

## PREPARATION, CHEMICAL AND STRUCTURAL STUDIES OF A NEW ( $\eta$ -ALLYL)DIHALOCARBONYLTUNGSTEN(II) COMPOUND \*

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### Summary

The complex  $(C_2H_5)_4N[(\eta-C_3H_5)Cl_2(CO)_2WP(C_6H_5)_3]$  (I) prepared from the anion  $W(CO)_5Cl^-$ , crystallizes in the triclinic system,  $P\bar{1}$ ,  $a$  11.264(5),  $b$  14.697(6),  $c$  10.318(4) Å;  $\alpha$  99.37(3),  $\beta$  111.87(5),  $\gamma$  90.21°;  $V$  1559 Å<sup>3</sup>;  $Z = 2$ . The structure was refined to  $R = 0.057$  for 4509 independent reflections. The crystal is made up of discrete monomeric ions. In the anion the tungsten atom is at the center of an octahedron, with two chlorine atoms and two CO groups in the equatorial plane, and the two remaining apices occupied by a ( $\eta$ -allyl) ligand and a triphenylphosphine group.

### Introduction

Allyl halides react with halogenopentacarbonyl anions of Mo and W to give the allyl complexes  $M_2X_3(\eta-C_3H_5)_2(CO)_4^-$  ( $M = Mo, W$ ;  $X = Cl, Br$ ) [1]. The reaction is thought to proceed through the intermediate complex anion  $M(CO)_3X_2(\eta-C_3H_5)^-$ , but no direct evidence for such a compound has yet been given. Furthermore the structures of these  $\eta$ -allyl carbonyl halide complexes of molybdenum and tungsten present some structural problems related to the positions of halogen atoms and the allyl group.

We describe below the preparation of a new  $\eta$ -allyl carbonyl halide of tungsten starting from the tetraethylammonium salts of the halopentacarbonyl anion  $W(CO)_5Cl^-$ . The route to this complex and its structure as determined by X-ray crystallography are discussed.

### Experimental

All preparations were carried out under dry nitrogen or argon using solvents free from moisture and oxygen. Infrared spectra were recorded on KBr discs

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with a Perkin Elmer 283 spectrophotometer. Solution spectra in the carbonyl region were recorded in acetonitrile. Microanalysis for W, Cl, C, H, N and P were performed by the Service central de microanalyse du CNRS.

#### *Preparation of $(C_2H_5)_4N[(CO)_5WCl]$*

The preparation of this complex in diglyme has already been reported [2]. We describe here a different preparation at a lower temperature. This involves refluxing 20 mmol (7 g) of  $W(CO)_6$  and 19 mmol (3.17 g) of  $(C_2H_5)_4NCl$  in 50 ml of dioxan for 45 minutes. Two phases appear, and crystallisation takes place upon cooling to room temperature. The product is filtered off, washed with dioxan and dried under vacuum. By sublimation under vacuum at  $60^\circ C$  the excess of  $W(CO)_6$  is removed. The complex is then recrystallised from a dichloromethane-ether mixture (yield 80%).

#### *Preparation of $(C_2H_5)_4N[(\eta-C_3H_5)Cl_2(CO)_2WP(C_6H_5)_3]$*

4 mmol  $(C_2H_5)_4N[W(CO)_5Cl]$  (2 g) are dissolved in 30 ml benzene and 5 ml acetonitrile. 5 ml  $C_3H_5Cl$  are added and the solution is stirred for one hour at  $40^\circ C$ . The solution, which is initially yellow, gradually turns red. An excess of triphenylphosphine is added (10 mmol) and the solution is stirred for five minutes at  $40^\circ C$ . The product appears as an orange powder, which is filtered off, washed with benzene and dried under vacuum (yield 60/70%).

Analysis, found: C, 48.81; H, 5.24; Cl, 9.62; N, 1.80; P, 4.23; W, 26.19,  $C_{31}H_{40}Cl_2NO_2PW$  calcd.: C, 50.02; H, 5.38; Cl, 9.54; N, 1.88; P, 4.16; W, 24.72%. Single crystals suitable for X ray study were obtained by dissolution of the powder at  $40^\circ C$  in acetonitrile, filtration, and slow cooling.

#### *Crystallographic studies*

A poorly shaped fragment of a large single crystal of  $(C_2H_5)_4N[(\eta-C_3H_5)Cl_2(CO)_2WP(C_6H_5)_3]$  was mounted in a Lindeman glass capillary. The space group  $P\bar{1}$  was determined from precession and Laue photographs (Mo- $K_\alpha$ ,  $\lambda$  0.71069 Å). The lattice constants were obtained from a least squares refinement of the setting angles of 9 strong reflections centered manually on a four circle diffractometer.  $a$  11.264(5),  $b$  14.697(6),  $c$  10.318(4) Å,  $\alpha$  99.37(3);  $\beta$  111.87(5);  $\gamma$  90.21(2)°. The density calculated with two molecules per unit cell is 1.57 g cm<sup>-3</sup>, in good agreement with the experimental value of 1.55 g cm<sup>-3</sup> measured by flotation technique in a  $CHCl_3$ - $CCl_4$  mixture. Intensity data were collected at room temperature with Mo- $K_\alpha$  radiation, a take-off angle of  $3^\circ$ , and a graphite monochromator set in front of the counter. The scintillation counter was fitted with a pulse-height analyser adjusted to Mo- $K_\alpha$  radiation in such a way that 90% of the diffracted intensity was counted. The intensity of every independent reflection with  $(\sin \theta)/\lambda < 0.572$  were automatically measured with a  $\theta/2\theta$  scan. Scan range in  $\theta$  was  $0.55^\circ + 0.345 \tan \theta$ , and scan speed was 2.5 deg min<sup>-1</sup>. Background was measured in fixed position before and after each scan. The intensities of two standard reflections  $\bar{6}22$ ,  $0\bar{1}4$ , were measured every 100 reflections. If the counting rate exceeded 7000 counts sec<sup>-1</sup>, counting loss was taken into account. Lorentz and polarization corrections were applied together with an empirical absorption correction [3] to yield a set of 4893 independent structure factors. The linear absorption coefficient,  $\mu$ , for this

compound is  $41.4 \text{ cm}^{-1}$ . Each structure factor  $F$  was assigned a standard deviation  $\sigma = \Delta I/F$  where  $\Delta I$  was the error on the integrated intensity. Of the 4893 independent reflections 384 with  $F < 3\sigma$  were not included in subsequent calculations.

Computations were performed using standard programs [4] on the CII IRIS 80. Scattering factors were taken from International Tables for X-ray Crystallography including  $\Delta f'$  and  $\Delta f''$  for tungsten and chlorine. The agreement factors were defined in the usual way as  $R = \Sigma(|F_{\text{obs}} - F_{\text{calc}}|)/\Sigma|F_{\text{obs}}|$  and  $R_w = \{\Sigma(W|F_{\text{obs}} - F_{\text{calc}}|)^2/\Sigma(W|F_{\text{obs}}|)^2\}^{1/2}$ . In all least squares refinements the quantity minimized was  $\Sigma(W|F_{\text{obs}} - F_{\text{calc}}|)^2$  and the full matrix were inverted. A weighting scheme based on counting statistics,  $W = 2F/\sigma$ , was used in least-squares refinement.

The position of the tungsten atom was unambiguously revealed by a Patterson

TABLE 1

FRACTIONAL ATOMIC COORDINATES WITH e.s.d.'s IN PARENTHESES

|       | x          | y           | z           |
|-------|------------|-------------|-------------|
| W     | 0.22297(4) | -0.19738(3) | -0.16087(5) |
| Cl(1) | 0.0057(2)  | -0.2641(2)  | -0.3527(3)  |
| Cl(2) | 0.2925(4)  | -0.3607(2)  | -0.1429(4)  |
| C(1)  | 0.393(1)   | -0.1386(9)  | -0.034(1)   |
| O(1)  | 0.483(1)   | -0.0961(8)  | 0.043(1)    |
| C(2)  | 0.2116(9)  | -0.0704(9)  | -0.181(1)   |
| O(2)  | 0.2119(9)  | 0.0099(6)   | -0.188(1)   |
| C(3)  | 0.082(2)   | -0.125(1)   | -0.068(2)   |
| C(4)  | 0.127(1)   | -0.209(1)   | -0.012(2)   |
| C(5)  | 0.258(2)   | -0.203(2)   | 0.076(2)    |
| P     | 0.2873(2)  | -0.2322(2)  | -0.3784(3)  |
| C(11) | 0.459(1)   | -0.2465(9)  | -0.330(1)   |
| C(12) | 0.547(1)   | -0.174(1)   | -0.242(1)   |
| C(13) | 0.675(2)   | -0.181(2)   | -0.205(2)   |
| C(14) | 0.721(1)   | -0.259(2)   | -0.251(2)   |
| C(15) | 0.637(2)   | -0.335(2)   | -0.339(2)   |
| C(16) | 0.504(1)   | -0.329(1)   | -0.379(1)   |
| C(21) | 0.2131(9)  | -0.3318(6)  | -0.525(1)   |
| C(22) | 0.213(1)   | -0.3298(8)  | -0.656(1)   |
| C(23) | 0.158(1)   | -0.4032(9)  | -0.767(1)   |
| C(24) | 0.107(1)   | -0.4808(8)  | -0.741(2)   |
| C(25) | 0.106(1)   | -0.4835(7)  | -0.610(1)   |
| C(26) | 0.159(1)   | -0.4098(7)  | -0.502(1)   |
| C(31) | 0.2624(9)  | -0.1376(6)  | -0.479(1)   |
| C(32) | 0.142(1)   | -0.1024(8)  | -0.518(1)   |
| C(33) | 0.112(1)   | -0.0330(8)  | -0.601(1)   |
| C(34) | 0.202(1)   | 0.0009(8)   | -0.645(1)   |
| C(35) | 0.320(1)   | -0.0325(8)  | -0.606(1)   |
| C(36) | 0.325(1)   | -0.1027(7)  | -0.524(1)   |
| N     | 0.2789(9)  | 0.3146(6)   | -0.199(1)   |
| C(41) | 0.349(1)   | 0.2313(9)   | -0.217(2)   |
| C(42) | 0.135(1)   | 0.2908(9)   | -0.245(1)   |
| C(43) | 0.337(1)   | 0.355(1)    | -0.037(1)   |
| C(44) | 0.291(2)   | 0.3851(9)   | -0.286(2)   |
| C(45) | 0.317(3)   | 0.184(1)    | -0.365(2)   |
| C(46) | 0.101(1)   | 0.228(1)    | -0.161(2)   |
| C(47) | 0.269(2)   | 0.435(1)    | 0.007(2)    |
| C(48) | 0.425(2)   | 0.416(1)    | -0.260(2)   |

synthesis. Subsequent tungsten-phased  $F_0$  Fourier syntheses showed the positions of all nonhydrogen atoms. Refinement of their coordinates, using isotropic temperature factors, gave the agreement indices  $R = 0.125$  and  $R_w = 0.147$ . The introduction of anisotropic thermal parameters dropped  $R$  to 0.071 and  $R_w$  to 0.074. At this stage, the observed structure factors were empirically corrected for absorption.  $R$  decreased to 0.060 and  $R_w$  0.066. H atoms of phenyl and allyl groups were found on slant difference Fourier maps, and an usual difference Fourier synthesis gave H atoms of the cation  $(C_2H_5)_4N^+$ . These atoms were included in later structure factor calculations but were not refined; they were assigned an isotropic thermal parameter 1.0 higher than those of the carbon atom to which they are attached. The final refinement of 344 variables

TABLE 2  
ANISOTROPIC PARAMETERS

|       | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{13}$ | $B_{23}$ |
|-------|----------|----------|----------|----------|----------|----------|
| W     | 3.44(2)  | 3.37(2)  | 4.02(2)  | 0.15(1)  | 1.40(1)  | 1.13(1)  |
| Cl(1) | 3.4(1)   | 5.2(1)   | 5.3(1)   | -0.39(9) | 1.83(9)  | 0.7(1)   |
| Cl(2) | 7.6(2)   | 4.3(1)   | 6.0(1)   | 1.0(1)   | 2.4(1)   | 2.6(1)   |
| C(1)  | 4.2(5)   | 5.5(6)   | 6.2(6)   | -0.2(4)  | 0.6(5)   | 2.6(5)   |
| O(1)  | 5.1(4)   | 7.8(6)   | 9.4(7)   | -1.5(4)  | -1.9(5)  | 2.9(5)   |
| C(2)  | 2.1(4)   | 6.0(6)   | 6.2(6)   | 0.1(4)   | -1.2(4)  | 1.0(5)   |
| O(2)  | 6.2(5)   | 3.2(3)   | 10.9(7)  | 0.9(3)   | -0.7(5)  | 1.4(4)   |
| C(3)  | 7.3(8)   | 7.8(9)   | 8.6(9)   | 2.0(7)   | 4.4(7)   | 0.4(7)   |
| C(4)  | 6.2(7)   | 9.4(9)   | 7.3(8)   | -0.6(7)  | 4.6(7)   | -0.1(7)  |
| C(5)  | 10(1)    | 13(1)    | 4.9(7)   | 0.0(9)   | 3.3(7)   | 4.1(8)   |
| P     | 3.07(9)  | 3.2(1)   | 4.9(1)   | 0.08(7)  | 1.47(9)  | 1.89(9)  |
| C(11) | 3.3(4)   | 6.6(6)   | 6.8(6)   | 1.4(4)   | 2.5(4)   | 4.4(5)   |
| C(12) | 3.1(4)   | 9.8(9)   | 6.4(6)   | -1.0(5)  | 0.5(4)   | 4.9(7)   |
| C(13) | 4.2(6)   | 12(1)    | 10(1)    | 0.5(7)   | 3.0(7)   | 6(1)     |
| C(14) | 3.4(6)   | 19(2)    | 8(1)     | -0.6(9)  | 1.8(7)   | 7(1)     |
| C(15) | 7.3(9)   | 14(1)    | 7.2(8)   | 6(1)     | 4.9(8)   | 6(1)     |
| C(16) | 4.7(6)   | 9.5(9)   | 6.2(6)   | 2.3(6)   | 2.6(5)   | 4.5(6)   |
| C(21) | 3.1(4)   | 3.7(4)   | 4.9(5)   | 0.8(3)   | 1.9(3)   | 1.3(3)   |
| C(22) | 5.7(6)   | 4.5(5)   | 5.1(5)   | 0.3(4)   | 2.5(4)   | 1.2(4)   |
| C(23) | 7.7(7)   | 5.6(6)   | 5.3(6)   | 1.2(5)   | 3.0(5)   | 1.0(5)   |
| C(24) | 6.1(7)   | 3.7(5)   | 7.7(8)   | 0.9(4)   | 2.5(6)   | -0.2(5)  |
| C(25) | 5.9(6)   | 3.5(4)   | 6.1(6)   | -0.2(4)  | 2.9(5)   | 0.3(4)   |
| C(26) | 5.0(5)   | 3.6(4)   | 6.7(6)   | 0.0(4)   | 3.1(4)   | 0.8(4)   |
| C(31) | 3.6(4)   | 3.5(4)   | 4.9(5)   | -0.5(3)  | 1.4(4)   | 1.5(3)   |
| C(32) | 4.3(5)   | 4.4(5)   | 5.4(5)   | 0.0(4)   | 1.0(4)   | 1.8(4)   |
| C(33) | 5.6(6)   | 4.6(5)   | 6.4(6)   | 0.9(4)   | 0.9(5)   | 2.2(5)   |
| C(34) | 6.3(7)   | 4.6(5)   | 5.9(6)   | 0.3(5)   | 1.6(5)   | 2.4(5)   |
| C(35) | 7.4(7)   | 4.4(5)   | 5.7(6)   | -1.3(5)  | 2.8(5)   | 1.4(4)   |
| C(36) | 4.5(5)   | 4.6(5)   | 4.3(5)   | -0.4(4)  | 1.5(4)   | 1.6(4)   |
| N     | 5.3(4)   | 3.8(4)   | 5.3(4)   | 0.6(3)   | 1.7(4)   | 1.5(3)   |
| C(41) | 6.8(7)   | 4.9(6)   | 7.9(8)   | 1.8(5)   | 2.6(6)   | 1.3(5)   |
| C(42) | 4.3(5)   | 6.1(6)   | 5.3(6)   | 0.4(4)   | 0.8(4)   | 1.1(5)   |
| C(43) | 6.5(7)   | 6.6(7)   | 5.3(6)   | -1.1(5)  | 0.9(5)   | 2.2(5)   |
| C(44) | 8.4(8)   | 4.8(6)   | 6.6(7)   | 0.9(5)   | 3.4(6)   | 2.1(5)   |
| C(45) | 13(2)    | 6.8(9)   | 8(1)     | 2.7(9)   | 3.7(9)   | -0.6(8)  |
| C(46) | 5.4(6)   | 6.8(7)   | 7.6(8)   | -0.1(5)  | 2.6(6)   | 2.1(6)   |
| C(47) | 13(1)    | 5.0(6)   | 6.8(8)   | -0.3(7)  | 5.2(8)   | 0.3(6)   |
| C(48) | 11(1)    | 9(1)     | 11(1)    | -2.3(9)  | 7(1)     | 1.4(9)   |

The parameters enter the expression for the structure factor in the form:  $\exp.[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$ .

TABLE 3

BOND DISTANCES (Å) WITH THEIR STANDARD DEVIATIONS

|           |          |             |         |
|-----------|----------|-------------|---------|
| W—Cl(1)   | 2.571(3) | C(11)—C(12) | 1.40(2) |
| W—Cl(2)   | 2.542(3) | C(12)—C(13) | 1.35(2) |
| W—C(1)    | 1.96(1)  | C(13)—C(14) | 1.33(3) |
| W—C(2)    | 1.91(1)  | C(14)—C(15) | 1.42(3) |
| W—P       | 2.581(3) | C(15)—C(16) | 1.42(2) |
| W—C(3)    | 2.33(2)  | C(16)—C(11) | 1.42(2) |
| W—C(4)    | 2.20(2)  | C(21)—C(22) | 1.36(2) |
| W—C(5)    | 2.35(2)  | C(22)—C(23) | 1.39(2) |
| C(1)—O(1) | 1.15(2)  | C(23)—C(24) | 1.39(2) |
| C(2)—O(2) | 1.20(2)  | C(24)—C(25) | 1.35(2) |
| C(3)—C(4) | 1.47(3)  | C(25)—C(26) | 1.38(1) |
| C(4)—C(5) | 1.41(2)  | C(26)—C(21) | 1.39(2) |
| P—C(11)   | 1.82(1)  | C(31)—C(32) | 1.40(2) |
| P—C(21)   | 1.86(1)  | C(32)—C(33) | 1.40(2) |
| P—C(31)   | 1.83(1)  | C(33)—C(34) | 1.38(2) |
|           |          | C(34)—C(35) | 1.35(2) |
|           |          | C(35)—C(36) | 1.40(2) |
|           |          | C(36)—C(31) | 1.37(2) |

using 4509 observations resulted in  $R = 0.057$  and  $R_w = 0.065$ . Agreement of  $F_o$  and  $F_c$  at low diffraction angles did not require introduction of a secondary extinction parameter.

Final atomic coordinates for all non hydrogen atoms, and anisotropic thermal parameters are reported in Tables 1 and 2. Bond distances and angles, and the equations of the main molecular planes are given in Tables 3, 4 and 5. A list of observed and calculated structure factors is available from the authors.

TABLE 4

BOND ANGLES (°) WITH THEIR STANDARD DEVIATIONS

|                |          |                   |        |
|----------------|----------|-------------------|--------|
| Cl(1)—W—Cl(2)  | 89.5(1)  | C(11)—C(12)—C(13) | 122(2) |
| Cl(1)—W—C(1)   | 172.5(5) | C(12)—C(13)—C(14) | 120(2) |
| Cl(1)—W—C(2)   | 99.4(3)  | C(13)—C(14)—C(15) | 121(2) |
| Cl(1)—W—P      | 80.1(1)  | C(14)—C(15)—C(16) | 119(2) |
| Cl(2)—W—C(1)   | 94.2(4)  | C(15)—C(16)—C(11) | 118(1) |
| Cl(2)—W—C(2)   | 165.2(4) | C(16)—C(11)—C(12) | 119(1) |
| Cl(2)—W—P      | 80.1(1)  | C(21)—C(22)—C(23) | 121(1) |
| C(1)—W—C(2)    | 75.6(5)  | C(22)—C(23)—C(24) | 118(1) |
| C(1)—W—P       | 94.1(5)  | C(23)—C(24)—C(25) | 121(1) |
| C(2)—W—P       | 89.8(5)  | C(24)—C(25)—C(26) | 120(1) |
| W—C(1)—O(1)    | 173(1)   | C(25)—C(26)—C(21) | 121(1) |
| W—C(2)—O(2)    | 176(1)   | C(26)—C(21)—C(22) | 119(1) |
| C(3)—C(4)—C(5) | 114(2)   | C(31)—C(32)—C(33) | 120(1) |
| W—P—C(11)      | 112.7(5) | C(32)—C(33)—C(34) | 119(1) |
| W—P—C(21)      | 112.5(4) | C(33)—C(34)—C(35) | 120(1) |
| W—P—C(31)      | 113.7(4) | C(34)—C(35)—C(36) | 121(2) |
| C(11)—P—C(21)  | 102.9(5) | C(35)—C(36)—C(31) | 120(1) |
| C(11)—P—C(31)  | 102.1(6) | C(36)—C(31)—C(32) | 119(1) |
| C(21)—P—C(31)  | 100.3(5) |                   |        |

TABLE 5

LEAST-SQUARES BEST PLANES DEFINED BY ATOMIC POSITIONS, AND DISTANCES (Å) OF ATOMS FROM THESE PLANES (X, Y, AND Z ARE FRACTIONAL COORDINATES)

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|                                                         |            |       |            |
|---------------------------------------------------------|------------|-------|------------|
| Plane 1: atoms C(1), C(2), Cl(1) and Cl(2)              |            |       |            |
| Equation of plane: $7.466X + 1.045Y - 9.695Z = 3.188$   |            |       |            |
| C(1)                                                    | -0.09(2)   | Cl(1) | -0.002(4)  |
| C(2)                                                    | 0.07(2)    | Cl(2) | 0.004(4)   |
| W                                                       | -0.17(3)   |       |            |
| Plane 2: atoms C(3), C(4) and C(5)                      |            |       |            |
| Equation of plane: $6.605X - 2.445Y - 9.451Z = 1.477$   |            |       |            |
| Plane 3: atoms C(11) to C(16)                           |            |       |            |
| Equation of plane: $-3.216X - 7.592Y + 9.576Z = -2.757$ |            |       |            |
| C(11)                                                   | -0.004(15) | C(14) | -0.004(30) |
| C(12)                                                   | 0.002(17)  | C(15) | -0.003(23) |
| C(13)                                                   | 0.003(25)  | C(16) | 0.005(17)  |
| P                                                       | -0.03(3)   |       |            |
| Plane 4: atoms C(21) to C(26)                           |            |       |            |
| Equation of plane: $9.635X - 6.704Y - 0.152Z = 4.352$   |            |       |            |
| C(21)                                                   | -0.002(9)  | C(24) | 0.008(14)  |
| C(22)                                                   | 0.006(13)  | C(25) | -0.004(13) |
| C(23)                                                   | -0.011(16) | C(26) | 0.002(12)  |
| P                                                       | 0.03(3)    |       |            |
| Plane 5: atoms C(31) to C(36)                           |            |       |            |
| Equation of plane: $0.155X + 8.183Y + 6.831Z = -4.358$  |            |       |            |
| C(31)                                                   | -0.002(9)  | C(34) | -0.005(12) |
| C(32)                                                   | 0.004(11)  | C(35) | 0.007(12)  |
| C(33)                                                   | -0.000(11) | C(36) | -0.002(10) |
| P                                                       | -0.08(2)   |       |            |
| Dihedral angles (°) between planes                      |            |       |            |
| 2-1                                                     | 14.6       |       |            |
| 3-4                                                     | 78.9       |       |            |
| 3-5                                                     | 67.8       |       |            |
| 4-5                                                     | 91.8       |       |            |

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## Description of the structure

The crystal structure is made up of discrete monomeric ions. A stereo view of the unit cell is presented in Fig. 1. The anion, formally a complex of  $W^{VI}$ , is shown in Fig. 2. From a structural point of view the tungsten atom can be regarded at the centre of an octahedron with the allyl group at one apex, two carbonyl groups and two chlorine atoms at the apices of the equatorial plane, and the remaining site, *trans* to the allyl group, occupied by a triphenylphosphine.

The allyl group and the carbonyl groups are in an *anti*-configuration with respect to the C(1), C(3), C(3), C(5) plane, as in  $Mo(\eta-C_3H_5)(CO)_2Cl(diphos)$  [5],  $Mo(\eta-C_3H_5)(CO)_2(pd)(NC_5H_5)$  ( $pd = 2,4$ -pentane dithionate) [6] or  $W(\eta-C_3H_5)(CO)_2(CF_3COO)$  [7]. There have been many structures reported containing terminal, unsubstituted allyl groups ( $\eta-C_3H_5$ ). An extensive study of the correlations between the geometric structure and the number of *d*-electrons for several ( $\eta$ -allyl) metal complexes were given by Kaduk, Poulos and Ibers [8]. C—C distances, 1.47(1) and 1.41(1) Å, and C—C—C angle, 115(2)°, in the present work, are consistent with values found for a  $d^4$  electron configuration, as is also the distance from the tungsten atom to the center of mass, G,

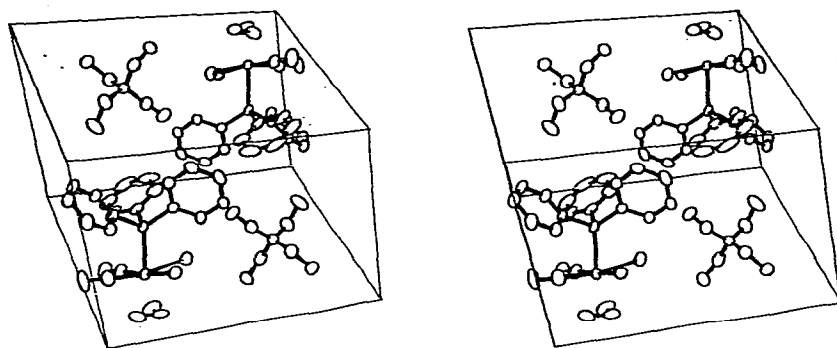


Fig. 1. Stereo view of the unit cell.

of the allyl group, 2.04 Å, and the tilt angle  $\tau$ , 101° (angle between the vectors W—G and G—C(4)).

The tungsten atom is 0.17(1) Å above the C(1), C(2), Cl(1) and Cl(2) best plane, in the direction of the allyl group. An interesting feature is the *cis* position of the chlorine atoms and the carbonyl groups. This may be related to the infrared spectrum (Fig. 3) in which the two main bands in the CO-stretch-

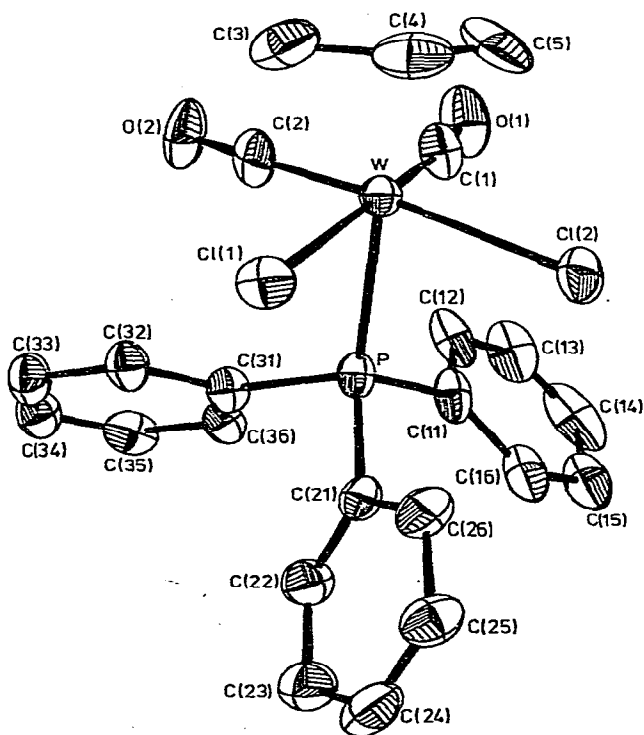


Fig. 2. ORTEP drawing of the anion (Thermal ellipsoids contain 50% of the electronic density).

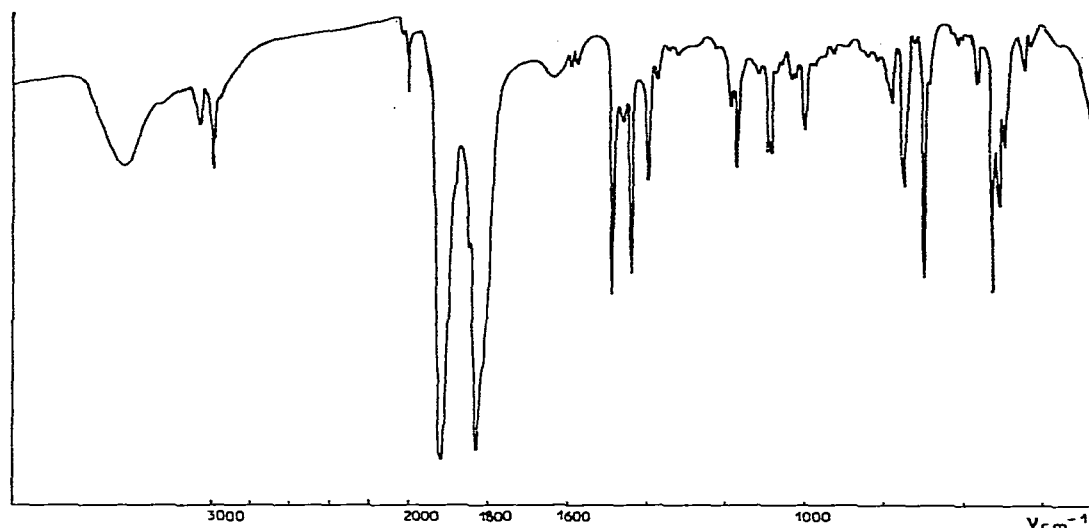


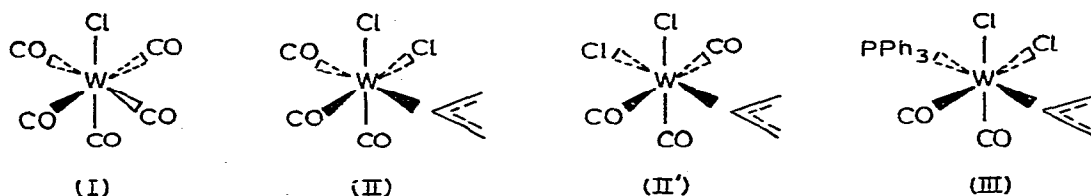
Fig. 3. Infrared spectra of solid complex  $(\text{C}_2\text{H}_5)_4\text{N}[(\eta\text{-C}_3\text{H}_5)(\text{CO})_2\text{WCl}_2\text{PPh}_3]$ .

ing region ( $1915$  and  $1830\text{ cm}^{-1}$ ) are consistent with a *cis* configuration [9].

Although there are several structures involving W—Cl bonds, none has yet been reported with such a configuration for the tungsten atom in such a low oxidation state. The two independent W—Cl lengths of  $2.542(3)$  and  $2.571(4)$  Å are about  $0.15$  Å longer than the  $2.417(3)$  Å distance observed in  $\text{WCl}(\text{CF}_3\text{C}_2\text{F}_3)_2(\eta\text{-C}_5\text{H}_5)$  [10]. This lengthening suggests a *trans* influence of the CO group, which is comparable to that found in other compounds where M—P and M—As (M = W, Mo) bonds are weakened by the influence of such a carbonyl group [11]. A similar distance of  $2.573(4)$  Å was observed in  $\text{MoCl}(\eta\text{-C}_3\text{H}_5)(\text{CO})_2(\text{diphos})$  [5], which also has a Cl atom *trans* to a CO group. Similarly it can be said that the W—CO bond is strengthened since it is *trans* to a W—Cl bond where Cl is a  $\pi$ -donor; indeed W—C (carbonyl),  $1.91(1)$  Å and  $1.97(1)$  Å are somewhat shorter than  $2.06(1)$  Å found in  $\text{W}(\text{CO})_6$  [12]. The W—P bond length,  $2.582$  Å, is similar to those found for tertiary phosphine complexes of metal tri-, and tetra-halides [13]. Each phenyl ring is planar within experimental error. Bond distances and angles in the triphenylphosphine are essentially the same as those reported, for example, by Schneider and Weiss in  $\text{V}(\eta\text{-C}_3\text{H}_5)(\text{CO})_4\text{-P}(\text{C}_6\text{H}_5)_3$  [14] or by Leipolt et al. in  $\text{Rh}(\text{ttfa})(\text{CO})\text{PPh}_3$ . [15] (ttfa = thenoyltri-fluoroacetato).

## Discussion

In the halogeno-pentacarbonyltungstate (I) the carbonyl groups which should be the most labile are those *cis* to the chlorine atom since chlorine has a lower *trans* effect than CO [16]. Therefore the substitution of CO in complex I by ligands L should give complexes in which ligands are *cis* to the chlorine atom. Then when allyl chloride reacts with  $\text{W}(\text{CO})_5\text{Cl}^-$ , complex II will be obtained rather than II', as suggested by M.D. Murdoch [1], in which one halogen is *trans* to the allyl group.



Attempts to obtain II in crystalline form failed. When the reaction mixture of  $C_3H_5Cl$  and  $(C_2H_5)_4N[ClW(CO)_5]$  in benzene-acetonitrile was evaporated under vacuum it gave an oil.

II has two kinds of carbonyl groups: two *trans* to the chlorine atoms, and one *trans* to the allyl group. Because of the stronger *trans* effect of the allyl group, triphenylphosphine should replace carbonyl *trans* to allyl more easily, to yield III, which was isolated as a solid. The crystalline structure of its tetraethylammonium salt supports the assumption made for structure II: in both complexes, the three ligands Cl, Cl, Allyl are in *facial* positions. In the absence of a crystal structure determination, the structure of  $MX(\eta\text{-allyl})(CO)_2L_2$  complexes ( $X = Cl, Br$ ;  $M = W, Mo$ ) are often written with the allyl group and the halide atom in the *trans* configuration (17–20). The structure we have determined for III, like that of  $Mo(\eta\text{-}C_3H_5)(CO)_2X(\text{diphos})$  [5], strongly suggests that allyl and chlorine are instead in the *cis* orientation.

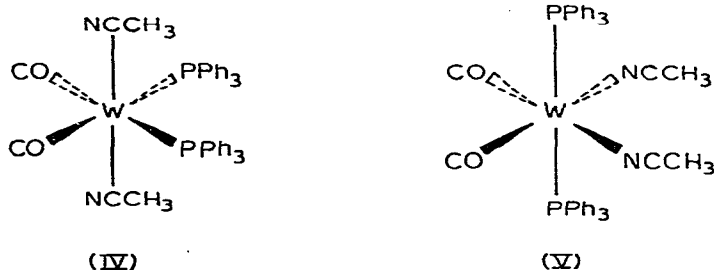
### Chemical properties of III

Crystals of III are stable in air for several days. They are soluble in acetonitrile giving a solution very sensitive to oxygen. They are insoluble in most other organic solvents.

Acetonitrile reacts with III when heated at  $70^\circ C$ . After one hour the red solution turns black. A complex reaction has occurred, and yellow crystals (IV) were obtained by cooling this black solution at  $0^\circ C$  for three or four days. Their chemical analysis indicates the formula  $W(CO)_2(NCCH_3)_2(P(C_6H_5)_3)_2$ .

Analysis, found: C, 57.62; H, 4.17; N, 3.15; P, 6.81; W, 20.99.  $C_{42}H_{36}N_2O_2 \cdot P_2W$  calcd.: C, 59.59; H, 4.25; N, 3.31; P, 7.32; W, 21.73%.

The IR spectrum of IV shows two main bands in the carbonyl region ( $1930$  and  $1810\text{ cm}^{-1}$ ) and one band in the C—N stretching region ( $2260\text{ cm}^{-1}$ ). The chemical analysis and infrared spectra agree with a compound which contains two CO groups in *cis* disposition, two acetonitrile, and two triphenylphosphine ligands. IV appears to have the same formula as a compound described by F. Hohmann [19], but not the same infrared spectra in the carbonyl stretching region ( $1803$  and  $1733\text{ cm}^{-1}$ ) [19]. The differences in stretching frequencies between the two products may be explained by structural isomerism (structures IV and V): triphenylphosphine and acetonitrile have the same  $\sigma$  donor ability but the phosphine is a better  $\pi$  acceptor than acetonitrile [21–22].



The two CO groups in *cis* disposition must give rise to two main bands in the IR in the region 1700–2000  $\text{cm}^{-1}$ . However, the difference in the nature of the ligands *trans* to the CO groups in the two isomers should result in higher CO frequencies for IV than for V because of lower back bonding to the CO groups in structure IV. We conclude that our route yields isomer IV while Hohmann's route yields isomer V.

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