Journal of Organometallic Chemistry, 49 (1973) C61–C63
© Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Preliminary communication

Mechanism of thermal elimination of ethane from iodotrimethylbis(dimethylphenylphosphine)platinum(IV)

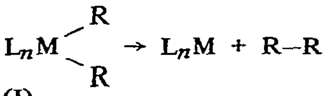
M.P. BROWN, R.J. PUDDEPHATT and C.E.E. UPTON
Donnan Laboratories, The University of Liverpool, Liverpool L69 3BX (Great Britain)

(Received December 28th, 1972)

SUMMARY

The isotope content of ethane formed by pyrolysis of the complex $(Me_2PPh)_2$-$PtMe_3I$ and its deuterated derivatives shows that the reaction is both intramolecular and first order with respect to substrate and gives the activation parameter $\Delta H^{\ddagger} = 129 \pm 5$ $kJ \cdot mol^{-1}$.

Reductive eliminations of the type shown in eq. (1) are often involved in the transition-metal catalysed coupling[1,2] of alkyl groups, R, and may provide a low energy pathway for decomposition of the transition-metal alkyl (I)[3,4]



$$L_nM\begin{matrix}R\\R\end{matrix} \rightarrow L_nM + R{-}R \qquad (1)$$

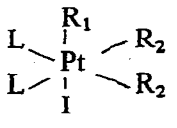
(I)

In order to determine the mechanism of this type of reaction, we have studied the elimination (eq. (2), L = PMe_2Ph) discovered by Ruddick and Shaw[5].

$$PtIMe_3L_2 \rightarrow trans\text{-}PtIMeL_2 + C_2H_6 \qquad (2)$$

(II)

Selectively deuterated derivatives, (IIa)–(IId) were synthesised for this study. The complex (IIb), for example, was prepared with isotopic purity greater than 95% by treatment of CD_3I with *cis*-$PtMe_2L_2$, L = PMe_2Ph.



(IIa: $R_1 = R_2 = Me$;
IIb: $R_1 = CD_3$, $R_2 = Me$;
IIc: $R_1 = Me$, $R_2 = CD_3$;
IId: $R_1 = R_2 = CD_3$)

The gases evolved on pyrolysis of (IIa)–(IId) were analysed by mass spectrometry (Table 1). NMR studies showed that no scrambling of methyl and methyl-d_3 groups took place prior to reductive elimination. The absence of C_2D_6 from pyrolysis of (IIb) and of C_2H_6 from (IIc) proves that the reductive elimination is an intramolecular process.

TABLE 1

Compound	*Gaseous products (%)*		
	C_2H_6	CH_3CD_3	C_2D_6
IIa	100	0	0
IIb	40[a]	60[a]	0
IIc	0	68[a]	32[a]
IId	0	0	100

[a] Reproducible to ± 2%.

Pyrolysis of (IIc) gave the 2/1 mixture of CH_3CD_3 and C_2D_6 expected from statistical considerations only, but (IIb) gave considerably more C_2H_6 than predicted on this basis. It seems that two effects influence the stereochemistry of elimination: (a) the groups *trans* to phosphorus are eliminated more readily than the group *trans* to iodine in (II), and (b) methyl groups are eliminated more readily than methyl-d_3 groups. In (IIb) these effects combine to favour formation of ethane rather than CH_3CD_3, but in (IIc) the effects cancel out and the statistical product ratio is found.

A kinetic study showed that the reaction depicted in eq. (2) follows first order kinetics over the temperature range 60–90°C in the solvent 1,4-dioxane, and confirmed that a secondary kinetic isotope effect was operative. Consistent values of k_1 (IIa)/k_1 (IId) = 1.10 ± 0.05 were obtained. Analysis of the kinetic data gave the activation parameters, $\Delta H^{\ddagger}$ (353 K) = 129 ± 5 $\text{kJ} \cdot \text{mol}^{-1}$ and $\Delta S^{\ddagger}$ (353 K) = 87 $\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ The activation energy is significantly lower than the value of $\bar{E}$(Pt–CH_3) in (IIa) of 144 ± 6 $\text{kJ} \cdot \text{mol}^{-1}$, which we determined by a study of the elimination reaction by differential scanning calorimetry. It is also lower than that of D(Pt–CH_3) = 163 $\text{kJ} \cdot \text{mol}^{-1}$, in $PtMe_3(\pi\text{-}C_5H_5)$ reported recently by Egger[6]. This strongly suggests that the reductive elimination of ethane from (IIa) is a concerted process in which C–C bond formation accompanies Pt–C bond cleavage.

The role of the phosphine ligands in promoting this concerted elimination, rather than decomposition initiated by homolysis of a single platinum–methyl bond as is found for $PtMe_3(\pi\text{-}C_5H_5)$[6] and probably for $PtIMe_3(2,2'\text{-}C_{10}H_8N_2)$ when methane is the chief gaseous product, is being studied further.

REFERENCES

1 P.M. Maitlis, *The Organic Chemistry of Palladium*, Vol. II, Academic Press, New York, 1971, p. 60–70.
2 K. Tamao, K. Sumitani and M. Kumada, *J. Amer. Chem. Soc.*, 94 (1972) 4374.

3 P.S. Braterman and R.J. Cross, *J. Chem. Soc. Dalton*, (1972) 657.
4 T. Yamamoto, A. Yamamoto and S. Ikeda, *J. Amer. Chem. Soc.*, 93 (1971) 3350.
5 J.D. Ruddick and B.L. Shaw, *J. Chem. Soc. A*, (1969) 2801, 2964, 2969.
6 K.W. Egger, *J. Organometal. Chem.*, 24 (1970) 501.