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Reaction of a Side-on Co-ordinated Carbene Ligand with the Wittig Reagent

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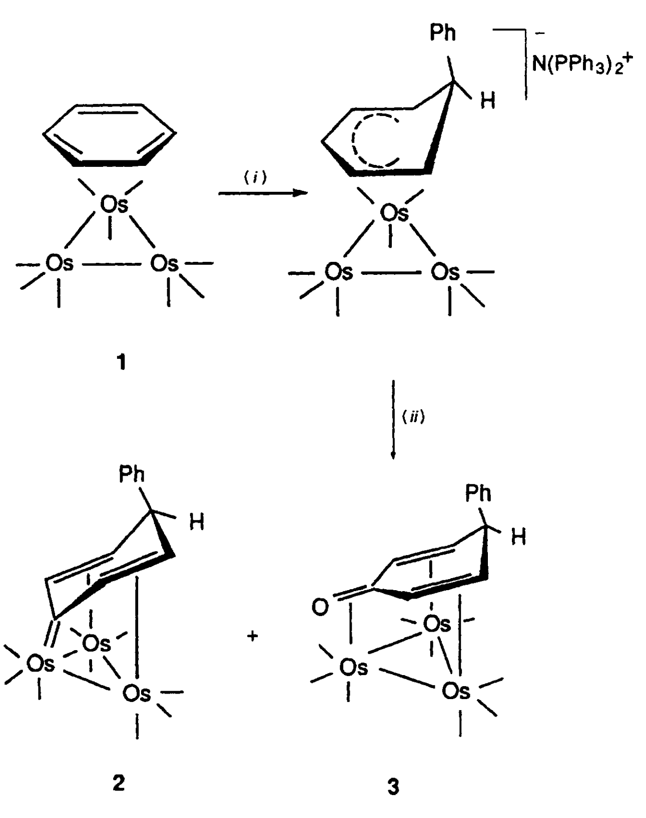
The 1-methylene-4-phenylcyclohexadiene triosmium complex $[Os_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}H_2C{=}C_6H_5Ph)]$ has been prepared from the reaction of $[Os_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^1{:}\eta^2\text{-}C_6H_5Ph)]$, which contains a side-on co-ordinated carbene group, with the Wittig reagent $H_2C{=}PPh_3$; the crystal and molecular structure of the product has been determined by an X-ray diffraction study.

Arenes can adopt a $\mu_3\text{-}\eta^2:\eta^2:\eta^2$-face-capping mode when they are co-ordinated to a triangular metal cluster core, and this mode has been observed in a variety of cluster compounds during the last few years.[1,2] These compounds are of interest as model complexes for the adsorption of arenes on metal surfaces.[3]

During our investigations of the reactivity of the triosmium cluster $[Os_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)]$ **1**[4,5] we recently synthesised a triosmium cluster complex **2** containing a carbene in an unusual side-on co-ordination mode (Scheme 1).[6] The cyclohexadienone triosmium complex **3** is formed during the purification of **2** on TLC plates. Complex **3** can also be obtained easily from **2** in the presence of air and a Lewis base (*e.g.* NEt_3). These reactions give a first hint that carbene carbon may act as an electrophilic centre which is attacked by Lewis bases (NEt_3 or surface groups bearing free electron pairs or even water in the case of silica gel).[6]

We were interested in the reactivity of the carbene complex **2** towards nucleophilic reagents and to compare these results with those obtained in the case of mononuclear Fischer carbene complexes in which the carbene is co-ordinated in the usual end-on mode. Our first comparative reaction involved the Wittig reagent, $H_2C{=}PPh_3$. For example, this compound reacts readily with the mononuclear tungsten complex $[(OC)_5W{=}CPh(OMe)]$ to form two products. One product is $[W(CO)_5(PPh_3)]$, which is simply formed by co-ordination of the PPh_3 group to the co-ordinatively unsaturated '$W(CO)_5$' fragment. The second product, $H_2C{=}CPh(OMe)$, in which a double C=C bond is formed between the carbene carbon and the methylene moiety of the Wittig reagent,[7] may be viewed as a dimerisation of two carbenes.

In the comparative reaction with the novel triosmium carbene complex **2** a solution of $H_2C{=}PPh_3$ (0.07 mmol) in tetrahydrofuran (thf) (5 cm^3) at −78 °C was added to the orange solution of **2** (0.05 mmol). During the addition the solution became yellow. The reaction mixture was purified by TLC. Product **4** (Scheme 2) was obtained as orange-yellow microcrystals in 50% yield and initially characterised from spectroscopic data.† Its molecular and crystal structure has been established by X-ray crystallography.‡ The asymmetric unit contains two independent but structurally similar molecules which are separated by normal van der Waals



Scheme 1 Synthesis of complexes **2** and **3**. (*i*) PhLi, thf, −78 °C; $[N(PPh_3)_2]Cl$, Pr^iOH; (*ii*) $[CPh_3]BF_4$, CH_2Cl_2, −78 °C

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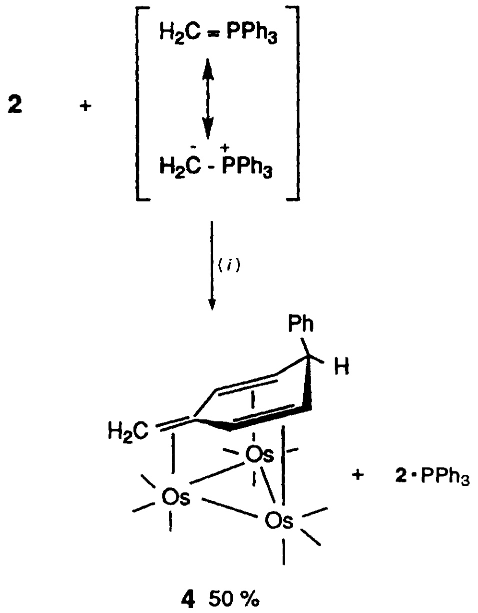
† IR (CH_2Cl_2): ν(CO) 2077m, 2033vs, 2024vs, 2002m, 1976m and 1950w cm^{-1}. NMR (CD_2Cl_2): ^1H, δ 7.3–7.6 (m, 5 H), 4.84 [t, *J*(HH) = 2.5, 1 H], 3.51 [dd, *J*(HH) = 8.0, 2.5, 2 H], 3.20 (s, 2 H) and 2.67 [d, *J*(HH) = 8.0 Hz, 2 H]. Positive-ion FAB mass spectrum: m/z 996 (M^+, calc. 996).

‡ Crystal data: $C_{22}H_{12}O_9Os_3$, $M = 990.92$, monoclinic, space group $P2_1/c$ (no. 14), $a = 18.811(4)$, $b = 14.155(3)$, $c = 17.463(3)$ Å, $\beta = 95.21(3)°$, $U = 4631(2)$ Å^3, $Z = 8$, $D_c = 2.843$ Mg m^{-3}, λ(Mo-Kα) = 0.710 73 Å, μ(Mo-Kα) = 16.473 mm^{-1}, $F(000) = 3552$, crystal dimensions 0.25 × 0.33 × 0.38 mm. Data collection at room temperature on a Stoe four-circle diffractometer. Structure solved by direct methods and subsequent Fourier-difference syntheses. Hydrogen atoms were placed in idealised positions and allowed to ride on the relevant carbon atom. Refinement by full-matrix least squares on F_o^2 using SHELXTL PLUS[8] and SHELXL 93[9] to give $R1 = 0.079$ $[F > 4\sigma(F)]$ and $wR2 = 0.237$ (all data), where $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = \{\Sigma w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{\frac{1}{2}}$ and $w = 1/[\sigma^2(F_o^2) + (0.153P)^2 + 149.34P]$ where $P = (F_o^2 + 2F_c^2)/3$. 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.



Scheme 2 Synthesis of complex **4**. (*i*) thf, −78 °C

distances. The molecular structure of one molecule is shown in Fig. 1.

In contrast to the reactions of the mononuclear complexes described above, the 1-methylene-4-phenylcyclohexadiene triosmium carbonyl product **4** contains a carbidic C=C double bond which remains in the co-ordination sphere of the triosmium cluster and the whole organic ligand still occupies a face-capping position. The ligand is co-ordinated formally by three C=C 'double bonds' which are slightly shorter than the non-co-ordinated C–C 'single bonds'. The co-ordinated part of the cyclohexadienyl ring is not strictly planar but is slightly bowed probably to enable a better interaction between the metals and the 'double bonds'. This is in contrast to the case of the cyclohexadienone complex **3** where the co-ordinated section of the ring remains planar.[6] The sp^3-hybridised carbon atom bearing the phenyl substituent is displaced out of the ring co-ordination plane so that the dihedral angle between the ring plane and the plane containing the two hinge carbons and this carbon is 24.8° compared to 19.5° in **3**.

The second product, which has not yet been characterised fully, is assumed to be an adduct between the phosphine and the carbene ligand forming a ylidic structure. The carbene complex **2** has in common with Fischer carbene complexes the reactivity towards this nucleophilic Wittig reagent. The product, however, is unique since the C=C double bond formed remains in a side-on co-ordination mode to the osmium cluster.

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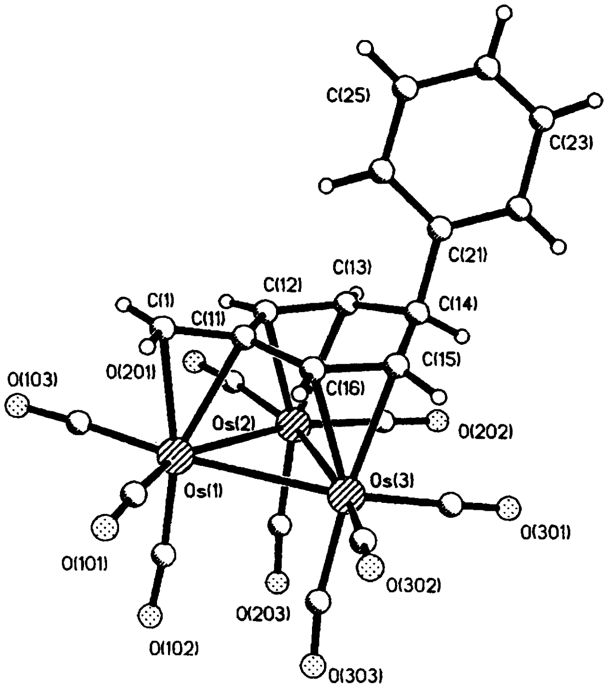

Fig. 1 Molecular structure of complex **4**. Selected bond lengths (Å) and angles (°) (parameters for the second molecule are given in square brackets): Os(1)–Os(2) 2.906(2) [2.920(2)], Os(1)–Os(3) 2.900(2) [2.892(2)], Os(2)–Os(3) 2.864(2) [2.888(2)], Os(1)–C(1) 2.30(3) [2.37(3)], Os(1)–C(11) 2.30(3) [2.31(3)], Os(2)–C(12) 2.32(3) [2.29(3)], Os(2)–C(13) 2.40(3) [2.31(3)], Os(3)–C(15) 2.30(3) [2.31(3)], Os(3)–C(16) 2.29(2) [2.28(3)], C(1)–C(11) 1.40(4) [1.36(4)], C(11)–C(12) 1.47(4) [1.48(4)], C(12)–C(13) 1.44(4) [1.39(4)], C(13)–C(14) 1.57(4) [1.52(4)], C(14)–C(15) 1.53(3) [1.51(4)], C(15)–C(16) 1.40(3) [1.27(4)] and C(11)–C(16) 1.50(4) [1.50(4)]; Os(3)–Os(1)–Os(2) 59.09(4) [59.59(4)], Os(3)–Os(2)–Os(1) 60.35(4) [59.73(4)], Os(2)–Os(3)–Os(1) 60.55(4) [60.67(4)], C(1)–C(11)–C(12) 122(2) [118(3)], C(1)–C(11)–C(16) 120(2) [124(3)], C(12)–C(11)–C(16) 118(2) [118(3)], C(11)–C(12)–C(13) 122(3) [116(3)], C(12)–C(13)–C(14) 119(3) [126(3)], C(13)–C(14)–C(15) 113(3) [106(3)], C(14)–C(15)–C(16) 120(2) [127(3)] and C(11)–C(16)–C(15) 122(2) [120(3)]

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