mosphere for 2 days or the solutions for a few minutes. The compound reacts rapidly with primary alcohols affording the carbonyl **1**.

Anal. Calcd for $C_{54}H_{45}ClP_3Ir$: C, 63.87; H, 4.47; P, 9.15; Cl, 3.49. Found: C, 63.77; H, 4.49; P, 9.11; Cl, 3.94.

Chlorobishydridotris(triphenylphosphine)iridium(III) (11). Hydrogen was bubbled through a solution of $IrClL_3$ in toluene. Crystals of the light yellow dihydride were collected on a filter and dried *in vacuo*, mp 165°. Infrared peaks at 2190, 2100, 850, and 815 cm^{-1} are assigned to Ir–H stretching and bending modes.

Anal. Calcd for $C_{54}H_{47}ClP_3Ir$: C, 63.78; H, 4.63. Found: C, 64.14; H, 4.87.

Acknowledgment. We are grateful to R. M, Ishikawa, T. T. Revak, and G. M. Nakamura for assistance with the kinetic experiments. Grants from the National Science Foundation, the Alfred P. Sloan Foundation, and the Advanced Projects Research Agency (Contract SD-100) supported this research.

Transition Metal Complexes of Alkyl Phosphites. III. Four- and Five-Coordination with Nickel(II) Cyanide[1,2]

K. J. Coskran, J. M. Jenkins, and J. G. Verkade[3]

Contribution from the Department of Chemistry, Iowa State University, Ames, Iowa, and the Department of Chemistry, Michigan State University, East Lansing, Michigan. Received March 20, 1968

Abstract: The spectral properties of the red-orange, diamagnetic, and nonelectrolytic dicyano complex $[Ni(P(OCH_3)_3)_3(CN)_2]$ indicate a *trans* trigonal-bipyramidal configuration. One molecule of phosphite is easily lost to form the yellow, diamagnetic, nonelectrolyte $[Ni(P(OCH_3)_3)_2(CN)_2]_x$. Ultraviolet–visible and infrared spectral evidence is presented which is consistent with the tentative postulate that in the solid the complex is a dicyano bridged dimer of two trigonal bipyramids such that $x = 2$. In solution, spectral data and molecular weight measurements are in agreement with partial dissociation of the dimer to a square-planar monomer which reverts to $[Ni(P(OCH_3)_3)_3(CN)_2]$ on adding excess ligand. The *trans* complexes $[NiL_3(CN)_2]$ where $L = P(O(CH_2)_3CH_3)_3$ and $C_6H_5P(OC_2H_5)_2$ are also shown to be dissociatively unstable in solution with respect to a lower complex or $Ni(CN)_2$ although no lower complexes could be isolated. The insolubility of the *trans*-$[NiL_3(CN)_2]$ where $L = P(OCH_2)_3CCH_3$ did not permit detection of dissociation in solution. An oily complex which according to spectral studies is probably *trans*-$[Ni(P(OC_6H_5)_3)_3(CN)_2]$ did not show evidence of dissociation in solution.

In a recent communication, Rick and Pruett described the preparation of the five-coordinate nickel(II) complex *trans*-$[Ni(C_6H_5P(OC_2H_5)_2)_3(CN)_2]$ which was reported to be a diamagnetic nonelectrolyte dissociatively stable in acetone.[4] In the paper by Chastain, Rick, Pruett, and Gray preceding ours,[5] additional examples of the type *trans*-$[NiL_3(CN)_2]$ (where $L = C_6H_5P(OC_2H_5)_2$, $(C_6H_5)_2POC_2H_5$, $C_6H_5P(OCH_3)_2$, and $P(OC_2H_5)_3$) are described and their electronic transitions assigned on the basis of self-consistent charge and configuration molecular orbital calculations. These complexes as well as the *trans* square-planar system $[Ni((C_6H_5)_2POC_2H_5)_2(CN)_2]$ were also reported to be quite stable in solution although some dissociation in acetonitrile was noticed for $[Ni(C_6H_5P(OC_2H_5)_2)_3(CN)_2]$. Prior to these disclosures, we had begun an investigation of the properties of alkyl phosphite–nickel(II) systems incorporating various coordinating anions. In view of the comparable ligand properties of organic phosphites and cyanides,[6,7] the structural and isomeric possibilities of such mixed complexes were of interest.

We report here the solid diamagnetic complexes *trans*-$[Ni(P(OCH_3)_3)_3(CN)_2]$, *trans*-$[Ni(P(OCH_2)_3CCH_3)_3(CN)_2]$, and $[Ni(P(OCH_3)_3)_2(CN)_2]_x$, where x is probably 2. Spectral evidence permits postulation of the presence of *trans*-$[Ni(P(OC_6H_5)_3)_3(CN)_2]$ and *trans*-$[Ni(P(O(CH_2)_3CH_3)_3)_3(CN)_2]$ in solution. All of the $[NiL_3(CN)_2]$ complexes except where $L = P(OC_6H_5)_3$ are shown to be reversibly unstable in solution with respect to $Ni(CN)_2$ and/or what is very likely a four-coordinate *trans*-$[NiL_2(CN)_2]$ species. Solid and solution spectral measurements of $[Ni(P(OCH_3)_3)_2(CN)_2]_2$ coupled with molecular weight determinations in solution admit the strong possibility of a five-coordinate dicyano-bridged dimer $[NiL_2(CN)_2]_2$ in the solid which is in equilibrium with the planar monomeric *trans*-$[NiL_2(CN)_2]$ in solution. Furthermore, *trans*-$[Ni(P(OCH_3)_3)_3(CN)_2]$ shows evidence of dissociating partially to the planar monomer and its dimer. These observations led us to reinvestigate the $[Ni(C_6H_5P(OC_2H_5)_2)_3(CN)_2]$ complex with the result that it too was shown from spectral studies to be reversibly unstable with respect to dissociation in acetone in contrast to the report of Rick and Pruett.[4]

Experimental Section

Reagents. $Ni(CN)_2 \cdot 4H_2O$ was prepared according to a previously given method.[8] Trimethyl phosphite, triphenyl phosphite, and tri-*n*-butyl phosphite were obtained from Eastman Kodak Co., Rochester, N. Y., and used without further purification. 4-Methyl-

---

(1) Presented in part at the 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967; Abstracts, No. O16.

(2) Part II of this series: J. M. Jenkins, T. J. Huttemann, and J. G. Verkade, Advances in Chemistry Series, No. 62, American Chemical Society, Washington, D. C., 1967, p 604.

(3) Alfred P. Sloan Fellow.

(4) E. A. Rick and R. L. Pruett, *Chem. Commun.*, 697 (1966).

(5) B. B. Chastain, E. A. Rick, R. L. Pruett, and H. B. Gray, *J. Am. Chem. Soc.*, 90, 3994 (1968).

(6) E. F. Riedel and R. A. Jacobson, Abstracts, Meeting of the American Crystallographic Association, Minneapolis, Minn., 1967, p P-10.

(7) J. G. Verkade and T. S. Piper, *Inorg. Chem.*, **2**, 944 (1963).

(8) W. C. Fernelius and J. J. Burbage, *Inorg. Syn.*, **2**, 227 (1946).

2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane ($P(OCH_2)_3CCH_3$) was prepared as reported previously,[9] and diethoxyphenylphosphine was prepared by slowly adding 2 moles of ethanol in ether to a stirred ether solution of dichlorophenylphosphine and 2 moles of N,N-dimethylaniline at room temperature under nitrogen. The N,N-dimethylaniline hydrochloride was filtered after stirring the reaction mixture for 30 min, and then the ether was stripped from the filtrate under vacuum. The middle fraction of the product distilling at 1 mm possessed a pnmr spectrum consistent with the expected formulation.

Physical Measurements. Ultraviolet–visible spectra were obtained on a Cary Model 14 spectrophotometer. Reflectance spectra were obtained with a Beckman DU spectrophotometer equipped with a Beckman 2580 reflectance attachment. Magnesium carbonate was used as a reference and diluent. Infrared spectra were obtained in KBr pellets, Nujol mulls, and $CHCl_3$ solutions using a Perkin-Elmer Model 21 double-beam and a Beckman IR-12 spectrophotometer. Proton nmr spectra were obtained on a Varian Associates Model A-60 spectrometer equipped with a variable-temperature attachment. Spectra were referenced to tetramethylsilane (TMS) as an internal standard. Molecular weight measurements performed on a Mechrolab vapor pressure osmometer (Model 301A) were made over a concentration range of 0.01–0.03 *M*. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn., and nickel analyses were carried out as described previously.[10]

$[Ni(P(OCH_3)_3)_3(CN)_2]$. To 1.83 g (10.0 mmoles) of $Ni(CN)_2 \cdot 4H_2O$ suspended in 25 ml of acetone, 3.72 g (30.0 mmoles) of $P(OCH_3)_3$ was added all at once. The solution was refluxed with stirring for 3 hr, filtered, and concentrated to give dark reddish-orange crystals, which could be recrystallized from acetone or ether (see following preparation). *Anal.* Calcd for $C_{11}H_{27}N_2O_9P_3Ni$: C, 27.35; H, 5.50; N, 5.81; Ni, 12.2. Found: C, 27.55; H, 5.50; N, 5.82; Ni, 12.2.

$[Ni(P(OCH_3)_3)_2(CN)_2]$. When $[Ni(P(OCH_3)_3)_3(CN)_2]$ was stirred in a large volume of ether for 1 hr, there appeared a pale yellow powder and a yellow solution. Cooling the yellow solution produced $[Ni(P(OCH_3)_3)_3(CN)_2]$, while the analysis of the yellow powder was consistent with the formulation $[Ni(P(OCH_3)_3)_2(CN)_2]$. The latter compound exhibited some solubility in CH_2Cl_2, CH_3CN, C_2H_5OH, and dimethyl sulfoxide but slowly decomposed to form a small amount of $Ni(CN)_2$. It is also unstable to decomposition in the atmosphere. *Anal.* Calcd for $C_8H_{18}N_2O_6P_2Ni$: C, 26.75; H, 5.02; N, 7.81; P, 17.27. Found: C, 26.75; H, 5.08; N, 8.08; P, 17.24.

$[Ni(P(OCH_2)_3CCH_3)_3(CN)_2]$. To 0.50 g (1.72 mmoles) of $Ni(NO_3)_2 \cdot 6H_2O$ dissolved in 10 ml of ethanol was added 1.28 g (8.60 mmoles) of $P(OCH_2)_3CCH_3$ dissolved in 5 ml of ethanol followed by 0.17 g (3.44 mmoles) of NaCN also dissolved in 5 ml of ethanol. Although a pale yellow powder was produced on adding the NaCN, the mixture was stirred for 12 hr and then filtered; the solid was washed thoroughly with boiling ethanol to remove all $NaNO_3$. The product was quite insoluble in polar and nonpolar solvents. *Anal.* Calcd for $C_{17}H_{27}N_2O_9P_3Ni$: C, 36.77; H, 4.87; N, 5.05; P, 16.78; Ni, 10.6. Found: C, 36.51; H, 5.01; N, 4.76; P, 16.29; Ni, 10.6.

$[Ni(P(O(CH_2)_3CH_3)_3)_3(CN)_2]$. To 1.83 g (10.0 mmoles) of $Ni(CN)_2 \cdot 4H_2O$ suspended in 25 ml of acetone, 7.50 g (30.0 mmoles) of $P(O(CH_2)_3CH_3)_3$ was added all at once. The solution was stirred and refluxed for 3 hr, filtered, and concentrated to a volume where the absence of solvent was evident from the pnmr spectrum. Cooling this dark red-orange oil produced no solid and addition of ether only diluted the oil. The similarities of the visible and infrared spectra of this solution with those of $[Ni(P(OCH_3)_3)_3(CN)_2]$ were taken as evidence for the presence of this compound in the oil.

$[Ni(P(OC_6H_5)_3)_3(CN)_2]$. To a solution of 1.97 g (5.38 mmoles) of $Ni(ClO_4)_2 \cdot 6H_2O$ dissolved in 10 ml of 2,2-dimethoxypropane and 5 ml of ethanol which was stirred for 1 hr at room temperature was added 5.01 g (16.14 mmoles) of $P(OC_6H_5)_3$. Further stirring of this solution for 0.25 hr was accompanied by an orange color formation. At this point 0.69 g (10.76 mmoles) of KCN was added all at once. After 3 hr of stirring, the very dark red-orange solution was filtered and concentrated under vacuum to remove all solvent. Efforts to crystallize the syrup were fruitless. Again the similarity of the visible and infrared spectra of this solution with those of $[Ni(P(OCH_3)_3)_3(CN)_2]$ was used as evidence for the presence of this compound.

Discussion

The nonelectrolytic nature of $[Ni(P(OCH_3)_3)_3(CN)_2]$ in acetone (molar conductivity = 0.9) and the single sharp band in the cyanide region of its solid-state infrared spectrum (2125 cm^{-1}) strongly favors a *trans* trigonal-bipyramidal structure for this neutral species. The molecular weight measurements on fresh solutions in acetone (Table I) also support a five-coordinate complex. The compound easily loses a ligand molecule under vacuum or upon washing with ether or hydrocarbons to yield a bright yellow powder whose analysis indicates the stoichiometry $[Ni(P(OCH_3)_3)_2(CN)_2]$. The red-orange complex can be recrystallized, however, from acetone or ether in the presence of excess ligand. In view of the diamagnetic nature of the complex ions $[Ni(P(OCH)_3(CH_2)_3)_5]^{2+}$ [10] and $Ni(CN)_5^{3-}$, [11] it is not surprising that $[Ni(P(OCH_3)_3)_3(CN)_2]$ also represents a low-spin d^8 configuration. Like $[Ni(P(OCH)_3(CH_2)_3)_5](ClO_4)_2$[6] and unlike $Ni(CN)_5^{-3}$,[11] $[Ni(P(OCH_3)_3)_3(CN)_2]$ may be expected to possess a regular trigonal-bipyramidal structure on the basis of the spectral evidence presented here. The complex $[Ni(P(OCH_2)_3CCH_3)_3(CN)_2]$ containing a polycyclic phosphite also exhibited a single sharp band in the cyanide region of the infrared spectrum (2135 cm^{-1}) and is undoubtedly also *trans* trigonal bipyramidal. Its extreme insolubility prevented characterization of its nature in solution. It should be noted that the experimental conditions found best for the preparation of this compound employed the initial formation of the $[Ni(P(OCH_2)_3CCH_3)_5]^{2+}$ cation.[10] Similarly, it was found that $[Ni(P(OCH_3)_3)_3(CN)_2]$ could also be made *via* the $[Ni(P(OCH_3)_3)_5]^{2+}$ complex reported by us earlier.[10]

Table I. Molecular Weight Data

Compound	Solvent	—Molecular weight— Obsd	Calcd
$[Ni(P(OCH_3)_3)_3(CN)_2]$	$(CH_3)_2CO$	483–520[a]	483
		430, 438[b]	
		459, 470[c]	
		494, 554[d]	
$[Ni(P(OCH_3)_3)_2(CN)_2]_x$	CH_2Cl_2	520, 502[e]	359 ($x = 1$)
			718 ($x = 2$)

[a] Range for four measurements made 5 min after solvent added to compound. The average of the four values is 498. [b] Two measurements made 20 min after solvent added to compound. [c] Two measurements made 30 min after solvent added to compound. [d] Two measurements made 40 min after solvent added to compound. [e] Two measurements made 3 min after solvent added to compound.

The yellow diamagnetic powder $[Ni(P(OCH_3)_3)_2(CN)_2]_x$ obtained by the facile removal of one molecule of trimethyl phosphite from *trans*-$[Ni(P(OCH_3)_3)_3(CN)_2]$ is definitely not a four-coordinate complex, since the solid-state infrared spectrum clearly shows three sharp cyanide modes at 2149, 2127, and 2122 cm^{-1} and a shoulder at 2144 cm^{-1} on the 2149-cm^{-1} band. Nickel(II) cyanide contamination of this compound was shown

---

[9] J. G. Verkade, T. J. Huttemann, M. K. Fung, and R. W. King, *Inorg. Chem.*, 4, 83 (1965).

[10] K. J. Coskran, T. J. Huttemann, and J. G. Verkade, in ref 2, p 590.

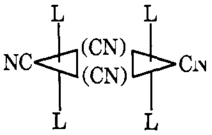
[11] K. N. Raymond, P. W. R. Corfield, and J. A. Ibers, Abstracts, Meeting of the American Crystallographic Association, Atlanta, Ga. 1967, p 65.

Table II. Ultraviolet–Visible Spectral Data

Compound	Phase	Absorption, cm^{-1} [a]
$[Ni(P(OCH_3)_3)_3(CN)_2]$	Solid	38,500, 25,300 (broad)
	CH_2Cl_2	33,900 (2.7 × 10^3), 28,200 (1.8 × 10^3), 23,800 (sh)
	C_2H_5OH	33,700 (1.3 × 10^3), 23,800 (1.9 × 10^3), 23,800 (sh)
	$(CH_3)_2CO$	28,600, (1.6 × 10^3), 23,800 (sh)
	$P(OCH_3)_3$	28,200 (2.8 × 10^3), 23,800 (sh)
$[Ni(P(OCH_3)_3)_2(CN)_2]_2$	Solid	38,500, 29,000 (sh), 23,800 (sh)
	CH_2Cl_2[b]	33,900, 28,200 (sh), 23,800 (sh)
	$(CH_3)_2SO$[b]	35,100, 33,900, 29,000 (sh)
$[Ni(P(OCH_2)_3CCH_3)_3(CN)_2]$	Solid	37,450, 27,400 (broad)
$[Ni(P(O(CH_2)_3CH_3)_3)_3(CN)_2]$[c]	CH_2Cl_2	33,700, 29,000 (sh), 23,800 (sh)
$[Ni(P(OC_6H_5)_3)_3(CN)_2]$[c]	CH_2Cl_2	37,750, 36,300, 35,800, 26,000, 24,600[d]
	C_2H_5OH	37,750 (sh), 36,400, 36,000 (sh), 26,100,[d] 22,200[d] (sh)
$P(OC_6H_5)_3$	CH_2Cl_2	37,750, 37,000 (sh)
	C_2H_5OH	38,000 (sh), 37,000, 36,700 (sh)
$[Ni(C_6H_5P(OC_2H_5)_2)_3(CN)_2]$	$n\text{-}C_6H_{14}$	37,400 (1.9 × 10^4), 33,600 (1.2 × 10^4) 27,800 (4 × 10^3), 24,400 (sh)
$C_6H_5P(OC_2H_5)_2$	$n\text{-}C_6H_{14}$	38,500 (1.5 × 10^3)
$[Ni(C_6H_5P(OC_2H_5)_2)_3(CN)_2]$	CH_3CN	38,500 (3.3 × 10^4), 33,900 (9.7 × 10^3), 27,800 (2.1 × 10^3), 24,400 (10^3)
$C_6H_5P(OC_2H_5)_2$	CH_3CN	38,500 (5.8 × 10^3)
$[Ni(C_6H_5P(OC_2H_5)_2)_3(CN)_2]$	C_2H_5OH[e]	28,600 (3.16 × 10^3), 24,100 (2.51 × 10^3)
	C_2H_5OH[f]	39,500, 33,900 (sh), 28,200 (2.4 × 10^3), 23,000 (sh)
$[Ni(C_6H_5P(OC_2H_5)_2)_3(CN)_2]$	CH_2Cl_2[b]	39,500, 33,700 (sh), 28,200 (sh), 23,000 (sh)
	$(CH_3)_2CO$[b]	28,200 (sh), 23,000 (sh)

[a] Molar extinction coefficients appear in parentheses. [b] Only a qualitative spectrum was possible due to the unstable nature of this compound in solution. [c] Oil. No changes in the spectra were observed when excess ligand was added. [d] This band is broadened in ethanol and the low-energy shoulder (22,200 cm^{-1}) resolves from the main peak (26,100 cm^{-1}) by Gaussian analysis. [e] See ref 4. [f] Since the ligand absorbs strongly only at 39,500 cm^{-1} in ethanol, the extra band in our measurement at 33,900 (sh) cm^{-1} belongs to a second complex species (see text).

to be negligible by the absence of its characteristic cyanide bands at 2176 and 2133 (sh) cm^{-1}. Molecular weight determinations in CH_2Cl_2 are consistent with the presence of the dimeric $[Ni(P(OCH_3)_3)_2(CN)_2]_2$ in appreciable quantities (Table I). If the solid complex exists entirely in the dimeric form, some difference in the solid and solution ultraviolet–visible spectra is expected. This is indeed the case, for in contrast to the spectrum in CH_2Cl_2 the band at 33,900 cm^{-1} is absent in the solid spectrum (Table II). In the solid, we find it attractive to tentatively postulate the existence of cyanide-bridged pentacoordinate dimers of the type shown below where the terminal cyanides and ligands can be interchanged to allow for possible isomer formation. The arrangement of atoms in the cyanide bridges is at present not known. Because of the somewhat intractable nature of this compound, the postulation of the existence of a dimer can only be based on the following evidence at present.[12] The solid-state ultraviolet–visible spectra of $[Ni(P(OCH_3)_3)_3(CN)_2]$ and $[Ni(P(OCH_3)_3)_2(CN)_2]_2$ (Table II) are very much alike if it is conceded that the very broad absorption in the former at 25,300 cm^{-1} is composed of two bands similar to those found in the latter at 29,000 and 23,800 cm^{-1}. That this concession is reasonable is shown by the presence of two bands at 28,200 and 23,800 cm^{-1} for $[Ni(P(OCH_3)_3)_3(CN)_2]$ in its solution spectra and in $P(OCH_3)_3$. Thus the complete similarity of these spectra in all probability means that both compounds are five-coordinate. The solid-state infrared spectrum in the cyanide region of the dimer consists of four bands which can be assigned to bridging (2149 and 2144 cm^{-1}) and terminal (2127 and 2122 cm^{-1}) cyanide groups. The latter values are near the value observed for the $[Ni(P(OCH_3)_3)_3(CN)_2]$, and the former values are in accord with the conclusion that bridging cyanide groups tend to absorb at lower wavelengths than terminal.[13] Lastly, molecular weight measurements (Table I) and its diamagnetism are consistent with association.



Instead of preferential dissociation of the five-coordinate $P(OCH_3)_3$ complex to a square-planar configuration as is the case, for instance, with $[Ni((C_6H_5)_2POC_2H_5)_3(CN)_2]$,[5] the five-coordinate trigonal-bipyramidal dimer may be more stable for three reasons. (a) Both $P(OCH_3)_3$ and CN^-[7,10] have been shown to have nearly equal ligand field strengths at least in the case of octahedral cobalt(III) complexes. Part of the high-field nature of phosphites can undoubtedly be attributed to the comparable π-acceptor properties of such ligands and cyanide. Since four filled nickel 3d orbitals are available for back-bonding in trigonal-bipyramidal symmetry as opposed to only three in the square-planar case, the trigonal-bipyramidal dimer is favored. (b) The well-known tendency of cyanide to bridge metal atoms affords a viable path to maintain five-coordination on loss of $P(OCH_3)_3$ from the five-coordinate monomer. (c) The low steric requirements of $P(OCH_3)_3$, compared to $(C_6H_5)_2POC_2H_5$,[5] would entail less repulsion between ligands on the threefold axes of the bipyramids in the dimer. The insolubility of the dimer *vs.* the parent five-coordinate monomer would indicate that dimer formation is favored by good packing in the crystal, a less favorable property of phosphites with longer alkoxy chains.

That *trans*-$[Ni(P(OCH_3)_3)_3(CN)_2]$ is dissociatively

---

(12) Efforts to grow suitable crystals of this compound for an X-ray structural study have only recently been successful.

(13) D. A. Dows, A. Haim, and W. K. Wilmarth, *J. Inorg. Nucl. Chem.*, **21**, 33 (1961).

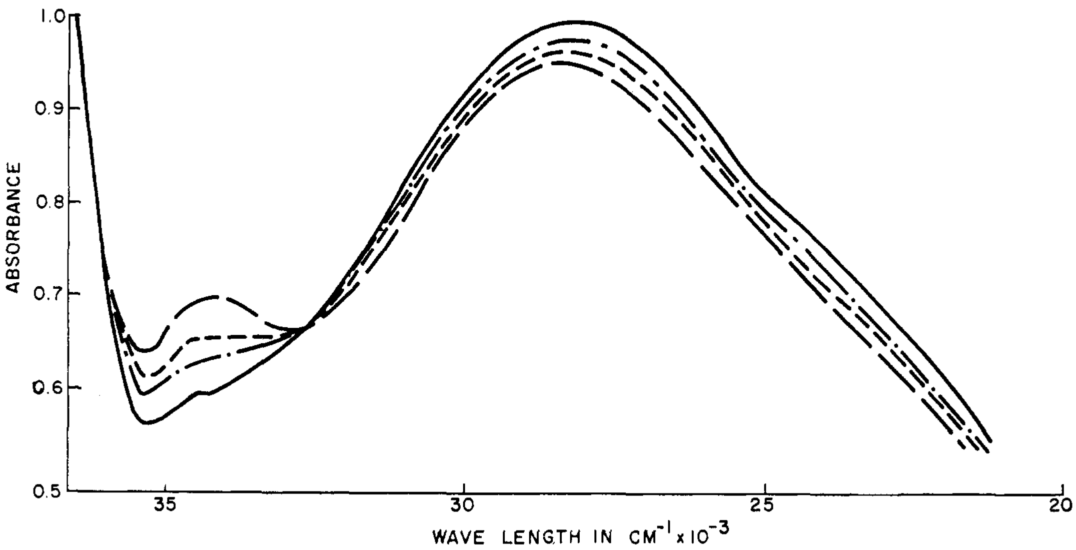


Figure 1. Ultraviolet–visible spectral changes for a 4.63 × 10^{-4} *M* ethanol solution of $[Ni(P(OCH_3)_3)_3(CN)_2]$ upon adding ligand in ratios to nickel present of 0 (— —), 0.3 (- - - - -), 0.5 (— - —), and 1 (——).

unstable in solution was confirmed by a comparison of the ultraviolet-visible spectra taken in a variety of solvents with that of the solid as well as by a low-temperature pnmr experiment. The band at 33,900 and 33,700 cm^{-1} in CH_2Cl_2 and C_2H_5OH, respectively, decreases in intensity upon addition of $P(OCH_3)_3$ and is absent in $P(OCH_3)_3$ as well as in the solid-state spectrum. Furthermore, the extinction coefficients of the 28,200-cm^{-1} band in three solvents increase upon addition of ligand and approach the value obtained in pure ligand (Table *II*). A pnmr spectrum of the complex in acetone at −50° revealed two broad peaks at 3.3 and 3.8 ppm with respect to TMS which coalesced into the more intense peak at 3.8 ppm at −20°.[14] At room temperature a doublet at 3.80 ppm persisted (J_{POCH} = 11 Hz), which upon addition of ligand shifted upfield toward the free ligand value in acetone (3.46 ppm), attesting to the lability of the complex with respect to exchange. The two peaks at low temperature can be ascribed to dissociated ligand (3.3 ppm) and dissociated complex (3.8 ppm). The simultaneous presence of some undissociated five-coordinate complex with a peak also at 3.8 ppm cannot be ruled out. Since the 33,900-cm^{-1} band cannot be associated with either the five-coordinate monomer or the five-coordinate dimer, we are forced to postulate the presence of a third species in the form of a four-coordinate monomeric $[Ni(P(OCH_3)_3)_2(CN)_2]$ complex in solutions of these complexes. This conclusion is based on the following evidence. (a) The band at 33,900 cm^{-1} present in solutions of the five-coordinate monomer and dimer involving organic solvents does not appear in the solid-state spectra. (b) This band decreases in intensity upon adding ligand to solutions of either complex and is not present when the ligand itself is the solvent. (c) The observation of an isosbestic point between the 39,000-cm^{-1} band and the 28,200-cm^{-1} band attributable to the five-coordinate complexes confirms the presence of a third species (see Figure 1). (d) In the spectrum of $[Ni(P(OCH_3)_3)_2(CN)_2]_2$ in CH_2Cl_2, the 33,900-cm^{-1} band is about four times as intense as the 28,200-cm^{-1} band, whereas for $[Ni(P(OCH_3)_3)_3(CN)_2]$ in CH_2Cl_2 the higher energy band is only 1.5 times as intense as the lower. This is expected on the reasonable assumption that more square-planar dissociation product would be present in a solution of the dimer than in a solution of the five-coordinate monomer since the latter first would yield the dimer on loss of ligand. (e) A solution of the dimer in CH_2Cl_2 (stabilized by a small amount of ligand) on warming to 60° shows the expected increase in intensity of the 33,900-cm^{-1} band and a decrease in the band at 28,200 cm^{-1} (Figure 2). The decrease in the latter band can be attributed to dissociation of either or both the five-coordinate monomer and dimer, both of which exhibit a broad absorption in this region. (f) The 33,900-cm^{-1} band has been observed by Gray and coworkers[5] for their isolated and characterized *trans*-$[Ni((C_6H_5)_2POC_2H_5)_2(CN)_2]$ complex and by Turco and coworkers[15] in *trans*-$[Ni(C_6H_5P(C_2H_5)_2)_2(CN)_2]$. The stronger intensity of this band reported for the previous complex[5] than is observed in our solutions of *trans*-$[Ni(P(OCH_3)_3)_3(CN)_2]$ is expected since only part of the five-coordinate monomer dissociates to the planar species.

The diamagnetic nature of solutions of the five-coordinate monomer and dimer indicates that the postulated four-coordinate complex also present is square planar rather than tetrahedral. Whether the four coordinate complex is *trans* as are the complexes of Gray and Turco cited above or perhaps *cis* is not known at this time. Infrared spectra of solutions of the five-coordinate monomer or dimer do not reveal a cyanide band(s) attributable to a square-planar species although the cyanide absorption of the parent complexes could mask such a band(s). It should not be inferred that the 33,900-cm^{-1} band is the only optical absorption associated with the planar compound since an additional weaker transition such as the 29,400-cm^{-1} peaks found in *trans*-$[Ni(C_6H_5)_2POC_2H_5)_2(CN)_2]^5$ might be hidden by the five-coordinate monomer and dimer band at 28,200 cm^{-1} with which the postulated planar species is in equilibrium. The existence of such a lower energy band

---

[14] The breadth of the peaks could have resulted in part from the crystals of solute which were observed to form.

[15] P. Rigo, C. Pecile, and A. Turco, *Inorg. Chem.*, **6**, 1636 (1967).

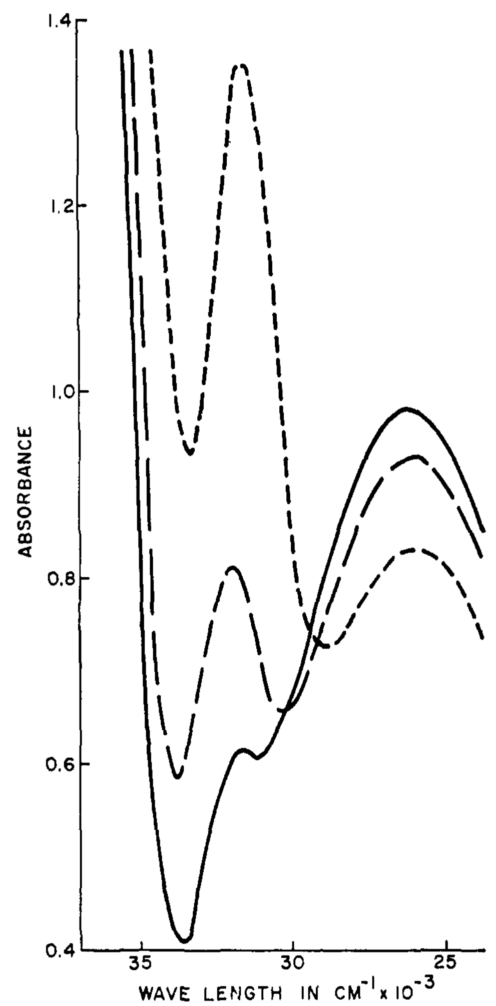


Figure 2. Intensity changes in the ultraviolet-visible spectrum as a CH_2Cl_2 solution of $[Ni(P(OCH_3)_3)_2(CN)_2]_2$ stabilized with a small quantity of ligand is heated to 60°: 25° (——), between 25 and 60° (— — —), and 60° (- - - - -).

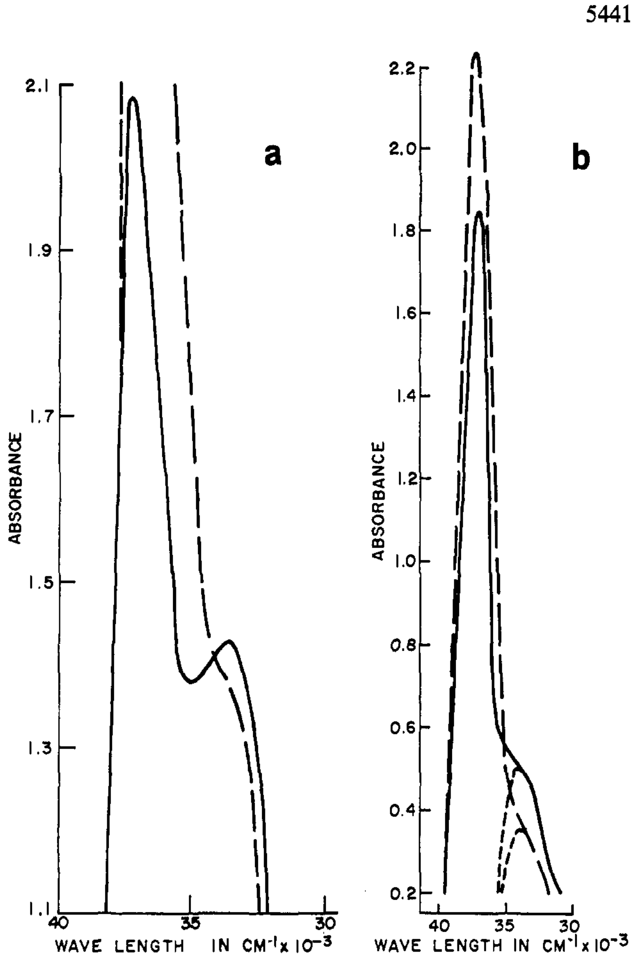


Figure 3. (a) Portion of the ultraviolet–visible spectrum of a 1.17 × 10^{-4} M $[Ni(C_6H_5P(OC_2H_5)_2)_3(CN)_2]$ in n-hexane (——) and the same solution containing 0.8 × 10^{-3} M additional ligand (— — —). (b) Portion of the ultraviolet–visible spectrum of a 0.57 × 10^{-4} M $[Ni(C_6H_5P(OC_2H_5)_2)_3(CN)_2]$ solution in acetonitrile (——) and the same solution containing 3.0 × 10^{-4} M additional ligand (— — —). The 33,900-cm^{-1} band in each spectrum was resolved (- - - - - -) by Gaussian analysis.

for the planar complex is supported, however, by the observations that adding ligand to the five-coordinate monomer (Figure 1) or heating the five-coordinate dimer (Figure 2) results in a faster change in the 33,900-cm^{-1} peak than in the 28,200-cm^{-1} band. Thus, as ligand is added in the first case, the intensity increase in the 28,200-cm^{-1} band is partially offset perhaps by a decrease in intensity of a planar species in this region, and in the latter experiment the expected intensity decrease in this region could be in part compensated by an increase in intensity of a square-planar absorption. It would appear that if a lower intensity square-planar absorption were hidden by the 28,200-cm^{-1} band, the isosbestic point in Figure 1 should not have been observed unless the low-intensity square-planar peak were small compared to the 28,200-cm^{-1} absorption assigned to the five-coordinate species. Where the relative proportion of square-planar species is higher (Figure 2), the lack of an isosbestic point is taken as further evidence that a square-planar band lies on the high-energy side of the 28,200-cm^{-1} peak.

The strange variation of the apparent molecular weight measurements with time of $[Ni(P(OCH_3)_3)_3(CN)_2]$ in acetone (Table I) now becomes reasonable assuming that the complex can dissociate to the four-coordinate compound and its five-coordinate dimer. Thus as the parent five-coordinate monomer releases ligand, dimer, and planar complex to solution, the apparent average molecular weight is decreased. At the time of the last reading which reveals an increase in average molecular weight, however, a yellow precipitate characteristic of the dimer was noted to form. Thus the apparent average molecular weight should rise toward the initial value since the same number of particles will be present in solution at the end of the reaction as at the start if all of the dimer should precipitate.

$$2[NiL_3(CN)_2] \rightleftharpoons 2L + 2[NiL_2(CN)_2] \rightleftharpoons [NiL_2(CN)_2]_2 \rightleftharpoons [NiL_2(CN)_2]_2\downarrow$$

The above observations and arguments led us to examine the spectra of $[NiL_3(CN)_2]$, where L = $P(O(CH_2)_3CH_3)_3$ and $P(OC_6H_5)_3$, prepared in this work, as well as that of $[Ni(C_6H_5P(OC_2H_5)_2)_3(CN)_2]$ reported by Rick and Pruett and by Gray and coworkers.[4,5] In the last complex the band observed at 33,600 cm^{-1} (ϵ 1.2 × 10^4) in hexane changed its shape slightly upon addition of ligand as shown in Figure 3a. In agreement with the results of Gray, *et al.*,[5] however, we find that the 33,600-cm^{-1} band definitely increases about 8%

in intensity when the excess ligand concentration of a 1.25×10^{-4} *M* solution of the complex in hexane is raised from 9.0×10^{-4} to 4.6×10^{-3} *M* in both the sample and reference cells. In acetonitrile the two bands in question have separated somewhat (38,500 cm^{-1} (ϵ 3.3×10^4) and 33,900 cm^{-1} (ϵ 9.7×10^3)), and we observe what appears to be a reasonably definite *decrease* in the 33,900-cm^{-1} peak on adding ligand (Figure 3b). This band is also quite intense in acetonitrile solutions of the isolated square-planar *trans*-[Ni(($C_6H_5)_2POC_2H_5)_2(CN)_2$] (33,900 cm^{-1} ($\epsilon$ 10^4)).[5] Apparently the five- and four-coordinate complexes of $C_6H_5P(OC_2H_5)_2$ both possess a band at about 33,900 cm^{-1}, and the five-coordinate species remains largely intact in hexane while it dissociates appreciably in acetonitrile. It is interesting that this band was neither observed in the solid state or ligand solution of *trans*-[Ni($P(OCH_3)_3)_3(CN)_2$] nor in an acetonitrile solution of *trans*-[Ni(($C_6H_5)_2POC_2H_5)_3(CN)_2$] and excess ligand. If this absorption exists in these compounds, it must be either too weak to be detected or it is significantly shifted to higher or lower energies and is therefore masked by ligand or other complex bands.

When L is $P(O(CH_2)_3CH_3)_3$, a single cyanide mode at 2120 cm^{-1} in the infrared of a smear is seen. The behavior of the 33,700-cm^{-1} band upon adding ligand to a solution of the red oil in CH_2Cl_2 (Table II) is similar to that in the analogous complexes where L = P $(OCH_3)_3$ and $C_6H_5P(OC_2H_5)_2$. No dissociation products could be isolated from the oil, however. For the liquid complex in which L is $P(OC_6H_5)_3$, the single cyanide band[16] at 2135 cm^{-1} is again characteristic of a *trans* configuration, but this time no 33,900-cm^{-1} band was observed. Moreover, addition of L to solutions of the compound resulted in no significant changes in the spectrum except an increase in the intensity of the free ligand bands. Thus it is concluded that a *trans* trigonal-bipyramidal complex is formed.

Gray and coworkers[5] conclude from their studies that, although $(C_6H_5)_3P$ and $(C_6H_5)_2POR$ would rather stabilize trigonal-bipyramidal complexes from orbital contraction arguments, these ligands are restricted to stabilizing square-planar environments because of larger steric requirements compared to $P(OR)_3$. Some caution in the application of these arguments might be indicated by our study of the visible spectrum of *trans*-[Ni($P(OC_6H_5)_3)_3(CN)_2$] and *trans*-[Ni($P(OCH_3)_3)_3(CN)_2$]. Gray *et al.*,[5] assign the lowest energy band in the spectra of their trigonal-bipyramidal and square-planar complexes to a d–d transition. Applying this criterion to the ethanol spectrum of the $P(OC_6H_5)_3$ complex, the series of ligands becomes $(C_6H_5)_3P < P(OC_6H_5)_3 \cong (C_6H_5)_2POR < C_6H_5P(OR)_2 \cong P(OR)_3$. Thus from the arguments put forth by Gray and coworkers at least some evidence for dissociation to a planar $P(OC_6H_5)_3$ complex would be expected. We could observe no evidence for such a dissociation, and this fact is all the more poignant in view of our evidence for dissociation to a planar species even with $P(OCH_3)_3$ and $P(O(CH_2)_3CH_3)_3$. Moreover, the position of $P(OC_6H_5)_3$ in the series (assuming correct spectral assignment) is reasonable on steric grounds since models reveal that ligand–ligand repulsions among $P(OC_6H_5)_3$ ligands in a complex are very nearly the same as among $P(C_6H_5)_3$ molecules if not greater, and thus some evidence of a planar species should be observable. We conclude, therefore, that the relationship between steric and electronic properties of the ligands and the structures of these complexes is at present somewhat unclear.

Acknowledgments. The authors thank the National Science Foundation for a grant in support of this research. Mr. J. Converse is thanked for the magnetic susceptibility measurements. We also thank Professor Gray and Dr. Pruett for discussing the results of their work before publication in several stimulating conversations.

---

(16) Although a weak shoulder on the 2135-cm^{-1} band appeared at 2125 cm^{-1}, it was found that the ligand in $CHCl_3$ also exhibited a rather weak but distinct band at 2125 cm^{-1}.