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A tungstendiiron cluster $[NEt_4][WFe_2\{\mu_3\text{-}\eta^3,\eta^5\text{-}CH{=}C{=}C(^tBu)C(O)C_2B_9H_8Me_2\}(CO)_8]$ derived from $[Fe_2(CO)_9]$ and $[NEt_4][W({\equiv}CC{\equiv}C^tBu)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ *

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Abstract

Treatment of a tetrahydrofuran solution of $[NEt_4][W({\equiv}CC{\equiv}C^tBu)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ with $[Fe_2(CO)_9]$ affords the trimetal complex $[NEt_4][WFe_2\{\mu_3\text{-}\eta^3,\eta^5\text{-}CH{=}C{=}C(^tBu)C(O)C_2B_9H_8Me_2\}(CO)_8]$, the structure of which has been established by X-ray diffraction. The anion has a core based on an essentially isosceles triangle of metal atoms [Fe–Fe 2.663(3), W–Fe 2.811(2) and 2.829(2) Å]. Each iron atom carries three CO groups, whereas the tungsten atom is co-ordinated by two such groups, and by the open face of a *nido*-icosahedral C_2B_9 cage. In the five-membered $\overline{BBBCC}$ ring forming the face of the cage, the boron atom occupying the β site with respect to the two carbon atoms is σ bonded to the carbon atom of a ketonic group [B–C 1.57(3) Å]. The latter in turn is linked to an allenyl fragment $C(^tBu){=}C{=}CH$ [C–C average 1.35(2) Å, C–C–C 150(1)°] which spans the face of the WFe_2 triangle. The terminal CH group is attached to the tungsten and to an iron atom [C–W 2.25(1), C–Fe 1.96(1) Å], and the central carbon is linked to the tungsten atom [C–W 2.07 (1) Å] and also to the second iron atom [C–Fe 2.05(1) Å]. The latter is also bonded to the $C(^tBu)$ fragment [C–Fe 2.20(2) Å] which in turn is connected to the ketonic group [$C(^tBu)$–C(O) 1.47(2) Å] linking the μ_3-C_3 moiety to the cage. The NMR data (^1H, $^{13}C\text{-}\{^1H\}$, and $^{11}B\text{-}\{^1H\}$) for the new cluster compound are reported and discussed.

Introduction

The alkynylmethylidyne compounds $[M({\equiv}CC{\equiv}C^tBu)(CO)_2L]$ {M = Mo or W, L = η^5-C_5H_5, $HB(pz)_3$ [hydrotris(pyrazol-1-yl)borate], or $HB(dmpz)_3$ [hydrotris(3,5-dimethylpyrazol-1-yl)borate]} [1] and $[NEt_4][W({\equiv}CC{\equiv}C^tBu)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ [2] are versatile reagents for preparing mixed-metal complexes. They are particularly interesting precursors since they contain two potentially active sites (C≡M or C≡C) for combination with metal-ligand fragments. Species containing the ligands η^5-C_5H_5 or η^5-$C_2B_9H_9Me_2$ generally react at the C≡M linkages, while the presence of the

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* This paper is dedicated to Professor Peter Pauson on the occasion of his retirement.

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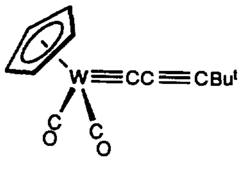
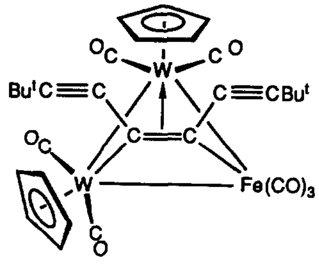


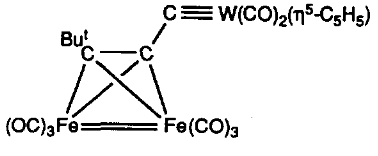
I



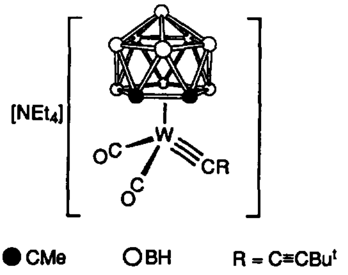
II

more bulky $HB(pz)_3$ or $HB(dmpz)_3$ groups favours addition of metal-ligand fragments at the C≡C bonds. During the course of these studies the reaction between $[W(\equiv CC\equiv C^tBu)(CO)_2(\eta^5\text{-}C_5H_5)]$ (I) and $[Fe_2(CO)_9]$ was investigated, and found to give $[W_2Fe\{\mu_3\text{-}C_2(C\equiv C^tBu)_2\}(CO)_7(\eta^5\text{-}C_5H_5)_2]$ (II) as the major product (ca. 60%), together with small amounts of $[Fe_2\{\mu\text{-}{}^tBuC_2C\equiv W(CO)_2(\eta^5\text{-}C_5H_5)\}(CO)_6]$ (III) [1b]. The latter species evidently results from addition of iron carbonyl fragments to the C≡C bond in I. The pathway to compound II is more complex, however, since its formation involves a coupling of two alkynylmethylidyne groups at some stage. For this process to occur, a plausible intermediate would be a dimetal species of formulation $[WFe(\mu\text{-}CC\equiv C^tBu)(CO)_5(\eta^5\text{-}C_5H_5)]$ in which an $Fe(CO)_3$ group ligates the C≡W bond of I. This intermediate could then react with a second molecule of I to afford compound II via a coupling of two alkynylmethylidyne groups on a trimetal cluster. The various steps in such a pathway have ample precedent [3].

The isolation of the complexes II and III prompted us to study the corresponding reaction between $[Fe_2(CO)_9]$ and the salt $[NEt_4][W(\equiv CC\equiv C^tBu)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ (IV). The latter is isolobal with the reagent I, but the nature of any products obtained in their reactions with low valent metal ligand fragments is likely to be different. This is because the carbaborane ligand frequently adopts a non-spectator role in the chemistry of species of the type $[NEt_4][W(\equiv CR)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ (R = alkyl or aryl) [4], and this is likely to occur also when R is an alkynyl group, as in IV.



III



IV

Results and discussion

Treatment of compound IV in THF (tetrahydrofuran) with $[Fe_2(CO)_9]$ affords a black salt, separated by column chromatography from small amounts of $[Fe_3(CO)_{12}]$ and $[NEt_4][Fe_3(\mu\text{-}H)(CO)_{11}]$, and formulated as $[NEt_4][WFe_2\{\mu_3\text{-}\eta^3,\eta^5\text{-}CH{=}C{=}C({}^tBu)C(O)C_2B_9H_8Me_2\}(CO)_8]$ (V). The nature of this product was not fully established until after an X-ray diffraction study had been carried out. Preliminary examination of the ^1H, $^{13}C\text{-}\{^1H\}$, and $^{11}B\text{-}\{^1H\}$ NMR spectra revealed that an unusual compound had formed. In particular, the $^{13}C\text{-}\{^1H\}$ NMR spectrum showed no resonance indicative of the presence of a ligated carbon atom of a bridging alkynylmethylidyne group [1], and the ^1H spectrum revealed no high-field signal attributable to a $B{-}H{\rightharpoondown}Fe$ three-centre two-electron bond, as in, for example, $[NEt_4][WFe(\mu\text{-}CC_6H_3Me_2\text{-}2,6)(CO)_4(\eta^6\text{-}C_2B_{10}H_{10}Me_2)]$ [5].

The structure of the anion of V is shown in Fig. 1, and selected bond distances and angles are listed in Table 1. The core of the anion consists of a metal triangle [W–Fe(1) 2.811(2), W–Fe(2) 2.829(2), and Fe(1)–Fe(2) 2.663(3) Å]. The two iron atoms each carry three CO ligands, and the tungsten atom has two such groups. The M (W or Fe)–C–O angles are in the range 167 to 176°. Thus although some of the carbonyl ligands are bound essentially terminally to their respective metal centers, others deviate appreciably from linearity, e.g. W–C(6)–O(6) 167(2)° and Fe(1)–C(7)–O(7) 169(2)°. The tungsten atom, as expected, is η^5 co-ordinated by the *nido*-icosahedral C_2B_9 cage system. However, a boron atom in the face of the cage, and in the β site with respect to the two carbon atoms C(1) and C(2) of the $\overline{BB\beta BCC}$ ring, forms a σ bond to the atom C(20). The latter is part of a ketonic group [C(20)–O(20) 1.17(2) Å] linking the cage to an allenyl fragment, C(15)–C(14)–C(13). This C_3 moiety spans the metal triangle, and important distances are C(13)–C(14) 1.32(2), C(14)–C(15) 1.37(2), C(13)–W 2.25(2), C(13)–Fe(1) 1.96(2), C(14)–W

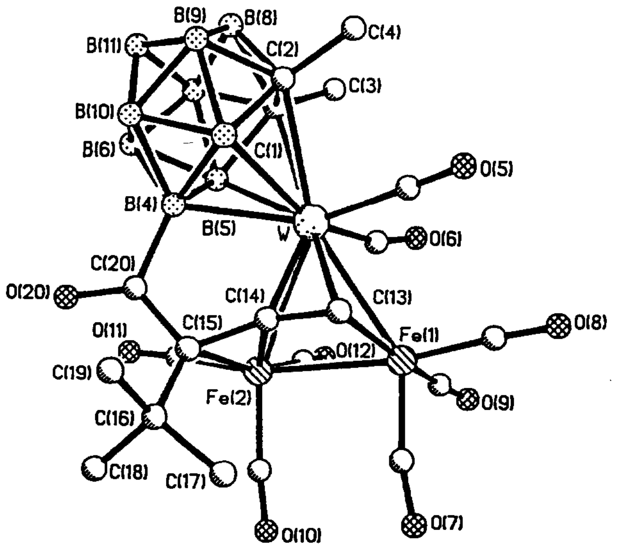


Fig. 1. The structure of the complex anion of the salt $[NEt_4][WFe_2\{\mu_3\text{-}\eta^3,\eta^5\text{-}CH{=}C{=}C({}^tBu)\text{-}C(O)C_2B_9H_8Me_2\}(CO)_8]$ (V) showing the crystallographic numbering scheme.

Table 1

Selected internuclear distances (Å) and angles (°) for the complex $[NEt_4][WFe_2\{\mu_3\text{-}\eta^3,\eta^5\text{-}CH{=}C{=}C(^tBu)C(O)C_2B_9H_8Me_2\}(CO)_8]$ (V)

W–Fe(1)	2.811(2)	W–Fe(2)	2.829(2)	Fe(1)–Fe(2)	2.663(3)	W–B(3)	2.36(2)
W–B(4)	2.35(2)	W–B(5)	2.38(2)	W–C(1)	2.48(2)	W–C(2)	2.47(2)
W–C(5)	1.94(2)	W–C(6)	1.90(3)	W–C(13)	2.25(2)	W–C(14)	2.07(1)
Fe(1)–C(13)	1.96(2)	Fe(2)–C(14)	2.05(1)	Fe(2)–C(15)	2.20(2)	Fe(1)–C(7)	1.77(2)
Fe(1)–C(8)	1.71(3)	Fe(1)–C(9)	1.76(2)	Fe(2)–C(10)	1.73(2)	Fe(2)–C(11)	1.74(2)
Fe(2)–C(12)	1.73(2)	C(1)–C(2)	1.68(3)	C(1)–B(5)	1.64(3)	C(2)–B(3)	1.63(3)
B(3)–B(4)	1.82(3)	B(4)–B(5)	1.81(3)	B(4)–C(20)	1.57(3)	C(5)–O(5)	1.16(3)
C(6)–O(6)	1.17(3)	C(7)–O(7)	1.14(3)	C(8)–O(8)	1.12(3)	C(9)–O(9)	1.11(3)
C(10)–O(10)	1.09(3)	C(11)–O(11)	1.13(2)	C(12)–O(12)	1.10(3)	C(20)–O(20)	1.17(2)
C(13)–C(14)	1.32(2)	C(14)–C(15)	1.37(2)	C(15)–C(16)	1.53(2)	C(15)–C(20)	1.47(2)

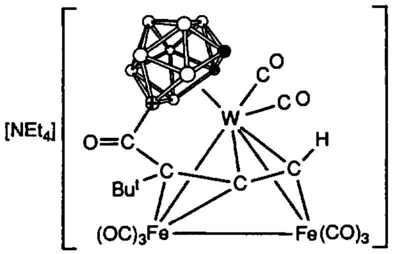
W–Fe(1)–Fe(2)	62.2(1)	W–Fe(2)–Fe(1)	61.5(1)	Fe(1)–W–Fe(2)	56.4(1)
W–Fe(1)–C(13)	52.6(5)	W–Fe(2)–C(14)	47.0(4)	W–C(13)–Fe(1)	83.6(5)
W–C(14)–Fe(2)	86.6(5)	Fe(1)–W–C(13)	43.8(4)	Fe(2)–W–C(13)	70.1(4)
Fe(2)–W–C(14)	46.4(3)	Fe(1)–W–C(14)	59.7(4)	W–Fe(2)–C(15)	75.6(4)
Fe(1)–Fe(2)–C(14)	62.9(4)	Fe(1)–Fe(2)–C(15)	97.1(4)	W–C(13)–C(14)	65.2(8)
W–C(14)–C(13)	79.6(9)	C(13)–W–C(14)	35.2(5)	Fe(1)–C(13)–C(14)	98(1)
W–C(14)–C(15)	129(1)	Fe(2)–C(14)–C(13)	121(1)	Fe(2)–C(14)–C(15)	77(1)
Fe(2)–C(15)–C(14)	66(1)	C(14)–Fe(2)–C(15)	37.5(6)	Fe(2)–C(15)–C(16)	124(1)
Fe(2)–C(15)–C(20)	97(1)	W–B(4)–C(20)	106(1)	B(4)–C(20)–C(15)	118(1)
B(4)–C(20)–O(20)	120(2)	C(15)–C(20)–O(20)	121(1)	C(13)–C(14)–C(15)	150(1)
C(14)–C(15)–C(16)	123(1)	C(14)–C(15)–C(20)	109(1)	C(16)–C(15)–C(20)	122(1)
W–C(5)–O(5)	173(2)	W–C(6)–O(6)	167(2)	Fe(1)–C(7)–O(7)	169(2)
Fe(1)–C(8)–O(8)	176(2)	Fe(1)–C(9)–O(9)	174(2)	Fe(2)–C(10)–O(10)	170(2)
Fe(2)–C(11)–O(11)	176(2)	Fe(2)–C(12)–O(12)	174(2)		

2.07(1), and C(14)–Fe(2) 2.05(1) Å. The carbon–carbon bond distances within the allene ligand are in the range (1.32 to 1.50 Å) for η^3 co-ordinated allene complexes [6] and the central carbon atom C(14) lies closer to the metal atoms than do the terminal carbon atoms, a feature which is commonly observed. Consistent with this, the C(13)–C(14)–C(15) bond angle of 150(1)° is typical of that found for allene groups co-ordinated through both double bonds.

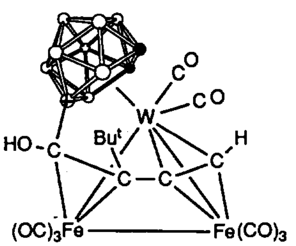
The atom C(15) carries the tertiary butyl group, and although the hydrogen atom on C(13) was not located in the electron density difference map its presence was clearly revealed in the ^1H NMR spectrum, discussed below. The source of this hydrogen atom is presumably the B(4)–H(4) linkage present in the precursor IV.

Having established the structure of V by X-ray diffraction, the spectroscopic data are readily interpreted. The weak and broad absorption at 1620 cm^{-1} in the IR spectrum may be assigned to the ketonic group C(20)–O(20). Examination of the $^{13}C\text{-}\{^1H\}$ NMR spectrum when measured at −55 °C revealed a very broad peak at δ 237.0 ppm which is assigned to C(20). This resonance is not seen in the spectrum measured at ambient temperature, presumably due to the ^{11}B quadrupolar effect and dynamic behaviour exhibited by V. The latter property was demonstrated by changes in the spectrum in the CO region with temperature. At room temperature four CO resonances are observed at δ 220.0, 214.9, 212.4, and 212.0 ppm with relative intensities ca. 1 : 3 : 3 : 1, while at −55 °C five signals are seen at δ 222.5, 218.7, 212.8, 211.3, and 209.0 ppm with relative intensities ca. 1 : 1 : 2 : 3 : 1. A limiting low temperature spectrum indicating the absence of CO site exchange could not be obtained. A peak seen at 72.7 ppm is assigned to C(15), and this signal becomes very broad in the room temperature spectrum. Resonances for the other allenic carbon atoms are observed at δ 163.1 [C(14)] and 95.2 ppm [C(13)]. These assignments are based on earlier studies on compounds with η^3-allenyl ligands [6c]. As expected, the non-equivalence of the CMe groups of the C_2B_9 cage leads to four peaks at δ 66.9 and 61.6 (*C*Me), and 31.8 and 30.6 ppm (C*Me*). Assignment of the two resonances for the ^{t}Bu group seen at δ 36.8 (*C*Me$_3$) and 28.1 ppm (C*Me*$_3$) is based on the observed intensities, and on a $^{13}C\text{-}\{^1H\}$ DEPT NMR spectrum. The ^1H NMR spectrum of V displays all the expected resonances (see Experimental section). The $^{11}B\text{-}\{^1H\}$ NMR spectrum showed a signal at δ 11.4 ppm which remained a singlet in a fully coupled spectrum, characteristic of an *exo*-polyhedral B–C bond [7].

The mechanism for the formation of compound V is complex, and probably involves several intermediates. Based on previous results [8a] it is very likely that a dimetal anionic complex $[WFe(\mu\text{-}CC{\equiv}C^tBu)(CO)_5(\eta^5\text{-}C_2B_9H_9Me_2)]^-$ is initially formed. Addition of a second iron carbonyl fragment to the C≡C group, followed by migration of a cage B–H hydrogen atom to the bridging alkynylmethylidyne group may then occur. The latter process has precedent in the formation of the anion $[WFe\{\mu\text{-}CH(C_6H_4Me\text{-}4)\}(\mu\text{-}\sigma,\eta^5\text{-}C_2B_9H_8Me_2)(\mu\text{-}CO)(CO)_5]^-$ [8b]. A WFe_2 species with a bridging alkylidene fragment might well undergo CO insertion and hydrogen migration to give the product V.



V



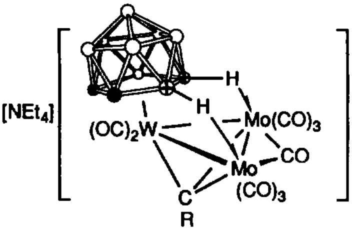
VI

● CMe ○ BH ⊕ B

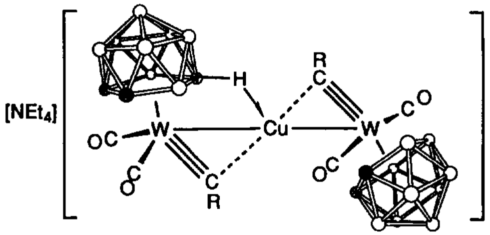
The protonation of V with $HBF_4 \cdot Et_2O$ was attempted, but only with partial success. The product obtained was a green oil which resisted crystallisation. The spectroscopic properties were informative, however, leading us to propose the formulation $[WFe_2\{\mu_3\text{-}CH{=}C{=}C(^tBu)C(OH)C_2B_9H_8Me_2\}(CO)_8]$ (VI), having the structure depicted. The IR spectrum, in addition to showing carbonyl stretching bands (see Experimental section), displayed a broad band at 3481 cm^{-1} assignable to an OH group. In agreement, the ^1H NMR spectrum had a resonance corresponding in intensity to one proton at δ 6.90, a region where signals for an OH group attached to a carbon which is part of a delocalised ring system would occur [9]. Moreover, the hydrogen atom giving rise to this peak underwent exchange with deuterium, since the signal disappeared in the presence of $(CD_3)_2CO$. A singlet resonance at δ 8.17 is assigned to the hydrogen atom of the allylenic moiety. The corresponding peak in the spectrum of compound V occurs at δ 8.13.

The ^{13}C-{^{1}H} NMR spectrum of VI displayed CO resonances at δ 217.1 (WCO), 211.0 (FeCO), 209.4 (FeCO), and 204.3 ppm (WCO), in the ratio 1:3:3:1. The signal observed at 237.0 ppm in the spectrum of V, and assigned to the B*C*(O) nucleus, was not seen in the spectrum of VI. Peaks in the spectrum at δ 136.1 and 87.9 ppm are assigned to the CH=*C*=C(^{t}Bu) and *C*H=C=C(^{t}Bu) nuclei, respectively. A peak assignable to the CH=C=*C*(^{t}Bu) nucleus was not observed, possibly being obscured by solvent resonances. The spectrum also revealed three broad peaks at δ 70.3, 70.2, and 64.3 ppm associated with the two *C*Me and the *C*(OH) groups. The ^{t}Bu signals are observed at δ 36.3 (*C*Me$_3$) and 28.5 (C*Me*$_3$) ppm. The ^{11}B-{^{1}H} NMR spectrum showed a peak at δ 3.4 ppm which may be assigned to the BC(OH) nucleus. In agreement, this resonance remained a singlet in a fully coupled spectrum. Resonances for the other boron nuclei of the carbaborane cage were observed in the expected range of δ −5.8 to −13.1 ppm.

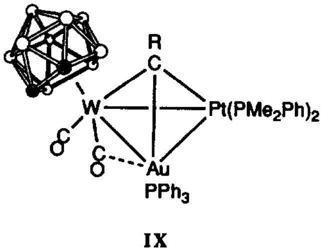
The characterisation of compound V increases the range of known polynuclear metal complex structures obtainable from reactions between the reagent IV and low valent metal species. We have previously reported that the reaction between [Mo(CO)$_3$(NCMe)$_3$] and IV affords the trimetal salt [NEt$_4$][Mo$_2$W(μ_3-CC≡C^{t}Bu)(μ-CO)(CO)$_8$(η^5-C$_2$B$_9$H$_9$Me$_2$)] (VII) [2b]. In this product the alkynylmethylidyne CC≡C^{t}Bu fragment is retained as a structural feature, in contrast with complex V. The CC≡C^{t}Bu group is also preserved in the salt [NEt$_4$][W$_2$Cu(μ-CC≡C^{t}Bu)$_2$(CO)$_4$(η^5-C$_2$B$_9$H$_9$Me$_2$)$_2$] (VIII) obtained by treating two equivalents of IV with one equivalent of CuCl in the presence of TlBF$_4$ [2d]. Other trimetal compounds derived from the reagent IV include the species [WPtAu(μ_3-CC≡C^{t}Bu)(CO)$_2$(PPh$_3$)(PMe$_2$Ph)$_2$(η^5-C$_2$B$_9$H$_9$Me$_2$)] (IX) [2b] and [NEt$_4$][WCu$_2$-Cl$_2$(μ_3-CC≡C^{t}Bu)(CO)$_2$(η^5-C$_2$B$_9$H$_9$Me$_2$)] (X) [2d]. It is noteworthy that the η^5-



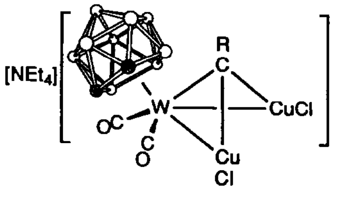
VII



VIII



IX



X

● CMe ○ BH ⊕ B R = C≡CBu^t

$C_2B_9H_9Me_2$ ligands in complexes IX and X adopt a spectator role, in contrast with the situation in the products V–VIII.

Experimental

All experiments were carried out under nitrogen using Schlenk tube techniques. Light petroleum refers to that fraction of b.p. 40–60 °C. All solvents were rigorously dried before use. The compound IV was prepared as described previously [2a]. NMR spectra, measured in CD_2Cl_2, were recorded with JEOL JNM GX 270 and GX 400 spectrometers. Chemical shifts are given in ppm, and coupling constants are in hertz. The ^{11}B chemical shifts are positive to high frequency of $BF_3 \cdot Et_2O$ (external). IR spectra were measured in CH_2Cl_2 with a Perkin–Elmer FT 1600 spectrometer.

Synthesis of the tungstendiiron compounds

(i). Compound IV (0.50 g, 0.80 mmol) in THF (20 cm^3) was treated with an excess of $[Fe_2(CO)_9]$ (0.87 g, 2.4 mmol), and the mixture was stirred for 2 h. Solvent was reduced in volume *in vacuo* to ca. 2 cm^3, and transferred to the top of a chromatography column packed with alumina. Elution with CH_2Cl_2 removed traces of $[Fe_3(CO)_{12}]$ and $[NEt_4][Fe_3(\mu\text{-}H)(CO)_{11}]$, identified by IR spectroscopy. Further elution with CH_2Cl_2-THF (1 : 1) removed a blue-black fraction. Solvent was reduced in volume *in vacuo* to ca. 2 cm^3, and Et_2O (10 cm^3) was added. Removal of supernatant liquid with a syringe afforded, after pumping *in vacuo*, black *microcrystals* of $[NEt_4][WFe_2\{\mu_3\text{-}\eta^3,\eta^5\text{-}CH{=}C{=}C({}^tBu)C(O)C_2B_9H_8Me_2\}(CO)_8]$ (V) (0.30 g, 40%) (Found: C, 36.1; H, 5.8; N, 1.6. $C_{28}H_{44}B_9Fe_2NO_9W$ calc.: C, 35.9; H, 5.3; N, 1.5%); IR: ν_{max}(CO) at 2046vs, 2000vs, 1971s, and 1620w(br) cm^{-1}; ν_{max}(BH) at 2560m(br) cm^{-1}. NMR: ^1H, δ 1.24 (s, 9H, ^{t}Bu), 1.33 [t, 12H, NCH_2*Me*, *J*(HH) 7], 2.22, 2.24 (s × 2, 6H, CMe), 3.37 [q, 8H, NCH_2Me with *H*$_2$, *J*(HH) 7], and 8.13 (s, 1H, CH); $^{13}C\text{-}\{^1H\}$ (at −55 °C), δ 237.0 [B*C*(O)C], 222.5 (WCO), 218.7 (FeCO), 212.8 (2 × FeCO), 211.3 (3 × FeCO), 209.0 (WCO), 163.1 (CH=*C*=C^{t}Bu), 95.2 (*C*H=C=C^{t}Bu), 72.7 (CH=C=*C*^{t}Bu), 66.9, 61.6 (*C*Me), 52.3 (*C*H$_2$Me), 36.8 (*C*Me$_3$), 31.8, 30.6 (C*Me*), 28.1 (C*Me*$_3$), and 7.8 (CH$_2$*Me*); $^{11}B\text{-}\{^1H\}$, δ 11.4 [1B, BC(O)], −6.0 to −13.0 (br, 8B).

(ii). Compound V (0.50 g, 0.54 mmol) in CH_2Cl_2 (10 cm^3) was treated with $HBF_4 \cdot Et_2O$ (90 μl, 0.54 mmol). The colour changed immediately to green. The mixture was stirred for 10 min, solvent was removed *in vacuo*, and the residue was extracted with Et_2O (5 × 10 cm^3). The combined extracts were filtered through a Celite pad (2 × 3 cm) and the olive green solution was reduced in volume *in vacuo* to ca. 2 cm^3. Light petroleum (5 cm^3) was added, and the mixture was cooled to −30 °C for 12 h. After this time removal of the supernatant liquid with a syringe afforded a green oil formulated as $[WFe_2\{\mu_3\text{-}CH{=}C{=}C({}^tBu)C(OH)C_2B_9H_8Me_2\}\text{-}(CO)_8]$ (VI); IR: ν_{max}(CO) at 2070vs, 2028vs, and 2024s cm^{-1}, ν_{max}(OH) at 3481w(br) cm^{-1}, and ν_{max}(BH) at 2560 cm^{-1}. NMR: ^1H, δ 1.23 (s, 9H, ^{t}Bu), 2.16, 2.30 (s × 2, 6H, CMe), 6.90 (s, 1H, OH), and 8.17 (s, 1H, CH); $^{13}C\text{-}\{^1H\}$, δ 217.1 (WCO), 211.0 (3 × FeCO), 209.4 (3 × FeCO), 204.3 (WCO), 136.1 (CH=*C*=C^{t}Bu), 87.9 (*C*H=C=C^{t}Bu), 70.3, 70.2, 64.3 (*C*Me and COH), 36.3 (*C*Me$_3$), 32.1, 30.4 (C*Me*), and 28.5 (C*Me*$_3$).

Table 2

Atomic positional parameters (fractional coordinates $\times 10^4$) for compound V with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
W	1509(1)	1666(1)	396(1)
Fe(1)	1497(2)	2079(1)	1726(1)
Fe(2)	2745(2)	1374(1)	1511(1)
O(5)	−347(16)	2305(7)	393(9)
O(6)	2771(15)	2548(7)	359(8)
O(7)	1230(15)	1934(6)	3210(7)
O(8)	26(18)	2781(8)	1764(10)
O(9)	3040(16)	2754(6)	1939(9)
O(10)	3270(11)	1348(8)	2930(8)
O(11)	4252(10)	759(5)	983(6)
O(12)	4231(12)	2043(6)	1220(18)
O(20)	2232(10)	227(4)	759(6)
N	1637(14)	953(5)	5521(10)
B(3)	645(15)	1091(8)	−244(10)
B(4)	1848(15)	893(7)	76(11)
B(5)	2706(14)	1293(7)	−336(11)
B(6)	2538(17)	761(6)	−680(9)
B(7)	2663(16)	1221(8)	−1215(10)
B(8)	1469(19)	1351(9)	−1501(10)
B(9)	565(17)	1003(7)	−1114(11)
B(10)	1222(18)	629(7)	−625(11)
B(11)	1772(18)	791(8)	−1420(11)
C(1)	2047(13)	1635(7)	−845(8)
C(2)	820(14)	1519(6)	−783(8)
C(3)	2402(16)	2099(6)	−1087(9)
C(4)	47(14)	1865(7)	−1008(9)
C(5)	390(17)	2091(8)	386(11)
C(6)	2335(18)	2200(9)	455(11)
C(7)	1377(16)	1950(6)	2626(11)
C(8)	588(19)	2494(9)	1734(12)
C(9)	2478(20)	2475(7)	1846(10)
C(10)	3009(15)	1328(10)	2391(11)
C(11)	3631(13)	995(7)	1172(8)
C(12)	3615(15)	1800(7)	1326(19)
C(13)	598(11)	1596(5)	1376(8)
C(14)	1266(9)	1266(5)	1279(7)
C(15)	1608(11)	827(5)	1425(7)
C(16)	1225(12)	538(6)	2038(8)
C(17)	788(13)	824(6)	2622(8)
C(18)	2042(15)	245(6)	2320(9)
C(19)	384(15)	242(7)	1742(9)
C(20)	1977(11)	615(5)	775(8)
C(21)	2489(21)	856(7)	5980(12)
C(22)	2494(22)	1104(8)	6677(15)
C(23)	1623(24)	1428(8)	5304(14)
C(24)	1181(35)	1595(8)	4703(11)
C(25)	1743(29)	609(11)	4961(15)
C(26)	2511(26)	647(10)	4484(12)
C(27)	719(21)	918(11)	5859(15)
C(28)	530(17)	443(9)	6214(16)

Crystal structure determination

Crystals of V were grown as black plates by slow diffusion of Et_2O into a CH_2Cl_2 solution of the complex. A crystal of suitable dimensions (ca. $0.65 \times 0.30 \times 0.15$ mm) was sealed in a Lindemann capillary tube under nitrogen, and diffracted intensities were measured (ω scans) on a Siemens R3m/V four-circle diffractometer at 298 K. Of 6707 unique data ($4 \leq 2\theta \leq 50°$), 3753 had $F \geq 3\sigma|F|$, and only these were used in the solution and refinement of the structure, after correction for Lorentz, polarisation, and X – ray absorption effects. The latter correction was by an empirical method based on azimuthal scan data [10].

Crystal data. $C_{28}H_{44}B_9Fe_2NO_9W$, $M = 931.5$, orthorhombic, space group *Pbca* (no. 61), a 13.381(3), b 28.829(4), c 19.144(3) Å, U 7385(2) Å^3, $Z = 8$, D_c 1.68 g cm^{-3}, $F(000) = 3696$, Mo-K_α X-radiation (graphite monochromator), $\bar{\lambda} = 0.71069$ Å, μ(Mo-K_α) 40.0 cm^{-1}.

The molecular structure of V was solved by direct methods. Only the metal atoms were initially located, the lighter atoms being subsequently found by successive difference Fourier syntheses. Hydrogen atoms were included at calculated positions (C–H 0.96 and B–H 1.10 Å) [11] with fixed isotropic thermal parameters (ca. $1.2U_{eq}$ of the parent carbon or boron atom). All other atoms were given anisotropic thermal parameters. Refinement by full matrix least-squares converged at $R = 0.071$ ($R' = 0.062$) with a weighting scheme of the form $w^{-1} = [\sigma^2|F| + 0.0005|F|^2]$ giving a satisfactory analysis of variance. The final electron density difference map showed no peaks ≥ 0.97 or ≤ -0.86 e Å^{-3}.

Calculations were performed on a DEC micro-Vax II computer with the SHELXTL PLUS system of programs [10]. Scattering factors with corrections for anomalous dispersion are from ref. 12. Atomic coordinates for compound V are given in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, comprises H-atom coordinates, thermal parameters, and remaining bond lengths and angles. Structure factors are available from the authors.

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