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The Synthesis of Six- and Seven-coordinate Molybdenum and Tungsten(II) Dicarbonyl Complexes Containing Monodentate Phosphine Ligands

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Abstract

On passing a stream of dry N_2 gas through a solution of $Mo(CO)_3(PR_3)_2X_2$ ($PR_3 = PEtPh_2$, PMe_2Ph or PEt_2Ph, $X = Br$; $PR_3 = PMePh_2$, $X = Cl$, Br or I) in acetonitrile at room temperature, or $W(CO)_3(PR_3)_2X_2$ ($PR_3 = PMePh_2$ or PMe_2Ph, $X = Br$) in boiling acetonitrile, the yellow, monomeric 7-coordinate dicarbonyls $M(CO)_2(NCMe)(PR_3)_2X_2$ are formed in high yields. The nitrile ligand is readily displaced from $M(CO)_2(NCMe)(PR_3)_2X_2$ ($M = Mo$, $PR_3 = PEtPh_2$ or PEt_2Ph, $X = Br$; $PR_3 = PMePh_2$, $X = I$; $M = W$, $PR_3 = PMePh_2$, $X = Br$) by passing a vigorous stream of N_2 gas through a solution of these complexes dissolved in chlorinated or ketonic solvents yielding new, highly coloured 6-coordinate d^4 $M(CO)_2(PR_3)_2X_2$ derivatives.

Introduction

The relationship between mononuclear 6- and 7-coordinate d^4 molybdenum and tungsten complexes has attracted considerable attention from both a theoretical [1] and synthetic viewpoint [2], but there are still relatively few complexes known in which the electronic and steric effects of the ligands are sufficiently well balanced to allow an easy interconversion between these two coordination numbers. Historically, the most important series of complexes of this type involved phosphine derivatives of molybdenum(II) carbonyl halides, some of which were shown by Colton and Tomkins to behave as CO carrier molecules [3].

$$MoBr_2(CO)_3(PR_3)_2 \overset{\Delta}{\rightleftharpoons} MoBr_2(CO)_2(PR_3)_2 + CO$$

Although this reaction can be extended to include tungsten analogues [4], the total number of complexes of this type which exhibit this facile change in coordination number is limited to some dozen reported examples, most of which contain triphenyl- or tritolylphosphine ligands [3, 4]. All dicarbonyl derivatives have been prepared, often in poor yields, by thermal decarbonylation of tricarbonyl precursors. Attempts to extend this reaction to several other phosphine derivatives yield the species $[MBr_2(CO)_2(PR_3)_2]_n$. These complexes generally have very low solubilities and hence the value of *n* cannot easily be determined. However, *n* is normally assumed to be 2, leading to a formulation in which 7-coordination is achieved at each metal atom via a pair of halide bridges. Additional credence for this proposal is provided by the recently determined structure of the parent carbonyl halide $[WBr_2(CO)_4]_2$ [6]. As a consequence of the difficulty in providing a facile synthesis of complexes of this type, much interesting chemistry has centred on the alternative series of 6- and 7-coordinate molybdenum and tungsten(II) dialkyldithiocarbamates $Mo(CO)_x(S_2CNR_2)_2$ ($x = 2$ or 3; R = alkyl) [7]. However, $M(CO)_2(PR_3)_2X_2$ complexes do not contain strong π-basic ligands, they adopt a different solid-state structure to the dialkyldithiocarbamate derivatives [8–11] and should be significantly more elctrophilic than $Mo(CO)_2(S_2CNR_2)_2$ (R = alkyl) in their subsequent reactions.

We considered that replacement of a CO ligand in $M(CO)_3(PR_3)_2X_2$ by a more labile, π-innocent, volatile ligand such as MeCN, might lead to an improved route to new 6-coordinate electrophilic d^4 monomers under reaction conditions which would avoid dimerisation. These materials should also be useful precursors for the preparation of new 7-coordinate d^4 species containing donor ligands not capable of directly displacing CO from $M(CO)_3(PR_3)_2X_2$.

Experimental

All work with air-sensitive materials was carried out in a dry, oxygen-free atmosphere using freshly distilled, deoxygenated solvents. Instrumentation and characterisation were identical to those of previous reports from this laboratory [12, 13].

The starting materials $M(CO)_3(PR_3)_2X_2$ ($M = Mo$, $PR_3 = PMePh_2$, $X = Cl$, Br or I; $PR_3 = PEtPh_2$,

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PEt_2Ph, PMe_2Ph, X = Br; M = W, $PR_3 = PMePh_2$, PMe_2Ph, X = Br) were prepared from $M(CO)_4X_2$ or $M(CO)_4(PR_3)_2$ by literature procedures or simple extensions thereof [3, 5, 8].

Preparation of $M(CO)_2(NCMe)(PR_3)_2X_2$ (M = Mo, PR_3 = $PEtPh_2$, PEt_2Ph or PMe_2Ph, X = Br; PR_3 = $PMePh_2$, X = Cl, Br or I; M = W, PR_3 = $PMePh_2$ or PMe_2Ph, X = Br)

A stream of N_2 gas was passed through a stirred suspension of $M(CO)_3(PR_3)_2X_2$ (0.5 mmol) in acetonitrile (15 cm^3). Reactions involving molybdenum complexes were carried out at room temperature, whilst those of tungsten were performed under gentle reflux conditions. The course of the reaction was monitored by infrared spectroscopy. When the three CO bands of the tricarbonyl had been replaced by two new CO bands of approximately equal intensity, the reaction was stopped and the solvent evaporated to low bulk *in vacuo*. Refrigeration yielded pale yellow microcrystalline crystals which were analytically pure.

Preparation of $Mo(CO)_2(PR_3)_2X_2$ (PR_3 = $PEtPh_2$ or PEt_2Ph, X = Br; PR_3 = $PMePh_2$, X = I)

A vigorous stream of N_2 gas was passed through a solution of either $Mo(CO)_3(PR_3)_2X_2$ (0.5 mmol) or $Mo(CO)_2(NCMe)(PR_3)_2X_2$ (0.5 mmol) in dichloromethane, acetone or 3-pentanone (15 cm^3). Reaction occurred at room temperature except for the tricarbonyl iodo-complex which was heated under reflux. The yellow solution turned blue as the reaction proceeded and the course of the reaction was monitored by infrared spectroscopy. Products were isolated as blue or purple powders by dropwise addition of hexane (10 cm^3) followed by slow partial evaporation of the solvent at room temperature. The filtered products were washed with hexane and dried *in vacuo*.

Preparation of $MoBr_2(CO)_2(PMePh_2)_2$

Nitrogen was bubbled through a suspension of $MoBr_2(CO)_3(PMePh_2)_2$ (0.15 g, 0.20 mmol) in dichloromethane (5 cm^3) as above. After 5 min the yellow solution became purple and at this point hexane (10 cm^3) was added dropwise and the total volume of solvent reduced *in vacuo* until the product precipitated as a powder. Extended reaction resulted in the formation of $[MoBr_2(CO)_2(PMePh_2)_2]_n$.

Preparation of $WBr_2(CO)_2(PMePh_2)_2$

A sample of $WBr_2(CO)_2(NCMe)(PMePh_2)_2$ (0.17 g, 0.20 mmol) was dissolved in chloroform (10 cm^3) and a stream of N_2 passed through the boiling solution. The orange solution darkened and became purple, and after 10 min the solution was cooled and treated with hexane (10 cm^3). On partial evaporation the product was formed as a purple microcrystalline solid which was collected, washed with hexane and dried *in vacuo*. Prolonged reaction under these conditions yielded a mixture of the product together with $[WBr_2(CO)_2(PMePh_2)_2]_n$.

Preparation of $[WBr_2(CO)_2(PR_3)_2]_n$ (where PR_3 = $PMePh_2$ or PMe_2Ph)

A solution of $WBr_2(CO)_3(PR_3)_2$ (0.5 mmol) dissolved in ethanol (40 cm^3) was heated under reflux for 2 h. The complex $[WBr_2(CO)_2(PMePh_2)]_n$ precipitated from solution as an insoluble orange powder which was filtered, washed with hexane and dried *in vacuo*. The corresponding dimethylphenylphosphine complex only precipitated after the volume of the solvent was reduced by 50% at –10 °C.

Preparation of $[Mo(CO)_2(PMePh_2)_2X_2]_n$ (where X = Cl or Br)

A suspension of $Mo(CO)_3(PMePh_2)_2X_2$ or $Mo(CO)_2(NCMe)(PMePh_2)X_2$ (0.5 mmol) in dichloromethane (10 cm^3) was bubbled vigorously with a stream of N_2 gas for 1 h. The product precipitated as an orange powder as the reaction proceeded, and was finally collected by filtration, washed with hexane and dried *in vacuo*.

Results and Discussion

Passing a stream of dinitrogen gas through a stirred suspension of $Mo(CO)_3(PR_3)_2X_2$ in dry MeCN at room temperature, or $W(CO)_3(PR_3)_2X_2$ in boiling MeCN, resulted in evolution of CO and dissolution of the solid with the formation of clear, yellow solutions from which yellow microcrystalline products could be isolated. Qualitatively, the rate of loss of CO from the tricarbonyl showed no appreciable dependence upon the nature of the halogen or the phosphine, and infrared spectroscopy revealed that the product $Mo(CO)_2(NCMe)(PR_3)_2X_2$ ($PR_3 = PMePh_2$, X = Cl, Br or I; $PR_3 = PEtPh_2$, PMe_2Ph or PEt_2Ph, X = Br) and $WBr_2(CO)_2(NCMe)(PR_3)_2$ ($PR_3 = PMePh_2$ or PMe_2Ph) (Table I) contained CO ligands occupying mutually *cis*-sites in the metal coordination sphere, with calculated OC–M–CO angles in the range 70–75°. These values compare well with those quoted by Day, Batscheler and Archer [14] for a large range of seven-coordinate Mo(II) and W(II) carbonyl complexes.

It was apparent from NMR measurements on the more soluble products that fast exchange occurred between free and coordinated nitrile, and that in other solvents MeCN was slowly lost from the metal coordination sphere. This process was accelerated by the rapid passage of N_2 through the solution and was accompanied by a marked colour change from yellow to mauve or blue. Addition of hexane and subsequent concentration of such solutions yielded

TABLE I. Analytical and Physical Data for $M(CO)_2(MeCN)(PR_3)_2X_2$ and $[M(CO)_2(PR_3)_2X_2]_n$

Complex	Colour	Yield (%)	ν(CO) (cm^{-1})		ν(CN) (cm^{-1})	Analysis (%)			
						C	H	N	X
$Mo(CO)_2(NCMe)(PMePh_2)_2Cl_2$	yellow	67	1935s	1853s	2275m	52.2 (54.2)	4.50 (4.35)	2.50 (2.10)	10.4 (10.7)
$Mo(CO)_2(NCMe)(PMePh_2)_2Br_2$	yellow	77	1945s	1843s	2273m	47.7 (47.8)	3.95 (3.85)	2.05 (1.85)	20.9 (21.2)
$Mo(CO)_2(NCMe)(PMePh_2)_2I_2$	yellow	53	1935s	1853s	2278m	42.5 (42.5)	3.65 (3.40)	1.80 (1.65)	
$Mo(CO)_2(NCMe)(PEtPh_2)_2Br_2$	yellow	68	1942s	1839s	2275m	53.0 (53.3)	4.40 (4.60)	1.95 (1.95)	22.1 (22.2)
$Mo(CO)_2(NCMe)(PMe_2Ph)Br_2$	yellow	64	1939s	1832s	2285m	38.1 (38.2)	3.90 (3.95)	2.15 (2.25)	25.3 (25.4)
$Mo(CO)_2(NCMe)(PEt_2Ph)Br_2$	yellow	68	1945s	1835s	2283m	42.1 (42.0)	4.80 (4.80)	2.10 (2.05)	23.2 (23.4)
$W(CO)_2(NCMe)(PMePh_2)_2Br_2$	yellow–green	63	1923s	1839s	2275m	42.8 (42.8)	3.40 (3.45)	1.65 (1.65)	18.9 (19.0)
$W(CO)_2(NCMe)(PMe_2Ph)_2Br_2$	yellow–green	59	1919s	1834s	2283m	36.4 (36.5)	3.80 (3.80)	2.05 (2.10)	24.2 (24.35)
$MoBr_2(CO)_2(PMePh_2)_2$	purple	56	1955s	1865s		47.2 (47.2)	3.60 (3.65)		21.3 (22.5)
$MoI_2(CO)_2(PMePh_2)_2$	blue	45	1943s	1861s		41.0 (41.7)	3.10 (3.25)		29.5 (31.5)
$MoBr_2(CO)_2(PEtPh_2)_2$	blue	51	1965s	1849s		48.4 (48.7)	3.95 (4.05)		21.3 (21.6)
$MoBr_2(CO)_2(PEtPh_2)_2$	mauve	59	1955s	1845s		48.5 (48.7)	4.00 (4.05)		21.0 (21.6)
$MoBr_2(CO)_2(PEt_2Ph)_2$	blue	85	1949s	1868s		40.7 (41.0)	4.70 (4.65)		25.0 (42.9)
$WBr_2(CO)_2(PMePh_2)_2$	purple	51	1944s	1850s		41.9 (42.0)	3.20 (3.25)		20.0 (20.0)
$[MoCl_2(CO)_2(PMePh_2)_2]_n$	orange	82	1942s	1860s		53.6 (53.9)	4.00 (4.15)		11.2 (11.4)
$[MoBr_2(CO)_2(PMePh_2)_2]_n$	orange	77	1943s	1868s		47.3 (47.2)	3.85 (3.65)		22.2 (22.5)
$[WBr_2(CO)_2(PMePh_2)_2]_n$	orange	74	2020vw 1927s	1830s		42.0 (42.0)	3.80 (3.25)		19.2 (20.0)
$[WBr_2(CO)_2(PMe_2Ph)_2]_n$	orange	59	2020vw 1910s	1810s		32.3 (32.0)	3.40 (3.25)		23.1 (23.7)

$Mo(CO)_2(PR_3)_2X_2$ ($PR_3 = PEtPh_2$, PEt_2Ph, $PMePh_2$, $X = Br$; $PR_3 = PMePh_2$, $X = I$) as the only isolable products. The mauve colouration of the PMe_2Ph analogue proved transient and faded as orange, insoluble $[Mo(CO)_2(PMe_2Ph)_2Br_2]_n$ finally precipitated from solution. The colour changes suggest that the 6-coordinate monomer $Mo(CO)_2(PMe_2Ph)_2Br_2$ is probably produced initially, but rapidly forms the product previously obtained by Moss and Shaw and formulated as a dimer, on heating $MoBr_2(CO)_3(PMe_2Ph)_2$ in methanol [5].

Bubbling N_2 through a boiling $CHCl_3$ solution of $WBr_2(CO)_2(NCMe)(PMePh_2)_2$ yielded a purple solution from which purple $WBr_2(CO)_2(PMePh_2)_2$ could be isolated, but on prolonged heating (*ca.* 0.5 h) traces of the orange species $[WBr_2(CO)_2(PMePh_2)_2]_n$ were also formed. All mauve monomers and orange oligomers reacted with refluxing MeCN and with CO to reform $M(CO)_2(NCMe)(PR_3)_2X_2$ and $M(CO)_3(PR_3)_2X_2$ respectively.

$$\begin{tikzcd}[column sep=small]
\mathrm{M(CO)_3(PR_3)_2X_2 + MeCN} \arrow[rr] & & \mathrm{M(CO)_2(NCMe)(PR_3)_2X_2} \arrow[dl, shift right, "\Delta"'] \\
& \mathrm{M(CO)_2(PR_3)_2X_2} \arrow[ul, "\mathrm{CO}"] \arrow[ur, shift right, "\mathrm{NCMe}"'] &
\end{tikzcd}$$

The new monomeric dicarbonyls prepared by this procedure, $MoBr_2(CO)_2(PR_3)_2$ (where $PR_3 = PEtPh_2$, PEt_2Ph, $PMePh_2$) and $MoI_2(CO)_2(PMePh_2)_2$ and $WBr_2(CO)_2(PMePh_2)_2$, are all intensely coloured blue or purple diamagnetic solids which show weak ($\epsilon = 400$–600 l mol^{-1} cm^{-1}) bands in their visible spectrum at 550 ± 50 nm. The origins of this low energy transition have been described previously

TABLE II. Correlation Between the Decarbonylation Product of $M(CO)_3(PR_3)_2X_2$, the Cone-angle of PR_3 and the Halide X

Phosphine	Cone-angle (°)	Halide	Product[a]
$PEtPh_2$	140	Br	A
PEt_2Ph	137	Br	A
$PMePh_2$	136	I	A
$PMePh_2$	136	Br	A, B
$PMePh_2$	136	Cl	B
PMe_2Ph	122	Br	B

[a] A = $M(CO)_2(PR_3)_2X_2$; B = $[M(CO)_2(PR_3)_2X_2]_n$.

[1, 9] but the band is diagnostically important in determining whether a complex is a 6-coordinate monomer or a halogen-bridged 7-coordinate species.

For comparative purposes, the direct decarbonylation of a range of $M(CO)_3(PR_3)_2Br_2$ derivatives in various solvents was attempted. In dichloromethane, acetone or 3-pentanone the more sterically crowded tricarbonyls formed the blue diamagnetic monomers $MoBr_2(CO)_2(PEtPh_2)_2$ and $MoBr_2(CO)_2(PEt_2Ph)_2$. The former was found to exist in two forms, blue or purple, with almost identical analyses but somewhat different CO stretching frequencies (Table I). On standing in solution, the blue form slowly converted into the more stable purple form. Decarbonylation of $MoBr_2(CO)_3(PMePh_2)_2$ initially produced the dicarbonyl monomer which at ambient temperature was converted within 0.5 h to the yellow species $[MoBr_2(CO)_2(PR_3)_2]_n$, whereas only the latter was isolated on decarbonylation of $MoBr_2(CO)_3(PMe_2Ph)_2$, in agreement with previous observations [5]. In the series examined, only those phosphines with cone angles >135° were able to stabilise 6-coordinate monomers under the reaction conditions described above (Table II).

In order to determine the influence of the halide ion on the ease of CO loss, the series $Mo(CO)_3(PMePh_2)_2X_2$ (X = Cl, Br or I) was decarbonylated and found to produce the complexes $[MoCl_2(CO)_2(PMePh_2)_2]_n$, $[MoBr_2(CO)_2(PMePh_2)_2]_n$ or $MoBr_2(CO)_2(PMePh_2)_2$, and $Mo(CO)_2(PMePh_2)_2I_2$ respectively. The rate of CO loss paralleled that found by Colton *et al.* who showed that the ease of CO loss increased in the triphenylphosphine containing series $Cl^- > Br^- > I^-$ [3, 4].

Interestingly, the passage of N_2 through a refluxing CH_2Cl_2 solution of $WBr_2(CO)_3(PMePh_2)_2$ produced a purple colouration, but only the halogen-bridged orange product $[WBr_2(CO)_2(PMePh_2)_2]_n$ could be isolated from the solution. This contrasts with the ready formation of the monomer $WBr_2(CO)_2(PMePh_2)_2$ from $WBr_2(CO)_2(NCMe)(PMePh_2)_2$ referred to earlier, showing that loss of MeCN rather than CO from the 7-coordinate derivative $WBr_2(CO)_2L(PMePh_2)_2$ (where L = MeCN or CO) favours monomer formation.

Reactions of these 6- and 7-coordinate complexes with various ionic and neutral ligands are currently under investigation.

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