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Tail-to-tail carbon–carbon bond coupling of acetylides on chalcogen-bridged Fe/W mixed-metal clusters

Pradeep Mathur,* Moawia O. Ahmed, Aswini K. Dash and Mrinalini G. Walawalkar

Chemistry Department, Indian Institute of Technology, Powai, Bombay-400 076, India

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On thermolysis of a toluene solution containing $[Fe_3(CO)_9(\mu_3\text{-}E)_2]$ (E = S **1a**, Se **16** or Te **1c**) and $[W(\eta^5\text{-}C_5Me_5)_2(CO)_3(C{\equiv}CPh)]$ **2** the new clusters $[W_2Fe_3(\eta^5\text{-}C_5Me_5)_2(CO)_6(\mu_3\text{-}E)_2\{\mu_4\text{-}CC(Ph)C(Ph)C\}]$ (E = S **3**, Se **4** or Te **5**) were isolated. Compounds **3**–**5** were characterised by IR and ^{1}H, ^{13}C, ^{77}Se and ^{125}Te NMR spectroscopy. The crystal structure of **3** was elucidated by X-ray diffraction methods. It shows a novel tail-to-tail coupling of substituted acetylides on a sulfur-bridged mixed-metal Fe–W cluster.

A wide range of organic transformations are supported and catalysed by a variety of inorganic and organometallic compounds, wherein the necessary steric and electronic requirements for such transformations are offered by the metal centres. Amongst these compounds the heteronuclear metal cluster complexes are of considerable interest, as they tend to possess reactivity due to a combination of the different properties of the constituent elements.[1] The preparation of heterometallic compounds, by several groups, using mononuclear acetylide precursors and the generation of acetylide bridged complexes has enriched our knowledge on the reactivity and bonding capability of acetylide ligands.[2–5]

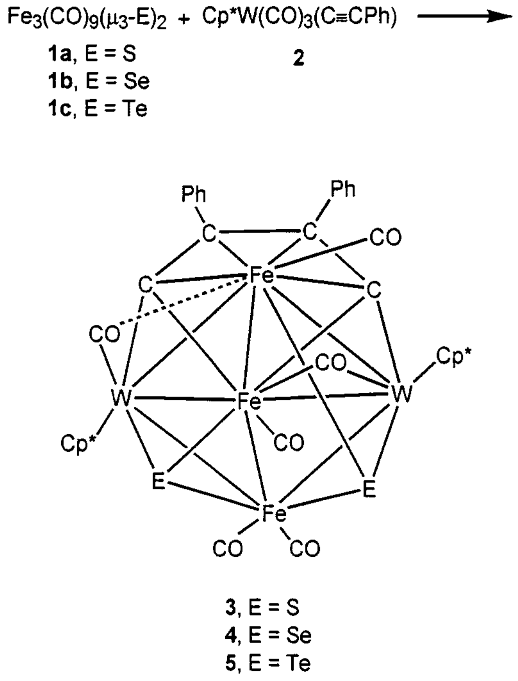
The coupling of terminal and functionalised metal acetylides has been extensively studied recently and through this route a number of polycarbon ligand-containing metal clusters have been realised.[3–5] In several cases it has been observed that either an oxidative or a Cadiot–Chodkiewicz coupling is operative.[6] In principle, there may occur a head-to-head, head-to-tail or a tail-to-tail linkage of acetylides or polyacetylides co-ordinated in a multisite fashion on a metal cluster, and it may be possible to synthesize new multimetallic polycarbon complexes in which the alkynyl groups use the full potential of σ and π electrons in bonding. The use of such a strategy in transition metal cluster chemistry has been limited but there are a few reports describing the stereospecific head-to-head coupling of the acetylide fragments attached to transition metals.[4] There have also been instances wherein a head-to-tail type of coupling of the C≡C unit has been favoured.[5] To our knowledge there is no report concerning the tail-to-tail coupling of monoacetylide groups attached to transition metals during the cluster build-up reactions.

We have a long-standing interest in chalcogenide ligand based cluster chemistry,[7] and have recently examined the aspect of cluster expansion reactions by addition of alkynyl Fischer carbene complexes to chalcogen-bridged metal carbonyl compounds.[8] Continuing our interest in this area, we are currently exploring the possibility of using transition metal acetylides as ligands towards chalcogen-bridged diiron and triiron carbonyl clusters. Here, we report our recent results in this area wherein an hitherto unknown tail-to-tail coupling of the acetylide fragments in a cluster environment has been observed.

Results and discussion

Synthesis and characterisation of $[(W_2Fe_3(\eta^5\text{-}C_5Me_5)_2(CO)_6(\mu_3\text{-}E)_2\{\mu_4\text{-}CC(Ph)C(Ph)C\}]$ (E = S 3, Se 4 or Te 5)

When a toluene solution containing $[Fe_3(CO)_9(\mu_3\text{-}E)_2]$ (E = S **1a**, Se **1b** or Te **1c**) and $[W(\eta^5\text{-}C_5Me_5)(CO)_3(C{\equiv}CPh)]$ **2** was subjected to reflux for 2 h new dark green mixed-metal clusters $[W_2Fe_3(\eta^5\text{-}C_5Me_5)_2(CO)_6(\mu_3\text{-}E)_2\{\mu_4\text{-}CC(Ph)C(Ph)C\}]$ (E = S **3**, Se **4** or Te **5**) were obtained (Scheme 1). The three new clusters are stable in air in the solid state but gradually decompose in solution over a period of hours at room temperature, with the relative stabilities being in the following order: **3** > **4** > **5**. The infrared spectra of **3**–**5** display identical *ν*(CO) patterns with bands corresponding to the presence of both terminal and bridging carbonyl groups. There is a shift of the corresponding bands to lower frequencies along the series **3** > **4** > **5**. The ^{1}H and ^{13}C NMR spectra of all three compounds indicate the presence of non-equivalent η^5-C_5Me_5 groups. For compounds **4** and **5**, the ^{77}Se and ^{125}Te NMR spectra indicate the presence of two types of selenide and telluride ligands respectively. Formation of **3**–**5** highlights the significance of the bridging chalcogen ligands in **1a**–**1c**. Overall, each chalcogen atom in **1a**–**1c** undergoes cleavage of a bond with one of the iron atoms, and formation of a new bond with a tungsten atom of the acetylide complex **2**. The two adding tungsten acetylide units are oriented



Scheme 1

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

C(11)–C(12)	1.428(5)	W(2)–S(2)	2.3174(10)
C(12)–C(13)	1.439(5)	Fe(1)–S(1)	2.1880(13)
C(13)–C(14)	1.421(6)	Fe(2)–S(1)	2.2256(11)
W(1)–C(11)	1.974(4)	Fe(1)–S(2)	2.2169(12)
W(2)–C(14)	1.977(4)	Fe(3)–S(2)	2.2638(12)
Fe(2)–C(11)	2.017(4)	W(1)–C(6)	2.000(5)
Fe(2)–C(14)	1.990(4)	W(2)–C(5)	2.085(4)
Fe(3)–C(11)	2.000(4)	Fe(2)–C(5)	2.035(4)
Fe(3)–C(12)	2.126(4)	Fe(3)–C(6)	2.500(4)
Fe(3)–C(13)	2.155(4)	C(5)–O(5)	1.184(5)
Fe(3)–C(14)	2.023(4)	C(6)–O(6)	1.161(6)
W(1)–Fe(1)	2.8510(6)	Fe(1)–C(1)	1.779(5)
W(2)–Fe(1)	2.8939(6)	Fe(1)–C(2)	1.773(5)
W(1)–Fe(2)	2.6764(6)	Fe(2)–C(3)	1.772(5)
W(2)–Fe(2)	2.5575(6)	Fe(3)–C(4)	1.777(5)
W(1)–Fe(3)	2.8487(6)	C(1)–O(1)	1.140(6)
W(2)–Fe(3)	2.7954(6)	C(2)–O(2)	1.145(6)
Fe(1)–Fe(2)	2.6062(8)	C(3)–O(3)	1.134(6)
Fe(2)–Fe(3)	2.5289(8)	C(4)–O(4)	1.148(6)
W(1)–S(1)	2.3475(10)		
O(5)–C(5)–Fe(2)	134.0(3)	Fe(1)–S(2)–W(2)	79.29(4)
O(5)–C(5)–W(2)	149.1(3)	C(14)–Fe(2)–C(11)	78.23(16)
O(6)–C(6)–W(1)	160.1(4)	C(11)–Fe(3)–C(14)	77.84(16)
O(6)–C(6)–Fe(3)	120.5(4)	C(12)–C(11)–W(1)	151.9(3)
Fe(1)–S(1)–Fe(2)	72.38(4)	C(11)–C(12)–C(13)	113.1(4)
Fe(1)–S(1)–W(1)	77.81(4)	C(14)–C(13)–C(12)	111.8(3)
Fe(1)–S(2)–Fe(3)	86.90(4)	C(13)–C(14)–W(2)	151.9(3)

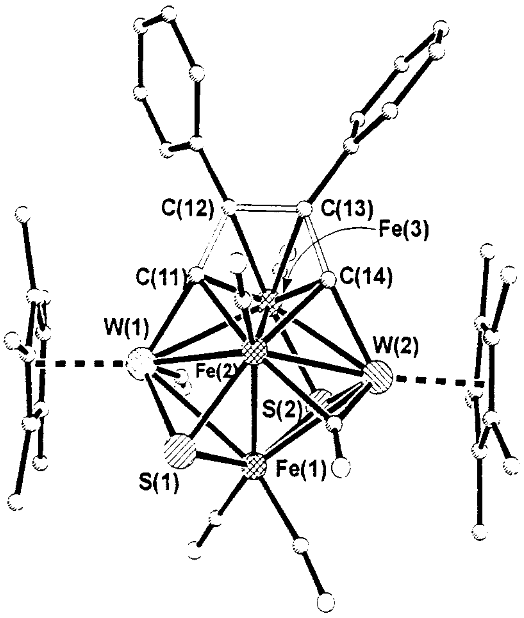


Fig. 1 Crystal structure of compound **3**.

such that the carbon atoms bearing the phenyl substituents are in close proximity to each other and a tail-to-tail acetylide coupling is facilitated.

Molecular structure of compound 3

The molecular structure of $[W_2Fe_3(\eta^5\text{-}C_5Me_5)_2(CO)_6(\mu_3\text{-}S)_2\text{-}\{\mu_4\text{-}CC(Ph)C(Ph)C\}]$ **3** is depicted in Fig. 1. Relevant structural parameters are listed in Table 1. The molecule is made up of a Fe_3W_2 metal core which is enveloped by terminal and bridging carbonyl ligands, and a μ_4-{CC(Ph)C(Ph)C} unit. The five metal atoms are arranged in the form of an open trigonal-bipyramidal polyhedron wherein the three Fe occupy the basal plane while the two W centres are at the axial positions. One of the two Fe–Fe bonds [Fe(2)–Fe(3) 2.5289(8) Å] is somewhat short whereas the second one [Fe(1)–Fe(2) 2.6062(8) Å] is closer to the Fe–Fe bond lengths reported for $[Fe_3(CO)_9(\mu_3\text{-}S_2]$ [2.589(1) and 2.598(1) Å].[9] Each tungsten atom also forms a short bond to one of the iron atoms [W(1)–Fe(2) 2.6764(6) and W(2)–Fe(2) 2.5575(6) Å]. The remaining W–Fe bonds, which lie in the range 2.7954(6)–2.8939(6) Å are similar to the W–Fe bond lengths in $[Fe_2W(CO)_{10}(\mu_3\text{-}Se)_2]$ [2.802(4) and 2.829(4) Å] and in $[Fe_2W(CO)_{10}(\mu_3\text{-}Se)(\mu_3\text{-}Te)]$ [2.840(1) and 2.869(1) Å].[10] Each tungsten atom is bonded to a C_5Me_5 ligand in η^5 fashion and to one carbonyl group. The carbonyl group associated with one of the tungsten atoms symmetrically bridges a Fe–W bond, W(2)–C(5)–O(5) 149.1(3)°, whereas the one which is attached to the other tungsten atom shows a semi-bridging character, W(1)–C(6)–O(6) 160.1(4)°. Among the three iron centres, Fe(1) has two terminal carbonyl groups, while both Fe(2) and Fe(3) atoms bear only one terminal CO group, in addition to the bridging CO ligands described above. Although the two sulfur atoms in the molecule act as triply bridging four electron donors and cap the triangle formed by the two Fe and one W, they show considerable differences in the co-ordination geometry around them. For example, the M–S–M bond angles around S(2) are wider [75.19(3), 79.29(4), 86.90(4)°] than those observed around the S(1) atom [71.58(3), 72.38(4), 77.81(4)°]. The most interesting structural feature of this molecule is the {CC(Ph)C(Ph)C} unit, which acts as an eight electron donor. While the two terminal carbon atoms are μ_3 bridging (two Fe and one W), the carbon atoms bearing the phenyl groups chelate the closest iron atom *viz.* Fe(3), and all the Fe–C bond distances lie in a very narrow range of 1.990(4) to 2.155(4) Å. Bond distances between tungsten and the end carbon atoms of the C_4 hydrocarbon ligand [W(1)–C(11) 1.974(4); W(2)–C(14) 1.977(4) Å] are considerably shorter than the bond length between tungsten and the carbon atom of the acetylide group in the mononuclear acetylide complexes $[W(C\equiv CR)(\equiv CH)(dmpe)_2]$ (R = H, $SiMe_3$ or Ph), which lie in the range 2.245(8) to 2.263(5) Å.[11] Surprisingly, all the C–C distances in the C_4 hydrocarbon ligand in **3** are almost equal and lie within the estimated standard deviation limits [1.421(6), 1.428(5), 1.439(5) Å]. This is in sharp contrast to the previously described examples of head-to-head and head-to-tail C–C coupling reactions of acetylides in the cluster environment which yield C_4 units containing different types of C–C bonds. For example, the C–C bond lengths in the C_4 fragment of head-to-tail coupled product $[C_2Mo_2Os_3(\eta^5\text{-}C_5H_5)_2(CO)_{11}\{CC(Ph)CC(Ph)\}]$ are 1.48(4), 1.44(5), 1.36(5) Å;[5] the corresponding distances in the head-to-head coupled complex $[Ru_4(CO)_8(PPh_2)_2\{C(Bu^t)\text{-}CCC(Bu^t)\}]$ are 1.332(7), 1.366(7), 1.321(7) Å.[4] Spectroscopic features indicate that clusters **4** and **5** are isostructural with **3**.

In conclusion, we have described in this report an unprecedented tail-to-tail coupling of acetylide groups attached to tungsten atoms resulting in the formation of pentanuclear Fe_3W_2 carbonyl clusters stabilised by the newly formed C_4 unit and triply bridging chalcogen caps. The strategy described herein can prove useful in the build-up of cluster complexes that contain unusual hydrocarbon chains.

Experimental

Reactions and manipulations were performed using standard Schlenk techniques under an atmosphere of pre-purified argon. Solvents were purified, dried and distilled under an argon or nitrogen atmosphere prior to use. Infrared spectra were recorded on a Nicolet Impact 400 FT spectrometer as dichloromethane solutions in 0.1 mm path length cells, NMR (^{13}C, ^{77}Se and ^{125}Te) spectra on a Varian VXR-300S spectrometer in $CDCl_3$. The ^{77}Se NMR measurements were made at an operating frequency of 57.23 MHz using 90° pulses with 1.0 s delay and 1.0 s acquisition time and referenced to Me_2Se (δ 0). The ^{125}Te NMR measurements were made similarly at 94.75 MHz and referenced to Me_2Te (δ 0). Elemental analyses were performed on a Carlo-Erba automatic analyser. The compounds $[Fe_3(CO)_9(\mu\text{-}E)_2]$ (E = S, Se or Te)[12] and $[W(\eta^5\text{-}C_5Me_5)(CO)_3(C\equiv CPh)]$[13] were prepared by established procedures.

Table 2 Crystal data and structure refinement for compound **3**

Empirical formula	$C_{42}H_{40}Fe_3O_6S_2W_2$
Formula weight	1240.11
T/K	296(2)
λ/Å	0.71073
Crystal system, space group	Monoclinic, $P2_1/c$
a/Å	18.40570(10)
b/Å	12.6864(10)
c/Å	18.31830(10)
β/°	107.477(5)
V/Å^3	4079.9(3)
Z, D_c/Mg m^{-3}	4, 2.019
μ/mm^{-1}	6.808
F(000)	2392
θ range for data collection/°	2.33 to 28.42
Reflections collected/unique	47204/10101 [R(int) = 0.0401]
Maximum and minimum transmission	0.4283 and 0.0738
Data/restraints/parameters	10101/0/497
Goodness of fit on F^2	1.244
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0291$, $wR2 = 0.0610$
(all data)	$R1 = 0.0356$, $wR2 = 0.0645$
Extinction coefficient	0.00030(4)
Largest difference peak and hole/e Å^{-3}	1.309 and −1.614

Preparation of [$W_2Fe_3(\eta^5\text{-}C_5Me_5)_2(CO)_6(\mu_3\text{-}E)_2\{\mu_4\text{-}CC(Ph)C(Ph)C\}$] (E = S 3, Se 4 or Te 5)

In a typical preparation a toluene solution (50 mL) containing [$W(\eta^5\text{-}C_5Me_5)(CO)_3(C{\equiv}CPh)$] **2** (140 mg, 0.28 mmol) and two equivalents of [$Fe_3(CO)_9(\mu_3\text{-}E)_2$] (E = S **1a**, Se **1b** or Te **1c**) was subjected to reflux for 2 h, during which the reaction mixture changed from dark purple to dark green. It 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: purple **1** (trace), dark green **3**, **4** or **5** and yellow **2** (trace). Compound **3** (57%): IR ν(CO) 1974m, 1939vs, 1788m and 1734m cm^{-1}; ^{1}H NMR δ 7.3–7.1 (m, C_6H_5, 10 H), 1.99 [s, $C_5(CH_3)_5$, 15 H] and 1.92 [s, $C_5(CH_3)_5$, 15 H]; ^{13}C NMR δ 10.6 (CH_3), 11.1 (CH_3), 106.5 [$C_5(CH_3)_5$], 107.8 [$C_5(CH_3)_5$], 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 and 220.4 (CO) (Found: C, 40.5; H, 3.38. $C_{42}H_{40}Fe_3O_6S_2W_2$ requires C, 40.7; H, 3.23%). Compound **4** (33%): IR ν (CO) 1968m, 1936vs, 1777m and 1734m cm^{-1}; ^{1}H NMR δ 7.3–7.1 (m, C_6H_5, 10H), 1.92 [s, $C_5(CH_3)_5$, 15 H] and 1.87 [s, $C_5(CH_3)_5$, 15 H]; ^{13}C NMR δ 11.1 (CH_3), 11.6 (CH_3), 105.7 [$C_5(CH_3)_5$], 107.1 [$C_5(CH_3)_5$], 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 and 222.6 (CO); ^{77}Se NMR δ 872 and 800 (Found: C, 37.5; H, 3.21. $C_{42}H_{40}Fe_3O_6Se_2W_2$ requires C, 37.8; H, 3.00%). Compound **5** (25%): IR ν(CO) 1959m, 1925vs, 1718m and 1608m cm^{-1}; ^{1}H NMR δ 7.26–7.17 (m, C_6H_5, 10 H), 1.93 [s, $C_5(CH_3)_5$, 15 H] and 1.90 [s, $C_5(CH_3)_5$, 15 H]; ^{13}C NMR δ 12.1 (CH_3), 12.4 (CH_3), 104.8 [$C_5(CH_3)_5$], 106.3 [$C_5(CH_3)_5$], 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 and 224.3 (CO); ^{77}Te NMR δ 971.1 and 1157.6 (Found: C, 35.0; H, 2.96. $C_{42}H_{40}Fe_3O_6Te_2W_2$ requires C, 35.2; H, 2.79%).

Crystal structure determination of compound 3

Crystals of compound **3** suitable for X-ray diffraction studies were grown from a dilute dichloromethane–*n*-hexane solution. Intensity data were collected using a 0.6 × 0.4 × 0.15 mm crystal on a SMART CCD detector (SCD system) in the 2θ range 0 to 57°. Data integration was carried out using SAINT program.[14] The structure was solved by direct methods (SHELXS 86)[15] and refined by full-matrix least squares against F^2 using SHELXL 97.[16] All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were geometrically constrained and allowed to ride over the atoms to which they are attached. Final R: $I > 2\sigma(I)$, $R1 = 0.0291$, $wR2 = 0.0610$; all data, $R1 = 0.0356$, $wR2 = 0.0645$. Other relevant data pertaining to cell constants, data collection and structure refinement are listed in Table 2.

CCDC reference number 186/1418.

See http://www.rsc.org/suppdata/dt/1999/1795/ for crystallographic files in .cif format.

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