CONTRIBUTION FROM THE ISTITUTO CHIMICA GENERALE ED INORGANICA (II SEZIONE),
UNIVERSITY OF PADUA, PADUA, ITALY

Complexes of Nickel(II) Cyanide with Ditertiary Phosphines

BY P. RIGO, B. CORAIN, AND A. TURCO

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The preparation and characterization of the diamagnetic complexes of $Ni(CN)_2$ with the ditertiary phosphines $(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2$ (n = 2, 3, or 4) are reported. In contrast to the analogous complexes with the nickel halides, the complexes with $Ni(CN)_2$ are shown to contain not only chelating but also nonchelating and bridging diphosphines. The complexes are of the type $Ni[(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2]_m(CN)_2$, where m = 1, 1.5, or 2. The visible spectra show that the complexes with m = 1.5 or 2 are five-coordinate. The five-coordinate compound $Ni[(C_6H_5)_2P(CH_2)_3P(C_6H_5)_2]P(C_4H_9)_3(CN)_2$ containing one ditertiary phosphine and one tertiary phosphine is also reported. The unusual composition of some of these complexes is attributed to the tendency of nickel(II) cyanide to coordinate three phosphorus atoms of trisubstituted phosphines.

Introduction

In a previous paper[1] we showed that tertiary phosphines do not yield five-coordinate adducts by reaction with the planar complexes *trans*-$Ni(PR_3)_2X_2$ (R = alkyl, aryl) when X = Cl, Br, NCO, NCS, whereas the reactions of the complexes *trans*-$Ni(PR_3)_2(CN)_2$ with the corresponding phosphines give in solution the stable five-coordinated compounds $Ni(PR_3)_3(CN)_2$. It had previously been shown that cobalt(II) gives the trisphosphine complexes $Co(PR_3)_3X_2$ when X = NCS but not when X = Cl, Br, NCO.[2] Recently, the complexes $Co(PR_3)_3(CN)_2$ have also been reported.[3]

All of these results point to the conclusion that trisphosphine complexes can be formed by nickel(II) and cobalt(II) only when the anionic partner X is a strong-field ligand. Recently, it has been shown that cobalt(II) cyanide coordinates three phosphorus atoms even in complexes with ditertiary phosphines, and compounds with the unusual composition $Co(diphos)_{1.5}(CN)_2$ have been reported.[3] We report here the preparation and characterization of the diamagnetic nickel(II) complexes $Ni[(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2]_m(CN)_2$ where n = 2, 3, or 4 and m = 1, 1.5, or 2. Those with m = 1.5 or 2 are five-coordinate. A number of complexes of nickel halides with ditertiary phosphines have been reported.[4] None of them appears to have the stoichiometry $Ni(diphos)_{1.5}X_2$.

Experimental Section

Apparatus.—Electronic spectra were obtained with an Optica CF4NI spectrophotometer, and infrared spectra, with a Perkin-Elmer 257 grating spectrophotometer. The reflection spectra were measured using solid compounds ground with $MgCO_3$ as the inert diluent.

The molecular weights were measured cryoscopically in $C_2H_4Cl_2$ or at 25° with the isopiestic Mechrolab 301 A osmometer.

Molar conductivities were determined in CH_2Cl_2 at 25°. All of the new complexes were nonconducting.

Magnetic susceptibilities were measured using the standard Gouy method at room temperature and were corrected for the diamagnetism of the ligands. All of the cyano complexes of nickel(II) were found to be diamagnetic.

The absence of quaternization processes of the diphosphines by reaction with CH_2Cl_2 or $C_2H_4Cl_2$ was ascertained by measuring the conductivity of the solutions. No significant increase in conductivity was found during the time required to carry out the various physicochemical observations described here (*e.g.*, spectrophotometric measurements).

Materials.—The ditertiary phosphines 1,2-bis(dipenylphosphino)ethane (dpe) and 1,3-bis(diphenylphosphino)propane (dpp) were prepared according to published methods.[5,6]

The tributylphosphine (Fluka) was distilled twice before use.

The ditertiary phosphine 1,4-bis(diphenylphosphino)butane (dpb) was prepared by allowing $P(C_6H_5)_2K$ and $Br(CH_2)_4Br$ to react in boiling dioxane for 5 min. After cooling, water was added to the reaction mixture, and the white solid which precipitated was collected, washed with ethanol, and recrystallized from ethanol–methylene chloride.

$Ni[(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2](CN)_2$.—Water was added dropwise with vigorous stirring to a suspension of $Ni(dpe)Br_2$[4] (2 mmol) and KCN (4 mmol) in ethanol, until the KCN was completely dissolved. The yellow crystals which precipitated were collected, washed with ethanol, and dried *in vacuo*. *Anal.* Calcd for $Ni[(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2](CN)_2$: C, 66.05; H, 4.75; N, 5.50; mol wt, 509. Found: C, 66.59; H, 4.60; N, 5.38; mol wt in CH_2Cl_2 at 25°, 530.

$Ni[(C_6H_5)_2P(CH_2)_3P(C_6H_5)_2](NCS)_2$.—The ligand dpp (2 mmol) dissolved in ethanol (20 ml) was added to a stirred warm solution of $Ni(SCN)_2$ (2 mmol) in 50 ml of ethanol. The yellow crystals which separated were collected, washed with ethanol and n-hexane, and dried *in vacuo*. *Anal.* Calcd for $Ni[(C_6H_5)_2P(CH_2)_3P(C_6H_5)_2](NCS)_2$: C, 59.31; H, 4.46; N, 4.77. Found: C, 59.67; H, 4.52; N, 4.76.

$Ni[(C_6H_5)_2P(CH_2)_3P(C_6H_5)_2]_{1.5}(CN)_2$.—Water was added 1 drop at a time with vigorous stirring to a solution of the ligand dpp (1 mmol) in ethanol containing suspended $Ni(dpp)(NCS)_2$ (2 mmol) and KCN (4 mmol) until the latter was completely dissolved. The red crystals obtained were collected, washed with water and ethanol, and dried *in vacuo*. *Anal.* Calcd for $Ni[(C_6H_5)_2P(CH_2)_3P(C_6H_5)_2]_{1.5}(CN)_2$: C, 69.98; H, 5.39; N, 3.84. Found: C, 69.39; H, 5.57; N, 3.87.

$Ni[P(C_4H_9)_3]_2(CN)_2$.—Nickel(II) cyanide (powder, 2 mmol) in n-hexane was treated with 2 mmol of the ligand $P(C_4H_9)_3$. The resultant yellow solution was refluxed for 1 hr. The unreacted nickel cyanide was filtered off and the yellow crystals obtained when the solvent volume was reduced and the solution cooled down to −20° were recrystallized from n-hexane by cooling; mp 70° (uncorrected). *Anal.* Calcd for $Ni[P(C_4H_9)_3]_2(CN)_2$: C, 60.59; H, 10.56; N, 5.43. Found: C, 60.70; H, 10.58; N, 5.47.

$Ni[(C_6H_5)_2P(CH_2)_3P(C_6H_5)_2]P(C_4H_9)_3(CN)_2$.—Ligand dpp (2

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

(2) T. Boschi, M. Nicolini, and A. Turco, *Coord. Chem. Rev.*, **1**, 269 (1966).

(3) P. Rigo, M. Bressan, and A. Turco, *Inorg. Chem.*, **7**, 1460 (1968).

(4) G. R. Van Hecke and W. D. Horrocks, Jr., *ibid.*, **5**, 1968 (1966), and ref 3–5 therein.

(5) W. Hewertson and H. R. Watson, *J. Chem. Soc.*, 1490 (1962).

(6) G. R. Van Hecke and W. D. Horrocks, Jr., *Inorg. Chem.*, **5**, 1960 (1966).

mmol) and previously prepared $Ni(P(C_4H_9)_3)_2(CN)_2$ (2 mmol) were heated 10 min at 40° in petroleum ether (bp 70–120°). The resulting red solution was aspirated to remove the solvent until red crystals began to precipitate. The product was collected and dried *in vacuo*; mp 143° (uncorrected). *Anal.* Calcd for $Ni[(C_6H_5)_2P(CH_2)_3P(C_6H_5)_2]P(C_4H_9)_3(CN)_2$: C, 67.88; H, 7.36; N, 3.86; mol wt, 725. Found: C, 68.00; H, 7.46; N, 3.80; mol wt in CH_2Cl_2 at 25°, 680.

$Ni[(C_6H_5)_2P(CH_2)_4P(C_6H_5)_2]_{1.5}(CN)_2$.—Prepared in a manner analogous to the complex $Ni(dpp)_{1.5}(CN)_2$ using $Ni(dpb)Br_2$ as starting material. The red solution yielded red crystals that were collected and dried *in vacuo*. *Anal.* Calcd for $Ni[(C_6H_5)_2P(CH_2)_4P(C_6H_5)_2]_{1.5}(CN)_2$: C, 70.42; H, 5.64; N, 3.73; mol wt (calcd for the simplest formula), 750. Found: C, 70.12; H, 5.77; N, 3.74; mol wt (found cryoscopically in $C_2H_4Cl_2$, concn 1.4% by weight), 1150.

$Ni[(C_6H_5)_2P(CH_2)_4P(C_6H_5)_2](CN)_2$.—$Ni(dpb)_{1.5}(CN)_2$ was heated 5 min in boiling 1:1 acetone–petroleum ether (bp 70–120°). In the boling solution the red starting material was converted (by loss of dpb) to a yellow crystalline product, which was collected, washed with acetone, and recrystallized from acetone–methylene chloride. *Anal.* Calcd for $Ni[(C_6H_5)_2P(CH_2)_4P(C_6H_5)_2](CN)_2$: C, 67.07; H, 5.25; N, 5.21; mol wt, 537. Found: C, 66.61; H, 5.16; N, 5.07; mol wt in CH_2Cl_2 at 25°, 1100.

Results and Discussion

The Complexes $Ni(dpe)(CN)_2$ and $Ni(dpe)_2(CN)_2$.—The reaction of the ligand dpe with $Ni(dpe)Br_2$ in ethanol containing KCN and small amounts of water yields a yellow compound which analyzes as $Ni(dpe)(CN)_2$. The determination of the molecular weight in CH_2Cl_2 indicates that the compound is monomeric in this solvent. The infrared spectra in Nujol mull show a strong doublet centered at 2125 cm^{-1}; the two peaks of equal intensity are separated by ~ 5 cm^{-1}. We attribute these peaks to the CN stretching of two CN groups in the *cis* position and not to crystal field effects or to a combination band. The visible spectrum in CH_2Cl_2 is reported in Figure 1. The spectra of $Ni(dpe)Cl_2$ and $Ni(dpe)Br_2$ in CH_2Cl_2 show one band at 21,600 and 20,800 cm^{-1}, respectively (ϵ_{max} 1.7×10^3), assigned to the $^1A_1 \rightarrow {}^1B_2$ transition in C_{2v} symmetry.[4] This band appears as a weak shoulder at about 28,200 cm^{-1} in the spectrum of $Ni(dpe)(CN)_2$ because the much stronger ligand field of CN^- shifts it toward the ultraviolet region where it is obscured by the strong intensity of the tail of the charge-transfer bands.

On addition of dpe to a solution of $Ni(dpe)(CN)_2$ in CH_2Cl_2 the color changes from yellow to red, and correspondingly a band appears at 20,800 cm^{-1} (Figure 1). A continuous-variation spectrophotometric study shows that the ligand dpe reacts with $Ni(dpe)(CN)_2$ in the molar ratio 1:1, forming the compound $Ni(dpe)_2(CN)_2$. The visible spectra of this compound (Figure 1) are completely different from those of Nujol mulls of the yellow $Ni(dpe)_2I_2$ to which has been attributed a hexacoordinated structure, with the chelating phosphines defining a plane and the halogens occupying axial positions.[4] Moreover the spectrum of $Ni(dpe)_2(CN)_2$, which shows two ligand-field bands (one band at 20,800 cm^{-1} (ϵ 1900) and a shoulder at about 26,500 cm^{-1}), is in agreement with the general patterns of the spectra of other diamagnetic five-coordinated complexes of nickel(II) with trigonal-bipyramidal structures.[7] The negligible conductivity of the CH_2Cl_2 solutions containing $Ni(dpe)_2(CN)_2$ rules out the dissociation of the complex to give a pentacoordinate cationic species $Ni(dpe)_2CN^+$. All of these observations consistently point to the conclusion that the sole possible structure for the molecule $Ni(dpe)_2(CN)_2$ is that in which one of the two diphosphines acts as a monodentate ligand. The infrared spectrum shows only one sharp absorption at 2110 cm^{-1}, attributable to CN groups in *trans* positions, and is consistent with a trigonal-bipyramidal structure with the cyanide groups occupying apical positions. Molecular framework models indicate considerable strain when the bond angles P–Ni–P are 120°. However, if the angle subtended by the chelating phosphine drops to about 110°, then the strain is released.

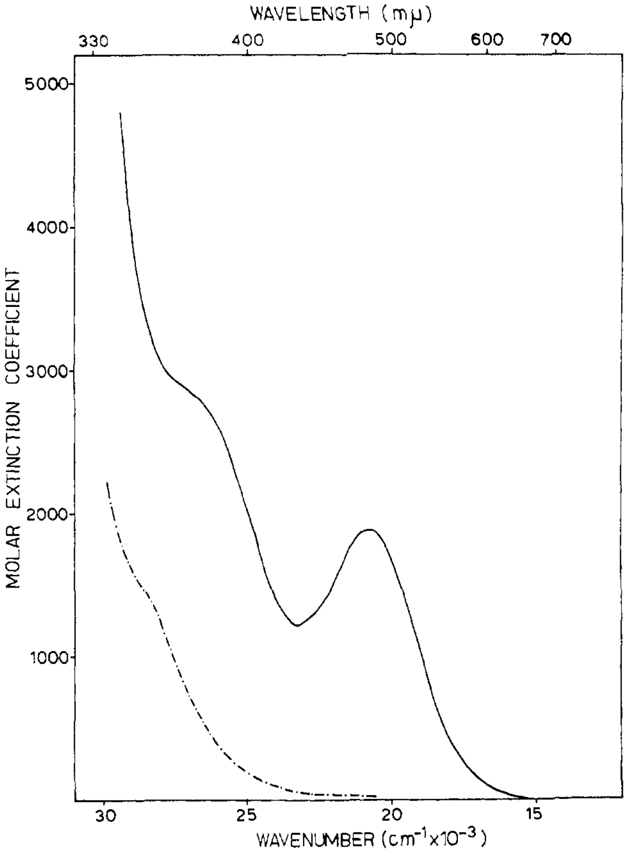

Figure 1.—Absorption spectra in CH_2Cl_2: – · – ·, $Ni(dpe)(CN)_2$; ———, 2.0×10^{-3} M $Ni(dpe)(CN)_2$, 2.0×10^{-1} M dpe.

The Complexes $Ni(dpp)(P(C_4H_9)_3)(CN)_2$ and $Ni(dpp)_{1.5}(CN)_2$.—Red crystals of $Ni(dpp)(P(C_4H_9)_3)(CN)_2$ are obtained on heating at moderate temperature a petroleum ether solution of $Ni(P(C_4H_9)_3)_2(CN)_2$ and of the ligand dpp; prolonged heating at higher temperature leads to the total replacement of $P(C_4H_9)_3$ and the final product of the reaction is then $Ni(dpp)_{1.5}(CN)_2$. The compound $Ni(dpp)(P(C_4H_9)_3)(CN)_2$ is monomeric and very slightly dissociated in CH_2Cl_2 (mol wt: found, 680; calcd, 725.5). The in-

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[7] M. J. Norgett, J. H. M. Thornley, and L. M. Venanzi, *J. Chem. Soc.*, 540 (1967), and references therein.

frared spectrum in Nujol shows a strong band at 2095 cm^{-1} and a weak but very sharp band at 2110 cm^{-1}. In CH_2Cl_2 the two bands are shifted to 2110 and 2115 cm^{-1}, respectively. The reflectance spectra and the solution spectra of the compound (Figure 2) are very similar and show one band at about 21,000 cm^{-1} and one weak but definite shoulder in the region of 27,000 cm^{-1}. The spectral patterns of this compound are comparable with those of $Ni(dpe)_2(CN)_2$. Thus analyses, optical spectra, and the molecular weight show that the compound is five-coordinate and therefore contains a chelated dpp molecule.

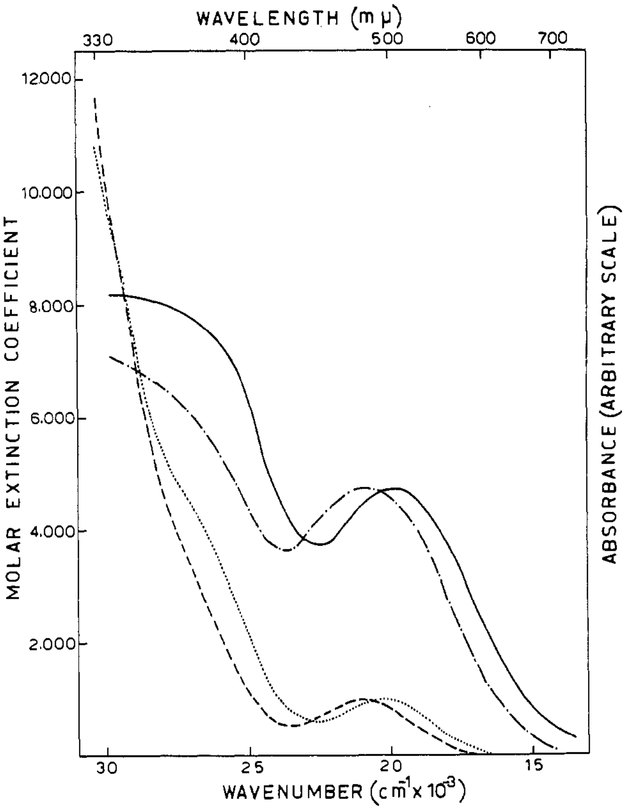

Figure 2.—Absorption spectra in CH_2Cl_2: · · · ·, 1.1 × 10^{-3} *M* $Ni(dpp)_{1.5}(CN)_2$, 4.0 × 10^{-2} *M* dpp; – – – –, 1.0 × 10^{-3} *M* $Ni(dpp)(P(C_4H_9)_3)(CN)_2$. Reflectance spectra: ———, $Ni(dpp)_{1.5}(CN)_2$; – · – ·, $Ni(dpp)(P(C_4H_9)_3)(CN)_2$.

The optical spectra of $Ni(dpp)_{1.5}(CN)_2$ (Figure 2) are very similar to those of $Ni(dpp)(P(C_4H_9)_3)(CN)_2$ suggesting that the symmetry of the binding sites of the ligands around the nickel atoms of the two complexes does not differ greatly. The red shift of about 800 cm^{-1} for the low-frequency band is essentially due to the replacement of one $P(C_4H_9)_3$ molecule by one $(C_6H_5)_2PCH_2$– group and parallels similar shifts observed in $Ni(PR_3)_3(CN)_2$ complexes in the series $P(C_2H_5)_3$, $P(C_2H_5)_2C_6H_5$, and $PC_2H_5(C_6H_5)_2$.[8] The infrared spectrum in Nujol mull shows a single, strong peak at 2100 cm^{-1}, indicating that the CN$^-$ groups are in *trans* positions. Owing to the limited solubility of the compound, it has not been possible to determine its molecular weight. Thus the molecular conformation can be deduced only from indirect arguments. The ligand dpp has always been found to act as a chelating agent as, for example, in $Ni(dpp)(P(C_4H_9)_3)(CN)_2$. However, to account for both five-coordination and composition, one must necessarily admit that there are also nonchelating diphosphines in $Ni(dpp)_{1.5}(CN)_2$. The only reasonable formulation which accounts for both stoichiometry and five-coordination is $(CN)_2(dpp)Ni(dpp)Ni(dpp)(CN)_2$ in which one dpp molecule bridges two different nickel atoms. The same structure has been attributed to the corresponding cobalt(II) complex $Co(dpp)_{1.5}(CN)_2$.[3]

The Complexes $Ni(dpb)(CN)_2$, $Ni(dpb)_2(CN)_2$, and $Ni(dpb)_{1.5}(CN)_2$.—The yellow complex $Ni(dpb)(CN)_2$ can be obtained by boiling a solution of the red $Ni(dpb)_{1.5}(CN)_2$ in an acetone–petroleum ether mixture. The compound is dimeric and not dissociated in CH_2Cl_2 at 25°. The infrared spectrum in Nujol mull shows a single peak at 2120 cm^{-1}, indicating that the CN$^-$ groups are in *trans* positions. The visible spectrum in CH_2Cl_2 is reported in Figure 3. It is identical with that of the *trans*-planar $Ni(P(C_2H_5)_2C_6H_5)_2(CN)_2$,[1] except that the band at 28,300 cm^{-1} in the latter is shifted to 28,600 cm^{-1}. The visible and infrared spectra are consistent with a planar D_{2h} structure. The observed molecular weight suggests that the compound is a binuclear complex in which two nickel atoms are joined by two bridging diphosphines.

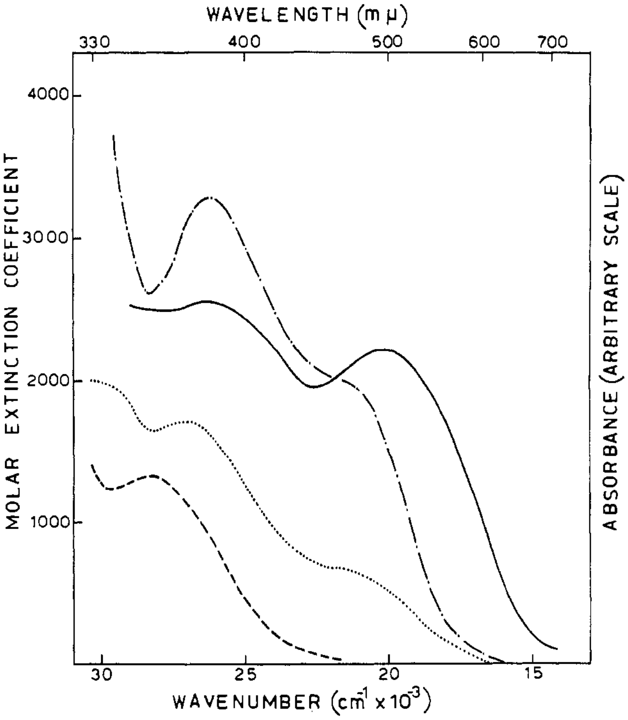

Figure 3.—Absorption spectra in CH_2Cl_2: – – – –, 3.5 × 10^{-3} *M* $Ni(dpb)(CN)_2$; · · · ·, 8.5 × 10^{-3} *M* $Ni(dpb)_{1.5}(CN)_2$; – · – ·, $Ni(dpb)_2(CN)_2$ (1.8 × 10^{-3} *M* $Ni(dpb)(CN)_2$ plus 4.7 × 10^{-2} dpb). Reflectance spectrum: ———, $Ni(dpb)_{1.5}(CN)_2$.

A continuous-variation spectrophotometric study shows that $[Ni(dpb)(CN)_2]_2$ reacts with dpb in CH_2Cl_2 in the 1:2 mole ratio, giving a compound the simplest

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(8) P. Rigo and A. Turco, unpublished results.

formula of which can be represented as $Ni(dpb)_2(CN)_2$. The spectral patterns of this compound (Figure 3) are in agreement with those of low-spin five-coordinate compounds. The two bands at about 21,000 and 26,300 cm^{-1} in the spectrum of solutions of $Ni(dpb)_2(CN)_2$ occur at the frequencies found in the spectra of the other five-coordinate complexes described here (Table I). The spectral evidence alone is not sufficient to establish the structure of this compound. However the stoichiometry and the demonstrated five-coordination allow one to conclude that one of the two diphosphines acts as a monodentate ligand.

TABLE I

ELECTRONIC SPECTRA OF $Ni(diphos)_m(CN)_2$ COMPLEXES

Complex	Absorption max, cm^{-1} [a]
$Ni(dpe)(CN)_2$	~28,200 sh (1250)
$Ni(dpe)_2(CN)_2$	20,800 (1900); ~26,500 sh (2750)
$Ni(dpp)(P(C_4H_9)_3)(CN)_2$	21,000 (1000);[b] ~27,000 sh (3000)
	20,800; ~27,000 sh[c]
$Ni(dpp)_{1.5}(CN)_2$	20,200 (1000); ~27,200 sh (4500)
	19,800[c]
$[Ni(dpb)(CN)_2]_2$	28,300 (1300)[d]
$Ni(dpb)_2(CN)_2$	~21,000 sh (1900); 26,300 (3300)
$Ni(dpb)_{1.5}(CN)_2$	20,200; 26,300[c]
	~21,000 (600); 27,000 (1700)[e]

[a] Methylene chloride solutions, unless otherwise stated; sh, shoulder; numbers in parentheses are molar absorptivities. [b] Apparent values for 10^{-3} *M* solution. [c] Reflectance spectrum. [d] Absorptivity calculated per $Ni(dpb)(CN)_2$ moiety. [e] Apparent values for 8.5×10^{-3} *M* solution.

The ligand dpb reacts with $Ni(dpb)Br_2$ in ethanol containing KCN and small amounts of water, yielding a red crystalline compound which analyzes as $Ni(dpb)_{1.5}(CN)_2$. The reflectance spectrum (Figure 3) is similar to that of the other five-coordinate complexes and demonstrates that there are five-coordinate nickel(II) atoms in the solid compound. The molecular weight is about 1150 in freezing $C_2H_4Cl_2$ (calcd for a dimer, 1500). The solubility in other solvents is too low to permit a molecular weight determination. The spectral patterns of the compound in CH_2Cl_2 (Figure 3) indicate that a five-coordinate species is present in solution.

Conclusions

As far as we know the diphosphines dpe, dpp, and dpb have always been found to act exclusively as chelating agents.[4,9] Only $(C_6H_5)_2PCH_2P(C_6H_5)_2$ (dpm) binds as a monodentate ligand[4] giving four-coordinate $Ni(dpm)_2X_2$ complexes. However, there are three kinds of ditertiary phosphines in the compounds investigated here: chelating, bridging, and nonchelating moieties. The occurrence of all possible modes of coordination is the result of the combined effects of the alkyl chain length in the diphosphine and of the possibility for nickel(II) to give four- as well as five-coordination.

The results obtained with the ditertiary phosphines confirm that the ability to coordinate three phosphorus atoms is a characteristic feature of the chemistry of nickel(II) cyanide. Other nickel salts of "strong" anions such as $\leftarrow C{\equiv}CR^-$ and $\leftarrow CNO^-$ can be expected to behave similarly. The red compound $Ni[P(C_2H_5)_2C_6H_5]_3(C{\equiv}CC_6H_5)_2$ has already been reported.[10] *Red* solutions are obtained in the reaction of $K_2Ni(CNO)_4$ with $P(C_2H_5)_3$ in ethanol. The yellow diamagnetic (four-coordinate) compound $Ni(P(C_2H_5)_3)_2(CNO)_2$ has been isolated from such solutions;[11] however, their red color leaves little doubt that they also contain the five-coordinate species $Ni(P(C_2H_5)_3)_3(CNO)_2$ in equilibrium with the planar compound.

In conclusion, it appears that both tertiary and ditertiary phosphines can give stable low-spin complexes MP_3X_2 (where M = Ni(II), Co(II); X = monovalent anion) only when the anion X is a good covalent bonder.

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(9) W. D. Horrocks, Jr., G. R. Van Hecke, and D. D. Hall, *Inorg. Chem.*, **6**, 694 (1967), and references quoted therein.

(10) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 1718 (1960).

(11) W. Beck and E. Schuvierer, *Chem. Ber.*, **98**, 298 (1965).