

Tertiary Phosphine Complexes of Nickel(0) and Nickel(I). New Dinitrogen Complexes of Nickel(0)

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Received August 5, 1974

The reduction of $NiX_2(PCy_3)_2$ ($X = Cl, Br; PCy_3 =$ tricyclohexylphosphine) in toluene with sodium sand under argon affords $[NiX(PCy_3)_2]_2$ or $Ni(PCy_3)_3$. In the same way starting from NiX_2P_2 [$X = Cl, Br; P = P(C_2H_5)_3, P(CH_2CH_2CH_2CH_3)_3, P(C_2H_5)_2C_6H_5$] the tetracoordinate Ni(0) complexes NiP_4 are obtained. These give $NiP_3(N_2)$ under nitrogen. The electronic spectra of Ni(0) and Ni(I) complexes, both in the solid state and solution, are reported.

Introduction

Ni(0) and Ni(I) complexes have received considerable attention as they have been found effective as catalysts in a number of reactions¹, especially in olefin oligomerization^{1a} and more recently in alkylene carbonate formation^{1b}. Ni(I) compounds² are not very common and usually they are reported to be tetra-^{2a-c} or pentacoordinate^{2f,g}. Tricoordinate Ni(I) complexes are supposed to exist in solution by dissociation of the tetracoordinated species^{2c} or produced in electrochemical reduction of Ni(II) phosphine complexes^{2h}, but not fully characterized.

This reports is concerned with the preparation of Ni(0) and Ni(I) complexes of formula NiP_4 ($P = PEt_3, P^nBu_3, PEt_2Ph$), $Ni(PCy_3)_3$, $[NiX(PCy_3)_2]_2$, and their electronic spectra in the solid state and solution are reported and discussed. The reaction of the NiP_4 complexes with nitrogen to give $Ni(N_2)P_3$ in solution is also reported.

Experimental

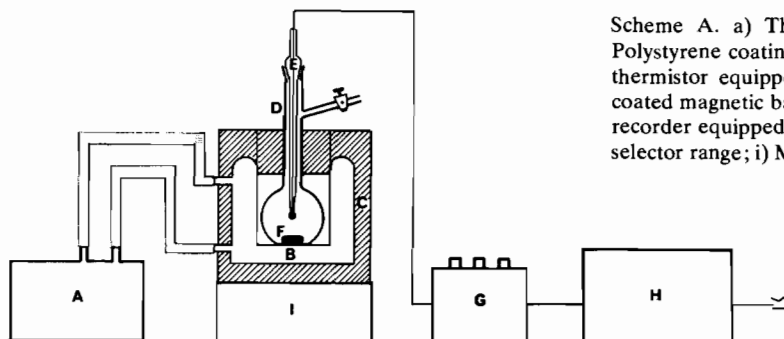
All the solvents were anhydriified in the usual manner and distilled under argon or nitrogen before use. They were handled out of the contact with air and moisture. The complexes were manipulated using the standard vacuum-line techniques. Samples for decomposition or melting points were sealed in capillary tubes under vacuum or an atmosphere of the specified gas.

Infrared spectra were recorded using a Perkin-Elmer 557 spectrophotometer. Bulk susceptibility measurements were obtained by the Faraday method in an argon or nitrogen atmosphere.³ Electronic spectra were recorded in the range 220–1000 nm with a CF4 Optica spectrophotometer which cell compartment was thermostated at 20° C, using 1.0 cm Teflon capped cells. Solid state (reflectance) spectra were recorded in a MgO mixture (MgO as reference) using a specially prepared cell, filled using a vacuum-line technique, where the solid complexes could be stored without any appreciable decomposition for the time needed to run the spectrum.

Determination of Molecular Weights

The molecular weights were determined cryoscopically in benzene using the apparatus shown in Scheme A.

A standard curve was obtained with chloranil or triphenylphosphine benzene solutions in the range $2-100 \times 10^{-3}$ molal. The solution of the complex was prepared apart and transferred under argon to the



Scheme A. a) Thermostatic bath; b) Jacketed beaker; c) Polystyrene coating; d) 10 ml flat bottomed flask; e) Sargent thermistor equipped with ground joint; f) 6 x 3 mm Teflon coated magnetic bar; g) Sargent thermistor bridge; h) Sargent recorder equipped with a 1.25–2.5–5.0–12.5–25–50–125 mV selector range; i) Magnetic stirrer.

flask(D) that was stopped up with the thermistor (E), that was provided with a ground joint. The temperature of the air bath around the flask was controlled by means of circulation of cold water from a thermostat (A) into the jacket (B) of the cell. The bridge resistance(G) was adjusted in such a way that the final part of the cooling curves of the pure benzene and of the solutions in the concentration range $2\text{--}35 \times 10^{-3}$ molal could be analyzed in the 0–200 divisions total width of the paper (2.5 mV full scale).

The standard curve was obtained by plotting ΔDiv (or ΔR) versus concentration. The ratio $\Delta T/\Delta\text{Div} = 1.02 \times 10^{-3} \text{ }^\circ\text{C}/\text{Div}$ has been calculated. For diluted solutions (4×10^{-3} molal) a $\Delta\text{Div} = 21$ has been found (between the freezing point of the solution and pure benzene) with a mean deviation of ± 0.4 divisions, giving thus an error of about 2%; for solutions approximately 15×10^{-3} molal the error was about 0.5%.

μ,μ -dibromotetrakis(tricyclohexylphosphine) dinickel(I), $[\text{NiBr}(\text{PCy}_3)_2]_2$.

A suspension of $\text{NiBr}_2(\text{PCy}_3)_2$ (6.5g; 8.5 mmol) and sodium sand (0.53g; 25.2 mmol) in toluene (20 ml) was stirred at room temperature under argon just until an orange-brown solution was produced (ca. 12 hours). After filtration the solution was concentrated *in vacuo* to 10 ml and by adding n-pentane (15 ml) orange-red crystals were obtained, which were filtered under argon, washed with n-pentane and dried *in vacuo*. Yield: 48%. D.p. 150–151 *in vacuo*. The complex is soluble in benzene, toluene, tetrahydrofuran, insoluble in pentane. It is paramagnetic ($\mu_{\text{eff}} = 2.2$ B.M. at 25°C). *Anal. Calcd. for $\text{C}_{72}\text{H}_{132}\text{Br}_2\text{Ni}_2\text{P}_4$: C, 61.82; H, 9.51; Br, 11.42; Ni, 8.39; P, 8.86. Found C, 63.00; H, 9.60; Br, 11.45; Ni, 8.25; P, 8.75%.*

μ,μ -dichlorotetrakis(tricyclohexylphosphine) dinickel(I), $[\text{NiCl}(\text{PCy}_3)_2]_2$.

This complex was obtained in a similar manner starting from $\text{NiCl}_2(\text{PCy}_3)_2$ and sodium sand (Na/Ni molar ratio = 4). The filtered solution was concentrated to a small volume (10 ml) and, after addition of n-pentane (10 ml), cooled to -20°C . The brown crystals that deposited on standing were filtered, washed with n-pentane and dried *in vacuo*. Yield = 47%. D.p. = 148–149°C *in vacuo*. The complex is soluble in benzene, toluene, tetrahydrofuran, not soluble in saturated hydrocarbons. It is paramagnetic ($\mu_{\text{eff}} = 2.1$ B.M. at 25°C). *Anal. Calcd for $\text{C}_{72}\text{H}_{132}\text{Cl}_2\text{Ni}_2\text{P}_4$: C, 65.95; H 10.14; Cl, 5.48; Ni, 8.96; P, 9.45. Found C, 66.10; H, 10.33; Cl, 5.45; Ni, 8.9 P, 9.43%.*

Tris(tricyclohexylphosphine)nickel(0), $\text{Ni}(\text{PCy}_3)_3$.

A suspension of $\text{NiBr}_2(\text{PCy}_3)_2$ (9.0 g; 11.56 mmol) and powdered sodium (1.1 g; 47.8 mmol) was stirred at room temperature under argon until the yellow–orange resulting solution gave a negative test for

bromine*. After filtration the solution was concentrated *in vacuo* to about 10 ml. On cooling to -80°C the solution became purple and violet crystals slowly precipitated.

The product was filtered at -30°C , washed with cold n-pentane and dried *in vacuo*. Yield = 43%. D.p. 86–88°C *in vacuo*. The complex is soluble in benzene, toluene, tetrahydrofuran, sparingly soluble in pentane, not soluble in ethanol. It is diamagnetic. *Anal. Calcd for $\text{C}_{54}\text{H}_{99}\text{NiP}_3$: C, 72.06; H, 11.09; Ni, 6.52; P, 10.32. Found C, 70.29; H, 10.73; Ni, 6.38; P, 9.90%.*

The same compound was obtained when argon was bubbled through a concentrated solution of $[\text{Ni}(\text{PCy}_3)_2]_2\text{N}_2$ in toluene at room temperature with a yield of about 50%.

From the mother solution different products were isolated, accounting for the total Ni and P. These products are at the moment under investigation. No metal nickel was detected during the reaction.

Tetrakis(tri-n-butylphosphine)nickel(0), $\text{Ni}(\text{P}^n\text{Bu}_3)_4$.

A solution of $\text{Ni}(\text{P}^n\text{Bu}_3)_2\text{Cl}_2$ (4.0 g; 7.5 mmol) in n-heptane (40 ml) was treated with sodium sand (0.72 g; 31 mmol) and stirred under argon for 24 hours. The red brown solution obtained was filtered and evaporated to dryness. Benzene (5 ml) and ethanol (10 ml) were added and the solution cooled to -20°C . Ivory needles deposited that were filtered at -20°C , washed with cold ethanol and dried *in vacuo*. Yield 2.1 g. M.p. under nitrogen: the compound becomes red at 44°C and melts at 52–55°C as a red liquid. The same values are found under vacuum. *Anal. Calcd. for $\text{C}_{48}\text{H}_{108}\text{NiP}_4$: Ni, 6.76; P, 14.27. Found: Ni, 6.94; P, 13.98%.*

Tetrakis(diethylphenylphosphine)nickel(0), $\text{Ni}(\text{PEt}_2\text{Ph})_4$.

This compound was similarly prepared under an argon atmosphere starting from $\text{NiBr}_2(\text{PEt}_2\text{Ph})_2$ (1.8 g; 3.2 mmol) and sodium (0.34 g; 15 mmol) in n-heptane. After filtration the red solution was concentrated to ca. 10 ml *in vacuo* and cooled to -20°C . Light yellow crystals deposited that were filtered and dried *in vacuo*. Yield 0.75 g. M.p.: under nitrogen the compound becomes red at 61°C and melts at 83–86°C as a red liquid. *Anal. Calcd for $\text{C}_{40}\text{H}_{60}\text{NiP}_4$: Ni, 8.11; P, 17.12. Found Ni, 8.11; P, 16.82%.*

Tetrakis(triethylphosphine)nickel(0), $\text{Ni}(\text{PEt}_3)_4$.

5.0 g (11.0 mmol) of $\text{NiBr}_2(\text{PEt}_3)_2$ were suspended in n-heptane (50 ml), treated with powdered sodium (1.05 g; 45 mmol) and stirred under argon until a purple solution was obtained. The solution was con-

* A good qualitative test is obtained upon exposure to air of one drop of the solution. This becomes colourless if only Ni(0) species are present in the solution, but gives a green coloration in the presence of Ni(I) or Ni(II) species.

centrated to 10 ml *in vacuo* and cooled to -20°C . On standing overnight a light yellow crystalline product was obtained which was isolated by filtration, washed with 5 ml of cold pentane and dried *in vacuo*. The product burns promptly when exposed to the air. It is soluble in non polar organic solvents giving purple solutions. In the solid state it is stable at -20°C , when heated to room temperature it becomes violet: the colour goes back to light yellow if it is promptly cooled to -20°C ; if it is left for a long time at room temperature it becomes irreversibly violet. The yellow complex can be obtained by recrystallization Yield: 2.5 g. D.p. decomposes at $93-94^{\circ}\text{C}$. *Anal.* Calcd for $\text{C}_{24}\text{H}_{60}\text{NiP}_4$: Ni, 11.05; P, 23.52. Found: Ni, 11.1; P, 22.8%.

μ -dinitrogen tetrakis(tricyclohexylphosphine) dinickel(0), $[\text{Ni}(\text{PCy}_3)_2]_2\text{N}_2$

A suspension of $\text{NiBr}_2(\text{PCy}_3)_2$ (2.0 g; 2.6 mmol) and sodium sand (0.25 g; 10.9 mmol) in toluene (15 ml) was stirred at room temperature under nitrogen until the resulting dark-red solution tested for bromine gave a negative test. The solution was filtered and cooled to -20°C . Dark red crystals of the dinitrogen complex were obtained which were filtered and dried *in vacuo*. Yield 50%. D.p. under nitrogen $136-138^{\circ}\text{C}$, *in vacuo* $118-121^{\circ}\text{C}$. *Anal.* Calcd for $\text{C}_{72}\text{H}_{132}\text{N}_2\text{Ni}_2\text{P}_4$: C, 68.24; H, 10.50; N, 2.21; Ni, 9.27; P, 9.78. Found C, 68.10; H, 9.95; N, 2.20; Ni, 9.15; P, 9.79%.

The same product was obtained when solid $\text{Ni}(\text{PCy}_3)_3$ was kept under nitrogen at room temperature for one hour (80% yield) or when it was suspended in warm petroleum ether (50°C) or dissolved in toluene (at room temperature) and exposed to nitrogen.

Trans-hydridochlorobis(tricyclohexylphosphine) nickel(II), $\text{NiHCl}(\text{PCy}_3)_2$

To a stirred solution of $\text{Ni}(\text{PCy}_3)_3$ (0.4 mmol) in petroleum ether (10 ml) 0.4 ml of a solution of HCl in ethanol (1 N) were added and a yellow crystalline compound precipitated, which was filtered, washed with cold ethanol and dried *in vacuo*. The compound was identified by means of its i.r. spectrum ($\nu_{\text{Ni-H}} = 1916\text{ cm}^{-1}$), D.p. (149°C under argon) and analysis. *Anal.*: Calcd for $\text{C}_{36}\text{H}_{67}\text{ClNiP}_2$: Cl, 5.40; Ni, 8.95; P, 9.44. Found Cl, 5.21; Ni, 8.70; P, 9.25%.

Trans-hydridochlorobis(triethylphosphine)nickel(II), $\text{NiHCl}(\text{PEt}_3)_2$

0.150 g of $\text{Ni}(\text{PEt}_3)_4$ were dissolved in benzene and treated with HCl in benzene under nitrogen. The red orange resulting solution was cooled to 0°C and red-orange crystals of the hydrido-complex precipitated, which were filtered and dried *in vacuo*. The complex was identified by means of its i.r. spectrum [band at 1920 cm^{-1} in nujol due to $\nu(\text{Ni-H})$] and analysis. *Anal.* Calcd for $\text{C}_{12}\text{H}_{31}\text{ClNiP}_2$: Cl, 10.69; Ni, 17.70; P, 18.68. Found Cl, 10.30; Ni, 17.06; P, 18.0%.

Reaction of $\text{Ni}(\text{PEt}_3)_4$, $\text{Ni}(\text{PEt}_2\text{Ph})_4$ and $\text{Ni}(\text{P}^n\text{Bu}_3)_4$ with Nitrogen

When the tetrakisphosphinenickel(0) complexes were dissolved in the appropriate solvent under nitrogen, deep violet solutions were obtained that showed in the i.r. spectrum strong bands in the region $2050-2100\text{ cm}^{-1}$, attributable to a terminal $\nu(\text{N}_2)$ stretching vibration of the N_2 bonded to a NiP_3 moiety. These bands disappear when argon is bubbled through the solutions and appear again when the solutions are exposed to N_2 .

Attempts to isolate the solid dinitrogen complexes failed so far; even working at low temperatures no pure samples of the dinitrogen complexes (terminal or bridging) were obtained.

Only very pure samples of the tetrakisphosphine complexes were isolated. The $\nu(\text{N}_2)$ stretching frequencies of the complexes in solution are as follows: $\text{Ni}(\text{PEt}_3)_3(\text{N}_2)$, 2070 cm^{-1} , very strong (n-heptane); $\text{Ni}(\text{PEt}_2\text{Ph})_3(\text{N}_2)$, 2065 cm^{-1} , strong (benzene); $\text{Ni}(\text{P}^n\text{Bu}_3)_3(\text{N}_2)$, 2063 cm^{-1} , very strong (toluene); $\text{Ni}(\text{P}^n\text{Bu}_3)_3(\text{N}_2)$, 2060 cm^{-1} , very strong (tetrahydrofuran).

Results and Discussion

Nickel(I) Complexes

The complexes $[\text{NiX}(\text{PCy}_3)_2]_2$ (X = Cl, Br) can be easily obtained by reduction of the corresponding Ni(II) complexes of formula $\text{NiX}_2(\text{PCy}_3)_2$ with sodium sand in toluene under argon. They are red-orange crystalline compounds (yellow when finely grounded), soluble in aromatic solvents and THF, readily oxidized by air both in the solid state and in solution. Their paramagnetism (2.1 B.M. for $[\text{NiCl}(\text{PCy}_3)_2]_2$ and 2.2 B.M. for $[\text{NiBr}(\text{PCy}_3)_2]_2$ at 25°C) accounts for the absence of any Ni-Ni bond in the solid state and is in accordance with a d^9 configuration with an orbital contribution. The values found agree with those reported for Ni(I) complexes by other Authors (see Table I)

The analysis of the i.r. and u.v. and visible spectra on solid samples suggests that the complexes are dimeric in the solid state.

TABLE I. Magnetic Data.

Compound	B.M.	Reference
$\text{Ni}(\text{PPh}_3)_3\text{Cl}$	2.2	2b
$\text{Ni}(\text{PPh}_3)_3\text{Cl}$	1.9	2c
$\text{Ni}(\text{PPh}_3)_3\text{Br}$	1.9	2c
$\text{Ni}(\text{dppe})_{1.5}\text{CN}$	2.0-2.3	2d
$\text{Ni}[\text{CH}_3\text{C}(\text{CH}_2\text{PPh}_2)_3]\text{Cl}$	1.98	2g

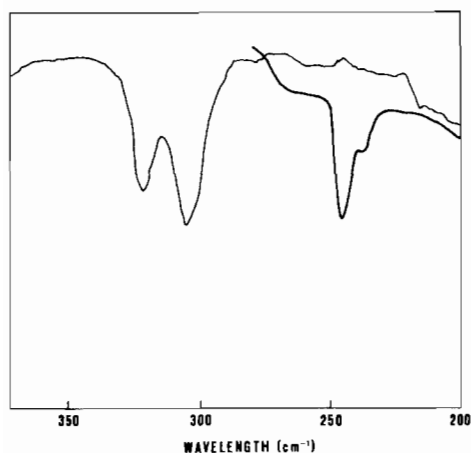


Figure 1. Far i.r. spectra (350–200 cm^{-1}) of: — $[\text{Ni}(\text{PCy}_3)_2\text{Cl}]_2$ in nujol mull; - - - $[\text{Ni}(\text{PCy}_3)_2\text{Br}]_2$ in nujol mull (CsI plates).

The far i.r. (600–200 cm^{-1}) spectrum of $[\text{NiCl}(\text{PCy}_3)_2]_2$ in nujol presents two bands of similar intensity at 321 and 306 cm^{-1} (see Fig. 1).

These bands are absent in the spectrum of $\text{NiCl}_2(\text{PCy}_3)_2$ that shows a strong band at 390 cm^{-1} that we assign to the $\nu(\text{Ni}-\text{Cl}_2)$ stretching in accordance with a *trans* configuration. The assignment agrees with those made for other *trans*- NiCl_2P_2 complexes. For example, for $\text{NiCl}_2(\text{PMe}_3)_2$ ^{4a} a band at 403 cm^{-1} is attributed to the *trans*- $\nu(\text{Ni}-\text{Cl}_2)$ stretching. The lower values of $\nu(\text{Ni}-\text{Cl})$ in $[\text{NiCl}(\text{PCy}_3)_2]_2$ than in $\text{NiCl}_2(\text{PCy}_3)_2$ is in accordance with the change of the oxidation state of the nickel atom from one to two. We propose a square planar configuration for the Ni(I)

complex with chlorine atoms bridging the two NiP_2 moieties.

For such a system two i.r. active metal-halogen stretching frequencies (b_{2u} and b_{3u}) are predicted and two bands are observed. For comparison $\text{Rh}_2\text{Cl}_2(1,5\text{-COD})_2$ shows bands at 278 and 260 cm^{-1} ^{4b}. The far i.r. spectrum of $[\text{NiBr}(\text{PCy}_3)_2]_2$ shows a medium band at 246 cm^{-1} and a weaker one at 238 cm^{-1} (Fig. 1). These bands are absent in the spectrum of the parent compound *trans*- $\text{NiBr}_2(\text{PCy}_3)_2$ that exhibits a band at 328 cm^{-1} .

The reflectance spectra of $[\text{NiCl}(\text{PCy}_3)_2]_2$ and $[\text{NiBr}(\text{PCy}_3)_2]_2$ are consistent with a square planar configuration. In fact the u.v. and visible spectra of solid $[\text{NiCl}(\text{PCy}_3)_2]_2$ and $[\text{NiBr}(\text{PCy}_3)_2]_2$ in the range 220–1000 nm (Fig. 2 and Table II) are comparable with that of the d^9 square planar dipyriddy-Ag(II) complex⁵ that presents a maximum at 357 $\text{m}\mu$ and a broad band at 454 $\text{m}\mu$. The adsorption at shorter wavelengths in Figure 2 could be associated with an electron transfer transition, while the band at 500 $\text{m}\mu$ can be ascribed to a forbidden transition because of the low value of the molar extinction. Therefore, we conclude that both the $\text{NiCl}(\text{PCy}_3)_2$ and $\text{NiBr}(\text{PCy}_3)_2$ complexes are dimeric in the solid state with a square planar configuration, which in the case of the bromo complex can be somewhat distorted because of the bigger size of the bromine atom with respect to the chlorine, thus accounting for the slight differences presented by the far i.r. spectrum.

Molecular weights in benzene show that both complexes dissociate in solution to give $\text{NiX}(\text{PCy}_3)_2$ ($\text{X} = \text{Cl}, \text{Br}$), in which the nickel atom is tricoordinate. We find the following values for the molecular weights:

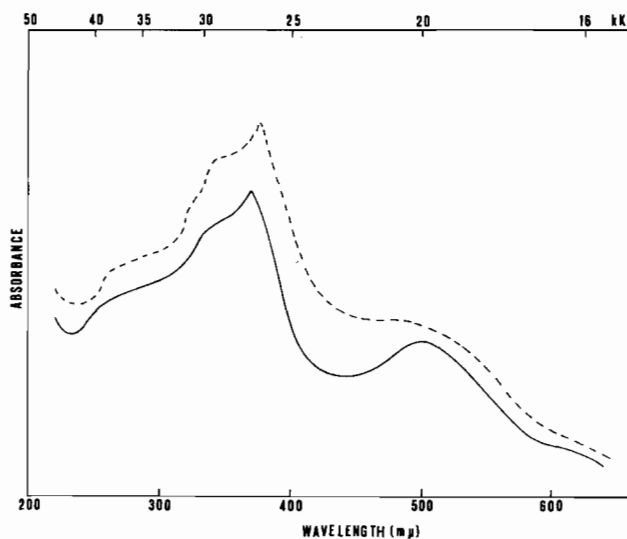


Figure 2. Electronic absorption spectra (reflectance), molar absorbance on arbitrary scale, - - - $[\text{Ni}(\text{PCy}_3)_2\text{Cl}]_2$; — $[\text{Ni}(\text{PCy}_3)_2\text{Br}]_2$.

TABLE II. Ultraviolet and Visible Spectral Data.

Compound	Absorption Maxima in $m\mu$		[Molar Extinction]	
$[\text{Ni}(\text{PCy}_3)_2\text{Cl}]_2^a$		345(sh)	370max	500(br)
$[\text{Ni}(\text{PCy}_3)_2\text{Br}]_2^a$		340(sh)	370max	500(br)
$\text{Ni}(\text{PCy}_3)_2\text{Cl}^b$	290 [$\epsilon = 1260$]	340 [$\epsilon = 2490$]	360 [$\epsilon = 2435$]	400 [$\epsilon = 600$]
$\text{Ni}(\text{PCy}_3)_2\text{Br}^b$	290 [$\epsilon = 2346$]	340 [$\epsilon = 2453$]	360 [$\epsilon = 2406$]	400 [$\epsilon = 570$]
$\text{Ni}(\text{PCy}_3)_3^a$	260	340		420(sh) 520max
$[\text{Ni}(\text{PCy}_3)_2]_2\text{N}_2^a$	260	340		400 520max
$\text{Ni}(\text{P}^n\text{Bu}_3)_4^a$	260(sh)	320max		490(vw,br)
$\text{Ni}(\text{P}^n\text{Bu}_3)_4^b$			360(sh)	485max
$\text{Ni}(\text{P}^n\text{Bu}_3)_3\text{N}_2^b$	275(sh)	290max	365(sh)	480(w,br)

^a Solid state in MgO. ^b Benzene solution; max: maximum; sh: shoulder; br: broad; w: weak; vw: very weak.

$\text{NiCl}(\text{PCy}_3)_2$

Calcd. for the monomer: 656

Found: 620 (5.62×10^{-3} molal)

Found: 643 (26.7×10^{-3} molal)

$\text{NiBr}(\text{PCy}_3)_2$

Calcd. for the monomer: 699

Found: 660 (6.35×10^{-3} molal)

Found: 680 (27.6×10^{-3} molal)

The values found of the molecular weights imply that no further dissociation of $\text{NiX}(\text{PCy}_3)_2$ takes place in solution.

The u.v. and visible spectrum of the monomer $\text{NiCl}(\text{PCy}_3)_2$ in benzene solution is quite different from that of the dimer in the solid state. Three maxima at 290 $m\mu$ ($\epsilon = 1260$) 340 $m\mu$ ($\epsilon = 2490$) and 360 $m\mu$ ($\epsilon = 2435$) and a shoulder at 400 $m\mu$ ($\epsilon = 600$) are evident (see Fig. 2 bis).

The spectrum of $\text{NiBr}(\text{PCy}_3)_2$ is very similar to that of the chloro complex, the unique difference being the higher molar extinction of the band at 290 $m\mu$ (see Table II). These spectra are the first to be reported for a d^9 tricoordinate species. The presence of a tetracoordinate species in the solutions of our Ni(I) complexes seems to be excluded on the basis of the fact that the d^9 tetracoordinate complexes, both square planar^{5,6} or tetrahedral^{2b,6} shows bands at wavelengths higher than 400 $m\mu$. Thus, the absence of bands in the range 400–1000 $m\mu$ precludes the existence of a Ni(I) tetracoordinate (dimer or solvated) in solution, in accordance with the results of the molecular weights determination.

The solutions of these complexes are very sensitive to oxygen and the u.v. spectra change rapidly if the solutions are exposed to air. The Ni(I) complexes react readily with perchloric acid in n-butylic alcohol with evolution of 0.5 mol of hydrogen per nickel atom.

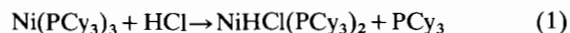
Ni(0) Complexes

Tricoordinate Ni(0)

The $\text{NiX}(\text{PCy}_3)_2$ (X = Cl, Br) can be easily reduced with Na in toluene at room temperature under argon

to give the Ni(0) complex of formula $\text{Ni}(\text{PCy}_3)_3$. This can be obtained as well by direct reduction of $\text{Ni}(\text{PCy}_3)_2\text{X}_2$ in toluene with Na under argon. Even in the presence of an excess of free phosphine the tetracoordinate complex of formula $\text{Ni}(\text{PCy}_3)_4$ could not be isolated, probably because PCy_3 is a bulky ligand. According to Tolman⁷ for the PCy_3 ligand a minimum cone angle of $179 \pm 10^\circ$ can be assumed, much larger than those relative to PET_3 ($132 \pm 4^\circ$), P^nBu_3 ($130 \pm 4^\circ$), or PET_2Ph^* ($135 \pm 5^\circ$), whose complexes of formula NiP_4 we have isolated.

The $\text{Ni}(\text{PCy}_3)_3$ forms diamagnetic purple crystals, unstable to the air both in the solid state and in solution, soluble in most organic solvents. It is oxidized by halogenated hydrocarbons and reacts readily with HCl in ethanol to give the already known $\text{NiHCl}(\text{PCy}_3)_2$ ⁸ according to (1):



$\text{Ni}(\text{PCy}_3)_3$ reacts with N_2 in the solid state (and in solution) to give the binuclear dinitrogen complex of formula $[\text{Ni}(\text{PCy}_3)_2]_2\text{N}_2$, reported by Jolly *et al.*⁹

In the solid state equilibrium is reached within an hour, with the 82% of nickel converted to the dinitrogen binuclear complex, according to (2):



The i.r. spectrum of the solid does not show at any time bands attributable to a terminal $\nu(\text{N}_2)$ stretching vibration. The amount of N_2 coordinated can be measured by means of gas chromatographic analysis³ of the gas evolved on decomposition of the solid samples (see Table III).

If the reduction of $\text{NiX}_2(\text{PCy}_3)_2$ (X = Cl, Br) with Na in toluene is conducted under nitrogen (instead of argon) $[\text{Ni}(\text{PCy}_3)_2]_2\text{N}_2$ is obtained in 50% yield (based on Ni). This reaction provides a further way

* For this phosphine the Author does not give any value of the cone angle but it can be assumed to range around $135 \pm 5^\circ$, averaging the effect of the substitution of a phenyl group for an ethyl group in $\text{P}(\text{C}_2\text{H}_5)_3$.

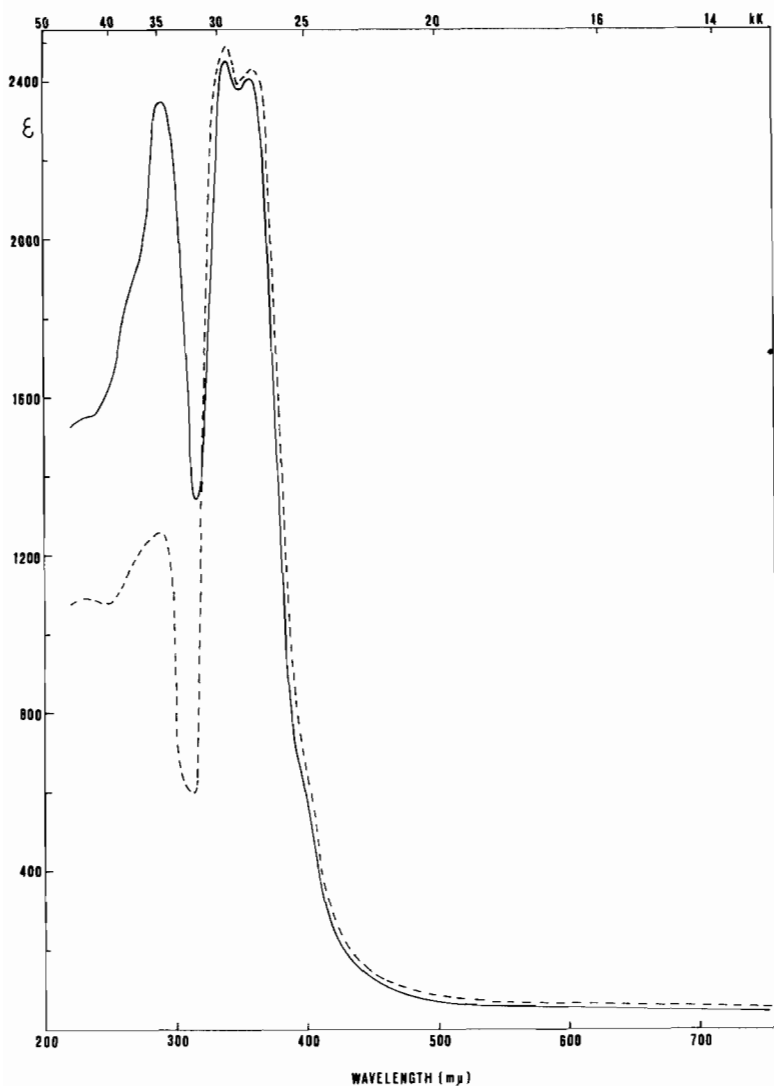


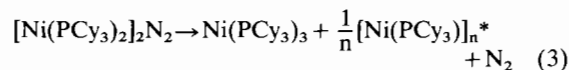
Figure 2 bis. Electronic absorption spectra in benzene solution: ---- Ni(PCy₃)₂Cl; — Ni(PCy₃)₂Br.

TABLE III. Gas chromatographic Determination of N₂ on the Product of Reaction of Solid Ni(PCy₃)₃ with N₂.

Ni(PCy ₃) ₃ μmol	Time in minutes	N ₂ Evolved μmol	N ₂ /Ni Molar Ratio
17.6	10	4.2	0.24
23.7	30	8.26	0.35
32.6	64	13.5	0.41
20.9	4500	8.55	0.41
23.8	8700	9.7	0.41

to the binuclear dinitrogen nickel complex. The dinitrogen complex is converted into the Ni(PCy₃)₃ complex when argon is bubbled through its concentrated solutions (47% yield).

The presence of metal nickel has never been revealed, thus supporting the equation (3):



From the mother solution several fractions of products containing Ni and phosphine (P/Ni molar ratio 0.5:1.5), accounting for the total nickel and phosphine, have been isolated, but no pure product has been isolated so far.

The Ni(PCy₃)₃ reflectance spectrum is very similar to that of [Ni(PCy₃)₂]₂N₂ apportioning thus the

* This residue could be as well a monomer or a polymer. Such a hypothesis has been suggested also by one of the referees.

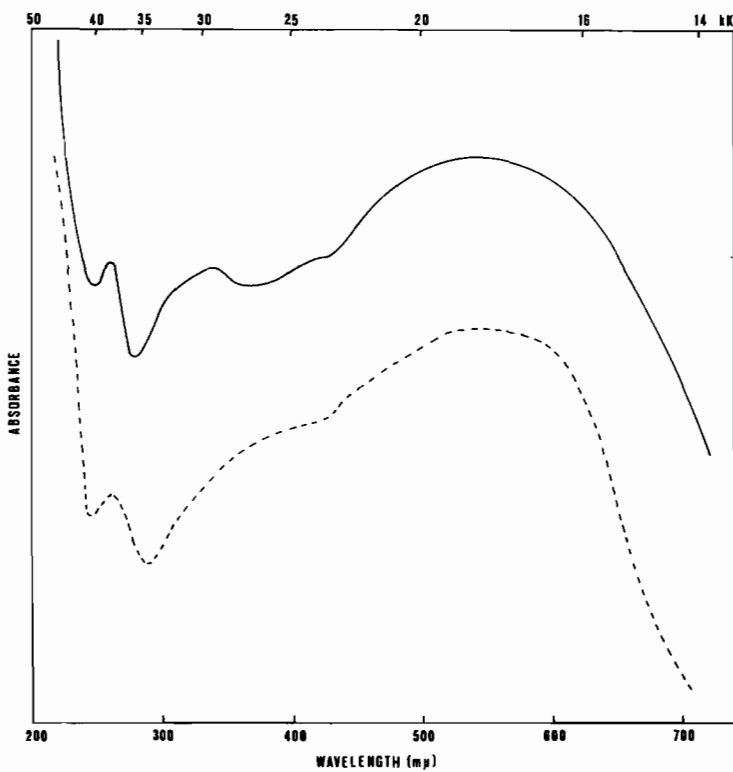


Figure 3. Electronic absorption spectra (reflectance), molar absorbance on arbitrary scale: ---- $[\text{Ni}(\text{PCy}_3)_2]_2\text{N}_2$; — $\text{Ni}(\text{PCy}_3)_3$.

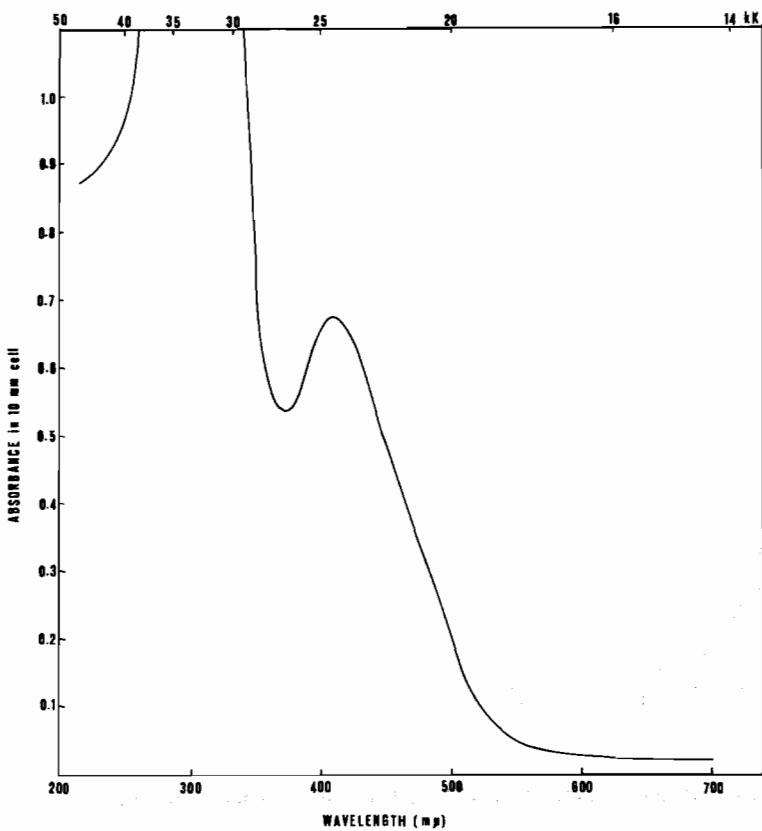


Figure 4. Electronic absorption spectrum of a $9.65 \times 10^{-4} M$ solution of $\text{Ni}(\text{PCy}_3)_3$ in benzene under argon.

idea that the two complexes have the same coordination number in the solid state (Fig. 3 and Table II). The dinitrogen complex in benzene (under nitrogen) presents a maximum at $410 \text{ m}\mu$ with a shoulder at $500 \text{ m}\mu$. When the nitrogen atmosphere is replaced by argon this spectrum becomes identical to that of $\text{Ni}(\text{PCy}_3)_3$ under argon (see Fig. 4 and 5). The difference between the reflectance spectra of $[\text{Ni}(\text{PCy}_3)_2]_2\text{N}_2$ and $\text{Ni}(\text{PCy}_3)_3$ and the spectra in solution of the same compounds can be explained assuming that in solution dissociation equilibria take place and, likely, the predominating species are not the tricoordinate $\text{Ni}(0)$ complexes.

We are investigating the reaction of the dinitrogen complex with trialkyl phosphines and other ligands*, and we present here the first results on the reaction of $[\text{Ni}(\text{PCy}_3)_2]_2\text{N}_2$ with PEt_3 .

Addition of PEt_3 to a solution of $[\text{Ni}(\text{PCy}_3)_2]_2\text{N}_2$ in toluene under nitrogen causes a gradual change of the i.r. spectrum of the solution and when a PEt_3/Ni molar ratio equal to one is reached the band at 2028 cm^{-1} , ascribed to the $\text{Ni}(\text{PCy}_3)_2\text{N}_2$ species in solution, disappears and a new very strong band appears

* The complete report on these reactions will be subject of a next paper.

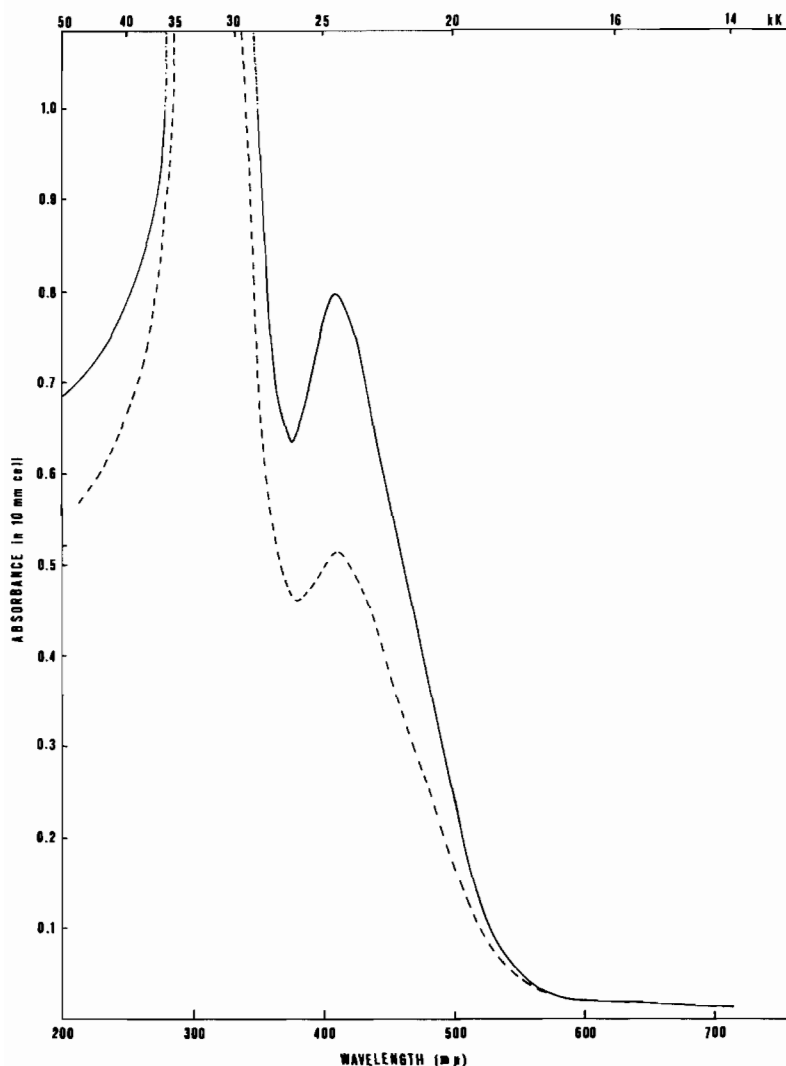
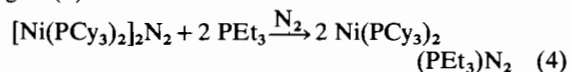


Figure 5. Electronic absorption spectra of a $3.57 \times 10^{-4} M$ solution of $[\text{Ni}(\text{PCy}_3)_2]_2\text{N}_2$ in benzene: — under nitrogen; ---- under argon.

at 2070 cm^{-1} . This band is much more intense than the band at 2028 cm^{-1} . We attribute the band at 2070 cm^{-1} to a $\text{Ni}(\text{PCy}_3)_2(\text{PEt}_3)\text{N}_2$ species according to (4):



The analysis of the u.v. spectrum of this system (Fig. 6) confirms the formation of a tetracoordinated species in solution. The final solution showed an absorbance maximum at $390\text{ m}\mu$ with a weak broadened band at $480\text{ m}\mu$. The disappearance of the absorbance above $400\text{ m}\mu$ is characteristic of the change of the coordination number from three to four for Ni(0) complexes. The same behaviour was found by Tol-

man¹⁰ for the system $\text{Ni}[\text{P}(\text{O}-o\text{-C}_6\text{H}_4\text{CH}_3)_3]_3 + \text{RCN}$. Addition of CH_3CN to the solution of the tricoordinate Ni(0) complex causes the disappearance of the bands at 410 and $460\text{ m}\mu$ in consequence of the formation of the $\text{Ni}[\text{P}(\text{O}-o\text{-C}_6\text{H}_4\text{CH}_3)_3]_3 \cdot \text{CH}_3\text{CN}$ complex. When $\text{C}_6\text{H}_5\text{CN}$ is used a new band appears at $396\text{ m}\mu$.

Tetracoordinate Ni(0) complexes

Commonly used pathways to complexes of formula NiP_4 (P = trialkyl-, triaryl-, alkylaryl-phosphines) include the reaction of nickelocenes with phosphines¹¹, and reaction of phosphines with $\text{Ni}(\pi\text{-allyl})_2$ ¹² or $\text{Ni}(1,5\text{ cyclooctadiene})_2$ ⁷. The replacement of CO in $\text{Ni}(\text{CO})_4$ was a convenient route to obtain complexes

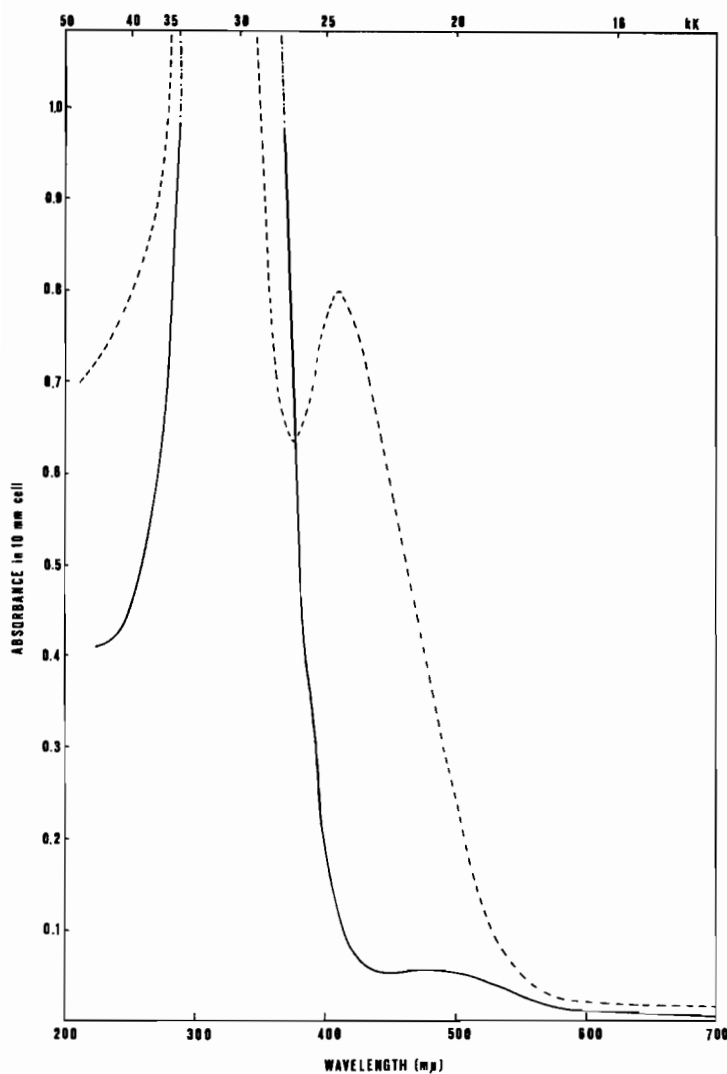
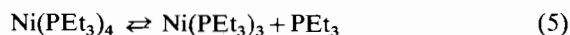


Figure 6. Electronic absorption spectra of: ---- a $3.57 \times 10^{-4}\text{ M}$ solution of $[\text{Ni}(\text{PCy}_3)_2]_2\text{N}_2$ in benzene under nitrogen; — the same after addition of PEt_3 in a molar ratio PEt_3/Ni equal to one.

of the type $\text{Ni}(\text{PX}_3)_4$ ($\text{X} = \text{Cl}^{13}$, F^{14}); and $\text{Ni}(\text{CH}_2 = \text{CH}-\text{CN})_2$ has been used as a starting material for obtaining phosphite complexes¹⁵ which can also be prepared by reaction of nickelocene¹⁶.

Only a few reports are available on the preparation of Ni(0) complexes by direct reduction of Ni(II): $\text{Ni}(\text{PPh}_3)_4$ has been prepared by reduction of Ni(2,4-pentanedionate)₂ with AlEt_3 in the presence of phosphine¹⁷ and $\text{Ni}(\text{PPh}^n\text{Bu}_2)_4$ by reduction of Ni(acac)₂ with AlEt_2OEt in the presence of phosphine¹¹; $\text{Ni}[\text{P}(\text{OR})_3]_4$ ($\text{R} = \text{Me}$, Et , ^iPr , ^nPr , ^nBu) have been obtained by reduction of $\text{NiX}_2[\text{P}(\text{OR})_3]_2$ with potassium graphitite¹⁸. We have prepared the NiP_4 complexes ($\text{P} = \text{PEt}_3$, P^nBu_3 , PEt_2Ph) by direct reduction of NiX_2P_2 complexes with sodium sand in toluene (or n-heptane) under argon in absence of free phosphine. When the reduction was carried out in the presence of the free ligand the isolation of the pure NiP_4 complexes was very difficult.

These complexes are diamagnetic and sensitive to air and moisture. They burn in air in the solid state and decompose easily in solution in the presence of traces of oxygen. They are white or light-yellow when freshly prepared. The $\text{Ni}(\text{PEt}_3)_4$ is white when stored at low temperatures (-20°C); when heated to room temperature its colour changes to violet and goes back to light-yellow if cooled promptly to -20°C . If the complex stays longer at room temperature it converts irreversibly into a violet compound, from which the white compound can be obtained by recrystallization. This behaviour can be explained assuming a dissociation of the tetracoordinate complex in the solid state according to (5):



The formation of the tricoordinate Ni(0) complex is responsible for the colour change. It can be assumed that the dissociation reaction is reversible as long as the free phosphine is trapped into the crystal lattice.

The $\text{Ni}(\text{P}^n\text{Bu}_3)_4$ is white and more stable than the PEt_3 complex and can be stored at room temperature without appreciable decomposition for some hours. The thermal stability increases going to the pale yellow $\text{Ni}(\text{PEt}_2\text{Ph})_4$ complex. The complexes are soluble in non polar solvents giving deep red solutions under argon as a result of the extensive dissociation. They react with HCl to give hydrido complexes of Ni(II). For example $\text{Ni}(\text{PEt}_3)_4$ reacts with HCl in n-butyl alcohol to give *trans*- $\text{NiHCl}(\text{PEt}_3)_2$.

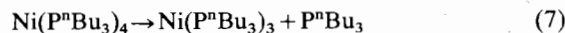
When exposed to nitrogen the solutions of the NiP_4 complexes take up nitrogen and the i.r. spectrum shows very strong bands at 2070 cm^{-1} (n-heptane), 2060 cm^{-1} (THF), 2065 cm^{-1} (benzene) respectively for $\text{Ni}(\text{PEt}_3)_4$, $\text{Ni}(\text{P}^n\text{Bu}_3)_4$ and $\text{Ni}(\text{PEt}_2\text{Ph})_4$. This situation is in contrast with what has been found for $\text{Ni}(\text{PPh}_3)_4$ and $\text{Ni}[\text{P}(\text{O}-o-\text{C}_6\text{H}_4\text{CH}_3)_3]_3$, which are

not able to coordinate nitrogen in solution, probably because of the low basicity of these phosphorus ligands.

These are one of the first example of tetracoordinate Ni(0) dinitrogen complexes obtained by reaction of NiP_4 complexes with nitrogen*, according to (6):



The presence of the tetracoordinate dinitrogen complexes is supported by the analysis of the u.v. and visible spectra (see below). In Fig. 7 we report the reflectance spectrum of the tetracoordinate $\text{Ni}(\text{P}^n\text{Bu}_3)_4$. The very weak absorption at $490\text{ m}\mu$ could be ascribed to a tricoordinate species formed upon slight dissociation of the NiP_4 complex. In fact, if the temperature of the cell compartment is raised to 35°C the colour of the complex becomes red and the reflectance spectrum of the compound changes to that in Fig. 7 bis. Moreover, the spectrum of the $\text{Ni}(\text{P}^n\text{Bu}_3)_4$ is consistent with those of the previously mentioned tetracoordinate complexes reported by Tolman. When the nickel complex is dissolved in benzene under argon the spectrum exhibits a shoulder at $360\text{ m}\mu$ and a maximum at $485\text{ m}\mu$ (Fig. 8). Such a change must be related to the dissociation of NiP_4 to give NiP_3 and free phosphine according to (7):



and accounts for the deep colour of the solution.

When the argon atmosphere is replaced by nitrogen the colour of the solution fades and the spectrum changes as shown in Fig. 8, owing to the formation of the NiP_3N_2 . The same behaviour is observed for the PEt_3 and PEt_2Ph complexes.

Unfortunately, so far we have not been able to isolate pure samples of NiP_3N_2 from these solutions, even working at temperatures as low as -70°C ; the only products isolated in good yields are the tetracoordinate NiP_4 species. Attempts are in progress to trap the phosphine liberated on dissociation in solution in order to isolate the crystalline dinitrogen complexes. It is evident that both the basicity and the steric hindrance of the phosphine play an important role on the stability of the dinitrogen complexes of Ni(0).

Acknowledgements

This research was supported by the Consiglio Nazionale delle Ricerche. The Authors wish to thank Mr. P. Bianco for analyses of metal and phosphorus, and Mr. U. Farella for drawings.

* After submission of this paper we had notice that Tolman *et al.*¹⁹ had reached independently our same conclusions for what concerns the behaviour of the $\text{Ni}(\text{PEt}_3)_4$ complex under nitrogen in solution.



Figure 7. Electronic absorption spectrum (reflectance), molar absorbance on arbitrary scale, of $\text{Ni}(\text{P}^n\text{Bu}_3)_4$ at 15°C

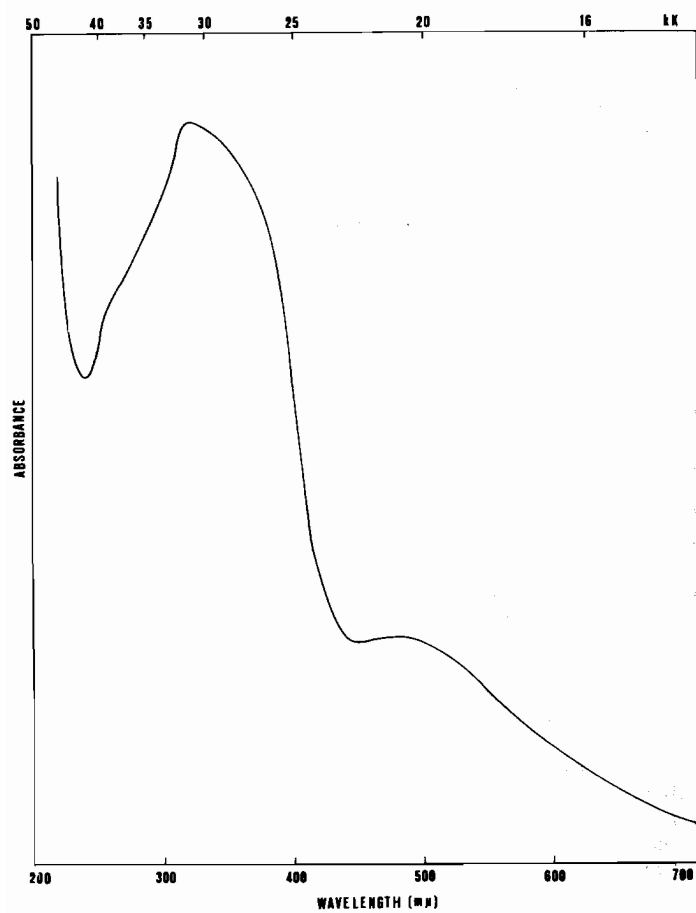


Figure 7 bis. Electronic absorption spectrum (reflectance), molar absorbance on arbitrary scale, of $\text{Ni}(\text{P}^n\text{Bu}_3)_4$ at 35°C .

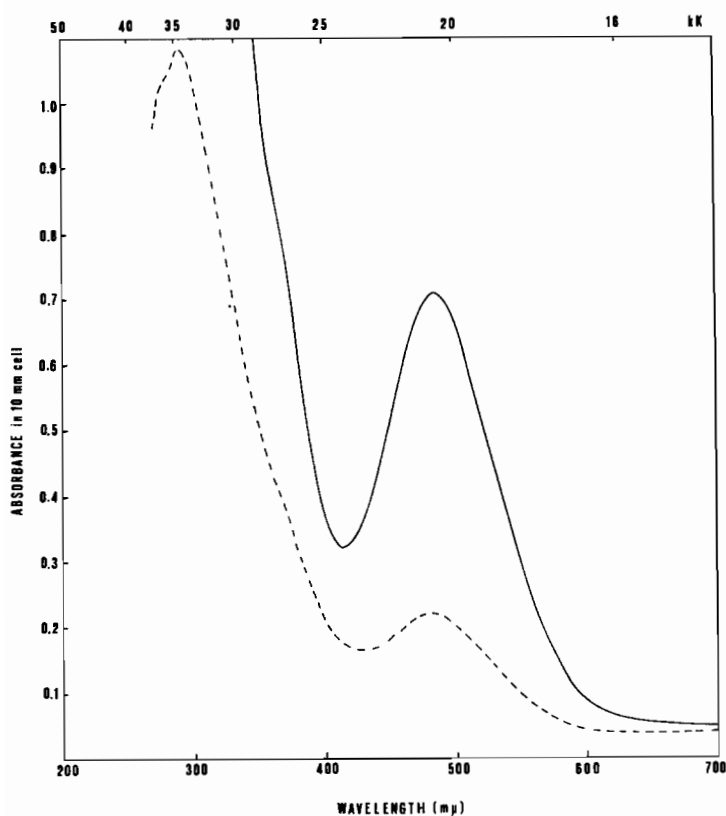


Figure 8. Electronic absorption spectra of a $1.04 \times 10^{-3} M$ solution of $Ni(P^tBu_3)_4$ in benzene: — under argon; --- under nitrogen.

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