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Preliminary communication

ortho-EFFECTS ON CARBON MONOXIDE INSERTION IN BENZYL-MOLYBDENUM COMPLEXES*

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Summary

The formation of phosphine-substituted acylmolybdenums $[(\eta^5\text{-}C_5H_5)(CO)_2(PPh_3)Mo(COR)]$, from reactions between substituted benzylmolybdenum complexes and triphenylphosphine in acetonitrile, is enhanced by the presence of a single bulky substituent in the *ortho*-position. However disubstitution (for i-Pr, Cl and OMe) causes a pronounced lowering of reactivity. The results are interpreted in terms of the steric demands of the reaction.

Recently we observed [1] that the insertion of carbon monoxide into iron—carbon σ bonds in the reaction was significantly enhanced by increas-

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

ing size of the alkyl substituent (e.g. k_1 for $(Me_3Si)_2CH \gg Me_3CCH_2 >$ i-Pr, i-Bu > Et > Me etc). In this paper we present a further comment on steric effects in the reactions of a series of mono- and di-substituted benzylmolybdenum complexes, $[(\eta^5\text{-}C_5H_5)(CO)_3MoR]$, with triphenylphosphine in acetonitrile which yield the phosphine-substituted acyl derivatives $[(\eta^5\text{-}C_5H_5)(CO)_2(PPh_3)Mo(COR)]$. The rate constant for this process, which is effectively first order in alkylmolybdenum [2], was obtained, for the several substituted benzyl complexes, at 30°C, by a proton NMR method in which the resonance of the cyclopentadienyl groups of starting material, initially 0.2 *M*, and acyl product were monitored. The concentration of triphenylphosphine was 0.2 *M* in each reaction.

The results for mono-*ortho* complexes are summarised in Table 1, and com-

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TABLE 1

k_{obs} VALUES FOR REACTION OF $[Cp(CO_3)_3Mo(CH_2C_6H_4X)]$ WITH PPh_3 IN CH_3CN AT 30°C

X	10^5 k_{obs} (s^{-1})		
	ortho	*meta*	*para*
H	32	32	32
Me	73	34	39
i-Pr	~1500	—	37
Cl	11	13	17
F	9	15	31
OCH_3	28	25	48
CF_3	10	11	8

pared with rate constants obtained previously [2] for *meta*- and *para*-substituents in the same system. The latter rate data, which should be uninfluenced by steric factors, demonstrated a moderate increase in reactivity (substituent parameter, $\rho \simeq -1.0$) with electron donation to the benzyl system.

Striking support for the concept of increased reactivity with size of the substituent came from the reaction of the *ortho*-isopropylbenzyl complex for which the rate constant is roughly twenty times higher than for *ortho*-methyl, which is a much smaller substituent with a similar electronic effect (as emphasised by the small differences in rate constants when the isopropyl and methyl substituents are in the *meta* and *para* positions and sterically remote from the reaction site). The approximately 40-fold rate enhancement for the *ortho*-isopropyl- over the *para*-isopropyl-benzyl complex, and the two-fold increase for *ortho*-methyl over the *meta*- and *para*-methyl complexes, again clearly suggest significant steric enhancement, although a slight increase might also be related to the mild electron inductive effect of the alkyl substituent which would operate more strongly from the *ortho*-position.

The observed differences for the trifluoromethyl substituent are less marked but again suggest a positive steric effect. The CF_3 group, which is strongly electron withdrawing both by resonance and induction, should on electronic grounds slow the reaction more in the *ortho*- than in the *para*-position. However *k(ortho)* is significantly higher than *k(para)*, and only slightly lower than *k(meta)*, for which position the electron-withdrawing resonance effects are inoperative.

No unambiguous evidence for *ortho*-enhancement can be obtained from the data for the mono-fluoro, -chloro and -methoxy substituents. For both chloro and fluoro, substituents which are electron donating by resonance and strongly electron withdrawing inductively, a rate sequence *para* > *meta* > *ortho* is observed. In these cases, the negative effect of the increased inductive effect from the *ortho*-position may be swamping any steric influence. For the methoxy group, which is more strongly electron donating by resonance, but less strongly inductively withdrawing than the halo groups, the sequence is *para* > *ortho* > *meta*.

With the aim of accentuating steric effects, we then explored the reactivity of corresponding complexes containing two *ortho* substituents in the benzyl group. For the 2,4,6-trimethylbenzylmolybdenum compound, a small, but not

substantial, increase in the rate constant ($k = 85 \times 10^{-5}$ s^{-1}) was observed over the mono-substituted *ortho*-methyl complex ($k = 73 \times 10^{-5}$ s^{-1}). On the basis of earlier results, this seemed more compatible with the electron-donating effect of the three methyl substituents rather than to the increased bulk. Unexpectedly however, on moving to the significantly more crowded 2,4,6-triisopropyl complex, the insertion of carbon monoxide was completely inhibited. Very slow reactions were also observed for the 2,6-dichloro ($k < 0.1 \times 10^{5}$ s^{-1}) and the 2,6-dimethoxy ($k = 0.9 \times 10^{-5}$ s^{-1}) complexes, but although it is not possible unambiguously to separate electronic and steric effects for these substituents, the large decreases strongly suggest that steric factors predominate.

Our explanation [1] of steric enhancement in the reaction of the alkyl-irons with DMSO involved the concept of relatively greater proportional release of steric strain, in the transition state leading to the formation of the DMSO-substituted acyl derivative, as the size of the alkyl group increased. In the transition state [3], as the partial bond to the solvent is formed, the metal—carbon σ bond lengthens, and the large substituent is partially removed from the crowded environment at the metal centre.

A similar explanation may apply when there is only one *ortho*-substituent in the benzyl-molybdenum complexes. Although in this case the reaction is two-stage and involves, first, the formation of an acetonitrile-stabilised intermediate, followed by displacement of solvent by triphenylphosphine, the conditions of the experiments were such that the observed rate constants approximate to those of the first reaction stage (i.e. metal—carbon bond breaking). While the overall steric effect clearly increase in the case of two *ortho*-substituents, the results cannot be interpreted on the same basis. For these systems we believe that the second *ortho*-substituent plays a specific role in restricting the access of the migrating benzylic carbon atom to the carbonyl carbon. Models show that the restriction is severe for the triisopropyl derivative. When there is a single bulky *ortho*-substituent, rotation of the aromatic ring into a vertical plane in the pseudo-square pyramidal molecule can alleviate this specific interaction, but necessary interactions between one of the *ortho*-substituents and the cyclopentadienyl ring must inhibit such rotation in the di-*ortho* compounds. Inevitably, then, the activation energy for reaction would increase markedly.

References

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