Electrophilic Reactivity of Arene Carbonyl Cluster Complexes with the Ru_6C Core. Crystal and Molecular Structure of $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_4Ph_2\text{-}1,4)]$

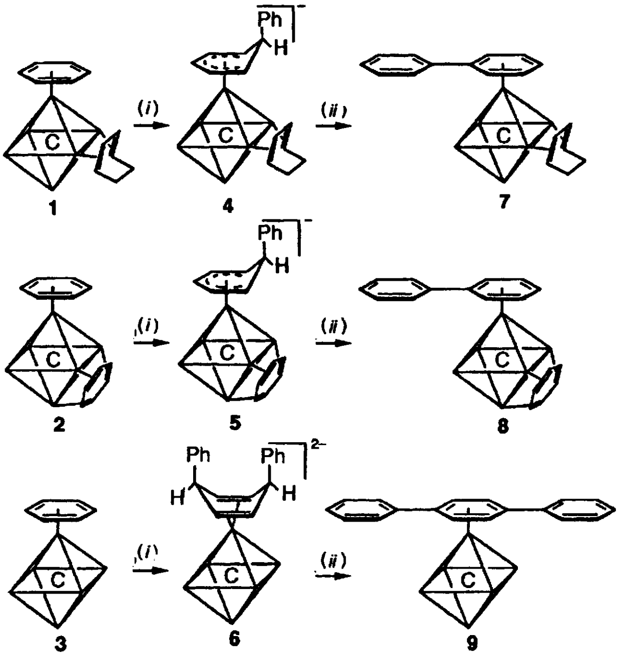
Till Borchert,[a,b] **Jack Lewis**,*[a] **Hans Pritzkow**,[b] **Paul R. Raithby**[a] and **Hubert Wadepohl***[b]
[a] *Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK*
[b] *Anorganisch-Chemisches Institut der Ruprecht-Karls-Universität, Im Neuenheimer Feld 270, D-69120 Heidelberg, Germany*

Addition of LiPh to $[Ru_6C(CO)_{12}(\eta^6\text{-}C_6H_6)(\mu\text{-}\eta^2:\eta^2\text{-}C_6H_8)]$, $[Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ and $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_6)]$, followed by treatment with $[CPh_3][BF_4]$, has led to the substituted arene cluster complexes $[Ru_6C(CO)_{12}(\mu\text{-}\eta^2:\eta^2\text{-}C_6H_8)(\eta^6\text{-}C_6H_5Ph)]$, $[Ru_6C(CO)_{11}(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)(\eta^6\text{-}C_6H_5\text{-}Ph)]$ and $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_4Ph_2\text{-}1,4)]$ (structure established by X-ray crystallography).

In contrast to mononuclear systems,[1] comparatively little is known about the reactivity of arenes co-ordinated to metal clusters.[2,3] In the latter systems both the η^6 (terminal) and μ_3-$\eta^2:\eta^2:\eta^2$ (face bridging) co-ordination modes of the arene have been found.[2,3] When co-ordinated to a triosmium carbonyl cluster in the face-bridging mode, benzene is activated towards nucleophiles such as H^-, Me^- or Ph^-, which add to the ring in the *exo* position.[4] This type of reaction is not observed with the face-capping arene ligands in the large class of tris(cyclopentadienylcobalt) cluster complexes $[\{Co(\eta^5\text{-}C_5H_5)\}_3(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-arene})]$ (arene = alkyl- or alkenyl-benzene).[2]

Here we report investigations of the reactivity of the hexanuclear ruthenium carbido cluster complexes $[Ru_6C(CO)_{12}(\eta^6\text{-}C_6H_6)(\mu\text{-}\eta^2:\eta^2\text{-}C_6H_8)]$ **1**,[5] $[Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ **2**[6] and $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_6)]$ **3**[7] (see Scheme 1). All these complexes have a terminal and, in the case of **2**, also a face-bridging arene ligand. Treatment of **1**–**3** with an excess (1.2–1.5 mol equivalents) of LiPh at −78 °C, followed by addition of $[N(PPh_3)_2]Cl$ in Pr^iOH gave red-brown solids in 65–90% yield.

Based on spectroscopic data† and on their reactivity towards $[CPh_3][BF_4]$ (see below), the structures $[Ru_6C(CO)_{12}(\eta^5\text{-}C_6H_6Ph)(\mu\text{-}\eta^2:\eta^2\text{-}C_6H_8)]^-$ **4**, $[Ru_6C(CO)_{11}(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)(\eta^5\text{-}C_6H_6Ph)]^-$ **5** and $[Ru_6C(CO)_{14}(\eta^4\text{-}C_6H_6Ph_2)]^{2-}$ **6** are assigned to the products of the reactions with complexes **1**, **2** and **3**, respectively. For **4** and **5** in particular, the observation of the molecular negative ions in the FAB mass spectra, and the low-frequency shift of the IR(ν_{CO}) bands ($\approx 30\ cm^{-1}$ as compared to the neutral starting materials) are consistent with the presence of anionic cluster complexes. Confirmation of a μ_3-$\eta^2:\eta^2:\eta^2$-benzene ligand in **5** comes from the ^1H NMR spectrum, which has a singlet (δ 4.03) in the region typical for face-capping benzene rings. Therefore it is likely that the terminal benzene of **2** was attacked by the nucleophile during the formation of **5**, although attack at the μ_3-benzene followed by a terminal-to-bridging site exchange of the two organic ligands cannot be ruled out completely.



Scheme 1 (*i*) LiPh, −78 °C; (*ii*) $[CPh_3][BF_4]$, −78 °C

The negative-ion FAB mass spectrum of the reaction product from complex **3** shows a peak envelope centred at *m*/*z* 1241, corresponding to the addition of two phenyl groups to the starting material. The observed low-frequency shift of the ν_{CO} bands ($\approx 60\ cm^{-1}$ relative to **3**, about twice as much as for **4** and **5**) suggests a dianion **6**, although only a peak for the monoanion is found in the negative-ion FAB mass spectrum. Owing to the large number of phenyl groups in the $[N(PPh_3)_2]^+$ salt of **6** the cyclohexadiene protons could not be detected in the ^1H NMR spectrum.

When complexes **4**–**6** were treated with an excess of $[CPh_3][BF_4]$ in dichloromethane at −78 °C the dark red

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† **4**: IR (ν_{CO} in CH_2Cl_2) 2032m, 1987s, 1976s, 1766w (br) cm^{-1}; negative-ion FAB *m*/*z* 1190. **5**: ν_{CO} 2011m, 1972s, 1916w, 1762w (br) cm^{-1}; *m*/*z* 1160; ^1H NMR (250 MHz, in $CDCl_3$) δ 7.70–7.01 (m, 35 H), 5.96 ('t', 1 H), 4.58 ('t', 2 H), 4.03 (s, 6 H), 3.90 ('t', 1 H), 3.05 ('t', 2 H). **6**: ν_{CO} 2014m, 1963s, 1919m, 1768w (br); *m*/*z* 1241.

neutral products $[Ru_6C(CO)_{12}(\mu\text{-}\eta^2{:}\eta^2\text{-}C_6H_8)(\eta^6\text{-}C_6H_5Ph)]$ **7**, $[Ru_6C(CO)_{11}(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(\eta^6\text{-}C_6H_5Ph)]$ **8** and $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_4Ph_2\text{-}1,4)]$ **9** were obtained (yield 20–30% after chromatographic work-up). The positive-ion FAB mass spectra (*m*/*z* 1189 **7**, 1159 **8**, 1243 **9**) are in accord with the abstraction of one (in the case of **7** and **8**) and two hydrogens (**9**). The infrared spectra* are similar to those of the neutral starting materials **1**–**3**. So far only **9** has been characterised completely. The very simple ^1H and ^{13}C NMR spectra (in CD_2Cl_2)† of this complex are indicative of a *p*-terphenyl ligand, co-ordinated to the Ru_6 cluster *via* the central phenylene ring. From the chemical shift of the four protons attached to this ring, a terminal η^6 co-ordination can be assumed. As shown by the single broad ^{13}C resonance in the carbonyl region ($\delta \approx 200$), **9** exhibits considerable fluxionality.

The structure of complex **9** in the solid state was determined by a single-crystal X-ray diffraction study‡ (Fig. 1). The Ru_6 metal framework is that of an octahedron, encapsulating a carbide carbon atom. One of the ruthenium atoms carries the *p*-terphenyl ligand, which is η^6-co-ordinated *via* the central arene ring. The carbide carbon atom C(1) is shifted from the centre of the Ru_6 octahedron towards the Ru atom bearing the arene ligand [Ru(1)–C(1) 1.924 *vs.* Ru(2–6)–C(1) 2.059 Å (average)]. A similar effect was observed in other (η^6-arene)Ru_6C carbonyl cluster complexes.[3,5,10] The distribution of the carbonyl ligands is also similar to that in related complexes and is characterised by the presence of one bridging CO spanning one Ru–Ru bond in the 'equatorial' plane defined by Ru(2)–Ru(5). Two more carbonyls lie within the same plane and are asymmetrically bridging two Ru–Ru edges. There are two terminal CO ligands on each ruthenium atom in the equatorial plane and three such ligands on the apical Ru(6).

There is a small, barely significant deviation from planarity of the co-ordinated arene ring, resulting in a slight elongation of the distances Ru(1)–C(2) and Ru(1)–C(5). The planar phenyl substituents are at 41 and 38° to the best plane through C(2)–C(7).

For the products **7** and **8** we assume structures with η^6-biphenyl and a bridging cyclohexadiene (**7**) or benzene (**8**) ligands, respectively.

The results presented here are different from those obtained earlier with the cluster complex $[Os_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)]$. In this case, the phenyl carbanion adds to the μ_3-benzene ligand to give a μ_3-cyclohexadienyl moiety. However, hydride abstraction occurs from the position '*para*' to the phenyl substituent, resulting in the formation of the carbene complex $[Os_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^1{:}\eta^2\text{-}C_6H_5Ph)]$.[4b]

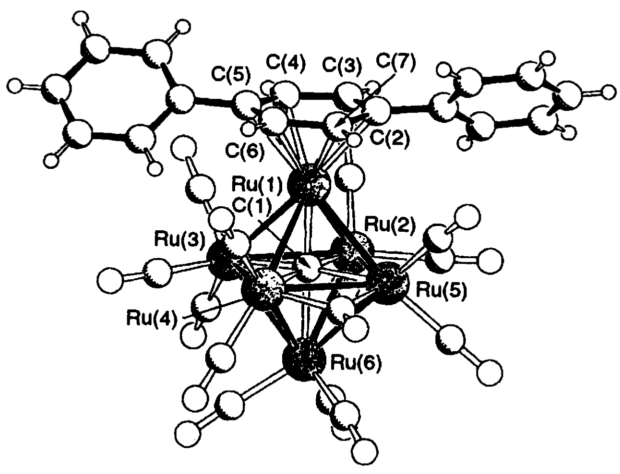

Fig. 1 Molecular structure of complex **9**. Selected distances (Å): Ru(1)–Ru(2–5) 2.855(1)–2.885(1), Ru(6)–Ru(2–5) 2.833(1)–2.900(1), Ru(2)–Ru(3) 2.800(1), Ru(2)–Ru(5) 2.982(1), Ru(3)–Ru(4) 3.017(1), Ru(4)–Ru(5) 2.811(1), Ru(1)–C(1) 1.924(6), Ru(2–6)–C(1) 2.044(6)–2.076(6), Ru(1)–C(2) 2.293(6), Ru(1)–C(3) 2.231(6), Ru(1)–C(4) 2.212(6), Ru(1)–C(5) 2.277(6), Ru(1)–C(6) 2.246(6), C(2)–C(3) 1.406(9), C(2)–C(7) 1.410(9), C(3)–C(4) 1.406(9), C(4)–C(5) 1.401(9), C(5)–C(6) 1.406(9), C(6)–C(7) 1.420(9)

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* IR(ν_{CO} in CH_2Cl_2): **7**, 2043m, 2002s, 1951w, 1816w (br); **8**, 2039m, 2002s, 1951w, 1816w (br); **9**, 2075m, 2026s, 1985w, 1811w (br) cm^{-1}.

† ^1H (200 MHz) δ 7.47–7.39 (m, 10 H), 6.20 (s, 4 H); $^{13}C\text{-}\{^1H\}$ (50.3 MHz) δ 200 (br, CO), 133.9 (C), 131.0 (CH), 129.3 (CH), 128.7 (CH), 106.7 (C), 87.2 (CH); a weak broad signal at $\delta \approx 420$ is tentatively assigned to the carbide carbon atom.

‡ Crystal data. $C_{33}H_{14}O_{14}Ru_6 \cdot 0.5C_6H_6$, monoclinic, space group $P2_1/n$, $a = 13.864(4)$, $b = 12.791(4)$, $c = 21.971(7)$ Å, $\beta = 106.88(3)°$, $U = 3728(2)$ Å^3, $Z = 4$, $\mu = 24.4$ cm^{-1}, $F(000) = 2424$. Syntex R3 four-circle diffractometer, Mo-Kα radiation (graphite monochromator, $\lambda = 0.710\,69$ Å), ω scan, $2\theta_{min} = 3$, $2\theta_{max} = 50°$, $0 \leqslant h \leqslant 16$, $0 \leqslant k \leqslant 15$, $-26 \leqslant l \leqslant 25$. Reflections: measured, 6897; unique, 6616. Empirical absorption correction ($T_{min} = 0.627$, $T_{max} = 0.974$). The structure was solved by direct methods and refined by full-matrix least squares. Residual electron density was successfully accounted for by assuming half a disordered benzene per asymmetric unit. Hydrogen atoms were inserted at calculated positions. Final $wR2 = 0.092$ (all data), $R1 = 0.038$ [5484 reflections with $I > 2\sigma(I)$], $w = 1/[\sigma^2(F_o^2) + (0.0308P)^2 + 10.31P]$, $P = [(F_o^2, 0)_{max} + 2F_c^2]/3$. Programs used were SHELXS 86[8] and SHELXL 93.[9] Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.