Journal of Organometallic Chemistry, 217 (1981) C25—C28
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

DYNAMIC BEHAVIOUR OF BIS(DIOP)PALLADIUM AND ITS REACTION WITH ALKENES

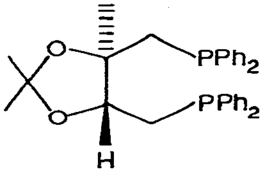
KATHLEEN BROWN and PENNY A. CHALONER*
Dyson Perrins Laboratory, South Parks Road, Oxford, 0X1 3QY (Great Britain)

(Received May 8th, 1981)

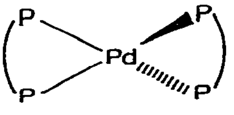
Summary

The dynamic behaviour of bis(DIOP)palladium is studied by complete line-shape analysis of its ^{31}P NMR spectrum. Its reaction with *trans*-disubstituted alkenes gives diastereomeric complexes, the selectivity depending on the nature of the substituents.

A number of asymmetric syntheses have been achieved in the presence of tetrakis(triphenylphosphine)palladium and excess 2,3-isopropylidene-2,3-*trans*-dihydroxy-1,4-bis(diphenylphosphino)butane, DIOP, I [1]. More recently, asymmetric addition of hydrogen cyanide to norbornadiene has been reported, catalysed by an isolated DIOP-palladium complex [2]. The catalyst was prepared by the reduction of ((+)-DIOP)PdCl$_2$ with sodium borohydride in acetone solution in the presence of (+)-DIOP. The ^{31}P NMR spectrum of the complex showed a singlet at room temperature but two signals below —70°C. On the basis, together with microanalytical data, the authors assigned to it the structure ((+)-DIOP)Pd, though they have since concluded that the complex was ((+)-DIOP)$_2$Pd [3]. In view of the apparent difference between their original suggestion and the known (DIOP)$_2$Pt [4] we investigated this compound in more detail.



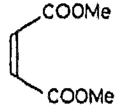
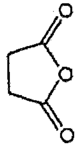
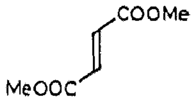
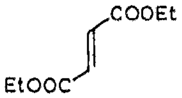
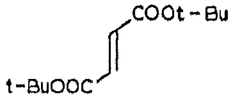
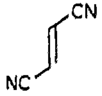
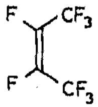
(I)



(II)

TABLE 1

RESULTS OF THE REACTION OF COMPLEX II WITH ALKENES

Alkene	% Pd converted to alkene complex		Diastereomer ratio	^{31}P NMR in toluene at 300 K (ppm)
	1:1 [a]	5:1 [a]		
	5	15	—	10.62 (d) $J(P_A-P_B)$ = 17 Hz 7.29 (d)
	60	100	—	11.7 (d) [b,c] $J(P_A-P_B)$ = 8 Hz 8.6 (d)
	40	80	3:2	9.42 [d] 9.31
	25	70	3:2	9.69 9.41
	5	10	2:1	9.21 8.28
	100	100	1:1	8.26 [b] 7.77
	—	10	Broad at all temperatures	6.5 [e]

[a] Ratio alkene:palladium; (DIOP)$_2$Pd ~ 0.018 *M*. [b] 228 K. [c] Spectrum recorded in acetone. [d] 203 K. [e] 253 K.

((—)—DIOP)$PdCl_2$ was reduced with sodium borohydride in acetone or hydrazine hydrate in ethanol in the presence of (—)-DIOP. Recrystallisation (toluene) and prolonged drying in vacuo gave in both cases yellow prisms (m.pt. 99—102°C, dec; α_D = + 56.3 c = 0.49, C_6H_6. ((—)-DIOP)$_2$Pt gives α_D = +18.67 c = 0.08, C_6H_6) which analysed correctly for ((—)-DIOP)$_2$Pt. A monomeric formula was confirmed by the field desorption mass spectrum; the characteristic palladium isotope pattern was noted with M^+ = 1102 for ^{106}Pd.

The ^{31}P NMR spectrum was recorded at various temperatures (Fig. 1). At 300 K a singlet (δ = 0.32 ppm [5] was observed while at 190 K an A_2B_2

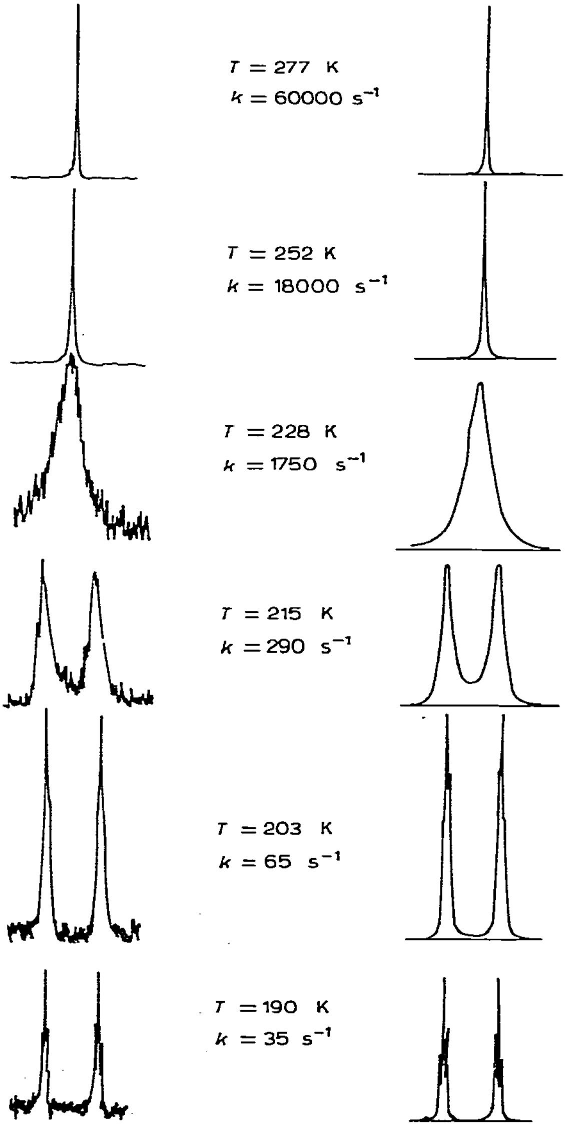


Fig. 1. Observed and calculated ^{31}P NMR spectra of ((—)-DIOP)$_2$Pd.

multiplet ($\delta(P_A) = 7.57$ ppm, $\delta(P_B) = -5.22$ ppm, $J(P_A-P_B) = 24$ Hz) was resolved. The dynamic exchange did not involve free phosphine. Complete line shape analysis [6] gave $\Delta G^\ddagger$ (228 K) = 41.2 kJ mol^{-1}. This compares closely with the process and activation energy for the analogous platinum complex and is consistent with a tetrahedral complex ((—)-DIOP)$_2$Pd, II, in which exchange is occurring between different conformations of the seven-membered chelate rings. It is noteworthy that when DIOP is added to tetrakis(triphenylphosphine)palladium, as in most alkylation reactions [1], (DIOP)$_2$Pd is also obtained, showing identical dynamic behaviour to the isolated complex.

The displacement of one molecule of DIOP from II by an alkene leads to a mixed complex. With a symmetrically *cis*-disubstituted alkene an AB pattern is expected in the ^{31}P NMR spectrum, whereas with a symmetrical *trans*-alkene two diastereomeric complexes may be observed. Results are given in Table 1. In the case of dimethyl maleate slow isomerisation occurs to give the dimethyl fumarate complex. The degree of binding is highest for alkenes bearing the most electron-withdrawing groups. Lower equilibrium constants but higher diastereomeric preference are observed for more hindered alkenes. The coordination of an alkene to palladium makes it more susceptible to nucleophilic attack and the binding of these simple substrates may provide a model for the role of DIOP palladium complexes as asymmetric catalysts.

Acknowledgements

KB thanks the Lancashire Education Authority for a grant and PAC thanks the Cephelasporin Trust for the award of a fellowship.

References

1 B.M. Trost and T.J. Dietsche, J. Amer. Chem. Soc., 95 (1973) 8200; B.M. Trost and P.E. Strege, J. Amer. Chem. Soc., 99 (1977) 1649.

2 P.S. Elmes and W.R. Jackson, J. Amer. Chem. Soc., 101 (1979) 6128.

3 W.R. Jackson, private communication.

4 J.M. Brown and P.A. Chaloner, J. Amer. Chem. Soc., 100 (1978) 4307.

5 ^{31}P chemical shifts are recorded in ppm downfield from external H_3PO_4.

6 Simulated spectra were calculated using the program DNMRS; G. Binsch, J. Amer. Chem. Soc., 91 (1969) 1304.