

## SHORT COMMUNICATIONS

### CARBONYL HALIDES OF THE GROUP VI TRANSITION METALS\*

#### II.† DERIVATIVES OF MOLYBDENUM TETRACARBONYL DIBROMIDE

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In Part I of this series we described the preparation of molybdenum tetracarbonyl dichloride and some of its triphenylphosphine and triphenylarsine derivatives. Recently<sup>1</sup> diphosphine derivatives of the Group VI metal carbonyls have been prepared which could be oxidized by halogens to give seven-coordinate complexes of molybdenum(II). Diarsines<sup>2</sup> and other bidentate ligands<sup>3</sup> have also been used to prepare seven-coordinate substituted carbonyl halides in an analogous way, but no similar compounds of molybdenum(II) with simple monodentate ligands have been prepared by this method.

We now report the preparation of a series of derivatives of molybdenum tetracarbonyl dibromide with triphenylphosphine, triphenylarsine, and triphenylstibine of the type bis(triphenylphosphine)molybdenum tricarbonyl dibromide. The triphenylphosphine compound only, like its chloro analogue, is thermally unstable in dichloromethane and decomposes to bis(triphenylphosphine)molybdenum dicarbonyl dibromide. The triphenylstibine derivative of the carbonyl chloride has been prepared to complete the series of chloro compounds.

Unlike molybdenum tetracarbonyl dichloride, whose preparation we described in Part I of this series, the tetracarbonyl dibromide has not been isolated in a pure state, but it is readily obtainable in solution and derivatives of it may readily be prepared. Addition of bromine in dichloromethane to a suspension of molybdenum hexacarbonyl in the same solvent at  $-78^{\circ}$  gave a smooth reaction with evolution of carbon monoxide. The solution was pumped to dryness and the solid consisting of excess molybdenum carbonyl, the tetracarbonyl dibromide, and probably a mixture of molybdenum bromides was extracted with acetone or dichloromethane. Addition of the appropriate ligand in dichloromethane gave the crystalline derivative.

The triphenylphosphine compound, only, is thermally unstable in refluxing dichloromethane. The product of the reaction, which goes to completion in about 2 hr, is the blue compound bis(triphenylphosphine)molybdenum dicarbonyl dichloride,  $[P(C_6H_5)_3]_2Mo(CO)_2Cl_2$ . Like the corresponding chloro compound, the blue

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<sup>1</sup> Lewis, J., and Whyman, R., *J. chem. Soc.*, 1965, 5486.

<sup>2</sup> Cook, C. D., Nyholm, R. S., and Tobe, M. L., *J. chem. Soc.*, 1965, 4194.

<sup>3</sup> Stiddard, M. H. B., *J. chem. Soc.*, 1962, 4712, and references therein; Mannerskantz, H. C. E., and Wilkinson, G., *J. chem. Soc.*, 1962, 4454.

complex is diamagnetic and shows two stretching carbonyl frequencies, both pieces of evidence suggesting a dimer molecule since a six-coordinate monomer should be paramagnetic. The infrared stretching frequencies are given in Table 1: there are no absorptions in the region associated with bridging carbonyl groups, and although definite evidence is lacking so far it is thought that the dimer is halogen-bridged. The formation of the dimer by loss of carbon monoxide from the monomer bears a striking resemblance to the decomposition of monomeric rhenium pentacarbonyl halides to give dimeric rhenium tetracarbonyl halides.<sup>4</sup>

TABLE 1  
CARBONYL STRETCHING FREQUENCIES

Compound	Frequencies	Medium
$[P(C_6H_5)_3]_2Mo(CO)_3Br_2$	2020m, 1955s, 1910m 2035m, 1970s, 1930m	Nujol CH <sub>2</sub> Cl <sub>2</sub>
$[As(C_6H_5)_3]_2Mo(CO)_3Br_2$	2020m, 1960s, 1915m 2040m, 1970s, 1935m	Nujol CH <sub>2</sub> Cl <sub>2</sub>
$[Sb(C_6H_5)_3]_2Mo(CO)_3Br_2$	2020s, 1960s, 1915s 2035m, 1965s, 1920m	Nujol CH <sub>2</sub> Cl <sub>2</sub>
$[Sb(C_6H_5)_3]_2Mo(CO)_3Cl_2$	2035s, 1965s, 1920s 2040m, 1965s, 1925m	Nujol CH <sub>2</sub> Cl <sub>2</sub>
$[P(C_6H_5)_3]_2Mo(CO)_2Br_2$	1975m, 1900s 1965m, 1890s	Nujol CH <sub>2</sub> Cl <sub>2</sub>

### Experimental

#### Analyses

The compounds were carefully fused with sodium hydroxide-sodium peroxide mixture for molybdenum, bromine, or chlorine analyses. After extracting with water the solution was made up to a standard volume and aliquots were taken to determine molybdenum as its 8-hydroxyquinolate<sup>5</sup> and the halogens by potentiometric titration with standard silver nitrate solution. Carbon, hydrogen, and phosphorus analyses were performed by the Australian Microanalytical Service, Melbourne.

#### *Bis(triphenylphosphine)molybdenum Tricarbonyl Dibromide*

Finely ground molybdenum hexacarbonyl (1 g) was suspended in 20 ml dichloromethane cooled to  $-78^\circ$  in an acetone/dry-ice bath. About 10 drops of bromine were added and the smooth reaction was allowed to proceed for about 5 min; the solvent was then pumped off. The impure tetracarbonyl dibromide was extracted with acetone, and the solution was then filtered into a solution of 2 g triphenylphosphine in 10 ml of acetone. The yellow crystalline precipitate was allowed to settle for 2 hr, then the supernatant liquid was poured off and the crystals were washed several times with small amounts of acetone. The crystals were finally dried by pumping (Found: Mo, 11.5; Br, 18.3; C, 52.1; H, 3.7; P, 7.0. Calc for  $[P(C_6H_5)_3]_2Mo(CO)_3Br_2$ : Mo, 11.1; Br, 18.5; C, 54.2; H, 3.5; P, 7.2%).

#### *Bis(triphenylphosphine)molybdenum Dicarbonyl Dibromide*

Bis(triphenylphosphine)molybdenum tricarbonyl dibromide (1 g) was refluxed in acetone (30 ml) for 4-5 hr. The supernatant liquid was decanted off, and the blue solid was washed with

<sup>4</sup> Abel, E. W., Hargreaves, G. B., and Wilkinson, G., *J. chem. Soc.*, 1959, 3149.

<sup>5</sup> Hollingshead, R. G. W., "Oxine and its Derivatives." (Butterworths: London 1954.)

small amounts of acetone and pumped dry (Found: Mo, 12.0; Br, 18.8; C, 54.0; H, 3.8; P, 7.1. Calc. for  $[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{Mo}(\text{CO})_2\text{Br}_2$ : Mo, 11.5; Br, 19.1; C, 54.6; H, 3.8; P, 7.4%).

*Bis(triphenylarsine)molybdenum Tricarbonyl Dibromide*

The procedure is identical with that given for the corresponding triphenylphosphine compound. The yellow-orange compound was washed with acetone and pumped dry (Found: Mo, 10.4; Br, 16.6; C, 48.6; H, 3.5. Calc. for  $[\text{As}(\text{C}_6\text{H}_5)_3]_2\text{Mo}(\text{CO})_3\text{Br}_2$ : Mo, 10.1; Br, 16.8; C, 49.2; H, 3.2%).

*Bis(triphenylstibine)molybdenum Tricarbonyl Dibromide*

The procedure is identical with that given for the corresponding triphenylphosphine compound. The orange crystals were washed with acetone and pumped dry (Found: Mo, 9.7; Br, 15.1; C, 44.7; H, 3.4. Calc. for  $[\text{Sb}(\text{C}_6\text{H}_5)_3]_2\text{Mo}(\text{CO})_3\text{Br}_2$ : Mo, 9.2; Br, 15.2; C, 44.8; H, 2.9%).

*Bis(triphenylstibine)molybdenum Tricarbonyl Dichloride*

Approximately 0.5 g of molybdenum tetracarbonyl dichloride, prepared as described in Part I of this series, was dissolved in acetone (20 ml). The solution was filtered into a solution of triphenylstibine (2 g) in acetone (10 ml). Carbon monoxide was evolved and the mixture was shaken vigorously. The precipitate was allowed to settle for 2 hr, then the supernatant liquid was decanted off. The crystals were washed with acetone ( $2 \times 4$  ml) and pumped dry (Found: Mo, 10.2; Cl, 7.6; C, 48.8; H, 3.5. Calc. for  $[\text{Sb}(\text{C}_6\text{H}_5)_3]_2\text{Mo}(\text{CO})_3\text{Cl}_2$ : Mo, 10.1; Cl, 7.4; C, 48.9; H, 3.2%).

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