

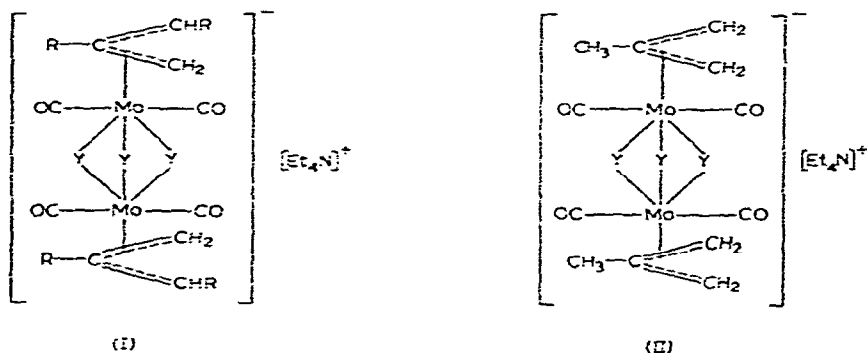
π -ALLYL COMPLEXES OF MOLYBDENUM. II*

H. D. MURDOCH** AND R. HENZI

Cyanamid European Research Institute, Cologne/Geneva (Switzerland)

(Received October 15th, 1965)

The preparation of the tetraethylammonium salts of tri- μ -halobis(π -allyldicarbonylmotals) (I, M = Mo or W; Y = Cl or Br) has been recently reported¹. The present work describes some reactions of these complexes with formation of new π -allylic derivatives. These reactions can be subdivided into metathetical bridge-replacement and bridge-splitting reactions.



BRIDGE-REPLACEMENT REACTIONS

Since the synthetic method for preparing the complexes (I) did not allow formation of iodo complexes, initial metathetical reactions were carried out to attempt replacement of the other halogens in the complexes with iodide ion¹. These were unsuccessful. However, several other metathetical reactions proved possible. For simplicity the reactions were restricted to the tetraethylammonium tri- μ -chlorobis(2-methyl- π -allyldicarbonylmolybdenum) (II, Y = Cl) although it is anticipated that the reactions will apply in general. Thus reaction of this complex with sodium hydroxide in aqueous methanol, sodium or sodium carbonate in anhydrous methanol gave the tri- μ -methoxy derivative (II, Y = OCH₃) in good yield. The corresponding tri- μ -ethoxy complex (II, Y = OC₂H₅) was prepared in the same manner using ethanol. That the bridging structure of (II, Y = Cl) was unchanged was confirmed by infrared and NMR data (*vide infra*).

These appear to be the first alkoxy-bridged carbonyl derivatives to be characterized.

* Ref. 1 is considered as Part I.

** Present address: Borax Consolidated Limited, Research Centre & Laboratories, Cox Lane, Chessington, Surrey.

Similarly, reaction of the tri- μ -chloro complex with sodium thiophenoxide, or sodium carbonate in thiophenol gave the tri- μ -thiophenoxy derivative (II, Y = SC₆H₅).

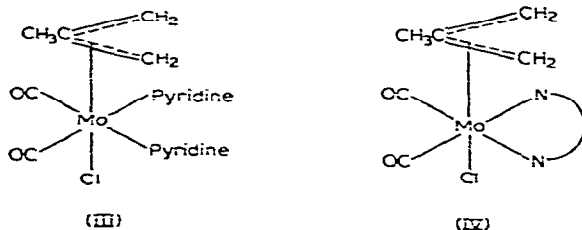
Attempts were also made to effect replacement with acetate and hydroxide ions. In both cases the reactions gave mixtures of products. Thus reaction of a suspension of the tri- μ -chloro complex with 40 % sodium hydroxide solution, gave two products which were separated by fractional crystallisation. These proved to be the tetraethylammonium and sodium salts of the tri- μ -hydroxy complex (II, Y = OH). Use of tetraethylammonium hydroxide, however, eliminated this complication. Treatment of the tri- μ -hydroxy complex with sodium methoxide in methanol gave the tri- μ -methoxy derivative in good yield.

However, reaction of the tri- μ -chloro complex with sodium, tetraethylammonium, or silver acetate invariably gave a mixture of compounds from which no crystalline product could be obtained.

All the products are pale yellow solids with stabilities very much lower than the parent halo complex. All are rapidly oxidised by air.

BRIDGE-SPLITTING REACTIONS

As described briefly¹ the tri- μ -chloro complex reacts with pyridine to give the corresponding chloro(2-methyl- π -allyl)dicarbonylbispyridinemolybdenum (III). This reaction has been extended and analogous products have been obtained from 2,2'-bipyridine (IV, N-N = bipyridine) and ethylenediamine (IV) (N-N = ethylenediamine). With piperidine the product could not be crystallised. The chelated amine products can be obtained either by direct reaction of the trichloro complex or the pyridine complex (III) with the amine. The latter method avoids the need for excess amine.



The amine derivatives are dark yellow (pyridine, ethylenediamine) to deep red (bipyridine) crystalline solids reasonably stable to air in the solid state.

An attempt to split the halo bridges by triphenylphosphine was unsuccessful.

INFRARED MEASUREMENTS

The bridged complexes (II, Y = OH, OCH₃, OC₂H₅ or SC₆H₅) have two bands of approximately equal intensity in the CO stretching region, similar to the parent halo complexes but with shifts to lower wavenumbers relative to the latter. These shifts, which correspond to an increase in the π -acceptor bonding in the CO groups, can be attributed to the lower electronegativity of the O- and S-bridges relative to halogen necessitating greater charge transfer to the carbonyls from the metals.

It was also observed that during the course of the reactions, the CO stretching vibrations of the reaction mixtures gradually shifted to lower frequencies, indicating the step-wise replacement of the halo bridges. No attempt was made to isolate intermediate products.

In addition to the above, the tris- μ -hydroxy complex showed OH stretching vibrations, and C—O stretching vibrations could be assigned for the tris- μ -alkoxy products.

TABLE I
INFRARED SPECTRA OF THE COMPLEXES

Compound	ν_{CO}^a	Other
(II) Y = Cl [†]	1940 (s) 1842 (s)	1070 (m)C—O (KBr)
(II) Y = OCH ₃	1904 (s) 1791 (s)	1105 (m)C—O (KBr)
(II), Y = OC ₂ H ₅	1900 (s) 1790 (s)	
(II), Y = OH	1900 (s) 1795 (s)	3650 (m)O—H (KBr)
(II), Y = SC ₆ H ₅	1921 (s) 1830 (s)	
(III), N = pyridine	1938 (s) 1840 (s) ^b	
(IV), N—N = ethylenediamine	1935 (s) 1835 (s)	
(IV), N—N = bipyridine	1950 (s) 1865 (s)	

^a In CH₂Cl₂. ^b In tetrahydrofuran.

The amine complexes, as expected, also show two CO stretching vibrations corresponding to the two CO groups. The spectra are recorded in Table I.

NUCLEAR MAGNETIC RESONANCE MEASUREMENTS

The bridged complexes all have spectra essentially similar to the corresponding tris- μ -halo complexes, with peaks for the tetraethylammonium cation and the 2-methyl- π -allyl groups in the required ratio of 1:2.

In addition, for the tri- μ -methoxy complex, (II, Y = OCH₃), two further sharp absorptions are observed in the region appropriate for OCH₃ group at 6.32 τ (intensity 6) and 5.18 τ (intensity 3). In the structure proposed for the tri- μ -halo complexes¹ it is evident that one of the bridging positions, being adjacent to two carbonyl groups on each metal, differs from the two other positions which are adjacent to one carbonyl and the π -allyl group.

On this basis the peak at 5.18 τ is assigned to the unique OCH₃ and that at 6.32 τ to the two equivalent OCH₃ groups.

That this assignment is correct is confirmed by the NMR spectra of the tri- μ -ethoxy product (II, Y = OC₂H₅). This complex has, in addition to the allylic and tetraethylammonium protons, two distinct quartet (at 6.26 τ and 5.12 τ) and two distinct triplet absorptions (at 8.78 τ and 8.33 τ) expected for two different types of OC₂H₅ groups, again in the ratio 2:1. This confirmation of the structures of these alkoxy derivatives, also confirms the initial structural proposals for the tri- μ -halo complexes¹, for which no means of distinguishing the different bridging positions was available.

For the tri-μ-thiophenoxy derivative (II, Y = SC₆H₅) the spectrum in the SC₆H₅ region is complicated, and two different SC₆H₅ groups could not be distinguished. However, the ratio of allylic to tetraethylammonium to phenyl groups is the expected 2:1:3. In contrast to the alkoxy derivatives, for the tri-μ-hydroxy complex only one peak (intensity 3) was observed in addition to the 2-methyl-π-allyl and tetraethylammonium protons, and this at very high field (9.90 τ). It was found that rapid exchange occurred in CDCl₃, and deuterated acetone, so that no OH peak could be observed. It is difficult to see why two types of OH are not discernible, but it is conceivable that exchange phenomena, perhaps through interbridge H-bonding make the protons equivalent.

For the pyridine and ethylenediamine complexes, the chemical shift of the high field protons of the 2-methyl-π-allyl groups is at lower field (~ 8.6 τ) than the anionic complexes (~ 9.3 τ). The two remaining expected absorptions are very little different. In addition the complexes show absorptions for the amine ligands. No assignments were attempted, but ratio of allylic to amine protons was as required. In the spectra of the pyridine complex, additional weak absorptions in the π-allyl region could not be eliminated on purification of the complex. These peaks may be attributed to isomers which are possible or to the formation in equilibrium of a small amount of dimeric halogen-bridged product formed by elimination of pyridine. Such equilibria are known for amine halogen derivatives of platinum and rhodium².

The insolubility of the bipyridine product prevented measurements of its NMR spectrum.

The NMR spectra are tabulated in Table 2.

TABLE 2
NUCLEAR MAGNETIC RESONANCE SPECTRA OF THE COMPLEXES

Complex	Absorptions ^a (ppm)			Solvent
	2-Methyl- π-allyl	Et ₄ N ⁺	Other ^b	
(II), Y = Cl ¹	9.2 (4) 8.1 (6) 7.25 (4)	8.83 (12) 6.8 (8)		(CD ₃) ₂ SO
(II), Y = OCH ₃	9.67 (4) 8.29 (6) 7.39 (4)	8.86 (12) 6.82 (8)	6.32 (6) 5.18 (3)	(CD ₃) ₂ SO
(II), Y = OC ₂ H ₅	9.75 (4) 8.2 (6) 7.4 (4)	8.84 ^c 6.82 (8)	8.78 ^c 8.33 (3) 6.26 (4) 5.12 (2)	(CD ₃) ₂ SO
(II), Y = OH	9.52 (4) 8.13 (6) 7.36 (4)	8.62 (12) 6.73 (8)	9.9 (3)	CH ₂ Cl ₂
(II), Y = SC ₆ H ₅	9.2 (4) 7.72 (6) 7.01 (4)	8.64 (12) 6.58 (8)	3.1-2.8 and 2.3-1.8 (multiplets, 15)	(CD ₃) ₂ CO
(III)	8.67 (2) 7.95 (3) 6.76 (2)		~ 2.7, ~ 2.4, ~ 1.2 broad multiplets (10)	CCl ₄
(IV), N-N = ethylenediamine	9.22 (2) 7.94 (3) 7.0 (2)		~ 7.5 (v. broad) (8) ~ 6.3 (v. broad)	(CD ₃) ₂ SO

^a Centres of multiplets. ^b See text. ^c Overlap of multiplets.

It is perhaps worth noting that although many of the spectra were recorded in dimethyl sulphoxide- d_6 , there was no evidence for the conversion of the π -allyl to σ -allyl which has been observed for π -allyl complexes of palladium in this solvent^{3,4}.

EXPERIMENTAL

Unless otherwise stated all operations were carried out in an atmosphere of pure nitrogen. The infrared spectra were recorded on grating spectrometers Perkin-Elmer models 521 and 337. The nuclear magnetic resonance spectra were measured on a Varian DP 60A spectrometer at 60 Mc.

Microanalyses are by Dr. K. EDER, Ecole de chimie, Geneva. All m.p.'s are uncorrected.

Tetraethylammonium tri- μ -methoxybis(2-methyl- π -allyldicarbonylmolybdenum)

(a) *From sodium hydroxide in aqueous methanol.* To a suspension of the tetraethylammonium tri- μ -chlorobis(2-methyl- π -allyldicarbonylmolybdenum)¹ (2 g) in 20% sodium hydroxide solution (100 ml), methanol (25 ml) was added and the mixture was heated to 40° for 2 h. The yellow solid was then filtered off, washed with water (20 ml) dried and recrystallised from CH_2Cl_2 /light petroleum as yellow crystals (1.6 g, 85%), m.p. 160–162° (dec.). (Found: C, 43.13; H, 6.62; Mo, 30.34. $\text{C}_{23}\text{H}_{43}\text{Mo}_2\text{NO}_7$ calcd.: C, 43.33; H, 6.8; Mo, 30.1%.)

(b) *From sodium carbonate in anhydrous methanol.* A mixture of the tri- μ -chloro complex (0.5 g), sodium carbonate (1 g) in anhydrous methanol (20 ml) was stirred for 4 h at 40°. The reaction was then filtered, and the solvent removed under reduced pressure. Extraction of the residue with methylene chloride and crystallisation from this solvent and light petroleum gave a product identical with that obtained above (0.3 g, 65%).

(c) *From sodium in methanol.* From 0.5 g tri- μ -chloro complex and 0.5 g sodium metal in methanol (30 ml) after allowing to stand at room temperature for 15 h, 0.4 g of the tri- μ -methoxy product was obtained by evaporation of the solvent and crystallisation of the residue from CH_2Cl_2 /petr. ether (85%).

Tetraethylammonium tri- μ -ethoxybis(2-methyl- π -allyldicarbonylmolybdenum)

By methods identical to the above, but using ethanol, the tri- μ -ethoxy product was isolated in 75–85% yield. Recrystallisation from methylene chloride/light petroleum gave the compound as yellow crystals, m.p. 157–159° (decomp.). (Found: C, 45.16; H, 7.00; Mo, 28.36; N, 2.29. $\text{C}_{25}\text{H}_{49}\text{Mo}_2\text{NO}_7$ calcd.: C, 45.95; H, 7.26; Mo, 28.3; N, 2.06%.)

Tetraethylammonium tri- μ -thiophenoxybis(2-methyl- π -allyldicarbonylmolybdenum)

(a) *From sodium thiophenoxide.* A mixture of the tri- μ -chloro complex (0.5 g) and sodium thiophenoxide (1.1 g) in tetrahydrofuran (50 ml) was allowed to stand for 24 h at room temperature. The mixture was then filtered, and evaporated to dryness and the residue extracted with benzene/methylene chloride. Further evaporation and crystallisation from methylene chloride gave the tri- μ -thiophenoxy complex as yellow brown needles (150 mg, 22%) m.p. 162–165° (Found: C, 52.26; H, 5.40; Mo, 22.09. $\text{C}_{28}\text{H}_{48}\text{Mo}_2\text{NO}_4\text{S}_2$ calcd.: C, 52.33; H, 5.67; Mo, 22.00%.)

(b) *From sodium carbonate and thiophenol.* A mixture of the tri- μ -chloro complex (0.5 g), thiophenol (5 ml) and sodium carbonate (1 g) was stirred at room temperature for 4 h. The excess thiophenol was then distilled off under reduced pressure, and the residue extracted with methylene chloride. The solution obtained was then filtered through an alumina column which was washed with methylene chloride. From the resultant eluate, the required product (0.32 g, 48%) was obtained after recrystallisation from methylene chloride/light petroleum.

Tetraethylammonium tri- μ -hydroxybis(2-methyl- π -allyldicarbonylmolybdenum)

(a) *From sodium hydroxide.* A mixture of the tri- μ -chloro complex (1 g) was stirred for three days with a solution of sodium hydroxide (25%, 150 ml). It was then filtered and the yellow solid residue was dried under high vacuum, and eluted with methylene chloride. The material was only part soluble. The solution was dried and the solvent evaporated to give the required tri- μ -hydroxy complex as the tetraethylammonium salt (0.25 g, 27%), m.p. 142–145° (dec.). (Found: C, 40.5; H, 6.44; Mo, 32.45. $C_{20}H_{37}Mo_2NO_7$ calcd.: C, 40.73; H, 6.27; Mo, 32.23%.) The residue, insoluble in methylene chloride, was washed briefly with water, and dried. This was the required product as the sodium salt (0.3 g, ~40%). No analysis was made.

(b) *From tetraethylammonium hydroxide.* From 1 g of the tri- μ -chloro complex and 30 ml of a 25% solution of tetraethylammonium hydroxide after 48 h stirring a yellow solid was obtained on filtration. This was dried, and eluted with methylene chloride. The solution obtained was dried with sodium sulphate and evaporated giving the tri- μ -hydroxy compound identical with that isolated above (0.45 g, 50%).

Reaction with sodium methoxide. The tri- μ -hydroxy complex (100 mg) was dissolved in methanol to which sodium had been added. After 0.5 h water was added to the mixture and the precipitated solid was filtered off, dried and crystallised from methylene chloride/light petroleum. It was proved by m.p. and infrared and NMR comparisons to be the tri- μ -methoxy compound identical with that prepared above.

Amine complexes

(a) *Pyridine.* This was prepared as described previously¹.

(b) *2,2'-Bipyridine.* To a solution of the tri- μ -chloro complex (1 g) in tetrahydrofuran (50 ml) an excess (0.5 g) of 2,2'-bipyridine was added. The solution became red in colour and after 2 h a red crystalline precipitate was formed. This was filtered off, washed quickly with dilute HCl, water, dried and crystallised from chloroform. The product was very insoluble but crystallisation could be effected using a large volume of solvent. The complex (0.3 g, 50%) had m.p. 234–238° (decomp.) (Found: C, 47.64; H, 3.99; Mo, 23.23; N, 7.5. $C_{16}H_{15}ClMoN_2O_2$ calcd.: C, 48.2; H, 3.79; Mo, 24.07; N, 7.93%.) It was found difficult to eliminate entirely small traces of the 2,2'-bipyridine from the product.

A further method of obtaining this product consisted in mixing equimolar quantities of the bis-pyridine complex above and 2,2'-bipyridine in tetrahydrofuran. The bipyridine complex is immediately precipitated in theoretical yield and can be purified as above.

(c) *Ethylenediamine.* The tri- μ -chloro complex (0.5 g) suspended in petroleum ether (25 ml) was treated with ethylenediamine (10 ml) and the mixture stirred for 12 h. The solid crystalline material was filtered off, washed with water, dried and re-

crystallised from methanol/carbon tetrachloride as yellow needles (0.2 g, 87%), m.p. 215–220° (dec.) (Found: C, 31.95; H, 5.14; Mo, 31.52; N, 9.16. $C_8H_{15}ClMoN_2O_2$ calcd.: C, 31.74; H, 5.00; Mo, 31.71; N, 9.26%.)

(d) *With triphenylphosphine.* Treatment of the tri- μ -chloro complex with a large excess of the triphenylphosphine at temperatures up to 60°, even with ultraviolet irradiation failed to cause reaction, the starting material being recovered.

ACKNOWLEDGEMENTS

The authors wish to thank Drs. CALDERAZZO and NOACK for helpful discussions.

SUMMARY

The reactions of the tetraethylammonium salts of tri- μ -chloro-bis(2-methyl- τ -allyldicarbonylmolybdenum) with replacement of the chlorine bridges by hydroxy-, alkoxy- and thiophenoxy-groups are described. Bridge-splitting reactions with amines with formation of chloro-2-methyl- τ -allyldicarbonyldiamine molybdenum derivatives are also discussed.

REFERENCES

- 1 H. D. MURDOCH, *J. Organometal. Chem.*, **4** (1965) 119.
 - 2 J. CHATT AND L. M. VENANZI, *J. Chem. Soc.*, (1957) 4735; S. D. ROBINSON AND B. L. SHAW, *J. Chem. Soc.*, (1963) 919, and references therein.
 - 3 J. C. W. CHIEN AND H. C. DEHM, *Chem. Ind. (London)*, (1961) 745.
 - 4 J. POWELL, S. D. ROBINSON AND B. L. SHAW, *Chem. Commun.*, (1965) 78.
- J. Organometal. Chem.*, **5** (1966) 552–558