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Preliminary communication

Facile cleavage of $[\text{RhRu}_3(\mu\text{-H})_2(\mu\text{-CO})(\text{CO})_9(\eta^5\text{-C}_5\text{H}_5)]$ with elimination of benzene on reaction with $(\text{Ph}_2\text{PCH}_2)_3\text{CMe}$ (triphos). Structural characterisation and non-rigidity of $[\text{Ru}_3(\mu\text{-H})\{\mu\text{-PPhCH}_2(\text{Ph}_2\text{PCH}_2)_2\text{CMe}\}(\text{CO})_8]$

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Abstract

Reaction of $[\text{RhRu}_3(\mu\text{-H})_2(\mu\text{-CO})(\text{CO})_9(\eta^5\text{-C}_5\text{H}_5)]$ with $(\text{Ph}_2\text{PCH}_2)_3\text{CMe}$ in tetrahydrofuran, at or below ambient temperature, causes extensive cleavage of the cluster and intramolecular elimination of a molecule of benzene to form structurally characterised $[\text{Ru}_3(\mu\text{-H})\{\mu\text{-Ph}_2\text{PCH}_2(\text{Ph}_2\text{PCH}_2)_2\text{CMe}\}(\text{CO})_8]$, for which fluxionality of the μ_2 -ligand system is reported.

The heteronuclear cluster $[\text{RhRu}_3(\mu\text{-H})_2(\mu\text{-CO})(\text{CO})_9\text{Cp}]$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) (**1**) [1] has been shown to undergo cleavage in solution on reaction with CO [1] and, to a large extent, on reaction with PPh_3 [2] at ambient temperature. Cluster **1** also reacts under mild conditions with a number of other phosphine ligands to give substitution or, more commonly, cleavage products containing Ru_n ($n = 3, 4$) and Rh_n ($n = 1-3$) units [2,3]. Similar cleavage reactions are known for other mixed-metal clusters [4,5] although in most cases, and especially with completely 4d or 5d transition metal systems, more vigorous reaction conditions are required.

Reaction of **1** with an equimolar quantity of the potentially tridentate, tripod ligand $(\text{Ph}_2\text{PCH}_2)_3\text{CMe}$ (triphos) in tetrahydrofuran (thf) at room temperature ($< 22^\circ\text{C}$) during 18 h gives only cleavage products. Separation by column chromatography (silica gel, 80–200 mesh) affords, as the main cluster product, $[\text{Ru}_3(\mu\text{-H})\{\mu\text{-PPhCH}_2(\text{PPh}_2\text{CH}_2)\text{CMe}\}(\text{CO})_8]$ (**2**) (15–20%; eluted with 60/80 petroleum ether/dichloromethane 2/1), characterised by analysis, ^1H and ^{31}P NMR spectroscopy [6*]. Complex **2** was obtained as a mono-solvate, $\mathbf{2} \cdot \text{CH}_2\text{Cl}_2$, in the form of orange prisms, from petroleum ether/dichloromethane at -15°C , and the crystal and molecular structure was determined by X-ray diffraction [7*]. The

* Reference numbers with asterisks indicate notes in the list of references.

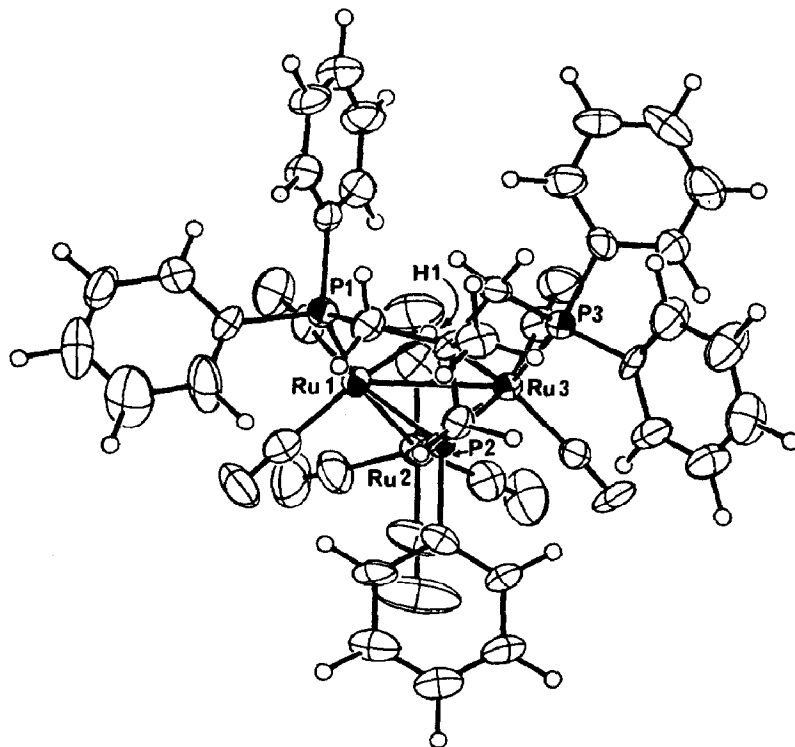
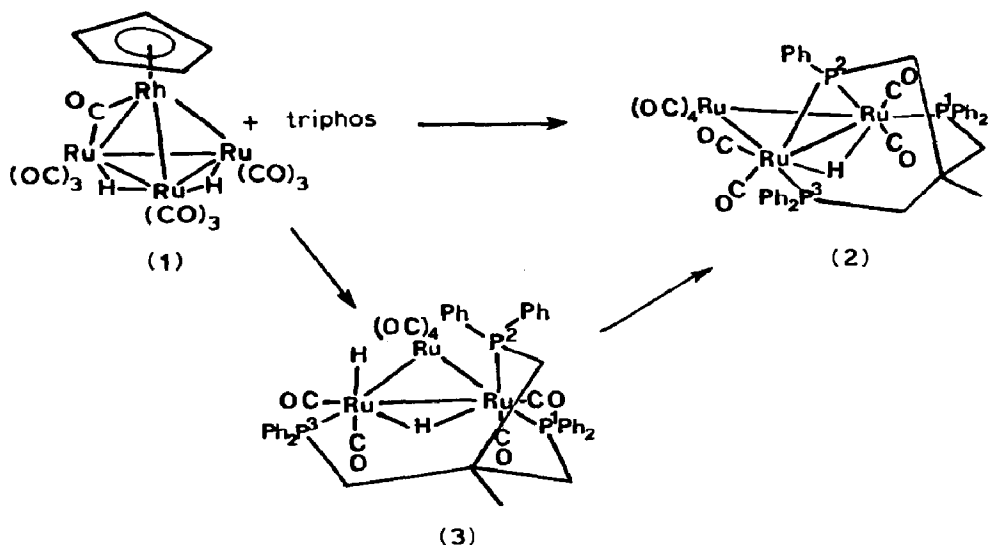


Fig. 1. The crystal structure of complex **2** [ORTEP [13], 50% ellipsoids]. Some important bond distances include: Ru(1)–Ru(2) 2.8803(18), Ru(1)–Ru(3) 2.9097(17), Ru(2)–Ru(3) 2.8765(18), Ru(1)–P(1) 2.324(4), Ru(1)–P(2) 2.341(4), Ru(3)–P(2) 2.330(4), Ru(3)–P(3) 2.318(4), Ru(1)–H(1) 1.61(17), Ru(3)–H(1) 1.90(17) Å.

structure of **2** is illustrated in Fig. 1, and is related to those of other species $[\text{Ru}_3(\mu\text{-H})(\mu\text{-X})(\text{CO})_{10}]$ [8]. Cleavage of a phenyl group from the triphos ligand has occurred under the mild reaction conditions, and a bridging phosphido function has been formed (Scheme 1). P–C bond fission is a well known reaction, but normally requires more vigorous conditions [9].

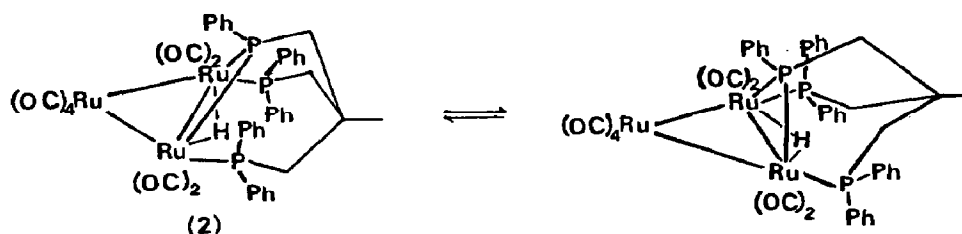
A by-product of reaction between **1** and triphos is $[\text{Ru}_3(\mu\text{-H})\text{H}(\text{CO})_8(\text{triphos})]$ (**3**) (ca. 4%, eluted with petroleum ether/dichloromethane 1/1) which, on the basis of ^1H and ^{31}P NMR (including selective ^{31}P decoupling) spectroscopy [10*] has a structure related to species $[\text{Os}_3(\mu\text{-H})\text{H}(\text{CO})_{10}\text{L}]$ [11], as shown in Scheme 1. Cluster **3** contains terminal and bridging hydrido ligands and a tridentate, intact triphos ligand spanning two Ru atoms, with two *cis* P atoms bonded to one Ru and the other P atom *cis* to the terminal H atom on the other Ru atom. There is no evidence for isomers or non-rigidity of **3** from the ^1H NMR spectra at temperatures between -100 and $+30^\circ\text{C}$. In solution at ca. 24°C complex **3** slowly decomposes (e.g. in CDCl_3 $t_{1/2} \sim 11$ h), to form **2** as the major product (minor by-products were also detected by NMR spectroscopy). The ready loss of benzene from **3** may be rationalised in terms of the co-elimination of a phenyl group from the axial- P^2Ph_2 function with the terminal H ligand on the adjacent Ru atom; these groups possess a favorable geometry for the intramolecular reaction (see Scheme 1) [12*].



Scheme 1.

The formation of **2** in the initial reaction must, at least in part, be via **3**, although a more direct reaction mechanism may also be operating. The reaction of **1** with triphos at 0–10 °C for 18 h gives more **3** (ca. 10%) and also a small amount of mixed substitution products [RhRu₃(μ-H)₂(CO)_n(triphos)Cp], but even under these milder conditions elimination of benzene to form significant amounts of **2** still occurs.

The ambient temperature ³¹P{¹H} and ¹H NMR spectra of cluster **2** are consistent with a symmetrical molecule containing two equivalent PPh₂ groups but variable temperature ³¹P{¹H} spectra (81.0 MHz) reveal fluxionality, with inequivalent PPh₂ groups at –114 °C [6*]: coalescence of these resonances at –99 °C corresponds to ΔG[‡] = 33 kJ mol^{–1}. Also, the symmetrical ¹H NMR resonance (dt) of the bridging hydrogen at ambient temperature becomes a broadened multiplet at –114 °C, probably approaching a ddd resonance. The solid state structure of **2** shows asymmetry in the chelating ligand system, and the observed fluxionality must be attributed to interchange between enantiomeric forms of the tricyclic Ru₂P₃C₄ cage. Inversion of this cage involving, in particular, motion of the methylene groups and the phenyl substituents attached to P(1) and P(3), is indicated in Scheme 2. Thus, ³¹P NMR spectroscopy provides a direct method for monitoring the non-rigidity of this heterocyclic cage.



Scheme 2.

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- 6 **2**: CH_2Cl_2 : Anal. Found: C, 45.5; H, 3.2. $\text{C}_{44}\text{H}_{37}\text{Cl}_2\text{O}_8\text{P}_3\text{Ru}_3$ calcd.: C, 45.1; H, 3.3%. IR (petroleum ether) $\nu(\text{CO})$: 2071m, 2010s, 2004sh, 1990m, 1952w cm^{-1} . ^1H NMR (CDCl_3 , 20 °C): 8.1, 7.7 and 7.4 (complex, 5 C_6H_5), 5.29 (s, CH_2Cl_2), 2.1 (complex ~ dq, 2 CH_2), 0.52 (s, CH_3), -17.06 (dt, $J(\text{P}^2\text{-H})$ 25.2, $J(\text{P}^1/3\text{-H})$ 8.6 Hz, $\mu\text{-H}$) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 20 °C): 107.6 (t, $J(\text{P-P})$ 27 Hz, P^2), 24.6 (d, 2 PPh_2); ($\text{CD}_2\text{Cl}_2/\text{CFCl}_3$, -114 °C): 108.4 (~ t, P^1), 26.7 (d, 22 Hz, PPh_2), 23.9 (d, 30 Hz, PPh_2) ppm.
- 7 Crystal data for **2**: $\text{C}_{43}\text{H}_{35}\text{O}_8\text{P}_3\text{Ru}_3 \cdot \text{CH}_2\text{Cl}_2$, orange/red prisms, monoclinic, a 19.549(3), b 14.2462(21), c 16.429(4) Å, β 90.271(18)°, U 4575.3 Å³, Z = 4, D_c = 1.685 gcm^{-3} , $\mu(\text{Mo-K}\alpha)$ = 12.3 cm^{-1} , data crystal 0.225 × 0.15 × 0.175 mm. Intensity data were collected on a CAD4 four-circle diffractometer (ω - 2θ scans, $1.5 < \theta < 22^\circ$, h : -20 to +20, k : 0 to +15, l : -17 to 0, $\text{Mo-K}\alpha$ X-radiation) and corrected for Lorentz and polarisation effects, and absorption [13]. Space group $P2_1/n$ (non-standard setting of No. 14) was determined from systematic absences and successful structure solution. After blocked-matrix least squares refinement [13], with anisotropic temperature factors for non-hydrogen atoms R and R_w were 0.051 and 0.060, respectively, for 2762 data with $I > 3\sigma(I)$. A table of atom coordinates and a full list of bond lengths and angles will be deposited at the Cambridge Crystallographic Data Centre.
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- 10 **3**: Anal. Found: C, 51.1; H, 3.8. $\text{C}_{49}\text{H}_{41}\text{O}_8\text{P}_3\text{Ru}_3$ calcd.: C, 51.0; H, 3.6%. IR (CH_2Cl_2) $\nu(\text{CO})$: 2038s, 2005s, 1985s, 1945m, 1918w cm^{-1} . ^1H NMR (CDCl_3 , -25 °C) 7.9–6.4 (complex, 6 C_6H_5), 3.35, 2.7 and 1.8 (m's, 3 CH_2), 1.1 (s, CH_3), -11.61 (m, $J(\text{H-H})$ 3, $J(\text{P}^3\text{-H})$ ~ 5 Hz, Ru-H), -17.14 (~ dt, $J(\text{P}^2\text{-H})$ 10, $J(\text{P}^1\text{-H})$ ~ $J(\text{P}^3\text{-H})$ -20 Hz, Ru-H-Ru) ppm, (this spectrum is essentially unaltered at -100 °C in $\text{CD}_2\text{Cl}_2/\text{CFCl}_3$). ^{31}P NMR (CDCl_3 , -25 °C) 34.2 (dd, $J(\text{P}^1\text{-P}^2)$ 30.8, $J(\text{P}^2\text{-P}^3)$ 3.8 Hz, P^2), 22.4 (dd, P^3), 15.4 (dd, $J(\text{P}^1\text{-P}^3)$ 2.7 Hz, P^1) ppm.
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