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FULL PAPER

Coupling of co-ordinated acetylide ligands with and without CO on chalcogen-stabilised mixed-metal clusters. Synthesis and characterisation of $[M_2Fe_3(L)_2(CO)_6(\mu_3\text{-}E)_2\{\mu\text{-}CC(Ph)C(Ph)C\}]$ and $[M_2Fe_2(L)_2(CO)_4(\mu_3\text{-}E)_2\{\mu\text{-}CC(Ph)(CO)C(Ph)C\}]$ (L = η^5-C_5Me_5 or η^5-C_5H_5, M = Mo or W, E = S, Se or Te)

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Thermolysis of a toluene solution containing $[Fe_3(CO)_9(\mu_3\text{-}E)_2]$ (E = S or Se) and $[M(L)(CO)_3(C{\equiv}CPh)]$, M = Mo or W, resulted in coupling of co-ordinated acetylide ligands with and without CO and formation of mixed-metal clusters $[M_2Fe_3(L)_2(CO)_6(\mu_3\text{-}E)_2\{\mu\text{-}CC(Ph)C(Ph)C\}]$ (L = η^5-C_5Me_5, M = Mo, E = S **1** or Se **2**; M = W, E = S **3** or Se **4**; M = W, E = Te **5**; L = η^5-C_5H_5, M = Mo, E = S **6** or Se **7**; M = W, E = S **8** or Se **9** and $[M_2Fe_2(L)_2(CO)_4(\mu_3\text{-}E)_2\{\mu\text{-}CC(Ph)(CO)C(Ph)C\}]$ (L = η^5-C_5H_5, M = Mo, E = S **10** or Se **11**; M = W, E = S **12** or Se **13**). From the thermolysis reaction of $[Mo(\eta^5\text{-}C_5H_5)(CO)_3(C{\equiv}CPh)]$, the new compound $[\{Mo(\eta^5\text{-}C_5H_5)(CO)_2\}_2\{\mu\text{-}C(Ph)C(CO)C{\equiv}C(Ph)\}]$ **15** was isolated. All compounds have been characterised by IR and ^{1}H, ^{13}C and ^{77}Se or ^{125}Te NMR spectroscopy. The crystal structures of **8**, **12** and **15** were elucidated by X-ray diffraction methods.

Considerable interest exists in metal acetylide complexes for the construction of organometallic polymers,[1–6] as components in non-linear optical materials[7,8] and as new liquid crystals.[9,10] A particularly interesting aspect of metal–acetylide chemistry has been the coupling of terminal and functionalised metal acetylides on metal clusters, and a number of polycarbon ligand-containing metal clusters have been prepared from mononuclear acetylide starting materials.[11–14] Metal acetylide complexes possess two reaction sites, the C≡C triple bond and the metal centre itself. Combination of the former to act as an electron donating alkyne ligand and the latter to be able to effect ligand transformation in its co-ordination sphere can give rise to novel and unusual reactivity features. Large variation in the chemistry of the acetylide moiety can be achieved by incorporating it into the co-ordination sphere of mixed-metal polynuclear complexes. Indeed, this strategy has been used in recent times and there exist a number of mixed-metal clusters which have been obtained from mononuclear acetylide precursors. Reactions leading to C–C bond formation with an additional C_2 fragment have constituted an important development in the study of acetylide–cluster complexes.[11,12,15–17] In the past we have investigated the use of chalcogen ligands as bridges in synthesis of mixed-metal clusters,[18] and have shown the contrasting influence of the different chalcogens in such reactions. We believe that when chalcogen-bridged metal carbonyl compounds are used as precursors to add metal acetylide molecules an equally rich and diverse set of reactions might be observed whereby the nature of metal acetylide additions and acetylide coupling reactions may strongly be dependent on what chalcogens are used. Further variation is also expected from using different types of metal acetylides. Our first report of this investigation detailed a novel tail-to-tail coupling of acetylides on a chalcogen-bridged Fe/W mixed-metal cluster by treating $[W(\eta^5\text{-}C_5Me_5)(CO)_3(C{\equiv}CPh)]$ with $[Fe_3(CO)_9(\mu_3\text{-}E)_2]$ (where E = S, Se or Te).[19] We have extended this study to using the complexes $[M(\eta^5\text{-}C_5Me_5)(CO)_3(C{\equiv}CPh)]$ and $[M(\eta^5\text{-}C_5H_5)(CO)_3(C{\equiv}CPh)]$ where M = Mo or W, and here we report on the complete synthesis and characterisation of the different clusters obtained from these reactions.

Results and discussion

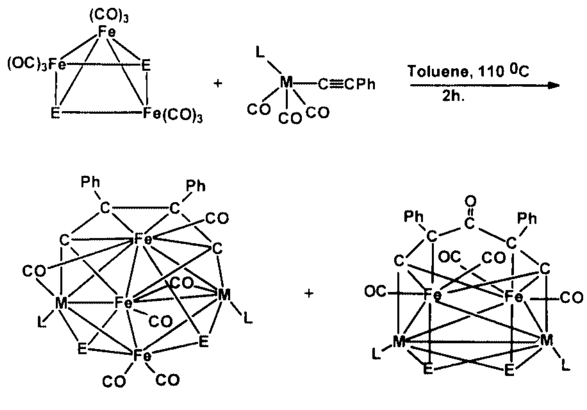
Reaction of $[ML(CO)_3(C{\equiv}CPh)]$ (L = η^5-C_5Me_5 or η^5-C_5H_5, M = Mo or W) with $[Fe_3(CO)_9(\mu_3\text{-}E)_2]$ (E = S, Se or Te)

When a toluene solution containing $[M(\eta^5\text{-}C_5Me_5)(CO)_3(C{\equiv}CPh)]$ and $[Fe_3(CO)_9(\mu_3\text{-}E)_2]$ (E = S, Se or Te) was subjected to reflux in all but one case (when M = Mo and E = Te) the tail-to-tail acetylide coupled clusters $[M_2Fe_3(\eta^5\text{-}C_5Me_5)_2(CO)_6(\mu_3\text{-}E)_2\{\mu\text{-}CC(Ph)C(Ph)C\}]$ (M = Mo, E = S **1** or Se **2**; M = W, E = S **3** or Se **4**; M = W, E = Te **5**) (Scheme 1, Table 1) were obtained as the sole products. The new clusters are stable in air in the solid state but slowly decompose in solution over a period of days. The synthesis of **3**–**5** and the crystal structure of **3** have been reported by us earlier,[19] and the identity of the new clusters **1** and **2** was established by comparison of their spectroscopic features with those of **3**–**5** (Table 2). Under the same conditions of thermolysis, if $[M(\eta^5\text{-}C_5H_5)(CO)_3(C{\equiv}CPh)]$ is used for reaction with $[Fe_3(CO)_9(\mu_3\text{-}E)_2]$ (E = S, Se or Te) we observe formation of the tail-to-tail acetylide coupled clusters $[M_2Fe_3(\eta^5\text{-}C_5H_5)(CO)_6(\mu_3\text{-}E)_2\{\mu\text{-}CC(Ph)C(Ph)C\}]$ (M = Mo, E = S **6** or Se **7**; M = W, E = S **8** or Se **9**) as well as the new type of mixed-metal clusters $[M_2Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_4(\mu_3\text{-}E)_2\{\mu\text{-}CC(Ph)(CO)C(Ph)C\}]$ (M = Mo, E = S **10** or Se **11**; M = W, E = S **12** or Se **13**). Reaction with the Te-bridged starting compound $[Fe_3(CO)_9(\mu_3\text{-}Te)_2]$ led to substantial decomposition and only trace amounts of the starting materials were isolated. Compounds **6**–**9** were characterised by IR and NMR spectroscopic

Table 1 Experimental conditions used for the preparation of compounds **1–15**

Reactants/mg (mmol)	Compound	Yield/mg (%)	Analysis (%) Calc. (Found)	mp[a]/°C
[MoCp*(CO)$_3$(C$_2$Ph)] + [Fe$_3$(CO)$_9$(μ$_3$-S)$_2$] 269 (0.56) 104 (0.25)	**1**	60 (45)	C, 47.4 (47.6); H, 3.79 (3.99)	242–243
[MoCp*(CO)$_3$(C$_2$Ph)] + [Fe$_3$(CO)$_9$(μ$_3$-Se)$_2$] 269 (0.56) 324 (0.56)	**2**	43 (30)	C, 43.3 (43.5); H, 3.46 (3.59)	240–241
[WCp*(CO)$_3$(C$_2$Ph)] + [Fe$_3$(CO)$_9$(μ$_3$-S)$_2$] 140 (0.28) 269 (0.56)	**3**	98 (57)	C, 40.5 (40.7); H, 3.23 (3.38)	237–238
[WCp*(CO)$_3$(C$_2$Ph)] + [Fe$_3$(CO)$_9$(μ$_3$-Se)$_2$] 140 (0.28) 324 (0.56)	**4**	67 (36)	C, 37.5 (37.8); H, 3.00 (3.21)	234–235
[WCp*(CO)$_3$(C$_2$Ph)] + [Fe$_3$(CO)$_9$(μ$_3$-Te)$_2$] 140 (0.28) 378 (0.56)	**5**	58 (29)	C, 35.0 (35.2); H, 2.79 (2.96)	231–232
[MoCp(CO)$_3$(C$_2$Ph)] + [Fe$_3$(CO)$_9$(μ$_3$-S)$_2$] 150 (0.433) 134 (0.28)	**6**	33 (33)	C, 41.59 (41.26); H, 2.18 (2.37)	227–230
[MoCp(CO)$_3$(C$_2$Ph)] + [Fe$_3$(CO)$_9$(μ$_3$-Se)$_2$] 150 (0.433) 126 (0.28)	**7**	31 (28)	C, 37.76 (37.45); H, 1.98 (2.21)	225–228
[WCp(CO)$_3$(C$_2$Ph)] + [Fe$_3$(CO)$_9$(μ$_3$-S)$_2$] 200 (0.461) 134 (0.28)	**8**	46 (37)	C, 34.95 (34.66); H, 1.83 (1.98)	223–227
[WCp(CO)$_3$(C$_2$Ph)] + [Fe$_3$(CO)$_9$(μ$_3$-Se)$_2$] 200 (0.461) 126 (0.28)	**9**	41 (30)	C, 32.20 (31.86); H, 1.69 (1.91)	222–225
[MoCp(CO)$_3$(C$_2$Ph)] + [Fe$_3$(CO)$_9$(μ$_3$-S)$_2$] 150 (0.433) 134 (0.28)	**10**	24 (40)	C, 44.32 (44.21); H, 2.40 (2.55)	220–222
[MoCp(CO)$_3$(C$_2$Ph)] + [Fe$_3$(CO)$_9$(μ$_3$-Se)$_2$] 150 (0.433) 126 (0.28)	**11**	24 (35)	C, 39.59 (39.47); H, 2.15 (2.28)	217–218
[WCp(CO)$_3$(C$_2$Ph)] + [Fe$_3$(CO)$_9$(μ$_3$-S)$_2$] 200 (0.461) 134 (0.28)	**12**	62 (40)	C, 36.64 (36.33); H, 1.97 (2.11)	212–213
[WCp(CO)$_3$(C$_2$Ph)] + [Fe$_3$(CO)$_9$(μ$_3$-Se)$_2$] 200 (0.461) 126 (0.28)	**13**	60 (35)	C, 33.53 (33.13); H, 1.8 (1.92)	209–211
[MoCp(CO)$_3$(C$_2$Ph)] 150 (0.433)	**14**	14 (20) 6 (9)[b]	C, 56.25 (56.03); H, 3.15 (3.40)	157–159
[MoCp(CO)$_3$(C$_2$Ph)] 150 (0.433)	**15**	23 (33) 41 (58)[b]	C, 56.04 (56.14); H, 3.03 (3.32)	176–178

[a] In all cases corresponds to decomposition point. [b] Sealed tube reaction.



Compound	L	M	E
1	η^5-C$_5$Me$_5$	Mo	S
2	η^5-C$_5$Me$_5$	Mo	Se
3	η^5-C$_5$Me$_5$	W	S
4	η^5-C$_5$Me$_5$	W	Se
5	η^5-C$_5$Me$_5$	W	Te
6	η^5-C$_5$H$_5$	Mo	S
7	η^5-C$_5$H$_5$	Mo	Se
8	η^5-C$_5$H$_5$	W	S
9	η^5-C$_5$H$_5$	W	Se

Compound	L	M	E
10	η^5-C$_5$H$_5$	Mo	S
11	η^5-C$_5$H$_5$	Mo	Se
12	η^5-C$_5$H$_5$	W	S
13	η^5-C$_5$H$_5$	W	Se

Scheme 1

techniques and their identification based on comparison of these spectral features with those of **1**–**5** (Table 2). Further, the structure of **8** was confirmed crystallographically. Table 3 lists selected bond lengths and angles. Its molecular structure, shown in Fig. 1, can be described as consisting of a Fe$_3$W$_2$ metal core which is arranged in the form of an open trigonal bipyramidal polyhedron, in which the Fe atoms occupy the equatorial positions. Two S atoms μ$_3$-cap two Fe$_2$W faces of the polyhedron and a μ$_4$-CC(Ph)C(Ph)C unit is attached to the polyhedron at the two W and two Fe atoms. Overall, the structure is similar to that of the previously reported **3**. The bond parameters of **3** and **8** are also quite similar.

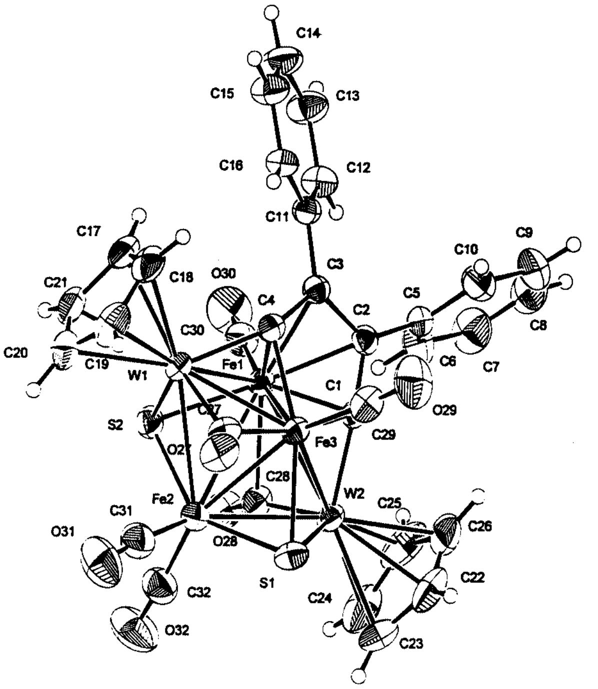


Fig. 1 An ORTEP[20] diagram of compound **8** (with 50% probability ellipsoids). Solvent molecule is not shown for clarity.

The infrared spectra of compounds **10**–**13** displayed an identical carbonyl stretching pattern, confirming the presence of only terminally bonded carbonyl groups, as well as a broad band corresponding to the presence of a ketonic carbonyl group. The ^{1}H NMR spectra displayed a single peak for the η^5-C$_5$H$_5$ groups and peaks for the phenyl group. For **11** and **13** the ^{77}Se spectra showed single peaks in the region typical for

Table 2 Spectroscopic data for compounds **1**–**15**

Compound	ν(CO)/cm^{-1}	^{1}H NMR (δ, $CDCl_3$)	^{13}C NMR (δ, $CDCl_3$)	^{77}Se NMR (δ, $CDCl_3$)	^{125}Te NMR (δ, $CDCl_3$)
1	1975s, 1943vs, 1755m	7.3–7.1 (m, C_6H_5, 10 H), 1.78 (s, $C_5(CH_3)_5$, 15 H), 1.71 (s, $C_5(CH_3)_5$, 15 H)	10.9 (CH_3), 11.8 (CH_3), 105.6 (s, $C_5(CH_3)_5$), 108.2 (s, $C_5(CH_3)_5$), 128.1–132.3 (C_6H_5), 139.1 (C_4Ph_2), 141.4 (C_4Ph_2), 209.8, 214.3, 218.7, 228.6, 229.9 (CO)		
2	1969s, 1940vs, 1792m	7.2–7.1 (m, C_6H_5, 10 H), 1.78 (s, $C_5(CH_3)_5$, 15 H), 1.72 (s, $C_5(CH_3)_5$, 15 H)	11.4 (CH_3), 12.5 (CH_3), 106.8 (s, $C_5(CH_3)_5$), 109.0 (s, $C_5(CH_3)_5$), 128.6–131.7 (C_6H_5), 139.8 (C_4Ph_2), 143.1 (C_4Ph_2), 211.2, 215.4, 217.8, 227.9, 230.6 (CO)	834, 958	
3	1974s, 1939vs, 1734m	7.3–7.1 (m, C_6H_5, 10 H), 1.93 (s, $C_5(CH_3)_5$, 15 H), 1.99 (s, $C_5(CH_3)_5$, 15 H)	10.6 (CH_3), 11.1 (CH_3), 106.5 (s, $C_5(CH_3)_5$), 107.8 (s, $C_5(CH_3)_5$), 127.6–130.8 (C_6H_5), 135.2 (C_4Ph_2), 137.2 (C_4Ph_2), 212.8, 213.2, 215.1, 216.6, 220.4 (CO)		
4	1968s, 1936vs, 1777m	7.3–7.1 (m, C_6H_5, 10 H), 1.92 (s, $C_5(CH_3)_5$, 15 H), 1.87 (s, $C_5(CH_3)_5$, 15 H)	11.1 (CH_3), 11.6 (CH_3), 105.7 (s, $C_5(CH_3)_5$), 107.1 (s, $C_5(CH_3)_5$), 127.6–131.1 (C_6H_5), 135.1 (C_4Ph_2), 136.9 (C_4Ph_2), 214.2, 214.4, 216.5, 220.3, 222.6 (CO)	880, 872	
5	1959m, 1926vs, 1718m	7.3–7.2 (m, C_6H_5, 10 H), 1.93 (s, $C_5(CH_3)_5$, 15 H), 1.90 (s, $C_5(CH_3)_5$, 15 H)	12.1 (CH_3), 12.4 (CH_3), 104.8 (s, $C_5(CH_3)_5$), 106.3 (s, $C_5(CH_3)_5$), 127.5–131.3 (C_6H_5), 135.6 (C_4Ph_2), 136.7 (C_4Ph_2), 217.1, 217.3, 220.7, 222.8, 224.3 (CO)		971, 1157
6	1992s, 1964vs, 1764w (br)	7.1–7.6 (m, C_6H_5, 10 H), 5.56 (s, C_5H_5, 5 H), 5.63 (s, C_5H_5, 5 H)	95.1 (s, C_5H_5), 96.8 (s, C_5H_5), 128–130 (C_6H_5), 137.3 (s, C_4Ph_2), 139.7 (s, C_4Ph_2), 207.1, 210.04, 213.2, 223.92 (CO)		
7	1987s, 1958vs, 1758w (br)	7.1–7.7 (m, C_6H_5, 10 H), 5.59 (s, C_5H_5, 5 H), 5.67 (s, C_5H_5, 5 H)	95.3 (s, C_5H_5), 96.7 (s, C_5H_5), 128.2–130.6 (C_6H_5), 136.6 (s, C_4Ph_2), 138.1 (s, C_4Ph_2), 208.2, 211.04, 214.4, 226.03 (CO)		642.71, 781.91
8	1990s, 1957vs, 1752w (br)	7.2–7.4 (m, C_6H_5, 10 H), 5.57 (s, C_5H_5, 5 H), 5.70 (s, C_5H_5, 5 H)	93.5 (s, C_5H_5), 95.2 (s, C_5H_5), 128.1–130.1 (C_6H_5), 135.4 (s, C_4Ph_2), 137.5 (s, C_4Ph_2), 208.6, 209.27, 213.65, 215.09 (CO)		
9	1982s, 1951vs, 1740w (br)	7.1–7.59 (m, C_6H_5, 10 H), 5.56 (s, C_5H_5, 5 H), 5.63 (s, C_5H_5, 5 H)	94 (s, C_5H_5), 95.74 (s, C_5H_5), 127.9–131.3 (C_6H_5), 138 (s, C_4Ph_2), 138.8 (s, C_4Ph_2), 212.2, 212.5, 214.6, 220.19 (CO)		764.21, 946.13
10	2000vs, 1958s, 1835w (br), 1744w	7.2–7.4 (m, C_6H_5, 10 H), 5.44 (s, C_5H_5, 10 H)	93.99 (s, C_5H_5), 104.1 (s, C_4Ph_2), 127.3–129.8 (C_6H_5), 138.7 (s, C_4Ph_2), 166.3, 209.12 (CO)		
11	1995vs, 1954s, 1831w (br), 1740w	7.2–7.5 (m, C_6H_5, 10 H), 5.44 (s, C_5H_5, 10 H)	91.02 (s, C_5H_5), 103.2 (s, C_4Ph_2), 127.3–130.2 (C_6H_5), 141.9 (s, C_4Ph_2), 165.03, 210.3 (CO)	1019.12	
12	1993vs, 1951s, 1828w (br), 1735w	7.5–7.3 (m, C_6H_5, 10 H), 5.59 (s, C_5H_5, 10 H)	93.9 (s, C_5H_5), 101.1 (s, C_4Ph_2), 127.1–130.1 (C_6H_5), 140.02 (s, C_4Ph_2), 163.8, 208.5 (CO)		
13	1991vs, 1947s, 1823w (br), 1731w	7.5–7.2 (m, C_6H_5, 10 H), 5.45 (s, C_5H_5, 10 H)	93.58 (s, C_5H_5), 102.3 (s, C_4Ph_2), 128.3–130.9 (C_6H_5), 141.9 (s, C_4Ph_2), 164.76, 208.9 (CO)	946	
14	1994s, 1936vs, 1841s	7.1–7.6 (m, C_6H_5, 10 H), 5.23 (s, C_5H_5, 10 H)	93.7 (s, C_5H_5), 91.5, 94.3 (s, C_2Ph), 126.2, 146.6 (s, C_2Ph), 126.4–132.5 (C_6H_5), 207.4, 209.3 (CO)		
15	2006s, 1950vs, 1851s, 1721w (br)	7.1–7.4 (m, C_6H_5, 10 H), 5.25 (s, C_5H_5, 10 H)	93.03 (s, C_5H_5), 87.5, 89.51 (s, C_2Ph), 120.65, 145.73 (s, C_2Ph), 126.4–132.5 (C_6H_5), 165.62, 205.8, 208.1 (CO)		

μ_3-Se caps. Suitable X-ray quality crystals of **12** were grown by slow evaporation of a hexane–dichloromethane solvent mixture. Its molecular structure, shown in Fig. 2, consists of a Fe_2W_2 butterfly tetrahedron, in which the W atoms occupy the hinge sites and are bonded to each other while the Fe atoms sit at the wing-tip positions. Each FeW_2 face is capped by a sulfide ligand. The W atoms bear one η^5-C_5H_5 group each and the Fe atoms have two terminally bound carbonyl groups each. The most significant feature of the structure is the presence of an organic backbone consisting of two phenylacetylide groups coupled tail-to-tail with one CO group to form a pentanone unit. In the pentanone backbone the carbon–carbon bond distance between the end carbon atoms is shorter (1.394(7) Å) than the distance between the carbon atom bearing the phenyl substituent and the ketonic carbon atom (1.503(6) Å) (Table 4). Each terminal carbon atom of the organic backbone is bonded to one W and both Fe atoms while each of the two inner carbon atoms is bonded to a Fe atom and bears the phenyl group. Assuming each S atom to be a 4-electron donor, each metal atom in **12** satisfies the 18-electron requirement.

The formation of compounds **10**–**13** involving coupling of acetylides with CO contrasts with the previously reported head-to-head and head-to-tail acetylide coupling on cluster compounds.[12,14,15,21–23] Although the exact mechanism of formation of these is unknown at present, formally it involves a number of new metal–metal, metal–chalcogen, metal–carbon and carbon–carbon bonds, as well as the formal loss of an iron carbonyl unit from the $[Fe_3(CO)_9(\mu_3\text{-}E)_2]$ molecule. The possibility that $[Fe_3(CO)_9(\mu_3\text{-}E)_2]$ first converts into a $Fe_2(CO)_6E_2$ moiety, which then reacts with two molecules of the metal acetylide units, seems unlikely because when we carried out room temperature reactions of $[Fe_2(CO)_6(\mu\text{-}E_2)]$ (E = S or Se) with $[M(\eta^5\text{-}C_5H_5)(CO)_3(C{\equiv}CPh)]$ no new product formation was observed and both starting materials were recovered intact; at higher temperatures $[Fe_2(CO)_6(\mu\text{-}E_2)]$ decomposes. Under the thermolytic reaction conditions it is likely that the metal acetylide complex undergoes loss of carbonyl groups and the electron deficient metal acetylide moiety then adds to the lone pairs of the triply bridging chalcogens of the iron cluster, as the first step. This may be followed by dissociation of one iron carbonyl

Table 3 Selected bond lengths (Å) and angles (°) for compound **8**

C(1)–C(2)	1.416(5)	Fe(3)–C(29)	1.777(5)
C(2)–C(3)	1.446(5)	Fe(3)–C(27)	1.995(4)
C(3)–C(4)	1.431(5)	Fe(3)–C(1)	1.996(4)
Fe(1)–C(30)	1.780(4)	Fe(3)–C(4)	2.000(4)
Fe(1)–C(1)	1.993(3)	Fe(3)–S(1)	2.2481(11)
Fe(1)–C(4)	2.013(4)	Fe(3)–W(1)	2.5454(6)
Fe(1)–C(3)	2.138(4)	Fe(3)–W(2)	2.6798(6)
Fe(1)–C(2)	2.140(4)	W(1)–C(4)	1.975(4)
Fe(1)–S(2)	2.2645(11)	W(1)–C(27)	2.093(4)
Fe(1)–C(28)	2.435(4)	W(1)–S(2)	2.3204(10)
Fe(1)–Fe(3)	2.5391(7)	W(2)–C(1)	1.975(4)
Fe(1)–W(1)	2.7852(6)	W(2)–C(28)	1.981(4)
Fe(1)–W(2)	2.7993(6)	W(2)–S(1)	2.3406(11)
Fe(2)–C(32)	1.762(5)	C(27)–O(27)	1.187(5)
Fe(2)–C(31)	1.773(5)	C(28)–O(28)	1.178(5)
Fe(2)–S(1)	2.2002(12)	C(29)–O(29)	1.131(5)
Fe(2)–S(2)	2.2201(12)	C(30)–O(30)	1.130(5)
Fe(2)–Fe(3)	2.6151(8)	C(31)–O(31)	1.149(5)
Fe(2)–W(2)	2.8430(6)	C(32)–O(32)	1.159(6)
Fe(2)–W(1)	2.8636(6)		
O(27)–C(27)–Fe(3)	138.1(3)	Fe(2)–S(1)–W(2)	77.43(4)
O(27)–C(27)–W(1)	144.5(3)	C(1)–Fe(1)–C(4)	76.66(15)
O(28)–C(28)–W(2)	159.2(3)	C(1)–Fe(3)–C(4)	76.90(15)
O(28)–C(28)–Fe(1)	120.7(3)	C(2)–C(1)–W(2)	148.7(3)
Fe(2)–S(2)–Fe(1)	85.42(4)	C(3)–C(4)–W(1)	151.1(3)
Fe(2)–S(2)–W(1)	78.16(4)	C(1)–C(2)–C(3)	112.0(3)
Fe(2)–S(1)–Fe(3)	72.00(4)	C(4)–C(3)–C(2)	110.7(3)

Table 4 Selected bond lengths (Å) and angles (°) for compound **12**

W–C(1)	1.978(5)	Fe–S	2.2386(13)
W–S	2.3148(11)	O(1)–C(3)	1.214(9)
W–Fe	2.7686(6)	C(1)–C(2)#1	1.395(6)
W–W#1	2.8274(3)	C(1)–Fe#1	2.038(4)
Fe–C(1)	2.094(4)	C(2)–C(4)	1.492(6)
Fe–C(2)	2.140(4)	C(2)–C(3)	1.503(6)
C(1)–W–S	100.26(12)	Fe–W–W#1	57.797(13)
S–W–S#1	98.98(4)	C(1)#1–Fe–C(1)	73.12(18)
C(1)–W–Fe#1	48.61(11)	C(1)#1–Fe–C(2)	38.91(17)
S–W–Fe#1	108.29(3)	C(1)–Fe–C(2)	79.59(17)
S#1–W–Fe#1	51.93(3)	C(1)#1–Fe–S	102.59(14)
C(1)–W–Fe	48.95(12)	C(1)–Fe–S	99.23(13)
S–W–Fe	51.31(3)	C(2)–Fe–S	140.61(12)
S#1–W–Fe	105.00(3)	C(1)#1–Fe–W#1	46.72(13)
Fe#1–W–Fe	73.32(2)	Fe–S–W	74.87(4)
C(1)–W–W#1	84.69(12)	W–S–W#1	74.46(3)
S–W–W#1	53.47(3)	C(2)#1–C(1)–W	154.6(3)
S#1–W–W#1	52.07(3)	C(2)#1–C(1)–Fe#1	74.5(2)
Fe#1–W–W#1	60.011(13)	W–C(1)–Fe#1	84.67(16)
C(1)–Fe–W#1	85.80(12)	C(2)#1–C(1)–Fe	113.3(3)
C(2)–Fe–W#1	84.77(12)	W–C(1)–Fe	85.64(17)
S–Fe–W#1	56.03(3)	Fe#1–C(1)–Fe	104.55(18)
C(1)#1–Fe–W	85.18(12)	C(1)#1–C(2)–Fe	66.6(2)
C(1)–Fe–W	45.41(13)	O(1)–C(3)–C(2)	124.0(3)
C(2)–Fe–W	114.03(12)	C(2)#1–C(3)–C(2)	112.0(6)
S–Fe–W	53.81(3)	W#1–Fe–W	62.193(14)

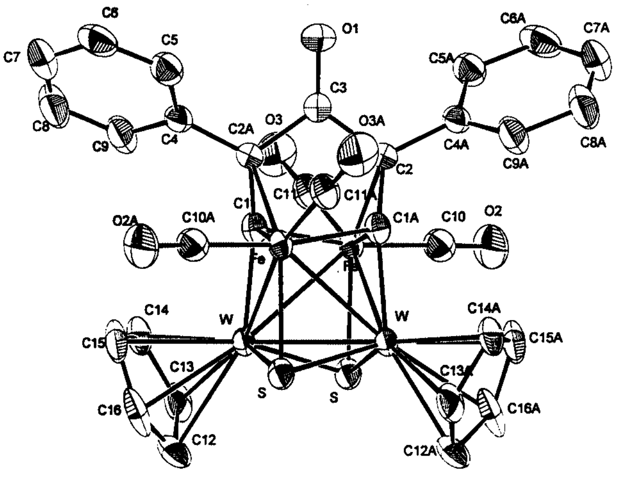
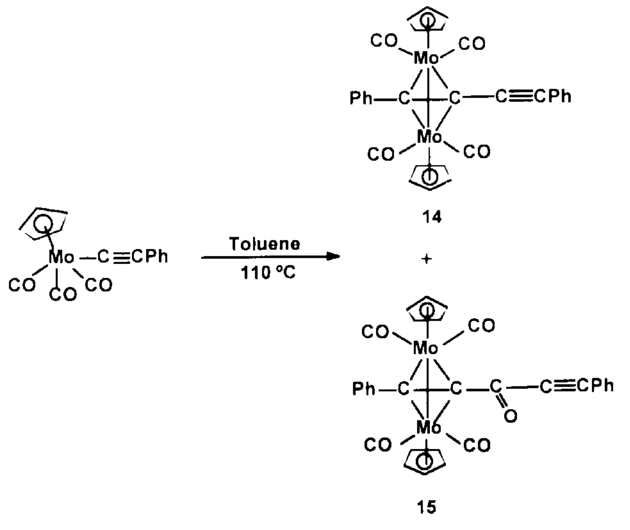


Fig. 2 An ORTEP diagram of compound **12** (with 50% probability ellipsoids).



Scheme 2

unit by cleavage of one Fe–Fe bond and two chalcogen–Fe bonds. The orientation of the two adding metal acetylide units is such that the tail ends of the acetylide groups come in close proximity to each other around the Fe_2W_2 cluster core and couple with a CO group to form a 2,4-diphenyl-3-pentanone organic backbone which is attached to the metal core as discussed before. The role of the chalcogen atoms in supporting the heteronuclear cluster framework is apparent here, as well as the importance of the cluster framework in supporting the organic unit.

Thermolysis of [Mo(η^5-C_5H_5)(CO)$_3$(C≡CPh)]

In continuation of our investigations on the utility of metal acetylide complexes for formation of metal clusters containing σ,π-alkynyl ligands we have looked at the thermolysis of [M(η^5-C_5H_5)(CO)$_3$(C≡CPh)] (M = Mo or W). In an earlier report the solid state and solution thermolyses at 120 and 115 °C respectively have been described.[24] While the tungsten acetylide compound was found to decompose, the molybdenum compound formed the acetylide-coupled dimer [{Mo(η^5-C_5H_5)(CO)$_2$}$_2$(μ-1,2-PhC≡CC≡CPh)] **14** (Scheme 2). We find that on thermolysis in a sealed tube of a toluene solution of [Mo(η^5-C_5H_5)(CO)$_3$(C≡CPh)], at 110 °C, a small amount of compound **14** and significant amount of hitherto unreported [{Mo(η^5-C_5H_5)(CO)$_2$}$_2$(μ-1,2-PhC≡C(CO)C≡CPh)] **15** are formed. Thermolysis of [W(η^5-C_5H_5)(CO)$_3$(C≡CPh)] under the same conditions led to substantial decomposition and even after several hours only a trace amount of the starting material was isolable from the solution. Compound **15** was characterised by IR and ^{1}H and ^{13}C NMR spectroscopy. The IR spectrum showed three strong bands for the terminal carbonyls and a broad band in the ketonic carbonyl region. The ^{1}H and ^{13}C NMR spectra showed one signal each for the two equivalent η^5-C_5H_5 groups. In addition to signals for the phenyl groups, the ^{13}C NMR spectrum showed five signals for the μ-1,2-PhC≡C(CO)C≡CPh group in the regions expected for co-ordinated and unco-ordinated C≡C atoms and for the ketonic carbonyl carbon atom. For an unambiguous structure elucidation, a single crystal X-ray analysis was undertaken. The molecular structure of **15**, shown in Fig. 3, consists of two (η^5-C_5H_5)Mo(CO)$_2$ units linked by a metal–metal bond while a PhC≡C(CO)C≡CPh molecule acts as a bridge, being bonded to each molybdenum atom by only one triple bond. The bond distance between the two carbon atoms which are attached to

Table 5 Selected bond lengths (Å) and angles (°) for compound **15**

Mo(1)–C(21)	2.177(5)	C(17)–C(18)	1.197(5)
Mo(1)–C(20)	2.196(5)	C(18)–C(19)	1.456(6)
Mo(1)–Mo(2)	2.966(7)	C(19)–O(19)	1.232(6)
Mo(2)–C(20)	2.164(5)	C(19)–C(20)	1.441(6)
Mo(2)–C(21)	2.190(5)	C(20)–C(21)	1.390(7)
C(11)–C(17)	1.442(6)	C(21)–C(22)	1.470(6)
C(21)–Mo(1)–C(20)	37.07(18)	C(20)–C(19)–C(18)	116.8(3)
C(28)–Mo(1)–C(5)	112.57(19)	C(21)–C(20)–C(19)	136.2(4)
C(21)–Mo(1)–Mo(2)	47.39(13)	C(21)–C(20)–Mo(2)	72.4(2)
C(20)–Mo(1)–Mo(2)	46.68(11)	C(19)–C(20)–Mo(2)	141.4(3)
C(31)–Mo(2)–C(30)	88.9(2)	C(21)–C(20)–Mo(1)	70.7(3)
C(20)–C(21)–C(22)	134.3(3)	C(19)–C(20)–Mo(1)	124.2(3)
C(20)–Mo(2)–C(21)	37.24(19)	Mo(2)–C(20)–Mo(1)	85.7(2)
C(20)–Mo(2)–Mo(1)	47.59(14)	C(20)–C(21)–C(22)	134.3(3)
C(21)–Mo(2)–Mo(1)	47.03(13)	C(20)–C(21)–Mo(1)	72.2(2)
C(18)–C(17)–C(11)	174.8(4)	C(22)–C(21)–Mo(1)	137.5(2)
C(17)–C(18)–C(19)	176.0(4)	C(20)–C(21)–Mo(2)	70.4(2)
O(19)–C(19)–C(20)	123.8(4)	C(22)–C(21)–Mo(2)	130.6(3)
O(19)–C(19)–C(18)	119.4(3)	Mo(1)–C(21)–Mo(2)	85.6(2)

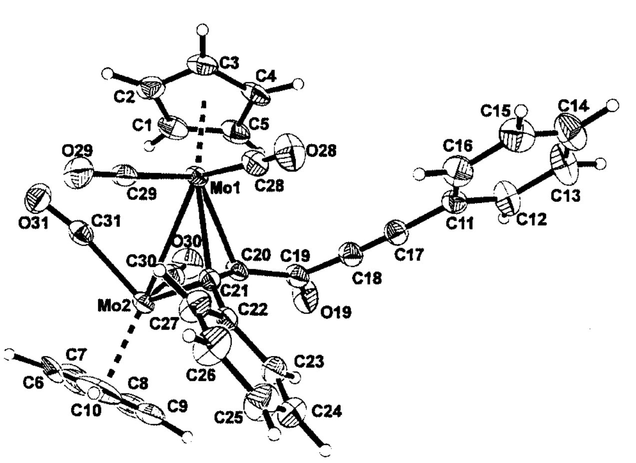


Fig. 3 An ORTEP diagram of compound **15** (with 40% probability ellipsoids).

the dimolybdenum centre, C(20)–C(21), 1.390(7) Å (Table 5), is slightly longer than observed in other [{Mo(η^5-C_5H_5)$(CO)_2$}$_2$(μ-RCCR)] compounds (R = H, 1.337(5); Et, 1.335(8); Ph, 1.329(6) Å).[25] The Mo–$C_{acetylene}$ bond distances (2.164(5)–2.196(5) Å), however, are within the range observed in [{Mo(η^5-C_5H_5)$(CO)_2$}$_2$(μ-RCCR)] (2.153(6)–2.2203(3) Å). The two (η^5-C_5H_5)Mo$(CO)_2$ units are structurally non-equivalent because one of the carbonyls is semi-bridging (Mo(2)–C(31)–O(31), 170.4(3) Å). The degree of bending of the Mo–C–O group is similar to what is observed for one carbonyl group in [{Mo(η^5-C_5H_5)$(CO)_2$}$_2$(μ-RCCR)] (R = H, 168.5; Et, 168.1; Ph, 168.6°).

To check whether compound **15** could be an intermediate in the formation of clusters of the type **10** and **11**, but one which results in a head-to-head coupling of acetylides with CO, we examined the sealed tube thermolysis of [$Fe_3(CO)_9$(μ_3-E)$_2$] and [Mo(η^5-C_5H_5)$(CO)_3$(C≡CPh)]. In each case we observed formation of small amounts of **10** or **11** and of **15** as the major product, along with considerable decomposition. Clusters of the type [Mo_2Fe_3(η^5-C_5H_5)$_2$$(CO)_6$($\mu_3$-E)$_2${$\mu$-CC(Ph)C(Ph)C}] were not observed on work-up of the reaction mixture.

Experimental

General procedures

All reactions and other manipulations were carried out using standard Schlenk techniques under an inert atmosphere of argon. All solvents were purified, dried and distilled under a nitrogen or argon atmosphere immediately prior to use. Reactions were monitored by TLC as well as by FT-IR spectroscopy. Infrared spectra were recorded on a Nicolet Impact 400 FTIR spectrophotometer as hexane solutions in 0.1 mm path length NaCl cells. Elemental analyses were performed using a Carlo Erba automatic analyser. ^{77}Se and ^{125}Te NMR spectra were recorded on a Varian VXR-300S spectrometer in $CDCl_3$. The operating frequency for ^{77}Se NMR was 57.23 MHz; 90° pulses were used with 1.0 s delay and 1.0 s acquisition time. The operating frequency for ^{125}Te was 94.705 MHz with a pulse of 90° and a delay of 1.0 s. ^{77}Se NMR spectra are referenced to Me_2Se (δ 0) and ^{125}Te NMR to Me_2Te (δ 0). The compounds [$Fe_3(CO)_9$(μ-E)$_2$] (E = S or Se)[26] and [M(η^5-C_5H_5)$(CO)_3$(C≡CPh)][27] were prepared by established procedures. Details of quantities of starting materials used and the yields of products obtained are given in Table 1.

Preparation of [Mo_2Fe_3(η^5-C_5Me_5)$_2$$(CO)_6$($\mu_3$-E)$_2${$\mu_4$-CC(Ph)-C(Ph)C}] 1 and 2

In a typical preparation a toluene solution (50 mL) containing [Mo(η^5-C_5Me_5)$(CO)_3$(C≡CPh)] (104 mg, 0.25 mmol) and two equivalents of [$Fe_3(CO)_9$(μ_3-E)$_2$] (E = S or Se) was subjected to reflux for 2 h, during which the reaction mixture changed from dark purple to dark green. The solution was filtered through Celite to remove insoluble material and the solvent removed *in vacuo*. The residue was subjected to chromatographic work-up on silica-gel TLC plates. Elution with CH_2Cl_2–hexane (30 : 70 v/v) yielded the following, in order of elution: dark green **1** (45) and **2** (35%).

Preparation of [M_2Fe_3(η^5-C_5H_5)$_2$$(CO)_6$($\mu_3$-E)$_2${$\mu_4$-CC(Ph)-C(Ph)C}] (M = Mo, E = S 6 or Se 7; M = W, E = S 8 or Se 9) and [M_2Fe_2(η^5-C_5H_5)$_2$$(CO)_4$($\mu_3$-E)$_2${$\mu$-CC(Ph)(CO)CPhC}] (M = Mo, E = S 10 or Se 11; M = W, E = S 12 or Se 13)

In a typical preparation a toluene solution (50 mL) containing [M(η^5-C_5H_5)$(CO)_3$(C≡CPh)] (M = Mo, 150 mg, 0.433 mmol; M = W, 200 mg, 0.461 mmol), and one equivalent of [$Fe_3(CO)_9$(μ_3-E)$_2$] (E = S or Se) was subjected to reflux for 2 h, under an atmosphere of nitrogen. The solution was cooled to room temperature, filtered through Celite to remove insoluble material and the solvent removed *in vacuo*. The residue was dissolved in dichloromethane and subjected to chromatographic work-up on silica-gel TLC plates. Elution with CH_2Cl_2–hexane (30 : 70 v/v) yielded the following two bands, in order of elution: dark green [M_2Fe_3(η^5-C_5H_5)$_2$$(CO)_6$($\mu_3$-E)$_2${$\mu_4$-CC(Ph)-C(Ph)C}], **6** (33), **7** (28), **8** (37) or **9** (30%); and dark red [M_2Fe_2(η^5-C_5H_5)$_2$$(CO)_4$($\mu_3$-E)$_2${$\mu$-CC(Ph)(CO)CPhC}], **10** (35), **11** (33), **12** (40) or **13** (35%).

Thermolysis of [Mo(η^5-C_5H_5)$(CO)_3$(C≡CPh)] in toluene

A toluene solution (40 ml) containing 150 mg (0.433 mmol) of [Mo(η^5-C_5H_5)$(CO)_3$(C≡CPh)] in an evacuated sealed tube was heated at 110 °C for 2 h. The solution was cooled to room temperature and the solvent removed *in vacuo*. The residue was subjected to chromatographic work-up using silica-gel TLC plates. Elution with dichloromethane–hexane (40 : 60 v/v) afforded the following two red bands, in order of elution: [{Mo(η^5-C_5H_5)$(CO)_2$}$_2${μ-1,2-η-PhCCCCPh}] **14** (9%) and [{Mo(η^5-C_5H_5)$(CO)_2$}$_2${μ-1,2-η-PhCC(CO)CCPh}] **15** (58%).

Thermolysis of [Mo(η^5-C_5H_5)$(CO)_3$(C≡CPh)] and [$Fe_3(CO)_9$-(μ_3-S)$_2$] in a sealed tube

A toluene solution (40 ml) containing 150 mg (0.433 mmol) of [Mo(η^5-C_5H_5)$(CO)_3$(C≡CPh)] and one equivalent (134 mg, 0.28 mmol) of [$Fe_3(CO)_9$(μ_3-S)$_2$] in an evacuated sealed tube was heated at 110 °C for 2 h. The solution was cooled to room temperature and the solvent removed *in vacuo*. The residue was subjected to chromatographic work-up using silica-gel TLC plates. Elution with dichloromethane–hexane (40 : 60 v/v)

Table 6 Crystal data and structure refinement for compounds **8**, **12** and **15**

	8	**12**	**15**
Formula	$C_{32.50}H_{20}ClFe_3O_6S_2W_2$	$C_{31}H_{20}Fe_2O_5S_2W_2$	$C_{31}H_{21}Mo_2O_{5.50}$
M	1141.30	507.99	673.36
T/K	294(2)	293(2)	221(2)
λ/Å	0.71073	0.71070	0.71073
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$C2/c$	$Pbcn$
a/Å	21.561(2)	15.0470(3)	13.38(5)
b/Å	8.1880(8)	9.50700(10)	19.69(5)
c/Å	21.932(2)	20.4070(4)	20.15(5)
β/°	116	95.1950(9)	
U/Å^3	3460.0(6)	2907.27(9)	5312(27)
Z	4	4	8
Reflections collected/unique	47103/13421 [R(int) = 0.0454]	3555/2484 [R(int) = 0.0000]	4819/4657 [R(int) = 0.0104]
Final $R1$, $wR2$ [$I > 2\sigma(I)$]	0.0288, 0.0631	0.0197, 0.0506	0.0329, 0.0860
(all data)	0.0608, 0.0705	0.0205, 0.0516	0.0415, 0.0892

afforded the following, in order of elution: dark red band of **10** (15%) and a red band of **15** (35%).

X-Ray crystallographic studies

Details of the crystallographic data collection and refinement parameters are given in Table 6. Crystals of all compounds were grown by slow evaporation of dichloromethane–hexane solvent mixtures. Compound **8** crystallised with disordered solvent molecule of dichloromethane.

[$W_2Fe_3(\eta^5$-$C_5H_5)_2(CO)_6(\mu_3$-$S)_2\{\mu$-CC(Ph)C(Ph)C$\}$] 8. Data were collected on a Bruker AXS SMART 1K CCD (platform with full three circle goniometer). Intensity measurements were performed using graphite monochromated Mo-Kα radiation from a sealed tube. SMART was used for preliminary determination of the cell constants and data collection control. The structure was solved by direct methods using SHELXS 93[28] and subsequent Fourier difference synthesis and refined by full matrix least squares on F^2. For the hydrogen atoms a riding model was employed under restriction of ideal geometry at the corresponding non-hydrogen atom attached. All non-hydrogen atoms were refined anisotropically, while the positions of hydrogen atoms were held fixed.

[$W_2Fe_2(\eta^5$-$C_5H_5)_2(CO)_4(\mu_3$-$S)_2\{\mu$-CC(Ph)(CO)C(Ph)C$\}$] 12. Data were collected on a Nonius Kappa CCD diffractometer with Mo-Kα radiation. A numerical absorption correction was applied. The structure was solved by direct methods using SHELXS 93[28] and refined by full-matrix least squares on F^2 using SHELXL 97.[29] Least squares refinement of scale, positional and anisotropic thermal parameters of non-hydrogen atoms was carried out while the positions of hydrogen atoms were held fixed.

[$\{Mo(\eta^5$-$C_5H_5)(CO)_2\}_2\{\mu$-1,2-η-PhCC(CO)CCPh$\}$] 15. A Nonius MACH3 diffractometer (graphite monochromatised Mo-Kα radiation) was used for the cell determination and intensity data collection. The unit cell parameters were derived and refined using randomly selected reflections in the θ range 11–16.2°. The structure was solved by direct methods using SHELXS 93[28] and refined isotropically. The crystals were of rather poor quality reflected in the poor quality of data. The ψ scans did not give a satisfactory absorption correction and therefore DIFABS[30] was applied to the raw data. The non-hydrogen atoms were refined using SHELXL 97 with anisotropic thermal parameters. All the hydrogen atoms were geometrically fixed and allowed to refine using a riding model.

CCDC reference number 186/2058.

See http://www.rsc.org/suppdata/dt/b0/b003517n/ for crystallographic files in .cif format.

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