SYNTHESIS OF UNSATURATED METHYL(ALKYLIDYNE)DITUNGSTEN COMPLEXES, $[W_2(\mu-CR)(Me)(CO)_3(\eta-C_5H_5)_2]$ (R = C₆H₄Me-4 OR C₆H₄OMe-2); CRYSTAL STRUCTURE OF THE COMPOUND WITH R = C₆H₄OMe-2

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Abstract—In light petroleum at reflux temperatures, the compounds $[W(Me)(\eta-C_2H_4)(CO)_2(\eta-C_3H_5)]$ and $[W(\equiv CR)(CO)_2(\eta-C_5H_5)]$ (R = C₆H₄Me-4 or C₆H₄OMe-2) afford the ditungsten complexes $[W_2(\mu-CR)(Me)(CO)_3(\eta-C_5H_5)_2]$. The structure of the product with R = C₆H₄OMe-2 has been established by X-ray diffraction. The W—W bond (2.761(1) Å) is spanned symmetrically by the CC₆H₄OMe-2 group (μ -C—W, 2.01(1) Å). One tungsten atom carries a cyclopentadienyl ligand and two carbonyl groups, one of which weakly semi-bridges the metal-metal bond (W—C—O, 168.3(9)°). The other tungsten atom is ligated by a cyclopentadienyl ring, and by a carbonyl and a methyl group (W—CH₃, 2.24(2) Å).

We have previously reported¹ that UV irradiation of mixtures of the compounds $[M(Me)(CO)_3(\eta-C_5H_5)]$ (M = Mo or W) and $[W(\equiv CR)(CO)_2(\eta-C_5H_5)]$ $(R = C_6H_4Me-4 \text{ or } C_6H_4OMe-2)$ in light petroleum affords the complexes $[MW{\mu-C(R)C(O)Me}(CO)_4$ $(\eta-C_5H_5)_2]$ (1). This reaction involves a coupling of methyl, carbonyl and alkylidyne groups at a dimetal centre. However, the pathway by which these products were formed was by no means clear. Herein we describe related reactions between the ethylene complex $[W(Me)(CO)_2(\eta-C_2H_4)(\eta-C_5H_5)]$ and the alkylidine-tungsten species $[W(\equiv CR)(CO)_2$ $(\eta-C_5H_5)]$, which yield products relevant to the formation of compounds 1.

RESULTS AND DISCUSSION

The complex $[W(Me)(CO)_2(\eta-C_2H_4)(\eta-C_5H_5)]$ was generated by irradiating $[W(Me)(CO)_3(\eta-C_5H_5)]$ with UV light in the presence of ethylene.² It was then treated with $[W(=CC_6H_4Me-4)(CO)_2(\eta-C_5H_5)]$; the mixture being refluxed in light petroleum. Separation of products by column chromatography on alumina gave purple crystals of the ditungsten compound $[W_2(\mu-CC_6H_4Me-4)(Me)(CO)_3(\eta-C_5H_5)_2]$ (2a), a trace of the previously characterized complex $[W_2{\mu-C(C_6H_4Me-4)C(O)Me}(CO)_4(\eta-C_5H_5)_2]$ (1b)¹ and an unidentified exceedingly insoluble green material. In a similar reaction, the compounds $[W(Me)(CO)_2(\eta-C_2H_4)(\eta-C_5H_5)]$ and $[W(\equiv CC_6H_4OMe-2)(CO)_2(\eta-C_3H_5)]$ gave a chromatographical separable mixture of $[W_2(\mu-CC_6H_4OMe-2)(Me)(CO)_3(\eta-C_5H_5)_2]$ (2b), a trace of 1d and the μ -alkyne complex $[W_2{\mu-C_2(C_6H_4OMe-2)_2}(CO)_4(\eta-C_5H_5)_2]$ (3).

The IR and NMR data for the compounds 2 and 3 were in accord with the formulations proposed. Moreover, as described below, the structure of 2b was confirmed by an X-ray diffraction study. The IR spectrum of 2a in the carbonyl region shows three bands at 1941, 1908 and 1835 cm^{-1} , as expected. The absorption at 1835 cm^{-1} may be attributed to a semi-bridging carbonyl group. The ¹H NMR spectrum showed all the expected peaks, including a resonance for the WMe group at -0.40ppm (J(WH) 7 Hz). The ¹³C-{¹H} NMR spectrum displayed a diagnostic resonance for the μ -C nucleus at δ 360.7 ppm, with two sets of $^{183}W-^{13}C$ satellite peaks [J(WC) 120 and 101 Hz]. This pattern is in agreement with the μ -CC₆H₄Me-4 ligand being attached to non-equivalent tungsten

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W(1)—W(2)	2.761(1)	W(2)-C(1)	2.01(1)	O(02)—C(02)	1.44(2)
W(1) - C(1)	2.01(1)	W(2)C(2)	1.94(1)	C(2)-O(2)	1.16(2)
W(1)-C(4)	1.92(1)	W(2)C(3)	1.99(1)	C(3)-O(3)	1.14(2)
W(1)C(5)	2.24(2)	C(1) - C(11)	1.47(1)	C(4)O(4)	1.17(1)
		C(12)—O(02)	1.39(1)		
C(1) - W(1) - W(2)	46.6(3)	C(1) - W(2) - W(1)	46.5(2)	W(1) - C(1) - W(2)	86.9(4)
C(1) - W(1) - C(4)	71.6(4)	C(1) - W(2) - C(2)	107.3(4)	W(2) - C(1) - C(11)	143.9(6)
C(1) - W(1) - C(5)	97.6(4)	C(1) - W(2) - C(3)	108.0(4)	W(2) - C(1) - C(11)	129.2(6)
C(4) - W(1) - W(2)	118.2(3)	C(2) - W(2) - W(1)	68.1(3)	C(11)-C(12)-O(02)	113.4(8)
C(4) - W(1) - C(5)	86.3(5)	C(3) - W(2) - W(1)	82.7(3)	C(12)-O(02)-C(02)	118.1(9)
C(5) - W(1) - W(2)	100.3(3)	C(2) - W(2) - C(3)	88.2(5)		
W(1)-C(4)-O(4)	173.8(10)	W(2)C(2)O(2)	168.3(9)	W(2)C(3)O(3)	175.7(9)

Table 1. Selected bond distances (Å) and angles (°) for $[W_2(\mu-CC_6H_4OMe-2)(Me)(CO)_3(\eta-C_5H_5)_2]$ (2b)



Fig. 1. The molecular structure of $[W_2(\mu$ -CC₆H₄OMe-2)(Me)(CO)₃(η -C₅H₅)₂] (2b) showing the atom-numbering scheme.

atoms. Moreover, the observed chemical shift is relatively deshielded. This is in accord with a structure in which the C=W fragment is functioning formally as a four-electron donor,³ thereby leading to a stable but electronically unsaturated 32 valence-electron species. The three carbonyl groups in **2a** give rise to resonances at δ 238.3, 223.2 and 221.9 ppm. There are two signals (δ 97.7 and 94.1 ppm) for the non-equivalent C₃H₃ ligands, and a characteristic⁴ peak for the WMe fragment at δ -15.9 ppm [J(WC) 88 Hz].

Examination of the NMR spectra of 2b showed that peaks were present corresponding to the presence of two isomers, but discussion is deferred until the results of the X-ray diffraction study are described. The structure is shown in Fig. 1, and selected bond distances and angles are listed in Table 1. The W-W bond (2.761(1) Å) is spanned symmetrically by the alkylidyne group (μ -C--W, 2.01(1) Å). The metal-metal distance is perceptibly shorter than the W-W single bond distances $[W_2(\mu-HC_2H)(CO)_4(\eta-C_5H_5)_2]$ (2.987) (1) Å),⁵ [W₂(μ -EtC₂Et)(CO)₄(η ⁵-C₅Et₄C₆H₄Me-4) $(\eta-C_5H_5)$] (3.003(1) Å)⁶ and [N(PPh_3)₂][W₂ { μ -C(H)C₆H₄Me-4}(CO)₇(η -C₅H₅)] (3.111(1) Å).⁷ However, the W-W separations in the electronically unsaturated 32 valence-electron ditungsten complexes, $[W_2(\mu-CC_6H_4Me-4)(CO)_2(L)]$ $(\eta^{5}-C_{9}H_{7})(\eta^{5}-C_{2}B_{9}H_{9}Me_{2})$ [L = N₂C(C₆H₄Me-4)₂ $(2.777(1) \text{ Å}) \text{ or } O (2.761(1) \text{ Å}), C_9H_7 = \text{indenyl}],^8$ are very similar to the metal-metal bond distance in 2b. Moreover, the fact that C(1) symmetrically spans the W(1)—W(2) bond is also in accord with the electronic unsaturation of 2b and with electron delocalization within the μ -CW₂ ring. In structures in which an alkylidyne ligand edgebridges a W-W bond, and the two metal centres have 18 electron shells, the two μ -C—W separations are perceptibly different,⁹ indicating the presence of more localized C-W and C=W bonds within the ring. It is noteworthy that the μ -C—W distances in **2b** (2.01(1) Å) are shorter than W=C separation



(2.14(2) Å) in $[W(=CPh_2)(CO)_5]$,¹⁰ a molecule in which tungsten has an 18 electron shell.

The W(2) atom in **2b** carries a C_5H_5 ring and two CO groups. However, whereas C(3)O(3) has an essentially linear attachment to the tungsten, the ligand C(2)O(2) weakly semi-bridges the metalmetal bond (W(2)—C(2)—O(2), 168.3(9)°). This is in agreement with the appearance of an IR band at 1835 cm⁻¹, mentioned above. The W(1) atom is ligated by a C_5H_5 ring, a terminal CO ligand and a methyl group. The W(1)—C(5) separation (2.24(2) Å) is within the range expected (2.1–2.3 Å)¹¹ for σ bonds between tungsten and sp^3 carbon atoms. The *o*-anisol ring in **2b** lies at 99.0° to the plane defined by C(1)W(1)W(2), but with the OMe group and the Me substituent on W(1) on the same side of the μ -CW₂ ring.

The compounds 2 are isolobally mapped with the complex [W(Me)(CO)(η -C₂H₂)(η -C₅H₅)], in which the ethyne molecule functions as a four-electron donor.¹² As mentioned above, complex 2b is formed as a mixture of two diastereoisomers, a property revealed by the ¹H and ¹³C-{¹H} NMR spectra (see Experimental). The relative intensity of peaks in the spectra indicate that in CDCl₃ solution the proportion of the two isomers was ca 3:1. We suggest that the isomerism arises as a result of the Me and OMe groups being either cisoid (on the same side), or transoid (on the opposite sides) of the μ -CW₂ ring. the reaction between $[W(\equiv CC_6H_4OMe-2)]$ In $(CO)_2(\eta-C_5H_5)$ and $[WMe(CO)_2(\eta-C_2H_4)(\eta-C_5H_5)]$ the formation of the μ -alkyne complex 3 was unexpected, because in the corresponding reaction involving $[W(\equiv CC_6H_4Me-4)(CO)_2(\eta-C_5H_5)]$, the compound $[W_2{\mu-C_2(C_6H_4Me-4)_2}(CO)_4(\eta C_{5}H_{5}$ was not formed. The latter complex is, however, often produced in reactions of $[W(\equiv CC_6H_4Me-4)(CO)_2(\eta-C_5H_5)]$ with low-valent metal species.^{9,13} Compounds of the type $[M_2(\mu$ $alkyne)(CO)_4(\eta - C_5H_5)_2$ (M = Mo or W) in solution show dynamic behaviour on the NMR timescale,^{14,15} and 3 is no exception. Although good quality spectra were not obtained, at -40° C, peaks corresponding to the presence of two isomers were observed, including four CO resonances in the ¹³C- ${^{1}H}$ NMR spectrum. At room temperature no CO resonances were seen in the spectrum.

In spite of its electronic unsaturation, compound **2a** was unreactive towards PMe_3 or PPh_3 in refluxing tetrahydrofuran (THF), and UV irradiation of **2a** in the presence of PMe_3 was equally fruitless. However, irradiation of **2a** in THF with a stream of CO gas passing through the solution, resulted in the disappearance of the IR bands due to **2a** and the appearance of new carbonyl absorptions at 2018vs, 1972s, 1926s, 1864m, 1678w and 1671w cm⁻¹. On

removing the UV source and replacing the CO atmosphere with N_2 , these bands gradually disappear, and are replaced by those due to **1b**. Column chromatography of the mixture led to the isolation of **1b** in yields greater than 70%.

Possible pathways to compounds 1b and 2a are shown in the Scheme 1, and similar processes can be invoked to account for the formation of the other species, 1 and 2. The synthesis of 1b from $[W(Me)(CO)_3(\eta-C_5H_5)]$ and $[W(\equiv CC_6H_4Me-4)]$ $(CO)_2(\eta - C_5H_5)$] proceeds upon UV irradiation of solutions containing a mixture of the two reagents.¹ It is likely that the methyltungsten compound is activated with release of a molecule of CO to the coordinatively unsaturated species give $[W(Me)(CO)_2(\eta-C_5H_5)]$.¹⁶ The latter could then capture a molecule of $[W(\equiv CC_6H_4Me-4)(CO)_2(\eta C_{5}H_{5}$ to give intermediate A. Reaction of A with CO, present in the solutions or scavenged from one of the reactants, might yield the acyl-dimetal complex, **B**, which could collapse to give 1b. The formation of 2a from $[W(Me(CO)_2(\eta-C_2H_4)(\eta$ $C_{5}H_{5}$ and $[W(\equiv CC_{6}H_{4}Me^{-4})(CO)_{2}(\eta^{-}C_{5}H_{5})]$ proceeds in hydrocarbon solvents but only under reflux conditions. Presumably intermediate A is again formed, but in the absence of appreciable amounts of free CO in the mixture it releases CO to afford primarily 2a. The observation that traces of 1b are formed in the reaction demonstrates the relationship between 2a and 1b with the probability of a common intermediate. As mentioned above, UV irradiation of 2a in the presence of CO gives 1b in high yield. However, during this conversion the IR spectrum of the mixture shows bands due to a transient species at 1678 and 1671 cm⁻¹, characteristic of an acyl group, as invoked for **B**. The presence of two absorptions near 1675 cm^{-1} may be due to the existence of more than one isomer of **B**. It is noteworthy that 2a does not react with CO in the absence of UV irradiation. This suggests that 2a requires initial activation, perhaps to give an intermediate $[W_2(\mu-CC_6H_4Me-4)(Me)(CO)_3(\eta$ in which the $(\eta - C_5 H_5)(OC)_2 W \equiv$ $C_{1}H_{1}$ CC₆H₄Me-4 moiety acts as a two-electron donor to the W(Me)(CO)(η -C₅H₅) fragment. The latter would then possess a 16 electron tungsten centre which would capture a CO molecule to give A; which via additional CO could yield 1b, through the intermediacy of **B**. The conversion of **B** into the product 1b may involve more than one step. Thus, transfer of the acyl group to the μ -CC₆H₄Me-4 fragment might produce a μ -C(C₆H₄Me-4)C(O)Me ligand in a species containing a W=W bond. This intermediate (not shown), with the bridging group functioning as a two-electron donor, could transform into 1b, in which the organic group contributes



four electrons to the ditungsten system. The process would be similar to the transfer of a terminally bound formyl group to a μ -thio-alkylidyne ligand, as in the formation of the complexes [Fe₂{ μ -C(SMe)C(H)O}(μ -CO)(CO)(η -C₅H₅)₂].¹⁷ We have attempted to isolate intermediates such as **A** or **B** by UV irradiation of CO saturated solutions of **1b**, but no reaction was observed.

EXPERIMENTAL

Light petroleum refers to that fraction of bp 40-60°C. All reactions were carried out under N₂, using Schlenk tube techniques. Chromatography columns employed BDH alumina (Brockman activity II). The compounds $[W(==CR)(CO)_2(\eta-C_5H_5)]$ $(R = C_6H_4Me-4 \text{ or } C_6H_4OMe-2)$ were prepared by procedures described elsewhere, ^{3,18} while $[W(Me)(CO)_2(\eta-C_2H_4)(\eta-C_5H_5)]^2$ was obtained by irradiating $[W(Me)(CO)_3(\eta-C_5H_5)]$ in light petroleum with UV light (Hanovia medium pressure mercury vapour lamp) under a stream of C_2H_4 , the reagent thus prepared being used *in situ*. IR spectra were measured (in CH_2Cl_2) with Nicolet MX-1 and 5ZDX FT spectrophotometers. The NMR spectra were recorded in CDCl₃ using JNM JEOL FX90Q, GX270 and GX400 FT spectrometers. The ¹³C-{¹H} chemical shifts are to high frequency of SiMe₄ (0.0 ppm).

Synthesis of the compounds $[W_2(\mu-CR)(Me)(CO)_3 (\eta-C_5H_5)_2]$

(i) The complex $[W(Me)(CO)_3(\eta - C_5H_5)]$ (1.75 g, 5.0 mmol) in light petroleum (300 cm³) was irradiated with UV light at -20° C for ca 4 h; the conversion to $[W(Me)(CO)_2(\eta - C_2H_4)(\eta - C_5H_5)]$ being monitored periodically by IR. The compound $[W(\equiv CC_6H_4Me-4)(CO)_2(\eta-C_5H_5)]$ (1.43 g, 3.5 mmol) was added, and the mixture was refluxed for 6 h. Removal of solvent in vacuo gave a brown residue which was dissolved in CH_2Cl_2 (10 cm³) and chromatographed $(3 \times 20 \text{ cm column})$. Elution light petroleum removed with traces of $[W(Me)(CO)_3(\eta-C_5H_5)]$. Elution with CH_2Cl_2 -light petroleum (2:1) gave a purple fraction and a red

fraction. Removal of solvent in vacuo from the purple eluate, and crystallization of the residue from CH₂Cl₂-light petroleum (15 cm³, 1:10) at -78° C gave purple *microcrystals* of $[W_2(\mu-CC_6H_4)]$ Me-4)(Me)(CO)₃(η -C₅H₅)₂] (2a) (0.51 g, 21%), v_{max} (CO) at 1941m, 1908vs and 1835m cm⁻¹ (Found: C, 35.3; H, 3.0. $C_{22}H_{20}O_3W_2 \cdot CH_2Cl_2$ requires : C, 35.2; H, 2.8%). NMR : 1 H, $\delta - 0.40$ [s, 3H, WMe, J(WH) 7 Hz], 2.43 (s, 3H, Me-4), 5.34, 5.36 (s \times 2, 10H, C₅H₅), 6.29–7.16 (m, 4H, C_6H_4). ¹³C-{¹H}, δ 360.7 [μ -C, J(WC) 120 and 101], 238.3 [CO, J(WC) 156], 223.2 [CO, J(WC) 170], 221.9 [CO, J(WC) 168], 165.5 [C¹(C₆H₄)], 134.2, 127.7, 127.4, 122.4, 119.0 (C₆H₄), 97.7, 94.1 (C_5H_5) , 21.1 (Me-4), and -15.9 ppm [MeW, J(WC) 88 Hz].

The red eluate from the column was identified by IR as containing a trace of **1b**. A final elution of the column with THF recovered a green eluate, which after removal of solvent *in vacuo* gave green microcrystals (ca 0.2 g), as yet unidentified.

(ii) In a similar experiment, the compound $[W(Me)(CO)_2(\eta-C_2H_4)(\eta-C_5H_5)]$ (prepared from $[W(Me)(CO)_3(\eta-C_5H_5)]$ (1.75 g, 5.0 mmol) and C_2H_4) was treated with $[W(\equiv CC_6H_4OMe-2)$ $(CO)_2(\eta-C_5H_5)]$ (1.48 g, 3.5 mmol). Separation of products, as described above, afforded purple *microcrystals* of $[W_2(\mu-CC_6H_4OMe-2)(Me)(CO)_3(\eta-C_5H_5)_2]$ (2b) (0.45 g, 18%), red *microcrystals* of $[W_2\{\mu-C_2(C_6H_4OMe-2)_2\}(CO)_4(\eta-C_5H_5)_2]$ (0.30 g) and a trace of red 1d.

For 2b, v_{max}(CO) at 1939m, 1907vs and 1830m cm^{-1} . NMR (peaks with asterisk due to minor isomer), ¹H, δ -0.41*, -0.25 [s × 2, 3H, MeW, J(WH) 7], 3.55*, 3.58 (s × 2, 3H, OMe), 5.30, 5.32*, 5.33, 5.36* (s×4, 10H, C₅H₅), 6.22–6.95 (m, 4H, C_6H_4). ¹³C-{¹H} (measured at -40°C), δ 359.9, 357.3^* (µ-C), 237.9 (CO, both isomers), 225.7, 224.0*, 223.2*, 222.2 (CO), 157.9, 157.8* $[C^{1}(C_{6}H_{4})], 150.4^{*}, 150.0, 127.3, 127.1^{*}, 125.2,$ 121.4^* , 120.5^* , 120.2, 112.1^* , 111.2 (C₆H₄), 98.4*, 98.0, 95.0*, 94.6 (C₅H₅), 56.8*, 56.4 (OMe), -12.3, and -15.7^* [MeW, J(WC) 87 Hz]. For $[W_2{C_2(C_6H_4OMe-2)_2}(CO)_4(\eta-C_5H_5)_2]$ (3), v_{max} (CO) at 1969vs, 1937s and 1845m cm⁻¹. NMR $(at - 40^{\circ}C)$; ¹H, δ 3.46*, 3.66 (s × 2, br, 6H, OMe), 5.56 (sbr, 10H, C_5H_5), 6.82–7.32 (m, 8H, C_6H_4). $^{13}C-\{^{1}H\}, \delta 231.1, 225.6, 221.4, 213.2 (CO), 164.2*,$ 157.0, 146.1, 144.3, 134.4*, 131.9*, 127.5, 124.5*,

122.2, 120.2, 112.6*, 110.6 (C_6H_4), 94.3, 91.7* (C_5H_5), 55.6* and 54.5 (OMe).

Crystal structure determination of $[W_2(\mu-CC_6H_4 OMe-2)(Me)(CO)_3(\eta-C_5H_5)_2]$ (2b)

Crystals of **2b** were grown as dark purple prisms from Et₂O-light petroleum. Diffracted intensities were recorded at 298 K on a crystal of dimensions $ca \ 0.2 \times 0.2 \times 0.4$ mm. Of the 3624 reflections $(2\theta \le 50^{\circ})$, measured on a Nicolet R3m/ μ fourcircle diffractometer (θ -2 θ scans), 2690 had $F \ge 3.0\sigma(F)$, and only these were used in the solution and refinement of the structure. Intensity data were corrected for Lorentz, polarization and X-ray absorption effects, the latter by an empirical method based on azimuthal scan data.¹⁹

Crystal data. $C_{22}H_{20}O_4W_2$, M = 716.1, monoclinic, a = 15.462(2), b = 16.354(2), c = 8.406(1) Å, $\beta = 105.31(1)^\circ$, U = 2050(1) Å³, $D_c = 2.32$ g cm⁻³, Z = 4, F(000) = 1328, space group $P2_1/a$ (No. 14), Mo- K_{α} X-radiation (graphite monochromator, $\overline{\lambda} = 0.71073$ Å), μ (Mo- K_{α}) = 114.8 cm⁻¹.

The structure was solved, and all non-hydrogen atoms were located, by conventional heavy-atom and difference-Fourier methods. Hydrogen atoms were included in calculated positions (C-H 0.96 Å) with common refined isotropic thermal parameters for groups of related hydrogen atoms. All remaining atoms were given anisotropic thermal parameters. Refinement by full-matrix leastsquares, with a weighting scheme of the form $w^{-1} = [\sigma^2(F) + 0.0009|F|^2]$, converged at R =0.034 (R' = 0.036).* The final electron-density difference synthesis showed no peaks ≥ 1.5 or ≤ -1.1 e Å⁻³. Scattering factors, with corrections for anomalous dispersion, were from ref. 20. All calculations were carried out on a DEC micro-Vax II computer with the SHELXTL PLUS system of programs.¹⁹

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^{*} Tables of atomic positional and thermal parameters and F_o/F_c values have been deposited as Supplementary Data with the Editor, from whom copies are available on request. Atomic coordinates have also been deposited with the Cambridge Crystallographic Data Centre.

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