

Preliminary communication

ADDITION OF METHYLENE GROUPS TO THE UNSATURATED COMPLEX $[\text{FeW}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_5(\eta\text{-C}_5\text{Me}_5)]$: μ -ALKENYL LIGAND REARRANGEMENTS AT A DIMETAL CENTRE

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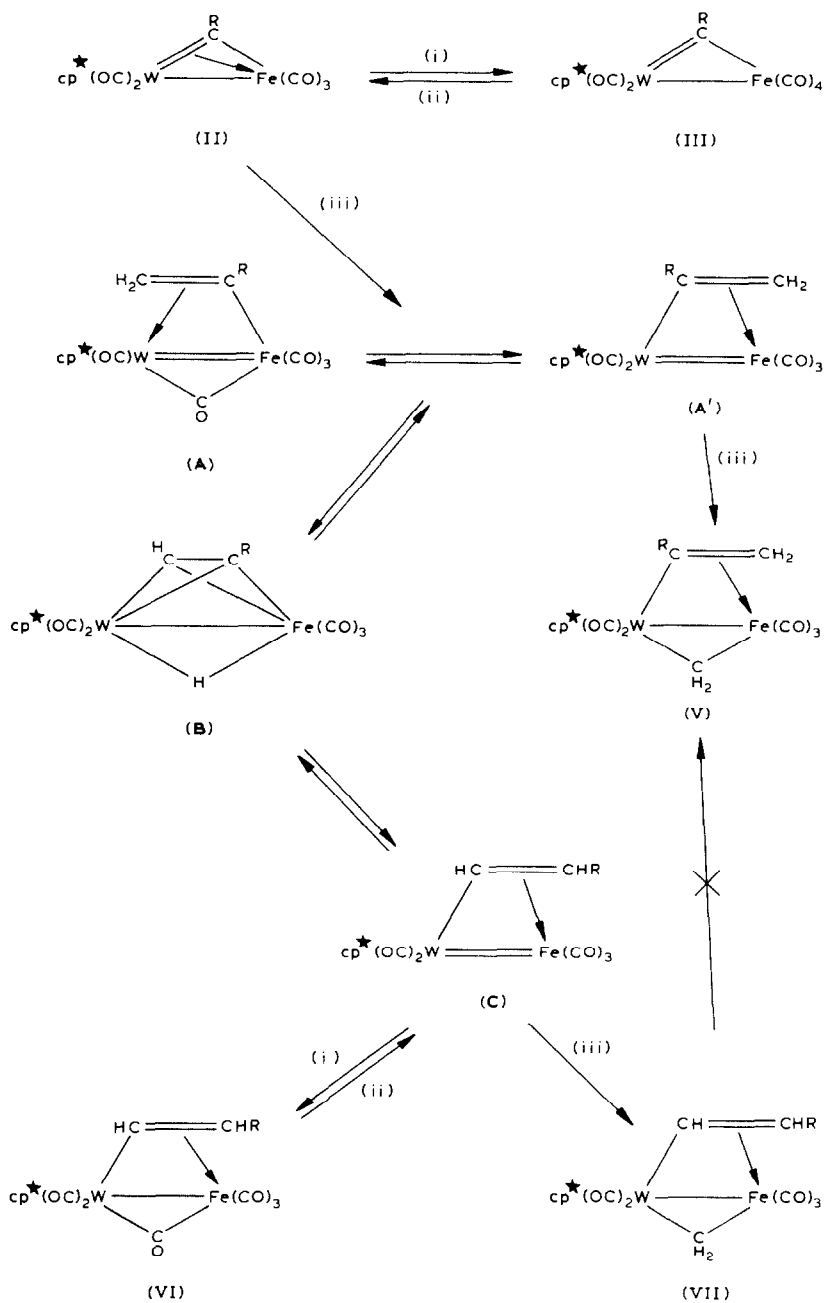
Summary

The unsaturated heteronuclear dimetal complex $[\text{FeW}(\mu\text{-CC}_6\text{H}_4\text{Me-4})(\text{CO})_5(\eta\text{-C}_5\text{Me}_5)]$ reacts with diazomethane to afford products corresponding to addition of either one or two methylene groups across the metal–metal bond.

The reactivity of alkylidyne or alkylidene groups when functioning as bridging ligands in dimetal compounds is currently a topic of interest in the context of hydrogenation of carbon monoxide, olefin dimerisation, acetylene oligomerisation, methylene transfer reactions, and other processes [1]. Most studies have involved homo-dinuclear metal complexes; the majority of these being electronically saturated, albeit with labile ligands. Herein we report the synthesis of an unsaturated heteronuclear dimetal compound which undergoes stepwise reaction with two methylene groups derived from diazomethane.

Treatment of the complex $[\text{W}(\equiv\text{CR})(\text{CO})_2(\eta\text{-C}_5\text{Me}_5)]$ ($\text{R} = \text{C}_6\text{H}_4\text{Me-4}$) (I) [2] with $[\text{Fe}(\text{CO})_3(\eta\text{-C}_8\text{H}_{14})_2]$ [3] in hexane at -50°C affords mainly the purple coloured compound $[\text{FeW}(\mu\text{-CR})(\text{CO})_5(\eta\text{-C}_5\text{Me}_5)]$ (II), together with small amounts of brown $[\text{FeW}(\mu\text{-CR})(\text{CO})_6(\eta\text{-C}_5\text{Me}_5)]$ (III) and brown $[\text{Fe}_2\text{W}(\mu_3\text{-CR})\text{-}(\mu\text{-CO})(\text{CO})_8(\eta\text{-C}_5\text{Me}_5)]$ (IV). Reaction between I and one equivalent of $[\text{Fe}_2(\text{CO})_9]$ in diethyl ether gives the same products, but with a relatively high yield (ca. 20%) of III [4]. Treatment of II with CO gives III which in vacuo tends to reform II via loss of CO. Compound IV may be prepared (ca. 60%) by treating I with three equivalents of $[\text{Fe}_2(\text{CO})_9]$ in diethyl ether. The related trimetal compound $[\text{Fe}_2\text{W}(\mu_3\text{-CR})(\mu\text{-CO})(\text{CO})_8(\eta\text{-C}_5\text{H}_5)]$ has been studied extensively [5].

*Dedicated to Professor Rafael Uson on the occasion of his 60th birthday on March 27th, 1986.



SCHEME 1. $\text{cp}^* = \eta\text{-C}_5\text{Me}_5$, $\text{R} = \text{C}_6\text{H}_4\text{Me-4}$. (i) $+\text{CO}$, (ii) $-\text{CO}$, (iii) CH_2N_2 .

In II, a 32 valence electron complex, the $\text{W}(\equiv\text{CR})(\text{CO})_2(\eta\text{-C}_5\text{Me}_5)$ fragment can be regarded formally as donating four electrons to the $\text{Fe}(\text{CO})_3$ group. The resonance for the $\mu\text{-CR}$ group in the $^{13}\text{C}\text{-}\{^1\text{H}\}$ NMR spectrum of II is ca. 54 ppm more deshielded than the corresponding signal for the alkyldiyn group in the spectrum of the 34 valence electron complex III [4]. A similar trend has been

observed in the $^{13}\text{C}\{-^1\text{H}\}$ NMR spectra of the compounds $[\text{FeW}(\mu\text{-CR})(\text{CO})_n(\eta\text{-C}_5\text{H}_5)]$ ($\mu\text{-C}$: $n = 5$, δ 392.5; $n = 6$, δ 331.3 ppm) and $[\text{FeW}(\mu\text{-CR})(\text{CO})_n(\text{HBpz}_3)]$ ($\text{HBpz}_3 = \text{hydrotis}(\text{pyrazol-1-yl})\text{borato}$) ($\mu\text{-C}$: $n = 5$, δ 408.8; $n = 6$, δ 290.9 ppm) [6, 7].

Complex II reacts readily with diazomethane, but the nature of the products depends markedly on the conditions employed. With excess of CH_2N_2 in Et_2O at -20°C , in the presence of CuCl catalyst, the green-brown complex $[\text{FeW}(\mu\text{-CR}=\text{CH}_2)(\mu\text{-CH}_2)(\text{CO})_5(\eta\text{-C}_5\text{Me}_5)]$ (V) is formed (ca. 50%) [8] (Scheme 1). If, however, II is treated slowly (1 h) with one equivalent of CH_2N_2 , the dark green compound $[\text{FeW}(\mu\text{-CH}=\text{CHR})(\mu\text{-CO})(\text{CO})_5(\eta\text{-C}_5\text{Me}_5)]$ (VI) is produced (ca. 50%) [8], together with a small amount of a mixture (ca. 2/3) of the complexes V and $[\text{FeW}(\mu\text{-CH}=\text{CHR})(\mu\text{-CH}_2)(\text{CO})_5(\eta\text{-C}_5\text{Me}_5)]$ (VII) [8]. Compound VI is separable by column chromatography from the $\mu\text{-CH}_2$ isomers V and VII. The stereochemistries of their bridging alkenyl groups are unequivocally established from the NMR data. Thus, for example, in the ^1H NMR spectrum of VI the observation of a 13 Hz coupling for the two CH protons of the vinyl group is diagnostic for a *trans*-CH=CHR arrangement [9].

Possible pathways to V and VI are shown in Scheme 1. Methylene group transfer to a bridging alkyldiyne group to give an alkenyl bridge, as in intermediate A, has been observed previously [1g]. Moreover, the $\sigma\text{-}\pi$ interconversion $A \rightleftharpoons A'$ is well established [9, 10], and would be expected to be facile for these unsaturated species. Predominant formation of the saturated complex V with excess of CH_2N_2 is thus understandable. With slow addition of CH_2N_2 to II the intermediates A and A' may have sufficient life time to rearrange via B to C. The latter could then capture CO or CH_2 to give the observed products VI or VII. The proposed intermediate B is structurally akin to the salts $[\text{W}_2(\mu\text{-H})(\mu\text{-RC}_2\text{R})(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2][\text{BF}_4]$ ($\text{R} = \text{Me}$ or $\text{C}_6\text{H}_4\text{Me-4}$) [11]. It is possible to reverse at least partially the pathway to VI. The latter reacts slowly with an excess of CH_2N_2 affording a mixture (ca. 1/4) of V and its isomer VII. Solutions of complex VII do not rearrange on standing to give V.

The chemistry described herein illustrates the high reactivity of the unsaturated complex II, and demonstrates the advantage of using a heteronuclear dimetal species in this field [1].

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- 2 This new complex was prepared by treating $[W(=CR)Br(CO)_4]$ with KC_5Me_5 in tetrahydrofuran. For I: $\nu(CO)(max)$ at 1981s and 1910s cm^{-1} (in hexane). $^{13}C\{-^1H\}$ NMR (in CD_2Cl_2/CH_2Cl_2), δ 301.3 (CR, $J(WC)$ 211 Hz) and 225.4 ppm (CO, $J(WC)$ 193 Hz).
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- 4 Selected spectroscopic data for II, III and IV. (IR measured in hexane, unless otherwise stated. $^{13}C\{-^1H\}$ NMR in CD_2Cl_2/CH_2Cl_2 , measured at ambient temperatures unless otherwise stated, coupling constants in Hz). Compound II: $\nu(CO)(max)$ 2045s, 1987s, 1970s, 1873w and 1851w $br\ cm^{-1}$. $^{13}C\{-^1H\}$ NMR (at $-70^\circ C$), δ 395.4 (μ -CR, $J(WC)$ 156), 228.9 ($W(CO)_2$, $J(WC)$ 175) and 216.3 ppm ($Fe(CO)_3$). Compound III: $\nu(CO)(max)$ 2068s, 2014m, 1991s, 1936m and 1873w cm^{-1} . $^{13}C\{-^1H\}$ NMR, δ 341.8 (br, μ -CR), 242.9 (br, $W(CO)_2$) and 216.6 ppm (br, $Fe(CO)_3$). Compound IV: $\nu(CO)(max)$ 2058m, 2018s, 2006s, 1965m, 1942sh, 1902w br, and 1769w $br\ cm^{-1}$ (in CH_2Cl_2). $^{13}C\{-^1H\}$ NMR, δ 276.2 ppm (μ_5 -CR, $J(WC)$ 83).
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- 7 Unlike II, both the unsaturated ($n = 5$) and saturated ($n = 6$) complexes $[FeW(\mu-CR)(CO)_n(\eta-C_5H_5)]$ are unstable, making studies of their reactions at best difficult. In contrast, II is relatively stable, may be purified by chromatography on Florisil, and gives satisfactory analytical data. It is thus evident that the presence of the $\eta-C_5Me_5$ ligand in II stabilises this unsaturated species.
- 8 Selected spectroscopic data for V, VI and VII (IR measured in hexane. NMR in CD_2Cl_2 (1H) and $CD_2Cl_2-CH_2Cl_2$ ($^{13}C\{-^1H\}$) at room temperature unless otherwise stated, coupling constants in Hz). Compound V: $\nu(CO)(max)$ 2039s, 1991s, 1977m, and 1921w cm^{-1} ; NMR, 1H , δ 1.34 (d, 1 H, $\mu-CH_2$, $J(HH)$ 4), 1.78 (s, 15 H, C_5Me_5), 1.87 (s, 1 H, $\mu-CR=CH_2$), 2.29 (s, 3 H, Me-4), 3.55 (s, 1 H, $\mu-CR=CH_2$), 4.04 (d, 1 H, $\mu-CH_2$, $J(HH)$ 4), and 7.01, 7.16 ((AB) $_2$, 4 H, C_6H_4 , J_{AB} 8); $^{13}C\{-^1H\}$ (at $-60^\circ C$), δ 225.3 (WCO, $J(WC)$ 129), 220.8 (WCO, $J(WC)$ 134), 214.6 (br, $Fe(CO)_3$), 181.4 ($\mu-CR=CH_2$, $J(WC)$ 67), 156.8, 136.3, 129.6, 127.6 (C_6H_4), 97.7 (C_5Me_5), 89.9 ($\mu-CH_2$, $J(WC)$ 58), 74.2 ($\mu-CR=CH_2$), 21.2 (Me-4) and 10.5 ppm (C_5Me_5); ^{13}C (at $-30^\circ C$), δ 89.9 (apparent t, $\mu-CH_2$, $J(CH)$ 143) and 74.2 ppm (apparent t, $\mu-CR=CH_2$, $J(CH)$ 156). Compound VI: $\nu(CO)(max)$ 2045m, 1993s, 1977m, 1939w and 1742m cm^{-1} . NMR, 1H , δ 1.99 (s, 15 H, C_5Me_5), 2.27 (s, 3 H, Me-4), 3.85 (d, 1 H, $\mu-CH=CHR$, $J(HH)$ 13), 7.06, 7.14 ((AB) $_2$, 4 H, C_6H_4 , J_{AB} 8) and 8.14 (d, 1 H, $\mu-CH=CHR$, $J(HH)$ 13); $^{13}C\{-^1H\}$ (at $-40^\circ C$), δ 281.6 ($\mu-CO$), 223.0 (WCO, $J(WC)$ 129), 220.5 (WCO, $J(WC)$ 148), 213.0 (br, $Fe(CO)_3$), 139.8, 137.7, 127.0, 125.8 (C_6H_4), 120.4 ($\mu-CH=CHR$, $J(WC)$ 58), 101.4 ($\mu-CH=CHR$), 99.2 (C_5Me_5), 21.4 (Me-4) and 10.5 ppm (C_5Me_5). Compound VII: NMR, 1H , δ 1.99 (s, 15 H, C_5Me_5), 1.87 (d, 1 H, $\mu-CH_2$, $J(HH)$ 4), 2.29 (s, 3 H, Me-4), 4.17 (d, 1 H, $\mu-CH=CHR$, $J(HH)$ 14), 4.18 (d, 1 H, $\mu-CH_2$, $J(HH)$ 4), 7.09, 7.19 ((AB) $_2$, C_6H_4 , J_{AB} 8), and 8.30 (d, 1 H, $\mu-CH=CHR$, $J(HH)$ 14); $^{13}C\{-^1H\}$, δ 225.5, 222.3 (br, $W(CO)_2$), 214.0 (br, $Fe(CO)_3$), 134.8 ($\mu-CH=CHR$, $J(WC)$ 62), 99.6 (br, $\mu-CH=CHR$), 88.2 ($\mu-CH_2$, $J(WC)$ 61); ^{13}C , δ 134.8 (d, $\mu-CH=CHR$, $J(CH)$ 140), 88.2 ppm (apparent t, $\mu-CH_2$, $J(CH)$ 139).
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