Reactions of metalloalkynes.‡ The reaction of the ethyne-1,2-diyl complex, [{Ru(CO)$_2$(η-C$_5$H$_5$)}$_2$(μ-C≡C)], with [Mo$_2$(CO)$_4$(η-C$_5$H$_5$)$_2$]. An example of μ_3,η^1-C≡C coordination of a carbide ligand

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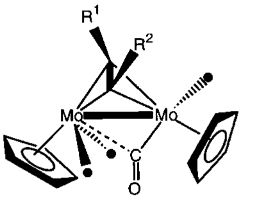
Reaction of [{Ru(CO)$_2$(η-C$_5$H$_5$)}$_2$(μ-C≡C)] with [Mo$_2$(CO)$_4$(η-C$_5$H$_5$)$_2$] gave [MoRu$_2$(μ_2-CO)$_3$[μ_3-C≡C{Ru-(CO)$_2$(η-C$_5$H$_5$)}](η-C$_5$H$_5$)$_3$] as the major product after chromatography and not the expected dimolybdenum 'alkynyl' adduct; this new complex contains a carbide (C$_2$) ligand bound, in triply bridging mode to the MoRu$_2$ triangle, through one carbon and the other in a monohapto fashion to the other ruthenium atom.

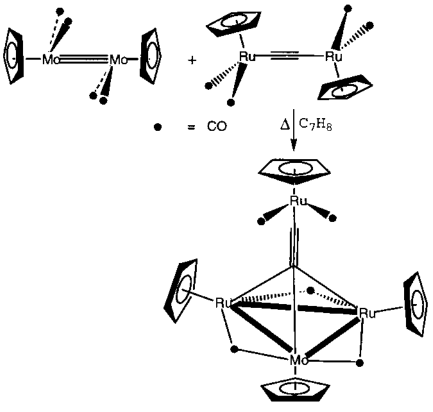
We are interested in the reactivity of metalloalkynes in so far as their reactivity is similar to that of simple organic alkynes.[1] The dimetalloalkynes, or ethyne-1,2-diyl complexes, are a special class of these complexes and their reactivity has been of particular interest to us.[2–14] Ethyne-1,2-diyl complexes contain the C$_2$ ligand which is often implicated in catalytic CO hydrogenation mechanisms. Multinuclear homo- and heterometallic complexes containing the C$_2$ molecule offer the opportunity to study and observe the reactivity of such species.[15]

Herein we report the unexpected course of the reaction between [Mo$_2$(CO)$_4$(η-C$_5$H$_5$)$_2$] **1** and the dimetalloalkyne, [{Ru(CO)$_2$(η-C$_5$H$_5$)$_2$}$_2$(μ-C≡C)] **2**. We have recently found[16] that metalloalkynes of ruthenium and iron, *viz.* [M(CO)$_2$(η-C$_5$H$_5$)(C≡CR)], react readily with complex **1**, giving, in the case of ruthenium, the expected 'alkyne' adduct **A**. The analogous iron compounds underwent Fe–C bond cleavage, by a yet to be determined mechanism, and resulted in the formation of complexes **B** in their reaction with **1**. It is of note that the analogous reaction with an iron congener of **2**, *viz.* [{Fe(CO)$_2$(η-C$_5$Me$_5$)$_2$}(μ-C≡C)], resulted in carbonyl transfer to **1** to give [Mo$_2$(CO)$_6$(η-C$_5$H$_5$)$_2$] with decomposition.[2b]



A: R^1 = Ru(CO)$_2$(C$_5$H$_5$), R^2 = Me or Ph
B: R^1 = H; R^2 = Me or Ph
G: R^1 = R^2 = Ru(CO)$_2$(C$_5$H$_5$)

The reaction (Scheme 1)§ in refluxing toluene gave a mixture of products and some unreacted starting material that were readily separated using column chromatography. The major red–black fraction provided a good yield of [MoRu$_2$(μ-CO)$_3$[μ_3-C≡C{Ru(CO)$_2$(η-C$_5$H$_5$)}](η-C$_5$H$_5$)$_3$] **3**, an electron deficient 45-electron cluster considering the μ_3,η^1-C≡C{Ru-(CO)$_2$(η-C$_5$H$_5$)} unit as only a two-electron donor. The compound remarkably contains a μ_3-CC fragment bound to the MoRu$_2$ triangle and is, to our knowledge, the only example of this type of coordination to any metal cluster other than those of Cu[17] or Li.[18] Moreover, the bonding mode of the C$_2$ ligand observed here is also unique in so far as it is surrounded by metals but not 'buried'. The range of bonding modes so far observed for the interaction of four metals with a carbide ligand (Fig. 1) implicates the π system of the triple bond more fully in bonding in multi-metallic systems.



Scheme 1

The ^{1}H NMR spectrum of **3** comprises two signals at δ 5.26 and 4.90 in a 1 : 3 ratio which are assigned to the Mo(η-C$_5$H$_5$) and Ru(η-C$_5$H$_5$) moieties, respectively. These signals remain unchanged in the temperature range 296–233 K. This implies that the Mo(η-C$_5$H$_5$) and Ru(η-C$_5$H$_5$) vertices are undergoing fluxional motion giving rise to an averaged signal for the three Ru(η-C$_5$H$_5$) vertices and a separate signal for the Mo(η-C$_5$H$_5$) vertex. This fluxionality is also reflected in the ^{13}C NMR spectrum of **3**. This contains two signals for cyclopentadienyl ligands and two signals are observed at δ 234.2 and 232.4 which are assigned to the terminal and bridging CO ligands. The signals observed at δ 308.4 and 87.2 are assigned to the μ_3-C and η^1-C of the carbide ligand, respectively.

These data and those reported in the footnote were insufficient to unequivocally assign the connectivity and as such a room-temperature single-crystal X-ray structure study¶ was undertaken. The structure determination is of limited utility given that the cell obtained in the tetragonal setting *P*4/*m* contains a pseudo-inversion centre, relating two independent molecules in the asymmetric unit, and with a crystallographic mirror plane coincident with the molecular symmetry plane in each of the independent molecules. In addition, the specimen obtained after many attempts was of marginal suitability for the experiment. However, the results are consistent with the

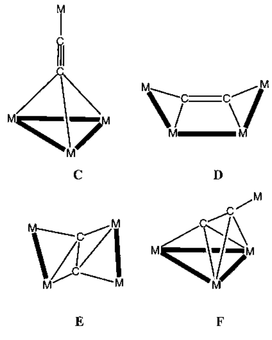


Fig. 1 Bonding modes for a carbide ligand bound to tetrametallic systems

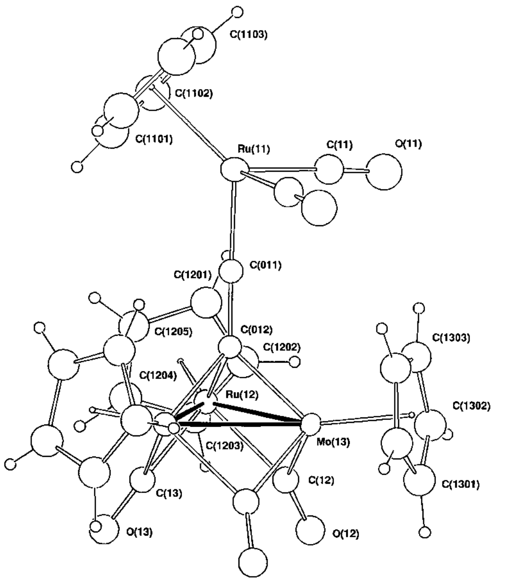


Fig. 2 Projection of one molecule of **3** approximately through the $MoRu_2$ plane. 20% thermal ellipsoids are shown for the metal atoms; other non-hydrogen atoms are shown as isotropic spheres; hydrogen atoms have arbitrary radii of 0.1 Å. Selected bond lengths (Å) and angles (°): Ru(n2)–Mo(n3) 2.701(2), 2.700(2); Ru(n2)–Ru(n2′) 2.704(2), 2.710(2); Ru(n1)–C(0n2) 2.01(1), 1.77(2); C(0n2)–C(0n1) 1.39(2), 1.46(3); Ru(n1)–C(0n1)–C(0n2) 179(1), 175(2); Ru(n2)–Mo(n3)–Ru(n2′) 60.09(6), 60.24(6); Mo(n3)–Ru(n2)–Ru(n2′) 59.96(4), 59.88(4) for the two molecules (molecule 1, n = 1; molecule 2, n = 2).

stoichiometry and connectivity as expressed in **3** and Fig. 2, albeit with interatomic parameters of a higher than desired uncertainty. The molecules are best considered as being composed of trinuclear heterometallic $MoRu_2$ triangles with each metal atom coordinated by a pentahapto cyclopentadienyl ligand which is essentially perpendicular to the plane of the triangle. The structure determination cannot rigorously exclude the possibility of scrambling of the molybdenum atom among other metal sites of the triangle in the solid. The metal cores are coordinated from 'above' by the μ_3,η^1-C≡C$\{Ru(CO)_2(\eta\text{-}C_5H_5)\}$ unit which has its CC axis at right angles to the metal triangles with the μ_3-C symmetrically bridging to each of the metal core atoms. Three bridging carbonyls complete the coordination of the metal core and these are directed 'below' the plane of the core.

The formal electron count gives this substituted triangular cluster 45 cluster valence electrons (CVE) with each Ru atom achieving an 18-electron count and the Mo formally electron deficient with a 16-electron count. In the various bonding modes and their valence bond representations hitherto observed for the carbide ligand bound to four metals (Fig. 1)[19] the CC unit has a formal bond order of three in mode **C** while in mode **D** the bond order is two and in **E** and **F** it is one. Theoretical calculations[19] have been performed that rationalise the bonding observed for **D**–**F** and it is noteworthy that complex **3** (mode **C**) does not adopt mode **F** where the electron deficiency experienced by the Mo atom could be alleviated.

The mechanism operating in this reaction is unclear. However, it is likely that the CC bond of **2** interacts initially with the unsaturated metal–metal bond in **1** to give a structure similar to **G** which presumably undergoes fragmentation, evidenced by the isolation of $[Ru(CO)_2(\eta\text{-}C_5H_5)]_2$ from the reaction. The reason for this fragmentation is presumably steric.[16] It is possible that **G** undergoes homolytic cleavage of a $Ru(CO)_2(\eta\text{-}C_5H_5)$ group and that this is the source of the dimer isolated from the mixture; this, however, seems unlikely given the ultimate stoichiometry of the product.

Work is in progress to identify the minor products from the reaction in the hope that they will shed further light on the mechanism operating in this reaction.

We thank the Australian Research Council for supporting this work. C. S. G. is the holder of an Australian Postgraduate Award.

Notes and References

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‡ Part 1, Parts 2 and 3 given in ref. 16.

§ *Synthesis* of **3**: an equimolar amount of $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$ **1** (29 mg, 0.085 mmol) and $[\{Ru(CO)_2(\eta\text{-}C_5H_5)\}_2(\mu\text{-}C{\equiv}C)]$ **2** (40 mg, 0.085 mmol) in toluene (25 mL) was heated at reflux for 15 h. After cooling the solvent was removed *in vacuo*, and the residue was dissolved in the minimum amount of CH_2Cl_2 and chromatographed on silica [CH_2Cl_2–hexanes (3 : 2)] to resolve four bands. The first band gave unreacted $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$, the second yellow band yielded $[Ru_2(CO)_4(\eta\text{-}C_5H_5)_2]$ (2 mg, 6%), the third yellow band remains unidentified and the fourth red–black band gave **3** (45 mg, 84%), mp 145 °C (decomp.). Found: C, 39.34; H, 2.59. FABMS: m/z 824 (M^+). $C_{27}H_{20}MoO_5Ru_3$ requires C, 39.34; H, 2.59. m/z 824. IR (toluene) ν(CO) 1959m, 1893m, 1823s, 1781m.

¶ *Crystal/refinement data* for **3**: $C_{27}H_{20}MoO_5Ru_3\cdot0.25CH_2Cl_2$, M = 844.8, tetragonal space group $P4/m$ (C^1_{4h}, no. 83), a = 20.996(15), c = 12.632(7) Å, U = 5568(7) Å^3, D_c (Z = 8) 2.02 g cm^{-3}, 6412 independent, absorption corrected and 3958 observed [$I > 3\sigma(I)$], diffractometer data refined by full matrix least squares to R = 0.072, R_w = 0.082 (statistical weights). 2θ–θ scan mode, $2\theta_{max}$ 55°; monochromatic Mo-Kα radiation, λ = 0.7107$_3$ Å; T = 295 K; anisotropic thermal parameter forms were refined for the metal atoms only, $(x, y, z, U_{iso})_H$ being constrained at estimated values.[20] The geometry of the disordered CH_2Cl_2 molecule of solvation was restrained to ideal values. CCDC 182/939.

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Received in Columbia, MO, USA, 2nd March 1998; 8/01744A