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Crystal and molecular structures of $[Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^3\text{-}C_{12}H_{17})(CO)_9]$: revision of a previous determination

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The complex obtained from $[Ru_3(CO)_{12}]$ and cyclododeca-1,5,9-triene, previously identified as $[Ru_3(\mu\text{-}H)(\mu_3\text{-}C_{12}H_{15})(CO)_9]$ from a crystal structure determination using photographic data, has now been shown to contain a $\mu_3\text{-}C_{12}H_{17}$ ligand, by a combination of diffractometer data, electrospray mass spectra and detailed ^1H and ^{13}C NMR spectrometry.

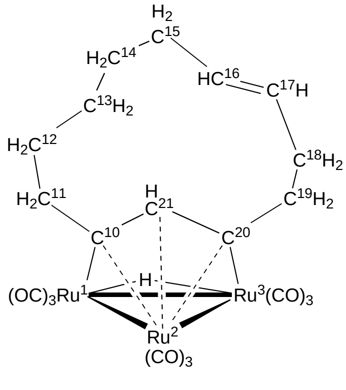
Over a quarter of a century ago one of us described the reaction between $[Ru_3(CO)_{12}]$ and cyclododeca-1,5,9-triene, which was carried out in refluxing light petroleum (b.p. 80–100 °C) for 30 h.[1] Four complexes were separated by column chromatography on Florisil. These were identified using elemental analyses, ^1H NMR spectra and high-resolution electron-impact mass spectrometry as $[Ru_3(\mu\text{-}H)(\mu_3\text{-}C_{12}H_{15})(CO)_9]$ **1**, $[Ru_3(CO)_9(C_{12}H_{18})]$ **2**, $[Ru_3(CO)_7(C_{24}H_{34})]$ **3** and $[Ru_4(CO)_{10}(C_{12}H_{16})]$ **4**. Complex **1** was obtained in *ca.* 70% yield and the preparation has been carried out on many occasions since. Complexes **1** and **4** have been subjected to X-ray single-crystal structure determinations,[1–4] the latter being shown to exist in two forms containing *syn* and *anti* allyl groups. Despite many attempts, single crystals of complex **3** of a quality suitable for a structure determination have not yet been obtained. The nature of **2** is somewhat of an enigma: the ν(CO) spectra of **1** and **2** were distinctly different but ^1H NMR spectra were obtained only for **1**. Although formulated as the expected product, containing hydride and $C_{12}H_{17}$ ligands, **2** was obtained in only 1% yield, and crystals suitable for an X-ray study have never been obtained.

On this occasion we wish to reconsider the structure of complex **1**. The point of discussion centres on the number of H atoms present on the ring (15 or 17) and consequently the number of uncomplexed double bonds in the C_{12} ligand (two or one, respectively). The original distinction between **1** and **2**, which are yellow and orange, respectively, was made on the basis of electron-impact mass spectrometry, a technique then in its infancy in terms of its application to organometallic cluster complexes. High-resolution measurements showed the parent ion to have a mass of 716, which is consistent with the presence of a $C_{12}H_{15}$ ligand.

The first crystal structure determination of **1** was carried out by a refinement of data obtained by photographic methods and afforded a structure which was interpreted as indicating that the hydrocarbon had undergone dehydrogenation to form a $C_{12}H_{15}$ ligand.[1,2] Of the three hydrogens that were lost, one had migrated to the cluster and was found bridging one of the Ru–Ru vectors. The fate of the other two was not determined. The refinement suffered from high thermal motions of the ring C atoms, with consequent rather low precision for the C–C distances [1.26–1.82(7) Å]. However, consideration of these distances suggested that ethylenic links occurred between C(6) and C(7) and C(9) and C(10). Further, the geometries about the respective C atoms [substantial coplanarity was found for the atom sequences C(5)–C(6)–C(7)–C(8) and C(8)–C(9)–C(10)–C(11)] were taken to indicate the presence of *trans* double bonds at C(6)–C(7) and at C(9)–C(10) in the C_{12} ring. These data, together with the ^1H NMR and mass spectra, enabled **1** to be formulated as containing a $C_{12}H_{15}$ ligand.

Subsequent investigations of the chemistry of complex **1** have afforded complexes containing tertiary phosphine, phosphite or arsine ligands,[1,5,6] diphenylethyne[7] or one, two or three $Au(PPh_3)$ units attached to the Ru_3 cluster.[8,9] The crystal structures of $[Ru_3(\mu\text{-}H)(\mu_3\text{-}C_{12}H_{15})(CO)_8(\text{dpam-}As)]$[6] (dpam = $Ph_2AsCH_2AsPh_2$) and $[Au_3Ru_3(\mu_3\text{-}C_{12}H_{15})(CO)_8(PPh_3)_3]$[8] have been reported and in each case the refinement has been consistent with the retention of the $C_{12}H_{15}$ ligand, albeit with considerable disorder in several of the ring carbons.

In the course of further studies involving insertion reactions of CO into a ring–metal bond in complex **1** a reassessment of the nature of the cyclic C_{12} ligand was prompted by the crystal structure of $[Ru_3(\mu\text{-}AsPh_2)(\mu\text{-}O{=}CC_{12}H_{17})(\mu\text{-}CO)(CO)_6]$, to be reported elsewhere.[10] As a result we now report that a combination of ^1H and ^{13}C NMR and electrospray mass spectrometric studies, together with a low-temperature redetermination of the crystal and molecular structures of **1** using modern counting methods, have shown conclusively that the hydrocarbon ligand contains 17 H atoms. Consequently, it is likely that all derivatives of **1** previously described should now be considered to have the same ligand.



Complex **1** with C=C double bond between C(16) and C(17)

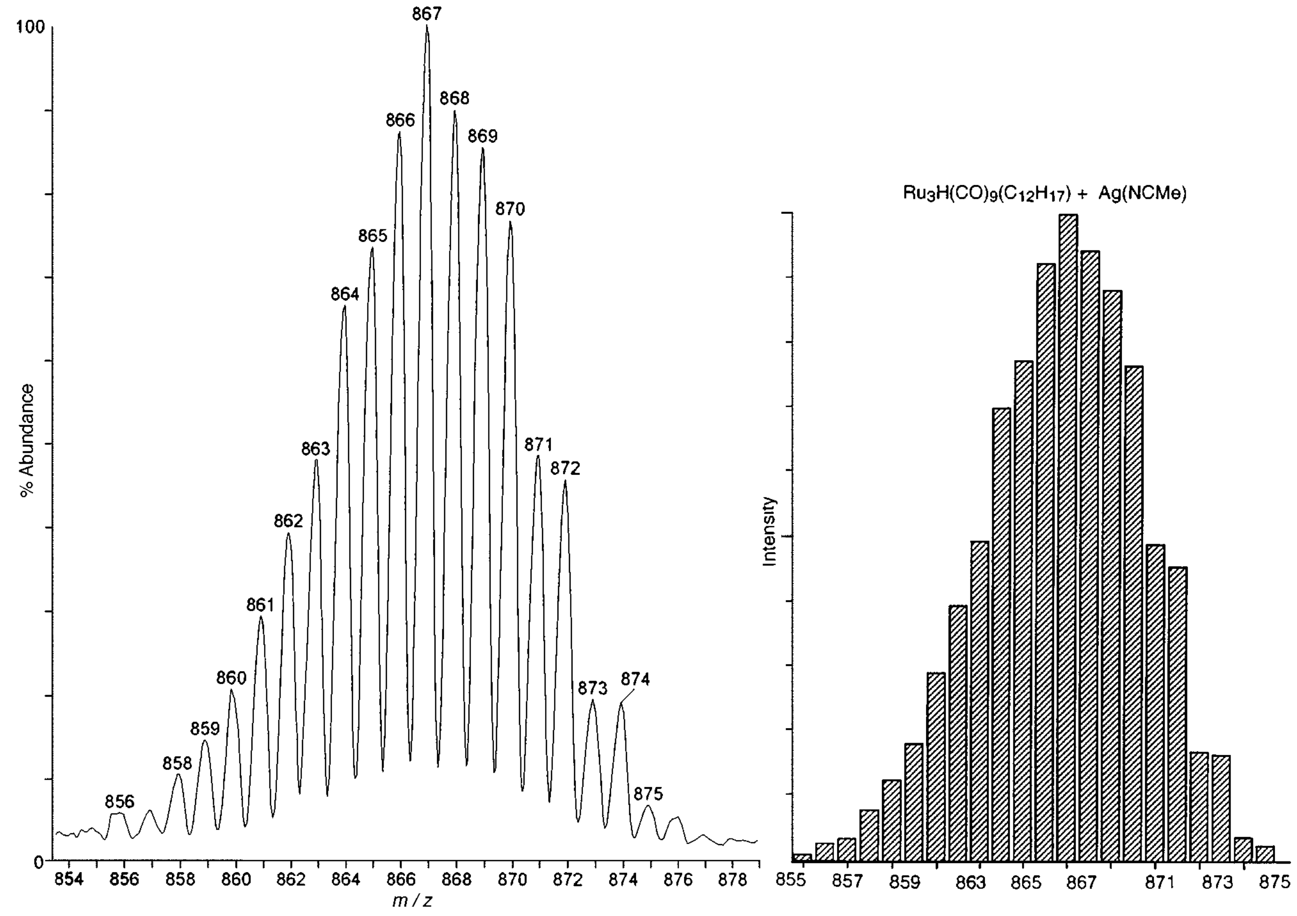


Fig. 1 Observed and calculated isotope patterns for the ion $[Ru_3H(CO)_9(C_{12}H_{17}) + Ag + MeCN]^+$ (*m*/*z* 867) in the electrospray mass spectrum of complex **1**

Results

Complex **1** was prepared in the same way as previously described,[1] except that the time of heating was reduced to 8 h. The IR spectroscopic data were similar to those previously reported.

Mass spectra

Samples of complex **1** were analysed by electrospray mass spectrometry. Solutions in MeCN–water (1 : 1) were used, with added Ag^+ ions to provide a source of chemical ionisation.[11] At low cone voltages the positive molecular ion pattern shown in Fig. 1 was obtained. The cluster of peaks centered around *m*/*z* 867 can be assigned to the ion $[Ru_3H(CO)_9(C_{12}H_{17}) + Ag + MeCN]^+$, an excellent match between the observed and calculated[12] isotope patterns being obtained (Fig. 1). The simulated pattern for the corresponding $C_{12}H_{15}$ species is clearly two mass units too low, and even a small percentage of this lower-mass species would have marred the excellent fit between the experimental and calculated patterns for **1**. At higher cone voltages (40 V) peaks arising from the loss of CO (*m*/*z* 839) and MeCN (*m*/*z* 826) from the ions centered at *m*/*z* 867 appear, and these also have isotopic distributions matching the $C_{12}H_{17}$ formulation. Similarly, the electrospray mass spectrum of **1** in MeCN–water (1 : 1) taken in the negative-ion mode gave a weak cluster of peaks around *m*/*z* 736 which can be assigned to $[Ru_3H(CO)_9(C_{12}H_{17}) + OH]^-$, again supporting the reformulation. Reviewing the previously published fast-atom bombardment mass spectral data obtained for $[Au_3Ru_3(\mu_3\text{-}C_{12}H_{15})(CO)_8(PPh_3)_3]$,[13] the ion at *m*/*z* 2063 which was assigned to $[M + 2H]^+$ can now be considered to be the molecular ion of the $C_{12}H_{17}$ complex.

Table 1 Proton and carbon chemical shifts for complex **1** *

Carbon shift (δ)	Attached proton(s) (δ)	Assignment
21.6	1.35, 1.52	C(13)
28.9	1.55 (2H)	C(14)
29.9	1.82, 2.18	C(15)
31.4	1.86, 1.93	C(12)
35.7	2.30, 2.76	C(18)
48.0	2.87, 3.03	C(11)
52.0	2.63, 3.27	C(19)
118.7	6.3	C(21)
129.6	5.4	C(17)
135.2	5.6	C(16)
190.6	—	CO
192.1	—	CO
192.6	—	CO
196.0	—	CO
196.2	—	C(20)
197.7	—	CO
199.3	—	C(10)

* The numbering system is that used in the X-ray diagram (Fig. 2) with the disordered double bond arbitrarily located at C(16)–C(17). The cluster-bound μ-H is at δ −20.5, with a 2.7 Hz coupling to the allylic CH at δ 6.3.

NMR Spectra

The ^1H and ^{13}C NMR data for complex **1** are listed in Table 1. The DEPT135 spectra showed the presence of three CH and seven CH_2 groups as expected for a $C_{12}H_{17}$ ligand with only one double bond within the ring. The number of peaks clearly shows the unsymmetrical nature of the ring. The NMR data also confirm that the arrangement of H atoms about the C=C bond is *trans*, as shown by the *J*[H(16)H(17)] value of 15.1 Hz.

Table 2 Selected bond distances (Å) and angles (°) for $[Ru_3(\mu\text{-}H)(\mu_3\text{-}C_{12}H_{17})(CO)_9]$ **1**

Ru(1)–Ru(2)	2.7782(11)	C(12)–C(13a,b)	1.529(11), 1.57(2)
Ru(1)–Ru(3)	2.9418(9)	C(13a)–C(14a)	1.534(12)
Ru(2)–Ru(3)	2.7861(10)	C(13b)–C(14b)	1.29(2)
Ru(1)–C(10)	2.065(5)	C(14a,14b)–C(15)	1.578(12), 1.46(2)
Ru(2)–C(10)	2.276(5)	C(15)–C(16a,b)	1.455(17), 1.55(2)
Ru(2)–C(20)	2.271(5)	C(16a)–C(17a)	1.301(14)
Ru(2)–C(21)	2.247(5)	C(16b)–C(17b)	1.55(2)
Ru(3)–C(20)	2.076(5)	C(17a,b)–C(18)	1.562(14), 1.51(2)
		C(18)–C(19)	1.548(9)
C(10)–C(11)	1.531(7)	C(19)–C(20)	1.530(7)
C(10)–C(21)	1.415(7)	C(20)–C(21)	1.415(7)
C(11)–C(12)	1.535(8)		
C(11)–C(10)–C(21)	113.5(4)	C(15)–C(16a)–C(17a)	125.6(11)
C(10)–C(11)–C(12)	111.0(4)	C(15)–C(16b)–C(17b)	116.0(14)
C(11)–C(12)–C(13a,b)	120.0(5), 100.5(7)	C(16a)–C(17a)–C(18)	123.7(9)
C(12)–C(13a)–C(14a)	109.9(7)	C(16b)–C(17b)–C(18)	107.3(13)
C(12)–C(13b)–C(14b)	122(2)	C(17a,b)–C(18)–C(19)	106.5(6), 118.8(7)
C(13a)–C(14a)–C(15)	111.7(8)	C(18)–C(19)–C(20)	111.8(5)
C(13b)–C(14b)–C(15)	125(2)	C(19)–C(20)–C(21)	114.0(5)
C(14a)–C(15)–C(16a)	112.4(10)	C(10)–C(21)–C(20)	124.5(4)
C(14b)–C(15)–C(16b)	112.4(10)		

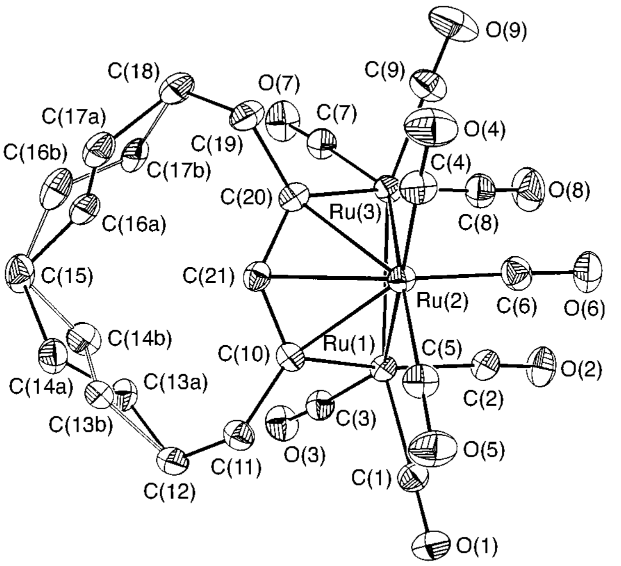


Fig. 2 Plot of a molecule of $[Ru_3(\mu\text{-}H)(\mu_3\text{-}C_{12}H_{17})(CO)_9]$ **1**, showing the atom numbering scheme

Two-dimensional X–H correlation experiments allowed assignment of the ^{13}C peak at δ 118.7 to the allylic CH leaving two signals at δ 135.2 and 129.6 for the two ring CH carbons. Full assignments of the other ^{13}C and ^1H signals are given in Table 1. The cluster-bound μ-H was observed at δ −20.5 and showed a 2.7 Hz coupling to the allylic CH at δ 6.3.

Molecular structure of complex 1

The present structure determination was carried out at 193 K and confirms the overall stereochemistry of complex **1** previously found. A plot of a molecule of **1** is shown in Fig. 2 and selected bond parameters are collected in Table 2. The C_{12} ring is attached to the Ru_3 cluster by a μ_3-$\eta^1:\eta^1:\eta^3$ interaction with atoms C(10)–C(21)–C(20). The geometry of the $Ru_3(\mu\text{-}H)\{\mu_3\text{-}C(10){-}C(21){-}C(20)\}(CO)_9$ fragment is similar to that found in the original determination and in other complexes containing this feature.[14] The Ru–Ru and Ru–C distances are somewhat longer than found originally [Ru–Ru 2.778–2.942(1) *vs.* 2.775–2.929(4) Å; Ru–C(σ) 2.065–2.076(5) *vs.* 2.01–2.02(3) Å; Ru–C(π) 2.247–2.276(5) *vs.* 2.18–2.23(3) Å].

The three atoms C(10)–C(21)–C(20) form part of the C_{12} ring. Considering the conformation of the remaining C atoms, we find that there is only one double bond which is disordered over two equivalent sites [C(13)–C(14) and C(16)–C(17)]. Refinement of the disorder on the basis of this model gave rather short C(13b)–C(14b) and C(16a)–C(17a) separations of 1.29(2) and 1.301(14) Å, respectively; other non-co-ordinated ring C–C distances range between 1.455(17) and 1.578(12) Å. Considering the geometries about C(13b)–C(14b) and C(16a)–C(17a), we find C–C–C angles at these carbons between 122(2) and 125(2)° [125.6(11) and 123.7(9)°] and torsion angles of 176(1) and 171.9(9)° for C(15)–C(14b)–C(13b)–C(12) and C(15)–C(16a)–C(17a)–C(18), respectively, for both conformations of the ring. This clearly shows that the C–C=C–C units are almost planar, and that the C=C bonds are *trans* in both conformations.

Discussion

The early crystal structure determination of complex **1** used photographic data, and the original description in terms of two double bonds in the ring was based on the apparent coplanarity of the carbon atoms at these sites since, as the original authors pointed out,[1,2] the standard deviations were too large to allow firm conclusions based on C–C bond lengths. With the hindsight benefitting from the structure determination described above, together with the cited spectroscopic data, it is clear that there is only one double bond which is disordered over two equivalent sites (site occupation factor, s.o.f. = 0.5) which, combined with a floppy ring, gave the illusion of two C=C bonds. The structure determination of the gold derivative of **1**, $[Au_3Ru_3(\mu_3\text{-}C_{12}H_{17})(CO)_8(PPh_3)_3]$, was also bedevilled by a poorly defined C_{12} ring with similar disorder and was (probably incorrectly) assigned as the $C_{12}H_{15}$ species on the basis of the presumed formula of the starting material in the synthesis.[8] The same conclusions can probably be drawn about other complexes derived from the subsequent chemistry of **1**.

Experimental

General

Electrospray mass spectra were recorded on a Fisons Platform II instrument, using MeCN–water (1 : 1) as mobile phase. Other details are given in ref. 11. A small sample of complex **1** was dissolved in a drop of MeCN and then diluted to *ca.* 0.5 cm^3 with water. The negative-ion spectrum was recorded using this solution, while the positive-ion spectrum was recorded after the addition of a drop of a dilute solution of $AgClO_4$ in MeCN.

The NMR spectra of solutions of complex **1** in $CDCl_3$ were recorded using Bruker AC300 and Avance DRX400 instruments, employing standard Bruker library pulse sequences. Spectra were referenced to the solvent signals at δ 7.26 in the ^1H spectra and at δ 77.06 in the ^{13}C spectra. The ^1H chemical shifts are strictly accurate only to one decimal place, but crowded signals have not been rounded off in order to maintain their relative positions.

Complex **1** was prepared in *ca.* 70% yield by heating a mixture of $[Ru_3(CO)_{12}]$ with *all-trans*-cyclododeca-1,5,9-triene (excess) for 8 h in refluxing hexane. Column chromatographic separation gave crude **1**, which was finally purified by thin-layer chromatography and crystallisation from *n*-hexane.

Crystallography

A data set was measured at 193 K using a Siemens P4 diffractometer (Mo-Kα radiation, graphite monochromator, $\lambda = 0.710\,73$ Å) with the θ–2θ scan technique, within the limits $\theta = 1.45–27.53°$. Although the crystal was unusually large, the collimator size was selected so that the crystal was entirely within the X-ray beam. The net intensities of three standard reflections were monitored after every 97 reflections had been recorded and these indicated that no decomposition of the crystal had occurred during data collection. 6801 Data were collected, 5503 of which were unique ($R_{int} = 0.0435$). Data were corrected for Lorentz-polarisation effects. The structure was solved by direct methods using SHELXTL-PC[15] and refined by full-matrix least-squares techniques on $|F^2|$ using SHELXL 93.[16] Absorption corrections using the ψ-scan technique were applied. Conventional residuals are $R1 = 0.0434$, $wR2 = 0.1201$ [data with $I > 2\sigma(I)$], $R1 = 0.0460$, $wR2 = 0.1219$ (all data); goodness of fit 1.142. The largest difference peak and hole were 0.893 and −1.408 e $Å^{-3}$.

With the exception of those attached to the disordered carbons C(13), C(14), C(16), C(17), the hydrogen atoms, including H(1Ru), were located from a difference map and refined. The H atoms on the disordered ring carbons were fixed in calculated positions. The largest residue was located 0.889 Å from Ru(2) and 1.160 Å from C(5).

Crystal data and refinement details. $C_{21}H_{18}O_9Ru_3$, $M = 717.56$, monoclinic, space group $P2_1/c$, $a = 14.862(7)$, $b = 15.505(5)$, $c = 11.053(5)$ Å, $\beta = 109.30(1)°$, $U = 2404$ $Å^3$, $Z = 4$, $D_c = 1.983$ g cm^{-3}, $\mu(\text{Mo-K}\alpha) = 1.908$ mm^{-1}, $F(000) = 1392$, crystal size 0.76 × 1.03 × 1.04 mm, $T_{max} = 0.868$, $T_{min} = 0.414$, number of parameters refined = 383.

CCDC reference number 186/835.

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