Synthesis and Characterization of the First Mononuclear Ni^{II} Phosphorane Imino Complex

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A recent contribution by Klein et al. describes the first examples of Ni^{II} phosphorane imido complexes.[1] These diamagnetic clusters, prepared by photochemical activation of the $[NiCl(N_3)(PMe_3)_2]$ azido precursor contain the trimethylphosphorane imido ligand as a triply bridging group. The authors suggest that their formation involves a nitrene intermediate which traps PMe_3 from the reaction mixture giving the phosphorane imido moiety, $Me_3P{=}N^-$. Further examples of tetrametallic paramagnetic Ni^{II} phosphorane imido clusters of the type $[NiX(NPEt_3)]_4$ (X = Cl, Br) have been reported by Dehnicke et al.[2]

We report here the synthesis and characterization of the unprecedented *mononuclear* Ni^{II} *N*-arylphosphino-substituted phosphorane imino complex $[NiCl(PMe_3)(PN{=}PMe_3)]PF_6$ (**3**) and of the corresponding free ligand (*o*-diphenylphosphino)-*N*-(trimethylphosphoranyl)phenylimine ($PN{=}PMe_3$). Complex **3** is formed when (*o*-diphenylphosphino)aniline (PNH_2) is present in the coordination sphere of the Ni^{II} phosphino amino starting compounds, as in $[NiCl_2(PMe_3)(PNH_2)]$ (**1**)[3] or $[NiCl(PMe_3)(PNH_2)]PF_6$ (**2**).[4] Evidence is also provided that the presence of $[HPMe_3]^+$ in solution and the evolution of molecular hydrogen play key roles in the formation of **3**.

During our studies of the reactivity of chelating phosphino amines with $[NiCl_2(PMe_3)_2]$, it was found that the bidentate phosphino amine (*o*-diphenylphosphino)-*N*-methylaniline (PNHMe) gave first a stable five-coordinated intermediate,[5,6] which, in the presence of KPF_6, produced the expected cationic[5,7] square-planar compounds of the type $[NiCl(PR^3)(PNHMe)]^+$ (R^3 = Ph_2Me, $PhMe_2$, and Me_3).

On the other hand, when equimolar amounts of $[NiCl_2(PMe_3)_2]$ and PNH_2 were reacted in the presence of KPF_6, molecular hydrogen was evolved,[8] and complexes **3**[9] (21% yield), *cis*-$[Ni(PNH)_2]$ (**5**),[10] and *cis*-$[Ni(PNH_2)_2]^{2+}$ (**6**)[10] were formed. ^{31}P NMR control spectra of the reaction mixture, performed after 20 min, indicated that the solution also contained **2** (two broad signals centered at 40.2 and −4.9 ppm),[11] a small amount of **3**, and $[HPMe_3]^+$. The signals arising from **2** disappear with time, as those for **3** and **5** concomitantly increase. Free $PN{=}PMe_3$ [12] can be recovered from complex **3**, by treatment with sodium cyanide in a H_2O/C_6H_6 mixture.

On the basis of these findings, one can propose the reaction pathways shown in Scheme 1. Here the Ni^{II} ion makes the N−H bonds of the coordinated phosphino amine in **2** sufficiently acidic to be deprotonated by the free PMe_3 present in solution with formation of $[HPMe_3]^+$ and the amido complex **2***. The latter reacts further through two competitive routes. The first one, **A**, produces the cationic bis-substituted phosphino amino derivative **6** through the intermediates binuclear **4** and uncharged **5**. The second one, **B**, consists of the nucleophilic attack of the activated amido nitrogen of **2*** at the trimethylphosphonium cation giving **3***. This step is followed by the intramolecular redox reaction which affords molecular hydrogen and the ylide-type fragment. The phosphorane imine ligand remains coordinated to the Ni^{II} ion as a neutral chelating agent.

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(1) Klein, H. F.; Haller, S.; König, H.; Dartiguenave, M.; Dartiguenave, Y.; Menu, M. J. *J. Am. Chem. Soc.* **1991**, *113*, 4673−4675.

(2) Mai, H.-J.; Kang, H.-C.; Wocadlo, S.; Massa, W.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1995**, *621*, 1963−1968.

(3) Synthesis of $[NiCl_2(PMe_3)(PNH_2)]$ (**1**): Solid PNH_2 [24] (0.315 g, 1.14 mmol) was added to a blood red solution of $[NiCl_2(PMe_3)_2]$ (0.319 g, 1.12 mmol) in CH_2Cl_2 (15 mL). The solution immediately turned red-violet. After 1 h of stirring under N_2 at room temperature, the reaction mixture was concentrated to 5 mL and treated with *n*-hexane (25 mL) to give a blue precipitate. The solid was filtered off, washed with *n*-hexane (2 × 5 mL), C_6H_6 (1 mL) and Et_2O (5 mL), and dried under vacuum (0.471 g, 87.0%). ^1H NMR (200 MHz, $CDCl_3$): δ 1.29 (s, 9 H; $P[CH_3]_3$), 2.53 (bs, 2 H; NH_2), 7.97−7.10 (m, 14 H; aromatic).

(4) Compound **2**: This species is not sufficiently stable to be characterized in the solid state. ^{31}P NMR spectra of the crude material show, inter alia, two broad singlets (centered at $\delta = 40.2$ and − 4.9 ppm) and the septet of the PF_6 anion.

(5) Crociani, L.; Refosco, F.; Tisato, F.; Gatto, S.; Corain, B. *Inorg. Chim. Acta* **1996**, *249*, 131−133.

(6) Crociani, L.; Refosco, F.; Tisato, F.; Dolmella, A.; Gatto, S. Bandoli, G. *Z. Kristallogr.* **1997,** *212*, 745−751.

(7) Bonnet, M. C.; Dahan, F.; Ecke, A.; Keim, W.; Schulz, R. P.; Tkachenko, I. *J. Chem. Soc., Chem. Commun.* **1994**, 615−616.

(8) To confirm the evolution of H_2, a gentle stream of N_2 was bubbled through the reaction mixture and the volatile products were collected by a cannula in an aqueous solution containing Na_2PdCl_4. A black powder (metallic Pd) accumulated in the aqueous solution according to the reduction $Pd^{II} \rightarrow Pd^{\circ}$ operated by H_2.

(9) Synthesis of $[NiCl(PMe_3)(PN{=}PMe_3)]PF_6$ (**3**): (a) From $[NiCl_2(PMe_3)_2]$. To a mixture of $[NiCl_2(PMe_3)_2]$ (0.115 g, 0.40 mmol) and KPF_6 (0.110 g, 0.59 mmol) in CH_2Cl_2 (10 mL) was added solid PNH_2 (0.114 g, 0.41 mmol). After 3 h of stirring at room temperature, a whitish precipitate (excess of KPF_6 and KCl) was filtered off. The filtrate was concentrated to 5 mL and treated with Et_2O (15 mL), which afforded initially an oil and, after vigorous stirring, gave a brown solid. This solid was collected by filtration and washed with water (3 mL), Et_2O (2 × 5 mL), and MeOH (0.5 mL). The resulting red compound was recrystallized from a $CH_2Cl_2/MeOH/C_6H_6$ mixture (3/1/3) and dried under vacuum (0.057 g, 21.5%). Crystals suitable for X-ray analysis were grown by slow evaporation of acetone solutions. ^1H NMR (200 MHz, CD_2Cl_2): δ 1.14 (d, $^2J(HP) = 12$ Hz, 9 H; $P[CH_3]_3$), 1.88 (d, $^2J(HP) = 13$ Hz, 9 H; $N{=}P[CH_3]_3$), 6.50−7.90 (m, 19 H; aromatic). $^{31}P\{^1H\}$ NMR (200 MHz, CD_2Cl_2): δ −144.3 (septet, $J(PF) = 713$ Hz, 1P; PF_6), −12.6 (dd, $^2J[P(2)P(1)] = 108$ Hz, $^3J(P(2)P(3)) = 5$ Hz, 1P; $P(2)[CH_3]_3$), 37.9 (d, $^2J[P(1)P(2)] = 108$ Hz, 1P; $P(1)N{=}P(3)[CH_3]_3$), 41.8 (d, $^3J[P(3)P(2)] = 5$ Hz, 1P, $P(1)N{=}P(3)[CH_3]_3$). (b) From complex **1**. To a solution of **1** (0.143 g, 0.3 mmol) in CH_2Cl_2 (10 mL) was added an excess of KPF_6 (0.074 g, 0.4 mmol) under stirring at room temperature. After 3 h, the inorganic salts were filtered off and the filtrate was concentrated to 5 mL and treated with Et_2O (20 mL) to give an oil and, finally, a brown powder as above. This solid was redissolved in EtOH (5 mL), and after the solution was allowed to stand in a closed test tube for 3 days, crystals of complex **3** (yield 9%) were obtained. This yield can be improved by addition of 1 equiv of both $[HPMe_3]^+$ and 2,4-lutidine to the starting reaction mixture containing complex **1** and excess KPF_6. After the reaction was completed as above, an additional equimolar amount of $[PPh_4]Cl$ was added as internal standard and an aliquot of the mixture was subjected to ^{31}P NMR. Relative integration yield a Ni^{II} complex **3**/tetraphenylphosphonium cation ratio of 85/100.

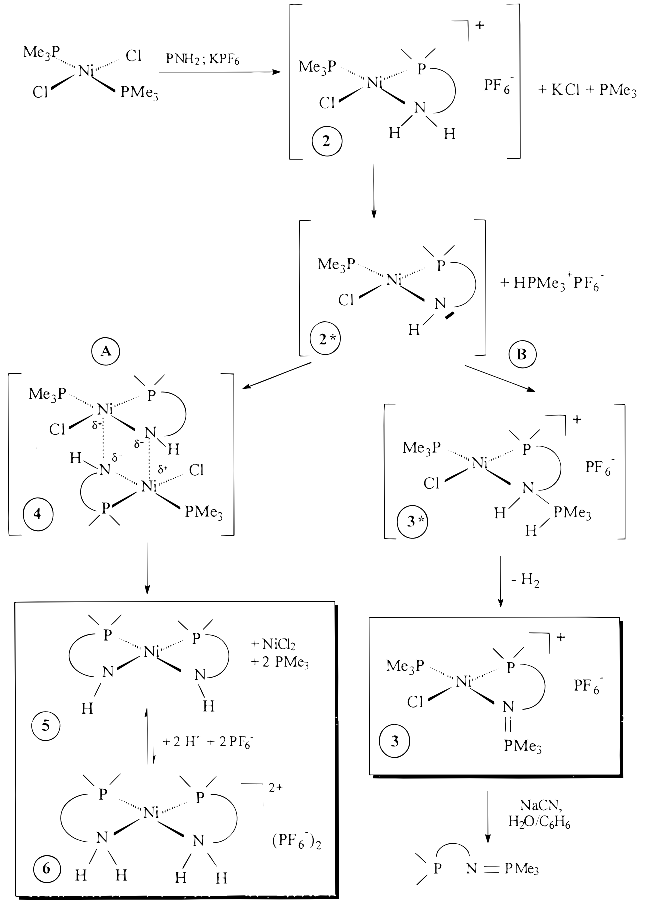
(10) Cooper, M. K.; Downes, J. M.; Duckworth, P. A.; Tiekink, E. R. T. *J. Chem. Soc., Dalton Trans.* **1989**, 1067−1073.

(11) Related square-planar complexes $[NiCl(PMe_2Ph)(PNMe_2)]^+$ and $[NiCl(PMePh_2)(PNMe_2)]^+$ (see also ref 6) show, analogously, a two broad singlet ^{31}P NMR pattern with values falling at $\delta = 38.6$, −5.7 ppm and 37.3, −6.4 ppm, respectively.

(12) Synthesis of $[Ph_2P(o\text{-}C_6H_4)NPMe_3]$ (abbreviated $PN{=}PMe_3$): To an orange-red suspension of **3** (0.300 g, 0.45 mmol) in benzene (50 mL) was added a 10% sodium cyanide solution (50 mL) with stirring. After 1 h, the color was discharged, and the organic phase was separated. The aqueous phase was treated twice with Et_2O (2 × 15 mL). The combined organic portions were dried over Na_2SO_4 and reduced in volume to a crude pale yellow oil. The ligand was then purified by alumina column chromatography (2.5 × 10 cm) eluted with benzene. ^1H NMR (200 MHz, $CDCl_3$): δ 1.28 (d, $^2J(HP) = 13$ Hz, 9H; $P[CH_3]_3$), 7.40−6.40 (m, 14 H; aromatic). $^{31}P\{^1H\}$ NMR (200 MHz, $CDCl_3$): δ −15.6 (s, $PN{=}P(CH_3)_3$), 6.2 (s, $PN{=}P(CH_3)_3$).

S0002-7863(97)03844-4 CCC: $15.00

Scheme 1



Although nitrene pathways have been postulated for the formation of phosphorane imines,[13−20] the nucleophilic amido pathway appears to be more plausible in the system we have investigated since (a) $[HPMe_3]^+$ is detected by ^{31}P NMR in the reaction mixture during the formation of **3** and (b) the concomitant addition of equimolar amounts of $[HPMe_3]^+$ [21] and 2,4-lutidine produces **3** in almost quantitative yield, upon starting from **1**. Indeed, under these experimental conditions, the lutidine (pK_a= 6.99) is expected to selectively deprotonate the coordinated PNH_2 ligand to give **2***, while the trimethylphosphonium cation (pK_a= 8.65) provides the electrophilic fragment for the metal-assisted formation of the final phosphorane imine ligand (Scheme 1**B**).

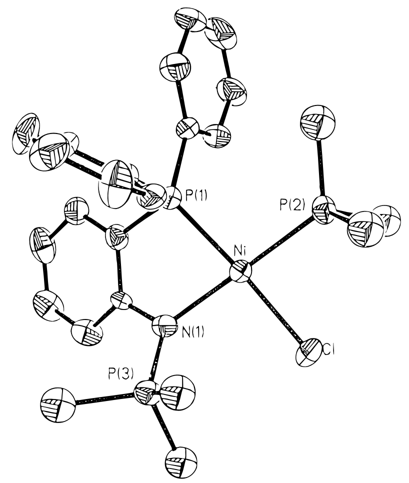


Figure 1. ORTEP drawing of the cation $[NiCl(PMe_3)(PN{=}PMe_3)]^+$ of **3**; the PF_6^- anion is omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (pm) and angles (deg): Ni−Cl 221.7(2), Ni−P(1) 215.9(2), Ni−P(2) 219.2(2), Ni−N(1) 201.1(7), N(1)−Ni−P(3) 158.9(7); Cl−Ni−P(1) 176.0(1), P(2)−Ni−N(1) 177.6(2), Cl−Ni−N(1) 93.4(2), N(1)−Ni−P(1) 83.1(2), P(1)−Ni−P(2) 97.5(1), P(2)−Ni−Cl 86.2(1), Ni−N(1)−P(3) 123.9(4), Ni−N(1)−C(6) 113.8(5), P(3)−N(1)−C(6) 121.2(5).

Complex **3**[22] was structurally characterized by X-ray diffraction, and Figure 1 shows the cation present in **3**.

In this complex, the metal atom is located in a distorted square-planar coordination sphere consisting of the P,N-donor atoms of the bidentate ligand, the P(2) atom from PMe_3, and the chloride ion. The trans angles in the Ni coordination sphere are 176.0(1) and 177.6(2)° while the cis angles range from 83.1(2) to 97.5(1)°. The four donor atoms deviate alternatively from the mean coordination plane by ±4 pm, the dihedral angle between this plane and the C(1)−(6) plane being 149.1°. The conformation of the five-membered chelate ring is envelope (C_s). The nitrogen atom is in an essentially trigonal-planar environment (Ni−N(1)−P(3) 123.9(4), Ni−N(1)−C(6) 113.8(5), and P(3)−N(1)-C(6) 121.2(5)°), and its hybridization does not affect the Ni−N distances which are 201.1(7) pm in **3** and 198.1(5) pm in $[NiCl(PMe_3)(PNHMe)]PF_6$ (PNHMe = (*o*-diphenylphosphino)-*N*-methylaniline),[23] which contains an sp^3-hybridized N-atom. The P−N bond distance of 158.9(7) pm in **3** is similar to the values observed in several closely related phosphorane imino complexes, and it is indicative of π interaction between P and N.[16,17]

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Supporting Information Available: Summary of data collection and refinement and tables of crystal data, bond distances and angles, final fractional coordinates, thermal parameters, and other spectroscopic data of complexes **1** and **3** (11 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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[13] Basolo, F. *J. Ind. Chem. Soc.* **1977**, *54*, 6−10.

[14] Poznyak, A. L.; Pavlovski, V. I. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 789−796.

[15] Sleiman, H. F.; Mercer, S.; McElwee White, L. *J. Am. Chem. Soc.* **1989**, *111*, 8007−8009.

[16] Fourquet, J. L.; Leblanc, M.; Saravanamuthu, A.; Bruce, M. R. M.; Bruce, A. E. *Inorg. Chem.* **1991**, *30*, 3241−3243.

[17] Saravanamuthu, A.; Ho, D. M.; Kerr, M. E.; Fitzgerald, C.; Bruce, M. R. M.; Bruce, A. E. *Inorg. Chem.* **1993**, *32*, 2202−2206.

[18] Staudinger, H.; Meyer, J. *Helv. Chim. Acta* **1919**, *2*, 635−638.

[19] Refosco, F.; Tisato, F.; Moresco, A.; Bandoli, G. *J. Chem. Soc., Dalton Trans.* **1995**, 3475−3482.

[20] Chatt, J.; Rove, G. J. *J. Chem. Soc.* **1962**, 4019−4023.

[21] $[HPMe_3]^+$ was generated in situ by bubbling anhydrous HCl into an anhydrous Et_2O solution containing PMe_3 originating from the $AgI{\cdot}PMe_3$ adduct.

[22] Crystal data for **3**: $C_{24}H_{32}ClF_6NNiP_4$, M_w = 666.5, red cuboid, monoclinic, space group $P2_1/n$, a = 14.464(4), b = 12.007(4), and c = 18.518(5) Å, β = 110.17(2)°, Z = 4, R(F) = 0.063, GOF = 1.19.

[23] L. Crociani, et al., unpublished results.

[24] Cooper, M. K.; Downes, J. M.; Duckworth, P. A.; Kerby, M. C.; Powell, R. J.; Soucek, M. D. *Inorg. Synth.* **1989**, *25*, 129−133.