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FORMATION OF A CHIRAL CARBON CENTRE BY DIRECT METALLATION INTO A METHYLENE GROUP

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SUMMARY

The preparation of an optically active organometallic compound through the reaction between 8-ethylquinoline and lithium tetrachloropalladate is reported. The optical activity of this compound is associated with the presence of a chiral carbon atom.

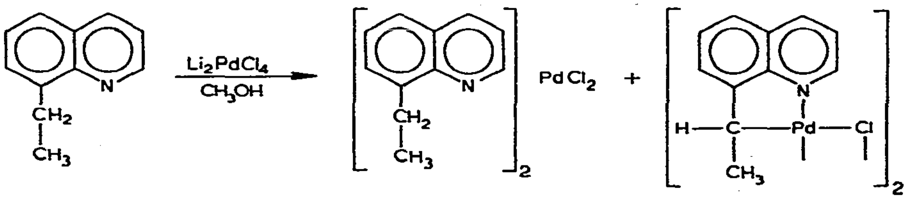
INTRODUCTION

Little work has been undertaken to date on optically active molecules having a σ-bonded transition metal atom linked to the chiral carbon centre. Such compounds could be of great importance in developing new approaches to model compounds.

We now wish to report a novel method for the formation of a chiral carbon centre through direct metallation (palladation) to an aliphatic methylene group by means of a reaction described recently involving 8-methylquinoline[1]. When the methyl group is replaced by an alkyl group of greater chain length a chiral centre is formed.

RESULTS AND DISCUSSION

The reaction between 8-ethylquinoline (L) and lithium tetrachloropalladate in methanol gave rise to a mixture of two products, a complex of type L_2PdCl_2 (I) and a dimer having the palladium atom σ-bonded to carbon (II)*.



(I) (II)

The latter could be purified by extraction with benzene. The composition of the

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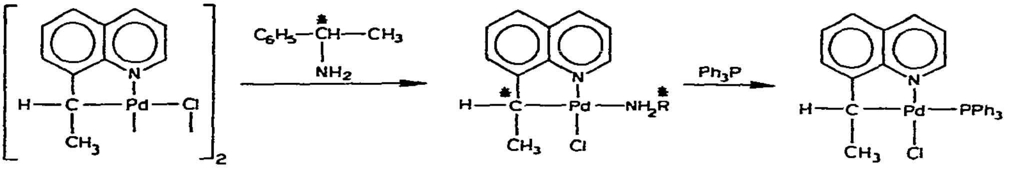
* We have observed that the palladation of 8-methylquinoline also yields a similar mixture, the complex L_2PdCl_2 being predominant in this case.

mixture was established through use of the well resolved methyl bands in the NMR spectrum: δ 1.22 ppm (triplet) and 0.93 ppm (doublet) for (I) and (II) respectively.



(II) (III) (IV)

It was found that the metal–chlorine bridges in the dimer could be easily cleaved upon treatment with optically active (1-phenylethyl)amine in dichloromethane, crystallization of the resulting product (III) affording one of the diastereoisomers, $[\alpha]_D + 29.2°$ (*c* 4; CH_2Cl_2). If the optically active amine in this complex was replaced by triphenylphosphine, compound (IV) was obtained, $[\alpha]_D + 41.5°$ (*c* 4.5; CH_2Cl_2)[*]. The optical activity of the latter compound is solely due to the presence of the chiral carbon atom[**].

The formation of organometallic compounds of this type suggests the possibility of studying the stereochemistry of metal–carbon σ-bond breaking, and as an extension of our work[2] we have used a related reaction pathway starting with *N*-methyl-*N*-ethyl-1-naphthylamine to examine the ability of nitrogen to act as a chiral centre when coordinated to a metal atom.

Work is at present in progress to elucidate how the chiroptical properties of the above complexes are affected by the replacement of palladium by platinum or nickel.

REFERENCES

1 J. E. HARTWELL, R. V. LAWRENCE AND M. J. SMAS, *Chem. Commun.*, (1970) 912.
2 V. I. SOKOLOV, L. L. TROITSKAYA *et al.*, *Izv. Akad. Nauk SSSR*, (1971) 2611.

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[*] All compounds mentioned analyzed satisfactorily for C, H, Cl and Pd.

[**] The four ligands at the palladium atom have a planar arrangement.