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Steric Effects of Tertiary Phosphines on Nucleophile-induced Insertion of Carbon Monoxide into Transition Metal–Carbon Bonds*

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Rate constants associated with the tertiary phosphine-induced formation of the metal acyls, $[(\eta^5\text{-}C_5H_5)(CO)(PR_3)FeCOCH_2Cy]$ *and* $[(\eta^5\text{-}C_5H_5)(CO)_2(PR_3)MoCOCH_2Ph]$*, show no correlation with the electronic properties of the phosphine, but exhibit a marked dependence on steric effects. Rates decrease slightly with increase in phosphine cone angles in the lower ranges, but drop very rapidly at higher cone angles. The behaviour is consistent with the concept of a pocket of limited size around the metal centre, with large intermolecular effects arising when the sizes of the tertiary phosphine and the pocket become comparable.*

Introduction

The mechanism of the insertion of carbon monoxide into transition metal to carbon bonds has been extensively studied and, in polar solvents, involves a two-stage process in which a solvent-stabilised acyl intermediate, formed initially, then reacts further with a nucleophile, L, such as a tertiary phosphine, to give the final acyl product [1].

$$[(OC)MR] \underset{k_{-1}}{\overset{\text{Solvent},k_1}{\rightleftharpoons}} [(\text{Solvent})M(COR)] \xrightarrow{k_2,L} [LM(COR)]$$

We have recently made several studies of the steric and electronic effects of the alkyl substituent on this insertion process [2, 3]. The reactions of a series of *meta-* and *para*-substituted benzylmolybdenum compounds, $[\eta^5\text{-}C_5H_5)(CO)_3Mo(CH_2C_6H_4X)]$, with triphenylphosphine in acetonitrile solution, demonstrated that the reactivity of the molybdenum–carbon sigma bond, which was reflected in the rate constant k_1, was moderately enhanced by electron donating substituents [2]. In this system, steric effects are essentially constant. However a pronounced increase in rate (k_1), with increasing size of the alkyl substituent, was detected [3] in the reactions of $[(\eta^5\text{-}C_5H_5)(CO)_2FeR]$, where R = Me, Et, ^{i}Pr, CH_2Cy, ^{s}Bu, Np, $(Me_3Si)_2CH$ *etc.*, with dimethylsulfoxide (DMSO) which yield the solvent-substituted acyls, $[(\eta^5\text{-}C_5H_5)(CO)(DMSO)Fe(COR)]$. This steric enhancement was interpreted in terms of the lengthening of the iron–alkyl bond in the transition state leading to the formation of the DMSO-substituted acyl complex, which has the effect of partially removing a large substituent from the crowded environment at the metal centre, and which might be expected to lead to relatively higher effects for larger alkyl groups.

In view of these results we were interested in probing further the factors which influence the second (k_2) step of the reaction in which an added nucleophile replaces a coordinated solvent molecule in the acyl complex. We report here the reactivity of a series of tertiary phosphines with the complexes $[(\eta^5\text{-}C_5H_5)(CO)_3MoCH_2Ph]$ and $[(\eta^5\text{-}C_5H_5)(CO)(DMSO)Fe(COCH_2Cy)]$, and our attempts to correlate such reactivity with the Tolman electronic and steric parameters [4] of tertiary phosphines.

Results and Discussion

The cyclohexylmethyliron complex, $[(\eta^5\text{-}C_5H_5)(CO)_2FeCH_2Cy]$, which is an easily-handled solid and shows convenient reactivity [3, 5] was selected for study. In all experiments, the pre-equilibrium

$$[(\eta^5\text{-}C_5H_5)(CO)_2FeCH_2Cy] + DMSO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [(\eta^5\text{-}C_5H_5)(CO)(DMSO)Fe(COCH_2Cy)]$$

was set up (12 h at 30 °C) and monitored by observation of the ^{1}H NMR resonances of the cyclopentadienyl groups in the complexes. Tertiary phosphine was added and the second-order reaction followed, at 30 °C, by observation of the cyclopentadienyl

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TABLE I. Rate Constants for CO Insertion for Tertiary Phosphines.

Phosphine	θ[a]	ν[b]	10^4 k_2 ($l\ mol^{-1}\ s^{-1}$) $FeCH_2Cy/DMSO$	10^4 k_1 (s^{-1})	k_2/k_{-1} ($l\ mol^{-1}$) $MoCH_2Ph/CH_3CN$	10^5 k_1 (s^{-1})	k_2/k_{-1} ($l\ mol^{-1}$) $FeEt/CH_3CN$[c]
PMe_2Ph	122°	2065.3	1.48 ± 0.06	3.4	217	14	4.0
$PMePh_2$	136°	2067.0	1.37 ± 0.09	3.2	250	14	3.9
$PEtPh_2$	140°	2066.7	1.12 ± 0.05	3.0	222		
PPh_3	145°	2068.9	1.04 ± 0.20	2.7[d]	64[d]	9	4.2
P^iPrPh_2	150°	2065.7	0.79 ± 0.07	3.0	44		
P^tBuPh_2	157°	2064.7	0.39 ± 0.03	3.0	~37		

[a] Tolman steric parameter. [b] Tolman electronic parameter. [c] Recalculated from data of Reference 10. [d] 29 °C.

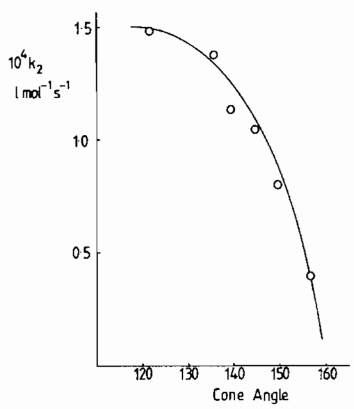

Fig. 1. Variation in k_2 ($l\ mol^{-1}\ s^{-1}$) with phosphine cone angle for the reaction of $[(\eta^5\text{-}C_5H_5)(CO)(DMSO)Fe(COCH_2Cy)]$ with tertiary phosphines in DMSO.

doublet associated with the phosphine-substituted acyl, and the disappearing cyclopentadienyl resonances of the starting material and the DMSO-acyl. The kinetic analysis for k_2 took into account the regeneration of the DMSO-acyl in the pre-equilibrium, the establishment of which was fast compared with the k_2 step. The results are shown in Table I. No correlation with the Tolman electronic factor, ν, for the several tertiary phosphines is apparent, but a well-defined decrease in k_2 with increasing cone angle occurs. The variation is depicted in Fig. 1. The decrease is gradual for cone angles from 120 to 130° but is pronounced at higher cone angles. Tertiary phosphines with very high cone angles (*e.g.* PCy_3, 170°) do not react observably.

In reactions with the larger phosphines, small amounts of the decarbonylation products, $[(\eta^5\text{-}C_5H_5)(CO)(PR_3)FeCH_2Cy]$, were also detected. Our observations, based on relative amounts, are compatible with the results of an extensive study of the thermal decarbonylation of phosphine-substituted acetyl molybdenum complexes in acetonitrile at 60 °C [6]. In this latter process, where dissociation of a terminal carbon monoxide ligand is the rate determining step, the rate of decarbonylation increased substantially with increased size of the tertiary phosphine, but electronic factors played only a minor role.

The variation in k_2 with phosphine for the reactions of the molybdenum complex, $[(\eta^5\text{-}C_5H_5)(CO)_3MoCH_2Ph]$, in acetonitrile can only be probed indirectly. In this process, the presence of the solvent-stabilised intermediate has been inferred kinetically [1, 2] but it has not been directly observed. In the overall reaction, (which is assumed to go to completion),

$$[(\eta^5\text{-}C_5H_5)(CO)_3MoCH_2Ph] + PR_3 \rightarrow [(\eta^5\text{-}C_5H_5)(CO)_2(PR_3)Mo(COCH_2Ph)],$$

the kinetics are effectively first order in the molybdenum benzyl if the concentration of phosphine is essentially constant throughout. On the basis of the steady-state approximation for the concentration of the intermediate, the overall rate constant, k_{obs}, can be expressed in terms of the rate constants for the two stages of reaction:

$$k_{obs} = \frac{k_1k_2[PR_3]}{k_{-1} + k_2[PR_3]}$$

The rate constant k_1 can be obtained, from k_{obs} data collected for a number of concentrations of tertiary phosphine, from the ordinate intercept of a plot of $1/k_{obs}$ *versus* $1/[PR_3]$, and the ratio k_2/k_{-1} is accessible from the gradient. Thus, unlike the iron–DMSO system, a separate determination of k_2 is not possible. However, in the formal reaction scheme k_{-1} is independent of the nature of the phosphine and although, in practice, small variations might occur because of minor changes in the overall characteristics of the solvent, the ratio k_2/k_{-1} should adequately reflect the variation in k_2.

To enable a reasonable spread of concentrations of phosphine while ensuring an essentially constant concentration throughout the reaction, a low concentration (0.008 *M*) of molybdenum benzyl was necessary. At this concentration the NMR technique was unsuitable and the reactions were followed by infrared spectrophotometry, monitoring the disappearance of the highest energy carbonyl absorption in the starting material.

Although the uncertainties (~10–20%) involved in the indirect evaluation are higher than for the direct k_2 measurements, the same general trend with cone angle is observed. Again there is no correlation with the electronic parameter (see Table). Little change in k_2/k_{-1} occurs in a plateau region from 120–140° but there is a marked decrease at higher cone angles. The reaction with t-butyldiphenylphosphine was very slow and significant deviations from linearity of the first order rate plots were observed. The expressed result for k_2/k_{-1} in this case is an estimate based on a best fit of the data to the general kinetic expression using an average value of k_1 calculated from the reactions with the smaller phosphines. The reason for the deviation is not understood; it may be associated with the approximation of the overall kinetic expression to $k_{obs} = k_1k_2[PR_3]/k_{-1}$, at very small k_2, in which small changes in the concentration of phosphine might be proportionally more important, or may arise from a breakdown in the steady-state approximation. As for the iron–DMSO system, there was no observable reaction with the very large nucleophile, tricyclohexylphosphine. In general, the kinetic data provide good support for the established mechanistic scheme. For example, within experimental error (approximately ±5%), the values of k_1 are independent of the tertiary phosphine used.

In summary, the results for both systems demonstrate the high sensitivity of the k_2 stage of the reaction to the steric demand of the tertiary phosphine, which is, not unexpectedly in view of the approach of a large nucleophile to the metal centre in this step, in the opposite sense to the steric effect of the alkyl group on the k_1 stage, where the transition state is postulated to involve its partial removal. The plots of k_2, and k_2/k_{-1} against cone angle, which show a relatively flat, or plateau, region and marked decreases above 'critical' angles, can be interpreted, pictorially, in terms of a pocket at the metal centre in which the phosphine must fit in order to react. For phosphines smaller than the pocket, steric interactions are minimal and the rate constants are little changed with cone angle. However, when the size of the phosphine becomes comparable with the pocket, intermolecular interactions increase rapidly with cone angle, resulting in an increasing activation energy for reaction. The repulsion eventually becomes extreme, and very large phosphines (*e.g.* PCy_3) are unable to approach close enough to establish a bonding interaction with the metal centre.

The more limited plateau for the cyclohexylmethyliron complex suggests that its pocket is significantly smaller than for the benzylmolybdenum compound. Unfortunately the comparison is not direct (the cyclohexylmethylmolybdenum complex is inaccessible, and the benzyliron complex does not react with DMSO), but the difference could be associated with the possibility of sterically favourable distortion of the pseudo-square pyramidal structure of the molybdenum complex to a pseudo-trigonal bipyramidal arrangement, such as proposed [7] for the *cis–trans* isomerisation of $[(\eta^5\text{-}C_5H_5)(CO)_2L(X)Mo]$. However, the sizes of the alkyl group and the ancillary ligands will clearly be important factors. Our preliminary studies with the pentamethylcyclopentadienyl analogue of the molybdenum complex in acetonitrile have indicated a significantly more restricted access: triphenylphosphine is completely unreactive in this case and diphenylmethylphosphine reacts slowly [8]. The effect of a large alkyl substituent is demonstrated by the fact that the cyclopentadienyl molybdenum compound containing the 2,4,6-tri-isopropylbenzyl ligand is able to differentiate phosphines with cone angles down to 122° [9]. Further support comes from reanalysed data quoted by Green and Westlake [10] for the reaction of $[(\eta^5\text{-}C_5H_5)(CO)_2FeEt]$ with tertiary phosphines at 47.5 °C in acetonitrile. The constancy of the k_2/k_{-1} values (obtained by linear least squares analysis, and listed in the Table) shows that the plateau region extends to about 145° in this case. Although our experiments with the cyclohexylmethyl iron complex were carried out in a different solvent (DMSO), the results may partially reflect the relative sizes of the alkyl groups.

Experimental

The compounds $[(\eta^5\text{-}C_5H_5)(CO)_3MoCH_2Ph]$ and $[(\eta^5\text{-}C_5H_5)(CO)_2FeCH_2Cy]$, were prepared by established procedures [11]. Acetonitrile was dried over Merck 'Sicapent' and distilled under nitrogen prior to use. Dimethylsulfoxide was dried over 4A molecular sieve, degassed and stored under nitrogen.

Proton NMR spectra, in kinetic runs in DMSO, were recorded on a Jeol PS-100 spectrometer, with DMSO as lock. Routinely, a solution (0.25 *M*) of the iron complex in DMSO was held at 30 °C over 12 h, when equilibrium with the solvated acyl was established, tertiary phosphine then added to give a 0.50 *M* solution, and a sample of the mixture quickly syringed into an NMR tube which was degassed and sealed. Kinetic observations were made by monitoring either the peak heights or the integrated area of the cyclopentadienyl resonances of the starting alkyl (4.99 ppm), the DMSO-substituted acyl (4.76 ppm) and the doublet associated with the phosphine-substituted acyl (~4.5 ppm). A plot of $[1/(a_o - p_o)] \cdot \ln[p_o(a_o - x_t)/a_o(p_o - x_t)]$ *versus* time gave $k_2K/(K + 1)$ directly [3]; (a_o = initial concentration of cyclohexylmethyliron complex, p_o = initial concentration of phosphine and x_t = concentration of phosphine-substituted acyl at time t, K = equilibrium constant for the first stage of reaction). Statistical errors in slopes were less than 5%.

Kinetic data for the benzylmolybdenum complex were collected at a substrate concentration of 0.008 *M* and for concentrations of tertiary phosphine from 0.025 to 0.25 *M*. Solutions were prepared in acetonitrile under nitrogen in a Schlenk tube fitted with a rubber septum and thermostatted at 30 °C. Samples were periodically removed by syringe and the absorbance of the highest energy carbonyl vibration (~2007 cm^{-1}) of the starting material monitored on a PE 283 spectrophotometer. Plots of ln(absorbance) *versus* time gave the rate constant k_{obs}, directly. Statistical errors in slope were less than 4%. For each tertiary phosphine, k_{obs} values were obtained for at least 8 different concentrations.

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