Journal of Organometallic Chemistry, 294 (1985) 213–217
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

CARBON MONOXIDE INSERTION REACTIONS IN SUBSTITUTED CYCLOPENTADIENYLMOLYBDENUM COMPLEXES *

J.D. COTTON ** and H.A. KIMLIN
Department of Chemistry, University of Queensland, Brisbane, Queensland, 4067 (Australia)
(Received April 15th, 1985)

Summary

The reactions of $[(\eta^5\text{-}C_5Me_5)(CO)_3MoCH_2Ph]$ and $[(\eta^5\text{-}C_5H_4Me)(CO)_3MoCH_2\text{-}Ph]$ with tertiary phosphines and alkyl isocyanides in polar solvents to yield phosphine-substituted molybdenum acyl complexes have been explored and compared with the behaviour of the unsubstituted cyclopentadienyl compound. For the pentamethylcyclopentadienyl complex, reaction is restricted to tertiary phosphines with small cone angles. Unlike the cyclopentadienyl system, a mixture of *cis*- and *trans*-acyl products is formed.

Introduction

In previous papers [1–5] we have discussed mechanistic features of the ligand-induced carbon monoxide insertion into metal–carbon bonds in η^5-cyclopentadienyl complexes in the reaction represented generally by eq. 1.

$$\left[(\eta^5\text{-}C_5H_5)(CO)_nMR\right] + L \rightleftarrows \left[(\eta^5\text{-}C_5H_5)(CO)_{n-1}LM(COR)\right] \quad (1)$$

Our major conclusions, for M = Fe ($n = 2$) and Mo ($n = 3$), have concerned the size and electronic effect of the alkyl group, R, and the nucleophile, L, which is typically a tertiary phosphine or an alkylisocyanide. In the k_1 reaction step in polar solvents, in which a solvent (S)-stabilised acyl complex, $[(\eta^5\text{-}C_5H_5)(CO)_{n-1}SM(COR)]$, is formed, enhanced reactivity is observed for electron-donating substituents in *meta*- and *para*-substituted benzylmolybdenum compounds $[(\eta^5\text{-}C_5H_5)(CO)_3MoCH_2C_6\text{-}H_4X]$ [1,2], and with increasing size of R in both *ortho*-substituted benzylmolybdenum complexes [3] and in a series of alkyliron compounds, $[(\eta^5\text{-}C_5H_5)(CO)_2FeR]$ [4]. The reverse steric effect has been noted by Wax and Bergman [6] for the k_1 step of the reaction of $[(\eta^5\text{-}C_5H_5)(CO)_3MoCH_3]$ with diphenylmethyl-

* No reprints available.
** Please address correspondence to this author.

phosphine, with reactivity decreasing with an increase in solvent size in a series of α-substituted tetrahydrofurans. Increase in the size of a tertiary phosphine, expressed as its cone angle [7], caused a decrease in the rate of the k_2 stage of the reaction, in which the solvent molecule in the intermediate acyl is replaced by the phosphine, for $[(\eta^5\text{-}C_5H_5)(CO)_3MoCH_2Ph]$ and $[(\eta^5\text{-}C_5H_5)(CO)_2FeCH_2Cy]$ [5].

The substantial steric influences which have become apparent in the carbon monoxide insertion process have led us to explore the effect of replacing the cyclopentadienyl ligand by the bulky pentamethylcyclopentadienyl group and we report here on the reactivity of $[(\eta^5\text{-}C_5Me_5)(CO)_3MoCH_2Ph]$ with tertiary phosphines and alkyl isocyanides in polar solvents. A comparison with the corresponding methylcyclopentadienyl system is also made.

Results and discussion

The reactions of $[(\eta^5\text{-}C_5H_4Me)(CO)_3MoCH_2Ph]$ and $[(\eta^5\text{-}C_5Me_5)(CO)_3MoCH_2Ph]$ with tertiary phosphines, in acetonitrile at 30°C, were monitored either by ^{31}P NMR spectroscopy, which detected the appearance of the acyl product, e.g. $[(\eta^5\text{-}C_5Me_5)(CO)_2(PMe_2Ph)Mo(COCH_2Ph)]$, or by infrared solution spectroscopy, in which the decreasing absorbance of the highest frequency carbonyl stretching vibration (around 2000 cm^{-1}) in the starting material was followed.

Two major differences from the reactivity of the corresponding cyclopentadienyl complex were immediately apparent. First, for the pentamethylcyclopentadienyl system, triphenylphosphine is unreactive, although enhanced rates are observed for smaller phosphines. Second, in the case of both the methyl- and pentamethyl-complexes, a mixture of the *cis*- and *trans*-isomers of the acyl product, based on the geometry in the basal plane below the molybdenum atom in the pseudo-square pyramidal system, results. For the corresponding cyclopentadienyl system, small amounts of the *cis*-isomer are observed only in the initial stages of the reaction with triphenylphosphine in dimethylsulfoxide [1].

Typically, in the reaction of a 0.2 *M* solution of $[(\eta^5\text{-}C_5Me_5)(CO)_3MoCH_2Ph]$ with 2 *M* dimethylphenylphosphine in acetonitrile at 26°C, the *cis*-product (^{31}P chemical shift, δ 65.31 ppm relative to free ligand) was the major product component (e.g. 70% *cis* after 4 min at 30% reaction). At around 75% reaction (ca. 15 min) the *cis* and *trans* (δ 78.96 ppm) forms were present in comparable amounts and, at equilibrium (2 h), the mixture contained only 17% of the *cis*-isomer. Assignment of the isomers was made on the basis of infrared spectra in the carbonyl stretching region. The spectrum (in cyclohexane) of the freshly dissolved solid product indicated the presence of a single isomer (1923 and 1838 cm^{-1}) with peak intensities compatible with a *trans*-$[(\eta^5\text{-Cp})(CO)_2LMoX]$ species [8]. With time, the characteristic absorptions associated with the *cis*-isomer (1936 and 1858 cm^{-1}) appeared. A scan of the ^{31}P spectrum of freshly dissolved product then allowed assignment of the resonances associated with the isomers. Substantial formation of the *cis*-isomer was also detected in a similar experiment with the monomethylated complex, $[(\eta^5\text{-}C_5H_4Me)(CO)_3MoCH_2Ph]$. The relative distribution of isomers followed a similar pattern and, at equilibrium, the mixture contained 15% of the *cis*-form. Both isomers were also observed in the reaction of $[(\eta^5\text{-}C_5Me_5)(CO)_3MoCH_2Ph]$ with dimethylphenylphosphine in dimethylsulfoxide. The distribution at equilibrium is unchanged but a slightly higher amount of the *cis*-isomer is present initially. This probably

reflects an increase in the rate of the insertion reaction in the more polar solvent relative to the rate of isomerisation. The higher proportion of the *cis*-isomer on ring methylation may be the result of an increased steric interaction between the ring and the tertiary phosphine which serves to tilt the plane of the ring away from the phosphine. The crystal structure of the *trans*-acyl complex, $[(\eta^5\text{-}C_5H_5)(CO)_2(PPh_3)Mo(COCH_3)]$ [9], in which the shortest Mo–cyclopentadienyl ring carbon distances are for the atoms lying above the acetyl group and *trans* to the triphenylphosphine ligand, provides some basis for this interpretation. Related, and possibly more definitive, evidence comes from a crystallographic study of $[(\eta^5\text{-}C_5H_5)(CO)_3MoCH_2Ph]$, $[(\eta^5\text{-}C_5H_5)(CO)_3MoCH_2C_6H_4\text{-}o\text{-}Me]$ and $[(\eta^5\text{-}C_5H_5)(CO)_3MoCH_2C_6H_3\text{-}2,4,6\text{-}Me_3]$ where the tilt of the cyclopentadienyl ring with respect to the plane of the carbonyl oxygen atoms varies regularly from 8.9 to 10.7 to 13.7° as the amount of steric congestion in the molecule increases [10]. The relatively greater amount of the *cis*-form could thus be viewed in terms of the greater ease of accommodation of the adjacent substituents in the aperture created by the ring tilt.

Ring substitution also had a significant effect on the rate of CO insertion. The reaction, in polar solvents, is traditionally analysed in terms of a two-stage process involving the initial formation of a solvent(S)-stabilised intermediate which further reacts with the inducing nucleophile (L) to give the acyl product (eq. 2) [11].

$$[(CO)MR] \underset{k_{-1},\,-S}{\overset{k_1,\,S}{\rightleftharpoons}} [SM(COR)] \underset{k_{-2},\,-L}{\overset{k_2,\,L}{\rightleftharpoons}} [LM(COR)] + S \qquad (2)$$

Under the conditions used, the reactions proceeded to completion which allowed the k_{-2} step and the rate of the subsequent *cis–trans* isomerisation to be kinetically ignored. The overall rate constant, k_{obs}, under the effective first-order conditions which apply at large concentrations of the inducing nucleophile, is then given by

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

The rate constant k_1 and the ratio k_{-1}/k_2 for the several systems (Table 1) were obtained from plots of $1/k_{obs}$ vs. $1/[L]$ in reactions using different nucleophile concentrations. Values for the corresponding reactions of the cyclopentadienyl complex are included for comparison.

The most striking feature, mentioned earlier, in the kinetic studies is the restriction of the reactivity of the pentamethylcyclopentadienyl complex to smaller phosphines. The tabulated data are for dimethylphenylphosphine for which good first-order plots were obtained. However, for diphenylmethylphosphine, even though reasonable reaction rates were observed, serious deviations from first-order kinetics occurred. The reason for the kinetic breakdown in this case, and for larger tertiary phosphines, probably lies with low values of k_2 in pentamethylcyclopentadienyl complexes which would make $k_2[L]$ comparable with, or even less than k_{-1}. The effect would be expected to be more pronounced at lower phosphine concentrations, as observed. In the extreme situation, which we have not yet encountered, with $k_2[L] \ll k_{-1}$, the reaction would become effectively second order with $k_{obs} = k_1k_2[L]/k_{-1}$.

With a common nucleophile, dimethylphenylphosphine, the k_1 values for the three cyclopentadienyl systems (C_5H_5, C_5H_4Me and C_5Me_5) show a significant increase as the extent of ring substitution increases. This is in line with the enhancement anticipated from the mild electron donating capacity of the methyl

TABLE 1

RATE CONSTANTS FOR THE REACTION OF $[Cp(CO)_3MoCH_2Ph]$ SYSTEMS WITH NUCLEOPHILES IN ACETONITRILE AT 30°C

Cp	L	$10^4 k_1$ (s^{-1})	$10^3 k_{-1}/k_2$ (mol l^{-1})	$10^3 k_3$ (l mol^{-1} s^{-1})
C_5H_5	PMe_2Ph	3.4 [a]	4.6 [a]	
C_5H_4Me	PMe_2Ph	4.7	4.3	
C_5Me_5	PMe_2Ph	9.2	140	
C_5H_5	^tBuNC	2.7 [b]	5.2 [b]	3.3 [b]
C_5H_4Me	^tBuNC	5.3	23	5.2
C_5Me_5	^tBuNC	7.9	160	11
C_5H_5	CyNC	2.8 [b]	28 [b]	
C_5Me_5	CyNC	12	250	

[a] Data from Ref. 5. [b] Data from Ref. 2.

group but our previous observation, that an increase in the size of the alkyl group in unsubstituted cyclopentadienyl systems causes an increase in k_1, means that both steric and electronic factors operate in the same direction and are inseparable. The trend in the reactions with t-butyl isocyanide (Table 1) is similar. As required by the mechanism, the k_1 values correspond, within experimental error, to those from the phosphine kinetics. The values for cyclohexyl isocyanide are approximate because of deviations from first-order conditions.

Although the values for k_{-1}/k_2 are subject to higher experimental uncertainty ($\pm 20\%$), their interpretation is more straightforward. For dimethylphenylphosphine, the values for the cyclopentadienyl and methylcyclopentadienyl complexes are comparable but the value for the pentamethylcyclopentadienyl compound is approximately 50 times greater. If the assumption is made that the k_{-1} values trend in approximately the same manner as k_1 (for which idea the individually determined values of k_1 and k_{-1} for the reactions of $[(\eta^5\text{-}C_5H_5)(CO)_2FeCH_2Cy]$ with DMSO provide some basis [4]), then the k_2 values for the reaction of dimethylphenylphosphine with the cyclopentadienyl and methylcyclopentadienyl molybdenum complexes are necessarily comparable. This suggests that the steric factors involved in this displacement of solvent by phosphine are similar. In the case of the corresponding reactions with t-butyl isocyanide a small decrease in k_2 is observed. In the corresponding comparison of the pentamethyl complex with the unsubstituted system, after allowance is made for the increase in k_1 (and k_{-1}), a decrease in k_2 of at least one order of magnitude results for both the dimethylphenylphosphine and t-butyl isocyanide reactions. This clearly highlights the substantially greater congestion in the pentamethylcyclopentadienyl complex and reinforces the previous qualitative observations to this effect, namely the non-reaction of triphenylphosphine and the deviations from first-order behaviour for diphenylmethylphosphine. The k_{-1}/k_2 value for the reaction of cyclohexyl isocyanide with $[(\eta^5\text{-}C_5Me_5)(CO)_3MoCH_2Ph]$ is significantly higher than for the corresponding reaction with t-butyl isocyanide. This, together with the fact that deviations from first-order behaviour occur, particularly at low concentrations, for cyclohexyl isocyanide, points to a smaller k_2 and to a larger effective size of cyclohexyl isocyanide in this process.

A limited study of the direct reaction of t-butyl isocyanide at high concentration with the cyclopentadienylmolybdenum complexes has been made. Under these conditions, the "k_3" reaction pathway, in which the acyl formation is initiated by direct attack of nucleophile, rather than solvent, on the metal, comes into play (eq. 3),

$$[(CO)MR] \underset{k_{-3},\,-L}{\overset{k_3,\,L}{\rightleftharpoons}} [LM(COR)] \qquad (3)$$

The overall rate constant (for $k_2[L] \gg k_{-1}$) is now given by $k_{obs} = k_1 + k_3$ [L]. The same trend in k_3 is observed as with k_1 ($k_3(C_5H_5)$ 3.3×10^{-3} l mol^{-1} s^{-1}; $k_3(C_5H_4Me)$ 5.2×10^{-3} l mol^{-1} s^{-1}; $k_3(C_5Me_5)$ 11×10^{-3} l mol^{-1} s^{-1}).

Experimental

The complexes $[(\eta^5\text{-}C_5H_5)(CO)_3MoCH_2Ph]$ and $[\eta^5\text{-}C_5H_4Me(CO)_3MoCH_2Ph]$ were prepared by the standard method [1] by refluxing a tetrahydrofuran solution of the sodium cyclopentadienide, prepared by treatment of sodium with the cyclopentadiene, and molybdenum hexacarbonyl, followed by addition of benzyl chloride. $[(\eta^5\text{-}C_5Me_5)(CO)_3MoCH_2Ph]$ was prepared in a related procedure which involved deprotonation of pentamethylcyclopentadiene with n-butyllithium. The products were purified by column chromatography (alumina II/III) in hexane and recrystallisation. Acetonitrile for kinetic studies was dried over Merck "Sicapent" and distilled under nitrogen. Dimethylsulfoxide was dried over a 4 Å molecular sieve. Tertiary phosphines were used as supplied (Strem) and alkyl isocyanides prepared by the standard procedure [12]. Kinetic measurements (for k_1 and k_{-1}/k_2) were made on solutions 8×10^{-3} *M* in molybdenum benzyl in acetonitrile at 30°C, with the concentration of nucleophile typically ranging from 0.22 to 0.25 *M*, by following the decrease in absorbance of the highest frequency carbonyl stretching band (around 2000 cm^{-1}) in the infrared spectrum of the molybdenum benzyl complex on a PE283 spectrophotometer. *Cis-trans* isomer distributions of phosphine-substituted acyl products were established by monitoring the ^{31}P resonances on a JEOL FX100 spectrometer at 40.26 MHz over a spectral width of 6000 Hz with 16 K data points, giving a digital resolution of 0.07 ppm.

Acknowledgements

We thank the Australian Research Grant Scheme for financial support of this work.

References

1 J.D. Cotton, G.T. Crisp and V.A. Daly, Inorg. Chim. Acta, 47 (1981) 165.
2 J.D. Cotton and P.R. Dunstan, Inorg. Chim. Acta, 88 (1984) 223.
3 J.D. Cotton, H.A. Kimlin and R.D. Markwell, J. Organomet. Chem., 232 (1982) C75.
4 J.D. Cotton, G.T. Crisp and L. Latif, Inorg. Chim. Acta, 47 (1981) 171.
5 J.D. Cotton and R.D. Markwell, Inorg. Chim. Acta, 63 (1982) 13.
6 M.J. Wax and R.G. Bergman, J. Am. Chem. Soc., 103 (1981) 7028.
7 C.A. Tolman, Chem. Rev., 77 (1977) 313.
8 P.J. Craig and J. Edwards, J. Less-Common Met., 36 (1974) 193.
9 M.R. Churchill and J.P. Fennessey, Inorg. Chem., 7 (1968) 953.
10 J.D. Cotton, C.H.L. Kennard, R.D. Markwell and A.H. White, to be published.
11 R.J. Mawby, F. Basolo and R.G. Pearson, J. Am. Chem. Soc., 86 (1964) 3994.