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; $J_{\mathrm{PF}} = 1230$ Hz, δ 59.9 ppm), as do peaks 9–12, whose new doublet appears as peaks B and D in Figure 1 ($J_{\mathrm{PF}} = 1230$ 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 ($J_{\mathrm{P'F}} = 20$ 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 $J_{\mathrm{PF}} = 1230$ Hz, $J_{\mathrm{PF'}} = 20$ Hz, $J_{\mathrm{PP'}} = 3.5$ Hz, and $J_{\mathrm{FH}} = 3.5$ Hz, with the signs of J_{PF} and $J_{\mathrm{P'F}}$ the same[15] (see Figure 2).

As temperature is further raised, these peaks broaden, coalesce, and reappear as a single doublet ($J_{\mathrm{PF}} = 1220$ 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 $J_{\mathrm{P'F}}$ seen in both conformers at −40°. Since the magnitude of $J_{\mathrm{P'F}}$ 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 $J_{\mathrm{P'F}}$ 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 $\delta \pm {}^1\!/_2 J_{\mathrm{PF}}$ 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.

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[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.

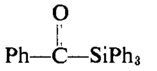
[17] C. J. Johnson, *Advan. Magn. Resonance*, **1**, 33 (1965).

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

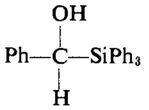
Sir:

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-


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

1


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

2

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[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).

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Table I. Observed $|F(hkl)|$ and Observed and Calculated Bijvoet Differences

$\|h\|$	$\|k\|$	$\|l\|$	$\|F_o(hkl)\|$	$\Delta F_{\mathrm{Bij,obsd}}$	$\Delta F_{\mathrm{Bij,calcd}}$	$\|h\|$	$\|k\|$	$\|l\|$	$\|F_o(hkl)\|$	$\Delta F_{\mathrm{Bij,obsd}}$	$\Delta F_{\mathrm{Bij,calcd}}$
6	1	2	34.5	−4.0	−3.8	3	3	6	42.0	6.1	5.4
5	1	1	29.6	4.8	4.5	3	3	8	16.6	4.7	5.5
5	1	4	45.5	5.7	4.9	2	3	6	12.1	−5.8	−6.6
4	1	5	30.2	−8.0	−7.7	2	3	1	50.0	8.2	8.0
4	1	4	32.1	2.0	2.4	1	3	4	44.5	2.4	2.2
4	1	3	21.0	4.6	4.1	1	3	6	31.1	5.3	5.3
3	1	1	34.4	−3.9	−4.0	1	3	9	26.7	−4.1	−4.1
3	1	3	30.2	4.7	4.1	2	4	2	33.2	5.3	5.5
3	1	4	65.2	6.1	5.5	2	4	3	57.8	−5.6	−5.4
3	1	7	38.2	5.7	5.5	3	4	6	39.5	−4.1	−4.2
2	1	5	48.2	5.7	5.2	3	4	4	23.4	−4.2	−4.7
2	1	4	58.6	−6.7	−6.9	3	4	3	39.4	−6.2	−5.6
2	1	3	28.7	−8.6	−8.1	3	4	1	22.2	2.8	3.4
2	1	2	145.4	9.8	8.8	4	5	3	27.1	4.9	4.8
1	1	1	78.0	−5.5	−5.3	3	5	4	35.4	8.5	8.1
1	1	5	73.1	−8.0	−8.1	2	5	7	30.2	2.8	2.5
1	1	6	30.2	−4.9	−5.2	1	5	2	62.6	−7.7	−7.3
1	1	8	67.6	−6.5	−6.6	1	5	5	17.3	−9.1	−8.9
1	1	9	40.0	3.5	3.3	1	6	9	55.3	6.5	6.4
2	2	3	57.8	−8.9	−8.2	1	6	3	45.7	6.6	6.0
2	2	4	38.3	−8.6	−8.5	2	6	3	19.2	4.0	3.9
4	2	6	38.8	−2.6	−2.8	2	6	4	24.2	−4.1	−3.8
4	3	3	16.2	−2.6	−6.1	2	7	5	41.8	3.9	3.5
3	3	3	24.4	5.7	6.1	4	8	1	25.0	−2.8	−3.5

tions, we initiated an X-ray crystallographic investigation of this silylcarbinol **2** with the objective of determining its absolute configuration.[5] Preliminary studies revealed that **2** crystallizes in the monoclinic space group $P2_1$ with four molecules in the unit cell, or two molecules per asymmetric unit. Due to the magnitude of this problem alternative possibilities were evaluated. Of the derivatives considered the (−)-bromobenzoate of the (+)-carbinol appeared quite promising. The crystals are orthorhombic, space group $P2_12_12_1$ with cell dimensions a = 10.143 (1), b = 15.503 (2), and c = 17.590 (2) Å as determined by a least-squares procedure. There are four molecules per unit cell, or one in the asymmetric unit.

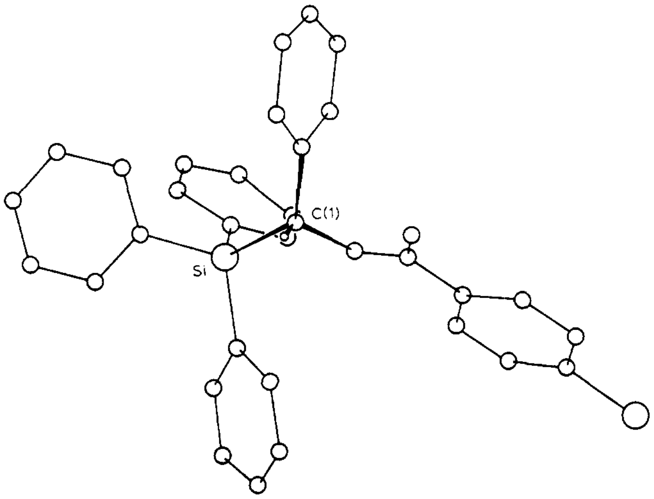

Figure 1. Projection of the molecule onto the mean molecular plane, showing the R configuration at C(1).

A crystal ground to a nearly spherical shape was used for data collection on a Picker automatic diffractometer with Ni-filtered Cu Kα radiation. A total of 2722 reflections below 2θ = 133° in one octant were measured by the 2θ-θ scan method. During data collection the crystal showed signs of decay, manifest both in decreasing reflection intensity and apparent changes in cell dimensions. After application of Lorentz, polarization, and absorption corrections as well as an approximate decay correction 2154 reflections were recorded as observed.

The structure was solved by a straightforward application of the heavy atom method and refined by least-squares techniques. The absolute configuration was determined at a stage with R = 0.14 by use of our program ABSCON.[6,7] The R configuration was unambiguously indicated for all levels of D; specifically, with $D > 100$, for the R configuration R = 0.097, $\Sigma w(\Delta F)^2 = 42$, and for the S configuration R = 0.108, $\Sigma w(\Delta F)^2 = 55$.

The final least-squares cycles (block diagonal approximation) were carried out with anisotropic B's for all C, O, Si, and Br atoms and isotropic B's for the hydrogens. Refinement was concluded with an R index of 0.063. Figure 1 shows a view of the molecule projected onto the mean plane through the molecule.

The average C(φ)–Si bond length is 1.86 (1) Å, and the C(1)–Si distance is 1.93 (1) Å. The average of the C(φ)–Si–C(φ) angles is 110.3° (3), and the average of the C(1)–Si–C(φ) angles is 108.6° (3). The dihedral angles defined by the silylphenyl rings and the C(1)–Si bond (C(1)–Si–C–C) are 62, 61, and 24°. The effective radius (from molecular dimensions plus van der Waals radii) of the triphenylsiliyl "propeller" is 6.6 Å. Calculations indicated a poor fit to a "rigid body" model.[8]

(5) We are grateful to Professor H. S. Mosher for pointing out the problem, for valuable discussions, and for providing the samples used in this study.

(6) H. Hope and U. de la Camp, *Nature* (*London*), **221**, 54 (1969).

(7) The program calculates R indices and weighted sums of squares of deviations for the two enantiomers for sets of reflections selected according to increasing values of $D = (|F_{\mathrm{calcd}}(hkl)| - |F_{\mathrm{calcd}}(\bar{h}\bar{k}\bar{l})|)^2/\sigma^2 \cdot (F_{\mathrm{obsd}})$.

Because of the relatively low quality of the Cu data set, it was felt that the credibility of the results would be enhanced by direct measurements of the most significant Bijvoet differences, and as an additional benefit we hoped to provide an experimental test of theoretical $\Delta f''$ values. For these measurements a freshly ground crystal was used with monochromatic Mo Kα radiation (graphite crystal).

Table I lists the observed and calculated[9] Bijvoet differences $[F(hkl) - F(\bar{h}\bar{k}\bar{l})]$ for the 48 pairs of reflections with $D > 100$.[7] Both in sign as well as in magnitude the agreement is excellent. If ΔF_{Bij} denotes a Bijvoet difference, we note that the value of $R_{\mathrm{Bij}} = \Sigma|\Delta F_{\mathrm{Bij,obsd}} - \Delta F_{\mathrm{Bij,calcd}}|/\Sigma|\Delta F_{\mathrm{Bij,obsd}}|$ is as low as 0.08. This index, together with the observation that for these reflections the magnitudes of ΔF_{Bij} in general correspond to about 10–20% of F_{obsd}, indicates that the theoretical $\Delta f''$ values are highly accurate.

As a result of this study it has been established with certainty that the absolute configuration of (−)-phenyltriphenylsilylcarbinyl *p*-bromobenzoate from (+)-phenyltriphenylsilylcarbinol is *R*. Comparison of our results with those reported by Biernbaum and Mosher[3] shows that stereochemical deductions based on extensions of Cram's rule to novel systems can be quite misleading.

The fact that Freudenberg's method of rotational shifts led to the incorrect answer, while Fredga's quasi-racemate method and Prelog's atrolactic asymmetric synthesis gave the correct prediction, does not imply that we are in a position to evaluate the relative merits of these methods. They all have the potential for failure, and should be applied with great caution. With present-day methods and equipment we think that an X-ray study very often affords the safest, fastest, and most economic solution to configurational problems.

[8] V. Schomaker and K. N. Trueblood, *Acta Crystallogr., Sect. B*, **24**, 63 (1968).

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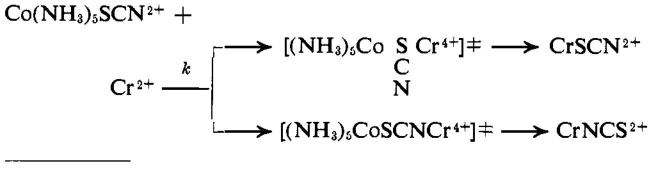
Adjacent and Remote Attacks in the Inner-Sphere Reductions of Thiocyanato- and Isothiocyanatopentaamminecobalt(III) Complexes by Chromium(II)[1]

Sir:

Following the report[2] on the bridged activated complex for electron-transfer reactions, a great deal of effort was devoted to the question of adjacent *vs.* remote attack for polyatomic bridging ligands,[3] but it was not until 1965 that definitive evidence was obtained for the remote-attack mechanism.[4–6] In contrast, direct evidence for adjacent attack in inner-sphere reactions with polyatomic bridging ligands has not been obtained thus far.[7] In the present communication, we report evidence for adjacent attack in the inner-sphere $Co(NH_3)_5SCN^{2+}$–Cr^{2+} reaction. The discovery of efficient electron transfer by attack of Cr^{2+} on S bound to Co(III) is of particular importance in the context of recent redox work with sulfur-containing ligands.[8,9]

When $Co(NH_3)_5SCN^{2+}$ [10] is mixed with an *excess* of Cr^{2+} in a rapid-flow apparatus, two reactions can be detected. The first is the rapid redox reaction between $Co(NH_3)_5SCN^{2+}$ and Cr^{2+} to produce a mixture of $CrSCN^{2+}$ and $CrNCS^{2+}$. The second, slower reaction is the chromium(II)-catalyzed isomerization[6] of $CrSCN^{2+}$ to $CrNCS^{2+}$. The rate constant for the first reaction ($[H^+] = 1.0\ M$, $[Co(III)] = 5.0 \times 10^{-5}\ M$, and $[Cr(II)] = 2.8\text{–}4.5 \times 10^{-5}\ M$) is $(2.7 \pm 0.1) \times 10^5\ M^{-1}\ sec^{-1}$ at 25°. The $CrSCN^{2+}$ produced was identified by its spectrum[7] and by its rate of chromium(II)-catalyzed isomerization to $CrNCS^{2+}$ (found, $40 \pm 1\ M^{-1}\ sec^{-1}$ at 25°, $[H^+] = 1.0\ M$, to be compared with the literature[6] value of $42 \pm 2\ M^{-1}\ sec^{-1}$). The yield of $CrSCN^{2+}$ was determined in three different manners. In the first method, $Co(NH_3)_5SCN^{2+}$ was mixed with an excess of Cr^{2+} in the rapid-flow apparatus. At 25° ($[H^+] = 1.0\ M$, $[Co(III)] = (1.3\text{–}1.6) \times 10^{-4}\ M$, $[Cr(II)] = (7.5\text{–}17.0) \times 10^{-3}\ M$) the Co(III)–Cr(II) reaction had a half-life shorter than 0.3 msec, and therefore the observed absorbance changes were associated with the Cr^{2+}-catalyzed isomerization of the $CrSCN^{2+}$ produced in the first stage. From the measured absorbance changes and the known extinction coefficients of $CrSCN^{2+}$ and $CrNCS^{2+}$, the fraction of $CrSCN^{2+}$ formed in the $Co(NH_3)_5SCN^{2+}$–Cr^{2+} reaction was found to be 0.30 ± 0.02. In the second method, Cr^{2+} ($4.8 \times 10^{-5}\ M$) and an excess of $Co(NH_3)_5SCN^{2+}$ ($1.9 \times 10^{-4}\ M$) were mixed ($[H^+] = 1.0\ M$, 25°) in the flow machine. The resulting solution was analyzed for $CrSCN^{2+}$ and $CrNCS^{2+}$ by ion-exchange and spectrophotometric techniques.[6,7] The fraction of $CrSCN^{2+}$ produced was 0.29. In the third method, the Cr^{2+} was mixed with an excess of $Co(NH_3)_5SCN^{2+}$ at 0° by conventional syringe techniques, and the resulting solution was analyzed as indicated above. The fraction of $CrSCN^{2+}$ produced was 0.26 ± 0.02. From these measurements, we conclude that the $Co(NH_3)_5SCN^{2+}$–Cr^{2+} reaction proceeds *via* parallel adjacent and remote attack mechanisms according to the scheme



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[1] This work was supported by the National Science Foundation under Grant No. GP-9669.

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[4] J. Halpern and S. Nakamura, *J. Amer. Chem. Soc.*, **87**, 3002 (1965).

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[6] A. Haim and N. Sutin, *ibid.*, **87**, 4210 (1965); **88**, 434 (1966).

[7] In the initial report on the $FeNCS^{2+}$–Cr^{2+} and *trans*-$Co(en)_2(OH_2)NCS^{2+}$–Cr^{2+} reactions, it was concluded that these reactions proceeded by adjacent and remote attack.[6] This conclusion was based on the belief that $CrSCN^{2+}$ reacted with Hg^{2+} to produce Cr^{3+} only. However, it was subsequently shown that Hg^{2+} was a catalyst for both the aquation and isomerizations reactions of $CrSCN^+$, and therefore there is no evidence for adjacent attack in the redox, isothiocyanate-bridged reactions: M. Orhanovic and N. Sutin, *ibid.*, **90**, 4286 (1968).

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