*Journal of Organometallic Chemistry*, 164 (1979) 83–96

# SOLUTION EQUILIBRIA STUDIES ON SOME MOLYBDENUM-ALLYL COMPLEXES

BRIAN J.BRISDON and MICHAEL CARTWRIGHT

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

(Received September 18th, 1978)

## SUMMARY

The complexes $[MoCl(\eta^3-C_3H_5)(CO)_2(RCN)_2]$,where R = Me or Ph, ionise extensively in both polar and non-polar solvents to $[Mo(\eta^3-C_3H_5)(CO)_2(RCN)_3]^+[Mo_2Cl_3(\eta^3-C_3H_5)_2(CO)_4]^-$ with the liberation of free nitrile. Both cations have been isolated and characterised in the form of hexafluorophosphate salts. The corresponding neutral bromo-complexes $[MoBr(\eta^3-C_3H_5)(CO)_2(RCN)_2]$ ionise similarly although to a lesser extent, whereas the iodides do not. Equilibrium constants for the ionisation reactions, and thermodynamic data for the system $[MoCl(\eta^3-C_3H_5)(CO)_2(PhCN)_2]$-PhCN, have been calculated.

## Introduction

Complexes of the type $[MX(CO)_2(\eta-C_3H_5)(MeCN)_2]$, where M = Mo or W and X = halide have been used extensively for the synthesis of many molybdenum- and tungsten-allyl derivatives, which may be obtained by replacement of the weakly bonded nitriles by nitrogen [1-3], phosphorus [4], arsenic [5] or carbocyclic [6,7] ligands. In some reactions attack on the coordinated allyl group results in elimination of allyl halide so providing a useful route to the cis-dicarbonyl complexes [$M(CO)_2(MeCN)_2L_2$], [$M(CO)_2(MeCN)L_3$], [$M(CO)_2(bidentate)L_2$] and [$M(CO)_2(bidentate)_2$], where M = Mo or W and L = monodentate ligand [5,8-10]. Since MeCN is frequently used as both the reactant and solvent for the substitution reactions, the intermediate nitrile complexes are often reacted in situ, and hence their exact nature has not been thoroughly investigated. Our interest in these complexes was first aroused by the sometimes anomolous behaviour of [$MoCl(CO)_2(\eta\text{-}C_3H_5)(MeCN)_2$] [11] and our inability to obtain $^1H$ NMR spectra for this complex in agreement with literature data [2]. Consequently a spectroscopic examination of solutions of some nitrile complexes [$MoX(CO)_2(\eta\text{-}C_3H_5)(RCN)_2$], where X= Cl, Br or I and R = Me or Ph, has been carried out in order to identify the species present. A preliminary report on our findings on the acetonitrile compounds has appeared previously [12].

## Experimental

Solvents were purified and dried by standard procedures and all reactions were carried out in an atmosphere of dry $N_2$ gas. The deuterated solvents used [$CDCl_3$, $CD_3CN$ and $(CD_3)_2CO$] were deoxygenated before use.

Infrared spectra were recorded on solid samples mulled in sodium dried nujol on Perkin-Elmer 237 and 597 spectrophotometers. Solution spectra in the carbonyl region were recorded in acetone or acetonitrile. NMR data were obtained using a JEOL PS100 instrument with tetramethylsilane as internal standard. Conductance measurements were made on a Wayne-Kerr Autobalance bridge at 295 K.

C, H and N analyses were carried out by Strauss Laboratories Ltd., and confirmation of some of the nitrogen figures was obtained by micro-Kjeldahl analysis. Phosphorus in the cationic species was determined gravimetrically as $Ph_4AsPF_6$.

## Preparation of complexes $[MoX(\eta-C_3H_5)(CO)_2(MeCN)_2]$, where X = Cl, Br and I

These complexes were prepared by either of two routes. The chloro- and bromo-derivatives were formed by the direct interaction of $Mo(CO)_6$ and allylhalide in a refluxing $MeCN-C_6H_6$ mixture as reported by Dieck et al [2]. This procedure was not successful for the analogous iodo-compound. Alternatively all three complexes were prepared by the room temperature reaction of allylhalide with $Mo(CO)_3(MeCN)_3$ as outlined by Hayter [6]. In all cases evaporation of the solvent to low bulk at room temperature caused precipitation of analytically pure products. Yields 80-90%.

## Preparation of $[MoX(\eta-C_3H_5)(CO)_2(PhCN)_2]$, where X = Cl, Br or I.

Attempts to prepare these complexes directly from $Mo(CO)_6$, PhCN and $C_3H_5X$ were successful for the chloro-complex only.

0.8 g (3 mmol) $Mo(CO)_6$ was heated with 3 ml PhCN and 3 ml $C_3H_5Cl$ in 15 ml refluxing benzene. After 8 h the solution was cooled and evaporated to low bulk *in vacuo*. Treatment of the residue with 25 ml diethyl ether precipitated $[MoCl(\eta-C_3H_5)(CO)_2(PhCN)_2]$ as a yellow powder. The product was filtered off, washed with $Et_2O$ and dried in a stream of $N_2$. Yield 60%.

All three title compounds were formed on dissolution of the corresponding bis-MeCN complex in excess PhCN at 40°C. The products were isolated by reducing the solution to low bulk *in vacuo* and precipitating the solid with petroleum ether. Yields 90-95%.

## Preparation of $R_4Z[Mo_2X_3(\eta-C_3H_5)_2(CO)_4]$, where $R_4Z = NEt_4$ or $Ph_4As$ and X = Cl or Br.

(i) $Et_4N$ salts. These were prepared by literature methods via the carbonyl halides $Et_4N[MoX(CO)_5]$ [13].

(ii) $Ph_4As$ salts. $Ph_4As[MoCl(CO)_5]$ was first prepared by refluxing 1 g (2.4 mmol) $Ph_4AsCl$ with 0.8 g (3.0 mmol) $Mo(CO)_6$ in 20 ml diglyme until no more carbon monoxide was evolved. The solution was filtered hot and the carbonyl halide precipitated by petroleum ether (Yield 90%). This was then dissolved in tetrahydrofuran and treated with a ten-fold excess of $C_3H_5X$, where X = Cl or Br. After stirring for 4 h, the solvent was removed *in vacuo* and the crude product recrystallised from $CHCl_3$-petroleum ether. Yields 85%.

### Preparation of $[Mo(\eta-C_3H_5)(CO)_2(RCN)_3]PF_6$, where R = Me or Ph

(i) R = Me. 2.0 mmol of $[MoCl(\eta-C_3H_5)(CO)_2(MeCN)_2]$ was dissolved in 15 ml MeCN and treated with 2.2 mmol $KPF_6$. After 48 h at room temperature, the precipitated KCl was filtered off and the solvent removed under reduced pressure. The yellow, air-sensitive solid was recrystallised from $CH_2Cl_2$ to remove unreacted $KPF_6$. Yields 75-80%. The corresponding bromo- and iodo-complexes reacted similarly but longer reaction times were required for complete conversion to $[Mo(\eta-C_3H_5)(CO)_2(MeCN)_3]PF_6$, and yields were correspondingly lower.

(ii) R = Ph. The complex was prepared in a 70% yield in an analogous manner from $[MoCl(\eta-C_3H_5)(CO)_2(PhCN)_2]$ and $KPF_6$ in PhCN solution. The product was precipitated with petroleum ether and recrystallised from $CH_2Cl_2$-petroleum ether. Alternatively, reaction of $[Mo(\eta-C_3H_5)(CO)_2(MeCN)_3]PF_6$ with excess PhCN at room temperature for 2 h yielded the required product in quantitative yields.

## Results and discussion

Dissolution of $[MoCl(\eta-C_3H_5)(CO)_2(MeCN)_2]$ in rigorously dried and deoxygenated solvents resulted in $^1H$ NMR spectra which were at variance with data in the literature [2]. In $CD_3CN$, $CDCl_3$, $(CD_3)_2CO$ and PhCN, three allyl-containing species were formed (Figure 1 and Table 3), whose relative concentrations, as determined from the intensity of the allyl signals, were solvent dependent. In order to exclude the possibility that the spectra resulted from hydrolysis or oxidation products, the spectrum of the deuterated complex $[MoCl(\eta-C_3H_5)(CO)_2(CD_3CN)_2]$ was recorded in $CD_3CN$, resulting in the same pattern of allyl signals. Evaporation of the solvent yielded unchanged $[MoCl(\eta-C_3H_5)(CO)_2(CD_3CN)_2]$.

Although the relative intensities of the allyl signals of the three species varied with the solvent, the ratio of the intensities of the lowest to highest field signals of the _anti_-allyl protons remained constant at just under 1:2 (Table 3), and their chemical shifts were as

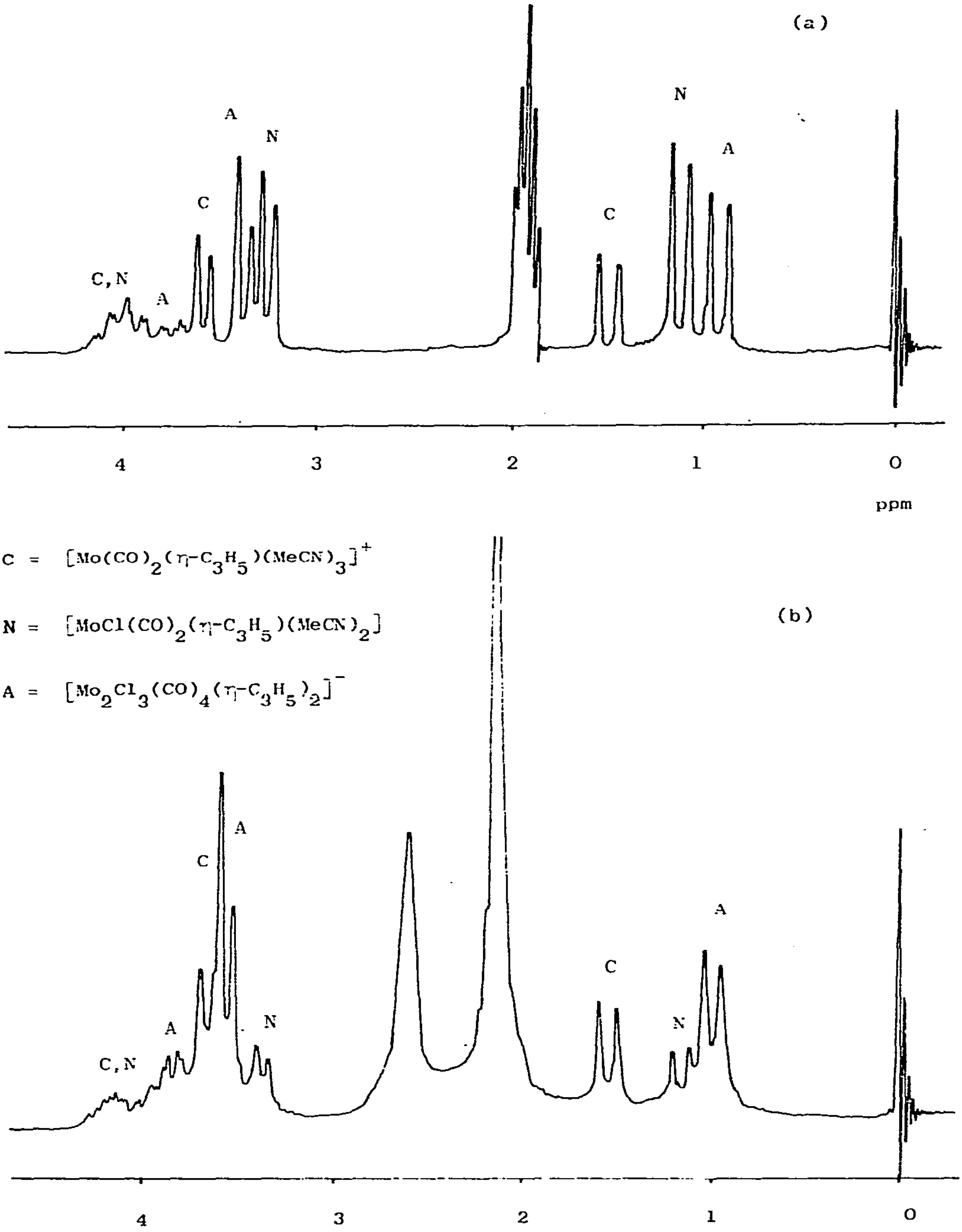

Fig.1 Proton NMR spectra of (a) $[MoCl(CO)_2(\eta\text{-}C_3H_5)(CD_3CN)_2]$ in $CD_3CN$ and (b). $[MoCl(CO)_2(\eta\text{-}C_3H_5)(CH_3CN)_2]$ in $CDCl_3$

Table 1. Analytical and Selected Infrared Data[a] on Allyl Complexes

| Complex | | Elemental analyses found (calcd.)(%) | | | | $\nu$(C-O) cm$^{-1}$ | $\nu$(C≡N) (cm$^{-1}$) |
|---|---|---|---|---|---|---|---|
| | | C | H | N | P | | |
| $[Mo(\eta\text{-}C_3H_5)(CO)_2(MeCN)_3]PF_6$ | (I) | 29.0 | 3.1 | 9.1 | 6.5 | 1865 | 2290 |
| | | (29.0) | (2.5) | (9.1) | (6.7) | 1955 | |
| $[Mo(\eta\text{-}C_3H_5)(CO)_2(PhCN)_3]PF_6$ | (II) | 48.4 | 3.5 | 6.4 | 4.6 | 1870 | 2250 |
| | | (48.2) | (3.1) | (6.5) | (4.8) | 1960 | |
| $Ph_4As[Mo_2Cl_3(\eta\text{-}C_3H_5)_2(CO)_4]$ | (III) | 46.1 | 3.6 | | | 1830; 1802 | |
| | | (46.6) | (3.5) | | | 1928; 1910 | |
| $Ph_4As[Mo_2Br_3(\eta\text{-}C_3H_5)_2(CO)_4]$ | (IV) | 40.4 | 3.2 | | | 1845; 1820 | |
| | | (40.5) | (3.0) | | | 1936; 1920 | |
| $MoCl(\eta\text{-}C_3H_5)(CO)_2(PhCN)_2$ | (V) | 52.2 | 3.6 | 6.5 | | 1865 | 2255 |
| | | (52.5) | (3.5) | (6.4) | | 1943 | |
| $MoBr(\eta\text{-}C_3H_5)(CO)_2(PhCN)_2$ | (VI) | 48.0 | 3.1 | 5.7 | | 1855 | 2250 |
| | | (47.6) | (3.2) | (5.9) | | 1938 | |
| $MoI(\eta\text{-}C_3H_5)(CO)_2(PhCN)_2$ | (VII) | 43.6 | 2.9 | 5.5 | | 1865 | 2253 |
| | | (43.4) | (3.1) | (5.3) | | 1948 | |

[a] on Nujol mulls

expected for cationic and anionic species respectively. Confirmation that ionic species were formed in solution was obtained from conductivity measurements. At low concentrations (~ $10^{-3}$ molar) in acetonitrile the chloro-complex showed appreciable conductivity ( ~30 S $cm^2$ $mol^{-1}$) although lower than expected for a simple ionisation to a 1:1 electrolyte in this medium [14]. Furthermore addition of $KPF_6$ to acetonitrile solutions of the complex resulted in the precipitation of KCl and complete conversion of the allyl-containing species to the cationic form. Filtration and evaporation of the solvent yielded pale yellow crystals of $[Mo(\eta\text{-}C_3H_5)(CO)_2(MeCN)_3]PF_6$. Addition of $Ph_4AsCl$ to a solution of $[MoCl(\eta\text{-}C_3H_5)(CO)_2(MeCN)_2]$ caused the two sets of allyl signals at low fields to diminish in intensity and the signals from the anionic form to increase. Comparison of the chemical shifts and coupling constants of the allyl protons in analytically pure samples of $Ph_4As[Mo_2Cl_3(\eta\text{-}C_3H_5)_2(CO)_4]$ and $[Mo(\eta\text{-}C_3H_5)(CO)_2(MeCN)_3]PF_6$ dissolved separately in various solvents gave good agreement with the chemical shifts and coupling constants of the high and low field sets of allyl protons in the spectra of $[MoCl(\eta\text{-}C_3H_5)(CO)_2(MeCN)_2]$ (Tables 2 and 3).

Only one reaction can account for the reversible formation of these ionic species in the observed ratios from the neutral bis-MeCN adduct:

$$3[MoCl(\eta^3\text{-}C_3H_5)(CO)_2(MeCN)_2] \rightleftharpoons [Mo(\eta^3\text{-}C_3H_5)(CO)_2(MeCN)_3]^+ + [Mo_2Cl_3(\eta^3\text{-}C_3H_5)_2(CO)_4]^- + 3\ MeCN \qquad (1)$$

Such an equilibrium involves the liberation of free MeCN, which together with the complexed MeCN in the cation and in the neutral adduct will result in a maximum of three methyl signals in the $^1H$ NMR spectrum, provided exchange of free and coordinated MeCN is slow. At room temperature in $CDCl_3$ the cationic MeCN signal occurs as a broad singlet at δ 2.4 ppm whereas the free and complexed MeCN in the neutral adduct gave one signal of the appropriate intensity at δ 2.08 ppm. Addition of free MeCN to a solution of the bis-MeCN adduct suppressed the ionisation as expected for the proposed equilibrium and caused the two methyl signals to collapse to a singlet,

Table 2

Room Temperature $^1H$ NMR Data on Charged Complexes

| Complex | Solvent | $^1H$ ($\delta$ rel.TMS, J in Hz)$^a$ | | | | |
|---|---|---|---|---|---|---|
| | | | Allyl | | RCN | Counter-ion |
| | | $H_a$ | $H_s$ | $H_c$ | | |
| I | $CDCl_3$ | 1.44d(9.6) | 3.50d(6.) | 4.06tt | 2.16s | |
| | $CD_3CN$ | 1.47 | 3.58 | 4.06 | | |
| II | $CDCl_3$ | 1.68d(9.5) | 3.72d(6.3) | 4.39tt | 7.60m | |
| | PhCN | 1.88 | 4.08 | 4.75 | | |
| III | $CDCl_3$ | 0.82d(9.4) | 3.36d(6.5) | 3.68tt | | 7.77 m |
| | $CD_3CN$ | 0.92 | 3.39 | 3.72 | | 7.82 m |
| | PhCN | 1.06 | 3.68 | 3.98 | | |
| IV | $CDCl_3$ | 0.92d(9.0) | 3.50d(6.1) | 3.90tt | | 7.76 m |
| | $CD_3CN$ | 1.06 | 3.32 | 4.00 | | 7.82 m |

[a] d = doublet, tt = triplet of triplets,
s = singlet and m = multiplet

presumably by facilitating exchange between the various types of MeCN.

The corresponding bromo-complex $[MoBr(\eta\text{-}C_3H_5)(CO)_2(MeCN)_2]$ showed a similar but less pronounced degree of ionisation to $[Mo(\eta\text{-}C_3H_5)(CO)_2(MeCN)_3]^+$ and $[Mo_2Br_3(\eta\text{-}C_3H_5)_2(CO)_4]^-$ in both $CDCl_3$ and $(CD_3)_2CO$, but in MeCN anion and cation signals were barely detectable. For the iodo-complex there was no NMR evidence of an anionic allyl species in any of the solvents examined, but traces of the $[Mo(\eta\text{-}C_3H_5)(CO)_2(MeCN)_3]^+$ cation were detected in MeCN, probably due to a simple solvolytic process.

Table 3

$^{1}H$ NMR Data for Neutral Complexes $[MoX(\eta\text{-}C_3H_5)(CO)_2(RCN)_2]$

| Complex | Solvent | Chem.shifts for allyl protons[a] | | | Assignments and relative concn.[b] | |
|---|---|---|---|---|---|---|
| | | $H_a$ | $H_s$ | $H_c$ | | |
| $[MoCl(\eta\text{-}C_3H_5)(CO)_2(MeCN)_2]$ | $CDCl_3$ | 0.94 | 3.46 | 3.76 | A | 1.4 |
| | | 1.13 | 3.29 | 3.76 | N | 1 |
| | | 1.48 | 3.54 | 4.08 | C | 1.5 |
| | $CD_3CN$ | 0.92 | 3.39 | 3.72 | A | 0.4 |
| | | 1.12(9.5) | 3.26(6.4) | 3.98 | N | 1 |
| | | 1.48 | 3.59 | 4.08 | C | 0.4 |
| $[MoBr(\eta\text{-}C_3H_5)(CO)_2(MeCN)_2]$ | $CDCl_3$ | 0.92 | 3.59 | 3.95 | A | 0.4 |
| | | 1.12 | 3.29 | 3.80 | N | 1 |
| | | 1.49 | 3.59 | 4.02 | C | 0.4 |
| | $CD_3CN$ | 1.16(9.2) | 3.27(6.0) | 4.02 | N | 1 |
| | | 1.47 | 3.57 | 4.03 | C | trace |
| $[MoI(\eta\text{-}C_3H_5)(CO)_2(MeCN)_2]$ | $(CD_3)_2CO$ | 1.26 | 3.28 | 4.07 | N | |
| | $CD_3CN$ | 1.23(9.3) | 3.34(6.2) | 4.12 | N | 1 |
| | | 1.48 | 3.60 | 4.08 | C | < 0.1 |
| $[MoCl(\eta\text{-}C_3H_5)(CO)_2(PhCN)_2]$ | PhCN | 1.08 | 3.66 | 3.93 | A | 0.3 |
| | | 1.50(9.6) | 3.66(6.4) | 4.48 | N | 1 |
| | | 1.88 | 4.04 | 4.72 | C | 0.3 |
| $[MoBr(\eta\text{-}C_3H_5)(CO)_2(PhCN)_2]$ | PhCN | 1.50(9.2) | 3.62(6.1) | 4.50 | N | |
| $[MoI(\eta\text{-}C_3H_5)(CO)_2(PhCN)_2]$ | PhCN | 1.58(9.4) | 3.72(6.3) | 4.67 | N | |

[a] $H_a$ and $H_s$ signals are doublets, coupling constants for the neutral species are given in parentheses

[b] based on the intensities of the signals from the allyl protons

$$[MoI(\eta^3\text{-}C_3H_5)(CO)_2(MeCN)_2] + MeCN \rightleftharpoons [Mo(\eta^3\text{-}C_3H_5)(CO)_2(MeCN)_3]^+ + I^- \quad (2)$$

Since the iodide ion is apparently unable to stabilize a halogen-bridged anion of the type $[Mo_2X_3(\eta\text{-}C_3H_5)_2(CO)_4]^-$ [13], no anionic allyl species of this stoichiometry would be formed from the displaced $I^-$. In $CD_2Cl_2$ at room temperature, the syn- and anti-allyl proton signals of the iodo-complex consisted of two sets of overlapping doublets of unequal intensities. On cooling the solution below 0°C, the weaker set of signals disappeared and partial evaporation of the solvent resulted in the recovery of unchanged $[MoI(\eta\text{-}C_3H_5)(CO)_2(MeCN)_2]$. Such behaviour is consistent with a low concentration of an isomeric or dissociated species in this solvent at ambient temperatures, but a more definite conclusion must await further investigations.

The NMR spectra of solutions of $[MoX(\eta\text{-}C_3H_5)(CO)_2(MeCN)_2]$ in PhCN at ambient temperatures were identical in the allyl region with the spectra of the corresponding neutral bis-PhCN adducts, indicating that total replacement of MeCN had occurred. This was confirmed by isolating analytically pure PhCN complexes from these solutions, and consequently literature data on the NMR spectra of bis-MeCN adducts dissolved in this solvent should be reinterpreted in terms of the PhCN species [2]. $[Mo(\eta\text{-}C_3H_5)(CO)_2(MeCN)_3]PF_6$ also reacted readily with PhCN to yield the corresponding cationic benzonitrile complex(II), which was detected spectroscopically together with $[Mo_2Cl_3(\eta\text{-}C_3H_5)_2(CO)_4]^-$ in solutions of the neutral chloro-complex in PhCN (Table 3). Thus an ionisation process analogous to that given in equation (1) is operative in this solvent although with a smaller equilibrium constant than in the MeCN system (Tables 4 and 5). The corresponding PhCN-bromo- and iodo-complexes each showed only one set of allyl signals in their proton NMR spectra in PhCN, which were assigned to the undissociated molecular species. The low solubilities of all the neutral PhCN derivatives in $CD_2Cl_2$ and $CDCl_3$ together with overlapping spectral bands precluded thorough investigations in these solvents, but both the chloro- and bromo-complexes exhibited at least two and probably three independent sets of allyl

Table 4

Equilibrium Constants at 300 K for the Ionisation of $[MoX(\eta\text{-}C_3H_5)(CO)_2(MeCN)_2]$

| Solvent | X = Cl | Br | I[a] |
|---|---|---|---|
| $CD_3CN$ | $7 \times 10^3$ | - | $< 1 \times 10^{-4}$ |
| $CDCl_3$ | $6 \times 10^2$ | $8 \times 10^{-3}$ | |
| $(CD_3)_2CO$ | $7 \times 10^3$ | $7 \times 10^{-2}$ | |

[a] based on replacement of $I^-$ by MeCN [equation (2)]

Table 5

Equilibrium Constants and Thermodynamic Data for the Ionisation of $[MoCl(\eta\text{-}C_3H_5)(CO)_2(PhCN)_2]$

| Temperature (K) | Equilibrium Constant ( $\times 10^3$) | $\Delta G^o$ (kJ $mol^{-1}$) |
|---|---|---|
| 303 | 1.04 | -17.5 |
| 323 | 1.72 | -20.0 |
| 343 | 2.39 | -22.2 |
| 363 | 3.45 | -24.6 |
| 373 | 4.39 | -26.0 |

signals in their NMR spectra, whereas the iodo-complex showed only one, thus indicating a close similarity between analogous MeCN and PhCN derivatives.

## Variable temperature $^1H$ NMR data on the charged species.

Several of the charged species under investigation showed temperature-dependent NMR phenomena. The changes which occurred were of two types (a) those affecting the conformation of a particular species and (b) those affecting the relative concentration of the various species in solution.

(a) Conformational changes

Several allyl complexes of molybdenum containing the $Mo(\eta^3-C_3H_5)(CO)_2$ unit have been shown recently to be fluxional at room temperature [5,15-17]. In all the structures so far determined the $Mo(\eta-C_3H_5)(CO)_2$ unit occupies one triangular face of an octahedron [15,18-24], and a trigonal twist mechanism has been suggested to account for the equivalence of the pairs of syn- and anti-allyl protons as shown in the room temperature NMR spectra of neutral complexes with inequivalent ligands cis to the $\eta^3$-allyl group [15,16]. For both the cations isolated (I) and (II), such a mechanism would result in only one signal for the coordinated RCN as observed in Table 2. However, on slowing down such a process, separate signals with intensity ratios 1:2 would be expected for the RCN groups trans to the allyl and trans to the carbonyl groups respectively. Experimentally this was observed to occur for (I) below approximately 285 K in $CDCl_3$. By 215 K sharp singlets centred at δ 2.34 and δ 2.62 ppm replaced the room temperature signal at δ 2.46 ppm. No significant changes in the NMR spectra of the anions occurred over the temperature range 220-400 K, indicating that these anions are either stereochemically non-rigid with a very low activation energy, or adopt a stereochemistry of high symmetry.

(b) Concentration effects

In view of the complex spectra and extreme sensitivity of solutions of most of these complexes, only the $[MoCl(\eta^3-C_3H_5)(CO)_2(PhCN)_2]$-PhCN system was studied in any detail. Over the temperature range 303-373 K, the ratio of the ionised to neutral species increased by a factor of almost two, allowing the calculation of the equilibrium constant of reaction (3) as a function of temperature (Table 5).

$$3[MoCl(\eta^3\text{-}C_3H_5)(CO)_2(PhCN)_2] \rightleftharpoons [Mo(\eta^3\text{-}C_3H_5)(CO)_2(PhCN)_3]^+ + [Mo_2Cl_3(\eta^3\text{-}C_3H_5)_2(CO)_4]^- + 3PhCN \quad (3)$$

The PhCN reaction analogous to equation (1) was found to be endothermic and within the limits of the measurements the heat of reaction $\Delta H^o$ was found to be constant over this temperature range at 19 ± 1 kJ mol$^{-1}$. The driving force for the reaction is the entropy increase ($\Delta S^o_{273-300}$ = 120 ± 6 J deg$^{-1}$) caused by the formation of two ionic species and three molecules of PhCN from every three molecules of the neutral bis-PhCN adduct.

## References

1. A.T.T.Hsieh and B.O.West, J.Organometal.Chem., 112 (1976) 285.
2. H.tom Dieck and H.Friedel, J.Organometal.Chem., 14 (1968) 375.
3. S.Trofimenko, J.Amer.Chem.Soc., 91 (1969) 3183.
4. B.J.Brisdon, J.Organometal.Chem., 125 (1977) 225.
5. B.J.Brisdon and K.E.Paddick, J.Organometal.Chem., 149 (1978) 113.
6. R.G.Hayter, J.Organometal.Chem., 13 (1968) C1.
7. J.W.Faller, Chin-Chun Chen, M.J.Mattina and A.Jakubowski, J.Organometal.Chem., 52 (1973) 361.
8. F.Hohmann, J.Organometal.Chem., 137 (1977) 315.
9. F.Hohmann and H.tom Dieck, J.Organometal.Chem., 85 (1975) 47.
10. H.Fridel, I.W.Renk and H.tom Dieck, J.Organometal.Chem., 26 (1971) 247.
11. B.J.Brisdon and M.Cartwright, unpublished observations.
12. B.J.Brisdon and M.Cartwright, J.Organometal.Chem., 128 (1977) C15.
13. H.D.Murdoch and R.Henzi, J.Organometal.Chem., 5 (1966) 552.
14. W.J.Geary, Co-ordination Chem.Rev., 7 (1971) 81.
15. B.J.Brisdon and A.A.Woolf, J.Chem.Soc.Dalton, (1978) 291.
16. J.W.Faller, D.A.Haitko, R.D.Adams and D.F.Chodosh, J.Amer.Chem.Soc., 99 (1977) 1654.

17. J.W.Faller and D.A.Haitko, J.Organometal.Chem., 149 (1978) C19.

18. A.J.Graham and R.H.Fenn, J.Organometal.Chem., 17 (1969) 405; 25 (1970) 173; 37 (1972) 137.

19. F.A.Cotton, B.A.Frenz and A.G.Stanislowski, Inorg.Chim.Acta., 7 (1973) 503.

20. F.Dewans, J.Dewailly, J.Meuniert-Piret and P.Piret, J.Organometal.Chem., 76 (1974) 53.

21. F.A.Cotton, T.La Coeur and A.G.Stanislowski, J.Amer.Chem.Soc., 96 (1974) 754.

22. J.L.Calderon, F.A.Cotton and A.Shaver, J.Organometal.Chem., 42 (1972) 419.

23. F.A.Cotton, B.A.Frenz and C.A.Murillo, J.Amer.Chem.Soc., 97 (1975) 2118.

24. C.A.Kosky, P.Ganis and G.Avitabile, Acta.Cryst., B27 (1971) 1859.