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ON THE FLUXIONALITY OF THE "PIANO-STOOL" CONFIGURATION OF CYCLOPENTADIENYLMOLYBDENUM COMPLEXES OF THE TYPE $[Mo(\eta^5\text{-}C_5H_5)L_2(L\text{—}L')]$

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Summary

The complexes $Mo(\eta^5\text{-}C_5H_5)(NO)X(p\text{-}MeC_6H_4N_3C_6H_4\text{-}p\text{-}Me)$ (X = Cl, Br or I), $Mo(\eta^5\text{-}C_5H_5)(CO)_2[p\text{-}MeC_6H_4N_3(R)O]$ (R = Me or i-Pr) and $Mo(\eta^5\text{-}C_5H_5)(CO)_2\text{-}(MeCOCHCOR)$ (β-diketonate, R = CF_3 or Ph) have been prepared and characterised. The fluxional behaviour of η^5-cyclopentadienylmolybdenum complexes having a "piano-stool" configuration (3,4 coordination), and which contain a *cis*-chelating ligand, is discussed generally and in relation to the new and some similar compounds.

Introduction

In a previous paper [1] we described the dynamic activity of the diaryltriazenido complexes $Mo(\eta^5\text{-}C_5H_5)(CO)_2(RNNNR')$ (R,R' = aryl) and showed, by using the prochiral group, $\eta^5\text{-}MeC_5H_4$ that the CO groups underwent site exchange via a Berry-type pseudo-rotation. However, somewhat surprisingly, we found that the related mixed alkyl—aryl triazenide, $Mo(\eta^5\text{-}C_5H_5)(CO)_2(ArNNNPr\text{-}i)$ appeared to be stereochemically rigid on the NMR time scale.

The fluxional behaviour of $Mo(\eta^5\text{-}C_5H_5)(CO)_2[HC(NR)N(CO)R']$ (R = R' = aryl) has also been explained [2] in terms of a Berry-type pseudo-rotation, but the non-rigidity of $Mo(\eta^5\text{-}C_5H_5)(CO)_2(RN{=}CR')$ has been interpreted [3] in terms of rotation of the imino group. A rotational process has also been advanced to account [4] for the epimerization of the optically active pyridyl-

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aldimine complex $[Mo(\eta^5\text{-}C_5H_5)(CO)_2\{2\text{-}C_5H_4NCH{=}NR\}]^+$ (R = $CH(Me)C_6H_5$). Only a few compounds of the general type $Mo(\eta^5\text{-}C_5H_5)L_2(L{-}L')$, where L—L′ may be a symmetrical or unsymmetrical bidentate ligand, have been reported to be rigid although, when L = CO, very few ^{13}C NMR spectral data are available which would confirm this point.

In order to investigate more fully the fluxional properties of $Mo(\eta^5\text{-}C_5H_5)L_2$-(L—L′) we have prepared some new complexes which have the usual square pyramidal or "4-legged piano stool" structure (3,4 coordination) of this type of system, and have examined their temperature dependent NMR spectra.

Results

The new complexes in this study were prepared according to the reactions 1, 2 and 3:

$$[Mo(\eta^5\text{-}C_5H_5)(NO)X_2]_2 + 2\ Ag(ArN_3Ar) \xrightarrow[RT]{THF} 2\ Mo(\eta^5\text{-}C_5H_5)(NO)X(ArN_3Ar) + 2\ AgX \quad (1)$$

(Ar = p-MeC$_6$H$_4$; X = Cl (Ia), Br (Ib) and I (Ic))

$$Mo(\eta^5\text{-}C_5H_5)(CO)_3Cl + Na[RNNN(R')O] \xrightarrow[RT]{MeOH} Mo(\eta^5\text{-}C_5H_5)(CO)_2[RNNN(R')O] + NaCl + CO \quad (2)$$

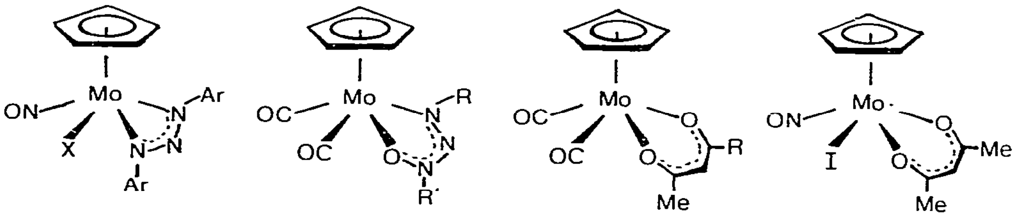
(R = p-MeC$_6$H$_4$; R′ = Me (IIa) or i-Pr (IIb))

$$Mo(\eta^5\text{-}C_5H_5)(CO)_3Cl + Na[\beta\text{-dik}] \xrightarrow[reflux]{MeOH} Mo(\eta^5\text{-}C_5H_5)(CO)_2(\beta\text{-dik}) + NaCl + CO \quad (3)$$

(β-dik = MeCOCHCOCF$_3$ (IIIa) or MeCOCHCOPh (IIIb))

The complexes were obtained in good yields as red or black crystalline solids which, with the exception of IIa and IIb (see below) analysed satisfactorily (Table 1).

The triazenido complex $Mo(\eta^5\text{-}C_5H_5)(NO)I(PhNNNPh)$ has been prepared before [5], and it may also be formed in higher yield by the reaction of Mo-$(\eta^5\text{-}C_5H_5)(NO)I(OAc)$ [6] with diphenyltriazene. However, reaction 1, involving silver(I) triazenides, is generally more convenient, more widely applicable, and affords high yields of the desired compounds. The possibility that Ia, Ib or Ic



I II III IV

Fig. 1. The proposed structures.

TABLE 1

COMPLEXES, MICROANALYSES, COLOURS AND MOLECULAR WEIGHTS

Compound[a]	Colour	Elemental analyses (found (calcd.) (%))				Mol. wt.[c] (found (calcd.))
		C	H	N	halide	
$Mo(\eta^5\text{-}C_5H_5)(NO)Cl(p\text{-}Tol_2N_3)$ (Ia)	red	50.8 (50.6)	4.42 (4.26)	12.2 (12.4)	7.90 (7.86)	
$Mo(\eta^5\text{-}C_5H_5)(NO)Br(p\text{-}Tol_2N_3)$ (Ib)	red	46.4 (46.1)	4.16 (3.84)	11.4 (11.3)	16.2 (16.1)	
$Mo(\eta^5\text{-}C_5H_5)(NO)I(p\text{-}Tol_2N_3)$ (Ic)	red	41.9 (42.1)	3.83 (3.51)	10.3 (10.3)	23.1 (23.4)	
$Mo(\eta^5\text{-}C_5H_5)(CO)_2[p\text{-}TolNNN(Me)O]$ (IIa)	black	[b]				365 (381)
$Mo(\eta^5\text{-}C_5H_5)(CO)_2[p\text{-}TolNNN(Pr\text{-}i)O]$ (IIb)	black	[b]				385 (409)
$Mo(\eta^5\text{-}C_5H_5)(CO)_2(tfac)$ (IIIa)	black	38.3 (38.9)	2.72 (2.46)			
$Mo(\eta^5\text{-}C_5H_5)(CO)_2(bzac)$ (IIIb)	black	54.1 (54.0)	3.80 (3.74)			
$Mo(\eta^5\text{-}C_5H_5)(NO)I(acac)$ (IV)	black	28.5 (28.8)	3.16 (2.91)	3.58 (3.36)		

[a] $RCOCHCOCH_3$: R = CF_3(tfac), R = Ph(bzac), R = Me(acac). [b] Combustion problems (see text). [c] Vapour osmometric in benzene (45.2°C). Due to limited solubility diluted solutions (0.01—0.05 M) could be used only.

might be binuclear with bridging triazenido groups may be discounted because of the presence in the IR spectrum (Table 2) of a band at 1280 cm^{-1} which is typical of a chelating triazenido ligand [7]. The values of ν(NO) are typical [6,8] of this type of Mo complex and indicate a linear Mo—N—O bonding mode.

The ^1H NMR spectra of Ia, Ib and Ic (Table 2) are consistent with the structure shown in Fig. 1 and show that the p-tolyl groups are magnetically inequivalent between +8 and +70°C in C_6D_6. It may be concluded, therefore, that these molecules are stereochemically rigid on the ^1H NMR time scale. Our attempts to replace X in I by neutral ligands L, e.g. CO, PR_3 etc., via treatment of I with $AgPF_6$ or $TlPF_6$ in the presence of L, were generally unsuccessful, complex and intractable reaction mixtures being obtained. However, when Ic was treated with an excess of PPh_3 over 24 h in the presence of $TlPF_6$ in DMSO at room temperature, the known $[Mo(\eta^5\text{-}C_5)(NO)I(PPh_3)_2][PF_6]$ [6] was obtained.

The complex $Mo(\eta^5\text{-}C_5H_5)(NO)I(MeCOCHCOMe)$ (IV) has been obtained previously [6]. In the ^1H NMR spectrum over the range +8—+50°C, the methyl protons remain inequivalent, indicating that this complex, too, is rigid on the NMR time scale. We may also note parenthetically that, although $Mo(\eta^5\text{-}C_5H_5)(NO)I(\eta^2\text{-}O_2CPr\text{-}i)$ [9] * exhibited only a doublet signal due to the methyl protons (^3J(HH)) down to −60°C, the ^{13}C NMR spectrum of this compound revealed that the C(methyl) atoms are inequivalent at room temperature, and therefore that the apparent degeneracy of the proton signals is accidental and this molecule also is non-fluxional.

The compounds IIa and IIb precipitated from reaction mixture 2 in

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* Prepared by treatment of $Mo(C_5H_5)_2(NO)I$ with i-$PrCO_2H$ or $[Mo(\eta^5\text{-}C_5H_5)(NO)I_2]_2$ with AgO_2CPr-i.

TABLE 2

SPECTROSCOPIC DATA

	Infrared[a]		^{1}H NMR[b]		^{13}C NMR	
	ν(NO), ν(CO)	ν(RN$_3$R)	δ(C$_5$H$_5$)	δ(Chel)	δ(CO)	δ(C$_5$H$_5$)
Ia	1655	1300	5.45[c]	7.4 (m), 2.37		
				7.2 (m), 2.37		
Ib	1680	1300	5.46[c]	7.4 (m), 2.34		
				7.2 (m), 2.35		
Ic	1670	1292	5.47[c]	7.4 (m), 2.34		
				7.2 (m), 2.34		
IIa	1816		5.14[c]	3.00	[e]	
	1948			7.2 (m), 2.15		
IIb	1835		5.20[c]	3.88 (sp), 1.00 (d)	263.8[d,f]	100.2
				0.98 (d)		
	1949			7.2 (m), 2.18	262.7	
IIIa	1857		4.95[c]	1.40, 5.37	262.5[c]	99.0
	1964				262.0	
IIIb	1843		5.14[c]	1.70, 5.77	262.3[c]	98.1
	1953			7.2 (m)	262.0	

[a] All spectra run as KBr discs. [b] ppm from internal TMS, d = doublet, sp = septet, m = multiplet. [c] In C_6D_6. [d] In CD_3CN. [e] Not sufficiently soluble. [f] Measured on Bruker WP-200.

methanol and were recrystallized from acetone. Although the IR and ^{1}H NMR spectra of both the crude and purified products are consistent with their formulation and showed the presence of neither impurities nor solvent, we were quite unable to obtain correct microanalytical data for any sample of IIa or IIb. We may only surmise that incomplete combustion of the compounds during the analytical process is responsible for this failure. However, the uncomplicated nature of reaction 2 and the straightforward spectroscopic data are, we believe, sufficient justification for our formulation of IIa and IIb.

The bonding mode of the hydroxytriazene ligand as indicated in Fig. 1 cannot be deduced unequivocally from the spectroscopic data. However, it has been shown that the hydroxytriazenes themselves exist predominantly in the triazene-oxide form [10], and the O,N-bonding mode is found in the two transition metal complexes which have been characterised crystallographically [11]. The *cis*-configuration of II is indicated by the relative intensities of the CO IR absorptions [12] and is confirmed in the magnetic inequivalency of the methyl resonances in the ^{1}H NMR spectrum of the prochiral i-Pr group in IIb. This last observation also reveals that IIb is rigid, and the occurrence of two carbonyl C-

Fig. 2. Schematic description of class A (symmetrical chelate) and class B (unsymmetrical chelate) for Mo(η^5-C_5H_5)L_2(L—L′).

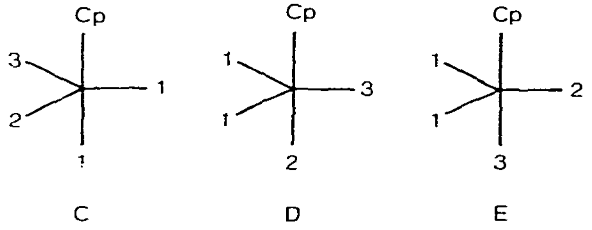

Fig. 3. The possible intermediates in a Berry-type rotation mechanism.

C-atom resonances in the ^{13}C NMR spectrum of IIb confirms this point.

The complexes III were prepared from Mo(η^5-C_5H_5)(CO)$_3$Cl and Na[β-diketonate] under strictly anhydrous conditions since the products are moisture-sensitive. Both products were characterised spectroscopically along lines similar to those described above. They too, are stereochemically rigid.

Discussion

The generalized polytopal rearrangements of Mo(η^5-C_5H_5)$L^1L^2L^3L^4$ have been discussed by Faller and Anderson [13]. In relation to the species under discussion in this paper, the general system is limited to one containing a chelating ligand occupying *cis*-sites and in which two of the four permutable sites are identical. Thus there are only two classes of compound, A and B (Fig. 2), existing in enantiomeric pairs, which may fulfil this condition.

The occurrence of fluxional behaviour in these systems may be monitored by observing the NMR signals associated with the identical groups (L^1). The introduction of prochiral groups or ligands with potential steric hindrance should enable the distinction between the three possible intermediates C, D and E, in which L^1, L^2 and L^3 groups occur respectively in the axial position of the Berry-type trigonal bipyramid (Fig. 3). Thus a prochiral group such as η^5-C_5H_5Me may distinguish intermediate C from D and E, and distinction between the latter two may be achieved by comparison of the rate constants for the interchange of sites 2 and 3 when a bulky group is introduced at L^2 or L^3. It is likely that the bulkier group will prefer an axial site in a trigonal bipyramidal intermediate, and this point has been nicely drawn out in the work of Brunner and Herrmann [4].

The dynamic processes in the systems described in this paper are very complicated and will be influenced as much by electronic as by steric factors. Hence we have not attempted to give a full account of the stability of the likely intermediates involved in Berry-type pseudo-rotation, or of the steric restrictions likely to occur in the pathways of the exchange processes. However, we can draw certain tentative conclusions from the available data.

In considering those systems which contain symmetric chelating ligands (A/A′), we may anticipate that a bulky group (L^2) will inhibit dynamic activity. Thus, although *Mo(η^5-C_5H_5)(CO)L[HC(NAr)$_2$]* (L = CO) is fluxional, those complexes where L = PPh_3, $AsPh_3$, $SbPh_3$, P(OPh)$_3$ and P(OMe)$_3$ are not [14]. Whereas Mo(η^5-C_5H_5)(CO)$_2$(ArNNNAr) exhibits dynamic activity, the species Ia, Ib and Ic and the closely related $Mo(\eta^5-C_5H_5)(NO)X(S_2CNR_2)$ [8] [*] are rigid, in spite of the fact that NO and X (L^2 and L^3) are not substantially more bulky than CO.

We may also compare the properties of the pairs of complexes $Mo(\eta^5-C_5H_5)(CO)_2(RC{=}NR)$ [3] with $Mo(\eta^5-C_5H_5)(CO)_2(R_2CN{=}O)$ [15] and $Mo(\eta^5-C_5H_5)(CO)_2[HC(NR)N(CO)R']$ [2] with $Mo(\eta^5-C_5H_5)(CO)_2[RNNN(R')O]$. The first in each pair is fluxional, whereas the second is not. Combining these observations, we may conclude that electronegative donor atoms, such as halogens or oxygen, or very strongly electron-withdrawing ligands, such as NO, inhibit the fluxional process.

A steric factor of obvious importance is the bite of the chelating ligand. Those complexes reported herein, taken with those also cited in the text, show clearly the trend that as the metal-chelate ring size increases so the energy barrier for the fluxional process also increases. This trend was originally observed in the scrambling processes in $M(chelate)_3$ complexes [16].

Experimental

All reactions were carried out under a nitrogen atmosphere, and all solvents were dried prior to use. The compounds $[Mo(\eta^5-C_5H_5)(NO)X_2]_2$ [17], $Mo(\eta^5-C_5H_5)(CO)_3Cl$ [18], $Ag[(p-MeC_6H_4)_2N_3]$ [19], the hydroxytriazenes [20] and Na(β-diketonate) [21] were prepared according to literature methods. The IR spectra were measured using a Beckman 4250A spectrometer and ^1H and ^{13}C NMR spectra were obtained using Varian HA-100 and Bruker WP-80 instruments. Elemental analyses were obtained by the Microanalytical Department of Sheffield University and by the Organic Laboratory of TNO (Utrecht).

$Mo(\eta^5-C_5H_5)(NO)X[p-C_6H_4N_3C_6H_4-p-Me]$. To a solution of $[Mo(\eta^5-C_5H_5)(NO)X_2]_2$ (1 mmol) in THF (20 ml) at room temperature was added solid $Ag[(p-MeC_6H_4)_2N_3]$ (2 mmol). After stirring for 0.5 h, the precipitated AgX was filtered off, the THF evaporated in vacuo and the product obtained by recrystallisation from THF/hexane mixtures (yield 80—90%).

These complexes are readily soluble in most organic solvents.

$Mo(\eta^5-C_5H_5)(CO)_2[p-MeC_6H_4N_3(R)O]$ (R = Me or i-Pr). Equimolar quantities (ca. 2 mmol) of NaCH and $H[p-MeC_6H_4N_3(R)O]$ were dissolved in methanol (50 ml) at room temperature. Solid $Mo(\eta^5-C_5H_5)(CO)_3Cl$ (ca. 2 mmol) was added, CO evolution occurred and a black precipitate formed. After precipitation was complete (ca. 10 min for R = Me and 0.5 h for R = i-Pr), the product was filtered off and recrystallised from acetone (yield 80%).

$Mo(\eta^5-C_5H_5)(CO)_2(MeCOCHCOR)$, ($R = CF_3$ or Ph). A solution of $Mo(\eta^5-C_5H_5)(CO)_3Cl$ (2 mmol) and Na(β-diketone) (2 mmol) was slowly heated to boiling in methanol (30 ml) and then refluxed for 0.5 h. If heating was too rapid, there

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[*] The ^1H NMR spectra of the dithiocarbamato species where X = halide, or $\eta^1-C_5H_5$ exhibit two inequivalent R groups over the range 30—90°C. Above this temperature coalescence of the protons of the Me group occurs due to rotation about the C—N bond of the $S_2C{-}NMe_2$ group. The species where $X = \eta^1-C_5H_5$ undergoes electronic interconversion of the two cyclopentadienyl rings via a process that does not require polytopal rearrangement of the whole molecule. However, it has been suggested that this complex is capable of undergoing a form of turnstile rotation assisted by bending of the Mo—N—O bond system [22].

was considerable formation of $[\mathrm{Mo}(\eta^5\text{-}\mathrm{C}_5\mathrm{H}_5)(\mathrm{CO})_3]_2$. Upon cooling, the solvent was removed in vacuo and the crude product was recrystallised from toluene (yield 60%).

Acknowledgements

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