Inorganica Chimica Acta, 18 (1976) L9
© Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

Stereochemistry of the Oxidative Addition of Optically Active 8-(α-bromoethyl)quinoline to Tris (triphenylphosphine)platinum*

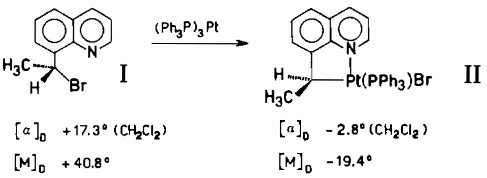
V. I. SOKOLOV

Institute of Organoelement Compounds, Moscow, U.S.S.R.

(Received January 13, 1976)

The oxidative addition to $(Ph_3P)_nPt$ was first observed as early as 1960.[1] However, the mechanism of this and related reactions is yet not clear and of current interest.[2-4] Until now, no examples of the reaction were known for secondary and tertiary alkyl halides and $L_nPt(0)$. Hence, no stereochemical information was available. Very recently, it was suggested[5] that secondary bromides are generally unable to afford σ-organoplatinum compounds in this reaction. Those authors have failed to obtain the respective complexes starting from sec-butyl bromide and α-phenylethyl bromide.

Now I wish to report the first study of the oxidative addition of an optically active bromide, 8-(α-bromoethyl)quinoline, to the zerovalent platinum complex $(Ph_3P)_3Pt$. This secondary bromide which is closely related to α-phenylethyl bromide differs in having a donor nitrogen atom in a position suitable to close a chelate ring. As we have shown[6,7] both 8-bromomethylquinoline and racemic 8-(α-bromoethyl)quinoline when reacted to $(Ph_3P)_3M$ or $(dba)_nM$ (M = Pt or Pd) afford exclusively σ-alkyl derivatives, not open forms. The latter was now partially resolved as *d*-camphorsulphonic acid salt. In a similar way, (+)bromide I gave (–)organoplatinum II in a 70% yield. The retention of optical activity suggests at least in part a heterolytic pathway.



It is necessary to know the maximal magnitudes of rotation angles to evaluate the extent of stereoselectivity. However, the qualitative conclusion may be drawn immediately using the Brewster helical model of optical activity,[8] which proved to be useful for various stereochemical problems. In terms of this model, the optical rotations of two molecules in question are determined only by atomic asymmetry. The sign of rotation should depend on the relative polarizabilities of the four groups around the chiral centre. As shown below, the order is the same for both structures:

$X > aryl > CH_3 > H$, when X = Br or $(Ph_3P)PtBr$. Therefrom it follows that the configurations of the carbon centres are *opposite* in the starting (+)bromide I and in the resulting (–)platinum complex II. Thus, inversion has occurred. This result is consistent with the S_N2 mechanism of oxidative addition. Recently Stille[4] established the high extent of inversion in the oxidative addition of alkyl halides to $(Ph_3P)_4Pd$.

References

1 J. Chatt and B. L. Shaw, *J. Chem. Soc.,* 705 (1959).
2 M. F. Lappert and P. W. Lednor, *Chem. Comm.,* 948 (1973).
3 A. V. Kramer and J. A. Osborn, *J. Am. Chem. Soc., 96,* 7832 (1974).
4 K. S. Y. Lau, R. W. Fries and J. K. Stille, *J. Am. Chem. Soc., 96,* 4983 (1974).
5 R. G. Pearson, W. Louw and J. Rajaram, *Inorg. Chim. Acta, 9,* 251 (1974).
6 V. I. Sokolov, *Abstracts of the VII ICOMC, SA5,* Venice (1975).
7 L. L. Troitskaya, V. I. Sokolov and O. A. Reutov, *DAN SSSR (Russ.),* in press.
8 J. H. Brewster, *J. Am. Chem. Soc., 81,* 5475 (1959).

---

*Presented as a part of Section Lecture at the VII International Conference on Organometallic Chemistry, Venice, September 1975.[6]