tively, and rearrangement to **5**. Leakage of **8** to **10** would lead to **6** and **7** through **11**.[18,19]

If formed, **12**[5] would not be expected to survive the photolysis conditions used for **1**. Irradiation[3] of a 0.0029 M solution of **12** in 50% aqueous methanol containing 0.0042 M methanesulfonic acid yielded (GLC analysis, *n*-octadecane internal standard) **4a** (26.2%), **6** (0.5%), **7** (2.1%), and no recovered **12**.[21,22] However, in photolyses of **1**, **12** is most likely an intermediate in a minor pathway to **4**. As noted, a small amount of deuterium was lost on going from **1b** to **4**, and this is consistent with the intermediacy of a deuterated analogue of **12** produced from **10b** and/or **11**.[23]

The nature of the interaction between excited 3,5-dimethoxyphenyl and the methanesulfonate group is unknown but will be the subject of further investigation. As noted, it is also unknown whether **8** is an intermediate or simply a transition state, but study of an appropriate chiral system may answer this question.

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(2) Photosolvolysis of 2-(4-hydroxy-3,5-di-*tert*-butylphenyl)ethyl *p*-toluenesulfonate in methanol has been reported, V. B. Vol'eva, V. V. Ershov, and A. A. Volod'kin, *Izv. Akad. Nauk SSSR*, *Ser. Khim.*, 1207 (1974). However, with this system it is not clear whether photosolvolysis is initiated by excitation of the aromatic leaving group or 2-aryl group.

(3) For each run 250 ml of solution was degassed with purified nitrogen for 40 min prior to and during irradiation for 40.0 min with a 450-W Hanovia lamp through Vycor.

(4) Methanesulfonate **1a,** bp 145 °C (0.02 mm) (Kugelrohr), was prepared from **2a** by an established procedure, R. K. Crossland and K. L. Servis, *J. Org. Chem.*, **35,** 3195–3196 (1970).

(5) The ^{1}H NMR, ir, and mass spectra were consistent with the structural assignment, and carbon and hydrogen analyses were within 0.40% of theory.

(6) (a) S. Winstein and R. Heck, *J. Am. Chem. Soc.*, **76,** 4801–4806 (1956); (b) J. P. Brown, N. J. Cartwright, A. Robertson, and W. B. Whalley, *J. Chem. Soc.*, 859–867 (1949); (c) H. S. Aaron and C. P. Ferguson, *J. Org. Chem.*, **33,** 684–689 (1968).

(7) (a) Figures are actual yields based on materials isolated from the crude product mixture by column chromatography on silica gel with ether–hexane. (b) No additional material ($>\sim1\%$) other than polymer was detected. (c) Methanesulfonic acid would have been lost on workup.

(8) High resolution mass spectrometry gave $M\cdot^+ = 164.083\ 23$; calculated for $C_{10}H_{12}O_2$, 164.083 73.

(9) Controls demonstrated the absence of thermal solvolysis of **1a** during photolysis and isolation.

(10) The ethylene protons of benzocyclobutene exhibit a chemical shift of δ 3.14 (CCl_4): G. Fraenkel, Y. Asahi, M. J. Mitchell, and M. P. Cava, *Tetrahedron*, **20,** 1179–1184 (1964).

(11) H. R. Williams and H. S. Mosher, *J. Am. Chem. Soc.*, **76,** 2984–2987 (1954).

(12) There is no evidence in the uv spectrum (50% aqueous methanol) of **1a** for ground state interaction of the aryl and methanesulfonate groups.

(13) Reduction of methyl 3,5-dimethoxyphenylacetate[14] with $LiAlD_4$ (99% D) gave **2b**, which was converted[4] to **1b**.

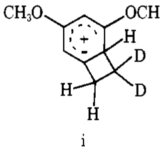
(14) E. Hardegger, W. Rieder, A. Walser, and F. Kugler, *Helv. Chim. Acta*, **49,** 1283–1290 (1966).

(15) For each compound analysis was based on flat-topped peaks of the molecular ion group at 12 eV.

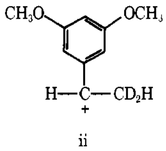
(16) In the spectrum of **5**, singlets in a ratio of 2.4:1 were observed at δ 3.03 and 3.18, respectively. At present it is not known which is the major isomer. However, in view of that fact than an almost equal isomer distribution was obtained for **2** and for **3** from **1b**, it is reasonably assumed that **5b** is the major isomer for purposes of mechanistic discussion.

(17) A control demonstrated that 1-(3,5-dimethoxyphenyl)ethyl methanesulfonate, if produced by a return process with **11**, would have decomposed completely during product isolation if not during photolysis.

(18) An alternative mechanism is formulated by substitution of ions i and ii for free radical **9**. The former ion could result along with **8** from the initial interaction of excited aryl group with methanesulfonate and would be responsible for the excess of **5b** over **5c**. Ion ii could result from hydride transfer concomitant with ionization, and its reduction (see below) would lead to **4b**.



i



ii

(19) Thermal solvolyses of 2-(3,5-dimethoxyphenyl)ethyl *p*-bromobenzenesulfonate,[6a] and its deuterated analogue, 2-(3,5-dimethoxyphenyl)ethyl-*1,1-d*$_2$ *p*-bromobenzenesulfonate,[20] have been reported; **4** and **5** and products analogous to **6** and **7** were not detected. Acetolysis and formolysis of deuterated sulfonate gave ester products containing only partially scrambled deuterium label.

(20) C. C. Lee and L. Noszkó, *Can. J. Chem.*, **44,** 2481–2489 (1966).

(21) By GLC only a few other unknown minor products ($\leq 4\%$) of comparable volatility were detected.

(22) (a) Photochemical reduction of styrenes in methanol and accompanying addition have been reported. For example, see P. J. Kropp, *J. Am. Chem. Soc.*, **95,** 4611–4619 (1973), and references therein. (b) A control demonstrated the absence of thermal reaction.

(23) (a) Irradiation[3] of a 0.0024 M solution of **6** in 50% aqueous methanol containing 0.0044 M methanesulfonic acid yielded (GLC analysis, *n*-octadecane internal standard) **4a** (33.1%), **7** (1.2%), and **6** (0.6%).[21] Likewise, irradiation[3] of a 0.0023 M solution of **7** in the same solvent containing 0.0047 M methanesulfonic acid yielded **4a** (34.8%), **6** (0.5%), and **7** (0.8%).[21] These results are consistent with photoinduced reduction of **12** since reductions of **6**, **7**, and **12** presumably proceed through **11**, which abstracts hydride from methanol. (b) Irradiation[3] of a 0.0023 M solution of **2a** in 50% aqueous methanol containing 0.0045 M methanesulfonic acid yielded (GLC analysis, *n*-octadecane internal standard) recovered **2a** (64.7%) and no **3**, **4**, **5**, **6**, or **7**.[21]

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Solution Structure and Ligand Exchange in the Five-Coordinate Molecular Complexes $NiX_2(PMe_3)_3$

Sir:

Synthesis and determination of the stereochemistries of five-coordinate metal complexes have been subject to a considerable increase of interest during the last decade, but few studies have reported the solution structures of these complexes or kinetic studies of five-coordinate metal centers.[1-7] We wish to present evidence for the solution structure and the ligand exchange mechanism in $NiX_2(PMe_3)_3$ complexes, obtained from $^{31}P\{^1H\}$ NMR spectroscopy.

In earlier papers we have shown[7] that trimethylphosphine Ni(II) complexes, $NiX_2(PMe_3)_3$ (X = CN, Cl, Br, I), are examples of five-coordinate d^8 complexes. They are reasonably stable as crystalline solids, but labile in solution, resulting in different species depending on the concentration, the nature of the solvent, and the presence of excess ligand. Thus the solution structures were not well understood.[5,7]

Figure 1 shows ^{1}H noise decoupled Fourier transform ^{31}P NMR spectra of solutions of $NiX_2(PMe_3)_3$ (X = CN, Cl, Br, I) in 1:1 CH_2Cl_2/CD_2Cl_2 solutions at −75 °C. The slow exchange limit spectra are obtained for the four complexes. They are among the very scarce five-coordinate complexes which exhibit stereochemical rigidity at not too low a temperature.[8]

At −75 °C, the solution spectra present an A_3 pattern for X = CN and an A_2B pattern for X = Cl, Br, and I. These results are consistent with the two trigonal bipyramid (= TBP) configurations: *trans*-TBP (X = CN) and *cis*-TBP (X = Cl, Br, I) previously reported for these complexes.[7] But NMR spectroscopy alone cannot determine unambiguously the geometry of the NiX_2L_3 species in solution for X = halide, since the same A_2B pattern is expected for the cis trigonal bipyramidal and square pyramidal geometries. Nevertheless, the existence of only one isomer in CH_2Cl_2 solution is clearly demonstrated (at least in concentrations detectable by NMR).

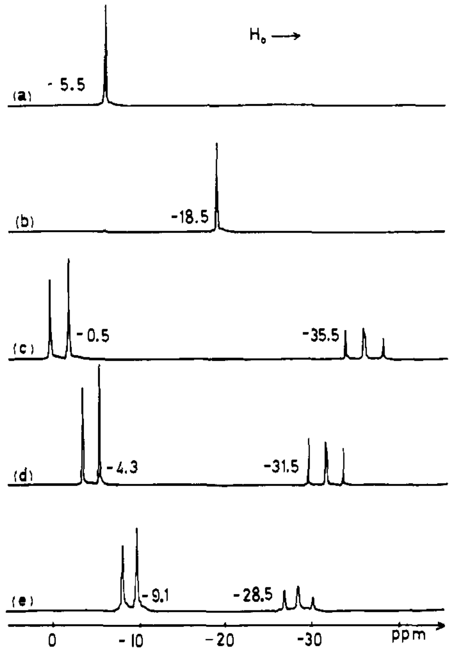

Figure 1. $^{31}P\{^1H\}$ FT NMR spectra at 36.43 MHz of (a) $Ni(CN)_2(PMe_3)_2$, 0.1 M, at −75 °C; (b) $Ni(CN)_2(PMe_3)_3$, 0.1 M, at −75 °C; (c) $NiCl_2(PMe_3)_3$, 0.05 M, at −90 °C (J_{PP} = 78.8 Hz); (d) $NiBr_2(PMe_3)_3$, 0.05 M, at −85 °C (J_{PP} = 70.3 Hz); (e) $NiI_2(PMe_3)_3$, 0.05 M, at −75 °C (J_{PP} = 58.8 Hz) in 1:1 CH_2Cl_2–CD_2Cl_2 solutions. The external reference is 65% H_3PO_4 (not shown).

As the temperature is increased, intramolecular exchange occurs. Broadening of the lines and the collapse of the doublet and the triplet into a single line are observed and the rate constants increase in the order I < Br < Cl.

At −75 °C, the ^{31}P NMR spectrum of $Ni(CN)_2(PMe_3)_3$ contains a weak singlet (<1%), characteristic of the trans square planar $Ni(CN)_2(PMe_3)_2$ species resulting from the dissociative process, although no free PMe_3 is detected:

$$Ni(CN)_2(PMe_3)_3 \rightleftarrows Ni(CN)_2(PMe_3)_2 + PMe_3$$

Addition of an excess of PMe_3 to a $Ni(CN)_2(PMe_3)_3$ solution shows two singlets due to $Ni(CN)_2(PMe_3)_3$ and free PMe_3, at −75 °C. This complex provides an opportunity to investigate exchange of free and coordinated PMe_3 at five-coordinate d^8 metal centers. We have studied the following two reactions:

$$Ni(CN)_2(PMe_3)_3 + 3{*}PMe_3 \leftrightarrows Ni(CN)_2({*}PMe_3)_3 + 3PMe_3$$

$$Ni(CN)_2({*}PMe_3)_2PMe_3 + Ni(CN)_2(PMe_3)_2 \leftrightarrows Ni(CN)_2({*}PMe_3)_2 + Ni(CN)_2(PMe_3)_3$$

A line shape analysis, as a function of the concentration of the reactants at −20 °C, shows that these processes are first order in $Ni(CN)_2(PMe_3)_3$, and zero order in PMe_3 and $Ni(CN)_2(PMe_3)_3$, respectively. The activation parameters are equal in both cases: $\Delta H^* = +13.7 \pm 0.5$ kcal/mol and $\Delta S^* = +10.4$ eu. For both reactions, we conclude a dissociative mechanism, with $Ni(CN)_2(PMe_3)_2$ acting as an intermediate.

When free PMe_3 is added to the five-coordinate halide complexes, the quantitative formation of a new species occurs with the following stoichiometry:

$$NiX_2(PMe_3)_3 + PMe_3 \overset{-75\ ^\circ C}{\rightleftarrows} NiX_2(PMe_3)_4$$

The product is characterized by a singlet at δ −14.9 ppm for X = Cl, δ −15.8 ppm for X = Br, and δ −18.5 ppm for X = I. When the molecular ratio $PMe_3/NiX_2(PMe_3)_3$ is greater than one, the singlet due to free PMe_3 appears at −61.2 ppm. No other species is detected at this temperature.

An increase of the solution conductivity is observed when the temperature is lowered, indicating the presence of ionic species. For X = Br, the ligand field spectrum recorded under the same conditions of temperature and concentration contains only one symmetrical ligand field band, the ϵ value (~1900) and energy (18 400 cm^{-1}) of which are characteristic of five-coordinate square pyramidal Ni(II) complexes.[9-11] Thus, the presence of only one ^{31}P NMR singlet and one nearly symmetrical ligand field transition favor the square pyramidal complex $[NiBr(PMe_3)_4]Br$, with the halide in the apical position. However, the recent report of the trigonal bipyramidal structure $[NiBr(P(OMe)_3)_4]BF_4$[12] is not consistent with our conclusions.

The very few square pyramidal Ni(II) complexes with monodentate tertiary phosphine ligands reported prompted us to continue structural studies along this line. Ligand exchange studies have also been initiated with a view to obtaining quantitative rate data. It is clear, from the results presented here, that ^{31}P NMR is a useful technique for providing insight into the complicated chemistry of five-coordinate metal complexes containing monodentate phosphine ligands.

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Anion Cryptates: Highly Stable and Selective Macrotricyclic Anion Inclusion Complexes

Sir:

Whereas very many metal cation complexes are known, stable anion complexes of organic ligands are very rare indeed. Spherical cations (e.g., alkali cations) form very stable and selective cryptates where the cation is included in the intramolecular cavity of a macropolycyclic ligand.[1] Similarly, it should be possible to obtain stable and selective anion complexes, anion cryptates, by inclusion into cavities lined with appropriate anion binding sites, i.e., especially sites able to form ionic hydrogen bonds like protonated amines: N^+-H···X^-.

Indeed, halide ions give inclusion complexes, the katapinates,[2] in which the anion is held in the cavity of biprotonated macrobicyclic diamines $^+HN[(CH_2)_n]_3NH^+$ by two hydrogen bonds, ^+N-H···X^-···H-N^+ as confirmed by a recent crystal structure determination.[3] Complexes of small anions with α- and β-cyclodextrins have also been reported.[4]