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DIRECT OBSERVATION OF SLOW ROTATION ABOUT CARBON-PHOSPHOROUS SINGLE BONDS. $^{31}P-^{1}H$ SPIN-SPIN COUPLING AS A PROBE OF CONFORMATIONAL PREFERENCE

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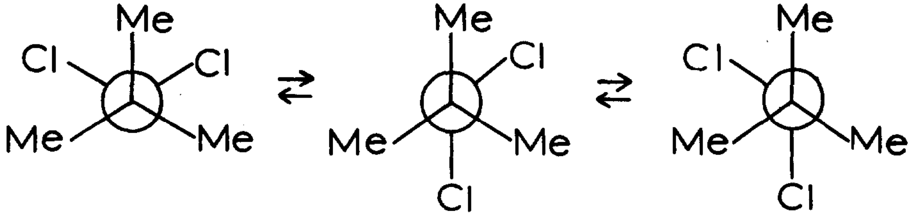
Knowledge of the magnitude and origins of potential barriers to internal rotation in simple, acyclic systems has important implications in understanding the conformational dynamics of more complex structures. Microwave and dynamic nuclear magnetic resonance (DNMR) spectroscopy have been especially effective in determining barriers to both rotation[2] and atomic inversion[3] in acyclic compounds.

Although extensive experimental studies suggesting the origins of barriers to pyramidal inversion at phosphorous have been performed,[3b] there exists a dearth of information regarding the magnitude of rotational barriers about carbon-phosphorous single bonds.[4] This report concerns the direct observation (DNMR method) of slow rotation about the C–P bond in tert-butyldichlorophosphine (1) and di(tert-butyl)chlorophosphine (2) as well as a dramatic dependence of the $^{1}H-^{31}P$ spin-spin coupling constants in 1 and 2 on the orientation of methyl within a given tert-butyl group.

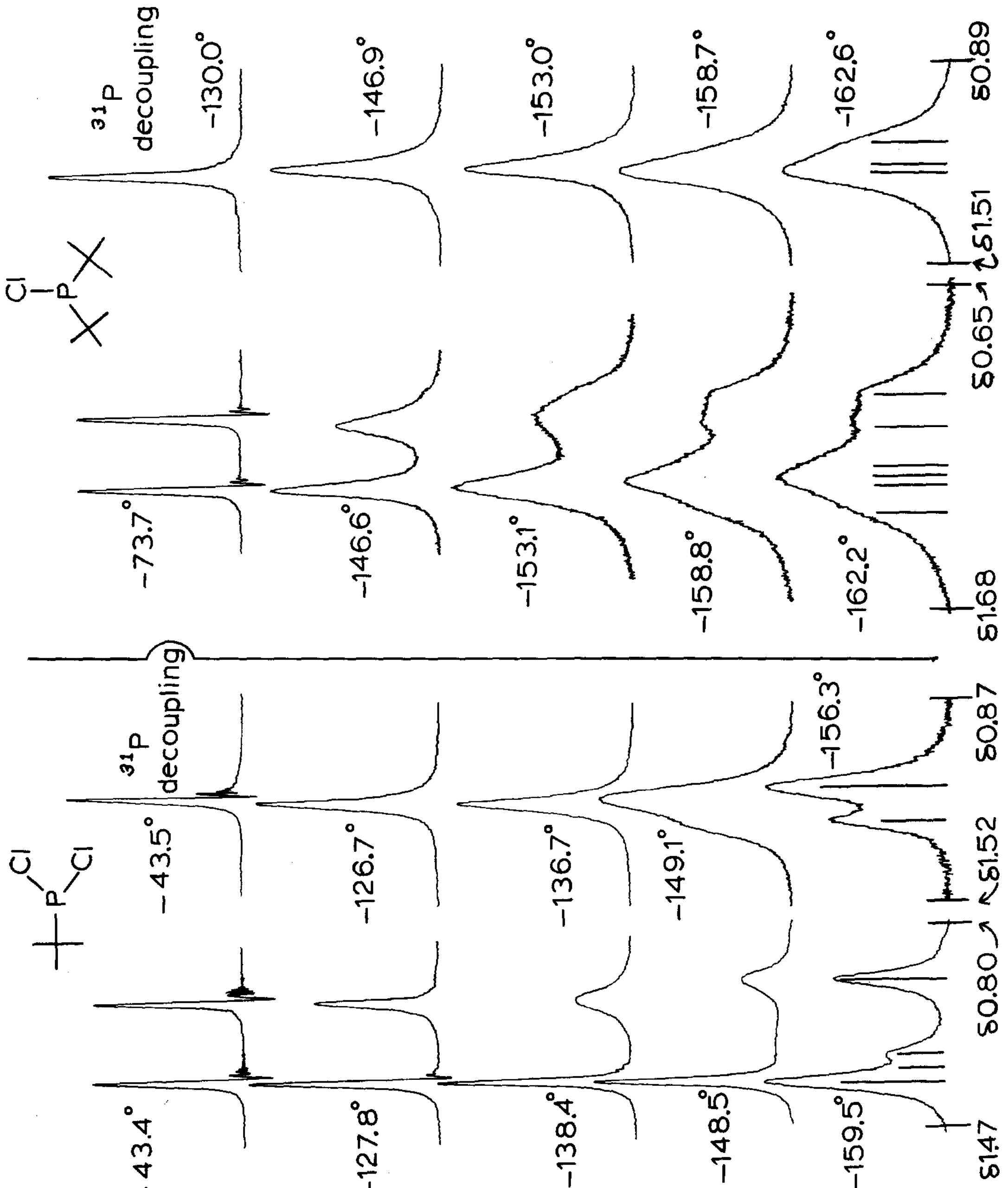
Examination of the ^1H DNMR spectrum of 1 (8% v/v in CH_2CHCl) at -43° revealed a doublet resonance (δ1.20; $J_{H,P}$ = 15.1 Hz) consistent with rapid tert-butyl rotation on the DNMR time scale (Figure). Upon lowering the temperature, the spectrum broadened and then sharpened consistent with slowing of tert-butyl rotation on the DNMR time scale (Equation 1). A complete line shape analysis of the ^1H DNMR spectrum of the methyl resonances in 1 at -160° (slow exchange) gave two resonances at δ1.15 (6H; $J_{H,P}$ = 20.9 Hz) and δ1.27 (3H; $J_{H,P}$ = 4.5 Hz). Subsequent examination of the DNMR spectrum of 1 with ^{31}P decoupling (Figure) also revealed a series of spectra entirely consistent with slowing of tert-butyl rotation. Derivation of rate constants from the DNMR spectra of 1 using a complete line shape analysis[5] gave E_a = 6.8 ±0.4 kcal/mole, $\Delta H^\ddagger$ = 6.5 ±0.4 kcal/mole, $\Delta S^\ddagger$ = 1 ±4 eu, and $\Delta G^\ddagger$ = 6.4 ±0.2 kcal/mole at -148.2°.



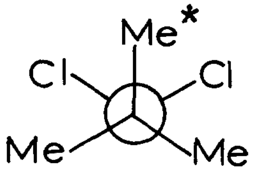
(1)

Examination of the ^1H DNMR spectrum of 2 (5% v/v in CH_2CHCl) also revealed changes consistent with slowing of tert-butyl rotation on the DNMR time scale (Figure) giving under conditions of slow exchange three methyl resonances at δ1.23 (3H; $J_{H,P}$ ≈3.5 Hz), δ1.22 (3H; $J_{H,P}$ ≈17 Hz), and δ1.11 (3H; $J_{H,P}$ ≈16 Hz) as well as $\Delta G^\ddagger$ = 6.0 ±0.3 kcal/mole at -158.3° for tert-butyl rotation.

Two important observations are reported above. First, although relatively small, the barriers to rotation about C–P bonds in 1 and 2 are within the experimental limits of the DNMR method and thus make possible a study of factors contributing to the magnitude of such barriers. For example the dramatic effect of bond length and possibly bond angle is seen in a comparison of the tert-butyl rotational barriers in 1 and 2 with that in N,N-dichloro-N-tert-


Cl
P
Cl
−43.4°
−43.5°
^{31}P decoupling
−127.8°
−126.7°
−138.4°
−136.7°
−148.5°
−149.1°
−159.5°
−156.3°
δ1.47
δ0.80
δ1.52
δ0.87
Cl
P
−73.7°
−130.0°
^{31}P decoupling
−146.6°
−146.9°
−153.1°
−153.0°
−158.8°
−158.7°
−162.2°
−162.6°
δ1.68
δ0.65
δ1.51
δ0.89

butylamine ($\Delta G^{\dagger}$ = 9.4 ±0.2 kcal/mole at -92°).[6] Second, as observed in other systems,[7] there exists in **1** and **2** a significant dependence of $J_{H,P}$ on the conformational environment of a methyl group. In **1**, the $^{1}H-^{31}P$ coupling constant associated with the methyl group gauche to two chlorines (Me^{*}; **3**) is dramatically smaller (4.5 Hz) than $J_{H,P}$ associated with the other two methyl groups (20.9 Hz). This trend will be useful in deriving conformational data from both time-averaged and slow exchange DNMR spectra.



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