CHEMISTRY LETTERS, pp. 1311-1314, 1994. © 1994 The Chemical Society of Japan

Further Studies on the Dependence of the Barriers for Gear Slippage on the Joint Group in Bis(9-triptycyl)X Type Molecules. Bis(9-triptycyl)phosphine, the Missing Link in the Series along the Third Row of the Periodic Table[1,2]

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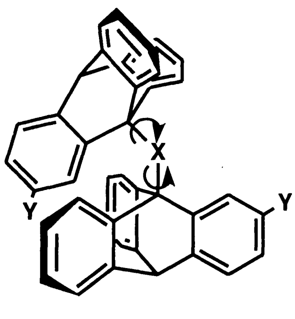
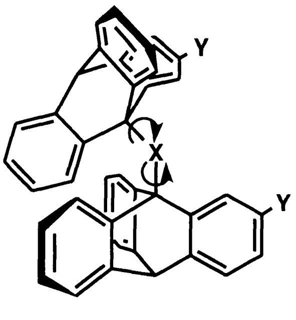
Bis(9-triptycyl)phosphines have been prepared. The two tortional degrees of freedom about the bonds from the bridgehead carbons to the phosphorus correlate in such a strength as to make it just possible to separate phase isomers under ambient conditions. The barrier for the loss of correlation has been accurately determined through the kinetics of the interconversion of the *meso* and *dl* isomer of bis(2-chloro-9-triptycyl)phosphine.($\Delta H^{\ddagger} = 24.0 \pm 0.1$ kcal/mol, $\Delta S^{\ddagger} = -4.2 \pm 0.2$ e.u.)

Tight coupled disrotation around the two bonds from the bridgehead carbons to the joint atom in bis(9-triptycyl)X type molecules (molecular bevel gear) begins to miss (gear slippage), when temperature is raised. The barrier heights for the process have been of our major concern and range from 31.4 kcal/mol for the methane ($\Delta H^{\ddagger}$ for conversion from the *dl* to *meso* isomer)[3] to 41.0 kcal/mol for the ether[3] as measured by the interconversion of the *meso* and *dl* isomers with labeled vanes (a chlorine atom on each C-2).[3] The barrier of the amine (38.1 kcal/mol)[4] is much closer to that of the ether(See Table 1).

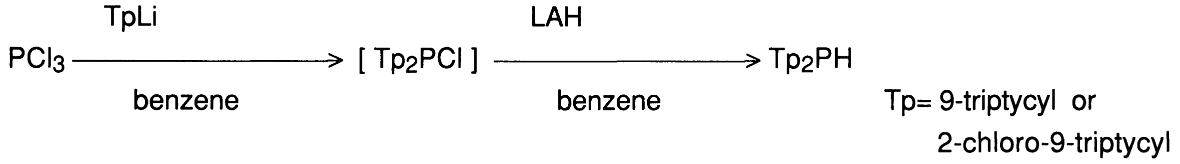
The compounds where the joint atom belongs to the third row of the periodic table have considerably smaller barriers. The silane gear can no more mesh tightly and the *meso* and *dl* isomers are not separable at room temperature. The barrier has been determined to be 20.4 kcal/mol through DNMR methods.[5] To the contrary, the sulfide gear retains tight meshing (28.8 kcal/mol) and the phase isomers of the sulfide interconvert each other at measurable rate only above 60 °C (1/*k* (*dl*→*meso*), about 100 d).[6] Effect of the long bond from the



meso



d or *l*



$$PCl_3 \xrightarrow[\text{benzene}]{\text{TpLi}} [\,Tp_2PCl\,] \xrightarrow[\text{benzene}]{\text{LAH}} Tp_2PH$$

Tp= 9-triptycyl or 2-chloro-9-triptycyl

Scheme 1.

bridgehead carbons to the sulfur atom, which must be one of the most important factors to make meshing looser, seems to be largely counterbalanced by some other factors. The barrier height for the phosphine, which should be somewhere between those of the silane and the sulfide, is yet to be determined and might give more insights into these unaccounted factors. In this paper we will report the preparation of bis(9-triptycyl)phosphines, the separation of the phase isomers with labeled vanes, and the kinetics of their interconversion to reveal that these phosphine gears rarely miss meshing under ambient conditions.

The phosphines were prepared according to Scheme 1. The experimental procedures for the unsubstituted bis(9-triptycyl)phosphine are as follows. A solution of 9-triptycyllithium in benzene7) was added dropwise to a solution of phosphorus trichloride dissolved in the same solvent through a syringe at ambient temperature over a period of about 10 min. After stirring for several hours, excess $LiAlH_4$(3-4 equiv.) was added and stirring was continued overnight. Usual workup and successive purification by chromatography on a short alumina column, GPC, and preparative TLC gave the target compound.8) Compared to the pyrolytic methods used to prepare the ether, amine, and sulfide (extrusion of CO_2, N_2, and SO_2 from the corresponding peroxyester, triazene, and thiosulfonate, respectively), the present synthetic sequence is very simple but far less efficient. The yield has been less than a few percent with a concomitant formation of a large amount of triptycene. It suggests that an intermediate dichloro(9-triptycyl)phosphine does not readily undergo S_N2 reaction with bulky nucleophiles like 9-triptycyllithium on steric reasons and that single electron transfer

Table 1. Activation Parameters for Gear Slippage(*dl* → *meso*) of Bis(2-chloro-9-triptycyl)X Type Compounds

X	$\Delta H^‡$ /kcal·mol $^{-1}$	$\Delta S^‡$ / e.u.	
CH_2	31.4 ± 0.1	- 6.0 ± 0.2	Ref. 3[a]
NH	38.1 ± 0.3	- 4.8 ± 0.7	Ref. 4[a]
O	41.0 ± 0.6	- 5.2 ± 0.6	Ref. 3[a]
SiH_2	20.4 ± 0.4	- 2.6 ± 1.2	Ref. 2
PH	24.0 ± 0.1	- 4.2 ± 0.2	this work
S	28.8 ± 0.2	- 4.2 ± 0.4	Ref. 6[a]

a) In the previous works,3,4,6) Arrhenius parameters have been reported instead of activation enthalpies and entropies.

occurs from 9-triptycyllithium to give 9-triptycyl radical, an avid hydrogen abstractor, instead.9)

The phase isomers of bis(2-chloro-9-triptycyl)phosphine similarly obtained have been separated by HPLC. Because of a little occurrence of interconversion even at slightly higher temperature than ambient one, the column packed with micro silica gel was kept below 10 °C using a water jacket. Furthermore the collected chromatographic fractions containing either the *meso* or the *dl* isomer were kept below 0 °C throughout the separation and the eluent (hexane-chloroform) was removed under a reduced pressure around 0 °C. They were easily identified because the two 2-chloro-9-triptycyl groups of the *meso* isomer are equivalent, whereas they are not in the *dl* isomer.10)

Kinetic measurements starting from the pure *meso* isomer were carried out in benzene as described previously3) in a temperature range of 20-90 °C. Similar precautions were paid against an unintended isomerization. Once the *meso* isomer was dissolved in benzene, the solution was always kept below 0 °C except when it was heated for interconversion at a fixed temperature for a fixed period. Especial cares were taken, when small glass ampoules containing the solution were sealed off. The results were summarized in Table 1 together with those previously obtained.11)

Compared to the compounds joined by a second row atom, those with a joint atom of the third row have decreased activation enthalpies by 11-14 kcal/mol and increased activation entropies by about 1-3 e.u. These facts reflect the less tight meshing in the ground state and the resultant lesser steric congestion in the transition state for gear slippage.

Among the factors which are possibly affecting the energy of the transition state for gear slippage other than the C-X bond length, important and dependent on the joint atom are probably the C-X-C angle, ease of the C-X stretching and/or C-X-C bending. As is inferred from the reported values for a series of Me_2X type molecules,12) the 30% increase in the activation enthalpy on going from the methane to the ether is brought about by combined effects of the 8% decrease in the C-X bond length and about the 30% increase of the both force constants.12a,d) To the contrary, more than the 40% increase of activation enthalpy from the silane to the sulfide is ascribable to the reduction of C-X-C bond angle by 12.1°, more than the 80% increase of the bending force constant, 12c,e) and the decrease in the C-X bond length (less than 4%). Counteracting is the decrease in stretching force constant (15%).12c) Although it should be noted that non-bonded repulsive terms are neglected and that an extensive deformation of the molecular geometry due to severe congestion13) renders it somewhat dubious to apply the molecular constants obtained from Me_2X to bis(9-triptycyl)$_2$X type molecules, these observations seem to point to the relative importance of the C-X-C angle and the C-X-C bending force constant. Now the barrier for the phosphine has been disclosed to be some 20% larger than that of the silane and lies in the middle of those of the silane and the sulfide. Considering that the decrease in the C-X bond length is only 1% on going from the silane to the phosphine, the increase of the barrier is ascribable to the decrease of the C-X-C angle to 99.7° and the considerably large force constants.12f)

It is evident that we cannot expect tight meshing of the rotation around the two carbon-arsenic bonds in bis(9-triptycyl)arsine, because the change in activation enthalpy on descending from the third to the fourth row is considered no less than a few kcal/mol and large enough to make the arsine gear loose. To the contrary, tightness of the meshing in bis(9-triptycyl) selenide is worthy of scrutiny, which is now in progress. This work was supported by the Grant-in-Aid for Scientific Research on Priority Areas No.048 from the Ministry of Education, Science, and Culture, Japanese Government. Prof. H. Iwamura of the University of Tokyo is greatly acknowledged for his encouragement and valuable comments throughout this work.

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6) Y. Kawada, J. Ishikawa, G. Koga, S. Murata, and H. Iwamura, *Tetrahedron Lett.*, **28**, 445 (1987).

7) 9-Bromotriptycene was treated with n-butyllithium as usual in a mixture of benzene and diethyl ether to give precipitate of 9-triptycyllithium: see experimental part of Ref. 3. Most of the ether was removed either by withdrawing the supernatant or by cooling down the solution to -78 °C to effect benzene to solidify followed by decantation and fresh benzene was added to retain the original volume. In the presence of diethyl ether, the yield of the phosphine decreases further.

8) mp 340-342 °C; ^{1}H NMR(270 MHz, $CDCl_3$) δ 5.45 (2H, s), 6.04 (1H, d, J_{PH}=237.2 Hz), 6.78 (6H, dt), 6.99 (6H, dt), 7.44 (3H, d), 7.92 (6H, d); ^{13}C NMR(67.5 MHz, $CDCl_3$) δ 54.7 (d, J_{CP}=41 Hz), 55.1, 123.5, 124.4, 125.5, 125.8 (d, J_{CP}=17 Hz), 145.7 (d, J_{CP}=8 Hz), 146.4 (d, J_{CP}=5 Hz); IR(KBr) ν_{PH} 2320cm^{-1}; HRMS Found: 538.1859, Calcd for $C_{40}H_{27}P$: 538.1850.

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10) *meso* mp 210-212 °C; ^{1}H NMR(400 MHz, $CDCl_3$) δ 5.44 (2H, s), 6.00 (1H, d, J_{PH}=236.7 Hz), 6.89-6.95 (6H, m), 7.07 (4H, m), 7.32 (2H, d), 7.46-7.49 (4H, m), 7.68 (2H, t, J≤1.8 Hz), 7.86 (2H, d), 8.11 (2H, dd); HRMS Found: 606.1063, Calcd for $C_{40}H_{25}Cl_2P$: 606.1070.
dl mp 210-212 °C; ^{1}H NMR(400 MHz, $CDCl_3$) δ 5.44 (2H, s), 5.97 (1H, d, J_{PH}=237.4 Hz), 6.68 (1H, dt), 6.72 (1H, dt), 6.90 (1H, dt), 6.93 (1H, dt), 6.96-7.02 (4H, m), 7.07 (1H, dt), 7.08(1H, dt), 7.37 (2H, d), 7.43 (2H, d), 7.47 (2H, d), 7.63 (1H, d), 7.77 (1H, d), 7.90 (1H, t, J≤1.8 Hz), 7.95–7.99 (2H, m), 8.06 (1H, t, 2.6 Hz); HRMS Found: 606.1031, Calcd for $C_{40}H_{25}Cl_2P$: 606.1070.
Presence of eleven and twentytwo kinds of signals for the aromatic protons of the *meso* and *dl* isomer, respectively, clearly indicates that configurational inversion at the joint phosphorus atom is slow on the NMR time scale. No difference between the melting points of the *meso* and *dl* isomer shows the equilibration of these isomers prior to melting.

11) k (*dl*→*meso*)/s^{-1} (temperature/°C) 9.67×10^{-7} (20.4); 8.18×10^{-6} (35.7); 3.56×10^{-5} (47.5); 1.99×10^{-4} (62.4); 1.40×10^{-3} (81.0); 2.89×10^{-3} (89.0). The equilibrium ratio of *dl* /*meso* remained constant (1.63) throughout the temperature range studied.

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(Received March 28, 1994)