2]	174.9, 159.5, 140.3, 119.0, 114.9, 31.0	54.2	71.2
9[b]	235.9, 206.4, 206.2 (d) {6.7}, 205.6 (d) {5.1}, 204.1 (d) {9.2}, 201.2, 194.2 (d) {11.9}[e]	173.8, 161.4, 138.9, 119.2, 111.9, 31.1		83.3
10a[b]	209.5 (d) {6.6}, 207.6, 204.1, 201.0 (d) {4.7}, 199.8 (d) {4.7}, 195.7 (d) {12.4}[e]	175.1, 161.4, 138.7, 118.9, 112.5, 31.1	11.6, 8.9	79.6

[a] The data given for the carbonyl resonances correspond to proton-coupled spectra; the other ones are proton decoupled. Chemical shifts (δ, ppm) are relative to internal $SiMe_4$. Unless otherwise stated, all resonances are singlets; other multiplicities are given in parentheses; coupling constants (Hz) ar given in brackets [J_{C-H}] or braces {J_{C-P}}. [b] In CD_2Cl_2. [c] In C_6D_6. [d] In $CDCl_3$. [e] Proton-decoupled.

was the only product of the reaction of complex **9** with $HSiEt_3$ in refluxing THF. These two reactions did not work at room temperature.

Characterization of the Compounds. All new products were characterized by microanalysis and by IR (Table I) and NMR (Tables II and III) spectroscopies. Particularly, the structures shown in Chart I for the compounds of type **4**–**6** are proposed on the basis of the similarity of many of their physical (color, solubility, order of elution in chromatography), chemical (reactions in which they have been produced), and spectroscopic data with those reported for the triorganotin derivatives [$Ru_3(\mu\text{-}H)(\mu_3,\eta^2\text{-}$ampy$)(SnR_3)_2(CO)_8$] (analogous to **4**) and [$Ru_3(\mu\text{-}H)(\mu_3,\eta^2\text{-}$ampy$)\{\mu,\eta^1{:}\eta^2\text{-}PhC{=}C(H)Ph\}(SnR_3)(CO)_7$] (two isomers, analogous to **5** and **6**, identified by X-ray diffraction for R = Ph).[14] Thus, the ^1H and ^{13}C NMR spectra (Tables II and III) clearly showed the characteristic resonances of the ampy ligand (two doublets and one triplet for the aromatic protons and singlets for the NH and Me groups)[8,10,11,14] and the SiR_3 groups, as well as the corresponding $CH_{alkenyl}$ resonances (3.8–4.4 ppm in ^1H, 71–83 ppm in ^{13}C) for compounds **5a**, **5b**, **6b**, **9**, and **10a**;[14] the ^1H NMR spectra also showed the hydride ligands.

The number of CO ligands in complex **9** was inferred from its ^{13}C NMR spectrum (Table III), which shows seven resonances in the carbonyl region. The high frequency of one of them (235.9 ppm) is indicative of the presence of a bridging carbonyl (this ligand is also responsible for an absorption at 1794 cm^{-1} in the IR spectrum). The presence of a diphenylalkenyl group coordinated in a $\mu,\eta^1{:}\eta^2$ fashion[9,12,14] was confirmed by the ^1H and ^{13}C NMR spectra, which also suggested the structure shown in Chart II, since a coupling of 3.0 Hz between the alkenyl proton and the phosphorus nucleus was observed.

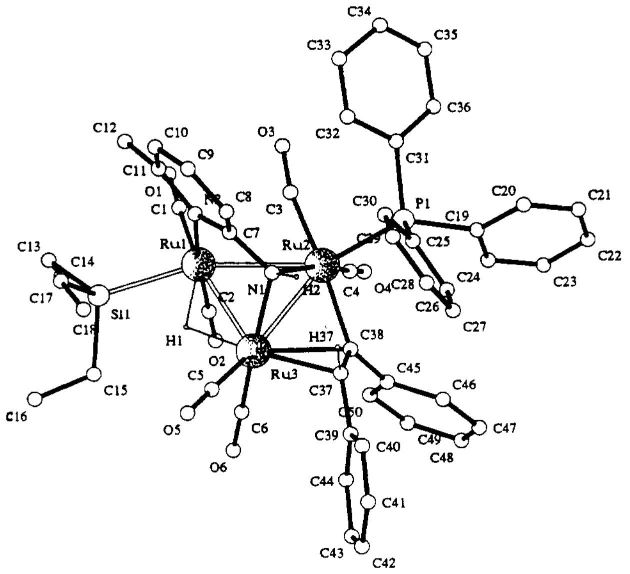


Figure 1. Molecular structure of [$Ru_3(\mu\text{-}H)(\mu_3,\eta^2\text{-}$ampy$)\{\mu,\eta^1{:}\eta^2\text{-}PhC{=}C(H)Ph\}(SiEt_3)(CO)_6(PPh_3)$] (**10a**).

The structure of complex **10a** (Figure 1) was determined by an X-ray diffraction study because its analytical and

---

(14) Cabeza, J. A.; García-Granda, S.; Llamazares, A.; Riera, V.; Van der Maelen, J. F. *Organometallics* **1993**, *12*, 157.

Table IV. Selected Bond Lengths (Å) and Bond Angles (deg) in 10a (with Esd's)

Bond Lengths			
Ru(1)-Ru(2)	2.929(1)	Ru(1)-Ru(3)	2.873(1)
Ru(2)-Ru(3)	2.692(1)	Ru(1)-Si(1)	2.432(2)
Ru(2)-P(1)	2.362(2)	Ru(1)-N(2)	2.228(6)
Ru(2)-N(1)	2.166(6)	Ru(3)-N(1)	2.135(6)
Ru(3)-C(37)	2.249(7)	Ru(3)-C(38)	2.232(7)
Ru(2)-C(38)	2.135(7)	C(37)-C(38)	1.40(1)
Ru(1)-H(1)	1.86(6)	Ru(3)-H(1)	1.74(6)
Bond Angles			
Ru(1)-Ru(2)-Ru(3)	61.30(4)	Ru(1)-Ru(3)-Ru(2)	63.44(4)
Ru(2)-Ru(1)-Ru(3)	55.27(4)	Ru(2)-Ru(1)-Si(1)	156.3(1)
Ru(3)-Ru(1)-Si(1)	101.3(1)	C(38)-Ru(2)-Ru(1)	100.9(2)
C(38)-Ru(2)-Ru(3)	53.6(3)	C(38)-Ru(3)-Ru(1)	109.9(2)
C(38)-Ru(3)-Ru(2)	50.3(2)	C(37)-Ru(3)-Ru(1)	141.4(2)
C(37)-Ru(3)-Ru(2)	78.0(2)	Ru(2)-C(38)-Ru(3)	76.1(2)
C(38)-C(37)-Ru(3)	71.1(4)	C(37)-C(38)-Ru(2)	123.2(6)
C(37)-C(38)-Ru(3)	72.5(4)	C(38)-Ru(2)-P(1)	94.9(2)

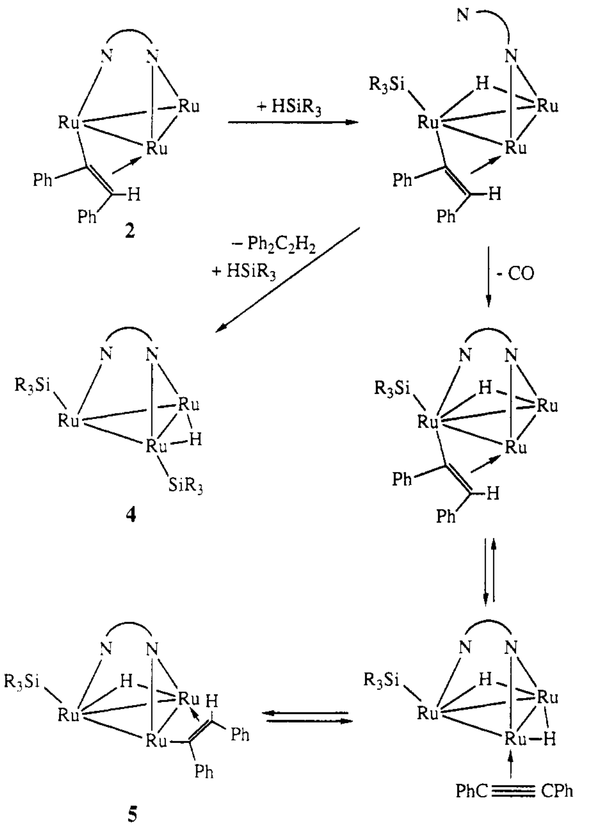
spectroscopic data, although confirming the presence of all the cluster ligands, were again insufficient to precisely assign the positions of the ligands on the cluster. The cluster consists in a triangular array of ruthenium atoms triply bridged by the ampy ligand, with the two shortest edges, Ru(1)-Ru(3) = 2.873(1) Å and Ru(2)-Ru(3) = 2.692(1) Å, also bridged by hydrido and diphenylalkenyl ligands, respectively. The μ_3,η^2-ampy ligand occupies three axial coordination sites, being linked to the Ru(1) atom through the pyridinic nitrogen N(2) and to the other two Ru atoms through the exocyclic nitrogen N(1). The alkenyl group spans the same metal edge as the amido fragment of the ampy ligand, being σ-bound to the Ru(2) atom through the α-carbon atom C(38) and π-bound to the Ru(3) atom through both the α- and β-carbon atoms C(38) and C(37). A $SiEt_3$ group is coordinated, in an equatorial position, to the Ru(1) atom through the silicon atom, being cis to the hydride H(1). The cluster coordination shell is completed by a PPh_3 ligand (in an equatorial site on Ru(2), cis to the alkenyl ligand) and by six carbonyl ligands (three in axial and three in equatorial positions).

The molecular structure of **10a** is related to that of complex **5a** and can be described as the result of a formal substitution of triphenylphosphine for the equatorial carbonyl of **5a** that is cis to the alkenyl group on the Ru atom unbound to the hydride ligand. In fact, the structural parameters of **10a** (Table IV) can be compared to those described for the cluster $[Ru_3(\mu\text{-}H)(\mu_3,\eta^2\text{-ampy})\{\mu,\eta^1:\eta^2\text{-}PhC{=}C(H)Ph\}(SnPh_3)(CO)_7]$, which is isostructural with **5a**.[14]

Discussion

The results described above for the reactions involving trimethoxysilyl (but not triethylsilyl) derivatives (as either reagents or products) match those reported in a previous work for analogous reactions involving triorganostannyl derivatives,[14] indicating that the chemical behavior of $HSi(OMe)_3$, although comparable to that of $HSiEt_3$ in many reactions, is more similar to that of $HSnR_3$ than that of $HSiEt_3$.[15] This, coupled to the fact that the hydrido–stannyl clusters are much more stable than the analogous hydrido–silyl derivatives toward the elimination of trialkylstannane or trialkylsilane, respectively,[11] may explain the results described by eqs 1–5.

Scheme I. Proposed Pathways for the Formation of 4 and 5 from 2 and $HSiR_3$[a]



[a] Carbonyl ligands have been omitted for clarity.

Thus, although the products of eqs 1 and 2, which involve the reactions of complex **2** with $HSiEt_3$ and $HSi(OMe)_3$, are entirely analogous (Scheme I), the reactions of the silyl derivatives **3a** and **3b** with diphenylacetylene are quite different; in fact, complex **2**, which is a product in eq 4 and the only product in eq 3 (a donor solvent seems to promote the substitution of diphenylacetylene for $HSiEt_3$ in complex **3a**), is absent in eq 5 (Scheme II). This seems to be a consequence of the fact that, as discussed above, the reductive elimination of $HSiEt_3$ from **3a** to give complex **2**, in the presence of diphenylacetylene (Scheme III), has to be easier than the elimination of $HSi(OMe)_3$ from **3b**.

The mechanistic aspects and reaction pathways that lead to the formation of complexes of types **4–6** in this class of reactions have been previously discussed[14] and are summarized in Schemes I and II. Similar principles would explain the formation of the phosphine-substituted derivative **10a** from **8a** and **9**.

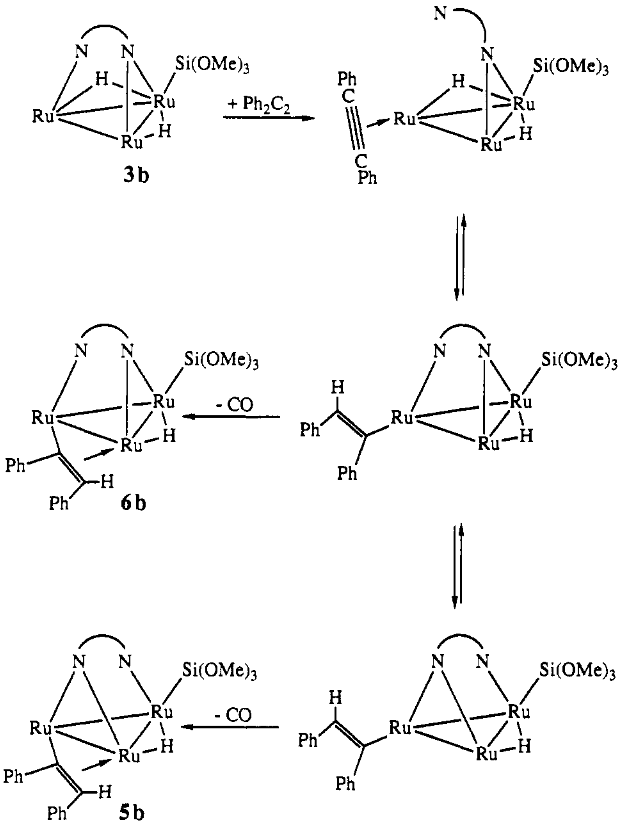
Concerning the structures of the compounds which contain diphenylalkenyl and silyl groups, it should be noted that, in all the instances, these ligands are attached to different ruthenium atoms. However, in order to reductively eliminate hydrosilylated diphenylacetylene, a metal complex should have the silyl group and the α-carbon atom of a diphenylalkenyl ligand coordinated in a cis arrangement to the same metal atom.[16] Therefore, the structures

---

(15) It is generally accepted that the reactions leading to hydrido–stannyl clusters are generally very similar to those leading to hydrido–silyl derivatives. See, for example: (a) Süss-Fink, G.; Ott, J.; Schmidkonz, B.; Guldner, K. *Chem. Ber.* **1982**, *115*, 2487. (b) Klein, H.-P.; Thewalt, U.; Herrmann, G.; Süss-Fink, G.; Moinet, C. *J. Organomet. Chem.* **1985**, *286*, 225. (c) Reference 11.

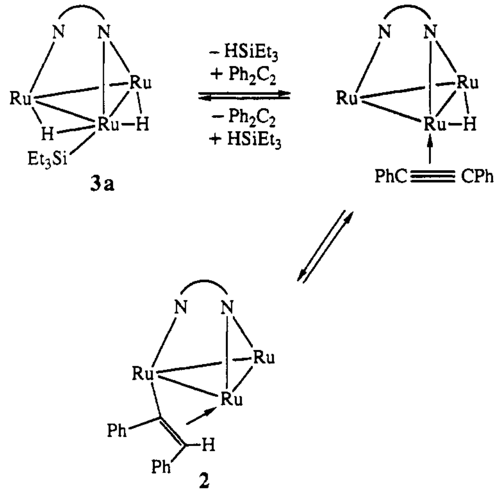
(16) It has been reported that the structurally characterized cluster $[Os_3\{\mu,\eta^1:\eta^2\text{-}HC{=}C(H)^tBu\}\{Si(OEt_3)\}(CO)_{10}]$, which has the alkenyl α-carbon and the silyl group bound to the same metal atom, decomposes, releasing $(EtO)_3SiC(H){=}C(H)^tBu$.[7]

Scheme II. Proposed Pathways for the Formation of 5b and 6b from 3b and Ph_2C_2[a]



[a] Carbonyl ligands have been omitted for clarity.

Scheme III. Proposed Pathway for the Formation of 2 from 3a and Ph_2C_2[a]



[a] Carbonyl ligands have been omitted for clarity.

of the cluster complexes described in this work may explain why no hydrosilylated diphenylacetylene is produced when complex 1 or its phosphine-substituted derivative 7 is allowed to react with diphenylacetylene and tertiary silanes.

Experimental Section

General Procedures. All reactions were carried out under nitrogen using standard Schlenk techniques and were monitored by solution IR spectroscopy (carbonyl stretching region). Solvents were purified according to standard literature procedures[17] and distilled under nitrogen prior to use. Alumina for column chromatography was deactivated by appropriate addition of deoxygenated water, under nitrogen, to the commercial material (Aldrich, neutral, activity I). The clusters 1,[8] 2,[9] 3a,[11] 7,[10a] and 8a[11] were prepared as described previously; all other reagents were purchased from Aldrich and used as received. Infrared spectra (Table I) were recorded in solution on a Perkin-Elmer FT 1720-X spectrophotometer, using 0.1-mm CaF_2 cells. ^1H (Table II), ^{13}C (Table III), and ^{31}P NMR spectra were run with Bruker AC-300 and AC-200 instruments, being referred ($\delta = 0$ ppm) to internal $SiMe_4$ (^1H, ^{13}C) or external 85% H_3PO_4 (^{31}P). GC analyses were performed with a Perkin-Elmer 8600 gas chromatograph equipped with a 12-m AQ2 capillary column and a flame ionization detector. Microanalyses were obtained from the University of Oviedo Analytical Service.

Preparation of $[Ru_3(\mu\text{-}H)_2(\mu_3,\eta^2\text{-ampy})\{Si(OMe)_3\}(CO)_8]$ (3b). This compound was prepared by the procedure previously described for 3a:[11] A solution of compound 1 (52 mg, 0.078 mmol) and $HSi(OMe)_3$ (12 μL, 0.086 mmol) in THF (10 mL) was heated at reflux temperature for 5 min. The color changed from orange to yellow. The solvent was removed under reduced pressure and the residue washed with cold pentane (1 mL) to give complex **3b** as a pale yellow solid (55 mg, 93%). Anal. Calcd for $C_{17}H_{18}N_2O_{11}Ru_3Si$: C, 26.95; H, 2.40; N, 3.70. Found: C, 27.12; H, 2.52; N, 3.43.

Reaction of $[Ru_3(\mu_3,\eta^2\text{-ampy})\{\mu,\eta^1{:}\eta^2\text{-PhC=C(H)Ph}\}(CO)_8]$ (2) with $HSiEt_3$. A solution of complex 1 (100 mg, 0.151 mmol) and diphenylacetylene (27 mg, 0.151 mmol) in THF (8 mL) was stirred at reflux temperature for 45 min. The IR spectrum of this solution showed the complete transformation of 1 into complex **2**. After the mixture was cooled to room temperature, $HSiEt_3$ (0.25 mL) was added. The resulting solution was stirred for 3.5 h and evaporated to dryness. The integrated ^1H NMR spectrum of the crude residue indicated the presence of **3a**, **4a**, and **5a** (in a 2:2.5:1 ratio). The residue was dissolved in toluene (0.75 mL), and the solution was chromatographed on a column (10 × 2 cm) of neutral alumina (activity IV). Hexane–toluene (4:1) eluted a red band which yielded complex **4a** as a red oil that could not be crystallized. Subsequent elution with hexane–toluene (2:1) gave a yellow fraction which contained complex **3a** (7 mg, 6.2%). Further elution with hexane–toluene (1:1) afforded complex **5a**, which was obtained as a violet solid (11 mg, 8.1%). Anal. Calcd for $C_{33}H_{34}N_2O_7Ru_3Si$: C, 43.95; H, 3.80; N, 3.11. Found: C, 43.55; H, 3.52; N, 3.06.

Reaction of $[Ru_3(\mu_3,\eta^2\text{-ampy})\{\mu,\eta^1{:}\eta^2\text{-PhC=C(H)Ph}\}(CO)_8]$ (2) with $HSi(OMe)_3$. A solution of complex 1 (79.5 mg, 0.120 mmol) and diphenylacetylene (22 mg, 0.122 mmol) in THF (10 mL) was stirred at reflux temperature for 45 min. The IR spectrum of this solution showed the complete transformation of 1 into complex 2. After the mixture was cooled to room temperature, $HSi(OMe)_3$ (0.15 mL) was added. The resulting solution was stirred for 4 h and evaporated to dryness. The integrated ^1H NMR spectrum of the crude residue indicated the presence of **3b**, **4b**, and **5b** (in a 1:12:3 ratio). The residue was dissolved in toluene (1 mL), and the solution was chromatographed on a column (10 × 2 cm) of neutral alumina (activity IV). Hexane–dichloromethane (2:1) eluted an orange band which yielded complex **5b** as red crystals (9 mg, 8.3%). Anal. Calcd for $C_{30}H_{28}N_2O_{10}Ru_3Si$: C, 39.69; H, 3.11; N, 3.09. Found: C, 40.01; H, 3.22; N, 2.91. Subsequent elution with the same eluant afforded trace amounts of complex **3b**. Further elution with dichloromethane afforded complex **4b**, which was obtained as an orange-red oil that could not be crystallized.

Reaction of $[Ru_3(\mu\text{-}H)_2(\mu_3,\eta^2\text{-ampy})(SiEt_3)(CO)_8]$ (3a) with Diphenylacetylene. A solution of complex 1 (97 mg, 0.146 mmol) and $HSiEt_3$ (0.25 mL) in THF (8 mL) was stirred at reflux temperature for 7 min. The IR spectrum of this solution showed the complete transformation of 1 into complex **3a**. The solvent was removed under reduced pressure, the residue dissolved in toluene (3 mL), and diphenylacetylene (52.6 mg, 0.292 mmol)

---

[17] Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon Press: Oxford, England, 1980.

Table V. Crystallographic and Refinement Data for Complex 10a

formula	$C_{50}H_{49}N_2O_6PRu_3Si$
fw	1136.22
cryst syst	monoclinic
space group	$P2_1/n$
a, Å	10.731(5)
b, Å	28.577(7)
c, Å	15.729(7)
β, deg	91.47(3)
V, Å^3	4822(3)
Z	4
$F(000)$	2288
D_{calcd}, g/cm^3	1.565
cryst size, mm	0.20 × 0.17 × 0.10
radiation (λ, Å)	Mo Kα (0.710 73)
diffractometer	Enraf-Nonius CAD4
monochromator	graphite
temp, K	293
scan method	ω–2θ
h, k, l ranges	±12, 0–33, 0–18
θ range, deg	0–25
no. of measd reflns	9097
no. of unique reflns	8408
$R_{int} = \sum(I - \langle I \rangle)/\sum I$	0.042
no. of reflns with $I > 3\sigma(I)$	3810
no. of variables	685
$R(F)^a$	0.034
$R_w(F)^b$	0.031
GOF^c	1.354
Δ/σ	0.04
max, min $\Delta\rho$, e/Å^3	0.38, −0.38

[a] $R(F) = \sum\|F_o/k| - |F_c\|[\sum|F_o/k|]^{-1}$. [b] $R_w(F) = \sum w^{1/2}\|F_o/k| - |F_c\|[\sum w^{1/2}|F_o/k|]^{-1}$; $w = [\sigma^2(F_o) + 0.0002|F_o|^2]^{-1}$; $\sigma(F_o)$ taken from counting statistics. [c] Goodness of fit (GOF) = $[\sum w(|F_o| - |F_c|)^2/(N_{obs} - N_{var})]^{1/2}$.

added. The resulting solution was stirred for 3.5 h and evaporated to dryness. The integrated ^{1}H NMR spectrum of the crude residue indicated the presence of **2**, **4a**, and **5a** (in a 2:3:1 ratio). The residue was extracted with hexane (10 mL) to give a solution and a red insoluble solid which was identified as complex **2** (37 mg, 31.1%). The hexane solution was evaporated to dryness, the residue dissolved in toluene (1 mL), and the solution chromatographed on a column (10 × 2 cm) of neutral alumina (activity IV). Hexane–toluene (4:1) eluted a red band which yielded complex **4a** as a red oil that could not be crystallized. Subsequent elution with hexane–toluene (1:1) afforded complex **5a**, which was obtained as a violet solid (10 mg, 7.6%).

Reaction of [$Ru_3(\mu\text{-}H)_2(\mu_3,\eta^2\text{-ampy})\{Si(OMe)_3\}(CO)_8$] (3b) with Diphenylacetylene. A solution of complex 1 (89 mg, 0.134 mmol) and $HSi(OMe)_3$ (20 μL, 0.149 mmol) in THF (7 mL) was stirred at reflux temperature for 7 min. The IR spectrum of this solution showed the complete transformation of 1 into complex **3b**. Diphenylacetylene (25 mg, 0.139 mmol) was then added, and the resulting solution was stirred at reflux temperature (no reaction was observed at room temperature) for 1 h and evaporated to dryness. The integrated ^{1}H NMR spectrum of the crude residue indicated the presence of complexes **5b** and **6b** (in a 1:4 ratio). The residue was dissolved in toluene (1 mL), and the solution was chromatographed on a column (11 × 2 cm) of neutral alumina (activity IV). Hexane–dichloromethane (2:1) eluted a red band which yielded complex **6b** as an orange solid (21 mg, 17.3%). Anal. Calcd for $C_{30}H_{28}N_2O_{10}Ru_3Si$: C, 39.69; H, 3.11; N, 3.09. Found: C, 39.82; H, 3.23; N, 3.12. Subsequent elution with hexane–dichloromethane (1.5:1) afforded trace amounts of complex **5b**.

Preparation of [$Ru_3(\mu_3,\eta^2\text{-ampy})\{\mu,\eta^1{:}\eta^2\text{-Ph-C{=}C(H)Ph}\}(CO)_7(PPh_3)$] (9). A solution of complex 7 (83 mg, 0.093 mmol) and diphenylacetylene (17 mg, 0.094 mmol) in THF (7 mL) was stirred at reflux temperature for 3 h. The solvent was removed under reduced pressure and the residue washed with pentane (three 6-mL portions) to give complex **9** as a red solid (61 mg, 63%). Anal. Calcd for $C_{45}H_{33}N_2O_7PRu_3$: C, 51.58; H, 3.17; N, 2.67. Found: C, 51.74; H, 3.32; N, 2.40.

Table VI. Fractional Atomic Coordinates and Isotropic Temperature Factors for 10a (with Esd's)

atom	x/a	y/b	z/c	U_{eq},^{a} Å^2 × 10^2
Ru(1)	0.06251(6)	0.21409(2)	0.36921(4)	3.43(2)
Ru(2)	−0.01054(6)	0.11814(2)	0.32536(4)	3.01(2)
Ru(3)	0.08301(6)	0.17304(2)	0.20345(4)	3.08(2)
P(1)	−0.1645(2)	0.05909(7)	0.3202(1)	3.39(7)
Si(1)	0.1297(2)	0.29390(8)	0.3424(2)	4.73(9)
N(1)	−0.1071(6)	0.1647(2)	0.2373(4)	3.0(2)
N(2)	−0.1378(6)	0.2259(2)	0.3349(4)	3.4(2)
C(1)	0.0566(8)	0.2273(3)	0.4848(6)	4.7(3)
O(1)	0.0615(7)	0.2333(3)	0.5575(4)	8.2(3)
C(2)	0.227(1)	0.1984(3)	0.3870(6)	5.1(4)
O(2)	0.3302(7)	0.1888(3)	0.3985(5)	8.5(3)
C(3)	−0.0800(8)	0.1434(3)	0.4290(5)	3.8(3)
O(3)	−0.1254(6)	0.1498(2)	0.4932(4)	5.5(2)
C(4)	0.1056(8)	0.0893(3)	0.3983(5)	3.7(3)
O(4)	0.1760(6)	0.0737(2)	0.4482(4)	6.5(3)
C(5)	0.0660(8)	0.2106(3)	0.1057(6)	4.7(3)
O(5)	0.0549(6)	0.2329(3)	0.0448(4)	8.2(3)
C(6)	0.2568(9)	0.1760(3)	0.1954(5)	4.4(3)
O(6)	0.3620(6)	0.1787(2)	0.1886(4)	6.7(3)
C(7)	−0.1813(7)	0.2008(3)	0.2675(5)	3.3(3)
C(8)	−0.2978(8)	0.2093(3)	0.2284(5)	4.2(3)
C(9)	−0.3716(9)	0.2430(4)	0.2623(7)	5.9(4)
C(10)	−0.3319(9)	0.2667(3)	0.3341(6)	5.6(4)
C(11)	−0.2174(8)	0.2580(3)	0.3701(5)	4.2(3)
C(12)	−0.1774(9)	0.2816(3)	0.4527(6)	5.8(4)
C(13)	0.169(1)	0.3300(3)	0.4411(7)	7.1(4)
C(14)	0.285(1)	0.3137(4)	0.4913(7)	8.4(5)
C(15)	0.273(1)	0.2938(3)	0.2751(7)	7.2(4)
C(16)	0.328(1)	0.3404(4)	0.256(1)	13.8(8)
C(17)	0.008(1)	0.3311(3)	0.2836(7)	6.5(4)
C(18)	−0.033(1)	0.3166(4)	0.1961(9)	11.8(7)
C(19)	−0.1248(8)	−0.0029(3)	0.3333(5)	3.8(3)
C(20)	−0.2181(9)	−0.0367(3)	0.3239(6)	4.6(3)
C(21)	−0.191(1)	−0.0830(3)	0.3373(6)	5.9(4)
C(22)	−0.071(1)	−0.0962(3)	0.3604(6)	6.2(4)
C(23)	0.022(1)	−0.0637(3)	0.3679(7)	6.6(4)
C(24)	−0.0049(9)	−0.0172(3)	0.3555(6)	5.2(4)
C(25)	−0.2487(7)	0.0578(3)	0.2167(5)	3.8(3)
C(26)	−0.1964(9)	0.0298(3)	0.1524(6)	4.9(3)
C(27)	−0.250(1)	0.0291(3)	0.0703(6)	6.1(4)
C(28)	−0.356(1)	0.0555(4)	0.0526(7)	7.7(5)
C(29)	−0.404(1)	0.0831(4)	0.1131(7)	7.3(5)
C(30)	−0.3515(9)	0.0851(3)	0.1968(6)	5.5(4)
C(31)	−0.2843(8)	0.0677(3)	0.3995(5)	3.9(3)
C(32)	−0.3518(9)	0.1092(3)	0.4004(6)	5.6(4)
C(33)	−0.441(1)	0.1176(5)	0.4614(8)	8.3(5)
C(34)	−0.457(1)	0.0838(5)	0.5247(9)	10.0(6)
C(35)	−0.389(1)	0.0448(5)	0.5262(8)	10.0(6)
C(36)	−0.302(1)	0.0359(3)	0.4646(6)	5.9(4)
C(37)	0.0390(8)	0.1069(2)	0.1313(5)	3.6(3)
C(38)	0.0802(7)	0.0951(2)	0.2136(5)	3.2(3)
C(39)	0.1030(8)	0.0987(3)	0.0487(5)	3.6(3)
C(40)	0.0314(9)	0.0944(3)	−0.0261(6)	5.2(4)
C(41)	0.088(1)	0.0898(3)	−0.1051(6)	6.2(4)
C(42)	0.217(1)	0.0897(3)	−0.1083(6)	6.5(4)
C(43)	0.288(1)	0.0929(3)	−0.0362(6)	5.4(4)
C(44)	0.2321(9)	0.0974(3)	0.0431(5)	4.5(3)
C(45)	0.1872(8)	0.0612(3)	0.2217(5)	3.4(3)
C(46)	0.1743(8)	0.0178(3)	0.1807(5)	4.4(3)
C(47)	0.267(1)	−0.0159(3)	0.1897(6)	6.3(4)
C(48)	0.376(1)	−0.0069(4)	0.2380(7)	6.7(4)
C(49)	0.3873(9)	0.0352(3)	0.2785(6)	5.8(4)
C(50)	0.2962(8)	0.0695(3)	0.2703(5)	4.3(3)

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_ia_ja^*_ia^*_j$.

Reaction of [$Ru_3(\mu\text{-}H)_2(\mu_3,\eta^2\text{-ampy})(SiEt_3)(CO)_7(PPh_3)$] (8a) with Diphenylacetylene. A solution of complex 1 (55.5 mg, 0.084 mmol), PPh_3 (22 mg, 0.084 mmol), and $HSiEt_3$ (0.25 mL) in THF (10 mL) was heated at reflux temperature for 25 min. The IR spectrum of this solution showed only the presence of complex **8a**. The THF solvent was removed under reduced pressure to give a solid which was redissolved in 1,2-dichloroethane (10 mL). After addition of diphenylacetylene (15.1 mg, 0.084 mmol), the resulting solution was heated at reflux temperature for 30 min and evaporated to dryness. The integrated

$^{31}P\{^1H\}$ NMR spectrum of the crude residue indicated the presence of complexes **7**, **8a**, **9**, and **10a** (in a 2:1:1:7 ratio). The residue was chromatographed on a column (11 × 2 cm) of neutral alumina (activity IV). Hexane–toluene (8:1) eluted a yellow band which was a mixture of compounds. Further elution with hexane–toluene (3:1) gave a red band corresponding to compound **10a** (30 mg, 31.6%). Anal. Calcd for $C_{50}H_{49}N_2O_6PRu_3Si$: C, 52.86; H, 4.35; N, 2.47. Found: C, 52.64; H, 4.30; N, 2.36.

Reaction of [Ru$_3$(μ_3,η^2-ampy){μ,η^1:η^2-PhC=C(H)Ph}(CO)$_7$(PPh$_3$)] (9) with HSiEt$_3$. A solution of complex **9** (66 mg, 0.063 mmol) and $HSiEt_3$ (0.25 mL) in THF (8 mL) was stirred at reflux temperature for 40 min. The solvent was removed under reduced pressure and the residue washed with hexane (two 6-mL portions) to give complex **10a** as a red solid (45 mg, 64%).

Crystal Structure of [Ru$_3$(μ-H)(μ_3,η^2-ampy){μ,η^1:η^2-PhC=C(H)Ph}(SiEt$_3$)(CO)$_6$(PPh$_3$)] (10a). Dark red crystals of **10a** were obtained by slow diffusion of a pentane layer carefully placed on a solution of the compound in dichloromethane. Selected crystallographic data are collected in Table V. Unit cell dimensions were determined from the angular settings of 25 reflections with $15 < \theta < 17°$. The space group was determined from systematic absences. The intensity was checked by monitoring three standard reflections every 60 min; final drift correction factors were between 0.96 and 1.03. Profile analysis was performed on all reflections.[18] A semiempirical absorption correction, using ψ scans,[19] was applied, $\mu = 10.15$ cm^{-1} (correction factors in the range 0.85–1.00). Lorentz and polarization corrections were applied and data reduced to $|F_o|$ values.

The structure was solved by Patterson interpretation, using SHELX-86,[20] and refined by full-matrix least-squares, using a modified version[21] of SHELX-76,[22] first with isotropic (empirical absorption correction applied,[23] maximum and minimum correction factors 1.10 and 0.85) and then with anisotropic thermal parameters in the last cycles for all the non-hydrogen atoms. A difference Fourier synthesis allowed the location of all the hydrogen atoms, which were refined isotropically with a common thermal parameter using a riding model, except H(1) and H(2) which were left free. Atomic scattering factors were taken from ref 24. Selected bond lengths and angles are given in Table IV. Final atomic coordinates are given in Table VI. Figure 1 was drawn with PLUTO.[25] Geometrical calculations were made with PARST.[26] All calculations were performed on a MicroVAX-3400 computer at the University of Oviedo Computer Centre.

Acknowledgment. This work was supported by the CICYT (Spain; Project MAT90-0173). A.L. is grateful to the FICYT (Asturias) for a postgraduate scholarship.

Supplementary Material Available: Tables of bond lengths and angles, anisotropic thermal parameters, H atom coordinates, and angles between least-squares planes and lines (7 pages). Ordering information is given on any current masthead page.

OM9301086

---

(18) Lehman, M. S.; Larsen, F. K. *Acta Crystallogr.* **1974**, *A30*, 580. Grant, D. F.; Gabe, E. J. *J. Appl. Crystallogr.* **1978**, *11*, 114.

(19) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr.* **1968**, *A24*, 351.

(20) Sheldrick, G. M. In *SHELX-86, Program for the Solution of Crystal Structures.* In *Crystallographic Computing 3*; Sheldrick, G. M., Krüger, C., Goddard, R., Eds.; Clarendon Press: Oxford, England, 1985; pp 175–189.

(21) This version allows to handle any number of atoms and parameters: Van der Maelen, J. F. Ph.D. Thesis, University of Oviedo, Oviedo, Spain, 1991.

(22) Sheldrick, G. M. *SHELX, Program for Crystal Structure Determination*; University Chemical Laboratory: Cambridge, England, 1976.

(23) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.

(24) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. 4.

(25) Motherwell, W. D. S.; Clegg, W. *PLUTO, Program for Plotting Molecular and Crystal Structures*; University Chemical Laboratory: Cambridge, England, 1978.

(26) Nardelli, M. *Comput. Chem.* **1983**, *7*, 95.