Preparation and Crystal Structure † of Nonacarbonyl-di-μ-hydrido-μ_3-phenylimido-*triangulo*-triruthenium, $[Ru_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}NPh)]$

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$[Ru_3(CO)_{10}(NPh)]$ (1) reacts with molecular hydrogen to give $[Ru_3H_2(CO)_9(NPh)]$ (2), which can be carbonylated to produce $[Ru_3(CO)_{12}]$. A single-crystal *X*-ray structure determination of (2) confirms the presence of a triply-bridging NPh group and two doubly-bridging hydrogen atoms: space group $P2_1/c$, a = 11.697(2), b = 9.265(2), c = 18.589(4) Å, β = 100.18(2)°, Z = 4, R = 0.039 for 3 019 unique observed reflections. Mean bond lengths include Ru–Ru 2.805(1) (H-bridged), 2.680(1) (unbridged), Ru–N 2.068(6), Ru–H 1.76(5) Å.

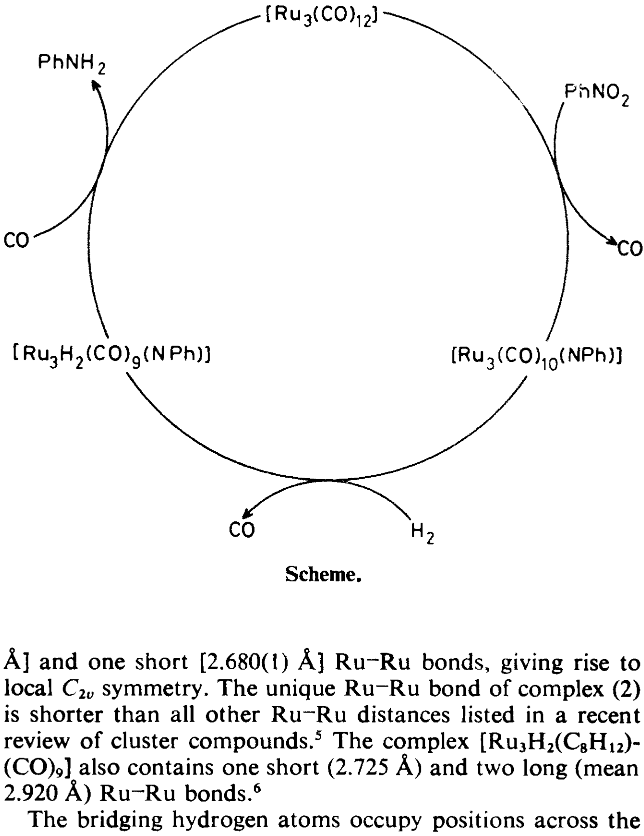
Reaction of hydrogen with $[Ru_3(CO)_{10}(NPh)]$ (1), obtained from the reaction of $[Ru_3(CO)_{12}]$ with $PhNO_2$, has been reported [1] to give $[Ru_3H_2(CO)_9(NPh)]$ (2). Unequivocal crystallographic data were not, however, available for either of these two complexes. In order to understand the role of $[Ru_3(CO)_{12}]$ as a catalyst in the hydrogenation of $PhNO_2$, it is necessary to have complete structural information on such imido-complexes, which are thought to be the probable catalytic intermediates.[2] In a previous paper [3] we reported an *X*-ray diffraction study of (1). This paper describes the syntheses, carbonylation, and crystal structure determination of (2).

Results and Discussion

Complex (1) is converted to (2) in high (>75%) yield at 60 °C under a hydrogen pressure of 3×10^5 Pa. However, one of the other isolable products [1,3] of the $[Ru_3(CO)_{12}]/PhNO_2$ reaction, $[Ru_3(CO)_9(NPh)_2]$, remains unchanged even under more forcing conditions (60 °C, 7×10^5 Pa hydrogen). Complex (2) can be carbonylated to give quantitative yields of $[Ru_3(CO)_{12}]$ under a carbon monoxide pressure of 1×10^6 Pa at 30 °C.

Among many other steps that are certainly involved in the catalytic hydrogenation of $PhNO_2$ with $[Ru_3(CO)_{12}]$ as the catalyst, evidence is therefore found for the reactions shown in the Scheme.

Microanalytical, and i.r. and n.m.r. spectroscopic data for (2) (see Experimental section) suggest removal of the local C_{3v} symmetry [3] of (1) on replacement of the triply-bridging CO group with two hydrides. It is known that the analogous osmium complex, obtained from the reaction of NH_2Ph with $[Os_3(CO)_{12}]$, can exist in two isomeric forms.[4] A crystal structure determination was therefore undertaken, in order to establish the nature of the complex (2).



Scheme.

The nine carbonyl groups in (2) are all terminal, with three bonded to each metal atom. There are two long [mean 2.805(1) Å] and one short [2.680(1) Å] Ru–Ru bonds, giving rise to local C_{2v} symmetry. The unique Ru–Ru bond of complex (2) is shorter than all other Ru–Ru distances listed in a recent review of cluster compounds.[5] The complex $[Ru_3H_2(C_8H_{12})(CO)_9]$ also contains one short (2.725 Å) and two long (mean 2.920 Å) Ru–Ru bonds.[6]

The bridging hydrogen atoms occupy positions across the two long Ru–Ru bonds. The Ru–H distances lie in the range 1.71(7)—1.81(7) Å, with a mean of 1.76(5) Å. Although the differences in Ru–H distances are not much larger than the e.s.d.s, both Ru–H–Ru bridges are observed to be asymmetric, with the hydrides *ca.* 0.09 Å closer to the unique Ru atom. Such pronounced asymmetry in Ru–H distances is not uncommon, as for example in $[Ru_4H_4(CO)_{10}(Ph_2PCH_2CH_2PPh_2)]$,[7] where the distances range from 1.64(6) to 1.81(4) Å. The mean Ru–H distance in (2) is similar to that observed in $[Ru_3H_3(CO)_9(CMe)]$ [1.72(7) Å],[8] a complex with a capping CMe ligand.

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† *Supplementary data available* (No. SUP 23914, 23 pp.): H-atom co-ordinates, full bond lengths and angles, thermal parameters, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

The two Ru_2H planes subtend angles of 130 and 127° with the Ru_3 plane. The N atom lies 1.315 Å above this Ru_3 triangle [*cf.* 1.308 Å in (1)]; the mean Ru–N bond lengths in (1) and (2) are similar [2.055(5) and 2.068(6) Å respectively]. The NPh ligand triply bridges the Ru atoms; there is no *o*-metallation of the phenyl ring.

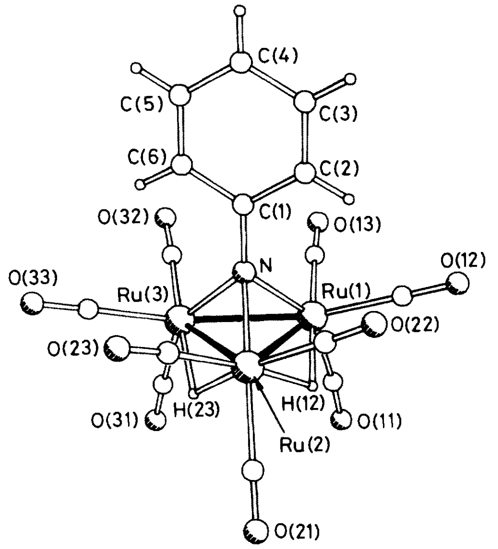

Figure. Molecular structure of (2) with atom numbering scheme. Carbonyl C atoms take the same numbers as the corresponding O atoms; phenyl H atoms take the same numbers as the corresponding C atoms

Experimental

Infrared and n.m.r. spectra were taken on a Perkin-Elmer 377 grating spectrometer and a Bruker 80-MHz instrument respectively. A Carlo-Erba 1106 instrument was used for microanalyses.

Synthesis of (2).—Complex (1) (0.135 g, 0.2 mmol) was treated with hydrogen (3×10^5 Pa) in n-hexane (20 cm^3) at 60 °C for 4 h in a low-pressure Parr hydrogenation apparatus. Removal of hexane, followed by thin-layer chromatography of the residue with n-hexane as eluant, gave a yellow band, from which (2) (0.116 g, 0.18 mmol) was obtained. The complex was recrystallised from n-hexane at 0 °C (Found: C, 27.8; H, 1.2; N, 2.1. Calc. for $C_{15}H_7NO_9Ru_3$: C, 27.8; H, 1.1; N, 2.2%). I.r. spectra (cyclohexane): (1), 2 100w, 2 076vs, 2 037vs, 2 020w, and 1 740m; (2), 2 119w, 2 080vs, 2 055vs, 2 045s(sh), 2 015vs, and 1 992m cm^{-1}. ^1H N.m.r. ($CDCl_3$): (1), aromatic H at 7.13 (multiplet); (2), aromatic H at 7.12 (multiplet), bridging H at −16.94 p.p.m. (singlet).

Carbonylation of (2).—Complex (2) (0.064 g, 0.1 mmol) was treated with CO (1×10^6 Pa) in n-hexane (15 cm^3) at 30 °C for 2 h in a Parr pressure reactor. Removal of solvent gave $[Ru_3(CO)_{12}]$ (0.06 g), identified on the basis of its i.r. spectrum. The presence of aniline in the products was confirmed by gas chromatography and mass spectroscopy.

Crystal Data.—$C_{15}H_7NO_9Ru_3$, $M = 648.4$, monoclinic, space group $P2_1/c$, $a = 11.697(2)$, $b = 9.265(2)$, $c = 18.589(4)$ Å, $\beta = 100.18(2)°$, $U = 1\,982.8$ Å^3, $Z = 4$, $D_c = 2.172$ g cm^{-3}, $F(000) = 1\,232$, $\lambda(\text{Mo-}K_\alpha) = 0.710\,69$ Å, $\mu = 22.6$ cm^{-1}, crystal dimensions 0.3 × 0.15 × 0.1 mm.

Data were collected by a real-time profile-fitting procedure [9]

Table 1. Atomic co-ordinates (× 10^4) with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ru(1)	2 332(1)	925(1)	1 114(1)	C(23)	2 348(5)	4 904(6)	−305(3)
Ru(2)	2 157(1)	2 921(1)	−35(1)	O(23)	2 481(4)	6 036(4)	−496(3)
Ru(3)	4 099(1)	2 755(1)	1 090(1)	C(31)	5 333(6)	1 523(8)	904(4)
H(12)	2 008(55)	1 117(72)	131(36)	O(31)	6 043(5)	757(7)	799(4)
H(23)	3 622(44)	2 557(55)	118(28)	C(32)	4 643(6)	2 719(7)	2 109(3)
C(11)	2 958(6)	−897(6)	896(3)	O(32)	4 982(5)	2 738(7)	2 722(3)
O(11)	3 381(5)	−1 945(5)	756(3)	C(33)	4 817(4)	4 596(7)	958(3)
C(12)	737(5)	364(6)	1 063(3)	O(33)	5 238(4)	5 670(5)	870(2)
O(12)	−195(4)	8(6)	1 046(3)	N	2 368(4)	3 159(5)	1 090(2)
C(13)	2 723(5)	555(6)	2 128(3)	C(1)	1 802(5)	4 181(5)	1 468(3)
O(13)	2 950(4)	273(5)	2 734(2)	C(2)	640(5)	4 013(6)	1 533(3)
C(21)	2 254(5)	2 241(6)	−1 014(3)	C(3)	76(6)	5 025(8)	1 896(4)
O(21)	2 327(5)	1 815(6)	−1 564(2)	C(4)	668(6)	6 221(7)	2 207(4)
C(22)	487(5)	3 027(6)	−225(3)	C(5)	1 817(7)	6 388(7)	2 155(4)
O(22)	−489(4)	3 071(5)	−307(3)	C(6)	2 378(5)	5 396(6)	1 792(3)

Table 2. Selected bond lengths (Å) and angles (°)

Ru(1)–Ru(2)	2.804(1)	Ru(2)–Ru(3)	2.806(1)	Ru(3)–C(32)	1.888(6)	Ru(3)–C(33)	1.935(6)
Ru(1)–Ru(3)	2.680(1)	Ru(1)–C(11)	1.911(6)	Ru(1)–H(12)	1.807(65)	Ru(2)–H(12)	1.714(67)
Ru(1)–C(12)	1.923(6)	Ru(1)–C(13)	1.891(6)	Ru(2)–H(23)	1.721(51)	Ru(3)–H(23)	1.804(51)
Ru(2)–C(21)	1.949(6)	Ru(2)–C(22)	1.925(6)	Ru(1)–N	2.072(4)	Ru(2)–N	2.074(4)
Ru(2)–C(23)	1.929(6)	Ru(3)–C(31)	1.919(7)	Ru(3)–N	2.059(4)		
Ru(2)–Ru(1)–Ru(3)	61.5(1)	Ru(1)–Ru(3)–Ru(2)	61.4(1)	Ru(3)–Ru(2)–N	47.0(1)	Ru(1)–Ru(2)–N	47.4(1)
Ru(1)–Ru(2)–Ru(3)	57.1(1)	Ru(2)–Ru(1)–H(12)	36.1(21)	Ru(2)–Ru(3)–N	47.5(1)	Ru(1)–Ru(3)–N	49.7(1)
Ru(1)–Ru(2)–H(12)	38.4(22)	Ru(3)–Ru(2)–H(23)	38.3(18)	Ru(1)–N–Ru(3)	80.9(2)	Ru(1)–N–Ru(2)	85.1(2)
Ru(2)–Ru(3)–H(23)	36.2(17)	Ru(1)–H(12)–Ru(2)	105.6(34)	Ru(1)–N–C(1)	130.3(4)	Ru(2)–N–Ru(3)	85.5(2)
Ru(2)–H(23)–Ru(3)	105.5(29)	Ru(2)–Ru(1)–N	47.5(1)	Ru(3)–N–C(1)	132.0(3)	Ru(2)–N–C(1)	126.2(3)
Ru(3)–Ru(1)–N	49.4(1)						

on a Stoe-Siemens AED diffractometer, to $2\theta_{max.} = 50°$, and were corrected for absorption by a semi-empirical method based on azimuthal scan data. Of 3 474 unique reflections, 3 019 with $F > 4\sigma(F)$ were used for structure solution, by Patterson and Fourier methods, and for least-squares refinement. Anisotropic thermal parameters were refined for all non-hydrogen atoms. Phenyl H atoms were constrained to lie on the C–C–C external bisectors with C–H = 0.96 Å and $U(H) = 1.2U_{eq.}(C)$. The bridging H atoms were located in a difference synthesis and refined freely with isotropic thermal parameters. $R = \Sigma|\Delta|/\Sigma|F_o|$ converged to 0.039, and $R' = (\Sigma w\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}}$ to 0.047, with $\Delta = |F_o| - |F_c|$ and $w^{-1} = \sigma^2(F) + 0.0005F^2$. There was no evidence of extinction effects, and an analysis of variance showed no systematic trends with indices, sin θ or $|F|$. Final co-ordinates are given in Table 1, selected bond lengths and angles in Table 2.

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Acknowledgements

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