

## Protonation of triruthenium carbonyl cluster complexes containing a bridging 1-azavinylidene ligand. Experimental results and EHMO calculations

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Received 24 July 1997; received in revised form 10 November 1997

### Abstract

The  $\eta^1$ -1-azavinylidene cluster complex  $[\text{Ru}_3(\mu\text{-H})(\mu\text{-N}=\text{CPh}_2)(\text{CO})_{10}]$  (**1**) cannot be protonated with tetrafluoroboric acid in dichloromethane solvent. However, under analogous conditions, the phosphine-substituted derivatives  $[\text{Ru}_3(\mu\text{-H})(\mu\text{-N}=\text{CPh}_2)(\mu\text{-dppm})(\text{CO})_8]$  (**2**),  $[\text{Ru}_3(\mu\text{-H})(\mu\text{-N}=\text{CPh}_2)(\text{PPh}_3)(\text{CO})_9]$  (**3**) and  $[\text{Ru}_3(\mu\text{-H})(\mu\text{-N}=\text{CPh}_2)(\text{PPh}_3)_2(\text{CO})_8]$  (**4**) undergo protonation at the metal atoms to give the cationic dihydrido derivatives  $[\text{Ru}_3(\mu\text{-H})_2(\mu\text{-N}=\text{CPh}_2)(\mu\text{-dppm})(\text{CO})_8][\text{BF}_4]$  (**5**),  $[\text{Ru}_3(\mu\text{-H})_2(\mu\text{-N}=\text{CPh}_2)(\text{PPh}_3)(\text{CO})_9][\text{BF}_4]$  (**6**) and  $[\text{Ru}_3(\mu\text{-H})_2(\mu\text{-N}=\text{CPh}_2)(\text{PPh}_3)_2(\text{CO})_8][\text{BF}_4]$  (**7**), respectively. EHMO calculations on complex **1** and on the phosphine-substituted model compound  $[\text{Ru}_3(\mu\text{-H})(\mu\text{-N}=\text{CPh}_2)(\text{PH}_3)_2(\text{CO})_8]$  (**8**) have shown that the protonation is expected to take place on the metal atoms (the highest ten occupied MOs of **1** and **8** are fundamentally of metallic character) and that the ruthenium atoms of **8** are electron richer, and therefore more basic, than those of **1**, suggesting that phosphine-substituted derivatives of **1** are more liable to undergo protonation than complex **1**. © 1998 Elsevier Science S.A. All rights reserved.

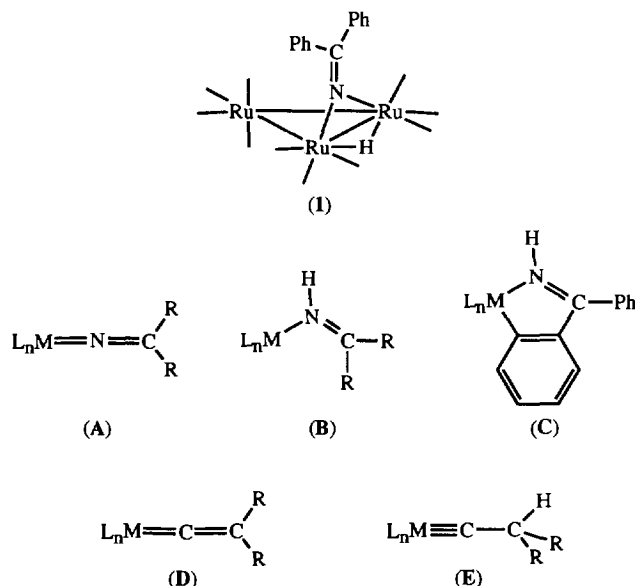
**Keywords:** Ruthenium; Clusters; Azavinylidene ligands; Protonation reactions; EHMO calculations

### 1. Introduction

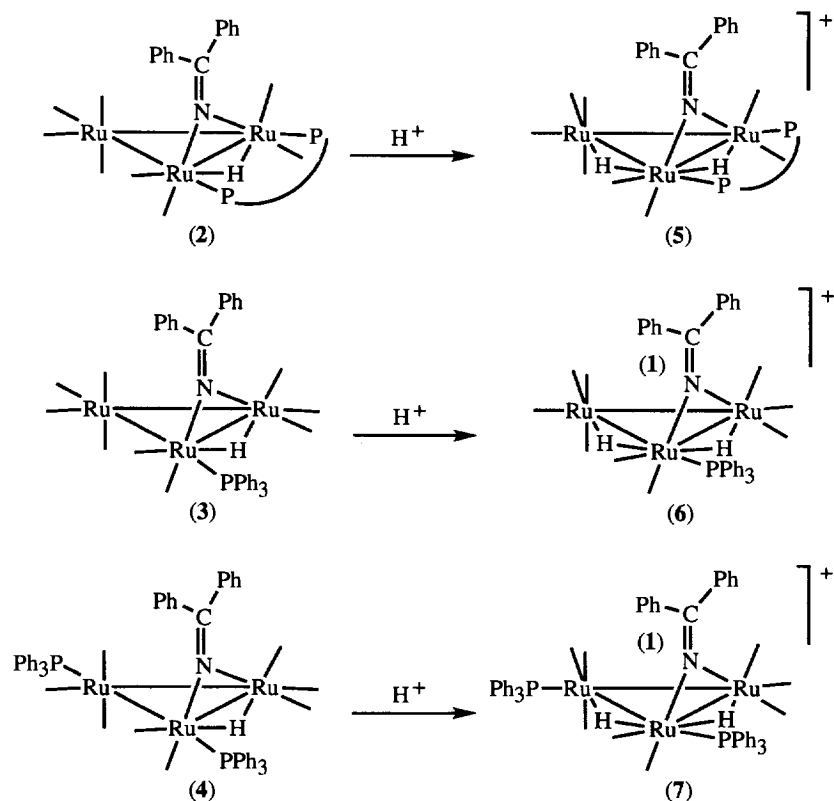
In a previous paper, we have reported a high-yield synthesis of the trinuclear 1-azavinylidene complex  $[\text{Ru}_3(\mu\text{-H})(\mu\text{-N}=\text{CPh}_2)(\text{CO})_{10}]$  (**1**) [1].

Reactivity studies on compound **1** have shown that (a) it easily replaces carbonyl ligands by phosphine ligands [1], (b) it reacts with diphenylacetylene undergoing an unusual insertion of the alkyne into a metal–nitrogen bond [2], and (c) the azavinylidene ligand can also coordinate to three metal atoms in a face-capping mode [1].

On the other hand, it has been reported that mononuclear 1-azavinylidene complexes of type A



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Scheme 1.

(Chart 1) can be protonated at the nitrogen atom to give derivatives of type **B**. These protonated compounds are unstable when  $R = \text{Ph}$ , undergoing a subsequent orthometallation process to afford metallacycles of type **C** [3]. Protonation of nucleophilic vinylidene complexes (**D**) occurs on the  $\beta$ -carbon atom and leads to carbyne derivatives of type **E** [4].

As, to our knowledge, no protonation reactions of complexes containing bridging 1-azavinylidene ligands have been reported, we decided to study the protonation of compound **1** and of some of its substituted derivatives. In this paper we also report some EHMO calculations that help rationalize the experimental results.

## 2. Results and discussion

No reaction was observed between compound **1** and an excess of  $\text{HBF}_4 \cdot \text{OEt}_2$  in dichloromethane at room temperature. However, under the same conditions, the phosphine-substituted derivatives  $[\text{Ru}_3(\mu\text{-H})(\mu\text{-N}=\text{CPh}_2)(\mu\text{-dppm})(\text{CO})_8]$  (**2**),  $[\text{Ru}_3(\mu\text{-H})(\mu\text{-N}=\text{CPh}_2)(\text{PPh}_3)(\text{CO})_9]$  (**3**) and  $[\text{Ru}_3(\mu\text{-H})(\mu\text{-N}=\text{CPh}_2)(\text{PPh}_3)_2(\text{CO})_8]$  (**4**) (Scheme 1) underwent protonation at an unbridged Ru–Ru edge to give the cationic dihydrido complexes  $[\text{Ru}_3(\mu\text{-H})_2(\mu\text{-N}=\text{CPh}_2)(\mu\text{-dppm})(\text{CO})_8][\text{BF}_4]$  (**5**),  $[\text{Ru}_3(\mu\text{-H})_2(\mu\text{-N}=\text{CPh}_2)(\text{PPh}_3)(\text{CO})_9][\text{BF}_4]$  (**6**) and  $[\text{Ru}_3(\mu\text{-H})_2(\mu\text{-N}=\text{CPh}_2)(\text{PPh}_3)_2(\text{CO})_8][\text{BF}_4]$  (**7**), respectively.

The structures proposed for compounds **5–7** in Scheme 1 are based on their analytical and spectroscopic data.

The cationic character of the protonated complexes was clearly evidenced by the higher wavenumbers of the  $\nu(\text{CO})$  absorptions of their IR spectra (Table 1), as compared to those of their neutral precursors [1]. In contrast with the results found for some mononuclear 1-azavinylidene compounds, which undergo protonation at the nitrogen atom [3], the NMR spectra of compounds **5–7** unambiguously indicated that the protonation of **2–4** had taken place on a metal–metal edge.

The addition of a proton to complex **2** diminishes the initial  $C_s$  symmetry into  $C_1$ , as manifested by the  $^1\text{H}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of **5**, which show two hydride ligands and two distinct phosphorus atoms

Table 1  
Selected IR data

Comp.	$\nu(\text{CO})/\text{cm}^{-1}$
<b>5</b> <sup>a</sup>	2117 (m), 2066 (s), 2044 (vs), 1981 (w)
<b>6</b> <sup>a</sup>	2130 (w), 2083 (m), 2072 (m), 2054 (vs), 2045 (vs), 2009 (s), 1955 (w)
<b>7</b> <sup>a</sup>	2138 (w), 2097 (m), 2066 (s), 2029 (vs), 2020 (m)

<sup>a</sup> In  $\text{CH}_2\text{Cl}_2$ .

Table 2  
Selected  $^1\text{H}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR data

Comp.	$\delta(\mu\text{-H})$ ppm <sup>a</sup>	$\delta(\text{P})$ ppm <sup>a</sup>
5 <sup>b</sup>	–12.99 (t) [13.2], –16.87 (dd) [26.9, 5.1]	15.7 (d) {28.1}, 12.4 (d) {28.1}
6	–12.75 (d) [12.8], –12.96 (d) [28.2]	38.6 (s)
7	–12.50 (ddd) <sup>c</sup> [12.4, 3.4], –16.74 (ddd) <sup>c</sup> [34.3, 8.7]	36.6 (s), 28.1 (s)

<sup>a</sup> Spectra were recorded in  $\text{CDCl}_3$ ; multiplicities are given in parentheses; coupling constants (Hz) are given in square brackets [ $J_{\text{H-P}}$ ] or braces  $\{J_{\text{H-P}}\}$ .

<sup>b</sup>  $\delta(\text{CH}_2) = 4.59$  (m, 1 H), 3.48 (m, 1 H) ppm.

<sup>c</sup>  $J_{\text{H-H}} = 1$  Hz.

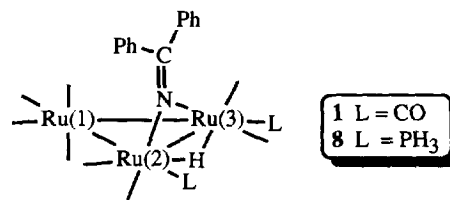
(Table 2). The  $J_{\text{H-P}}$  coupling constants measured in the hydride resonances clearly indicate that the triplet (with  $J_{\text{H-P}} = 13.2$  Hz, typical of a *cis* coupling [5]) corresponds to the hydride which spans the same Ru–Ru edge as the dppm ligand, while the doublet of doublets corresponds to the other hydride, which is *trans* to one phosphorus atom ( $J_{\text{H-P}} = 26.9$  Hz, typical of a *trans* coupling [5]) and is far away from the other one ( $J_{\text{H-P}} = 5.1$  Hz).

Complexes **3** and **4** are asymmetric and have two distinct unbridged Ru–Ru edges accessible to the entering protons. However, the  $^1\text{H}$  NMR spectra of the protonated products **6** and **7** (Table 2) indicate that both protonations are regioselective, taking place at the Ru–Ru edges containing the maximum number of phosphine ligands (Scheme 1). In fact, the presence of phosphine ligands is expected to increase the basicity of the metal atoms attached to them, making these atoms more liable to be protonated than the other metal atoms. Thus, both hydride resonances of complex **6** are doublets, with  $J_{\text{H-P}}$  coupling constants which suggest that the phosphorus atom is *cis* to one hydride (12.8 Hz) and *trans* to the other (28.2 Hz) [6,7]. In the case of complex **7**, one hydride is *cis* to one phosphorus atom (12.4 Hz) and far away from the other phosphorus (3.4 Hz), while the other hydride is *cis* to one phosphorus (8.7 Hz) and *trans* to the other (34.3 Hz) [6,7], as shown in Scheme 1. This structural assignment for compound **7** implies that, on protonation, the phosphine ligand which in complex **4** is attached to the unbridged ruthenium atom changes its coordination site to the adjacent equatorial position, thus resulting *cis* to the new hydride ligand. These processes can in fact be associated to the color changes observed during the protonation of the red complex **4**, which immediately changed to dark brown (protonation), ending orange after only 2 min (coordination shift of the phosphine ligand). The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of the orange complex **7** is also consistent with this change of coordination site of the phosphine ligand, since the phosphorus atoms of **7**

are not coupled to each other, while  $J_{\text{P-P}}$  in complex **4** is 31.2 Hz. Related changes of coordination sites of phosphine ligands occurring on protonation of neutral precursors have been reported previously [6,7].

All these data suggest that, in compounds **1–4**, the nitrogen atom of the bridging 1-azavinylidene ligand is not basic enough to be protonated. In addition, the introduction of phosphine ligands into carbonyl complexes increases the basic character of the metal atoms, making them more susceptible to undergo reactions with electrophilic reagents than their unsubstituted precursors [8]. Protonation reactions of other neutral triruthenium carbonyl clusters have been described previously and they generally lead to cationic hydride-bridged derivatives [5–7,9]. However, as commented above, the protonation of some mononuclear 1-azavinylidene complexes takes place at the nitrogen atom [3]. In view of these findings, we decided to carry out some theoretical calculations in order to rationalize the situation.

EHMO calculations were carried out on complex **1** and on the model phosphine-substituted derivative  $[\text{Ru}_3(\mu\text{-H})(\mu\text{-N}=\text{CPh}_2)(\text{PH}_3)_2(\text{CO})_8]$  (**8**) (both idealized to  $C_s$  symmetry). Selected results are collected in Tables 3–5.



Tables 3 and 4 show the composition of the highest ten occupied MOs of compounds **1** and **8**, respectively. Since some of these orbitals are expected to be among the most responsible ones for the reactivity of these complexes, the high contribution of metal atomic orbitals to these OMs indicates that protonation (if at all occurs) should preferably take place on the metal

Table 3  
Composition of the highest ten occupied MOs of complex **1**

OM <sup>a</sup>	Ru <sub>3</sub> (%)	N (%) <sup>b</sup>	C (%) <sup>b</sup>	Other (%)
53a' (HOMO)	39.5	2.3	1.2	57.0
43a''	78.6	0.0	0.0	21.4
52a'	62.2	2.4	2.7	32.2
51a'	64.8	0.9	0.2	34.1
42a''	63.8	1.5	0.8	33.9
50a'	77.5	0.4	0.2	34.1
41a''	68.5	2.2	0.9	28.4
40a''	31.5	1.7	4.5	62.3
39a''	45.9	0.2	0.5	53.4
49a'	59.3	4.3	0.6	35.8

<sup>a</sup> The energies of these orbitals range from –11.254 eV for 53a' to –12.425 eV for 49a'.

<sup>b</sup> Of the 1-azavinylidene ligand.

Table 4  
Composition of the highest ten occupied MOs of complex 8

OM <sup>a</sup>	Ru <sub>3</sub> (%)	N (%) <sup>b</sup>	C (%) <sup>b</sup>	Other (%)
52a' (HOMO)	64.4	1.9	3.7	30.0
42a''	79.7	0.0	0.0	20.3
51a'	76.4	1.2	1.7	20.7
41a''	72.1	5.7	1.5	20.7
50a'	68.1	2.2	0.8	29.9
40a''	84.1	0.1	0.2	15.6
39a''	17.8	2.0	5.6	74.6
49a'	67.3	1.3	0.2	31.2
38a''	46.8	3.3	0.2	29.6
48a'	67.9	2.3	1.4	59.3

<sup>a</sup> The energies of these orbitals range from –10.752 eV for 52a' to –12.380 eV for 48a'.

<sup>b</sup> Of the 1-azavinylidene ligand.

atoms, ruling out the possibility of protonation on the nitrogen or carbon atoms of the 1-azavinylidene ligand.

Table 5 clearly shows that the replacement of carbonyl ligands of compound 1 by phosphine ligands is accompanied by a considerable decrease of the positive charges allocated on the metal atoms. This effect is not only observed on the ruthenium atoms attached to the phosphine ligands, but also on the unsubstituted Ru(1) atom. It should also be noticed that the effect of ligand substitution on the charges allocated on the 1-azavinylidene ligand N and C atoms is nearly negligible.

In conclusion, in spite of the limited reliability of the numerical results obtained by the EH calculation method, the calculations described in this work have helped rationalize the experimental results obtained on protonation reactions of the 1-azavinylidene-bridged compound 1 and of some of its phosphine-substituted derivatives, since they have shown that (a) if protonation occurs, it should take place on the metal atoms, and (b) the phosphine substituted derivatives are more prone to undergo protonation than their unsubstituted predecessors.

Table 5  
Selected results of EHMO calculations on compounds 1 and 8

	1	8
Charge on Ru(1)	+0.565	+0.291
Charge on Ru(2) and Ru(3)	+0.071	–0.385
Charge on N <sup>a</sup>	–0.418	–0.500
Charge on C <sup>a</sup>	+0.546	+0.514

<sup>a</sup> Of the 1-azavinylidene ligand.

### 3. Experimental details

#### 3.1. General data

Solvents were dried over sodium diphenyl ketyl (diethyl ether, hydrocarbons) or CaH<sub>2</sub> (dichloromethane) and distilled under nitrogen prior to use. The reactions were carried out under nitrogen at room temperature, using Schlenk-vacuum line techniques, and were routinely monitored by solution IR spectroscopy (carbonyl stretching region). Compounds 1–4 were prepared as described previously [1]. HBF<sub>4</sub> · OEt<sub>2</sub> was used as received from Aldrich. Infrared spectra were recorded on a Perkin–Elmer FT 1720-X spectrophotometer, using 0.1-mm CaF<sub>2</sub> cells. <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectra were run at 20°C with Bruker AC-200 and AC-300 instruments, using SiMe<sub>4</sub> (internal, for <sup>1</sup>H) or 85% H<sub>3</sub>PO<sub>4</sub> (external, for <sup>31</sup>P) as standards (δ = 0 ppm). Microanalyses were obtained from the University of Oviedo Analytical Service. Carbonyl IR absorptions and relevant <sup>1</sup>H and <sup>31</sup>P NMR data are given in Tables 1 and 2, respectively.

#### 3.2. [Ru<sub>3</sub>(μ-H)<sub>2</sub>(μ-N=CPh<sub>2</sub>)(μ-dppm)(CO)<sub>8</sub>][BF<sub>4</sub>] (5)

A solution of compound 2 (50 mg, 0.046 mmol) in dichloromethane (10 ml) was treated with an excess of HBF<sub>4</sub> · OEt<sub>2</sub> (0.1 ml). The color changed from red to orange. The solvent was removed under reduced pressure and the residue was washed with diethyl ether (3 × 5 ml) to give compound 5 as an orange solid (45 mg, 83%). Anal. Calcd for C<sub>46</sub>H<sub>34</sub>BF<sub>4</sub>NO<sub>8</sub>P<sub>2</sub>Ru<sub>3</sub>: C, 46.79; H, 2.90; N, 1.19. Found: C, 47.21; H, 2.97; N, 1.08.

#### 3.3. [Ru<sub>3</sub>(μ-H)<sub>2</sub>(μ-N=CPh<sub>2</sub>)(PPh<sub>3</sub>)(CO)<sub>9</sub>][BF<sub>4</sub>] (6)

A solution of compound 3 (50 mg, 0.050 mmol) in dichloromethane (10 ml) was treated with an excess of HBF<sub>4</sub> · OEt<sub>2</sub> (0.5 ml). The color changed from orange to yellow. The solvent was removed under reduced pressure and the residue was washed with diethyl ether (3 × 5 ml) to give compound 6 as a yellow solid (50 mg, 92%). Anal. Calcd for C<sub>40</sub>H<sub>27</sub>BF<sub>4</sub>NO<sub>9</sub>PRu<sub>3</sub>: C, 44.21; H, 2.50; N, 1.29. Found: C, 44.32; H, 2.49; N, 1.25.

#### 3.4. [Ru<sub>3</sub>(μ-H)<sub>2</sub>(μ-N=CPh<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>(CO)<sub>8</sub>][BF<sub>4</sub>] (7)

An excess of HBF<sub>4</sub> · OEt<sub>2</sub> (0.1 ml) was added to a solution of compound 4 in dichloromethane (10 ml). The color changed immediately from bright red to dark brown, becoming orange after 2 min. The solution was evaporated to dryness and the oily residue was washed with 1:1 pentane-diethyl ether (3 × 10 ml) and then with diethyl ether (3 × 10 ml) to give complex 7 as an orange solid (48.2 mg, 90%). Anal. Calcd for

C<sub>57</sub>H<sub>42</sub>BF<sub>4</sub>NO<sub>8</sub>P<sub>2</sub>Ru<sub>3</sub>: C, 51.83; H, 3.21; N, 1.06.  
Found: C, 51.38; H, 3.12; N, 0.87.

### 3.5. EHMO calculations

Theoretical MO calculations were carried out at the Extended Hückel level [10] using the CACAO program [11]. The atomic orbital parameters for H, C, N, O [10]c, P [12] and Ru [13] were taken from the literature. The structural parameters used for **1** and **8** were based on the X-ray diffraction data published for the compound [Ru<sub>3</sub>(μ-H)(μ-N=CPh<sub>2</sub>)(μ-dppm)(dppm)(CO)<sub>7</sub>] [1], averaging the appropriate distances and angles in order to obtain ideal C<sub>s</sub> symmetry. For compound **8**, two sets of input data were used, including and excluding the phosphorus 3d atomic orbitals, but both resulted in similar calculation results as far as atom charges and MO composition (atom %) are concerned. The data shown in Tables 3–5 correspond to calculations excluding the phosphorus 3d atomic orbitals.

### Acknowledgements

This research was supported by the DGES (Spain, Grant PB95-1042).

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