From Butadiynyl (–C≡C–C≡CR) Ligands to Alkylidyne–Carbides: Synthesis and Characterisation of the Unusual Hexanuclear Ruthenium Carbido Clusters $[Ru_6(CO)_{13}(\mu\text{-}CO)_2(\mu\text{-}PPh_2)(\mu_5\text{-}C)(\mu_3\text{-}C\text{–}C{\equiv}CR)]$ (R = Bu^t, Ph)

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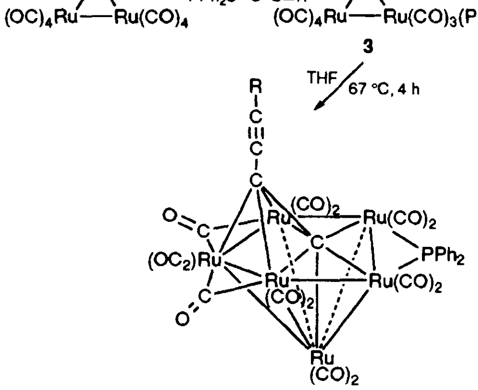
The preparation from $[Ru_3(CO)_{11}(PPh_2C{\equiv}C\text{–}C{\equiv}C\text{–}R)]$ (R = Bu^t, Ph) of the hexanuclear complexes $[Ru_6(CO)_{13}(\mu\text{-}CO)_2(\mu\text{-}PPh_2)(\mu_5\text{-}C)(\mu_3\text{-}C\text{–}C{\equiv}CR)]$ (R = Bu^t **1**, Ph **2**) containing a novel alkylidyne–carbide ligand is described; the structure of **1** is determined by a single-crystal X-ray diffraction study.

Since the discovery of the first carbidocarbonyl cluster $[Fe_5C(CO)_{15}]$,[1] molecules containing a single carbon atom bound only to metal atoms have been a continued focus of attention.[2] A principal reason for this is the belief that partially exposed carbides in clusters such as $[Fe_4C(CO)_{12}]^{2-}$ may mimic, structurally and chemically, the behaviour of surface-bound carbide intermediates in Fischer–Tropsch chemistry.[3] We describe herein the synthesis and characterisation of two novel hexanuclear clusters $[Ru_6(CO)_{13}(\mu\text{-}CO)_2(\mu\text{-}PPh_2)(\mu_5\text{-}C)(\mu_3\text{-}C\text{–}C{\equiv}CR)]$ (R = Bu^t **1**, Ph **2**) which contain semi-interstitial carbide-like carbon atoms bound to five metal atoms, as established by X-ray crystallography for **1**. A unique feature of the carbidic carbon atoms in **1** and **2** is that they are also attached to a single alkylidyne ligand. Thus these clusters are best described as alkylidyne–carbides with both carbide and alkylidyne fragments derived from a diynyl –C≡C–C≡CR group. Although a structural analogy between μ-η-acetylides and alkylidyne carbides has been suggested,[4] **1** and **2** represent the best intermediate models yet described for the transformation of an alkynyl group to a carbide and alkylidyne. In addition, they are the first Ru_6 clusters to be reported with a pentagonal-pyramidal core. As a fragment isoelectronic with CO and CNR, the usual precursors of carbides, the acetylide anion $[\text{–}C{\equiv}C\text{–}R]^-$ is a potential source of μ-C ligands but only a single very recent account of the conversion of a cluster bound alkynyl group to carbide and alkylidyne has been reported.[5]

As a continuation of our investigation into the interaction of polyunsaturated organic fragments with bi- and poly-nuclear centres, the thermolysis of the triruthenium clusters $[Ru_3(CO)_{11}(PPh_2C{\equiv}C\text{–}C{\equiv}C\text{–}R)]$ (**3**, R = Bu^t, Ph) was studied, Scheme 1. After 4 h in refluxing THF, chromatographic separation of the reaction mixture[†] afforded the title complexes in low yield [**1**, 3.2%; **2**, 1.2%, based on $Ru_3(CO)_{12}$], after crystallisation from diethyl ether–hexane at −20 °C. In addition, one major product and several minor products were obtained, the details of which will be reported elsewhere. The presence of bridging carbonyl ligands was evident from IR spectroscopy while the ^{31}P NMR spectra were consistent with the incorporation of a phosphido bridge across an Ru–Ru bond.[‡] The most unusual spectroscopic feature of **1** and **2** was the appearance of a signal at very low field (δ ≈ 303) in the ^{13}C NMR spectra, a chemical shift more commonly associated with interstitial carbon in transition metal clusters.[2,6] This, along with the occurrence of three quaternary carbon peaks at higher field, suggested the incorporation of the diyne ligand into the metallic framework in an unorthodox fashion.



R
1 Bu^t
2 Ph

Scheme 1

In order to elucidate the structure of **1**, a single-crystal X-ray diffraction study was undertaken, Fig. 1.[§] The metallic framework describes a pentagonal pyramid, a geometry hitherto unknown for Ru_6 clusters. Evidently, P–C bond cleavage in the starting complex liberates a diyne fragment which becomes attached to the Ru_6 system *via* C(16) and C(17), with the latter bearing a pendant –C≡C–Bu^t. Thus carbidic C(16) is μ_5 bonded to Ru(1)Ru(2)Ru(3)Ru(5)Ru(6), while attachment to C(17) confers μ_6 coordination. The associated PPh_2 group assumes a bridging position across the Ru(1)–Ru(2) bond. An approximate plane is formed by Ru(1)Ru(2)Ru(3)Ru(5) with Ru(4) deviating by 0.48 Å below the plane to facilitate linking with apical Ru(6). The μ_5-carbide carbon C(16) is displaced above the plane by 0.26 Å, a distance significantly greater than that found in $[Ru_5C(CO)_{15}]$ (0.11 Å),[7] and presumably a consequence of attachment to the alkylidyne carbon C(17). The short Ru(6)–C(16) [2.103(4) Å], Ru(1)–C(16) [2.108(4) Å] and Ru(2)–C(16) [2.119(4) Å] contacts in **1** may be compared with similarly strong Ru–C interactions in the μ_4-η^2 acetylide $[Ru_5(CO)_{13}(C{\equiv}CPh)(PPh_2)]$[4a] [average Ru–$C_\alpha$(acetylide) 2.105 Å] and in the dicarbide species $[Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{11}]$[8] [average Ru–C($\eta^1$) 2.133 Å]. The net effect of these interactions is a lengthening of the $C_\alpha{\equiv}C_\beta$ bond to 1.458(7) Å, a distance greater than the formally single C(17)–C(18) bond [1.435(6) Å].

The effect of the alkylidyne–carbide ligand in **1** is evident from the variation in metal–metal bonding distances found. While the metal separations in the Ru(5)Ru(1)Ru(2)Ru(3) chain [Ru(5)–Ru(1) 2.775(1), Ru(1)–Ru(2) 2.782(1), Ru(2)–Ru(3) 2.756(1) Å] are only slightly shorter than those found in $[Ru_3(CO)_{12}]$ (2.85 Å), the Ru(3)Ru(4)Ru(5) unit exhibits strong metal–metal interactions [Ru(3)–Ru(4) 2.656(1), Ru(4)–Ru(5) 2.671(1) Å]. This contrasts sharply with the interatomic separation of 3.03 Å between Ru(4) and capping Ru(6), a value not atypical of those observed in electron-rich Ru_4 and Ru_5 clusters.[9] The long Ru(4)–Ru(6) contact is responsible for the deviation from planarity of the Ru(1)–Ru(5) ring, giving a dihedral angle Ru(1)Ru(2)Ru(3)Ru(5)–Ru(3)Ru(4)Ru(5) of 15.2(1)°. An eight-skeletal electron pair count for clusters **1** and **2**, with the intact hydrocarbyl fragment contributing seven electrons, is consistent with a six-vertex pentagonal-pyramidal structure. The EAN rule (6M, 10 M–M bonds) also requires an 88 electron count with the carbon ligands acting as carbide (μ_5-C, 4e) and alkylidyne (μ_3-CC_2R, 3e) donors. An alternative description is a fused octahedron Ru(3)Ru(4)Ru(5)-

Ru(16)C(17)/bicapped tetrahedron Ru(1)Ru(2)Ru(3)Ru(5)-(Ru(6)C(16).[10]

Although μ_6 coordination of C in M_6 systems is now well documented, such examples are usually characterised by octahedral metal-encapsulation of the carbidic atom. In μ_5 carbide clusters, {*e.g.* $[M_5C(CO)_{15}]$, M = Fe, Ru, Os}, a square-pyramidal or distorted octahedral geometry is most commonly found. In the latter case the carbidic atom can be considered to occupy one of the vertices and this description may be applied to the pseudooctahedral C(16)Ru(1)Ru(2)-Ru(3)Ru(5)Ru(6) fragment of **1**, when viewed in isolation.

To our knowledge, the coordination mode of the diyne ligand in **1** and **2** is unprecedented. Perhaps its closest relative in the literature is $[Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{11}]$[11] where the dicarbon fragment is coordinated in a μ-η^5 fashion across a grossly distorted pentagonal Ru_5 face. Fission of the phosphino–diyne bond in the precursors to **1** and **2** facilitates attachment of the activated triple bond to the metal skeleton, albeit with the integrity of the C_4 chain being barely preserved. The formation of dicarbide-containing ligands through the linking of acetylide[12a] and diyne[12b] units to square Ru_4 faces has been noted previously, although these exhibit lower coordination of carbon (μ_4).

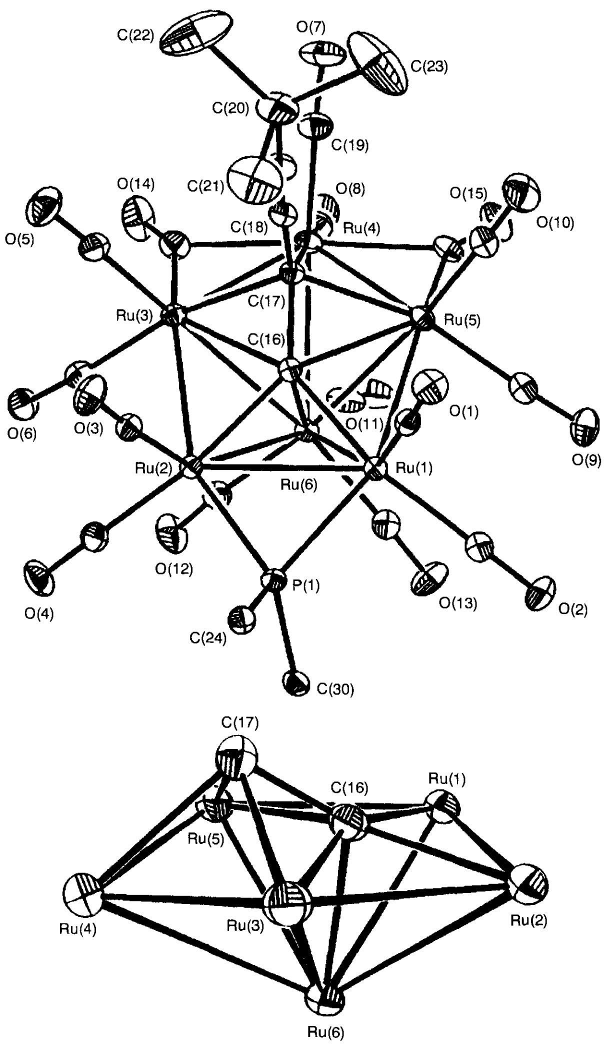


Fig. 1 A perspective view of the molecular structure of $[Ru_6(CO)_{13}(\mu\text{-}CO)_2(\mu\text{-}PPh_2)(\mu_5\text{-}C)(\mu_3\text{-}C\text{-}C{\equiv}CBu^t)]$ **1** with the Ru_6 skeleton drawn separately to illustrate the coordination of the μ_5-carbido and the μ_3-alkylidyne ligands. Important bond lengths (Å) and angles (°) not mentioned in the text are: Ru(1)–Ru(6) 2.916(1), Ru(2)–Ru(6) 2.876(1), Ru(3)–Ru(6) 2.861(1), Ru(5)–Ru(6) 2.814(1), Ru(3)···Ru(5) 3.888(1), Ru(3)–C(16) 2.271(4), Ru(3)–C(17) 2.186(4), Ru(5)–C(16) 2.265(3), Ru(5)–C(17) 2.182(4), Ru(4)–C(17) 2.194(3); C(16)–C(17)–C(18) 121.8(3), Ru(1)–P(1)–Ru(2) 75.1(1).

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Footnotes

† A dark red-brown band removed from a silica column [hexane–CH_2Cl_2 (9 : 1)] was subsequently purified by TLC on silica plates [hexane–CH_2Cl_2 (7 : 3)].

‡ *Selected spectroscopic data*: IR(CH_2Cl_2) ν(CO)/cm^{-1}, **1** 2080w, 2049m, 2041vs, 2019s, 1872w br; **2** 2080w, 2050m, 2042vs, 2020s, 1873w br; ^1H NMR ($CDCl_3$) δ **1** 7.82–7.40 (m, 10H, Ph), 1.10 (s, 9H, Bu^t); **2** 7.86–6.60 (m, Ph); $^{13}C\{^1H\}$ NMR, **1** ([$^2H_8$]THF) δ 302.7 (d, J_{PC} 6 Hz, C_α), 218.6 (s, μ-CO), 204.2 (d, J_{PC} 4 Hz, CO), 200.6 (s, CO), 197.9 (s, CO), 197.1 (d, J_{PC} 6 Hz, CO), 185.2 (s, C_β), 137.9 (d, J_{PC} 44 Hz, PC_{ipso}), 136.0–129.8 (m, Ph), 126.0 (s, C_δ), 98.9 (s, C_γ), 31.0 (s, CMe_3), 30.2 (s, CMe_3); **2** ($CDCl_3$) δ 302.8 (d, J_{PC} 6 Hz, C_α), 213.5 (s, μ-CO), 203.0 (d, J_{PC} 4 Hz, CO), 199.2 (s, CO), 196.4 (s, CO), 195.9 (d, J_{PC} 6 Hz, CO), 183.9 (s, C_β), 137.5–126.8 (m, Ph), 123.2 (s, C_δ), 111.2 (s, C_γ); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ **1** 251.6(s); **2** 235.9(2). Satisfactory elemental analyses were obtained.

§ *Crystal data for* **1**: dark red-brown prisms grown from diethyl ether–hexane at −20 °C; $C_{35}H_{19}O_{15}PRu_6 \cdot 0.5C_4H_{10}O$, M = 1354.0; triclinic, space group $P\bar{1}$, a = 12.588(2), b = 13.391(3), c = 13.923(5) Å, α = 78.05(2), β = 68.56(2), γ = 83.84(2)°, U = 2135.8(9) Å^3, Z = 2, T = 200 K, D_c = 2.105 g cm^{-3}, $F(000)$ = 1298, λ = 0.71073 Å, μ(Mo-Kα) = 21.72 cm^{-1}. Intensity data were collected for a crystal of dimensions 0.15 × 0.32 × 0.14 mm mounted on a Siemens R3 m/V diffractometer by the ω-scan method ($2\theta < 50°$). Of 7900 reflections measured, 6434 were considered observed [$F > 6.0\sigma(F)$]. The structure was solved (Patterson, Fourier methods) and refined (full-matrix least squares) using the Siemens SHELXTL PLUS program, giving final R and R_w values of 0.0207 and 0.0264 respectively.

Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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