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Preliminary communication

SYNTHESIS OF μ-ALKYLIDENE COMPLEXES OF TUNGSTEN

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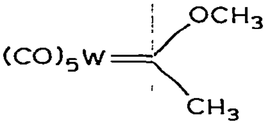
Summary

Treatment of $EtOCMe{=}W(CO)_5$ with MeLi, followed by acidification with CF_3CO_2H, afforded a red crystalline compound. This was found to be the binuclear complex $(CO)_4\overline{W{-}W(CO)_4C}HCH{=}CMe_2$ by X ray analysis and NMR spectroscopy. A mechanism for the formation of this binuclear complex is outlined.

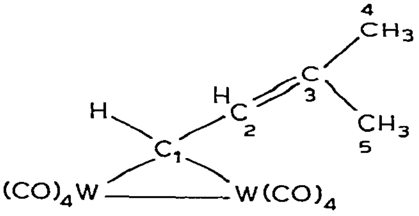
In the course of our studies [1—4] on the mechanism of the olefin-metathesis reaction, we became interested in making compounds of the type $RR'C{=}W(CO)_5$, a hitherto unreported species when both R and R′ are alkyl groups. When R = R′ = Ph, the metal complex has been isolated and characterised [5,6], while the complexes with R = Ph, R′ = Me and H have been prepared in solution [7,8]. A classical method of making such compounds is to treat an alkoxycarbene derivative with an alkylmetal. As applied to $MeOC(Me){=}W(CO)_5$ (I) and MeLi, the reaction, after treatment of the resulting solution with CF_3CO_2H, afforded a mixture which could be separated by fast silicagel chromatography into I and a red crystalline compound, to which structure II was assigned on the basis of spectral and radiocrystallographic data (see experimental). The ORTEP plot for II is shown in Fig. 1. Bond lengths and bond angles are given in Table 1.

The spectral data are in agreement with structure II: the off-resonance ^{13}C NMR spectrum shows that both C(1) and C(2) each bear one hydrogen atom, and the noise decoupled ^{13}C NMR spectrum shows that C(1) is coupled to both tungsten atoms ($J(W{-}C)$ = 45 Hz) [9].

The geometry of II (from X-ray data) and the chemical shifts of both C(1), C(2) and H(1) suggest that II could be regarded as resulting formally from the interaction of W=W double bond with a singlet alkylidene moiety, leading to a three-membered ring with a W—W single bond: this picture would amount to the



(I)



(II)

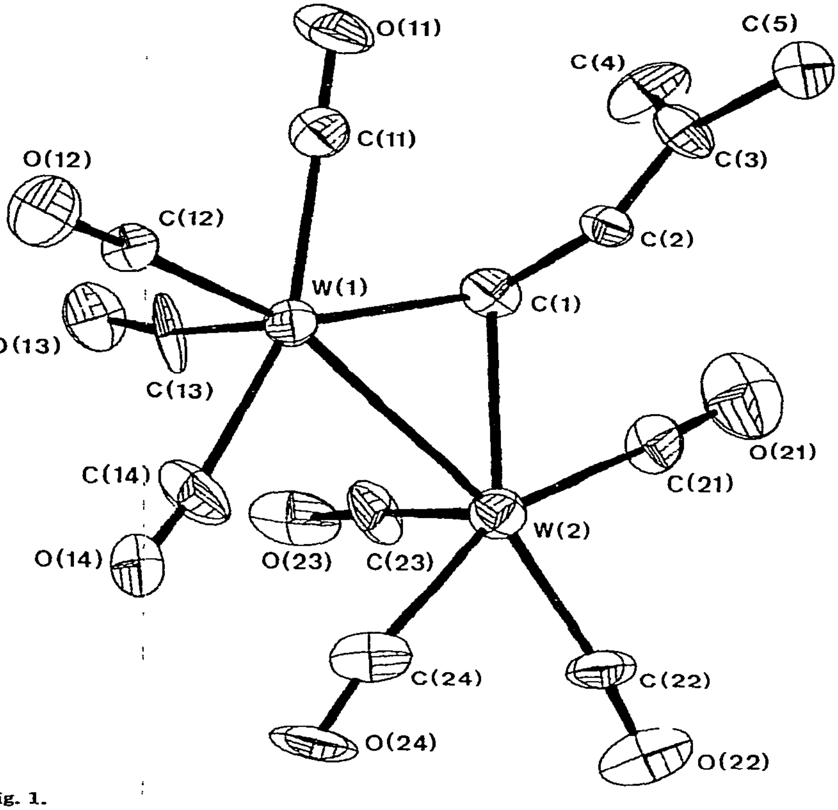


Fig. 1.

TABLE 1

BOND LENGTHS (Å) AND BOND ANGLES (°) OF $(CO)_4W_2CHCH{=}CMe_2$

W(1)—W(2)	3.157(1)	W(1)—C(1)—C(2)	122(1)
W(1)—C(1)	2.30(2)	W(1)—C(1)—W(2)	85.8(5)
W(2)—C(1)	2.34(2)	C(1)—W(1)—W(2)	47.7(4)
C(1)—C(2)	1.40(2)	C(1)—W(2)—W(1)	46.5(4)
C(2)—C(3)	1.33(2)	C(1)—C(2)—C(3)	132(2)
C(3)—C(4)	1.63(3)	C(2)—C(3)—C(4)	115(2)
C(3)—C(5)	1.57(3)	C(2)—C(3)—C(5)	120(2)
		C(4)—C(3)—C(5)	124(2)
		W(2)—C(1)—C(2)	120(1)

reverse of the classical Dewar—Chatt description of the interaction of the C=C double bond with a metal atom (or ion)*.

In order to shed light on the mechanism of the transformation of I into II, the experiments shown in Scheme 1 were carried out. Compounds III, IV and V were isolated as a mixture of both possible geometrical isomers. On the basis of these experiments, the mechanism shown in Scheme 2 can be proposed.

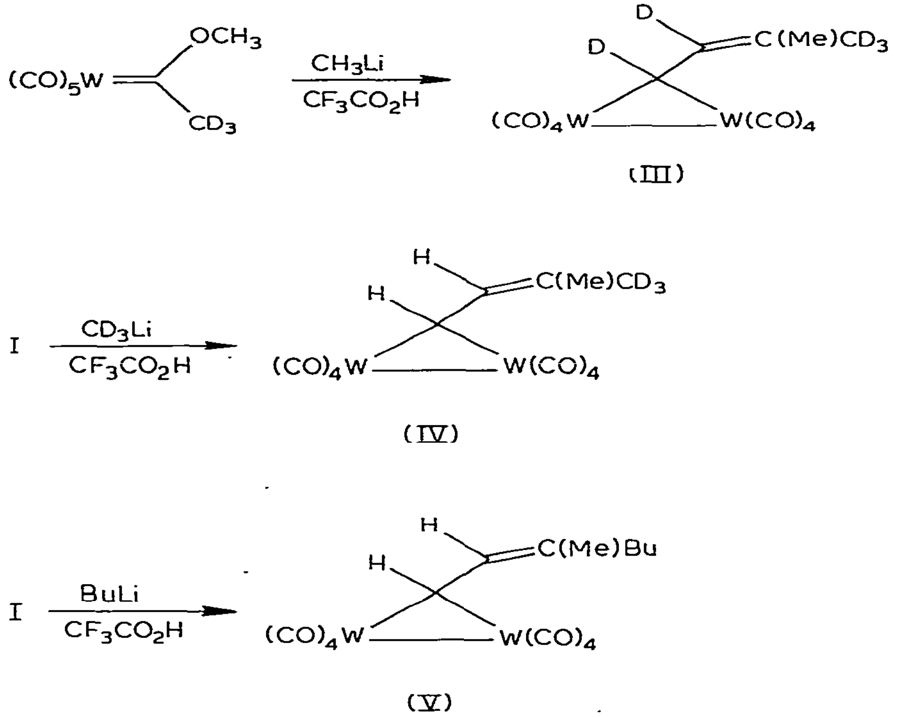
Intermediate VI was detected by Casey [11] in an analogous reaction with BuLi. Intermediate IX is of the type postulated for the formation of $Ph_2C=W(CO)_5$ [12]. Further work is in progress to establish the generality of the formation of type II complexes and, since II shows activity in the metathesis reaction, its possible role in this reaction.

Experimental

Procedure

All operations were performed under nitrogen using anhydrous solvents.

To a cooled (−40°C) solution $EtOCMe=W(CO)_5$ (I) (3.68 g, 10^{-2} mol) in ether (100 ml) was added first a 1.4 *N* ether solution of MeLi (7.5 ml, 10^{-2} mol), then CF_3CO_2H (0.75 ml, 10^{-2} mol), stirring being continued for 5 min. Fast column chromatography of the crude reaction product on Kieselgel (Merck 60,



SCHEME 1

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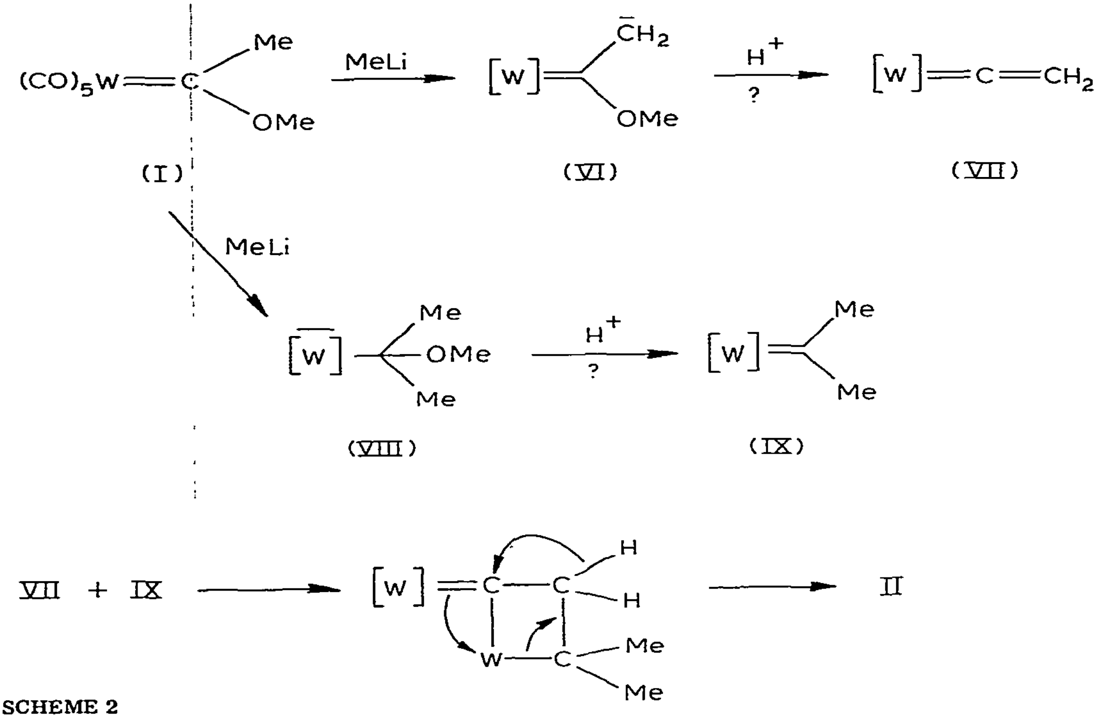
*The C(1)—C(2) bond length of 1.40(2) Å in II is conspicuous in being close to the C(1)—C(2) bond in acrolein $C(3)H_2=C(2)H—C(1)H=O$ (1.44 Å).

μ-Alkylidene complexes of other transition metals have already been described [10].



SCHEME 2

0.063—0.200) with elution with pentane gave red crystals of complex II (650 mg; yield 18%). The complex was recrystallized from pentane.

Spectroscopic data of II, III and IV: $(CO)_4W_2CHCH{=}C(Me)_2$ (II): red needles; m.p. 64—65°C; ^1H NMR ($CDCl_3$, δ (ppm), TMS int): 10.16 d (C(1)—H) J 14 Hz; 6.58d (C(2)—H) J 14 Hz; 2.13s (C_4H_3); 2.00 s (C_5H_3). IR (cm^{-1}): 1992vs, 2038w, 2058m, 2100w cm^{-1} ($CHCl_3$). ^{13}C NMR (noise decoupled, $CDCl_3$, δ (ppm), TMS int): 196.3 (CO), 148.6 (C(2)), 145.1 (C(1)), 129.8 (C(3)), 25.4 (C(4)), 18.2 (C(5)) (off resonance): 148.6d (C(2)), 145.1d (C(1)).

$(CO)_4W_2CDCD{=}C(Me)(CD_3)$ (III): ^1H NMR ($CDCl_3$; δ (ppm), TMS int): 2.13d (C_4H_3) (J 1.8 Hz); 2.00d (C_5H_3) (J 1.8 Hz).

$(CO)_4W_2CHCH{=}C(Me)(CD_3)$ (IV): ^1H NMR ($CDCl_3$, δ (ppm), TMS int): 10.16d (C(1)—H) (J 14 Hz); 6.58d (C(2)—H) (J 14 Hz); 2.13 (C_4H_3); 2.00 (C_5H_3).

Crystal data. $C_{13}H_8O_8W_2$, mol. wt. 659.7, orthorhombic, a 7.147(2), b 16.422(5), c 16.649(5) Å, V 1954 Å^3, D_c 2.24 g cm^{-3} with $Z = 4$, space group $P2_12_12_1$. Intensity data ($2\theta < 50°$) were recorded on an Enraf-Nonius CAD-3 automatic diffractometer, using Cr filtered Mo-K_α radiation by the θ—2θ scan technique. 1340 observed reflexions were used in the analysis. ($R = 0.058$, $R_w = 0.076$). High thermal parameters may explain the large error standard deviations.

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