Journal of Organometallic Chemistry, 277 (1984) 85–90
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

AQUEOUS ALLYLMOLYBDENUM(II) CHEMISTRY

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(Received June 28th, 1984)

Summary

Dissolution of $[MoCl(CO)_2(\eta^3\text{-}C_3H_4R)(NCMe)_2]$ (R = H or Me) in methanol yields yellow conducting solutions containing the $[Mo(CO)_2(\eta^3\text{-}C_3H_4R)(HOMe)_3]^+$ cations. The same species are formed on dissolution of $[Mo(CO)_2(\eta^3\text{-}C_3H_4R)(NCMe)_3]BF_4$ in methanol, and one of the cations (R = Me) has been isolated as its tetrafluoroborate salt. There is strong spectroscopic evidence that hydrated allyldicarbonylmolybdenum(II) cations $[Mo(CO)_2(\eta^3\text{-}C_3H_4R)(H_2O)_x]^+$ are present on dissolution of $[MoCl(CO)_2(\eta^3\text{-}C_3H_4R)(NCMe)_2]$ in deoxygenated water, and treatment of these solutions with bi- and tridentate ligands yields neutral complexes $[MoCl(CO)_2(\eta^3\text{-}C_3H_4R)L_2]$ (R = H or Me; L_2 = 2,2′-bipyridine (bipy) or 2,2′-bipyridylamine (bpa)), and cationic species $[Mo(CO)_2(\eta^3\text{-}C_3H_4R)L_3]^+$ (R = H or Me; L_3 = diethylenetriamine (dien) or bis(2-pyridylmethyl)amine (bpma)) respectively. The latter were isolated as their hexafluorophosphate salts. Addition of Ph_4AsCl to basic methanolic solutions of $[MoCl(CO)_2(\eta^3\text{-}C_3H_4R)(NCMe)_2]$ causes the precipitation of the anionic molybdenum derivatives $Ph_4As[Mo_2(CO)_4(\eta^3\text{-}C_3H_4R)_2(\mu\text{-}OMe)_3]$ (R = H or Me).

Introduction

As part of our investigations into the solution behaviour of organomolybdenum complexes [1], we recently reported that the ionisation of $[MoCl(CO)_2(\eta^3\text{-}C_3H_4R)(NCMe)_2]$ (R = H (I) or Me (II)) into $[Mo(CO)_2(\eta^3\text{-}C_3H_4R)(NCMe)_3]^+$ and $[Mo_2(CO)_4(\eta^3\text{-}C_3H_4R)_2Cl_3]^-$ was highly solvent dependent [2,3]. In addition, we observed that reactions of I and II in methanol differ in some respects from those in other solvents [4], and that these solutions could be used to catalyse Diels–Alder cycloadditions [5], and to promote alkyne polymerisation reactions [6]. We were therefore interested in identifying the species present in this solvent, and determining whether any aqueous allylmolybdenum(II) chemistry could be developed from these readily available starting materials.

0022-328X/84/$03.00

Results and discussion

Dissolution of I or II in CD_3OD or warm D_2O yielded yellow conducting solutions which only slowly decolourised on standing in air. Both ^{13}C and ^{1}H NMR data revealed the presence of free nitrile, and single allyl containing moieties (Tables 1 and 2) as the major metal-containing species, whilst solution infrared measurements in methanol confirmed the presence of *cis*-dicarbonyl groupings in both metal

TABLE 1

INFRARED AND ^{1}H NMR DATA

Complex	ν(CO) (cm^{-1})	Solvent	Chemical shifts (δ (ppm) rel. to TMS, (J in Hz))				
			Allyl			Aliphatics	Aromatics
			H_{anti}	H_{syn}	$H_{central}$ or Me		
I[a]	1848, 1942[b]	CD_3OD	1.06d(9.5)	3 40d(6.4)	3.74m	2 09s	
		D_2O	1.22d(9.5)	3.47d(6.4)	3.64m	2.07s	
II[c]	1844,1937[b]	CD_3OD	0.91s	3 13s	2.16s	2.10s	
		D_2O	1.05s	3 21s	2.08s	2.08s	
III	1846,1939[b]	CD_3OD	0 95s	3.16s	2.11s	2 07s	
IV	1845,1944	$(CD_3)_2CO$	1.02d(9.3)	3.21d(6.5)	3.81tt	2 94m, 3 25m	
V	1843,1940	$(CD_3)_2CO$	0.93s	3.06s	2.06s	2.88m, 3 34m	
VI	1856,1946	$(CD_3)_2CO$	1.58d(9.5)	3.95d(6.3)	4.15tt	4.64[d]	7.48m, 7.90m, 9.00m
VII	1860,1947	$(CD_3)_2CO$	1.56s	3.48s	1.92s	4 60[d]	7 52m, 7.96m, 9.02m
XII	1790,1902	$(CD_3)_2CO$	0.36d(9.0)	2.90d(6.3)	2.92m	4 07s, 4.62s	7 88br.s
XIII	1792,1904	$(CD_3)_2CO$	0 34s	2.70s	1.80s	3.81s, 4 96s	7 88br.s

[a] Conductivities of 14.1 and 72.1 S cm^2 mol^{-1} for 10^{-3} molar solutions in water and methanol respectively. [b] MeOH as solvent. [c] Conductivities of 14.3 and 72 0 S cm^2 mol^{-1} for 10^{-3} molar solutions in water and methanol respectively. [d] Centre of *AB* quartet (deuterated solutions).

TABLE 2

^{13}C NMR DATA

Complex	Solvent	Chemical shifts (δ (ppm) rel. to TMS)					
		CO	Allyl			Aliphatics	Aromatics
			C(terminal)	C(central)	Me		
I	D_2O	227.2	59.0	73.2		1.1	
	CD_3OD		57.8	73.9		1.6	
II	D_2O	227.9	57.3	83.8	18.4	1.1	
	CD_3OD		57.1	84.2	20 0	1 3	
III	CD_3OD	227.8	57.1	84.0	19.8		
IV	$(CD_3)_2CO$	226 1	55 4	68.2		42.0, 52.3	
V	$(CD_3)_2CO$	226.4	55.2	80.5	20.0	41.8, 51.2	
VI	$(CD_3)_2CO$	226.5	58.2	71 5		61 6	124.0, 126.0, 140 6, 152.1, 159.0
VII	$(CD_3)_2CO$	226.7	60.8	84.8	20.3	60.8	124.1, 126.0, 140.6, 151.9, 159 0
XII	$(CD_3)_2CO$	234.1	55.0	74.9		49.4	131.8, 133.9, 135.4
XIII	$(CD_3)_2CO$	233.6	55.9	79.4	19.6	49.4	131.9, 133 9, 135.4

species. Removal of excess solvent in vacuo yielded only decomposition products from aqueous solutions of either nitrile complex, but tan-coloured, nitrogen-free hygroscopic solids could be recovered from methanol. These solids had a somewhat variable methanol content, but when redissolved in CD_3OD they gave ^{13}C NMR spectra which were virtually identical in the allyl region with those of fresh CD_3OD solutions of $[MoCl(CO)_2(\eta^3\text{-}C_3H_4R)(NCMe)_2]$. Very similar spectra to those produced by II were obtained on dissolution of $[Mo(CO)_2(\eta^3\text{-}C_3H_4Me)(NCMe)_3]BF_4$ in CD_3OD, and this time removal of excess solvent (CH_3OH) and displaced MeCN from a methanol solution of this cationic complex produced $[Mo(CO)_2(\eta^3\text{-}C_3H_4Me)(HOMe)_3]BF_4$ (III) as an air-sensitive solid. Thus we conclude that dissolution of I or II in CD_3OD produces $[Mo(CO)_2(\eta^3\text{-}C_3H_4R)(DOCD_3)_3]^+Cl^-$ as the major metal containing product, and it seems likely from conductimetric and spectroscopic evidence that $[Mo(CO)_2(\eta^3\text{-}C_3H_4R)(H_2O)_x]^+$ cations exist in aqueous solutions, although attempts to isolate salts by addition of various anions have been unsuccessful to date.

Aqueous solutions containing the allyldicarbonyl–molybdenum moiety have been used to prepare several neutral and cationic complexes as shown in the scheme below:

$$[Mo(CO)_2(\eta^3\text{-}C_3H_4R)(H_2O)_x]Cl \xrightarrow[NH_4PF_6]{L_3} [Mo(CO)_2(\eta^3\text{-}C_3H_4R)L_3]PF_6$$

	R	L_3
IV	H	dien
V	Me	dien
VI	H	bpma
VII	Me	bpma

$$[Mo(CO)_2(\eta^3\text{-}C_3H_4R)(H_2O)_x]Cl \xrightarrow{L_2} [MoCl(CO)_2(\eta^3\text{-}C_3H_4R)L_2]$$

	R	L_2
VIII	H	bipy
IX	Me	bipy
X	H	bpa
XI	Me	bpa

The neutral complexes VIII–XI are identical to those formed previously by other routes [7,8], but the new cationic derivatives IV–VII are very conveniently synthesised in high yields from aqeuous media. The spectroscopic properties of these latter complexes at ambient temperatures are summarised in Tables 1 and 2. The proton chemical shifts of the allyl ligand are highly sensitive to the nature of the tridentate ligand, and low temperature ^1H NMR studies showed the cations to be dynamic. Thus for complex IV at −102 °C, all three allyl resonances and the two *AA'BB'* multiplet signals of the methylene protons of the dien ligand lost their fine structure, with the latter showing an upfield shift of ca. 0.3 ppm. In addition the NH and NH_2 signals of the coordinated amine were resolved as broad singlets with chemical shifts of 7.84, 4.24 and 3.25 ppm. For the corresponding bpma derivative (complex VI), the proton signals for the allyl and amine ligands did not overlap and clearly resolved spectra were obtained at −80 °C. Two different chemical environments for the pyridine rings of the bpma ligand were apparent from the splitting of each of the three aromatic signals (Table 1) into two components of equal intensity, and an

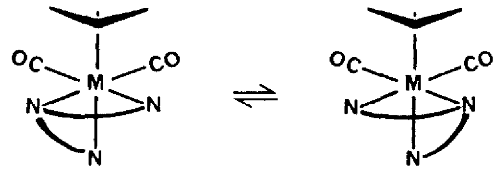

Fig. 1. Triganol twist rearrangement proposed for [Mo(CO)$_2$(η^3-C$_3$H$_5$)L$_3$]$^+$ where L$_3$ = diethylenetriamine or bis(2-pyridylmethyl)amine.

ABMNX spin pattern was observed for the allyl moiety under these conditions. At room temperature and above, the methylene protons of the bpma ligand gave rise to a single *AB* quartet (approximating to an *AX* system) when spectra were recorded in the presence of D$_2$O. In the absence of D$_2$O, NH coupling (ca. 6 Hz) to two of the four methylene protons was observed. At −80 °C the decoupled spectrum revealed that the methylene groups were inequivalent as shown by the appearance of two overlapping *AB* quartets. A restricted trigonal twist rearrangement in which the molecule interconverts between S and R configurations (Fig. 1) at ambient temperatures is fully consistent with the spectral information. Such a process has been proposed for several other [Mo(CO)$_2$(η^3-C$_3$H$_5$)L$_2$X] complexes (L$_2$ = bidentate and X = anion) and results in enantiomerisation at the metal centre [1,9]. This process is also compatible with the observation that over the entire temperature range +80 to −80 °C, only half of the methylene protons are strongly coupled with the NH group. Molecular models of [Mo(CO)$_2$(η^3-C$_3$H$_5$)bpma]$^+$, in which the tridentate ligand occupies one face in the pseudooctahedral structure as shown in Fig. 1, reveal that the dihedral angles (θ) between H–N–C and N–C–H planes are small (ca. 20 °) for two of the methylene protons and large (ca. 90 °) for the others. Correlations between ^3J(NH–CH) and the interplanar angle θ have been explored previously [10]. For θ values of approximately 90 ° these couplings are very small, whereas for a θ value of 20–30 ° ^3J(NH–CH) couplings of the size observed are expected.

Although there is no spectroscopic evidence for the formation of anionic molybdenum–allyl entities on dissolving I or II in ROH (R = H or Me), such species can be prepared in the presence of base. Thus treating methanolic solutions of I or II with Ph$_4$AsCl dissolved in 2 *M* NaOH solution yielded the binuclear anionic complexes Ph$_4$As[Mo$_2$(CO)$_4$(η^3-C$_3$H$_4$R)$_2$(μ-OMe)$_3$] (R = H or Me) as yellow air-sensitive solids. The spectroscopic properties of complexes XII and XIII are very similar to those of the known trichloro-bridged analogues, and show the expected changes in ν(CO) and in ^{1}H and ^{13}C chemical shifts when compared with the related cations (Tables 1 and 2).

Experimental

Infrared specta were recorded on solid samples mulled in Nujol on a Perkin–Elmer 597 spectrophotometer. Solution spectra in the carbonyl region were recorded in CH$_2$Cl$_2$ or CH$_3$OH. NMR data were obtaining using JEOL PS 100 and FX 90Q instruments with either tetramethylsilane or sodium 2,2-dimethyl-2-silapentane-5-sulphonate as internal reference. Conductance measurements were made on a

Wayne–Kerr Autobalance bridge at 295 K on 10^{-3} *M* solutions. Microanalyses are by Butterworth Laboratories Ltd.

The starting materials $[MoCl(CO)_2(\eta^3\text{-}C_3H_4R)(NCMe)_2]$ and $[Mo(CO)_2(\eta^3\text{-}C_3H_4R)(NCMe)_3]BF_4$ (R = H or Me) were synthesised according to literature methods [11,3], and the ligand bis(2-pyridylmethyl)amine (bpma) was prepared in 75% yield from chloromethylpyridine, using the method outlined in ref. 12.

All subsequent reactions were carried out under an atmosphere of nitrogen gas.

Preparation of $[Mo(CO)_2(\eta^3\text{-}C_3H_4Me)(HOMe)_3]BF_4$

$[Mo(CO)_2(\eta^3\text{-}C_3H_4Me)(NCMe)_3]BF_4$ (0.83 g, 2.0 mmol) was stirred at 35 °C with dry, deoxygenated MeOH for 10 min. Solvent was evaporated from the clear yellow solution in vacuo at room temperature, leaving the product as a tan-coloured, hygroscopic solid in quantitative yield. Found: C, 28.1; H, 4.8. $MoC_9H_{19}O_5BF_4$ calcd.: C, 27.7; H, 4.9%.

Preparation of $[Mo(CO)_2(\eta^3\text{-}C_3H_4R)L_3]PF_6$ *(R = H or Me;* L_3 *= dien or bpma)*

A solution of $[MoCl(CO)_2(\eta^3\text{-}C_3H_4R)(NCMe)_2]$ (1.0 mmol) in hot (40 °C) deoxygenated water (50 cm^3) was stirred with excess dien (2 cm^3) or with bpma (0.20 g, 1.0 mmol) for 0.5 h. Excess aqueous NH_4PF_6 was added dropwise to the solution, and the mixture stirred at 40 °C for 0.5 h prior to filtration. The yellow product was washed with water, dried in vacuo and recrystallised from aqueous acetone. Yields 80–90%. Complex IV. Found: C, 24.1; H, 3.7; N, 9.7. $MoC_9H_{18}N_3O_2PF_6$ calcd.: C, 24.3; H, 4.1; N, 9.5%. Complex V. Found: C, 26.8; H, 4.2; N, 9.6. $MoC_{10}H_{20}N_3O_2PF_6$ calcd.: C, 26.2; H, 4.5; N, 9.2%. Complex VI. Found: C, 38.0; H, 3.4; N, 7.7. $MoC_{17}H_{18}N_3O_2PF_6$ calcd.: C, 38.0; H, 3.4; N, 7.8%. Complex VII. Found: C, 39.8; H, 3.6; N, 7.2. $MoC_{18}H_{20}N_3O_2PF_6$ calcd.: C, 39.2; H, 3.6; N, 7.6%.

Preparation of $[MoCl(CO)_2(\eta^3\text{-}C_3H_4R)L_2]$ *(R = H or Me;* L_2 *= 2,2′-bipyridine or 2,2′-bipyridylamine)*

A solution of $[MoCl(CO)_2(\eta^3\text{-}C_3H_4R)(NCMe)_2]$ (2.0 mmol) in hot (40 °C) deoxygenated water (20 cm^3) was treated dropwise with a hot solution of 2,2′-bipyridine or 2,2′-bipyridylamine (2.0 mmol) in the minimum volume of 10% aqueous acetone. The mixture was stirred for 0.5 h while cooling to room temperature, and the product filtered, washed with hot water and dried in vacuo. Yield 40–50%.

The physical and spectroscopic properties of complexes VIII–XI were identical to those of $[MoCl(CO)_2(\eta^3\text{-}C_3H_4R)L_2]$ (R = H or Me; L_2 = bipy or bpa) prepared from $[Mo(CO)_4L_2]$ and the appropriate allyl halide [7,8].

Preparation of $Ph_4As[Mo_2(CO)_4(\eta^3\text{-}C_3H_4R)_2(\mu\text{-}OMe)_3]$ *(R = H or Me)*

A stirred solution of $[MoCl(CO)_2(\eta^3\text{-}C_3H_4R)(NCMe)_2]$ (1.0 mmol) in methanol (10 cm^3) was treated dropwise with Ph_4AsCl (0.21 g, 0.5 mmol) dissolved in 2 *M* NaOH solution (20 cm^3). After 0.5 h the yellow product was filtered, washed with cold water, dried and recrystallised from methanol containing a few drops of aqueous NaOH solution. Yields 45–50%. Complex XII. Found: C, 50.6; H, 4.6. $Mo_2C_{37}H_{39}O_7As$ calcd.: C, 51.5; H, 4.5%. calcd. Complex XIII. Found: C, 52.4; H, 4.8. $Mo_2C_{39}H_{43}O_7As$ calcd.: C, 52.6; H, 4.8%.

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