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Preliminary communication

DINUCLEAR μ-ALKYLIDENE COMPLEXES OF TUNGSTEN FROM MONONUCLEAR, HETEROATOM-SUBSTITUTED VINYL-ALKYLIDENE COMPLEXES OF THIS METAL

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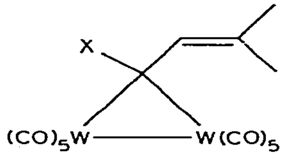
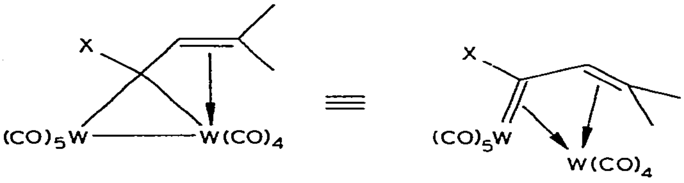
Summary

A general synthesis of homodinuclear μ-alkylidene complexes of tungsten, starting from Fischer type alkylidene complexes of tungsten is outlined. Thus the vinyl-alkylidene complexes $(CO)_5W{=}C(OMe)CHCHR$ react with $(CO)_5W{=}CPh_2$, as a source of coordinatively unsaturated $W(CO)_4$, to give the dinuclear complexes $W_2(CO)_9(OMe)CHCHR$, and the complex $(CO)_5W{=}C(OMe)CHCH_2$ reacts slowly in hydrocarbon solution, in the absence of $(CO)_5W{=}CPh_2$, to give a dinuclear complex $W_2(CO)_{10}C(OMe)CHCH_2$ in which the two metal centers are not bound together: this product is the result of coordination of the double bond of the starting material to a $W(CO)_5$ species.

The search for a general approach to μ-alkylidene complexes of tungsten was undertaken, because of their interesting reactions [1,2]. Although heterodinuclear complexes have been obtained by Stone et al. [3,4], starting from mononuclear alkylidene complexes of tungsten, no straightforward synthesis of homodinuclear μ-alkylidene complexes of tungsten has been described. The only indirect synthesis so far outlined [6] starts from $(CO)_5W{=}C(OMe)Me$ and leads to μ-alkylidene complexes I and II in which the organic ligand is



(I)



(II, X = H)

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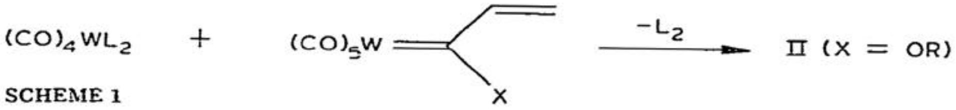
the result of a rather complicated reaction between unstable intermediates. This communication describes a general approach to these systems.

Two importants points were taken into account in devising such an approach: (1) as far as their reactivity is concerned, mononuclear alkylidene complexes can be compared to organic carbonyl compounds [7]; (2) organic carbonyl compounds, and especially conjugated carbonyl compounds, react with $W(CO)_6$ to give substitution products in which the organic substrate acts as a bidentate ligand [8].

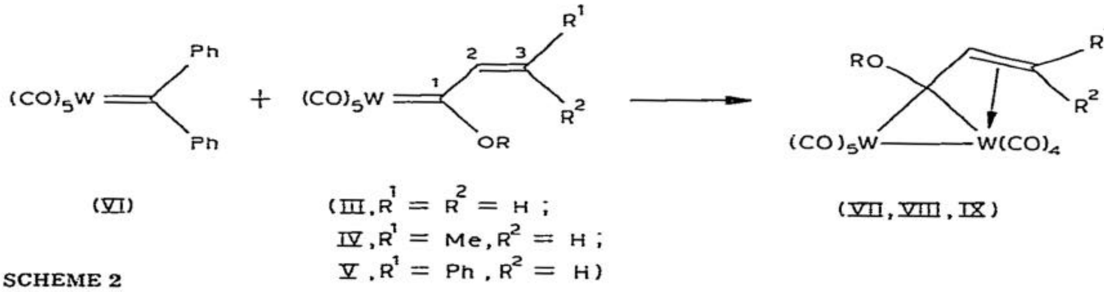
Thus we attempted the synthesis of complexes of type II (X = OR) by treating conjugated alkylidene complexes (the analog of a conjugated carbonyl compound) with $W(CO)_4L_2$ (Scheme 1). A suitable source of $W(CO)_4$ was found when we observed [9] that $(CO)_5W{=}CPh_2$ (VI) reacts with 1,5-cyclooctadiene (COD) to give inter alia $W(CO)_4COD$.



SCHEME 1

Results and discussion

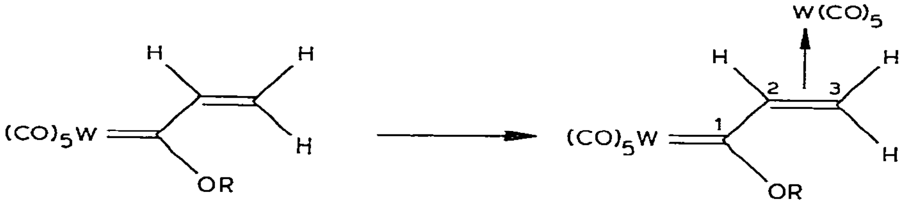
The conjugated alkylidene complexes III—V as well as VI were prepared by published methods [10—12]. For example, complex IV reacts with VI (Scheme 2) at 50°C, in hexane, during about 12 h to give a new purple com-



SCHEME 2

plex VIII in about 20% yield. The formation of this dinuclear complex can be monitored by ^{13}C NMR spectroscopy: the characteristic signal of the carbene carbon atom C^1 at 307 ppm in IV disappears while a new signal appears at 231 ppm which corresponding to literature data [13], is assigned to the bridging carbon atom C^1 in VIII. The signals of the double bond carbon atoms C^2 and C^3 in IV are shifted upfield, from 149 and 136 ppm to 96 and 68 ppm, respectively.

Complex VIII (m.p. 106°C, dec.) (^1H NMR ($CDCl_3$) 1H at 5.8 ppm (d, *J* 9 Hz), 3H at 4 ppm (s), 1H at 3.3 ppm (d.q. *J* 9 and 6 Hz) and 3H at 2.3 ppm (d, *J* 6 Hz), is rather unstable in solution and slowly regenerates the starting material. When $R^1 = R^2 =$ Me, the dinuclear complex was not observed. The reactivity of complex III is somewhat unusual, thus it reacts slowly in hexane at room temperature and in the absence of VI to give a new dinuclear complex X (m.p. 96—98°C, dec.) different from VII (Scheme 3). The mass spectrum of complex X (m/e = 708, 10 CO groups) as well as the ^1H NMR spectrum (C^2H at 5.55 ppm, quartet, *J* 8.2 and 14.2 Hz, C^3H_2 at 3.6 ppm, d. of d. *J*



(III) (X)

SCHEME 3

8.2 and 14.2 Hz) and the ^{13}C NMR spectrum (C^1 at 311 ppm, C^2 at 48 ppm, C^3 at 91 ppm and CO at 194 and 197 ppm) are in agreement with this structure. Complex X is very stable in solution and heating for long periods is required to regenerate complex III.

It is clear that the synthesis of μ-alkylidene complexes of tungsten can be carried out starting from Fischer-type α,β-unsaturated mononuclear alkylidene complexes.

However, very small electronic (or steric) factors can change the nature of the reaction and greatly affect the stability of the products.

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