Journal of Organometallic Chemistry, 221 (1981) 279—285
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

ISOMERIC ORGANOMOLYBDENUM CARBOXYLATE DERIVATIVES

B.J. BRISDON and A. DAY

School of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY (Great Britain)

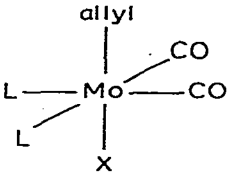
(Received June 9th, 1981)

Summary

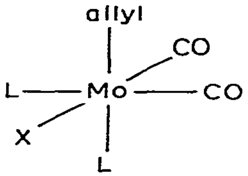
A series of carboxylate complexes $[Mo(CO)_2(\eta^3\text{-}RC_3H_4)bipy(O_2CR')]$ (R = H, R' = Me, Ph, CF_3, C_2F_5 or C_3F_7; R = Me, R' = CF_3, C_2F_5 or C_3F_7; bipy = 2,2'-bipyridine) have been prepared and the solution properties of the fluorinated derivatives examined, Each β-methylallyl compound contains a symmetrical trihapto ligand and adopts a pseudooctahedral structure with approximate C_s symmetry over the temperature range —90 to +50°C. The allyl derivatives exist in two isomeric forms in solution at room temperature, one has local C_s symmetry as above, and the other is dynamic, but assumes C_1 symmetry at low temperatures. The spectral observations on the dynamic species and high temperature interconversion of these two isomers can be accounted for an intramolecular trigonal twist rearrangement.

Introduction

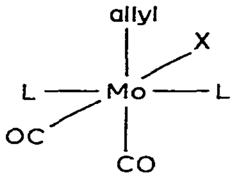
The stereochemistry, fluxionality and reactivity of complexes containing the $Mo(CO)_2(\eta^3\text{-allyl})$ moiety has been shown to be markedly dependent upon the nature of the ligands completing the coordination sphere [1—8]. X-ray crystallographic studies have so far revealed three different solid-state structures (A—C) for complexes $[Mo(CO)_2(\eta^3\text{-}C_3H_5)L_2X]^{0,+}$.



(A)



(B)



(C)

0022-328X/81/0000—0000/$02.50

TABLE 1

ANALYTICAL AND SELECTED INFRARED DATA

Complex		Yield (%)	Found (calcd. (%))			Λ_M [a] (Ω^{-1} cm^2 mol^{-1})	ν(CO) (cm^{-1}) [b]
			C	H	N		
I	$Mo(CO)_2(\eta^3\text{-}C_3H_5)(bipy)(O_2CCH_3)$	51	49.3 (50.0)	3.7 (3.9)	6.7 (6.9)		1845, 1937 [c]
II	$Mo(CO)_2(\eta^3\text{-}C_3H_5)(bipy)(O_2CPh)$	53	55.2 (56.2)	4.2 (3.8)	5.8 (6.0)		1854, 1934 [c]
III	$Mo(CO)_2(\eta^3\text{-}C_3H_5)(bipy)(O_2CCF_3)$	68	44.0 (44.2)	2.8 (2.8)	6.0 (6.1)	9.1	1855, 1940 1865, 1952
IV	$Mo(CO)_2(\eta^3\text{-}C_3H_5)(bipy)(O_2CC_2F_5)$	52	42.2 (42.2)	2.3 (2.5)	5.7 (5.5)	5.9	1838, 1955 1844, 1962
V	$Mo(CO)_2(\eta^3\text{-}C_3H_5)(bipy)(O_2CC_3F_7)$	62	41.0 (40.6)	2.3 (2.3)	5.0 (5.0)	8.2	1864, 1935 1872, 1941
VI	$Mo(CO)_2(\eta^3\text{-}2\text{-}MeC_3H_4)(bipy)(O_2CCF_3)$	71	45.1 (45.4)	3.2 (3.2)	5.6 (5.6)	4.0	1869, 1954
VII	$Mo(CO)_2(\eta^3\text{-}2\text{-}MeC_3H_4)(bipy)(O_2CC_2F_5)$	75	43.4 (43.4)	2.8 (2.9)	5.4 (5.3)	5.3	1871, 1955
VIII	$Mo(CO)_2(\eta^3\text{-}2\text{-}MeC_3H_4)(bipy)(O_2CC_3F_7)$	60	41.2 (41.7)	2.8 (2.6)	5.0 (4.9)	4.9	1872, 1955

[a] Molar conductance at 10^{-3} M in acetone. [b] Acetone solution unless otherwise stated. [c] Nujol mull.

The complex adopting structure C has been described previously in terms of a pentagonal bipyramid in which the allyl group is regarded as a bidentate ligand occupying two coordination positions in the equatorial plane [4], but its relationship to complexes of structures A and B may be seen by the alternative pseudooctahedral description shown above (these are idealised structures in which distortions are not shown). There appears to be a correlation between the solid-state structure and dynamic behaviour of these complexes, with types B and C normally undergoing facile rearrangement in solution at ambient temperatures, whereas no complex of type A has been shown to behave in this way.

So far, only one complex has been shown to contain the correct combination of ligands which will allow more than one of these three isomeric forms to co-exist. $[Mo(CO)_2(\eta^3\text{-}C_3H_5)(pd)(py)]$ (pd = pentane-2,4-dionate, py = pyridine) adopts structure A in the solid state but exists as a solvent dependent mixture of isomers with structures A and B in solution [2].

We were interested in further defining the factors which determine the adoption of a particular isomeric form and here report a series of complexes containing the $Mo(CO)_2(\eta^3\text{-}RC_3H_4)$ (R = H or 2-Me) moiety which show similar solution behaviour to the β-diketonate complex referred to above.

Experimental

Solvents for preparative and spectroscopic use were degassed before use and all preparations were carried out under an oxygen-free, dry, nitrogen atmosphere. Infrared spectra were recorded on Nujol mulls or in acetone solution using a Perkin-Elmer 577 spectrophotometer. ^1H and ^{13}C NMR measurements were recorded on JEOL PS 100 and FX 90Q instruments with tetramethylsilane as internal reference. Conductance measurements were carried out at 25°C on 10^{-3} molar solutions in acetone using a Wayne-Kerr bridge. The starting materials $[Mo(\eta^3\text{-}RC_3H_4)(CO)_2(bipy)Cl]$, (R = H or Me) were prepared by literature methods [9,10].

Preparation of $[Mo(\eta^3\text{-}RC_3H_4)(CO)_2(bipy)(O_2CR')]$

A mixture of $[Mo(\eta^3\text{-}RC_3H_4)(CO)_2(bipy)Cl]$ (1.0 mmol) and $AgBF_4$ (0.20 g, 1.0 mmol) was stirred in acetone (20 cm^3) at room temperature for 0.3 h. Silver chloride was filtered off and the orange solution treated with NaO_2CR' (1.0 mmol) dissolved in the minimum of acetone. The solution was stirred for a further 0.3 h to ensure complete reaction and then evaporated to low bulk in vacuo. The slow addition of water (70 cm^3) produced small orange-red crystals of the products, which were filtered off, washed with water and dried in vacuo. On standing the filtrate at 0°C overnight, further (but less pure) product precipitated out, which was recrystallised from aqueous acetone. Yields, analytical and infrared data are given in Table 1.

Results and discussion

Powell [11] has shown that the chloride ion is readily abstracted from $[Mo(CO)_2(\eta^3\text{-}C_3H_5)(bipy)Cl]$ by $AgBF_4$ dissolved in acetone, and has synthesised several cationic derivatives $[Mo(CO)_2(\eta^3\text{-}RC_3H_4)(bipy)(L)]BF_4$ (L = neutral monodentate ligand) by this route. We have adapted this procedure to prepare a series of neutral carboxylate derivatives of molybdenum (Table 1).

$$[Mo(CO)_2(\eta^3\text{-}RC_3H_4)(bipy)Cl] + AgBF_4 \xrightarrow{\text{acetone}} [Mo(CO)_2(\eta^3\text{-}RC_3H_4)(bipy)(acetone)]BF_4$$

$$\downarrow NaO_2CR'$$

$$[Mo(CO)_2(\eta^3\text{-}RC_3H_4)(bipy)(O_2CR')]$$

Although the acetate and benzoate complexes (I and II) were insouble, derivatives containing fluorinated carboxylate groups were sufficiently soluble for infrared and NMR studies. In both the solid and solution states these compounds all show two strong, and sometimes split, absorption bands of approximately equal intensities in the terminal carbonyl stretching region, indicative of *cis*-carbonyl groups with an $M(CO)_2$ angle of slightly less than 90°. The CO_2 asymmetric and symmetric stretching modes occur as single strong bands at approximately 1690 and 1400 cm^{-1} in the solid state spectrum of the $O_2CC_nF_{2n+1}$ complexes, and the separations [$\nu(CO_2\text{ asym}) - \nu(CO_2\text{ sym})$] of approximately 290 cm^{-1} show these carboxylate ligands to be monodentate [12] as expected for an 18-electron metal atom configuration.

All the spectroscopic properties of the complexes are consistent with a pseudooctahedral structure in which the allyl and carbonyl ligands occupy adjacent sites on one face of the octahedron as in structural types A or B. The appearance of four carbonyl absorptions in the solution spectra of the η^3-C_3H_5 derivatives, but only two in the η^3-2-MeC_3H_4 complexes, indicates that some form of isomerism is occurring in the unsubstituted allyl compounds. The low conductivity of these complexes precluded ionisation as a possible source of new species and ^1H NMR measurements confirmed that more than one allyl-containing compound is present in $CDCl_3$, CD_2Cl_2 and $(CD_3)_2CO$ solutions of the soluble η^3-C_3H_5 complexes, but only a single isomer for each 2-MeC_3H_4 complex. At room temperature the spectra of these substituted allyl derivatives (Table 2) were typical of complexes with a symmetrically bound allyl group, and no significant spectral changes occurred on cooling the solutions to −90°C. The ^{13}C NMR spectra of complexes VI and VII (Table 3) support a structure in which the terminal carbon atoms of the allyl ligand are equivalent (resonating at 54.9 and 54.8 ppm in VI and VII, respectively), and a plane of symmetry bisects the carbonyl and bipyridine ligands. Therefore unless a very low energy rearrangement is occurring, the 2-MeC_3H_4 derivatives adopt structure A in solution.

In contrast, dynamic behaviour was observed for the η^3-C_3H_5 derivatives, and the properties of complex III were typical of this class of compound. At room temperature in $CDCl_3$, CD_2Cl_2 or $(CD_3)_2CO$ two sets of allyl signals were observed and decoupling experiments showed the presence of two independent species whose relative concentrations were solvent dependent [approximately 1 : 1 in CD_2Cl_2 and 3 : 2 in $(CD_3)_2CO$], but temperature independent between −90 and 0°C. On recording the spectrum of complex III in PhCN and increasing the temperature from 30 to 120°C, the two pairs of doublets characterising

TABLE 2

^{1}H NMR DATA (δ, ppm relative to TMS)

Complex	Solvent	Temperature (K)	Isomer	Allyl[a]			Bipyridine			
				H_c or Me	H_{anti}	H_{syn}				
III	CD_2Cl_2	302	A	3.10m	1.22d	3.22d	7.60m	8.10m	8.96d	
			B	4.00tt	1.42d	3.53d	7.60m	8.10m	9.24d	
		183	A	3.10m	1.32d	3.16d	7.62m	8.10m	8.95d	
			B	4.00tt	1.20d	~3.3(br)	7.62m	8.20m	8.34d	9.76d
					1.72d	~3.7(br)				
IV	CD_2Cl_2	302	A	3.15m	1.21d	3.22d	7.70m	8.21m	9.00d	
			B	3.90tt	1.42	3.52	7.70m	8.48m	9.30d	
V	$(CD_3)_2CO$	302	A	3.15m	1.21d	3.22d	7.68m	8.20m	9.00d	
			B	3.92tt	1.41d	3.50d	7.68m	8.46m	9.32d	
VI	$(CD_3)_2CO$	302	A	1.14s	1.23s	3.08s	7.72m	8.28t	8.56d	9.02d
VII	$(CD_3)_2CO$	302	A	1.09s	1.20s	3.04s	7.58m	8.10d	8.42d	8.90d
VIII	$(CD_3)_2CO$	302	A	1.10s	1.21s	3.04s	7.60m	8.13t	8.44d	8.92d

[a] In the allyl ligand, *anti*-proton resonances were doublets [$^3J(H_{anti}—H_{syn})$ = 9 Hz], as were *syn*-proton resonances [$^3J(H_{syn}—H_c)$ = 6 Hz] and the central proton resonances were triplets of triplets, or multiplets where partially masked by other bands.

TABLE 3

^{13}C NMR DATA [a] (δ ppm relative to TMS)

Complex	CO	Me	Allyl		Bipyridine			
			$C_{central}$	$C_{terminal}$	$C_{\alpha\alpha'}$	C_{γ}	C_{β}	$C_{\beta'}$
III (CD_2Cl_2)	226.5 226.6		73.6 70.6	59.9 [b] 55.9	152.6 [c]	139.4	126.4 126.3	122.4
IV	227.0 226.9		74.2 71.0	59.8 56.1	153.2	140.4	127.1 127.0	123.5 123.4
V	226.9		74.1 70.9	59.8 56.0	153.2	140.3	127.1 126.9	123.5 123.4
VI	226.8	19.4	81.4	54.9	153.2	140.4	127.0	123.6
VIII	227.1	19.4	81.6	54.8	153.0	140.3	126.9	123.6
VIII	227.1	19.4	81.6	54.9	153.0	140.4	127.0	123.6

[a] $(CD_3)_2CO$ as solvent with the exception of III. [b] At 193 K this resonance was replaced by two signals at 66.7 and 52.8 ppm. [c] This signal split into two components at 193 K.

the *syn* and *anti* allyl protons (Table 2) coalesced and finally approached a single AM_2X_2 pattern, typical of a single dynamic allyl species. On cooling CD_2Cl_2 solutions of this complex below room temperature, the signals assigned to isomer A in Table 2, remained invariant in position and bandwidth and are typical of a species with structure A in which the proton on the central allyl carbon atom lies above the plane of the bipyridine ligand (and consequently appears at high field in the ^1H NMR spectrum). However, the allyl signals for isomer B split further on cooling, finally resulting in the ABMNX pattern of an unsymmetrically bonded η^3-allyl group. The simultaneous split of the *ortho*-proton signal of the bipyridine ligand into two doublets of equal intensities (Table 2), also revealed the inequivalence of the two aromatic ring systems in the low temperature limiting spectrum. Thus isomer B is dynamic at room temperature and adopts a low symmetry structure at low temperatures. Although a complete analysis of the ^{13}C NMR spectra of the two η^3-C_3H_5 containing isomers of III proved impossible because of the relatively low solubility of the complex and overlapping spectral bands, a sufficiently detailed assignment can be made to support the above conclusions. Thus the two signals at 73.6 and 70.6 ppm for the central carbon atoms of the allyl groups establish the presence of two allyl-containing species at room temperature (Table 3), and the replacement of one of the two C (terminal) allyl resonances by two new signals at −80°C indicates the generation of a low symmetry allyl complex from a dynamic one. By comparison with the data on [$Mo(CO)_2(\eta^3$-$C_3H_5)$(pd)(py)], which is known to adopt structure B in the solid state [2], it seems likely that the dynamic isomer B also assumes this type of structure at low temperatures in solution.

An intramolecular rearrangement mechanism has been established for some other [$Mo(CO)_2(\eta^3$-$C_3H_5)$(bidentate)L] complexes of structural type B, involving a restricted rotation of the triangular face formed by the allyl and two carbonyl groups relative to that formed by the three donor atoms of the other ligands [6]. Such a mechanism seems likely to account for the dynamic behaviour of the B isomers, and complete rotation of these two faces about the same axis will interconvert isomers A and B, as observed experimentally at elevated temperatures. Molecular models show that the increased size of the β-methyl substituted allyl ligand destabilises isomer B relative to A, due to steric interactions with the inflexible bipyridine ligand, and accounts for the formation of just a single isomer for these complexes.

Acknowledgement

We thank the S.R.C. for a studentship to A.D.

References

1 J.W. Faller, D.F. Chodosh and D. Katahira, J. Organometal. Chem., 187 (1980) 227.
2 B.J. Brisdon and A.A. Woolf, J. Chem. Soc. Dalton, (1978) 291.
3 M.G.B. Drew, B.J. Brisdon and M. Cartwright, Inorg. Chim. Acta, 36 (1979) 127.
4 B.J. Brisdon, D.A. Edwards, K.E. Paddick and M.G.B. Drew, J. Chem. Soc. Dalton, (1980) 317.
5 B.J. Brisdon and M. Cartwright, J. Organometal. Chem., 164 (1979) 83.
6 J.W. Faller, D.A. Haitko, R.D. Adams and D.F. Chodosh, J. Amer. Chem. Soc., 101 (1979) 1654.
7 D.J. Bevan and R.J. Mawby, J. Chem. Soc. Dalton, (1980) 1904.
8 G. Doyle, J. Organometal. Chem., 50 (1978) 67.
9 B.J. Brisdon and G.F. Griffin, J. Chem. Soc. Dalton, (1975) 1999.
10 C.G. Hull and M.H.B. Stiddard, J. Organometal. Chem., 9 (1967) 519.
11 P. Powell, J. Organometal. Chem., 129 (1977) 175.
12 G.B. Deacon and R.J. Phillips, Coord. Chem. Rev., 33 (1980) 227.