metry to effective C_s symmetry by virtue of unequal P–Ru—P and N–Ru–P bond angles. These results are thus in close agreement with those found very recently for the isoelectronic $Ir(NO)H(P(C_6H_5)_3)_3^+$ complex.[6]

The coordination geometry of complex **2** is also best described as a distorted trigonal bipyramid with a linear nitrosyl group as shown in Figure 2, but in this structure, the nitrosyl occupies an *equatorial* position in the coordination polyhedron. The bond angles about the Ru atom (see Figure 2 caption) give the complex effective C_{2v} symmetry in its inner coordination geometry. One further point of structural interest is that the conformations of the two diphos rings differ, as has been found in other diphos-containing complexes such as $Rh(diphos)_2^+$ [7] and $M(O_2)(diphos)_2^+$ (M = Rh, Ir).[8]

The structural results for complexes **1** and **2** show that in each case the nitrosyl group coordinates to the ruthenium in a linear manner with considerable metal → ligand π bonding. This linear bonding mode is conventionally described in terms of NO^+ and, hence, these systems are coordinatively saturated complexes of Ru(0). These results contrast with those found for the related complex $Ru(NO)_2Cl(P(C_6H_5)_3)_2^+$ [2d] in which the coordination geometry is a tetragonal pyramid with a bent apical nitrosyl coordinating as NO^- and a linear equatorial nitrosyl bonding as NO^+. This dinitrosyl complex is therefore a d^6 coordinatively unsaturated Ru(II) system. The differences in the coordination geometries and the degree of coordinative saturation in these relatively similar complexes thus strongly support the notion that the nitrosyl group in certain catalytically active systems functions as an "electron pair reservoir" capable of donating and withdrawing an electron pair from the metal center.[9,10] In this regard, Collman and coworkers[11] have recently shown that the two nitrosyl groups in $Ru(NO)_2Cl(P(C_6H_5)_3)_2^+$ interconvert, presumably through a trigonal-bipyramidal structure analogous to **1** or **2**. Finally, the nitrosyl stretching frequencies for the three Ru–nitrosyl complexes (ν(NO) values for $Ru(NO)_2Cl(P(C_2H_5)_3)_2^+$ are 1687 and 1845 cm^{-1}) clearly illustrate the danger associated with correlating ν(NO) with the M–N–O bond angle and underscore the notion that ν(NO) is sensitive to the *composition* of filled bonding molecular orbitals regardless of the formal assignment of metal and ligand charges.[12]

Acknowledgment. We thank Professor John Osborn and Dr. Robert E. Townsend for generous samples of their complexes and for their helpful comments, and acknowledge the National Science Foundation (Grant No. GP-23139) and the Advanced Research Projects Agency for support of this work.

(6) D. M. P. Mingos and J. A. Ibers, *Inorg. Chem.*, **10**, 1035 (1971).

(7) M. C. Hall, B. T. Kilbourn, and K. A. Taylor, *J. Chem. Soc. A*, 2539 (1970).

(8) J. A. McGinnety, N. C. Payne, and J. A. Ibers, *J. Amer. Chem. Soc.*, **91**, 6301 (1969).

(9) J. P. Collman, N. W. Hoffman, and D. E. Morris, *ibid.*, **91**, 5659 (1969).

(10) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, p 573.

(11) J. P. Collman, P. Farnham, and G. Dolcetti, *J. Amer. Chem. Soc.*, **93**, 1788 (1971); J. P. Collman, personal communication.

(12) P. T. Manoharan and H. B. Gray, *Inorg. Chem.*, **5**, 823 (1966).

(13) National Institutes of Health Predoctoral Fellow, 1969–1971.

Cortlandt G. Pierpont,[13] Amleto Pucci, Richard Eisenberg*
Department of Chemistry, Brown University
Providence, Rhode Island 02912

Received April 9, 1971

Restricted Rotation in a Bisphosphinohydrazine[1]

Sir:

Large torsional barriers about P–N bonds[2–7] and rotational and/or inversional barriers in hydrazines[8–12] have been reported. We have recently isolated $F_2PN(CH_3)N(CH_3)PF_2$ [13] and have observed similar stereochemical processes occurring in this molecule. Figure 1 shows representative ^{19}F nmr spectra taken between −145 and +160° on a Varian HA-100 spectrometer operating at 94.1 MHz. Spectra were run between about −110 and +60° in $FCCl_3$, between −145 and +20° in isopentane, between +20 and +160° in *n*-undecane and 1,1,2,2-tetrachloroethane, and between −145 and +20° in F_2CCl_2. Within experimental uncertainty, the temper-

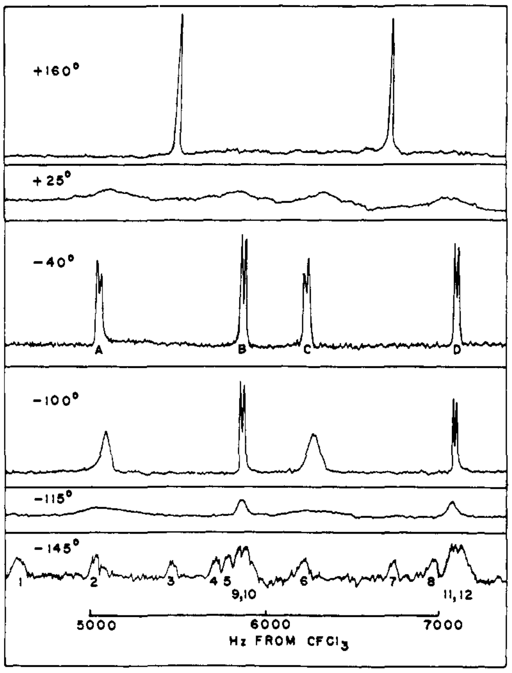


Figure 1. ^{19}F nmr spectrum of $F_2PN(CH_3)N(CH_3)PF_2$ between +160 and −145°.

(1) Acknowledgment is gratefully made to the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

(2) M. P. Simonnin, J. J. Basselier, and C. Charrier, *Bull. Soc. Chim. Fr.*, 3544 (1967).

(3) A. H. Cowley, M. J. S. Dewar, and W. R. Jackson, *J. Amer. Chem. Soc.*, **90**, 4185 (1968).

(4) D. Imbery and H. Friebolin, *Z. Naturforsch. B*, **23**, 759 (1968).

(5) H. Goldwhite and D. G. Rowsell, *Chem. Commun.*, 713 (1969).

(6) A. H. Cowley, M. J. S. Dewar, W. R. Jackson, and W. B. Jennings, *J. Amer. Chem. Soc.*, **92**, 1085 (1970).

(7) A. H. Cowley, M. J. S. Dewar, W. R. Jackson, and W. B. Jennings, *ibid.*, **92**, 5206 (1970).

(8) G. J. Bishop, B. J. Price, and I. O. Sutherland, *Chem. Commun.*, 672 (1967).

(9) M. J. S. Dewar and W. B. Jennings, *J. Amer. Chem. Soc.*, **91**, 3655 (1969).

(10) J. R. Fletcher and I. O. Sutherland, *Chem. Commun.*, 707 (1969).

(11) J. E. Anderson, D. L. Griffith, and J. D. Roberts, *J. Amer. Chem. Soc.*, **91**, 6371 (1969).

(12) M. J. S. Dewar and W. B. Jennings, *Tetrahedron Lett.*, 339 (1970).

(13) Synthesized by fluorination of $Cl_2PN(CH_3)N(CH_3)PCl_2$, a product of the reaction between PCl_3 and either $HN(CH_3)N(CH_3)H$ or $P[N(CH_3)N(CH_3)]_3P$. $F_2PN(CH_3)N(CH_3)PF_2$ is a volatile, fairly unstable liquid. Its characterization is lengthy and is based upon ^1H and ^{19}F nmr, including ^{31}P and ^1H double resonance and crude indor experiments, mass and ir spectra, as well as chemical behavior and physical properties. The details of these reactions and experiments will appear in a full paper now being prepared.

Table I. Rotational Activation Parameters for $F_2PN(CH_3)N(CH_3)PF_2$

Temp range, °C	Assigned conformational change	T_c, °C	$\Delta G_c^{\ddagger}$, kcal/mol	E_a, kcal/mol	$\Delta H^{\ddagger}$, kcal/mol
+160 to −40	N-N bond rotation	+30	13.0 ± 1	9.0 ± 1	8.4 ± 1
−40 to −145	P-N bond rotation (cis)	−120	6.4 ± 1		
−110 to −145	P-N bond rotation (trans)	−120	6.9 ± 1		

ature dependence of the spectra was independent of both solvent and concentration. All chemical shifts are referenced to internal $FCCl_3$.

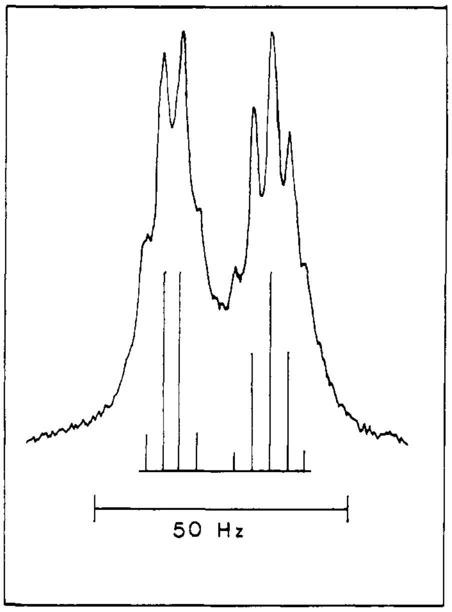
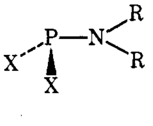
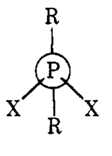


Figure 2. Peak B from Figure 1 compared to the line spectrum calculated using the parameters described in the text.

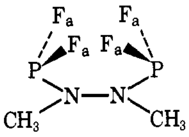
Interpretation of these spectra is hindered by the fact that there is at present no detailed information available on the structure of the hydrazinophosphines. However, recent investigations indicate that the stereochemistry of the related aminohalophosphines both as solids[14] and in solution[6,7] is



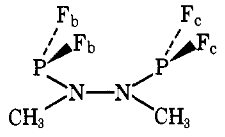
or



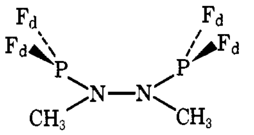
If $F_2PN(CH_3)N(CH_3)PF_2$ can be imagined as being derived from $F_2PN(CH_3)_2$ by substitution of a CH_3 group by a $F_2PN(CH_3)$ moiety, a number of rotamers would be expected if rotation about the N-N and P-N bonds were slow. Thus, if the two $F_2PN(CH_3)$ units are joined so that the P-N-N-P framework is planar, six structures (I-VI) can be drawn. For either this cis (I-III) or trans (IV-VI) geometry about the N-N bond the fluorine atoms would be expected to occupy four distinct magnetic environments (a total of eight fluorine environments in the six conformers). Double statistical weight is given to II and V, however, since they may arise in twice as many ways as the other four rotamers. Thus, at sufficiently low temperatures (where bond rotations would be slow) a complicated ^{19}F spectrum might be anticipated. Indeed, at −145° the spectrum consists of eight lines (1-8 in Figure 1) of approximate relative intensity one, and four peaks (9-12 in Figure 1) of relative intensity about two. (The approximate 60-Hz separation of 9 from 10 and 11 from 12 is not clearly resolved on the scale used in Figure 1.) Peaks 1-8 are assigned as four doublets, arising from coupling of a ^{19}F with an adjacent ^{31}P, whose respective members are peaks 1 and 5 (J_{PF} = 1220 Hz, δ 55.2 ppm), 2 and 6 (J_{PF} = 1190 Hz, δ 59.9 ppm), 3 and 7 (J_{PF} = 1240 Hz, δ 64.8 ppm), and 4 and 8 (J_{PF} = 1230 Hz, δ 67.6 ppm). Peaks 9-12 likewise represent two doublets; peaks 9 and 11 (J_{PF} = 1250 Hz, δ 67.6 ppm) and 10 and 12 (J_{PF} = 1250 Hz, δ 68.2 ppm).



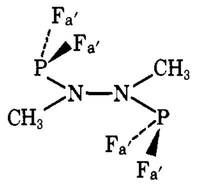
I



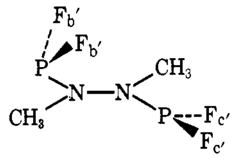
II



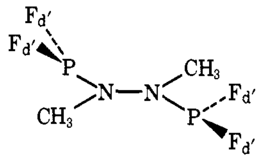
III



IV



V



VI

If the rotamers of $F_2PN(CH_3)N(CH_3)PF_2$ at −145° can be represented by I-VI and if all are of approximately equal energy, four ^{19}F resonances (each appearing as a doublet due to P-F coupling) of equal intensity would be expected for I-III. These can be assigned to peaks 1-8 in the −145° spectrum. While IV-VI also formally contain four different kinds of fluorine, it is possible that the chemical shift differences between $PF_2^{a'}$ and $PF_2^{b'}$ groups and $PF_2^{c'}$ and $PF_2^{d'}$ groups would be small, resulting in the resolution of only two doublets for IV-VI. Each of these peaks, however, should be twice as intense as each peak arising from I-III. Peaks 9-12 are thus assigned to IV-VI.

For symmetrically substituted aminophosphines, X_2PNR_2, P-N torsional barriers are about 8 kcal/mol;[6,7] typical N-N barriers are often considerably greater.[8-12] Assuming such a relationship in $F_2PN(CH_3)N(CH_3)PF_2$ and approximately equal Arrehnius

---

[14] E. D. Morris, Jr., and C. E. Nordman, *Inorg. Chem.*, **8**, 1673 (1969).

frequency factors, the P–N rotation should be observed at a lower temperature than N–N rotation. Rapid rotation about the P–N bonds should lead to time averaging and to equivalence of the fluorines in I–III and likewise among those in IV–VI. Indeed, between −145 and −40° peaks 1–8 broaden, coalesce, and reappear as a single doublet (peaks A and C in Figure 1; $J_{PF} = 1230$ Hz, δ 59.9 ppm), as do peaks 9–12, whose new doublet appears as peaks B and D in Figure 1 ($J_{PF} = 1230$ Hz, δ 68.6 ppm). In view of the arguments used to assign the −145° spectrum, peaks A and C correspond to the conformer in which the two PF_2 groups are cis, while B and D represent the trans configuration. In assigning the −145° spectrum, structures I–IV were assumed to be of nearly equal energy. If this is true, the energy of the cis configuration must be very close to that of the trans conformer even when rotation about the P–N bonds is rapid. Consistent with this assumption, the integrated relative intensities of A, B, C, and D are equal within the uncertainties of the measurement; about ±5%. Each member of the low-field doublet, peaks A and C, is itself split into a doublet ($J_{P'F} = 20$ Hz) by interaction with the nonadjacent ^{31}P and shows even further incipient, but unresolved splitting. Peaks B and D are also complex multiplets which closely approximate a calculated spectrum with $J_{PF} = 1230$ Hz, $J_{PF'} = 20$ Hz, $J_{PP'} = 3.5$ Hz, and $J_{FH} = 3.5$ Hz, with the signs of J_{PF} and $J_{P'F}$ the same[15] (see Figure 2).

As temperature is further raised, these peaks broaden, coalesce, and reappear as a single doublet ($J_{PF} = 1220$ Hz, δ 65.0 ppm), as expected for $F_2PN(CH_3)N(CH_3)PF_2$ if rapid rotation occurs about all bonds. While each of these peaks at +160° shows unresolved fine structure, no observed splitting is as large as the 20-Hz $J_{P'F}$ seen in both conformers at −40°. Since the magnitude of $J_{P'F}$ at this temperature should be an average of the P′F couplings observed for the two rotamers at −40°, the clear indication is that the sign of $J_{P'F}$ differs between the two conformers observed at −40°.

Using the structures which result from easing the requirement that the PNNP framework be planar, that the nitrogen be planar, and/or that the stereochemistry of the $F_2P–N(CH_3)$ moiety resemble that in the aminophosphines, we have been unable to explain the observed spectra. Similarly, arguments utilizing other exchange processes such as slow nitrogen inversion and/or hindered rotation about other bonds also have proven to be inconsistent with the observed spectra.[16] Thus we feel confident that the stereochemistry of $F_2PN(CH_3)N(CH_3)PF_2$ can be represented by I–VI.

In principle, the most reliable method of obtaining exchange times from nmr spectra involves complete line-shape analysis. However, the ^{19}F spectra herein presented are all largely first order, and the more approximate methods are to be expected to yield reasonably reliable values. Thus, the spectra between −40 and +160° were treated as representing a pair of two-site exchange processes[17] with effective chemical shifts $\delta \pm {}^1\!/_2 J_{PF}$ for each site. Similar approximations were made for the spectra at lower temperatures. Because of the large temperature range involved, data for the N–N bond rotation are the most reliable. Within experimental error, both P–N bonds have the same activation energy and coalescence temperature; the much larger chemical shifts between fluorine "sites" in the cis compounds (I–III) cause these peaks to broaden appreciably at −100°, while peaks arising from the trans compounds (IV–VI) are still in the fast-exchange limit. The results are shown in Table I. While no torsional barriers about an $F_2P–N$ bond have previously been reported, for both $(F_3C)_2PN(CH_3)_2$ and $Cl_2PN(CH_3)_2$ $\Delta G_c^{\ddagger} \approx 8–9$ kcal/mol.[7] This barrier has been attributed to $p\pi–d\pi$ bonding, which also may explain the source of the barrier in $F_2PN(CH_3)N(CH_3)PF_2$. Previous N–N barriers have been attributed to lone pair–lone pair repulsions;[8–12] however, in view of the probable stereochemistry of $F_2PN(CH_3)N(CH_3)PF_2$, $p\pi–p\pi$ overlap may also contribute to the barrier.

Thomas T. Bopp, Mary D. Havlicek, John W. Gilje*
Department of Chemistry, University of Hawaii
Honolulu, Hawaii 96822

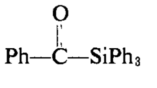
Received February 1, 1971

X-Ray Determination of the Absolute Configuration of (+)-Phenyltriphenylsilylcarbinol[1,2]

Sir:

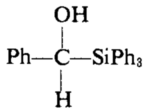
A key compound in connection with asymmetric reduction studies,[3] silylcarbinol to silyl ether rearrangements, and other stereochemical interrelationships is phenyltriphenylsilylcarbinol (**2**), obtained by the reduction of phenyl triphenylsilyl ketone (**1**).

Attempts at using established configurational correlation schemes such as Freudenberg's rule of rotational shifts, ORD correlations, Fredga's quasi-racemate method, Prelog's atrolactic asymmetric synthesis, as well as asymmetric reductions, led to conflicting or equivocal results.[3] The one published determination of a configuration at a carbinol carbon attached to silicon[4] was based upon an untested application of Cram's rule to optically active 1-naphthylphenylmethylsilyl phenyl ketone followed by a silylcarbinol to silyl ether rearrangement. If the other correlation schemes[3] are ambiguous when applied to compounds of this type, this determination is also suspect. Before a rational interpretation of a number of stereochemical questions in such systems can be made, the absolute configuration of some key compound must be rigorously established. As a consequence of the silicon–carbon bond at the asymmetric carbon center in this particular system, the standard chemical methods of configurational correlations apparently do not provide the necessary answer. Since phenyltriphenylsilylcarbinol was an accessible and central compound in these correla-



$$\mathrm{Ph{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}SiPh_3}$$

1



$$\mathrm{Ph{-}\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}{-}SiPh_3}$$

2

---

(15) Double irradiation of the ^{31}P confirmed that both the 20- and the 1230-Hz splittings arose from $^{19}F–^{31}P$ coupling.

(16) Arguments based on energetics have previously been made which eliminate phosphorus inversion from being rate limiting in stereochemical processes such as those observed here. See ref 7.

(17) C. J. Johnson, *Advan. Magn. Resonance*, **1**, 33 (1965).

(1) Study supported by the National Science Foundation.

(2) K. T. Black, undergraduate research project.

(3) M. S. Biernbaum and H. S. Mosher, *Tetrahedron Lett.*, 5789 (1968).

(4) A. G. Brook and W. W. Limburg, *J. Amer. Chem. Soc.*, **85**, 832 (1963).