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Nickel complexes with a *O,N,O′*-ligand and a phosphane co-ligand – Monometallic versus bimetallic complexes

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The coordination chemistry of 5-hydroxypyrazoline ligand precursor **1** with $Ni(OAc)_2{\cdot}4H_2O$ and 1,1-bis(diphenylphosphino)methane (DPPM) as co-ligand to form the monometallic nickel complex **2** [Ni(**1**–2H)(DPPM)] was studied. The complex was characterized and investigated by various techniques, pointing out a square planar geometry at the nickel center with η^1-coordination of the DPPM ligand. Moreover, addition of $Fe_2(CO)_9$ revealed the formation of the bimetallic complex **3** [Ni(**1**–2H)(DPPM)Ni(**1**–2H)] with DPPM as bridging ligand between two nickel centers and the abstraction of one DPPM ligand by the iron to form $Fe(CO)_4(\eta^1\text{-dppm})$.

1. Introduction

Recently, the coordination chemistry of ligand precursor **1** was examined and different coordination modes (e.g., *O,N,O′*; *O,N*; *O,O′*; and *N,O′*) were realized, depending on the metal and the added co-ligands [1–4]. Moreover, the obtained complexes demonstrated interesting catalytic potential in various organic transformations. For instance, the flexibility of the ligand precursor **1** was shown in the reaction with $ZnMe_2$. On the one hand, an *O,O′*-coordination after deprotonation was observed, while the addition of base revealed a second deprotonation and a *O,N*-coordination [5,6]. A similar *O,O′*-motif was observed for coordination to molybdenum, resulting in attractive precatalysts for the reduction of organic amides to amines [7]. In case of copper a *N,O′*-coordination was detected with triphenylphosphane as co-ligand and application in copper-catalyzed amination of CH bond was realized [8]. In contrast to that, with iron(II) or iron(III) as complex metal center a *O,N,O′*-coordination was observed with 4-dimethylaminopyridine (DMAP) or triphenylphosphane oxide as co-ligands [9]. Moreover, the reaction of ligand precursor **1** with $Ni(OAc)_2{\cdot}4H_2O$ and DMAP resulted after double deprotonation in the formation of an octahedral complex with a *O,N,O′*-coordination, while in the presence of ammonia or phosphane co-ligands a square planar geometry was observed [10–17]. Importantly, at this stage only monometallic nickel complexes were reported. Based on the flexibility of the co-ligands the formation of bimetallic complexes with bridging bidentate co-ligands can be a straightforward target (Fig. 1). For instance such bimetallic complexes can be useful precatalysts for catalytic applications (e.g., cooperative catalysis, consecutive catalysis) [18,19]. Based on that, we report herein on the synthesis and characterization of monometallic and bimetallic nickel(II) complexes with a *O,N,O′*-ligand and a (bridging) DPPM co-ligand.

2. Results and discussion

The 1-benzoyl-5-hydroxypyrazoline **1** was synthesized in accordance to the procedure reported in the literature [20]. Benzohydrazide was reacted with equimolar amounts of 1,1,1,5,5,5-hexafluoroacetylacetone and heated to reflux for 5 h in ethanol. After work-up the desired ligand precursor **1** was obtained as colourless crystalline compounds. With **1** in hand we examined the coordination to nickel (Scheme 1). In agreement to our previously established protocol a methanol solution of ligand precursor **1** and an excess of 1,1-bis(diphenylphosphino)methane (DPPM, 3.0 equiv.) was added to a solution of $Ni(OAc)_2{\cdot}4H_2O$ in methanol at room temperature [10–17]. After stirring overnight, all volatiles were removed to obtain a brown powder, which was extracted with toluene and purified by crystallization to obtain red–brown crystals.

Crystals suitable for X-ray measurements were grown from toluene by slow evaporation of the solvent at room temperature. The solid–state structure of complex **2** has been characterized by single–crystal X-ray diffraction analysis. Thermal ellipsoid plots and selected bond lengths and angles are shown in Fig. 2. Interestingly, only one phosphorous unit of the bidentate DPPM

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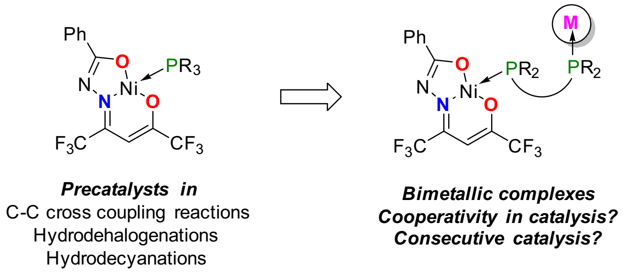


Fig. 1. Monometallic vs. bimetallic nickel complexes.

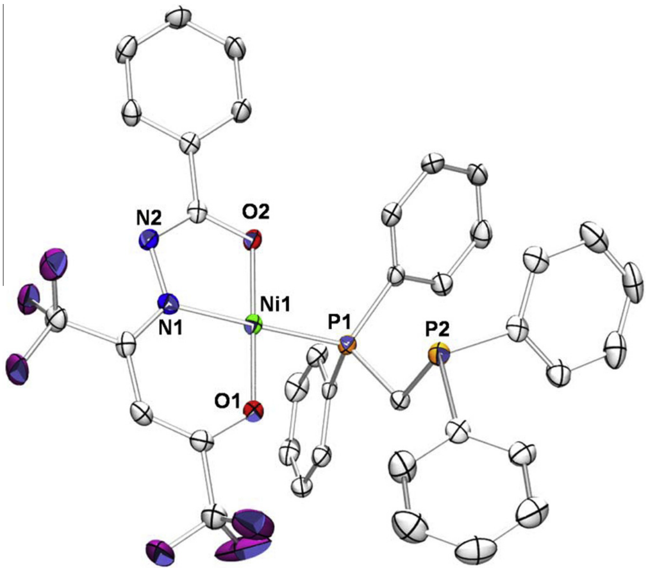


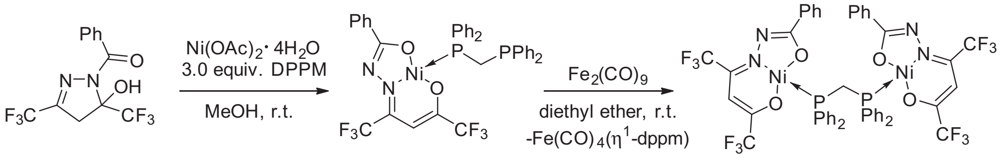
Fig. 2. Molecular structure of **2**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ni1–N1: 1.8672(19), Ni1–O1: 1.8298(16), Ni1–O2: 1.8317(15), Ni1–P1: 2.2097(7), O1–Ni1–O2: 179.61(8), N1–Ni1–P1: 171.70(6).

ligand is coordinated to the nickel center, while the other one is uncoordinated. The tridentate ligand is coordinated in a *O*,*N*,*O*′-mode creating a five-membered as well as a six-membered ring system and therefore shielding one side of the metal. The DPPM ligand is *cis*-positioned to the oxygen donors, while N1 of the ligand is connected to the nickel centre in the *trans*-position. Overall a square planar nickel center was observed, which is in accordance to (**1**–2H)-nickel complexes with monodentate phosphane co-ligands. In more detail, the Ni–P1 bond distance of 2.2097(7) Å is to some extend shorter in comparison to nickel(II) complexes (2.2252–2.2422 Å) having the same coordinating atoms [12,13,16,17]. For instance, in case of triphenylphosphane as co-ligand a Ni–P1 bond distance of 2.2252(10) Å was observed [17]. On the other hand, the Ni–O and Ni–N1 bond lengths are in the range of comparable nickel(II) complexes [12,13,16,17]. Moreover, the N1–Ni–P1 bond angle of 171.70(6)° deviates from the ideal angle of 180° (comparable complexes: 172.23–177.32°) [12,13,16,17].

The complex **2** was characterized by ^{1}H NMR spectroscopy applying C_6D_6 as solvent, showing the C–*H* proton in the six-membered ring at 6.16 ppm and the CH_2 bridge between the two phosphorous with a chemical shift of $\delta = 2.95$ ppm. In the ^{19}F NMR spectrum two sharp signals for the two CF_3 groups at −65.0 ppm and −71.2 ppm were observed. The coordination of the DPPM ligand was confirmed by $^{31}P\{^{1}H\}$ NMR; here a signal at 5.85 ppm for the phosphorous coordinated to the nickel was detected, while the uncoordinated phosporous has a chemical shift of −26.1 ppm. Afterwards attempts were undertaken to coordinate the free phosphane unit in complex **2** to other metals (e.g., iron, platinum, copper) to allow access to heterobimetallic complexes. In case of the reaction of complex **2** with one equivalent of $Fe_2(CO)_9$ in refluxing diethyl ether a new complex was obtained after work-up. Crystals suitable for X-ray measurements were grown from ethanol by slow evaporation of the solvent at room temperature. The solid–state structure of the complex **3** has been characterized by single–crystal X-ray diffraction analysis. Thermal ellipsoid plots and selected bond lengths and angles are shown in Fig. 3.

Surprisingly, the structure revealed the formation of a homobimetallic complex instead of the desired heterobimetallic complex in which the DPPM ligand acts as bridging ligand between two (**1**–2H)-nickel center, which pointing in opposite directions. In accordance to complex **2** the tridentate ligands are coordinated in a *O*,*N*,*O*′-mode creating five-membered as well as six-membered ring systems and the DPPM ligand is *cis*-positioned to the oxygen donors, while the nitrogen of the tridentate ligand is connected to the nickel centers in the *trans*-position. The Ni–P bonds (Ni–P1: 2.2024(9), Ni–P2: 2.2018(8)) are in the same range as observed for complex **2**. In comparison to complex **2** smaller N–Ni–P angles were found (N1–Ni1–P1: 169.18(8), N3–Ni2–P2: 169.73(10)).

Moreover, the bimetallic complex was characterized by NMR analysis. The crystals of complex **3** were investigated by ^{1}H NMR spectroscopy applying C_6D_6 as solvent, showing the C–*H* proton in the six-membered ring at 5.99 ppm. In the ^{19}F NMR spectrum two sharp signals for the two CF_3 groups at −65.1 ppm and −70.9 ppm were observed. The coordination of the DPPM ligand to both nickel center was confirmed by $^{31}P\{^{1}H\}$ NMR; here a signal at 0.4 ppm was detected. On the other hand, the investigation of the reaction mixture by $^{31}P\{^{1}H\}$ NMR revealed the formation of other phosphorous containing species. For instance the signals with a chemical shift of −26.0 ppm and 66.6 ppm with a coupling constant of $^{2}J_{P\text{–}P} = 84.62$ Hz can be assigned to the complex $Fe(CO)_4(\eta^1\text{-dppm})$ **4** [21,22], which was furthermore proven by single–crystal X-ray diffraction analysis and is in accordance with the structure reported by Dias Rodrigues, Lechat and Francisco [23]. Based on this results the $Fe_2(CO)_9$ acts as a DPPM abstraction reagent from complex **2**. The DPPM-free nickel intermediate probably reacts with an additional complex **2** to form the homobimetallic complex **3**. Moreover, a singlet signal at 67.0 ppm was monitored, which can be assigned to the complex $Fe_2(CO)_5(dppm)_2$. Interestingly, reacting complex **2** with other metal sources for instance $CpFe(CO)_2I$ or $PtCl_2(cod)$ revealed the formation of complex **3** and the additional complex acts as abstraction reagent for DPPM.



1 **2** (yield: 12%) **3** (yield: 56%)

Scheme 1. Synthesis of nickel complexes **2** and **3**.

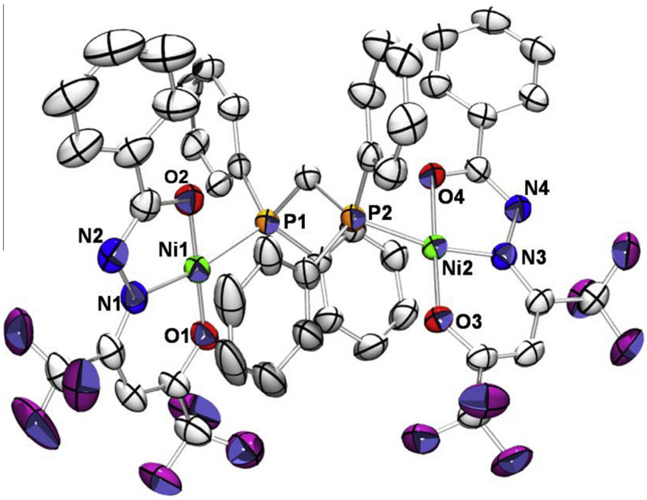


Fig. 3. Molecular structure of **3**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ni1–O1: 1.823(2), Ni1–O2: 1.8356(19), Ni1–N1: 1.854(3), Ni1–P1: 2.2024(9), Ni2–O3: 1.821(2), Ni2–O4: 1.837(2), Ni2–N3: 1.868(3), Ni2–P2: 2.2018(8), O1–Ni1–O2: 178.24(10), O3–Ni2–O4: 179.46(11), N1–Ni1–P1: 169.18(8), N3–Ni2–P2: 169.73(10).

3. Conclusion

In summary we have investigated the coordination chemistry of 5-hydroxypyrazoline ligand **1** with $Ni(OAc)_2 \cdot 4H_2O$ and 1,1-bis(diphenylphosphino)methane (DPPM) as co-ligand to form the monometallic nickel complex **2** [Ni(**1**–2H)(DPPM)]. The complex was characterized and investigated by various techniques, pointing out a square planar geometry at the nickel center with η^1-coordination of the DPPM ligand. Moreover, addition of $Fe_2(CO)_9$ revealed the formation of the bimetallic complex **3** [Ni(**1**–2H)(DPPM)Ni(**1**–2H)] with DPPM as bridge between two nickel centers. In ongoing studies the application of complex **2** and **3** as precatalysts will be investigated [24].

4. Experimental section

4.1. General

^1H, ^{19}F, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker Avance 200 spectrometer (^1H: 200.13 MHz; ^{13}C: 50.32 MHz; ^{19}F: 188.31 MHz, ^{31}P: 81.01 MHz) and 400 spectrometer (^{13}C: 100.61 MHz) using the signals of the deuterated solvents (^1H NMR, ^{13}C NMR), $CFCl_3$ (^{19}F NMR) or 85% H_3PO_4 (^{31}P NMR) as reference. IR spectra were recorded on a Perkin Elmer Spectrum 100 FT-IR.

*4.2. 3,5-di(trifluoromethyl)-1-(benzoyl)-5-hydroxy-pyrazoline (**1**)*

To a solution of 1,1,1,5,5,5-hexafluoropeta-2,4-dione (55.8 mmol) in ethanol (60 mL) was added a solution of benzohydrazide (55.8 mmol) in ethanol (60 mL). After refluxing the mixture for 5 h the solvent was removed in vacuum. The colourless residue was purified by recrystallization from ethanol/*n*-hexane (9:1). Yield = 15.9 g (87%, colourless crystals). ^1H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 7.84–7.92$ (m, 2H; Ar), 7.40–7.65 (m, 3H, Ar), 6.40 (s, br, 1H, OH), 3.00–3.66 (m 2H, CH_2) ppm. $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$, 25 °C) $\delta = 171.6$, 144.1, 143.7, 133.3, 131.6, 130.5, 128.3, 94.2, 93.8, 41.4 (CH_2) ppm. ^{19}F NMR (50 MHz, $CDCl_3$, 25 °C) $\delta = -67.4$, -80.5 ppm. IR (KBr): $\nu = 3390$ (m), 3324 (m), 1680 (s), 1637 (m), 1451 (m), 1434 (m), 1333 (m), 1305 (m), 1275 (s), 1176 (s), 1152 (s), 1078 (m), 1028 (w), 1009 (m), 1009 (m), 905 (w), 792 (w), 757 (w), 715 (w), 672 (w), 631 (w) cm^{-1}. HRMS calc. for $C_{12}H_8F_6N_2O_2$+H: 327.05627, found: 327.05569.

*4.3. Synthesis of **2***

To a mixture of **1** (3.06 mmol) and bis(diphenylphosphino)methane (3 equiv., 9.17 mmol) in methanol (10 mL) was added a solution of $Ni(OAc)_2 \cdot 4H_2O$ (3.06 mmol) at room temperature. The solution was stirred overnight. After stirring overnight, the volatiles were removed in vacuum to obtain a brown powder, which was extracted from toluene and purified by crystallization. Crystals suitable for X-ray diffraction analysis were obtained from toluene solution at room temperature by slow evaporation. Yield = 290 mg (12%, first crop, red crystals). Mp: 151 °C. ^1H NMR (200 MHz, C_6D_6, 25 °C) $\delta = 8.03–8.08$ (m, 2H), 7.55 (br, 7H), 6.98–7.08 (m, 16H), 6.16 (s, 1H, C*H*), 2.95 (s, 2H, C*H*$_2$) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6, 25 °C) $\delta = 173.0$, 156.4 (q, $^2J_{C-F} = 33.5$ Hz), 141.6 (q, $^2J_{C-F} = 30.3$ Hz), 133.7, 131.4, 130.7, 129.5, 129.2, 128.8, 119.5 (q, $^1J_{C-F} = 282.2$ Hz), 118.9 (q, $^1J_{C-F} = 282.2$ Hz), 91.3, 30.2 ppm (some peaks were overlapped with solvent's peaks). ^{19}F NMR (188 MHz, C_6D_6, 25 °C) $\delta = -65.0$, -71.2 ppm. $^{31}P\{^1H\}$ NMR (81 MHz, C_6D_6, 25 °C) $\delta = 5.85$, -26.1 ppm. IR (KBr): $\nu = 3433$ (br), 1608 (m), 1592 (m), 1531 (m), 1516 (m), 1483 (w), 1455 (w), 1434 (m), 1366 (m), 1347 (m), 1267 (s), 1203 (s), 1175 (s), 1166 (s), 1156 (s), 1135 (s), 1108 (m), 1067 (m), 1025 (w), 999 (w), 890 (w), 848 (w), 798 (w), 775 (w), 742 (m), 736 (m), 716 (m), 695 (s), 585 (w), 581 (w), 484 (w) cm^{-1}. HRMS calc. for $C_{37}H_{29}F_6N_2NiO_2P_2$+H: 767.09619, found: 767.09356. elemental analysis: $C_{37}H_{29}F_6N_2NiO_2P_2$: calc. C 57.92, H 3.68, N 3.65; found C 57.65, H 3.91, N 3.44.

*4.4. Synthesis of **3***

A mixture of **2** (0.65 mmol) and $Fe_2(CO)_9$ (0.65 mmol) in diethylether (50 mL) was stirred for 24 h at room temperature. The volatiles were removed in vacuum to obtain a brown powder, which was dissolved in a small amount of acetone (10 mL) and purified by filtration over a plug of silica. After elution of the plug of silica with acetone (200 mL) and removal of the solvent in vacuum a red–brown residue was obtained (Note: This procedure removed undesired side products and yields a mixture of **3**, **4** and $Fe_2(CO)_5(dppm)_2$). The residue was dissolved in ethanol (50 mL) and purified by filtration over a plug of silica. After elution of the plug of silica with ethanol (200 mL) and removal of the solvent in vacuum a brown residue was obtained, which contains **4** (Note: suitable crystals for X-ray diffraction analysis were obtained from slow evaporation of the solvent) and $Fe_2(CO)_5(dppm)_2$. After elution of the plug of silica with acetone and removal of the solvent in vacuum a red–brown residue was obtained. The red–brown residue was purified by crystallization with ethanol. Crystals suitable for X-ray diffraction analysis were obtained from an ethanol solution at room temperature by slow evaporation. Yield = 210 mg (56%, red crystals). Mp: 254 °C. ^1H NMR (200 MHz, C_6D_6, 25 °C) $\delta = 8.02–8.06$ (m, 4H), 7.78–7.92 (m, 8H), 6.89–7.05 (m, 18H), 5.99 (s, 2H, C*H*), 3.10–3.30 (m, 2H, C*H*$_2$) ppm. $^{13}C\{^1H\}$ NMR was not measured, due to poor solubility of complex **3**. ^{19}F NMR (188 MHz, C_6D_6, 25 °C) $\delta = -65.1$, -71.2 ppm. $^{31}P\{^1H\}$ NMR (81 MHz, C_6D_6, 25 °C) $\delta = 0.37$ ppm. IR (KBr): $\nu = 1945$ (w), 1610 (w), 1596 (w), 1535 (m), 1518 (m), 1455 (w), 1437 (m), 1362 (m), 1347 (m), 1267 (s), 1197 (s), 1185 (s), 1154 (s), 1129 (m), 1100 (w), 1065 (w), 801 (w), 784 (w), 744 (w), 735 (w), 716 (w), 691 (m) cm^{-1}. HRMS calc. for $C_{49}H_{34}F_{12}N_4Ni_2O_4P_2$+H: 1149.06434, found: 1149.06678. elemental analysis: $C_{49}H_{34}F_{12}N_4Ni_2O_4P_2$: calc. C 51.17, H 2.98, N 4.87; found C 51.43, H 3.11, N 4.64.

4.5. Single–crystal X-ray structure determination [25]

Crystals were each mounted on a glass capillary in perfluorinated oil and measured in a cold N_2 flow. The data were collected using an Oxford Diffraction Xcalibur S Sapphire at 150(2) K ($Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å) or an Agilent Technologies SuperNova (single source) at 150 K $Cu_{K\alpha}$ radiation, $\lambda = 1.5418$ Å). The structures were solved by direct methods and refined on F^2 with the SHELX-97 software package. The positions of the hydrogen atoms were calculated and considered isotropically according to a riding model. The Figures were created with ORTEP and POV-Ray.

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Appendix A. Supplementary material

CCDC 949640 (for **2**), 1050190 (for **3**) and 1050191 (for **4**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2015.05.008.

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