Cluster Formation Assisted by Alkyne Ligands: Synthesis and *X*-Ray Crystal Structure of $[Co_2W(\mu\text{-}C_2Et_2)(\mu\text{-}C_4Et_4)(CO)_8]$

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The tri(alkyne)monocarbonyltungsten complex $[W(CO)(C_2Et_2)_3]$ reacts with $[Co_2(CO)_8]$ to form $[Co_2W(\mu\text{-}C_2Et_2)(\mu\text{-}C_4Et_4)(CO)_8]$, the structure of which has been established by *X*-ray diffraction.

There is considerable interest in the synthesis of mixed-metal cluster compounds and in the reactivity of hydrocarbon moieties ligated to such systems.[1] The term 'bridge-assisted' has been coined for reactions in which phosphido ligands originally bonded to a single metal centre promote the formation of binuclear complexes by co-ordinating in a bridging mode to a second transition metal.[2] In a similar manner alkyne molecules ligated in a mononuclear system can be viewed as potentially bridging ligands and have been observed to participate in the formation of binuclear compounds, containing molybdenum–rhenium and molybdenum– or tungsten–cobalt bonds.[3,4] The majority of clusters containing alkyne ligands have been prepared by the thermal or photochemical reactions of mono- or poly-nuclear complexes with alkynes.[5] We report the first example of cluster synthesis *via* the reaction of a mononuclear alkyne complex with a source of metal ligand fragments.

The complex $[W(CO)(C_2Et_2)_3]$[6] reacts smoothly with $[Co_2(CO)_8]$ in light petroleum at room temperature to afford the orange trinuclear cluster $[Co_2W(\mu\text{-}C_2Et_2)(\mu\text{-}C_4Et_4)(CO)_8]$ (**1**) in high yield (*ca.* 68%).† The molecular structure of (**1**) has

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† Spectroscopic data for compound (**1**), ν_{CO} (max) at 2087s, 2036vs, 2029s, 1990m, 1970s, 1959s, and 1948m cm^{-1} (light petroleum); n.m.r.: ^1H (CD_2Cl_2), δ 3.15—2.86 (m, 8H, CH_2), 2.53 (q, 4H, CH_2, J_{HH} 7 Hz), 1.33 (t, 6H, CH_3, J_{HH} 7 Hz), 1.24 (t, 6H, CH_3, J_{HH} 8Hz), and 1.20 (t, 6H, CH_3, J_{HH} 7Hz); $^{13}C\{^1H\}$ $(CD_2Cl_2\text{–}CH_2Cl_2)$, δ 210.9 (s, WCO, J_{WC} 152 Hz), 205.6, 198.9, 193.2 (3 × s, CoCO), 173.9 [s, C(11), C(14)], 135.1 [s, C(12), C(13)], 92.8 [s, C(21), C(22)], 35.0, 26.7, 23.3 (3 × s, CH_2), and 21.0, 15.8, 14.6 (3 × s, CH_3).

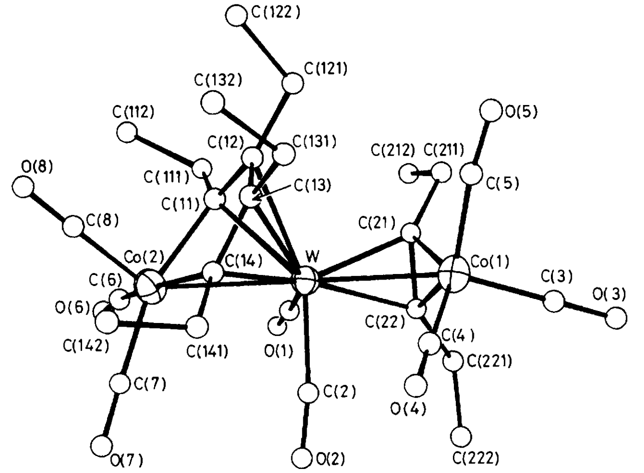

Figure 1. Molecular structure of $[Co_2W(\mu\text{-}C_2Et_2)(\mu\text{-}C_4Et_4)(CO)_8]$ (**1**). Dimensions: W–Co(1) 2.732(1), W–Co(2) 2.673(1), W–C(11) 2.25(1), W–C(12) 2.38(1), W–C(13) 2.40(1), W–C(14) 2.25(1), W–C(21) 2.15(1), W–C(22) 2.16(1), Co(1)–C(21) 2.04(1), Co(1)–C(22) 2.01(1), Co(2)–C(11) 1.99(1), Co(2)–C(14) 1.98(1) Å; Co(1)–W–Co(2) 153.6(1)°.

been established by a single crystal *X*-ray diffraction study and is shown in Figure 1.‡ The molecule has an open metal-chain structure as expected for a 50 electron cluster.[7] The chain is non-linear [Co(1)–W–Co(2) 153.6(1)°], the Co(1)–W bond being spanned by a hex-3-yne ligand in a perpendicular bridging mode, while the Co(2)–W bond is bridged by a butadiene ligand, formed by the coupling of two alkyne ligands, σ-bonded to the cobalt centre and π-bonded to the tungsten. Although the solid-state structure of (**1**) possesses no symmetry, the solution n.m.r. spectra† reveal that fluxional processes cause equivalence of both halves of the alkyne and butadiene ligands even at 193 K, the lowest temperature at which spectra were recorded.

Attempts to expel a carbonyl ligand from compound (**1**) either thermally or photochemically to produce a triangular 48 electron cluster have been unsuccessful, but (**1**) does display reactivity towards a variety of 2e donor ligands such as phosphines, phosphites, and alkynes which will be the subject of a full paper.

The synthesis of compound (**1**) demonstrates how alkyne-containing clusters can be built up from mononuclear alkyne complexes. Several other systems are being investigated and it is becoming apparent that when $[Co_2(CO)_8]$ is used in cluster building, complexes containing alkynes donating more than 2 electrons are the best precursors.[8] Several 2 electron alkyne systems, such as $[Co(PPh_3)(Ph_2C_2)(\eta\text{-}C_5H_5)]$, undergo complete alkyne transfer to afford complexes of the type $[Co_2(CO)_6(RC_2R')]$.[9]

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‡ *Crystal Data* for (**1**): $C_{26}H_{30}Co_2O_8W$, $M = 772.24$, monoclinic, space group $P2_1$ (No. 4, C_2^2), $a = 9.372(3)$, $b = 14.547(3)$, $c = 10.525(2)$ Å, $\beta = 89.95(2)°$, $U = 1434.9(6)$ Å^3, $Z = 2$, $D_c = 1.79$ g cm^{-3}, $F(000) = 756$, Mo-K_α *X*-radiation, $\bar{\lambda} = 0.71069$ Å, μ(Mo-K_α) = 52.7 cm^{-1}. $R = 0.031$ ($R_w = 0.036$) for 2981 absorption corrected reflections [293 K, $\theta/2\theta$ scans, $2 < \theta < 30°$, $I > 2.5(\sigma)I$]. Data were collected on an Enraf- Nonius CAD4F diffractometer and the structure was solved by direct and Fourier methods, with refinement by full matrix least squares. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.