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# Reaction of [(tmeda)NiMe<sub>2</sub>] with 2-pyridylmethylamine and (2-pyridylmethyl)(diphenylphosphanyl)amine

Astrid Malassa, Helmar Görls, Matthias Westerhausen\*

Institut für Anorganische und Analytische Chemie, Friedrich-Schiller-Universität Jena, August-Bebel-Street 2, D-07743 Jena, Germany

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#### Abstract

2-Aminomethylpyridine (Amp) substitutes the bis(dimethylamino)ethane ligand (TMEDA) of [(tmeda)NiMe<sub>2</sub>] leading to the formation of N,N'-(2-aminomethylpyridine)dimethylnickel (1). The reaction of bulkier N-diphenylphosphanyl-2-aminomethylpyridine with [(tmeda)NiMe<sub>2</sub>] yields tetrakis(N-diphenylphosphanyl-2-aminomethylpyridine)nickel(0) (2), ethane and TMEDA. The nickel(II) complex 1 shows a distorted square planar environment for the metal center, whereas nickel(0) in 2 displays a distorted tetrahedral coordination sphere with an average Ni–P bond length of 217.35 pm.

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The synthesis of many late transition metal bis[(2-pyridylmethyl)(trialkylsilyl)amides] succeeds via a transamination starting from  $[M{N(SiMe_3)_2}]$  [1]. However, nickel bis[bis(trimethylsilyl)amide] decomposes very fast [2] and therefore, another starting material has to be employed. The metallation of *N*-trialkylsilyl-8-aminoquinoline with nickelocene yields the corresponding paramagnetic complex with the nickel(II) atom in a distorted tetrahedral environment [3]. The metallation of 8-aminoquinoline with [(tmeda)NiMe<sub>2</sub>] leads to the formation of diamagnetic nickel di(8-amidoquinoline) with a distorted square planar metal center [4].

Strongly related *N*-trialkylsilyl-2-pyridylmethylamides can easily undergo an oxidative C–C coupling reaction according to Eq. (1) with dimethylzinc at elevated temperatures [5,6]. Without protecting trialkylsilyl groups, the reaction of  $H_2N$ – $CH_2$ –Py with ZnMe<sub>2</sub> at elevated temperatures does lead to oxidative C–C coupling reactions, but a variety of compounds are obtained [7]. This C–C coupling of 2-pyridylmethylamines strongly depends on the redox potential  $E^0$  of the employed reagents: Initiation of the coupling with ZnMe<sub>2</sub> [ $E^0(Zn/Zn^{2+}) = -0.763$  V] requires elevated temperatures, whereas this reaction can be performed at room temperature with [Sn{N(SiMe\_3)\_2}\_2] [ $E^0(Sn/Sn^{2+}) = -0.137$  V] and no coupling was observed with MgR<sub>2</sub> [ $E^0(Mg/Mg^{2+}) = -2.356$  V]. Taking these observations into account nickel(II) compounds [ $E^0(Ni/Ni^{2+}) = -0.257$  V] seem to be a suitable reagent for a C–C coupling of 2-pyridylmethylamines.



The nickel(II) complex [(tmeda)NiMe<sub>2</sub>] shows several reaction pathways [8]: addition of bipyridine and bidentate phosphanes give an exchange of the tmeda ligand and the formation of LNiMe<sub>2</sub> whereas strong  $\pi$ -acceptor molecules

<sup>\*</sup> Corresponding author. Tel.: +49 3641 948110; fax: +49 3641 948102. *E-mail address:* m.we@uni-jena.de (M. Westerhausen).

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lead to reductive elimination of ethane and the formation of  $[(\text{tmeda})\text{Ni}(\pi-\text{ligand})_n]$  (n = 1, 2). The reaction of terpyridine (tpy) with  $[(\text{tmeda})\text{NiMe}_2]$  yields the nickel(I) complex [(tpy)NiMe] as shown in Eq. (2) [9,10] via a nonradical reaction mechanism [10]. This complex shows a Ni–C distance of 195 pm [9].



The reaction of [(tmeda)NiMe<sub>2</sub>] with 2-aminomethylpyridine (Amp) leads to an exchange of the tmeda ligand and to the formation of (Amp)NiMe<sub>2</sub> 1 [11]. This complex is poorly soluble in toluene and therefore, it precipitates immediately giving a yield of more than 70%. A reaction in THF gives lower yields of approximately 20% due to accompanying decomposition reactions. The bulkier N-diphenylphosphanyl-2-aminomethylpyridine [12] reacts with [(tmeda)NiMe<sub>2</sub>] tetrakis(N-diphenylphosphanyl-2-aminomethylvielding pyridine)nickel(0) 2 [13]. Rather poor yields of 2 were obtained due to the fact that also decomposition takes place during this reaction yielding ethane and nickel(0). A higher yield was obtained starting from  $[(cod)_2Ni]$  (cod = 1,5cyclooctadiene) and Ph<sub>2</sub>P-N(H)-CH<sub>2</sub>-Py. The soft nickel(0) atom prefers the coordination to the soft phosphorus rather than to the harder nitrogen bases.



The crystal structure determinations of 1 [14] and 2 [15] were performed on a Nonius KappaCCD diffractometer, using graphite-monochromated Mo–K<sub> $\alpha$ </sub> radiation. Data were corrected for Lorentz and polarization effects, and not for absorption effects [16,17]. The structures were solved by direct methods (SHELXS [18]) and refined by full-matrix least squares techniques against  $F_o^2$  (SHELXL-97 [19]). The hydrogen atoms of the four amine groups of **2** were located by difference Fourier synthesis and refined isotropically. All other hydrogen atoms were included at calculated positions with fixed thermal parameters. All nonhydrogen, non solvent atoms were refined anisotropically [19]. XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

The nickel(II) complex **1** crystallizes in the shape of extremely thin needles with two molecules in the asymmet-

ric unit, distinguished by the letters "A" and "B" [14]. Molecular structure and numbering scheme of molecule A are represented in Fig. 1. The metal atom of this diamagnetic complex is in a distorted square planar environment with average Ni–C and Ni–N bond lengths of 192.6 and 197.2 pm.

The molecular structure of molecule A of **2** is shown in Fig. 2. The asymmetric unit contains two half molecules distinguished by "A" and "B" [15]. The structure of this aminophosphane complex is rather similar to the complex of tetrakis(anilino-diphenylphosphane)nickel(0) [20] which was prepared from the appropriate phosphane, nickel(II) chloride and zinc. The nickel atoms of **2** are in slightly distorted tetrahedral environments with an average Ni–P bond length of 216.9 pm. The P–N distances show an average value of 169.5 pm which is comparable to the P–N bonds of [MeZn–N(CH<sub>2</sub>Py)PPh<sub>2</sub>]<sub>2</sub> but smaller than observed for Py–CH<sub>2</sub>–N(PPh<sub>2</sub>)<sub>2</sub> [12].

The organometallic chemistry of [(tmeda)NiMe<sub>2</sub>] is rather complex because this compound offers a variety of different reaction pathways:

- (i) Substitution of the neutral coligand TMEDA: 2-Aminomethylpyridine substitutes the TMEDA molecule giving the nickel(II) complex (2-aminomethylpyridine-N,N')dimethylnickel **1**. Similar observations were made for 2,2'-bipyridine and 1,2-bis(dimethylphosphino)ethane [8].
- (ii) Metallation of H-acidic substrates: the metallation force of (tmeda)NiMe<sub>2</sub> was shown in the reaction with 8-aminoquinoline leading to the formation of square planar bis(8-amidoquinoline)nickel(II) [4].



Fig. 1. Molecular structure of molecule A of (amp)NiMe<sub>2</sub> 1. The ellipsoids represent a probability of 40%. Selected bond lengths (pm): NiA–C7A 192.1(9), NiA–C8A 193.6(9), NiA–N1A 196.8(7), NiA–N2A 198.1(7); angles (°): C7A–NiA–C8A 88.2(5), N1A–NiA–N2A 82.2(3), C7A–NiA–N1A 98.3(4), C7A–NiA–N2A 179.5(4), C8A–NiA–N1A 172.2(4), C8A–NiA–N2A 91.3(4).



Fig. 2. Molecular structure of molecule A of Ni[P(Ph<sub>2</sub>)–N(H)–CH<sub>2</sub>Py]<sub>4</sub> **2**. The ellipsoids represent a probability of 40%. Symmetry equivalent atoms are marked with an apostrophe. The H atoms are omitted for clarity reasons. Selected bond lengths (pm): NiA–P1A 217.12(7), NiA–P2A 217.58(7), P1A–N1A 170.0(2), P1A–C7A 185.3(3), P1A–C13A 183.9(3), P2A–N3A 169.3(2), P2A–C25A 184.3(3), P2A–C31A 184.8(3), N1A–C1A 145.9(4), N3A–C19A 146.2(4); angles (°): P1A–NiA–P2A 105.51(3), P1A–NiA–P2A' 115.49(4), P1A–N1A–C1A 123.9(2), P2A–N3A–C19A 126.3(2).

- (iii) Reductive elimination of ethane yields nickel(0) complexes.
- (iv) Comproportionation of Ni(0) and Ni(II) compounds: occasionally, comproportionation of nickel(0) and nickel(II) complexes can lead to nickel(I) compounds as observed for the reaction of [(tmeda)NiMe<sub>2</sub>] with terpyridine [9,10].

Often these reactions are competitive and many side reactions can occur leading to low yields. 2-Pyridylmethylamino-diphenylphosphane initiates the formation of nickel(0) yielding tetrakis(*N*-diphenylphosphanyl-2-aminomethylpyridine)nickel(0) **2**, TMEDA and ethane. Even though the redox potential  $E^0(\text{Ni/Ni}^{2+})$  should allow the oxidative C–C coupling of 2-aminomethylpyridine derivatives similar to Eq. (1), this reaction was not observed in our case. The reductive elimination of ethane is favoured instead.

#### Supplementary material

CCDC 669029 and 669030 contain the supplementary crystallographic data for 1 and 2. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

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- [11] (2-Aminomethylpyridine-N,N')dimethylnickel 1: A solution of 84 mg of 2-aminomethylpyridine (0.78 mmol) in 7 ml of toluene was layered on a toluene solution of 92 mg of [(TMEDA)NiMe<sub>2</sub>] (0.45 mmol). Diffusion at r.t. leads to the formation of red needles which were collected and washed with toluene. Recrystallization from THF gave single crystals of 1 suitable for X-ray diffraction experiments. Yield: 62 mg (0.31 mmol, 70%). M.p. 136 °C (dec.). <sup>1</sup>H NMR (THF-*d*<sub>8</sub>): 8.31 (d, 1H, Py1), 7.62 (t, 1H, Py3), 7.07 (m, 2H, Py4, Py2), 3.91 (t, 2H, CH<sub>2</sub>), 2.91 (s, br, 2H, NH<sub>2</sub>), -0.83 (s, 3H, CH<sub>3</sub>), -1.01 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (THF-*d*<sub>8</sub>): 163.7 (Py5), 147.6 (Py1), 135.1 (Py3), 135.6 (Py3), 123.3 (Py4/2), 120.7 (Py2/4), 48.2 (CH2), -9.2 (CH3), -15.1 (CH<sub>3</sub>). IR (Nujol, KBr windows, cm<sup>-1</sup>): 3331 s, 3160 w, 3085 m br, 1604 m, 1446 s, 1275 m, 1154 m, 1063 s, 1027 m, 932 w, 750 vs, 667 m, 526 m. MS (DEI, m/z): 181 ([amp-NiCH<sub>3</sub>]<sup>+</sup>, 4%), 166 ([amp-Ni]<sup>+</sup>, 46%), 108 ( $[amp]^+$ , 100%). Elemental analysis ( $C_8H_{14}N_2Ni$ , 196,90): calc.: C, 48.80; H, 7.17, N, 14.23; found: C, 47.78; H, 7.12, N, 14.16.
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- [13] Tetrakis(*N*-diphenylphosphanyl-2-aminomethylpyridine)nickel(0) 2: Method A (from [(tmeda)NiMe<sub>2</sub>]): A solution of 0.43 g of Ndiphenylphosphanyl-2-aminomethylpyridine (1.46 mmol) in 14 ml of THF was dropped into a solution of 75 mg of [(tmeda)NiMe<sub>2</sub>] (0.36 mmol) in 6 ml of THF. Ethane gas was liberated from this mixture immediately. Yellow cuboid crystals were obtained during storage at -20 °C which were washed with THF. A second crop of crystals can be isolated after concentration of the motherliquor and cooling again to -20 °C. Yield: 0.18 g (0.15 mmol, 40%). Method B (from [Ni(cod)<sub>2</sub>]): At r.t. a solution of 0.51 g of N-diphenylphosphanyl-2-aminomethylpyridine (1.7 mmol) in 10 ml of toluene was added dropwise to a solution of 124 mg (0.45 mmol) of [Ni(cod)<sub>2</sub>] in 10 ml of toluene. All solids were removed by filtration. Then the volume of the filtrate was reduced and the remaining solution was stored at -20 °C. After a week the product was collected and washed with toluene. Yield: 0.30 g (0.25 mmol, 54%). Physical properties: M.p. 192 °C (dec.). <sup>1</sup>H NMR (benzene- $d_6$ ): 8.37 (d, <sup>3</sup>J(HH) = 4.0 Hz, 4H, Py1),

7.56 (s, br, 16H, Ph), 6.97 (m, br, 28H, Py3, Ph), 6.73 (d,  ${}^{3}J(\text{HH}) = 7.8 \text{ Hz}$ , 4H, Py4), 6.60 (t,  ${}^{3}J(\text{HH}) = 6.0 \text{ Hz}$ , 4H, Py2), 3.78 (m, 8H, CH<sub>2</sub>), 3.37 (m, br, 4H, NH).  ${}^{13}\text{C}{}^{1}\text{H}$  NMR (benzene- $d_{6}$ ): 161.1 (Py5), 149.3 (Py1), 141.6 (br, Ph), 135.6 (Py3), 131.5 (br, Ph), 128.3 (Ph), 121.8 (Py4), 121.2 (Py2), 50.3 (CH<sub>2</sub>).  ${}^{31}\text{P}{}^{1}\text{H}$  NMR (benzene- $d_{6}$ ): 69.3 (PPh<sub>2</sub>). IR (Nujol, KBr windows, cm<sup>-1</sup>): 3400 m, 3382 s, 3365 s, 3051 m, 1964 w, 1903 w, 1586 s, 1569 m, 1432 vs, 1402 m, 1336 w, 1308w, 1276 w, 1207 m, 1154 m, 1102 s, 1075 vs, 1027 m, 994 m, 911 m, br, 836 m, br, 802 m, br, 750 s, 707 s, 696 vs, 680 m, 630 w, 620 w, 596 m, 543 m, 518 s, 486 m, 463 s. MS (DEI, *m/z*): 292 ([amp-PPh<sub>2</sub>]<sup>+</sup>, 100%), 215 ([amp-PPh]<sup>+</sup>, 100%), 200 ([amp-PPh<sub>2</sub> - C<sub>6</sub>H<sub>6</sub>N]<sup>+</sup>, 100%). Elemental analysis (C<sub>72</sub>H<sub>68</sub>N<sub>8</sub>P<sub>4</sub>Ni, 1227.95): calc.: C, 70.42; H, 5.58; N, 9.13; found: C, 69.20; H, 6.21; N, 7.87.

[14] Crystal data for 1:  $C_8H_{14}N_2Ni$ ,  $M_r = 196.92 \text{ g mol}^{-1}$ , red prism, size  $0.05 \times 0.05 \times 0.05 \text{ mm}^3$ , monoclinic, space group  $P2_1/c$ , a = 12.8428(4), b = 7.2276(4), c = 18.9577(9) Å,  $\beta = 91.159(3)^\circ$ , V = 1759.34(14) Å<sup>3</sup>, T = -90 °C, Z = 8,  $\rho_{calcd.} = 1.487 \text{ g cm}^{-3}$ ,  $\mu$ (Mo-K<sub> $\alpha$ </sub>) = 21.42 cm<sup>-1</sup>, F(000) = 832, 11,960 reflections in h(-16/16), k(-9/9), l(-24/24), measured in the range  $1.59^\circ \leq \Theta \leq 27.49^\circ$ , completeness  $\Theta_{max} = 99.4\%$ , 4008 independent reflections,  $R_{int} = 0.0668$ , 2642 reflections with  $F_o > 4\sigma(F_o)$ , 203 parameters, 0 restraints,  $R_{1,obs} = 0.0880$ ,  $wR_{obs}^2 = 0.2420$ ,  $R_{1,all} = 0.1266$ ,  $wR_{all}^2 =$ 0.2633, GOOF = 1.051, largest difference peak and hole: 2.168/ -1.377 e Å<sup>-3</sup>. The crystals of **1** were extremely thin and of low quality resulting in a substandard data set and a rather high final  $wR_{all^2}$  value.

- [15] Crystal data for **2**: C<sub>72</sub>H<sub>68</sub>N<sub>8</sub>NiP<sub>4</sub> · 1.5 C<sub>4</sub>H<sub>8</sub>O,  $M_r = 1332.06 \text{ g mol}^{-1}$ , yellow prism, size  $0.05 \times 0.05 \times 0.04 \text{ mm}^3$ , monoclinic, space group P2/c, a = 26.9743(4), b = 11.7894(1), c = 25.1820(4) Å,  $\beta = 116.626(1)^\circ$ , V = 7158.9(2) Å<sup>3</sup>, T = -90 °C, Z = 4,  $\rho_{calcd} = 1.236 \text{ g cm}^{-3}$ ,  $\mu$  (Mo-K<sub> $\alpha$ </sub>) = 4.11 cm<sup>-1</sup>, F(000) = 2800, 81,216 reflections in h(-33/34), k(-14/15), l(-32/32), measured in the range  $1.73^\circ \leq \Theta \leq 27.41^\circ$ , completeness  $\Theta_{max} = 99.4\%$ , 16,214 independent reflections,  $R_{int} = 0.0720$ , 11,459 reflections with  $F_o > 4\sigma(F_o)$ , 843 parameters, 0 restraints,  $R_{1,obs} = 0.0577$ ,  $wR_{obs}^2 = 0.1464$ ,  $R_{1,all} = 0.0925$ ,  $wR_{all}^2 = 0.1667$ , GOOF = 1.021, largest difference peak and hole: 1.091/-0.475 e Å<sup>-3</sup>.
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