

Reactions of low valent metal species with the compound $[W(\equiv CSiPh_3)(CO)_2(\eta-C_5H_5)]$; crystal structure of the ketylenyl complex $[WFe\{\mu-C(SiPh_3)CO\}(CO)_5(\eta-C_5H_5)]^*$

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Abstract

Treatment of $[W(\equiv CSiPh_3)(CO)_2(\eta-C_5H_5)]$ with $[Fe_2(CO)_9]$ in Et_2O yields the μ -ketylenyl complex $[WFe\{\mu-C(SiPh_3)CO\}(CO)_5(\eta-C_5H_5)]$, structurally characterized by X-ray diffraction. The very short W–Fe bond (2.516(1) Å) is bridged by the $\mu-C(SiPh_3)CO$ group ($\mu-C-W$ 2.214(6), $\mu-C-Fe$, 2.121(7), $C-CO$ 1.317(9), $CC-O$ 1.164(9) Å). The two CO groups ligating tungsten weakly semi-bridge the metal–metal bond (W–C–O 170°). Treatment of $[W(\equiv CSiPh_3)(CO)_2(\eta-C_5H_5)]$ with $[Pt(C_2H_4)_2(PPR_3^i)]$ in light petroleum affords the unsaturated (30 valence electron) compound $[WPt(\mu-CSiPh_3)(\mu-CO)(CO)(PPR_3^i)(\eta-C_5H_5)]$. Reactions of the latter with CuCl and $[Fe_2(CO)_9]$ have been studied, leading to the isolation of the tri-metal compounds $[WPtCuCl(\mu_3-CSiPh_3)(\mu-CO)(CO)(PPR_3^i)(\eta-C_5H_5)]$, $[WPtFe(\mu_3-CSiPh_3)(\mu-CO)(CO)_4(PPR_3^i)(\eta-C_5H_5)]$, and $[WPtFe(\mu_3-CSiPh_3)(CO)_6(PPR_3^i)(\eta-C_5H_5)]$. The two iron compounds are readily interconverted by addition or removal of CO. NMR data (1H , ^{13}C - $\{^1H\}$, ^{31}P - $\{^1H\}$, or ^{195}Pt - $\{^1H\}$) for the new compounds are reported.

Introduction

The compounds $[M(\equiv CR)(CO)_2L]$ ($M = Cr, Mo$ or W ; $R =$ alkyl or aryl; $L = \eta-C_5H_5, \eta-C_5Me_5$, or $HB(pz)_3$ {hydrotris(pyrazol-1-yl)borate}) are versatile reagents for the synthesis of polynuclear metal compounds with bonds between dissimilar transition elements [1,2]. However, the electronic and steric effects of the R groups and L ligands in the reagents $[M(\equiv CR)(CO)_2L]$ markedly influence the nature of the products obtained [2–4]. Extending our studies in this area, we have investigated

* Dedicated to Professor Ernst Otto Fischer on the occasion of his 70th birthday on 10th November 1988.

reactions of $[\text{Fe}_2(\text{CO})_9]$ and $[\text{Pt}(\text{C}_2\text{H}_4)_2(\text{PPr}_3^i)]$ with the alkylidyne tungsten compound $[\text{W}(\equiv\text{CSiPh}_3)(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ (I), first prepared by Fischer and co-workers [5]. It was anticipated that the presence of the SiPh_3 group in I would lead to the isolation of novel heteronuclear dimetal species different from those isolated from similar reactions involving the compounds $[\text{W}(\equiv\text{CR})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ ($\text{R} = \text{Me}, \text{Ph}, \text{C}_6\text{H}_4\text{Me-4}, \text{C}_6\text{H}_4\text{Me-2}$ or $\text{C}_6\text{H}_3\text{Me}_2\text{-2,6}$).

Results and discussion

Treatment of compound I with $[\text{Fe}_2(\text{CO})_9]$ in Et_2O at room temperature affords the black dimetal complex $[\text{WFe}\{\mu\text{-C}(\text{SiPh}_3)\text{CO}\}(\text{CO})_5(\eta\text{-C}_5\text{H}_5)]$ (II); analytical and spectroscopic data for which are given in Tables 1 and 2. In practice the nature of II was not recognised until the results of an X-ray diffraction study became available. Selected bond distances and angles are listed in Table 3, and the structure is shown in Fig. 1.

The W-Fe bond is spanned by a ketyne ligand $\text{C}(\text{SiPh}_3)\text{CO}$, formed by a combination of the alkylidyne group in I with a CO molecule. The tungsten atom carries the cyclopentadienyl ring and two CO groups, the latter perceptibly semi-bridging the W-Fe bond ($\text{W-C-O} \approx 170^\circ$). The iron centre is ligated by three CO molecules, the Fe-C-O groups being essentially linear. The W-Fe separation (2.516(1) Å) is significantly shorter than those found in several other tungsten-iron compounds we have studied [6] including $[\text{WFe}\{\mu\text{-PPh}_2\text{CHCH}_2\text{C}(\text{C}_6\text{H}_4\text{Me-4})\}(\text{CO})_5(\eta^5\text{-C}_5\text{Me}_5)]$ (2.828(1) Å) [6a], $[\text{WFe}\{\mu\text{-C}(\text{C}_6\text{H}_4\text{Me-4})\text{C}(\text{O})\text{C}(\text{Me})\text{C}(\text{Me})\}(\text{CO})_5(\eta\text{-C}_5\text{Me}_5)]$ (2.722(1) Å) [6b], $[\text{WFe}\{\mu\text{-C}(\text{C}_6\text{H}_4\text{Me-4})\text{C}(\text{Me})\text{C}(\text{Me})\}(\text{CO})_5(\eta\text{-C}_5\text{H}_5)]$ (2.720(1) Å) [6c], $[\text{WFe}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_5\{\text{HB}(\text{pz})_3\}]$ ($\text{HB}(\text{pz})_3 = \text{hydrotris}(\text{pyrazol-1-yl})\text{borate}$) (2.612(2) Å) [6d], and $[\text{NEt}_4][\text{WFe}(\mu\text{CC}_6\text{H}_3\text{Me}_2\text{-2,6})(\text{CO})_5(\eta^5\text{-C}_2\text{B}_9\text{H}_9\text{Me}_2)]$ (2.600(1) Å) [6e]. The data for the last two species have been interpreted in terms of the presence in these compounds of appreciable W=Fe double bonding, and this seems likely in II also, as discussed below.

Table 1

Analytical and other data

Compound	Colour	Yield (%)	$\nu_{\text{max}}(\text{CO})$ (cm^{-1})			Analysis (Found calcd.) (%)	
						C	H
$[\text{WFe}\{\mu\text{-C}(\text{SiPh}_3)\text{CO}\}(\text{CO})_5(\eta\text{-C}_5\text{H}_5)]$ (II)	Black	77	^a 2061s, 1893w,	2026vs, 1854w,	1974s,	47.8 (48.6)	3.0 (2.8)
$[\text{WFe}\{\mu\text{-C}(\text{SiPh}_3)\text{C}(\text{O})\text{O}\}(\text{CO})_5(\eta\text{-C}_5\text{H}_5)]$ (VI)	Orange	— ^b	^a 2069vs, 1945w,	2018s, 1697w	1995s,	47.9 (47.4)	3.0 (2.7)
$[\text{WPt}(\mu\text{-CSiPh}_3)(\mu\text{-CO})(\text{CO})\text{-}(\text{PPr}_3^i)(\eta\text{-C}_5\text{H}_5)]$ (VII)	Red-brown	89	^c 1943vs,	1764m		45.2 (45.1)	4.7 (4.4)
$[\text{WPtCuCl}(\mu_3\text{-CSiPh}_3)(\mu\text{-CO})(\text{CO})\text{-}(\text{PPr}_3^i)(\eta\text{-C}_5\text{H}_5)]$ (VIII)	Red-brown	91	^d 1918sbr,	1775vs		41.8 (40.8)	4.3 (4.1)
$[\text{WFePt}(\mu_3\text{-CSiPh}_3)(\mu\text{-CO})(\text{CO})_4\text{-}(\text{PPr}_3^i)(\eta\text{-C}_5\text{H}_5)]$ (IX)	Brown-purple	73	^d 2023vs, 1846m,	1961s, 1767m	1944s,	43.0 (42.6)	4.0 (3.9)
$[\text{WFePt}(\mu_3\text{-CSiPh}_3)(\text{CO})_6(\text{PPr}_3^i)(\eta\text{-C}_5\text{H}_5)]$ (X)	Dark green	80	^d 2015s, 1934m,	1984s, 1870w	1948vs,	43.7 (42.6)	3.9 (3.8)

^a In Et_2O . ^b Compound formed from II in presence of oxygen (see text). ^c In light petroleum. ^d In thf.

Table 2

 ^1H and ^{13}C - $\{^1\text{H}\}$ NMR data ^a

Com- pound	$\delta(^1\text{H})$	$\delta(^{13}\text{C})$ ^b
II	^c 4.64 (s, 5 H, C ₅ H ₅), 7.1–7.30, 7.51–7.54 (m, 15 H, Ph)	^d 228.3, 218.9 (WCO), 212.0 (br, FeCO), 155.5 (μ -CCO) 137.4, 134.3, 131.1, 129.0, 128.7, 128.4, 128.0 (Ph), 93.7 (C ₅ H ₅), 7.5 (μ -CCO)
VI	^c 5.56 (s, 5 H, C ₅ H ₅), 7.37–7.40, 7.85–7.90 (m, 15 H, Ph)	^e 216.9, [WCO, <i>J</i> (WC) 146], 215.2 [WCO, <i>J</i> (WC) 161], 206.4 (br, FeCO), 165.9 (C=O), 136.2, 135.8, 129.1, 127.5 (Ph), 91.5 (C ₅ H ₅), 64.5 (CSiPh ₃)
VII	^c 1.02 [d of d, 18 H, Me, <i>J</i> (PH) 15, <i>J</i> (HH) 7], 2.05 (m, 3 H, CHMe ₂), 4.96 (s, 5 H, C ₅ H ₅), 7.20–7.26, 7.93–8.04 (m, 15 H, Ph)	^c 339.4 [d, μ -C, <i>J</i> (PC) 31, <i>J</i> (PtC) 382, <i>J</i> (WC) 150], 235.0 [d, CO, <i>J</i> (PC) 5, <i>J</i> (PtC) 131, <i>J</i> (WC) 186], 136.8, 136.4, 129.4, 127.8 (Ph), 91.9 (C ₅ H ₅), 25.2 [d, CHMe ₂ , <i>J</i> (PC) 24], 20.3 (Me)
VIII	^c 1.01 [d of d, Me, 18 H, <i>J</i> (PH) 15, <i>J</i> (HH) 7], 1.90 (m, 3 H, CHMe ₂), 4.73 (s, 5 H, C ₅ H ₅), 7.15–7.30, 8.00–8.10 (m, 15 H, Ph)	^f 303.7 [dbr, μ_3 -C, <i>J</i> (PC) 28], 235.9 [d, CO, <i>J</i> (PC) 6], 229.8 [CO, <i>J</i> (WC) 167], 136.9, 132.2, 130.3, 128.4 (Ph), 93.2 (C ₅ H ₅), 25.8 [d, CHMe ₂ , <i>J</i> (PC) 25], 19.9, 19.7 (Me)
IX	^g 0.94 [d of d, Me, 9 H, <i>J</i> (PH) 15, <i>J</i> (HH) 7], 1.02 [d of d, 9 H, Me, <i>J</i> (PH) 15, <i>J</i> (HH) 7], 2.32 (m, 3 H, CHMe ₂), 5.21 (s, 5 H, C ₅ H ₅), 7.30–7.40, 7.60–7.70 (m, 15 H, Ph)	^f 315.8 [d, μ_3 -C, <i>J</i> (PC) 28], 250.7 (μ -CO), 230.0 [d, WCO, <i>J</i> (PC) 9], 217.0 (br, FeCO), 138.2, 136.8, 129.4, 128.0 (Ph), 93.8 (C ₅ H ₅), 24.4 [d, CHMe ₂ , <i>J</i> (PC) 26], 20.1, 19.9 (Me)
X	^g 1.04 [d of d, Me, 9 H, <i>J</i> (PH) 15, <i>J</i> (HH) 7], 1.24 [d of d, 9 H, Me, <i>J</i> (PH) 14, <i>J</i> (HH) 7], 2.71 (m, 3 H, CHMe ₂), 5.54 (s, 5 H, C ₅ H ₅), 7.20–7.38, 7.57–7.61 (m, 15H, Ph)	^g 302.7 [d, μ_3 -C, <i>J</i> (PC) 14], 137.5, 137.4, 129.3, 128.0 (Ph), 94.6 (C ₅ H ₅), 27.8 [d, CHMe ₂ , <i>J</i> (PC) 22], 20.0, 19.7 (Me)

^a Chemical shifts (δ) in ppm, coupling constants in Hz. Measurements at room temperature unless otherwise stated. ^b Hydrogen-1 decoupled, chemical shifts are positive to high frequency of SiMe₄ (0.0 ppm). ^c In C₆D₆. ^d In thf/C₆D₆ (10/1). ^e In CDCl₃. ^f In CD₂Cl₂/CH₂Cl₂ at –60 °C. ^g In CD₂Cl₂.

The presence of the μ - η^1 -ketenyl ligand in II is of major interest in several respects. This group has an extensive chemistry, since it can ligate both mono- and di-metal centres [7]. For dimetal compounds both μ - η^1 and μ - η^2 bonding modes have been identified by X-ray diffraction studies. The μ - η^2 form of attachment, with both carbon atoms of the C(R)CO group linked to metal centres, is found in the heteronuclear dimetal compound [WPt{ μ -C(C₆H₄Me-4)CO}(CO)(PMe₃)(cod)(η -C₅H₅)] (cod = cycloocta-1,5-diene) [8] and also in the tetra-metal compound [W₃Ru(μ -CO)(μ_3 - η -CO){ μ -C(Ph)CO}(μ -CPh)(μ_3 -CPh)(CO)(PMePh₂)(η -C₅H₅)₃] [9]. In dimetal complexes the μ - η^1 structure, as found in compound II, also occurs in [MnRe{ μ -C(Ph)CO}(CO)₆(η -C₅H₅)] [10], and in the homonuclear species [Mn₂{ μ -C(C₆H₄Me-4)CO}(CO)₆(η -C₅H₅)] [11] and [Fe₂{ μ -C(H)CO}(μ -CO)(CO)₂(η -C₅H₅)₂][PF₆] [12]. Attack of CO on ligated alkylidyne groups to produce the ketenyl ligand may proceed by an inter- or an intra-molecular process. Indeed, the former has been established for the complex [Fe₂(μ -CH)(μ -CO)(CO)₂(η -C₅H₅)₂][PF₆] [12]. Whatever mechanism is involved for CO addition to alkylidyne ligands, ketenyl moieties bridging dimetal centres have been implicated as intermediates in several reactions [6b,13–17], reflecting the importance of this group.

Table 3

Selected internuclear distances (Å) and angles (°) for $[\text{WFe}(\mu\text{-C}(\text{SiPh}_3)\text{CO})(\text{CO})_5(\eta\text{-C}_5\text{H}_5)]$ (II), with estimated standard deviations in parentheses

W-Fe	2.516(1)	W-C(1)	1.949(5)
W-C(51)	2.31(1)	W-C(52)	2.32(1)
W-C(55)	2.34(1)	Fe-C(3)	1.806(8)
Fe-C(6)	2.121(7)	C(1)-O(1)	1.162(7)
C(4)-O(4)	1.13(1)	C(5)-O(5)	1.129(9)
C(7)-O(7)	1.164(9)	Si-C(21)	1.871(5)
W-C(2)	1.953(8)	W-C(6)	2.214(6)
W-C(53)	2.31(1)	W-C(54)	2.36(1)
Fe-C(4)	1.806(8)	Fe-C(5)	1.782(7)
C(2)-O(2)	1.16(1)	C(3)-O(3)	1.13(1)
C(6)-C(7)	1.317(9)	C(6)-Si	1.873(5)
Si-C(31)	1.878(7)	Si-C(41)	1.867(7)
C(1)-W-C(2)	88.3(3)	Fe-W-C(6)	52.8(2)
C(4)-Fe-C(5)	92.5(3)	W-Fe-C(6)	56.3(2)
Fe-C(3)-O(3)	179.7(8)	Fe-C(4)-O(4)	174.1(7)
W-C(6)-C(7)	103.7(4)	Fe-C(6)-C(7)	101.2(4)
C(7)-C(6)-Si	117.6(5)	C(6)-C(7)-O(7)	177.7(6)
C(21)-Si-C(31)	108.9(3)	C(6)-Si-C(41)	110.0(3)
C(3)-Fe-C(4)	99.2(4)	C(3)-Fe-C(5)	92.8(3)
W-C(1)-O(1)	169.7(7)	W-C(2)-O(2)	169.8(7)
Fe-C(5)-O(5)	179.5(7)	W-C(6)-Fe	70.9(2)
W-C(6)-Si	127.0(3)	Fe-C(6)-Si	126.1(4)
C(6)-Si-C(21)	109.8(2)	C(6)-Si-C(31)	108.7(3)
C(21)-Si-C(41)	110.2(3)	C(31)-Si-C(41)	109.3(3)

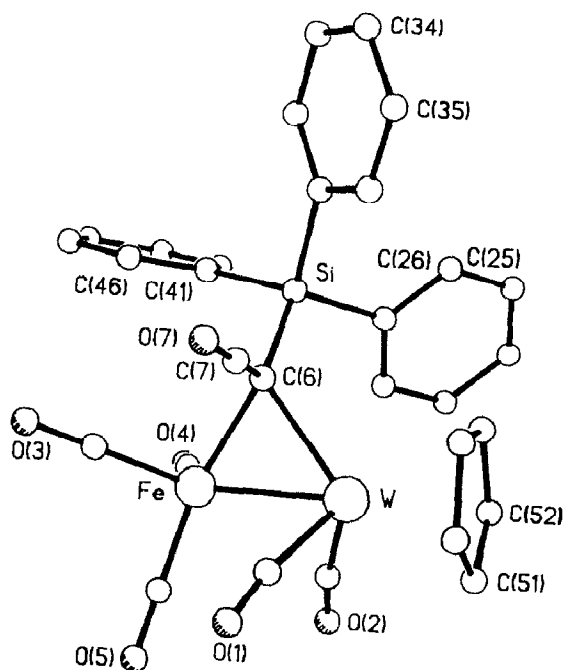


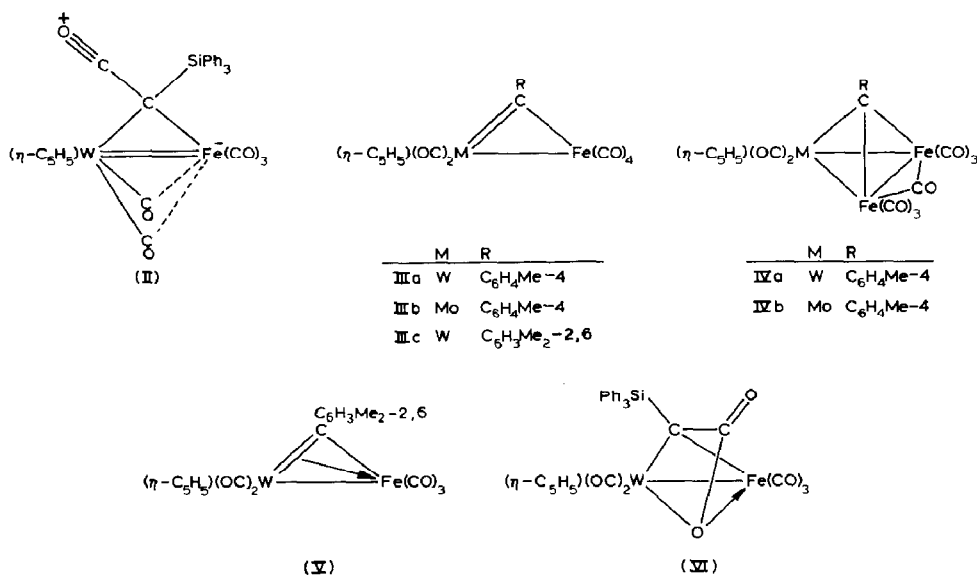
Fig. 1. The molecular structure of $[\text{WFe}(\mu\text{-C}(\text{SiPh}_3)\text{CO})(\text{CO})_5(\eta\text{-C}_5\text{H}_5)]$ (II) showing the crystallographic numbering scheme.

In II, the C(6)–C(7) (1.317(9) Å) and C(7)–O(7) (1.164(9) Å) distances are similar to those found (C–C, C–O) in [MnRe{ μ -C(Ph)CO}(CO)₆(η -C₅H₅)] (1.32(4), 1.18(4) Å) [10], [Mn₂{ μ -C(C₆H₄Me-4)CO}(CO)₆(η -C₅H₅)] (1.326(6), 1.167(5) Å) [11], and [Fe₂{ μ -C(H)CO}(μ -CO)(CO)₂(η -C₅H₅)₂][PF₆] (1.338(8), 1.135(7) Å) [12]. The earlier data for the Mn–Re, Mn–Mn and Fe–Fe species have been interpreted as indicating resonance between acylium and ketene resonance forms:



However, the previously mentioned very short metal–metal bond in II leads us to prefer the acylium formulation shown below for this species, with a formal W=Fe bond and a negative charge on the iron centre.

The formation of II is surprising in view of results obtained earlier. The compounds [M(\equiv CC₆H₄Me-4)(CO)₂(η -C₅H₅)] (M = Mo or W) react with [Fe₂(CO)₉] to give the bridging alkylidyne complexes III and IV [18]. Even though an excess of [Fe₂(CO)₉] was used in the syntheses of II, no trimetal complex was obtained. The reaction between the alkylidyne-tungsten compound [W(\equiv CC₆H₃Me₂-2,6)(CO)₂(η -C₅H₅)] and [Fe₂(CO)₉] affords the electronically unsaturated 32 valence electron complex [WFe(μ -CC₆H₃Me-2,6)(CO)₅(η -C₅H₅)] (V); carbon monoxide saturated solutions of which yield the unstable but electronically saturated species IIIc [2]. The formation of 32 valence-electron iron tricarbonyl derivatives like V is favoured by the presence of bulky substituents on the alkylidyne-carbon atom or on the tungsten centre [3b,6d,19]. It might therefore have been expected that I and [Fe₂(CO)₉] would initially have afforded an unstable saturated “Fe(CO)₄” intermediate [WFe(μ -CSiPh₃)(CO)₆(η -C₅H₅)], which would readily decarbonylate



to give $[\text{WFe}(\mu\text{-CSiPh}_3)(\text{CO})_5(\eta\text{-C}_5\text{H}_5)]$. Evidently however, an electronic effect of the SiPh_3 substituent leads to formation of the ketenyl complex II. This could arise via intramolecular carbonyl migration in $[\text{WFe}(\mu\text{-CSiPh}_3)(\text{CO})_6(\eta\text{-C}_5\text{H}_5)]$ or by capture of a molecule of CO by the coordinatively unsaturated complex $[\text{WFe}(\mu\text{-CSiPh}_3)(\text{CO})_5(\eta\text{-C}_5\text{H}_5)]$.

The spectroscopic data for II can be interpreted following determination of the structure by X-ray diffraction. In the IR spectrum (Table 1) there are five bands in the CO region. Those at 1893 and 1854 cm^{-1} may be ascribed to the two semi-bridging ligands C(1)O(1) and C(2)O(2). The remaining three bands (2061, 2026 and 1974 cm^{-1}) may be assigned to the $\text{Fe}(\text{CO})_3$ and $\text{C}(\text{SiPh}_3)\text{CO}$ groups. In dimetal compounds with $\mu\text{-}\eta^1$ -ketenyl ligands the CO absorption occurs in the range 1850–2100 cm^{-1} [7], and in the cation $[\text{Fe}_2\{\mu\text{-C}(\text{H})\text{CO}\}(\mu\text{-CO})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)_2]^+$ the band is at 2092 cm^{-1} [12].

The $^{13}\text{C}\text{-}\{^1\text{H}\}$ NMR spectrum of II (Table 2) shows two resonances attributable to the tungsten-ligated CO groups at δ 228.3 and 218.9 ppm. There is a very broad peak at δ 212.0 ppm which may be assigned to the $\text{Fe}(\text{CO})_3$ fragment. The CO ligands of the latter evidently undergo site-exchange at room temperature. However, cooling the sample to -60°C produced no change in the spectrum. Assignment of the peaks for the μ -ketenyl group is more difficult, but a signal at δ 155.5 ppm is likely to be due to the carbonyl-carbon of the $\text{C}(\text{SiPh}_3)\text{CO}$ fragment, and a resonance at δ 7.5 ppm is probably due to the $\text{C}(\text{SiPh}_3)$ nucleus. In the $^{13}\text{C}\text{-}\{^1\text{H}\}$ NMR spectrum of $[\text{Fe}_2\{\mu\text{-C}(\text{H})\text{CO}\}(\mu\text{-CO})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)_2]^+$ the corresponding resonances have been firmly assigned at δ 162.6 and 27.5 ppm, respectively [12].

During the synthesis of II, and during handling of the compound, small amounts of an orange material formed. Column chromatography of the mixture, eluting with light petroleum/thf (tetrahydrofuran) (3/2), allowed isolation of an orange complex which was identified as $[\text{WFe}\{\mu\text{-C}(\text{SiPh}_3)\text{C}(\text{O})\text{O}\}(\text{CO})_5(\eta\text{-C}_5\text{H}_5)]$ (VI). This species, which results from reaction of II with oxygen, is similar to the compound $[\text{WFe}\{\mu\text{-C}(\text{C}_6\text{H}_4\text{Me-4})\text{C}(\text{O})\text{O}\}(\text{CO})_5(\eta\text{-C}_5\text{Me}_5)]$ previously obtained from $[\text{WFe}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_5(\eta\text{-C}_5\text{Me}_5)]$ and oxygen, and characterised by X-ray diffraction [19]. A band in the IR spectrum of VI at 1697 cm^{-1} may be assigned to the $\text{C}=\text{O}$ group. A similar band occurs at 1685 cm^{-1} in the IR spectrum of $[\text{WFe}\{\mu\text{-C}(\text{C}_6\text{H}_4\text{Me-4})\text{C}(\text{O})\text{O}\}(\text{CO})_5(\eta\text{-C}_5\text{Me}_5)]$.

The $^{13}\text{C}\text{-}\{^1\text{H}\}$ NMR spectrum of VI (Table 2) shows resonances for the two tungsten-ligand CO groups at δ 216.9 and 215.2 ppm, and there is broad peak at δ 206.4 ppm due to the $\text{Fe}(\text{CO})_3$ moiety. When the spectrum is measured at -60°C the latter signal is replaced by three peaks at δ 210.7, 207.5 and 206.7 ppm. Evidently at the lower temperatures site-exchange of the carbonyl ligands attached to the iron ceases on the NMR time-scale. A resonance in the $^{13}\text{C}\text{-}\{^1\text{H}\}$ NMR spectrum of VI at δ 165.9 ppm is ascribed to the $\text{C}=\text{O}$ group present in the $\mu\text{-C}_3$ fragment. In the $^{13}\text{C}\text{-}\{^1\text{H}\}$ NMR spectrum of $[\text{WFe}\{\mu\text{-C}(\text{C}_6\text{H}_4\text{Me-4})\text{C}(\text{O})\text{O}\}(\text{CO})_5(\eta\text{-C}_5\text{Me}_5)]$ the signal for the $\text{C}=\text{O}$ group occurs at δ 163.4 ppm [19].

The reaction between I and $[\text{Pt}(\text{C}_2\text{H}_4)_2(\text{PPr}_3^1)]$ in light petroleum gave a red-brown product, characterised as the complex $[\text{WPt}(\mu\text{-CSiPh}_3)(\mu\text{-CO})(\text{CO})(\text{PPr}_3^1)(\eta\text{-C}_5\text{H}_5)]$ (VII) (Tables 1, 2 and 4). The IR spectrum in the carbonyl stretching region showed two bands at 1943 and 1674 cm^{-1} . The latter absorption strongly suggests that one of the CO ligands bridges the metal-metal bond.

The $^{13}\text{C}\text{-}\{^1\text{H}\}$ NMR spectrum of VII was informative. The observation of one

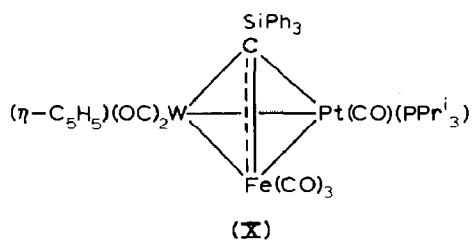
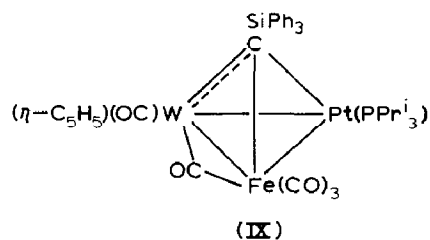
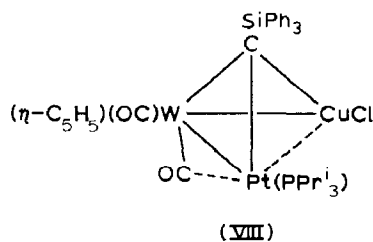
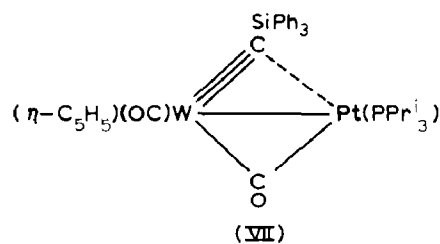
Table 4

 ^{31}P - $\{^1\text{H}\}$ and ^{195}Pt - $\{^1\text{H}\}$ NMR data ^a

Compound	$\delta(^{31}\text{P})$ ^b	$\delta(^{195}\text{Pt})$ ^c
VII	^d 78.7 [$J(\text{PtP})$ 5281]	^d 493.2 [d, $J(\text{PPt})$ 5281, $J(\text{WPt})$ 175]
VIII	^d 79.5 [$J(\text{PtP})$ 5322]	^{e,f} 747.4 [d, $J(\text{PPt})$ 5322, $J(\text{WPt})$ 186]
IX	^f 91.8 [$J(\text{PtP})$ 5200]	^g -112.6 [d, $J(\text{PPt})$ 5200]
X	^g 59.9 [$J(\text{PtP})$ 3555]	^g 27.5 [d, $J(\text{PPt})$ 3555]

^a Chemical shifts (δ) in ppm, coupling constants in Hz. Measurements at room temperature unless otherwise stated. ^b Chemical shifts to high frequency of 85% H_3PO_4 (external). ^c Chemical shifts to high frequency of $\Xi(^{195}\text{Pt})$ 21.4 MHz. ^d In C_6D_6 . ^e -20°C . ^f In $\text{CD}_2\text{Cl}_2/\text{CH}_2\text{Cl}_2$. ^g In CD_2Cl_2 .

CO resonance (δ 235.0 ppm) implies that at room temperature the two CO ligands undergo site-exchange between terminal and bridging positions. However, the occurrence of ^{31}P and ^{195}Pt couplings on the CO signal is in accord with the IR evidence for a bridging carbonyl group. The resonance at δ 339.4 ppm is diagnostic for a $\mu\text{-C}$ nucleus bridging a W–Pt bond [20]. The signal is a doublet due to ^{31}P – ^{13}C coupling (31 Hz), and there are ^{195}Pt and ^{183}W satellite peaks ($J(\text{PtC})$ 382, $J(\text{WC})$ 150 Hz). The values of the coupling constants suggest, however, that the $\mu\text{-CSiPh}_3$ ligand asymmetrically bridges the W–Pt bond. Generally when $\mu\text{-C}$ groups span W–PtPR₃ linkages the ^{13}C – ^{31}P , ^{13}C – ^{195}Pt and ^{13}C – ^{183}W coupling constants are remarkably constant at ca. 60, 750 and 140 Hz, respectively. The relatively low ^{31}P – ^{13}C and ^{195}Pt – ^{13}C couplings observed for VII are in agreement with the asymmetrically bridging alkylidyne formulation depicted, which would imply 18 and 14 electron configurations at the tungsten and platinum centres, respectively. It may be noted that heteronuclear dimetal compounds in which an alkylidyne ligand asymmetrically bridges the metal–metal bond are well established [21]. The ^{31}P - $\{^1\text{H}\}$ NMR spectrum of VII (Table 4) shows a singlet signal at δ 78.7 ppm, as expected.



The magnitude (5281 Hz) of the ^{31}P - ^{195}Pt coupling suggests a transoid arrangement for the W-Pt-PPr_3^1 group [20].

It was of interest to establish whether low-valent metal fragments would add to VII in an extension to the methodology employed earlier to prepare trimetal compounds containing dissimilar transition elements [1]. Treatment of VII with CuCl in thf gave the complex $[\text{WPtCuCl}(\mu_3\text{-CSiPh}_3)(\mu\text{-CO})(\text{CO})(\text{PPr}_3^1)(\eta\text{-C}_5\text{H}_5)]$ (VIII) (Tables 1, 2 and 4). Two CO bands are observed in the IR spectrum. The absorption at 1775 cm^{-1} suggests the presence of a semi-bridging or bridging environment for one of these groups. This is supported by the $^{13}\text{C}\text{-}\{^1\text{H}\}$ NMR spectrum, since one of the two CO resonances shows $^{31}\text{P}\text{-}^{13}\text{C}$ coupling (6 Hz) (Table 2). The $\mu_3\text{-C}$ nucleus resonates at δ 307.7 ppm.

It is unlikely that VII contains a direct Cu-Pt bond, even though both metal centres have 14 electron-shells. Only one compound with a $\mu_3\text{-CWPtCu}$ core structure $[\text{WPtCu}(\mu_3\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_2(\text{PMe}_3)_2(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_5\text{Me}_5)]$ has been described previously. An X-ray diffraction study revealed the absence of a copper-platinum bond [22].

The reaction between VII and $[\text{Fe}_2(\text{CO})_9]$ was next investigated. If the two reagents are mixed in Et_2O , with a nitrogen purge through the mixture, the product isolated after column chromatography is the pentacarbonyl compound $[\text{WFePt}(\mu_3\text{-CSiPh}_3)(\mu\text{-CO})(\text{CO})_4(\text{PPr}_3^1)(\eta\text{-C}_5\text{H}_5)]$ (IX). Data for this species are given in Tables 1, 2 and 4. If the two reagents are mixed in Et_2O , and the mixture treated with a stream of CO gas, the reaction product is the hexacarbonyl compound $[\text{WFePt}(\mu_3\text{-CSiPh}_3)(\text{CO})_6(\text{PPr}_3^1)(\eta\text{-C}_5\text{H}_5)]$ (X), also characterised by the data given in Tables 1, 2 and 4. In solution the two complexes exist in equilibrium in the presence of CO. Excess of carbon monoxide affords X, while a nitrogen purge of the mixture yields IX.

The presence of the bridging CO ligand in IX is indicated by the band at 1767 cm^{-1} in the IR spectrum. Moreover, the absorption at 1846 cm^{-1} suggests that another CO group semi-bridges one of the metal-metal bonds. In the $^{13}\text{C}\text{-}\{^1\text{H}\}$ NMR spectrum the resonance at δ 250.7 ppm may be ascribed to the $\mu\text{-CO}$ ligand on the basis of its chemical shift. The signal at 230.0 ppm, a doublet ($J(\text{PC})$ 9 Hz), would then be assigned to a CO group semi-bridging the W-Pt bond. The broad peak at δ 217.0 ppm is characteristic for an $\text{Fe}(\text{CO})_3$ group undergoing dynamic behaviour.

The IR spectrum of X in the carbonyl region shows no evidence for a bridging ligand, apart from a weak absorption at 1870 cm^{-1} , which may be due to a semi-bridging group. The molecule undergoes rapid site-exchange of the CO ligands on the NMR time-scale since in the $^{13}\text{C}\text{-}\{^1\text{H}\}$ spectrum measured at room temperature no carbonyl resonances are observed (Table 2). However, at -80°C signals are seen at δ 223.6, 222.1 (WCO), 219.2, 217.4, 214.6 (FeCO), and 187.5 ppm (PtCO, $J(\text{PC})$ ca. 12 Hz). This pattern corresponds to that expected for a low temperature limiting spectrum.

In their $^{13}\text{C}\text{-}\{^1\text{H}\}$ NMR spectra both compounds show characteristic doublet resonances for the $\mu_3\text{-C}$ nuclei (δ 315.8 (IX) and 302.7 ppm (X), with $J(\text{PC})$ 28 and 14 Hz, respectively). The $^{31}\text{P}\text{-}\{^1\text{H}\}$ and $^{195}\text{Pt}\text{-}\{^1\text{H}\}$ NMR spectra (Table 4) are as expected. However, the relatively low $^{31}\text{P}\text{-}^{195}\text{Pt}$ coupling found for X (3555 Hz), compared with VII-IX, is in accord with the presence of the CO ligand terminally bound to platinum.

Compound X is not the first of this class. We have previously reported [20c] the complexes $[\text{WFePt}(\mu_3\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_6(\text{PR}_3)(\eta\text{-C}_5\text{H}_5)]$ ($\text{PR}_3 = \text{PMePh}_2$, PMe_3 or PEt_3), which were prepared from reactions between $[\text{WPt}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_2(\text{PR}_3)_2(\eta\text{-C}_5\text{H}_5)]$ and $[\text{Fe}_2(\text{CO})_9]$. The structure of the PEt_3 derivative was established by X-ray diffraction. An interesting feature of this structure was the presence of an asymmetric $\mu\text{-CC}_6\text{H}_4\text{Me-4}$ ligand having only a weak interaction with the platinum centre. In view of the relatively deshielded $\mu_3\text{-C}$ resonance in the $^{13}\text{C}\text{-}\{^1\text{H}\}$ NMR spectra of IX and X a similar asymmetry of alkylidyne-metal bonding may well be present in these species also [20c.23].

The results described herein show that I is a useful precursor to a variety of heteronuclear di- or tri-metal compounds. Moreover, compounds II, VII, VIII and IX represent structural types not previously identified in reactions involving alkylidyne tungsten species.

Experimental

All experiments were carried out under nitrogen by Schlenk tube techniques. Light petroleum refers to that fraction of b.p. 40–60°C. The compound $[\text{W}(\equiv\text{CSiPh}_3)(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ was prepared by the method described in the literature [5]. The reagent $[\text{Pt}(\text{C}_2\text{H}_4)_2(\text{PPr}_3^i)]$ was generated in situ by treating an ethylene-saturated light petroleum solution of $[\text{Pt}(\text{cod})_2]$ ($\text{cod} = \text{cyclooctadiene}$) with an equivalent amount of the phosphine PPr_3^i , a method previously employed for related complexes [24]. NMR spectra were recorded with JEOL JNM FX90Q, GX270 and GX400 spectrometers, and IR spectra were measured with Nicolet MX5 and MX10 spectrometers.

Reactions of $[\text{W}(\equiv\text{CSiPh}_3)(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$

(i) A mixture of I (0.58 g, 1.0 mmol) and $[\text{Fe}_2(\text{CO})_9]$ (0.55 g, 1.5 mmol) was stirred in Et_2O (30 cm^3) at room temperature for 3 h. Carbon monoxide was evolved and removed by pumping in vacuo ca. every 15 min. After removal of solvent in vacuo, the residue was redissolved in Et_2O (30 cm^3) and treated with additional $[\text{Fe}_2(\text{CO})_9]$ (0.09 g, 0.25 mmol) for 3 h. Solvent was again removed in vacuo, and the residue was extracted with Et_2O (6 \times 5 cm^3). The extracts were chromatographed on a silica gel column (50 \times 3 cm). Elution with light petroleum/ Et_2O (1/1) removed a purple eluate. The latter, after removal of solvent in vacuo and washing the residue with light petroleum, gave black microcrystals of $[\text{WFe}(\mu\text{-C}(\text{SiPh}_3)\text{CO})(\text{CO})_5(\eta\text{-C}_5\text{H}_5)]$ (II) (0.55 g).

(ii) A sample of $[\text{Pt}(\text{cod})_2]$ (0.20 g, 0.49 mmol) in light petroleum (15 cm^3) at 0°C was treated with a stream of C_2H_4 , and PPr_3^i (0.50 mmol, 0.50 cm^3 of a 1.0 mmol dm^{-3} solution in light petroleum) was added to generate $[\text{Pt}(\text{C}_2\text{H}_4)_2(\text{PPr}_3^i)]$. The solution was transferred via a cannula into a suspension of I (0.28 g, 0.49 mmol) in light petroleum (20 cm^3) at 0°C. The mixture was slowly warmed to room temperature and stirred for 8 h. It was then filtered through a Celite pad (ca. 2 cm). Removal of solvent in vacuo, and washing the residue with light petroleum (2 \times 5 cm^3 at 0°C), gave red-brown microcrystals of $[\text{WPt}(\mu\text{-CSiPh}_3)(\mu\text{-CO})(\text{CO})(\text{PPr}_3^i)(\eta\text{-C}_5\text{H}_5)]$ (VII) (0.41 g).

(iii) A mixture of (VII) (0.06 g, 0.064 mmol) and CuCl (0.02 g, 0.20 mmol) was stirred in thf (10 cm^3) at room temperature for 10 min. The red-brown reaction

mixture was filtered through a Celite pad. Solvent was removed in vacuo, and the residue was washed with light petroleum ($2 \times 10 \text{ cm}^3$) affording red-brown microcrystals of $[\text{WPtCuCl}(\mu_3\text{-CSiPh}_3)(\mu\text{-CO})(\text{CO})(\text{PPr}_3^1)(\eta\text{-C}_5\text{H}_5)]$ (VIII) (0.06 g).

(iv) A mixture of VII (0.06 g, 0.064 mmol) and $[\text{Fe}_2(\text{CO})_9]$ (0.04 g, 0.11 mmol) was stirred in Et_2O (15 cm^3) at room temperature for 1 h, under a gentle stream of nitrogen. The mixture was then passed through a Celite pad, and solvent was removed in vacuo. The residue was dissolved in the minimum of thf (ca. 10 cm^3) and chromatographed on a Florisil column ($15 \times 1.5 \text{ cm}$) at -20°C . Elution initially with light petroleum (ca. 50 cm^3) to remove traces of $[\text{Fe}_3(\text{CO})_{12}]$ followed by light petroleum/thf (4/1) gave a purple eluate. Removal of solvent in vacuo gave brown-purple microcrystals of $[\text{WFePt}(\mu_3\text{-CSiPh}_3)(\mu\text{-CO})(\text{CO})_4(\text{PPr}_3^1)(\eta\text{-C}_5\text{H}_5)]$ (IX) (0.05 g).

(v) Compound VII (0.06, 0.064 mmol) and $[\text{Fe}_2(\text{CO})_9]$ (0.04, 0.11 mmol) were stirred in Et_2O (15 cm^3) for 2 h at room temperature, giving a dark green solution. The latter was then treated with a stream of CO for 3 min. Solvent was removed in vacuo, and the residue was dissolved in the minimum of thf (ca. 10 cm^3) and chromatographed on Florisil ($15 \times 1.5 \text{ cm}$ column, at -20°C). Elution with light petroleum (ca. 50 cm^3) removed traces of $[\text{Fe}_3(\text{CO})_{12}]$. Elution with light petroleum/thf (4/1) gave a green eluate. Removal of solvent in vacuo afforded dark green microcrystals of $[\text{WFePt}(\mu_3\text{-CSiPh}_3)(\text{CO})_6(\text{PPr}_3^1)(\eta\text{-C}_5\text{H}_5)]$ (X) (0.06 g).

Crystal structure determination

Crystals of II were grown from dichloromethane/light petroleum (1/4). Diffracted intensities were collected at 293 K from a crystal of dimensions ca. $0.50 \times 0.40 \times 0.13 \text{ mm}$ on a Nicolet P3m diffractometer. Of the 5261 data collected (Wyckoff ω -scans, $2\theta \leq 50^\circ$), 4211 unique data had $I \geq 2.5\sigma(I)$, and only these were used for structure solution and refinement. The data were corrected for Lorentz and polarisation effects and for X-ray absorption, the latter by an analytical method [25].

Crystal data. $\text{C}_{30}\text{H}_{20}\text{FeO}_6\text{SiW}$, $M = 744.3$, triclinic, space group $P\bar{1}$, a 9.077(2), b 15.759(3), c 10.955(2) Å, α 89.89(2), β 105.57(2), γ 67.70(2)°, U 1387.1(5) Å³, $Z = 2$, D_c 1.78 g cm⁻³, $F(000) = 724$, Mo- K_α X-radiation (graphite monochromator), $\bar{\lambda}$ 0.71069 Å, $\mu(\text{Mo-}K_\alpha)$ 48.4 cm⁻¹.

The structure was solved by conventional heavy-atom methods, and successive difference Fourier syntheses were used to locate all non-hydrogen atoms, which were refined with anisotropic thermal parameters. Hydrogen atoms were included in calculated positions (C-H 0.96 Å) with fixed isotropic thermal parameters ca. $1.2 \times U_{\text{equiv}}$ of the parent carbon atoms. Refinement by blocked-cascade least squares led to $R = 0.038$ ($R' = 0.038$) with a weighting scheme of the form $w^{-1} = [\sigma^2(F) + 0.00078|F|^2]$ giving a satisfactory analysis of variance. The final electron density difference synthesis showed no peaks > 2.4 or $< -1.8 \text{ e \AA}^{-3}$, the largest lying close to the tungsten atom. All calculations were performed on a Data General 'Eclipse' computer with the SHELXTL system of programs [25]. Scattering factors with corrections for anomalous dispersion were taken from reference [26]. The atom coordinates are given in Table 5. Full listing of bond distances and angles, and thermal parameters have been deposited with the Cambridge Crystallographic Data

Table 5

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

Atom	x	y	z
W	211(1)	2390(1)	203(1)
Fe	2598(1)	2361(1)	-571(1)
C(1)	2331(8)	1595(4)	1400(6)
O(1)	3449(7)	1103(4)	2219(5)
C(2)	759(8)	3448(5)	705(5)
O(2)	886(7)	4113(4)	1077(5)
C(3)	4261(9)	1512(6)	-1062(7)
O(3)	5300(7)	985(5)	-1373(7)
C(4)	2288(8)	3370(5)	-1555(6)
O(4)	2130(8)	4033(4)	-2077(6)
C(5)	4007(7)	2582(5)	741(6)
O(5)	4894(6)	2720(4)	1579(5)
C(6)	681(8)	1967(4)	-1628(5)
C(7)	1423(8)	1060(5)	-1406(6)
O(7)	2059(8)	257(4)	-1252(5)
Si	-731(2)	2481(1)	-3271(1)
C(21)	-2529(7)	3545(4)	-3176(5)
C(22)	-2324(8)	4292(5)	-2587(7)
C(23)	-3669(9)	5060(5)	-2521(7)
C(24)	-5272(9)	5117(5)	-3048(8)
C(25)	-5507(8)	4395(5)	-3638(7)
C(26)	-4148(8)	3611(5)	-3705(6)
C(31)	-1544(7)	1616(4)	-4026(5)
C(32)	-1819(10)	1560(5)	-5329(6)
C(33)	-2538(12)	974(7)	-5915(8)
C(34)	-2944(10)	427(5)	-5228(8)
C(35)	-2679(10)	472(5)	-3958(8)
C(36)	-1989(9)	1057(5)	-3358(7)
C(41)	443(7)	2766(4)	-4259(5)
C(42)	-148(8)	3626(4)	-4969(6)
C(43)	711(10)	3818(5)	-5716(6)
C(44)	2198(10)	3149(6)	-5783(6)
C(45)	2808(9)	2297(6)	-5095(7)
C(46)	1958(8)	2114(5)	-4340(6)
C(51)	-1291(12)	2683(9)	1665(9)
C(52)	-2410(12)	3208(7)	443(13)
C(53)	-2528(11)	2552(9)	-330(8)
C(54)	-1643(13)	1695(7)	312(9)
C(55)	-913(11)	1783(8)	1500(9)

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Structure factors are available from the authors.

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