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Solvent and nucleophile effects on the carbonyl insertion reaction into metal–carbon bonds

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Abstract

The rate constant, k_3, for the direct insertion of carbon monoxide induced by tertiary phosphines into $[(\eta^5\text{-}C_5H_5)(CO)_3MoCH_2C_6H_5]$ in toluene solution decreases steadily with increasing cone angle of the phosphine. In contrast, for $[(CO)_5MnCH_2C_6H_5]$, k_3 increases with decrease in the Tolman electronic parameter, ν, of the phosphine (i.e., with increasing electron donation) and does not correlate with the cone angle. However, k_3 reflects the size of the phosphine to a greater degree as the size of the benzyl substituent on manganese increases. An analysis of k_1 values in the solvent-assisted insertion pathway has been made for both the molybdenum and manganese systems in THF, 2-MeTHF and 2,5-Me_2THF solutions. The general decrease in k_1 with increasing size of the solvent for the cyclopentadienyl-molybdenum system becomes less marked as the size of the benzyl substituent increases. The manganese complexes are relatively less sensitive to solvent size. A comparison has been made between the nucleophilic role of a solvent molecule in the k_1 step and that of a tertiary phosphine in the k_3 step.

Introduction

Two reaction pathways for the ligand-induced insertion of carbon monoxide into a metal–carbon sigma bond in transition metal carbonyl systems, leading to a ligand-substituted acyl product, have been proposed [1]. In the k_1 step of the solvent-assisted pathway a polar solvent molecule induces the formation of an acyl intermediate, from which coordinated solvent is displaced by the nucleophilic ligand in the k_2 step. The second pathway (k_3), which is favoured in non-polar solvents, involves the direct reaction of the nucleophile with the metal alkyl.

Formally, the solvent in the solvent-assisted path and the ligand, e.g. a tertiary phosphine or an alkylisocyanide, in the direct route are performing a similar role as nucleophiles in inducing the intramolecular migration [2] of an alkyl group to a

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carbonyl carbon atom. In this paper we try to evaluate, where possible, the steric and electronic factors which affect their relative reactivities.

Specifically, we have explored steric and electronic effects, on the rate constant, k_3, of the alkyl group (R) and of the nucleophile (L), for reactions of the complexes, $[(CO)_5MnCH_2C_6H_{5-n}X_n]$ and $[(\eta^5\text{-}C_5H_5)(CO)_3MoCH_2C_6H_{5-n}X_n]$, where X = H, 2-Me, 2,4,6-Me_3 and 2,4,6-i-Pr_3, with tertiary phosphines in toluene.

In respect of k_1, we have extended the work of Wax and Bergman [3] on the variation in k_1 for the $[(\eta^5\text{-}C_5H_5)(CO)_3MoMe]$ system in tetrahydrofuran and α-methyl-substituted tetrahydrofurans of similar dielectric constant but with markedly different donicity. The large decrease in k_1 as the extent of α-methyl substitution is increased was interpreted by Wax and Bergman in terms of increased steric hindrance to direct coordination of solvent to molybdenum in the transition state. Our further investigation is directed particularly to an evaluation of the relative solvent effect, within this series of tetrahydrofurans, as the size of the alkyl group on molybdenum is changed. An extension to $[(CO)_5MnR]$ complexes has also been made; a preliminary report of this work has appeared [4].

Results and discussion

The observed rate constant, k_{obs}, which expresses the competition between the two reaction paths, is given by eq. 1. The derivation assumed that a steady-state

$$k_{obs} = \{k_1k_2[L]/(k_{-1} + k_2[L])\} + k_3[L] \qquad (1)$$

concentration of a solvated-intermediate exists and that, as observed in the systems under study, the reaction proceeds to completion.

In polar solvents, such as DMSO or acetonitrile, the k_1,k_2 path predominates [1,4–8] and the k_3 contribution can generally be ignored. If $[L] \gg [(CO)_nMR]$, the reaction is effectively first order in metal alkyl. For high nucleophilicity and at high concentrations of L, $k_2[L] \gg k_{-1}$ and $k_{obs} \simeq k_1$. At very high concentrations of L [9] and/or for less polar solvents [3], a mixed pathway may be followed and $k_{obs} \simeq (k_1 + k_3[L])$. For cyclohexane and toluene, the effect of the k_1,k_2 steps is insignificant and $k_{obs} \simeq k_3[L]$, [7,9].

The measurements of k_3 in the $[(\eta^5\text{-}C_5H_5)(CO)_3MoCH_2C_6H_{5-n}X_n]$ and $[(CO)_5MnCH_2C_6H_{5-n}X_n]$ systems were made in toluene, at 30 °C, using a range of concentrations of tertiary phosphine, as nucleophile, up to 1 *M*.

For the manganese system, the concentration of the metal alkyl was monitored by observation of the decreasing infrared absorbance of the sharp carbonyl vibration around 2100 cm^{-1}. The k_{obs} values varied linearly with concentration of phosphine and the gradient yielded k_3 directly (Table 1). For the unsubstituted benzyl compound (X_n = H), there is a large variation in k_3 with tertiary phosphine, with Cy_3P being exceptionally reactive. The very high nucleophilicity of Cy_3P was also apparent from a significant k_3 contribution to k_{obs}, even at moderate nucleophile concentration, in the reaction in acetonitrile [10]. The k_3 values in toluene increase with decrease in the Tolman electronic parameter, ν, [11] of the phosphine, that is with increasing electron-donating capacity of the nucleophile. The plot of log k_3 versus ν is approximately linear. There is no correlation of k_3 with the cone angle [11] of the phosphine. As the size of the alkyl group increases, the relative difference in reactivity between Ph_3P and Cy_3P is much reduced (the

Table 1

Variation in k_3 with cone angle (θ) and electronic parameter (ν) for the reactions of $[(\eta^5\text{-}C_5H_5)(CO)_3MoCH_2C_6H_{5-n}X_n]$ and $[(CO)_5MnCH_2C_6H_{5-n}X_n]$ with tertiary phosphines in toluene at 30 °C

Metal	X	L	10^6k^3 (L mol^{-1} s^{-1})	θ	ν
Mo	H	$PhMe_2P$	19.3	122	2065.3
	H	Et_3P	19.2	132	2061.7
	H	Ph_2MeP	9.9	136	2067.0
	H	Ph_3P	4.3	145	2068.9
	H	$i\text{-}Bu_3P$	3.4	143	2059.7
	H	$t\text{-}BuPh_2P$	1.9	157	2064.7
Mn	H	Ph_3P	3.2	145	2068.9
	H	$PhMe_2P$	9.2	122	2065.3
	H	Et_3P	49	132	2061.7
	H	Cy_3P	1560	170	2056.4
Mn	2-Me	Ph_3P	5.0		
	2-Me	Cy_3P	100		
Mn	2,4,6-Me_3	Ph_3P	11.9		
	2,4,6-Me_3	Ph_3P	10.5 [a]		
	2,4,6-Me_3	Cy_3P	52		
Mn	2,4,6-i-Pr_3	Ph_3P	12.0		

[a] Measured in $CHCl_3$.

reactivity ratio is approximately 500 for X = H; 20 for X = 2-Me; 4 for X = 2,4,6-Me_3).

We have also examined the trend in k_3 values with change in the alkyl group for reactions of $[(CO)_5MnCH_2C_6H_{5-n}X_n]$ for a given tertiary phosphine in toluene. For the reaction of $[(CO)_5MnCH_2C_6H_{5-n}X_n]$ with Ph_3P, there is a steady increase in k_3 as the degree of *ortho*-methyl substitution in the benzyl group increases. In view of the small electronic effect of the substituent, we interpret the change as reflecting the increased size of the benzyl group. The effect is broadly similar to the effect of these alkyl groups on k_1, for the reactions of $[(CO)_5MnCH_2C_6H_{5-n}X_n]$ [4,8] and $[(\eta^5\text{-}C_5H_5)(CO)_3MoCH_2C_6H_{5-n}X_n]$ [12] with tertiary phosphines in acetonitrile, which we interpreted (see previous paper [8]) in terms of a weakening of the metal–alkyl bond as the size of the alkyl group becomes larger, with effective lowering of the activation energy of this step. However, the trend in k_3 with alkyl group is reversed in the case of the larger phosphine, Cy_3P. The explanation may lie in the competition between two steric factors; one, a ground state effect, is, effectively, enhancement from metal–carbon bond weakening as the size of the alkyl group increases, and the other, an inhibition, results from steric restraints in the transition state of the migration pathway. The second effect is probably predominant in the case of k_1 in reactions of $[(\eta^5\text{-}C_5H_5)(CO)_3MoCH_2C_6H_{5-n}X_n]$ with Ph_3P in acetonitrile, when the benzyl group contains two large *ortho* substituents (e.g. i-Pr) [12], and may also assume relatively greater importance in the present study of k_3 for a bulky nucleophile such as tricyclohexylphosphine.

The fact that in the manganese system the major effect of a tertiary phosphine on k_3 is electronic and not steric is of considerable significance in relation to the observed dependence of k_2 on steric factors [8]. The k_3 step is necessarily associative, and would be expected to show a more pronounced steric effect than the k_2 step if, as claimed [13,14], this involves attack of the nucleophile on a coordinatively unsaturated species formed by prior dissociation of the solvent molecule from the intermediate. We believe that the results suggest that the k_2 process is associative, albeit with a substantial degree of bond breaking to the solvent molecule before significant bond formation to the incoming nucleophile occurs.

Measurements of k_3 values for the cyclopentadienyl-molybdenum system were obtained from reactions of $[(\eta^5\text{-}C_5H_5)(CO)_3MoCH_2C_6H_5]$ with tertiary phosphines in toluene by monitoring Cp resonances in the ^1H NMR spectrum. Small amounts of $[(\eta^5\text{-}C_5H_5)(CO)_2(L)MoCH_2C_6H_5]$ were also formed, by decarbonylation of the acyl product, but, kinetically, as with the manganese reactions, this further reaction has no effect on the analysis of k_3 because the reverse (k_{-2} and k_{-3}) processes are very slow, i.e. reactions proceed to completion. The extent of decarbonylation was most pronounced in the case of the large phosphines, $i\text{-}Bu_3P$ and $t\text{-}BuPh_2P$, consistent with observations from previous work [15]. The k_3 values for molybdenum decrease with increasing cone angle, in contrast to depending on the electronic parameter, as in the manganese system. For the large (cone angle = 184°) and highly basic tris(2,4,6-trimethoxyphenyl)phosphine [16], the surprisingly high k_3 value ($\sim 3 \times 10^{-4}$ L mol^{-1} s^{-1}) suggests that, in extreme cases, the electronic effect may override the effect of cone angle [17].

The variation in k_3 values in the molybdenum system is in line with that observed previously ($n\text{-}Bu_3P > (n\text{-}BuO)_3P > Ph_3P > (PhO)_3P$) by Basolo and coworkers [7] for the reactions of $[(\eta^5\text{-}C_5H_5)(CO)_3MoCH_3]$, in toluene at 50.7 °C. The choice of nucleophiles in these experiments did not, though, allow for the variations in k_3 to be separately analysed in terms of steric and electronic factors.

We have previously obtained k_3 values for the reactions of $[(\eta^5\text{-}C_5H_5)(CO)_3MoCH_2C_6H_5]$ with t-butylisocyanide and cyclohexylisocyanide at 30 °C in acetonitrile, THF and cyclohexane [9]. The k_3 values, (4×10^{-5} L mol^{-1} s^{-1} and 2×10^{-5} L mol^{-1} s^{-1} respectively and, within experimental error, insensitive to solvent) were slightly higher than k_3 for the smallest phosphine studied.

The formal similarity between the nucleophilic role of the solvent in the k_1 step and that of the ligand in the k_3 step was noted in the Introduction. A direct comparison of their relative nucleophilicity can be made if the rate constant, k_1, which is effectively first order because of the large solvent excess, is converted to a second order constant, k_1, by dividing k_1 by the solvent concentration in mol L^{-1}. For $[(CO)_5MnCH_2C_6H_{5-n}X_n]$, k_1' in acetonitrile [4,8] is 1.6×10^{-5} L mol^{-1} s^{-1} (and, as the mechanism requires, independent of phosphine) and, for tetrahydrofuran, 5.4×10^{-6} L mol^{-1} s^{-1} (Table 2). Both values are higher than the value of k_3 in the $[(CO)_5MnCH_2C_6H_5]$ series for the least reactive phosphine (Ph_3P, 3.2×10^{-6} L mol^{-1} s^{-1}) but very much less than k_3 for the very reactive Cy_3P (1.56×10^{-3} L mol^{-1} s^{-1}). For $[(\eta^5\text{-}C_5H_5)(CO)_3MoCH_2C_6H_5]$, the k_1' value in acetonitrile (1.5×10^{-5} L mol^{-1} s^{-1}) is about 3 times higher than the observed k_3 (toluene) for Ph_3P; the value for DMSO (2.9×10^{-4} L mol^{-1} s^{-1} is about 700 times higher and for THF (1.3×10^{-6} L mol^{-1} s^{-1}) about 4 times less.

The effect of the size of the alkyl group in the manganese complexes on the

Table 2

Variation in rate constants, k_1 and k_1', for the reactions of $[(CO)_5MnCH_3]$ and $[(CO)_5MnCH_2C_6H_{5-n}X_n]$ with Ph_3P in tetrahydrofuran and substituted tetrahydrofurans at 30 °C

	Solvent	10^5k_1 (s^{-1})	$10^6k_1'$ ($L\ mol^{-1}\ s^{-1}$)
R = Me	THF	17.9	14.5
	2-MeTHF	11.6	11.6
	2,5-Me_2THF	0.53	0.64
X = H	THF	6.7	5.4
	2-MeTHF	4.1	4.1
	2,5-Me_2THF	2.8	0.34
2-Me	THF	5.8	4.7
	2-MeTHF	3.3	3.3
	2,5-Me_2THF	3.7	4.5
2,4,6-Me_3	THF	19.2	15.6
	2-MeTHF	10.9	10.9
	2,5-Me_2THF	5.1	6.1
2,4,6-i-Pr_3	THF	51	41
	2,5-Me_2THF	17	20

sensitivity to change of the k_3 value, among the set of phosphine ligands, encouraged us to explore the effect of the size of the alkyl group on relative k_1 values, measured in tetrahydrofuran and α-methyl-tetrahydrofurans as the reaction solvent. Previously, for the $[(\eta^5\text{-}C_5H_5)(CO)_3MoCH_3]/PhMe_2P$ system, a reactivity order for k_1, THF > 2-MeTHF ≫ 2,5-Me_2THF, had been observed [3]. This result, which is in line with the observed decrease in k_3 with increasing cone angle of tertiary phosphine in this system, has been confirmed at several temperatures. The reactions, which were monitored by infrared spectroscopy of the carbonyl region, were carried out at high concentrations of phosphine, in the domain where $k_{obs} = (k_1 + k_3[L])$. The plots of k_{obs} versus concentration of $PhMe_2P$ were consistently linear; extrapolation to zero ligand concentration gave k_1 and the gradient, k_3. The k_{obs} plots were, with the exception of one case noted below, approximately parallel. There is thus no experimentally detectable solvent effect on k_3.

Our values of k_1 for $[(\eta^5\text{-}C_5H_5)(CO)_3MoCH_2C_6H_5]$ show a similar trend to those of the methyl compound (Table 3). Unexpectedly though, the differentiation in k_1 between the solvents was reduced, rather than increased, as the size of the alkyl group became larger; for example, the k_1 values for $[(\eta^5\text{-}C_5H_5)(CO)_3MoCH_2C_6H_2Me_3\text{-}2,4,6]$ in 2-MeTHF and 2,5-Me_2THF were comparable. For reactions at 40 °C, while there is a roughly 15-fold increase in k_1 for THF compared with 2,5-Me_2THF for R = Me and $CH_2C_6H_5$, it is only approximately 4-fold for R = $CH_2C_6H_4Me$-2, and 2-fold for R = $CH_2C_6H_2Me_3$-2,4,6. Also, the relative change in the k_1 value with changing size of the alkyl group, for a given solvent, becomes larger as the solvent size increases.

The result is the opposite of that predicted from the simple concept of increased steric restriction in the migration pathway as the alkyl group becomes larger. The explanation may lie with the degree to which the bond with the solvent molecule is

Table 3

Variation in rate constants, k_1, k_1' and k_3, for the reactions of $[(\eta^5\text{-}C_5H_5)(CO)_3MoCH_3]$ and $[(\eta^5\text{-}C_5H_5)(CO)_3MoCH_2C_6H_{5-n}X_n]$ with Ph_2MeP in tetrahydrofuran and substituted tetrahydrofurans

	Solvent	T (°C)	10^4k_1 (s^{-1})	$10^6k_1'$ ($L\ mol^{-1}\ s^{-1}$)	10^6k_3 ($L\ mol^{-1}\ s^{-1}$)
R = Me	THF	40	1.53	12.4	30
	2-MeTHF	40	0.38	0.38	30
	2,5-Me_2THF	40	0.10	0.12	30
	THF	50	3.75	30.4	53
	2-MeTHF	50	0.86	0.86	52
	2,5-Me_2THF	50	0.15	0.18	57
	THF	60	8.07	65.4	140
	2-MeTHF	60	1.77	1.77	122
	2,5-Me_2THF	60	0.31	0.37	123
X = H	THF	40	0.60	4.9	25
	2-MeTHF	40	0.18	1.8	22
	2,5-Me_2THF	40	0.03	0.36	18
	THF	50	1.47	11.9	48
	2-MeTHF	50	0.32	3.2	50
	2,5-Me_2THF	50	0.10	0.12	54
2-Me	THF	40	1.45	11.8	32
	2-MeTHF	40	0.35	3.5	37
	2,5-Me_2THF	40	0.17	2.0	38
	THF	50	3.55	29	40
	2-MeTHF	50	0.88	8.8	50
	2,5-Me_2THF	50	0.36	4.3	120, 170
2,4,6-Me_3	THF	40	1.31	10.6	58
	2-MeTHF	40	0.53	5.3	42
	2,5-Me_2THF	40	0.46	5.5	40
	THF	50	4.30	35	133
	2-MeTHF	50	2.23	22	117
	2,5-Me_2THF	50	1.97	20	128

formed in the transition state of the k_1 step. For larger alkyl groups, and a correspondingly weaker metal–carbon bond, the degree of metal–carbon bond breaking may be enhanced relative to the extent of metal–solvent bond formation. If this is the case, then relative differences in reactivity between the solvents will be reduced.

We note that a similar explanation could be applied to the trend, discussed earlier, in the relative k_3 reactivity of Ph_3P and Cy_3P with $[(CO)_5MnCH_2C_6H_{5-n}X_n]$ as the degree of substitution of the benzyl group increased. The issue is, though, less clear-cut here because of the significant differences between both the steric and the electronic effects of the phosphines.

Values of k_3 for reactions of $[(\eta^5\text{-}C_5H_5)(CO)_3MoCH_2C_6H_{5-n}X_n]$ in the tetrahydrofurans were also obtained. Although they are approximate, a clear trend exists with alkyl substituent ($R = CH_2C_6H_2Me_3\text{-}2,4,6 > CH_2C_6H_4Me\text{-}2 > CH_2C_6H_5$, and $CH_3 > CH_2C_6H_5$). There is, within experimental error, no variation in k_3 between the tetrahydrofurans. The k_3 value (for Ph_2MeP as the nucleophile) is significantly higher than the corresponding k_1' values, obtained by dividing k_1 by the solvent concentration, for the several tetrahydrofurans.

Although, in the reactions of the molybdenum complexes in the tetrahydrofurans, the normally pale yellow reaction solutions developed pale pink/dark red colours, particularly in light, we do not believe that the result is pertinent to the mechanistic discussion. For $[(\eta^5\text{-}C_5H_5)(CO)_3MoCH_2C_6H_{5-n}X_n]$, the degree of the discolouration was $X = 2,4,6\text{-}Me_3 \gg 2\text{-}Me > H$, and $2,5\text{-}Me_2THF \gg 2\text{-}MeTHF > THF$. To minimise this side reaction, all reactions were carried out in the dark. In all cases, except for $X = 2\text{-}Me$ in $2,5\text{-}Me_2THF$, where different k_3 values (but similar k_1) were obtained in separate sets of experiments, results were reproducible.

The results observed for $[(\eta^5\text{-}C_5H_5)(CO)_3MoCH_2C_6H_4Me\text{-}2]$ in $2,5\text{-}Me_2THF$ (common k_1, different k_3), and some degree of scatter in and increased magnitude of the k_1 values for reactions carried out in the light, raised the question of whether there could be specific catalysis by the photolytically-produced product. We have been unable to characterise the decomposition product, which is present only in very small amounts, but we believe that the pink to red colouration of the solutions results from the formation of the dimer, $[(\eta^5\text{-}C_5H_5)(CO)_3Mo]_2$, or a phosphine-substituted analogue, both of which can form either by photolytic or thermal decomposition of $[(\eta^5\text{-}C_5H_5)(CO)_3MoCH_2C_6H_{5-n}X_n]$ or phosphine-substituted analogues [18]. In view of the report [19] that $[(\eta^5\text{-}C_5H_5)(CO)_2Fe]_2$, catalyses Lewis-base substitution reactions of metal carbonyls and metal carbonyl halides, and although there is, to our knowledge, no evidence that similar catalysis occurs for $[(\eta^5\text{-}C_5H_5)(CO)_3Mo]_2$, or for substitution in metal carbonyl alkyls, we made a preliminary study of the reactivity in the THF solvents in the presence of added $[(\eta^5\text{-}C_5H_5)(CO)_3Mo]_2$; no rate enhancement was detectable. The reason for the erratic kinetic behaviour induced by photolysis remains unclear.

Our observations show that the tendency towards photolytic decomposition is greater for $X = 2,4,6\text{-}Me_3 > 2\text{-}Me > H$, for benzyl > methyl complexes and for $2,5\text{-}Me_2THF > 2\text{-}MeTHF > THF$. If the photolysis involves the decomposition of $[(\eta^5\text{-}C_5H_5)(CO)_2(Ph_2MeP)MoR]$, the trends may be reflecting the extent to which decarbonylation of the acyl, or the direct formation of a phosphine-substituted metal alkyl, occurs. While no direct evidence on solvent effects on either process is available, decarbonylation of $[(\eta^5\text{-}C_5H_5)(CO)(L)FeCOR]$ is known to be enhanced in less polar solvents [20].

A similar investigation for the $[(CO)_5MnCH_2C_6H_{5-n}X_n]$ system, in tetrahydrofuran and in the α-methyl-substituted tetrahydrofurans, showed that k_1 values, although generally trending in the same manner, were less sensitive to solvent than in the cyclopentadienyl-molybdenum system. The result is consistent with the relatively lower influence of steric factors previously observed in the reactivity of $[(CO)_5MnR]$ complexes [4,8]. Although there is some irregularity in the k_1 values, the order of reactivity with alkyl substituent, $R = CH_2C_6H_2Me_3\text{-}2,4,6 > CH_2C_6H_4Me\text{-}2 > CH_2C_6H_5$, is the same as observed for the molybdenum complexes. The k_1 values for $R = CH_3$ are, as for the molybdenum system, larger than for $R = CH_2C_6H_5$, but a similar relative difference between the tetrahydrofurans exists.

We note that our first unsuccessful attempts to measure k_3 for the reactions of $[(\eta^5\text{-}C_5H_5)(CO)_3MoCH_2C_6H_{5-n}X_n]$ with phosphines were made in acetonitrile, at high ligand concentrations where $k_{obs} = (k_1 + k_3[L])$. The method had worked

Table 4

Variation of k_{obs} for the reactions of [(η^5-C_5H_5)(CO)$_3$MoCH$_2$C$_6$H$_5$] with tertiary phosphines in acetonitrile at 30 ° C

[L]	10^4k_{obs}/s^{-1} (mol L^{-1})	[L]	10^4k_{obs}/s^{-1} (mol L^{-1})	[L]	10^4k_{obs}/s^{-1} (mol L^{-1})
PhMe$_2$P		*Ph$_2$MeP*		*t-BuPh$_2$P*	
0.47	3.0	0.49	2.5	0.31	2.5
0.75	3.6	0.75	2.6	0.51	2.4
0.91	3.5	1.01	2.5	0.69	1.2
1.40	3.5	2.00	2.3	0.83	1.1
2.00	4.6	2.50	2.3	1.47	0.9
2.33	4.3	3.00	2.1		
2.99	4.4	neat	0.9		
3.49	4.5				
neat	2.1				
Ph$_2$EtP		*Et$_3$P*			
0.56	2.5	0.75	2.9		
0.97	2.3	2.26	2.6		
1.50	1.9	5.65	2.0		
2.03	1.72	neat	1.8		
neat	0.4				

reasonably well previously (for X = H) in reactions with alkyl isocyanides, but a decrease in k_{obs} occurred at high (greater than 5 *M*) concentrations of isocyanide, with the value tending towards that in neat isocyanide. The decrease was exaggerated in solvents (e.g., DMSO) for which k_1 was high, but was insignificant in THF and cyclohexane [9]. The decrease in k_{obs} was interpreted in terms of the effective lowering in the contribution from k_1 (i.e. k_1' [S]) as the solvent concentration decreased significantly.

In the reactions of tertiary phosphines with [(η^5-C_5H_5)(CO)$_3$MoCH$_2$C$_6$H$_5$] in acetonitrile, an increase in k_{obs} with increasing concentration of phosphine was only observed for PhMe$_2$P. The results are shown in Table 4. With all other phosphines studied, decreases in k_{obs} were observed with increasing concentrations of phosphine. The degree of the decrease increased with cone angle and molecular weight. As with the isocyanide system, the results reflect the decrease in the contribution from k_1 to k_{obs} as the concentration of the solvent, in the mixture with the phosphine, becomes less. If concentrations are expressed on a molarity scale, the decrease in solvent concentration will effectively come into play at lower phosphine molarities, the higher is the molecular weight of the phosphine. However, the decreases in k_{obs} are more substantial than calculated on this scheme.

The approximate k_3 value (2.70×10^{-5} L mol^{-1} s^{-1}), obtained from the PhMe$_2$P experiment in acetonitrile by dividing the k_{obs} value for neat phosphine by its molar concentration, is comparable to that obtained, for this phosphine, from the experiment in toluene (1.93×10^{-5} L mol^{-1} s^{-1}). Similar correlation exists between the values for Et$_3$P (2.67×10^{-5} versus 1.92×10^{-5}) and Ph$_2$MeP (1.61×10^{-5} versus 0.99×10^{-5}). This additional set of k_3 values, together with that obtained for neat Ph$_2$EtP (0.76×10^{-5} L mol^{-1} s^{-1}) again trends with the cone angle of the phosphine.

An estimate of k_3 ($\sim 10^{-5}$ L mol^{-1} s^{-1}) for the reactions of $[(\eta^5\text{-}C_5H_5)(CO)_3MoCH_2C_6H_5]$ with Ph_2MeP in the tetrahydrofurans at 30 ° C, extrapolated from the rate constants measured at 40 ° and 50 ° C, is close to the value measured in toluene.

Experimental

Metal carbonyl alkyls were prepared and characterised as previously described [4,5,8]. Schlenk techniques were used for the manipulation of air-sensitive compounds and for the handling of solutions for spectroscopic analysis. Tertiary phosphines (Strem Chemical Company) were used as supplied. Acetonitrile was dried over phosphorus pentoxide (Merck "Sicapent"), and toluene, tetrahydrofuran, 2-methyltetrahydrofuran and 2,5-dimethyltetrahydrofuran over calcium hydride. All solvents were distilled under nitrogen immediately prior to use.

Measurement of k_3 for $[(\eta_5\text{-}C_5H_5)(CO)_3MoR]$ in toluene

Kinetic data were collected, at 30 ° C for concentrations of tertiary phosphine up to 1.5 *M*, for 0.04 *M* solutions of $[(\eta^5\text{-}C_5H_5)(CO)_3MoCH_2C_6H_{5-n}X_n]$. Solutions were transferred from Schlenk tubes to NMR tubes and degassed. Rates were followed by monitoring the ^1H resonances in the cyclopentadienyl region (typically around δ4.6 for starting material, and 4.9 (d, $J(^{31}P\text{-}^1H) \simeq 1$ Hz) for the acyl product, $[(\eta^5\text{-}C_5H_5)(CO)_2(Ph_3P)MoCH_2C_6H_{5-n}X_n]$) on a JEOL PS100 NMR spectrometer. The resonances were independent of concentration. Particularly for large phosphines, a peak for the decarbonylated acyl was also detected. Interestingly, the resonance, which was either slightly to low or high field of the starting material, was sensitive to both the nature of the tertiary phosphine and its concentration; the more alkylated the phosphine, the greater the shift to high field and the greater the concentration dependence. The observation presumably reflects the variation in the solvent shift associated with the aromatic solvent. Compared with non-aromatic solvents, the cyclopentadienyl resonance for the acyl product in toluene lies significantly to low field, rather than to high field, of the resonance for the starting alkyl. Concentration of solution species were established by peak integration. Good first-order plots (up to three half lives) were obtained, even for the case of Ph_3P where small amounts of product precipitated out in the later stages of reaction. The k_3 value (uncertainty ~ 10%) for each phosphine was obtained from the gradient of the $k_{obs}/[L]$ plot.

Attempted k_3 measurement for $[(\eta_5\text{-}C_5H_5)(CO)_3MoCH_2C_6H_{5-n}X_n]$ in acetonitrile

Kinetic data were collected by the NMR method described above, using 0.2 *M* solutions of $[(\eta^5\text{-}C_5H_5)(CO)_3MoCH_2C_6H_{5-n}X_n]$ at 30 ° C and phosphine concentrations from 0.5 *M* up to the limit of pure phosphine (only the more soluble liquid alkyl phosphines were studied). The reactions were cleaner than those in toluene and decarbonylation was not significant.

Measurement of k_3 for $[(CO)_5MnCH_2C_6H_{5-n}X_n]$ in toluene

Kinetic data were collected by monitoring the decrease in intensity of the A_1 vibration of the starting material around 2100 cm^{-1} on a Perkin Elmer PE283B spectrophotometer. A solution of 10 ml of 0.008 *M* manganese complex in toluene was added to a known amount of the phosphine in a Schlenk tube sealed with a serum cap and placed in a constant temperature bath at 30 °C. A range of phosphine concentrations between 0.2 and 1.0 *M* was used. After degassing of the sample, aliquots were removed periodically and the infrared absorbance measured using the attached ordinate data-processing facility. A plot of ln(Absorbance) against time yielded k_{obs}. Statistical errors in the k_{obs} values are generally around 2%. Values of k_3, determined from the gradient of the plot of k_{obs} versus concentration of phosphine, are of the same precision.

Measurement of k_1 for $[(CO)_5MnCH_2C_6H_{5-n}X_n]$ in THF, 2-MeTHF and 2,5-Me_2THF

Rates were followed by the infrared method described above using 0.008 *M* solutions of the manganese complexes, and concentrations of tertiary phosphine up to 0.2 *M*. In this concentration domain, only the k_1, k_2 pathway is followed and $1/k_1$ is obtained from the intercept of the plot of $1/k_{obs}$ versus 1/[L].

Measurement of k_1 for $[(\eta_5\text{-}C_5H_5)(CO)_3MoCH_2C_6H_{5-n}X_n]$ in THF, 2-MeTHF and 2,5-Me_2THF

Rates were followed, with the exclusion of light, by the infrared method using 0.004 *M* solutions of the molybdenum complexes, and concentrations of tertiary phosphine up to 1.0 *M*. The sharp A_1 vibration around 2000 cm^{-1} was monitored.

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