Journal of Organometallic Chemistry, 371 (1989) 393–395
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 09998

Dynamic behaviour of bis(diop)metal(0) compounds

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(Received February 24th, 1989)

Abstract

The dynamic behaviour of the enantiomerically pure [(R,R)- or (S,S)-(diop)]$_2$M (M = Pt,Pd) and the corresponding *meso* compounds [(R,R)-diop][(S,S)-diop]M have been reinvestigated by ^{31}P NMR spectroscopy, and somewhat different conclusions from those presented by Brown and Chaloner are drawn. In addition, data for the analogous nickel compounds are reported.

Introduction

Brown and Chaloner have discussed the dynamic ^{31}P NMR spectra of [(R,R)-diop]$_2$Pt [1*], the corresponding *meso* compounds [(R,R)-diop][(S,S)-diop]Pt [2,3], and the spectra of the corresponding palladium compounds. In this communication we present our studies of the variable temperature ^{31}P NMR spectra of these compounds and also those of the corresponding nickel analogues.

Samples of the [(R,R)- or (S,S)-diop]$_2$M compounds were prepared either by reduction of [(R,R)- or (S,S)-diop]MCl$_2$ in the presence of the same enantiomer of diop (M = Pd, Ni) or directly from potassium tetrachloroplatinate(II) and (R,R)- or (S,S)-diop [5]. The variable temperature ^{31}P NMR spectra of the platinum and palladium compounds showed very similar behaviour to those reported by Brown and Chaloner. Coalescence temperatures and $\Delta G^{\neq}$ values [6 *] for these compounds and for the corresponding nickel compound are summarised in Table 1, together with literature values.

It can be seen that the two sets of values for platinum and palladium compounds are in good agreement, and that the nickel compound, not unexpectedly, gives comparable values.

Samples of "*meso*"-complexes [(R,R)-diop][(S,S)-diop]metal(0) were prepared by reduction of [(R,R)-diop]MCl$_2$, (M = Pd, Ni) in the presence of (S,S)-diop or

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* Reference number with asterisk indicates a note in the list of references.

Table 1

Coalescence temperatures for ^{31}P NMR spectra of $[(R,R)\text{-diop}]_2M$ (M = Pt, Pd, Ni) and calculated $\Delta G^{\neq}$ values

Metal	Coalescence temp. (K) [a]	Lit. value (K)	$\Delta G^{\neq}$ at coalescence temperature (kJ mol^{-1})	Lit. value
Pt	244 [b], 253 [c]	250 [2]	45	48 [2]
Pd	219 [b]	228 [4]	40	41.2 [4]
Ni	254 [b], 278 [c]	–	49	–

[a] Spectrometer temperatures calibrated using methanol chemical shifts. [b] Spectra recorded on a Bruker HX90R, operating frequency 36.435 MHz. [c] Spectra recorded on a Bruker AM300, operating frequency 121.497 MHz.

in situ from reaction of equimolar amounts of (R,R)- and (S,S)-diop with bis(dibenzylideneacetone)palladium or potassium tetrachloroplatinate(II) in the presence of ethanolic potassium hydroxide [5]. All these preparative methods led to the formation of mixtures of *meso* and racemic materials. Close examination of the spectra of the mixtures obtained for the Pd and Pt compounds recorded at 121 MHz and at 300 K revealed two peaks, one significantly sharper than the other but of lower intensity. On cooling of the toluene solutions of the compounds, the ^{31}P NMR spectra showed similar behaviour to that reported by Brown and Chaloner. In particular the signals due to the racemic platinum compound broadened and separated into two triplets, while the signal due to the *meso* compound remained a sharp singlet for spectra recorded above ca. 240 K (see Fig. 1). On further cooling, however, the signal due to the *meso* compound also broadened and eventually merged into the baseline. Careful examination of ^{31}P spectra recorded at 121 MHz failed to reveal signals due to the *meso* compound in the slow exchange limit. The expected triplets were either too weak in intensity and/or too closely similar in chemical shift values to those of the racemic compound to be detected. The variable temperature effects were completely reversible. Integration of the central peak attributed to the meso compound indicated that its area was ca. 5% of the area of that for the racemic compound. (R,R)-diop (0.3 mol equiv.) was added to the mixture, which was heated to 333 K and cooled again to 240 K. The spectra showed the same behaviour as before, but the intensity of the peak due to the *meso* compound had increased and was ca. 15% of the intensity of the peak due to the racemic compound. This latter value (15%) is similar to that reported previously (5%) [2] when allowance is made for the difficulties in obtaining accurate integration values. Thus the equilibrium between the *meso* and racemic compound appears to be ca. 10/90 in favour of the racemic compound. Interestingly, preparation of the *meso* compound by reduction of $[(R,R)\text{-diop}]PtCl_2$ in the presence of (S,S)-diop gives a product which is even richer in the racemic compound ($\leq 5\%$ *meso*), whereas addition of a mixture of (R,R)- and (S,S)-diop to $(cod)_2Pt$ gives a ratio of 30 *meso* to 70 racemic [2]. Both of these preparations must be at least partially kinetically controlled, and the difference between them is difficult to explain.

The *meso* compound in addition to being thermodynamically less stable than the racemic compound also showed a lower barrier in its fluxional behaviour. An approximate value of $\Delta G^{\neq}$ 37 kJ mol^{-1} can be calculated on the assumption that the coalescence temperature is that at which the central peak first appears above the

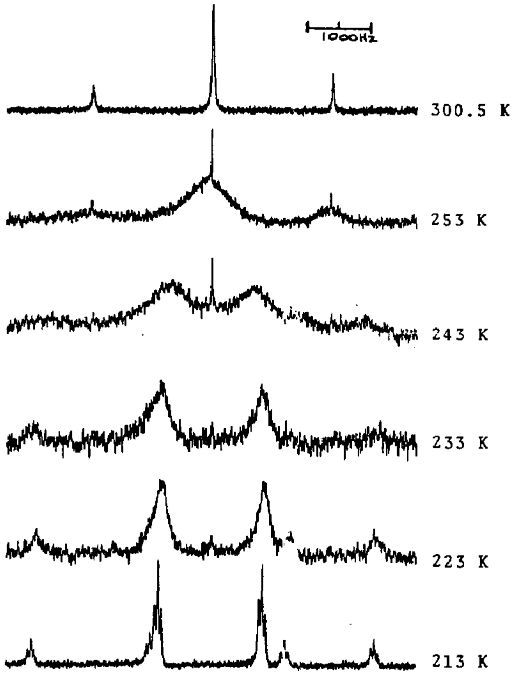

Fig. 1. Variable-temperature proton-decoupled ^{31}P NMR spectra of *meso*/racemic $(\text{diop})_2\text{Pt}$ in C_7D_8 at stated temperatures, 121.497 MHz platinum coupled satellites are shown.

baseline (ca. 213 K) and that the final peaks have the same $\Delta\nu$ value as the racemic compound in the slow exchange limit (1640 Hz). Similar values were obtained for the Pd and Ni compounds ($\Delta G^{\neq}$ 36 kJ mol^{-1} Pd, $\Delta G^{\neq}$ 44 kJ mol^{-1} Ni).

One explanation of these results is that the diop ligands in the *meso* compounds adopt chair and boat conformations in the slow exchange limit but that the barrier to interconversion is lower than that for the corresponding racemic compounds. An alternative explanation is that the diop ligands adopt a conformation in the slow exchange limit in which the two phosphorus atoms are non-equivalent and that the torsional barriers leading to equivalence are greater for the racemic than for the *meso* compounds.

Acknowledgements

We thank Dr. J.M. Brown for comments, the Australian Research Committee for support, and Johnson-Matthey Ltd. for a loan of metals.

References

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