Evidently, this effect need not be reflected in the ground-state geometry.[3]

The synthesis of **1** was accomplished through phenylsilane reduction of methyl isopropylphenylphosphinate[8] to isopropylphenylphosphine, which was subsequently treated with sodium dispersion in refluxing dioxane followed by trimethylsilyl chloride.[11] Purification of the silylphosphine by fractional distillation (*ca.* 52°, 0.05 mm) afforded a sample of **1** which contained a small amount of unidentified material, as judged by nmr.[12] The nmr spectrum of **1**, together with data for similar phosphines,[13] provides convincing evidence for the assigned structure: δ 7.1–7.7 (m, C_6H_5), 0.10 (d, $^3J_{PH} = 4.0$ Hz, $Si(CH_3)_3$), 2.14–2.83 (m, $C\mathit{H}(CH_3)_2$), 1.20 (dd, $^3J_{PH} = 16.5$ Hz, $^3J_{HH} = 6.9$ Hz, $CH_{3(a)}$), 1.15 (dd, $^3J_{PH} = 14.6$ Hz, $^3J_{HH} = 6.7$ Hz, $CH_{3(b)}$).

As the temperature is increased above 31°, the eight initially well-resolved signals in the isopropyl methyl region coalesce smoothly into four (in the range 55–75°). A line-shape analysis[14] was used to simulate[15] spectra at various rates of exchange. A comparison of these with experimental spectra recorded near coalescence provided a value for the above-cited barrier. Additional evidence that pyramidal inversion at phosphorus is the rate-determining step which corresponds to the measured barrier was provided by a similar nmr analysis of a (crude) sample of **2**, which yielded a barrier of $\Delta G^{\ddagger}_{70} \sim 19.1$ kcal/mol. The fact that the barrier remains essentially unaltered whether the diastereotopic methyl groups are bound to carbon (in **1**) or silicon (in **2**) greatly reduces the remote possibility that a torsional rather than an inversional process is being observed.

The low inversion barriers found in **1** and **2** may be ascribed, in part, to (p–d)π conjugation.[16,18] Such stabilization has been invoked to explain the relatively low barriers to inversion found in diphosphines[20,21] and, possibly, in thiophosphinites.[22] That (p–d)π conjugation may be a dominant effect is suggested by the observation (unpublished work) that the germanium analog of **1** (isopropylphenyltrimethylgermylphosphine) has a pyramidal inversion barrier of $\Delta G^{\ddagger}_{109} = 21.4$ kcal/mol. Since the electronegativity of Ge is closely similar to that of Si,[19] the slightly lower (by 2.5 kcal/mol) barrier of **1** might tentatively be ascribable to more effective (3p–3d)π as compared to (3p–4d)π orbital overlap.

The experimental results justify the expectation[23] that the low electronegativity and the absence of lone pairs on the adjacent silicon atom render this element far more effective than neighboring phosphorus[20] or sulfur[22] in lowering the barrier to pyramidal inversion at phosphorus.

pyramidal arsenic may also be lowered by adjacent silicon. Unfortunately, interpretation of the observed coalescences, which may be due to interconversions of ring conformers, is ambiguous, and no quantitative estimates of barrier heights have been reported.

[7] The only other comparably low barrier to phosphorus inversion previously reported involves a phosphole system ($\Delta G_{25}^{\ddagger} = 16$ kcal/mol) for which aromatic stabilization has been invoked: W. Egan, R. Tang, G. Zon, and K. Mislow, *J. Amer. Chem. Soc.*, **92**, 1442 (1970). It is noteworthy that in this case also the analogous nitrogen compound (pyrrole) is planar: L. Nygaard, J. T. Nielson, J. Kirchheiner, G. Mattesen, J. Rastrup-Anderson, and G. O. Sorensen, *J. Mol. Struct.*, **3**, 491 (1969).

[8] This previously reported[9] phosphinate was here prepared from the corresponding phosphinic acid, itself obtained by Arbuzov rearrangement of diisopropyl phenylphosphonite.[10]

[9] T. H. Siddall, III, and C. A. Prohaska, *J. Amer. Chem. Soc.*, **84**, 2502 (1962).

[10] A. E. Arbuzov, G. Kh. Kamai, and O. N. Belorossova, *J. Gen. Chem. USSR*, **15**, 766 (1945); *Chem. Abstr.*, **41**, 105 (1947).

[11] For the synthesis of related silylphosphines, see W. Kuchen and H. Buchwald, *Chem. Ber.*, **92**, 227 (1959); G. Fritz, *Angew. Chem., Int. Ed. Engl.*, **5**, 53 (1966).

[12] These compounds are extremely sensitive to oxygen (E. W. Abel and I. H. Sabherwal, *J. Chem. Soc. A*, 1105 (1968)) and moisture.

[13] W. McFarlane, *Chem. Commun.*, 229 (1968); G. Märkl and H. Olbrich, *Tetrahedron Lett.*, 3813 (1968).

[14] The line-shape analysis was based on data obtained on a Varian A-60A spectrometer. The sample was a *ca.* 20% v/v solution in C_6D_6 with *ca.* 5% v/v dioxane as internal standard.

[15] G. Binsch, *J. Amer. Chem. Soc.*, **91**, 1304 (1969).

[16] This conjugation[17] should be enhanced in the transition state for inversion.

[17] E. A. V. Ebsworth, *Chem. Commun.*, 530 (1966).

[18] At present, claims for (p–d)π conjugation in silylphosphines are based predominantly upon chemical evidence such as their very low basicity.[19]

[19] For a thorough discussion of the molecular properties which may be functions of (p–d)π conjugation, see E. A. V. Ebsworth in "Organometallic Compounds of the Group IV Elements," Vol. 1, Part 1, A. G. MacDiarmid, Ed., Marcel Dekker, Inc., New York, N. Y., 1968, Chapter 1.

[20] (a) J. B. Lambert, G. F. Jackson, III, and D. C. Mueller, *J. Amer. Chem. Soc.*, **90**, 6401 (1968); (b) J. B. Lambert, G. F. Jackson, III, and D. C. Mueller, *ibid.*, **92**, 3093 (1970).

[21] The barrier ($E_a = 26$ kcal/mol) in 1,2-dimethyl-1,2-diphenyldiphosphine[20a] reflects a decrease of *ca.* 6 kcal/mol relative to the dialkylarylphosphines.[5]

[22] W. B. Farnham, A. W. Herriott, and K. Mislow, *J. Amer. Chem. Soc.*, **91**, 6878 (1969).

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Bis(O-fluorosulfato)tetrafluoroxenon(VI) and Bis(O-fluorosulfato)difluoroxenon(IV)

Sir:

The ability of xenon to form compounds with ligands other than fluorine or oxygen has been demonstrated recently for Xe(II).[1–4] There have, however, been no reports of similar compounds for Xe(VI) and Xe(IV).[5] We have prepared $F_4Xe(OSO_2F)_2$ and $F_2Xe(OSO_2F)_2$ from XeF_6 and XeF_4 by reactions with fluorosulfuric acid at −25 to −5°. The reactions occur almost quantitatively when carried out stoichiometrically according to the equations (mmol)

$$XeF_6\ (0.95) + 2HOSO_2F\ (1.87) \longrightarrow F_4Xe(OSO_2F)_2\ (0.93) + 2HF\ (1.8)$$

$$XeF_4\ (0.75) + 2HOSO_2F\ (1.5) \longrightarrow F_2Xe(OSO_2F)_2\ (0.71) + 2HF\ (1.5)$$

Only traces of O_2, $S_2O_5F_2$, and $S_2O_6F_2$ were observed when the HF was removed at −5° after a 1 day reaction time. The progress of the reaction was monitored by observing the disappearance of the solid xenon fluorides in the Kel-F reaction tubes.

The new compounds are yellow-green liquids at 22°. They tend to form glasses at low temperature, but have been observed to crystallize slowly to white solids at −78°. Both compounds are thermally unstable

[1] M. Eisenberg and D. D. DesMarteau, *Inorg. Nucl. Chem. Lett.*, **6**, 29 (1970).

[2] N. Bartlett, M. Wechsberg, F. O. Sladky, P. A. Bulliner, G. R. Jones, and R. D. Burbank, *Chem. Commun.*, 703 (1969).

[3] F. Sladky, *Angew. Chem.*, **81**, 330 (1969).

[4] F. Sladky, *ibid.*, **81**, 536 (1969).

[5] The compound $Xe(O_2CCF_3)_4$ was reported by A. Iskraut, R. Taubenest, and E. Schumacher, *Chimia*, **18**, 188 (1964), but this claim has been disputed: J. G. Malm and E. H. Appelman, *At. Energy Rev.*, **8**, 38 (1969).

and a sample of $F_4Xe(OSO_2F)_2$ ($\sim$1 mmol) was decomposed after 2 weeks at 22° to the peroxide $S_2O_6F_2$ and XeF_4. Bis(O-fluorosulfato)difluoroxenon(IV) is more stable, but the decomposition is more complex, forming $S_2O_6F_2$, Xe, and XeF_4.

$$F_4Xe(OSO_2F)_2\ (0.90) \longrightarrow XeF_4\ (0.85) + S_2O_6F_2\ (0.94)$$

$$F_2Xe(OSO_2F)_2\ (1.0) \longrightarrow XeF_4\ (0.50) + Xe\ (0.45) + S_2O_6F_2\ (1.0)$$

This decomposition is similar to the Xe(II) fluorosulfates,[1,2] and the decomposition products were easily identified by their infrared spectra.[6-8] The decomposition of $F_4Xe(OSO_2F)_2$ provides a very convenient method for the formation of pure XeF_4, which is the most difficult of the xenon fluorides to obtain in high purity.[9,10]

The liquid compounds are extremely reactive and are comparable to XeF_6 in their reactivity. They react instantly with AgCl, forming a dark brown solid. The only suitable solvent we have found to date is $S_2O_6F_2$. The compounds are insoluble in *n*-perfluorohexane, slightly soluble with reaction in CCl_4, and react explosively with CH_3CN. They darken Kel-F No. 3 polymer oil but are unreactive toward polychlorofluoroethylene waxes and polyperfluoroether liquids. Their reaction with water is violent, and preliminary results indicate that the reactions parallel those of XeF_6 and XeF_4.

Caution! Both $F_4Xe(OSO_2F)_2$ and $F_2Xe(OSO_2F)_2$ can form the highly explosive xenon trioxide with water and extreme care must be used in handling these compounds.

The ^{19}F nmr obtained in Kel-F tubes at 35° on a Varian A56-60 instrument showed the following adsorptions relative to external $CFCl_3$: $F_4Xe(OSO_2F)_2$, δ 129 (XeF) and 45 (SF); $F_2Xe(OSO_2F)_2$, δ 130 (XeF) and 46 (SF). The relative areas as shown by integration were 2.1:1.0 for $F_4Xe(OSO_2F)_2$ and 1.0:1.0 for $F_2Xe(OSO_2F)_2$. The observed chemical shifts for XeF show large changes compared to XeF_4 and XeF_6, while the SF resonance is very close to that of other covalent fluorosulfates.[11-13] The presence of small amounts of $S_2O_6F_2$ was evident by an adsorption at δ 44.8.[13,14]

The nmr resonances were broad at 35.0° with widths at half-height of about 3 Hz for SF and 25 Hz for XeF in both compounds. A variable-temperature study down to −70° resulted in further differential broadening of the lines with no resolvable coupling between the different fluorines. At −70° the samples were essentially solid. At −60° the XeF resonances were weak and broad and the SF absorptions were broadened to 26 and 9 Hz, respectively, for $F_4Xe(OSO_2F)_2$ and $F_2Xe(OSO_2F)_2$. When the samples were run as 50% solutions in $S_2O_6F_2$ further line broadening was observed. The mechanism for the line broadening of the XeF and SF resonance is unclear and the question is under study.

The Raman spectra of the samples contained in 1/8-in. o.d. Kel-F tubes were taken on a Spex 4001 helium–neon laser instrument employing the 6328-Å line for excitation. The spectra recorded over the range of 300–1600 cm^{-1} show two very intense bands at 666 and 610 cm^{-1} for $F_4Xe(OSO_2F)_2$ and 670 and 614 cm^{-1} for $F_2Xe(OSO_2F)_2$. Xenon hexafluoride, $OXeF_4$, and XeF_4 show similar vibrational spectra.[8,15] These bands can be assigned to XeF stretching in the compounds. They are both shifted compared to the parent XeF_6 and XeF_4, with $F_2Xe(OSO_2F)_2$ showing the largest change. Several other weak bands similar to those observed for liquid $S_2O_6F_2$ run under the same conditions were also observed.

Attempts to obtain infrared spectra of the compounds have been frustrated by the high reactivity of the compounds and their low vapor pressure. No suitable ir solvent has been found and attempts to observe the gas-phase spectra at 35° are inconclusive.

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A Ruthenium Complex Having Both Linear and Bent Nitrosyl Groups

Sir:

The addition of small molecules to transition metal complexes and oxidative addition reactions in general have been extensively studied during the last 8 years,[1] with several very recent reports focusing on the oxidative addition properites of nitrosyl complexes of second and third transition series elements.[2-7] The recent communication of the synthesis of a ruthenium(0) nitrosyl analog[6] of the well-studied Ir(I) complex named after Vaska, $IrCl(CO)(P(C_6H_5)_3)_2$,[8] together with the established molecular geometry of the NO^+ adducts of $IrX(CO)(P(C_6H_5)_3)_2$ (X = Cl, I)[4,9,10] prompted us to consider the possibility of obtaining a complex having both linear and bent coordinated nitrosyl groups. We now wish to report the synthesis and structural

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