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SYNTHESIS AND X-RAY STRUCTURES OF SOME HOMONUCLEAR μ-ALKYLIDENETUNGSTEN COMPLEXES

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Summary

The complexes $W_2\{[\mu\text{-}CHCH{=}C(CH_3)_2][(CO)_{10}]\}$ and $W_2\{[\mu\text{-}CHCH{=}C(CH_3)(CH_2)_3CH_3][(CO)_{10}]\}$ have been synthesized, and an X-ray diffraction study has revealed the presence of five CO groups on each metal center. The analogy between $W_2\{[\mu\text{-}CHCH{=}C(CH_3)_2][(CO)_9]\}$ and a complex of $W(CO)_4$ and a tungstabutadiene $(CO)_5W{=}CHCH{=}C(CH_3)_2$ prompted the synthesis of the first heteroatom-substituted μ-alkylidene complexes of tungsten, starting from conjugated Fischer-type carbene complexes $(CO)_5W{=}C(OR)CH{=}CHR$. The X-ray structure of the complex $W_2\{[\mu\text{-}C(OEt)CH{=}CH(CH_3)][(CO)_9]\}$ has also been determined. In the case of the simplest conjugated complex $(CO)_5W{=}C(OR)CH{=}CH_2$, an interesting rearrangement initiated by addition of $W(CO)_5$ to the terminal C=C double bond giving a dinuclear complex $W(CO)_5[\eta^2\text{-}CH_2{=}CHC(OMe)W(CO)_5]$ in which the two metal centers are not directly linked, has been observed.

Introduction

Since the discovery of the first μ-methylene complex of manganese by Herrmann [1], much work has been described on the synthesis and chemistry of μ-alkylidene complexes of transition metals. Several methods, extensively reviewed, are now available for the synthesis of such species [2–4]. One of the most interesting and efficient approaches to the problem is that by Stone and his coworkers [5]. This approach is based on the isolobal analogy developed by Hoffmann [6], between organic groups and metal-ligand fragments.

Stone and his coworkers found that Fischer-type carbene complexes react in the same way as alkenes with low-valent platinum complexes, to give heterodinuclear

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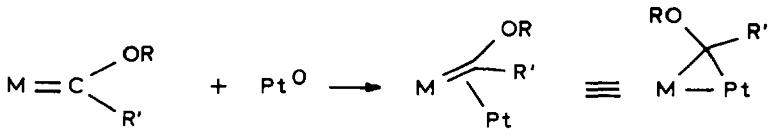

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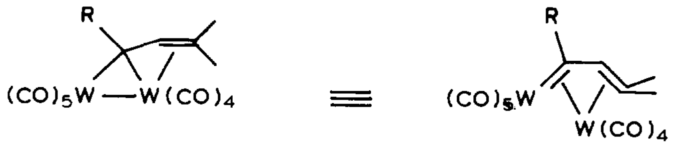

(3 : R = H) (4 : R = H)

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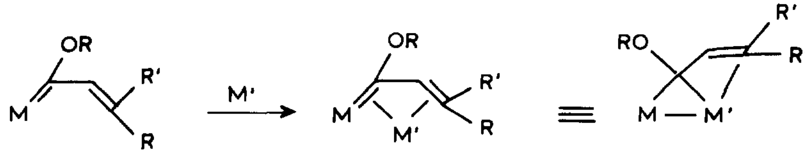


(6) (7) (8)

(3)

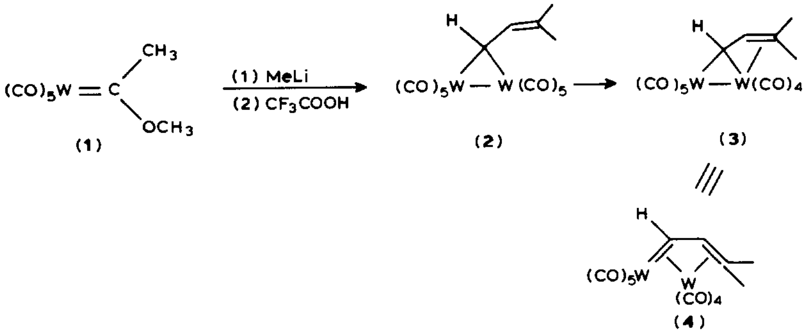
μ-alkylidene complexes, as shown in eq. 1. Our approach to the problem of synthesizing μ-alkylidenetungsten complexes bearing a heteroatom on the bridging carbon atom was rather similar [10] and followed the serendipitous synthesis of the first μ-alkylidenetungsten complex (**2**); it is possible to describe this complex as a complex of $W(CO)_4$ and of a metal-ligand, here a tungstadimethylbutadiene (eq. 2) [7]. We therefore explored the application of this analogy to the synthesis of μ-alkylidene complexes of the general structure **7** in which M = W, Fe and M' = W, Fe and the bridging carbon atom bears an alkoxy group, as shown in eq. 3.

The purpose of the present paper is therefore to describe first, the revised structure of complex **2**, and second the synthesis of the first μ-alkylidenetungsten complexes, the dinuclear analogues of the Fischer-type mononuclear carbene complexes, starting from mononuclear carbene complexes **6**.

Synthesis

Complexes **2** and **5** were synthesized as described previously starting from $(CO)_5W{=}C(OMe)Me$ and MeLi or BuLi (eq. 4) [8,9]. The synthesis of complexes of the type **7**, where M = M' = W, started from conjugated complexes; some of these had been described previously [11], whereas others were synthesized by a general route derived in our laboratory [12]. Two methods were used to generate coordinatively unsaturated $W(CO)_4$: (a) the photochemical decomposition of $W(CO)_6$, at room temperature and (b) the thermal decomposition of $(CO)_5W{=}C(Ph)_2$. We had previously observed that this complex reacts with dienes such as 1,5-cyclooctadiene (COD) to give inter alia, $W(CO)_4(COD)$ [13].

Complex **9** was found to react with **12**, at 60 °C, in hexane, to give the purple dinuclear complex **13** ($R = CH_3$), in 20% yield (eq. 8). The same complex was



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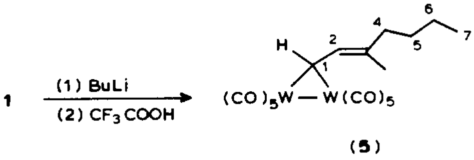

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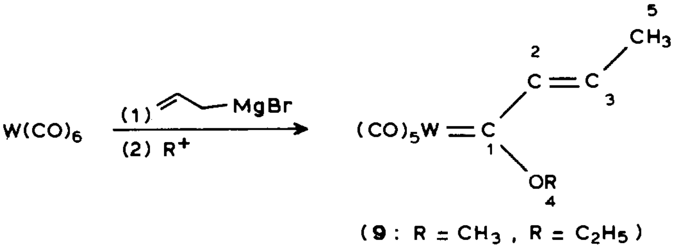

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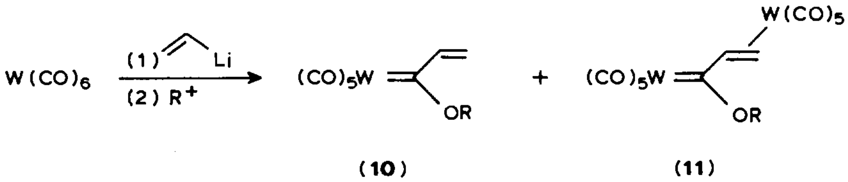

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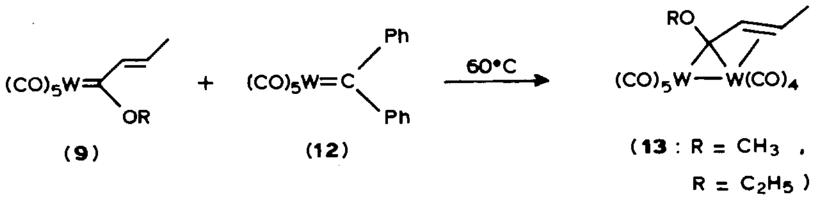


(8)

$$9 \quad + \quad W(CO)_6 \xrightarrow{h\nu} 13 \qquad (9)$$

TABLE 1

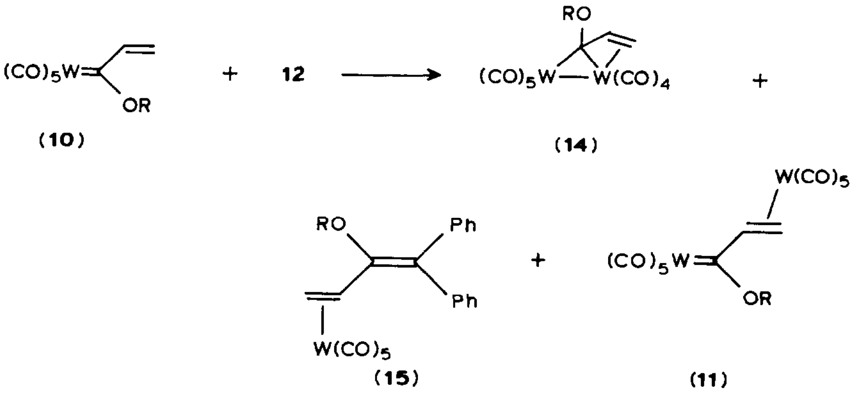
IMPORTANT ^1H AND ^{13}C NMR DATA FOR THE NEW COMPLEXES (δ, ppm)

	Solvent	C_2H	C_3H	C_5H	OCH_2X
9	C_6D_6	7.3	6.57	1.82	4.55 (X = H)
10	$CDCl_3$	7.4	5.72 5.25		4.6 (X = H)
13	C_6D_6	5.05	3.05	1.75	3.15 (X = H)
11	$CDCl_3$	5.55	3.60		4.40 (X = CH_3)
15	C_6D_6	4.33	2.64 1.88		3.90 (X = H)

		C(1)	C(2)	C(3)	C(5)	OCH_3
9	C_6D_6	307.2	149.4	136.8	18.4	78.9
13	C_6D_6	231.1	88.6	68.4	20.0	82.0
11	$CDCl_3$	311.1	90.9	47.8		67.7

obtained in 30% yield by irradiation of $W(CO)_6$ in the presence of **9** (eq. 9). Complex **13** gives a mass spectrum characteristic of dinuclear complexes of tungsten with the molecular ion at 718 followed by ions due to the successive loss of 9 CO groups. Comparison of the ^1H and ^{13}C NMR spectra of the starting complex **9** with those of complex **13** reveal a general upfield shift in the latter of the signals of both the hydrogens and the carbons of the double bond (Table 1). Moreover, the signal of the carbene function which appears at 307 ppm in **9** is shifted to 231 ppm, a shift consistent with literature data on bridging carbon atoms. An X-ray diffraction study confirmed the nature of **13**. An ORTEP view of its structure is shown in Fig. 4.

In the case of complex **10**, the reaction was somewhat more complex. Thermal decomposition of complex **12**, in the presence of complex **10**, did give complex **14**; in addition we observed the formation of two new complexes, which could be separated by silica gel chromatography at low temperature (eq. 10). The least polar complex, isolated as a purple-black oil, was assigned structure **14** on the basis of its mass spectrum and its ^1H NMR spectrum (Table 1). The next complex eluted was **11**, which was isolated as orange crystals. Its mass spectrum indicated that it also contains two metal centers and 10 CO groups, as well as the organic ligand of the



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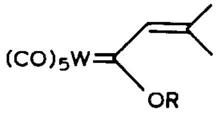

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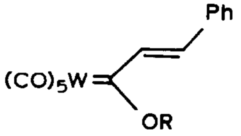

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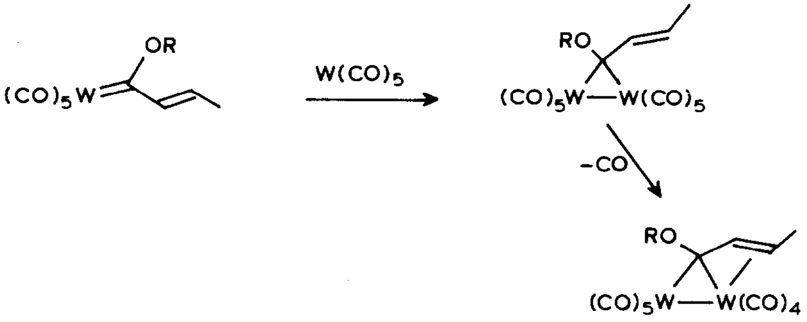


(11)

(13)

starting complex **10**. The ^1H NMR spectrum shows the presence of an ethoxy group and of a coordinated double bond. There is, however, a striking difference between complex **14** and complex **11** in the ^{13}C NMR spectrum, complex **11** showing a signal at 311 ppm characteristic of a heteroatom-substituted Fischer-type carbene complex. Consequently, a structure in which the two metal centers are not directly linked and in which the double bond of the starting complex **10** is coordinated to a second $W(CO)_5$ group was assigned to complex **(11)**, and this was confirmed by an X-ray diffraction study (Fig. 3).

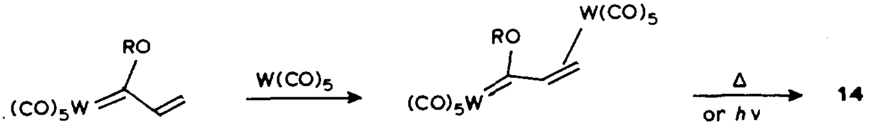
The last complex eluted, obtained as a yellow oil, was assigned structure **15** on the basis of its mass spectrum, which shows the presence of one $W(CO)_5$ moiety, and of its ^1H NMR spectrum, which shows signals due to a coordinated double bond (Table 1), an ethoxy group, and to ten aromatic protons.

Whereas complexes **11** and **15** are stable in solution at room temperature, complexes **13** and **14** slowly regenerate the starting complexes **9** and **10**. In the case of complexes **16** and **17**, no reaction was observed under our standard conditions.

Discussion

As expected, conjugated carbene complexes react with coordinatively unsaturated $W(CO)_4$ moieties to give heteroatom-substituted μ-alkylidene complexes.

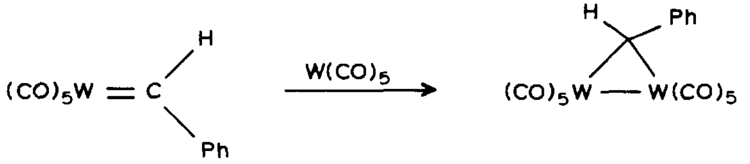
Whether this reaction occurs via a multi-step process is difficult to assess. It is conceivable that the mononuclear complex first reacts with $W(CO)_5$ to give an unstable intermediate, in which the carbene function is bound to $W(CO)_5$, and which then loses CO upon coordination of the C=C double bond, as in the known transformation 2 → 3 (eq. 11). Another possibility, which seems more likely, involves coordination of $W(CO)_5$ to the terminal C=C double bond followed by the coordination of the W=C double bond, as shown in eq. 12. Such a process does indeed take place during the decomposition of complex **10**, which leads to **11**; **11**, in turn slowly gives **14** upon UV irradiation (eq. 12).



(12)

A noteworthy observation, is the instability of complexes of type **8**, which contrasts with the stability of complexes of type **3**: this observation has recently been nicely explained by Goddard [14] in terms of the donor/acceptor bonding prefered by electronegative substituted carbene complexes, which means that, as observed, W^0 complexes of type **6** should be more stable than those of type **7**, and complexes of type **4** more stable than those of type **7**.

Also of interest is the formation of complexes **11** and **15**: as far as complex **11** is concerned, we were able to show that this complex is slowly formed when complex **10** is kept in solution at room temperature. It is likely that **10** reacts with $W(CO)_5$, itself formed by the decomposition of **10**. Such a reaction has also been observed by Fischer [15] in the case of a benzylidene complex of tungsten (eq. 13).



(18) (19) (13)

The formation of complex **15** could be firmally represented as the result of the coupling of the organic moieties of carbene complexes **10** and **12**, a type of reaction which is well documented for carbene complexes. The fact that complexes **16** and **17** give only traces of the expected dinuclear complexes can be ascribed to electronic and steric factors.

Comments on the structures of complexes 2, 5, 11 and 13

A structure in which each metal center bears four CO groups was previously assigned to complex **2** on the basis of an X-ray analysis [8]. As the mass spectrum and the chemical behaviour of complex **2**, especially the ready transformation 2 → 3, were not consistent with this structure, a new X-ray diffraction study was carried out on complex **2**. A similar study was also undertaken on complex **5**, a dinuclear complex of the same type obtained from methylmethoxytungstacarbene by use of BuLi instead of MeLi, under the best experimental conditions, to check carefully the number of CO groups on each metal center. These studies established clearly the

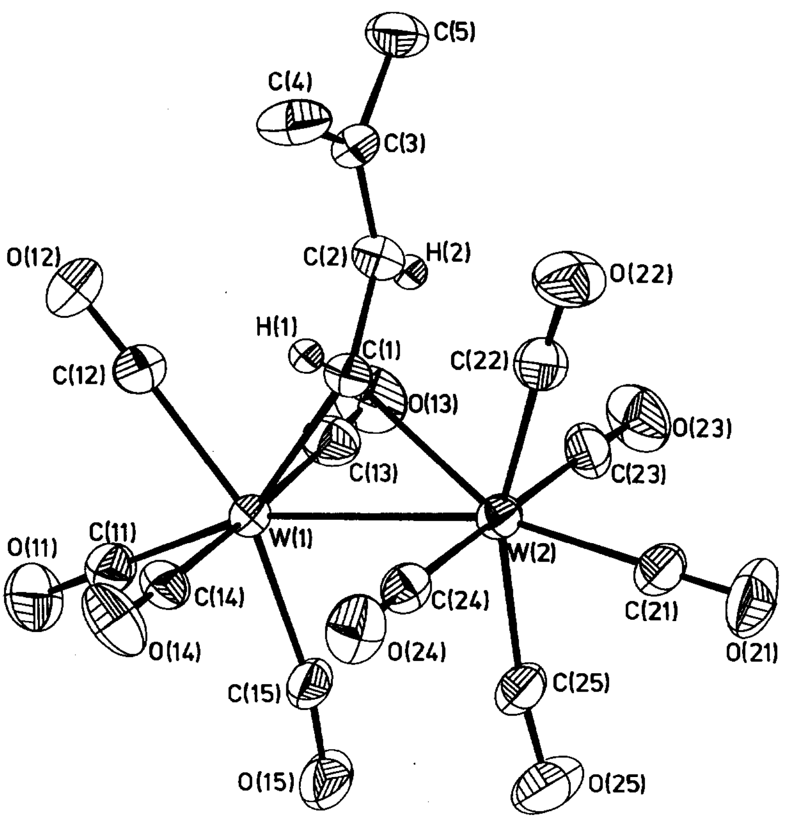
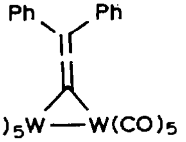


Fig. 1. ORTEP projection for complex 2.

presence of 10 CO groups and therefore the previously assigned structure for 2, with



(**20**)

8 CO groups, was incorrect. The new structure is fully consistent with the observed experimental data. The ORTEP projections for 2 and 5 appear in Fig. 1 and 2. The W–W distances in complexes 2, 5 and 13 (3.1450, 3.1354 and 3.150 Å) can be compared with the corresponding metal–metal distances in complexes **19** and **20** (3.118 and 3.156 Å) [15,16]. The W(1)–C(1)–W(2) angles (87.6 and 87.1°) can also be compared with the corresponding values in complexes **19** and **20** (86.4 and 90.1°). In complex **11**, the two metal centers are not directly linked. An interesting feature is the geometry of the W=C double bond with respect to the C=C double bond: these conjugated double bonds are no longer coplanar, the torsional angle between their two planes being 25°.

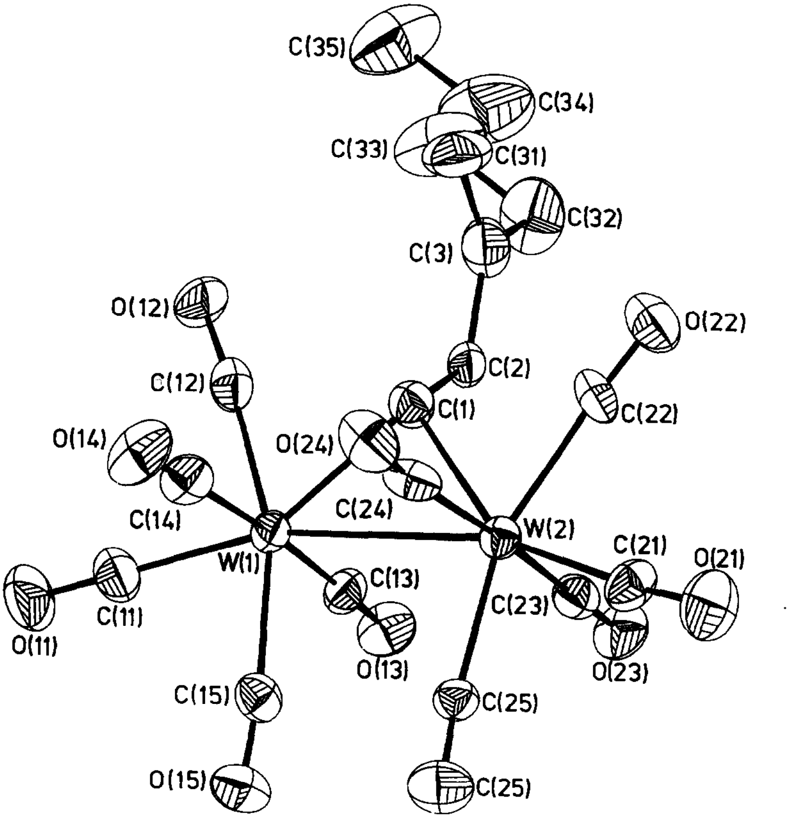


Fig. 2. ORTEP projection for complex **5**.

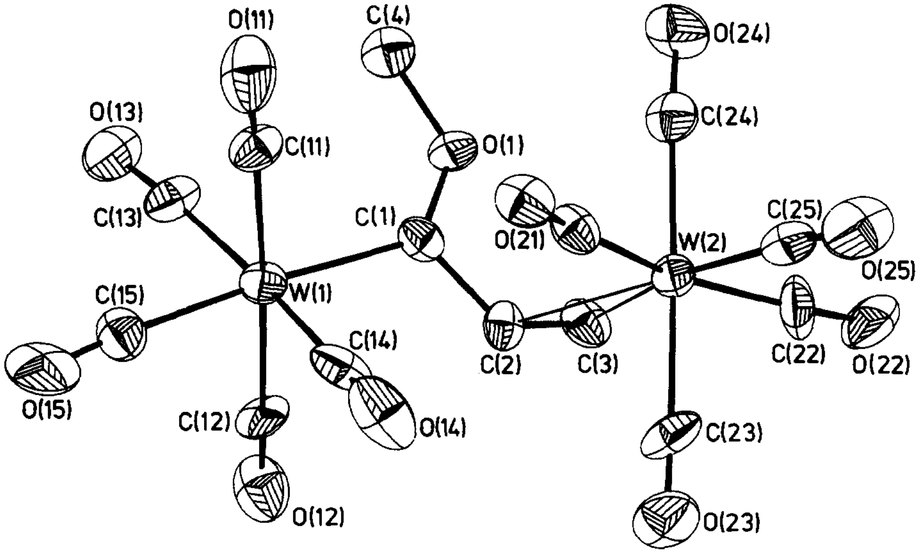


Fig. 3. ORTEP projection for complex **11**.

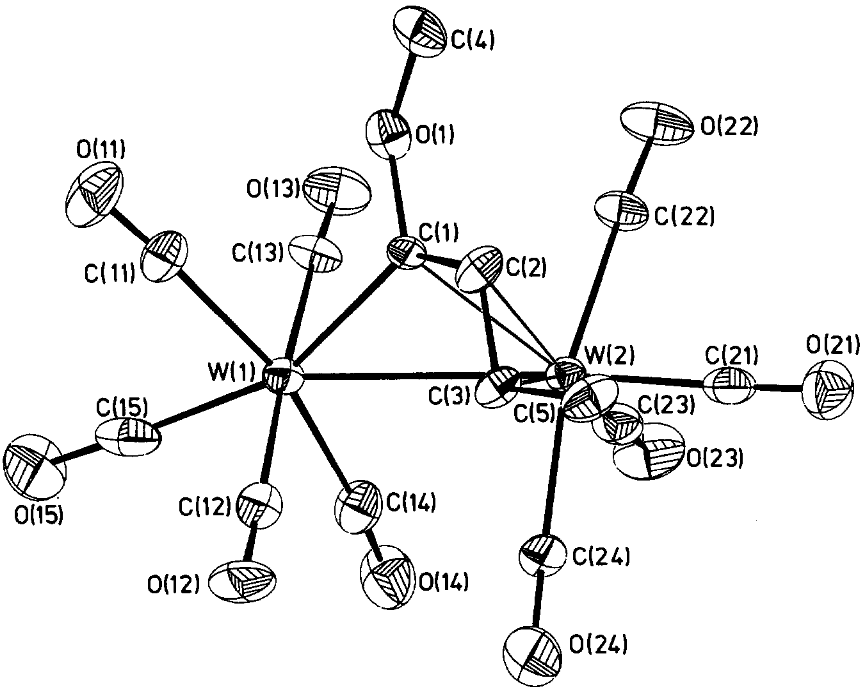


Fig. 4. ORTEP projection for complex **13**.

X-ray studies

In each case preliminary unit cell dimensions and symmetry information were derived from precession and Laue photographs. The crystal was then set up on an automatic diffractometer and the accurate cell dimensions and orientation matrix were obtained from least-squares refinements of the setting angles of 25 well defined reflections.

Crystal data and data collection parameters are listed in Table 2. Intensities of standard reflections showed no change during data collection. Corrections were made for Lorentz and polarization effects. For compounds **2** and **5**, the absorption correction was applied by use of an empirical correction technique [17], whereas a calculated absorption correction was applied in the case of compounds **11** and **13** [18]; transmission factors ranged from 0.125 to 0.238 for **11** and from 0.047 to 0.347 for **13**. Computations were performed by using the CRYSTALS system [19] adapted for a VAX 11/725 computer for compounds **2** and **5**, and the SHELX76 system [20] for the other two compounds. Atomic scattering factors for neutral W, O, C and H were taken from the international Tables for Crystallography [21]; anomalous dispersion for W atoms was taken into account.

The positions of W atoms were derived by Harker vector analysis of three dimensional Patterson maps. All remaining non-hydrogen atoms were found from successive electron density maps. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were fixed at their calculated positions (C–H 0.96 Å); only H atoms attached to carbon atoms C(1) and C(2) in compound **2** were located on a

TABLE 2

CRYSTAL DATA FOR COMPLEXES **2**, **5**, **11** AND **13**

Compound	**2**	**5**	**11**	**13**
Empirical formula	$C_{15}H_8O_{10}W_2$	$C_{18}H_{15}O_{10}W_2$	$C_{14}H_6O_{11}W_2$	$C_{14}H_8O_{10}W_2$
Formula wt.	715.9	759.0	717.9	703.9
Crystal system	orthorhombic	monoclinic	monoclinic	monoclinic
Space group	$P2_12_12_1$	$P2_1/c$	$P2_1/n$	$P2_1/c$
a (Å)	7.081(3)	7.054(5)	9.899(2)	8.593(2)
b (Å)	16.375(2)	22.674(6)	14.381(1)	13.342(3)
c (Å)	16.570(3)	13.801(3)	14.370(4)	15.947(4)
β (deg)		91.36(6)	112.65(2)	90.90(2)
V (Å^3)	1921(1)	2207(2)	1887.9(9)	1828.1(8)
Z	4	4	4	4
crystal size (mm)	0.48×0.15×0.09	0.39×0.2×0.17	0.2×0.18×0.14	0.55×0.3×0.8
μ(Mo-K_α) (cm^{-1})	127.3	110.9	129.6	133.8
ρ calcd. (g cm^{-3})	2.47	2.28	2.53	2.56
Radiation	Mo-K_α(0.71069)	Mo-K_α	Mo-K_α	Mo-K_α
Diffractometer	Nonius CAD4	Nonius CAD4	Philips PW1100	Philips PW1100
Monochromator	graphite	graphite	graphite	graphite
Scan range θ (deg)	$1.2+0.345\text{tg}\theta$	$1.2+0.345\text{tg}\theta$	$0.9+0.345\text{tg}\theta$	$1.2+0.345\text{tg}\theta$
Scan speed s (deg s^{-1})	$0.017<s<0.092$	$0.017<s<0.092$	0.03	0.03
Scan type	$\omega-1.67\theta$	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$
Standard reflections	2, every hour	2, every hour	3, every 3 hours	3, every 3 hours
Reflections measured	*hkl*	− *hkl*, *hkl*	− *hkl*, *hkl*	− *hkl*, *hkl*
Reflections collected	3010	4547	3617	1890
Reflections merged	2685	3880	3094	1778
Reflections used	2101	2502	2664	1671
Criteria	$I>2\sigma(I)$	$I>2\sigma(I)$	$F>3\sigma(F)$	$F>2\sigma(F)$
2θ range (deg)	$3<2\theta<56$	$3<2\theta<50$	$4<2\theta<50$	$4<2\theta<40$
$R=\Sigma\|\,|F_o|-|F_c|\,\|/\Sigma|F_o|$	0.0201	0.0482	0.0520	0.0280
$R_w=[\Sigma w(F_o-F_c)^2/\Sigma w(F_o)^2]^{1/2}$	0.0212	0.0550	0.0391	0.0316
Weighting scheme	1.0	1.0	$1.86/\sigma^2(F_o)$	$0.23/\sigma^2(F_o)$
Shift/esd	0.04	0.08	0.15	0.1

difference Fourier map and their coordinates refined. They were all an assigned isotropic thermal parameter of 0.05. Refinement was by least squares with a large-block approximation to the normal matrix for compounds **2** and **5**; full matrix least squares were used for **11** and **13**. The criteria for a satisfactory completed analysis were the ratio of the parameter shifts to standard deviations (Table 2) and no significant features in the final difference map.

Lists of thermal parameters and observed and calculated structure factors are available from the authors. Atomic coordinates are given in Table 3 and bond lengths and bond angles in Table 4, for compounds **2**, **5**, **11** and **13**.

Experimental

All reactions were carried out in oven-dried glassware under argon. Benzene, diethyl ether (Et_2O), and tetrahydrofuran (THF) were distilled from $LiAlH_4$. Preparative column chromatography was performed with 70–230 mesh Merck silica

(*Continued on p. 365*)

TABLE 3

FRACTIONAL ATOMIC COORDINATES WITH STANDARD DEVIATIONS

Atom	x/a	y/b	z/c
Compound 2			
W(1)	0.66127(6)	0.79796(2)	0.82856(2)
W(2)	0.75658(6)	0.66389(2)	0.69890(2)
C(1)	0.793(1)	0.8017(5)	0.7035(5)
C(2)	0.704(1)	0.8526(7)	0.6414(6)
C(3)	0.786(2)	0.9082(5)	0.5934(6)
C(4)	0.990(2)	0.9279(8)	0.5948(8)
C(5)	0.669(2)	0.9524(6)	0.5316(6)
H(1)	0.56(1)	0.184(5)	0.202(5)
H(2)	0.90(1)	0.159(6)	0.141(6)
C(11)	0.564(2)	0.8527(6)	0.9298(6)
O(11)	0.505(2)	0.8827(5)	0.9859(5)
C(12)	0.739(2)	0.9141(6)	0.8079(6)
O(12)	0.781(2)	0.9808(5)	0.7981(5)
C(13)	0.405(2)	0.8205(7)	0.7764(6)
O(13)	0.265(1)	0.8357(6)	0.7494(5)
C(14)	0.924(2)	0.7797(6)	0.8799(6)
O(14)	1.064(1)	0.7730(6)	0.9088(5)
C(15)	0.545(2)	0.7009(6)	0.8874(6)
O(15)	0.478(2)	0.6542(5)	0.9299(5)
C(21)	0.789(2)	0.5569(6)	0.6431(6)
O(21)	0.806(2)	0.4958(5)	0.6098(6)
C(22)	0.886(2)	0.7022(7)	0.5967(6)
O(22)	0.955(1)	0.7216(5)	0.5374(5)
C(23)	0.496(2)	0.6798(7)	0.6484(6)
O(23)	0.351(1)	0.6859(6)	0.6212(5)
C(24)	1.011(2)	0.6488(6)	0.7553(6)
O(24)	1.151(1)	0.6393(5)	0.7867(5)
C(25)	0.637(2)	0.5843(6)	0.7789(7)
O(25)	0.580(2)	0.5316(4)	0.8158(6)
Compound 5			
W(1)	0.30780(8)	0.11487(2)	0.02337(4)
W(2)	0.26203(7)	0.23709(2)	−0.08082(4)
C(1)	0.182(2)	0.1437(7)	−0.123(1)
C(2)	0.269(2)	0.1161(6)	−0.2080(9)
C(3)	0.155(3)	0.0916(7)	−0.284(1)
C(31)	−0.062(3)	0.093(1)	−0.288(2)
C(32)	0.255(4)	0.0609(8)	−0.361(2)
C(33)	0.201(4)	−0.0062(8)	−0.358(2)
C(34)	0.302(4)	−0.039(1)	−0.438(2)
C(35)	0.250(4)	−0.105(1)	−0.432(2)
C(11)	0.362(3)	0.0539(8)	0.126(1)
O(11)	0.390(3)	0.0194(6)	0.183(1)
C(12)	0.201(2)	0.0437(8)	−0.048(1)
O(12)	0.138(2)	0.0010(5)	−0.0830(9)
C(13)	0.565(2)	0.1014(7)	−0.037(1)
O(13)	0.714(1)	0.0948(6)	−0.0674(9)
C(14)	0.051(2)	0.1291(7)	0.094(1)
O(14)	−0.080(2)	0.1343(7)	0.132(1)
C(15)	0.450(2)	0.1632(7)	0.128(1)
O(15)	0.529(2)	0.1836(6)	0.1912(9)

continued

TABLE 3 (continued)

Atom	x/a	y/b	z/c
C(21)	0.271(2)	0.3220(7)	−0.113(1)
O(21)	0.267(2)	0.3711(6)	−0.137(1)
C(22)	0.136(2)	0.2370(8)	−0.215(1)
O(22)	0.066(2)	0.2412(7)	−0.2860(9)
C(23)	0.524(2)	0.2223(7)	−0.143(1)
O(23)	0.665(1)	0.2176(6)	−0.1760(9)
C(24)	0.007(2)	0.2461(8)	−0.014(1)
O(24)	−0.141(2)	0.2510(7)	0.0172(9)
C(25)	0.395(2)	0.2718(6)	0.040(1)
O(25)	0.459(2)	0.2963(6)	0.1026(9)
Compound 13			
W(1)	0.75653(7)	0.12709(4)	0.35816(4)
W(2)	0.31945(7)	0.31811(4)	0.33661(4)
C(1)	0.654(1)	0.2371(9)	0.417(1)
O(1)	0.698(1)	0.3188(7)	0.4496(8)
C(2)	0.517(2)	0.2137(9)	0.4314(9)
C(3)	0.472(2)	0.2605(9)	0.500(1)
C(4)	0.829(2)	0.360(1)	0.445(1)
C(11)	0.796(2)	0.210(1)	0.255(1)
O(11)	0.821(1)	0.254(1)	0.1983(9)
C(12)	0.725(2)	0.040(1)	0.462(1)
O(12)	0.712(1)	−0.0063(8)	0.5220(8)
C(13)	0.963(2)	0.156(1)	0.455(1)
O(13)	1.085(1)	0.1665(8)	0.5058(8)
C(14)	0.559(2)	0.090(1)	0.255(1)
O(14)	0.450(1)	0.0692(8)	0.1929(8)
C(15)	0.842(2)	0.019(1)	0.309(1)
O(15)	0.885(2)	−0.0452(9)	0.281(1)
C(21)	0.389(2)	0.2944(9)	0.223(1)
O(21)	0.422(1)	0.2847(7)	0.1560(7)
C(22)	0.220(2)	0.362(1)	0.429(1)
O(22)	0.163(1)	0.3904(9)	0.480(1)
C(23)	0.194(2)	0.197(10	0.301(1)
O(23)	0.132(1)	0.1312(9)	0.285(1)
C(24)	0.449(2)	0.436(1)	0.375(1)
O(24)	0.512(1)	0.5024(8)	0.3943(8)
C(25)	0.159(2)	0.383(1)	0.228(1)
O(25)	0.061(1)	0.4192(9)	0.1647(9)
Compound 11			
W(1)	0.26417(5)	−0.04132(3)	0.34198(3)
W(2)	0.14611(5)	0.09149(3)	0.19059(3)
C(1)	0.232(1)	−0.0702(8)	0.2051(8)
O(1)	0.3658(9)	−0.1098(6)	0.1725(5)
C(2)	0.095(1)	−0.0745(7)	0.1506(9)
C(3)	−0.051(1)	−0.0406(7)	0.1796(8)
C(4)	0.367(1)	−0.1677(9)	0.0962(9)
C(5)	−0.182(1)	−0.0334(9)	0.115(1)
C(11)	0.311(1)	−0.193(1)	0.3307(9)
O(11)	0.339(1)	−0.2748(7)	0.3292(7)
C(12)	0.039(2)	−0.0657(8)	0.3772(9)
O(12)	−0.085(1)	−0.0773(7)	0.4017(7)
C(13)	0.490(2)	−0.0060(9)	0.3078(8)
O(13)	0.608(1)	0.0175(7)	0.2888(7)

TABLE 3 (continued)

Atom	x/a	y/b	z/c
C(14)	0.246(1)	0.103(1)	0.386(1)
O(14)	0.246(1)	0.1783(8)	0.4170(7)
C(15)	0.325(2)	−0.069(1)	0.461(1)
O(15)	0.363(2)	−0.0895(8)	0.5292(8)
C(21)	0.035(1)	0.1567(9)	0.100(1)
O(21)	−0.034(1)	0.1933(7)	0.0433(7)
C(22)	0.325(1)	0.0880(9)	0.1093(9)
O(22)	0.425(1)	0.0922(7)	0.0645(7)
C(23)	0.255(1)	0.218(1)	0.2254(9)
O(23)	0.317(1)	0.2911(7)	0.2440(7)
C(24)	−0.023(1)	0.1357(9)	0.2711(9)
O(24)	−0.108(1)	0.1669(7)	0.3177(7)

gel, and preparative (PLC) and analytical thin layer chromatography (TLC) with Merck G60 silica gel.

NMR spectra were recorded on a JEOL C 60HL or FX-90 spectrometer or on a Bruker WM 250 or WM 500 spectrometer. IR spectra were recorded with a Beckman 4240 spectrophotometer, and mass spectra with a Kratos MS 3P. Melting points were determined on a Reichert Köfler block, and are uncorrected.

μ-Alkylidene complex 5

A solution of BuLi (1.8 *N*, 10 mmol) in hexane was added to a solution of pentacarbonyl(methylmethoxycarbene)tungsten(0) (4.0 g, 10 mmol) in Et_2O (100 ml), at −40 °C. The mixture was stirred for 10 min, then CF_3COOH (1.14 g, 10 mmol) was added, followed by water and then aqueous $NaHCO_3$. The usual work up gave a red oil which was chromatographed on SiO_2. Elution with light petroleum first gave a dark red oil of complex **3** (193 mg, 5%) as a 1/3 mixture of two isomers. Recrystallization from hexane gave red crystals of one isomer, m.p. 65 °C, suitable for an X-ray analysis, followed by starting material contaminated with complex **3** (2.5 g).

Complexes **5a** and **5b**: ^1H NMR (250 MHz, C_6D_6) δ(ppm): **5a**: 10.5 (1H, d, J 13 Hz, C(1)H), 6.78 (1H, d, J 13 Hz, C(2)H), 2.42 (2H, t, J 3 Hz, C(4)H_2), 1.77 (3H, d, J 1.1 Hz, CH_3), 1.29 (m, 4H, C(5)H_2 and C(6)H_2), 0.88 (3H, t, J 7.1 Hz, CH_2CH_3). **5b**: 10.32 (1H, J 13 Hz, C(1)H), 6.77 (1H, d, J 13 Hz, C(2)H), 2.06 (2H, d, J 7.5 Hz, C(4)H_2), 1.84 (3H, d, J 1.3 Hz, CH_3), 1.29 (4H, m, C(5)H_2 and C(6)H_2), 0.85 (3H, t, J 7.1 Hz, CH_2CH_3).

Pentacarbonyl(vinylmethoxycarbene)tungsten(0) (10)

Vinyllithium (20 mmol) (prepared from tetravinyltin and phenyllithium in Et_2O) was added to $W(CO)_6$ (7 g, 20 mmol) in Et_2O (250 ml), at room temperature. The solvent was evaporated under vacuum and the residue taken up in water (100 ml). The solution was filtered through glass wool to remove residual $W(CO)_6$ then 1 equivalent of Me_3OBF_4 was added. Extracting with light petroleum, followed by chromatography of the extract on silica gel first gave complex **10** (800 mg, 10%) as a red oil.

(*Continued on p. 369*)

TABLE 4

INTERATOMIC DISTANCES (Å) AND BOND ANGLES (°), WITH e.s.d.'s IN PARENTHESES

Compound 2			
W(1)-W(2)	3.1450(5)	C(2)-C(3)	1.34(1)
W(1)-C(1)	2.273(8)	C(3)-C(4)	1.48(2)
W(1)-C(11)	2.02(1)	C(3)-C(5)	1.50(1)
W(1)-C(12)	2.01(1)	C(11)-O(11)	1.13(1)
W(1)-C(13)	2.05(1)	C(12)-O(12)	1.14(1)
W(1)-C(14)	2.07(1)	C(13)-O(13)	1.11(1)
W(1)-C(15)	2.04(1)	C(14)-O(14)	1.10(1)
W(2)-C(1)	2.273(9)	C(15)-O(15)	1.14(1)
W(2)-C(21)	1.99(1)	C(21)-O(21)	1.15(1)
W(2)-C(22)	2.03(1)	C(22)-O(22)	1.14(1)
W(2)-C(23)	2.04(1)	C(23)-O(23)	1.13(1)
W(2)-C(24)	2.04(1)	C(24)-O(24)	1.13(1)
W(2)-C(25)	2.04(1)	C(25)-O(25)	1.13(1)
C(1)-C(2)	1.47(1)		
C(11)-W(1)-W(2)	161.6(2)	C(23)-W(2)-C(22)	91.6(4)
C(11)-W(1)-C(1)	152.1(4)	C(24)-W(2)-W(1)	87.8(3)
C(12)-W(1)-W(2)	119.0(3)	C(24)-W(2)-C(1)	90.3(3)
C(12)-W(1)-C(1)	72.9(4)	C(24)-W(2)-C(21)	90.2(5)
C(12)-W(1)-C(11)	79.3(4)	C(24)-W(2)-C(22)	91.1(4)
C(13)-W(1)-W(2)	91.6(3)	C(24)-W(2)-C(23)	177.0(4)
C(13)-W(1)-C(1)	88.5(4)	C(25)-W(2)-W(1)	85.0(3)
C(13)-W(1)-C(11)	88.2(4)	C(25)-W(2)-C(1)	131.2(4)
C(13)-W(1)-C(12)	90.1(5)	C(25)-W(2)-C(21)	77.7(4)
C(14)-W(1)-W(2)	89.3(3)	C(25)-W(2)-C(22)	158.1(4)
C(14)-W(1)-C(1)	90.6(3)	C(25)-W(2)-C(23)	88.5(5)
C(14)-W(1)-C(11)	91.6(4)	C(25)-W(2)-C(24)	89.4(5)
C(14)-W(1)-C(12)	87.7(5)	W(2)-C(1)-W(1)	87.6(3)
C(14)-W(1)-C(13)	177.8(4)	C(2)-C(1)-W(1)	118.7(6)
C(15)-W(1)-W(2)	82.5(3)	C(2)-C(1)-W(2)	119.5(6)
C(15)-W(1)-C(1)	128.5(3)	C(3)-C(2)-C(1)	127.9(10)
C(15)-W(1)-C(11)	79.1(4)	C(4)-C(3)-C(2)	124.3(10)
C(15)-W(1)-C(12)	158.5(4)	C(5)-C(3)-C(2)	119.3(10)
C(15)-W(1)-C(13)	89.1(5)	C(5)-C(3)-C(4)	116.3(10)
C(15)-W(1)-C(14)	93.0(5)	O(11)-C(11)-W(1)	178.2(11)
C(21)-W(2)-W(1)	162.7(3)	O(12)-C(12)-W(1)	178.0(12)
C(21)-W(2)-C(1)	151.1(4)	O(13)-C(13)-W(1)	177.2(12)
C(22)-W(2)-W(1)	116.9(3)	O(14)-C(14)-W(1)	177.1(10)
C(22)-W(2)-C(1)	70.7(4)	O(15)-C(15)-W(1)	169.8(8)
C(22)-W(2)-C(21)	80.4(4)	O(21)-C(21)-W(2)	178.7(11)
C(23)-W(2)-W(1)	89.8(3)	O(22)-C(22)-W(2)	177.2(10)
C(23)-W(2)-C(1)	89.4(4)	O(23)-C(23)-W(2)	177.7(11)
C(23)-W(2)-C(21)	91.5(5)	O(24)-C(24)-W(2)	179.1(9)
		O(25)-C(25)-W(2)	170.1(9)
Compound 5			
W(1)-W(2)	3.1354(8)	C(12)-O(13)	1.17(2)
W(1)-C(13)	2.03(2)	C(15)-O(14)	1.12(2)
W(1)-C(14)	2.11(2)	C(11)-O(15)	1.13(2)
W(1)-C(12)	2.03(2)	C(23)-O(21)	1.11(2)
W(1)-C(15)	2.06(2)	C(24)-O(22)	1.14(2)
W(1)-C(11)	2.01(2)	C(22)-O(23)	1.10(2)
W(1)-C(1)	2.28(1)	C(25)-O(24)	1.11(2)

TABLE 4 (continued)

W(2)–C(23)	2.08(2)	C(21)–O(25)	1.16(2)
W(2)–C(24)	2.05(2)	C(1)–C(2)	1.48(2)
W(2)–C(22)	2.03(1)	C(2)–C(3)	1.42(2)
W(2)–C(25)	2.05(1)	C(3)–C(31)	1.53(3)
W(2)–C(21)	1.98(2)	C(3)–C(32)	1.47(3)
W(2)–C(1)	2.27(1)	C(32)–C(33)	1.57(2)
C(13)–O(11)	1.15(2)	C(33)–C(34)	1.52(2)
C(14)–O(12)	1.08(2)	C(34)–C(35)	1.54(2)
C(14)–W(1)–C(13)	176.4(6)	C(1)–W(2)–C(23)	87.8(6)
C(12)–W(1)–C(13)	90.3(6)	C(1)–W(2)–C(24)	89.6(6)
C(12)–W(1)–C(14)	92.0(6)	C(1)–W(2)–C(22)	70.3(6)
C(15)–W(1)–C(13)	86.9(6)	C(1)–W(2)–C(25)	132.5(5)
C(15)–W(1)–C(14)	90.0(6)	C(1)–W(2)–C(21)	149.4(6)
C(15)–W(1)–C(12)	159.3(6)	O(11)–C(13)–W(1)	177.0(13)
C(11)–W(1)–C(13)	91.5(7)	O(12)–C(14)–W(1)	177.2(16)
C(11)–W(1)–C(14)	86.1(7)	O(13)–C(12)–W(1)	175.2(13)
C(11)–W(1)–C(12)	81.8(7)	O(14)–C(15)–W(1)	172.0(14)
C(11)–W(1)–C(15)	77.8(7)	O(15)–C(11)–W(1)	178.9(17)
C(1)–W(1)–C(13)	90.7(6)	O(21)–C(23)–W(2)	176.2(14)
C(1)–W(1)–C(14)	92.7(6)	O(22)–C(24)–W(2)	175.4(13)
C(1)–W(1)–C(12)	70.4(6)	O(23)–C(22)–W(2)	174.8(16)
C(1)–W(1)–C(15)	130.0(6)	O(24)–C(25)–W(2)	172.6(14)
C(1)–W(1)–C(11)	152.1(6)	O(25)–C(21)–W(2)	175.3(16)
C(24)–W(2)–C(23)	175.8(6)	W(2)–C(1)–W(1)	87.1(5)
C(22)–W(2)–C(23)	89.9(6)	C(2)–C(1)–W(1)	114.9(10)
C(22)–W(2)–C(24)	92.3(6)	C(2)–C(1)–W(2)	119.6(10)
C(25)–W(2)–C(23)	90.2(6)	C(3)–C(2)–C(1)	120.6(15)
C(25)–W(2)–C(24)	89.2(6)	C(31)–C(3)–C(2)	125.1(17)
C(25)–W(2)–C(22)	157.2(6)	C(32)–C(3)–C(2)	116.5(19)
C(21)–W(2)–C(23)	91.6(7)	C(32)–C(3)–C(31)	118.4(19)
C(21)–W(2)–C(24)	92.3(7)	C(33)–C(32)–C(3)	108.4(6)
C(21)–W(2)–C(22)	79.1(7)	C(34)–C(33)–C(32)	109.5(6)
C(21)–W(2)–C(25)	78.1(7)	C(35)–C(34)–C(33)	108.8(6)
Compound 13			
W(1)–C(11)	2.07(1)	O(1)–C(4)	1.44(1)
W(1)–C(12)	2.05(2)	C(1)–C(2)	1.45(2)
W(1)–C(13)	2.08(1)	C(2)–C(3)	1.42(2)
W(1)–C(14)	2.06(1)	C(3)–C(5)	1.52(2)
W(1)–C(15)	1.99(2)	C(11)–O(11)	1.12(1)
W(1)–C(1)	2.23(1)	C(12)–O(12)	1.15(1)
W(2)–C(1)	2.29(1)	C(13)–O(13)	1.11(1)
W(2)–C(2)	2.34(1)	C(14)–O(14)	1.12(1)
W(2)–C(3)	2.45(1)	C(15)–O(15)	1.17(2)
W(2)–C(21)	1.93(2)	C(21)–O(21)	1.18(2)
W(2)–C(22)	2.03(1)	C(22)–O(22)	1.13(1)
W(2)–C(23)	2.01(1)	C(23)–O(23)	1.14(1)
W(2)–C(24)	2.04(1)	C(24)–O(24)	1.13(1)
C(1)–O(1)	1.37(1)		
C(11)–W(1)–C(1)	76.5(4)	C(22)–W(2)–C(23)	80.8(5)
C(11)–W(1)–C(12)	93.0(4)	C(22)–W(2)–C(24)	164.5(4)
C(11)–W(1)–C(13)	91.0(4)	C(23)–W(2)–C(1)	128.1(4)
C(11)–W(1)–C(14)	163.8(5)	C(23)–W(2)–C(24)	85.2(5)
C(11)–W(1)–C(15)	81.7(5)	C(24)–W(2)–C(1)	116.1(4)
C(12)–W(1)–C(1)	97.9(5)	W(1)–C(1)–O(1)	110.2(8)

continued

TABLE 4 (continued)

C(12)-W(1)-C(13)	176.0(4)	W(1)-C(1)-C(2)	132.9(8)
C(12)-W(1)-C(14)	88.8(5)	O(1)-C(1)-C(2)	115.6(11)
C(12)-W(1)-C(15)	86.8(5)	C(1)-C(2)-C(3)	120.3(12)
C(13)-W(1)-C(1)	83.4(4)	C(2)-C(3)-C(5)	116.7(12)
C(13)-W(1)-C(14)	87.3(5)	C(1)-O(1)-C(4)	122.7(10)
C(13)-W(1)-C(15)	93.4(5)	W(1)-C(11)-O(11)	176.0(12)
C(14)-W(1)-C(1)	119.2(5)	W(1)-C(12)-O(12)	175.9(12)
C(14)-W(1)-C(15)	82.4(5)	W(1)-C(13)-O(13)	176.6(11)
C(15)-W(1)-C(1)	157.9(5)	W(1)-C(14)-O(14)	172.4(12)
C(21)-W(2)-C(1)	130.9(5)	W(1)-C(15)-O(15)	176.5(13)
C(21)-W(2)-C(22)	84.5(5)	W(2)-C(21)-O(21)	177.9(11)
C(21)-W(2)-C(23)	93.0(5)	W(2)-C(22)-O(22)	175.7(11)
C(21)-W(2)-C(24)	89.6(5)	W(2)-C(23)-O(23)	178.9(13)
C(22)-W(2)-C(1)	78.2(4)	W(2)-C(24)-O(24)	174.1(10)
Compound 11			
W(1)-C(11)	2.05(2)	O(1)-C(4)	1.44(2)
W(1)-C(12)	2.06(2)	C(1)-C(2)	1.49(2)
W(1)-C(13)	2.02(2)	C(2)-C(3)	1.40(2)
W(1)-C(14)	2.02(2)	C(11)-O(11)	1.13(2)
W(1)-C(15)	2.03(2)	C(12)-O(12)	1.14(2)
W(1)-C(1)	2.22(2)	C(13)-O(13)	1.16(2)
W(2)-C(21)	2.03(2)	C(14)-O(14)	1.15(2)
W(2)-C(22)	2.04(2)	C(15)-O(15)	1.15(2)
W(2)-C(23)	2.08(2)	C(21)-O(21)	1.14(2)
W(2)-C(24)	2.06(2)	C(22)-O(22)	1.15(3)
W(2)-C(25)	1.98(1)	C(23)-O(23)	1.11(2)
W(2)-C(2)	2.43(1)	C(24)-O(24)	1.12(2)
W(2)-C(3)	2.40(1)	C(25)-O(25)	1.16(2)
C(1)-O(1)	1.28(2)		
C(11)-W(1)-C(1)	95.9(6)	C(22)-W(2)-C(24)	88.7(7)
C(11)-W(1)-C(12)	177.3(6)	C(22)-W(2)-C(25)	85.6(7)
C(11)-W(1)-C(13)	87.6(6)	C(23)-W(2)-C(24)	178.3(6)
C(11)-W(1)-C(14)	91.1(6)	C(23)-W(2)-C(25)	88.7(6)
C(11)-W(1)-C(15)	88.5(7)	C(24)-W(2)-C(25)	93.0(6)
C(12)-W(1)-C(1)	86.5(6)	W(1)-C(1)-O(1)	130.9(11)
C(12)-W(1)-C(13)	91.1(6)	W(1)-C(1)-C(2)	117.9(9)
C(12)-W(1)-C(14)	90.0(6)	O(1)-C(1)-C(2)	110.9(13)
C(12)-W(1)-C(15)	89.1(7)	C(1)-C(2)-C(3)	122.9(12)
C(13)-W(1)-C(1)	94.9(6)	C(1)-O(1)-C(4)	122.8(12)
C(13)-W(1)-C(14)	174.5(8)	W(1)-C(11)-O(11)	177.9(14)
C(13)-W(1)-C(15)	87.0(6)	W(1)-C(12)-O(12)	177.6(14)
C(14)-W(1)-C(1)	90.6(6)	W(1)-C(13)-O(13)	174.2(13)
C(14)-W(1)-C(15)	87.7(6)	W(1)-C(14)-O(14)	176.8(16)
C(15)-W(1)-C(1)	175.2(6)	W(1)-C(15)-O(15)	176.8(15)
C(21)-W(2)-C(22)	167.5(6)	W(2)-C(21)-O(21)	176.1(12)
C(21)-W(2)-C(23)	90.8(7)	W(2)-C(22)-O(22)	177.4(15)
C(21)-W(2)-C(24)	89.1(6)	W(2)-C(23)-O(23)	177.0(17)
C(21)-W(2)-C(25)	82.3(5)	W(2)-C(24)-O(24)	175.7(15)
C(22)-W(2)-C(23)	91.8(7)	W(2)-C(25)-O(25)	177.9(16)

^{1}H NMR (60 MHz, CDCl$_3$) δ(ppm): 7.4 (1H, dd, J 14 and 22 Hz, CH=CH$_2$), 5.72 (1H, dd, J 22 and 2 Hz, CH=CHH *cis*), 5.25 (1H, dd, J 14 and 2 Hz, CH=CHH *trans*), 4.6 (3H, OCH_3). Further elution with light petroleum gave complex **11** (1.1 g, 15%), as dark purple crystals after recrystallization from hexane, m.p. 97 °C; ^{1}H NMR (60 MHz, CDCl$_3$) δ (ppm): 5.55 (1H, dd, J 14.2 and 8.2 Hz, CH=CH$_2$), 4.4 (3H, s, OCH_3), 3.6 (2H, dd, J 14.2 and 8.2 Hz, CH=CH_2). ^{13}C NMR 90 MHz, CDCl$_3$) δ (ppm): 311.1 (carbene), 197.2 (CO), 194.7 (CO), 90.9 (CH=CH$_2$), 67.8 (OCH$_3$), 47.7 (CH=CH$_2$).

The corresponding ethoxycarbene complexes were prepared by the same procedure. Mass spectrum: m/e 732 (M^+).

Pentacarbonyl(1-propenyl)methoxytungsten(0) (9, R = CH$_3$)

Formation of a Grignard reagent was started with Mg (2 g) in Et$_2$O (12 ml) and a few drops of allyl bromide, then W(CO)$_6$ (5.2 g) and more allyl bromide (4 g) in Et$_2$O (50 ml) were added and the mixture was stirred until the suspended W(CO)$_6$ disappeared. After evaporation of the solvent, followed by hydrolysis of the residue, Me$_3$OBF$_4$ (3 g) was added, and the mixture extracted with light petroleum. Passage of the extract through silica gel gave complex **9** (R = CH$_3$) as a red oil (2.4 g, 40%).

^{1}H NMR (60 MHz, C$_6$D$_6$) δ(ppm): 7.3 (1H, d, J 20 Hz, C(2)H), 6.57 (1H, dq, J 20 and 9 Hz, C(3)H), 4.55 (3H, s, OCH_3), 1.82 (3H, d, J 9 Hz, CH_3).

Pentacarbonyl(1-propenyl)ethoxycarbenetungsten(0) was prepared by the same procedure.

^{13}C NMR (90 MHz, C$_6$D$_6$) δ(ppm): 307.2 (carbene, 197.6 (CO), 149.4 (C(2)H), 136.8 (C(3)H$_2$), 78.9 (OCH$_2$), 18.4 (C-CH$_3$), 14.7 (CH$_2$$CH_3$).

μ-Alkylidene complex 13 (R = CH$_3$, CH$_2$CH$_3$)

Photochemical reaction. A solution of complex **9** (810 mg, 2 mmol) and W(CO)$_6$ (700 mg, 2 mmol) in hexane (100 ml) was irradiated with a water-cooled Philips lamp for 12 h at room temperature. Evaporation of the solvent followed by silica gel chromatography gave complex **13** (R = Et) (327 mg, 23%), m.p. 106 °C.

^{13}C NMR (R = OEt) δ(ppm): 231.1 (carbene), 197.1 (CO), 88.6 (CH=C), 82.0 (OCH$_2$), 68.4 (HC=CHCH$_3$), 20.0 (=CHCH$_3$), 14.6 (CH$_2$$CH_3$). Mass spectrum: m/e 718 (M^+).

Thermal reaction. A solution of complex **9** (R = Me) (1.428 g, 3.5 mmol) and complex **12** (3.4 g, 74 mmol) in hexane (50 ml) was heated at 40 °C for 17 h. TLC showed that no **12** remained in the solution. Silica gel chromatography, at 0 °C, gave first the starting carbene **9** (880 mg), then complex **13** (1.2 g, 49%) as black crystals.

^{1}H NMR (60 MHz, C$_6$D$_6$) δ(ppm): 5.05 (1H, d, J 12 Hz, CH=C), 3.15 (3H, s, OCH_3), 3.05 (1H, m, CH=CH-CH$_3$), 1.75 (3H, d, J 8 Hz, =CH-CH_3).

μ-Alkylidene complex 14. Complex **10** (R = Me) (0.2 g, 0.5 mmol) was heated in the presence of complex **2** (0.5 g, 1 mmol) in hexane (50 ml) for 14 h. After evaporation of the solvent at room temperature, the residue was chromatographed through silica gel, at −15 °C. Elution with light petroleum first gave complex **14** (60 mg).

^{1}H NMR (C$_6$D$_6$, 60 MHz) δ(ppm): 4.92 (1H, dd, J 12 and 10 Hz, CH=CH$_2$), 3.20 (3H, s, OCH_3), 3.10 (1H, dd, J 10 and 2 Hz, CH=CHH), 2.05 (1H, dd, J 12 and 2 Hz, CH=CHH), m/e 718 (M^+). Complex **15** (65 mg) was next eluted and isolated as a yellow oil.

IR ($CHCl_3$): ν(CO) 2080, 2050, 1980, 1970, 1940 cm^{-1}. ^1H NMR (250 MHz, C_6D_6) δ(ppm): 7.28 (10H, m, aromatic) 4.33 (1H, dd, J 7.4 and 5.8 Hz, $CH=CH_2$), 2.64 (1H, dd, J 5.8 and 4.4 Hz), 1.88 (1H, dd, J 7.4 and 4.4 Hz). ^{13}C NMR (C_6D_6) δ(ppm): 197.5 (CO), 144.2 (=COR), 139.5 (Ph_2C=), 130.9, 128.8, 128.1, 127.2, 127.0 (aromatic), 68.1 (OCH_3), 59.4 (HC=C), 2.7.7 (CH_2=C). Mass spectrum m/e 690 (M^+). Finally complex **11** (25 mg) was eluted, and isolated as black crystals, and identified by comparison with an authentic sample.

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