

CARBONYL HALIDES OF THE GROUP VI TRANSITION METALS

IV.* NITROGEN LIGAND COMPLEXES OF MOLYBDENUM HALOCARBONYLS

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Summary

Unstable seven-coordinate complexes of molybdenum(II) have been obtained by the interaction, under mild conditions, of the molybdenum halocarbonyls with pyridine (py), 2,2'-dipyridyl (dipy), and 1,10-phenanthroline (phen).

INTRODUCTION

In previous papers in this series^{1,2} we described the preparation of dichlorotetracarbonylmolybdenum(II) and dibromotetracarbonylmolybdenum(II). Quite stable seven-coordinate complexes of molybdenum(II) were readily obtained by interaction of the carbonyl halides with triphenylphosphine, triphenylarsine, and triphenylstibine.

Stiddard³ has reported the preparation of dihalotricarbonyldipyridylmolybdenum(II) (chlorine and bromine) by the action of the halogen on tetracarbonyldipyridylmolybdenum, and the corresponding tungsten compounds were prepared in an analogous manner. We now report the preparation of a series of molybdenum derivatives of this type by interaction of the nitrogen ligand with the halocarbonyls.

RESULTS AND DISCUSSION

The compounds dichlorotricarbonylbis(pyridine)molybdenum(II), dihalotricarbonylmono-2,2'-dipyridylmolybdenum(II) (chloride and bromide), and dihalotricarbonylmono-1,10-phenanthrolinemolybdenum(II) (chloride and bromide) have been prepared and characterized. As noted by Stiddard³ for his dipyridyl complexes, all of these compounds are unstable to light and exposure to air. This is in marked contrast to the stability of the complexes obtained using triphenylphosphine;^{1,2} the reduction in stability may be ascribed to the lack of back-bonding (π -bonding) ability of nitrogen compared with phosphorus. Although the infrared pattern in the carbonyl stretching region of these complexes is very similar to that obtained with the phosphines, all of the frequencies are higher (except the pyridine compound) suggesting a somewhat higher bond order for the carbonyl groups. The general similarity of the spectra given by complexes with these bidentate ligands to those given by the phosphines suggests that in the phosphine, arsine, and stibine series the two phosphine groups are *cis* to each other in their complexes. The carbonyl stretching frequencies are given in Table 1.

* Part III, *Aust. J. Chem.*, 1967, **20**, 9.

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¹ Colton, R., and Tomkins, I. B., *Aust. J. Chem.*, 1966, **19**, 1143.

² Colton, R., and Tomkins, I. B., *Aust. J. Chem.*, 1966, **19**, 1519.

³ Stiddard, M. H. B., *J. chem. Soc.*, 1962, 4712.

EXPERIMENTAL

Analyses

The compounds were fused carefully with sodium hydroxide and sodium hydroxide/sodium nitrate mixture for halogen and molybdenum analyses, respectively. Halogen was determined by potentiometric titration against standard silver nitrate solution, and molybdenum was determined gravimetrically as its 8-hydroxyquinolate.⁴

Solvent

Dichloromethane was distilled and dried over molecular sieves (Type 4A, 1/16 in. pellets, Union Carbide).

Ligands

Solutions of pyridine, 2,2'-dipyridyl, and 1,10-phenanthroline in dichloromethane were dried by refluxing over molecular sieves for 4-5 hr.

TABLE 1
CARBONYL STRETCHING FREQUENCIES IN NUJOL MULL

Compound	Description	Frequencies		
$\text{MoCl}_2(\text{CO})_3 \text{ py}_2$	yellow crystals	2020s	1930s	1875m
$\text{MoCl}_2(\text{CO})_3 \text{ dipy}$	yellow crystals	2050m	1975s	1925m
$\text{MoCl}_2(\text{CO})_3 \text{ phen}$	yellow crystals	2045m	1970s	1920s
$\text{MoBr}_2(\text{CO})_3 \text{ dipy}$	orange crystals	2060s	1985s	1930m
$\text{MoBr}_2(\text{CO})_3 \text{ phen}$	orange crystals	2060m	2000s	1930s

TABLE 2
ANALYTICAL DATA

Compound	Found (%)		Calc. (%)	
	Mo	Halogen	Mo	Halogen
$\text{MoCl}_2(\text{CO})_3 \text{ py}_2$	25.0	17.9	23.5	17.4
$\text{MoCl}_2(\text{CO})_3 \text{ dipy}$	23.8	17.3	23.6	17.4
$\text{MoCl}_2(\text{CO})_3 \text{ phen}$	22.4	16.9	22.3	16.5
$\text{MoBr}_2(\text{CO})_3 \text{ dipy}$	18.7	32.3	19.3	31.0
$\text{MoBr}_2(\text{CO})_3 \text{ phen}$	19.0	30.7	18.5	30.5

Preparation of Compounds

After the preparation of the parent halocarbonyls the procedures to obtain all of the complexes are identical. Thus only the preparation of dichlorotricarbonylbis(pyridine)molybdenum(II) will be described. Dichlorotetracarbonylmolybdenum(II) (1 g), prepared as described previously,¹ was dissolved in dry dichloromethane and filtered into a dry solution of pyridine (1 ml) in dichloromethane (20 ml). The yellow crystals were allowed to settle and then the supernatant liquid was poured off. The compound was washed with small amounts of acetone and pumped dry. The analytical figures for all of the compounds are given in Table 2; these are not as good as usually expected for organometallic compounds because of the unstable nature of the complexes.

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⁴ Hollingshead, R. G. W., "Oxine and its Derivatives." (Butterworths: London 1954.)