Carbon–Carbon Bond Formation by Alkyne–μ,η^2-Acetylide and Alkyne–CO Coupling in the Reaction of $(OC)_5MC{\equiv}CPh$ (M = Mn, Re) with $HOs_3(CO)_{10}(\mu,\eta^2\text{-}C{\equiv}CPh)$. *X*-Ray Structure of $HOs_3Re(CO)_{14}(C_2Ph)_2$

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Addition of $(OC)_5MC{\equiv}CPh$ (M = Mn,Re) to $HOs_3(CO)_{10}(\mu,\eta^2\text{-}C{\equiv}CPh)$ leads to the formation of carbon–carbon bonds under mild conditions to yield metal cluster compounds $HOs_3M(CO)_{14}(C_2Ph)_2$; the cluster $HOs_3Re(CO)_{14}(C_2Ph)_2$ has been characterized by an *X*-ray structure analysis.

Carbon–carbon bond formation involving CO groups and small multidentate hydrocarbon ligands bound to metal cluster compounds is of considerable interest in the elucidation of the mechanisms of Fischer–Tropsch synthesis reactions.[1] Here we report an example of formation of two carbon–carbon bonds by coupling of neutral acetylene derivatives $(OC)_5MC{\equiv}CPh$ (M = Mn,Re)[2] with the μ,η^2-acetylide and CO ligands of the neutral triosmium cluster $HOs_3(CO)_{10}(\mu,\eta^2\text{-}C{\equiv}CPh)$,[3] (**1**).

$HOs_3(CO)_{10}(\mu,\eta^2\text{-}C{\equiv}CPh)$
(**1**)

$HOs_3M(CO)_{14}(C_2Ph)_2$
(**2**) **a**; M = Re
b; M = Mn

Reaction of $(OC)_5ReC{\equiv}CPh$ with (**1**) (2:1 molar ratio) in dichloromethane at 25 °C affords a yellow crystalline complex $HOs_3Re(CO)_{14}(C_2Ph)_2$ (**2a**) as a single cluster product. The complex was identified by an *X*-ray diffraction study.† In the reaction of $(OC)_5MnC{\equiv}CPh$ with (**1**) under the same conditions $HOs_3Mn(CO)_{14}(C_2Ph)_2$ (**2b**) is obtained. The spectral data‡ indicate that complexes (**2a**) and (**2b**) have the same structure.

Crystals of (**2a**) suitable for an *X*-ray study were obtained by slow crystallization from hexane solution at 0 °C. The molecular structure of (**2a**) is shown in Figure 1.

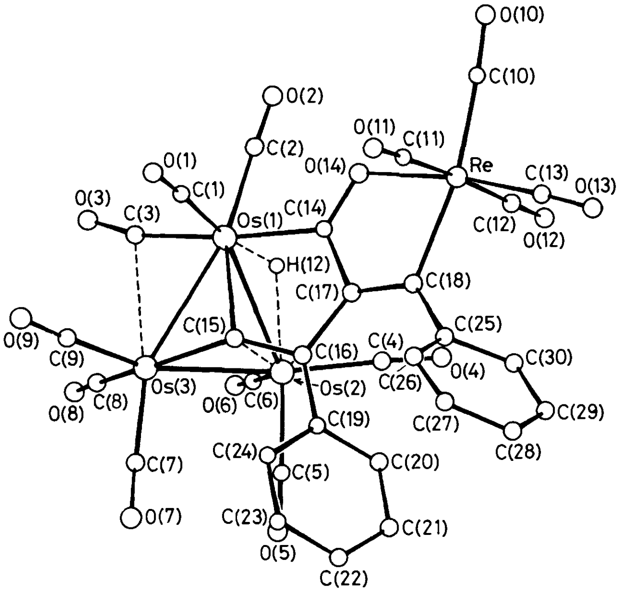

Figure 1. Molecular structure of (**2a**). Bond lengths: Os(1)–Os(2) 2.899, Os(1)–Os(3) 2.874, Os(2)–Os(3) 2.769, Os(1)–H(12) 1.8, Os(2)–H(12) 2.0, Os(1)–C(14) 2.11, Os(1)–C(15) 2.14, Os(2)–C(15) 2.21, Os(2)–C(16) 2.46, Os(3)–C(15) 1.97, Re–O(14) 2.164, Re–C(18) 2.18, C(14)–O(14) 1.25, C(14)–C(17) 1.45, C(15)–C(16) 1.40, C(16)–C(17) 1.51, C(17)–C(18) 1.37, Os–C(CO) 1.89—2.00, Re–C(CO) 1.92—2.00, e.s.d.s Os–Os 0.001, Os,Re–C,O 0.007—0.012, C–C 0.011—0.018, Os–H 0.1 Å.

Complex (**2a**) may be considered as a derivative of the ethylidene complex $HOs_3(CO)_9(\mu_3,\eta^2\text{-}C{=}CH_2)$ reported previously.[5] As in the latter complex, in (**2a**) one of the carbon atoms, *viz.* C(15), is σ-bonded to two osmium atoms Os(1) and Os(3), and Os(2) is co-ordinated *via* the C(15)=C(16) π-system. The 1,3-diene system C(15)=C(16)–C(17)=C(18) is a result of coupling between the PhC≡C-groups of $(OC)_5ReC{\equiv}CPh$ and (**1**), which is accompanied by migration of the rhenium carbonyl fragment to the C(18) atom bearing a phenyl group, and by substitution of a CO ligand at the rhenium atom by an oxygen atom of one of the osmium carbonyl groups. The latter is converted into a metal σ-acyl group owing to bond formation between C(14) and C(17). As a consequence of these transformations, two five-membered metallocycles fused along the C(14)–C(17) bond are formed.

The hydride ligand, directly located by an *X*-ray analysis, bridges the longest edge of the osmium triangle, Os(1)–Os(2) 2.899(1) Å. The μ_2-H ligand causes the adjacent equatorial carbonyl ligands to be pushed back relative to their position in dodecacarbonyltriosmium.[6] Thus, the Os(2)Os(1)C(2) and Os(1)Os(2)C(4) angles are increased to 120.6(3) and 108.3(3)° respectively, whereas for the other equatorial carbonyls in (**2a**) these angles are in the range 89.1—100.8°.

A formal electron count for the individual osmium atoms leads to 17 for Os(3), and 19 and 18 for Os(1) and Os(2), or

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† *Crystal data* for (**2a**) at −120 °C; $C_{30}H_{11}O_{14}Os_3Re$, M = 1352.2, monoclinic, a = 15.536(7), b = 11.743(6), c = 18.461(9) Å, β = 101.08(4)°, space group $P2_1/c$, Z = 4. Intensities of 4325 reflections with $F^2 \geqslant 6\sigma$ were measured with a Syntex $P2_1$ diffractometer at −120 °C (Mo-K_α radiation, θ—2θ scan, $2\theta \leqslant 52°$; an absorption correction based on the crystal shape was applied). The structure was solved by direct methods; non-hydrogen atoms were refined in the anisotropic approximation. All hydrogen atoms were located in the difference map and included in the subsequent refinement with isotropic thermal parameters. The final discrepancy factors are R = 0.031, R_w = 0.037. All calculations were carried out using the modified[4] EXTL programme package.

The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

‡ Compounds (**2a**) and (**2b**) have similar ^1H n.m.r. spectra ($CDCl_3$, 25 °C): (**2a**), δ −20.04 [s, 1H, $J(^{187}Os\text{–}^1H)$ 34.5, 30.3 Hz], 5.9—7.5 (m, 10H); (**2b**), δ −19.92 [s, 1H, $J(^{187}Os\text{–}^1H)$ 34.6, 30.2 Hz], 5.9—7.5 (m, 10H).

vice versa, depending on which of the osmium atoms the hydride ligand electron is assigned to. This imbalance of electron allocation in carbonyl clusters is usually redressed by the presence of semibridging carbonyl groups.[7] In (**2a**) there is such a carbonyl group, C(3)O(3), with an Os(1)C(3)O(3) bond angle of 166.3(9)° (for the other terminal carbonyl groups OsCO bond angles are in the range 174—178°), and an Os(3) · · · C(3) distance of 2.75(1) Å. To our knowledge complex (**2a**) represents the first example of an hydrido-carbonyl M_3 cluster with a semibridging carbonyl group.

The ^{13}C n.m.r. spectrum (−40 °C, $CDCl_3$) for (**2a**)§ is consistent with the *X*-ray structure of the complex. The peaks at δ 191.7, 191.5, 189.1, and 188.8 are assigned to the carbonyls of the $Re(CO)_4$ moiety; resonances at 180.7, 176.6, 172.6, 172.4, 170.9, 168.1, 167.7, 166.2, and 160.0 are due to nine terminal carbonyl groups co-ordinated by osmium atoms. The three resonances observed at lowest field, 252.9, 217.2, and 214.6, are assigned to the σ-acyl group, C(15), and C(16) carbon atoms. Signals for the hydrocarbon moiety of the cluster (**2a**) fall within the range δ 113—127.

The synthesis of complexes (**2a**) and (**2b**) is an interesting example of direct formation of C–C bonds on the face of a neutral cluster by coupling of an alkyne with bridging acetylide and CO ligands. Only a few examples of C–C bond formation *via* coupling of multisite-bound and bridging acetylides with neutral carbon nucleophiles, such as carbenes and isocyanides, have been reported.[8] Examples of the participation of co-ordinated CO groups in C–C bond formation reactions with neutral reagents are concerned with carbyne–carbonyl coupling.[9]

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§ The peaks were assigned on the basis of values of $^2J(^{13}C{-}^1H)$ and $^2J(^{13}C{-}^{13}C)$ in the ^{13}C spectra for $HOs_3Re(^{13}CO)_{10}(CO)_4(C_2Ph)_2$ (obtained from the osmium carbonyl *ca.* 40% ^{13}CO enriched). Complex (**2a**) is stereochemically nonrigid owing to localized carbonyl scrambling at Os(3): as the temperature is raised, peaks at δ 180.7, 176.6, and 170 broaden, and an averaged resonance is observed at 176.8 (toluene, 100 °C).