Journal of Organometallic Chemistry, 388 (1990) 123–132
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20674

Substituent effects on the alkyl migration reaction in pentacarbonylbenzylmanganese(I) systems

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(Received November 3rd, 1989)

Abstract

The k_1 step of the formal insertion of carbon monoxide into a Mn–C σ bond in the reaction of substituted benzylmanganese complexes, $[(CO)_5MnCH_2C_6H_{5-n}X_n]$, with tertiary phosphines in acetonitrile is enhanced by electron-donating substituents in *meta*- and *para*-positions. *Ortho*-substitution by a methyl group causes a reduction in k_1 compared with *para*-methyl substitution but di-substitution and single *ortho*-substitution by large alkyl groups increases reactivity. Similar behaviour occurs with Cl, F and CF_3 as *ortho*-substituents. The value of k_{-1}/k_2, which reflects $1/k_2$, increases with increasing cone angle of the tertiary phosphine but the strongly basic phosphine, PCy_3, although unreactive towards $[(\eta^5\text{-}C_5H_5)(CO)_3MoR]$ and $[(\eta^5\text{-}C_5H_5)(CO)_2FeR]$, induces insertion. Steric influences on the *cis/trans* isomerisation of the acyl product and its decarbonylation are discussed. Direct insertion of CO is observed for 2,4,6-triisopropyl- and 2,4,6-trimethyl-benzylmanganese complexes.

Introduction

A number of our recent papers have discussed the influence of the alkyl group, R, and the nucleophile, L, on the ligand-induced insertion of carbon monoxide (eq. 1) into transition metal–carbon σ bonds in η^5-cyclopentadienyl complexes, such as

$$[(CO)_nMR] + L \rightleftharpoons [(CO)_{n-1}LM(COR)] \quad (1)$$

$[(\eta^5\text{-}C_5H_5)(CO)_3MoR]$ [1–3] and $[(\eta^5\text{-}C_5H_5)(CO)_2FeR]$ [4] in polar solvents. In this paper, we extend our study to the $[(CO)_5MnR]$ system; a preliminary report on steric influences has been published [5]. Background information relating to CO insertion into metal–carbon bonds is available in several reviews [6]. Recent literature on CO insertion for $[(CO)_5MnR]$ complexes has been summarised [7].

Results and discussion

Although, for direct comparison with our earlier steric studies on the $[(\eta^5\text{-}C_5H_5)(CO)_2FeR]$ system [4], it was desirable to study a range of $[(CO)_5MnR]$ compounds with simple alkyl groups, e.g. Me, Et, i-Pr, Np etc., the required complexes, other than for R = Me, could be prepared only in low yield and were thermally unstable. For this reason, we studied benzylmanganese compounds, $[(CO)_5MnCH_2C_6H_{5-n}X_n]$, strategically substituted in the *ortho* (2), *meta* (3) and *para* (4) ring positions, in order to provide a wide variation in the electronic and steric characteristics of the alkyl group. Tertiary phosphines were used as nucleophiles, again to allow substantial variation in steric and electronic parameters. Reactions were carried out in acetonitrile, generally at 30 °C, and interpreted on the basis of the mechanistic scheme originally proposed by Mawby, Basolo and Pearson [8] (eq. 2 and 3).

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

$$[(CO)_nMR] + L \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} [(CO)_{n-1}LM(COR)] \qquad (3)$$

Under the conditions of the experiment (concentration of nucleophile less than 0.2 *M*, unless otherwise stated), there was no detectable contribution from the direct reaction path (k_3, eq. 3) except at high concentrations of the strongly basic tricyclohexylphosphine. The rate data are thus analysed simply in terms of the k_1, k_2 pathway (eq. 2). In the scheme originally proposed, the k_1 step is pictured as a bimolecular process in which a solvent molecule (S), as the nucleophile, induces an interaction (believed [9] to involve an alkyl migration) between the α-carbon atom of the alkyl group and a carbonyl carbon atom. An intermediate solvent-coordinated species, which is detectable only in few cases (for $[(\eta^5\text{-}C_5H_5)(CO)_2FeR]$ in dimethylsulfoxide [4,10], for $[(CO)_5MnCH_3]$ in acetonitrile and DMSO [11], and for $[(CO)_5ReEt]$ in acetonitrile [12]), but which is implied by the observation of a substantial solvent influence on k_1 [1,8,13], then reacts, in the k_2 step, with, for example, tertiary phosphine, with displacement of the solvent molecule to yield an acyl product, $[(CO)_{n-1}LM(COR)]$. Within the limits of observation, the reactions proceed to completion (i.e. k_{-2} and k_{-3} are negligible) and, under the effectively first-order conditions imposed by a high concentration of the tertiary phosphine relative to the manganese-alkyl compound, the rate constant, k_{obs}, is given by eq. 4:

$$k_{obs} = \frac{k_1 k_2 [L]}{(k_{-1} + k_2[L])} \qquad (4)$$

This rate constant refers to the formation of the *cis*-acyl product which, as observed previously [14] and confirmed here, is formed initially. The fact that k_{-2} is very small means that the isomerisation to the *trans*-acyl, and the slow decarbonylation to form *cis*-$[(CO)_4LMnR]$, do not complicate the kinetic analysis of the k_1, k_2 step.

We have used this model for the kinetic analysis even though recent investigations of the reaction of $[(CO)_4(CH_3CN)ReCOEt]$ with $[(CO)_5ReH]$ in acetonitrile [15], and of $[(CO)_5MnCH_2C_6H_4(OCH_3)\text{-}4]$ with *cis*-$[(CO)_4(PMe_2Ph)MnH]$ and triphenylphosphine oxide in C_6D_6 [16], both of which lead to the formation of an

Table 1

Rate constants for reaction of Ph_3P with $[(CO)_5MnCH_2C_6H_{5-n}X_n]$ in acetonitrile at 30 °C

Substituent, X_n	$10^5 k_1$ (s^{-1})	$10^3 k_{-1}/k_2$ (mol L^{-1})	log k_X/k_H	Hammett σ [16]
H	29.0	5.3	0	0
2-Me	24.6	2.3	−0.07	
3-Me	36.0	7.1	0.09	−0.06
4-Me	43.2	6.6	0.17	−0.14
2,3-Me_2	37.4	6.0		
2,4,6-Me_3	127	~0		
Me_5	180	~0		
2-i-Pr	32 [a]	4 [a]		
4-i-Pr	30 [a]	9 [a]		
2,4,6-i-Pr_3	330	~0		
2-t-Bu	440	4		
2-Cl	1.8	5.2		
3-Cl	12.1	4.0	−0.39	0.37
4-Cl	17.3	4.6	−0.23	0.22
2,6-Cl_2	0.8	4.9		
2-F	3.7	7.8		
3-F	12.0	7.0	−0.39	0.34
4-F	34.2	8.2	0.07	0.06
2-CF_3	3.3	~0		
3-CF_3	9.8	0.5	−0.48	0.46
4-CF_3	7.0	8.4	−0.63	0.53
2-OMe	7.8	~0	−0.58	
3-OMe	22.9	6.6	−0.11	0.10
4-OMe	60.2	3.1	0.31	−0.28

[a] Measured at 22 °C.

aldehyde in a C–H bond-forming reductive elimination process, suggest that the nucleophile (CH_3CN or Ph_3PO), which promotes the initial migratory insertion to form the acyl intermediate, dissociates from it prior to its reaction with the metal hydride. There is no evidence that such pre-dissociation occurs in reactions of metal alkyls with tertiary phosphines in polar solvents. Indeed the dependence of k_2 on the size of the tertiary phosphine suggests that complete predissociation of the solvent molecule does not occur.

The rate constants, k_1, and the ratios k_{-1}/k_2, obtained from plots of $1/k_{obs}$ against 1/[L], are given in Table 1 for reactions of series of *meta*- and *para*-substituted benzylmanganese complexes with triphenylphosphine. As is the case for the $[(\eta^5\text{-}C_5H_5)(CO)_3MoR]$ system [1], k_1 is enhanced moderately by electron-donating substituents. With the exception of the 4-F compound which consistently reacted faster than expected, the Hammett plot, log k_X/k_H versus substituent constant, σ, [17] is linear (see Fig. 1) with the sensitivity parameter, ρ, for the manganese system (−1.1) slightly greater than for molybdenum (−0.9). The negative sign of ρ, and its modest value, imply that, in the transition state of the k_1 step, there is an electron demand at a reaction centre situated beyond the benzylic carbon atom.

The overall direction of the electronic effect is the same as that observed previously in reactivity sequences for the direct reaction of CO with $[(CO)_5MnR]$ in 1,2-diethoxydiethyl ether, i.e. R = $CH_3 \gg CF_3$ [18] and R = i-Pr > Et > $CyCH_2$ > H

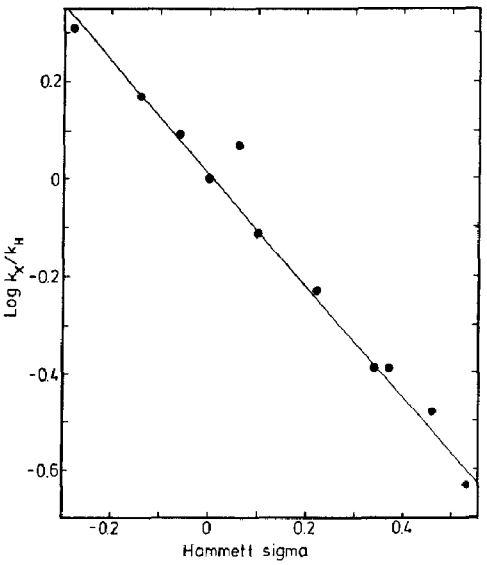

Fig. 1. Plot of $\log k_X/k_H$ against σ for the reaction of Ph_3P with $[(CO)_5MnCH_2C_6H_{5-n}X_n]$ in acetonitrile at 30 °C.

> CH_3OCH_2 > $C_6H_5CH_2$ > $HOC(O)CH_2$ [19]. In these reactions, the observed rate constant is approximately equal to $k_1k_2[CO]/k_{-1}$, rather than k_1, as a result of the low concentration of CO. However, in our separate measurement of k_1, k_{-1} and k_2 in the reaction of $[(\eta^5\text{-}C_5H_5)(CO)_2FeR]$, where R = Me, Et, Np, CH_2Cy, CH_2SiMe_3 etc., with DMSO, yielding $[(\eta^5\text{-}C_5H_5)(CO)(DMSO)FeCOR]$, and its further reaction with triphenylphosphine [4], we observed that the variation in each of k_{-1} and k_2 was in the same direction as in k_1 but an order of magnitude less. On this basis, the major change in the composite rate constant, $k_1k_2[CO]/k_{-1}$, should occur in k_1 thus allowing a direct comparison with the k_1 values in Table 1. No trend in k_{-1}/k_2 was observed for the *meta*- and *para*-substituted benzylmanganese complexes; potential analysis is complicated by the fact that each rate constant is separately affected by the electronic nature of the benzyl group.

We have observed previously, from the k_1 values for the reactions of $[(\eta^5\text{-}C_5H_5)(CO)_2FeR]$ complexes with DMSO, that reactivity is enhanced as the size of R increases, and have interpreted the result as reflecting the weakening of the iron–alkyl bond with increasing intramolecular interaction [4]. The observations were supported by the trend in k_1 values measured for the reaction of a series of *ortho*-substituted benzylmolybdenum complexes, $[(\eta^5\text{-}C_5H_5)(CO)_3MoCH_2C_6H_{5-n}X_n]$, with triphenylphosphine in acetonitrile; in this case, a large increase in k_1 occurs particularly for large alkyl substituents, e.g. X = 2-i-Pr compared with 4-i-Pr, and is also apparent in the reactivity order, 2-Me > 4-Me > 3-Me, [2].

For benzylmanganese complexes (Table 1), under the same conditions, the methyl substituent reactivity sequence is 4-Me > 3-Me > 2-Me, which is incompatible with the concept of steric enhancement. Indeed the trend is also at variance with that expected electronically; although the electronic effect of the methyl group is small, the group is electron-donating both inductively and by resonance, and its influence should be relatively greater from the *ortho* compared with the *para* position. However, as the steric influence in the *ortho* position(s) is increased, rate

enhancement is observed. Thus k_1 for the 2-isopropyl compound is comparable with k_1 for the 4-isopropyl (i.e., the *ortho* "inhibition" observed for the methyl substituent is overcome), and significant rate enhancement (far greater than predicted electronically) occurs for the 2,4,6-triisopropyl complex. The 2-t-butyl compound reacted very rapidly. Also, the k_1 value for the 2,4,6-trimethylbenzylmanganese complex is approximately three times higher than that for the 4-methyl compound and k_1 for the 2,3-dimethyl complex is higher than k_1 for the 3-methyl. The observed reactivities for these compounds and the pentamethylbenzyl compound are, though, basically compatible with predictions based on the additivity of substituent electronic effects.

The low reactivity of the 2-methylbenzylmanganese compound may reflect competition between two steric influences. In addition to enhancement engendered by non-bonded interactions in the starting material, which effectively serve to weaken the metal–carbon bond in the ground state, inhibition will result from steric interactions in the transition state associated with the migration of the alkyl group to a carbonyl carbon atom. The latter factor is highlighted by the substantial decreases in k_1 in reactions of benzylmolybdenum compounds which are di-*ortho*-substituted with large alkyl groups, e.g. $[(\eta^5\text{-}C_5H_5)(CO)_3MoCH_2C_6H_2\text{-i-}Pr_3\text{-}2,4,6]$, compared with their singly substituted counterparts [2]. With the manganese complexes, the limiting size necessary for the onset of this effect as a major influence on reactivity has not been reached. The 2,4,6-t-butylbenzyl manganese compound, which potentially could have provided a test of whether there is a similar retarding effect in the manganese system, decomposed during preparation at $-78\,^{\circ}C$. For the concept of two competing influences to be valid, it would be necessary for the profile of each effect, with respect to substituent, to be quite different and for the profile to vary from metal to metal. We propose that the overall effect is essentially to create a "steric window" within which reactivity is enhanced. Comparison of the relative reactivities of the manganese and cyclopentadienylmolybdenum compounds suggests that the window for the manganese system encompasses relatively larger alkyl groups and that manganese compounds are, overall, significantly less congested.

No clear trend in k_{-1}/k_2 is observed but, for some large *ortho* substituents, e.g. 2,4,6-Me_3, (but not 2-t-Bu), the ratio is very small.

The k_1 values for *ortho*-halobenzylmanganese compounds show similar trends. As expected from the higher contribution from the electron-withdrawing inductive effect from the *ortho* position, the k_1 value for the 2-chlorobenzylmanganese complex (1.8×10^{-5} s^{-1} is significantly less than k_1 for the 4-chloro complex (17.3×10^{-5} s^{-1}); the decrease is somewhat greater than for the corresponding cyclopentadienylmolybdenum compounds (11.2×10^{-5} s^{-1} versus 16.8×10^{-5} s^{-1}) [1,2] which suggests a further contribution from steric inhibition. Similar behaviour was observed for the corresponding fluorobenzylmanganese compounds (k_1 for 2-F, 3.7×10^{-5} s^{-1} compared with 4-F, 34.2×10^{-5} s^{-1}). The 2,6-dichlorobenzylmanganese complex was significantly more reactive ($k_1 = 0.8 \times 10^{-5}$ s^{-1}) than predicted on the basis of additivity of the effect observed for the 2-Cl complex. This contrasts with the cyclopentadienyl-molybdenum system where di-*ortho*-substitution resulted in almost complete inhibition of reaction. The k_1 (7.6×10^{-5} s^{-1}) observed for the 2-methoxybenzylmanganese system, where the substituent is again electron-withdrawing by induction and electron-donating by resonance, can be interpreted in

Table 2

Rate constants for reaction of tertiary phosphines with $[(CO)_5MnCH_2C_6H_{5-n}X_n]$ in acetonitrile at 30 °C

Substituent, X_n	Phosphine	Cone Angle	$10^5 k_1$ (s^{-1})	$10^3 k_{-1}/k_2$ (mol L^{-1})
H	PMe_2Ph	122	30.3	1.4
H	P-n-Bu_3	132	31.4	1.8
H	$PMePh_2$	136	30.6	2.3
H	$PEtPh_2$	140	29.6	2.6
H	PPh_3	145	29.0	5.3
H	P-i-$PrPh_2$	150	29.7	5.2
H	P-t-$BuPh_2$	157	31.8	21
H	PCy_3	170	29.4	33
2-Me	PMe_2Ph	122	25.3	~0
2-Me	$PEtPh_2$	140	24.5	~0
2-Me	PPh_3	145	24.6	2.3
2-Me	PCy_3	170	24.6	22
2,4,6-Me_3	PMe_2Ph	122	127	~0
2,4,6-Me_3	PPh_3	145	127	~0
2,4,6-Me_3	PCy_3	170	123	5
2,4,6-i-Pr_3	PMe_2Ph	122	326	~0
2,4,6-i-Pr_3	PPh_3	145	330	~0
2,4,6-i-Pr_3	PCy_3	170	332	~0

a manner similar to the *ortho*-halo compounds. Although the CF_3 group is strongly electron-withdrawing both by induction and resonance from *ortho* and *para* positions, which on electronic grounds should result in much reduced reactivity for the 2-CF_3 relative to the 4-CF_3 compound, the difference in k_1 (3.3×10^{-5} s^{-1} compared with 7.0×10^{-5} s^{-1}) is small. This is consistent with the onset of an enhancing steric effect for this larger substituent.

Steric and electronic effects of the nucleophile, L, on the k_2 stage were evaluated from the variation in the ratio, k_{-1}/k_2, measured for the unsubstituted benzylmanganese complex with a series of tertiary phosphines with a wide range of cone angle and electronic parameter [20]. The reaction scheme requires that k_1 and k_{-1} should be independent of the phosphine and, accordingly, the values of the ratio k_{-1}/k_2 will reflect the trend in k_2. The k_{-1}/k_2 values (Table 2) increase (i.e. decreasing k_2) with increasing cone angle in a similar manner to those observed in the $[(\eta^5\text{-}C_5H_5)(CO)_3MoCH_2Ph]$ system and to the k_2 values for the reaction of $[(\eta^5\text{-}C_5H_5)(CO)(DMSO)FeCH_2Cy]$ with phosphines [3]. There is no correlation with the Tolman electronic parameter. For the manganese system, the region of rapid decrease in k_2 occurs at a higher cone angle than for the cyclopentadienyl complexes. Indeed, for manganese, even tricyclohexylphosphine (cone angle = 170°) is quite reactive. Cone angle dependences for *ortho*-substituted benzylmanganese complexes show a similar general trend (Table 2). The k_2 results suggest that steric effects on this step are relatively less important in the manganese than in the cyclopentadienyl-molybdenum and -iron systems. In each case, though, it seems unlikely that the observed dependence on cone angle would arise if the solvent molecule had completely dissociated from the intermediate prior to reaction with tertiary phosphine. In this regard, it is interesting to note that, for the k_3 step for the manganese system, which involves the direct interaction of phosphine with the

metal in the intramolecular (and associative) alkyl migration process, the reactivity trend is with the Tolman electronic parameter of the phosphine rather than its cone angle [21].

Consistent with previous observations on the stereochemistry of the products $[(CO)_4LMnCOCH_3]$ [22] and $[(CO)_4LMnCOCH_2Ph]$ [23], the *cis* isomer of the acyl compound is obtained exclusively for relatively small phosphines, such as PMe_2Ph and $PMePh_2$, even in the case of bulky benzyl substituents. For larger phosphines, a mixture of *cis* and *trans* isomers of $[(CO)_4LMnCOCH_2Ph]$, is observed (for PPh_3, 71% *cis*; P-t-$BuPh_2$, 50% *cis*, at equilibrium).

Interestingly, and contrary to our expectation based on enhanced decarbonylation rates of $[(\eta^5\text{-}C_5H_5)(CO)_2LMoCOR]$ as the size of the tertiary phosphine increases [24], decarbonylation in $[(CO)_4LMnCOCH_2C_6H_{5-n}X_n]$ was completely inhibited in the case of bulky benzyl groups (X_n = 2-i-Pr, 2-t-Bu, 2,4,6-Me_3, 2,4,6-i-Pr_3 and Me_5). Qualitatively, decarbonylation for the benzylmanganese complex was considerably more facile than for the methyl complex and was significantly enhanced, as with the cyclopentadienylmolybdenum system, by increasing size of the tertiary phosphine. Strangely, however, $[(CO)_4(PCy_3)MnCOCH_2Ph]$ decarbonylated only slowly in acetonitrile solution at 60°, perhaps reflecting unfavourable steric effects in the *cis*-product, $[(CO)_4(PCy_3)MnCH_2Ph]$. A rate constant, $k_{isom} = 1.1 \times 10^{-4}$ s^{-1} for the *cis/trans* isomerisation of $[(CO)_4(PPh_3)MnCOCH_2C_6H_2Me_3\text{-}2,4,6]$ was measured, in CD_3CN at 22°C, by monitoring the ^1H NMR spectrum in the benzylic region. Likewise an approximate $k_{isom} = 7 \times 10^{-4}$ s^{-1}, at 27° in CH_3CN, was obtained for $[(CO)_4(PPh_3)MnCOCH_2Ph]$; the measurement was complicated by the competing (but slower) decarbonylation process ($k_{decarb} \sim 1.4 \times 10^{-5}$ s^{-1}). The rate constants for the isomerisation are comparable with that reported ($k_{isom} = 2.5 \times 10^{-4}$ s^{-1}) for $[(CO)_4(PPh_3)MnCOCH_3]$ at 30°C in acetone [14].

The preparation of the 2,4,6-triisopropylbenzylmanganese complex, from $[Mn(CO)_5]^-$ and the benzyl chloride, surprisingly led to a mixture of the alkyl, $[(CO)_5MnR]$, and acyl products, $[(CO)_5MnCOR]$. We believe that the acyl arises by direct insertion of carbon monoxide formed by decomposition of $[(CO)_5MnR]$ during the synthesis. The decomposition is presumably enhanced for large R because of significant Mn–C bond weakening. The 2,4,6-triisopropylbenzylmanganese compound will, unlike the benzyl complex [25], insert carbon monoxide directly (reaction proceeds to completion in THF at 25°C for $P = 1$ atm with $t_{1/2} \sim 1$ h). The high reactivity for direct insertion of CO is compatible with the high k_1 value for this alkyl group in the phosphine-induced process. The reaction of CO with the 2,4,6-trimethylbenzyl compound does not go to completion and is significantly slower under the same conditions (~ 66% acyl after 10 h). Spontaneous insertion of carbon monoxide was also observed in the preparation of $[(CO)_4(PPh_3)MnCH_2C_6H_2Me_3\text{-}2,4,6]$ from $[(CO)_4(PPh_3)Mn]^-$ and 2,4,6-trimethylbenzyl chloride. Similar behaviour has been observed for the $[(CO)_5MnCH_2CH_3]$ system [26].

The ^1H and ^{13}C NMR spectra of the alkyl complex, $[(CO)_5MnCH_2C_6H_2\text{-}i\text{-}Pr_3\text{-}2,4,6]$, and its acyl, $[(CO)_5MnCOCH_2C_6H_2\text{-}i\text{-}Pr_3\text{-}2,4,6]$, indicate that there is substantial intramolecular steric interaction in each molecule; while the two *ortho*-isopropyl groups are equivalent overall, the two methyl groups within each *ortho*-isopropyl group are chemically inequivalent. The inequivalence probably results from restricted rotation about the methylene to aryl–carbon bond or about the bond between the isopropyl methine carbon and *ortho* ring carbon. The methyl groups in

the *para*-isopropyl group are equivalent. This could result from either accidental degeneracy in the first case or, in the second, because no significant restriction to rotation exists for the less sterically congested *para*-isopropyl group. Peak broadening arising from decomposition of the alkyl at higher temperatures prevented an evaluation of the extent of the barrier to rotation. Such analysis was likewise not possible for the acyl which decarbonylated to the decomposing alkyl at higher temperatures.

Experimental

General

Manipulation of air-sensitive compounds was carried out under high purity nitrogen using Schlenk methods. Acetonitrile (dried over Merck "Sicapent"), tetrahydrofuran (dried over CaH_2) and diethylether (CaH_2 followed by $LiAlH_4$) were distilled under nitrogen immediately prior to use. Microanalyses were carried out in the Department on a Carlo Erba automatic analyser. Most benzyl chlorides used were available commercially and were used directly; 4-isopropylbenzyl chloride (Tokyo Kasei) contained ~ 15% of the 2-isopropyl isomer which could not be separated. Samples of 2-t-butylbenzyl chloride (prepared in low yield by permanganate oxidation of 2-t-butyltoluene [27], followed by $LiAlH_4$ reduction of the benzoic acid to give the alcohol, and final treatment with thionyl chloride), 2,4,6-tri-t-butylbenzylchloride (bromination of 2,4,6-tri-t-butylbenzene by bromine/trimethylphosphate, followed by lithiation with n-butyl lithium, treatment with formaldehyde, and chlorination by thionyl chloride) and 2,4,6-triisopropylbenzyl chloride (lithiation of the bromobenzene, followed by reaction with carbon dioxide, reduction to the alcohol with $LiAlH_4$ and chlorination with thionyl chloride) were prepared by Dr K.G. Penman in this Department.

Preparation of $[(CO)_5MnCH_2C_6H_{5-n}X_n]$ complexes

Dimanganese decacarbonyl (2 g, 5 mmol) in THF solution (40 ml) was added to sodium amalgam (0.6 g Na, 26 mmol/6 ml Hg) and stirred under an atmosphere of nitrogen at room temperature for 1 h until the yellow colour disappeared. The amalgam was drained from the reaction vessel and the solution washed with mercury (2 × 3 ml). The solution was then poured onto the substituted benzyl chloride (10 mmol) in another vessel under an atmosphere of nitrogen. After 2 h, the mixture was evaporated to dryness and extracted with CH_2Cl_2. The filtered solution was then chromatographed on a column of alumina (grade II–III), eluting with hexane. On evaporation of the hexane solution to dryness, a yellow solid was obtained, in generally in 40–60% yield, which was further purified by sublimation (60 °C/10 mmHg). The compounds with 3-F and 3-CF_3 substituents, and the mixture obtained from the reaction with 2- and 4-isopropylbenzyl chloride, were yellow oils which remained so after short-path distillation and repeated chromatography.

Compounds were characterised microanalytically (representatively; for $[(CO)_5MnCH_2C_6H_4Me$-2], found C, 51.9; H, 3.1. $C_{13}H_9MnO_5$ calc.: C, 52.0; H, 3.0%) and spectroscopically (^1H, ^{13}C, ^{55}Mn NMR and IR) [28].

Kinetics

Kinetic data for CO insertion were generally obtained by monitoring the decrease in intensity of the A_1 infrared band of the manganese benzyl at around 2100 cm^{-1}. Infrared spectra were recorded on a Perkin Elmer PE283B infrared spectrophotometer. A solution of 10 ml of 0.008 *M* manganese complex in acetonitrile was added to a known amount of the tertiary 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 0.025 and 0.20 *M* was used. After degassing 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 1–2%. Values of k_1, determined from the plot of $1/k_{obs}$ versus 1/[L], are of the same precision while k_{-1}/k_2 values are less precise (~ 5%).

For the 2- and 4-isopropylbenzylmanganese complexes, an 85/15 mixture was used in the kinetic study. The rate constants were measured on a JEOL GX-400 spectrometer by ^1H NMR at 399.65 MHz in acetonitrile solution at 22 °C at a total concentration of 0.008 *M* manganese. The height of the CH_2 benzylic proton resonance was followed with time using the JEOL Plexus StackS program, comparing the starting material resonances (δ 2.5) with the product peaks (δ 4.5) to obtain relative concentrations of these species. A substrate concentration of 0.008 *M* was again used in CD_3CN solution at 22 °C.

Cis–trans isomerisations of $[(CO)_4LMnCOR]$ were followed, at 22 °C, by ^1H NMR at 399.65 MHz on a JEOL GX-400 spectrometer (the height of the CH_2 benzylic proton resonances was followed with time using the JEOL Plexus StackS program, monitoring the *cis*-acyl (δ 4.5) and *trans*-acyl (δ 5.0) resonances to obtain relative concentrations of these species) or by observing the CH_2 proton resonances at 100 MHz and 27 ° using a JEOL JNM-PS-100 NMR spectrometer.

NMR spectroscopic study of $[(CO)_5MnCH_2C_6H_2$-i-Pr_3-2,4,6]

The ^{13}C NMR spectrum (measured in $CDCl_3$ at 25 °C at 25.00 MHz on a JEOL FX100 spectrometer and referenced to $CDCl_3$ at δ 77.00) showed isopropyl methine signals at δ 29.82 (*para*) and δ 34.00 (*ortho*) and three isopropyl methyl signals at δ 24.05 (*para*) and δ 22.14 and δ 25.96 (*ortho*). The ^1H NMR spectrum (measured in $CDCl_3$ at 25 °C at 300.066 MHz on a Bruker CXP300 spectrometer and referenced to TMS) showed two well separated apparent septets, (δ 2.81 (^3J(H–H) 6.7 Hz) in $CDCl_3$ of relative intensity 1, and δ 3.18 of relative intensity 2) and three isopropyl methyl doublets (δ 1.19 (^3J(H–H) 6.5 Hz) overlapping with δ 1.21, and δ 1.32) of equal intensity. Irradiation of the *para* septet collapses the central doublet and irradiation of (*ortho*) "septet" collapses the outer doublets. Irradiation of the δ 1.32 doublet (i.e., at one set of methyl protons on the *ortho* groups) collapses the (*ortho*) "septet" at δ 3.18 into a quartet.

NMR spectroscopic study of $[(CO)_5MnCOCH_2C_6H_2$-i-Pr_3-2,4,6]

The ^{13}C NMR spectrum shows two isopropyl methine signals (δ 29.74 (*para*) and δ 34.19 (*ortho*)) and three methyl signals (δ 21.27, 24.01 and 26.55). The ^1H NMR spectrum shows two overlapping apparent methine septets (δ 2.86 and 2.92, of relative intensity 1/2) and three methyl doublets (δ 1.06, ^3J(H–H) 6.7 Hz; δ 1.24, ^3J(H–H) 6.9 Hz; δ 1.37, ^3J(H–H) 6.7 Hz). Irradiation of the central (*para*) methyl

doublet collapses the smaller methine septet into a singlet whereas irradiation of either of the outer (*ortho*) doublets collapses the larger methine signal into a quartet.

Acknowledgements

We thank the Australian Research Grants Scheme for financial support and Dr K.G. Penman and Miss J. Boon for technical assistance.

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