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The NMR Study on *Trans-Trans*-Dibenzylideneacetone Complex of Palladium(II)

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The complex [(L-L)Pd(dba)], wherse (L-L) is 1,2-bis(di-tert-butylphosphinomethyl) benzene and dba is (*trans-trans*-dibenzylideneacetone), has been prepared and characterized by variable temperature multinuclear NMR spectroscopy. The environment around palladium seems to be essentially trigonal planar, with small dihedral angles between P_2Pd- and PdC_2 planes. Tertiary phosphine ligands (PR_3) play an extremely important role in the coordination chemistry of the late transition elements. They are important because they constitute one of the few series of ligands in which electronic and steric properties can be altered in a systematic and predictable way over a wide range by varying R. They also stabilize an exceptionally wide variety of metal species of interest to the organometallic chemist as their phosphine complexes $(R_3P)_nM$–L.

INTRODUCTION

Palladium and its complexes have been widely studied as potential catalysts for the production of industrially important materials, as well as for synthetic transformation, where enantioselectivity rather than turnover frequency is important. In this work the ligand whose synthesis is known[1] is then utilized in the synthesis of palladium(0) alkene complex. The synthesis of complexes of the type [(P-P)Pd(alkene)] has been developed for use as potential pre-catalysts in the methoxycarbonylation of ethene.

EXPERIMENTAL

The phosphine ligand L-L detailed above was synthesized according to the method of Show and Moulton[2]. In this method, the secondary phosphine was treated with 1,2-dibromo-*o*-xylene in acetone to yield the diphosphonium bromide as a precipitate. This material was then treated with an excess of sodium acetate in degassed water to liberate the desired phosphine as a precipitate, which was extracted into ether.

The reaction of $Pd(dba)_2$ with 1 equivalent L-L was done by known procedure[3], which results in the formation of $[Pd(L\text{-}L)_2]$ at short reaction times (10 min), whilst at long reaction times (4 h), a complex in which the two phosphorus atoms are not equivalent. This complex has been assigned as the [(P-P)Pd(dba)] complex where the phosphine is chelating and the dba is coordinated η-2 *via* one of its alkene moieties. The complex is air-stable in the solid state and is an orange powder. The stability of the compounds in solution depends on several factors, which include the structure of this type of ligands, the nature of coordinated alkene, solvent type and the presence of oxygen and the temperature of the solution.

The ^{31}P NMR spectra were recorded on JEOL FT FX NMR 90 Q spectrophotometer for solution of complexes in deuteidio dichloromethane; chemical shifts (high frequency is positive) are quoted relative to external 85% H_3PO_4. The value of δ_p was obtained with solutions containing 100 mg of the complex. Infrared spectra were recorded on a Perkin-Elmer 457 spectrophotometer (in dichloromethane and nujol).

RESULTS AND DISCUSSION

The ^{31}P NMR of complex at room temperature in dichloromethane shows 2 resonances at 48 ppm and 50 ppm, indicative of exchange processes occurring within the molecule, not resolved on the NMR time scale. On cooling to −80°C, 7 sharp peaks are resolved from the broad resonances. The integration of this spectrum is consistent with there being 3 major conformational species and 1 minor one, giving rise to 8 signals in total; one of the peaks from the minor species is coincident with one of the major species (Table-1).

TABLE-1

^{1}H NMR DATA FOR THE COMPLEX [(L-L)Pd(dba)]

	Tert-butyl CH_3	Ligand CH_2	Coordinated dba CH	Aromatics and dba
In CD_2Cl_2, at room temp.	0.9 (br), 1.2 (br), 1.5 (br) ppm	3.5 (br) ppm	4.3 (br), 4.6 (br) ppm	6.8–7.8 (br) ppm
In CD_2Cl_2, at −80°C	0.0689 (d, j = 18.7 Hz), 0.31 (d, j = 18.4 Hz), 0.65 (d, j = 13.4 Hz) ppm	3.2–3.5 (br) ppm	4.1 (m), 4.3(m), 4.35 (m), 4.5 (m), 4.7 (m)	6.8–7.8 (br) ppm

The obsevation from the VT ^{31}P NMR can be rationalized with reference to published literature[4]. On cooling to −80°C, 7 sharp signals are assigned to 4 conformational isomers, each isomer having inequivalent phosphorus centres (Fig. 1).

These conformational isomers are proposed to result from the restricted motion in both the biphenyl bridge and the coordinated dba. In the dba, rotation about the carbon-carbon bond (to which the carbonyl carbon is attached nearest to the coordinated alkene), is suggested to be restricted.

The molecule is illustrated in plane view in Fig. 1 looking down the carbon-carbon bond of the coordinated dba. Four conformers are thought to be possible. These are suggested to be a result of freezing out: (i) two possible dispositions of the aromatic ring of the phosphine ligand relative to the dba, and (ii) two different orientations of the dba carbonyl resulting from a low energy barrier to rotation about the carbon-carbon bond between the coordinated alkene carbon and the carbonyl carbon. The broadness in the spectra recorded at room temperature is thought to be due to the latter process as molecular modelling calculations suggest that the ligand aromatic ring flipping is a high energy process and unlikely to occur.

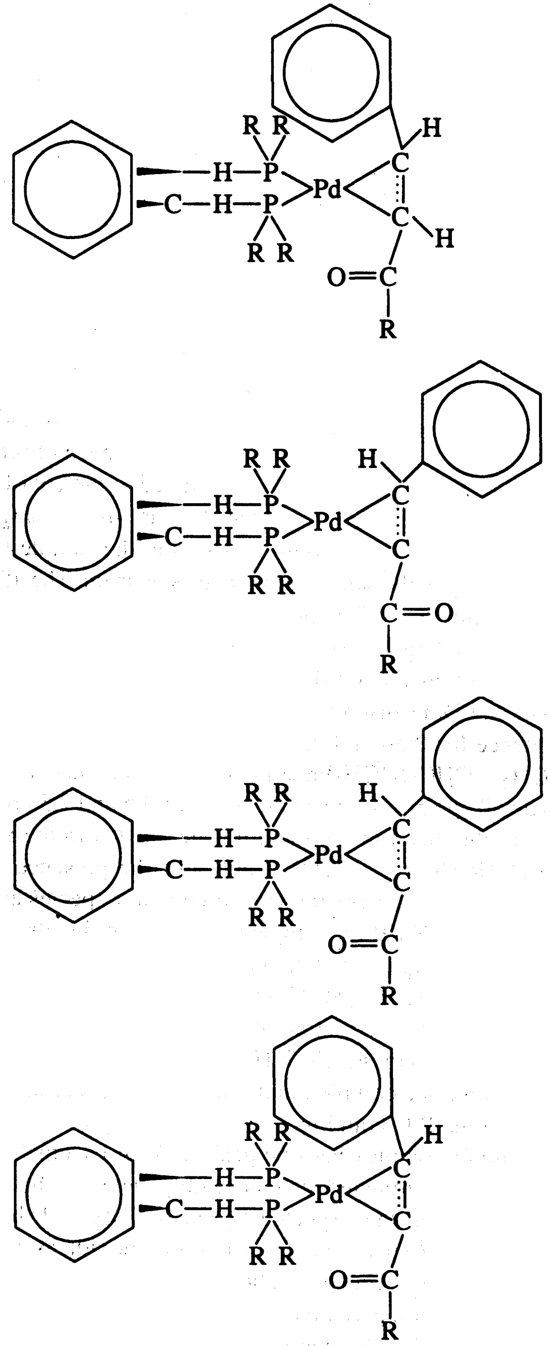

Fig. 1. Possible conformation of [(L-L)Pd(dba)] on cooling at –80°C

The ^1H and ^{13}C NMR spectra of complex in dichloromethane also have temperature dependent features as shown in Table-2.

TABLE-2
SELECTED ^{13}C NMR DATA FOR THE COMPLEX [(L-L)Pd(dba)]

	Coordinated dba CH	Carbonyl
In CD_2CL_2 solvent	60.7 (d, j = 31.6 Hz)	193.1 (s)
at −80°C	61.3 (d, j = 29.9 Hz),	192.4 (s)
	72.0 (d, j = 21.8 Hz)	190.4 (s) ppm
	73.1 (m) ppm	

In the ^1H NMR spectrum. the tert-butyl methyl resonances appear as three broad signals in dichloromethane. On cooling to −80°C these signals increase in complexity, with the appearance of new signals at 0.068, 0.31 and 0.65 ppm. The appearance of signals to high field on cooling has also been observed by Spencer *et al.*[5] in the related complexes. The signals assigned to the coordinated dba CH's appear as two broad humps suggesting that the various exchange processes are occurring at different rates in the solution. Cooling the sample to −80°C results in increased complexity in the same region in the spectrum. The alkene CH signals of noncoordinated *trans trans* dba appear as two doublets at 6.8 and 7.8 ppm; the coupling is a relatively large ^3j (H—H) *trans* vicinal coupling. The move to low field of these dba protons on coordination can be rationalized with reference to the Dewar, Chatt and Duncanson model for alkene bonding to transition metals.[6] Supporting evidence for these assignments comes also from the synthesis of the complex $[Pt(CH_2{=}CHCOOCH_2Ph)(PPh_3)_2]$ by Chaloner *et al.*[7] where the phenylpropionate alkene protons resonate between 3.5 and 3.5 ppm to higher field on coordination to the metal in the same manner as dba in the above complex.

The carbon NMR shown in Table-2 indicates the presence of three distinct carbonyl species at 193 K suggesting that three major species are present which is consistent with the ^{31}P NMR for complex. The carbon signals of the coordinated dba are broad at room temperature and on cooling fine structure develops. If only one conformer were present at −80°C then we would expect to see each carbon atom as a doublet of doublets cosisting of a larger P-C *trans* coupling (24–30 Hz) and a smaller P-C *cis* coupling (3–7 Hz). In fact because of the presence of conformers (Fig. 1) we see complex multiplets; in the spectrum however we can discern the larger *trans* P-C coupling.

The IR spectrum of complex has one peak (KBr discs, cm^{-1}): $\nu(CO)$ 1643 vs. The carbonyl of the coordinated dba is readily detected by IR but no clear correlation exists between the expected ligand basicity and the position of the carbonyl absorption in IR spectrum. The carbon monoxide as an ancillary ligand changes in CO stretching frequency reflecting the balance between σ-donation and π-back acceptance for a given phospine ligand.[8] The absence of a correlation in this study is suggested to be due to the conjugated π-electron system in the alkenes used in this study, of which the carbonyl forms a part.

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RFERENCES

1. F.R. Hartely, The Chemistry of Organophosphorus Compounds, Vol. 1, J. Wiley & Sons (1994).
2. J. Moulton and B.L. Shaw, *J. Chem. Soc., Chem Comm.*, 365 (1976).
3. C. Amatore, G. Broeker, A Jutand and F. Khalil, *J. Am. Chem. Soc.*, **119**, 5176 (1997).
4. W.A. Herrmann, W.R. Thiel, C. Brosmer, K. Ofele, T. Priemeier and W.J. Scherer, *J. Organomet. Chem.*, **461**, 51 (1993).
5. N. Carr, L. Mole, A.G. Orpen and J.L. Spencer, *J. Chem. Soc., Dalton Trans.*, 2653 (1992).
6. J.P. Collman, L.S. Hegedus, R.G. Norton and R.G. Finke, Principle and Application of Organotransition Metal Chemistry, University Science Books, Mill Valley (CA), USA (1987).
7. P.A. Chaloner, S.E. Davies and P.B. Hitchcock, *J. Organomet. Chem.*, **527**, 145 (1997).
8. R.H. Crabtree, The Organometallic Chemistry of Transition Metals, J. Wiley & Sons, New York (1988).

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