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Reaction of ruthenium and iron alkynyl complexes with $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$ ‡

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The reaction of the molybdenum dimer $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$ with $[M(CCR)(CO)_2(\eta\text{-}C_5H_5)]$ (M = Ru or Fe, R = Me or Ph) has given different products dependent on the alkynylmetal. The ruthenium-containing starting materials gave the expected dimolybdenum alkynyl adducts as the only isolable materials in moderate yield. In contrast the iron alkynyls underwent Fe–C bond cleavage to give the simple known alkyne adducts $[Mo_2(\mu\text{-}\eta^2\text{-}HC_2R)(CO)_4(\eta\text{-}C_5H_5)_2]$ by a yet to be determined mechanism. The fluxional nature of the complex $[Mo_2\{Ru(\mu\text{-}CCMe)(CO)_2(\eta\text{-}C_5H_5)\}(CO)_4(\eta\text{-}C_5H_5)_2]$ was observed by solution NMR studies; the mechanism for equilibration of the molybdenum carbonyl groups at room temperature must involve disruption of the central Mo_2C_2 core.

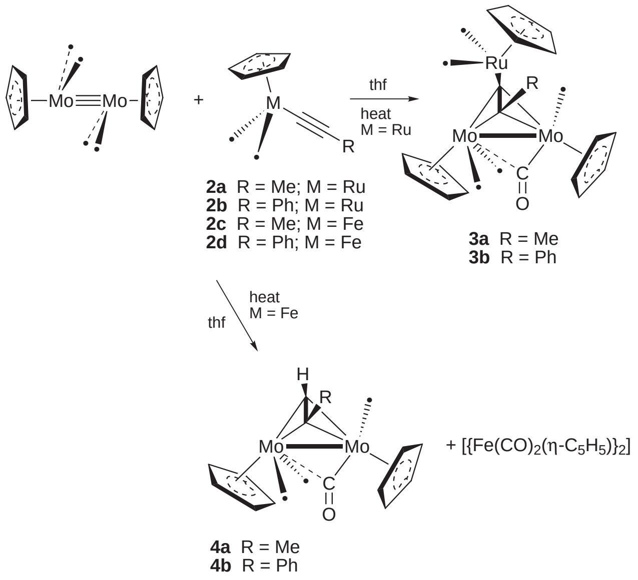
The interaction of alkynes with metal substrates has provided a rich source of novel chemistry over the last thirty years. The ability of alkynes to act as two- to four-electron donors has ensured the isolation of expected and, more often than not, unexpected, products as a result of oligomerisation or polymerisation.

We are interested in examining the reactivity of metalloalkynes, probably better known as acetylide or alkynyl complexes. The preparation and reactivity of these complexes has not been adequately reviewed since Nast[1] in 1982 but their bonding has attracted much interest.[2] The putative application in materials synthesis[3–11] has been a major driving force for the current interest in metalloalkynes. Our interest, in particular, is the reactivity of the dimetalloalkynes or ethyne-1,2-diyl complexes.[12–24] The binuclear complex $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$ has a rich alkyne chemistry[25,26] and we have recently observed the unexpected course of the reaction of $[\{Ru(CO)_2(\eta\text{-}C_5H_5)\}_2(\mu\text{-}C{\equiv}C)]$ with $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$[27] and decided to gauge the effect of removing one metal centre from the dimetalloalkyne on the course of the reaction.

In this paper we report the reaction of the molybdenum dimer $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$ **1** with $[M(CCR)(CO)_2(\eta\text{-}C_5H_5)]$ **2** (M = Ru or Fe, R = Me or Ph) which has given different products dependent on the alkynylmetal. The ruthenium-containing starting materials gave the expected dimolybdenum alkynyl adducts as the only isolable materials. In contrast the iron alkynyls underwent Fe–C bond cleavage to give the simple, known alkyne adducts, $[Mo_2(\mu\text{-}HC_2R)(CO)_4(\eta\text{-}C_5H_5)_2]$. It is noteworthy that Akita *et al.*[28] have reported the reaction of analogous iron ethynyl complexes, $[Fe(CCH)(CO)_2(\eta\text{-}C_5R'_4R)]$, with **1** also giving the expected ethynyl adducts. These were prepared using less vigorous conditions than those required to initiate a reaction between **1** and **2** but were found to be unstable with respect to decomposition above 70 °C.

Results and Discussion

The reactions between the molybdenum dimer **1** and the alkynyl complexes **2** were conducted at reflux in thf for varying times (Scheme 1). The products, **3**, were isolated from the reaction mixture by column chromatography. The ruthenium-containing starting materials **2a** and **2b** gave the expected dimolybdenum alkynyl adducts, **3**, as the only isolable materials in moderate yield. In contrast the iron alkynyls, **2c** and **2d**, underwent Fe–C bond cleavage to give the simple alkyne adducts **4**. These compounds are known and were characterised by comparison of their spectroscopic properties with those reported in the literature. In addition, the phenylethynyl adduct **4b** was structurally characterised (see below).



Scheme 1 —• = CO

The new compounds **3** were characterised by microanalysis, spectroscopy and single-crystal structure determination. The solution infrared spectra obtained for both compounds contained terminal ν(CO) bands and lower-frequency bands assigned to the semibridging carbonyl groups. The proton NMR spectra contained resonances at δ 2.66 and *ca.* 7.3 that are assigned to the Me group in **3a** and the phenyl substituent in **3b**, respectively. The spectra contained resonances at *ca.* δ 4.7 and 5.0 which are assigned to $Ru(\eta\text{-}C_5H_5)$ and $Mo(\eta\text{-}C_5H_5)$ units, respectively. This assignment is based partly on the values observed for other moieties of this type and partly on the variable-temperature NMR study reported below. The room-temperature ^{13}C NMR spectra are at the fast-exchange limit with the spectrum of **3a** containing single resonances for the Mo–*C*O and Ru–*C*O at δ 235.1 and 200.1, respectively. The $Mo(\eta\text{-}C_5H_5)$ and $Ru(\eta\text{-}C_5H_5)$ groups give singlets at δ 92.7 and

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‡ Reactions of metalloalkynes. Part 2; ref. 27 regarded as Part 1.

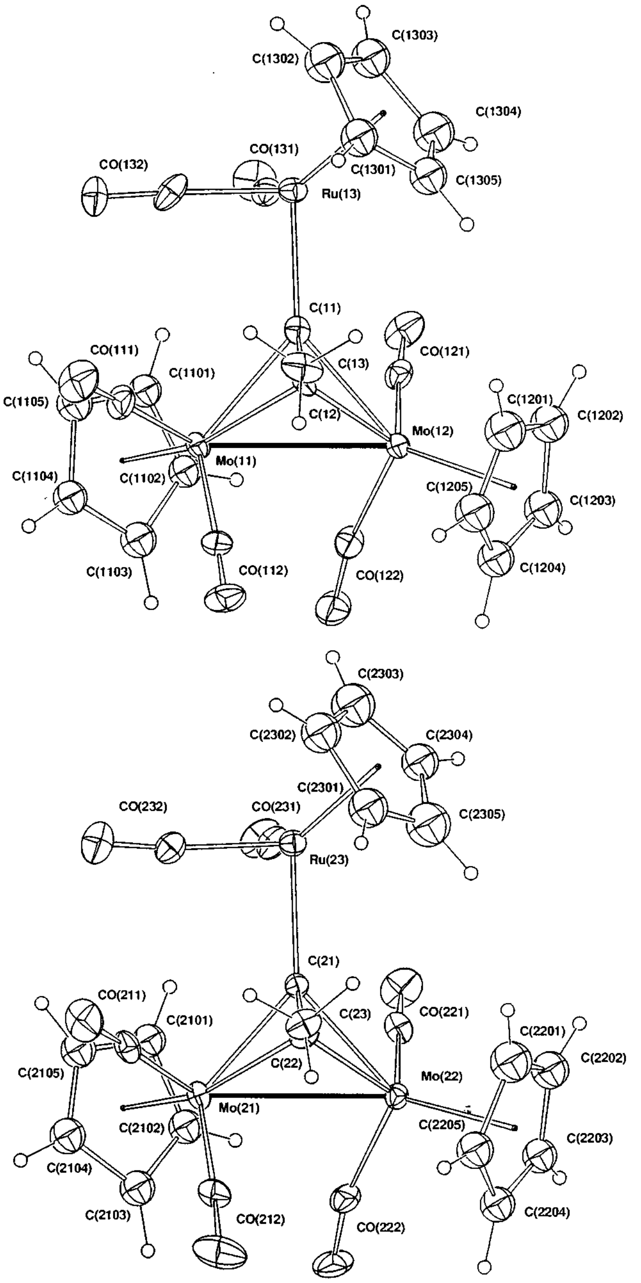


Fig. 1 Molecular structure of compound **3a** (molecule 1 above, 2 below): 20% probability ellipsoids are shown for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å

89.3 which at the slow exchange limit (203 K) show the asymmetry found in the solid-state structures with two resonances now found for the two Mo(η-C_5H_5) groups at δ 93.6 and 92.7 while the Ru(η-C_5H_5) signal remains unchanged. The resonance at δ 109.9 is assigned to the Ru–C_α carbon with C_β also observed as a singlet at δ 93.2. FAB Mass spectra showed molecular ions for complexes **3** that fragmented by sequential loss of CO groups.

Molecular structures of complexes 3 and 4b

(*a*) In the solid state. The results of the room-temperature structure determinations are presented in Figs. 1–3, with relevant interatomic parameters in Tables 1 and 2.

The structure determination of compound **3a** is of limited utility given that the cell obtained in the orthorhombic setting $Pca2_1$ contains a pseudo-inversion centre, relating two complete independent similar molecules, with consequent correlation problems in refinement. Thus, the asymmetric unit comprises two complete molecules which show slight variations in structure of dubious significance. The most noticeable of these differences is seen in the Cp–Mo–Mo–Cp torsion angles (Table 2). The structure of the simple phenylethyne adduct has not been previously reported and as such we have included details of its determination also.

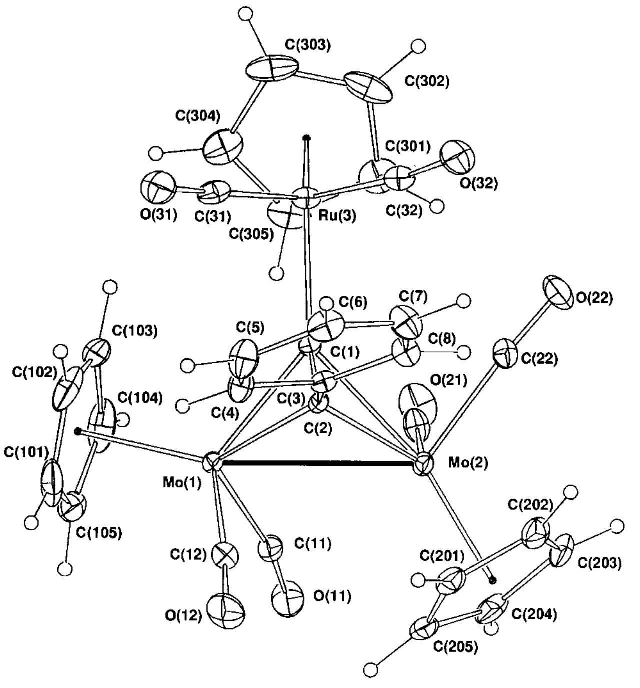


Fig. 2 Molecular structure of compound **3b**; details as in Fig. 1

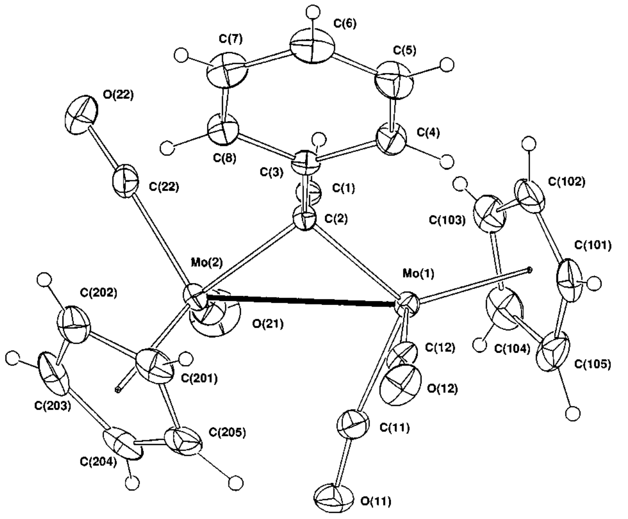


Fig. 3 Molecular structure of compound **4b**; details as in Fig. 1

All four molecules **3** and **4b** are comprised of a central dimetallotetrahedrane core involving the alkynyl carbons and the two Mo atoms. The C–C bonds are essentially perpendicular to the Mo–Mo vectors. The geometry of these tetrahedral cores is similar to that found for the closely related compounds $[\{Mo(CO)_2(\eta\text{-}C_5H_5)\}_2(\mu_3\text{-}\eta^1:\eta^2:\eta^2\text{-}CCH)Fe(CO)_2(\eta\text{-}C_5H_4R)]$ **5** reported by Akita *et al.*[28] The determination of complex **3b** is uncomplicated and precise compared with **3a** and shows a higher degree of asymmetry in the core when compared to the simple alkyne adducts **4b** and **4c**–**4e**.[29–31] Thus there is a *ca.* 0.16 Å difference in the attachment of C(1) to the molybdenum atoms in the core, presumably a result of the steric encumbrance of the bulky $Ru(CO)_2(\eta\text{-}C_5H_5)$ group attached to C(1). A similar observation[28] was made for the structures of complexes **5**. The CC bond of the alkynyl ligand in **2** has lengthened from the expected[2] 1.192(12) Å by *ca.* 0.16 Å in **3b** and by a similar amount in the structure of **4b**. The geometry of the

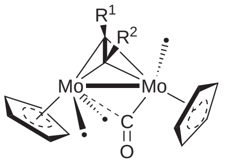
Table 1 Selected bond lengths (Å) and angles (°) for complexes **3** and **4**

	3a (molecule 1)	**3a** (molecule 2)	**3b**	**4b**
Mo(1)–Mo(2)	2.965(2)	2.965(2)	2.978(1)	2.972(1)
Mo(1), Mo(2)–C(1)	2.28(1), 2.30(1)	2.22(1), 2.26(1)	2.188(6), 2.351(6)	2.111(4), 2.178(4)
Mo(1), Mo(2)–C(2)	2.24(1), 2.14(1)	2.25(2), 2.14(1)	2.210(6), 2.208(6)	2.221(3), 2.176(3)
Ru(3)–C(1)	2.08(1)	2.15(1)	2.112(6)	—
C(1)–C(2)	1.35(2)	1.31(2)	1.345(9)	1.354(5)
C(2)–C(3)	1.48(2)	1.52(2)	1.468(9)	1.476(5)
Mo(1)–C(11), C(12)	1.93(2), 1.92(2)	1.97(2), 1.97(2)	1.961(7), 1.951(8)	1.951(5), 1.963(4)
Mo(2)–C(21), C(22)	1.93(2), 1.91(2)	1.93(1), 1.96(2)	1.961(8), 1.955(7)	1.994(4), 1.967(4)
Ru(3)–C(31), C(32)	1.87(2), 1.84(2)	1.88(2), 1.86(2)	1.878(7), 1.865(8)	—
Mo(1)–Mo(2)–C(1)	49.2(3)	48.6(4)	46.7(2)	45.23(9)
Mo(1)–Mo(2)–C(2)	48.9(4)	49.2(5)	47.6(2)	48.12(9)
Mo(2)–Mo(1)–C(1)	50.0(3)	49.3(3)	51.4(2)	47.1(1)
Mo(2)–Mo(1)–C(2)	45.9(3)	46.0(3)	47.6(1)	46.83(9)
Mo(1)–C(1)–Mo(2)	80.7(4)	82.7(4)	81.9(2)	87.7(1)
Mo(1)–C(2)–Mo(2)	85.2(5)	84.8(6)	84.8(2)	85(1)
C(1)–Mo(1)–C(2)	34.7(5)	34.1(5)	35.6(2)	36.3(1)
C(1)–Mo(2)–C(2)	35.1(5)	34.5(5)	34.1(2)	36.3(1)
Ru(3)–C(1)–C(2)	133(1)	131(1)	136.0(5)	—
Mo(1)–C(11)–O(11)	175(2)	178(2)	166.9(7)	170.5(4)
Mo(1)–C(12)–O(12)	174(2)	177(2)	175.4(7)	178.4(4)
Mo(2)–C(21)–O(21)	176(2)	178(1)	175.7(7)	179.1(4)
Mo(2)–C(22)–O(22)	169(2)	166(2)	174.4(6)	176.5(4)
C(12)–Mo(1)–C(11)	83.0(9)	81.6(7)	91.2(3)	87.7(2)
C(22)–Mo(2)–C(21)	88.5(7)	89.9(7)	80.2(3)	83.3(2)
Mo(1)–Mo(2)–C(21)	90.3(5)	90.4(5)	87.1(2)	83.0(1)
Mo(1)–Mo(2)–C(22)	67.8(5)	67.6(5)	126.1(2)	121.8(1)
Mo(2)–Mo(1)–C(11)	126.4(6)	123.4(5)	65.1(2)	69.5(1)
Mo(2)–Mo(1)–C(12)	81.2(6)	82.5(5)	84.7(2)	87.3(1)

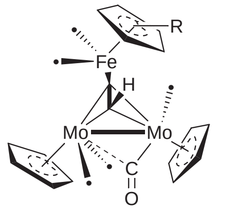
Table 2 Selected interatomic parameters (distances in Å, angles in °) for complexes **3** and **4***

	3a (molecule 1)	**3a** (molecule 2)	**3b**	**4b**
Cp$_1$–Mo(1)–C(11)	$108._6$	$110._5$	$110._8$	$113._5$
–C(12)	$121._7$	$123._1$	$115._0$	$123._0$
–Mo(2)	$123._3$	$123._5$	$160._3$	$149._1$
–C(1)	$121._4$	$121._6$	$117._6$	$110._1$
–C(2)	$156._0$	$155._6$	$135._7$	$131._1$
Cp$_2$–Mo(2)–C(21)	$123._1$	$119._2$	$122._5$	$121._2$
–C(22)	$109._8$	$111._6$	$111._4$	$112._7$
–Mo(1)	$146._6$	$150._3$	$119._4$	$122._7$
–C(1)	$136._4$	$134._8$	$151._8$	$154._2$
–C(2)	$113._3$	$113._4$	$117._7$	$118._0$
Cp$_3$–Ru(3)–C(31)	$123._9$	$122._8$	$129._2$	—
–C(32)	$128._1$	$127._1$	$123._6$	—
–C(1)	$120._8$	$121._6$	$124._4$	—
Dihedral angles				
C(1)–C(2)/Mo(1)–Mo(2)	$94._2$	$95._1$	$84._6$	$93._4$
Torsion angles				
Cp$_1$–Mo(1)–Mo(2)–Cp$_2$	$-139._4$	$-145._5$	$-150._0$	$159._2$
Q–R–Mo(1)–Cp$_1$	$127._8$	$127._8$	$84._8$	$-76._2$
Q–R–Mo(2)–Cp$_2$	$92._9$	$86._8$	$126._3$	$-124._6$
C(2)–C(1)–Ru(3)–Cp$_3$	$52._6$	$48._5$	$172._8$	—
Distance from the Mo$_2$Q plane				
Cp$_1$	-1.3_4	-1.3_5	-0.6_8	-1.0_1
Cp$_2$	1.1_3	1.0_0	1.4_2	1.3_9

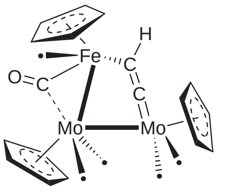
* Q defines the midpoint of C(1)–C(2) and R the midpoint of Mo–Mo bonds. Cp$_n$ is the centroid of ring *n*.



4c R^1 = R^2 = H
4d R^1 = Ph, R^2 = cyclopentenyl
4e R^1 = Ph, R^2 = nornbornyl



5a R = H
5b R = Me



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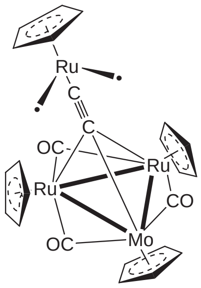

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Ru(CO)$_2$(η-C$_5$H$_5$) moiety in all the complexes is similar to that reported for [{Ru(CO)$_2$(η-C$_5$H$_5$)}$_2$(μ-C≡C)].[17] The orientation of the Ru(CO)$_2$(η-C$_5$H$_5$) group is twisted in the two molecules of **3a** with respect to **3b** as seen in the different torsion angles C(2)–C(1)–Ru(3)–Cp(3). Thus we appear to have different rotamers in the solid-state structures of **3a** and **3b** with respect to rotation about the C(1)–Ru(3) bond given that the Cp$_3$–Ru(3)–C(1) angle varies little amongst the complexes **3**.

The NMR fluxionality of alkyne adducts of the type reported here has long been known[31] and a recent crystallographic and theoretical study[32] has elegantly implicated Mo(CO)$_2$(η-C$_5$H$_5$) vertex rotation in the equilibration. In the present work the geometry of the Mo(CO)$_2$(η-C$_5$H$_5$) vertices is similar to that found in the preceding survey of 22 related vertices[32] where the Cp$_{\text{centroid}}$–Mo–CO angles were found to lie in a narrow range of 114.3 ± 3.7°. These workers applied a Bürgi-Dunitz analysis of the trajectory of the ring centroid associated with the molybdenum cyclopentadienyl fragment to a number of crystallographically characterised compounds and concluded that racemisation of these inherently chiral molecules proceeds *via* vertex rotation giving initially a molecule

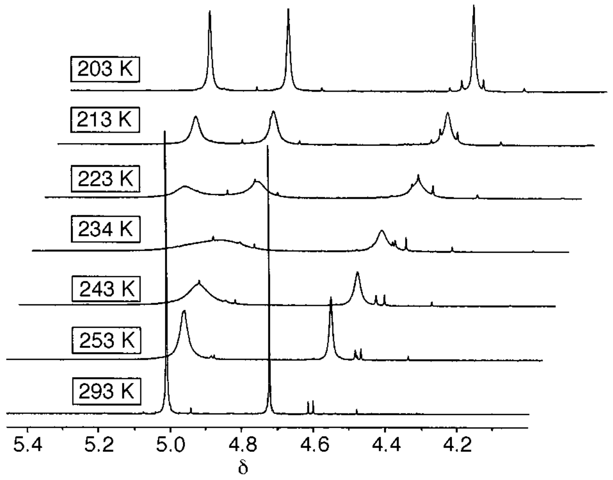
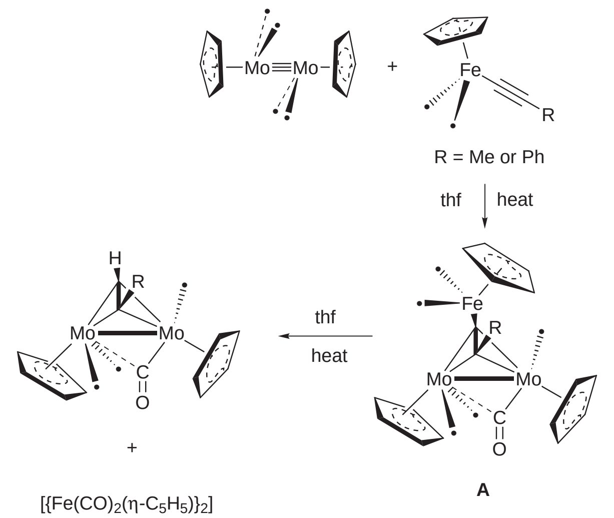


Fig. 4 Variable-temperature ^{1}H NMR spectra of complex **3a**



Scheme 2 ▬• = CO

with C_s symmetry, with the Mo(η-C_5H_5) groups in a *syn* arrangement, and that the lowest-energy rotamer has C_2 symmetry. It is of note that the complex [Mo{μ-$C_2(SiMe_3)$}$(CO)_2$(η-$C_5H_5)_2$] with its sterically demanding alkyne, crystallises with C_2 symmetry.[33] In the present work the solid-state structures of the molecules **3** provide evidence for the existence of rotamers. The Mo_2C_2 core varies little between the three molecules and the torsion angle Cp_1–Mo(1)–Mo(2)–Cp_2 is also similar between the structures. The diagrams projected onto the Mo_2Ru plane (Figs. 1 and 2) illustrate that the $Mo(CO)_2$(η-C_5H_5) vertices must rotate to accommodate the larger phenyl substituent in **3b**. In consequence the $Ru(CO)_2$(η-C_5H_5) unit also rotates to avoid steric congestion from the interaction with Mo–C≡O and Mo(η-C_5H_5) groups on the vertices. The other interesting feature evident in these structures is the switching of the semibridging carbonyl from bridging to Mo(*n*1) (molecule 1, *n* = 1; molecule 2, *n* = 2) in **3a** to bridging to Mo(2) in **3b**. If the steric demand of the alkyne is further increased to say [{$Ru(CO)_2$(η-C_5H_5)}$_2$(μ-C≡C)] then the simple alkyne adduct appears to be unstable and Ru–C bond cleavage occurs giving the new tetranuclear cluster **7**.[27]

(*b*) In solution. Complex **3a** exhibits fluxional behaviour in solution, previously observed for simple alkyne adducts[31] and the complexes **5**.[28] The results of the ^{1}H NMR variable-temperature experiment are presented in Fig. 4. There are several features to note. First, the two Mo(η-C_5H_5) groups are equivalent at room temperature but on cooling the signal corresponding to them broadens and splits into two signals below *ca.* 234 K. Secondly, the Ru(η-C_5H_5) signal broadens on cooling, becoming sharper at the lowest attained temperature where all the lines are slightly broadened as the complex precipitates from solution. In addition, the signal observed for the CC*Me* (not shown) group is barely affected through the coalescence of the two Mo(η-C_5H_5) signals in the range 234 to 229 K. Thirdly, in the low-temperature ^{13}C NMR spectrum, at 203 K, two Mo(CO) signals are observed which become equivalent in the room-temperature spectrum.

The mechanisms of exchange for fluxional processes in these types of molecules have been considered by several authors.[30–32] A number of processes are thought to occur: (1) a relatively low-energy process interchanges semibridging and terminal CO groups on the molybdenum vertices and (2) a higher-energy process equilibrates the C_5H_5 groups on the Mo atoms, which is thought to occur with some degree of vertex rotation.[32] In the present work the alkyne is unsymmetrical and as such we have not reached the slow exchange limit at the lowest temperature measured, in spite of the steric demand of the alkyne. The pairwise exchange of CO groups[31] must be occurring rapidly even at this temperature. The equilibration of the Mo(η-C_5H_5) groups occurs through vertex rotation as mentioned previously but in the present complex **3a** this is accompanied by rotation of the $Ru(CO)_2$(η-C_5H_5) unit to accommodate the steric requirements of the swivelling vertices. Cotton and co-workers[31] found that the variable-temperature ^{13}C NMR spectra of **4b**, containing an unsymmetrical alkyne, comprise two signals for the Mo(CO) groups at 353 K and reasonably suggested that the Mo_2C_2 core must remain rigid, at least up to that temperature. In the present case we find only one signal for the Mo(CO) groups above *ca.* 230 K and as such we must make the assumption that there is some degree of rotation of the Ru(CCMe)$(CO)_2$(η-C_5H_5) fragment with respect to the Mo–Mo bond that facilitates the scrambling of Mo(CO) groups. Another possible explanation would require the unlikely exchange of carbonyl groups on individual molybdenum atoms. Similar observations[28] with respect to Mo(CO) scrambling were made in the variable-temperature ^{13}C NMR spectra of complexes **5** where the fluxional processes observed were ascribed to binuclear alkynyl–vinylidene tautomerism. These authors were unable unequivocally to account for the mechanism of carbonyl scrambling and proposed several possible scenarios involving hydrogen shifts or rotations of putative vinylidene intermediates; clearly such intermediates are not possible for complex **3a** and the rigidity of the Mo_2C_2 core is compromised.

Formation of complexes 4

Perhaps the most interesting observation reported here is the formation of the known complexes **4**, Scheme 2, through formal Fe–C(sp) bond cleavage. We were unable to prepare any dimolybdenum adducts of iron alkynyl complexes analogous to compounds **3** or **5a**. The latter complex was prepared using more mild conditions than those reported here but was found to be unstable above 70 °C, no mention being made of the thermal decomposition products. The photoinduced decomposition of **5a** caused decarbonylation and the formation of a μ-vinylidenyl complex, **6**.

We have discounted the presence of adventitious moisture in the formation of complexes **4** and have accounted for the mass balance in the reaction. The exact mechanism for the reaction is still unclear but we surmise that the initial intermediate is a dimolybdenum adduct, **A**, that undergoes Fe–C(sp) bond cleavage with or without Mo_2C_2 core rearrangement. Presumably a radical cleavage mechanism followed by H atom abstraction from the solvent can also not be discounted. It is of note that the iron-containing complexes **5** are stable thermally to 70 °C[28] but the more sterically encumbered starting materials **2c** and **2d** do not react with $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$ at room temperature and require greater thermal activation ultimately yielding complexes **4**. The putative intermediate **A** or subsequent intermediates undergo facile bond cleavage as a result of the more demanding bulk of the Me group in **A**. If the steric demand of the alkyne is further increased to $[\{Ru(CO)_2(\eta\text{-}C_5H_5)\}_2(\mu\text{-}C{\equiv}C)]$ then even the Ru–C(sp) bond becomes labile and a major fragmentation of the initially formed simple dimolybdenum adduct occurs giving **7**. The analogous iron compound $[\{Fe(CO)_2(\eta\text{-}C_5Me_5)\}_2(\mu\text{-}C{\equiv}C)]$ does not react with $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$[28] to form an adduct but prolonged reaction results in carbonyl transfer to give $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$.

Conclusion

The reaction of metalloalkynes with $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$ was found to mimic the reaction of simple organic alkynes in the main. Thus the ruthenium alkynyl adducts readily reacted to give the dimolybdenum adducts **3** with a distorted tetrahedral Mo_2C_2 core and a semibridging carbonyl group. These compounds exist as rotamers in the solid state with respect to the Ru–C(sp) bond. However, it is clear that if the steric requirements of the 'alkyne' are large then the simple adduct is unstable, if formed at all, and will fragment if a suitable pathway is available.

The fluxional nature of this class of complex was observed by variable-temperature solution NMR studies and rotation about the Ru–C(sp) bond, suggested by the solid-state structures, was established. The molybdenum carbonyl groups are all observed equivalently at room temperature which is surprising given the unsymmetrical nature of the adduct. The mechanism for the equilibration must involve disruption of the Mo_2C_2 core with rotation about an axis that passes through the midpoints of both the C–C and Mo–Mo bonds.

Experimental

General conditions

Oxygen- and moisture-sensitive compounds were manipulated under an atmosphere of high-purity argon using standard Schlenk techniques or in a dry-box (Miller Howe).

Infrared spectra were recorded using a Bio-Rad FTS 45 or 40 FTIR spectrometer, ^1H and ^{13}C NMR spectra using Varian Gemini 200 or Bruker ARX 500 spectrometers and ^{31}P NMR spectra using a Bruker ARX 500 spectrometer. The ^1H and ^{13}C NMR spectra were referenced with respect to incompletely deuteriated solvent signals, ^{31}P NMR spectra to external H_3PO_4 (δ 0.0) and proton decoupled. Mass spectra were obtained on a VG AutoSpec spectrometer employing a fast atom bombardment (FAB) ionisation source unless otherwise specified.

Elemental analyses were performed by Chemical and Micro Analytical Services Pty. Ltd., Melbourne, Australia.

Tetrahydrofuran was dried over sodium metal and distilled from potassium–benzophenone under an atmosphere of argon. *n*-Hexane and toluene were dried over sodium metal and distilled from sodium–benzophenone under an atmosphere of argon. Distilled solvents were stored over sodium or potassium mirrors until use.

Syntheses

$[Mo_2Ru(\mu\text{-}CCMe)(CO)_6(\eta\text{-}C_5H_5)_3]$ 3a. A solution of $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$ (82 mg, 0.191 mmol) and $[Ru(C{\equiv}CMe)(CO)_2(\eta\text{-}C_5H_5)]$ (50 mg, 0.191 mmol) in tetrahydrofuran (30 cm^3) was stirred at reflux (12 h). The solvent was removed *in vacuo* and the residue eluted through a silica column (2 × 10 cm, 60% CH_2Cl_2–40% *n*-hexane eluent) to produce a single black band. Recrystallisation (toluene–*n*-hexane, −28 °C) yielded black crystals of compound **3a** (74 mg, 56%), m.p. 182–184 °C (Found: C, 40.5; H, 2.68. Calc. for $C_{24}H_{18}Mo_2O_6Ru$: C, 41.45; H, 2.61%). IR (thf): $\tilde{\nu}$(CO) 2022m, 1968s, 1951m, 1908 (sh), 1891s and 1822m. ^1H NMR ($C_6D_5CD_3$): δ 5.01 (s, 10 H, $\eta\text{-}C_5H_5$), 4.73 (s, 5 H, $\eta\text{-}C_5H_5$) and 2.66 (s, 3 H, CH_3). ^{13}C NMR ($C_6D_5CD_3$): δ 235.1 (s, CO), 200.1 (s, CO), 109.9 (s, C_α), 93.2 (s, C_β), 92.7 (s, $\eta\text{-}C_5H_5$), 89.3 (s, $\eta\text{-}C_5H_5$) and 27.1 (s, CH_3). FAB mass spectrum: *m*/*z* 696 (M^+, 100), 612 ($[M - 3CO]^+$, 22), 586 ($[M - 4CO]^+$, 18) and 528 ($[M - 6CO]^+$, 42%).

$[Mo_2Ru(\mu\text{-}CCPh)(CO)_6(\eta\text{-}C_5H_5)_3]$ 3b. A solution of $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$ (58 mg, 0.133 mmol) and $[Ru(CO)_2(C{\equiv}CPh)(\eta\text{-}C_5H_5)]$ (43 mg, 0.133 mmol) in tetrahydrofuran (20 cm^3) was stirred at reflux (18 h). The solvent was removed *in vacuo* and the residue eluted through a silica column (2 × 10 cm, 100% CH_2Cl_2 eluent) to produce a single black band. Recrystallisation (CH_2Cl_2–*n*-hexane) yielded black crystals of compound **3b** (60 mg, 59%), m.p. 188–190 °C (Found: C, 45.70; H, 2.68. Calc. for $C_{29}H_{20}Mo_2O_6Ru$: C, 45.98; H, 2.66%). IR (thf): $\tilde{\nu}$(CO) 2027s, 1970s, 1954s, 1905s, 1893s and 1824m. ^1H NMR (C_6D_6): δ 7.35–7.20 (m, 5 H, Ph), 5.04 (s, 10 H, $\eta\text{-}C_5H_5$) and 4.70 (s, 5 H, $\eta\text{-}C_5H_5$). ^{13}C NMR (CD_2Cl_2): δ 229.3 (s, CO), 196.4 (s, CO), 131.6–125.7 (m, Ph), 111.9 (C_α), 94.8 (C_β), 94.2 (s, C_5H_5) and 91.1 (s, C_5H_5). FAB mass spectrum: *m*/*z* 758 (M^+, 20), 674 ($[M - 3CO]^+$, 17), 646 ($[M - 4CO]^+$, 10) and 588 ($[M - 6CO]^+$, 22%).

$[Mo_2(\mu\text{-}HC_2Me)(CO)_4(\eta\text{-}C_5H_5)_2]$ 4a. A solution of $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$ (51 mg, 0.12 mmol) and $[Fe(CO)_2(C{\equiv}CMe)(\eta\text{-}C_5H_5)]$ (26 mg, 0.12 mmol) in tetrahydrofuran (15 cm^3) was stirred at reflux (10 h). The solvent was removed *in vacuo* and the residues eluted through a silica column (2 × 10 cm; CH_2Cl_2–hexanes, 2:3) to produce two dark coloured bands. The first band was collected and recrystallised from hexane to yield dark red crystals of compound **4a** (45 mg, 81%), the second was collected and gave $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$ (18 mg, 85%). The compounds exhibited spectroscopic properties identical with those reported.[34]

$[Mo_2(\mu\text{-}HC_2Ph)(CO)_4(\eta\text{-}C_5H_5)_2]$ 4b. A solution of $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$ (58 mg, 0.134 mmol) and $[Fe(CO)_2(C{\equiv}CPh)(\eta\text{-}C_5H_5)]$ (43 mg, 0.133 mmol) in tetrahydrofuran (20 cm^3) were stirred at reflux (24 h). The solvent was removed *in vacuo* and the residues washed with *n*-hexane until the filtrates were clear. Recrystallisation (CH_2Cl_2–*n*-hexane) gave red needles of compound **4b** (20 mg, 28%), which exhibited spectroscopic properties identical with those reported.[34]

Crystallography

Unique room-temperature diffractometer data sets were measured (2θ–θ scan mode, $2\theta_{max}$ 50°; monochromatic Mo-Kα radiation, $\lambda = 0.7107_3$ Å; $T = 295$ K), yielding N independent reflections, N_o of these with $I > 3\sigma(I)$ considered 'observed' and used in the full-matrix least-squares refinement after Gaussian absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms, $(x, y, z, U_{iso})_H$ being constrained at estimated values. Conventional residuals R, R' on $|F|$ are quoted at convergence, statistical weights being derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$. Neutral atom complex scattering factors were employed. Computation used the XTAL 3.4 program system implemented by S. R. Hall.[35] Pertinent results are given in Table 3, variants being noted below.

Two pseudo-centrosymmetrically related molecules of compound **3a** comprise the asymmetric unit in the space group $Pca2_1$. A hemisphere of data was measured in order to explore the possibilities of refinement of alternative chiralities (inclusive of 'Flack x') in order definitively to establish the same, and of the symmetry being less than orthorhombic. In the event none of these excursions yielded meaningful results, and the data were merged ($R_{int} = 0.060$) and the structure refined to

Table 3 Summary of diffraction data for complexes **3a**, **3b** and **4b**

	3a	**3b**	**4b**
Formula	$C_{24}H_{18}Mo_2O_6Ru$	$C_{29}H_{20}Mo_2O_6Ru$	$C_{22}H_{16}Mo_2O_4$
M_r	695.4	757.4	536.3
Crystal system	Orthorhombic	Monoclinic	Orthorhombic
Space group	$Pca2_1$ (C_{2v}^5, no. 29)	$P2_1/c$ (C_{2h}^5, no. 14)	$P2_12_12_1$ (D_2^4, no. 19)
a/Å	18.332(8)	10.848(6)	16.578(7)
b/Å	9.669(6)	15.081(8)	15.952(7)
c/Å	26.229(5)	15.877(6)	7.452(1)
β/°	—	91.48(4)	—
U/Å^3	4649	2597	1971
D_c/g cm^{-3}	1.98_7	1.93_7	1.80_7
Z	8	4	4
F(000)	2704	1480	1056
μ_{Mo}/cm^{-1}	17.4	15.7	13.0
Specimen size/mm	0.42 × 0.20 × 0.60	0.42 × 0.65 × 0.48	0.18 × 0.18 × 0.55
$A^*_{min,max}$	1.48, 2.06	1.65, 2.19	1.23, 1.29
$2\theta_{max}$/°	50	55	60
N	3791	5944	3249
N_o	3477	4981	2849
R	0.044	0.056	0.025
R'	0.046	0.065	0.024

convergence in space group $Pca2_1$, chirality being indeterminate. Isotropic thermal parameters were refined for the cyclopentadienyl carbon atoms in respect of correlative behaviour in refinement; geometrical parameters should be treated with caution despite the relatively auspicious residuals. For **4** residuals quoted apply to the preferred chirality.

CCDC reference number 186/931.

See http://www.rsc.org/suppdata/dt/1998/1575/ for crystallographic files in .cif format.

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