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Alkyl Substituent Effects in Ligand-induced Carbon Monoxide Insertion Reactions in $[(\eta^5\text{-}C_5H_5)(CO)_3Mo(\text{benzyl})]$ Systems*

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The first order reactions of benzyl-molybdenum complexes, $[(\eta^5\text{-}C_5H_5)(CO)_3Mo(CH_2C_6H_4X)]$, with triphenylphosphine in acetonitrile to yield the trans-*substituted acyl complexes, $[(\eta^5\text{-}C_5H_5)(CO)_2(PPh_3)Mo(COCH_2C_6H_4X)]$, have an overall rate constant which tends towards a limiting value at high triphenylphosphine concentration The reactivity of the molybdenum–carbon bond is enhanced by electron donating substituents, X, and can be analysed in terms of Hammett substituent parameters A marked enhancement of rate is observed in dimethylsulfoxide, in which solvent the* cis-*acyl complex is the unexpected initial product*

Introduction

The nucleophile-induced insertion of carbon monoxide into transition metal to carbon sigma bonds, to yield acyl–metal products, has been extensively studied, both synthetically and mechanistically, and comprehensively reviewed [1, 2] While many of the factors affecting the reaction, *e g* nature of the solvent, nucleophile, metal and ancillary ligands, are well documented, there has been comparatively little attention given to the variation in reactivity of the metal–carbon bond with change in the alkyl substituent attached to the metal In this paper, we describe our studies of triphenylphosphine-promoted insertion reactions on a series of meta- and para-substituted benzyl compounds, of general formula $[(\eta^5\text{-}C_5H_5)(CO)_3Mo(CH_2C_6H_4X)]$, in polar solvents In this system, a discrete analysis of electronic effects on reactivity is made possible by the relatively constant steric environment at the reacting carbon in the alkyl substituent

Reactivity studies on the corresponding systems $[(CO)_5MnR]$ [3] and $[(\eta^5\text{-}C_5H_5)(CO)_2FeR]$ [4] have suggested a mechanism for this insertion reaction in polar solvents The first stage of the process involves the formation of a (kinetically-inferred) intermediate acyl compound, which may be solvent stabilised, *e g*

$$[(\eta^5\text{-}C_5H_5)(CO)_2FeR] + \text{solvent} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [(\eta^5\text{-}C_5H_5(CO)Fe(COR)]$$

The intermediate, in the second stage, reacts with the nucleophile, L, to give the acyl product,

$$[(\eta^5\text{-}C_5H_5)(CO)Fe(COR)] + L \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [(\eta^5\text{-}C_5H_5)(CO)(L)Fe(COR)]$$

If a steady-state concentration of intermediate is assumed, and if reaction proceeds to completion, the overall rate constant for the reaction, k_{obs}, is given by

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

At high concentrations of nucleophile, k_{obs} thus tends towards k_1, the rate constant for the forward stage of the initial process

Although this mechanism has also become accepted for molybdenum alkyl complexes, the relevant kinetic data is in conflict Thus Craig and Green observed [5], for $[(\eta^5\text{-}C_5H_5)(CO)_3MoR]$ in acetonitrile solution, that k_{obs} was independent of the ligand concentration ($L = {}^nBu_3P$, Ph_3P, or $(PhO)_3P$) A similar observation was made by Hart-Davis and Mawby in similar studies of the corresponding η^5-indenyl compounds in tetrahydrofuran, except in the case of $(PhO)_3P$ where a limiting dependence of k_{obs} on ligand concentration was noted [6] Butler, Basolo and Pearson [7] found that, for $[(\eta^5\text{-}C_5H_5)(CO)_3MoR]$ in tetrahydrofuran, the k_{obs} values were independent of ligand concentration for $L = Ph_3P$ or $(PhO)_3P$ For $L = {}^nBu_3P$, however, the observed rate constant was given by

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TABLE I. Variation of k_{obs} with Triphenylphosphine Concentration in Acetonitrile at 29 °C.

Conc. of PPh_3 ($mol\ l^{-1}$)	$10^4\ k_{obs}$ (s^{-1})
0.0177	1.46
0.0271	1.62
0.0490	2.02
0.0842	2.32
0.128	2.41
0.171	2.44
0.256	2.56

TABLE II. Rate Constants (k_1) for Reaction of $[(\eta^5\text{-}C_5H_5)(CO)_3Mo(CH_2C_6H_4X)]$ with PPh_3 in acetonitrile at 29 °C.

X	$10^4\ k_1$ (s^{-1})
H	2.7
p-MeO	4.5
m-MeO	2.3
p-CF_3	0.7
m-CF_3	1.1
p-F	2.9
m-F	1.4
p-Me	3.6

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

where k_3 is the rate constant for a separate second order reaction which involves the direct nucleophilic attack of ligand on the metal-alkyl complex.

In view of these differing observations, a careful re-analysis has been made in acetonitrile of the effect of ligand concentration on the rate constants of the systems under study. Our experimental aim, given the applicability of the reaction scheme described, was to measure, accurately, k_1 values for the various substituted benzyl molybdenum complexes. In view of the substantial metal–carbon bond breaking likely to occur in this step of the reaction, a significant substituent effect on this rate constant was anticipated.

Results and Discussion

In order to facilitate the comparison of substituent effects it was desirable that the carbonyl insertion reactions proceeded to completion and were free of interference from the subsequent decarbonylation process which yields $[(\eta^5\text{-}C_5H_5)(CO)_2(Ph_3P)MoR]$. For these purposes, acetonitrile, in which the reactions were conveniently rapid and clean at around ambient temperature, was a suitable solvent and triphenylphosphine an appropriate nucleophile.

The analysis of the variation of k_{obs} with nucleophile concentration was carried out for $[(\eta^5\text{-}C_5H_5)(CO)_3Mo(CH_2Ph)]$ by the established [5] infrared method (in which the highest energy carbonyl absorption of the molybdenum alkyl is monitored), using a molybdenum-benzyl concentration of 8×10^{-3} *M*. In all reactions, a substantial excess of triphenylphosphine was present such that the overall reaction was effectively first order in $[(\eta^5\text{-}C_5H_5)(CO)_3Mo(CH_2Ph)]$. The results (Table I) show a smooth increase in k_{obs}, which reaches a limiting value at a concentration of triphenylphosphine of around 0.1–0.2 *M*, and give a good straight line plot of $1/k_{obs}$ *versus* $1/[PPh_3]$, which yields the values, $k_1 = 2.60 \times 10^{-4}\ s^{-1}$ and $k_{-1}/k_2 = 1.57 \times 10^{-2}\ mol\ l^{-1}$. Similar (but less definitive) observations were made for all the substituted benzyl complexes at the higher, but kinetically more convenient, substrate concentration of 2×10^{-2} *M*.

The molybdenum benzyl/acetonitrile/triphenylphosphine reactivity pattern clearly fits the overall reaction scheme discussed earlier. We believe that our successful observation of the trend in k_{obs} with ligand concentration in these experiments is associated with the substantially lower substrate concentration used, and that further experiments under similar conditions might resolve the several apparent conflicts in the previous studies. It is noteworthy that the k_{-1}/k_2 value for the Mo-benzyl system is very much lower than that observed previously [4] for $[(\eta^5\text{-}C_5H_5)(CO)_2FeEt]$ ($k_{-1}/k_2 = 0.36\ mol\ l^{-1}$ in acetonitrile at 47.5 °C) and lower than that for $[(CO)_5MnMe]$, ($5.4 \times 10^{-2}\ mol\ l^{-1}$ in methanol at 25.5 °C with cyclohexylamine as nucleophile [3]). The effect of the low k_{-1}/k_2 ratio is that the limiting k_{obs} is reached at relatively low concentrations of nucleophile; accordingly, the requirement that a substantial excess of nucleophile must be present in order that the overall reaction becomes effectively first order, means that low substrate concentrations are necessary if the appropriate dependence of k_{obs} on nucleophile concentration is to be observed.

The k_1 values (limiting k_{obs} values by the infrared method) for eight substitued benzyl complexes are shown in Table II. The rate constants increased significantly with increasing electron-donating ability of the substituent with the most reactive system (*p*-methoxy) reacting approximately five times faster than the least reactive (*p*-trifluoromethyl). The results were analysed in terms of Hammet σ substituent parameters and yield a straight line plot (correlation coefficient, 0.98), and a modest value of the reaction parameter, ρ, of -0.97. Rate data were also obtained by a ^1H NMR method, in which the η^5-C_5H_5 resonances of the starting benzyl complex and the acyl product were monitored, and gave a closely similar Hammett plot.

The observed enhancement of reaction by electron donating substituents is in line with earlier observations [8, 9], for the $[(CO)_5MnR]/CO$ system in 2,2′-diethoxydiethylether, of a reactivity order R = Me > CH_2F > CF_3. Although the conclusion regarding electronic effects in the latter case formally requires qualification because of the substantial change in the steric environment at the reacting carbon atom, our results for carbonyl insertion reactions in $[(\eta^5\text{-}C_5H_5)(CO)_2FeR]$ systems, in dimethylsulfoxide [10], suggest strongly that steric enhancement of such reactions occurs. If this is also the case for the manganese complexes, the steric and electronic factors along the series (Me, CH_2F, CF_3) would operate in opposite directions, and the above conclusion regarding electronic effects would, then, be unambiguous.

A related decarbonylation process, which involves C–C bond breaking, and which formally corresponds to the k_{-1} step has been studied by Kubota *et al.* in the process,

$$[(Ph_3P)_2Cl_2Ir(COR)] \rightarrow [(Ph_3P)_2Cl_2(CO)IrR],$$

where R represents benzyl and the substituted benzyl systems (*p*-methoxy, *p*-methyl and *p*-nitro) [11]. An enhancement of rate with electron-donating substituent was again observed, with a reaction parameter, ρ, of –0.30. Unfortunately it is not possible to study a comparable reaction for the molybdenum complexes. The first-order decarbonylation process, $[(\eta^5\text{-}C_5H_5)(CO)_2(Ph_3P)Mo(COR)] \rightarrow [(\eta^5\text{-}C_5H_5)(CO)_2(Ph_3P)MoR] + CO$, is observed in acetonitrile at 60 °C in the presence of free triphenylphosphine but the rate determining step is believed to involve the dissociation of a terminal carbon monoxide group from the acyl complex [12]. Our observed rate constants for this process (*p*-CF_3 benzyl, $k = 10.4 \times 10^{-6}\ s^{-1}$; benzyl, $4.7 \times 10^{-6}\ s^{-1}$; *p*-MeO benzyl, $4.0 \times 10^{-6}\ s^{-1}$), while in the reverse order of that observed by Kubota *et al.*, are explicable simply in terms of the greater effect which more strongly electron-withdrawing acyl substituents on weakening the Mo–CO bond.

The impossibility of separating k_{-1} and k_2 from the reactivity data for the molybdenum complexes with triphenylphosphine in acetonitrile prompted us to explore similar reactions in dimethylsulfoxide. In the latter solvent, $[(\eta^5\text{-}C_5H_5)(CO)_2FeR]$ complexes have been observed [13] to yield a solvent-stabilised acyl complex, $[(\eta^5\text{-}C_5H_5)(CO)(DMSO)Fe(COR)]$, which can then be further reacted with triphenylphosphine, which displaces the coordinated dimethylsulfoxide. The rate constants k_1, k_{-1} and k_2 can be separately obtained from studies of the individual reactions. Unfortunately, for a number of molybdenum alkyls (R = Me, Et, benzyl), at temperatures from 20–70 °C, and over long periods, no comparable solvated acyl complex could be detected (NMR). However, not unexpectedly, the addition of triphenylphosphine to the solutions at ambient temperature caused a rapid reaction which yielded the acyl compounds, $[(\eta^5\text{-}C_5H_5)(Ph_3P)(CO)_2Mo(COR)]$. A striking difference in these reactions from those in acetonitrile (monitored by ^1H NMR) was the appearance of a relatively broad (~2 Hz) resonance slightly (0.1 ppm) to low field of the $(\eta^5\text{-}C_5H_5)$ resonance of the starting alkyl, in addition to the expected doublet at higher field associated with the normal acyl product, $[(\eta^5\text{-}C_5H_5)(Ph_3P)(CO)_2Mo(COR)]$. The latter, for R = Me, has been characterised crystallographically [14] as *trans* (on an idealised square pyramidal structure for the complex), and is routinely identified spectroscopically on the basis of this feature of its ^1H NMR spectrum [15]. The additional peak in the spectrum is, we believe, attributable to the hitherto unobserved *cis*-acyl complex, in view of the correspondence of the chemical shift of the $(\eta^5\text{-}C_5H_5)$ protons with that noted [15, 16] for the isolable compounds *cis*-$[(\eta^5\text{-}C_5H_5)(CO)_2(Ph_3P)MoX]$, [X = Me, H, I *etc.*], for which ^{31}P–^1H coupling is also unresolved. More thorough identification of the proposed *cis*-form has been hindered by the fact that its relative proportion is greater in the early stages of reaction but drops off rapidly as the reaction proceeds (*e.g.* for R = benzyl, at 29 °C, the *cis*-product constituted 13% of the product at 20% reaction after 1.5 minutes, 14% at 49% reaction after 5 minutes, 5% at 70% reaction after 8 minutes, and 1% at 91% reaction after 16 minutes). Attempts to attenuate the relative concentration of the *cis*-form were unsuccessful; for $^nBu_3P$ and the *m*-methoxybenzyl complex, the *cis*-resonance had disappeared completely within three minutes, and for $(MeO)_3P$ and the sterically undemanding phosphite, $Et(CH_2O)_3P$, only the *trans*-product was observed. A very delicate balance of steric and electronic factors, which may affect not only the insertion process but also the *cis–trans* isomerisation, is clearly involved. The same phenomenon, for molybdenum ethyl and *p*-methoxybenzyl complexes, was also noted for the reaction with triphenylphosphine in N,N-dimethylformamide, although, for corresponding reactions, the intensity of the lower field resonance was approximately half that in dimethylsulfoxide.

The observations in dimethylsulfoxide are of interest in view of speculation [5] on the possible involvement of the *cis*-acyl species in the general reaction scheme for molybdenum complexes. Although the *cis* form has not previously been detected, it has been postulated [17] as an intermediate,

TABLE III Analytical Data for $[(\eta^5\text{-}C_5H_5)(CO)_3Mo(CH_2\text{-}C_6H_4X)]$ Complexes

X	M Pt °C	Found		Calculated	
		%C	%H	%C	%H
H	88–89	53 59	3 87	53 58	3 57
p-OMe	103–105	52 26	3 87	52 47	3 83
m-OMe	102–104	52 53	3 89	52 47	3 83
p-CF_3	96–98	47 32	2 83	47 53	2 72
m-CF_3	115–116	47 51	2 81	47 53	2 72
p-F	88–89	51 17	3 13	50 86	3 11
m-F	105–107	50 80	3 23	50 86	3 11
p-Me	94–95	54 66	4 13	54 87	4 00

in the reaction of $[(\eta^5\text{-}C_5H_5)(CO)_3Mo(CH_2)_3Br]$ with triphenylphosphine, which undergoes spontaneous internal cyclisation to give a *cis*-2-oxacyclopentylidenemolybdenum cation This *cis* cation then slowly rearranges to the corresponding *trans* species *Cis*- and *trans*- forms of the molecules, $[(\eta^5\text{-}C_5H_5)(CO)_2(^tBuNC)MoR]$, (R = Me or CH_2Ph), have also been observed, by ^1H NMR, in chloroform solution [18] Our recent studies [19] of the reaction of $[(\eta^5\text{-}C_5H_5)(CO)_3Mo(CH_2Ph)]$ with ^tBuNC in acetonitrile have, in fact, shown the same general ^1H NMR features as for the DMSO/triphenylphosphine reaction, with a relatively higher amount of the *cis*-form being present in the initial stages

The reactions of molybdenum alkyls in dimethylsulfoxide show, as for acetonitrile, an increase in overall rate constant with increase in the concentration of triphenylphosphine At 29 °C, for R = CH_2Ph, k_1 ($4\ 05 \times 10^{-3}\ s^{-1}$) is substantially higher than for the same reaction in acetonitrile ($2\ 69 \times 10^{-4}\ s^{-1}$), as is the value of k_{-1}/k_2 ($2\ 3 \times 10^{-1}$ compared with $1\ 6 \times 10^{-2}\ mol\ l^{-1}$) The marked solvent effect on k_1 provides further support for the view that the metal–carbon bond breaking process in the transition state leading to the acyl intermediate, is solvent-assisted [3] The higher value of k_{-1}/k_2 may be interpretable in terms of the higher activation energy required for the displacement of the more strongly coordinated dimethylsulfoxide by triphenylphosphine, but definitive comment is impossible because of the inability to separate k_{-1} and k_2

Experimental

General Conditions

All preparative and kinetic work was carried out under nitrogen using Schlenk techniques Solvents were distilled, under nitrogen, from the drying agents indicated, immediately prior to use acetonitrile (phosphorus pentoxide), tetrahydrofuran (calcium hydride), dichloromethane (phosphorus pentoxide), hexane (calcium hydride) Dimethylsulfoxide was dried over molecular sieve 4A Infrared spectra were recorded on a PE457 spectrophotometer and ^1H NMR spectra on Varian EM360 and Jeol PS100 spectrometers Analyses were performed by the Microanalytical Laboratory of this Department and by the Australian Microanalytical Service, C S I R O , Melbourne

Preparation of Molybdenum Benzyl Complexes

These were prepared in good yield (~50%) from the reaction of the appropriate benzyl chloride (or bromide) with the $[(\eta^5\text{-}C_5H_5)(CO)_3Mo]^-$ anion, according to the standard procedure [20] The crude product was purified by column chromatography (alumina Grade II–III, in hexane) and recrystallised from hexane The complexes all showed the characteristic two peak infrared spectrum (in acetonitrile ~2008s, 1922vs cm^{-1}) and, in the ^1H NMR spectrum in $CDCl_3$ a $(\eta^5\text{-}C_5H_5)$ singlet at ~5 2 ppm and a CH_2 singlet at ~2 9 ppm The compounds were further characterised analytically and showed sharp melting points (Table III)

Kinetic Measurements

Infrared method

The reaction of the molybdenum benzyl complex (generally 0 02 *M* in the appropriate solvent) was followed by observation of the decrease in intensity of its high energy carbonyl stretching vibration A Beer's law calibration plot was constructed for each substrate Plots of $\log_{10}$ [complex] *versus* time were linear (least squares), provided that triphenylphosphine was in better than two-fold excess, up to 3 half-lives Experiments involving at least four different nucleophile concentrations were carried out for each substrate Reactions were carried out in the dark, in thermostatted baths Samples were withdrawn periodically by syringe and injected into 0 2 mm sodium chloride solution cells, or, in the case of the experiments at 0 008 *M* for $[(\eta^5\text{-}C_5H_5)(CO)_3Mo(CH_2Ph)]$, into 0 5 mm cells

^1H NMR method

The reactions of equimolar quantities of $[(\eta^5\text{-}C_5H_5)(CO)_3Mo(CH_2C_6H_4X)]$ and triphenylphosphine, at 0 2 *M* in either CH_3CN or d_6-DMSO, were followed by changes in peak height of the $(\eta^5\text{-}C_5H_5)$ resonances of substrate (~5 4 ppm) and acyl product (~5 05 ppm, $J_{^{31}P-^1H} \sim 1$ Hz) NMR tubes were made up under nitrogen Good linear plots of $\log_{10}$ (substrate) *versus* time were obtained up to about two half-lives, at which point deviations arising from the substantial reduction in nucleophile concentration started to become apparent

Characterisation of trans-*Acyl Products*

All compounds exhibited the expected carbonyl stretching frequencies (~1936 s; 1850vs cm^{-1} in acetonitrile) and an acyl stretch (~1620 cm^{-1}). The ^{1}H NMR spectra showed a (η^5-C_5H_5) doublet around 5.05 ppm ($J_{^{31}P-^{1}H}$ ~ 1 Hz) and a benzylic singlet ~4.3 ppm in acetonitrile.

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