

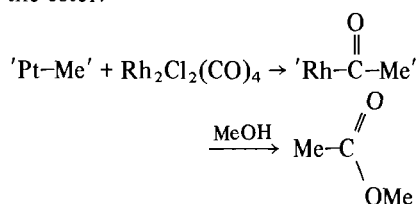
Alkyl Isomerization *via* Intermetallic Transfer

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We have recently reported^{1,2} that methyl transfer between two metal centres is a facile process and further that, following the transfer, reactions specific to the second metal can be effected. Thus transfer of a methyl group from a platinum–methyl complex to di- μ -chlorotetracarbonyldirhodium(I) in methanol results in the transferred methyl group being trapped as the ester:²



Using this reaction with platinum–alkyl complexes of the type $\text{cis-[PtR}_2(\text{PPh}_3)_2]$, where $\text{R} = \text{CH}_2\text{CD}_3$, CD_2CH_3 , $\text{n-C}_3\text{H}_7$, $\text{n-C}_4\text{H}_9$, $\text{CH}_2\text{CH}(\text{CH}_3)_2$ or $\text{n-C}_5\text{H}_{11}$, we have now investigated the occurrence of alkyl isomerization during the intermetallic transfer.

From the data presented in the Table it is clear that the propyl group occupies a somewhat unique position among the alkyl groups studied in being the only one which undergoes appreciable (20%) isomerization. With $\text{R} = \text{CH}_2\text{CD}_3$ we observed no isomerization. This is clearly not due to an H/D isotope effect as an analogous result was obtained with $\text{R} = \text{CD}_2\text{CH}_3$. We suggest that the difference between the fates of the ethyl and propyl groups is related to the *ca.* 14 kJ mol⁻¹ difference in bond energy between a primary and secondary C–H bond as found at the β -carbon atom of ethyl and propyl, respectively. We have attempted to check this hypothesis by preparing the platinum complex with $\text{R} = \text{CH}_2\text{CH}(\text{CH}_3)_2$, *i.e.* a complex with a tertiary C–H bond at the β -carbon, in the hope that this complex, because of the relatively weak tertiary C–H bond (bond energy *ca.* 14 kJ mol⁻¹ less than that of a secondary C–H bond), would give rise to a high degree of isomerization during the transfer reaction. However, the

TABLE. Product Esters Obtained as a Result of the Transfer of R from *cis*-PtR₂(PPh₃)₂ to Rh₂Cl₂(CO)₄ in CD₃OD.

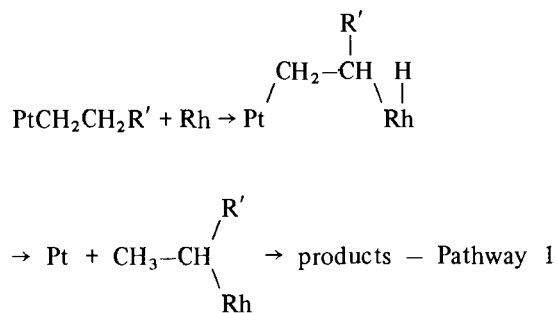
R	Product Ester(s) ^a	
CD ₂ CH ₃	CH ₃ CD ₂ COOCD ₃	(100%)
CH ₂ CD ₃	CD ₃ CH ₂ COOCD ₃	(100%)
CH ₂ CH ₂ CH ₃	CH ₃ CH ₂ CH ₂ COOCD ₃	(80%)
	CH ₃ CH(CH ₃)COOCD ₃	(20%)
CH ₂ CH ₂ CH ₂ CH ₃	CH ₃ CH ₂ CH ₂ CH ₂ COOCD ₃	(97%)
	CH ₃ CH ₂ CH(CH ₃)COOCD ₃	(3%)
CH ₂ CH ₂ CH ₂ CH ₂ CH ₃	CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ COOCD ₃	(99%)
	CH ₃ CH ₂ CH ₂ CH(CH ₃)COOCD ₃	(1%)

^a The values given in parentheses refer to the ester product composition at 10% conversion of *cis*-PtR₂(PPh₃)₂. The 10% limit was chosen to avoid any competing side reactions.

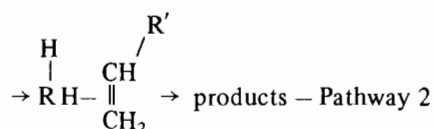
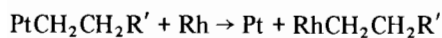
resulting platinum complex was thermally unstable and, in the presence of the rhodium dimer, rapidly decomposed to give a complex mixture of products in which we were unable to detect the expected esters.

As can be seen from the data in the Table the degree of isomerization decreases rapidly on going from propyl to butyl to pentyl. Although we do not, as yet, fully understand this marked decrease we would tentatively suggest that it may result from steric factors, *i.e.* the increase in size on going from propyl to butyl to pentyl. It is now well recognized³⁻⁷ that in organometallic chemistry many reactions are extremely sensitive to subtle changes in the steric requirements of the reactant groups and associated ligands.

We consider that the observed isomerization occurs *via* insertion of the rhodium into the β -carbon C–H bond (pathway 1) rather than *via* normal transfer of propyl to rhodium followed by β -elimination to give a hydride–alkene–rhodium intermediate, which then undergoes carbonylation (pathway 2):



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$\text{R}' = \text{CH}_3, \text{C}_2\text{H}_5$ or C_3H_7 (for clarity all other ligands present on the metals have been omitted).

If pathway 2 were the preferred course for the reaction then not only would we expect the usual normal/branched ratio of products, *i.e.* *ca.* 1, found in rhodium-catalysed carbonylation, but we would also expect no drastic difference in the degree of isomerization between the propyl, butyl and pentyl complexes. Furthermore, if a β -elimination process, such as depicted in pathway 2, were to play a significant role in the isomerization reaction we would expect to find free alkene during the reaction. In none of the exchange reactions described above did we detect free alkene.

Isomerization *via* homogeneous intermetallic transfer between two transition metal centres has not previously been reported and we would suggest that it may well play a role in metal-catalysed reactions where isomerization is encountered.

References

- 1 J. P. Visser, W. W. Jager and C. Masters, *Rec. Trav. Chim.*, **94**, 70 (1975).
- 2 J. P. Visser and C. Masters, *Abstracts of Papers, Seventh International Conference on Organometallic Chemistry, Venice, Italy, Sept. 1975*, Paper No. 245.
- 3 B. L. Shaw, *J. Am. Chem. Soc.*, **97**, 3856 (1975).
- 4 G. K. N. Reddy and B. R. Ramesh, *J. Organometal. Chem.*, **67**, 443 (1974).
- 5 M. Bressen and P. Rigo, *Inorg. Chem.*, **14**, 38 (1975).
- 6 A. A. Kiffen, C. Masters and L. Raynaud, *J. Chem. Soc. Dalton*, 853 (1975).
- 7 F. K. Schmidt, V. S. Tkach and A. V. Kalabina, *Nefte-kimiya*, **12**, 76 (1972).