Synthesis of New Exceedingly Strong Non-Ionic Bases: $RN{=}P(MeNCH_2CH_2)_3N$

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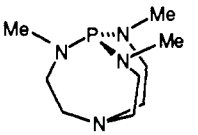
Abstract: The syntheses of $MeN{=}P(MeNCH_2CH_2)_3N$ (**4**), $[HRNP(MeNCH_2CH_2)_3N](CF_3CO_2)$ (R = Ph, **5**(CF_3CO_2); R = Me, **6**(CF_3CO_2)), $[MePhNP(MeNCH_2CH_2)_3N]I$ (**7**(I)), the stable azide adduct $MeN_3P(MeNCH_2CH_2)_3N$ (**8**), and $[HRNP(NMe_2)_3](CF_3CO_2)$ (R = Ph, **9**(CF_3CO_2)) are reported. Equilibria measured by ^{31}P NMR spectroscopy reveal the relative ordering of basicity: *t*-BuN=P[N=P(NMe_2)$_3$]$_3$ > $P(MeNCH_2CH_2)_3N$ (**1**) > $MeN{=}P(MeNCH_2CH_2)_3N$ (**4**) > $MeN{=}P(NMe_2)_3$ > DBU > $PhN{=}P(MeNCH_2CH_2)_3N$ (**3**) > $PhN{=}P(NMe_2)_3$ in CD_3CN. The unusually strong basicities of the polycyclic cage bases (e.g., those of **1** and **4** are *ca.* 17 and more than 3 pK_b units stronger than DBU, respectively) and the stability of adduct **8** is rationalized on the basis of partial transannulation from the bridgehead nitrogen to phosphorus which effectively delocalizes positive charge. The structure of **5**(CF_3CO_2) determined by X-ray means is also reported, revealing a transannular distance of 2.559(4) Å which is facilitated by a widened average MeN–P–NMe bond angle of 114.9(2)°.

Introduction

Strong non-ionic bases play an important role in organic synthesis because of the generally milder reaction conditions they generally permit,[2] the enhanced reactivity of the more naked anions in the poorly associating ion pairs formed upon substrate deprotonation by such bases (in contrast to ionic bases),[3] and the better solubility of non-ionic bases at room temperature and at the low temperatures required for some reactions.[4] Non-ionic bases are typically sterically hindered nitrogen compounds such as Proton Sponge,[5] DBU,[6] DBN,[6a,7] and peralkylated guanidines.[8] P_4-*t*-Bu, (*t*-BuN=P[N=P(NMe_2)$_3$]$_3$) is a base whose conjugate acid (which is protonated on the *t*-BuN nitrogen) is about 18 pK_a units weaker than that of $HDBU^+$.[4] Recently reported from our laboratories was the unusual non-ionic base **1**[9] which is protonated at phosphorus (rather than at nitrogen) to give cation **2**, whose structure has been obtained by X-ray means.[9a]

The pK_a of **2**, though surprisingly large in DMSO (with an upper limit of 26.8[9c,d]), is not quite as large as that reported for the conjugate acid of P_4-*t*-Bu in THF (28.04). The use of base **1** in organic synthesis, however, would appear to have two main advantages over P_4-*t*-Bu: (1) **1** is easier and less expensive to synthesize (requiring three steps from commercially available starting materials)[9e] while P_4-*t*-Bu requires seven steps (one of them requiring six days),[4] and (2) salts of **2** formed in reactions utilizing **1** as a strong base are quite insoluble in common organic solvents, whereas this is not the case with salts of the conjugate acid of P_4-*t*-Bu. Thus the separation of the organic product from salts of **2** is not only more facile, but the recovery of base **1** from such salts is easy, requiring only treatment with *t*-BuO^-. Base **1** is also a superior catalyst for the trimerization of aryl isocyanates to triisocyanurates.[10]



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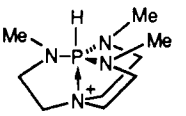

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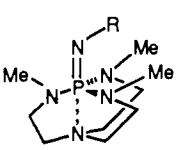
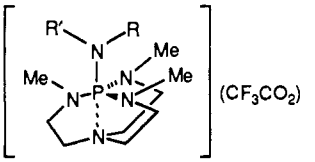
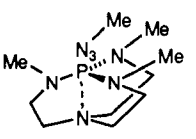
In view of the strong basicity of **1** that results from transannulation, it was of interest to determine how the basicity and transannulation capability of **1** changes when it is transformed into an imidophosphine such as **3**[11] and **4**, and how the basicities of the latter compounds compare with those of the analogous acyclic analogues $PhN{=}P(NMe_2)_3$ and $MeN{=}P(NMe_2)_3$, and with P_4-*t*-Bu. In this paper we report the synthesis and isolation of the new imidophosphine **4**; the conjugate acid cations of **3** and **4**, namely, **5** and **6**, respectively; the methylated cation of **3**, namely, **7**; the azide intermediate of **4**, namely, **8**; the conjugate



3: R = Ph
4: R = Me



5(CF_3CO_2): R = Ph, R′ = H
6(CF_3CO_2): R = Me, R′ = H
7(I): R = Ph, R′ = Me



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(1) Ames Laboratory Summer Trainee from St. Norbert College, De Pere, Wisconsin.
(2) Schwesinger, R. *Chimia* **1985**, *39*, 269.
(3) Pietzonka, T.; Seebach, D. *Chem. Ber.* **1991**, *124*, 1837.
(4) Schwesinger, R.; Schlemper, H. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1167.
(5) (a) Alder, R. W.; Bowman, P. S.; Steele, W. R. S.; Winterman, D. R. *J. Chem. Soc., Chem. Commun.* **1968**, 723. (b) Evans, D. A.; Weber, A. E. *J. Am. Chem. Soc.* **1986**, *108*, 6757. (c) Evans, D. A.; Miller, S. J.; Ennis, M. D. *J. Org. Chem.* **1993**, *58*, 471.
(6) (a) Oediger, H.; Muller, F.; Eiter, K. *Synthesis* **1972**, 591. (b) Burton, L.; White, J. *J. Am. Chem. Soc.* **1981**, *103*, 3226.
(7) Liu, H.-J.; Ho, L.-K.; Lao, H. K. *Can. J. Chem.* **1981**, *59*, 1685.
(8) (a) Wieland, G.; Simchen, G. *Liebigs Ann. Chem.* **1985**, 2178. (b) Barton, D. H. R.; Elliott, J. D.; Gero, S. D. *J. Chem. Soc., Perkin Trans. I* **1982**, 2085. (c) Barton, D. H. R.; Kervagoret, J. K.; Zard, S. Z. *Tetrahedron* **1990**, *46*, 7587.
(9) (a) Lensink, C.; Xi, S.-K.; Daniels, L. M.; Verkade, J. G. *J. Am. Chem. Soc.* **1989**, *111*, 3478. (b) Verkade, J. G. US Patent 5,051,533, 1991; *Chem. Abstr.* **1992**, *116*, 50379q. (c) Laramay, M. A. H.; Verkade, J. G. *J. Am. Chem. Soc.* **1990**, *112*, 9421. (d) Laramay, M. A. H.; Verkade, J. G. *Z. Anorg. Allg. Chem.* **1991**, *605*, 163. (e) Tang, J.-S.; Verkade, J. G. *Tetrahedron Lett.*, in press.
(10) (a) Tang, J.-S.; Verkade, J. G. *Angew. Chem.*, in press. (b) Tang, J.-S.; Verkade, J. G., US Patent Application pending.
(11) Schmidt, H.; Lensink, C.; Xi, S. K.; Verkade, J. G. *Z. Anorg. Allg. Chem.* **1989**, *578*, 75.

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acid cations of $PhN{=}P(NMe_2)_3$ and $MeN{=}P(NMe_2)_3$, namely, **9** and **10**, respectively; and the conjugate acid of P_4-*t*-Bu, namely

$$[HPhNP(NMe_2)_3](CF_3CO_2)$$
$$\mathbf{9}(CF_3CO_2)$$

$$[HMeNP(NMe_2)_3](CF_3CO_2) \qquad [HP_4\text{-}t\text{-}Bu](CF_3CO_2)$$
$$\mathbf{10}(CF_3CO_2) \qquad \mathbf{11}(CF_3CO_2)$$

11. We also report the structure of $\mathbf{5}(CF_3CO_2)$ as determined by X-ray means and the relative basicities of **3**, **4**, $PhN{=}P(NMe_2)_3$, $MeN{=}P(NMe_2)_3$, DBU, **1**, and P_4-*t*-Bu.

Experimental Section

Acetonitrile and benzene were dried with CaH_2, and THF, toluene, and pentane were dried with sodium. All solvents were freshly distilled and all reactions were done under argon. ^1H and ^{13}C NMR spectra were recorded on a Nicolet NT-300 and a Varian VXR-300 NMR spectrometer, respectively. ^{31}P NMR spectra were recorded on a Bruker WM-200 NMR spectrometer using 85% H_3PO_4 as the external standard. High-resolution and FAB mass spectra were recorded on a KRATOS MS-50 spectrometer. Elemental analyses were performed by Desert Analytics.

Compounds **1** and **2**(Cl) were synthesized according to our previously published method.[9,11] Phenyl[12] and methyl[13] azides were synthesized following earlier reports.

WARNING. Azides can decompose explosively and should be handled with appropriate care.[12]

$PhN{=}P(NMe_2)_3$. Although this compound is known,[14] we found the following procedure convenient. To a solution of hexamethylphosphorus triamide (5.0 g, 85%, 2.6 mmol) in benzene (15 mL) at 70 °C was added dropwise a solution of phenyl azide (3.182 g, 2.674 mmol) in benzene (15 mL) over a period of 30 min. The mixture was refluxed for 10 h and allowed to cool to room temperature. The solvent was removed in vacuo, and the residue was distilled at 127 °C/0.4 Torr (127 °C/0.4 Torr[14]) to give a yellowish liquid (5.9 g, 90%; lit.[14] 91%). ^{31}P NMR (CD_3CN): δ 20.66. ^1H (CD_3CN): δ 2.63 (d, 18H, NCH_3, $^3J_{PH}$ = 9.6 Hz); 6.50–7.01 (m, 5H, Ph). ^{13}C (CD_3CN): δ 37.69 (d, NCH_3, $^2J_{PC}$ = 3.2 Hz), 116.71, 123.38, 123.60, and 129.47 (d, $^2J_{PC}$ = 1.1 Hz, Ph). HRMS *m/z* calcd for $C_{12}H_{23}N_4P$: 254.16604. Found 254.16611 (33, M^+).

$MeN{=}P(NMe_2)_3$. Although this is a known compound,[15] we found the following procedure convenient. To a solution of $P(NMe_2)_3$ (5.0 g, 85%, 3.1 mmol) in toluene (50 mL) at 0–5 °C was added with a syringe precooled in a refrigerator cold methyl azide (8.7 g, 15 mmol). The mixture (in a flask closed by a septum) was stirred at 0–5 °C for 1.5 h, then at room temperature for 1 h with the flask vented by a needle, and finally at 50–60 °C for 5 h. The volatiles were removed in vacuo and the crude product was distilled in vacuo to give a colorless liquid (3.75 g, 63% (lit.[15] 81%), 36–39 °C/~0.4 Torr, 48–52 °C/vacuum[15]). ^{31}P (CD_3CN): δ 30.60. ^1H (CD_3CN): δ 2.56 (d, 18H, $N(CH_3)_2$, $^3J_{PH}$ = 9.3 Hz), 2.72 (d, 3H, NCH_3, $^3J_{PH}$ = 23.1 Hz). ^{13}C (CD_3CN): δ 31.73 (d, NCH_3, $^2J_{PC}$ = 4.3 Hz), 37.65 (d, $N(CH_3)_2$, $^2J_{PC}$ = 4.5 Hz). HRMS *m/z* calcd for $C_7H_{21}N_4P$: 192.15039. Found: 192.15012 (7, M^+).

$PhN{=}P(MeNCH_2CH_2)_3N$, 3. This compound was synthesized according to our previously reported method[11] with a minor modification. To a solution of **1** (2.192 g, 1.015 mmol) in benzene (60 mL) at 70 °C was added dropwise a solution of phenyl azide (1.227 g, 1.031 mmol) in benzene (50 mL) over a period of 45 min. The mixture was refluxed for 12 h and allowed to cool to room temperature. The solution was concentrated to about 20 mL. Crystallization was induced by adding pentane and allowing the solution to remain in a freezer for 4 h. The supernatant liquid was removed with a syringe and the yellowish solid product was dried in vacuo to give ^1H NMR spectroscopically pure **3** (2.7 g, 88%; lit.[11] 84%[11]). ^{31}P NMR (CD_3CN): δ 16.17. ^1H NMR (CD_3CN): consistent with that in the literature.[11] HRMS *m/z* calcd for $C_{15}H_{26}N_5P$: 307.19259. Found: 307.19251 (31, M^+).

$MeN{=}P(MeNCH_2CH_2)_3N$, 4. Method A. A solution of 0.50 g (1.8 mmol) of **8** (see later) in benzene (20 mL) was refluxed for 10 h. The solution was concentrated in vacuo to about 2 mL. This concentrate was crystallized by adding pentane and allowing the solution to remain in a freezer overnight. The supernatant liquid was removed by syringe to give the yellowish solid **4** (0.42 g, 94%) after drying in vacuo. ^{31}P (CD_3CN): δ 26.65. ^1H (CD_3CN): δ 2.62 (d, 9H, $N_{eq}CH_3$, $^3J_{PH}$ = 7.8 Hz), 2.71 (t, 6H, $N_{ax}CH_2$, $^3J_{HH}$ = 5.5 Hz), 2.79 (d, 3H, $N_{exo}CH_3$, $^3J_{PH}$ = 22.2 Hz), 2.83 (dt, 6H, $N_{eq}CH_2$, $^3J_{PH}$ = 12.3 Hz, $^3J_{HH}$ = 5.5 Hz). ^{13}C (CD_3CN): δ 31.42 (d, $N_{exo}CH_3$, $^2J_{PC}$ = 2.2 Hz), 34.44 (d, $N_{eq}CH_3$, $^2J_{PC}$ = 4.8 Hz), 49.16 (s, $N_{ax}CH_2$), 51.37 (d, $N_{eq}CH_2$, $^2J_{PC}$ = 2.2 Hz). HRMS *m/z* calcd for $C_{10}H_{24}N_5P$: 245.17694. Found: 245.17679 (32, M^+).

Method B. To a solution of **1** (0.705 g, 3.26 mmol) in toluene (20 mL) at 0–5 °C was added by syringe cold methyl azide (3 mL). The mixture (in a flask closed by a septum) was stirred at 0–5 °C for 3 h, at room temperature for 0.5 h with the flask vented by a needle, and then at 80–90 °C for 10 h. The solution was concentrated in vacuo to about a 3 mL concentrate which was crystallized by adding pentane and allowing the solution to stand in a freezer overnight. The supernatant liquid was removed by syringe to give a yellowish solid (0.73 g, 91%) after drying in vacuo.

$[HPhNP(MeNCH_2CH_2)_3N]CF_3CO_2$, $\mathbf{5}(CF_3CO_2)$. To a solution of **3** (0.193 g, 0.629 mmol) in CH_3CN (2 mL) was added by syringe trifluoroacetic acid (0.076 g, 0.67 mmol). The solution was stirred for 1 h at room temperature and then evaporated in vacuo to remove the solvent. The residue was washed with ethyl acetate and dried in vacuo to give $\mathbf{5}(CF_3CO_2)$ as a ^1H NMR spectroscopically pure white solid (0.26 g, 97%). Colorless crystals were grown from THF/ethyl acetate in a freezer. ^{31}P (CD_3CN): δ 18.35. ^1H (CD_3CN): δ 2.74 (d, 9H, $N_{eq}CH_3$, $^3J_{PH}$ = 11.7 Hz), 2.82 (t, 6H, $N_{ax}CH_2$, $^3J_{HH}$ = 5.4 Hz), 3.04 (dt, 6H, $N_{eq}CH_2$, $^3J_{PH}$ = 15.0 Hz, $^3J_{HH}$ = 5.4 Hz), 6.79 (bd, s, 1H, NHPh), 6.93–7.28 (m, 5H, Ph). ^{13}C (CD_3CN) 37.47 (d, $N_{eq}CH_3$, $^2J_{PC}$ = 4.3 Hz), 50.37 ($N_{ax}CH_2$), 50.38 (d, $N_{eq}CH_2$, $^2J_{PC}$ = 7.0 Hz), 119.98, 120.06, 122.45, and 130.17 (Ph). (The CF_3CO_2 signals were weak and were not recorded.) MS (FAB) *m/z*: 308.1 (100, $[PhNHP(MeNCH_2CH_2)_3N]^+$), 729.4 (0.1, $[(PhNH(MeNCH_2CH_2)_3N)_2CF_3CO_2]^+$). Elemental analysis calculated for $C_{17}H_{27}F_3N_5O_2P$: C, 48.43; H, 6.46; N, 16.62. Found: C, 48.34; H, 6.81; N, 15.94.

$[HMeNP(MeNCH_2CH_2)_3N]CF_3CO_2$, $\mathbf{6}(CF_3CO_2)$. To a solution of **4** (0.366 g, 1.49 mmol) in CH_3CN (4 mL) was added by syringe trifluoroacetic acid (0.169 g, 1.49 mmol). The mixture was stirred for 1 h and evaporated in vacuo to remove the solvent. The residue was recrystallized from ethyl acetate/pentane in a freezer overnight. The supernatant liquid was removed by syringe to give a white solid (0.51 g, 96%) after drying in vacuo. ^{31}P (CD_3CN): δ 37.88. ^1H (CD_3CN): δ 2.65 ($N_{ax}CH_2$, overlapping with $N_{eq}CH_3$), 2.70 (d, $N_{exo}CH_3$, $^3J_{PH}$ = 10.2 Hz, partially overlapping with $N_{eq}CH_3$), 2.72 (d, $N_{eq}CH_3$, $^3J_{PH}$ = 9.6 Hz), 2.86 (dt, 6H, $N_{eq}CH_2$, $^3J_{PH}$ = 14.7, $^3J_{HH}$ = 4.8 Hz), 4.06 (bd s, 1H, $N_{exo}H$). ^{13}C (CD_3CN): δ 29.05 ($N_{exo}CH_3$), 35.50 (d, $N_{eq}CH_3$, $^2J_{PC}$ = 2.7 Hz), 50.03 (d, $N_{ax}CH_2$, $^3J_{PC}$ = 1.1 Hz), 51.43 (d, $N_{eq}CH_2$, $^2J_{PC}$ = 2.7 Hz). MS (FAB) *m/z*: 246.2 (100, $[MeNHP(MeNCH_2CH_2)_3N]^+$), 605.3 (0.7, $[(MeNHP(MeNCH_2CH_2)_3N)_2CF_3CO_2]^+$). Elemental analysis calculated for $C_{12}H_{25}F_3N_5O_2P$: C, 40.09; H, 7.01; N, 19.49. Found: C, 39.72; H, 7.20; N, 19.15.

$[MePhNP(MeNCH_2CH_2)_3N]I$, 7(I). To a solution of **3** (0.202 g, 0.658 mmol) in CH_3CN (2 mL) was added by syringe methyl iodide (0.104 g, 0.731 mmol). The mixture was stirred for 5 h and evaporated in vacuo to remove volatiles. The residue (0.295 g, 100%) was ^1H NMR spectroscopically pure **15**(I). ^{31}P NMR (CD_3CN): δ 36.31. ^1H (CD_3CN): δ 2.55 (d, 9H, $N_{eq}CH_3$, $^3J_{HH}$ = 9.6 Hz), 2.76 (t, 6H, $N_{ax}CH_2$, $^3J_{HH}$ = 4.7 Hz), 2.89 (dt, 6H, $N_{eq}CH_2$, $^3J_{PH}$ = 15.0 Hz, $^3J_{HH}$ = 4.7 Hz), 3.19 (d, 3H, $N_{exo}CH_3$, $^3J_{PH}$ = 8.4 Hz), 7.36–7.48 (m, 5H, Ph). ^{13}C (CD_3CN): δ 35.95 (d, $N_{exo}CH_3$, $^2J_{PC}$ = 3.2 Hz), 43.62 (d, $N_{eq}CH_3$, $^2J_{PC}$ = 5.4 Hz), 49.92 (d, $N_{ax}CH_2$, $^3J_{PC}$ = 1.1 Hz), 52.28 (d, $N_{eq}CH_2$, $^2J_{PC}$ = 2.7 Hz), 128.64 (d, Ph, J_{PC} = 1.1 Hz), 130.50 (d, Ph, J_{PC} = 2.7 Hz), 130.88 (d, Ph, J_{PC} = 1.1 Hz), 144.11 (d, Ph, J_{PC} = 4.3 Hz). MS (FAB) *m/z*: 322.1 (100, $[MeNPhP(MeNCH_2CH_2)_3N]^+$), 771.3 (1.7, $[(MeNPhP(MeNCH_2CH_2)_3N)_2I]^+$). Elemental analysis calculated for $C_{16}H_{29}IN_5P$: C, 42.75; H, 6.51; N, 15.59. Found: C, 41.99; H, 6.64; N, 15.12.

$MeN_3P(MeNCH_2CH_2)_3N$, 8. To a solution of **1** (2.388 g, 1.165 mmol) in toluene (15 mL) at 0–5 °C was added by a precooled syringe cold methyl azide (3.1 g, 5.4 mmol). The mixture was stirred in a flask closed by a septum at 0–5 °C for 2 h, then at room temperature for 0.5 h with the flask vented by a needle, and finally at 50–60 °C for 2 h. The solution was concentrated to about 5 mL and pentane added, and then it was placed in a freezer for 5 h. The parent liquid was removed by syringe and the solid product dried in vacuo to give 2.85 g (95%) of **17**. ^1H (CD_3CN): δ 2.67 (d, 9H, $N_{eq}CH_3$, $^3J_{PH}$ = 7.8 Hz), 2.78 (t, 6H, $N_{ax}CH_2$, $^3J_{HH}$ = 6.5 Hz), 2.90 (dt, 6H, $N_{eq}CH_2$, $^3J_{PH}$ = 17.1 Hz, $^3J_{HH}$ = 6.5 Hz),

(12) Lindsay, R. O.; Allen, C. F. H. *Organic Syntheses*; Wiley: New York, 1955; Collect. Vol. III, p 710.
(13) Bock, H.; Dammel, R. *J. Am. Chem. Soc.* **1988**, *110*, 5261.
(14) Vetter, H.-J.; Nöth, H. *Chem. Ber.* **1963**, *96*, 1308.
(15) Haasemann, P.; Goubeau, J. *Z. Anorg. Allg. Chem.* **1974**, *408*, 293.

3.25 (s, 3 H, N_3CH_3). ^{13}C (CD_3CN): δ 35.55 (d, $N_{eq}CH_3$, $^2J_{PC}$ = 2.7 Hz), 48.27 (s, N_3CH_3), 50.09 (s, $N_{ax}CH_2$), 52.11 (d, $N_{eq}CH_2$, $^2J_{PC}$ = 1.6 Hz). HRMS *m/z* calcd for $C_{10}H_{24}N_7P$: 273.18309. Found: 273.18406 (1, M^+), 245.17652 (4, $M^+ - N_2$).

[HPhNP(NMe$_2$)$_3$]CF$_3$CO$_2$, 9(CF$_3$CO$_2$). To a solution of PhN=P(NMe$_2$)$_3$ (1.50 g, 5.90 mmol) in CH_3CN (8 mL) was added by syringe trifluoroacetic acid (0.67 g, 5.9 mmol). The mixture was stirred for 1 h and evaporated in vacuo to remove volatiles. The residue was washed with ethyl acetate and dried in vacuo to give white solid **9** (CF_3CO_2) (2.1 g, 95%). ^{31}P (CD_3CN): δ 36.62. ^1H (CD_3CN): δ 2.71 (d, 18H, NCH_3, $^3J_{PH}$ = 9.9 Hz), 7.06–7.34 (m, 5H, Ph), 8.95 (b, 1 H, NHPh). ^{13}C (CD_3CN): δ 37.48 (d, $N(CH_3)_2$, $^2J_{PC}$ = 4.8 Hz), 121.67 (d, Ph, $^2J_{PC}$ = 7.0 Hz), 124.35, 130.46, and 140.28 (Ph). (CF_3CO_2 signals were not recorded because of weakness.) MS (FAB) *m/z*: 255.0 (100, $[(Me_2N)_3PNHPh]^+$), 622.9 (2.1, $[((Me_2N)_3PNHPh)_2CF_3CO_2]^+$).

HMeNP(NMe$_2$)$_3$, 10(CF$_3$CO$_2$). To a solution of MeN=P(NMe$_2$)$_3$ (0.765 g, 3.98 mmol) in acetonitrile (5 mL) was added by syringe trifluoroacetic acid (0.454 g, 3.98 mmol). The mixture was stirred for 1 h and then evaporated under vacuum to remove the solvent. The residue was recrystallized from ethyl acetate/pentane at freezer temperature for 4 h. The supernatant liquid was removed with a syringe and the crystalline product dried in vacuo to give **10**(CF_3CO_2) (1.1 g, 93%). ^{31}P (CD_3CN): δ 43.09. ^1H (CD_3CN): δ 2.59 (d, 3H, NCH_3, $^3J_{PH}$ = 12.6 Hz), 2.68 (d, 18H, $N(CH_3)_2$, $^3J_{PH}$ = 9.6 Hz), 5.41 (br, 1 H, N*H*CH_3). ^{13}C (CD_3CN): δ 27.58 (NCH_3), 37.06 (d, $N(CH_3)_2$, $^2J_{PC}$ = 4.8 Hz). MS (FAB) *m/z*: 193.1 (100, $[MeHNP(NMe_2)_3]^+$), 499.2 (2.4, $[(MeNHP(NMe_2)_3)_2CF_3CO]^+$).

[HP$_4$-*t*-Bu]CF$_3$CO$_2$, 11(CF$_3$CO$_2$). To a solution of P_4-*t*-Bu (0.347 g, 0.547 mmol) in THF (5 mL) was added by syringe trifluoroacetic acid (0.062 g, 0.547 mmol) and the mixture was stirred for 2 h. The clear solution was evaporated in vacuo to give NMR spectroscopically pure **11**(CF_3CO_2) (0.4 g, 100%): ^{31}P (THF, CD_3CN external lock solvent): δ –22.90 (q, 1P, $^2J_{PP}$ = 50.5 Hz), 13.39 (d, 3P, $^2J_{PP}$ = 50.5 Hz). ^1H NMR (CD_3CN): δ 1.28 (s, 9H, *t*-Bu), 2.63 (d, 55 H, NMe_2, $^3J_{PH}$ = 9.9 Hz, *H*N$^+$(*t*-Bu)). MS (FAB) *m/z*: 634.4 (100, [P_4-*t*-Bu-H]$^+$. ^{31}P NMR of P_4-*t*-Bu (THF, CD_3CN external lock solvent): δ –24.44 (q, 1P, $^2J_{PP}$ = 20.2 Hz), 5.73 (d, 3P, $^2J_{PP}$ = 20.2 Hz).

pK_a Value of 2. The pK_a of **2** was measured by ^{31}P NMR spectroscopy in an equilibration experiment (see Discussion). **Method A.** To an NMR tube containing the acid [HP_4-*t*-Bu]CF_3CO_2, **11**(CF_3CO_2) (0.0426 g, 0.0569 mmol), and 1.5 mol % of Cr(acac)$_3$ as a relaxagent was added a solution of the base **1** (0.0123 g, 0.0569 mmol) in THF. The mixture was diluted to 1 mL with THF and shaken for 30 min. The ^{31}P NMR spectrum (CD_3CN as the external lock solvent) of the mixture showed signals of all four components (i.e. **1**, **2**, **11** and P_4-*t*-Bu) and their ratios did not change over 24 h. The pK_a value of **2** in THF was then calculated to be 26.7 from the integration ratios of the four components and the known pK_a value (28.0 in THF) of P_4-*t*-Bu.[4]

Method B. To an NMR tube containing 0.0273 g (0.108 mmol) of acid **2**(Cl) and 1.5 mol % of Cr(acac)$_3$ was added a solution of P_4-*t*-Bu (0.0808 g, 0.108 mmol) in THF. The mixture was diluted to 1 mL with THF. The pK_a value of **2** in THF calculated by the same method as in Method A is 26.5, giving an average value of 26.6 in THF.

Using the method of Schwesinger,[4] the pK_a value of cation **2** in MeCN (41.2) was obtained by interpolation from its pK_a value in THF (26.6) and the corresponding pK_a values of 28.0 in THF and 42.6 in MeCN of [HP_4-*t*-Bu]$^+$.

Equilibria 2–13. For each of these equilibria (see Discussion) the pairs of acid–base reactants and products in CD_3CN were run independently and the equilibrium composition for each reaction was measured by ^{31}P NMR spectroscopy. In each case only the two compounds on the right side (i.e., the products) of these equilibria could be observed in the ^{31}P NMR spectra upon mixing the pairs of reactants or products. The formation of [HDBU]$^+$ in these equilibria was accomplished by mixing equimolar amounts of DBU and CF_3CO_2H in CD_3CN.

Crystal Structure Analysis of 5(CF$_3$CO$_2$). A colorless crystal in the shape of an elongated cube was attached to the tip of a glass fiber. The cell constants for data collection were determined from reflections found by a rotation photograph. Pertinent data collection and reduction information are given in Table I. Lorentz and polarization corrections, a correction based on decay in the standard reflections and an absorption correction, were applied to the data. The agreement factor for the averaging of observed reflections was 2.1%. The space group $P2_12_12_1$ was chosen on the basis of the systematic absences. This assumption proved to be correct as shown by a successful direct-methods solution[16] and subsequent refinement. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms with the exception of H10A (bonded to N5) were modeled as riding atoms with a bond distance of 0.96 Å with refined isotropic thermal parameters. In the case of methyl groups, the three hydrogens were constrained to have a single thermal parameter. H10A was refined isotropically. The absolute configuration was determined to be the initial model. Refinement calculations were performed on a Digital Equipment Corp. MicroVAX 3100/76 computer using the SHELXTYL-Plus programs.[16]

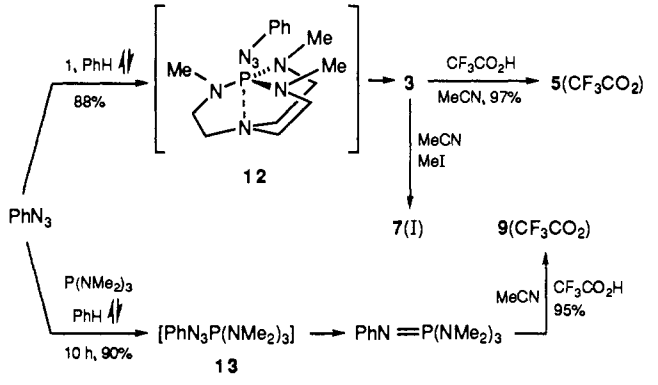
Table I. Summary of Crystallographic Data for **5**(CF_3CO_2)

Crystal Parameters	
crystal system	orthorhombic
space group	$P2_12_12_1$
formula	$C_{17}H_{27}F_3N_5O_2P$
formula wt, g mol^{-1}	421.4
a, Å	11.031(4)
b, Å	11.788(4)
c, Å	15.355(5)
V, Å^3	1996.6(12)
Z	4
ρ(calcd), g cm^{-3}	1.402
temp, °C	–50
abs coeff, mm^{-1}	0.188
crystal dimens, mm	0.5 × 0.45 × 0.40
trans. factors, max to min %	0.7789–0.6355
abs corr applied	semi-empirical
Measurement of Intensity Data	
diffractometer	Siemens P4/RA
radiation	Mo Kα (k = 0.71073 Å)
monochromator	highly oriented graphite crystal
method of structure soln	direct methods
refinement method	full matrix least squares
scan type	2θ–θ
scan range, deg	1.00 plus K_α-separation
reflcns meas	6233
no. of unique reflcns	5796
no. of reflcns used	2943
R	5.19
R_w	5.45
goodness-of-fit	1.77

Discussion

Syntheses. In Schemes I and II are summarized the syntheses of compounds **3**–**10**. Intermediate **12** in Scheme I was isolated

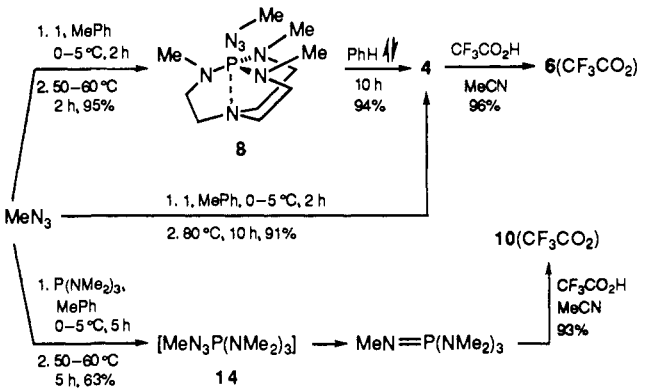
Scheme I



earlier by us.[11] In contrast to intermediate **14** in Scheme II, its polycyclic analogue **8** is isolable after heating the initial reaction mixture at 50–60 °C for 2 h, and it requires harsher treatment than **14** to convert it to the corresponding imido derivative **4**. A rationale for this observation is put forth in the last section. Spectroscopically pure **11**(CF_3CO_2) formed in quantitative yield upon addition of 1 equiv of CF_3CO_2H to P_4-*t*-Bu.

(16) SHELXTL-PLUS, Siemens Analytical X-ray Inc., Madison, WI.

Scheme II



Basicity Measurements. Equilibria 1–13 were established by mixing pairs of reactants and also by mixing pairs of products.

$$1 + 11 \overset{\text{THF}}{\rightleftharpoons} 2 + P_4\text{-}t\text{-Bu} \quad (1)$$

$$1 + 6 \overset{\text{MeCN}}{\rightleftharpoons} 2 + 4 \quad (2)$$

$$1 + 10 \overset{\text{MeCN}}{\rightleftharpoons} 2 + \text{MeN=P(NMe}_2)_3 \quad (3)$$

$$1 + [\text{HDBU}]^+ \overset{\text{MeCN}}{\rightleftharpoons} 2 + \text{DBU} \quad (4)$$

$$1 + 5 \overset{\text{MeCN}}{\rightleftharpoons} 2 + 3 \quad (5)$$

$$4 + 10 \overset{\text{MeCN}}{\rightleftharpoons} 6 + \text{MeN=P(NMe}_2)_3 \quad (6)$$

$$4 + [\text{HDBU}]^+ \overset{\text{MeCN}}{\rightleftharpoons} 6 + \text{DBU} \quad (7)$$

$$\text{MeN=P(NMe}_2)_3 + [\text{HDBU}]^+ \overset{\text{MeCN}}{\rightleftharpoons} 10 + \text{DBU} \quad (8)$$

$$3 + 9 \overset{\text{MeCN}}{\rightleftharpoons} 5 + \text{PhN=P(NMe}_2)_3 \quad (9)$$

$$\text{DBU} + 5 \overset{\text{MeCN}}{\rightleftharpoons} [\text{HDBU}]^+ + 3 \quad (10)$$

$$\text{DBU} + 9 \overset{\text{MeCN}}{\rightleftharpoons} [\text{HDBU}]^+ + \text{PhN=P(NMe}_2)_3 \quad (11)$$

$$4 + 5 \overset{\text{MeCN}}{\rightleftharpoons} 6 + 3 \quad (12)$$

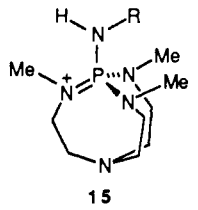
$$\text{MeN=P(NMe}_2)_3 + 9 \overset{\text{MeCN}}{\rightleftharpoons} 10 + \text{PhN=P(NMe}_2)_3 \quad (13)$$

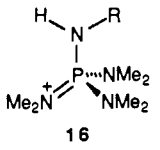
Reactants and products could be detected by ^{31}P NMR spectroscopy in the case of equilibrium 1 in THF, therefore allowing the determination of an average pK_a for cation **2** of 26.6. The analogous equilibrium in MeCN could not be established owing to the instability of this solvent with respect to polymerization in the presence of P_4-*t*-Bu.[4] The pK_a value of cation **2** in MeCN was obtained by interpolation (see Experimental Section) to be 41.2, thus rendering it higher than HDBU$^+$ by a factor of $\sim 10^{17}$. Because equilibria 2–13 are strongly shifted to the right, only the phosphorus-containing products could be detected by ^{31}P NMR spectroscopy, and therefore only a relative ordering of the basicities could be obtained in CD_3CN:

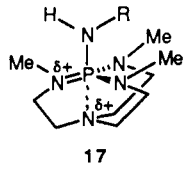
$$P_4\text{-}t\text{-Bu} > \mathbf{1} > \mathbf{4} > \text{MeN=P(NMe}_2)_3 > \text{DBU} > \mathbf{3} > \text{PhN=P(NMe}_2)_3$$

From this order it can be deduced that **4** is more than 1500 times a stronger base than DBU in MeCN since **4** is stronger than MeN=P(NMe$_2$)$_3$, which in turn was determined earlier to be 1500 times stronger than DBU.[2]

Structural Considerations. A striking feature of this series of basicities in CD_3CN is that **1** is quite comparable to P_4-*t*-Bu in basicity since the pK_a values of the corresponding conjugate acids in this solvent are 41.2 and 42.6,[4] respectively. This is especially interesting in view of the different protonation sites in these bases and the different sources of stability of the conjugate acids (i.e., extensive resonance stabilization in the case of cation **11** and a robust chelated structure in the case of cation **2**). A second striking feature of the above basicity sequence is that **4** and **3** are more basic than their corresponding acyclic analogues MeN=P(NMe$_2$)$_3$ and PhN=P(NMe$_2$)$_3$, respectively. It could be argued that resonance structures of type **15** may be favored over those of type **16**. Another possibility is that transannulation from the bridgehead nitrogen in cations **5** and **6** inductively enhances the basicity of the imido nitrogen and delocalizes the positive charge as in **17**. We do not believe resonance structures such as **15** are


15


16


17

primarily responsible for the stronger basicity of **3** and **4** over their acyclic counterparts. First of all **16** would have more structural flexibility than **15**, and might therefore be expected to adopt a less strained configuration to accommodate the delocalized π bonds inherent in the resonance structures. Secondly, any greater delocalization of positive charge out to the Me$_2$N nitrogens of **15** than in **16** might be expected to cause the CH_3 carbon and hydrogens in **15** to appear at lower field than in **16**. An examination of the NMR data for these atoms in **5**, **6**, **9**, and **10**, however, reveals no consistent trends (see Experimental Section).

If resonance structures of type **15** for **5** and **6** were enhanced by some degree of transannulation as shown in **17**, the positive charge could be predominantly delocalized to the bridgehead nitrogen (N_{ax}). The most convincing evidence for such transannulation is found in the structure of **5**(CF_3CO_2) shown in Figure 1 which we have determined by X-ray means. Here the P–N_{ax} distance of 2.551(3) Å is 23% shorter than the sum of the van der Waals radii (3.35 Å).[18] To accommodate transannulation, the average MeN–P–NMe angle in **5**(CF_3CO_2) (115.1(2)°) is considerably larger than tetrahedral. In an earlier publication[17a] we described a series of eight structures determined by X-ray means in which the MeN–P–NMe angle opened from 104.5° to 119.6° while the transannular distance closed from 3.33 to 1.967 Å. This plot is shown in Figure 2 with the insertion of these data for **5**(CF_3CO_2). The linearity of the plot prior to inclusion of this compound (r^2 = 0.98) is essentially preserved when the data for cation **5** are added (r^2 = 0.97). It is interesting to note from Figure 2 how protonation at or near the bridgehead of **1** affects its structure. Protonation of the phosphorus of **1** to give cation

(17) (a) Tang, J.-S.; Laramay, M. A. H.; Young, V.; Ringrose, S.; Jacobson, R. A.; Verkade, J. G. *J. Am. Chem. Soc.* **1992**, *114*, 221. (b) Tang, J.-S.; Verkade, J. G. *J. Am. Chem. Soc.* **1993**, *115*, 1660.

(18) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

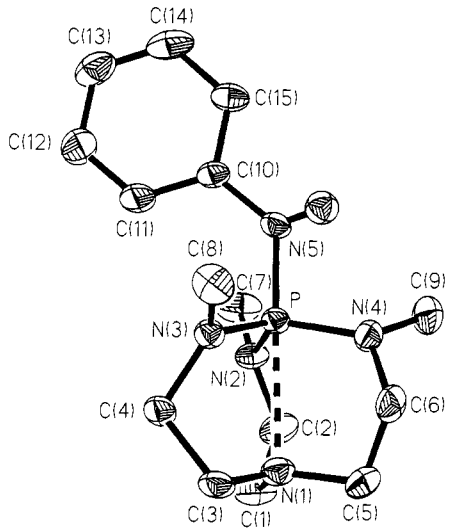


Figure 1. ORTEP drawing of $5(CF_3CO_2)$ with ellipsoids drawn at the 50% level.

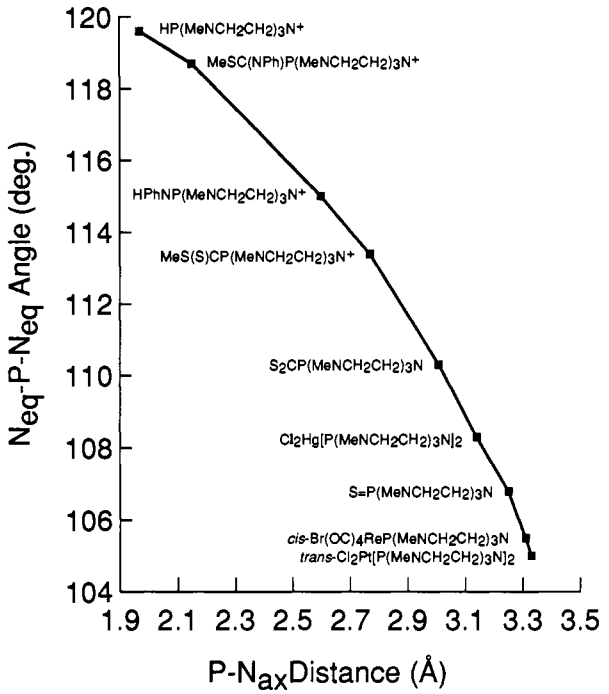


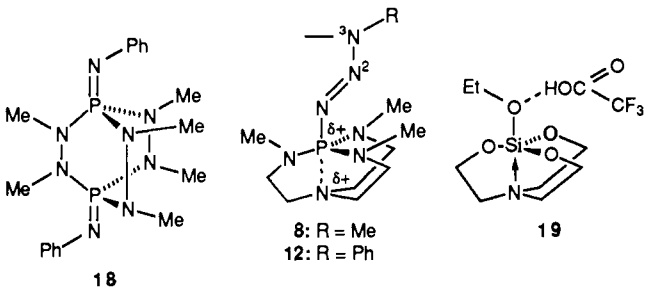
Figure 2. Plot of $P-N_{ax}$ distances against MeN–P–NMe angles in $ZP(MeNCH_2CH_2)_3N$ compounds.

2 results in a 1.4 Å reduction in $P-N_{ax}$ distance if it is assumed[19] that the structural metrics of **1** are similar to those of its platinum complex[20] in Figure 2. As might be expected, protonation of the imido nitrogen adjacent to phosphorus in **3** to give cation **5** gives rise to a smaller decrease (0.7 Å) in the $P-N_{ax}$ distance, if it can be assumed that the transannular distance in **3** is at least as long as that in $S{=}P(MeNCH_2CH_2)_3N$[20] in Figure 2, which contains the less electronegative sulfur substituent. Interestingly, methylation[17] of a sulfur in $S_2CP(MeNCH_2CH_2)_3N$,[17,20] which is two atoms removed from the phosphorus, results in a larger decrease in $P-N_{ax}$ distance (0.8 Å) than the aforementioned protonation of the adjacent imido nitrogen.

(19) This assumption is made reasonable by the observation that the P- -N_{ax} distance in the Pt complex[20] (Figure 2) is near the van der Waals sum of 3.35 Å. The platinum moiety is bulky and Pt(II) is electron rich (d^8) and can engage in retrodative π bonding. Thus no large shift of phosphorus lone pair density to Pt is expected and hence no transannulation is seen. The presence of only a phosphorus lone pair as the fourth phosphorus substituent in **1** is therefore not expected to favor transannulation.

(20) Xi, S. K.; Schmidt, H.; Lensink, C.; Kim, S.; Wintergrass, D.; Daniels, L. M.; Jacobson, R. A.; Verkade, J. G. *Inorg. Chem.* **1990**, *29*, 2214.

Although the protonating proton in $5(CF_3CO_2)$ was located in the crystal structure determination (H–N = 0.895(43) Å), its position on the imido nitrogen is further ascertained from the lengthening of the P=NPh multiple bond in the structurally related compound **18** (1.52(1) Å)[21] to $5(CF_3CO_2)$ (1.644(4) Å). The latter distance is comparable to that of the MeN–P single



bonds in $5(CF_3CO_2)$ (av 1.636(4) Å[21]) and in **18** (1.66(8) Å). The expected compression of the PhNP bond angle from **18** (134.3-(7)°[21]) to that in $5(CF_3CO_2)$ (130.7(4)°) owing to protonation of the imido nitrogen is obscured if one invokes three times the esd values as the margin of error. That protonation has not occurred on the bridgehead nitrogen (N_{ax}) of $5(CF_3CO_2)$ is evident from the protrusion of this nitrogen above the plane of its substituent carbons. It is also unlikely that a CH_3N nitrogen is protonated since the sum of the angles around each of these nitrogens is very similar (N2, 352.8°; N3, 355.8°; N4, 353.3°) as are the CH_3N–P bond lengths (P–N(2), 1.636(4) Å; P–N(3), 1.633(3) Å; P–N(4), 1.638(4) Å). It is interesting to note that the proton on the imido nitrogen is hydrogen bound to an oxygen of the $CF_3CO_2^-$ ion (H- - -O, 2.059(50) Å). This interaction is reminiscent of that in **19** for which we determined from the structural metrics that in contrast to $5(CFCO_2)$, the proton of CF_3CO_2H hydrogen bonds to the atrane, rather than protonating it.[22]

As a consequence of imido-nitrogen protonation in $5(CF_3CO_2)$ and $6(CF_3CO_2)$, the $CH_3N{=}P$ proton and carbon resonances of **4** move *upfield* upon protonation (0.1 and 2.3 ppm, respectively). This result is made reasonable by considering that the imido double bond has been converted to an amino single bond and that the positive charge has been delocalized onto the cage nitrogens. This reasoning is also consistent with the concomitant decrease in $^2J_{PC}$ (from 2.2 Hz to undetectable) and $^3J_{PH}$ (from 22.2 to 10.2 Hz) in the CH_3 group of this substituent, reflecting a decrease in *s*-character in the N–C linkage. These effects are also seen in comparing the ^1H and ^{13}C NMR spectra of $MeN{=}P(NMe_2)_3$ and $10(CF_3CO_2)$.

A rationale is now put forth for the comparative stability to N_2 elimination of **8** and **12**[11] with their respective acyclic counterparts $MeN_3P(NMe_2)_3$ and $PhN_3P(NMe_2)_3$. Structure determinations carried out by X-ray means of such intermediates reveal a nearly planar PN_3C chain and an E configuration around N^1–N^2 which has partial double bond character, the E configuration of P=N—N=NR being a second resonance form.[21] Clearly, partial transannulation (as shown in the proposed structures for **8** and **12**) would delocalize the phosphonium positive charge, thereby stabilizing these intermediates by strengthening the $N^1{=}N^2$ double bond and making rotation around N^1—N^2 (a proposed requirement for N_2 elimination[23]) more difficult.

Concluding Remarks. Nitrogen-to-phosphorus transannulation plays a surprisingly large role in conferring exceedingly strong basicities on the systems studied herein. While **1** (pK_a of **2**, 26.6) is not quite as strong a base as P_4-*t*-Bu (pK_a of $[HP_4$-*t*-$Bu]^+$,

(21) Cordes, A. W.; Fair, C. K.; Bermann, M.; Van Wazer, *J. Cryst. Mol. Struct.* **1975**, *5*, 279.

(22) Garant, R. J.; Daniels, L. M.; Das, S. K.; Janikiraman, M. N.; Jacobson, R. A.; Verkade, J. G. *J. Am. Chem. Soc.* **1991**, *113*, 5728.

(23) Golobov, Y. G.; Kasukhin, L. F. *Tetrahedron* **1992**, *48*, 1353.

28.0) in THF, it is possible that derivatives of **1** may even more closely rival P_4-*t*-Bu in basicity. Thus, for example, the pK_a of $P(HNCH_2CH_2)_3N$ (29.6) in DMSO is significantly higher in this solvent than the upper limit measured for **1** (26.8).[9c,d] Also included in studies underway is an examination of the potential advantages of non-nucleophilic non-ionic bases of the type studied here in organic reactions requiring this type of base, e.g., DBU and DBN.

Acknowledgment. The authors are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for a grant supporting this research. They also thank Dr. Victor G. Young, Jr., of the Iowa State Molecular Structure Laboratory for the solution by X-ray means to the structure of $\mathbf{5}(CF_3CO_2)$ and the W. R. Grace Co. for a research sample of $(H_2NCH_2CH_2)_3N$.

Supplementary Material Available: Tables of atomic coordinates, bond lengths, bond angles and thermal parameters for $\mathbf{5}(CF_3CO_2)$ (5 pages); listing of structure factors (21 pages). Ordering information is given on any current masthead page.