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HALOGEN DERIVATIVES OF AMINETUNGSTEN CARBONYLS

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Summary

Aminetungsten pentacarbonyls and bis(amine)tungsten tetracarbonyls react with bromine or iodine in hexane or benzene to give $W(CO)_4(amine)X_2$ and $W(CO)_3(amine)_2X_2$ (X = Br, I), respectively. The iodine compounds are stable as solids as well as in benzene solution, but the analogous bromo-complexes are stable in solution only. All the complexes are non-electrolytes in benzene.

Introduction

The halogen derivatives of substituted metal carbonyls are prepared either by the action of ligands on metal halocarbonyls or by the treatment of halogens with substituted metal carbonyls. The known types of neutral, cationic and anionic derivatives include $M(CO)_3L_2X_2$ [1,2], $M(CO)_3(L{-}L)X_2$ [1,3], $M(CO)_3(L{-}L')X_2$ [4], $M(CO)_2L_3X_2$ [2,5], $M(CO)_2(L{-}L{-}L)X_2$ [6—8], $M(CO)L_4X_2$ [2], $[M(CO)_4(L{-}L)X]^+$ [9], $[M(CO)_3(L{-}L{-}L)X]^+$ [6,7], $[M(CO)_2(L{-}L{-}L{-}L)X]^+$ [8], $[M(CO)_2(L{-}L)_2X]^+$ [1,3] and $[M(CO)_3LX_3]^-$ [10], which contain phosphorus or arsenic donors. The halogenation of such complexes containing nitrogen donors has not previously been described, and the neutral derivatives containing four carbonyl groups were not previously known. We describe below the bromination and iodination of several aminetungsten carbonyls, some of which give the neutral tetracarbonyl halides.

Results and discussion

Aminetungsten pentacarbonyls (amine = butylamine, cyclohexylamine, piperidine, and morpholine) reacted with one equivalent of bromine or iodine in inert solvents such as hexane or benzene to give $W(CO)_4(amine)X_2$ derivatives.

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TABLE 1

C—O STRETCHING FREQUENCIES OF $W(CO)_4(AMINE)X_2$ DERIVATIVES

Compound	ν(CO) (benzene solution) (cm^{-1})
$W(CO)_4(C_4H_9NH_2)Br_2$	2072s, 2000s, 1950s, 1836(sh), 1818vw
$W(CO)_4(C_4H_9NH_2)I_2$	2074s, 2000vs, 1950s, 1828vw, 1802w
$W(CO)_4(C_6H_{11}NH_2)Br_2$	2075s, 1998s, 1945s
$W(CO)_4(C_6H_{11}NH_2)I_2$	2070s, 1987s, 1930s
$W(CO)_4(C_5H_{11}N)Br_2$	2100s, 2010-1980s(br), 1950s, 1833w
$W(CO)_4(C_5H_{11}N)I_2$	2080s, 1985vs, 1930s
$W(CO)_4(C_4H_9NO)Br_2$	2070s, 2006s, 1922s
$W(CO)_4(C_4H_9NO)I_2$	2070s, 1990vs, 1930s

(With an excess of bromine or iodine, only unidentified sticky products were obtained.) Bis(amine)tungsten tetracarbonyls gave $W(CO)_3(amine)_2X_2$ derivatives. Chlorination of aminetungsten pentacarbonyls and bis(amine)tungsten tetracarbonyls seemed to take place similarly but the products were too unstable to be isolated. The iodine complexes were more stable than their bromo analogues in both cases; the iodinated derivatives were isolated as solids, but the bromo-complexes decomposed on crystallisation and hence were studied only in benzene solution. The iodine derivatives, which are moisture-sensitive, are orange in colour; they are insoluble in aliphatic hydrocarbons and light petroleum (60-80°) but soluble in aromatic hydrocarbons, tetrahydrofuran, dichloromethane, acetone, etc. In oxygenated solvents immediate decomposition is observed. It is noteworthy that the halogenated products are more stable in benzene solution than in the solid state, though the parent aminetungsten carbonyls are more stable as solids than in solution. The stoichiometric composition of the iodine derivatives, together with IR and molar conductivity data (2.5-3.0 Ω^{-1} cm^2), suggest that they are low symmetry hepta-coordinated complexes of divalent tungsten.

The IR spectra of $W(CO)_4(amine)X_2$ derivatives exhibit three strong C—O bands in the region 2100-1922 cm^{-1}. Two shoulders or weak intensity C—O bands also appear in some cases (Table 1). The spectra closely resembled those of the $Mo(CO)_4(amine)X_2$ derivatives [11] in the frequencies and intensities of the bands.

TABLE 2

C—O STRETCHING BANDS OF $W(CO)_3(AMINE)_2X_2$ DERIVATIVES

Compound	ν(CO) (benzene solution) (cm^{-1})
$W(CO)_3(C_4H_9NH_2)_2Br_2$	2040s, 1980s, 1935s
$W(CO)_3(C_4H_9NH_2)_2I_2$	2030s(br), 1972s, 1910s
$W(CO)_3(C_5H_{11}N)_2Br_2$	2045s, 1982s, 1935s
$W(CO)_3(C_5H_{11}N)_2I_2$	2035s(br), 1969s, 1912s
$W(CO)_3(C_4H_9NO)_2Br_2$	2035s, 1980s, 1935s
$W(CO)_3(C_4H_9NO)_2I_2$	2030s(br), 1978s, 1915s

There are only three strong C—O bands also in the IR spectra of $W(CO)_3(amine)_2X_2$ derivatives (Table 2). They had considerably lower frequencies than those for $W(CO)_4(amine)X_2$ derivatives, and this may be attributed to the presence in the $W(CO)_3(amine)_2X_2$ derivatives of two amine ligands, which do not possess any acceptor capability. The marked differences in the frequencies of the C—O bands between $W(CO)_3(amine)_2X_2$ and $W(CO)_3(amine)_3$ [12] derivatives may be due to the presence of halogen atoms in the former. The halogen atoms are very good electron acceptors, and usually raise the C—O frequencies.

Experimental

General

All experiments were performed under dry nitrogen. Aminetungsten pentacarbonyls and bis(amine)tungsten tetracarbonyls were prepared as previously described [13]. Evolved CO was measured with a gas burette. Iodine complexes were characterised by micro analysis, IR spectra and conductivity measurements. The analogous bromo-complexes were identified by the close similarity of their IR spectra to those of the iodinated products. Spectra were measured on a Perkin—Elmer IR spectrophotometer model 221.

Preparation of diiodo(butylamine)tungsten tetracarbonyl

A hexane solution of iodine (0.15 g in 30 ml) was added dropwise with stirring to a solution of butylaminetungsten pentacarbonyl (0.2 g in 30 ml hexane) under nitrogen at room temperature. The colour of the iodine disappeared during the addition, and an orange brown precipitate settled out. On completion of reaction the volume of liberated CO was 11.8 ml (calculated 12.3 ml). The supernatant liquid was decanted under nitrogen and the precipitate washed well with hexane (to remove the excess of iodine and any unchanged butylaminetungsten pentacarbonyl) and dried in vacuo. Recrystallisation from several solvents under nitrogen gave only blue coloured decomposition products. The crude product was shown to be diiodo(butylamine)tungsten tetracarbonyl (Found: C, 15.1; H, 1.6; I, 39.8; N, 2.4. $C_8H_{11}I_2NO_4W$ calcd.: C, 15.4; H, 1.7; I, 40.7; N, 2.2%). Molar conductivity: 2.5 Ω^{-1} cm^2 in 0.0001 *M* benzene solution.

Preparation of dibromo(butylamine)tungsten tetracarbonyl

A hexane solution of bromine (0.1 g in 25 ml) was added dropwise with stirring to a hexane solution of butylaminetungsten pentacarbonyl (0.2 g in 30 ml) under nitrogen at room temperature. The orange brown precipitate was washed well with nitrogen-saturated hexane to remove the unchanged reactants, and then filtered off under nitrogen. Attempts to dry the precipitate even in vacuo caused decomposition of the product into a yellowish green substance. Extraction with benzene left a small amount of blue residue. The IR spectrum of the benzene extract was identical to that of the analogous iodine complex.

Preparation of diiodo(cyclohexylamine)tungsten tetracarbonyl

Iodine (0.15 g in 30 ml hexane) and cyclohexylaminetungsten pentacarbonyl (0.2 g in 30 ml hexane) reacted at room temperature under nitrogen to give an orange solid. This was identified as diiodo(cyclohexylamine)tungsten tetracarbonyl (Found: C, 17.8; H, 1.8; I, 38.7; N, 2.0. $C_{10}H_{13}I_2NO_4W$ calcd.: C, 18.4; H, 2.0; I, 37.5; N, 2.1%). Molar cond.: 2.9 Ω^{-1} cm^2 in 0.0001 *M* benzene solution.

Preparation of dibromo(cyclohexylamine)tungsten tetracarbonyl

Bromine (0.1 g in 25 ml hexane) and cyclohexylaminetungsten pentacarbonyl (0.2 g in 30 ml hexane) similarly gave a yellowish brown solid which was extracted into benzene. The IR spectrum of the benzene extract in the C—O stretching region closely resembled that of the other dihalo-aminetungsten tetracarbonyls.

Preparation of diiodo(piperidine)tungsten tetracarbonyl

Iodine (0.15 g in 30 ml hexane) and piperidinetungsten pentacarbonyl (0.2 g in 30 ml hexane) similarly gave yellowish orange diiodo(piperidine)tungsten tetracarbonyl (Found: C, 16.2; H, 1.7; I, 41.2; N, 2.1. $C_9H_{11}I_2NO_4W$ calcd.: C, 17.0; H, 1.7; I, 40.0; N, 2.2%). Molar cond.: 3.0 Ω^{-1} cm^2 in 0.0001 *M* benzene solution.

Preparation of dibromo(piperidine)tungsten tetracarbonyl

Bromine (0.1 g in 25 ml hexane) and piperidinetungsten pentacarbonyl (0.2 g in 30 ml hexane) similarly gave a product which was extracted into benzene as in the case of dibromo(butylamine)tungsten tetracarbonyl. Its IR spectrum was recorded.

Preparation of diiodo(morpholine)tungsten tetracarbonyl

Iodine (0.15 g) in hexane (30 ml) reacted with morpholinetungsten pentacarbonyl (0.2 g in 30 ml hexane) at room temperature under nitrogen. Work up as for the butylamine analogue yielded an orange brown solid which was shown to be diiodo(morpholine)tungsten tetracarbonyl (Found: C, 15.6; H, 1.5; I, 40.1; N, 2.0. $C_8H_9I_2NO_5W$ calcd.: C, 15.0; H, 1.4; I, 39.9; N, 2.1%). Molar cond.: 2.5 Ω^{-1} cm^2 in 0.0001 *M* benzene solution.

Preparation of dibromo(morpholine)tungsten tetracarbonyl

Bromine (0.1 g in 25 ml hexane) and morpholinetungsten pentacarbonyl (0.2 g in 30 ml hexane) reacted at room temperature under nitrogen. The IR spectrum of the benzene extract showed the usual three C—O bands.

Preparation of diiodo(bis(butylamine))tungsten tricarbonyl

A hexane solution of iodine (0.15 g in 30 ml) was added dropwise with stirring to solid bis(butylamine)tungsten tetracarbonyl (0.2 g) at room temperature under nitrogen. The colour of the iodine disappeared and the bis(butylamine)tungsten tetracarbonyl dissolved, and a flocculent yellowish brown precipitate appeared. The volume of evolved CO was 8.8 ml (calcd. 10.7 ml). The solvent was decanted under nitrogen and the residue washed several times with hexane. It was dried in vacuo and was shown to be diiodo-bis(butylamine)tungsten tricarbonyl (Found: C, 18.9; H, 3.4; I, 40.0; N, 3.9. $C_{11}H_{22}I_2N_2O_3W$ calcd.: C, 19.7; H, 3.2; I, 38.0; N, 4.1%). Molar cond.: 2.7 Ω^{-1} cm^2 in 0.0001 *M* solution.

It was soluble in most organic solvents except aliphatic hydrocarbons and light petroleum (60-80°).

Preparation of dibromo(bis(butylamine))tungsten tricarbonyl

Similarly bromine (0.1 g in 25 ml) reacted with solid bis(butylamine)tungsten tetracarbonyl (0.2 g in 30 ml) in hexane to give a yellowish orange precipitate. This was washed well and extracted with benzene. The IR spectrum of the benzene solution resembled that of the iodine analogue.

Preparation of diiodo(bis(piperidine))tungsten tricarbonyl

Similarly iodine (0.15 g in 30 ml hexane) and solid bis(piperidine)tungsten tetracarbonyl (0.2 g) gave the orange diiodo-bis(piperidine)tungsten tricarbonyl (Found: C, 20.8; H, 3.1; I, 35.2; N, 3.7. $C_{13}H_{22}I_2N_2O_3W$ calcd.: C, 21.5; H, 3.0; I, 35.0; N, 3.8%). Molar cond.: 2.9 Ω^{-1} cm^2 in 0.0001 *M* benzene solution.

Preparation of dibromo(bis(piperidine))tungsten tricarbonyl

Bromine (0.1 g in 25 ml hexane) and solid bis(piperidine)tungsten tetracarbonyl (0.2 g) gave an orange product, which was extracted into benzene. Its IR spectrum was similar to that of its iodine analogue.

Preparation of diiodo(bis(morpholine))tungsten tricarbonyl

Similarly iodine (0.15 g in 30 ml hexane) and solid bis(morpholine)tungsten tetracarbonyl (0.2 g) gave a yellowish orange product which was shown to be diiodo(bis(morpholine))tungsten tricarbonyl (Found: C, 18.3; H, 2.7; I, 33.1; N, 4.0. $C_{11}H_{18}I_2N_2O_5W$ calcd.: C, 18.1; H, 2.5; I, 34.8; N, 3.8%). Molar cond.: 3.0 Ω^{-1} cm^2 in 0.0001 *M* benzene solution.

Preparation of dibromo(bis(morpholine))tungsten tricarbonyl

Similarly bromine (0.1 g in 25 ml hexane) and solid bis(morpholine)tungsten tetracarbonyl (0.2 g) gave an orange product which was extracted into benzene and identified by its IR spectrum in the C—O region.

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