Journal of Organometallic Chemistry, 51 (1973) C30–C32

Preliminary communication

Resolution and absolute configuration of an organopalladium(II) complex

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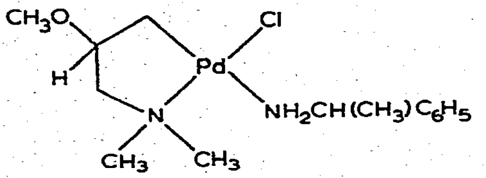
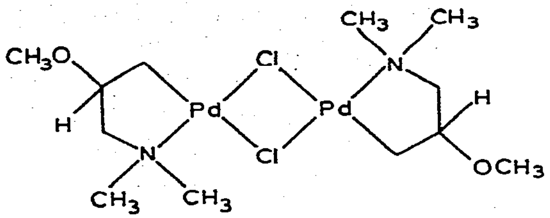
(Received February 14th, 1973)

We describe here the resolution of chloro(2-methoxy-3-*N,N*-dimethylaminopropyl-*C*^{1},*N*)[(*S*)-α-methylbenzylamine] palladium(II) (complex I). This complex possesses a σ carbon–metal bond adjacent to a chiral center. The absolute configuration of a diastereoisomeric form of (I) has been determinated by X-ray diffraction analysis.



(I)



(II)

Complex (I) is a derivative of the binuclear complex (II), isolated and characterized by Cope and coworkers[1]. It is obtained from (II) by rupture of the bridge with amine, following the procedure described[2] for the analogous reaction between (II) and $(C_6H_5)_3P$. Fractional crystallization of crude (I) from benzene/n-heptane (1/2) allows separation of two diastereoisomers; Ia ([α] −42.3; *c* 1.2, $CHCl_3$) and Ib ([α] +39.5; *c* 1.2, $CHCl_3$). Reductive disruption of (Ia) (with $LiAlH_4$ in Et_2O suspension), followed by standard separation procedures yielded levorotatory *N,N*-dimethyl-2-methoxypropylamine.

Product Ia crystallizes in the orthorombic system, space group $P2_12_12_1$, $a = 14.537 \pm 0.03$, $b = 11.570 \pm 0.02$, $c = 9.892 \pm 0.02$, $Z = 4$, $Dm = 1.55$ g·cm^{-3}, $Dc = 1.55$ g·cm^{-3}.

A total of 900 independent non-zero reflections, recorded with a Siemens four-circles automated diffractometer (Mo-K_α radiation), were used for the structure determination. The structure was solved by standard heavy atom procedures and refined by least squares calculations to a current conventional factor $R = 0.065$. The data were not corrected for adsorption or anomalous dispersion.

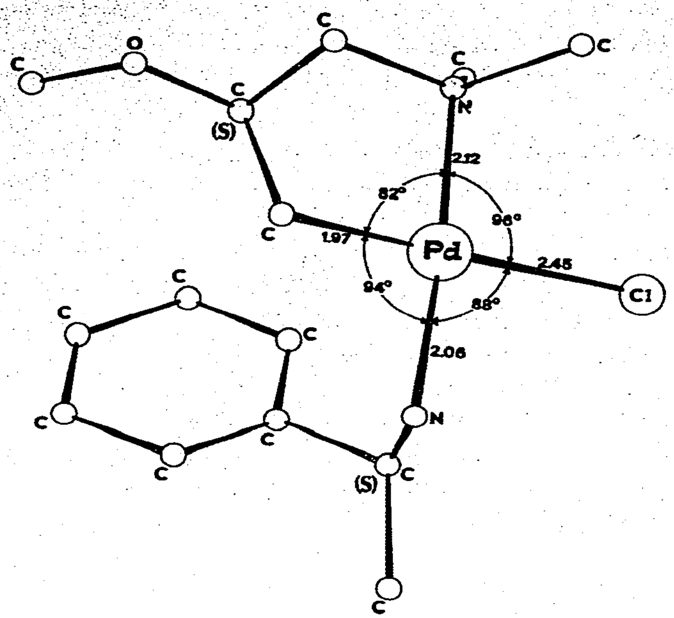


Fig. 1. Molecular structure of (Ia) including geometrical parameters.

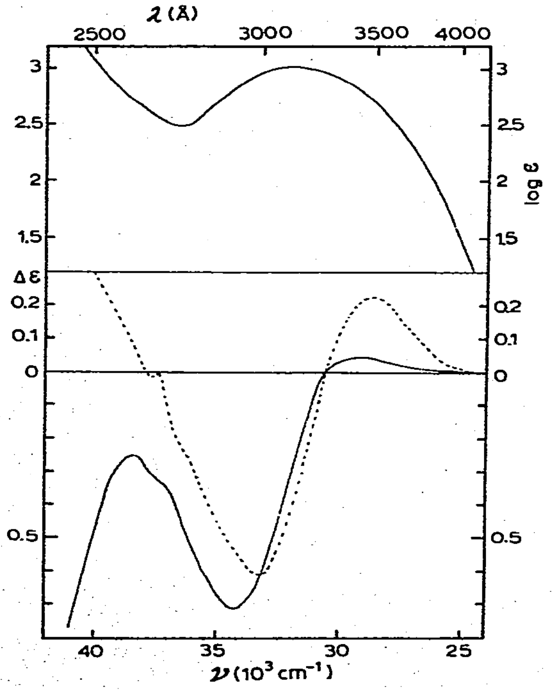


Fig. 2. Electronic absorption of (Ia) and circular dichroism of Ia (——) and Ib (----) in MeOH.

A molecular model is shown in Fig. 1 together with some geometrical parameters. The square-planar coordination at palladium is slightly distorted; the Pd—Cl distance (2.45 Å) is larger than the figure usually quoted[2], possibly due to the high *trans*-effect of the σ bond.

The presence of the amine chiral center of known absolute configuration (*S*) allows assignment of the absolute configuration, (*S*), to the asymmetric center adjacent to the σ C—Pd bond.

The electronic absorption and circular dichroism spectra of Ia and Ib are reported in Fig. 2. In the region of the $d \rightarrow d$ electronic transitions of palladium(II), *i.e.* between 25 000 and 35 000 cm^{-1}, the CD spectra of the two diastereoisomers are very similar, showing two absorption maxima of opposite sign (Ia, 29 000 cm^{-1}, $\Delta\epsilon + 0.05$, 34 250 cm^{-1}, $\Delta\epsilon - 0.72$; Ib, 28 500 cm^{-1}, $\Delta\epsilon + 0.22$, 33 300 cm^{-1}, $\Delta\epsilon - 0.61$).

This phenomenon, although permitting unambiguous correlations between the sign of the CD absorption bands and the absolute configuration of the chelate ligand, can be attributed to the presence of the coordinated (*S*)-α-methylbenzylamine[3] and to the poor contribution of the asymmetric ligand*.

REFERENCES

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2 See J. Powell, *Organometal. Chem. Rev.*, *B*, 6 (1970) 791 and references therein.
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*CD bonds of very low magnitude, associated to $d \rightarrow d$ transitions, have already been observed for other chelate four-membered ligands coordinated to Pd^{II}, *cf.* ref.4.