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Reactivity of the 1-azavinylidene cluster $[Ru_3(\mu\text{-}H)(\mu\text{-}N{=}CPh_2)(CO)_{10}]$ with hydrogen, tertiary silanes and tertiary stannanes

Claudette Bois [a], Javier A. Cabeza [b,*], R. Jesús Franco [b], Víctor Riera [b], Enrique Saborit [b]

[a] *Laboratoire de Chimie des Métaux de Transition, Université Pierre et Marie Curie, URA-CNRS 419, 4 Place Jussieu, F-75252 Paris Cedex, France*

[b] *Departamento de Química Orgánica e Inorgánica, Instituto de Química Organometálica 'Enrique Moles', Universidad de Oviedo-CSIC, E-33071 Oviedo, Spain*

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Abstract

The reactivity of the 1-azavinylidene cluster $[Ru_3(\mu\text{-}H)(\mu\text{-}N{=}CPh_2)(CO)_{10}]$ (**1**) with hydrogen, tertiary silanes and tertiary stannanes has been investigated. The reaction of **1** with hydrogen (1 atm, 110°C) gives $[Ru_4(\mu\text{-}H)_4(CO)_{12}]$ and H_2NCHPh_2 as end-products, proceeding via the imido and amido intermediates $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-}NCHPh_2)(CO)_9]$ (**2**) and $[Ru_3(\mu\text{-}H)(\mu\text{-}HNCHPh_2)(CO)_{10}]$ (**3**), respectively. Although no reaction is observed between compound **1** and tertiary organosilanes at 110°C, **1** reacts readily with tertiary organostannanes to give $[Ru_3(\mu\text{-}H)_2(\mu\text{-}N{=}CPh_2)(SnR_3)(CO)_9]$ (**4**: R = Ph; **5**: R = Bu). ^{1}H-NMR spectroscopy and the X-ray structure of the triphenylstannyl derivative **4** demonstrate that the addition of the stannane reagents to **1** takes place on the cluster metal framework. No transfer of the stannyl group from the metal to the azavinylidene ligand is observed at 110°C. This is in contrast with the results obtained in the hydrogenation of **1**, where reduction of the azavinylidene ligand is observed under comparable reaction conditions.

Keywords: Ruthenium; Cluster; Azavinylidene; Hydrogenation; Tertiary stannane; X-ray structure

1. Introduction

We have recently reported a high-yield synthesis of the trinuclear 1-azavinylidene complex $[Ru_3(\mu\text{-}H)(\mu\text{-}N{=}CPh_2)(CO)_{10}]$ (**1**), starting from $[Ru_3(CO)_{12}]$ and benzophenone imine [1]. Reactivity studies on compound **1** have shown that: (a) it easily undergoes substitution of carbonyl ligands by phosphine ligands [1]; (b) it reacts with diphenylacetylene experiencing an unusual insertion of the alkyne into a metal–nitrogen bond [2]; (c) its carbonyl-substituted phosphine derivatives undergo protonation at the metal atoms but not at the azavinylidene fragment [3]; and (d) the azavinylidene ligand can also coordinate to three metal atoms in a face-capping mode [1].

On the other hand, all the other previous examples of transition metal carbonyl cluster compounds containing 1-azavinylidene ligands are of the type $[M_3(\mu\text{-}H)(\mu\text{-}N{=}CHR)(CO)_{10}]$ and have been prepared in low yields by hydrogenation of nitriles on iron [4], ruthenium [5–9] and osmium [10–12] carbonyl clusters, but the low efficiency of these syntheses has prevented a subsequent development of their derivative chemistry.

We now report the reactivity of compound **1** with hydrogen. We undertook this study having in mind that compounds of the type $[Ru_3(\mu\text{-}H)(\mu\text{-}N{=}CHR)(CO)_{10}]$ are intermediates in the hydrogenation of nitriles to amines promoted by $[M_3(CO)_{12}]$ (M = Fe [4,13,14], Ru [7], Os [12]) and that, therefore, a study of the reactivity of the readily available compound **1** with hydrogen would shed more light on the mechanism of this hydrogenation reaction.

* Corresponding author. Tel.: +34 98 5103501: fax: +34 98 5103446; e-mail: jac@sauron.quimica.uniovi.es

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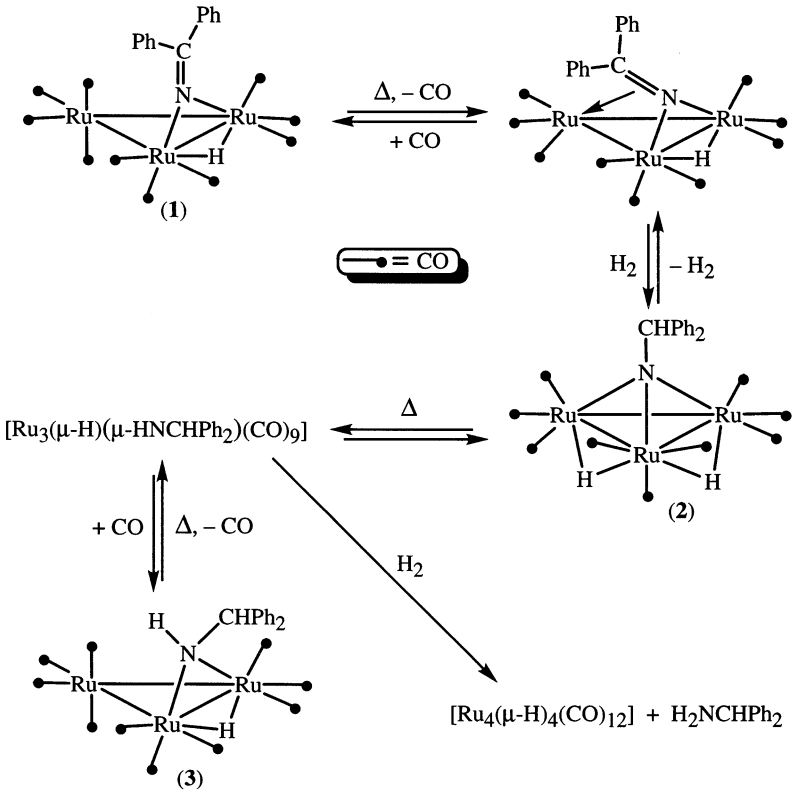


Scheme 1

In addition, the reactivity of compound **1** with triorganosilanes and triorganostannanes is also reported and compared with that observed with hydrogen. Hydrosilylated and hydrostannanted products are also of interest [15,16], and triorganosilanes and triorganostannanes often react with unsaturated organic molecules [15,16] and transition metal clusters [17] in a similar way as hydrogen.

2. Results and discussion

2.1. Hydrogenation reactions

Treatment of the 1-azavinylidene cluster $[Ru_3(\mu\text{-}H)(\mu\text{-}N{=}CPh_2)(CO)_{10}]$ (**1**) with hydrogen (1 atm) in toluene at reflux temperature gave $[Ru_4(\mu\text{-}H)_4(CO)_{12}]$ and H_2NCHPh_2 as end-products. The reaction required at least 6 h to be completed. The imido and amido derivatives $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-}NCHPh_2)(CO)_9]$ (**2**) and $[Ru_3(\mu\text{-}H)(\mu\text{-}HNCHPh_2)(CO)_{10}]$ (**3**), respectively (Scheme 1), were identified in the reacting solution with the help of NMR spectroscopy at intermediate reaction times.

Compounds **2** and **3** were separated by chromatographic means from the other components of the reaction mixtures, but all attempts to separate these complexes from each other resulted unsuccessful. Nevertheless, they could be identified by analysing the ^{1}H-NMR spectra the mixtures obtained at various reaction times (Table 1). Thus, excluding the resonances due to the phenyl groups, compound **2** is characterized by two singlet resonances in a 2:1 ratio, while compound **3** is characterized by three resonances, in a 1:1:1 integral ratio, whose chemical shifts and multiplicities unequivocally allow their assignment (Table 1). Confirming our assignment, the ratio of the resonances belonging to the same compound is maintained constant

Table 1
Selected ^{1}H-NMR data (δ ppm)[a]

Compound	μ-H	Other
2[b]	−17.16 (s, 2H)	5.64 (s, 1H), C*H*Ph$_2$
3[b]	−13.73 (d, 1H) [1.1]	5.81 (dd, 1H) [11.6, 1.1], N*H* 3.93 (d, 1H) [11.6], C*H*Ph$_2$
4	−12.06 (s[c], 1H), −13.43 (s, 1H)	7.5–6.5 (m, 25H), 5*Ph*
5	−12.41 (s[d], 1H), −12.69 (s, 1H)	7.4–7.1 (m, 10H), 2*Ph* 1.6–0.8 (m, 27H), 3*Bu*

[a] Spectra were recorded in $CDCl_3$; multiplicities are given in parentheses; coupling constants (Hz) are given in square brackets.
[b] The resonances of the phenyl groups of **2** cannot be distinguished from those of **3**.
[c] With tin satellites, $J(^{117}Sn-^1H)$ Å ca. $J(^{119}Sn-^1H)$ Å 39 Hz.
[d] With tin satellites, $J(^{117}Sn\text{-}^1H)$ Å ca. $J(^{119}Sn-^1H)$ Å 37 Hz.

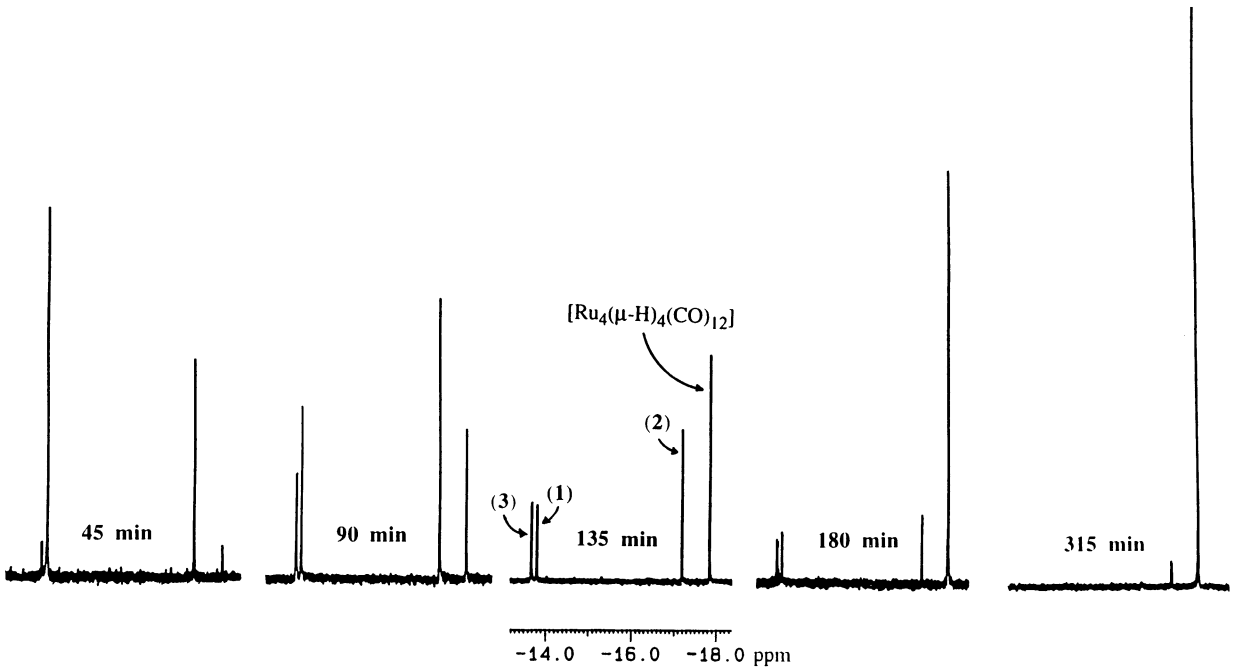


Fig. 1. Hydride region of the ^{1}H-NMR spectra of samples obtained at different reaction times during the hydrogenation (1 atm) of compound **1** in refluxing toluene. The scale and peak assignments are only given in the central spectrum but are common to the five spectra.

in the spectra of samples obtained after different reaction times, where the ratio of **2** and **3** is not maintained. Furthermore, the chemical shifts reported for the hydride ligands of the X-ray structurally characterized imido and amido compounds $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-}NCH_2\text{-}p\text{-}C_6H_4OMe)(CO)_9]$ (-17.17 ppm) [6] and $[Ru_3(\mu\text{-}H)(\mu\text{-}HNCH_2Ph)(CO)_{10}]$ (-13.52 ppm) [18] are comparable to those we report here for **2** and **3**, respectively.

Monitoring the reaction of compound **1** with hydrogen by ^{1}H-NMR spectroscopy (Fig. 1) revealed that: (a) complex **2** is the first intermediate cluster formed at the expenses of **1** (major product after 45 min); (b) the amount of the amido complex **3** increases very slowly during the first 90 min; (c) after 90 min, the amounts of both **2** and **3** slowly decrease until they completely disappear; and (d) the amount of $[Ru_4(\mu\text{-}H)_4(CO)_{12}]$ continuously increases as the reaction progresses.

As **2** seems to be formed prior than **3** in the reaction and as the hydrogenation of the C=N moiety of **1** requires its π-coordination to a metal atom in order to allow the transfer of a hydride from the metal to the carbon atom, we propose the existence of an elusive (not detected) intermediate, $[Ru_3(\mu\text{-}H)(\mu_3\text{-}N{=}CPh_2)(CO)_9]$, which contains the azavinylidene ligand in a face-capping mode (Scheme 1). Such a coordination mode for an azavinylidene ligand has precedents in iron [4] and ruthenium [1] carbonyl cluster chemistry. The equilibrium that leads from **1** to $[Ru_3(\mu\text{-}H)(\mu_3\text{-}N{=}CPh_2)(CO)_9]$ should be very displaced to the left, since the latter was not detected when complex **1** was stirred in toluene at reflux temperaure for several hours. A subsequent reaction of $[Ru_3(\mu\text{-}H)(\mu_3\text{-}N{=}CPh_2)(CO)_9]$ with hydrogen would lead to compound **2** (in several steps).

In order to establish the connection between **2** and **3** in the hydrogenation reaction of **1**, the thermolysis under nitrogen of a mixture of these two compounds in refluxing toluene was monitored by ^{1}H-NMR spectroscopy. Interestingly, the amounts of both **2** and **3** decreased with time, while **1** and $[Ru_4(\mu\text{-}H)_4(CO)_{12}]$ were progressively formed (Fig. 2). An IR spectrum and a spot TLC analysis of the resulting solution also showed the presence of $[Ru_3(CO)_{12}]$ in the reaction mixture. These data, coupled to the fact that both **2** and **3** give $[Ru_4(\mu\text{-}H)_4(CO)_{12}]$ under hydrogen (Fig. 1), suggest that both compounds are connected through a common, very unstable, intermediate which is a common product of their thermolysis, which reacts with hydrogen (in several steps) to give $[Ru_4(\mu\text{-}H)_4(CO)_{12}]$,

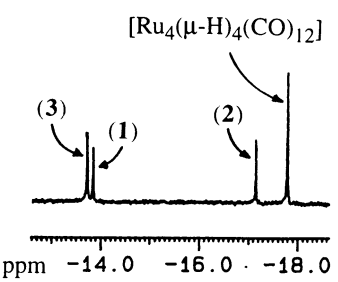
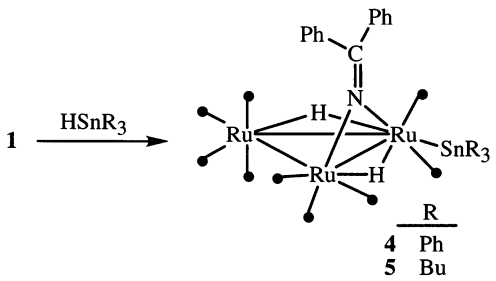


Fig. 2. Hydride region of the ^{1}H-NMR spectrum of a sample obtained by thermolysis under nitrogen of a ca. 1:1 mixture of **2** and **3** in refluxing toluene for 2.5 h.



Scheme 2.

and which decomposes on heating in the absence of hydrogen to give a mixture of compound **1**, $[Ru_3(CO)_{12}]$ and $[Ru_4(\mu\text{-}H)_4(CO)_{12}]$. The unsaturated 46-electron derivative $[Ru_3(\mu\text{-}H)(\mu\text{-}HNCHPh_2)(CO)_9]$, which would arise under thermal conditions from the hydrogen transfer of a hydride from the metal to the nitrogen atom of **2** and from the release of a CO ligand from **3**, would be a reasonable proposal for such an unstable intermediate. This would also account for the small amount of complex **3** formed during the hydrogenation reaction, since the formation of **3** from the unsaturated intermediate $[Ru_3(\mu\text{-}H)(\mu\text{-}HNCHPh_2)(CO)_9]$ requires carbon monoxide and only a small amount of the latter should be available in solution.

All this data, coupled to previous data on related systems, have allowed us to propose Scheme 1 as a mechanism for the hydrogenation of compound **1**.

As commented in the introductory section, 1-azavinylidene derivatives of type $[M_3(\mu\text{-}H)(\mu\text{-}N{=}CHR)(CO)_{10}]$ (M = Fe, Ru, Os) are intermediates in the hydrogenation of nitriles to amines promoted by the corresponding carbonyl metal cluster; therefore, the mechanism shown in Scheme 1 also represents a mechanism for that reaction, being the most complete proposal reported so far [12,14].

2.2. Reactions with tertiary silanes and tertiary stannanes

No reaction was observed between compound **1** and an excess of triethylsilane or triphenylsilane (toluene, reflux temperature, 1 h). However, under milder reaction conditions (1,2-dichloroetane, reflux temperature, 15 min), compound **1** reacted with triphenylstannane and tributylstannane to give the stannyl derivatives $[Ru_3(\mu\text{-}H)_2(\mu\text{-}N{=}CPh_2)(SnR_3)(CO)_9]$ (**4**: R = Ph; **5**: R = Bu) in high yields (Scheme 2). Compound **4** was obtained as a crystalline yellow solid, but compound **5** was obtained as a tan oil which could not be crystallized. Other tributylstannyl derivatives of triruthenium clusters have also been reported as oils [17,19–21]. The IR spectra of **4** and **5** are very similar, suggesting an analogous structure for both compounds, and show the ν(CO) absorptions shifted to higher wavenumbers than those of complex **1** [1], as expected for a higher formal oxidation state of the metal atoms. Their ^{1}H-NMR spectra (Table 1) clearly indicate the incorporation of a new hydride and one SnR_3 group to the original complex. However, with all these spectroscopic data it was not possible to precisely locate the position of the corresponding SnR_3 group on the clusters and, thus, an X-ray diffraction study was carried out.

Fig. 3 represents the X-ray molecular structure of compound **4**. Selected bond lengths and angles are given in Table 2. The cluster consists on a triangular array of ruthenium atoms with one of the edges being spanned by the nitrogen atom of the 1-azavinylidene ligand, which occupies two axial coordination sites. That edge and one of the two remaining edges are also bridged by hydride ligands. Although the location of hydrides by X-ray methods has always to be considered cautiously, in this case the X-ray data fit consistently with the NMR data. The $SnPh_3$ group is coordinated, in an equatorial position, to the ruthenium atom attached to the two hydrides. The ligand shell of the cluster is completed by nine CO ligands. Overall, this structure can be compared to that of the cluster $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-ampy})(SiEt_3)(CO)_8]$ (Hampy = 2-amino-6-methylpyridine), in which the ampy ligand occupies three axial coordination sites [22], although it differs in that the $SnPh_3$ group of **4** is *cis* to the hydride which spans the same edge as the bridging ligand, whereas the $SiEt_3$ group of the ampy complex is *trans* to the analogous hydride ligand.

All attempts to efficiently promote the transfer of the stannyl group of complex **4** from the metal to the azavinylidene ligand (refluxing in toluene, treatment with carbon monoxide or with triphenylphosphine in refluxing toluene) were unsuccessful, since they failed to give a tractable product. Therefore, no products derived from hydrostannated 1-azavinylidene could be prepared and this contrasts with the results commented above on the reaction of compound **1** with hydrogen, where the hydrogenation of the 1-azavinylidene ligand is achieved. However, the synthesis and structural characterization of compounds **4** and **5** may shed some more light on the mechanism of the reaction of compound **1** with hydrogen. In fact, a compound which would result from the formal substitution of the SnR_3 group in **4** or **5** by a hydrogen atom would well be one of the missing intermediates that link the complex $[Ru_3(\mu\text{-}H)(\mu\text{-}N{=}CPh_2)(CO)_9]$ with cluster **2** in Scheme 1.

3. Experimental details

3.1. General data

Solvents were dried over sodium diphenyl ketyl (diethyl ether, hydrocarbons) or CaH_2 (dichloromethane, 1,2-dichloroethane) and distilled under nitrogen prior to use. The reactions were carried out under hydrogen or nitrogen, as necessary, using Schlenk-vacuum line techniques, and were routinely monitored by solution IR spectroscopy (carbonyl stretching region). Compound **1** was prepared as described previously [1]. Hydrogen (99.995%) was obtained from Air Liquide. All the other reagents and chromatographic supports were purchased from Aldrich and were used as received. Infrared spectra were recorded on a Perkin-Elmer FT 1720-X spectrophotometer, using 0.1 mm CaF_2 cells. ^{1}H-NMR spectra were run at 20°C with Bruker AC-200 and AC-300 instruments, using $SiMe_4$ as internal standard ($\delta = 0$ ppm). Microanalyses were obtained from the University of Oviedo Analytical Service.

3.2. Reaction of complex *1* with hydrogen

A solution of compound **1** (300 mg, 0.390 mmol) in toluene (20 ml) was stirred at reflux temperature for 1.5 h, while a hydrogen flow was continuously bubbled through the solution. The solvent was removed under reduced pressure and the residue was separated by preparative TLC on silica gel. Three yellow bands were eluted with hexane as eluant and were extracted from the support with dichloromethane. The corresponding solutions were evaporated to dryness to give yellow solids. The first and second bands contained [$Ru_4(\mu$-$H)_4(CO)_{12}$] and compound **1**, respectively (identified by their IR and ^{1}H-NMR spectra). The third band was identified as a mixture of compounds **2** and **3**, in ca. 1:1 ratio, by ^{1}H-NMR spectroscopy. All attempts to separate these compounds by chromatographic means were unsuccessful. Longer reaction times resulted in higher yields of [$Ru_4(\mu$-$H)_4(CO)_{12}$] and in lower yields of the mixture **2** + **3**. [$Ru_4(\mu$-$H)_4(CO)_{12}$] was the only complex obtained after 6 h of reaction, while the presence of H_2NCHPh_2 in the solution was confirmed by GC-MS.

3.3. ^{1}H-NMR monitoring of the reaction of complex *1* with hydrogen

A solution of compound **1** (300 mg, 0.390 mmol) in toluene (40 ml) was stirred at reflux temperature while a hydrogen flow was continuously bubbled through the solution. At different reaction times, 5 ml aliquots of

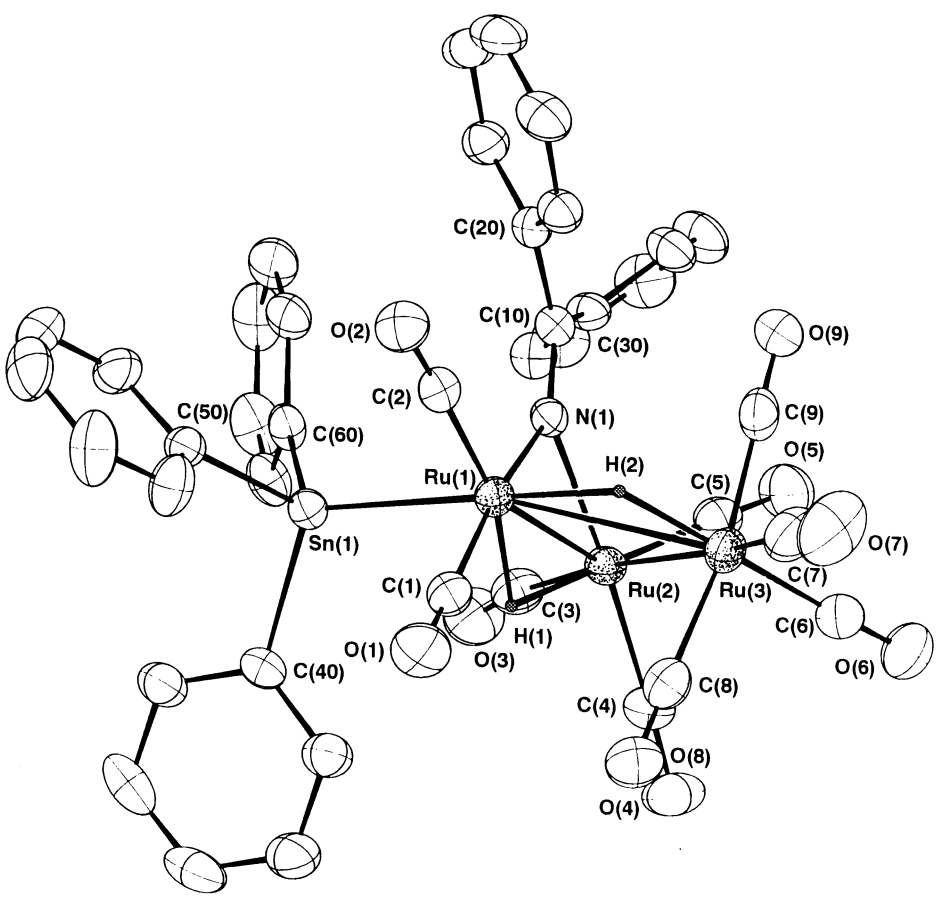


Fig. 3. Molecular structure of compound **4**.

Table 2
Selected bond lengths (Å) and angles (°) in $4\cdot(Et_2O)_{0.5}$

Ru(1)–Ru(2)	2.7942(7)	Ru(3)–C(9)	1.887(7)
Ru(1)–Ru(3)	3.0888(7)	O(1)–C(1)	1.129(7)
Ru(2)–Ru(3)	2.8654(7)	O(2)–C(2)	1.148(7)
Ru(1)–Sn(1)	2.6382(6)	O(3)–C(3)	1.128(7)
Ru(1)–N(1)	2.076(4)	O(4)–C(4)	1.140(7)
Ru(2)–N(1)	2.096(4)	O(5)–C(5)	1.134(8)
Ru(1)–C(1)	1.887(7)	O(6)–C(6)	1.128(9)
Ru(1)–C(2)	1.863(6)	O(7)–C(7)	1.132(9)
Ru(2)–C(3)	1.914(7)	O(8)–C(8)	1.133(8)
Ru(2)–C(4)	1.897(7)	O(9)–C(9)	1.140(8)
Ru(2)–C(5)	1.926(7)	N(1)–C(20)	1.272(7)
Ru(3)–C(6)	1.930(8)	C(10)–C(20)	1.484(8)
Ru(3)–C(7)	1.944(8)	C(10)–C(30)	1.511(8)
Ru(3)–C(8)	1.937(8)		
Ru(1)–Ru(2)–Ru(3)	66.14(2)	Ru(1)–N(1)–Ru(2)	84.1(2)
Ru(1)–Ru(3)–Ru(2)	55.82(4)	Ru(2)–Ru(3)–C(6)	89.9(2)
Ru(2)–Ru(1)–Ru(3)	58.04(2)	Ru(3)–Ru(2)–N(1)	84.2(1)
Ru(2)–Ru(1)–Sn(1)	98.29(2)	Ru(1)–N(1)-C(10)	142.6(4)
Ru(3)–Ru(1)–Sn(1)	154.46(2)	Ru(2)–N(1)–C(10)	133.2(4)
Ru(2)–Ru(1)–N(1)	48.3(1)	N(1)–C(10)–C(20)	124.5(5)
Ru(1)–Ru(2)–N(1)	47.7(1)	N(1)–C(10)–C(30)	121.3(5)

the solution were syringed out. The solvent of each aliquot was removed under reduced pressure and the residue was dissolved in $CDCl_3$ (1 ml) and was analysed by ^{1}H-NMR spectroscopy (Fig. 1).

3.4. Thermolysis of a mixture of compounds **2** and **3**

A solution containing a ca. 1:1 mixture of compounds **2** and **3** (20 mg) in toluene (10 ml) was stirred under nitrogen at reflux temperature for 2.5 h and then concentrated to ca. 2 ml. A spot TLC analysis of this solution indicated the presence of $[Ru_3(CO)_{12}]$, $[Ru_4(\mu\text{-}H)_4(CO)_{12}]$, **1** and **2** or/and **3**. The presence of H_2NCHPh_2 was confirmed by GC-MS. The solvent was removed under reduced pressure and the residue was dissolved in $CDCl_3$ and was analysed by ^{1}H-NMR spectroscopy (Fig. 2).

3.5. Preparation of $[Ru_3(\mu\text{-}H)_2(\mu\text{-}N{=}CPh_2)(SnPh_3)(CO)_9]$ (**4**)

A solution of compound **1** (50 mg, 0.065 mmol) and $HSnPh_3$ (46 mg, 0.130 mmol) in 1,2-dichloroethane (10 ml) was stirred at reflux temperature for 20 min. The colour changed from orange to yellow. The solution was concentrated under reduced pressure to ca. 1.5 ml and then it was applied to a column of neutral alumina (2×7 cm, activity I, packed in hexane) in order to remove the excess of stannane reagent. A hexane/dichloromethane (10:1) mixture eluted a yellow band which afforded compound **4** as a yellow solid after solvent removal (65 mg, 72%). Anal. Calc. for $C_{40}H_{27}NO_9Ru_3Sn$: C, 44.17; H, 2.50; N, 1.28. Found: C, 44.51; H, 2.79; N, 1.15. IR (CH_2ClCH_2Cl): 2115 (s), 2072 (s), 2050 (sh), 2039 (vs), 2019 (sh), 1963 (m) cm^{-1}.

3.6. Preparation of $[Ru_3(\mu\text{-}H)_2(\mu\text{-}N{=}CPh_2)(SnBu_3)(CO)_9]$ (**5**)

A solution of compound **1** (100 mg, 0.130 mmol) and $HSnBu_3$ (80 μl, 0.261 mmol) in 1,2-dichloroethane (10 ml) was stirred at reflux temperature for 20 min. The colour changed from orange to red. The solution was concentrated under reduced pressure to ca. 1.5 ml and then it was applied to a column of neutral alumina (2×10 cm, activity I, packed in hexane). A hexane/dichloromethane (10:1) mixture eluted a red band which afforded compound **5** as a tan oil after solvent removal. IR (CH_2ClCH_2Cl): 2112 (s), 2065 (s), 2050 (sh), 2035 (vs), 2009 (s), 1951 (m) cm^{-1}.

3.7. Crystal structure determination of $4\cdot(Et_2O)_{0.5}$

A yellow crystal, selected from a batch obtained at −20°C by slow diffusion of hexane into a diethyl-

Table 3
Crystallographic and refinement data for $4\cdot(Et_2O)_{0.5}$

Formula	$C_{40}H_{27}NO_9Ru_3Sn\cdot(Et_2O)_{0.5}$
Formula weight	1124.62
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
a (Å)	10.274(2)
b (Å)	21.283(6)
c (Å)	19.497(4)
β (°)	95.90(2)
V (Å^3)	4241(3)
Z	4
$F(000)$	1736
$D_{calc.}$ (g cm^{-3})	1.76
μ (mm^{-1})	16.66
Crystal size (mm)	$0.30\times0.20\times0.20$
Radiation, λ (Å)	Mo–K$_\alpha$, 0.71073
Diffractometer	Enraf-Nonius CAD4
Monochromator	Graphite
Temperature (K)	293(2)
Scan method	$\omega-2\theta$
Scan range (°)	$0.8+0.345\ \mathrm{tg}\theta$
θ limits (°)	1–25
h, k, l ranges	(−12, 0, 0) to (12, 25, 23)
Reflections collected	7921
Independent reflections	7437
$R_{int}=\Sigma(I-<I>)/\Sigma I$	0.047
Reflections with $F_o^2>3\sigma(F_o^2)$	5171
Parameters	508
Absorption coefficient	DIFABS (min = 0.81, max = 1.26)
R[a]	0.030
R_w[b]	0.032
Max, min $\Delta\rho$ (e Å^{-3})	0.87, −0.60

[a] $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$.
[b] $R_w=[\Sigma w(|F_o|-|F_c|)^2/\Sigma wF_o^2]^{1/2}$, unit weight.

ether solution of complex **4**, was used for the X-ray diffraction study. A selection of crystal and refinement data is given in Table 3. The space group $P2_1/n$ was determined from systematic absences. Two standard reflections were monitored periodically, revealing no intensity fluctuations. An empirical absorption correction (DIFABS) [23] and Lorentz and polarization corrections were applied.

The structure was solved by direct methods and successive Fourier maps. Computations were performed using the CRYSTALS package [24]. Atomic form factors were taken from the literature [25]. Real and imaginary parts of anomalous dispersion were taken into account. A disordered diethylether molecule was found on an inversion center, but it did not appear clearly and was refined with constraints with an overall isotropic thermal parameter. Almost all hydrogen atoms were found on difference maps, but their positions were not refined, except those of the hydrides H(1) and H(2) which were given individual isotropic thermal parameters. Non-hydrogen atoms were anisotropicaly refined, except those of the solvent molecule. Refinements were carried out in three blocks by minimising the function $[\Sigma w(|F_o| - |F_c|)]$. The structure plot was drawn with CAMERON [26]. Final atomic coordinates have been deposited within the Cambridge Crystallographic Data Centre.

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