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STEREODYNAMICS OF TERT-BUTYLPHOSPHINE BORANE COMPLEXES. BARRIERS TO TERT-BUTYL ROTATION. STEREOCHEMICAL DEPENDENCE OF $^3J_{PCCH}$

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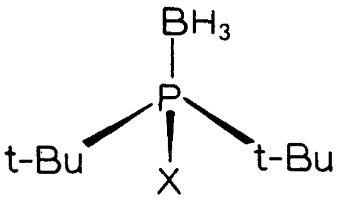
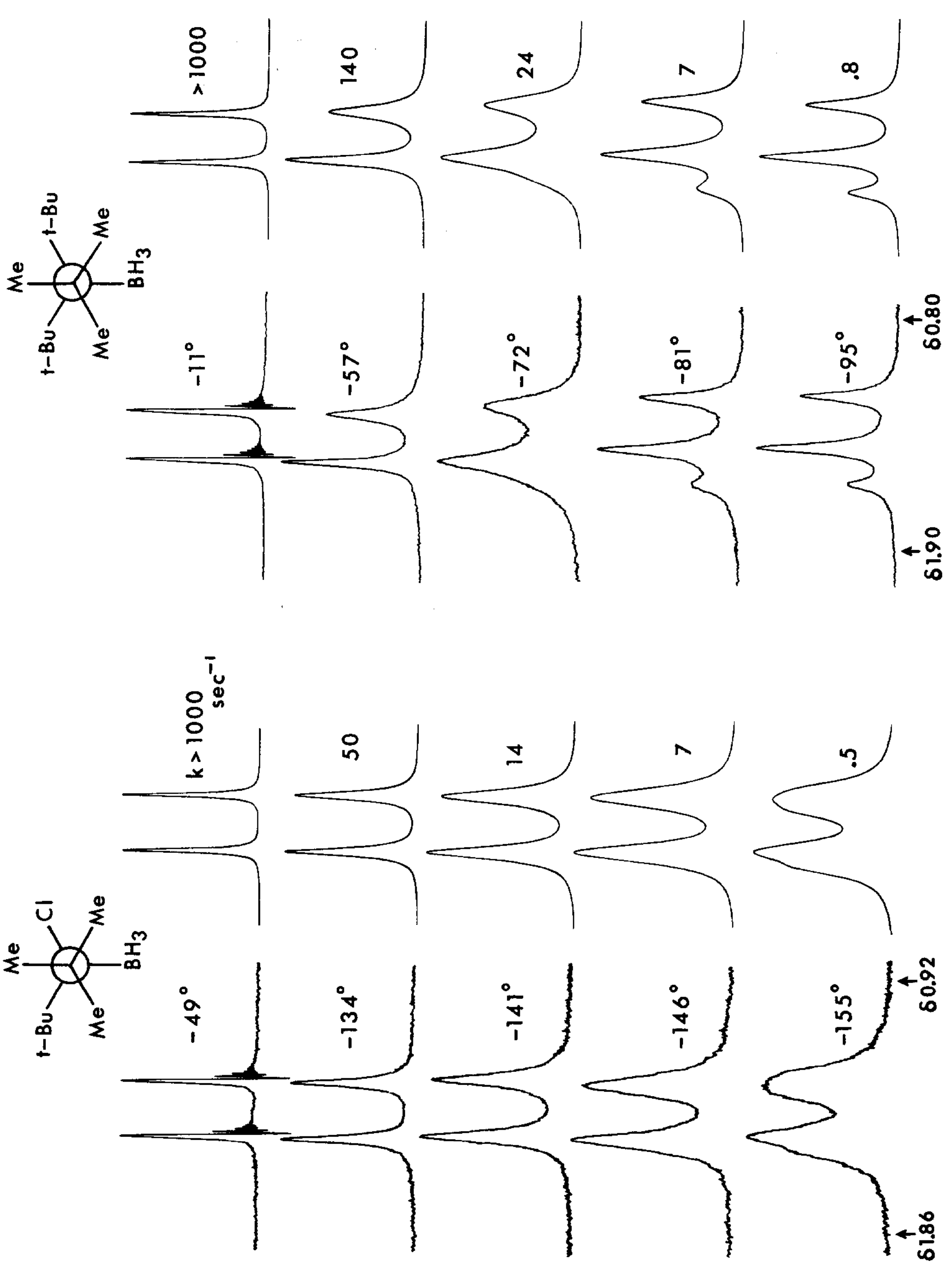
Although there exists a limited amount of information regarding the dynamics of rotation about carbon-phosphorus single bonds in hindered phosphines,[3] there is essentially no data regarding the effect of Lewis acid complexation on this rate process. This report concerns the direct observation of slow tert-butyl rotation in tri-tert-butylphosphine borane (1) and di-tert-butylchlorophosphine borane (2) using ^1H dnmr spectroscopy.



1 X = t-Bu

2 X = Cl

Examination of the ^1H dnmr spectrum (60 MHz) of 1 (0.2M in 60% CH_2Cl_2/40% CD_3OD v/v) at -11° (Figure) revealed a time-averaged doublet resonance (δ1.42; $^3J_{PCCH}$ = 11.7 Hz) consistent with rapid tert-butyl rotation on the dnmr time scale. At lower temperatures, the dnmr spectrum undergoes complex changes giving under conditions of slow exchange two doublet resonances at δ1.53 (3H; methyl trans to BH_3; $^3J_{PCCH}$ = 9.1 Hz) and 1.36 (6H; two methyls gauche to BH_3; $^3J_{PCCH}$ = 13.0 Hz) consistent with the symmetry experienced by a slowly rotating tert-butyl. Changes in the ^1H dnmr spectrum of 2 (0.1M in 5% CD_3OD/60% CH_2CHCl/35% $ClFCCF_2$ v/v) are also consistent with slowing tert-butyl rotation (Figure). Under conditions of slow, intermediate, and fast rates of


Me
t-Bu
Me
BH3
Me
t-Bu
-11°
-57°
-72°
-81°
-95°
>1000
140
24
7
.8
61.90
60.80
Me
Cl
Me
BH3
Me
t-Bu
-49°
-134°
-141°
-146°
-155°
k > 1000 sec^{-1}
50
14
7
.5
61.86
60.92

tert-butyl rotation in 2 , it was found necessary for the purpose of calculating theoretical spectra to employ three different coupling constants and chemical shifts for the tert-butyl methyls at δ1.39 (3H; methyl gauche to BH_3; $^3J_{PCCH}$ = 17.4 Hz), 1.38 (3H; methyl trans to BH_3; $^3J_{PCCH}$ = 11.1 Hz), and 1.23 (3H; methyl gauche to BH_3; $^3J_{PCCH}$ = 15.4 Hz). Activation parameters derived from total dnmr line shape analysis are compiled in Table I with data for other phosphines.

A perusal of Table I indicates some interesting trends. In comparing rates of tert-butyl rotation in Table I, it is most appropriate to compare the various $\Delta G^\ddagger$ values which are less subject to systematic errors than $\Delta H^\ddagger$ and $\Delta S^\ddagger$. The barriers ($\Delta G^\ddagger$) in $(t\text{-Bu})_3P$ and $(t\text{-Bu})_3PBH_3$ reveal BH_3 to be significantly more hindering to tert-butyl rotation than a lone pair and comparable to a coordinate covalently bonded sulfur. However, a comparison of $(t\text{-Bu})_2ClP$ and $(t\text{-Bu})_2ClPBH_3$ indicates that the effect is not additive and in these two compounds the barrier difference is much smaller as compared to $(t\text{-Bu})_3P$ and $(t\text{-Bu})_3PBH_3$. Although derived from data for only two pairs of compounds, there exists an apparent correlation between complex stability and the effective hindering of rotation by BH_3. Complex 2 would be expected to be less stable than 1 due to the electronegative chlorine and any resultant changes in bond length and/or force constants for bond angle deformation may play a role in determining the effective steric size of BH_3 in the context of retarding rotational processes.

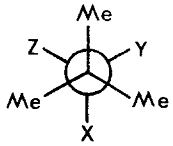
Also compiled in Table II are $^3J_{PCCH}$ values for 1 , 2 , selected tert-butylphosphines, and $(t\text{-Bu})_3PS$. Complexes 1 and 2 are similar to the free phosphines in that $^3J_{PCCH}(t)$ is smaller than $^3J_{PCCH}(g)$, although in 1 and 2 , the differences between $^3J_{PCCH}(t)$ and $^3J_{PCCH}(g)$ are much smaller than in the corresponding free phosphines. In the case of $(t\text{-Bu})_3PS$, $^3J_{PCCH}(t)$ and $^3J_{PCCH}(g)$ are essentially equal. Such coupling constant data will prove to be useful in subsequent conformational studies and may be developed as a probe into the nature of bonding involving the phosphorus lone pair.

Table I. Activation Parameters for tert-Butyl Rotation

Compd	$\Delta H^{\ddagger}$, kcal/mole	$\Delta S^{\ddagger}$, gibbs	$\Delta G^{\ddagger}$, kcal/mole (temp., °C)
$(t\text{-Bu})_3P$	9.0 ± 0.4[a]	2 ± 4	8.6 ± 0.1 (-103)
$(t\text{-Bu})_3PS$	9.5 ± 0.4[a]	-5 ± 4	10.5 ± 0.1 (-72)
$(t\text{-Bu})_3PBH_3$	10.0 ± 0.2[b]	-2 ± 2	10.4 ± 0.1 (-68)
$(t\text{-Bu})_2ClP$	6.3 ± 0.4[a]	0 ± 4	6.3 ± 0.1 (-149)
$(t\text{-Bu})_2ClPBH_3$	7.0 ± 0.4[b]	0 ± 5	6.8 ± 0.1 (-141)

(a) See ref. 3. (b) This work.

Table II. ^1H-^{31}P Spin-Spin Coupling Constants for Methyl Groups in tert-Butylphosphines and Derivatives



Compd	$^3J_{PCCH}(t)$, Hz[a]	$^3J_{PCCH}(g)$, Hz[b]
X = lone pair, Y = Z = t-Bu	2.4	13.4
X = S, Y = Z = t-Bu	13.3	14.0
X = BH_3, Y = Z = t-Bu	9.1	13.0
X = lone pair, Y = t-Bu, Z = Cl	4.5	15.9, 16.6
X = BH_3, Y = t-Bu, Z = Cl	11.1	15.4, 17.4

(a) $^3J_{PCCH}$ for methyl trans to X.

(b) $^3J_{PCCH}$ for methyls gauche to X.

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(2) NDEA Title IV Fellow, 1971-74.

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