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The Activation Barrier to Axial Torsion in 2,2'-Bis(diphenylphosphino)biphenyl

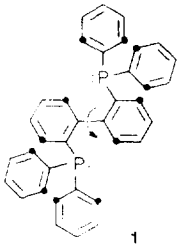
Olivier Desponds and M. Schlosser *

Institut de Chimie organique de l'Université
Bâtiment de Chimie (BCh), CH-1015 Lausanne-Dorigny, Switzerland

Abstract: After selective deuteriation of 2,2'-bis(diphenylphosphino)biphenyl, it was possible to determine the nmr coalescence temperature of the diastereotopic phenyl groups. On this basis, a torsional barrier of 22 kcal/mol was calculated. Thus, the bisphosphine, even if it could be resolved into pure enantiomers, would rapidly reracemize at temperatures around or above 25 °C.

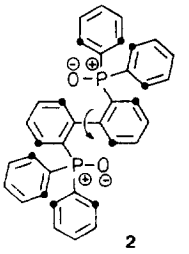
2,2'-Bis(diphenylphosphino)biphenyl [1,1'-biphenyl-2,2'-diylbis(diphenylphosphine), **1**] is the parent member of an impressive series of axially dissymmetric ligands. It can be readily prepared by the Ullmann coupling of (2-iodophenyl)diphenylphosphine oxide and the subsequent reduction of the resulting bis(phosphine oxide) **2** with trichlorosilane [1]. In contrast, the claimed access [2] by condensation of 2,2'-dilithiobiphenyl with two equivalents of chlorodiphenylphosphine was found to be irreproducible [1, 3]. The amazing configurational stability of the recently described 2,2'-bis(diphenylphosphino)-6,6'-difluorobiphenyl [4] at 210 °C ($\Delta G^{\neq} > 35$ kcal/mol) nourished the hope that also the 6,6'-unsubstituted bisphosphine might conserve atropisomerism at ordinary temperature. This is not the case, as we shall demonstrate. The energy required for the planarization of the biaryl moiety amounts to only 22 (± 1) kcal/mol.

This number follows from the nmr spectroscopically determined coalescence temperature above which the, in pairs, diastereotopic phenyl groups become equivalent [5]. However, the spectrum of the bisphosphine **1** had to be drastically simplified before these measurements could be successfully accomplished. To this end, the bis(phosphine oxide) **2** was submitted to a platinate catalyzed [6] replacement of all hydrogen atoms by deuterium, except at the *ortho* positions. The remaining ^1H signals did not overlap any more and could be unequivocally assigned. The pronounced temperature dependence of certain chemical shifts [7] represented an additional complication, but did not compromise the study.



1

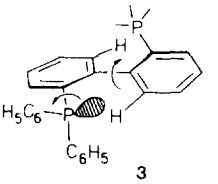
• means C-^{1}H
other positions: C-^{2}H



2

The racemization barrier of the bis(phosphine oxide) **2**, evaluated in the same way as that of bisphosphine **1**, proved to be identical with the latter (approximating again 22 kcal/mol). [8] This coincidence points at a

cogwheel motion coupling the untwisting of the central biaryl core with rotations around the P-C^{ortho} bonds (see partial structure **3**). The lone pair electrons of the halogen atoms in the 6,6'-difluoro analogue [4] of bisphosphine **1** should, of course, severely impede a process synchronized in this manner.



3

Selective H/D Exchange (Working Procedure) : Under nitrogen atmosphere, sodium tetrachloroplatinate tetrahydrate (0.090 g, 24 mmol) in *O*-[^{2}H]acetic acid (9.0 mL) and deuterium chloride (0.24 mmol) in degassed heavy water (2.5 mL) were added to 2,2'-bis(diphenylphosphinoyl)biphenyl (**2**; 1.7 g, 3.0 mmol; mp 221 - 223 °C). The suspension was heated under stirring in a well stoppered Schlenk vessel 30 min to 75 °C, 30 min to 100 °C and 15 h to 125 °C. The initially orange colored reaction mixture became grey in the course of this interval. It was poured into water (30 mL) and extracted with dichloromethane (2 × 30 mL). The combined organic layers were washed with a saturated aqueous solution (2 × 30 mL) of sodium carbonate and dried with sodium sulfate. The residue (1.4 g) left after the evaporation of the solvent was submitted to a second hydrogen/deuterium exchange, applying the same protocol as above. According to nmr analysis, the product (1.0 g; mp 214 - 219 °C) thus obtained carried an average of 95% of deuterium in all *meta* and *para* positions. ^{1}H-NMR : (400 MHz, $CDCl_3$) : δ 7.70 (4 H, d, *J* 11.7), 7.64 (4 H, d, *J* 12.1), 7.17 (2 H, d, *J* 14.1), 7.09 (2 H, d, *J* 4.2).

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7. For example, $\delta_{H(6,6')}$ 6.89 and 7.04 (in [^{2}H]chloroform) and $\delta_{H(3,3')}$ 7.07 and 6.95 (in [$^2H_8$]tetrahydrofuran) at +50 and -50 °C, respectively.
8. The *o,o'*-hydrogen signals of the phenyl groups in the bisphosphine **1** (ν 2878.7 and 2872.2 Hz) showed coalescence at 125 °C, whereas those in the bis(phosphine oxide) **2** (ν 3063.4 and 3043.0 Hz) merged at 160 °C, 1,1,2,2-tetrachloro[$^2H_2$]ethane being used as the solvent in both cases.

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