green crystals of bis(imidotetramethyldithiodiphosphino-S,S)nickel(II), $[SPMe_2NPMe_2S]_2Ni^{II}$. *Anal.* Calcd for $C_8H_{24}N_2NiP_4S_4$: C, 20.92; H, 5.28; N, 6.10; mol wt, 459.15. Found: C, 20.80; H, 5.48; N, 5.76; mol wt, 402 ($CHCl_3$). The complex (mp 194–195°) is paramagnetic both in the solid state (3.40 BM) and in solution (3.20 BM: $CHCl_3$) and has an optical spectrum typical of that found for tetrahedral nickel-(II) chelate complexes:[1–5] λ_{max} (cm^{-1}) 14,000, 12,750, 10,700, 8700; ϵ (l. $mole^{-1}$ cm^{-1}) 170.7, 240, 55.9, 34.0 in CH_2Cl_2 solution.

The complex crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ (C_{2h}^5; no. 14) with a = 15.437, b = 8.796, c = 16.237 Å, β = 106.35°, V = 2115.6 $Å^3$, ρ_{obsd} = 1.40 ± 0.02 g cm^{-3}, and ρ_{calcd} = 1.44 g cm^{-3} for M = 459.15, Z = 4. A total of 1791 independent reflections, representing complete three-dimensional data ($\sin \theta_{max} = 0.42$; Mo Kα radiation) were collected with a Buerger automated diffractometer. The structure was solved by direct methods, Sayre's equation being applied[10] to the 159 reflections with $E \geq 1.5$. Of the eight possible combinations of phase for the three starting reflections, one set achieved internal consistency in three iteration cycles with a consistency index of C = 0.945. An F-map based on these phases clearly showed the NiS_4P_4 fragment of the molecule. Subsequent Fourier and least-squares refinement processes have led to the location of all nonhydrogen atoms, the present discrepancy index being

$$R_F = \frac{\sum||F_o| - |F_c||}{\sum|F_o|} = 12.6\%$$

Refinement is continuing.

The over-all geometry of the molecule is shown in Figure 1. The central nickel atom is tetrahedrally coordinated by the four sulfur atoms of the two chelate rings. There is a slight flattening of the coordination tetrahedron: the intraligand angles are S(1)–Ni–S(2) = 107.9 (2)° and S(3)–Ni–S(4) = 109.1 (3)°, while other angles at the nickel are S(1)–Ni–S(3) = 106.2 (2)°, S(2)–Ni–S(4) = 105.9 (3)°, S(1)–Ni–S(4) = 111.4 (3)°, and S(2)–Ni–S(3) = 116.3 (3)°. The rings are markedly nonplanar; the dimensions and orientation of the P–N–P backbone are remarkably similar to those found in imidotetraphenyldiphosphinic diamide chloride.[11] The phosphorus atoms are each approximately tetrahedral and the disposition of the methyl groups clearly does not preclude the adoption of a planar NiS_4 structure. Nickel–sulfur distances in the present structure range from 2.270 (7) to 2.306 (7) Å, averaging 2.291 Å, slightly longer than the distances found in *planar* NiS_4 chelates (2.10–2.24 Å).[6] The average P—S distance of 2.033 Å is intermediate between that expected for P═S (1.94–1.96 Å) and for P—S (2.08–2.19 Å).[12]

The single most important feature of the present molecule is undoubtedly the tetrahedral configuration about the nickel atom. The significance of this result and the utility of imidodiphosphinates as ligands is even more apparent when changes in both the donor set and the substituents are made. Thus, the purple complex bis(imidotetraphenyldiiminodiphosphinato-NH,NH)-nickel(II), $[NHPPh_2NPPh_2NH]_2Ni^{II}$, which has a $Ni(-NH)_4$ core and bulky substituents, is diamagnetic and presumably planar. *Anal.* Calcd for $C_{48}H_{44}N_6NiP_4$: C, 64.95; H, 5.01; N, 9.47; mol wt, 887.57. Found: C, 65.67; H, 4.91; N, 9.20; mol wt, 795 ($CHCl_3$); mp 201–203°; λ_{max} (cm^{-1}) 15,000, 12,120, 11,420, 6570; ϵ (l. $mole^{-1}$ cm^{-1}) 98.9, 3.6, 4.3, 4.7.

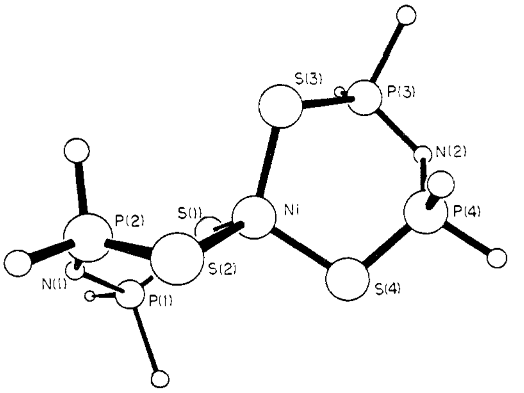

Figure 1. The stereochemistry of $[SPMe_2NPMe_2S]_2Ni^{II}$. Average distances and angles are: Ni–S = 2.291 ± 0.014 Å, S–P = 2.033 ± 0.008 Å, P–N = 1.606 ± 0.035 Å, P–Me = 1.820 ± 0.042 Å; Ni–S–P = 104.2 ± 1.3°, S–P–N = 116.7 ± 1.6°, P–N–P = 127.3 ± 1.5°, S–P–Me = 108.2 ± 1.0°, Me–P–Me = 105.9 ± 1.0°, Me–P–N = 109.6 ± 1.5°.

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The Mechanism of a Metal-Catalyzed Cycloaddition Reaction

Sir:

Little is known about why transition metals are effective in catalyzing cycloaddition reactions. For example, rhodium on carbon[1] and various coordination complexes of rhodium[2] transform I into II, but whether the carbon–carbon bonds are broken and formed in the same[2,3] or in subsequent[1,4] steps is unclear. For cycloaddition reactions in general, it is difficult to establish

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[2] H. C. Volger, H. Hogeveen, and M. M. P. Gaasbeek, *ibid.*, 91, 218 (1969).

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[4] Related systems: (a) T. J. Katz and N. Acton, *Tetrahedron Lett.*, 2601 (1967); (b) T. J. Katz, N. Acton, and I. C. Paul, *J. Am. Chem. Soc.*, 91, 206 (1969); (c) G. Wilke, *Angew. Chem. Intern. Ed. Engl.*, 2, 105 (1963); (d) G. Wilke *et al.*, *ibid.*, 5, 151 (1966).

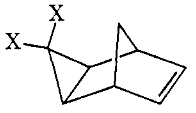
Table I. Experimental Determination of the Value of F

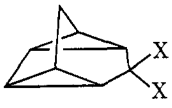
Run	Ratio of I-d_2/I By weighing[a]	By mass spectrometry[b] Before reaction	 After reaction	% reaction	Ratio of II-d_2/II[b,c]	F[d,e]
1	0.992 ± 0.02		1.094 ± 0.010	13	1.80 ± 0.04	1.88 ± 0.06
2	1.003 ± 0.02	1.012 ± 0.015		11	1.72 ± 0.05	1.77 ± 0.07
3	1.000 ± 0.02	1.010 ± 0.008	1.059 ± 0.008	12	1.71 ± 0.03	1.77 ± 0.05
4	1.000 ± 0.02	1.027 ± 0.008	1.050 ± 0.008	10	1.74 ± 0.03	1.79 ± 0.06
					Av	1.80 ± 0.10[f]

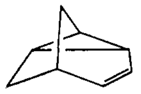
[a] The major source of error is that of determining the purity of the samples. The sample of I contained (by nmr) no detectable IV, but the detection limit is about 2%. By glpc it contained 1 ± 0.5% other materials. The sample of I-d_2 contained (by nmr of the IV formed by reaction with catalyst) 0.4 ± 0.3% deuterated IV, and by glpc 0.4 ± 0.3% other materials. Weighing errors are negligible. Account was taken of isotopic purity, and the error of the mass spectrometric analysis introduces errors of less than 0.6%. [b] The mass spectrometric errors are estimated from standard deviations in the measured peak heights. [c] Systematic errors that would be introduced if the M − 1 peak were appreciable are negligible. The intensity of the peak at *m/e* 105 was ≤1% that at *m/e* 106. [d] The ratio of I-d_2/I used is that in the first column. [e] Determined using eq 2 of M. J. Goldstein and G. L. Thayer, Jr., *J. Am. Chem. Soc.*, **87**, 1933 (1965). We are grateful to Professor Goldstein for suggesting its use. [f] The error is the standard deviation in F.

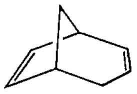
this difference experimentally.[5] We report here a method showing that in the metal-catalyzed transformation of I to II the rate-determining step produces not II, but an intermediate from which II is formed.

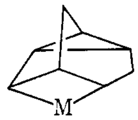
Catalytic amounts (1.3 mole %) of tris(triphenylphosphine)rhodium(I) chloride at 90° for 2 hr convert I not only into II but also into III and IV. These products are in the ratio 32:62:6, and under the reaction conditions the products do not change.[1] The transformation of I to III (and II also) has been shown to be intramolecular.[1] Because similar amounts of II and III are produced, the following experiment could be performed. Approximately equal amounts of the dideuterated hydrocarbon I-d_2 and undeuterated hydrocarbon I could be combined with the catalyst for a short time, so as to convert only a small amount of the starting material into products. The product II could then be isolated and its ratio of dideuterated and undeuterated material analyzed. If II is formed from I in a reaction involving concerted formation of the carbon–carbon bonds and independent of the formation of III, then the factor F in eq 1 must differ little from unity. At most


I, X = H
I-d_2, X = D


II, X = H
II-d_2, X = D


III


IV


V, M = RhCl[$(C_6H_5)_3P$]$_n$

$$\frac{d[\text{II-}d_2]}{d[\text{II}]} = F\frac{[\text{I-}d_2]}{[\text{I}]} \qquad (1)$$

there should be a secondary deuterium isotope effect, which precedents indicate would be minuscule. A reasonable estimate is $F = 0.96$.[6]

In contrast, if, as in eq 2, the products II and III are

$$\begin{tikzcd} & & \text{II} \\ \text{I} \arrow[r, "k_1", "\text{slow}"'] & \text{X} \arrow[ur, "k_2"] \arrow[dr, "k_3"] & \\ & & \text{III} \end{tikzcd} \qquad (2)$$

formed from a common intermediate (X, possibly of structure V)[1] that is itself formed from I in the rate-determining step, then eq 3 and 4 obtain, where the superscript D refers to the rate constants for the deuterated

$$\frac{d[\text{II-}d_2]}{d[\text{II}]} = \left(\frac{k_1{}^{\text{D}}}{k_1}\right)\left(\frac{k_2{}^{\text{D}}}{k_2}\right)\left(\frac{k_3}{k_3{}^{\text{D}}}\right)\left(\frac{1 + k_2/k_3}{1 + k_2{}^{\text{D}}/k_3{}^{\text{D}}}\right)\frac{[\text{I-}d_2]}{[\text{I}]} \qquad (3)$$

$$= \left(\frac{k_1{}^{\text{D}}}{k_1}\right)\frac{(1 + k_3/k_2)}{(1 + k_3{}^{\text{D}}/k_2{}^{\text{D}})}\frac{[\text{I-}d_2]}{[\text{I}]} \qquad (4)$$

compounds. The first two factors on the right-hand side of eq 3 should be approximately 1,[7] the third should be much larger than 1 (a primary isotope effect),[9] and, if k_2 is not much larger than k_3, then, even though no carbon–hydrogen bonds are broken during the formation of II, the ratios of the dideuterated and undeuterated II and the dideuterated and undeuterated I from which they are formed should differ greatly: the factor F in eq 1 should differ appreciably from unity. The value of F can be calculated as follows. If eq 2 is correct, then k_3/k_2 can be determined by glpc analysis of the ratio of the products formed from I, and $k_3{}^{\text{D}}/k_2{}^{\text{D}}$ from the ratio of the products formed from I-d_2. The experimentally determined ratios after 5–12% reaction at 60° are $k_3/k_2 = 1.74 \pm 0.09$ and $k_3{}^{\text{D}}/k_2{}^{\text{D}} = 0.60 \pm 0.03$. If $k_1{}^{\text{D}}/k_1$ is assumed to be 1,[7] then F is calculated (eq 4) to be 1.71 ± 0.06.

The experiment was performed as follows. Mixtures of I-d_2 and I were prepared and the ratio of I-d_2 to I determined by weighing and carefully mixing samples of I with samples of I-d_2 containing 96.6 ± 0.5% dideuterated material.[10] The ratio of I-d_2 to I was also determined by mass spectrometric analysis before and after reaction.[10] The mixtures were allowed to react with tris(triphenylphosphine)rhodium(I) chloride (1.3 mole %) at 60° for 0.5 hr, whereupon 10–13% of the starting hydrocarbon had been converted to products.

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(5) J. Sauer, *Angew. Chem. Intern. Ed. Engl.*, **6**, 16 (1967).

(6) Substitution of deuterium for hydrogen β to a center undergoing homolytic decomposition slows the rate by about 2% per deuterium.[7] If the isotope effect is larger, because in I-d_2 the deuteriums are β to two centers undergoing change or because the effect should be larger as in heterolytic decompositions,[8] the value of F will be even smaller.

(7) T. Koenig and R. Wolf, *J. Am. Chem. Soc.*, **91**, 2574 (1969), and references therein.

(8) A. Streitwieser, Jr., and G. A. Dafforn, *Tetrahedron Lett.*, 1263 (1969), and references therein.

(9) L. Melander, "Isotope Effects on Reaction Rates," The Ronald Press Co., New York, N. Y., 1960.

(10) K. Biemann, "Mass Spectrometry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, Chapter 5.

II was isolated by glpc and the ratio of II-d_2 to II determined by mass spectrometric analysis.[10] The analysis was calibrated using weighed and carefully mixed samples of II and II-d_2 (the latter containing 97.2 ± 1.0% dideuterated material as determined by mass spectrometry).[11]

The results of four experiments are given in Table I. Thus factor F is determined experimentally to be 1.80 ± 0.10. This is remarkably similar to the independently determined value required by the theory of eq 2–4. More significantly, the value differs by many times the error of the analysis from the value of unity required if the reactions yielding II and III were independent and the former concerted.

Acknowledgment. We are grateful to the National Science Foundation (NSF GP-7809) for its support.

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[12] P. K. Freeman, D. G. Kuper, and V. N. M. Rao, *Tetrahedron Lett.*, 3301 (1965).

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Fluoride Ion Transfer Reactions. Negative Ion–Molecule Reactions of SF_6^-

Sir:

Sulfur hexafluoride is remarkably inert chemically, a fact which appears to be the result of kinetic rather than thermodynamic stability.[1] Compounds containing the PF_6^- and SiF_6^{2-} ions, which are isoelectronic with SF_6, are well known. The formation of SF_6^- in gaseous SF_6 by resonance electron capture[2] of thermal electrons at 0.08 eV is often used to calibrate the electron energy scale in studies of gaseous negative ions produced in the mass spectrometer. However, no compounds containing the SF_6^- ion have been identified in condensed phases.

Recent descriptions[3] of the electronic distribution in SF_6 suggest that a net shift of electron density to the fluorine atoms occurs. A consideration[4] of the distribution of electrons in SF_6^- revealed that the unpaired electron could be incorporated in a molecular orbital where contributions from sulfur atomic orbitals were predominant. These conclusions lend support to the notion that electron density on fluorine is significant.

Demitras and MacDiarmid[5] have reported the reactions of sodium with SF_6 in liquid ammonia and in diphenylethylene glycol–dimethyl ether solutions. It was suggested that SF_6^- was formed in a rate-controlling step by electron transfer from the diphenyl radical ion, and that the reaction of SF_6^- involved elimination of F^- and formation of the SF_5 radical. From these results it appears likely that SF_6^-, which is itself a radical ion, might be reactive in the gas phase under conditions in the mass spectrometer where single collision events could occur. In this communication we wish to report that a reaction process similar to that suggested[5] in the condensed phase has been observed in the gas-phase reaction of SF_6^- with PF_5 and with PF_3.

Negative ions are formed in the mass spectrometer[6] at low electron energies (0–10 eV) by resonance electron capture reactions (reaction 1) or by dissociative electron capture processes (reaction 2). Dissociative ionization reactions or ion-pair processes may occur at electron energies sufficient to produce a positive and a negative ion simultaneously (reaction 3). At electron energies above about 10 eV where positive ions are formed, it is noted[7] that parent negative ions are formed by capture of secondary electrons. In this study, advantage is taken of the fact that at low electron energies the primary ion or ions in the ionization chamber may be controlled by selecting an electron energy where resonance capture reactions occur.

$$AB + e^- \longrightarrow AB^- \tag{1}$$

$$AB + e^- \longrightarrow A + B^- \tag{2}$$

$$AB + e^- \longrightarrow A^+ + B^- + e^- \tag{3}$$

The predominant negative ions formed in SF_6 at low energies are SF_6^- and SF_5^- with maxima in the electron capture ionization efficiency curves at 0.08 and 0.15 eV, respectively.[2] The shapes of the curves for these ions depend on the thermal distribution on the electron beam and on space charge effects which occur at high filament emission currents. In the results reported here, the energy distribution was always measured at low emission currents and low filament currents with SF_6 only in the ionization chamber. No significant changes in the distribution were observed upon addition of the reactant gas PF_5 or PF_3. Furthermore, the position of the maximum in the resonance capture process varied less than about 0.15 eV for the pressure range studied (0.2–2.2 μ).

The reactions were studied by the addition of PF_5 (or PF_3) and SF_6 to the ionization chamber from a dual inlet system. With PF_5 (or PF_3) in the ionization chamber at a known pressure, SF_6 was added and the resonance capture ionization efficiency curves determined for SF_6^-, SF_5^-, and any secondary ions which appeared in the spectrum. The significant ions detected at low energies in these experiments were PF_6^- and PF_4^- from mixtures containing SF_6 and PF_5 or PF_3, respectively. The reverse procedure, addition of PF_5 or PF_3 to SF_6, gave identical results. Neither PF_6^- nor PF_4^- was detected in pure PF_5 or PF_3 at high pressures.

Probable reactions to explain the occurrence of PF_6^- and PF_4^- are (using PF_5 as the example)

$$SF_6^- + PF_5 \longrightarrow PF_6^- + SF_5 \tag{4}$$

$$SF_5^- + PF_5 \longrightarrow PF_6^- + SF_4 \tag{5}$$

$$SF_6^-(SF_5^-) + PF_5 + M \longrightarrow PF_6^- + SF_5(SF_4) + M \tag{6}$$

Reactions 4 and 5 are typical bimolecular processes involving the formation of the secondary negative ion and neutral SF_5 or SF_4, respectively. An alternate explanation of the formation of PF_6^- (or PF_4^-) involves collisional stabilization of the secondary ion by a bath molecule, either SF_6 or PF_5 (PF_3). Reaction 6 is eliminated since a plot of the ratio of secondary to primary ion current varies linearly with pressure.[8] Since PF_6^- (or

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[4] K. A. R. Mitchell, *Chem. Commun.*, 368 (1969).

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[6] R. W. Kiser, "Introduction to Mass Spectrometry," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1965, p 192.

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