Table III. Results of Data Fitting with Reagent Dimerization Taken into Account (K_d = 10 mM)

	Acetone	DMSO	2-Propanol	β-Picoline
K_1, mM	4.64	1.39	4.1	7.01
K_2, mM	>120	21.86	40.0	5.75
Δ_1, Hz	784.0	424.0	590.0	178.0
Δ_2, Hz	0	406.0	788.0	252.0
Std, Hz	3.0	2.4	2.4	0.7

and assuming that the dimers do not react with substrate, a new set of adduct dissociation constants and limiting shifts was obtained. The results are summarized in Table III.

It is seen that as far as general trends are concerned the results are only slightly altered compared to those in Table II; for β-picoline still $K_2 < 4K_1$ and $\Delta_1 < \Delta_2$ and for DMSO $\Delta_1 \approx \Delta_2$. The only dramatic change is that acetone appears to be forming practically only 1:1 adducts. This lends further support to our tentative interpretation (*vide supra*) that substrate binding induces a ligand rearrangement around the central ion of the shift reagent molecule and that the new arrangement determines the affinity of the 1:1 adduct toward a second substrate molecule.

Acknowledgment. The assistance of Leonard Feigenbaum, a summer research student, in the early stages of this work, is gratefully acknowledged.

Nickel(II) and Palladium(II) Complexes with Polyfluoroaryl Polydentate Phosphorus–Sulfur Ligands[1-3]

P. Gary Eller,[4] Jeanette M. Riker, and Devon W. Meek*

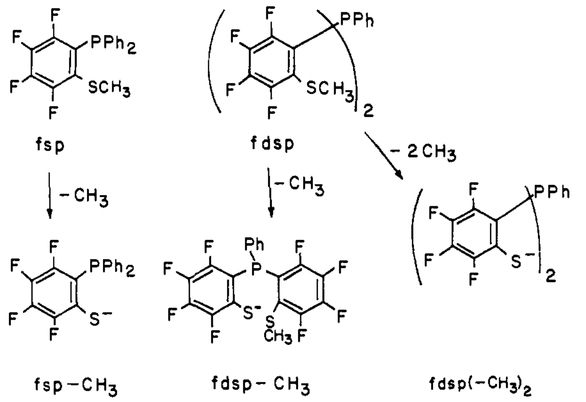
Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210. *Received September 16, 1972*

Abstract: Several different types of nickel(II) and palladium(II) complexes of the polyfluoroaryl ligands 2-methylthio-3,4,5,6-tetrafluorophenyldiphenylphosphine (fsp) and bis(2-methylthio-3,4,5,6-tetrafluorophenyl)phenylphosphine (fdsp) have been prepared and characterized. Conductance, magnetic, nmr, and electronic spectral data indicate that all the palladium complexes, except Pd(fdsp)I_2, possess planar geometries, whereas the nickel complexes have planar, tetrahedral, and octahedral structures. The potentially tridentate ligand fdsp functions as a bidentate ligand in the palladium complexes with only one of the two sulfur atoms coordinated. Several mercaptide complexes have also been prepared by demethylation of the corresponding fsp and fdsp complexes. Complexes of analogous fluorinated and unfluorinated ligands are compared, and the effect of fluorination on the σ- and π-bonding properties of the ligands is discussed.

Unusual coordination numbers and different geometries are often observed when the steric or electronic properties of the polydentate phosphine, arsine, thioether, and selenoether ligands are changed only slightly.[5-8] Unfortunately, both steric and electronic parameters are generally changed simultaneously when one of the substituents on a tertiary phosphine or arsine is varied. In order to separate these two parameters we have chosen sets of ligands whose donor groups and structural features are comparable, but whose coordination properties can be influenced by changing the electronic properties of the molecule. Thus we have been investigating the effect of substituting a fluoroaryl group for an aryl group in aryl and *o*-phenylene polydentate ligands. Since the van der Waals radii of hydrogen and fluorine are very similar (1.2 and 1.35 Å, respectively),[9] steric considerations should be minimal in comparisons of the donor properties of ligands containing comparable aryl and fluoroaryl substituents.

The electronegativity of the fluoroaryl group is higher than that of an aryl group.[10,11] A variety of

[1] The term "fluoro ligand" will be used to refer to a ligand in which some of the hydrogen atoms have been replaced by fluorine, *e.g.*, fsp or fdsp; the term "perfluoro ligand" will be reserved for those cases where *all* hydrogen atoms are replaced by fluorine, *e.g.*, PF_3, $P(CF_3)$, etc. Because the thioethers fsp and fdsp lose one (or two) methyl groups in certain reactions to form complexes nominally of anionic mercaptide ligands, establishing a brief but descriptive acronym for the different forms of the ligands is necessarily somewhat complex. We believe the following nomenclature scheme presents a minimum of confusion and a maximum of brevity.



[2] Presented in part at the 2nd Central Regional Meeting of the American Chemical Society, Columbus, Ohio, June 1970.

[3] Abstracted from the M.S. thesis of J. R., Aug 1970, and from the Ph.D. dissertation of P. G. E., The Ohio State University, Dec 1971.

[4] NDEA Predoctoral Fellow, 1967–1970; Lubrizol Fellow, 1970–1971.

[5] G. Dyer and D. W. Meek, *Inorg. Chem.*, 4, 1398 (1965); **6**, 149 (1967).

[6] G. Dyer, M. O. Workman, and D. W. Meek, *ibid.*, **6**, 1404 (1967).

[7] L. Sacconi, *J. Chem. Soc. A*, 248 (1970).

[8] (a) E. C. Alyea and D. W. Meek, *J. Amer. Chem. Soc.*, **91**, 5761 (1969); (b) P. G. Eller and D. W. Meek, *Inorg, Chem.*, **11**, 2518 (1972).

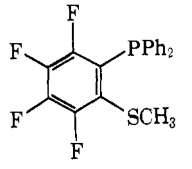
[9] F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Interscience, New York, N. Y., 1966.

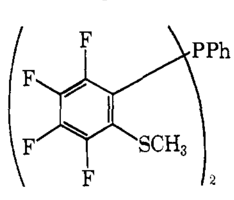
[10] M. G. Hogben and W. A. G. Graham, *J. Amer. Chem. Soc.*, **91**, 283 (1969), and references therein.

[11] M. G. Hogben, R. S. Gay, A. J. Oliver, J. A. J. Thompson, and W. A. G. Graham, *ibid.*, **91**, 291 (1969).

techniques also indicates a net π^*(fluoroaryl) → d_π-(phosphorus) donation from a C_6F_5 ring to the phosphorus atom in pentafluorophenylphosphines.[10-14] The concomitant inductive and mesomeric effects should reduce *both* the σ-donor and the π-acceptor properties of fluoroarylphosphine ligands. However, the problem is not so simple, as our initial electronic spectral studies have shown that the spectrochemical effects of similar fluorinated and unfluorinated phosphine ligands are virtually identical.[8] For example, the "d-d" absorption maxima of the complexes $Ni[C_6H_5P(CH_3)_2]_2X_2$ and $Ni[C_6F_5P(CH_3)_2]_2X_2$ occur at comparable values, even though the coordination properties of the individual ligands are somewhat different.[8a] To evaluate further the effect of fluorine substitution, nickel and palladium complexes of two new fluoro ligands, fsp and fdsp, have been synthesized and characterized; they are reported in this paper.

In addition to influencing the spectrochemical position and the coordination properties of the ligand, fluorination exerts one particularly interesting effect on the coordinated fsp and fdsp ligands. Facile demethylation reactions are observed in solution, leading to complexes of the corresponding mercaptide ligands fsp-CH_3 and fdsp-CH_3.


fsp


fdsp

Experimental Section

Reagents. The detailed syntheses of the fsp and fdsp ligands have been reported previously.[15] All organic solvents and other reagents were the best commercial grades and were used without additional purification. Characterization measurements were performed as previously described.[6,8]

Preparation of the Complexes. **$Ni(fsp)_2Cl_2$.** A slurry of 0.260 g (2 mmol) of anhydrous $NiCl_2$ in 10 ml of acetone was added to a solution of 0.758 g (2 mmol) of the ligand fsp in 10 ml of acetone. The color of the mixture gradually deepened to a deep red and a voluminous pale-green precipitate formed. The mixture was refluxed for 4 hr, then cooled and filtered to give 0.58 g (65% yield) of the pale green, powdery $[Ni(fsp)_2Cl_2]$. The compound was recrystallized from dichloromethane–ethanol. The pale green complex forms red solutions when dissolved in common organic solvents such as chloroform, acetone, and ethanol.

$Ni(fsp)_2Br_2$. The ligand fsp (0.760 g, 2 mmol) was dissolved in 5 ml of dichloromethane and added to a slurry of 0.219 g (1 mmol) of anhydrous $NiBr_2$ in 30 ml of warm 1-butanol. After a few minutes of stirring, the solution became red and a green precipitate formed. After stirring for 3 hr, the mixture was cooled and filtered to give the pale-green $[Ni(fsp)_2Br_2]$. The complex, like the analogous chloro complex, dissolves in acetone, ethanol, dichloromethane, and chloroform to give red solutions.

$Ni(fsp)Br_2 \cdot C_6H_6$. The complex $Ni(fsp)_2Br_2$ was stirred for 15 min in hot benzene. The resultant well-formed, deep red prisms were collected on a filter and washed with cold benzene. This complex is quite sensitive to polar solvents, reverting to the $Ni(fsp)_2Br_2$ complex in the presence of alcohols, water, etc. The benzene solvate was retained even after drying *in vacuo* overnight at room temperature.

$Ni(fsp\text{-}CH_3)_2$. A solution containing 0.421 g (1 mmol) of $NiI_2 \cdot 6H_2O$ in 15 ml of ethanol was added to a solution of 0.760 g (2 mmol) of fsp in 5 ml of dichloromethane. An immediate deep green solution resulted and bright green needles formed when the volume of solvent was reduced to 15 ml. Bright green needles separated when the complex was redissolved in a minimum of dichloromethane and filtered into ethanol.

Alternate Preparations of $Ni(fsp\text{-}CH_3)_2$. A quantity of $Ni(fsp)_2Br_2$ was dissolved in 20 ml of dichloromethane to give a saturated solution. After 2 days exposure to the atmosphere, the red color of the solution had changed to a characteristic deep green color. Reducing the volume of solution gave deep green needles, which were identified by infrared and visible spectroscopy to be the mercaptide complex $Ni(fsp\text{-}CH_3)_2$.

The same mercaptide complex was also prepared by refluxing solutions of $Ni(fsp)_2X_2$ (X = Cl, Br) in ethanol–DMF and by addition of iodide ion to solutions of $Ni(fsp)_2X_2$ (X = Cl, Br, NCS) at room temperature.

$Ni(fsp)_2(NCS)_2$. A solution of 0.366 g (1 mmol) of $Ni(ClO_4)_2 \cdot 6H_2O$ and 0.130 g (2 mmol) of LiNCS in 20 ml of ethanol was added to a solution of 0.760 g (2 mmol) of fsp in 5 ml of dichloromethane. After stirring for 15 min, the resultant brown powder was collected on a filter and washed with ether. Red-brown microcrystals were obtained upon recrystallization of the compound from an ethanol–dichloromethane solution.

$Ni(fsp)(NCS)_2$. The brown $[Ni(fsp)_2(NCS)_2]$ complex was dissolved in a minimum of dichloromethane to give a green solution. After standing for 15 min, a light green powder precipitated. The complex was collected on a filter and washed with light petroleum ether. This green complex rapidly reverts to the brown $[Ni(fsp)_2(NCS)_2]$ species upon contact with polar solvents and moisture.

$Ni(sp)I_2$. To a solution of 0.616 g (2 mmol) of sp in 10 ml of hot ethanol was added a solution of 0.421 g (1 mmol) of $NiI_2 \cdot 6H_2O$ in 10 ml of ethanol. The solution immediately became red and, after sitrring for a few minutes, a brick-red solid precipitated. The red solid was dissolved in dichloromethane and filtered, yielding a deep blue solution. Addition of ether to the filtrate produced intensely colored blue-black needles of $Ni(sp)I_2$. The crystals were collected on a filter and washed with ethanol and ether. All attempts to purify the red-brown precipitate, which immediately forms upon mixing NiI_2 and sp, yielded only $[Ni(sp)I_2]$.

$Ni(sp)_2(NCS)_2$. To a solution containing 0.120 g (1.48 mmol) of NaSCN and 0.272 g (0.74 mmol) of $Ni(ClO_4)_2 \cdot 6H_2O$ in 15 ml of ethanol was added a solution of 0.457 g (1.48 mmol) of sp in 8 ml of dichloromethane; a red-brown precipitate formed immediately. The mixture was stirred for 10 min, filtered, and the precipitate was washed with ether. The solid was air-dried, dissolved in a minimum quantity of dichloromethane, and the brown-orange solution was filtered. A small quantity of pale green solid precipitated when the solution was evaported nearly to dryness. The solid was redissolved by adding a few milliliters of dichloromethane; brown microcrystals (0.30 g, 51% yield) separated on addition of light petroleum ether.

$Ni(sp\text{-}CH_3)_2$. The ligand sp (0.616 g, 2 mmol) and $NiI_2 \cdot 6H_2O$ (0.421 g, 1 mmol) were combined in 10 ml of hot ethanol; a brick-red precipitate formed immediately. A deep green solution resulted when the mixture was refluxed for 1 hr and a bright green solid separated when the solution cooled to room temperature. Green microcrystals of $Ni(sp\text{-}CH_3)_2$ were obtained by recrystallizing the precipitate from a dichloromethane–ethanol mixture.

Methylation of $Ni(sp\text{-}CH_3)_2$ to Form $Ni(sp)I_2$. A solution of 0.3 g of $Ni(sp\text{-}CH_3)_2$ in 20 ml of methyl iodide was refluxed. The initial green color changed rapidly to red during the first 5 min of refluxing and then gradually changed to a deep blue-black color. After refluxing for 2 hr, no further color change was noted and the reaction mixture was evaporated to a dark oil. Addition of ethanol and ether to the oil resulted in formation of deep blue-black crystals, which were identified as the thioether complex $Ni(sp)I_2$ by infrared and visible absorption spectra.

Refluxing an equimolar mixture of $Ni(sp)I_2$ and sp in an ethanol–DMF mixture for 30 min regenerated the characteristic deep green color of $Ni(sp\text{-}CH_3)_2$.

$Ni(fdsp\text{-}CH_3)_2$. A solution of 0.30 g (2 mmol) of NaI and 0.366 g (1 mmol) of $Ni(ClO_4)_2 \cdot 6H_2O$ in ethanol was combined with a solution of 1.00 g (2 mmol) of fdsp in warm ethanol. After refluxing the solution for 15 min and reducing the volume of solvent, a green powder precipitated. The compound was collected on a filter, washed with hot ethanol, and dried *in vacuo*.

---

(12) J. H. Letcher and J. R. VanWazer, *J. Chem. Phys.*, **44**, 815 (1966).

(13) B. M. Brooke, B. S. Furniss, W. K. R. Musgrave, and M. A. Quasem, *Tetrahedron Lett.*, 34, 2991 (1965).

(14) M. Fild, I. Hollenberg, and O. Glemser, *Z. Naturforsch. B*, **22**, 253 (1967).

(15) P. G. Eller and D. W. Meek, *J. Organometal. Chem.*, **22**, 631 (1970).

Table I. Characterization Data for the Nickel(II) Complexes

Complex	Color	μ_{eff} [a],BM	Λ_M,[b] cm^2 ohm^{-1} M^{-1}	Elemental analyses							
				% C		% H		% other		% P	
				Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$Ni(fsp)_2Cl_2$	Pale green	3.22	15.1	51.27	51.14	2.94	3.17	7.96 (Cl)	8.12		
$Ni(fsp)_2Br_2$	Apple green	3.15	8.1	46.61	46.23	2.68	2.51	16.32 (Br)	16.11		
$Ni(fsp)_2(NCS)_2$	Tan	2.18[e]	13.4	51.35	51.06	2.80	2.83	2.72 (N)	2.99		
$Ni(fsp)(NCS)_2$	Pale green	3.48	*c*	45.42	45.61	2.36	2.43	5.10 (N)	5.06	5.58	5.62
$Ni(fsp)Br_2 \cdot C_6H_6$	Purple	0.67	1.6[f]	44.33	45.21	2.82	3.06	23.62 (Br)	23.86	4.58	4.61
$Ni(fsp\text{-}CH_3)_2$	Green	0.30	1.9	54.78	54.69	2.55	2.67	0.00 (I)	0.32		
$Ni(fdsp\text{-}CH_3)_2$	Green		0.4	44.51	44.28	1.57	1.61	12.51 (S)	12.55		
$Ni(sp)I_2$	Royal blue	0.47	6.8	36.75	37.49	2.76	2.41	40.88 (I)	41.06	4.99	4.73
$Ni(sp)_2(NCS)_2$	Brown	1.22[e]	*c*	60.70	60.43	4.33	4.33	3.54 (N)	3.24		
$Ni(sp)(NCS)_2$	Pale green	2.20[e]	*c*	52.20	52.37	3.55	3.81	5.80 (N)	3.36		
$Ni(sp\text{-}CH_3)_2$	Green	0.0	*d*	66.99	66.74	4.57	4.58	0.00 (I)	<0.30	9.61	9.59

[a] Determined by the Faraday method. [b] Measured in approximately 10^{-3} *M* nitromethane solution unless noted otherwise. [c] Decomposes in nitromethane. [d] Insufficiently soluble in nitromethane. [e] See Results and Discussion section for a rationalization of these values. [f] Measured in 1,2-dichloroethane.

$Pd(fsp)Cl_2$. A solution of 0.295 g (1 mmol) of Na_2PdCl_4 in 20 ml of 1-butanol was combined with a solution of 0.760 g (2 mmol) of fsp in 5 ml of dichloromethane. After the solution had been stirred for several minutes a yellow crystalline material separated. The complex was collected on a filter and washed with diethyl ether. The $Pd(fsp)Cl_2$ complex was recrystallized by dissolving it in a minimum volume of dichloromethane, filtering, and adding ethanol to the filtrate.

$Pd(fsp)X_2$ (X = Br, I, SCN). These complexes were prepared in the same manner as the chloro complex, using 1 mmol of Na_2PdCl_4 and 4 mmol of NaBr, NaI, or LiSCN in butanol as the source of PdX_4^{2-}.

$[Pd(fsp)_2](ClO_4)_2$. A solution of 0.760 g (2 mmol) of fsp in 5 ml of dichloromethane was combined with a solution of 0.295 g (1 mmol) of Na_2PdCl_4 in 20 ml of hot 1-butanol. After 1 min a solution of 0.5 g of $LiClO_4$ in 5 ml of hot butanol was added to the orange-brown solution. The resulting solution was stirred for 10 min, cooled to room temperature, and filtered to give a yellow solid. The solid was dissolved in a minimum volume of dichloromethane, and the red-orange solution was filtered into 10 ml of butanol. On reducing the volume of solvent by one-half and cooling, the complex separated as a yellow powder.

$Pd(fsp\text{-}CH_3)_2$. Equimolar amounts of $Pd(fsp)Cl_2$ and fsp were refluxed for 4 hr in *N,N*-dimethylformamide. The volume of solvent was reduced to a few milliliters and a yellow-orange solid separated on cooling the solution. The complex was recrystallized by dissolving it in dichloromethane, filtering, and adding ethanol to the filtrate.

$[Pd(fsp\text{-}CH_3)Cl]_2 \cdot {}^1/_3DMF$. The complex $Pd(fsp)Cl_2$ was refluxed 4 hr in *N,N*-dimethylformamide. The volume of solvent was reduced to a few milliliters and a yellow-orange solid was obtained on cooling. The solid was recrystallized by dissolving it in dichloromethane, filtering, and adding butanol to the filtrate.

$Pd(fdsp)Cl_2$. A solution of 0.214 g (1 mmol) of $PdCl_2$ and 0.08 g (2 mmol) of LiCl in 10 ml of absolute ethanol was combined with a solution of 0.498 g (1 mmol) of fdsp in 4 ml of warm ethanol. A yellow precipitate formed after about 5 min. The $Pd(fdsp)Cl_2$ was collected on a filter, recrystallized from a dichloromethane–ethanol solution, and dried *in vacuo*.

$Pd(fdsp)X_2$ (X = Br, I, SCN). These complexes were prepared in the same manner as the chloro complex above, using 0.214 g (1 mmol) of $PdCl_2$ and 0.084 g (2 mmol) of LiCl and 0.435 g (5 mmol) of LiBr, 0.669 g (5 mmol) of LiI, or 0.41 g (5 mmol) of NaSCN as the source of PdX_4^{2-}.

$[Pd(fdsp\text{-}CH_3)SCN]_2$. A 0.3 g sample of $Pd(fdsp)(SCN)_2$ was refluxed with 1 ml of *N,N*-dimethylformamide and 18 ml of butanol for 1.5 hr. The solvents were removed *in vacuo* to leave a red oil. Stirring the oil with 2 ml of ethanol induced crystallization of an orange solid. The complex was recrystallized from a 50/50 mixture of acetone and ethanol.

$Pd(fdsp\text{-}CH_3)_2$. A 0.360 g (0.5 mmol) sample of $Pd(fdsp)(SCN)_2$ was combined with 0.250 g (0.5 mmol) of fdsp in 18 ml of ethanol and 2 ml of *N,N*-dimethylformamide. The solution was refluxed for 0.5 hr; on cooling an orange solid formed. The complex was collected on a filter and recrystallized from an ethanol–dichloromethane mixture.

Space Group Determination for $Ni(fsp)_2(NCS)_2$. Red-brown needles were obtained by slow evaporation of a chloroform solution of the complex. Weissenberg and precession photographs of the 0*kl*, 1*kl*, 2*kl*, *h*0*l*, and *h*1*l* reciprocal lattice nets revealed the systematic absences ($0k0$, $k = 2n + 1$ and $h0l$, $h + l = 2n + 1$) and lattice symmetry (2/*m*) defining uniquely the monoclinic space group $P2_1/n$. The unit cell constants are $a = 17.6$ (1), $b = 21.1$ (1), and $c = 11.5$ (1) Å and $\beta = 82.7°$. The calculated density, assuming four $Ni(fsp)_2(NCS)_2$ units in the cell, is 1.47 g/cm^3, in good agreement with the observed density (1.49 g/cm^3), by flotation in a carbon tetrachloride–ethanol solution.

Results and Discussion

Nickel(II) Complexes. The characterization data for the nickel(II) complexes isolated in this study with fdsp, fsp, and sp are given in Tables I and II. All the fdsp and fsp complexes are reported herein for the first time; four of the sp complexes have been briefly mentioned previously.[16–18] The different reactions and interconversions for the nickel complexes are diagramed in Scheme I.

Both fsp and sp react with nickel(II) chloride in ethanol to produce deep red solutions from which pale green complexes of elemental composition $Ni(lig)_2Cl_2$ precipitate. In the presence of excess ligand sp gives the deep red, five-coordinate cations $[Ni(sp)_2X]^+$, which can be isolated if a large anion such as PF_6^-, ClO_4^-, or BPh_4^- is added to the red solutions.[6] However, similar five-coordinate complexes of fsp have not been obtained. The green $Ni(fsp)_2Cl_2$ and $Ni(sp)_2Cl_2$ complexes have magnetic moments of 3.22 and 3.15 BM, respectively, typical for six-coordinate nickel(II) compounds.[19] The electronic spectra (Table II) of the solid $Ni(lig)_2Cl_2$ compounds also support a six-coordinate geometry. The weak bands that are observed near 11,000 and 17,000 cm^{-1} are assignable to the $^3A_{2g} \rightarrow {}^3T_{2g}$ and $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ transitions of octahedral geometry,[19] although the highest possible symmetry for these complexes would be C_{2v}. Intense charge transfer absorptions commencing ~21,000 cm^{-1} probably obscure the $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transition expected for six-coordinate nickel(II) complexes.

The green $Ni(lig)_2Cl_2$ complexes readily dissolve in polar organic solvents such as dichloromethane to give deep red, nonconducting solutions whose visible spectra

---

(16) M. O. Workman, G. Dyer, and D. W. Meek, *Inorg. Chem.*, **6**, 1543 (1967).

(17) S. E. Livingstone and T. N. Lockyer, *Inorg. Nucl. Chem. Lett.*, **3**, 35 (1967).

(18) L. F. Lindoy, S. E. Livingstone, and T. N. Lockyer, *Inorg. Chem.*, **6**, 652 (1967).

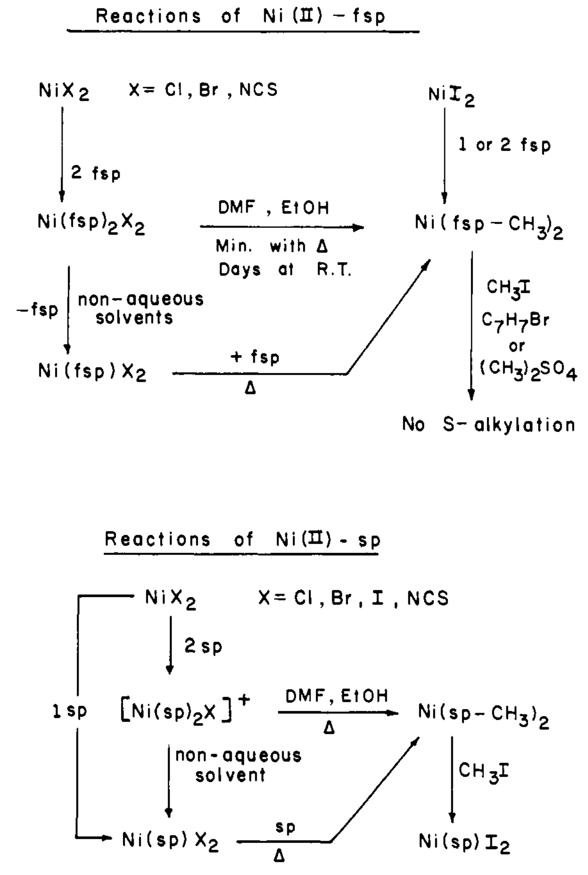
(19) B. N. Figgis, "Introduction to Ligand Fields," Interscience, New York, N. Y., 1966.

Table II. Electronic Spectra of Ni(II) Complexes

Complexes	Energy,[a] cm^{-1} CH₂Cl₂ solution	Energy,[a] cm^{-1} Nujol mull
$Ni(sp)_2Cl_2$[b,c,f]	19,620 (826), 29,200 (sh)[e]	11,110 ± 700, 16,400 ± 150
$Ni(sp)Cl_2$[f]	19,400 (572), 29,400 (sh)[e]	19,600, 29,000 (sh)[e]
$Ni(sp)Br_2$	18,950 (530), 25,000 (846), 31,000 (sh)[e]	18,200 (sh), 20,800, 25,600
$Ni(sp)_2(NCS)_2$	b	18,100 (sh), 22,400
$Ni(sp)I_2$	17,230 (1670), 25,000 (sh), 29,400 (sh)	16,500, 23,800 (sh)[e]
$Ni(sp\text{-}CH_3)_2$	16,500 ± 100 (150), 23,700 ± 100 (4710)	16,500 ± 150, 22,500 ± 100
$[Ni(sp)_2](ClO_4)_2$[f]	21,500 (259), 27,200 (1640)	g
$[Ni(sp)_2Br]ClO_4$[f]	21,200 (1240)	g
$Ni(fsp)_2Cl_2$[b]	19,600 (522)	11,200 ± 300, 17,400 ± 150
$Ni(fsp)_2Br_2$[b]	18,900 (937), 24,400 (1018)	10,600 ± 100, 16,950 ± 30
$Ni(fsp)_2(CNS)_2$[b]	11,500 (45), 20,200 (1260), 25,500 (2940)	12,500, 18,900 (sh), 24,000
$Ni(fsp)(NCS)_2$	d	8700, 10,800, 16,900
$Ni(fsp)Br_2 \cdot C_6H_6$	19,000 ± 30 (733), 24,200 (1080)	18,000 (br), 26,000
$Ni(fsp\text{-}CH_3)_2$	16,400 ± 50 (141), 24,000 ± 50 (5180)	16,530 ± 100, 23,700 ± 100
$Ni(fdsp\text{-}CH_3)_2$	16,000 (113), 25,100 (5542)	g

[a] Extinction coefficients are given in parentheses. ± denotes estimated uncertainties in band positions. Solutions were *ca.* 10^{-3} *M.* [b] Structure changes upon dissolving, see text. [c] Decomposes in solution. [d] Insufficiently soluble. [e] sh = shoulder, br = broad, wk = weak. [f] Reference 16. [g] Not determined.

Scheme I



show a single transition near 20,000 cm^{-1}, typical of planar nickel(II) complexes. Heating a suspension of $Ni(sp)_2Cl_2$ in benzene gives diamagnetic, deep red crystals of $Ni(sp)Cl_2$. The electronic spectra of $Ni(sp)Cl_2$ and $Ni(sp)_2Cl_2$ in dichloromethane solutions are virtually indistinguishable; thus the following dissociation takes place in solution.

$$\underset{\text{pale green}}{Ni(lig)_2Cl_2} \longrightarrow \underset{\text{red}}{Ni(lig)Cl_2} + lig \qquad (1)$$

Repeated attempts to prepare an analytically pure sample of the red compound $Ni(fsp)Cl_2$ from a variety of solvents were unsuccessful despite its apparent presence in solutions of $Ni(fsp)_2Cl_2$. In each case paramagnetic green solids were obtained from the red solutions.

When solutions of sp and nickel(II) bromide were mixed in a 1:1 mole ratio, the red, diamagnetic complex $Ni(sp)Br_2$ crystallized. The diamagnetism, stoichiometry, and characteristic electronic spectrum indicate a planar geometry for this compound. In contrast to sp, an ethanol solution of fsp and nickel(II) bromide immediately produces a pale green precipitate of composition $Ni(fsp)_2Br_2$. The electronic spectrum, which is very similar to those of $Ni(fsp)_2Cl_2$ and $Ni(sp)_2Cl_2$, and the magnetic moment (3.15 BM) are diagnostic of six-coordinate nickel(II). When the pale green $Ni(fsp)_2Br_2$ is heated in benzene, red crystals of composition $Ni(fsp)Br_2 \cdot C_6H_6$ separate. The electronic spectrum, diamagnetism, and nonelectrolyte behavior in dichloroethane indicate a planar structure for the latter compound. Since the electronic spectra of $Ni(fsp)_2Br_2$ and $Ni(fsp)Br_2 \cdot C_6H_6$ in dichloromethane solutions are virtually indistinguishable, ligand dissociation is again proposed (eq 1).

When ethanol solutions of sp and nickel(II) iodide are mixed, a brick red precipitate forms immediately. The red solid dissolves in halocarbon solvents and acetone to give intensely blue solutions from which deep blue-green needles of $Ni(sp)I_2$ crystallize. The blue $Ni(sp)I_2$ complex is diamagnetic and forms nonconducting solutions in nitromethane. The electronic spectrum

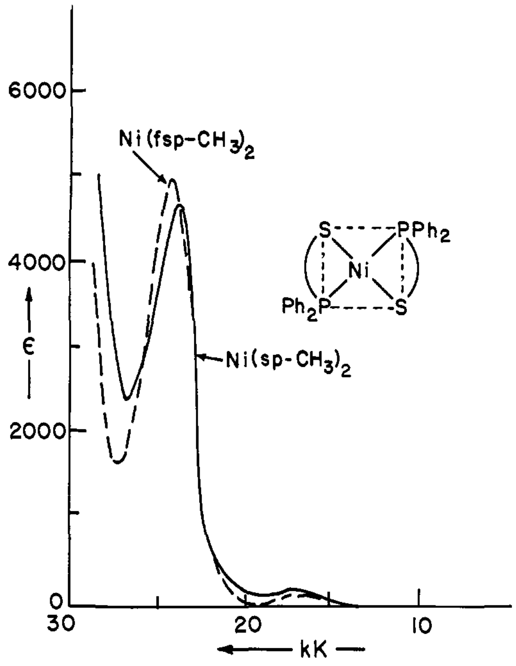


Figure 1. Electronic spectra of *ca.* 10^{-3} *M* solutions of Ni(sp-CH_3)$_2$ (——) and Ni(fsp-CH_3)$_2$ (- - - -) in nitromethane.

of Ni(sp)I_2 in solution and in the solid state consists of intense, symmetrical bands at ~17,000 and ~25,000 cm^{-1}, consistent with a planar structure.

Demethylation of the Nickel(II) Thioether Complexes. Although Ni(sp)I_2 and Ni(dsp)I_2 were synthesized easily, the corresponding complexes of fsp and fdsp could not be isolated. The presence of iodide ion in solutions containing nickel(II) and fsp or fdsp invariably gave deep green solutions of Ni(fsp-CH_3)$_2$ or Ni(fdsp-CH_3)$_2$; *i.e.*, the coordinated thioether in fsp or fdsp rapidly loses the methyl group to form the corresponding mercaptide in the presence of nickel iodide. Attempts to prepare Ni(fsp)I_2 were performed at lower temperatures (as low as −78°) and in a variety of solvents (benzene, acetone, ethanol, 1-butanol, THF, and dichloromethane). In each case the demethylated product Ni(fsp-CH_3)$_2$ was formed within seconds after adding iodide to a solution containing nickel and fsp (eq 2).

$$Ni^{2+} + 2fsp + 2I^- \longrightarrow Ni(fsp\text{-}CH_3)_2 + 2CH_3I \qquad (2)$$

The deep green complex Ni(fsp-CH_3)$_2$ is diamagnetic, a nonelectrolyte in nitromethane, and a monomer in acetone (calcd mol wt, 789; found 769). These data, along with the characteristic electronic spectrum, indicate a planar structure similar to the known planar structure of *trans*-Ni[*o*-$SeC_6H_4P(C_6H_5)_2$]$_2$.[20] The loss of the methyl group from fsp is particularly conspicuous in the proton nmr spectrum of Ni(fsp-CH_3)$_2$, which shows no methyl proton resonance.

Addition of iodide ion, even at −78°, to solutions of any of the fsp complexes listed in Table I instantly produced the deep green color characteristic of Ni(fsp-CH_3)$_2$. Quantitative demethylation was also observed when dichloromethane solutions of Ni(fsp)Cl_2 and Ni(fsp)Br_2 were allowed to stand at 25° for 2 and 7 days, respectively, although solutions of Ni(sp)$_2Cl_2$ appear to be stable for several weeks before significant amounts of Ni(sp-CH_3)$_2$ are formed. Quantitative formation of Ni(fsp-CH_3)$_2$ also was observed when 1:10 DMF–ethanol solutions of Ni(fsp)$_2Cl_2$ and Ni(fsp)$_2Br_2$ were refluxed for 12 and 1 hr, respectively.

Livingstone has briefly described the formation of Ni(sp-CH_3)$_2$ when solutions of nickel(II)–sp complexes are heated.[17,18] We have confirmed the demethylation of sp and find that its complexes undergo the demethylation reactions with more difficulty than the analogous complexes of the fluoro ligand fsp. For example, Ni(sp)I_2 was easily prepared, whereas the presence of fsp in solutions containing nickel(II) and iodide instantly gives the mercaptide complex Ni(fsp-CH_3)$_2$, even at −78°. Realkylation of Ni(fsp-CH_3)$_2$ was attempted using benzyl bromide, methyl iodide, and dimethyl sulfate; however, in each case the original mercaptide complex was recovered quantitatively. In contrast, a solution of Ni(sp-CH_3)$_2$ in refluxing methyl iodide is converted quantitatively to the thioether complex Ni(sp)I_2 in 1 hr. The interconversion of Ni(sp-CH_3)$_2$ and Ni(sp)I_2 (eq 3) may

$$Ni(sp\text{-}CH_3)_2 \underset{\Delta,\,-2CH_3I}{\overset{+2CH_3I}{\rightleftharpoons}} Ni(sp)I_2 + sp \qquad (3)$$

be repeated numerous times with very little decomposition.

Although demethylation of coordinated fsp occurs more readily than coordinated sp in analogous complexes, the electronic spectra of the two resulting mercaptide complexes Ni(fsp-CH_3)$_2$ and Ni(sp-CH_3)$_2$ are remarkably similar (Figure 1). The inductive effect of the four fluorine atoms in fsp-CH_3 would be expected to decrease the ligand field strength of fsp-CH_3 as compared to sp-CH_3.[10] However, the apparent ligand field strength and band intensities are slightly greater for the fluoro ligand fsp-CH_3 (Figure 1 and Table II).

Both fsp and sp give two different types of nickel thiocyanate complexes. The brown Ni(lig)$_2$(NCS)$_2$ complexes are formed when an ethanol solution of hydrated nickel(II) thiocyanate and a dichloromethane solution of the appropriate ligand are mixed. The infrared spectrum of Ni(fsp)$_2$(NCS)$_2$ shows two sharp, strong bands in the C≡N stretching region at 2095 and 2040 cm^{-1}, which are indicative of N-bonded and ionic thiocyanate groups, respectively.[21] The Ni(sp)$_2$(NCS)$_2$ complex exhibits two sharp, strong C≡N stretching frequencies at 2095 and 2070 cm^{-1}.

The magnetic moments of Ni(fsp)$_2$(NCS)$_2$ and Ni(sp)$_2$(NCS)$_2$ gave the anomalous values μ_{eff} 2.25 and 1.25 BM, respectively, calculated on the basis of monomeric NiL_2(NCS)$_2$ units. Since the μ_{eff} value for Ni(fsp)$_2$(NCS)$_2$ was reproducible for several independently prepared samples and showed no variation with the magnetic field strength, the odd moment is probably not due to paramagnetic or ferromagnetic impurities. The magnetic susceptibility of Ni(fsp)$_2$(NCS)$_2$ was found to obey a Curie–Weiss relationship from 73°K to ambient temperature and gave a Weiss constant θ of −4°. The temperature independence of the anomalous μ_{eff} excludes both a magnetically coupled polynuclear structure and a spin-equilibrium model, *e.g.*, a pentacoordinate nickel complex such as [Ni(fsp)$_2$NCS]NCS involving high and low spin states.[7,22] The magnetic data are

---

(20) R. Curran, J. A. Cunningham, and R. Eisenberg, *Inorg. Chem.*, **9**, 2749 (1970).

(21) D. W. Meek, P. E. Nicpon, and V. I. Meek, *J. Amer. Chem. Soc.*, **92**, 5351 (1970).

(22) G. R. Brubaker and D. H. Busch, *Inorg. Chem.*, **5**, 2114 (1966).

Table III. Characterization Data for the Palladium(II) Complexes

Compound[a]	Color	Λ_M,[b] cm^2/(ohm mol)	Analyses % C Calcd	% C Found	% H Calcd	% H Found	% other Calcd	% other Found	% P Calcd	% P Found
$Pd(fsp)Cl_2$	Bright yellow	2.6	41.0	40.7	2.3	2.4	12.76 (Cl)	13.60		
$Pd(fsp)Br_2$	Yellow	3.9	35.30	35.75	2.03	1.57				
$Pd(fsp)I_2$	Red-orange	8.3	30.81	30.38	1.77	1.77	4.18 (I)	4.39		
$Pd(fsp)(SCN)_2$	Yellow	1.3	41.82	41.65	2.08	2.37	4.65 (N)	4.57	5.14	4.79
$[Pd(fsp)_2](ClO_4)_2$	Pale yellow	159	42.81	43.02	2.46	2.46			5.82	6.12
$Pd(fsp\text{-}CH_3)_2$	Yellow-orange	5.9	51.65	50.65	2.41	2.77	0.00 (Cl)	0.32		
$[Pd(fsp\text{-}CH_3)Cl]_2 \cdot {}^1/_3DMF$	Yellow-orange	9.7	42.93	43.41	2.31	2.90	0.88 (N)	0.89		
$Pd(fdsp)Cl_2$	Yellow	0.22	35.55	35.34	1.64	1.49	10.49 (Cl)	10.31	4.58	4.46
$Pd(fdsp)Br_2$	Orange	0.36	31.42	31.31	1.45	1.68	20.90 (Br)	21.12	4.05	4.06
$Pd(fdsp)I_2$	Red	0.36	27.98	27.81	1.29	1.28	29.56 (I)	28.87	3.61	3.64
$Pd(fdsp)(SCN)_2$	Orange	0.38	36.65	36.40	1.54	1.49	3.88 (N)	3.64		
$[Pd(fdsp\text{-}CH_3)(SCN)]_2$	Orange	3.79	37.08	36.51	1.25	1.36	2.16 (N)	2.12		
$Pd(fdsp\text{-}CH_3)_2$	Orange	0.01	42.53	42.36	1.50	1.75	11.95 (S)	12.23		

[a] The complexes are all diamagnetic; the ligand abbreviations are explained in ref 1 and shown in the introductory section. [b] Molar conductance values were measured on approximately 10^{-3} *M* solutions in nitromethane.

interpretable if the $Ni(lig)_2(CNS)_2$ complexes are, in fact, composed of equal numbers of diamagnetic and paramagnetic nickel(II) species. The formulation of the fsp complex as $[Ni(fsp)_2(NCS)_2][Ni(fsp)_2](NCS)_2$, *i.e.*, a six-coordinate paramagnetic and a planar diamagnetic nickel(II) species, gives a calculated μ_{eff} for the paramagnetic center of 3.08 BM, assuming a reasonable TIP correction of 100 cgsu for the diamagnetic nickel species. This value is typical for six-coordinate nickel(II).[19] The mixed formulation also is consistent with the solid-state infrared spectra in the C≡N stretching region, since infrared bands corresponding to both ionic and N-bonded thiocyanate groups are observed.

The observed electronic spectra of the thiocyanate complexes (Table II) may be interpreted as a composite of the six-coordinate and four-coordinate units. The electronic spectrum of solid "$Ni(fsp)_2(NCS)_2$" contains two weak bands at 12,500 and 18,900 cm^{-1}, which are assigned as the ${}^3A_{2g} \rightarrow {}^3T_{2g}$ and ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ transitions of the six-coordinate $Ni(fsp)_2(NCS)_2$ species, and a much stronger band at 24,400 cm^{-1}, which is assigned to the ${}^1A_{1g} \rightarrow {}^1E_g$ transition of the planar $[Ni(fsp)_2]^{2+}$ species.[23] If the thiocyanate spectrum is treated in this manner, the spectra of the six-coordinate series $Ni(lig)_2X_2$ (X = Cl, Br, NCS) produce the usual spectrochemical series -NCS > Cl > Br (Table II).

Single-crystal X-ray photographs of "$Ni(fsp)_2(NCS)_2$" showed that the space group is $P2_1/n$ of the monoclinic system. The observed and calculated densities (1.49 and 1.47 g/cm^3, respectively) agree closely if four formula units having the molecular weight "$Ni(fsp)_2(NCS)_2$" are in the unit cell. Space group requirements would impose no symmetry if all four "$Ni(fsp)_2(NCS)_2$" units are identical, but would require centrosymmetric complexes for a formulation involving two different complexes, *i.e.*, $[Ni(fsp)_2(NCS)_2]$ and $[Ni(fsp)_2](NCS)_2$. Thus, the total data are best interpreted in terms of the mixed formulation with planar $[Ni(fsp)_2]^{2+}$ and two NCS^- ions along with tetragonal $[Ni(fsp)_2(NCS)_2]$ units involving N-bonded thiocyanate groups.

The brown $Ni(fsp)_2(NCS)_2$ complex dissolves in dichloromethane to give an intensely green-brown solution. The visible electronic spectrum of this solution is similar to the solid-state spectrum of $Ni(fsp)_2(NCS)_2$, suggesting a similar structure in solution despite the slight color change. However, the low conductance value observed for a 10^{-3} *M* nitromethane solution (13.4 for monomer, 26.8 for dimer) suggests that the amount of thiocyanate dissociation is minor. The infrared spectrum of a dichloromethane solution of $Ni(fsp)_2(NCS)_2$ consists of a broad absorption at 2078 cm^{-1} with an integrated intensity of 10.1×10^4 cm^{-2} M^{-1}; the band position and half-band width clearly indicate N-bonded groups, but the molar intensity is slightly low for isothiocyanato bonding.[21] The low value may be due to the presence of a moderate quantity of bridging thiocyanate, as evidenced by a new absorption at 2130 cm^{-1}. When light petroleum ether is added to the dark solution of $Ni(fsp)_2(NCS)_2$ or when the solution is allowed to stand for a few hours, the green complex $Ni(fsp)(NCS)_2$ is obtained. The magnetic moment of $Ni(fsp)(NCS)_2$, 3.48 BM, is in the range for a "tetrahedral" Ni(II) complex.[24] The solid-state electronic spectrum of this compound contained discrete maxima with increasing intensity at 8700, 10,800, and 16,900 cm^{-1}. The spectrum is consistent with a tetrahedral nickel(II) compound if the band at 16,900 cm^{-1} is assigned to the ${}^3T_1(F) \rightarrow {}^3T_1(P)$ transition, and the two lower energy bands are attributed to splitting of the ${}^3T_1(F) \rightarrow {}^3A_2$ transition in the pseudotetrahedral ligand field.[19]

If the six-coordinate complex $Ni(sp)_2(NCS)_2$ is dissolved in halocarbon solvents, a rapid precipitation of green $Ni(sp)(NCS)_2$ occurs. Samples of the latter compound rapidly change color on being ground with Nujol from pale green to a dark brown color similar to that of $Ni(sp)_2(NCS)_2$. The mull spectrum contained a band at 24,700 cm^{-1}, a shoulder at 18,500 cm^{-1}, and a much weaker maximum at 9000 cm^{-1}. The two higher energy bands agree reasonably well with the mull spectrum of $Ni(sp)_2(NCS)_2$ (Table II). The weak band at 9000 cm^{-1} may be due to contamination by a tetrahedral form.

Palladium Complexes. Characterization data for the palladium(II) complexes of fsp and fdsp are given in Tables III, IV, and V. The conductivity values of all the complexes except $[Pd(fsp)_2](ClO_4)_2$ indicate that they

---

(23) J. R. Preer and H. B. Gray, *J. Amer. Chem. Soc.*, 92, 7306 (1970).

(24) Both $Ni(lig)(NCS)_2$ compounds (lig = sp or fsp) were either insoluble or decomposed in solvents suitable for measuring visible absorption spectra.

Table IV. Electronic Spectra of the Palladium(II) Complexes

Compound	Energy,^{a,b} cm^{-1}
Pd(fsp)Cl$_2$	27,520 ± 40 (2510)
Pd(sp)Cl$_2$	27,500 ± 100 (2300)
Pd(fsp)Br$_2$	25,800 (3800)
Pd(fsp)(SCN)$_2$	23,400 (1171)
Pd(sp)(SCN)$_2$	24,200 (1120)
Pd(fsp)I$_2$	22,000 (4930)
Pd(sp)I$_2$	22,100 (4000)
Pd(fsp-CH$_3$)$_2$	27,200 (4620), 22,000 (250)
Pd(sp-CH$_3$)$_2$	26,300 (2750), 21,500 (200)
[Pd(fsp-CH$_3$)Cl]$_2$ · $^1/_3$DMF	28,400 (9900)
Pd(fdsp)Cl$_2$	26,670 (2174)^c
Pd(fdsp)Br$_2$	24,690 (2479)^c
Pd(fdsp)I$_2$	20,530 (3622), 25,190 (1063)^c
Pd(fdsp)(SCN)$_2$	22,990 (1142)^c
[Pd(fd-spCH$_3$)(SCN)]$_2$	19,610 (sh) (274)^c
Pd(fdsp-CH$_3$)$_2$	19,880 (126), 26,600 (7942)^c

[a] Band positions are given in cm^{-1} with extinction coefficients in parentheses. (±) represent estimated errors in band positions. [b] Measured on approximately 10^{-3} *M* dichloromethane solutions, except as noted by *c*. [c] Measured on approximately 10^{-3} *M* chloroform solutions.

Table V. Proton Magnetic Resonance Data

Compound	Solvent	τ CH$_3$^{c}	τ aryl^c
fsp	*a*	7.67	2.67
sp	*a*	7.67	2.70
Pd(fsp)Cl$_2$	*a*	6.83	2.55
Pd(sp)Cl$_2$	*a*	6.95	2.42
Pd(fsp)Br$_2$	*a*	6.77	2.35
Pd(fsp)(SCN)$_2$	*a*	6.85	2.35
Pd(fsp)I$_2$	*a*	6.76	2.38
Pd(sp)I$_2$	*a*	6.95	2.43
Pd(fsp)$_2$(ClO$_4$)$_2$	*a*	6.90, 6.97	2.50
fdsp	*b*	7.59	2.57
dsp	*b*	7.62	2.56
Pd(fdsp)Cl$_2$	*b*	7.04	2.43
Pd(fdsp)Br$_2$	*b*	7.11	2.48
Pd(fdsp)(SCN)$_2$	*a*	7.09	2.28
Pd(dsp)(SCN)$_2$	*b*	7.23	2.40
Pd(fdsp)I$_2$	*a*	7.09	2.39
[Pd(fdsp-CH$_3$)(SCN)]$_2$	*b*	7.42	2.40
Pd(fdsp-CH$_3$)$_2$	*b*	8.25	2.42

[a] Measured in dichloromethane solution. [b] Measured in chloroform-*d* solution. [c] Chemical shifts were determined from the internal standard TMS.

are nonelectrolytes in nitromethane. The conductance value for [Pd(fsp)$_2$](ClO$_4$)$_2$ (159 cm^2/(ohm mol)) is typical of a divalent–univalent electrolyte and suggests that both perchlorate groups are ionic in solution. A single, broad infrared absorption near 1100 cm^{-1} for the solid compound shows that the perchlorate groups are ionic in the solid state also.[25]

Molecular weights of Pd(fsp)I$_2$ (calcd, 741; found, 730) and Pd(fdsp)I$_2$ (calcd, 836; found, 840), determined in chloroform, are in excellent agreement with monomeric formulations. Since higher coordination numbers involving halogen bridging are expected to be most likely in palladium(II) iodide complexes,[26] we assume the other Pd(fsp)X$_2$ and Pd(fdsp)X$_2$ complexes are monomeric also.

With the exception of Pd(fdsp)I$_2$, the electronic spectra of all the fsp and fdsp complexes in solution (Table IV) are consistent with square-planar geometries.[23] The normal spectrochemical series, Cl > Br > -SCN > I, is followed for each set of complexes, indicating that the halide ions are present in the first coordination sphere. As can be seen in Table IV, the ligand field characteristics of the fluoro ligands are surprisingly similar to their unfluorinated analogs. In each case where stoichiometrically analogous complexes were isolated with the fluoro and the corresponding unfluorinated ligands, the ligand field strengths are identical within experimental error. The extinction coefficients are slightly greater for the fluoro complexes, however. The same pattern of ligand field and intensity effects were noted above for the nickel complexes.

The electronic spectra of the Pd(fsp)X$_2$ and Pd(fdsp)X$_2$ (X = Cl, Br, I) are very similar (Table IV), with the maxima of the fdsp complexes occurring at slightly lower energies. Since a phosphine is a better donor than a thioether group to palladium,[5] we conclude that the potentially tridentate ligand fdsp functions as a bidentate with one of the two thioether groups uncoordinated. The proton nmr spectra (Table V) confirm that fdsp acts only as a bidentate in the Pd(fdsp)X$_2$ complexes. The nmr spectrum of fsp in CDCl$_3$ consists of a singlet at τ 7.67 and a multiplet at τ 2.67 with relative intensities of 3:10, respectively. In the Pd(fsp)I$_2$ complex the two peaks are shifted downfield to τ 6.76 and 2.38, respectively. A singlet is observed at τ 7.59 for fdsp and at 7.09 for the complex Pd(fdsp)I$_2$. Since the sharp singlet occurs midway between the resonance positions of a free -SCH$_3$ group (τ 7.59) and a coordinated -SCH$_3$ group (τ $\sim$6.76), the two thiomethyl groups of coordinated fdsp apparently become equivalent *via* rapid exchange between coordinated and noncoordinated sites. In those cases where stoichiometrically identical complexes of fsp and sp were isolated, *e.g.*, Pd(fsp)I$_2$ and Pd(sp)I$_2$, the methyl resonance of the fluoro complex always occurs at lower field. Presumably the downfield shift in the free fsp ligand and in the sp coordination compounds is a result of the electronegative tetrafluorophenyl connecting linkage.

The infrared spectrum of Pd(fsp)(SCN)$_2$ in dichloromethane contains two very sharp C≡N peaks at 2124 and 2113 cm^{-1} with integrated intensities of 2.70 × 10^4 and 1.86 × 10^4 cm^{-1} mol^{-1}, respectively. The two bands are consistent with two sulfur-bonded thiocyanate groups trans to phosphorus and sulfur.[21] The spectrum of the solid complex is very similar.

An infrared spectrum (Nujol mull) of the thiocyanate complex of the tridentate ligand, Pd(fdsp)(SCN)$_2$, revealed three C≡N peaks at 2103, 2111, and 2121 cm^{-1} indicative of sulfur-bonded thiocyanates. The infrared spectrum of Pd(fdsp)(SCN)$_2$ in dichloromethane solution contains a broad peak centered at 2074 cm^{-1} and a sharp peak at 2117 cm^{-1} with integrated intensities of 10.4 × 10^4 and 2.83 × 10^4 cm^{-2} *M*$^{-1}$, respectively, indicating the presence of both N- and S-bonded thiocyanate in solution.[21] For this compound an increase in the polarity of the solvent increases the integrated intensity of the C≡N stretching peak at 2074 cm^{-1} and simultaneously decreases the intensity of the 2117 cm^{-1} peak. When both N- and S-bonded thiocyanate groups are observed in Pd(II) complexes of chelating phosphine ligands, increasing the polarity of the solvent generally increases the relative amount of

---

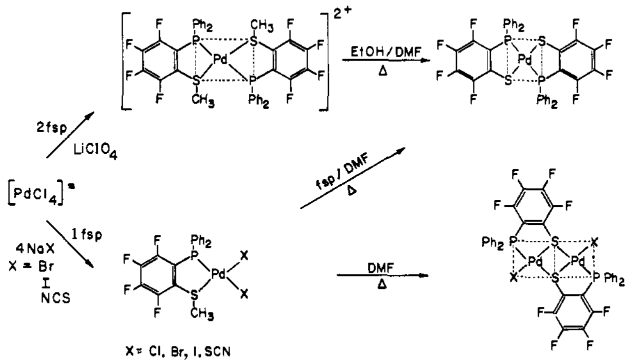
(25) S. F. Pavkovic and D. W. Meek, *Inorg. Chem.*, **4**, 1091 (1965), and references contained therein.

(26) A. D. Westland, *J. Chem. Soc.*, 3060 (1965); C. M. Harris and R. S. Nyholm, *ibid.*, 4375 (1956).

N-bonded thiocyanate present in solution,[27] as observed here for Pd(fdsp)(SCN)$_2$.

Demethylation of the Palladium(II) Thioether Complexes. The coordinated sulfur–phosphorus fluoro ligands undergo facile S demethylation reactions as shown by Scheme II. For example, the dimer [Pd(fsp-CH$_3$)Cl]$_2$ is obtained readily by heating a solution of Pd(fsp)Cl$_2$ in a 9:1 ethanol–DMF mixture for several minutes. Heating Pd(fsp)X$_2$ in the presence of an equimolar quantity of fsp rapidly gives Pd(fsp-CH$_3$)$_2$, which exists as a monomer (mol wt calcd, 837; found, 855 in chloroform). The fdsp ligand has one more thioether group than fsp, and the first demethylation step of Pd(fdsp)(SCN)$_2$ leads to a binuclear complex [Pd(fdsp-CH$_3$)SCN]$_2$. The methyl peak in the nmr of [Pd(fdsp-CH$_3$)SCN]$_2$ shifts toward that of the free ligand (Table V) indicating that the remaining thiomethyl group is uncoordinated in the mercaptide bridged dimer. The latter compound and Pd(fdsp)(SCN)$_2$ are both converted to the completely demethylated complex [Pd(fdsp(-CH$_3$)$_2$)]$_2$ in the mass spectrometer.

Scheme II



The previously reported[17,18] demethylation reactions of sp in Pd(II) complexes have been verified. Moreover, we find that the corresponding reactions with the fluoro ligands are facile by comparison. For example, the quantitative formation of [Pd(lig-CH$_3$)X]$_2$ by heating an ethanol–DMF solution of Pd(lig)X$_2$ required 1–2 hr with lig = sp but is complete within a few minutes with lig = fsp. The relative ease of demethylation is consistent with the results obtained on the Ni(II) complexes of sp and fsp; this suggests that the electronegativity of the perfluoroaryl connecting linkage in the fluoro ligands facilitates cleavage of the S–CH$_3$ bond.

The S dealkylation reactions of sp in Pd(II) complexes are reversible.[17,18] Thus, refluxing Pd(sp-CH$_3$)$_2$ in methyl iodide for a few minutes regenerates the thioether complex Pd(sp)I$_2$. However, the analogous fluoro complexes Pd(fsp-CH$_3$)$_2$ and [Pd(fsp-CH$_3$)X]$_2$ are not realkylated in refluxing methyl iodide even after several days.

As with the nickel(II) complexes, the effect of X in promoting S demethylation in the Pd(lig)X$_2$ series is I > Br > Cl; *i.e.*, the most nucleophilic anion is most effective in promoting demethylation. Such an order is consistent with a "Zeisel-type" thioether cleavage *via* an S$_N$2 mechanism.[18,28,29]

Pentacoordinate palladium(II) complexes have been reported with rigid "tripod-like" tetradentate ligands of group V.[30] However, neither the fluorinated nor the unfluorinated sulfur–phosphorus ligands showed any tendency to form stable pentacoordinate palladium(II) compounds under our preparative conditions. For example, careful addition of halide ion to solutions of [Pd(fsp)$_2$]$^{2+}$ failed to generate a pentacoordinate Pd(fsp)$_2$X$^+$ species. Instead, ligand displacement occurred to form Pd(fsp)X$_2$ by a reaction analogous to that shown by eq 1.

Conclusions

From our comparisons of the coordination properties of fsp and sp, the following general observations may be made. (1) The fluoro-ligand fsp shows a decreased propensity to form pentacoordinate nickel(II) complexes compared to the unfluorinated ligand sp. For example, one may easily prepare the five-coordinate [Ni(sp)$_2$Br]ClO$_4$,[6] whereas we have been unable to prepare any five-coordinate nickel(II) fsp complexes in either polar or nonpolar nonaqueous solvents. (2) In those cases where stoichiometrically analogous sp and fsp complexes could be isolated, the methyl proton resonances of the fsp complexes were invariably further downfield than the methyl resonances of the corresponding sp complexes, just as the methyl resonance of free fsp is downfield from that of sp. (3) Demethylation reactions of thioether complexes are much more facile in the cases of the fsp complexes. (4) The ease of demethylation of the fsp and sp complexes strongly depends on the presence of halide ions and decreases in the order I ≫ Br > Cl. (5) For fsp and sp complexes the spectrochemical effects for the two ligands are very similar. Molar extinction coefficients were usually slightly higher for the fluoro compounds.

These observations are in agreement with our findings with the ligand pairs $C_6H_5P(CH_3)_2$–$C_6F_5P(CH_3)_2$[8a] and $C_6H_5P(o\text{-}C_6H_4P(C_6H_5)_2)_2$–$C_6H_5P(o\text{-}C_6F_4P(C_6H_5)_2)_2$.[8b] From observations (2) and (3) we conclude that the perfluoroaryl group exerts a σ-electron withdrawing effect on the phosphorus and sulfur donor atoms. Such an inductive effect should deshield the thiomethyl protons and facilitate cleavage of the S–CH$_3$ bond by polarizing the bond and stabilizing the negative charge of the resultant mercaptide group. A reduced σ character for the donor atoms may also be related to the decreased tendency of the fluoro ligands to promote five coordination.

Although the perfluoroaryl group clearly seems to exert a σ-electron withdrawing effect on the donor atoms, the ligand field properties of fsp and sp are nevertheless very similar. We conclude that a cooperative (synergic) effect compensates for the reduced σ-donor nature of the fluoro ligand by increasing the π-acceptor properties of the fluoro ligands. A similar mechanism has been postulated to explain the excellent π-acceptor properties of phosphines, *e.g.*, PF$_3$, which contain highly electronegative substituents.[31,32] Further support for this hypothesis comes from a ^{31}P study which shows an increased shielding of phosphorus in $P(C_6H_5)_x(C_6F_5)_{3-x}$ compounds as the number of C$_6$F$_5$ groups increases,[12–14] and from an excellent ^{19}F nmr study with C$_6$F$_5$X deriva-

---

(27) M. Li and D. W. Meek, unpublished data, 1971.

(28) D. H. Busch, J. A. Burke, Jr., D. C. Jicka, M. C. Thompson, and M. L. Morris, *Advan. Chem. Ser.*, **No. 37**, 125 (1963).

(29) P. Karrer, "Organic Chemistry," Elsevier, New York, N. Y., 1950, p 431.

(30) L. M. Venanzi, *Angew. Chem., Int. Ed., Engl.*, **3**, 453 (1964); G. Dyer, J. G. Hartley, and L. M. Venanzi, *J. Chem. Soc.*, 1293 (1965).

(31) R. S. Nyholm, *Quart. Rev., Chem. Soc.*, **24**, 1 (1970).

(32) T. H. Kruck, *Angew. Chem., Int. Ed. Engl.*, **6**, 53 (1967).

tives which indicated an increased π acidity for phosphorus when $X = PR_2$.[10,11]

Finally, we note that the ease of demethylation of the sp and fsp metal halide complexes increases in the order of nucleophilicity of X, *viz.*, $I^- \gg Br^- > Cl^-$. This order is consistent with a Zeisel-type nucleophilic mechanism for cleavage of the $S-CH_3$ bond in the thioether.[18,28,29] A Zeisel mechanism is also consistent with the fluoro complexes undergoing more facile S demethylation than the sp complexes; the electronegative fluoroaryl ring would increase the positive charge on sulfur, thus increasing the susceptibility for nucleophilic attack by X^-.

Acknowledgment. The authors are grateful for the financial support of the National Science Foundation (Grant GP-23204).

Delineation of Shift Reagent–Substrate Equilibria

R. Porter, T. J. Marks,* and D. F. Shriver*

Contribution from the Department of Chemistry, Northwestern University, Evanston, Illinois 60201. *Received December 1, 1972*

Abstract: The equilibria between $Ln(fod)_3$ (Ln = Pr, Eu, Ho, or Yb; fod = 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctanedionate) and the basic substrate $(\pi\text{-}C_5H_5)Fe(CO)_2(CN)$ have been studied by vapor pressure osmometry on benzene solutions. Dimers and, in some cases, higher aggregates of the shift reagents are found in pure $Ln(fod)_3$ solutions. In general, the shift reagent: substrate systems form 1:1 and 1:2 complexes. In the case of $Pr(fod)_3$, 1:3 complex formation is also observed. The relative successive formation constants for 1:2 adduct formation decrease from light to heavy lanthanide. This, as well as the 1:3 formation with $Pr(fod)_3$, is thought to reflect greater steric crowding with the heavier members. The osmometry results are compared with nmr shifts determined under similar conditions, and the factors determining the shapes of plots of substrate shift *vs.* shift reagent to substrate ratio are discussed.

Central to the quantitative application of nmr shift reagents as structural and chemical probes[1-4] are the stoichiometry and equilibria of interaction between lanthanide shift reagent, Ln, and substrate, S. Surprisingly, little is actually known about the identity of the species which exist at ambient temperature in typical reagent–substrate solutions. Crystallographic studies[2,5,6] have identified 1:2 lanthanide: substrate adducts in the solid state; however, the situation in solution is far from clear. Until the recent, elegant experiments of Shapiro and Johnston[7] analyses of substrate chemical shifts as a function of lanthanide: substrate ratio have supported 1:1 adduct formation at room temperature,[1,8-10] and in some cases,[8-10] equilibrium constants have been calculated. Another nmr experiment,[11] which unfortunately may not apply at room temperature, detected only 1:2 adducts in the presence of excess base at −80°. Shapiro and Johnston's precision nmr analysis of $Eu(fod)_3$–substrate equilibria[7] yielded successive formation constants for both 1:1 and 1:2 adduct formation. The inherent possible complexity of the equilibria occurring in these systems indicated to us that an alternative physiochemical technique, in this case vapor pressure osmometry, would be a useful if not necessary supplement to even the most rigorous analysis of substrate nmr shift data. The possibility of extensive shift reagent association or 1:3 (or even 1:4) adduct formation cannot, *a priori*, be ruled out in shift reagent–substrate solutions.

We present here correlated osmometric and pmr studies with the model substrate $(C_5H_5)Fe(CO)_2CN$, which was chosen because it displays a single sharp resonance in the nmr, the site of coordination is known,[4] and it can be accurately weighed. Because of recent interest[2,3,12] in using lanthanides other than europium for shift reagents, we present data on the systems $Ln(fod)_3$,[13] where fod = 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionate and Ln = Pr, Eu, Ho, and Yb. The scope of equilibria occurring is considerably richer than heretofore believed. Some insight is provided into the systematic nature of lanthanide β-diketonate coordination chemistry and into what factors determine the utility of a given shift reagent.

Experimental Section

The substrate $(C_5H_5)Fe(CO)_2CN$ was prepared and purified

---

(1) J. K. M. Sanders, S. W. Hanson, and D. H. Williams, *J. Amer. Chem. Soc.*, **94**, 5325 (1972), and references therein.

(2) W. D. Horrocks, Jr., and J. P. Sipe, III, *J. Amer. Chem. Soc.*, **93**, 6800 (1971), and references therein.

(3) R. Von Ammon and R. D. Fischer, *Angew. Chem., Int. Ed. Engl.*, **11**, 675 (1972), and references therein.

(4) T. J. Marks, J. S. Kristoff, A. Alich, and D. F. Shriver, *J. Organometal. Chem.*, **33**, C35 (1971).

(5) W. D. Horrocks, Jr., J. P. Sipe, III, and J. R. Luber, *J. Amer. Chem. Soc.*, **93**, 5258 (1971).

(6) R. E. Cramer and K. Seff, *Acta Crystallogr., Sect. B*, **28**, 3281 (1972).

(7) B. L. Shapiro and M. D. Johnston, Jr., *J. Amer. Chem. Soc.*, **94**, 8185 (1972).

(8) I. Armitage, G. Dunsmore, L. D. Hall, and A. G. Marshall, *Chem. Commun.*, 1281 (1971).

(9) K. Roth, M. Grosse, and D. Rewicki, *Tetrahedron Lett.*, 435 (1972).

(10) L. Goldberg and W. M. Ritchey, *Spectrosc. Lett.*, **5**, 20 (1972).

(11) D. F. Evans and M. Wyatt, *J. Chem. Soc., Chem. Commun.*, 312 (1972).

(12) N. Ahmad, N. S. Bhacca, J. Selbin, and J. D. Wander, *J. Amer. Chem. Soc.*, **93**, 2564 (1971).

(13) (a) K. J. Eisentraut and R. E. Sievers, *J. Amer. Chem. Soc.*, **87**, 5254 (1965); (b) R. E. Rondeau and R. E. Sievers, *ibid.*, **93**, 1522 (1971).