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Preliminary communication

The synthesis, characterisation and crystal structure of $[Ru_3(\mu_2\text{-}H)(CO)_9(\mu_3\text{-}\sigma:\sigma:\eta^2\text{-}COPh)]$

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Abstract

The reaction of $[Ru_3(CO)_{12}]$ with potassium-benzophenone in tetrahydrofuran affords the new acyl cluster $[Ru_3(\mu_2\text{-}H)(CO)_9(\mu_3\text{-}\sigma:\sigma:\eta^2\text{-}COPh)]$ **1** in modest yield; the COPh ligand is believed to be derived from benzophenone. The solid-state structure of **1** has been established by an X-ray crystallographic study at 150 K.

Keywords: Ruthenium; Carbonyl; Hydride; Acyl; Crystal structure

There have been several reports on the reaction of aldehydes and ketones with the triosmium clusters $[Os_3(CO)_{12}]$, $[Os_3(\mu_2\text{-}H)_2(CO)_{10}]$ or $[Os_3(CO)_{10}(MeCN)_2]$ [1]. These reactions led to the isolation of acyl complexes of general formula $[Os_3(\mu_2\text{-}H)(CO)_{10}(\mu_2\text{-}COR)]$ (R = Me, Me_2CH, C_5H_{11}, Ph, CH_2Ph, C_6H_{13}). In these complexes the COR ligand is coordinated along an Os–Os edge with the CO fragment bonded to the second metal atom via the lone pair of electrons on the oxygen. The $\mu_3\text{-}\eta^2$-acyl group has also been observed in a number of clusters [2] and has been shown to undergo facile thermal C–O bond scission [3]. The new complex reported in this communication provides a further example of a cluster bearing a face-capping acyl ligand.

The two-electron reduction of $[Ru_3(CO)_{12}]$ by use of potassium-benzophenone in tetrahydrofuran under an inert atmosphere and the use of the reagent so formed as an electron transfer catalyst in $[Ru_3(CO)_{12}]$ substitution reactions has been described before [4]. In our study we were motivated by the possibility of ionic coupling reactions between the triruthenium cluster in a reduced form and cationic metal fragments. These reactions did not yield extractable products except for the new trinuclear acyl-cluster $[Ru_3(\mu_2\text{-}H)(CO)_9(\mu_3\text{-}\sigma:\sigma:\eta^2\text{-}COPh)]$ **1**, isolated in modest yield [5]. It was found that the same product could be produced even without the presence of a cationic fragment, merely by treating $[Ru_3(CO)_{12}]$ with potassium-benzophenone. This cluster was initially characterised by the usual spectroscopic techniques [7]. However, in order to fully establish the identity of **1** its molecular structure was determined by a single crystal X-ray diffraction study at 150 K [8].

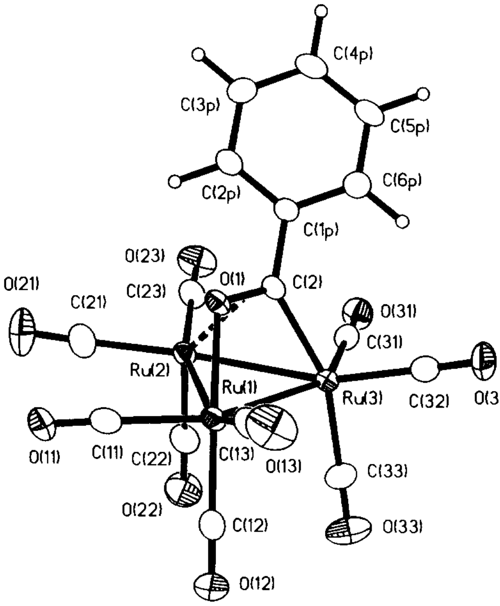

Fig. 1. The molecular structure of $[Ru_3(\mu_2\text{-}H)(CO)_9(\mu_3\text{-}\sigma:\sigma:\eta^2\text{-}COPh)]$ **1** in the solid state showing the atom labelling scheme.

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Table 1
Bond lengths (Å) with standard deviations

Ru(1)–Ru(2)	2.6894 (4)	O(1)–C(2)	1.368 (5)
Ru(1)–Ru(3)	2.9330 (4)	C(2)–C(1p)	1.501 (5)
Ru(2)–Ru(3)	2.7525 (4)		
Ru(1)–O(1)	2.096 (3)	Ru–C(mean)	1.926 (5)
Ru(2)–O(1)	2.177 (3)	C–O(mean)	1.126 (6)
Ru(2)–C(2)	2.297 (4)		
Ru(3)–C(2)	2.059 (4)		

The solid-state structure of **1** is shown in Fig. 1 and selected bond lengths are listed in Table 1. The three ruthenium atoms define a triangle; the edge [Ru(1)–Ru(3)] that is parallel with the PhC–O bond is significantly longer than the other two [2.9330(4) vs 2.6894(4) and 2.7525(4) Å]. Each ruthenium atom bears a tricarbonyl unit made up of two equatorial and one axial CO ligand, all of which are essentially linear. The hydride ligand could not be located directly, but presumably bridges the edge connecting Ru(1)–Ru(3) since this is significantly longer than the other two edges. The most noteworthy feature of the structure is the face-bridging coordination mode adopted by the COPh ligand over the ruthenium triangle. The CO fragment formally donates five electrons to the metal triangle, bonding to Ru(1) and Ru(3) via two σ-interactions [C(2)–Ru(3), and O(1)–Ru(1) via the lone pair on the oxygen] and to Ru(2) through the C–O π-electrons. The C–O bond of 1.368(5) Å is considerably elongated indicating a large decrease in bond order.

We may assume that the COPh fragment in complex **1** is derived from the electron transfer reagent benzophenone despite its high thermodynamic stability. The mechanism by which it is produced remains uncertain, and since **1** is produced in only low yield, we can only speculate about the route by which it is formed. It has been shown that the radical, $[Ru_3(CO)_{12}]^{-}$, readily undergoes CO substitution by two electron donors, presumably by Ru–Ru bond cleavage to generate a seventeen electron Ru-centre [4]. In the present reaction, no suitable ligand is present, and reaction of the seventeen electron Ru-centre with the ketyl radical may take place in such a way that the metal atom is inserted between the carbonyl C-atom and one of the phenyl rings. Additional oxidative addition and reductive elimination must take place, with formation of **1** and presumably biphenyl. Clearly, the re-formation of $[Ru_3(CO)_{12}]$ is more likely than such a reaction, and this is reflected in the large amount of $[Ru_3(CO)_{12}]$ recovered from the reaction and the low yield of **1**.

Acknowledgements

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[5] The method employed is similar to that previously described for the preparation of $[Ru_3(CO)_{12}]^{2-}$ [6] Tetrahydrofuran (6 ml) was added to an evacuated Schlenk tube containing benzophenone (105 mg) and metallic potassium (24 mg). The potassium-benzophenone solution was stirred for several hours until all the potassium metal had dissolved; $[Ru_3(CO)_{12}]$ (166 mg) was then added (in 10–20 mg portions every 15 min) to the stirred mixture at room temperature. After approximately 3 h the solvent was removed in vacuo, and the products separated by TLC. Two bands were observed and characterised as the starting material $[Ru_3(CO)_{12}]$ and $[Ru_3(\mu_2\text{-}H)(CO)_9(\mu_3\text{-}\sigma:\sigma:\eta^2\text{-}COPh)]$, **1** (approximately 4%). Crystals suitable for an X-ray analysis were grown from a toluene solution at −25°C over a period of several days.

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[7] Spectroscopic data for **1**: IR ν_{CO} (CH_2Cl_2) 2092(m), 2066(s), 2037(vs), 2018(m), 2003(sh) and 1974(w) cm^{-1}; mass spectrum $m/z = 661$ (Calc. = 661) amu, together with peaks representing the sequential loss of nine carbonyl groups; ^1H NMR ($CDCl_3$) δ7.3 (m, 5H), −18.11 (s, 1H) ppm.

[8] Crystal data. (**1**), $C_{16}H_6O_{10}Ru_3$, $M = 661.4$, triclinic, space group $P\bar{1}$, $a = 9.809(4)$, $b = 10.233(8)$, $c = 11.286(7)$ Å, $\alpha = 90.01(3)$, $\beta = 92.68(4)$, $\gamma = 99.76(5)°$, $U = 1115$ Å^3 [from 2θ values of 24 reflections measured at $\pm\omega$ ($2\theta = 30$–$32°$, $\lambda = 0.71073$ Å)], $Z = 2$, $D_c = 1.969$ g cm^{-3}, $T = 150.0(1)$ K, yellow rhombic crystal $0.82 \times 0.82 \times 0.43$ mm, $\mu = 2.013$ mm^{-1}, $F(000) = 628$. Data collection and processing. Diffraction data were collected on a Stoë Stadi-4 four-circle diffractometer equipped with an Oxford Cryosystems low-temperature device [9] and graphite-monochromated Mo Kα X-radiation, $T = 150$K, ω-2θ scans, 2704 unique data collected ($2\theta_{max}$ 45°, h −10 to 10, k −10 to 11, l 0 to 12), semi-empirical absorption correction [10] applied (minimum and maximum transmission factors 0.461 and 0.831 respectively), giving 2649 reflections with $F \geq 4\sigma(F)$ for use in all calculations. Structure solution and refinement. The ruthenium atoms were located by automatic direct methods [11] and subsequent iterative cycles of least-squares refinement and Fourier difference synthesis located all non-H atoms [12]. The Ru, C and O atoms were then refined (by least-squares on F) with anisotropic thermal parameters. The phenyl carbon atoms were refined as a rigid hexagon with the phenyl H atoms included at fixed, calculated positions. The hydride was not located. At final convergence R, $R' = 0.0283$, 0.0457 respectively, $S = 1.256$ for 282 refined parameters and the final ΔF synthesis showed no $\Delta\rho$ above 0.66 or below −0.70 e$Å^{-3}$, the major features lying near the Ru atoms. A secondary extinction parameter refined to 2.97×10^{-7}, the weighting scheme $w^{-1} =$

$\sigma^2(F) + 0.000072\ F^2$ gave satisfactory agreement analyses and in the final cycle $(\Delta/\sigma)_{max}$ was 0.05. Additional material available from the Cambridge Crystallographic Data Centre comprises of H-atom coordinates, thermal parameters and the remaining bond lengths and angles.

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