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Nickel(II) and nickel(0) complexes containing 2-pyridylphosphine ligands, including water-soluble species ☆

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Abstract

The paramagnetic, S = 1, NiX₂L₂ (X = Cl or Br, L = PPh_{3-n}py_n, n = 1-3), and diamagnetic NiBr₂[d(py)pe] (4b) complexes have been isolated, generally as solvates, where py = 2-pyridyl and d(py)pe = py₂P(CH₂)₂Ppy₂. Also isolated are the diamagnetic Ni(CO)₂(PPh₂py)₂ (5), Ni(CO)₂[d(py)pe] (7), Ni(PPh₂py)₄, Ni(PPhy₂)₄ and Ni[d(py)pe]₂, sometimes as hydrates. The complexes, except for 5 which contains paramagnetic impurities, analyze well, and have been characterized by ¹H and ³¹P{¹H} NMR (for diamagnetic species), IR (for the carbonyls) or magnetic moment data (for the paramagnetic species). NMR evidence for in situ formation of Ni(CO)₂(PPhpy₂)₂ and Ni(Ppy₃)₄ is also presented. Of note, NiX₂L₂, 4b and 7 are water-soluble, possibly because of protonation of the pyridyl-N atoms, although this remains to be established; even non-aqueous solutions of these Ni(II) species are moisture-sensitive. In contrast to Ni(PPh₃)₄, at ambient conditions the NiL₄ species show little tendency to dissociate in benzene or toluene.

Keywords: Nickel(II) complexes; Nickel(0) complexes; 2-Pyridylphosphine complexes

1. Introduction

Interest remains high in development of homogeneous catalytic systems that are effective in aqueous solution [1]. The reasons are clear: the cheapness of, and familiarity of dealing with, aqueous solutions, and the ease of separation of the catalyst and the product(s), particularly using biphasic systems. Contributions from this laboratory have focussed thus far on the use of the 2-pyridylphosphine ligands PPh_{3-n}py_n, where py = 2-pyridyl [2-4]. The aqueous solubilities of these ligands do increase with increasing number of pyridyl substituents and, for example, Ppy₃ readily dissolves at pH ~3, because the first protonation equilibrium corresponds to a pK_a value of 4.2 at 20 °C [5]; some dinuclear Pd₂(I) and monomeric Pd(II) complexes of Ppy₃ dissolve, however, at neutral pH [2].

We have reported previously on 2-pyridylphosphine complexes of monomeric Pt(0) [3], monomeric Pd(II) and Pt(II) [2-4,6], and dinuclear $Pd_2(I)$ and $Pt_2(I)$

[2,4,6]. The Pt(0) species were reactive toward small molecules such as O₂, HCl, MeI and olefins [2], and we tested unsuccessfully species such as Pt(Ppy₃)₄ and $Pt(PPh_2py)_3$ for catalytic hydration of olefins [2]. The well established catalytic properties of Pd(0) and Ni(0)tertiary phosphine complexes in non-aqueous solvents, e.g. for polymerization of olefins and acetylenes, and for formation of substituted products of allylic compounds [7], encouraged us to synthesize pyridylphosphine complexes of Pd(0) and Ni(0). This paper reports on the nickel work including potentially useful Ni(II) precursor species. Synthesis and use of the chelating 2-pyridyl ligand, py2P(CH2)2Ppy2 or 1,2-bis[bis(2-pyridyl)phosphino]ethane, abbreviated d(py)pe, is also described; this ligand has been used in conjunction with some studies on the biological properties of some Au(I) complexes [8], but details on its synthesis and characterization have not appeared. Our studies on Pd(0)complexes containing $PPh_{3-n}py_n$ and d(py)pe will be reported elsewhere [9]. We have also synthesized Pt(0) and Pt(II) complexes containing d(py)pe [9], a range of Ru(II) complexes containing pyridylphosphines [10], and trans-1,2-bis[bis(2-pyridyl)phosphino]cyclopentane, a ligand related to d(py)pe, but with a cyclopentane backbone [9]. A review on pyridylphosphines and their metal complexes appeared recently [11].

Abbreviations: COD = 1,5-cyclooctadiene; py = 2-pyridyl; d(py)pe = 1,2-bis[bis(2-pyridyl)phosphino]ethane; dp = 1,2-bis(diphenylphosphino)ethane; THF = tetrahydrofuran; BuOH = n-butanol; r.t. = room temperature.

^{*} Dedicated to the memory of Professor Ugo Croatto.

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2. Experimental

2.1. General

All preparations were performed under an atmosphere of dry N_2 (Union Carbide of Canada) by either conventional Schlenk tube techniques or in a glovebox. Solution NMR spectra (s = singlet, t = triplet, m = multiplet, dd = doublet of doublets, p = pseudo,br = broad) were acquired at room temperature using a Bruker AC-200 MHz spectrometer on samples prepared in 5 mm NMR tubes. The ³¹P NMR spectra (81 MHz) were ¹H broad-band decoupled, and were referenced to external 85% H₃PO₄; the ¹H shifts were referenced to the residual proton shift of the internal deuterated solvent. Solid state ³¹P{¹H} NMR spectra (81 MHz) were obtained using a Bruker CXP 200 instrument with the CP/MAS readout. IR spectra were recorded on either a BOMEM Michelson or an ATi Mattson Genesis instrument, using KBr pellets (s = strong, m = medium, w = weak, br = broad). UV-Vis spectra were obtained using 1 cm Spectrosil precision cells and an HP 8452A diode array spectrophotometer; extinction coefficients are given in units of M^{-1} cm⁻¹. Liquid secondary ion mass spectrometry (LSIMS) was carried out on a Kratos Concept II HQ instrument, using samples in a thioglycerol/H₂O matrix. Magnetic susceptibility measurements were made using the Guoy method. Elemental analyses were performed by Mr P. Borda of this department.

2.2. Materials

All organic solvents were dried over a suitable drying agent, and degassed using three freeze-pump-thaw cycles. Deuterated solvents for NMR were from MSD isotopes and were deoxygenated prior to use by freeze-pump-thaw cycles. Nickel(II) salts (Alfa Inorganics or Anachemia Chemicals), Ni(COD)₂ and PPh₃ (Strem Chemicals) and Zn dust (Fisher Scientific), were used as received. Purified CO was supplied by Union Carbide of Canada. The complexes $NiX_2(PPh_3)_2$, $X = Cl_1$, Br [12], and Ni(CO)₂(PPh₃)₂ [13] were made according to the literature procedures, and characterized by elemental analysis, magnetic susceptibility and UV-Vis data (for the Ni(II) species), and by elemental analysis, ¹H and ³¹P{¹H} NMR and IR (for the Ni(0) species); the spectroscopic data agreed with those in the literature [12-14].

The $PPh_{3-n}py_n$ ligands were synthesized and characterized as described previously [2,3,6]; the syntheses were adapted from a literature procedure [15].

2.2.1. 1, 2-Bis[bis(2-pyridyl)phosphino]ethane (d(py)pe) This ligand was obtained as outlined in Eq. (1):

$$B_{r} \bigvee_{N} \xrightarrow{n-BuLi}_{E_{12}O.-78^{\circ}C} \bigvee_{Li} \bigvee_{N} \xrightarrow{Cl_{2}PCH_{2}CH_{2}PCl_{2}}_{Py_{2}P} py_{2}P \xrightarrow{Ppy_{2}}_{Py_{2}}$$
(1)

the 2-bromopyridine and n-BuLi reagents were acquired from Aldrich, and the 1,2-bis(dichlorophosphino) ethane was made from C₂H₄, white phosphorus, and PCl_3 (all used as received from commercial sources) according to a literature method [16]. The 2-bromopyridine (16 ml, 0.17 mol) was added to a stirred mixture of n-BuLi (100 ml, 1.6 M hexane solution, 0.16 mol) and dried and degassed Et_2O (100 ml) at -78°C under a flow of N₂; the initially formed red solution soon deposited a precipitate, and the mixture was stirred for 4 h at -78 °C. Cl₂P(CH₂)₂PCl₂ (6 ml, 0.04 mol) in Et₂O (50 ml) was then added via cannula from a second flask, and the mixture allowed to warm slowly to r.t. with stirring for 3 h. Degassed 2 M H_2SO_4 (100 ml) was then added, and the mixture stirred rapidly for 10 min before the two layers were allowed to settle. The lower, aqueous acidic layer was cannulated off, and the Et₂O layer subsequently washed again with 100 ml H₂SO₄. Saturated NaOH solution (60 ml) was then added to the combined acid layers to generate a yellow-brown precipitate which was collected in air, washed with water, and dried in vacuo (14 g, 87%). The solid was then dissolved in a minimum of warm acetone; cool hexane was then added to the orange solution to the point of cloudiness. Slow evaporation of the acetone component generated a pale orange solid that was collected and dried in vacuo (10.9 g, 68%). Anal. Calc. for C₂₂H₂₀N₄P₂: C, 65.66; H, 5.01; N, 13.92. Found: C, 65.60; H, 5.33; N, 13.61%. ¹H NMR (CDCl₃): δ 8.6 (p.d, H₆), 7.5 (m, H₄), 7.4 (m, H₃), 7.1 (m, H₅), 2.5 (p.t, CH₂). ³¹P{¹H} NMR (CDCl₃): $\delta - 6.1$ (s). ¹³C{¹H} NMR (CDCl₃): δ 162.8 (C₂, by APT), 150.0, 135.3, 128.4, 122.4 (C₃-C₆), 22.0 (CH₂).

2.3. Complexes

The synthesized complexes 1a-3a, 1b-3b, 4b and 7 gave a single spot on a TLC plate (alumina) developed with 2:1 CHCl₃/EtOAc; 8, 9 and 11 were too airsensitive for TLC treatment.

2.3.1. $NiCl_2(PPh_2py)_2 \cdot H_2O$ (1a)

NiCl₂·6H₂O (0.056 g, 0.24 mmol) and PPh₂py (0.13 g, 0.48 mmol) were added to a sealed Schlenk tube, and 2.5 ml of glacial acetic acid were introduced via syringe. The clear, bright green reaction mixture became darker on warming as the reaction proceeded. After 2 h at 40 °C, the solvent was removed via a vacuum line to yield a dark green solid (0.12 g, 77%). Anal.

Calc. for $C_{34}H_{30}N_2Cl_2NiOP_2$: C, 60.67; H, 4.49; N, 4.16. Found: C, 60.94; H, 4.53; N, 4.08%. IR (cm⁻¹): 3390 (m, br, H–OH); 1584, 1561, 1457, 1419 (s, py skeletal bands) [17]. μ_{eff} =3.09 BM.

2.3.2. $NiCl_2(PPhpy_2)_2$ (2a)

The procedure was as for 1a; the use of NiCl₂·6H₂O (0.036 g, 0.15 mmol) and PPhpy₂ (0.079 g, 0.30 mmol) yielded a light green powdered solid (0.088 g, 89%). *Anal.* Calc. for C₃₂H₂₆N₄Cl₂NiP₂: C, 58.40; H, 3.98; N, 8.51. Found: C, 58.18; H, 4.03; N, 8.78%. IR (cm⁻¹): 1582, 1559, 1456, 1419 (s, py skeletal bands). μ_{eff} =2.92 BM.

2.3.3. $NiCl_2(Ppy_3) \cdot H_2O$ (3a)

The procedure was similar to that used for 1a, but the reaction mixture, NiCl₂ · 6H₂O (0.035 g, 0.15 mmol) and Ppy₃ (0.079 g, 0.30 mmol), was allowed to stir at 40 °C for 3.5 h, when the precipitated pale green solid was isolated via filtration, washed with minimal acetic acid, and dried in vacuo (0.047 g, 48%). Anal. Calc. for C₁₅H₁₄N₃Cl₂NiOP: C, 43.64; H, 3.42; N, 10.81. Found: C, 43.77; H, 3.56; N, 9.91%. IR (cm⁻¹): 3365 (m, br, H–OH); 1582, 1562, 1456, 1421 (s, py skeletal bands). μ_{eff} = 3.03 BM. LSIMS (*m*/*z*): 414 [*M*+1], 360–358 [*M*-Cl-H₂O].

2.3.4. $NiBr_2(PPh_2py)_2 \cdot 2H_2O$ (1b)

NiBr₂ (0.033 g, 0.15 mmol) was stirred in 2.5 ml toluene to produce a yellow-brown slurry. To this was added a methanolic (1.5 ml) solution of PPh₂py (0.081 g, 0.31 mmol); on being warmed to 50 °C, the slurry became green. After 1.5 h the precipitated lime green solid was isolated via filtration, washed with toluene, and dried in vacuo (0.066 g, 58%). *Anal.* Calc. for C₃₄H₃₂N₂Br₂NiO₂P₂: C, 52.28; H, 4.13; N, 3.59. Found: C, 52.47; H, 3.96; N, 3.60%. IR (cm⁻¹): 3395 (m, br, H-OH); 1581, 1562, 1448, 1432 (s, py skeletal bands). $\mu_{eff} = 2.96$ BM.

2.3.5. $NiBr_2(PPhpy_2)_2 \cdot 2H_2O$ (2b)

A warm BuOH (0.8 ml) solution of PPhpy₂ (0.084 g, 0.32 mmol) was added to a light green, BuOH (0.8 ml) solution of NiBr₂ (0.037 g, 0.16 mmol) via syringe. This mixture was stirred and heated at 60 °C for 0.5 h, before being taken to dryness on the vacuum line at r.t. to yield a pale green, powdered solid (0.086 g, 69%). *Anal.* Calc. for $C_{32}H_{30}N_4Br_2NiO_2P_2$: C, 49.08; H, 3.86; N, 7.14. Found: C, 49.14; H, 3.79; N, 6.84%. IR (cm⁻¹): 3255 (m, br, H–OH); 1584, 1560, 1457, 1419 (s, py skeletal bands). μ_{eff} =3.02 BM.

2.3.6. $NiBr_2(Ppy_3)_2 \cdot 2H_2O$ (3b)

To a warm BuOH solution (0.5 ml) of NiBr₂ (0.03 g, 0.14 mmol) was added a warm BuOH solution (0.6 ml) of Ppy₃ (0.08 g, 0.30 mmol); the resulting purple

solution quickly formed a precipitate when the reaction vessel was submersed in an ice-bath. The pale pink solid was isolated via filtration, washed with butanol, and dried in vacuo (0.10 g, 95%). *Anal.* Calc. for $C_{30}H_{28}N_6Br_2NiO_2P_2$: C, 45.86; H, 3.59; N, 10.70. Found: C, 45.65; H, 3.89; N, 10.56%. IR (cm⁻¹): 3280 (m, br, H–OH); 1620, 1577, 1455, 1422 (s, py skeletal bands). $\mu_{eff} = 3.06$ BM.

2.3.7. $NiBr_2(py_2PCH_2CH_2Ppy_2) \cdot toluene$ (4b)

To a warm toluene slurry (1.5 ml) of NiBr₂ (0.043 g, 0.20 mmol), a warm orange solution of Ppy₂CH₂CH₂-Ppy₂ (0.079 g, 0.20 mmol) in MeOH (1.0 ml) was added; the mixture became dark brown instantaneously and a brown precipitate formed. The mixture was stirred for 0.5 h at 50 °C before the solvents were removed via evacuation; the dried solid was then dissolved in CHCl₃ (3 ml), the mixture filtered, and the filtrate then taken to dryness to yield a dark reddish-brown solid (0.052 g, 43%). Anal. Calc. for C₂₉H₂₈N₄Br₂NiP₂: C, 48.85; H, 3.96; N, 7.86. Found: C, 48.64; H, 4.06; N, 7.51%. ¹H NMR (CDCl₃): δ 8.7 (p.d, H₆), 8.4 (m, H₄), 7.7 (m, H₃), 7.3 (m, H₅), 2.7 (dd, -CH₂-), 2.1 (m, toluene). ³¹P{¹H} NMR (CDCl₃): δ 71.7 (s).

2.3.8. $Ni(CO)_2(PPh_2py)_2$ (5)

To an N₂-flushed Schlenk tube containing NiBr₂ (0.05 g, 0.22 mmol) and PPh₂py (0.12 g, 0.44 mmol) was added THF (8 ml); the initial yellow solution became dark green in 5 min presumably due to in situ formation of NiBr₂(PPh₂py)₂. The solution was stirred for 0.5 h when Zn dust (0.03 g, 0.46 mmol) was added and CO was bubbled through the solution for 1.5 h. The Zn was then filtered off, and the filtrate taken to dryness to yield an off-white solid (0.077 g, 55%). A satisfactory elemental analysis could not be obtained; the ¹H NMR (CDCl₃) showed broad resonances at δ 3.7 (THF) and δ 6.8–8.0 (Ph and py), while no definitive ³¹P{¹H} signals were seen. Paramagnetic Ni(II) impurities are probably present in the isolated compound. IR (cm⁻¹): 1998, 1946 (s, CO).

2.3.9. $Ni(CO)_2(PPhpy_2)_2$ (6)

The presence of compound **6** was determined using ³¹P{¹H} NMR for the in situ reaction of Ni(CO)₂(PPh₃)₂ with PPhpy₂ in an NMR tube. The dicarbonyl (0.015 g, 0.024 mmol) and PPhpy₂ (0.013 g, 0.048 mmol) were dissolved in CDCl₃ (0.6 ml) to give a pale yellow solution; the spectra were then run at various intervals (1, 22, 45 and 115 h) to study the phosphine exchange and formation of **6**. After 115 h, the reaction was ~20% complete, as determined from a ratio of the ³¹P peaks. Use of a larger excess of PPhpy₂ causes the displacement reaction to proceed more quickly. ¹H NMR (CDCl₃): δ 7.0–7.9 and 8.4–8.8 (Ph and py groups). ³¹P{¹H} NMR (CDCl₃): δ –5.5 (s, free PPh₃), –2.7 (s, free PPhpy₂),

32.7 (s, Ni–PPh₃), 31.2 (s, Ni–PPhpy₂); a weak AB type signal at δ 37.5 and 32.9 presumably corresponds to the mixed phosphine species Ni(CO)₂(PPh₃)(PPhpy₂).

2.3.10. $Ni(CO)_2(py_2PCH_2CH_2Ppy_2) \cdot 2H_2O$ (7)

In a Schlenk tube Ni(CO)₂(PPh₃)₂ (0.077 g, 0.12 mmol) and d(py)pe (0.049 g, 0.12 mmol) were dissolved in 2.5 ml of CH₂Cl₂ to give a pale yellow solution. The mixture was stirred for 18 h at 50 °C to give a dark yellow solution which was then cooled to r.t. Cool Et₂O (5 ml) was added to yield a yellow precipitate which was collected, then washed with 2×2.5 ml of warm Et₂O to give pure 7 (0.030 g, 48%). Anal. Calc. for C₂₄H₂₄N₄NiO₄P₂: C, 52.12; H, 4.37; N, 10.13. Found: C, 52.37; H, 3.99; N, 9.91%. IR (cm⁻¹): 1994, 1939 (s, CO). ¹H NMR (CDCl₃): δ 8.6 (p.d, H₆), 7.8, 7.7, 7.1 (m, H₃-H₅), 2.8 (dd, -CH₂-). ³¹P{¹H} NMR (CDCl₃): δ 55.3 (s).

2.3.11. $Ni(PPh_2py)_4 \cdot H_2O(8)$

On mixing Ni(COD)₂ (0.045 g, 0.16 mmol) and PPh₂py (0.172 g, 0.64 mmol) in 5 ml of hexanes, there was a rapid colour change from bright yellow to orange and finally red, with formation of a precipitate. With continued stirring (1.5 h) the precipitate became darker red, when it was collected and then dried under vacuum for several days (0.103 g, 57%). *Anal.* Calc. for C₆₈H₅₈N₄NiOP₄: C, 72.29; H, 5.17; N, 4.96. Found: C, 72.22; H, 5.24; N, 4.71%. ¹H NMR (C₇D₈): δ 8.5 (p.d, H₆), 7.5 (br. s, H₇-H₉), 7.2, 6.9, 6.5 (m, H₃-H₅). ³¹P{¹H} NMR (C₇D₈): δ 31.4 (s). ³¹P{¹H} NMR (solid state): δ 32.8 (s).

2.3.12. Ni(PPhpy₂)₄ (9)

The procedure was the same as that given for 8, but using PPhpy₂; the isolated solid was bright orange. ¹H NMR (C₆D₆): δ 8.5 (p.d, H₆), 7.7, 7.3, 7.1, 6.9, 6.5 (m or br. s, H₃-H₉). ³¹P{¹H} NMR (solid state): δ 41.9 (s, Ni-PPhpy₂), -7.1 (s, free PPhpy₂).

2.3.13. Ni(Ppy₃)₄ (10)

This species was formed in situ completely and rapidly in C₆D₆ on mixing Ni(COD)₂ (0.015 g, 0.05 mmol) and Ppy₃ (0.055 g, 0.20 mmol). ¹H NMR (C₆D₆): δ 8.5 (p.d, H₆), 7.5–6.5 (m, H₃–H₅); the COD singlet resonances are seen at δ 5.5 (–CH=) and 2.2 (–CH₂–). ³¹P{¹H} NMR (C₆D₆): δ 28.9 (s).

2.3.14. $Ni(py_2PCH_2CH_2Ppy_2)_2$ (11)

The procedure was similar to that given for 8, but using 0.32 mmol of the bidentate ligand and a reaction temperature of 50 °C instead of r.t. Compound 11 was isolated as a yellow-orange solid. Yield 59%. Anal. Calc. for $C_{44}H_{40}N_8NiP_4$: C, 61.20; H, 4.67; N, 12.98. Found: C, 60.88; H, 4.59; N, 12.67%. ¹H NMR (C₆D₆): δ 8.5 (p.d, H₆), 7.3, 7.0, 6.5 (m, H₃-H₅), 3.1 (dd, -CH₂-). ³¹P{¹H} NMR (C₆D₆): δ 55.9 (s).

3. Results and discussion

3.1. Paramagnetic nickel(II) complexes

Syntheses of the dichloro and dibromo nickel(II) complexes of the pyridylphosphines were generally made by the procedure first reported by Venanzi for the PPh₃ analogues [12], using Ni(II) salts and the phosphine in glacial acetic acid or butanol for the chloro and bromo complexes, respectively. $NiBr_2(PPh_2py)_2$ (1b) and NiBr₂[d(py)pe] (4b), however, were isolated from toluene-MeOH solutions. The complexes containing the $PPh_{3-n}py_n$ ligands are all paramagnetic with magnetic moments corresponding to the spin-only value for S=1systems, the data being consistent with distorted tetrahedral structures [12]. The monohydrate formulations for two of the dichloro complexes, and dihydrate formulations for the NiBr₂L₂ complexes $(L = PPh_{3-n}py_n)$, are needed to satisfy the elemental analyses; in each case the hydrated species show a broad IR band in the 3200-3400 cm⁻¹ region, typical of non-coordinated water [18]. There is no direct evidence for the presence of coordinated water (but see below for 3a). The ¹H NMR spectra in CDCl₃ reveal qualitatively the presence of water at δ 1.5 (slightly broadened because of the presence of the paramagnetic species), but other peaks due to the pyridylphosphine ligands are very weak and broad; similarly, meaningful ³¹P{¹H} spectra were not measurable. As with PPh₃ [19], it is presumably the bulk of the pyridylphosphines with the small Ni(II) that forces the NiX₂L₂ species (X = Cl, Br) into distorted tetrahedral geometry (versus d⁸ diamagnetic, square planar).

Of considerable interest is isolation of the $NiCl_2(Ppy_3) \cdot H_2O$ (3a) complex containing just a single phosphine per Ni, particularly when the dibromo complex is prepared as NiBr₂(Ppy₃)₂·2H₂O (3b). Complex **3a** is again paramagnetic, and on steric grounds the bulkier bromo system would be expected to accommodate fewer phosphines in a tetrahedral environment. One possibility is that an N atom of the pyridyl group coordinates with the formation of a four-membered, chelate ring; such chelate formation has been documented previously within square planar Pt(II) species containing PPh₂py [20], PPhpy₂ [6] and Ppy₃ [6], as well as octahedral Ru(II) species [21]. In 3a, the harder Cl (versus Br) might favour bonding of the N atom. However, unlike all the other dihalo derivatives, 3a is insoluble in CH₂Cl₂ or CHCl₃, and a polymeric or dimeric formulation (possibly with H-bonding interactions) containing solely P-bonded or even P-N bridging Ppy₃ [2,4,11] is possible, although the highest molecular weight peak in the mass spectroscopic data (from a thioglycerol/H₂O matrix) corresponds to a monomeric species, including the water molecule. The pale green colour of **3a** is typical of tetrahedral, S = 1, Ni(II) species [19]. The other dichloro compounds **1a** and **2a**, and the dibromo complexes **1b** and **2b**, are also green, but the dibromo complex NiBr₂(Ppy₃)₂·2H₂O (**3b**) is actually a pale pink colour. Attempts to measure solution UV-Vis absorption spectra were hampered by decomposition/reactivity of the species in common solvents.

Complex 2b, NiBr₂(PPhpy₂)₂ \cdot 2H₂O, dissolves in H₂O, CH₂Cl₂ or benzene and initially absorption peaks are seen in the 560 and 420 nm regions, but the peak intensities decrease within seconds and colourless solutions result. The water-insoluble $NiX_2(PPh_3)_2$ complexes dissolve in CH₂Cl₂ to generate stable solutions showing an absorption maximum in both the 580-540 ($\epsilon \sim 100$) and 425-405 ($\epsilon \sim 1200$) regions (our data agreeing with those in the literature [12]); thus the transient spectrum of 2b resembles that for the PPh₃ analogue. Complex 1b, $NiBr_2(PPh_2py)_2 \cdot 2H_2O$, behaves somewhat analogously to 2b although the initially green CH₂Cl₂ solution now rapidly becomes yellow; 3b dissolves more slowly and generates colourless solutions in CH₂Cl₂ and in H₂O. D₂O solutions of the bromides give uninformative paramagnetic NMR spectra, but the pyridylphosphines clearly remain coordinated. The solution behaviour of the dichloro complexes varies with the pyridylphosphine: the PPh₂py species (1a) is insoluble in H₂O, but becomes brown on contact with moisture, a similar 'decomposition' being observed on exposure of solid 1a to air; the PPhpy₂ and Ppy₃ species (2a and 3a) are air-stable, but slowly dissolve in H_2O to give colourless solutions; 1a and 2a dissolve in CH₂Cl₂ to give colourless, air-stable solutions, while as noted above 3a is insoluble in CH₂Cl₂. All the chloro and bromo species (1a-3a, 1b-3b) dissolve in MeOH to form colourless solutions. Dissolution of 2a and 3a in water or MeOH containing chloride ion occurs in the same way as in the chloride-free solvent, but this does not necessarily rule out the possibility of formation of cationic, solvated species via loss of Cl⁻. More detailed studies on the solution behaviour, particularly that in aqueous media, are in progress; protonation of the pyridyl-nitrogen(s) seems likely and, even in CH₂Cl₂, water will be present in all cases except one (2a) because of the presence of the solvate molecules of the complexes. It is possible that the non-aqueous solutions of the complexes might be particularly moisture-sensitive, and measurements in more rigorously controlled conditions are being undertaken.

3.2. Diamagnetic nickel(II) complexes

Complexes of the type NiX₂[$R_2P(CH_2)_nPR_2$] (X = halide) are well known [20], and the dpe species (n = 2)



Fig. 1. Labelling of protons for 2-pyridylphosphine ligands.

are square planar and diamagnetic, giving rise to airstable, reddish solutions (e.g. in CH₂Cl₂) with an absorption maximum in the 520–460 nm region ($\epsilon \sim 2000$) [21]. Following our successful synthesis of the d(py)pe ligand according to standard procedures [11] outlined in Eq. (1), we attempted to synthesize the $NiX_2[d(py)pe]$ complexes by treating the Ni(II) salts with the ligand in alcohol or alcohol-toluene mixtures as done for other chelating P-P ligands [21], but have successfully characterized only the dibromo species (4b) which was isolated with a toluene solvate molecule. The complex is reddish (with an absorption maximum at 478 nm (ϵ \sim 300) in CH₂Cl₂) and diamagnetic, and thus square planar. Of the 2-pyridyl ¹H NMR signals, that for the H_6 proton (see Fig. 1) always gives the most downfield signal [9,10,22]. Of the H_3-H_5 protons, the multiplet signal for H₃ is the simplest pattern, approximating closely to a doublet, while the multiplet signal for H_4 is always downfield from that for H_5 [9,10,22]. More generally, the relative positions of H₃-H₅ for 2-pyridyl protons are found to vary with the solvent, and the nature of the complex; details will be presented elsewhere [9,10]. The specific assignments given for the H_3-H_5 protons of the free d(py)pe ligand (see Section 2) are based on those determined for the Ppy₃ ligand [22], and these agree with the generalizations noted above. The expected doublet of doublets for the -CH₂protons in 4b is seen at δ 2.7, while in the free ligand, the doublets overlap and a pseudo-triplet is observed. The ³¹P{¹H} singlet of the free ligand (δ -6.1) is a few ppm downfield of that for dpe [23], and, like the latter, on formation of a five-membered chelate ring undergoes a large downfield shift [24], with $\delta_{\rm P}$ at 71.7 for 4b. Like the monodentate pyridylphosphine complexes, 4b undergoes 'transformation' in solution. The pink solutions (in CH₂Cl₂ or CHCl₃) slowly generate yellow solutions with concomitant decreases in intensity of the NMR signals; 4b dissolves in MeOH or H₂O to generate yellow species directly. The pink solutions of 4b are not O₂-sensitive, and subsequent formation of Ni(III) species such as NiBr₃(P-P), which can be made for dpe using Br₂ as oxidant [21], appears unlikely, but again more work is needed to elucidate the solution chemistry.

3.3. Nickel(0) complexes

Attempts to isolate pure, diamagnetic $Ni(CO)_2L_2$ complexes (L = a monodentate pyridylphosphine) were unsuccessful, but there is good evidence for their formation, and the chelate-containing $Ni(CO)_2[d(py)pe]$ (7) was synthesized and characterized as a dihydrate.

We tried to synthesize the Ni(CO)₂L₂ species via the documented Zn/CO reduction of NiX₂L₂ complexes (X=halogen) in THF [13], the method we used successfully to isolate Ni(CO)₂(PPh₃)₂; however, the isolated products contain paramagnetic, presumably Ni(II) species, and THF impurities, as described, for example, in Section 2 for Ni(CO)₂(PPh₂py)₂ (5). The isolated, off-white solid did exhibit CO IR bands at 1998 and 1946 cm⁻¹, comparable to the anti-symmetric and symmetric ν (CO) bands of Ni(CO)₂(PPh₃)₂ (1997 and 1928 cm⁻¹, respectively). (The literature values for the PPh₃ species are 1998 and 1932 cm⁻¹ [13].) The somewhat higher ν (CO) values for the PPh₂py species imply somewhat stronger π -acceptor properties for the PPh_{3-n}py_n ligands relative to PPh₃.

To avoid the problem of paramagnetic impurities, an alternative phosphine displacement procedure was studied using Ni(CO)₂(PPh₃)₂ (A) as precursor, for example Eqns. (2) and (3). In situ NMR experiments in CDCl₃ at ambient conditions using an initial

$$Ni(CO)_{2}(PPh_{3})_{2} (\mathbf{A}) + PPhpy_{2} \xrightarrow{CDCl_{3}}$$

$$Ni(CO)_{2}(PPh_{3})(PPhpy_{2}) (\mathbf{6a}) + PPh_{3} (2)$$

$$\mathbf{6a} + PPhpy_{2} \xrightarrow{CDCl_{3}} Ni(CO)_{2}(PPhpy_{2})_{2} (\mathbf{6}) + PPh_{3} (3)$$

PPhpy₂:A ratio of 2.0 revealed slow partial formation (20% over 5d), probably governed by the solution equilibria, of a species with a ³¹P{¹H} singlet at δ 31.2, attributed to 6, while a weak AB type signal at δ 37.5 and 32.9 is attributed to the intermediate mixed phosphine species 6a; the ³¹P{¹H} singlet for A is observed at δ 32.7. The equilibria can also be monitored using the $\delta_{\rm P}$ signals of the phosphines (-5.5, PPh₃; -2.7, PPhpy₂). The studies reveal also formation, over extended periods, of the phosphine oxides (δ 28.9 and 16.9 for OPPh₃ and OPPhpy₂, respectively). Use of higher initial ratios of PPh_{3-n}py_n:A gave more effective conversions to species of type 6, but we have been unable to isolate pure samples of the complexes.

Of some interest, the overall equilibrium constant for reactions (2) and (3), assuming 20% equilibrium formation of 6 under the conditions noted, is estimated to be ~0.015, and the formation of the PPh₃ species (versus PPhpy₂) is favoured thermodynamically. The 2pyridyl group is electron-withdrawing relative to a phenyl substituent [25], and the weaker σ -basicity of the phosphorus of the PPh_{3-n}py_n ligands (versus PPh₃) likely accounts for the relative stabilities, because the somewhat better π -acceptor properties of the pyridylphosphines (as reflected in the relative ν (CO) values of the Ni(CO)₂L₂ species – see above and below) would be expected to enhance the stability of the Ni(0) species. Synthetic application of the phosphine displacement method for d(py)pe worked well, and the air-stable Ni(CO)₂[d(py)pe]·2H₂O complex (7) was readily isolated. The elemental analysis, NMR and IR data establish the formulation; the downfield ³¹P{¹H} singlet again reflects the presence of the five-membered ring, while, of the ν (CO) values, the symmetric stretch is about 10 cm⁻¹ higher than that for Ni(CO)₂(PPh₃)₂. The formation of the chelate ring clearly drives the forward displacement reaction, which is virtually complete in ~20 h. Noteworthy is that 7 dissolves in water to give a very pale yellow solution, the nature of which is under investigation.

It should be noted that the crystal structure of complex 5, $Ni(CO)_2(PPh_2py)_2$, has been reported [26], and the species has been used to synthesize NiRh(PPh_2py)_2-(CO)Cl₃ which effects carbonylation of MeOH [27]; however, details, including the synthetic procedure for 5, were not given in the literature available to us [11].

Carbonyl-free Ni(0) species were made by adding stoichiometric amounts of the pyridylphosphines to Ni(COD)₂ in hexanes at ambient conditions, as described by Ittel for the synthesis of Ni(PPh₃)₄ [28]; the labile COD ligands become the co-product which is readily removed via the vacuum line.

Compound 8, Ni(PPh₂py)₄·H₂O, was isolated as a bright red, powdered solid and, much like Ni(PPh₃)₄ [28], is extremely sensitive to O_2 and moisture; solution NMR spectra could be measured if done rapidly after dissolution of the solid, because decomposition to give a dark coloured mixture occurred in minutes even under 'O₂- and moisture-free' conditions. The broad singlet at δ 7.5 in the ¹H NMR is assigned to H₇-H₉, based on relative integrations with the other proton signals; the 'immediate' ³¹P{¹H} NMR solution spectrum is a sharp singlet at δ 31.4, which is correspondingly observed at δ 32.8 in the solid state spectrum. No free PPh₂py signal is seen, showing that the tetrakis(phosphine) formulation is correct. $Ni(PPh_3)_4$ in the solid state has been considered to be a tris(phosphine) complex containing lattice phosphine [29], and some room temperature ³¹P{¹H} NMR and titration data are also consistent with dissociation into Ni(PPh₃)₃ and PPh₃ [29,30], although at low temperature a single signal at δ 24.1 is consistent with the presence of Ni(PPh₃)₄ [29].

The supposed Ni(PPhpy₂)₄ (9) was isolated as an orange, very air-sensitive solid; because of decomposition, a satisfactory elemental analysis has not been obtained. A solution ¹H NMR was measured, but with only H₆ being assigned, while a ³¹P{¹H} NMR spectrum could be recorded in the solid state only; the singlet for the complex is seen at δ 41.9 and that of some free phosphine at δ -7.1. We were unable to isolate samples of Ni(Ppy₃)₄ (10), but its in situ formation in C₆D₆ from Ni(COD)₂ was readily demonstrated by the sharp singlet seen in the ³¹P{¹H} NMR at a 4:1 ligand to Ni ratio, with the absence of a signal for the free ligand (δ 0.0). There is no evidence for phospine dissociation from the Ni(PPh_{3-n}py_n)₄ species at ambient conditions in solution, behaviour that contrasts with that of Ni(PPh₃)₄, and we attribute this to the stronger π -acid character of the pyridylphosphines.

The chelate complex Ni[d(py)pe]₂ (11) requires heat (to ~50 °C) for its formation, but, once formed, is significantly more stable in air and in solution than the tetrakis(monodentate ligand) species; the NMR signals are sharp and the ³¹P{¹H} resonance, because of the presence of the five-membered ring, is again downfield, in the same region as the ³¹P{¹H} peak for 7. Complex 11 appears to be of comparable stability to Ni(dpe)₂ [20,21].

4. Conclusions

In summary, we have shown that 2-pyridylphosphine complexes of the type NiX₂L₂ (X = Cl, Br), Ni(CO)₂L₂ and NiL₄ (L=PPh_{3-n}py_n) may be formed, as well as corresponding species with a chelating bis(pyridylphosphine) ligand, L₂ = py₂P(CH₂)₂Ppy₂. Preliminary studies reveal generally more complex solution chemistry than for the corresponding PPh₃ and dpe complexes, and, of note, water solubility for at least the NiX₂L₂ species (all but one) and Ni(CO)₂[py₂P(CH₂)₂Ppy₂]; more detailed studies on the solution behaviour and potential catalytic properties are in progress.

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