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The Room Temperature Reaction of $[Mo_2(\eta\text{-}C_5H_5)_2(CO)_6]$ with Alkyl and Aryl Isocyanides

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Although organo-isocyanides react with $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ to give, ultimately, $[Fe_2(\eta\text{-}C_5H_5)_2(CNR)_4]$ [1, 2], aryl isocyanides are significantly more reactive than alkyl isocyanides. Consequently, we thought that it might be possible to prepare per-isocyanide complexes $[Mo_2(\eta\text{-}C_5H_5)_2(CNR)_6]$ of aryl isocyanides from $[Mo_2(\eta\text{-}C_5H_5)_2(CO)_6]$ by a straight-forward CO substitution reaction.

It has already been shown that the principal products of the reaction of $[Mo_2(\eta\text{-}C_5H_5)_2(CO)_6]$ with MeNC are the $[Mo(\eta\text{-}C_5H_5)(CO)_{4-n}(CNMe)_n][Mo(\eta\text{-}C_5H_5)(CO)_3]$ (n = 1 or 2) salts although trace amounts (1% yield) of the covalent $[Mo_2(\eta\text{-}C_5H_5)_2(CO)_5(CNMe)]$ were obtained [3]. At elevated temperatures $Mo_2(\eta\text{-}C_5H_5)_2(CO)_6$ and another alkyl isocyanide, t-BuNC, give the ionic $[Mo(\eta\text{-}C_5H_5)(CNBu\text{-}t)_4][Mo(\eta\text{-}C_5H_5)(CO)_3]$ [4].

Experimental

Literature methods were used to prepare $[Mo_2(\eta\text{-}C_5H_5)_2(CO)_6]$ [5] and organoisocyanides [6].

Benzene was dried and deoxygenated by refluxing over calcium hydride under an atmosphere of nitrogen.

^{1}H NMR spectra were run on a JEOL PFT 100 nmr spectrometer using Me_4Si as an internal standard. IR spectra were run on Perkin Elmer 283B or 337 spectrometers using samples dispersed in CsBr discs and they were calibrated with polystyrene. Relevant features of the spectra are summarised in Table I.

Analyses were obtained in the Analytical Laboratory of University College, Dublin.

Reaction of $[Mo_2(\eta\text{-}C_5H_5)_2(CO)_6]$ with MeNC and other Alkyl Isocyanides

MeNC (0.17 ml) was added to a solution of $Mo_2(\eta\text{-}C_5H_5)_2(CO)_6$ (0.25 g, mol ratio 6:1) in C_6H_6 (60 ml) in the dark. The reaction was monitored by IR spectroscopy and found to be complete after 1 hr at room temperature. The solvent was then removed at reduced pressure and the residue recrystallized from ethanol containing KPF_6. Yellow crystals of $[Mo(\eta\text{-}C_5H_5)(CNMe)_3(CO)][PF_6]$ were obtained in 70% yield. M.p. 124–125 °C. *Anal.* Found (calculated) %C = 30.7 (31.4), H = 3.4 (3.1), N = 8.5 (9.1) and F = 24.4 (24.9).

Related $[Mo(\eta\text{-}C_5H_5)(CNR)_3(CO)][PF_6]$ salts were prepared similar in ~70% yield when R = i-Pr (1.5 hr, 113–115 °C) and t-Bu (2 hr, 165–167 °C). Reaction times and melting points are given in parentheses. In some instances, these complexes were further purified by chromatography (alumina; CH_2Cl_2/acetone).

Reaction of $[Mo_2(\eta\text{-}C_5H_5)_2(CO)_6]$ with PhNC and other Aryl Isocyanides

PhNC (0.23 g) was added to a solution of $[Mo_2(\eta\text{-}C_5H_5)_2(CO)_6]$ (0.25 g, mol ratio 4:1) in benzene

TABLE I. IR and ^{1}H NMR Spectra of the $[Mo(\eta\text{-}C_5H_5(CNR)_3(CO)][PF_6]$ and $[Mo(\eta\text{-}C_5H_5)(CNAr)_4][PF_6]$ Complexes Described in the text.

R or Ar	IR Spectra^a	^{1}H NMR Spectra^b		
	$[Mo(\eta\text{-}C_5H_5)(CNR)_3(CO)][PF_6]$			
Me	1926(s.br)*, 2172(s), 2212(m)	5.34(s.5)†	3.67(s.9)	
i-Pr	1927(s.br)*, 2146(s), 2187(m)	5.34(s.5)†	1.46(d.18)^c, 4.28(q.3)^c	
t-Bu	1928(s.br)*, 2140(s), 2177(m)	5.34(s.5)†	1.54(s.27)	
	$[Mo(\eta\text{-}C_5H_5)(CNAr)_4][PF_6]$			
C_6H_5	2075(s), 2151(m)	5.62(s.5)†		7.40(s.20)
$o\text{-}MeC_6H_4$	2071(s), 2148(m)	5.62(s.5)†	2.38(s.12)	7.27(s.16)
$p\text{-}MeC_6C_4$	2078(s), 2150(m)	5.57(s.5)†	2.38(s.12)	7.22(s.16)

[a] Peak positions (cm^{-1}) of absorprtion bands due to ν(CO) (*) or ν(CN) vibrations with relative intensities in parentheses. (s = strong, m = medium, br = broad. Measured in KBr discs. [b] Chemical shifts (p.p.m. downfield from Me_4S) of C_5H_5 (†) and Ar or R protons with integrated intensities in parentheses. s = singlet, d = doublet and q = quartet. Measured in $CDCl_3$ solution. [c] J = 6.35 Hz.

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(60 ml). The reaction was complete within 5 min at room temperature in the dark. The solvent was removed from the reaction mixture at reduced pressure and the residue crystallized from ethanol containing KPF_6. Yellow crystals of $[Mo(\eta\text{-}C_5H_5)(CNPh)_4][PF_6]$ were obtained in 80% yield. M.p. 95–97 °C. *Anal.* Found (calculated) % C = 55.2 (55.1), H = 3.7 (3.5), N = 7.5 (7.8) and F = 16.3 (15.9). Related $[Mo(\eta\text{-}C_5H_5)(CNAr)_4][PF_6]$ complexes were prepared similarly in 70% yield when Ar = *p*-MeC_6H_4 (126–127 °C) and *o*-MeC_6H_4 (120–122 °C). Melting points are given in parentheses.

Results and Discussion

The reactions of $[Mo_2(\eta\text{-}C_5H_5)_2(CO)_6]$ with aryl isocyanides, ArNC are very fast. They are complete within less than five minutes at room temperature to give $[Mo(\eta\text{-}C_5H_5)(CNAr)_4][Mo(\eta\text{-}C_5H_5)(CO)_3]$ salts as the only detectable products. The related reactions with alkyl isocyanides RNC are also facile, but much slower and even with a large excess of the organo-isocyanide only give $[Mo(\eta\text{-}C_5H_5)(CNR)_3(CO)][Mo(\eta\text{-}C_5H_5)(CO)_3]$ with their less highly-substituted cations. The times required for these reactions to go to completion increase for R = Me < i-Pr < t-Bu.

Although the $[Mo(\eta\text{-}C_5H_5)(CNAr)_4][Mo(\eta\text{-}C_5H_5)(CO)_3]$ and $[Mo(\eta\text{-}C_5H_5)(CNR)_3(CO)][Mo(\eta\text{-}C_5H_5)(CO)_3]$ salts were the only significant products of these reactions, they were somewhat air-sensitive. Consequently we detected the anions by IR spectroscopy, and isolated the cations as their analytically pure, air-stable hexafluorophosphate salts in yield ~70%.

It is probable that the $[Mo(\eta\text{-}C_5H_5)(CNAr)_4]^+$ and $[Mo(\eta\text{-}C_5H_5)(CNR)_3(CO)]^+$ cations have the piano-stool structures which are similar to that found for $[Mo(\eta\text{-}C_5H_5)(CO)_3Cl]$ [7], for example. The IR and NMR spectra discussed below are consistent with this supposition.

The IR spectra of the $[Mo(\eta\text{-}C_5H_5)(CNAr)_4][PF_6]$ salts show strong absorption bands at *ca.* 560 and 840 cm^{-1} characteristic of the $[PF_6]^-$ ion and two others at *ca.* 2100 cm^{-1} due to the two anticipated IR active $\nu(CN)$ vibrations of the cations' $Mo(CNAr)_4$ moieties of C_{4v} symmetry. The weaker at *ca.* 2150 cm^{-1} are attributed to the modes of a_1 symmetry; the more intense at *ca.* 2070 cm^{-1} to the modes of *e* symmetry. Apart from absorption bands due to the $[PF_6]^-$ ions, the IR spectra of $[Mo(\eta\text{-}C_5H_5)(CNR)_3(CO)][PF_6]$ show single absorption bands at *ca.* 1930 cm^{-1} due to the $\nu(CO)$ modes of the cations and two at *ca.* 2170 and 2210 cm^{-1} due to their $\nu(CN)$ vibrations. Three of the latter would be expected, but it is clear that two are coincident and make up the 2170 cm^{-1} bands.

The ^1H NMR spectra of both series of salts are consistent with the proposed formulae. They show resonances characteristic of their cyclopentadienyl and isocyanide ligands with the correct integrated intensities (Table I). However whereas all four isocyanide ligands in the $[Mo(\eta\text{-}C_5H_5)(CNAr)_4]^+$ cations are equivalent, the three in $[Mo(\eta\text{-}C_5H_5)(CNR)_3(CO)]^+$ are not, as two are *cis* to CO and one is not. This inequivalence is not reflected in the ^1H NMR spectra at room temperature (Table I) which suggests that the two types of RNC ligands are interchanging rapidly on the NMR time scale (*cf.* ref. [8]).

Although a covalent complex, $[Mo_2(\eta\text{-}C_5H_5)_2(CO)_5(CNMe)]$, has been isolated in trace amounts from the reactions of organo-isocyanides with $[Mo_2(\eta\text{-}C_5H_5)_2(CO)_6]$ [3], the overwhelmingly important products are salts arising from the heterolytic cleavage of the metal–metal bond. This is in contrast with $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ which gives only covalent $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_{4-n}(CNR)_n]$ products (n = 1–4) [1, 2]. It is not unreasonable to attribute this behaviour to the steric interactions between adjacent ligands across the metal–metal bond which are already large in $[Mo_2(\eta\text{-}C_5H_5)_2(CO)_6]$ [9] and which are likely to be even greater in its isocyanide-substituted derivatives with their attendant organo-groups. Alternatively it is possible that the electronic asymmetry in the initially formed $[Mo_2(\eta\text{-}C_5H_5)_2(CO)_5(CNR)]$ may mean that it reacts with a further isocyanide molecule by loss of $[Mo(\eta\text{-}C_5H_5)(CO)_3]^-$ rather than CO. The differing stoichiometries of the products is another example of the known abilities of aryl isocyanides to replace more CO ligands of a substrate than do alkyl isocyanides [1]. Under more vigorous reaction conditions than those which we utilized, $[Mo_2(\eta\text{-}C_5H_5)_2(CO)_6]$ and the alkyl isocyanide t-BuNC give $[Mo(\eta\text{-}C_5H_5)(CNBu\text{-}t)_4][Mo(\eta\text{-}C_5H_5)(CO)_3]$ [4].

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