

Preliminary communication

SOLVENT INDUCED IONISATION OF η -ALLYLDICARBONYLMOLYBDENUM(II) COMPLEXES

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Summary

$[\text{MoCl}(\eta\text{-C}_3\text{H}_5)(\text{CO})_2(\text{MeCN})_2]$ dissolved in aprotic solvents is extensively ionised to $[\text{Mo}(\eta\text{-C}_3\text{H}_5)(\text{CO})_2(\text{MeCN})_3]^+[\text{Mo}_2\text{Cl}_3(\eta\text{-C}_3\text{H}_5)_2(\text{CO})_4]^-$ with the liberation of free acetonitrile. The corresponding bromo-complex shows similar but less pronounced ionisation in $(\text{CD}_3)_2\text{CO}$, whereas the iodo-complex retains its molecular structure.

While investigating some substitution reactions of complexes of the type $[\text{MoX}(\eta\text{-C}_3\text{H}_5)(\text{CO})_2(\text{MeCN})_2]$, where X = halide, it was noted that the reactions of the chloro-complex (I) dissolved in acetonitrile were sometimes anomalous [1]. Despite the frequent use of these compounds for the synthesis of a wide variety of molybdenum(0) and (II) complexes [2-5], only one report on the spectroscopic properties of this series of compounds has appeared [6], consequently the exact nature of the species present in solution was reinvestigated in an attempt to clarify our observations.

In CD_3CN solutions of (I), ^1H NMR revealed three allyl-containing species with chemical shifts typical of anionic, cationic and neutral complexes (Table 1). Addition of KPF_6 resulted in the precipitation of KCl and the complete conversion of the allyl-containing species to the

TABLE 1

100 MHz PMR DATA FOR THE ALLYL PROTONS OF COMPLEXES I - V
IN CD₃CN (IN PPM RELATIVE TO TMS)

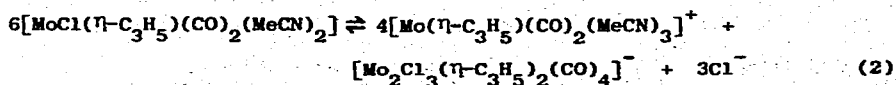
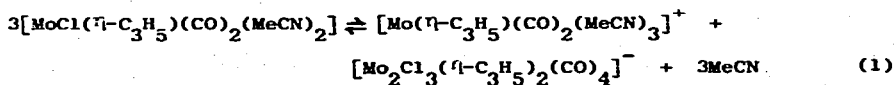
Complex	CH ₂ (anti) J(Hz)	CH ₂ (syn) J(Hz)	CH	Assignment
(I)	0.92(d)*	9.2	3.39(d) 6.4	3.72(m) A**
	1.12(d)	9.4	3.26(d) 6.6	3.98(tt) N
	1.48(d)	9.7	3.59(d) 6.6	4.08(tt) C
(II)	1.47(d)	9.7	3.58(d) 6.6	4.06(tt) C
(III)	0.92(d)	9.2	3.39(d) 6.5	3.72(tt) A
(IV)	1.15(d)	9.0	3.28(d) 6.2	4.00(tt) N
(V)	1.23(d)	9.5	3.34(d) 6.2	4.16(tt) N

* d = doublet, m = multiplet, tt = triplet of triplets

** A = anion, N = neutral complex, C = cation

cationic form. Filtration and evaporation of the solvent yielded the new complex $[\text{Mo}(\eta\text{-C}_3\text{H}_5)(\text{CO})_2(\text{MeCN})_3]\text{PF}_6$ (II). Addition of excess Ph_4AsCl to solutions of (I) or (II) in acetonitrile resulted in the formation of the known [7] anionic species $[\text{Mo}_2\text{Cl}_3(\eta\text{-C}_3\text{H}_5)_2(\text{CO})_4]^-$ (III).

Two equilibria can account for the formation of these ionic species from the neutral bis-MeCN adduct.



Measurements of the relative intensities of the allyl signals in the NMR spectrum of CD_3CN and $(\text{CD}_3)_2\text{CO}$ solutions of (I) indicated that reaction (1) was occurring with an equilibrium constant (K) of approximately $7 \times 10^3 \text{ mol}^2 \text{ dm}^{-2}$ at 300K. In CDCl_3 , the same ionisation process occurred but with a smaller value of K ($6 \times 10^2 \text{ mol}^2 \text{ dm}^{-2}$).

The corresponding neutral bromo (IV) and iodo (V) complexes dissolved in CD_3CN , each showed one strong set of allyl signals which were attributable to the neutral complex with only trace amounts of other allyl species. In $(\text{CD}_3)_2\text{CO}$, (IV) also formed anionic and cationic allyl complexes (K, $7 \times 10^{-2} \text{ mol}^2 \text{ dm}^{-2}$), whereas (V) did not. Addition of CD_3CN to solutions of (IV) in $(\text{CD}_3)_2\text{CO}$ suppressed the ionisation as expected for an equilibrium of type (1). The non-ionisation of the iodo-complex may be related to the inability of the iodide ion to stabilize a halogen-bridged anion of the type $[\text{Mo}_2\text{X}_3(\text{H-C}_3\text{H}_5)_2(\text{CO})_4]^-$ [8].

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