

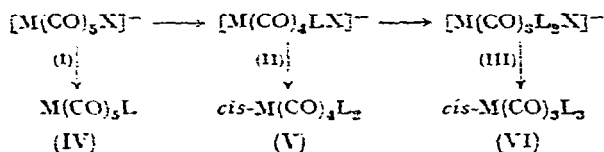
AMINE AND HYDRAZINE COMPLEXES OF MOLYBDENUM CARBONYL

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(Received September 16th, 1965)

The reactions of the halopentacarbonylmetal anions (I, $M = Cr, Mo$ or W ; $X = Cl, Br$ or I) with isonitriles has recently been described¹. Mono-, bis-, and tris-isonitrile carbonyl metal derivatives were obtained. The degree of substitution is mainly dependent on the halide X of the anion employed, being lowest for the iodide and highest for the chloride. It was also shown that the reaction followed a scheme as below, involving intermediates of the type (II and III, $L =$ isonitrile).



It was therefore of interest also to investigate the corresponding reactions of the halopentacarbonyl anions with amines. It was anticipated that the reactions would be more complicated since under the reaction conditions the mono-amine complexes (IV, $L =$ amine) can react with excess amine to give bis-amine products, whereas further reaction of the neutral isonitrile complexes with isonitrile did not occur.

The reactions were restricted to the molybdenum complexes, although it is anticipated that the method will apply in general to the corresponding chromium and tungsten compounds.

MONO-AMINES

Initial reactions were carried out using cyclohexylamine, pyridine, diphenylamine and triethylamine. It was found that, as with the isonitriles the tetraethylammonium iodopentacarbonylmolybdenum (I, $M = Mo, X = I$) gives virtually only the monocyclohexylaminepentacarbonylmolybdenum (IV, $M = Mo, L =$ cyclohexylamine) whereas, judging from the infrared spectrum of the reaction the corresponding chloro-anion affords a mixture of mono- and bis-cyclohexylamine derivatives (IV and V, $M = Mo, L =$ cyclohexylamine).

In the absence of solvent, however, both the iodo- and chloro-anions give the mono-derivative as the sole product of reaction, provided reaction times are short. The slow formation of the bis-product from the mono- is observed if the reactions are allowed to continue.

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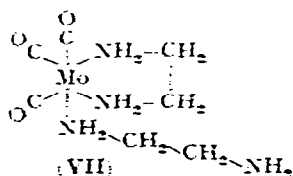
However, it was found impossible to isolate the bis(cyclohexylamine)tetracarbonylmolybdenum. All attempts led to decomposition or disproportionation.

For the reaction of the anions with pyridine, in tetrahydrofuran, the infrared spectra of the reaction mixtures indicated product ratios similar to those observed above. However, the reactions were exceedingly slow, being uncompleted in 5-7 days, and hence, as above, reactions using pyridine both as solvent and reactant were carried out. Fast reactions were obtained for which, unlike the solvent-free cyclohexylamine reactions, a greater control of the degree of substitution was observed. Thus, reaction of the iodo-complex anion gave virtually pure monopyridine-pentacarbonylmolybdenum, whereas the bispyridinetetracarbonylmolybdenum was obtained from the chloro complex with traces only of the mono complex. From the bromo complex a mixture of the two products was obtained.

With diphenylamine and triethylamine, no reaction with the halopentacarbonyl-anions could be observed even at temperatures up to 50°. This failure can be attributed to the weak basic strength of the former amine, and the steric requirements of the latter.

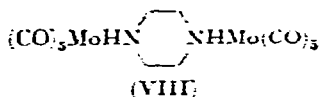
CHELATING DIAMINES

The second series of reactions were carried out using chelating diamines. Thus, reaction of ethylenediamine or its tetramethyl derivative in tetrahydrofuran with either the iodo- or chloro-anion resulted only in the formation of the chelated diamine-tetracarbonylmolybdenum [V, M = Mo, L₂ = NH₂CH₂CH₂NH₂ or (CH₃)₂NCH₂CH₂N(CH₃)₂], together, in the case of the ethylenediamine reaction, with some bis-(ethylenediamine)tricarboxylmolybdenum (VII). This latter product is formed by further reaction of the chelated diamine tetracarbonyl product with excess amine. It can also be obtained in almost theoretical yield by reaction of the anions with ethylenediamine without solvent at 120°. Infrared spectra of the reaction using the iodo-anion show evidence for intermediate formation of the *aminepentacarbonyl* complex (*vide infra*).



NON-CHELATING DIAMINES

Reaction of the iodopentacarbonylmolybdenum anion with the non-chelating diamine, piperazine in tetrahydrofuran gave piperazinepentacarbonylmolybdenum (IV, M = Mo, L = piperazine) as the sole product. This contrasts with the reaction of the amine with the hexacarbonylmolybdenum which gave only piperazinedecacarbonyldimolybdenum² (VIII).



REACTIONS IN AQUEOUS MEDIA

A further practical application of the method was also developed. It was found that if the reactions are carried out using water as solvent, then the mono-amine-pentacarbonylmetals are obtained as the sole products of reaction. Thus, reaction of aqueous solutions of pyridine, cyclohexylamine, or piperazine with the halopentacarbonylmolybdenum anions gives good yields of the mono-amine pentacarbonylmolybdenum complexes. In this fashion, the ammoniapentacarbonylmolybdenum (IV, $M = Mo$, $L = NH_3$), hydrazinepentacarbonylmolybdenum (IV, $M = Mo$, $L = NH_2NH_2$) and (phenylhydrazine)pentacarbonylmolybdenum (IV, $M = Mo$, $L = C_6H_5NHNH_2$) could also be obtained. Further, when reaction with ethylenediamine was carried out in aqueous medium, the product isolated is (ethylenediamine)pentacarbonylmolybdenum (IV, $M = Mo$, $L = NH_2CH_2CH_2NH_2$) with only one of the amine groups bonded to the metal. In organic solvents and even on standing in the solid phase, this product forms the chelated (ethylenediamine)tetracarbonylmolybdenum, normally isolated. The formation of the mono-products applies irrespective of the halopentacarbonylmetal anion employed.

Thus, the reactions of amines with halopentacarbonylmolybdenum anion provide a convenient method of preparation of mixed amine carbonyl derivatives of the Group VI metals with some measure of control of the degree of substitution. The reactions carried out in aqueous media especially, offer a simple method of preparing monoaminepentacarbonylmetal complexes and also enable the synthesis of hydrazine derivatives, not previously reported.

Unlike the reactions of the anions with isonitriles, no evidence for the formation of intermediates of the types (II and III, $L = \text{amine}$) was obtained. However, by comparison with isonitrile reactions⁴, it seems reasonable that the bis-amine derivatives are also formed from complexes (II, $L = \text{amine}$), and that formation from the preformed monoaminepentacarbonyl complexes by further reaction with the amine is a secondary process. Thus, in the ethylenediamine reactions the initial formation of an aminepentacarbonyl species is only observed for the iodo-anion as expected from the isonitrile reactions. This product then cyclises to give the bis-complex in a secondary reaction. In the reaction with the chloro-anion a careful infrared control of the reaction throughout failed to show this pentacarbonyl species, the bis-product appearing in place of the anion, most probably via the complex (II, $M = Mo$, $X = Cl$, $L = NH_2CH_2CH_2NH_2$).

PROPERTIES

All of the amine products are yellow crystalline solids, relatively stable to air in the solid state but less so in solution. Some of the complexes have been previously described³⁻⁵ and the properties found largely correspond with those reported. However, some discrepancies were found in the literature with respect to the reported melting points of certain of the complexes, and since in general the melting-decomposition points occur over a 10-15° range, purity was ascertained by elemental analyses.

The hydrazine- and (phenylhydrazine)pentacarbonylmolybdenum complexes, which have not been previously reported, are also pale yellow solids. The former

complex has properties similar to the corresponding amine complexes, but the latter compound darkens on standing even under nitrogen, and decomposes completely in 48 h at room temperature.

INFRARED MEASUREMENTS

The spectra of the complexes for the CO stretching region agree with reported spectra^{2,3,6}. Thus, for the pentacarbonyl derivatives, four bands are obtained corresponding to the two A_1 , the E and B_1 modes^{3,7}. The latter vibration appears as a very weak shoulder to the high frequency side of the lower A_1 band. The bis-amine tetracarbonyl complexes also have four bands in this region, in agreement with the *cis*-configuration of the amines. The bis(ethylenediamine)tricarbonylmolybdenum has two ν_{CO} stretching vibrations, one very broad, similar to other tris-amine complexes^{3,6}. For new complexes the spectra (Table 1) agree with the proposed formulations.

TABLE 1

INFRARED SPECTRA OF NEW COMPLEXES

Complex	ν_{CO}^a			
1. $NH_2CH_2CH_2NH_2Mo(CO)_5^b$	2070 w	—	1931 vs	~ 1889 m
2. $C_4H_{10}N_2Mo(CO)_5$	2071 w	1975 wsh	1939 vs	1900 m
3. $NH_3Mo(CO)_5^d$	2070 w	—	1930 vs	1887 m
4. $NH_2NH_2Mo(CO)_5$	2072 w	1978 wsh	1930 vs	1898 m
5. $C_4H_9NHNH_2Mo(CO)_5$	2072 w	1980 wsh	1935 vs	1897 m
6. $(C_2H_{11}NH_2)_2Mo(CO)_4^e$	2007 w	1877 vs	~ 1864 sh	1820 s
7. $(CH_3)_2NCH_2CH_2N(CH_3)_2Mo(CO)_4$	2013 w	1880 vs	~ 1875 sh	1840 s
8. $(NH_2CH_2CH_2NH_2)_2Mo(CO)_3^e$	—	1891 s	1755 broad (s)	

^a In tetrahydrofuran unless otherwise stated. ^b Rapidly converts to tetracarbonyl complex. ^c Nitromethane. ^d Behrens² does not report the ν_{CO} bands for this complex. ^e Not isolated.

EXPERIMENTAL

Unless otherwise stated all operations were carried out in an atmosphere of pure dry nitrogen. Infrared spectra were recorded on Perkin-Elmer Models 521 and 337 with grating units. Microanalyses are by Dr. K. EDER, Ecole de Chimie, Geneva. All melting points were recorded on a Kofler hotplate and are uncorrected.

Reactions were judged complete by the absence in the CO stretching region of the infrared, of the bands characteristic of the halopentacarbonylmolybdenum anions.

Cyclohexylamine

In tetrahydrofuran. A mixture of the tetraethylammonium iodo- or chloropentacarbonylmolybdenum³ (1 g) cyclohexylamine (5 ml) and THF (75 ml) was allowed to stand for 1 h (I⁻) or 0.5 hour (Cl⁻). The precipitated tetraethylammonium halide was then filtered off, and the solvent evaporated. The resultant solid was washed with water and extracted with benzene (50 ml) to give soluble and insoluble fractions. From the benzene-soluble fraction, the mono-cyclohexylaminepentacarbonylmolybdenum can be isolated by elimination of the solvent and recrystallisation from light

petroleum at -80° [yield 0.6 g, 88% (I^{-}); 0.35 g, 42% (Cl^{-})], m.p. $95-96^{\circ}$ (dec.) (lit.³ 102°). (Found: C, 39.71; H, 4.05. $C_{11}H_{13}MoO_5N$ calcd.: C, 39.42; H, 3.91%.) It was found that the benzene-insoluble material was not the bis-cyclohexylamine complex expected. The material was insoluble in all normal solvents and could thus not be purified. The analytical figures were inconsistent and the product was not studied further.

Without solvent. The anions (1 g) were stirred for 45 min with cyclohexylamine (10 ml), and then a large volume of water was added. The cyclohexylaminepentacarbonylmolybdenum which was precipitated was purified as above. The yield was $\sim 80\%$.

In water. A suspension of the tetraethylammonium halopentacarbonylmolybdenum (1 g) was stirred with cyclohexylamine (20 ml) in water (100 ml) for 2 h. The monocyclohexylaminepentacarbonylmolybdenum was then filtered off, washed with water, dried and purified as above. The yield is almost theoretical.

Pyridine

Without solvent. The tetraethylammonium iodopentacarbonylmolybdenum (0.5 g) was dissolved in pyridine (5 ml) and allowed to stand for 30 min. An excess of water was then added and the solid precipitated was filtered, washed thoroughly with water, dried and crystallised from light petroleum to give monopyridinepentacarbonylmolybdenum (0.2 g, 63%), m.p. $83-84^{\circ}$ (dec. at $\sim 120^{\circ}$) (Strohmeier¹ reports decomposition at 120° but did not report the m.p.). (Found: C, 38.14; H, 1.64. $C_{10}H_5MoNO_5$ calcd.: C, 38.12; H, 1.60%.)

If the above is repeated using the chloroanion, the product precipitated is the bispyridinetetracarbonylmolybdenum. This is treated as above and purified by precipitation from tetrahydrofuran/water, (0.35 g, $\sim 80\%$), 120° (dec.) (Strohmeier¹ also reports decomposition at 115° , but Cotton *et al.*³ report m.p. 163° dec. for this compound.). (Found: C, 45.70; H, 2.83. $C_{14}H_{10}MoN_2O_4$ calcd.: C, 46.04; H, 2.76%.)

From the bromopentacarbonylmolybdenum anion and pyridine, reaction as above gave a mixture of the mono- and bis-pyridine complexes. No attempt was made to separate and isolate the products.

In water. When the tetraethylammonium halopentacarbonylmolybdenum (1 g) is treated for 30 min with pyridine (20 ml) in water (100 ml), and the resultant mixture diluted with water, the monopyridinepentacarbonylmolybdenum is precipitated and can be purified as above. Yield is 95%.

Diphenylamine and triethylamine. When the halopentacarbonylmolybdenum anions were treated with these amines either in solution in THF, or as pure liquid in the latter case, no reaction occurs and the starting material can be recovered.

Ethylenediamine

In tetrahydrofuran. A mixture of the tetraethylammonium halopentacarbonylmolybdenum (1 g) and ethylenediamine (2 g) in THF (100 ml) was stirred for 1 h (Cl^{-}) or 3 h (I^{-}) at 30° . The reactions were filtered, water was added, the solvent volume was reduced under vacuum, and the solid precipitated was crystallised from methanol/water to give (ethylenediamine)tetracarbonylmolybdenum (0.5 g, $\sim 92\%$, from I^{-} and 0.56 g, 82%, from Cl^{-}), m.p. ~ 290 (dec.) (lit.³ 290 dec.). (Found: C, 27.15; H, 3.05; mol. wt. in dimethoxyethane, 272. $C_8H_{12}MoN_2O_4$ calcd.: C, 26.88; H, 3.01%;

mol. wt., 268.) Cotton³ reports C, 22.88 calcd., 22.2 found, for this product. The solid, obtained by filtration of the reaction, was washed thoroughly with water and was purified by precipitation from ethylenediamine/water by slow elimination of water and amine under reduced pressure to give bis(ethylenediamine)tricarbonylmolybdenum (trace), dec. $\sim 230\text{--}235^\circ$. (Found: C, 27.66; H, 5.13. $\text{C}_7\text{H}_{16}\text{MoN}_3\text{O}_3$ calcd.: C, 28.00; H, 5.38%.)

Without solvent. The above product can also be obtained by heating the chloro-anion (2 g) with ethylenediamine (10 ml) to 120° for 10 min. Water is then added and the excess amine distilled off with the water under reduced pressure. The product (1.1 g, 75%) is gradually precipitated, and is filtered, washed briefly with light petroleum, and purified as above.

It is also obtained by allowing the isolated (ethylenediamine)tetracarbonylmolybdenum to react at 30° with ethylenediamine in THF. The product is very slowly formed and is precipitated from solution. It is purified as above.

In water. Reaction of the tetraethylammonium chloropentacarbonylmolybdenum (1 g) with ethylenediamine (10 ml) in water (100 ml), for 2 h and filtration of the resultant solid, which was thoroughly washed with water, light petroleum and dried, gave the (ethylenediamine)pentacarbonylmolybdenum as an off-white solid (0.7 g, 95%) dec. $213\text{--}225^\circ$. (Found: C, 28.42; H, 3.01. $\text{C}_7\text{H}_5\text{MoN}_2\text{O}_5$ calcd.: C, 28.40; H, 2.73%.) If the complex is dissolved in an organic solvent, rapid formation of the chelated (ethylenediamine)tetracarbonylmolybdenum occurs, and hence, crystallisation was impossible.

N,N,N',N'-tetramethylethylenediamine

The reactions were only attempted in THF, and the (N,N,N',N'-tetramethylethylenediamine)tetracarbonylmolybdenum, m.p. $125\text{--}130^\circ$ (dec.), was isolated and purified as described for ethylenediamine. The yields were $\sim 80\%$. (Found: C, 37.14; H, 5.26. $\text{C}_{13}\text{H}_{16}\text{MoN}_2\text{O}_4$ calcd.: C, 37.05; H, 5.29%.)

Piperazine

In tetrahydrofuran. A mixture of piperazine (1 g), the iodo-anion (1 g) in THF (75 ml) was stirred for 3 h. Filtration and evaporation of the solvent gave the piperazinepentacarbonylmolybdenum, which was crystallized from THF/water (0.5 g, 76%), m.p. $138\text{--}140^\circ$. (Found: C, 33.67; H, 3.19; N, 8.7. $\text{C}_9\text{H}_{10}\text{MoN}_2\text{O}_5$ calcd.: C, 33.56; H, 3.03; N, 8.7%.)

In water. The same product was also obtained from the chloro- or iodo-anion (1.0 g), piperazine (2 g) and water (100 ml). After 18 h the solid material was filtered off, washed with water, dried and crystallised from THF/water, [0.5 g, 75% (I^-), or 0.58 g, 62% (Cl^-)]. No attempt was made to recover product from the aqueous phases.

Hydrazine and phenylhydrazine

A mixture of the chloropentacarbonylmolybdenum anion (1 g), hydrazine hydrate (5 ml) or phenylhydrazine (4 ml) in water (75 ml) was stirred for 30 min. The solid material was then filtered, washed with water, briefly with light petroleum and dried. Purification was effected by precipitation from THF/water. In this manner are obtained hydrazinepentacarbonylmolybdenum (0.4 g, 60%), m.p. $85\text{--}90^\circ$ (dec.) (Found: C, 22.61; H, 1.49. $\text{C}_5\text{H}_4\text{MoN}_2\text{O}_5$ calcd.: C, 22.41; H, 1.50%) and (phenyl-

hydrazine)pentacarbonylmolybdenum (0.8 g, ~ 90%), m.p. 95–96° (dec.). (Found: C, 38.40; H, 2.68. $C_{11}H_8MoN_2O_5$ calcd.: C, 38.38; H, 2.34%.) The same products can be also obtained in a similar fashion from the iodopentacarbonylmolybdenum anion.

Ammonia

The halopentacarbonylmolybdenum anions (1 g) were stirred with ammonia (30 ml, 25%) for 3–4 h. The solid was then filtered, washed with water, and dried to give the ammoniapentacarbonylmolybdenum [0.4 g (Cl^-), 63% or 0.4 g (I^-), 78%], m.p. 102–108° (dec.) (Behrens⁵ reports no dec. pt.). (Found: C, 23.64; H, 1.64. $C_5H_3MoNO_5$ calcd.: C, 23.74; H, 1.20%.)

ACKNOWLEDGEMENTS

The authors wish to thank Dr. F. CALDERAZZO for helpful discussions.

SUMMARY

The reactions of the tetraethylammonium salts of the halopentacarbonylmolybdenum anions with amines are described. Mono- and, in some cases, bis-amine carbonyl derivatives of molybdenum are obtained depending on the halogen of the anion. In aqueous media, the reactions invariably give the mono-aminepentacarbonylmolybdenum compounds. By this latter method hydrazinepentacarbonylmolybdenum derivatives can also be prepared.

REFERENCES

- 1 H. D. MURDOCH AND R. HENZI, *J. Organometal. Chem.*, 5 (1966) 166.
- 2 G. W. A. FOWLES AND D. K. JENKINS, *Inorg. Chem.*, 3 (1964) 257.
- 3 C. S. KRAHMANZEL AND F. A. COTTON, *Inorg. Chem.*, 2 (1963) 533.
- 4 W. STROHMEIER AND K. GERLACH, *Chem. Ber.*, 93 (1960) 2087.
- 5 H. BEHRENS AND J. VOGL, *Chem. Ber.*, 96 (1963) 2220.
- 6 E. ABEL, M. BENNETT AND G. WILKINSON, *J. Chem. Soc.*, (1959) 2325.
- 7 L. E. ORGEL, *Inorg. Chem.*, 1 (1962) 25.
- 8 E. W. ABEL, I. S. BUTLER AND I. G. REID, *J. Chem. Soc.*, (1963) 2068.