Solvent Isotope Effects in the Cleavage of Benzyltrimethyl-silanes and -stannanes by Alkali

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Product isotope effects, given by the product ratio $XC_6H_4{\cdot}CH_3/XC_6H_4{\cdot}CH_2D$, have been measured for cleavage at *ca.* 21° of some compounds of the type $XC_6H_4{\cdot}CH_2{\cdot}MMe_3$ (M = Sn or Si) in 1 : 1 MeOH–MeOD containing sodium methoxide (2 mol l^{-1}). Values for various substituents X and M = Sn are: *p*-Me, 2·4; H, 2·1; *p*-Cl, 2·1; *m*-CF_3, 2·1 (all ±0·15); and for M = Si; H, 1·17; *m*-OMe, 1·25; *p*-Cl, 1·07; *m*-CF_3, 1·19 (all ±0·05). The corresponding value for $C_6F_5{\cdot}CH_2{\cdot}SiMe_3$ is 1·16. Overall solvent isotope effects, $(k_{SH}/k_{SD})_s$ given by the individual rates in non-deuteriated and deuteriated media at 50° have been determined for the compounds with X = *m*-CF_3; the values are: for M = Si, 0·50 in MeOH or in MeOH containing 18·6 mole % H_2O; for M = Sn, 0·95 in MeOH and 0·97 in MeOH containing 20 mole % H_2O.

It is concluded that, in the cleavage of the tin compounds certainly, and probably also in that of the silicon compounds, a free carbanion is not formed. It is suggested that the rate-determining step involves proton transfer from the solvent to the carbon atom of the breaking $M{-}CH_2{\cdot}C_6H_4{\cdot}X$ bond, with the MeO–M bond fully or almost fully formed in the transition state. Initial formation of the M^V intermediates $[(MeO)Me_3M{\cdot}CH_2{\cdot}C_6H_4X]^-$ is favoured.

THE main feature of the published information relevant to the mechanism of cleavage of $R_3M{-}CH_2{\cdot}C_6H_4{\cdot}X$ bonds, where M = Si or Sn, in aqueous methanolic alkali can be summarised as follows. (*a*) For the compounds $Me_3Si{\cdot}CH_2{\cdot}C_6H_4X$ the effects of the substituents X can be related with considerable precision to their σ, or where appropriate (*e.g.* X = *p*-NO_2), σ^- constants; the relationship $\log k_{rel} = 4{\cdot}9\sigma$ (or σ^-) applies for 39 wt. % H_2O–MeOH at 50°, where k_{rel} is the rate for the substituted compound relative to that for the parent compound with X = H.[1,2] (*b*) Benzyltrimethylstannane is 29 times as reactive as its silicon analogue in 1 : 5 v/v H_2O–MeOH at 50°. The Hammett relationship applies to the compounds $Me_3Sn{\cdot}CH_2{\cdot}C_6H_4X$ with a value of ρ (4·2) smaller than that (4·7) for the corresponding silicon compounds in the same medium.[3]

The mechanistic choices can best be discussed in terms of the three steps (1)—(3), which may, as we shall see, be real or only notional. For simplicity we have written the base as methoxide ion, and the solvent as methanol, although in aqueous methanol hydroxide ion and water are also involved.

$$Me_3M{\cdot}CH_2{\cdot}C_6H_4X + MeO^- \rightleftharpoons \underset{\text{(I)}}{[(MeO)Me_3M{\cdot}CH_2{\cdot}C_6H_4X]^-} \quad (1)$$

$$[(MeO)Me_3M{\cdot}CH_2{\cdot}C_6H_4X]^- \longrightarrow MeOMMe_3 + XC_6H_4{\cdot}CH_2^- \quad (2)$$

$$XC_6H_4{\cdot}CH_2^- + MeOH \longrightarrow XC_6H_4{\cdot}CH_3 + MeO^- \quad (3)$$

The magnitude of the ρ factor, and the need to use σ^- constants for certain groups X, mean that the $M{-}CH_2{\cdot}C_6H_4X$ bond must be broken in the rate-determining step,[2] with substantial carbanionic character being developed at the benzylic carbon atom in the transition state. A mechanism with step (1) [formation of the M^V intermediate (I)] rate-determining can thus be discarded.[2] The remote possibility that the large ρ factor could arise from the effects of the substituents X, on the stability of the M^V intermediate is ruled out by the observation that a ρ factor of only +1·7 applies for substituents Y in cleavage of $YC_6H_4{\cdot}Me_2Si{-}CH_2{\cdot}C_6H_4Cl$-*p* bonds by methanol containing 10% aqueous potassium hydroxide at 50°.[4] The values of these ρ factors indicate that in the highest-energy transition state a considerable proportion of the negative charge lies on the benzylic carbon atom, and a smaller, but still substantial amount on the silicon atom, which means that the MeO–M bond must be fully or almost fully formed.

There remains a wide choice of mechanism.[2,5] Thus, (A) the intermediate (I) could be formed reversibly in a fast process (1); the benzyl carbanion then separates in the rate-determining step (2), and is rapidly destroyed in step (3) [*i.e.* (1) fast, (2) slow, (3) fast]. Alternatively, (B) (2) and (3) could be synchronous, the benzyl carbanion never being free [*i.e.* (1) fast, (2) + (3) slow]. In a third alternative (C) the attack of methoxide ion is concerted with the separation of a free carbanion [*i.e.* (1) + (2) slow, then (3) fast]. A fourth possibility (D) is that steps (1), (2), and (3) are all concerted [(1) + (2) + (3) slow]. In a concerted mechanism, bond making and bond breaking need not be quantitatively synchronous.

In order to throw further light on the mechanism, and in particular to ascertain whether or not a free benzyl carbanion separates, we have examined the solvent isotope effects for cleavage of the compounds $Me_3M{\cdot}CH_2{\cdot}C_6H_4X$ by methoxide ion in methanol.†

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† A brief account of a less accurate preliminary study has appeared.[6] Our application of solvent isotope effects to these problems followed the precedent set by Dr. D. L. Stiggall working in association with Professor T. G. Traylor.[7]

[1] C. Eaborn and S. H. Parker, *J. Chem. Soc.*, 1955, 126.

[2] R. W. Bott, C. Eaborn, and B. M. Rushton, *J. Organometallic Chem.*, 1965, **3**, 448.

[3] R. W. Bott, C. Eaborn, and T. W. Swaddle, *J. Chem. Soc.*, 1963, 2342.

[4] B. Bøe and C. Eaborn, unpublished work.

[5] C. Eaborn and R. W. Bott, 'Organometallic Compounds of the Group IV Elements,' ed. A. G. MacDiarmid, Dekker, New York, vol. 1, Part 1, 1968, pp. 402—405.

[6] R. Alexander, C. Eaborn, and T. G. Traylor, *J. Organometallic Chem.*, 1970, **21**, P65.

[7] D. L. Stiggall, Ph.D. Thesis, University of California, San Diego, 1968; *Diss. Abs.* (*B*), 1968, **29**, 1991.

In the main we have concentrated on the product isotope effects (PIE), given by the ratio ($CH_3{\cdot}C_6H_4X/DH_2C{\cdot}C_6H_4X$) of products obtained by cleavage in 1 : 1 MeOH–MeOD containing sodium methoxide (2 mol l^{-1}) at room temperature (21 ± 2°). This quantity is effectively equal to the primary solvent isotope effect $(k_{MeOH}/k_{MeOD})_I$ for the product-determining step. The results are shown in Table 1.

TABLE 1

Product isotope effects (PIE) in cleavage of $XC_6H_4{\cdot}CH_2{\cdot}MMe_3$ and $C_6F_5CH_2SiMe_3$ by 2·0M-sodium methoxide in 1 : 1 MeOH–MeOD

M	X	PIE [a]	M	X	PIE [b]
Sn	*p*-Me	2·4	Si	H	1·17
	H	2·14		*m*-OMe	1·25
	p-Cl	2·14		*p*-Cl	1·07 [c]
	m-CF_3	2·12		*m*-CF_3	1·19
				(F_5) [d]	1·16

[a] At 21°; estimated uncertainty ±0·15, based on reproducibility and calculation of errors arising from allowance for ^{13}C content. [b] At 50°; estimated uncertainty, ±0·05. [c] A value of 1·10 was obtained with 1·35M–NaOMe in 1 : 2 MeOH–MeOD. [d] Refers to $C_6F_5{\cdot}CH_2{\cdot}SiMe_3$.

For the representative compounds $Me_3M{\cdot}CH_2{\cdot}C_6H_4{\cdot}CF_3$-*m* (M = Si or Sn), we have also determined the overall solvent isotope effect, $(k_{MeOH}/k_{MeOD})_s$, by measurement of the individual rates in MeOH and in MeOD; the results are shown in Table 2. Because of the possibility that traces of water might have a substantial influence on the isotope effect, we measured the overall $(k_{SH}/k_{SD})_s$ ratios also in some MeOH–H_2O and MeOD–D_2O mixtures; the values were essentially identical with those for cleavage in methanol alone.

TABLE 2

Overall solvent isotope effects for *m*-$CF_3{\cdot}C_6H_4{\cdot}CH_2{\cdot}MMe_3$ at 50·0°

M	Medium [a]	$10^5\ k/s^{-1}$	k_{SH}/k_{SD}
Si	MeOH	6·8	0·50
	MeOD	13·5	
	MeOH with 18·6 mole % H_2O	7·2	0·50
	MeOD with 18·6 mole % H_2O	14·4	
Sn	MeOH	75·8	0·95
	MeOD	80·1	
	MeOH with 20·0 mole % H_2O	98	0·97
	MeOD with 20·0 mole % H_2O	100·5	

[a] Containing 2·0M-NaOMe or 2·0M-(NaOMe + NaOH) in each case.

If a free carbanion were formed at any stage of the reaction, it would react rapidly and unselectively with the solvent to give a PIE of, or close to, unity.* The magnitudes of the PIE values for the tin compounds (2·1—2·4) show that a free carbanion is not produced in this case. The fact that the value of the ratio $(k_{MeOH}/k_{MeOD})_s$/PIE exactly corresponds to the expected secondary isotope effect $(k_{MeOH}/k_{MeOD})_{II}$ arising from the transfer of the methoxide ion from its solvent shell to the metal atom,[10] indicates that the PIE is determined in the slow step of the reaction.† It rules out, for example, the suggestion that the slow step might produce a so-called 'ion-pair' [$MeOMe_3M \cdots {}^{-}CH_2{\cdot}C_6H_4X$], which then reacts rapidly with the solvent;[11] for such a case the overall solvent isotope effect would be the same as the secondary isotope effect, *i.e.* $(k_{MeOH}/k_{MeOD})_s$ would be *ca.* 0·44—0·50.[10] Very similar values of the ratio $(k_{MeOH}/k_{MeOD})_s$/PIE are also observed in the base-catalysed methanolysis of triphenylsilane[12] and of aryltrimethylstannanes[13] (Table 3).

TABLE 3

Product isotope effects (PIE), overall solvent isotope effects $(k_{MeOH}/k_{MeOD})_s$, and the derived secondary isotope effects $(k_{MeOH}/k_{MeOD})_s$/PIE in solvolysis by methanolic sodium methoxide

Reactant	PIE	$(k_{MeOH}/k_{MeOD})_s$	$(k_{MeOH}/k_{MeOD})_s$/PIE	Ref.
Ph_3SiH	4·0	1·97	0·49	12
p-$MeO{\cdot}C_6H_4{\cdot}SnMe_3$	5·2	2·4	0·46	13
m-$CF_3{\cdot}C_6H_4{\cdot}SnMe_3$	4·3	2·0	0·45	13
m-$CF_3{\cdot}C_6H_4{\cdot}CH_2{\cdot}SiMe_3$	1·2	0·50	0·42	This work
m-$CF_3{\cdot}C_6H_4{\cdot}CH_2{\cdot}SnMe_3$	2·1	0·97	0·46	This work

The situation is not so clear for the silicon compounds, since the PIE values are not far from unity, but we think it likely that free carbanions are not produced. This view is based partly on the fact that the PIE values are greater than unity outside experimental error, and partly on the absence of any significant variation in the PIE values for the compounds $Me_3Si{\cdot}CH_2{\cdot}C_6H_4X$ and $Me_3Si{\cdot}CH_2{\cdot}C_6F_5$; if the PIE values did arise from reactions of the free carbanions with the solvent, the much more stable $C_6F_5{\cdot}CH_2^-$ ion would be expected to be markedly more selective than the $C_6H_5{\cdot}CH_2^-$ ion. The value of the overall solvent isotope effect $(k_{MeOH}/k_{MeOD})_s$, *viz.* 0·50, for the *m*-trifluoromethyl derivative is consistent with a mechanism involving a small but significant degree of proton transfer to the separating benzyl group in the rate-determining step, but would also be fairly consistent with rate-determining separation of a carbanion. Certainly, in view of the similarity of the ρ values, coupled with the similarity in the rates for the silicon and tin compounds, it seems most unlikely that a change in mechanism (as distinct from a change in emphasis

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* Values slightly greater than unity, *viz.* 1·06, have been observed for reactions of methanol with benzyl-lithium in ether or tetrahydrofuran,[8] but in these the benzyl group is not fully carbanionic, and lies within a solvated aggregate. Reactions of a range of organometallic compounds with tritiated oxygen acids have given values close to unity.[9]

† We have neglected the difference for the tin compound in the temperatures of measurement of the product and overall solvent isotope effects. We found, in fact, in the few cases examined, that the PIE values were not significantly different at 50°.

[8] Y. Pocker and J. H. Exner, *J. Amer. Chem. Soc.*, 1968, **90**, 6764.

[9] L. O. Assarsson, *Acta Chem. Scand.*, 1958, **12**, 1545, and references therein.

[10] R. A. More O'Ferall, *Chem. Comm.*, 1969, 114; C. G. Mitton, M. Gresser, and R. L. Schowen, *J. Amer. Chem. Soc.*, 1969, **91**, 2045; K. O'Donnell, R. Bacon, K. L. Chellapa, R. L. Schowen, and J. K. Lee, *ibid.*, 1972, **94**, 2500.

[11] I. P. Beletskaya, K. P. Butin, and O. A. Reutov, *Organometallic Chem. Rev.*, 1971, **7**, 51.

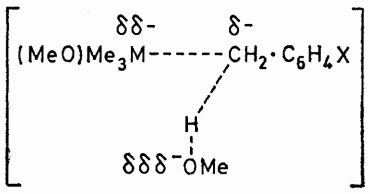
[12] C. Eaborn and I. D. Jenkins, *J. Organometallic Chem.*, 1974, in the press.

[13] R. Alexander, W. A. Asomaning, C. Eaborn, I. D. Jenkins, and D. R. M. Walton, *J.C.S. Perkin II*, 1974, 304.

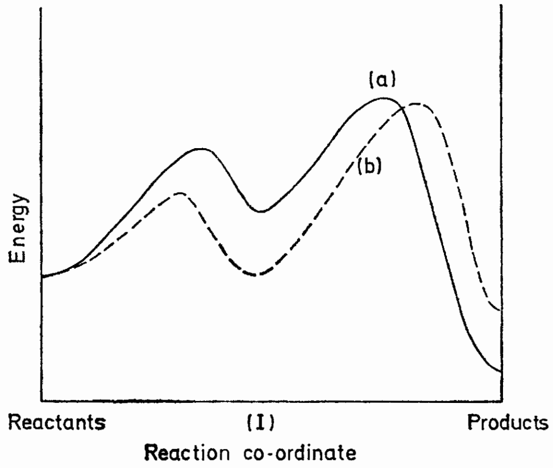
within a given mechanism) is involved, and we shall assume in the subsequent discussion that the same mechanism does, indeed, apply in both cases, but that the H–O bond breaking is less advanced in the highest energy transition state for the silicon compound.

Small PIE values could, in principle, arise from a very *advanced* degree of proton transfer, the influence of the breaking of the H–O bond being more than compensated by that of the making of the C–H bond, but this possibility is ruled out in the present case by the conclusion, based on ρ values, that a good deal of negative charge must reside on the benzylic carbon atom in the highest energy transition state. A large degree of proton transfer would also be inconsistent with the magnitude of the overall solvent isotope effect, since the secondary isotope effect associated with transfer of the methoxide ion from its solvent shell would be balanced by the generation of a methoxide ion from the methanol giving up the proton.[10]

While we cannot conclusively rule out the fully concerted mechanism (D), with the methoxide ion almost fully attached to the metal atom in the transition state, we favour the mechanism (A), involving rapid reversible formation of the M^V intermediate followed by rate-determining breaking of the $M-CH_2{\cdot}C_6H_4X$ bond concerted with the proton transfer from the solvent. The highest energy transition state will be as in (II), with a good proportion of the negative charge located on the benzyl group. In this transition state the formation of the C–H bond (and thus the breaking of the H–O bond) lags well behind the breaking of the M–C bond; the bond orders of the M–C and C–H bonds could, perhaps, be in the region of 0·4—0·3 and 0·05—0·2, respectively. (We cannot represent the M–C bond as more fully broken, in spite of the large proportion of negative charge on the benzyl group, because a smaller but substantial amount of negative charge must also be located on the metal atom, as indicated.) The fact that the H–O bond breaking is little advanced at the transition state, especially for the silicon compounds, does not mean that the electrophilic assistance by the solvent is unimportant. Even a small degree of proton transfer could reduce the energy of activation substantially below that needed for separation of a wholly free carbanion. It is not immediately apparent why the C–H bond making should lag so far behind the M–C bond breaking, but one factor may be the substantial steric hindrance to attack of the reactant methanol molecule, with its associated solvent molecules, into the M–C bond (see later), so that C–H bond formation will be severely limited until substantial stretching of the M–C bond has occurred. Because of the difference in the M–C bond lengths, this steric effect would be greater for the silicon than for the tin compounds.*



(II)



Possible energy profile for cleavages of $Me_3M{\cdot}CH_2Ph$ *via* the M^V intermediates (I); (a) M = Si, (b) M = Sn

In terms of the proposed mechanism, the slightly lower ρ value for the tin compounds could be associated with a greater degree of M–C bond breaking, with the increased degree of negative charge transferred from the metal being more than balanced by the greater degree of proton transfer to the benzyl group. The similarity in rates for the silicon and tin compounds in spite of the weakness of the Sn–C compared with the Si–C bond can be associated with a greater stability of the M^V intermediate for M = Sn, some of this originating in the smaller steric compression in the intermediate in the case of the larger tin atom. The energy profiles might be as in the Figure, in which the initial energies are for convenience placed at the same level, but we emphasise that this Figure is intended only to present a diagrammatic comparison of the situation for the silicon and tin compounds, and no significance should be attached to the absolute position of the highest energy transition state along the reaction co-ordinate, for the reasons discussed later.

A difficulty associated with the picture of the rate-determining process is that since the conversion of the M^V intermediate into products will be markedly exothermic, the transition state should lie over towards the reactants.† Transition state (II) is consistent with this as far as the reactant methanol molecule is concerned, in that the H–OMe bond is very little broken, but inconsistent with it if attention is focused on the other

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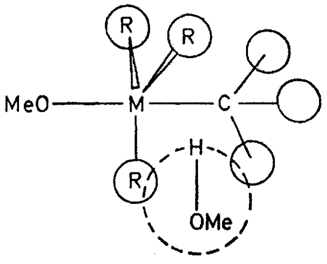
* The greater assistance received from the proton transfer for the tin compounds is consistent with the much greater ease of acid cleavage of $Sn-CH_2Ph$ than of $Si-CH_2Ph$ bonds.

† The same would apply, with less force, for the concerted process (D), since the overall reaction is also exothermic, though less so than the disappearance of the intermediate (I).

reactant (I), since the M–C bond must be more than half broken. If, however, the degree of conversion of the reactants into products can validly be related to the average of the suggested C–M and H–O bond orders, transition state (II) lies clearly on the side of the reactants.

Finally, we consider the possible relevance of the foregoing conclusions to interpretation of the large steric effects which can operate in cleavage of some Si–C bonds by base. The representation (III) of the transition state illustrates how serious steric hindrance could be for approach to the M–C bond of the proton-donating methanol molecule with its associated solvent molecules (indicated by the broken-line circle) still largely attached to it.* It is reasonable to attribute to such hindrance, for example, the marked drop in reactivity which occurs on going along the series $\text{PhCH}_2\text{SiMe}_3$, $\text{PhCH(SiMe}_3)_2$, and $\text{PhC(SiMe}_3)_3$,[14] in which an increase in reactivity, associated with stabilisation of the forming negative charge by interaction with the *d*-orbitals of the non-cleaved silicon atom ($\text{Ph}\overset{-}{\text{C}}\text{H–SiMe}_3 \leftrightarrow \text{PhCH=SiMe}_3^-$), would be expected on electronic grounds. We have previously suggested that there may be face-to-face interaction between the groups on the metal atom and those on the leaving carbon atom in the cleavage of di- and tri-phenylmethyl- and fluoren-9-yl-trimethylsilane (for a diagrammatic representation see ref. 3), and clearly even a very small degree of electrophilic assistance to the leaving carbanion, requiring the proton to approach between the two sets of groups, could result in a marked increase in the compression. This type of hindrance could hardly be of major importance, however, in the cleavage of the $\text{PhC}\vdots\text{C–MR}_3$ bond, because not only are there no interfering groups on the leaving carbon atom but furthermore the proton can attack into the π-cloud around this atom rather than the C–M bond, and yet the existence of serious steric hindrance is revealed by the 280-fold fall in the rate of cleavage by aqueous methanolic alkali on going from the Me_3Si to the Et_3Si derivative.[15] We have suggested a special explanation in this case, based on the steric hindrance to solvation of the forming negative charge on the leaving carbon atom, since this charge must in this case lie substantially in the line of the M–C bond,[15] and there is no reason to doubt the importance of such an effect. However, we must also take account of the fact that the large $\text{Me}_3\text{Si}/\text{Et}_3\text{Si}$ reactivity ratios in cleavage of $\text{R}_3\text{M–R}'$ bonds by aqueous methanolic alkali (*e.g.* R′ = fluoren-9-yl, 960;[3] R′ = PhCH=CH·CH_2, $>10^3$;[16] R′ = PhC≡C, 280) seem to be associated with the more reactive systems (*cf.* the ratio of only 5 for R′ = $\text{CH}_2\text{·C}_6\text{H}_4\text{·CO}_2^-\text{-}p$ [17]). The explanation of this may be that, in terms of the two-step mechanism favoured for the $\text{R}_3\text{M–R}'$ cleavage, there is likely to be serious steric compression in the Si^V intermediate for large R and R′ groups, and in the highest energy transition state the compression will be the greater the closer this state is to the intermediate, *i.e.* the more easily the group R′ leaves.† Furthermore, for such cases, in which the Si–R′ bond is little stretched in this transition state, even a very small degree of proton transfer to the leaving carbon atom would greatly compound the compression.



(III)

EXPERIMENTAL

Organo-silanes and -stannanes. Except for *p*-nitrobenzyltrimethylsilane, the preparation of which will be described elsewhere,[18] the compounds $\text{XC}_6\text{H}_4\text{·CH}_2\text{·MMe}_3$ were made by treatment of the appropriate Grignard reagent with chlorotrimethyl-silane or -stannane, and purified by fractional distillation. G.l.c. revealed no significant quantities of impurities, and physical constants agreed with those previously reported.[1–3]

Measurement of Product Isotope Effects.—The 1 : 1 MeOH–MeOD medium containing sodium methoxide (2 mol l^{-1}) was made up by mixing 10·0 volumes of 3·8M sodium methoxide in methanol with 9·0 volumes of methan[^{2}H]ol (Ryvan; >99% ^{2}H). Details of the procedure and analytical technique have been given previously.[13] Reactions were carried out in sealed ampoules for 48 h at 50° in the case of the silicon compounds and for 7 days at room temperature (*ca.* 21 ± 2°) in the case of the tin compounds.

Kinetic Isotopic Effects.—Rates were measured spectrophotometrically on a Unicam SP 500 spectrometer.[1] For the *m*-trifluoromethylbenzyltrimethylsilane the reaction was carried out in a flask kept in a thermostat at 50·0°, and aliquot portions were withdrawn at appropriate intervals, as described for studies on aryltin compounds.[13] For *m*-trifluoromethylbenzyltrimethylstannane the reaction mixture was contained in a stoppered quartz cell which was then placed in the thermostatically controlled cell compartment of the spectrophotometer. Rates for the deuterium-containing and non-deuterium-containing media were measured simultaneously, or consecutively under conditions as closely similar as possible, the emphasis being more on the

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* It is only for convenience and emphasis that we have depicted in (III) a transition state corresponding to inversion of configuration at the metal atom; the argument would not be changed significantly if other arrangements about the metal atom were adopted.

† With exceptionally good leaving groups R′ the formation of the M^V intermediate could become rate-determining.

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[16] R. M. G. Roberts and F. El Kaissi, *J. Organometallic Chem.*, 1968, **12**, 79.

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accuracy of the ($k_{\mathrm{MeOH}}/k_{\mathrm{MeOD}}$) ratio than on the separate rates.

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