# π-ALLYL COMPLEXES OF MOLYBDENUM AND TUNGSTEN

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Considerable interest has centred recently on π-allyl complexes of the transition metals, but few examples of this type of complex with the Group VI metals have been described, and these invariably have a cyclopentadienyl group also attached to the metal atom. Thus, Fischer and Ulm formulate the compound obtained from di-π-cyclopentadienylchromium, carbon monoxide and hydrogen under pressure, as π-cyclopentadienyl-π-cyclopentenyldicarbonylchromium[1]. π-Cyclopentadienyl-π-allyl-dicarbonyl complexes of molybdenum and tungsten have been described more recently by Green and co-workers[2,3]. An unsuccessful attempt to prepare π-allyl carbonyl derivatives of the Group VI metals by treating the hexacarbonyls with allyl halides, has also been reported[4].

This paper describes the preparation of new π-allyl complexes of molybdenum and tungsten starting from the tetraethylammonium salts of the halopentacarbonylmetal anions, $[Et_4N]^+[M(CO)_5X]^-$ (I). Treatment of these salts (where M = Mo or W; X = Cl, Br or I) with allyl halides ($C_3H_5Y$, Y = Cl or Br) gives excellent yields of products of the general formula $[Et_4N]^+[M_2Y_3(C_3H_5)_2(CO)_4]^-$ (II) according to the following equation:

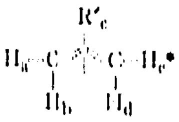
$$2[Et_4N]^+[M(CO)_5X]^- + 3C_3H_5Y \longrightarrow 6CO + [Et_4N]^+[M_2Y_3(C_3H_5)_2(CO)_4]^- + C_3H_5X + [Et_4N]^+X^- \quad (1)$$

That all the halogen in the complexes is derived from the allyl halide, is ascertained by proving the identity of the complexes obtained by reaction of (I) (M = Mo; X = Cl, Br or I) with allyl bromide. The tetraethylammonium halide $[Et_4N]X$ and the carbon monoxide formed were quantitatively determined. The formation of allyl bromide was qualitatively determined for the reaction using allyl chloride and (I) (M = Mo; X = Br). The reaction appears to be general for allyl chlorides and bromides. However, no reaction could be observed even under relatively drastic conditions with allyl iodides and any of the starting materials (I). Further, the corresponding chromium complexes could not be prepared, again there being no evidence of reaction.

The complexes are yellow crystalline solids, moderately soluble in methylene chloride, and very soluble in more polar solvents. They are relatively stable in air in the solid state, but are much less so in solution. In all cases the tungsten complexes are markedly less stable to oxidation than those of molybdenum and, with the exception of the chloro complexes, crystallise with difficulty. In agreement with their ionic character, attempted sublimation only led to decomposition.

TABLE 2

NUCLEAR MAGNETIC RESONANCE DATA
All spectra in deuterated acetone.



$H_a{-}C(H_b){\cdots}C(R'_e){\cdots}C(H_d){-}H_c$*

| *Complex* | *Intensity* | *Relative position*** | *Complexity* | *Assignment* | *J (cps)* |
|---|---|---|---|---|---|
| (II) M = Mo, R = R′ = H, Y = Cl | 4 | 9.2 | Doublet | $H_b$ ($H_d$) coupled to $H_c$ | 9.5 |
| | 4 | 6.6 | Doublet | $H_a$ ($H_e$) coupled to $H_c$ | 6.5 |
| | 2 | ~ 6.3 | Multiplet | $H_c$ coupled to $H_a$ and $H_b$ | |
| | 12 | 8.6 | Triplet | $N{-}CH_2CH_3$ | |
| | 8 | 6.5 | Quartet | $N{-}CH_2CH_3$ | 7.4 |
| (II) M = Mo, R = R′ = H, Y = Br | 4 | 9.1 | Doublet | $H_b$ ($H_d$) coupled to $H_c$ | 9.7 |
| | 4 | 6.54 | Doublet | $H_a$ ($H_e$) coupled to $H_c$ and text | 6.5 |
| | 2 | ~ 6.2 | Complex multiplet | $H_c$ | |
| | 12 | 8.51 | Triplet | as above | |
| | 8 | 6.39 | Quartet | | ~ 7.6 |
| (II) M = Mo, R = Me, R′ = H, Y = Br | 2 | 9.3 | Doublet | $H_b$ coupled to $H_c$ | ~ 9.2 |
| | 14 | ~ 6.4 | Multiplet | $H_a$, $H_d$ + $H_c$ | — |
| | 6 | 7.92 | Doublet | $CH_3$ split by coupling with $H_d$ | 7.5 |
| | 12 | 8.54 | Triplet | as above | |
| | | 6.5 | Quartet | | 7.0 |
| (II) M = Mo, R = H, R′ = Me, Y = Cl | 4 | 9.25 | Singlet | $H_b$ | — |
| | 6 | 7.91 | Singlet | $CH_3$ (R′) | — |
| | 4 | 7.03 | Singlet | $H_a$ | — |
| | 12 | 8.56 | Triplet | as above | |
| | 8 | 6.53 | Quartet | | ~ 7.2 |
| (II) M = W, R = R′ = H, Y = Cl | 4 | 8.84 | Doublet | $H_b$ ($H_d$) coupled to $H_c$ | ~ 8.6 |
| | 4 | 6.78 | Doublet | $H_a$ ($H_e$) coupled to $H_c$ | ~ 7 |
| | 2 | ~ 6.9 | Multiplet | $H_c$ | — |
| | 12 | 8.56 | Triplet | as above | |
| | 8 | 6.44 | Quartet | | 7.2 |
| (II) M = W, R = H, R′ = Me, Y = Cl | 4 | 8.82 | Singlet | $H_b$ ($H_d$) | |
| | 6 | 7.67 | Singlet | $CH_3$ (R′) | |
| | 4 | 7.08 | Singlet | $H_a$ ($H_e$) | |
| | 12 | 8.58 | Triplet | as above | |
| | 8 | 6.42 | Quartet | | ~ 7.2 |

* No stereochemistry is implied. ** Relative to tetramethylsilane as internal standard. Refers to centre of multiplet.

On the basis of the sharp peaks obtained in the nuclear magnetic resonance measurements (*vide infra*) the complexes are assumed to be diamagnetic.

## RESULTS

### *Infrared measurements*

The spectra of the complexes in the region 1800–2100 cm$^{-1}$ are summarized in Table 1. As is seen, two bands together with a shoulder are given by the four carbonyl groups. For the spectra taken in methanol the shoulder is not observed and the peaks are sharper. This indicates a rather symmetrical arrangement of the four CO groups in the molecule. The compounds show no evidence for free C=C stretching vibrations in the region 1500–1700 cm$^{-1}$ indicating that the allyl groups are $\pi$-bonded to the metal. The tetraethylammonium cations in the complexes give rise to peaks similar to those given by tetraethylammonium halides. The region of 1400–1500 cm$^{-1}$ is too complicated by the presence of absorption due to the tetraethylammonium cation to permit an assignment of the bands for the C=C stretching vibration of the complexed double bonds.

TABLE 1

INFRARED SPECTRA OF THE COMPLEXES

| *Complex* | $\nu_{(CO)}$ (*cm*$^{-1}$) | *Solvent* |
|---|---|---|
| (II) M = Mo, R = R′ = H, Y = Cl | 1950 sh, 1942, 1857 | THF[*] |
| (II) M = Mo, R = R′ = H, Y = Br | 1950 sh, 1940, 1858 | THF |
| (II) M = Mo, R = Me, R′ = H, Y = Cl | 1939 sh, 1929, 1849 | THF |
| (II) M = Mo, R = Me, R′ = H, Y = Br | 1940 sh, 1930, 1845 | THF |
| (II) M = Mo, R = H, R′ = Me, Y = Cl | 1947 sh, 1937, 1851 | THF |
| | — 1942, 1852 | Methanol |
| (II) M = W, R = R′ = H, Y = Cl | 1944 sh, 1930, 1842 | THF |
| (II) M = W, R = R′ = H, Y = Br | 1944 sh, 1935, 1849 | THF |
| (II) M = W, R = H, R′ = Me, Y = Cl | 1940 sh, 1930, 1840 | THF |

[*] THF is tetrahydrofuran.

### *Proton magnetic resonance spectra*

The proton magnetic resonance spectra of the complexes are relatively simple and can be interpreted on the basis of the data of complex (II) (M = Mo, R = R′ = H, Y = Br) (see Table 2).

The sharp high field doublet of intensity 4 can be assigned to the $H_b$ protons of two identical $\pi$-allyl groups split by coupling with $H_c$. The coupling constant (9.7 cps) is in agreement with an *anti*-configuration in a $\pi$-allyl system[5]. The high chemical shift value is similar to that for similar protons in the $\pi$-cyclopentadienyl-$\pi$-allyl-dicarbonyl complexes of molybdenum and tungsten[2,3], but the broadening of the peaks in these complexes, attributed to asymmetric bonding of the $\pi$-allyl groups, is not observed. From this it can be concluded that the two $\pi$-allyl groups are both *identically* and *symmetrically bonded* to the metal. The $H_a$ protons of the $\pi$-allyl groups give a doublet, intensity 4 at 6.54 $\tau$, the coupling constant, $J_{ac}$ (6.7 cps) being again in good agreement with the *syn*-assignment. The expected multiplet for $H_c$ is found at 6.18 $\tau$. Hence the complex shows what is now a classical spectrum for $\pi$-allyl complexes[5].

The tetraethylammonium cation gives a triplet at 8.51 $\tau$ and a quartet at 6.39 $\tau$ as expected for the ethyl groups. The peaks of the triplet are split equally into three by coupling with the nitrogen atom.

The replacement of the molybdenum by tungsten and interchange of halogen atoms causes only relatively small changes in the chemical shift values without altering the total pattern.

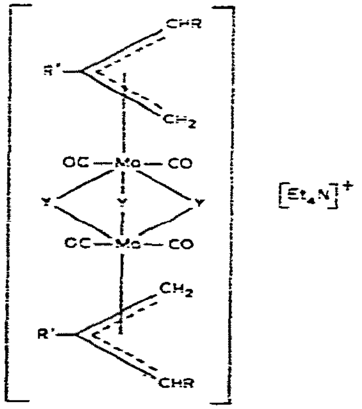
The 2-methylallyl complexes (II) ($M = Mo, W$; $R = H$; $R' = Me$; $Y = Cl$) give especially simple spectra. The assignments are given in Table 2. The sharpness of the three peaks confirms the symmetry of the bonding of the $\pi$-allyl groups in the complexes.

The 1-methylallyl complexes (II) ($R = Me$; $R' = H$) give spectra which are difficult to resolve because of gross overlapping of the bands. However, the spectra (Table 2) are in agreement with the $\pi$-allyl assignment.

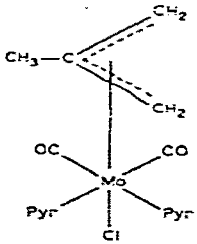
*Chemical studies*

Thermal decomposition of the complex (II) ($M = Mo$; $R = R' = H$; $Y = Cl$) affords as gaseous products, ethylene, triethylamine, propene, carbon monoxide, and allyl chloride. These products can be rationalised on the basis of the degradation of the $\pi$-allyl group and the tetraethylammonium cation.

More informative however, was the reaction of the complex (II) ($M = Mo$; $R = H$; $R' = Me$; $Y = Cl$) with pyridine. A high yield of a product which analyses for $C_4H_7Mo(CO)_2(C_5H_5N)_2Cl$ (together with tetraethylammonium chloride) is obtained.



(II)



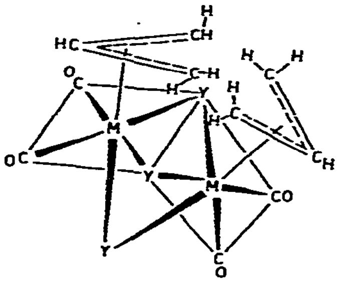
(III)

This new complex shows only two sharp peaks in the "carbonyl" region of the infrared. The proton magnetic resonance spectrum confirms the presence of the 2-methyl-$\pi$-allyl group and the pyridine molecules in the ratio 1:2. Hence the complex is chloro(2-methyl-$\pi$-allyl)bis(pyridine)dicarbonylmolybdenum (III). Geometrical isomers of (III) can be expected and some evidence for such isomerism can be seen in the proton magnetic resonance spectra. From the above it can be concluded that the complexes

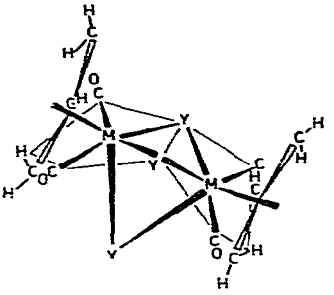
(II) have one π-allyl group and two carbon monoxide molecules per metal atom. A fuller discussion of this and other reactions of the complexes is, however, deferred until later.

## DISCUSSION

On the basis of the analytical, spectroscopic and chemical evidence, the complexes are formulated as tri-μ-halobis(π-allyldicarbonylmetal) anions (II). For this formulation the structures (IIA), in which two octahedra share a face, and (IIB) in which two pentagonal bipyramids share a face can be considered. On the basis that the metals are formally univalent in the complexes, and that the π-allyl groups will occupy two coordination sites, as has been shown for the π-allyl palladium chloride dimer[6], structure (IIB) in which the metals are 7-coordinate seems the most likely. However, the π-allyl groups can not be symmetrically bonded in this structure as required by the proton magnetic resonance data, and hence it is felt that a distortion of (IIB) to allow for the symmetry element, or of (IIA) to accommodate the steric requirements of the π-allyl group will represent the true structure.



(IIA)



(IIB)

It is possible that the failure of the corresponding anionic halopentacarbonyls of chromium to form these π-allyl complexes lies in the reluctance of the chromium to form 7-coordination complexes, together with the steric requirements of the π-allyl groups, and the halogen bridges. This steric factor may also be sufficient to prevent the complexes with iodine bridges from forming even with molybdenum or tungsten.

The complexes show some novel and interesting features. They are the first π-allyl complexes of Group VIA elements to be prepared without the stabilising influence of the cyclopentadienyl group. The formation of three halogen bridges has not been observed in the halocarbonyls of the transition metals although it is known for the higher oxidation state of molybdenum, in its polymeric triiodide and -bromide[7].

### *Mechanism of reaction*

Since the product isolated invariably contains the halogen derived from the allyl halide (see Eqn. 1) it is evident that halogen exchange must occur at some stage in the reaction. It can be shown, by observing the $A_1$ "carbonyl" band of the halopentacarbonyl anions, that some exchange occurs between the anions and the allyl halides in the case of the chloro complexes. However, no definite evidence for exchange can be observed for either the bromo- and iodopentacarbonyl anions. It is also dif-

TABLE 3

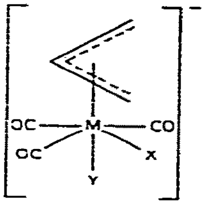
DETAILS OF THE REACTIONS

| *Reactants* | *Product* | *M.p.* | *Yield** | *Analysis found* | | | | | *Required* | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | *C* | *H* | *M* | *N* | *X* | *C* | *H* | *M* | *N* | *X* |
| (I) M = Mo, X = Cl; allyl bromide | (II) R = R′ = H, Y = Br | 142–3° | 85 | 28.7 | 4.61 | 24.6 | 1.97 | 32.4 | 28.6 | 3.97 | 25.4 | 1.85 | 31.7 |
| (I) M = Mo, X = Br; allyl bromide | (II) R = R′ = H, Y = Br | | 90 | | | | | | | | | | |
| (I) M = Mo, X = I; allyl bromide | (II) R = R′ = H, Y = Br | | 95 | | | | | | | | | | |
| (I) M = Mo, X = Cl; 2-methylallyl chloride | (II) R = H, R′ = Me, Y = Cl | 108–9° | 92 | 37.1 | 5.12 | 29.5 | — | 16.46 | 36.9 | 5.26 | 29.5 | — | 16.34 |
| (I) M = Mo, X = Br; 2-methylallyl chloride | (II) R = H, R′ = Me, Y = Cl | | 80 | | | | | | | | | | |
| (I) M = Mo, X = I; allyl chloride | (II) R = R′ = H, Y = Cl | 151–2° | 95 | 35.1 | 5.14 | 29.8 | 2.37 | 17.03 | 34.7 | 4.85 | 30.8 | 2.25 | 17.08 |
| (I) M = Mo, X = I; 1-methylallyl chloride | (II) R = Me, R′ = H, Y = Cl | 123–4° | 55 | ... | ... | 28.8 | ... | 16.00 | — | — | 29.5 | — | 16.34 |
| (I) M = Mo, X = Br; 1-methylallyl bromide | (II) R = Me, R′ = H, Y = Br | 131–2° | 80 | 30.3 | 4.05 | 23.9 | 1.91 | 29.8 | 30.6 | 4.34 | 24.4 | 1.78 | 30.6 |
| (I) M = W, X = Br allyl bromide | (II) R = R′ = H, Y = Br** | 115–20° | ... | | | | | | | | | | |
| (I) M = W, X = Br allyl chloride | (II) R = R′ = H, Y = Cl | 137–8° | 92 | 28.1 | 4.53 | 45.7 | 1.87 | 13.67 | 27.1 | 3.78 | 46.1 | 1.78 | 13.35 |
| (I) M = W, X = I 2-methylallyl chloride | (II) R = H, R′ = Me, Y = Cl | 147–8° | 80 | 28.8 | 4.31 | 44.1 | — | — | 29.2 | 4.15 | 44.5 | — | — |

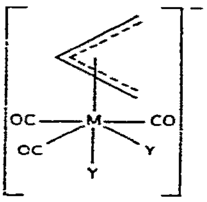
* Based on the metal. ** Crystallises with difficulty and gives inconsistent analyses.

ficult to envisage exchange as the final stage of the reaction since the tetraethylammonium halide formed is almost quantitatively precipitated from solution. It can be shown that the tri-μ-halobis(π-allyldicarbonylmetal) anions exchange only very slowly with lithium chloride, even at 50°, and not at all with allyl halides.

Hence the reaction is envisaged as proceeding through intermediate formation of the complexes (IV) (no prior exchange) and (V) (with prior exchange), formed by reaction of the allyl halide with the halopentacarbonyl anion.



(IV)



(V)

Product formation can now occur by dimerisation and elimination of tetraethylammonium halide. It is reasonable that this dimerisation will be controlled by the steric requirements of the final product, such that a symmetrically bridged product will be obtained. To this end it is felt that exchange occurs at this stage in the reaction and that the product is formed largely by combination of one molecule of (IV) with one of (V), and that dimerisation of (IV) to an asymmetrical product is less favoured. The dimerisation of (V) will also give the required product.

## EXPERIMENTAL

Unless otherwise stated all the reactions and operations described were carried out under an atmosphere of pure nitrogen. The infrared spectra were recorded on Perkin-Elmer Models 221 and 337 with grating units. The nuclear magnetic resonance spectra were measured on a Varian DP 60A spectrometer at 60 mc.

Microanalyses are by Dr. EDER, École de Chimie, Geneva. All melting points are uncorrected.

### *Preparation of the complexes*

Since the method of preparation was essentially the same for all the complexes a general method only will be described. The yields of products, the analyses carried out, and the physical properties of the materials are listed in Table 3.

A mixture of the tetraethylammonium halopentacarbonylmetallate[8] (3 g) and a large excess of the allyl halide (2 g) were stirred in tetrahydrofuran (75 ml) at room temperature (Mo) or at 40° (W) until the infrared bands of the former in the region 2070 to 1800 cm$^{-1}$ had disappeared (4–6 h). The reaction mixture was then filtered and the solvent removed by distillation under reduced pressure. The products, which were normally solid, were then kept at 50° for 1 h under high vacuum to remove traces of metal hexacarbonyl and were recrystallised from methylene chloride–petroleum ether.

In the reaction of tetraethylammonium bromopentacarbonyl molybdenum with methyl 4-bromocrotonate, a liquid product was obtained and all attempts to crystallise this were unsuccessful.

### *Reactions*

(*a*) *Thermal decomposition.* A quantity of the tetraethylammonium tri-$\mu$-chloro-bis($\pi$-allyldicarbonylmolybdenum) was heated to 350° and the gases which were formed were analysed by infrared and vapour phase chromatographic techniques. Ethylene, triethylamine, propene, carbon monoxide and allyl chloride were found. The proportions of the different gases were not determined. However, the CO evolved was determined accurately; 4 CO/mole complex were found.

(*b*) *With lithium iodide.* Reaction of the bromo complex corresponding to the above complex in tetrahydrofuran with a large excess of lithium iodide failed to cause any displacement of the bromine bridges by iodine, the starting material being recovered unchanged.

(*c*) *With pyridine.* To a suspension of the tetraethylammonium tri-$\mu$-chloro-bis(2-methyl-$\pi$-allyldicarbonylmolybdenum) (0.5 g) in carbon tetrachloride (25 ml) sufficient pyridine to effect solution was added (5 ml). After 1 h the reaction mixture was filtered free from the tetraethylammonium chloride which was precipitated and the solution was evaporated to dryness. The yellow solid obtained was crystallised from methylene chloride–petroleum ether as yellow plates, m.p. 115–7° (decomp.) (0.54 g, 88 %). (Found: C, 48.06; H, 4.17; Mo, 23.13. $C_{16}H_{17}ClMoN_2O_2$ calcd.: C, 47.96; H, 4.27; Mo, 23.94 %.)

## ACKNOWLEDGEMENTS

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## SUMMARY

The reaction of the tetraethylammonium salts of the anionic halopentacarbonyl complexes of molybdenum and tungsten with allyl halides gives novel dimeric $\pi$-allyl complexes whose structures are discussed on the basis of spectroscopic, chemical and analytical data.

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