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Solvent and Substituent Effects in Isocyanide-induced Insertion of Carbon Monoxide into Molybdenum–Carbon Bonds

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The mechanism of reaction of alkyl isocyanides with $[(\eta^5\text{-}C_5H_5)(CO)_3MoCH_2C_6H_5]$ *to yield isocyanide-substituted acyl complexes is similar to that of the corresponding reaction with tertiary phosphines in that two pathways, one an indirect route involving solvent assistance and the other a direct nucleophilic attack by isocyanide, exist. At very high isocyanide concentrations, decreases in reaction rate, which can be related to the lowering of solvent concentration are observed. The reaction is mildly enhanced by electron-donating substituents. The reaction with cyclohexylisocyanide in benzene yields, in addition to the acyl product, a chelated imino-acyl complex which probably forms by photodecarbonylation of the acyl derivative.*

Introduction

As an extension of our recent work [1–4] on the mechanism of insertion of carbon monoxide into transition metal–carbon bonds induced by tertiary phosphines, we report here a kinetic study of a corresponding reaction (eqn. 1), in several solvents, of t-butylisocyanide with a series of substituted benzyl complexes, $[(\eta^5\text{-}C_5H_5)(CO)_3MoCH_2C_6H_4X]$.

$$[(\eta^5\text{-}C_5H_5)(CO)_3MoCH_2C_6H_4X] + {}^tBuNC \longrightarrow [(\eta^5\text{-}C_5H_5)(CO)_2({}^tBuNC)MoCOCH_2C_6H_4X] \quad (1)$$

The general synthetic aspects of this reaction have been explored previously [5–7]. Yamamoto and Yamazaki observed that, in benzene at room temperature, an equilibrium mixture of *cis*- and *trans*-isomers, $[(\eta^5\text{-}C_5H_5)(CO)_2({}^tBuNC)MoCOR]$, (R = CH_3 or CH_2Ph), was formed [5, 6]. This contrasts with the same reaction with tertiary phosphines which, except for the initial stages of the reaction in dimethylsulfoxide where a small amount of the *cis*- isomer is present, gives only the *trans*- form. A further difference for alkylisocyanides is the reported additional formation of an isocyanide-insertion product, $[(\eta^5\text{-}C_5H_5)(CO)_3MoC(CH_2C_6H_4X){=}NC_6H_{11}]$, in the reaction of several *para*-substituted benzyl molybdenum complexes with cyclohexylisocyanide in benzene solution [6].

This paper is concerned mainly with a mechanistic evaluation of the role of the solvent on the formation of the acyl complexes using t-butylisocyanide as the inducing nucleophile. Electronic effects, as controlled by variation of *meta*- and *para*- substituents in benzylmolybdenum complexes are also explored, and a brief comment on the nature of the additional isocyanide insertion product is made.

Experimental

General

Operations were carried out under an atmosphere of high purity nitrogen using standard techniques. Solvents were dried, as indicated, and distilled prior to use. (Acetonitrile, P_2O_5; hexane, CaH_2; tetrahydrofuran, CaH_2; dimethylsulfoxide, molecular sieve 4A). Infrared measurements were made on a PE283B spectrophotometer and ^1H NMR spectra were recorded on a Jeol PS100 spectrometer. Microanalyses were carried out by Mr J. Kent of this Department. Molybdenum benzyl complexes, $[(\eta^5\text{-}C_5H_5)(CO)_3MoCH_2C_6H_4X]$ were prepared from the reaction of $[(\eta^5\text{-}C_5H_5)(CO)_3Mo]^-$ and the appropriate benzyl halide in tetrahydrofuran, using the standard procedure [8]. Cyclohexyl- and t-butyl-isocyanide were synthesised by the literature method [9].

Acyl Complexes

The compounds, $[(\eta^5\text{-}C_5H_5)(CO)_2(RNC)MoCOCH_2C_6H_4X]$, were prepared by the reaction of the molybdenum benzyl complex (*ca.* 3 mmol) and isocyanide (*ca.* 6 mmol) in acetonitrile (30 ml) at room temperature, in the absence of light, over 24 hours. After removal of solvent and excess isocyanide by evacuation, the solid residue was chromatographed on alumina (Grade II–III). The acyl product was eluted with dichloromethane/hexane (1:1) and crystallised. Yields ~40%. The compounds were characterised by microanalysis, IR and NMR; representatively $[(\eta^5\text{-}C_5H_5)(CO)_2({}^tBuNC)MoCOCH_2C_6H_4\text{-}OMe\text{-}p]$: Found: C, 56.13; H, 5.16; N, 3.12; Calculat-

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ed C, 56.41; H, 5.25; N, 3.03%; IR (in cyclohexane) $\nu_{C\equiv N}$, 2111m; $\nu_{C\equiv O}$, 1954s and 1889vs; $\nu_{C\equiv O}$, 1623w cm^{-1}; and ^{1}H NMR, $\delta(C_5H_5)$ (5.31 (*cis*), 5.17 (*trans*) in $CDCl_3$ relative to internal TMS.

Kinetic Measurements

Kinetic data were obtained generally using at least a ten-fold excess of ligand. Solutions were mixed in a Schlenk tube and transferred by syringe to a 5 mm NMR tube which was degassed and filled with nitrogen. Reactions, at 28 °C, were followed by monitoring the peak heights of the cyclopentadienyl resonances, around 5 ppm, of the starting material and the *cis-* and *trans-* acyl products. The peak widths at half-height were essentially constant (~0.5 Hz) and the method gave good quality rate data which were indistinguishable from those collected by more cumbersome integration methods. Overall uncertainties in rate constants, which are best gauged from differences observed in data collected for identical reactions under similar conditions, were about 5%. Reactions were followed at least to two half-lives.

Preparation of Isocyanide Insertion Product $[(\eta^5\text{-}C_5H_5)(CO)_2\overline{Mo\text{–}C(CH_2Ph)\text{=}N}C_6H_{11}]$

A solution of $[(\eta^5\text{-}C_5H_5)(CO)_3MoCH_2Ph]$, (1.0 g, 3.0 mmol) and cyclohexylisocyanide (0.4 ml, 3.8 mmol) in benzene (25 ml) was stirred under nitrogen at room temperature for 24 hours. The yellow precipitate which formed was redissolved in dichloromethane and chromatographed on alumina (Grade II–III). The isocyanide insertion product was eluted with chloroform after removal of unreacted starting material and the acyl complex. Crystallisation from chloroform gave a yellow powder (0.5 g, 40%). Found: C, 60.06; H, 5.20; N, 3.02; Calc. for $C_{21}H_{22}MoNO_2$: C, 60.43; H, 5.55; N, 3.16%; infrared (benzene solution): $\nu_{C\equiv O}$ 1967, 1895; $\nu_{C=N}$, 1595 cm^{-1}; ^{1}H NMR: $\delta(C_5H_5)$ 5.27, $\delta(CH_2)$ 4.17, 4.27 in $CDCl_3$ relative to internal TMS.

Results and Discussion

Reactions of t-butylisocyanide and substituted benzylmolybdenum complexes, $[(\eta^5\text{-}C_5H_5)(CO)_3MoCH_2C_6H_4X]$, were carried out in four solvents, cyclohexane, tetrahydrofuran, acetonitrile and dimethylsulfoxide, and the kinetics at 28 °C monitored by ^{1}H NMR spectroscopy. In each case, the formation of the isocyanide-substituted acyl derivative, $[(\eta^5\text{-}C_5H_5)(CO)_2(^tBuNC)MoCOCH_2C_6H_4X]$ was clean, and no significant side reactions, such as decarbonylation or isocyanide insertion, were observed.

When a significant excess (~5:1) of t-butylisocyanide over $[(\eta^5\text{-}C_5H_5)(CO)_3MoCH_2C_6H_4X]$ was used, the reactions were found to be effectively first order in the molybdenum benzyl, and the rate constant (*e.g.* $k_{obs} = (2.84 \pm 0.1)10^{-4}$ s^{-1} for $[(\eta^5\text{-}C_5H_5)(CO)_3MoCH_2C_6H_5]$ at 28 °C) was independent of its concentration over the tested range from 0.02 to 0.2 *M*, for a constant t-butylisocyanide concentration of 0.3 *M*.

The observation of a first order process is compatible with the mechanism previously proposed for analogous reactions promoted by tertiary phosphines which contain two competing pathways [10]. The first (Eqn. 2) is predominant in solvents (S) of relatively high donicity at low concentrations of inducing nucleophiles of moderate strength.

$$[(OC)MR] \underset{k_{-1}}{\overset{k_1,S}{\rightleftharpoons}} [(S)M(COR)] \underset{k_{-1}}{\overset{k_2,L}{\rightleftharpoons}} [(L)M(COR)] + S \tag{2}$$

The first (k_1) step yields a 'solvent-stabilised intermediate' which is kinetically inferred and which has only been observed directly in reactions of $[(\eta^5\text{-}C_5H_5)(CO)_2FeR]$ in the strongly donor solvent, dimethylsulfoxide [2, 11]. The second (k_2) stage involves the replacement of solvent by the nucleophile. The competing pathway (Eqn. 3), which is relatively favoured in non-polar solvents and for high concentrations of strong nucleophiles, is a direct attack of nucleophile on the metal alkyl to give the acyl product.

$$[(OC)MR] \underset{k_{-3}}{\overset{k_3,L}{\rightleftharpoons}} [(L)M(COR)] \tag{3}$$

In the system studied, reactions proceeded essentially to completion, allowing k_{-2} and k_{-3} to be ignored and, with the usual assumption [16] of a steady state concentration of the intermediate in Eqn. (2), the overall rate constant, k_{obs}, is thus given by

$$k_{obs} = \frac{k_1k_2[L]}{k_{-1} + k_2[L]} + k_3[L]$$

which, at high [L], reduces to

$$k_{obs} = (k_1 + k_3[L]).$$

Appropriately, as the concentration of L is effectively unchanged during reaction, the reaction is observed to be first order in [(OC)MR].

Unlike the corresponding reactions with tertiary phosphines, an equilibrium mixture of *cis-* and *trans-*isomers of the acyl product $[(\eta^5\text{-}C_5H_5)(CO)_2(^tBuNC)MoCOCH_2C_6H_4X]$ is obtained. There is no change in the *cis*/*trans* ratio during reaction and the rate of isomerisation is rapid compared with the rate of carbon monoxide insertion. Accordingly the isomerisation process does not effect the observed kinetics of the reaction as monitored by the disappearance of the molybdenum alkyl and the appearance of the two products. The result is consistent with an earlier report [5] where the rate constant for the isomerisation of *trans-*$[(\eta^5\text{-}C_5H_5)(CO)_2(^tBuNC)MoCOCH_2C_6H_5]$, obtained by low

TABLE I. Rate Constants for Reaction of $[(\eta^5\text{-}C_5H_5)(CO)_3MoCH_2C_6H_5]$ with t-Butylisocyanide at 28 °C.

Solvent	$10^4k_1/s^{-1}$	$10^4k_1'/s^{-1}$ L mol^{-1}	$10^4k_3/s^{-1}$ L mol^{-1}	$10^4k_1/s^{-1}$
Cyclohexane	0	0	0.39	
Tetrahydrofuran	~0	~0	0.4	0.16^a
Acetonitrile	2.84	0.15	0.33	2.60^a
Dimethylsulfoxide	40	2.9	–	40.5^a

^{a}For the reaction of $[(\eta^5\text{-}C_5H_5)(CO)_3MoCH_2C_6H_5]$ with PPh_3 at 29 °C. Data from Ref. 1.

temperature crystallisation, to *cis*, in deuterochloroform, was found to be 3.38 × 10^{-2} s^{-1} at –3 °C, which is over a hundred times higher than our k_{obs} value for carbon monoxide insertion in acetonitrile at 28 °C.

We confirm the somewhat surprising feature observed previously [5] that the position of the *cis/trans* equilibrium is independent, within experimental error, of the solvent, the amount of the *cis*- form being (38 ± 2)% for cyclohexane, tetrahydrofuran, acetonitrile and dimethylsulfoxide. In addition, different steric and electronic effects imposed by a variety of substituted benzyl groups (*o*-Me, 2,4,6-Me_3, *p*-CF_3, *p*-MeO *etc.*) had no influence, and there was no change in the ratio in going from t-butyl- to cyclohexyl-isocyanide. The observations are in marked contrast with those of Faller and Anderson [12] for *cis-trans* isomer ratios for phosphine-substituted molybdenum complexes, $[(\eta^5\text{-}C_5H_5)(CO)_2(PR_3)MoX]$, where X = alkyl, halide and hydride, and may be reflecting both the lower steric demand of an acyl compared to an alkyl substituent, and of an alkylisocyanide compared with a tertiary phosphine. A substantial variation in the equilibrium *cis/trans* ratio in $[(OC)_4(PR_3)MnCOR]$ complexes has been noted for different phosphines [13, 14] but there is a suggestion that the ratio is relatively independent of isocyanide for $[(OC)_4(RNC)MnCOCH_3]$, [15].

The nature of solvent influence on the overall reaction rate is illustrated, for cyclohexane, acetonitrile and dimethylsulfoxide, in Fig. 1. The range of nucleophile concentration, from approximately 0.2 *M* up to neat t-butylisocyanide, is in a significantly higher domain than that used in previous related studies and allows a new aspect of solvent involvement to emerge.

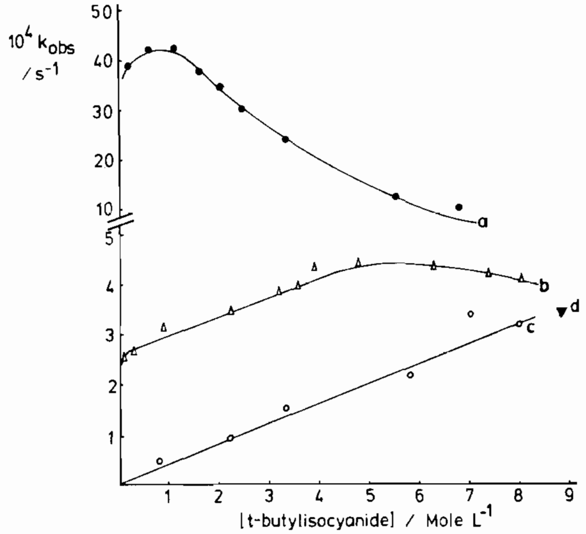

Fig. 1. Rate constants for reaction of t-butylisocyanide with $[(\eta^5\text{-}C_5H_5)(CO)_3MoCH_2Ph]$ in (a) dimethylsulfoxide, (b) acetonitrile (c) cyclohexane and (d) neat t-butylisocyanide.

The simplest trend is observed for cyclohexane for which a linear relationship between k_{obs} and concentration is seen. The line tends towards the value of k_{obs} measured in neat t-butylisocyanide (8.85 *M*). The data is consistent with the essentially zero k_1 value in this non-coordinating solvent, which gives rise to the approximation, $k_{obs} \cong k_3[L]$. In acetonitrile, the reaction, overall, is faster; there is a rapid initial rise in k_{obs} which corresponds to the approach of the first term in the composite rate constant towards k_1 at a relatively high concentration of nucleophile. This is followed by a linear portion, reflecting the competing influence of the second order k_3 pathway, which yields a $k_{obs} = k_1 + k_3[L]$. Finally a decrease in k_{obs} occurs at very high concentrations of isocyanide and the value tends towards that for the reaction in neat t-butylisocyanide (8.85 *M*). Such a decrease has not been previously detected in the carbon monoxide insertion process and it can be interpreted simply in terms of an effective lowering of the concentration of the solvent, which reduces the value of k_1 which, formally, is a second order rate constant, perhaps better represented as $k_1 = k_1'[S]$. The results for dimethylsulfoxide are consistent with this interpretation, even though the linear, $k_1 + k_3[L]$, portion of the graph is not clearly defined. The k_1 value for dimethylsulfoxide, a solvent of high donor strength, is clearly very much higher than for the other solvents, a factor which shifts the maximum in the k_{obs} plot to lower concentrations and into the linear, $k_1 + k_3[L]$, region of the graph. Data collected in tetrahydrofuran were closely similar to those for cyclohexane. Although this was at first surprising in terms of the k_1 values anticipated for these solvents from related previous studies [1, 10], they are interpretable on the simple basis that, in the high concentration range used, the k_3 path is the predominant one in both solvents, and any small differences in k_1 are submerged in the experimental uncertainties.

Analysis of the $k_1 + k_3[L]$ region of the graphs gave the values of k_1 and k_3 shown in Table I. A value for a rate constant, k_1', which is simply k_1 divided by the concentration of the solvent in mol L^{-1}, is also listed. This is an attempt to represent the first reaction stage as a second order process to enable a more realistic comparison of the relative donor abilities of solvent and isocyanide in the competing pathways. The values of k_1 and k_1' for dimethylsulfoxide are estimates taken from the maximum value of k_{obs}, which at this concentration, should not contain a significant k_3 contribution. The k_1 values for acetonitrile and dimethylsulfoxide correspond closely with those obtained using triphenylphosphine as the nucleophile in these solvents, as required by the proposed mechanistic scheme. There is a substantial variation in k_1 with solvent which, as suggested previously [1, 16], is indicative of discrete solvent–metal interactions rather than being simply a reflection of the overall polarity of the medium. The k_3 value might be expected to be effected by solvent in the latter sense, and the fact that the values were comparable in cyclohexane, tetrahydrofuran and acetonitrile suggests that bulk medium effects are not large. It is interesting that the k_{obs} value, obtained in neat t-butylisocyanide, divided by the concentration of the isocyanide in mol L^{-1}, yields a rate constant of 0.38 which is in the range of those obtained graphically in the three solvents. No direct k_3 measurement was possible for dimethylsulfoxide. Although a guesstimate is possible by assuming a k_1 and k_3 contribution to each point of the curve, inconsistent results were obtained. Essentially, the extent of decrease of the rate constant, k_{obs}, after the maximum is greater than can be accounted for by the decreasing concentration of the solvent, and the mechanistic pattern which is applied is clearly incomplete.

The question of the style of solvent involvement in this process has been widely debated [1, 11, 16, 17] but the most definitive evidence for direct solvent involvement is that of Wax and Bergman [17] who, by using a series of substituted tetrahydrofurans of similar polarity but substantially different donor ability arising from steric differences, found a large variation in the k_1 values for the reactions of methyldiphenylphosphine with $[(\eta^5\text{-}C_5H_5)(CO)_3MoCH_3]$. However, problems of interpretation still remain. For example, while in tetrahydrofuran the value of k_1' (the second order rate constant for the first stage of the solvent-induced pathway) is roughly an order of magnitude less than k_3, the two rate constants are similar in acetonitrile, which suggests a comparable nucleophilicity of this solvent with t-butylisocyanide. Although we have been unable to measure k_3 in dimethylsulfoxide, it is likely that it is about an order of magnitude lower than k_1', which could, assuming a common mechanism, be interpreted in terms of a relatively high nucleophilicity for the solvent. Intuitively this seems unlikely but it may be that such simple considerations, which ignore factors such as size of the ligands, are inadequate. For example it is known that the cone angle of a tertiary phosphine has a large influence on the k_2 value in this carbon monoxide insertion reaction [4] and that the size of the alkyl group dramatically effects k_1 [2, 3]. In addition, and importantly, it was the size of the substituted tetrahydrofurans which drastically affected the k_1 values in the reactions of methyldiphenylphosphine with $[(\eta^5\text{-}C_5H_5)(CO)_3MoCH_3]$, [17]. In this regard, it is noteworthy that cyclohexyl- and t-butyl- isocyanide yield significantly different k_3 values (0.22×10^{-4} and 0.33×10^{-4} s^{-1} L mol^{-1} respectively), in their reaction with $[(\eta^5\text{-}C_5H_5)(CO)_3MoCH_2C_6H_5]$ in acetonitrile at 28 °C, suggesting that steric factors are also important in the k_3 step and that, in this situation, cyclohexylisocyanide is effectively the larger ligand.

TABLE II. Substituent Effect on Rate Constants for the Reaction of $[(\eta^5\text{-}C_5H_5)(CO)_3MoCH_2C_6H_4X]$ and t-Butylisocyanide in Acetonitrile at 29 °C.

Substituent (X)	$10^4k_1/s^{-1}$	$10^4k_3/s^{-1}$ L mol^{-1}
p-OCH_3	4.55	1.65
p-CH_3	3.94	0.45
p-H	2.84	0.33
m-CF_3	1.09	0.09
p-CF_3	0.58	0.06

The electronic effect on k_1 of *meta*- and *para*-substituents in the benzyl group (see Table II) was analysed by a Hammett Plot and yielded a reaction sensitivity parameter, ρ, of –0.90 which, as benefits the proposed mechanism, was within experimental error of that obtained in the corresponding reactions [1] with triphenylphosphine (–0.94). The ρ value for the k_3 step of the isocyanide reaction was significantly higher ($\rho = -1.94$); this may be associated with the π-acceptor properties of the isocyanide ligand which could have a significant effect on the electronic properties of the transition state in this pathway.

We confirm the observation of Yamamoto and Yamazaki [6] that, for $[(\eta^5\text{-}C_5H_5)(CO)_3MoCH_2Ph]$ in benzene solution, the reaction with cyclohexylisocyanide yields both the normal carbon monoxide insertion product and an 'imino-acyl' compound which results from isocyanide insertion into the molybdenum–benzyl bond. Our characterisation of this material is presently incomplete because of difficulties of purification resulting from its limited solubility in a variety of solvents and because of problems, for the same reason, of obtaining good quality ^{1}H and ^{13}C NMR spectra. However, we believe that, on the basis of microanalytical results, the pattern of its carbonyl absorptions in its infrared solution spectrum and from its mass spectrum (parent ion observed) that the compound is not as formulated earlier, namely $[(\eta^5\text{-}C_5H_5)(CO)_3MoC(CH_2C_6H_5){=}NC_6H_{11}]$, but rather is a dicarbonyl compound $[(\eta^5\text{-}C_5H_5)(CO)_2MoC(CH_2C_6H_5){=}NC_6H_{11}]$ in which the imino-acyl group acts as a chelating ligand. A similar complex, $[(\eta^5\text{-}C_5H_5)(CO)_2MoC(CH_3){=}NC_6H_5]$, prepared from the reaction of $[(\eta^5\text{-}C_5H_5)(CO)_2Mo(CNC_6H_5)]^-$ with methyl iodide [18], has been characterised crystallographically [19]. The non-equivalence of the benzylic protons of $[(\eta^5\text{-}C_5H_5)(CO)_2MoC(CH_2C_6H_5){=}NC_6H_{11}]$, which we have also observed, is more appropriately explained in terms of diastereotopic nonequivalence rather than by the proposed syn- and anti- isomers in the mono-hapto formulation proposed earlier [6].

Monitoring by ^{1}H NMR of the reaction of cyclohexylisocyanide with $[(\eta^5\text{-}C_5H_5)(CO)_3MoCH_2C_6H_5]$ in benzene indicates that the formation of the chelated imino-acyl complex occurs *via* the normal carbon monoxide insertion product and that the reaction is dramatically accelerated by light. The process could could thus be interpreted as a photolytically-assisted decarbonylation in which the alkyl group migrates to the coordinated carbon atom of the isocyanide moiety rather than to the metal, as is the case in the decarbonylation of phosphine-substituted metal acyls. It is possible that the effectively greater steric influence of cyclohexyl- over t-butylisocyanide, which is suggested by the relative magnitudes of the k_3 values, might provide the necessary driving force for the reaction. Support for this comes from the decarbonylation of phosphine-substituted metal acyls which are known to be positively influenced by increasing cone angle of the coordinated phosphine [20]. This suggestion is clearly incompatible with concepts based on the steric effects around secondary and tertiary carbon atoms, but, in the crowded environment around the metal centre, the greater steric extension and less symmetrical nature of the cyclohexyl group may become significant.

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