(5) Reports of the preparation of $MoCr(O_2CR)_4$ derivatives have been made, but none has been substantiated as pure compounds, free of $Mo_2(O_2CR)_4$ which always appears to accompany formation of the heteronuclear species; cf. ref 1 and C. D. Garner and R. G. Senior, *J. Chem. Soc., Chem. Commun.*, 580 (1974).
(6) This stability is in contrast to that observed for the species $[Mo_2(O_2CR)_4]^+$ obtained by electrochemical oxidation of $Mo_2(O_2CR)_4$ in acetonitrile; cf. F. A. Cotton and E. Pedersen, *Inorg. Chem.*, **14**, 399 (1975).
(7) Details of the X-ray structure elucidation, including tables of final atomic and thermal parameters and structure factors will be provided in a full publication.
(8) On leave from the University of Zagreb, Zagreb, Croatia, Yugoslavia.

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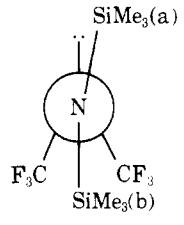
Stereochemistry of *N,N*-Bis(trimethylsilyl)amino- and *N-tert*-Butyl-*N*-(trimethylsilyl)aminobis-(trifluoromethyl)phosphine

Sir:

The structures[1] and stereochemistry[2] of aminophosphines have received considerable attention in recent years. Our interest in this area is being extended to include compounds containing the silicon-nitrogen-phophorus linkage.[3] The new silylaminophosphines, $(Me_3Si)_2NP(CF_3)_2$ (**1**) and $(Me_3Si)(t\text{-Bu})NP(CF_3)_2$ (**2**), were prepared by the reaction of $(CF_3)_2PCl$ with the *N*-lithium derivative of the appropriate silylamine.[4]

At ambient temperature the ^1H NMR spectrum of **1** consists of a single broad resonance which on cooling broadens further before splitting into two sharp lines and a multiplet (Figure 1a). By recording the ^1H spectra at both 60 and 100 MHz it was determined that: (i) the 2.8 Hz spacing between the two sharp lines is a coupling constant, as is the 0.7 Hz splitting within the multiplet, and (ii) the separation (6.3 Hz at 100 MHz, 3.7 Hz at 60 MHz) between the doublet and the multiplet results from a chemical shift difference. The ^{19}F NMR spectrum of **1** is a doublet (+59.2 ppm from $CFCl_3$, J_{PCF} = 93.1 Hz) which remains unchanged down to −130°.

These observations are consistent with hindered rotation about the N-P bond and the characteristic[1,2] ground state structure, in which the CF_3 groups are isochronous and the Me_3Si groups are anisochronous. The doublet Me_3Si resonance in the ^1H NMR spectrum of **1** can be assigned to the Me_3Si(a) group with J_{PNSiCH} = 2.8 Hz. Such an assignment is based on the observations[5,6] that the analogous *P*-N-C-*H* and *P*-N-^{13}C coupling constants in dimethylaminophosphines are larger when the methyl resides cis to the phosphorus lone pair than for the trans conformation. For the Me_3Si(b) group J_{PNSiCH} ~0 and $J_{FCPNSiCH}$ = 0.7 Hz. Possibly the proximity of the Me_3Si(b) and CF_3 groups promotes a through space interaction. A similar preferential phosphorus coupling has been found to exist in the low temperature ^1H NMR spectra of $(Me_3Si)_2NPCl_2$ and a long range proton-fluorine coupling has been observed in the aminoarsine $(Me_3Si)_2NAs(CF_3)_2$.[3]



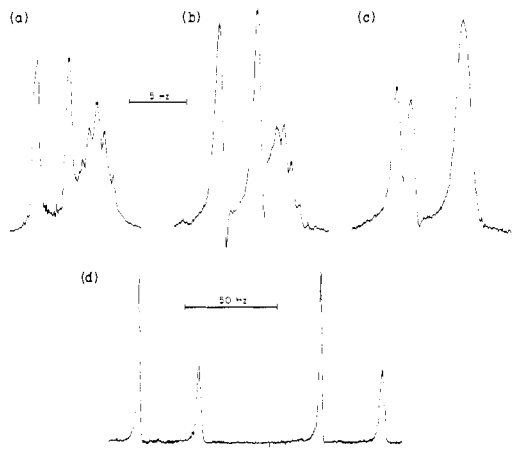
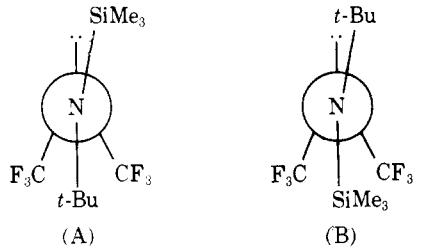


Figure 1. NMR spectra of $(Me_3Si)_2NP(CF_3)_2$ (**1**) and $(Me_3Si)(t\text{-Bu})NP(CF_3)_2$ (**2**): (a) 60-MHz ^1H spectrum of **1** at −40°; (b) 60-MHz ^1H spectrum of the Me_3Si group of **2** at ambient temperature; (c) 60-MHz ^1H spectrum of the *t*-Bu group of **2** at ambient temperature; (d) 56.45-MHz ^{19}F spectrum of **2** at ambient temperature.

Typically $\Delta G_{NP}^{\ddagger}$ values for other acyclic aminophosphines fall in the range 7-10 kcal/mol.[2] The high $\Delta G_{NP}^{\ddagger}$ value of 15.3 kcal/mol which is calculated[7] for **1** is most reasonably attributed to the steric bulk of the Me_3Si moiety.

Compound **2** is apparently unique among aminophosphines since both the ^1H and ^{19}F NMR spectra (Figure 1) indicate the presence of two rotational isomers at ambient temperature. The Me_3Si region of the ^1H spectrum is strikingly similar to that observed at low temperature for **1** except that the doublet:multiplet ratio is ca. 1.3:1 rather than 1:1. Two *tert*-butyl resonances, a doublet and a broad singlet, of unequal intensities are also observed. The ^{19}F NMR spectrum consists of two doublets (+54.9 ppm, J_{PCF} = 100.0 Hz, and 55.4 ppm, J_{PCF} = 101.0 Hz) in the intensity ratio 1.3:1. These results are consistent with the existence of two rotamers of slightly different energy which undergo slow interconversion on the NMR time scale at ambient temperature.



In view of the earlier discussion of the angular dependence of coupling constants the more intense Me_3Si doublet (J_{PNSiCH} = 3.2 Hz) and the *tert*-butyl singlet are attributed to rotamer A in which the Me_3Si group is cis to the phosphorus lone pair. Similarly the doublet in the *tert*-butyl region (J_{PNCCH} = 1.2 Hz) and the Me_3Si multiplet ($J_{FCPNSiCH}$ = 0.7 Hz) are ascribed to rotamer B. Furthermore, it is noted that the less intense doublet in the ^{19}F spectrum (presumably resulting from rotamer B) has the larger peak width which correlates with the larger H-F coupling observed for the less intense Me_3Si resonance in the ^1H spectrum.

The high temperature ^1H NMR spectrum of **2** revealed a coalescence of the *tert*-butyl signals at +110° from which a value of $\Delta G_{NP}^{\ddagger}$ = 20.8 kcal/mol is calculated.[7] This very high value of $\Delta G_{NP}^{\ddagger}$ is not easily explained. The shorter

C-N bond in the *tert*-butyl compound **2** relative to the Si-N bond in the disilyl analog **1** might, however, cause greater steric interaction with the CF_3 groups in the rotational transition state resulting in a higher barrier to N-P rotation.

The results of this study have a bearing on a report by Scherer and Schieder[8] in which the preparation of the phosphine imine, **3**, was described. Assignment of the imine

$$(t\text{-Bu})_2\text{PN(H)SiMe}_3 \xrightarrow[2.\ \text{Me}_3\text{SiCl}]{1.\ n\text{-BuLi}} (t\text{-Bu})_2\text{P}(\text{SiMe}_3)\text{=NSiMe}_3$$

3

structure to **3** was based largely on the observation of two different Me_3Si signals, a doublet (J_{PSiCH} = 2.2 Hz) and a singlet (J_{PNSiCH} = 0.0), of equal area in the ^1H spectrum. In light of the high N-P rotational barriers and preferential phosphorus couplings reported here for the aminophosphines **1** and **2**, the spectrum of **3** would also be consistent with the isomeric aminophosphine structure $(t\text{-Bu})_2\text{PN}(\text{SiMe}_3)_2$ in which nonequivalent Me_3Si groups result from hindered rotation about the N-P bond.

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(3) R. H. Neilson and A. H. Cowley, to be submitted for publication.

(4) Full details of the syntheses of **1**, **2**, and related compounds will be published elsewhere.[3] Compounds **1** and **2** were fully characterized by ir, mass, and ^1H and ^{19}F NMR spectroscopy.

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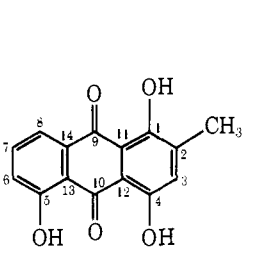
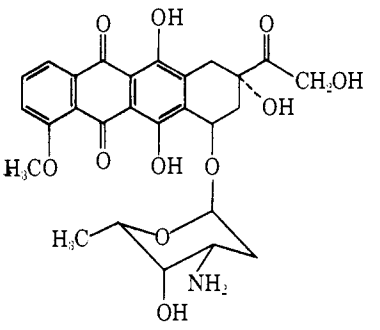
A ^{13}C Nuclear Magnetic Resonance Study of the Biosynthesis of Islandicin from $^{13}CH_3{}^{13}CO_2Na$

Sir:

Islandicin (**1**), a red pigment isolated[1] from the mold *P. islandicum* may be viewed as a biosynthetic prototype of the potent anticancer antibiotic adriamycin (**2**).[2] The former has been shown by Gatenbeck[3] to be biosynthesized



1



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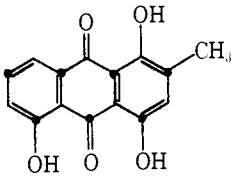
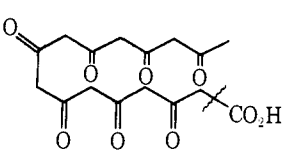
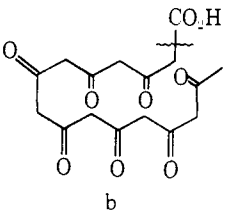
from a polyketide precursor. His experiments demonstrated that incorporation of $CH_3{}^{14}CO_2Na$ gives the following labeling pattern



which we have confirmed through incorporation of $CH_3{}^{13}CO_2Na$ and subsequent ^{13}C NMR. This pattern could arise from one of two possible foldings of a polyketide chain, a or b. We have demonstrated via the Tanabe tech-



a



b

nique,[4] the use of ^{13}C doubly labeled acetate ($^{13}CH_3$-$^{13}CO_2Na$, 90% enriched), that islandicin is biosynthesized via configuration a.

P. islandicum Sopp was obtained from ATCC (no. 10127) and was maintained on Czapek-Dox-2% agar at 19-24°C. Petri dishes (100 × 15 mm) containing the growing organism were pulsed daily, each with 0.5 ml of $^{13}CH_3{}^{13}CO_2Na$ (8 mg/ml) from day 7 through day 16. Cultures were harvested[1] after 24 days, and the islandicin was purified by chromatography (benzene-silica gel) and sublimation. The isolated product (>90% pure) was chemically converted (Ac_2O/py) to the triacetate prior to ^{13}C NMR experiments. A small amount of $^{14}CH_3CO_2Na$ was added along with the ^{13}C acetate to accurately determine the incorporation level (2.0-2.5%).

Conversion of islandicin to the triacetate increased its solubility in $CDCl_3$ and made possible the use of $Cr(acac)_3$[5] for the ^{13}C NMR experiments. Under these conditions all the ^{13}C NMR signals were of approximately the same height (Figure 1A) which ensured that enrichment of carbon by labeled acetate would be readily apparent. This use of $Cr(acac)_3$ was especially helpful in determining incorporation levels and positions of singly-labeled precursors. The chemical shifts of islandicin triacetate are given in Table I and are based on known chemical shift data,[6] comparison with a number of model compounds (1,2-, 1,4-, 1,5-, 1,8-diacetoxyanthraquinones, 5-hydroxy-1,4-naphthaquinone and its corresponding acetate), and off-resonance decoupling experiments. C-1 was distinguished from C-4 and C-5 in off-resonance irradiation spectra where the former appeared as a sharp singlet and the two latter as broad signals; C-4 and C-5 were assigned by comparison of the spectrum