Group VI metal tricarbonyl complexes containing a unidentate diphosphine ligand

II *. A study of thermal behaviour of M(CO)$_3$(η^2-bpy)(η^1-dppm) (M = Mo, W)

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(Received March 26th, 1990)

Abstract

fac-W(CO)$_3$(η^2-$\widehat{NN}$)(η^1-dppm) ($\widehat{NN}$ = 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen), 2,9-dimethyl-1,10-phenanthroline (dmp); dppm = bis(diphenylphosphine)methane) have been prepared in high yields by thermal reactions of W(CO)$_4$(η^2-$\widehat{NN}$) with dppm. The behaviour of one of these complexes, W(CO)$_3$(η^2-bpy)(η^1-dppm), and of its molybdenum analogue upon heating of their solutions in various solvents has been studied. Conversion of these complexes into dihalodicarbonyl derivatives, M(CO)$_2$Cl$_2$(η^2-bpy)(η^1-dppm) (M = Mo, W), appears to be promoted by halogenated solvents at the reflux temperature.

Introduction

Synthesis of substituted carbonyl complexes containing a diphosphine ($\widehat{PP}$) ligand, such as dppm, dppe or dppp (dppm = bis(diphenylphosphine)methane, dppe = 1,2-bis(diphenylphosphine)ethane, dppp = 1,3-bis(diphenylphosphine)propane), by thermolytic and photolytic techniques, has been judged to be unsastifactory because there are various possibilities for coordination of the ($\widehat{PP}$) ligand, such as (μ-$\widehat{PP}$), (η^2-$\widehat{PP}$) or (η^1-$\widehat{PP}$). It was decided that this route was not sufficiently selective towards the required species [1–4]. However, we have described [5] the formation in high yield of the complexes Mo(CO)$_3$(η^2-$\widehat{NN}$)(η^1-dppm) ($\widehat{NN}$ = 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen), 2,9-dimethyl-1,10- ·

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* For Part I. see ref. 5.

phenanthroline (dmp)), by heating $Mo(CO)_4(\eta^2\text{-}\widehat{NN})$ with dppm. *Fac* or *mer* isomers were obtained, depending on the nature of the $(\widehat{NN})$ ligand and on the reaction conditions.

In this paper we confirm the value of this approach by describing the syntheses of analogous tungsten complexes. We also compare the thermal behaviour of these complexes with those of the related molybdenum derivatives.

Results and discussion

The complexes $M(CO)_3(\eta^2\text{-}\widehat{NN})(\eta^1\text{-}dppm)$ ($M = Cr, Mo, W$; $\widehat{NN} = bpy$, phen) were prepared previously by a two step reaction of $M(CO)_6$ with $(\widehat{NN})$ and dppm ligands, with TMNO (trimethylamine-*N*-oxide) present as a decarbonylating agent in order to prevent the chelation or bridge formation by $(\widehat{PP})$ ligand [1,2].

We found earlier [5] that the same molybdenum species could be obtained by a simple thermal reaction. In extension of this work we prepared the analogous tungsten species in the same way (see Experimental section). The reaction was monitored by examining at intervals the IR spectra of isolated solids. Figure 1 shows the change in the spectrum in the case of the bpy derivative.
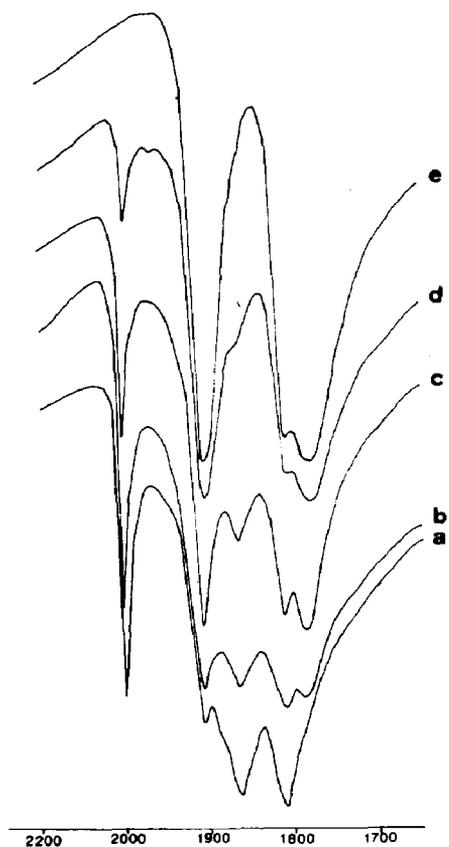
Fig. 1. IR spectra in the $\nu(C\equiv O)$ region of the reaction $W(CO)_4(\eta^2\text{-}bpy)$ with dppm at different times: (a) 15 min; (b) 30 min; (c) 1 h; (d) 1.5h; (e) 2 h.

Table 1

Spectroscopic data for the $W(CO)_3(\eta^2\text{-}\widehat{NN})(\eta^1\text{-dppm})$ ($\widehat{NN}$ = bpy, phen, dmp) complexes

Complex	$\nu(C{\equiv}O)$ (cm^{-1}) [a]		$\delta\,^1H$ (ppm) [b] $(CH_2$ in dppm)	$\delta\,^{31}P$ (ppm) [b]
	KBr discs	CH_2Cl_2 solution		
$W(CO)_3(\eta^2\text{-bpy})(\eta^1\text{-dppm})$	1902vs	1908vs	2.71 (dd)	19.7 (d, P_a)
	1808s	1812s	$^2J(P_a\text{–}H) = 5.7$	-27.7 (d, P_b)
	1780vs	1785vs	$^2J(P_b\text{–}H) = 2.1$	$^2J(P_a\text{–}P_b) = 61.6$
				$^1J(P_a\text{–}W) = 224$
$W(CO)_3(\eta^2\text{-phen})(\eta^1\text{-dppm})$	1890vs	1905vs	2.56 (dd)	20.0 (d, P_a)
	1790sh	1815s	$^2J(P_a\text{–}H) = 5.7$	-27.8 (d, P_b)
	1778vs	1785s	$^2J(P_b\text{–}H) = 3.6$	$^2J(P_a\text{–}P_b) = 61.1$
				$^1J(P_a\text{–}W) = 225$
$W(CO)_3(\eta^2\text{-dmp})(\eta^1\text{-dppm})$	1895vs	1890vs	2.20 (dd)	19.5 (d, P_a)
	1795sh	1795s	$^2J(P_a\text{–}H) = 5.7$	-28.3 (d, P_b)
	1780vs	1765s	$^2J(P_b\text{–}H) = 3.6$	$^2J(P_a\text{–}P_b) = 58.7$
			3.22, 3.21	
			(s, CH_3 in dmp)	

[a] vs = very strong; s = strong; sh = shoulder. [b] P_a = coordinated phosphorus atom; P_b = uncoordinated phosphorus atom; J in Hz.

The identities of the products were evident from the analytical and spectroscopic (IR, ^1H and ^{31}P-NMR) data (Table 1). The dmp derivative is a new compound, but the bpy and phen derivatives have been previously described [1,2]. The IR and NMR spectra indicated that only one isomer was formed in each case, and a *fac* configuration was suggested for them [5].

The high stability of the tungsten complexes was somewhat unexpected, and so we carried out a study of thermal behaviour of one of them, $W(CO)_3(\eta^2\text{-bpy})(\eta^1\text{-dppm})$ in solution, and compared it with that of the analogous molybdenum complex. Table 2 summarizes the results.

Solutions of $W(CO)_3(\eta^2\text{-bpy})(\eta^1\text{-dppm})$ in $CHCl_3$, CCl_4, or toluene were heated for different times (1–24 h). In all cases, the IR spectra were recorded for the solids subsequently isolated. The complex was stable in $CHCl_3$ at room temperature for a long time, and, even when its solution in toluene was refluxed for 5 h there was no significant change in the IR spectrum. Only when solutions in $CHCl_3$ or CCl_4 were refluxed for 4 h was there a marked change in the colour from blue to scarlet occurred and formation of a new carbonyl compound (**A**).

Figure 2 shows some of the changes observed in the IR spectra of solids isolated from the $CHCl_3$ solutions after heating. It can be seen that the pattern of the carbonyl bands after 4 h at room temperature (point line) remains that of the starting complex $W(CO)_3(\eta^2\text{-bpy})(\eta^1\text{-dppm})$. The two new bands observed after refluxing for 4 h in $CHCl_3$ (full line) are attributed to a new carbonylic species (**A**). After 24 h in refluxing toluene only decarbonilation products were present.

The related molybdenum compound $Mo(CO)_3(\eta^2\text{-bpy})(\eta^1\text{-dppm})$ behaves differently. In this case, after only a short time (5 to 10 min) in refluxing $CHCl_3$ there are significant changes in colour (violet to orange-brown), and the IR spectra of the isolated solid (**B**) show that it is a mixture of complexes.

We studied both **A** and **B** by IR and NMR (^1H, ^{31}P) spectroscopy. Table 3 lists the NMR data and the $\nu(C{\equiv}O)$ frequencies.

Table 2

Results of thermal treatings of $M(CO)_3(\eta^2\text{-bpy})(\eta^1\text{-dppm})$ (M = Mo, W)

Starting compound	Solvent	Temp. (°C)	Time (h)	Atmosphere	Species observed [a]
$W(CO)_3(\eta^2\text{-bpy})(\eta^1\text{-dppm})$	$CHCl_3$	20	5	N_2	starting compound
	$CHCl_3$	20	24	N_2	starting compound
	$CHCl_3$	62	1	N_2	starting compound
	$CHCl_3$	62	4	N_2	A
	CCl_4	77	2	N_2	starting compound + A
	CCl_4	77	4	N_2	A
	$CH_3C_6H_5$	111	3	N_2	starting compound
	$CH_3C_6H_5$	111	5	N_2	starting compound
	$CHCl_3$	20	24	CO	starting compound
	$CHCl_3$	62	3	CO	starting compound + A
	$CHCl_3$	62	4	CO	A
$Mo(CO)_3(\eta^2\text{-bpy})(\eta^1\text{-dppm})$	$CHCl_3$	20	3	N_2	starting compound
	$CHCl_3$	20	24	N_2	decarbonylation products
	$CHCl_3$	62	10 min	N_2	B
	CCl_4	77	10 min	N_2	B
	CCl_4	77	2	N_2	decarbonylation products
	$CHCl_3$	20	4	CO	starting compound
	$CHCl_3$	62	10 min	CO	B

[a] Solids obtained by precipitation from the solution.

The ^{31}P-NMR spectrum of A indicates the presence of two types of phosphorus atoms. The doublets at low and high field (δ = 21.84 and −26.51 ppm; $^2J(P_a-P_b)$ = 23.8 Hz) are assigned to the coordinated and uncoordinated phosphorus atoms, respectively. The ^{1}H-NMR spectrum of A shows the characteristic signals of aromatic and CH_2 groups. Two multiplets at 4.03 and 4.15 ppm are consistent with
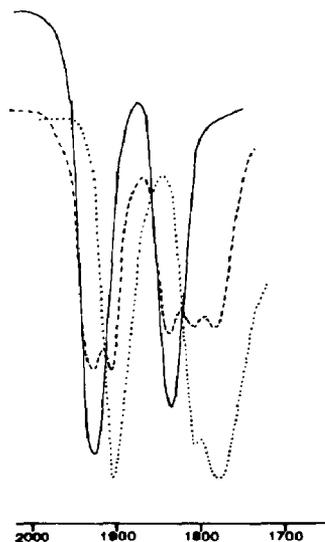
Fig. 2. IR spectra in the $\nu(C\equiv O)$ region of $W(CO)_3(\eta^2\text{-bpy})(\eta^1\text{-dppm})$ in $CHCl_3$: $\cdots\cdots$ 4 h at room temperature under N_2; ———— 4 h at reflux under N_2; ------ 3 h at reflux under CO.

Table 3

Spectroscopic data for $M(CO)_2Cl_2(\eta^2\text{-bpy})(\eta^1\text{-dppm})$ (M = Mo, W)

Complex	IR data (cm^{-1}) [a] $\nu(C\equiv O)$	$\delta\,^1H$ (ppm) [b] $(CH_2$ in dppm)	$\delta\,^{31}P$ (ppm) [b]
$Mo(CO)_2Cl_2(\eta^2\text{-bpy})(\eta^1\text{-dppm})$	1940vs 1850s	3.55m	42.1 (d, P_a) -25.8 (d, P_b) $^2J(P_a-P_b) = 23.0$
$W(CO)_2Cl_2(\eta^2\text{-bpy})(\eta^1\text{-dppm})$	1922vs 1830s	4.03m 4.15m	21.8 (d, P_a) -26.5 (d, P_b) $^2J(P_a-P_b) = 23.8$

[a] vs = very strong; s = strong. [b] m = multiplet; d = doublet; P_a = coordinated phosphorus atom; P_b = uncoordinated phosphorus atom; J in Hz.

the inequivalence of CH_2 protons of dppm ligand. The IR spectrum shows two carbonyl stretching bands (1922 and 1830 cm^{-1}); a similar pattern was previously observed in the IR spectra of dihalo complexes such as $W(CO)_2Cl_2(\eta^2\text{-dppm})(\eta^1\text{-}$dppm) (1930 and 1850 cm^{-1}) [6] and $W(CO)_2Cl_2(\eta^2\text{-dam})(\eta^1\text{-dam})$ (1934 and 1849 cm^{-1}; dam = bisdiphenilarsinomethane) [7].

Complex **A** shows a non-ionic behaviour in acetone ($\Lambda = 10.9$ ohm^{-1} cm^2 mol^{-1}). In view of the presence of chloride ligands in **A**, together with the above spectroscopic data and the analytical data, indicate the formulation $W(CO)_2Cl_2(\eta^2\text{-}$bpy)($\eta^1$-dppm). We thus suggest that there has been an oxidative reaction between $W(CO)_3(\eta^2\text{-bpy})(\eta^1\text{-dppm})$ and the halogenated solvent ($CHCl_3$ or CCl_4). The diamagnetism of the complex is consistent with a heptacoordinate environment of W^{II}.

The IR spectrum of solid **B** was recorded with KBr discs. Two strong carbonyl bands (1940 and 1850 cm^{-1}) appear in the same range as for other heptacoordinated dihalodicarbonyl complexes containing bidentate and monodentate $\widehat{(PP)}$ or $\widehat{(AsAs)}$ ligands, such as $Mo(CO)_2Cl_2(\eta^2\text{-dppm})(\eta^1\text{-dppm})$ (1940 and 1865 cm^{-1}) [6] and $Mo(CO)_2Cl_2(\eta^2\text{-dam})(\eta^1\text{-dam})$ (1950 and 1870 cm^{-1}) [7]. Other bands, of low intensity, appear in the carbonyl region at 2000, 1895 and 1790 cm^{-1}, and are attributed to the presence of the complex $Mo(CO)_4(\eta^2\text{-bpy})$. It seems that the major component in solid **B** is $Mo(CO)_2Cl_2(\eta^2\text{-bpy})(\eta^1\text{-dppm})$. We were unable to obtain analytical data, because the compound was always mixed with others products.

In the ^{31}P-NMR of **B**, two doublets at 42.1 and -25.8 ppm ($^2J(P_a-P_b) = 23.0$ Hz) are consistent with the presence of two types of phosphorus atoms (coordinated and uncoordinated), as in the tungsten complex (**A**). Other signals observed in the characteristic region for coordinated phosphorus are consistent with the formation of a new species through further reaction of the dicarbonyl complex in solution.

We finally studied the effect of carbon monoxide on the thermal behaviour. When the reaction were carried out in refluxing $CHCl_3$ under CO for 3 h for the tungsten derivative, a mixture of a new dicarbonyl and the starting tricarbonyl specie was obtained (Fig. 2, broken line). After 4 h, the same dicarbonyl species (full line) was observed. For the molybdenum complex, only short times were necessary to give the dicarbonyl compound mixed with the tetracarbonyl derivative, suggesting that the reaction is not inhibited by the presence of carbon monoxide.

Our success in synthesizing $Mo(CO)_3(\eta^2\text{-}\overset{\frown}{NN})(\eta^1\text{-dppm})$ by a direct replacement of CO ligand in $Mo(CO)_4(\eta^2\text{-}\overset{\frown}{NN})$ by dppm, has thus been repeated with the related tungsten derivatives. The tungsten derivatives are more stable than the molybdenum compounds. However, in both cases, these complexes are oxidized by halogenated solvents at the reflux temperature to yield new heptacoordinated dihalodicarbonyl compounds in which the dppm ligand appears to be monodentate.

Experimental

All reactions were carried out under oxygen-free dry nitrogen. Analytical grade solvents were used. The complexes $W(CO)_4(\eta^2\text{-}\overset{\frown}{NN})$ ($\overset{\frown}{NN}$ = bpy, phen, dmp) were prepared as previously described [8–10]. C, H and N analyses were carried out by Elemental Micro-Analysis Ltd. Laboratories (Devon). IR spectra were recorded on a Perkin Elmer 1300 spectrophotometer with KBr discs or CH_2Cl_2 solutions. The NMR spectra were recorded on a Varian XL-300 spectrometer at room temperature, operated at 299.95 MHz for ^1H and 121.42 MHz for ^{31}P, with $(CH_3)_4Si$ as internal standard for ^1H and 85% phosphoric acid as external standard for ^{31}P; the solvent in all cases was $CDCl_3$.

Preparation of $W(CO)_3(\eta^2\text{-}\overset{\frown}{NN})(\eta^1\text{-dppm})$ ($\overset{\frown}{NN}$ = bpy, phen, dmp)

The synthesis was carried out as described for the related molybdenum derivatives [5], with xylene as solvent and reaction times of 2 (bpy and phen compounds) and 5 h (dmp derivative) (yield: 65–80%; Analyses for $W(CO)_3(\eta^2\text{-dmp})(\eta^1\text{-dppm})$. Found: C, 58.17; H, 3.71; N, 3.19. $C_{42}H_{34}N_2O_3P_2W$ calcd.: C, 58.62; H, 3.99; N, 3.26%).

$W(CO)_2Cl_2(\eta^2\text{-bpy})(\eta^1\text{-dppm})$. A solution of $W(CO)_3(\eta^2\text{-bpy})(\eta^1\text{-dppm})$ (1.0 mmol) in $CHCl_3$ or CCl_4 (15 ml) was refluxed for 4 h then cooled to room temperature. Light petroleum (b.p.: 40–60 °C) was added (30 ml) and the precipitate formed was filtered off, washed with light petroleum, and dried in vacuo (yield: 50%. Analysis. Found: C, 51.44; H, 3.21; N, 3.22. $C_{37}H_{30}WP_2N_2O_2Cl_2$ calcd.: C, 52.20; H, 3.56; N, 3.29%).

$Mo(CO)_2Cl_2(\eta^2\text{-bpy})(\eta^1\text{-dppm})$. The procedure used for the tungsten derivative was used but with only 10 min refluxing.

Acknowledgement

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