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Reactions of the bis(iminophosphoranyl)methane ligand $CH_2(Ph_2P{=}NSiMe_3)_2$ with nickel(II) halides and the structural characterization of ligand fragmentation products

Mani Ganesan, Phillip E. Fanwick, Richard A. Walton *

Department of Chemistry, Purdue University, 1393 Brown Building, West Lafayette, IN 47907-1393, USA

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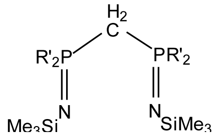
Abstract

While anhydrous nickel(II) chloride reacts with $CH_2(Ph_2P{=}NSiMe_3)_2$ to afford the pseudotetrahedral complex $NiCl_2[CH_2(Ph_2P{=}NSiMe_3)_2]$ (**2**), the analogous reaction with anhydrous nickel(II) iodide gives the structurally related complex $NiI_2[CH_2(PPh_2{=}NSiMe_3)(PPh_2{=}NH)]$ (**3**) in which one of the trimethylsilyl groups of **1** has been replaced by hydrogen. Another reaction in which the fragmentation of **1** occurs is that with the hydrate $NiCl_2{\cdot}6H_2O$; in this case a square-planar nickel(II) complex of composition $[Ni\{Ph_2PCH_2PPh_2({=}NH)\}_2]Cl_{1.25}(NO_3)_{0.75}$ (**4**) was identified as one of the products. The phosphonium salt $[Ph_2P(NH_2)\text{-}NPPh_2(CH_3)]I$ (**5**) is found to be a major product of the reaction between **3** and CO. The structures of **2**–**5** have been established by X-ray crystallography.

Keywords: Crystal structures; Nickel complexes; Iminophosphoranyl complexes

1. Introduction

In recent years the coordination of bis(iminophosphoranyl)methane ligands $CH_2(R'_2P{=}NSiMe_3)_2$ (**I**) and their monoanions $[CH(R'_2P{=}NSiMe_3)_2]^-$ (**II**), as well as other ligands of a closely similar type,[1] to main group [1], transition metal [2] and lanthanide metal [3] centers has yielded a diverse array of interesting complexes in which these ligands exhibit a variety of intriguing coordination modes. To date, the bulk of the transition metal chemistry that has been developed involves the Group 4 elements [2a,b] and various platinum metals [2e–j]. In the present report we describe the reactions of the ligand $CH_2(Ph_2P{=}NSiMe_3)_2$ (**1**), bis[trimethylsilyliminodi(phenyl)phosphoranyl]methane, with nickel(II) halides which yield cases of products in which the ligand **1** remains intact or has undergone fragmentation. The crystal structures of four products are reported.



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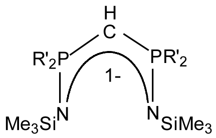

II

2. Experimental

2.1. Starting materials and reaction procedures

The bis(iminophosphoranyl)methane $CH_2(Ph_2P{=}NSiMe_3)_2$ (**1**) was prepared by the literature method [4]. Samples of anhydrous NiI_2 were purchased from Strem Chemicals and the hydrate $NiCl_2{\cdot}6H_2O$ from J.T. Baker Chemical Co. Anhydrous $NiCl_2$ was obtained by

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* Corresponding author. Tel.: +1-765-494-5464; fax: +1-765-494-0239.

E-mail address: rawalton@purdue.edu (R.A. Walton).

[1] These include the dianionic form of these ligands as well as derivatives where the bridgehead –CH_2– group is changed to –CH(R′)–.

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dehydrating the hexahydrate with the use of thionyl chloride. Organic solvents were purchased from commercial sources and deoxygenated by purging with N_2(g) prior to use. Reactions were carried out under an atmosphere of N_2.

IR spectra were recorded as KBr pellets on a Perkin–Elmer 2000 FT-IR spectrometer. ^1H and $^{31}P\{^1H\}$ NMR spectra were obtained with the use of a Varian INOVA 300 spectrometer. Proton resonances were referenced internally to the residual protons in the incompletely deuteriated solvent. The $^{31}P\{^1H\}$ spectra were recorded at 121.6 MHz, with 85% H_3PO_4 as an external standard. Electronic absorption spectra were obtained with use of a Cary 300 spectrophotometer. The magnetic moment of **3** was determined at Texas A&M University with the use of a SQUID magnetometer. Elemental microanalyses were performed by Dr. H.D. Lee of the Purdue University Microanalytical Laboratory.

2.2. Synthesis of $NiCl_2[CH_2(PPh_2{=}NSiMe_3)_2]$ (2)

A mixture of anhydrous $NiCl_2$ (0.22 g, 1.70 mmol) and ligand **1** (0.94 g, 1.68 mmol) in 50 ml of toluene was refluxed for 3 days, the solvent evaporated, the residue dissolved in 25 ml of dichloromethane and centrifuged to remove any insoluble materials. The supernatent was concentrated to ca. 15 ml and then carefully layered with hexanes. Crystals of composition **2**$\cdot CH_2Cl_2$ (as characterized by X-ray crystallography) were isolated and dried under a vacuum which led to partial loss of the lattice dichloromethane solvent molecule. Yield 0.13 g (11%). *Anal.* Found: C, 51.99; H, 5.64; N, 4.07. Calc for $C_{31.5}H_{41}Cl_3N_2NiP_2Si_2$ (i.e. **2**$\cdot 0.5CH_2Cl_2$): C, 51.02; H, 5.65; N, 3.83%.

IR spectrum (KBr pellet, 1600–400 cm^{-1}): 1591(w), 1488(w), 1439(m-s), 1353(m-w), 1262(s), 1249(s), 1186(m), 1123(vs), 1114(s), 1092(s), 1075(m-s), 1029(w), 999(w), 840(w), 804(vs), 764(m-s), 737(s), 719(s), 693(s), 621(w), 533(m-w), 513(m-w), 494(m-w), 469(m-w), 416(w).

2.3. Synthesis of $NiI_2[CH_2(PPh_2{=}NSiMe_3)(PPh_2{=}NH)]$ (3)

A mixture of anhydrous NiI_2 (0.25 g, 0.80 mmol) and ligand **1** (0.90 g, 1.61 mmol) was refluxed for 4 days in 50 ml of toluene to give an insoluble green solid that was filtered off, washed with diethyl ether and dried under a vacuum. Yield: 0.55 g (86%). The product was recrystallized from dichloromethane/hexanes. *Anal.* Found: C, 41.36; H, 3.74; N, 3.58. Calc for $C_{28}H_{31}I_2N_2NiP_2Si$: C, 42.10; H, 3.88; N, 3.50%.

IR spectrum (KBr pellet, 1600–400 cm^{-1}): 1589 (m-w), 1545(w), 1484(m-w), 1438(s), 1352(w), 1335(vw), 1312(w), 1251(m-s), 1177(m), 1115(vs), 1085(s), 1042(m-w), 1021(m-w), 997(m), 886(vw), 841(s), 790(s), 741(vs), 690(vs), 667(vw), 618(w), 555(w), 524(w), 491(m-s), 476(m-w), 422(vw).

2.4. Synthesis of $[Ni\{Ph_2PCH_2PPh_2({=}NH)\}_2]Cl_{1.25}(NO_3)_{0.75}$ (4)

A mixture of $NiCl_2\cdot 6H_2O$ (0.10 g, 0.42 mmol) and ligand **1** (0.50 g, 0.90 mmol) in 50 ml of dichloromethane was stirred at room temperature (r.t.) for 4 days. The light green reaction mixture was centrifuged, and the clear solution concentrated to 10 ml and then carefully layered with hexanes. A mixture of orange–yellow crystals of **4** and an unidentified pale green microcrystalline material formed. The crystals of **4** were separated by hand, washed with a dichloromethane/hexane mixture and dried under vacuum. Yield 0.026 g (6%). *Anal.* Found: C, 58.53; H, 4.92; N, 4.50. Calc for $C_{51}H_{48}Cl_{3.25}N_{2.75}NiO_{2.25}P_4$ (i.e. **4**$\cdot CH_2Cl_2$): C, 59.28; H, 4.68; N, 3.73%. A single crystal X-ray structure determination of the product prior to drying under a vacuum showed the orange–yellow crystals to be of composition **4**$\cdot 2CH_2Cl_2$.

IR spectrum (KBr pellet, 1650–400 cm^{-1}): 1621(m), 1589(m-w), 1574(w), 1484(m), 1438(vs), 1373(s), 1337(vs,br), 1241(w), 1162(m-s), 1118(vs), 1100(s), 1073(w), 991(vs), 902(m-w), 829(w), 786(m-s), 745(vs), 734(s), 691(vs), 616(w), 566(w), 534(m-w), 508(s), 481(m), 453(w).

2.5. Synthesis of $[Ph_2P(NH_2)NPPh_2(CH_3)]I$ (5)

A stream of CO gas was passed through a solution of **3** (0.20 g, 0.25 mmol) in 25 ml of dichloromethane for 30 min. and the resulting solution kept under a CO atmosphere for 4 days. During this time the solution turned colorless. The reaction mixture was then centrifuged and the supernatent concentrated to 15 ml and treated with hexane (10 ml). After 7 days a crop of colorless crystals were filtered off and carefully dried. Yield 0.065 g. *Anal.* Found: C, 55.53; H, 4.63; N, 5.08. Calc. for $C_{25}H_{25}IN_2P_2$: C, 55.36; H, 4.65; N, 5.16%.

IR spectrum (KBr pellet, 1600–400 cm^{-1}): 1589(m-w), 1558(m-w), 1483(m-w), 1438(m-s), 1416(w), 1318(vs), 1291(s), 1274(s), 1183(m), 1162(w), 1121(s), 1073(vw), 1029(vw), 998(m-w), 943(m-s), 896(m-s), 801(m), 757(m-s), 746(s), 721(m-s), 692(vs), 644(w), 616(vw), 520(s), 488(m), 470(m-s), 449(w), 438(w).

$^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): +20.9 (d, $^2J(PP) = 3$ Hz), +21.7(d, $^2J(PP) = 3$ Hz). ^1H NMR ($CDCl_3$, δ): +2.54 (dd, CH_3, $^2J(PH) = 12.9$ Hz, $^4J(PH) = 1.2$ Hz), +4.82 (s, br, NH_2), +7.3 to +7.9 (m, Ph).

2.6. X-ray crystallography

Single crystals of compounds **2**–**5** were obtained as described in Sections 2.2, 2.3, 2.4 and 2.5. Data collections were performed at 150 (±1) K with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) on a Nonius Kappa CCD diffractometer. Lorentz and polarization corrections were applied to the data sets. The key crystallographic data are given in Table 1.

The structures of **2** and **5** were solved by direct methods using SIR97[5], the structure of **3** was solved with use of SHELXS-97 [6], and that of **4** with the structure solution program PATTY in DIRDIF-99 [7]. The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were placed in calculated positions according to idealized geometries with C–H = 0.95 Å and $U(\mathrm{H}) = 1.3U_{\mathrm{eq}}(\mathrm{C})$. They were included in the refinement but constrained to ride on the atom to which they are bonded. An empirical absorption correction using SCALEPACK [8] was applied. The final refinements were performed by the use of the program SHELXL-97 [9]. The highest peak in the final difference Fouriers of **2**–**5** had a height of 0.59, 3.21, 0.63 and 0.47 e Å^{-3}, respectively.

The structure solution and refinement for **2** proceeded routinely. The atoms Ni, Cl(1), Cl(2) and C(1b) of the nickel complex are located on a crystallographic plane of symmetry. The lattice molecule of dichloromethane solvent, which is also located on a special position, was modeled satisfactorily with minimal disorder and anisotropic thermal parameters for its C and Cl atoms. For complex **3**, in which the ligand **1** has lost a trimethylsilyl group, the hydrogen atom bound to N(2) was not located but its presence can be inferred from the other properties of this normal paramagnetic, tetrahedral Ni(II) complex. All non-hydrogen atoms were refined anisotropically. The only problem encountered in the structure solution of **4** concerned the nature of the counter anions. A satisfactory and chemically reasonable model involved three different anion positions for $[\mathrm{Cl}]^-$ and/or $[\mathrm{NO_3}]^-$ within the asymmetric unit, such that there is one $[\mathrm{Cl}]^-$ at full occupancy, one $[\mathrm{Cl}]^-$ position at 20% occupancy, and one position which was modeled as a disorder between $[\mathrm{NO_3}]^-$ and $[\mathrm{Cl}^-]$ with 75 and 5% occupancies, respectively. This model gives an appropriate charge balance for the nickel(II) dication. There are also two independent, well-behaved $\mathrm{CH_2Cl_2}$ molecules in the asymmetric unit. All non-hydrogen atoms of **4** were refined with anisotropic thermal parameters. The structure solution and refinement of **5**, with all non-hydrogen atoms anisotropic, proceeded routinely.

3. Results and discussion

The reaction of anhydrous $\mathrm{NiCl_2}$ with bis[trimethylsilyliminodi(phenyl)phosphoranyl]methane (**1**) in refluxing toluene for periods of up to 3–4 days affords crystalline $\mathrm{NiCl_2[CH_2(PPh_2{=}NSiMe_3)_2]}$ (**2**). This tetrahedral nickel(II) complex was characterized by X-ray crystallography. An ORTEP [10] representation of this conventional structure is shown in Fig. 1. A similar reaction between anhydrous $\mathrm{NiI_2}$ and **1** also gave a tetrahedral nickel(II) complex, but in this case one of the trimethylsilyl groups of the ligand had been replaced by hydrogen to give $\mathrm{NiI_2[CH_2(PPh_2{=}NSiMe_3)(PPh_2{=}NH)]}$ (**3**) in high yield. The structure of **3** (Fig. 2) is otherwise similar to that of **2** with the exception of differences engendered by changes in the size of the halide ligands and the unsymmetrical nature of the chelating ligand in **3**. The N–Ni–X angles (not listed in the captions to Figs. 1 and 2) are in the ranges 103.8–115.5° (X = Cl) and 101.7–112.7° (X = I). When compared to the

Table 1
Crystallographic data for $\mathrm{NiCl_2[CH_2(PPh_2{=}NSiMe_3)_2]\cdot CH_2Cl_2}$ (**2**), $\mathrm{NiI_2[CH_2(PPh_2{=}NSiMe_3)(PPh_2{=}NH)]}$ (**3**), $\mathrm{[Ni\{Ph_2PCH_2PPh_2({=}NH)\}_2]Cl_{1.25}(NO_3)_{0.75}\cdot 2CH_2Cl_2}$ (**4**) and $\mathrm{[Ph_2P(NH_2)NPPh_2(CH_3)]I}$ (**5**)

Compound	**2**	**3**	**4**	**5**
Empirical formula	$\mathrm{C_{32}H_{42}Cl_4N_2NiP_2Si_2}$	$\mathrm{C_{28}H_{31}I_2N_2NiP_2Si}$	$\mathrm{C_{52}H_{50}Cl_{5.25}N_{2.75}NiO_{2.25}P_4}$	$\mathrm{C_{25}H_{25}IN_2P_2}$
Formula weight	773.35	798.12	1118.23	542.34
Space group	$P2_1/m$ (no. 11)	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)	$P1$ (no. 2)
a (Å)	9.1894(3)	10.5919(4)	16.3023(2)	8.88560(10)
b (Å)	20.1040(7)	14.8366(6)	12.2896(2)	12.0669(2)
c (Å)	10.6672(4)	19.5188(6)	27.2235(7)	13.3459(3)
α (°)	90	90	90	106.6690(10)
β (°)	103.9260(10)	89.978(3)	103.3459(7)	98.0920(10)
γ (°)	90	90	90	111.3460(10)
V (Å^3)	1912.8(2)	3067.3(3)	5306.9(3)	1227.65(9)
Z	2	4	4	2
ρ_{calc} (g cm^{-3})	1.343	1.728	1.399	1.467
μ(Mo Kα) (mm^{-1})	0.959	2.788	0.793	1.431
R (F_o) [a]	0.041	0.067	0.042	0.028
R_w (F_o^2) [b]	0.102	0.171	0.108	0.070
GOF	1.030	1.003	1.037	1.094

[a] $R = \Sigma|F_o| - |F_c|/\Sigma|F_o|$ with $F_o^2 > 2\sigma(F_o^2)$.

[b] $R_w = [\Sigma\, w(|F_o^2| - |F_c^2|)^2/\Sigma\, w|F_o^2|^2]^{1/2}$.

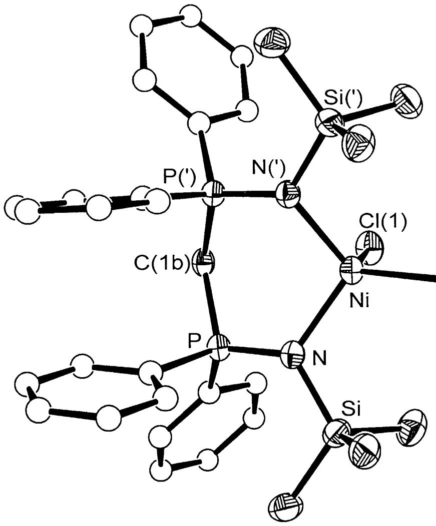

Fig. 1. ORTEP [10] representation of the structure of the nickel(II) complex $NiCl_2[CH_2(PPh_2{=}NSiMe_3)_2]$ as present in crystals of **2**$\cdot CH_2Cl_2$. Thermal ellipsoids are drawn at the 50% probability level except for the carbon atoms of the phenyl rings which are circles of arbitrary radius. This molecule contains a plane of symmetry comprising atoms Ni, Cl(1), Cl(2) and C(1b). Selected bond distances (Å) and bond angles (°) are as follows: Ni–Cl(1) 2.2664(10), Ni–Cl(2) 2.2747(9), Ni–N 2.0182(19), N–P 1.5910(19), N–Si 1.757(2); Cl(1)–Ni–Cl(2) 111.87(4), N–Ni–N′ 104.97(11), Ni–N–P 119.13(11), N–P–C(1b) 110.42(12), P–C(1b)–P′ 118.71(18).

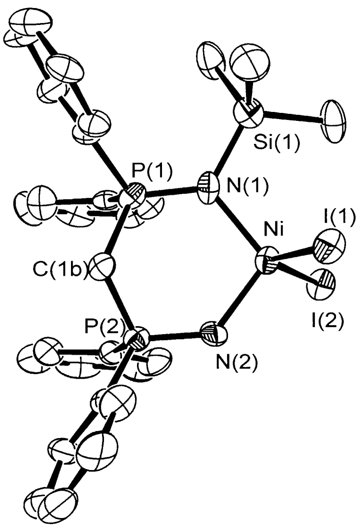

Fig. 2. ORTEP [10] representation of the structure of the nickel(II) complex $NiI_2[CH_2(PPh_2{=}NSiMe_3)(PPh_2{=}NH)]$ (**3**). Thermal ellipsoids are drawn at the 50% probability level except for the carbon atoms of the phenyl rings which are circles of arbitrary radius. Selected bond distances (Å) and bond angles (°) are as follows: Ni–I(1) 2.6058(16), Ni–I(2) 2.6112(16), Ni–N(1) 1.998(10), Ni–N(2) 1.950(9), N(1)–P(1) 1.596(10), N(2)–P(2) 1.603(9), N(1)–Si(1) 1.816(11); I(1)–Ni–I(2) 125.87(5), N(1)–Ni–N(2) 107.1(4), Ni–N(1)–P(1) 122.2(6), Ni–N(2)–P(2) 128.1(5), N(1)–P(1)–C(1b) 112.2(5), N(2)–P(2)–C(1b) 107.1(5), P(1)–C(1b)–P(2) 118.9(5).

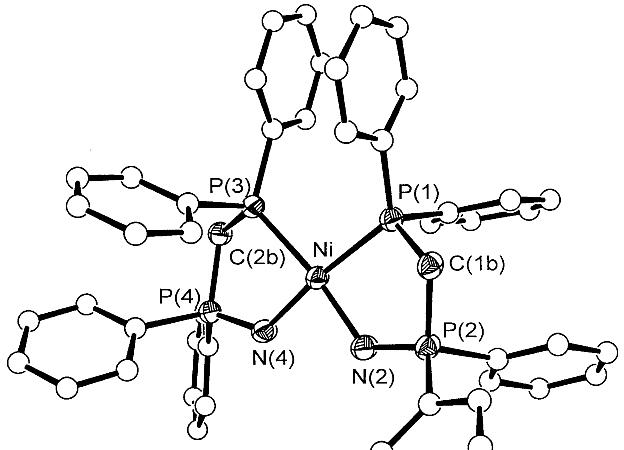

Fig. 3. ORTEP [10] representation of the structure of the $[Ni\{Ph_2PCH_2PPh_2({=}NH)\}_2]^{2+}$ cation as present in the crystals of **4**$\cdot 2CH_2Cl_2$. The thermal ellipsoids are drawn at the 50% probability level except for the carbon atoms of the phenyl groups which are circles of arbitrary radius. Selected bond distances (Å) and bond angles (°) are as follows: Ni–N(2) 1.907(2), Ni–N(4) 1.905(2), Ni–P(1) 2.1636(7), Ni–P(3) 2.1646(7), N(2)–P(2) 1.600(2), N(4)–P(4) 1.598(2); N(2)–Ni–N(4) 89.99(10), P(1)–Ni–P(3) 98.91(3), N(2)–Ni–P(1) 86.62(8), N(2)–Ni–P(3) 170.20(8), N(4)–Ni–P(1) 170.47(8), N(4)–Ni–P(3) 85.75(7), Ni–N(2)–P(2) 126.91(15), Ni–N(4)–P(4) 126.81(14).

structural data available for phosphoraneimine complexes of halides of the first transition series that contain monodentate ligands of the types $Me_3SiN{=}PR_3$ and $HN{=}PR_3$ [11], the P=N distances in **2** and **3** (range 1.591–1.603 Å) are quite normal. These results, which accord with data reported for bis(iminophosphoranyl)methane ligands bound to main group [1a] and heavier transition metals [2g,j], also show that these P–N distances are significantly longer than those associated with uncoordinated ligands [1a,2a,g,12]. Furthermore, there is no indication that the chelating ligand in **3** is monoanionic and deprotonated $[CH_2(PPh_2{=}NSiMe_3)(PPh_2{=}N)]^-$ which would make it a complex of nickel(III); differences between the pairs of Ni–N and P–N distances in **3** are at most small and attributable to the replacement of Me_3Si by H.

The electronic absorption spectra of **2** and **3** in dichloromethane (800–400 nm) are consistent with their formulation as pseudotetrahedral nickel(II) species; each shows the characteristic $^3T_1(P) \rightarrow {}^3T_1$ transition (ν_3) [13], which for **2** is at 15,300 cm^{-1} ($\epsilon \sim 150$) with a broad shoulder at 17,480 cm^{-1}, and for **3** at 14,265 cm^{-1} ($\epsilon \sim 450$) with a shoulder at $\sim$16,400 cm^{-1}. The magnetic moment of **3** is 3.26 μ_B at 300 K which is in further accord with its pseudotetrahedral nickel(II) structure [14,15].

When the hexahydrate $NiCl_2 \cdot 6H_2O$ was used in place of anhydrous $NiCl_2$, and the reaction with ligand **1** was carried out in dichloromethane at room temperature for 4 days, a mixture of products was formed, one of which was obtained as orange–yellow crystals (**4**) from a

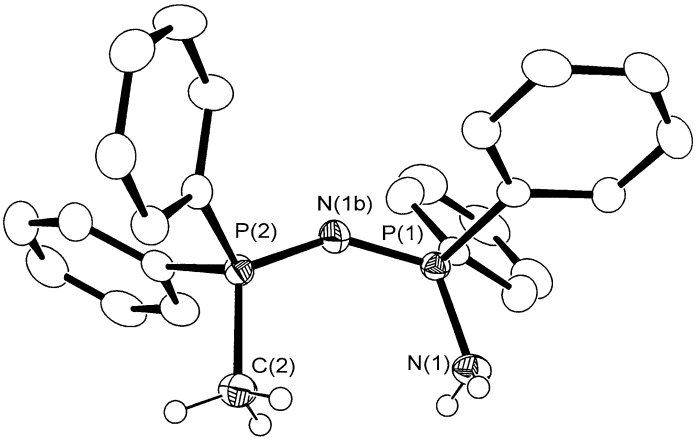

Fig. 4. ORTEP [10] representation of the structure of the $[Ph_2P(NH_2)NPPh_2(CH_3)]^+$ cation as present in the crystals of its iodide salt **5**. Thermal ellipsoids are drawn at the 50% probability level except for the hydrogen atoms associated with C(2) and N(1). Selected bond distances (Å) and bond angles (°) are as follows: N(1)–P(1) 1.633(2), P(1)–N(1b) 1.5761(18), N(1b)–P(2) 1.5722(18), P(2)–C(2) 1.792(2); N(1)–P(1)–N(1b) 121.36(10), P(1)–N(1b)–P(2) 142.91(13), N(1b)–P(2)–C(2) 114.79(10).

dichloromethane/hexane mixture. This product was identified as being of composition $[Ni\{Ph_2PCH_2PPh_2(=NH)\}_2]Cl_{1.25}(NO_3)_{0.75}\cdot 2CH_2Cl_2$ (**4**·$2CH_2Cl_2$) and its structure established by a single crystal X-ray structure determination. The presence of $[NO_3]^-$ in **4** was confirmed by IR spectroscopy (KBr pellet) which showed a strong band at 1337 cm^{-1} assigned to the ν_3 mode of this anion. An ORTEP [10] representation of the square planar nickel(II) cation is shown in Fig. 3 and demonstrates that like **3** it is obtained by fragmentation of ligand **1** but in this instance the bidentate ligand contains a mixed phosphane/phosphoraneimine donor set. The low yield has prevented us from carrying out more extensive investigations of **4**. The structural parameters for the phosphoraneimine portion of this ligand resemble those found for complex **2** (Fig. 2).

A third ligand fragmentation/rearrangement product obtained during the course of this study was isolated in quite high yield during attempts to carbonylate the nickel(II) iodide complex **3**. Quite unexpectedly we obtained the salt $[Ph_2P(NH_2)NPPh_2(CH_3)]I$ (**5**), amino[methyldiphenylphosphoranylidenamido]diphenylphosphonium iodide; this is a known compound [16], as is its chloride salt [12]. The spectroscopic data for **5** are given in Section 2.5; NMR spectral data for the chloride salt have previously been measured in methanol [16]. The ORTEP [10] representation of the structure of the cation is shown in Fig. 4 and confirms the identity of this compound. The mechanism of the reaction that produces **5** through the decomposition of **3** has yet to be established, although the chloride salt is known to be formed by the reaction of the ligand **1** with HCl which leads to the loss of the trimethylsilyl groups as Me_3SiCl [12].

The reactions of **1** described in this report provide examples of ligand fragmentation reactions in which pseudotetrahedral and square-planar nickel(II) complexes that contain these fragments have been structurally characterized. In addition, the full structural characterization of the phosphonium salt **5** confirms the identity of this previously reported cation [12,16].

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 192891–192894 for compounds **2**–**5**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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