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Preliminary communication

THE MECHANISM OF FLUXIONALITY OF (1,2,7-η^3-2-Me-benzyl)(η^5-C_5H_5)Mo(CO)$_2$

BRIAN E. MANN* and SUSAN D. SHAW

Department of Chemistry, The University, Sheffield, S3 7HF (Great Brittain)

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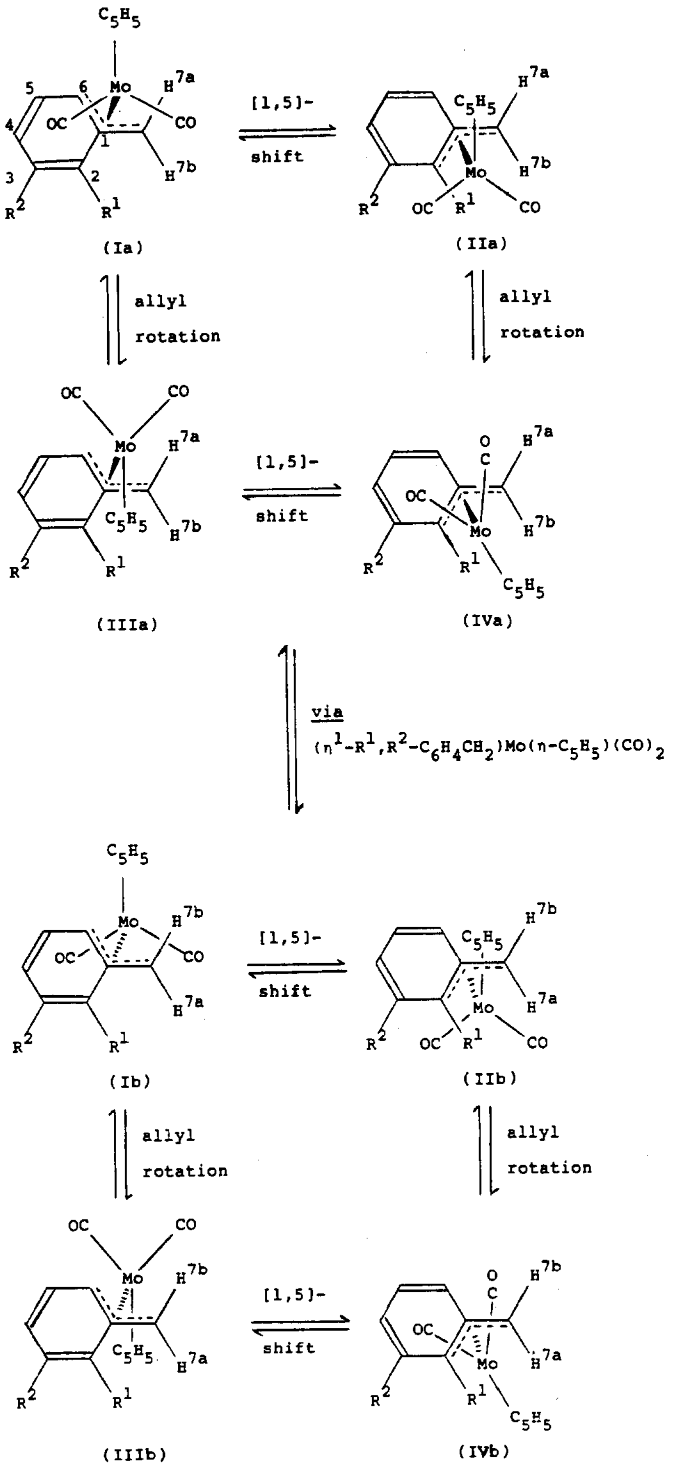
Summary

It is shown that (1,2,7-η^3-2-Me-benzyl)(η^5-C_5H_5)Mo(CO)$_2$ exists in solution as one isomer which is fluxional, probably via (7-η^1-2-Me-benzyl)(η^5-C_5H_5)Mo(CO)$_2$, with $\Delta G^{\neq}_{370} = 23.6 \pm 1.0$ kcal mol^{-1}. In contrast, (1,2,7-η^3-3-Me-benzyl)(η^5-C_5H_5)Mo(CO)$_2$ exists as two isomers at $-20\,^\circ$C, which undergo interconversion at room temperature with $\Delta G^{\neq}_{293}$ 15.7 kcal mol^{-1}. This dynamic process is an allyl rotation. It is probable that there is also a low energy [1,5]-sigmatropic shift.

In 1969, Cotton and Marks carried out a very elegant study of the fluxionality of (1,2,7-η^3-benzyl)(η^5-C_5H_5)Mo(CO)$_2$ derivatives [1]. By examining the (1,2,7-η^3-3,5-Pr^1-benzyl)(η^5-C_5H_5)Mo(CO)$_2$ derivative they concluded that the mechanism of fluxionality involves a 16-electron (7-η^1-3,5-Pr^i-benzyl)(η^5-C_5H_5)Mo(CO)$_2$ intermediate. Subsequent work has shown their interpretation to be oversimplified, and possibly wrong. Two additional mechanisms have been identified for this type of system: a very low energy [1,5]-sigmatropic shift [2], as in Pd(η^3-CPh$_3$)(acac) [3,4], with $\Delta G^{\neq} < 8$ kcal mol^{-1}, and rotation of the allyl group, as found in (η^3-C_3H_5)(η^5-C_5H_5)Mo(CO)$_2$ [5], with $\Delta G^{\neq}$ ca. 15 kcal mol^{-1}. The three mechanisms can be combined to produce the overall fluxional process given in Scheme 1.

In order to study the problem, it is necessary to reduce the symmetry of (1,2,7-η^3-benzyl)(η^5-C_5H_5)Mo(CO)$_2$, and this was achieved by synthesising (1,2,7-η^3-2-Me-benzyl)(η^5-C_5H_5)Mo(CO)$_2$ and (1,2,7-η^3-3-Me-benzyl)(η^5-C_5H_5)Mo(CO)$_2$, advantage being taken of a recently described synthetic procedure [6]. (η^5-C_5H_5)Mo(CO)$_3$Me was treated with LiBHEt$_3$ to generate (η^5-C_5H_5)Mo(CO)$_2$(η^2-MeCHO), which was then treated with the 2- or 3-methyl benzyl chloride in THF at low temperatures to generate (1,2,7-η^3-*n*-Me-benzyl)(η^5-C_5H_5)Mo(CO)$_2$, $n = 2$ or 3, respectively, isolated in moderate yield after chromatography on alumina [6].

At room temperature, the ^{1}H NMR spectrum of (1,2,7-η^3-2-Me-benzyl)(η^5-C_5H_5)Mo(CO)$_2$ in C_6H_6 is consistent with the major isomer present being Ia/Ib, R^1 = Me, R^2 = H. The ^{1}H chemical shifts and coupling constants are H^3, δ 6.70,



SCHEME 1. The fluxional processes occurring in (1,2,7-η^3-2,3-R^1,R^2-benzyl)(η^5-C_5H_5)Mo(CO)$_2$. Note that Ia, IIa, IIIa, and IVa are related to Ib, IIb, IIIb, and IVb as enantiomers.

$J(H^3, H^4)$ 6.5 Hz, H^4, 6.96, $J(H^4, H^5)$ 8 Hz; H^5, 6.82, $J(H^5, H^5)$ 6 Hz; H^6, 4.41; H^{7a}, 1.22, $J(H^{7a}, H^{7b})$ 2 Hz; H^{7b}, 3.34; Me, 2.07; C_5H_5, 4.70 ppm [7]. The assignments of H^{7a} and H^{7b} are made on chemical shift grounds, by analogy to known compounds [5]. This assumption was confirmed by NOE measurements. Irradiation of H^{7a} produced an NOE into H^{7b}, as would be expected for the H^4 group and the cyclopentadienyl group. Similarly irradiation of H^{7b} produced an NOE into the methyl group and H^{7a}. The chemical shift of H^5 being δ 4.41 ppm is consistent with the major isomer being Ia/Ib, R^1 = Me, R^2 = H. During the NOE experiments, no effects of exchange were detected. If exchange occurs via a 16-electron (7-η^1-2-Me-benzyl)(η^5-C_5H_5)Mo(CO)$_2$, interconverting Ia and Ib, R^1 = Me, R^2 = H, then H^{7a} and H^{7b} must also exchange. No such exchange was detected at room temperature. In order to investigate the exhcange further, the solvent was changed to toluene-d_8. At 97 ° C, irradiation of H^{7a} produced a small, 8%, decrease in the intensity of H^{7b}, and vice versa. It was not possible to obtain quantitative exchange data from this observation owing to the expected NOE between H^{7a} and H^{7b} but, it corresponds to an exchange rate of between 0.2 and 0.02 s^{-1} depending on the assumptions made about the NOE. This corresponds to $\Delta G^{\neq}_{370}$ 23.6 ± 1.0 kcal mol^{-1}. Considerable sample decomposition occurred during this experiment, and no NOE was observed into other protons in the molecule, probably because the presence of paramagnetic decomposition products. If it is assumed that there is no NOE, then $\Delta G^{\neq}_{370}$ is ca. 24.5 kcal mol^{-1}. It is probable that the dynamic process involves a 16-electron (7-η^1-2-Me-benzyl)(η^5-C_5H_5)Mo(CO)$_2$ intermediate rather than rotation about the tolyl-CH_2 bond in (1,2,7-η^3-2-Me-benzyl)(η^5-C_5H_5)Mo(CO)$_2$. This activation energy can be compared with the value of $\Delta G^{\neq}_{348}$ of $\leq$ 18.8 kcal mol^{-1} estimated from data published by Cotton and Marks for (1,2,7-η^3-3,5-Pr^i-benzyl)(η^5-C_5H_5)Mo(CO)$_2$ [1]. It is improbable that Cotton observed this process. His evidence is based on the collapse of four doublets of the isopropyl-methyl groups to one doublet, with a line width of ca. 2 Hz. He notes that if the molybdenum remains on one face of the benzyl ligand, then the isopropyl-methyl signals will be two doublets separated by 1 Hz. This conclusion assumes that the methyl groups in the isopropyl substituents have temperature invariant chemical shifts. In (1,2,7-η^3-2-Me-benzyl)(η^5-C_5H_5)Mo(CO)$_2$ in toluene-d_8 the methyl signal moves from δ 2.02 ppm at −33 ° C to δ 1.94 ppm at 97 ° C. In the light of the data reported here, it is probable that Cotton's isopropyl-methyl doublet is acutally two unresolved doublets.

At −20 ° C, the ^1H NMR spectrum of (1,2,7-η^3-3-Me-benzyl)(η^5-C_5H_5)Mo(CO)$_2$ in toluene-d_8 shows the presence of two isomers in the ratio 1/2.2. The major isomer has ^1H NMR data: H^2, δ 4.00; H^4, ca. 6.70; H^5, ca. 6.70; H^6, 6.60, $J(H^5, H^6)$ 8 Hz; H^{7a}, 3.15; H^{7b}, 1.32; C_5H_5, 4.56; Me, 2.01 ppm, while the minor isomer has ^1H NMR data: H^2, δ 5.64; H^4, 6.70; H^5, 6.74; H^6, 4.81; H^{7a}, 1.81; H^{7b}, 2.55; C_5H_5, 4.41; Me, 2.14 ppm. Magnetisation transfer measurements at 20 ° C show pairwise exchange of signals between the two isomers, completely consistent with allyl rotation as in Scheme 1. No exchange corresponding to rotation about the C^1–C^7 bond was detected at room temperature, showing that a mechanism involving (1-η^1-3-Me-benzyl)(η^5-C_5H_5)Mo(CO)$_2$ is not significant. The line broadening gave $\Delta G^{\neq}_{293}$ 15.7 kcal mol^{-1} for going from the major to minor isomer. This can be compared with $\Delta G^{\neq}_{293}$ 14.1 kcal mol^{-1} for (1,2,7-η^3-4-Me-benzyl)(η^5-C_5H_5)Mo(CO)$_2$, and $\Delta G^{\neq}_{293}$ 15.9 kcal mol^{-1} for (1,2,7-η^3-3,5-Pr^i-benzyl)(η^5-C_5H_5)Mo(CO)$_2$ [1]. It therefore appears that the dynamic process normally observed in (1,2,7-η^3-benzyl)(η^5-C_5H_5)Mo(CO)$_2$ derivatives at around room temperature is allyl rotation.

The major isomer of (1,2,7-η^3-3-Me-benzyl)(η^5-C_5H_5)Mo(CO)$_2$ is IVa/IVb, R^1 = R^3 = H, R^2 = Me. This is consistent with the observation of H^2 at δ 4.00 ppm and H^6 at δ 6.60 ppm. This structure is preferred over IIa/IIb, R^1 = H, R^2 = Me because of the steric hindrance expected between the cyclopentadienyl ring and the benzyl group. The minor isomer can be taken to be predominantly Ia/Ib, R^1 = H, R^2 = Me, on the basis of the chemical shifts for H^2 of δ 5.64 ppm and H^6 of δ 4.81 ppm, but as the shift for H^2 is markedly different from that expected, viz. ca. δ 6.6 ppm, on the basis of structure Ia/Ib, R^1 = H, R^2 = Me, structure IIa/IIb, R^1 = H, R^2 = Me, must make a significant contribution. This contribution is reflected in the shifts of H^{7a} and H^{7b}, with rapid interconversion of Ia $\rightleftharpoons$ IIa and Ib $\rightleftharpoons$ IIb causing complete averaging.

All the observations reported here are consistent with the [1,5]-sigmatropic shift being very facile. The [1,5]-shift does provide a facile mechanism for the interconversion of pairs of isomers I/II and III/IV, giving rise to temperature dependent chemical shifts. The dynamic process observed at room temperature is allyl rotation, and then at high temperature there is metal movement from one face of the benzyl to the other.

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References

1 F.A. Cotton and T.J. Marks, J. Am. Chem. Soc., 91 (1969) 1339.

2 B.E. Mann, in E.W. Abel, F.G.A. Stone, and G. Wilkinson (Eds.), 'Comprehensive Organometallic Chemistry', Pergamon Press, Oxford, 1982, Vol. 3, p. 141.

3 A. Sonoda, B.E. Mann, and P.M. Maitlis, J. Chem. Soc., Chem. Commun., (1975) 108.

4 B.E. Mann, A. Keasey, A. Sonoda, and P.M. Maitlis, J. Chem. Soc., Dalton Trans., (1979) 338.

5 J.W. Faller and M.J. Incorvia, Inorg. Chem., 7 (1968) 840.

6 J.T. Gauntlet, B.F. Taylor, and M.J. Winter, J. Chem. Soc., Dalton Trans., (1985) 1815.

7 H^{7a} and H^{7b} refer to the numbering in Ia, IIa, IIIa, and IVa given in Scheme 1, throughout the paper.