Reactivity of a Face-Bridged Trinuclear Ruthenium Carbonyl Cluster with Diphenylacetylene and Triorganotin Hydrides. Attempted Hydrostannation of Diphenylacetylene

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The cluster complex $[Ru_3(\mu\text{-H})(\mu_3,\eta^2\text{-ampy})(CO)_9]$ (**1**; Hampy = 2-amino-6-methylpyridine) does not promote the hydrostannation of diphenylacetylene. A study of the sequential reactions of **1** with diphenylacetylene and R_3SnH (R = Bu, Ph) and of **1** with R_3SnH and diphenylacetylene has allowed the isolation of $[Ru_3(\mu\text{-H})(\mu_3,\eta^2\text{-ampy})(SnR_3)_2(CO)_8]$ and of two isomers of $[Ru_3(\mu\text{-H})(\mu_3,\eta^2\text{-ampy})(SnR_3)\{\mu,\eta^1{:}\eta^2\text{-PhC=C(H)Ph}\}(CO)_7]$. The X-ray structures of the latter (R = Ph) have shown that both isomers have the $SnPh_3$ and diphenylalkenyl groups attached to different ruthenium atoms; this may explain why no hydrostannated diphenylacetylene is observed when diphenylacetylene and triorganotin hydrides are allowed to react with complex **1**.

Introduction

Hydrosilation[2] and hydrostannation[3] of unsaturated organic substrates are important catalytic reactions. However, despite the obvious interest,[2,3] it is rather remarkable that metal carbonyl clusters have received little attention as catalyst precursors in hydrosilation reactions[4] and that no examples are known about their use in hydrostannation reactions.

In a previous paper,[5] we described the incorporation of trialkylsilyl and trialkylstannyl groups into the triruthenium carbonyl cluster $[Ru_3(\mu\text{-H})(\mu_3,\eta^2\text{-ampy})(CO)_9]$ (**1**; Hampy = 2-amino-6-methylpyridine)[6] and into some of its phosphine-substituted derivatives.[7] As a continuation of that work, we thought it of interest to attempt the hydrostannation of diphenylacetylene promoted by **1**.[8] We now report that the sequential reactions of **1** with diphenylacetylene and R_3SnH (R = Bu, Ph) and of **1** with R_3SnH and diphenylacetylene have provided stable compounds in which R_3Sn, alkenyl, and hydrido groups are tied together through a Ru_3 unit and that their X-ray structures have shed light about why no hydrostannated diphenylacetylene is observed when this alkyne and triorganotin hydrides are allowed to react with complex **1**. To our knowledge, apart from those described in our previous paper,[5] the only known examples of triruthenium carbonyl clusters containing triorganosilyl or triorganotin groups are of the type $[Ru_3(\mu\text{-H})(ER_3)_2(CO)_{10}]^-$ (E = Si,[9,10] Sn[10]).

Results and Discussion

No hydrostannated diphenylacetylene was produced when tributyltin hydride, diphenylacetylene, and complex **1** (65:33:1 mole ratio) were allowed to react in toluene at 80 °C for 2.5 h. However, from previous works, we knew that complex **1** reacts with diphenylacetylene and tributyltin hydride to give $[Ru_3(\mu_3,\eta^2\text{-ampy})\{\mu,\eta^1{:}\eta^2\text{-PhC=C(H)Ph}\}(\mu\text{-CO})(CO)_7]$[11,12] (**2**) and $[Ru_3(\mu\text{-H})_2(\mu_3,\eta^2\text{-ampy})(SnBu_3)(CO)_8]$[5] (**3a**), respectively (see Chart I); furthermore, complex **1** is an efficient catalyst precursor for the homogeneous hydrogenation of unsaturated organic substrates under mild conditions.[11] These facts prompted us to study the reactivity of complex **2** with tributyltin hydride and that of complex **3a** with diphenylacetylene, in order to explain the failure of complex **1** to promote the hydrostannation of diphenylacetylene. We initially used tributyltin hydride as the tin reagent, but as most of its products were obtained as oils which proved to be very difficult to crystallize, we also carried out the reactions using triphenyltin hydride.

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

(2) See, for example: (a) Ojima, I. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Chapter 25. (b) Speier, J. L. *Adv. Organomet. Chem.* **1979**, *17*, 407. (c) 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.

(3) (a) Pereyre, M.; Quintard, J. P.; Rahm, A. *Tin in Organic Synthesis*; Butterworths: London, 1986. (b) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508. (c) Zhang, H. X.; Guibé, F.; Balavoine, G. *J. Org. Chem.* **1990**, *55*, 1857 and references cited therein.

(4) (a) 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. (b) Ojima, I.; Donovan, R. J.; Clos, N. *Organometallics* **1991**, *10*, 2606 and references cited therein. (c) Seki, Y.; Takeshita, K.; Kawamoto, K.; Murai, S.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 928. (d) Süss-Fink, G.; Reiner, J. *J. Mol. Catal.* **1982**, *16*, 231. (e) Süss-Fink, G. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 73. (f) Süss-Fink, G.; Reiner, J. *J. Organomet. Chem.* **1981**, *221*, C36. (g) Adams, R. D.; Cortopassi, J. E.; Pompeo, M. P. *Organometallics* **1992**, *11*, 1.

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

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

(7) (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**, *20*, 4611.

(8) We have used complex **1** as the starting ruthenium carbonyl cluster because, as reported in previous works,[6,7] the face-bridging ampy ligand has proved to hold the metal atoms firmly, preventing cluster degradation.

(9) Klein, H.-P.; Thewalt, U.; Herrmann, G.; Süss-Fink, G.; Moinet, C. *J. Organomet. Chem.* **1985**, *286*, 225.

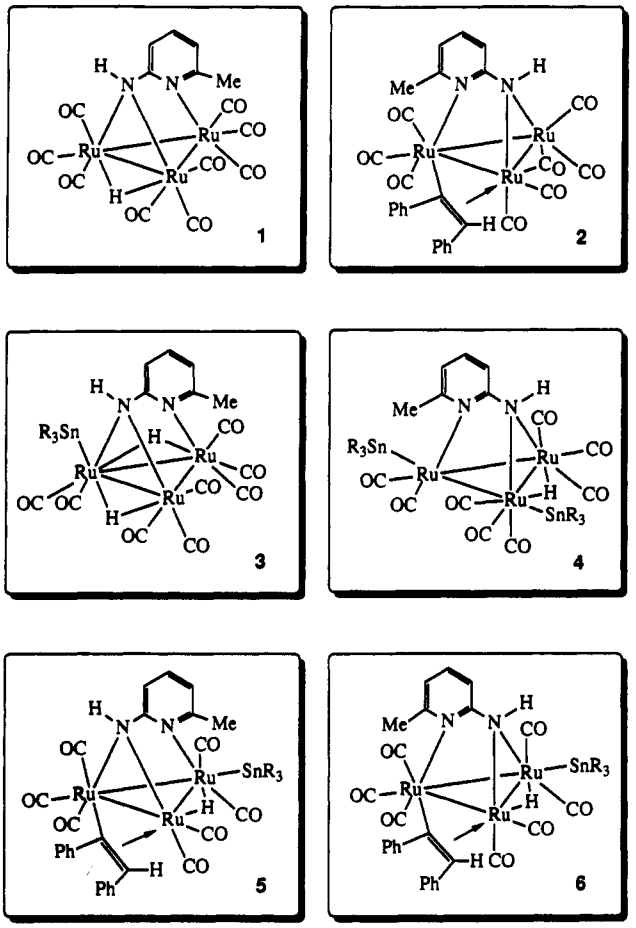
(10) Süss-Fink, G.; Ott, J.; Schmidkonz, B.; Guldner, K. *Chem. Ber.* **1982**, *115*, 2487.

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

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

0276-7333/93/2312-0157$04.00/0

Chart I[a]



[a] R = Bu (**a**), Ph (**b**).

Reactions of Complex 2 with R_3SnH (R = Bu, Ph). The reaction of complex **2** with an excess of tributyltin hydride or triphenyltin hydride, at room temperature, gave a mixture of products (eqs 1 and 2) which could be separated by chromatographic methods. The yields shown in eqs 1 and 2 were estimated by integrating the ^1H NMR spectra of the reaction mixtures.

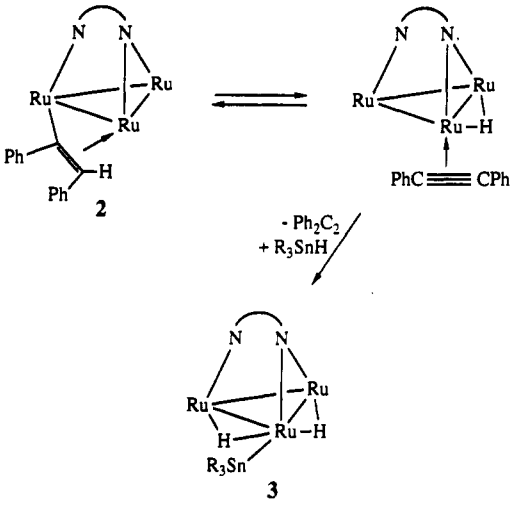
$$2 + Bu_3SnH \rightarrow \mathbf{3a}\ (5\%) + \mathbf{4a}\ (63\%) + \mathbf{5a}\ (32\%) \quad (1)$$

$$2 + Ph_3SnH \rightarrow \mathbf{3b}\ (\text{trace}) + \mathbf{4b}\ (88\%) + \mathbf{5b}\ (12\%) \quad (2)$$

In both cases, the minor products (**3a** and **3b**) corresponded to the substitution of triorganotin hydride for diphenylacetylene in complex **2**. Their identity was confirmed by comparing their spectroscopic data with those of the known complex **3a**.[5] A plausible reaction pathway is outlined in Scheme I. This would involve the isomerization of the alkenyl complex **2** into a hydrido–alkyne species which, after the elimination of diphenylacetylene, would add the corresponding triorganotin hydride.

The major products of these reactions corresponded to the bis(triorganotin) derivatives **4a** and **4b**. The carbonyl regions of their IR spectra were very similar to each other (Table I), and their ^1H NMR spectra (Table II) confirmed the presence of one hydrido and two R_3Sn ligands per ampy ligand and the absence of alkenyl and bridging carbonyl ligands. The relative positions of the ligands in these clusters were inferred from the ^{13}C and ^{119}Sn NMR

Scheme I. Proposed Pathway for the Formation of 3 from 2 and R_3SnH[a]



[a] Carbonyl ligands have been omitted for clarity.

Table I. Carbonyl Stretching Absorptions in Hexane Solution

compd	ν(CO),[a] cm^{-1}
3b	2086 (s), 2055 (s), 2028 (s), 2009 (m), 2004 (m), 1993 (m), 1971 (m)
4a	2065 (s), 2043 (w), 2016 (s), 1995 (m), 1978 (w), 1960 (m), 1928 (w)
4b	2072 (s), 2054 (w), 2027 (s), 2003 (m), 1989 (w), 1971 (m), 1944 (w)
5a	2062 (m), 2028 (s), 2008 (s), 1996 (m), 1976 (s), 1939 (w)
5b	2065 (m), 2035 (s), 2012 (s), 2001 (w), 1985 (m), 1946 (w)
6a	2056 (m), 2025 (s), 2006 (s), 1995 (m), 1978 (m), 1972 (sh), 1943 (w)
6b	2058 (m), 2031 (s), 2012 (s), 1998 (m), 1983 (m), 1952 (m)

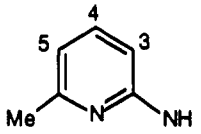
[a] Abbreviations are as follows: s = strong, m = medium, w = weak, sh = shoulder.

spectra of **4b** (complex **4a** decomposes during overnight NMR experiments at room temperature). The number of CO ligands was evident from the proton-decoupled ^{13}C NMR spectrum (see the supplementary material), which shows eight CO singlet resonances (indicating an asymmetric structure), two of which (those at 200.7 and 188.8 ppm) split into doublets in the proton-coupled spectrum with considerable $J(^{13}C–^1H)$ coupling constants (17.8 and 12.0 Hz), as expected for two CO groups trans to the hydrido ligand,[13] thus ruling out the possibility that the two Ph_3Sn groups were in positions trans to the hydride. The ^{119}Sn NMR spectrum of **4b**, with selective decoupling of aromatic protons, contains two resonances, a singlet at −15.2 ppm and a doublet at −2.4 ppm, indicating that the hydrido ligand does not span the Ru atoms bound to the SnR_3 groups (two doublets should be expected in this case). All these spectroscopic data strongly suggest that the structure of compound **4b** is that depicted in Chart I.

The compounds **5a** and **5b** were also obtained in these reactions, though in lower yields than **4a** and **4b**. Their spectroscopic data (Tables I and II), which were very similar, confirmed the presence of hydrido, alkenyl, and triorganotin ligands in a 1:1:1 ratio but were insufficient

(13) In hydrido carbonyl clusters, it is known that the $J_{trans}(^{13}C–^1H)$ coupling constants are normally greater than 10 Hz, whereas the $J_{cis}(^{13}C–^1H)$ couplings are smaller and often negligible. See, for example, refs 5 and 7.

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



compd	H^5	H^4	H^3	NH	Me	μ-H	CH_{vinyl}
3b[b]	6.46 (d)	6.79 (t)	5.45 (d)	3.79 (s)	2.31 (s)	−9.77 (s, sat), −11.86 (s, sat)	
4a[c]	5.69 (d)	5.85 (t)	5.35 (d)	3.36 (s)	1.61 (s)	−10.81 (s, sat)	
4b[c]	5.61 (d)	6.01 (t)	4.87 (d)	3.71 (s)	1.81 (s)	−10.99 (s, sat)	
5a[c]	6.04 (d)	6.44 (t)	5.29 (d)	2.85 (s)	2.69 (s)	−11.21 (s, sat)	3.91 (s)
5b[c]	5.70 (d)	6.43 (t)	5.41 (d)	3.07 (s)	2.60 (s)	−10.98 (s, sat)	3.98 (s)
6a[c]	5.98 (d)	6.55 (t)	5.85 (d)	*d*	2.02 (s)	−10.82 (s, sat)	4.44 (s)
6b[c]	5.81 (d)	6.55 (t)	5.68 (d)	4.21 (s)	1.97 (s)	−10.55 (s, sat)	4.28 (s)

[a] General information and conditions: spectra recorded at 300 MHz, 25 °C; chemical shifts (δ, ppm) relative to internal $SiMe_4$; multiplicities (s = singlet, d = doublet, t = triplet, sat = with tin satellites) in parentheses; coupling constants J_{H-H} for H^3, H^4, and H^5 are ca. 7.4 Hz in all cases. The ^1H resonances of the phenyl and butyl fragments, although confirming their presence in the clusters, are uninformative multiplets. [b] In $CDCl_3$. [c] In C_6D_6. [d] Unobserved.

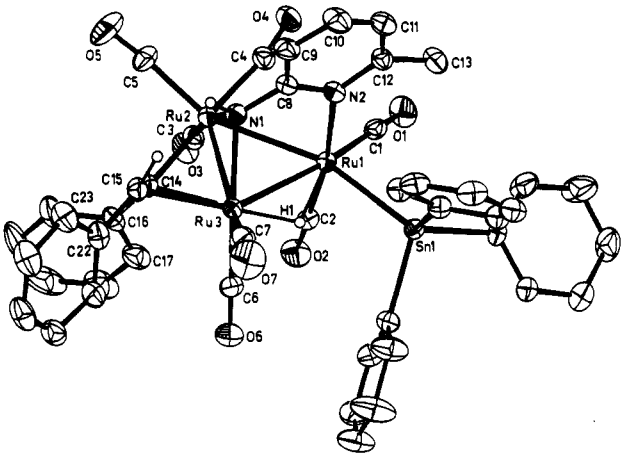


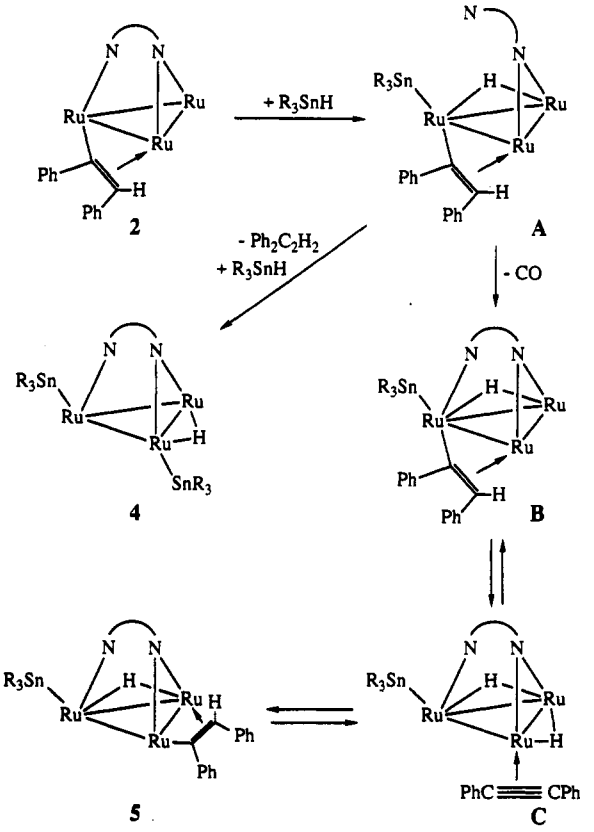
Figure 1. Molecular structure of $[Ru_3(\mu\text{-H})(\mu_3,\eta^2\text{-ampy})\{\mu,\eta^1:\eta^2\text{-PhC=C(H)Ph}\}(SnPh_3)(CO)_7]$ (isomer **5b**) with thermal ellipsoids drawn at the 30% probability level.

to unambiguously assign a structure; therefore, a single-crystal X-ray diffraction study of **5b** (vide infra) was carried out (Figure 1).

The mild conditions under which these transformations take place (room temperature) suggest that a low-energy path is being used in the reactions. As indicated by Lavigne et al.,[12] the aperture of one of the Ru–ligand bonds of a saturated $Ru_3(\mu_3\text{-ligand})$ cluster would provide a reactive 46-electron species as a low-energy transition state. Such a $\mu_3 \leftrightarrow \mu_2$ bridge transformation has been observed by Lavigne et al.[12] and Süss-Fink et al.[14] in related (phenyl-2-pyridylamido)- and (camphorhydrazonato)ruthenium carbonyl clusters, respectively. Thus, reasonable pathways that would lead to complexes **4** and **5** from complex **2** and triorganotin hydrides are outlined in Scheme II. First, complex **2** would open the pyridine arm to provide the vacant site necessary for the reaction with R_3SnH. Subsequently, the tin-containing intermediate A, which has the alkenyl α-carbon attached to the same Ru atom as the hydrido ligand, may evolve through two different paths: (a) closing the pyridine arm and releasing stilbene (in fact, *cis*- and *trans*-stilbene are observed in the reaction solution by gas chromatography) to give an unsaturated species which would react with R_3SnH (which is present in excess in solution) to end in **4** or (b) closing the pyridine arm and releasing CO to give B, which subsequently isomerizes into **5** through the intermediate C.

(14) Jenke, T.; Bodensieck, U.; Stoeckli-Evans, H.; Süss-Fink, G. *J. Organomet. Chem.* **1991**, *414*, C28.

Scheme II. Proposed Pathways for the Formation of 4 and 5 from 2 and R_3SnH[a]



[a] Carbonyl ligands have been omitted for clarity.

It is interesting to note that complexes **3a** and **3b** are stable in the presence of an excess of the corresponding triorganotin hydride and, therefore, the bis(triorganotin) derivatives **4a** and **4b** cannot arise from the direct interaction of **3a** and **3b** with R_3SnH. This constrasts with the reaction of $[Ru_3(\mu\text{-H})(CO)_{11}]^-$ with an excess of triphenyltin hydride, which has been reported to give the bis(triphenyltin) derivative $[Ru_3(\mu\text{-H})(SnPh_3)_2(CO)_{10}]^-$.[10]

Reactions of Complexes 3a and 3b with Diphenylacetylene. No reaction was observed when complexes **3a** and **3b** were treated with an excess of diphenylacetylene at room temperature. At 80 °C, a mixture of two products, which could be separated by chromatography, was obtained in each reaction (eqs 3 and 4). The yields shown in eqs 3 and 4 were estimated by integrating the ^1H NMR spectra of the reaction mixtures.

$$\mathbf{3a} + Ph_2C_2 \rightarrow \mathbf{5a}\ (25\%) + \mathbf{6a}\ (75\%) \quad (3)$$

$$\mathbf{3b} + Ph_2C_2 \rightarrow \mathbf{5b}\ (\text{trace}) + \mathbf{6b}\ (100\%) \quad (4)$$

The analytical and spectroscopic data of **6a** and **6b** (Tables I and II) confirmed that these compounds are isomers of **5a** and **5b**, respectively; but, again, they were insufficient to precisely locate the ligands on the clusters. The structure of **6b** (Figure 2) was determined by an X-ray diffraction study (vide infra).

Most probably, the first step in these reactions is the opening of one arm of the ampy ligand to allow the incorporation of diphenylacetylene in the clusters (Scheme III). A subsequent hydride insertion in D followed by recoordination of the pyridine ring would give the σ-alkenyl intermediate E, which upon CO elimination would render complex **6**. To account for the presence of complex **5** in the reaction mixture, a 120° rotation of the ampy ligand on the Ru_3 unit of intermediate E to give F has to be assumed. Complexes **5** and **6** are not fluxional at room temperature and do not interconvert into each other in refluxing toluene; therefore, the rotation of the ampy ligand has to take place in one of the reaction intermediates. In intermediate F, a steric interaction of the methyl substituent on the 6-position of the pyridine ring with the SnR_3 group (particularly when R = Ph) would account for the observed relative amounts of **5** and **6** in the reaction mixtures (**5** is always the minor product). Very recently, the rotation of a face-bridging μ_3 ligand on a Ru_3 unit has been observed by NMR spectroscopy, namely in the cluster $[Ru_3(\mu\text{-H})(\mu_3,\eta^2\text{-}C_2{}^t\text{Bu})(CO)_9]$.[15]

Molecular Structures of Complexes 5b and 6b. The molecular structures of **5b** (Figure 1) and **6b** (Figure 2) were determined by X-ray diffraction methods; selected bond lengths and angles are given in Tables III and IV, respectively.

The cluster **5b** consists of a triangular array of ruthenium atoms triply bridged by the ampy ligand, with the two shortest edges (Ru(1)–Ru(3) = 2.878 (1) Å and Ru(2)–Ru(3) = 2.695 (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 planes Ru(2)–N(1)–Ru(3) and that of the pyridine ring are almost perpendicular to the Ru_3 plane, with dihedral angles of 89.8 (4)° and 88.4 (3)°, respectively. The bridging hydrido ligand H(1) spans the Ru(1)–Ru(3) edge, with the plane Ru(1)–Ru(3)–H(1) forming a dihedral angle of 135 (3)° with the Ru_3 triangle. Although the location of hydrides by X-ray diffraction methods always has to be considered cautiously, in this case the X-ray data fit consistently with the NMR data. The alkenyl group spans the same Ru_2 edge as the amido fragment of the ampy ligand, being σ-bound to the Ru(2) atom through the α-carbon atom C(14) and π-bound to the Ru(3) atom through both the α- and β-carbon atoms C(14) and C(15). The structural parameters of this alkenyl group compare well with those found in other polynuclear ruthenium alkenyl complexes.[12] A $SnPh_3$ group is coordinated, in an equatorial position, to the Ru(1) atom through the tin atom, being nearly cis to the hydride H(1). The cluster coordination shell is completed by seven terminal CO ligands, three in axial sites (trans to the nitrogen atoms of the ampy ligand) and four in equatorial sites.

(15) Farrugia, L. J.; Rae, S. E. *Organometallics* **1992**, *11*, 196.

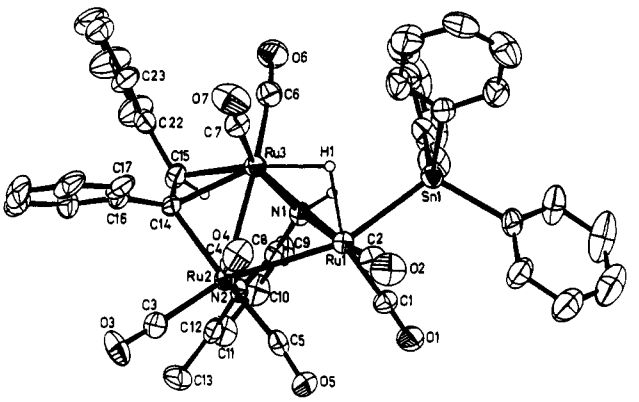
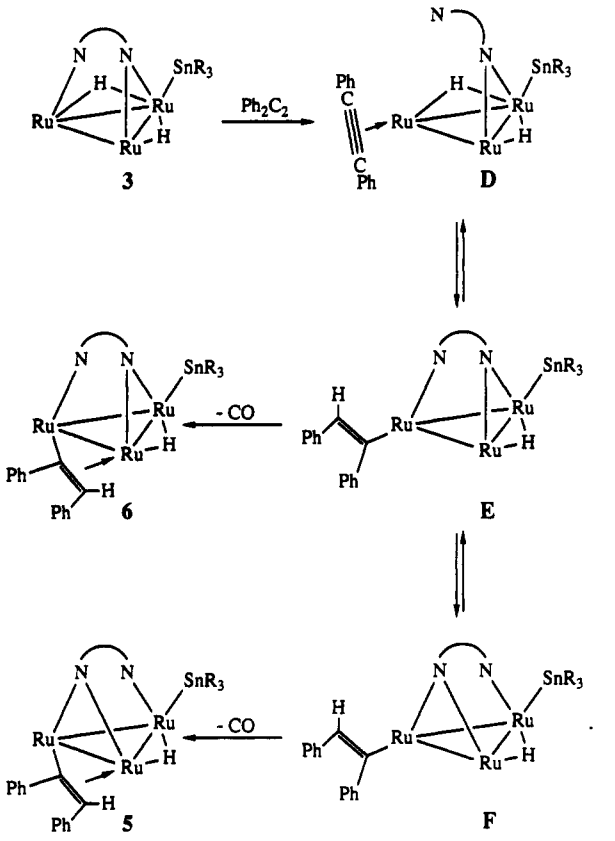


Figure 2. Molecular structure of $[Ru_3(\mu\text{-H})(\mu_3,\eta^2\text{-ampy})\{\mu,\eta^1\text{:}\ \eta^2\text{-PhC=C(H)Ph}\}(SnPh_3)(CO)_7]$ (isomer **6b**) with thermal ellipsoids drawn at the 30% probability level.

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



[a] Carbonyl ligands have been omitted for clarity.

The structural features of complex **6b**, apart from the orientation of the ampy ligand with respect to the other ligands, are entirely analogous to those of complex **5b**, commented on above. Overall, the structure of **6b** could be described as the result of a formal 120° rotation of the ampy ligand about an axis perpendicular to the Ru_3 plane of cluster **5b**, in such a way that the ampy ligand in **6b** is bound to the Ru(2) atom through the pyridinic nitrogen N(2), while the exocyclic nitrogen N(1) spans the same Ru_2 edge as the hydrido ligand. The dihedral angle between the planes Ru(1)–H(1)–Ru(3) and the metal triangle is 174 (6)°.

Table III. Selected Bond Lengths (Å) and Bond Angles (deg) in 5b (with Esd's)

Bond Lengths			
Ru(1)–Ru(2)	2.893 (1)	Ru(1)–Ru(3)	2.878 (1)
Ru(2)–Ru(3)	2.695 (1)	Ru(1)–Sn(1)	2.662 (1)
Ru(1)–N(2)	2.235 (8)	Ru(2)–N(1)	2.133 (9)
Ru(3)–N(1)	2.135 (9)	Ru(2)–C(14)	2.170 (9)
Ru(3)–C(14)	2.20 (1)	Ru(3)–C(15)	2.27 (1)
C(14)–C(15)	1.38 (1)	Ru(1)–H(1)	2.0 (1)
Ru(3)–H(1)	1.6 (1)		
Bond Angles			
Ru(1)–Ru(2)–Ru(3)	61.90 (1)	Ru(1)–Ru(3)–Ru(2)	62.40 (1)
Ru(2)–Ru(1)–Ru(3)	55.70 (1)	Ru(2)–Ru(1)–Sn(1)	155.90 (1)
Ru(3)–Ru(1)–Sn(1)	100.30 (1)	C(14)–Ru(2)–Ru(1)	109.5 (3)
C(14)–Ru(2)–Ru(3)	52.3 (3)	C(14)–Ru(3)–Ru(1)	109.2 (3)
C(14)–Ru(3)–Ru(2)	51.4 (2)	C(15)–Ru(3)–Ru(1)	138.6 (3)
C(15)–Ru(3)–Ru(2)	76.3 (3)	Ru(2)–C(14)–Ru(3)	76.2 (3)
C(14)–C(15)–Ru(3)	69.2 (6)	C(15)–C(14)–Ru(2)	119.2 (8)
C(15)–C(14)–Ru(3)	74.9 (6)		

Table IV. Selected Bond Lengths (Å) and Bond Angles (deg) in 6b·0.5C_6D_6 (with Esd's)

Bond Lengths			
Ru(1)–Ru(2)	2.936 (1)	Ru(1)–Ru(3)	2.732 (1)
Ru(2)–Ru(3)	2.762 (1)	Ru(1)–Sn(1)	2.623 (1)
Ru(1)–N(1)	2.136 (8)	Ru(2)–N(2)	2.204 (7)
Ru(3)–N(1)	2.150 (8)	Ru(2)–C(14)	2.17 (1)
Ru(3)–C(14)	2.20 (1)	Ru(3)–C(15)	2.28 (1)
C(14)–C(15)	1.42 (1)	Ru(1)–H(1)	2.0 (1)
Ru(3)–H(1)	2.0 (1)		
Bond Angles			
Ru(1)–Ru(2)–Ru(3)	57.20 (1)	Ru(1)–Ru(3)–Ru(2)	64.60 (1)
Ru(2)–Ru(1)–Ru(3)	58.20 (1)	Ru(2)–Ru(1)–Sn(1)	160.80 (1)
Ru(3)–Ru(1)–Sn(1)	102.80 (1)	C(14)–Ru(2)–Ru(1)	108.2 (3)
C(14)–Ru(2)–Ru(3)	51.2 (3)	C(14)–Ru(3)–Ru(1)	114.6 (3)
C(14)–Ru(3)–Ru(2)	50.2 (3)	C(15)–Ru(3)–Ru(1)	125.5 (3)
C(15)–Ru(3)–Ru(2)	76.3 (3)	Ru(2)–C(14)–Ru(3)	78.5 (3)
C(14)–C(15)–Ru(3)	68.3 (6)	C(15)–C(14)–Ru(2)	120.4 (7)
C(15)–C(14)–Ru(3)	74.7 (6)		

Concluding Remarks

One necessary condition to reductively eliminate hydrostannated diphenylacetylene from a complex is to have the SnR_3 group and the α-carbon atom of the alkenyl ligand coordinated in a cis arrangement to the same metal atom. Although other types of arguments might also be considered, the failure of complex **1** to promote the hydrostannation of diphenylacetylene can be rationalized on the basis of the structures of the cluster complexes described in this work, since none of them has the appropriate ligand arrangement. Moreover, the remarkable stability of complexes **5** and **6** has to be related to the fact that their respective alkenyl α-carbon atoms are σ-bound to Ru atoms different from those that support the hydrido and SnR_3 ligands.

The results described herein can be contrasted with those reported recently by Adams et al. about the hydrosilation of alkynes promoted by an osmium cluster complex.[4g] In that work, the structurally characterized intermediate $[Os_3\{\mu,\eta^1{:}\eta^2\text{-}HC{=}C(H)^tBu\}\{Si(OEt)_3\}(CO)_{10}]$ decomposes, giving the silylated alkene because the alkenyl α-carbon and the silyl group are attached to the same Os atom.

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[16] and distilled under nitrogen prior to use. Alumina for column chromatography was deactivated by appropriate addition of water under nitrogen to the commercial material (Aldrich, neutral, activity I). The clusters **1**,[6] **2**,[11] and **3a**[5] were prepared as described previously; ^{13}CO-enriched compounds were made from ^{13}CO-enriched $[Ru_3(CO)_{12}]$.[17] 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, and ^{119}Sn NMR spectra were run with a Bruker AC-300 instrument, being referred (δ 0 ppm) to $SiMe_4$ (^1H, ^{13}C) or $SnMe_4$ (^{119}Sn). 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.

Attempted Hydrostannation of Diphenylacetylene. A toluene solution (20 mL) of tributyltin hydride (0.5 mL, 1.803 mmol), diphenylacetylene (164.5 mg, 0.922 mmol), and complex **1** (20 mg, 0.030 mmol), maintained at 80 °C in a thermostated bath, was vigorously shaken for 2.5 h. Throughout this time, periodical gas chromatography analyses of aliquots of the reaction solution showed the presence of a constant amount of diphenylacetylene and the absence of any hydrostannated product.

Preparation of $[Ru_3(\mu\text{-}H)_2(\mu_3,\eta^2\text{-ampy})(SnPh_3)(CO)_8]$ (3b). A solution of compound **1** (40 mg, 0.060 mmol) and Ph_3SnH (21.5 mg, 0.061 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 pentane (1 mL) to give complex **3b** as a yellow solid (45 mg, 76%). Anal. Found: C, 39.53; H, 2.62; N, 2.43. Calcd for $C_{32}H_{24}N_2O_8Ru_3Sn$: C, 38.96; H, 2.45; N, 2.84. Selected $^{13}C\{^1H\}$ NMR data (CD_2Cl_2, 75.5 MHz, 25 °C): 201.0, 200.4, 198.3, 195.5, 194.6, 191.0, 186.6, 181.8 (8 CO ligands), 177.5, 158.4, 137.7, 118.6, 110.3, 28.7 (ampy ligand) ppm.

Reaction of Complex 2 with Tributyltin Hydride. A solution of complex **1** (95.7 mg, 0.144 mmol) and diphenylacetylene (26 mg, 0.144 mmol) in THF (10 mL) was stirred at reflux temperature for 40 min. The IR spectrum of this solution showed the complete transformation of **1** into complex **2**. After the solution was cooled to room temperature, tributyltin hydride (80 μL, 0.288 mmol) was injected. The resulting solution was stirred for 20 min and evaporated to dryness. The integrated ^1H NMR spectrum of the crude residue indicated the presence of **3a**, **4a**, and **5a** (in a 1:12:6 ratio). The residue was dissolved in toluene (1 mL) and chromatographed on a column (10 × 2 cm) of neutral alumina (activity IV). Hexane 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 an orange fraction which contained complex **3a** (IR identification). Further elution with toluene afforded complex **5a**, which was obtained as a violet solid (5 mg, 3% based on the amount of **1**). Anal. Found: C, 43.83; H, 4.62; N, 2.43. Calcd for $C_{39}H_{46}N_2O_7Ru_3Sn$: C, 43.51; H, 4.31; N, 2.60. Selected $^{13}C\{^1H\}$ NMR data (CD_2Cl_2, 75.5 MHz, 25 °C, sample enriched in ^{13}CO): 205.8, 203.4, 202.8, 199.4, 196.7, 195.1, 184.8 (7 CO ligands), 175.1, 161.4, 139.5, 119.7, 112.5, 31.0 (ampy ligand), 141.8, 80.5 (alkenyl group) ppm.

Reaction of Complex 2 with Triphenyltin Hydride. A solution of complex **1** (72.4 mg, 0.109 mmol) and diphenylacetylene (19.6 mg, 0.109 mmol) in THF (10 mL) was stirred at reflux temperature for 40 min. The IR spectrum of this solution showed the complete transformation of **1** into complex **2**. After the solution was cooled to room temperature, triphenyltin hydride (76.6 mg, 0.218 mmol) was added. The resulting solution was stirred for 25 min and evaporated to dryness. The integrated ^1H NMR spectrum of the crude residue indicated the presence of **4b**, **5b** (in a 7:1 ratio), and a trace amount of **3b**. The residue was dissolved in dichloromethane (1 mL) and chromatographed on

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a column (10 × 2 cm) of neutral alumina (activity IV). Hexane–toluene (2:1) eluted a red band which yielded complex **4b** as a red solid (36 mg, 25% based on the amount of **1**). Anal. Found: C, 45.14; H, 3.01; N, 2.03. Calcd for $C_{50}H_{38}N_2O_8Ru_3Sn_2$: C, 44.97; H, 2.87; N, 2.10. Selected $^{13}C\{^1H\}$ NMR data (CD_2Cl_2, 75.5 MHz, 25 °C): 206.6, 204.6, 200.7, 199.4, 198.7, 197.2, 188.8, 187.3 (8 CO ligands), 175.6, 158.6, 137.6, 118.8, 110.1, 30.8 (ampy ligand) ppm. ^{119}Sn NMR ($CDCl_3$, 111.9 MHz, 25 °C, aromatic protons selectively decoupled): −2.4 (d, J = 29.6 Hz), −15.2 (s) ppm. Subsequent elution with hexane–toluene (1:1) afforded an orange fraction which contained a trace amount of complex **3b** (IR identification). Further elution with toluene afforded complex **5b**, which was obtained as a violet solid (6 mg, 4% based on the amount of **1**). Anal. Found: C, 48.06; H, 3.27; N, 2.23. Calcd for $C_{45}H_{34}N_2O_7Ru_3Sn$: C, 47.55; H, 3.01; N, 2.46.

Reaction of Complex 3a with Diphenylacetylene. A solution of complex **1** (130 mg, 0.196 mmol) and tributyltin hydride (55 μL, 0.196 mmol) in THF (10 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 (4 mL), and diphenylacetylene (70.7 mg, 0.393 mmol) added. The resulting solution was stirred for 1 h at 80 °C and evaporated to dryness. The integrated ^1H NMR spectrum of the crude residue indicated the presence of **5a** and **6a** (in a 1:3 ratio). The residue was dissolved in toluene (1 mL) and chromatographed on a column (10 × 2 cm) of neutral alumina (activity IV). Hexane–toluene (4:1) eluted a red band which yielded complex **6a** as a red oil that could not be crystallized. Selected $^{13}C\{^1H\}$ NMR data (CD_2Cl_2, 75.5 MHz, 25 °C, sample enriched in ^{13}CO): 206.9, 205.3, 202.7, 196.7, 195.9, 195.3, 192.3 (7 CO ligands) ppm. Subsequent elution with toluene afforded complex **5a**, which was obtained as a violet solid (20 mg, 10% based on the amount of **1**).

Reaction of Complex 3b with Diphenylacetylene. A solution of complex **1** (121.7 mg, 0.183 mmol) and triphenyltin hydride (54.4 mg, 0.183 mmol) in THF (8 mL) was stirred at reflux temperature for 5 min. The IR spectrum of this solution showed the complete transformation of **1** into complex **3b**. The solvent was removed under reduced pressure, the residue dissolved in toluene (3 mL), and diphenylacetylene (66.6 mg, 0.367 mmol) added. The resulting solution was stirred for 40 min at 80 °C and evaporated to dryness. The integrated ^1H NMR spectrum of the crude residue indicated the presence of **6b** and a trace amount of **5b**. The residue was dissolved in dichloromethane (1 mL) and chromatographed on a column (10 × 2 cm) of neutral alumina (activity IV). Hexane–toluene (2:1) eluted a red band which yielded complex **6b** as a red solid (80 mg, 24% based on the amount of **1**). Anal. Found: C, 45.76; H, 3.25; N, 2.22. Calcd for $C_{45}H_{34}N_2O_7Ru_3Sn$: C, 47.55; H, 3.01; N, 2.46. Selected $^{13}C\{^1H\}$ NMR data (CD_2Cl_2, 75.5 MHz, 25 °C, sample enriched in ^{13}CO): 205.4, 203.5, 202.0, 201.1, 194.9, 194.4, 193.3 (7 CO ligands), 173.5, 158.2, 139.2, 117.9, 112.9, 29.8 (ampy ligand), 142.2, 70.2 (alkenyl group) ppm. Subsequent elution with toluene afforded a trace amount of complex **5b**.

Crystal Structures of 5b and 6b·0.5C$_6$D$_6$. Dark red crystals of **5b** and **6b**·0.5C_6D_6 were made by slow diffusion of an *n*-pentane layer carefully placed on solutions of the compounds in dichloromethane or benzene-d_6, respectively. Selected crystallographic data for both compounds are collected in Table V. Unit cell dimensions were determined from the angular settings of 25 reflections with $15 < \theta < 17°$. Space groups were determined from structure determination (**5b**) and systematic absences (**6b**). The intensity was checked by monitoring three standard reflections every 60 min; final drift correction factors were between 0.99 and 1.14 (**5b**) and 0.98 and 1.06 (**6b**). Profile analysis was performed on all reflections.[18] Semiempirical absorption corrections, using ψ scans,[19] were applied: μ = 14.75 cm^{-1} (**5b**) and 15.08 cm^{-1} (**6b**) (correction factors in the ranges 0.95–1.00 (**5b**) and 0.98–1.00 (**6b**)). Lorentz and polarization corrections were applied and data reduced to $|F_o|$ values.

Table V. Crystallographic and Refinement Data for 5b and 6b·0.5C$_6$D$_6$

	5b	**6b**·0.5C_6D_6
formula	$C_{45}H_{34}N_2O_7Ru_3Sn$	$C_{45}H_{34}N_2O_7Ru_3Sn{\cdot}0.5C_6D_6$
fw	1136.67	1178.73
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$
a, Å	11.086 (7)	11.032 (6)
b, Å	12.75 (1)	37.006 (6)
c, Å	19.069 (7)	12.16 (1)
α, deg	74.14 (7)	90
β, deg	86.6 (1)	109.19 (5)
γ, deg	67.46 (7)	90
V, Å^3	2392.0 (3)	4688.0 (5)
Z	2	4
$F(000)$	1112	2308
D_{calcd}, g/cm^3	1.58	1.67
cryst size, mm	0.46 × 0.17 × 0.17	0.30 × 0.13 × 0.10
radiation (λ, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
diffractometer	Enraf-Nonius CAD4	Enraf-Nonius CAD4
monochromator	graphite	graphite
temp, K	293	293
scan method	ω–2θ	ω–2θ
hkl range	±13; −14 to +15; 0–22	±12; 0–43; 0–14
θ range, deg	0–25	0–25
no. of measd reflns	8634	8728
no. of unique reflns	8357	8155
no. of reflns with $I \geq 3\sigma(I)$	5556	3786
$R_{int} = \Sigma(I - \langle I \rangle)/\Sigma I$	0.031	0.037
no. of variables	532	539
$R(F)^a$	0.046	0.042
$R_w(F)^b$	0.049[c]	0.040[c]
GOF[d]	2.206	2.367
Δ/σ	0.05	0.001
max, min $\Delta\rho$, e/Å^3	0.92, −0.99	0.42, −0.68

[a] $R(F) = \Sigma||F_o/k| - |F_c||[\Sigma|F_o/k|]^{-1}$. [b] $R_w(F) = \Sigma w^{1/2}||F_o/k| - |F_c||[\Sigma w^{1/2}|F_o/k|]^{-1}$. [c] $w = [\sigma^2(F_o) + g|F_o|^2]^{-1}$; g = 0.0006 (**5b**), 0.0002 (**6b**·0.5C_6D_6); $\sigma(F_o)$ taken from counting statistics. [d] Goodness of fit (GOF) = $[\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{var})]^{1/2}$.

The structures were 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 1.29 and 0.73 (**5b**) and 1.20 and 0.77 (**6b**)) and then with anisotropic thermal parameters in the last cycles for all the non-hydrogen atoms, except for the carbon atoms of the solvent molecule (located in a symmetry center) of **6b**·0.5C_6D_6, which were refined with a common variable occupation factor and with thermal parameters fixed to 15.0 Å^2. All hydrogen atoms were refined isotropically (the D atoms of the solvent molecule of **6b**·0.5C_6D_6 were treated as H atoms), with a common thermal parameter using a riding model, except H(1) and H(2) of **5b** and H(1) of **6b**, which were left free, and H(2), H(46), and H(48) of **6b**, which were fixed in positions located in difference Fourier syntheses. No corrections for the presence of extinction were made. Atomic scattering factors were taken from ref 24. Selected bond lengths and angles are given in Tables III and IV. Final atomic coordinates are given in Tables VI and VII. Geometrical calculations were made with PARST.[25] Plots were drawn with

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Table VI. Fractional Atomic Coordinates and Isotropic Temperature Factors for 5b (with Esd's)

atom	x/a	y/b	z/c	U_{eq}, Å² × 100[a]
Sn(1)	0.01554 (7)	0.45045 (6)	0.31922 (4)	3.66 (3)
Ru(1)	0.03563 (8)	0.38115 (7)	0.19793 (4)	3.36 (3)
Ru(2)	0.09998 (8)	0.21292 (7)	0.11240 (4)	3.70 (3)
Ru(3)	0.16017 (8)	0.12956 (7)	0.25711 (4)	3.66 (3)
C(1)	−0.024 (1)	0.541 (1)	0.1424 (5)	4.3 (4)
O(1)	−0.0519 (9)	0.6357 (6)	0.1089 (4)	6.7 (4)
C(2)	0.201 (1)	0.3823 (9)	0.1896 (6)	4.4 (4)
O(2)	0.3027 (8)	0.3854 (8)	0.1814 (5)	6.7 (4)
C(3)	0.220 (1)	0.2684 (8)	0.0540 (6)	4.5 (4)
O(3)	0.2887 (8)	0.3029 (7)	0.0175 (5)	6.4 (4)
C(4)	−0.039 (1)	0.3627 (9)	0.0658 (6)	4.7 (4)
O(4)	−0.1182 (8)	0.4436 (7)	0.0282 (4)	6.6 (4)
C(5)	0.071 (1)	0.135 (1)	0.0450 (7)	5.9 (6)
O(5)	0.063 (1)	0.088 (1)	0.0048 (6)	10.3 (7)
C(6)	0.319 (1)	0.1207 (9)	0.2934 (6)	4.9 (5)
O(6)	0.4156 (9)	0.1125 (8)	0.3161 (5)	7.3 (4)
C(7)	0.133 (1)	0.044 (1)	0.3533 (7)	6.1 (5)
O(7)	0.121 (1)	−0.0080 (9)	0.4101 (5)	10.2 (6)
N(1)	−0.0148 (8)	0.1623 (8)	0.1988 (5)	3.9 (4)
N(2)	−0.1506 (7)	0.3502 (7)	0.2074 (4)	3.7 (3)
C(8)	−0.1370 (9)	0.2408 (8)	0.2103 (5)	3.8 (4)
C(9)	−0.240 (1)	0.203 (1)	0.2249 (7)	5.3 (5)
C(10)	−0.362 (1)	0.281 (1)	0.2364 (8)	6.6 (6)
C(11)	−0.379 (1)	0.393 (1)	0.2281 (6)	5.5 (5)
C(12)	−0.273 (1)	0.4284 (9)	0.2134 (6)	4.4 (4)
C(13)	−0.296 (1)	0.5586 (9)	0.2022 (7)	5.9 (5)
C(14)	0.255 (1)	0.0497 (8)	0.1696 (5)	4.2 (4)
C(15)	0.222 (1)	−0.0358 (8)	0.2183 (6)	4.6 (4)
C(16)	0.389 (1)	0.0247 (9)	0.1445 (6)	5.1 (4)
C(17)	0.464 (1)	0.091 (1)	0.1463 (7)	6.4 (6)
C(18)	0.586 (1)	0.066 (2)	0.1188 (9)	9.2 (8)
C(19)	0.642 (2)	−0.023 (2)	0.093 (1)	13 (1)
C(20)	0.570 (2)	−0.101 (2)	0.0915 (8)	11.8 (9)
C(21)	0.445 (1)	−0.075 (1)	0.1160 (6)	7.1 (6)
C(22)	0.319 (1)	−0.1529 (9)	0.2644 (6)	5.4 (5)
C(23)	0.284 (1)	−0.250 (1)	0.2771 (7)	6.5 (6)
C(24)	0.373 (2)	−0.359 (1)	0.3179 (8)	7.6 (7)
C(25)	0.486 (1)	−0.376 (1)	0.3448 (7)	7.2 (6)
C(26)	0.519 (1)	−0.287 (1)	0.3346 (6)	6.4 (5)
C(27)	0.439 (1)	−0.170 (1)	0.2936 (7)	6.3 (5)
C(28)	−0.129 (1)	0.4037 (9)	0.3890 (6)	4.5 (4)
C(29)	−0.193 (1)	0.472 (1)	0.4359 (6)	4.9 (5)
C(30)	−0.274 (1)	0.436 (1)	0.4860 (6)	6.8 (6)
C(31)	−0.293 (1)	0.332 (1)	0.4931 (7)	6.1 (6)
C(32)	−0.228 (1)	0.263 (1)	0.4473 (6)	5.6 (5)
C(33)	−0.148 (1)	0.301 (1)	0.3943 (6)	5.0 (5)
C(34)	−0.031 (1)	0.6345 (8)	0.3155 (6)	4.3 (4)
C(35)	0.029 (1)	0.6542 (9)	0.3722 (6)	5.2 (5)
C(36)	0.001 (1)	0.766 (1)	0.3785 (7)	6.6 (6)
C(37)	−0.096 (2)	0.862 (1)	0.3283 (8)	8.4 (7)
C(38)	−0.158 (2)	0.841 (1)	0.274 (1)	11 (1)
C(39)	−0.120 (2)	0.730 (1)	0.2663 (8)	8.5 (7)
C(40)	0.194 (1)	0.3546 (9)	0.3876 (6)	4.7 (4)
C(41)	0.311 (1)	0.362 (1)	0.3655 (7)	5.9 (6)
C(42)	0.422 (1)	0.299 (1)	0.4096 (9)	7.7 (7)
C(43)	0.421 (1)	0.228 (2)	0.4784 (9)	9.4 (8)
C(44)	0.307 (2)	0.221 (2)	0.5004 (9)	10.9 (9)
C(45)	0.192 (1)	0.284 (1)	0.4546 (7)	8.0 (7)

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

Table VII. Fractional Atomic Coordinates and Isotropic Temperature Factors for 6b·0.5C_6D_6 (with Esd's)

atom	x/a	y/b	z/c	U_{eq}, Å² × 100[a]
Sn(1)	0.54248 (7)	0.12169 (2)	0.46079 (7)	4.99 (3)
Ru(1)	0.41175 (8)	0.16714 (2)	0.29999 (8)	4.21 (4)
Ru(2)	0.23714 (9)	0.19522 (2)	0.07876 (8)	4.21 (4)
Ru(3)	0.30463 (9)	0.12319 (3)	0.11256 (8)	4.53 (4)
C(1)	0.386 (1)	0.1946 (3)	0.420 (1)	5.1 (5)
O(1)	0.3698 (8)	0.2113 (2)	0.4927 (7)	7.3 (4)
C(2)	0.568 (1)	0.1903 (3)	0.317 (1)	6.1 (6)
O(2)	0.6602 (8)	0.2046 (3)	0.3237 (9)	9.1 (5)
C(3)	0.140 (1)	0.2275 (3)	−0.048 (1)	5.2 (5)
O(3)	0.1009 (9)	0.2457 (3)	−0.1242 (8)	9.0 (5)
C(4)	0.389 (1)	0.2000 (3)	0.039 (1)	5.3 (5)
O(4)	0.4802 (8)	0.2047 (2)	0.0198 (8)	7.7 (4)
C(5)	0.306 (1)	0.2334 (3)	0.195 (1)	5.1 (5)
O(5)	0.3355 (9)	0.2583 (2)	0.2536 (8)	8.6 (5)
C(6)	0.296 (1)	0.0727 (4)	0.139 (1)	6.3 (6)
O(6)	0.276 (1)	0.0434 (3)	0.1493 (9)	10.2 (5)
C(7)	0.410 (1)	0.1123 (3)	0.023 (1)	6.3 (6)
O(7)	0.484 (1)	0.1059 (3)	−0.0212 (9)	11.0 (6)
N(1)	0.2373 (8)	0.1369 (2)	0.2543 (7)	4.4 (4)
N(2)	0.0960 (7)	0.1833 (2)	0.1667 (7)	3.9 (3)
C(8)	0.122 (1)	0.1542 (3)	0.2378 (9)	4.2 (4)
C(9)	0.036 (1)	0.1409 (4)	0.292 (1)	6.2 (5)
C(10)	−0.079 (1)	0.1590 (4)	0.272 (1)	6.8 (6)
C(11)	−0.106 (1)	0.1891 (4)	0.207 (1)	6.8 (6)
C(12)	−0.021 (1)	0.2010 (3)	0.151 (1)	6.2 (5)
C(13)	−0.045 (1)	0.2359 (3)	0.079 (1)	7.0 (6)
C(14)	0.165 (1)	0.1499 (3)	−0.0372 (9)	4.2 (4)
C(15)	0.096 (1)	0.1217 (3)	−0.0051 (9)	5.1 (5)
C(16)	0.155 (1)	0.1539 (3)	−0.162 (1)	5.2 (5)
C(17)	0.264 (2)	0.1594 (3)	−0.199 (1)	7.9 (7)
C(18)	0.243 (2)	0.1657 (4)	−0.316 (1)	9.1 (8)
C(19)	0.125 (2)	0.1672 (4)	−0.398 (1)	10.0 (9)
C(20)	0.017 (2)	0.1624 (4)	−0.361 (1)	9.6 (8)
C(21)	0.038 (1)	0.1553 (3)	−0.244 (1)	7.4 (6)
C(22)	0.050 (1)	0.0875 (3)	−0.073 (1)	5.9 (5)
C(23)	0.105 (1)	0.0706 (4)	−0.147 (1)	7.5 (7)
C(24)	0.058 (1)	0.0383 (4)	−0.200 (1)	8.0 (7)
C(25)	−0.043 (2)	0.0222 (4)	−0.184 (2)	10.4 (9)
C(26)	−0.103 (2)	0.0384 (5)	−0.111 (2)	13 (1)
C(27)	−0.057 (1)	0.0702 (4)	−0.058 (1)	9.4 (8)
C(28)	0.417 (1)	0.0798 (3)	0.480 (1)	5.6 (5)
C(29)	0.334 (1)	0.0878 (4)	0.539 (1)	9.5 (8)
C(30)	0.255 (2)	0.0600 (6)	0.556 (2)	12 (1)
C(31)	0.249 (2)	0.0269 (6)	0.513 (2)	12 (1)
C(32)	0.327 (2)	0.0199 (5)	0.450 (2)	11 (1)
C(33)	0.414 (1)	0.0464 (4)	0.437 (1)	7.3 (6)
C(34)	0.698 (1)	0.0945 (3)	0.422 (1)	5.5 (5)
C(35)	0.806 (1)	0.0843 (4)	0.511 (1)	8.1 (7)
C(36)	0.908 (1)	0.0665 (5)	0.489 (2)	10.3 (9)
C(37)	0.899 (2)	0.0582 (4)	0.381 (2)	9.3 (9)
C(38)	0.788 (2)	0.0663 (4)	0.292 (1)	9.7 (8)
C(39)	0.692 (1)	0.0855 (4)	0.311 (1)	8.7 (7)
C(40)	0.627 (1)	0.1448 (4)	0.633 (1)	6.2 (6)
C(41)	0.664 (1)	0.1809 (4)	0.645 (1)	8.7 (7)
C(42)	0.699 (2)	0.1963 (5)	0.752 (2)	15 (1)
C(43)	0.709 (2)	0.1760 (7)	0.851 (2)	13 (1)
C(44)	0.670 (2)	0.1415 (7)	0.839 (2)	13 (1)
C(45)	0.631 (1)	0.1256 (5)	0.731 (1)	9.6 (8)
C(46)	0.490 (3)	0.5292 (8)	0.673 (2)	15.00[b]
C(47)	0.539 (3)	0.5112 (7)	0.622 (2)	15.00[b]
C(48)	0.444 (2)	0.5071 (8)	0.503 (3)	15.00[b]

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_ia_ja^*_ia^*_j$. [b] U_{iso} (Å² × 100), SOF = 0.76 (1).

the EUCLID package.[26] All calculations were performed on a Micro VAX-3400 computer at the Centro de Cálculo Científico of the University of Oviedo.

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(26) Spek, A. L. The EUCLID Package. In *Computational Crystallography*; Sayre, D., Ed.; Clarendon Press: Oxford, England, 1982; p 528.

Supplementary Material Available: Tables of bond lengths and angles, anisotropic thermal parameters, H atom coordinates, and angles between least-squares planes and lines and diagrams with complete atomic numbering schemes for both structural analyses (**5b** and **6b**) and a figure containing the carbonyl region of the proton-coupled and proton-decoupled ^{13}C NMR spectra of **4b** (17 pages). Ordering information is given on any current masthead page.

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