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THE SYNTHESIS AND SPECTRAL PROPERTIES OF SOME HIGHLY REACTIVE NEW SEVEN-COORDINATE MOLYBDENUM(II) AND TUNGSTEN(II) BISACETONITRILE DIHALOGENOTRICARBONYL COMPLEXES

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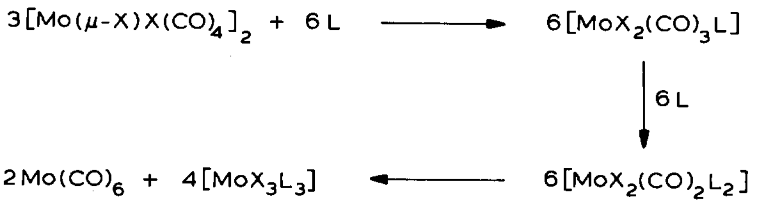
Summary

The complexes $[M(CO)_3(NCMe)_3]$ (M = Mo and W) react with X_2 (X = Br and I) in NCMe to afford high yields of the new seven-coordinate complexes $[MX_2(CO)_3(NCMe)_2]$.

Introduction

The complexes $[MX_2(CO)_3L_2]$ (M = Mo and W; L = PPh_3 and $AsPh_3$; X = Cl and Br) are currently under investigation as catalysts for the ring-opening polymerisation of norbornene [1,2], and the phosphine or arsine dissociation in these complexes is the rate-determining step in the mechanism. Although a wide variety of bisphosphine complexes of the type $[MX_2(CO)_3L_2]$ (L = phosphine) have been described [3], very few seven-coordinate complexes of molybdenum(II) and tungsten(II) containing nitrogen donor ligands have been reported [4] and it has been found [5] that reaction of the halide bridged dimers $[Mo(\mu\text{-}X)X(CO)_4]_2$ (X = Cl and Br) with ligands with low π-acceptor ability such as nitriles proceeds via a dispro-



(X = Cl and Br; L = nitriles, pyridine, thf, etc.)

SCHEME 1

0022-328X/86/$03.50

TABLE 1

IR, ^{1}H AND ^{13}C NMR DATA FOR $[MX_2(CO)_3(NCMe)_2]$

M	X	$\bar{\nu}$(CO) [a] (cm^{-1})	$\bar{\nu}$ (C≡N) [a] (cm^{-1})	^{1}H NMR NCCH$_3$ [b]	^{13}C NMR		
					C≡O [b]	N≡C-CH$_3$ [b]	N≡C-CH$_3$ [b]
Mo	I	2038 (s), 1968 (s) 1940 (m)	2355, 2316 (w)	2.39	225.97	117.86	3.9
Mo	Br	2040 (s), 1985 (s) 1948 (m)	2318, 2286 (w)	–	–	–	–
W	I	2040 (m), 1980 (s), 1945 (s)	2300, 2245 (w)	2.53	218.44	117.08	3.9
W	Br	2030 (m), 1980 (s) 1945 (s)	2310, 2295 (w)	2.4	–	–	–

[a] Spectra recorded in $CHCl_3$; w, weak; m, medium; s, strong. [b] Spectra recorded in $CDCl_3$ (+25°C) and referenced to Me_4Si.

portionation of Mo^{II} to Mo^{III} and Mo^0 at the last step (Scheme 1). We now describe the synthesis of the new highly reactive bisacetonitrile complexes, $[MX_2(CO)_3(NCMe)_2]$ (M = Mo and W; X = Br and I).

Results and discussion

The complexes $[MI_2(CO)_3(NCMe)_2]$ (M = Mo and W; X = Br and I) are prepared by treating $[M(CO)_3(NCMe)_3]$ (generated in situ) X_2 at 0°C to afford the brown crystalline complexes in quantitative yield. The diiodo complexes are stable in the solid state when stored under argon in the dark, and have been fully characterised by elemental analysis (C, H and N) and by IR, ^{1}H and ^{13}C NMR spectroscopy (Table 1).

The bromide complexes are much less stable, although some spectral data have been recorded, and the dichloro complexes are extremely unstable.

The previously reported X-ray crystal structures of seven-coordinate complexes [6–17] all reveal capped octahedral geometry, and it is highly likely that the bisacetonitrile complexes have a similar geometry since their carbonyl infrared pattern closely resembles those of the analogous bisphosphine compounds.

The diiodo complexes $[MI_2(CO)_3(NCMe)_2]$ were prepared many times, and quantitative yields of analytically pure products upon removal of acetonitrile. The complexes have proved to be excellent precursors for a wide range of new organotransition-metal compounds, mainly owing to the ease of displacement of the acetonitrile ligands, which is in contrast to the previously reported bisphosphine compounds $[MX_2(CO)_3L_2]$ [3] in which the metal–phosphorus bonds are very strong.

Experimental

All preparations were carried out under argon. $[M(CO)_6]$ (M = Mo and W), I_2, Br_2 and acetonitrile were purchased from commercial sources, $[M(CO)_3(NCMe)_3]$ (M = Mo and W) were prepared by published methods [18]. ^{1}H and ^{13}C NMR spectra were recorded on a Jeol FX 60 NMR spectrometer (all spectra were calibrated against tetramethylsilane). Infrared spectra were recorded on a Perkin–Elmer 197 infrared spectrophotometer. Elemental analyses for carbon, hydrogen and nitrogen were recorded on a Carlo Erba Elemental Analyser MOD1106 (using a helium carrier gas).

Preparation of [MoI$_2$(CO)$_3$(NCMe)$_2$]

A suspension of [Mo(CO)$_6$] (4.00 g, 15.2 mmol) in degassed acetonitrile (120 cm^3) was refluxed under argon for 24 h. The solution obtained was cooled to 0°C, then I_2 (3.85 g, 15.2 mmol) was added, resulting in the immediate formation of a red-brown solution. Removal of the solvent in vacuo gave the analytically pure brown crystalline complex [MoI$_2$(CO)$_3$(NCMe)$_2$] in quantitative yield. (Found: C, 16.28; H, 1.16; N, 5.21. $C_7H_6N_2O_3I_2Mo$ calcd.: C, 16.28; H, 1.16; N, 5.43%.)

Preparation of [WI$_2$(CO)$_3$(NCMe)$_2$]

A suspension of [W(CO)$_6$] (4.00 g, 11.4 mmol) in degassed acetonitrile (120 cm^3) was refluxed under argon for 72 h. The solution obtained was cooled to 0°C, then I_2 (2.88 g, 11.3 mmol) was added, resulting in the immediate formation of a red-brown solution. Removal of the solvent in vacuo gave the analytically pure brown crystalline complex [WI$_2$(CO)$_3$(NCMe)$_2$] in quantitative yield. (Found: C, 13.72; H, 1.22; N, 4.83. $C_7H_6N_2O_3I_2W$ calcd.: C, 13.91; H, 0.99; N, 4.64%.)

The dibromo complexes [MBr$_2$(CO)$_3$(NCMe)$_2$] (M = Mo and W) were prepared analogously but were found to be much more air-sensitive and thermally unstable than the diiodo compounds, and satisfactory analytical data were not obtained.

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