Synthesis and Characterization of Heterotrinuclear Complexes of Nickel and Palladium with Pyridinecarboxylate as Bridging Ligands

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Heterotrinuclear pyridinecarboxylate complexes of nickel(II) and palladium(II) of the types [Ni(mcN$_3$)(pyridinecarboxylate)]$_2${μ-[Pd(C$_6$F$_5$)$_2$]}(PF$_6$)$_2$ [mcN$_3$ = 2,4,4-trimethyl-1,5,9-triazacyclododec-1-ene (Me$_3$-mcN$_3$) or 2,4,4,9-tetramethyl-1,5,9-triazacyclododec-1-ene (Me$_4$-mcN$_3$)] have been prepared by two different routes. The corresponding monomeric pyridinecarboxylate complexes of nickel and the monomeric pyridinecarboxylic acid/ester complexes of palladium have also been prepared. The crystal structures of two precursors [Ni(Me$_4$-mcN$_3$)(NC$_5$H$_4$-3-COO)]PF$_6$ and *cis*-[Pd(C$_6$F$_5$)$_2$(NC$_5$H$_4$-4-CH$_2$COOCH$_3$)$_2$] have been established by X-ray diffraction.

Introduction

Pyridinecarboxylate ligands tend to bind metal ions with both, pyridine and carboxylate groups to form extended networks, where the carboxylate groups balance the metal charges.[1–6] The deliberate, stepwise and controlled synthesis of molecular squares and dinuclear macrocycles using pyridinecarboxylates as spacers has been recently reported by Hor et al.[7]

The versatile carboxylate anion can adopt a wide range of bonding modes including monodentate, symmetric and asymmetric chelating and bidentate and monodentate bridging.[8] It is generally agreed that the carboxylate complexes of the 3d elements, including several examples of nickel derivatives, play an important role in biochemistry.[9]

In this paper we report the preparation by two different routes and the spectroscopic behavior of heterotrinuclear pyridinecarboxylate complexes of nickel and palladium in which the two nickel(II) ions are in a pentacoordinate environment. The corresponding monomeric pyridinecarboxylate complexes of nickel and the monomeric pyridinecarboxylic acid/ester complexes of palladium have also been prepared.

Results and Discussion

Synthesis and Characterization of Monomeric Pyridinecarboxylate Complexes of Nickel(II)

The reaction between [Ni(mcN$_3$)(μ-OH)]$_2$(PF$_6$)$_2$ [mcN$_3$ = 2,4,4-trimethyl-1,5,9-triazacyclododec-1-ene (Me$_3$-mcN$_3$) or 2,4,4,9-tetramethyl-1,5,9-triazacyclododec-1-ene (Me$_4$-mcN$_3$)] and carboxylic acids [HA = isonicotinic (Hisonic) or nicotinic (Hnic) acid] leads to the formation of the carboxylate complexes [Ni(mcN$_3$)(A)](PF$_6$) **1**–**4** shown in Scheme 1.

The acid-base reaction occurs at room temperature in acetone with the concomitant liberation of water. This synthetic method has previously been used for the preparation of pentacoordinate nickel(II) complexes containing N,S-donor,[10] oxamidate,[11] hydroxamate,[12] and pyridonate ligands,[13] as well as phosphate esters and phosphinate derivatives.[14]

Complexes **1**–**4** are air-stable both in the solid state and in solution. They have been characterized by partial elemental analyses, FAB$^+$ mass spectrometry and spectroscopic (IR, UV/Vis, and ^{1}H NMR) methods. The IR spectra of complexes **1**–**4** show characteristic absorptions for the mcN$_3$ ligands:[12,14] 3287–3121 cm^{-1} for $\tilde{\nu}$(N–H), ca. 1660 cm^{-1} for $\tilde{\nu}$(C=N), and two strong bands as a result of the PF$_6^-$ ion at 840 and 560 cm^{-1}. The κ^2-coordination mode in compounds **1**–**4** is revealed by the IR spectra, which contain symmetric OCO stretching bands at ca. 1550 cm^{-1}.[15,16] The κ^2-coordination mode in **4** was authenticated by an X-ray crystal structure determination (vide infra). The electronic spectra of **1**–**4** are quite similar and show two d-d transitions in acetone solution with λ_{max} ≈

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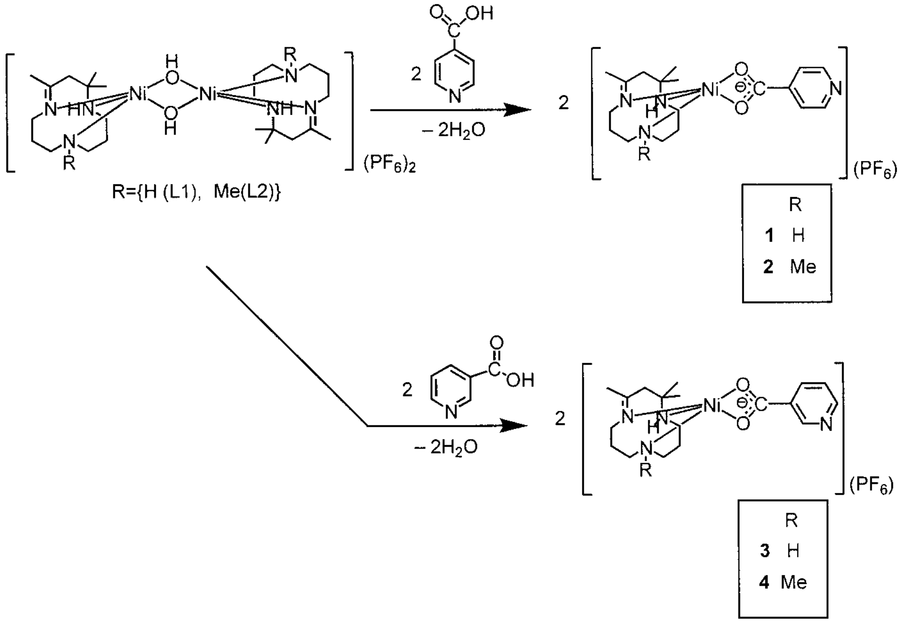


Scheme 1. Monomeric nickel complexes.

63 (ca. 80 $M^{-1}cm^{-1}$) and 390 nm (ca. 200 $M^{-1}cm^{-1}$) which could be assigned to $^3B_1(F) \rightarrow {}^3E(F)$ and $^3B_1(F) \rightarrow {}^3A_2, {}^3E(P)$ transitions, respectively. Both λ_{max} values and molar absorptivities are consistent with a pentacoordinate environment around the nickel(II) center.[17]

NMR Spectroscopic Study of Complexes 1–4

All of the complexes exhibit sharp hyperfine-shifted ^1H NMR signals in acetone solution in the 370 to –35 ppm chemical shift range. The ^1H NMR spectra of complexes **1**–**4** show the resonance line pattern observed for the mcN_3 ligands that was assigned on the basis of previous studies of (macrocycle)nickel complexes[10–14] and from the temperature dependence of the resonances. A representative ^1H NMR spectrum for complex **4** is shown in Figure 1. The α-methylene proton signals shift downfield whereas the β-methylene proton signals shift upfield with regard to the diamagnetic position.[18] Moreover, the signals of the equatorial protons are expected to experience larger contact shifts than those of the axial protons[19] and therefore the most downfield resonances are due to α-CH_{eq} and the most upfield ones to β-CH_{eq}. The isotropically shifted ^1H NMR signals observed for the methyl groups [2-Me, 4-Me(a,b), and 9-Me-N] and phenyl groups of carboxylates can be initially assigned by inspection of their peak areas. All the resonances of the phenyl rings are downfield to TMS in accordance with a dominant σ-delocalization pattern of spin density, consistent with the ground state of nickel(II), although the unpaired electrons could polarize the net spin density in the d_π orbitals. A similar behavior has been observed elsewhere.[20] Curie plots of proton resonances of complex **4** in [D6]acetone are shown in Figure 2. These plots illustrate the general tendency for the contact shifts to increase more rapidly at lower temperatures and exhibit a temperature dependence closely proportional to T^{-1}.

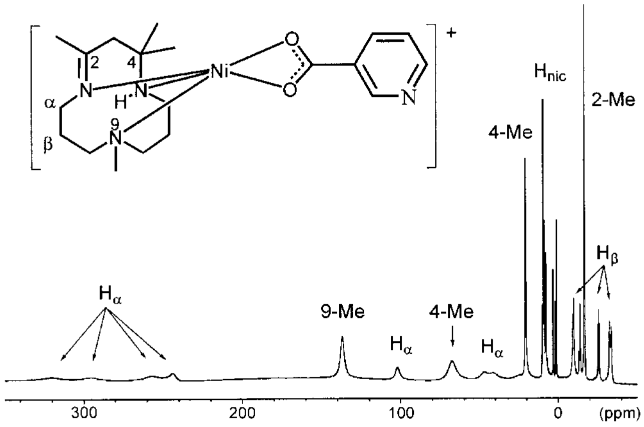


Figure 1. ^1H NMR spectra (in [D6]acetone solution at room temperature) of complex **4**.

Description of the Crystal Structure of Complex 4

The crystal structure of the cation of complex **4** is shown in Figure 3. Selected geometric data are given in Table 1. In each crystallized cation of complex **4**, the nickel atom is five-coordinate, with a square-pyramid arrangement of the chelating atoms. The Reedijk τ parameter[21] (τ = 0 and 1 for square-pyramidal and trigonal-bipyramidal structures, respectively) shows a value of 0.005. The three nitrogen atoms of the N_3 macrocycle are found at the apical position and two adjacent basal ones, whereas the other two basal positions correspond to the *O,O'*-carboxylate group. The basal plane is formed by N(1), N(2), O(1), and O(2), with an r.m.s. deviation of fitted atoms of 0.0108 Å. The Ni atom is 0.3054(13) Å above the corresponding basal plane towards the apical N(3) atom. The coordinated macrocycle exhibits a chairlike conformation for the two six-membered rings that do not contain the C=N bond. This is the most

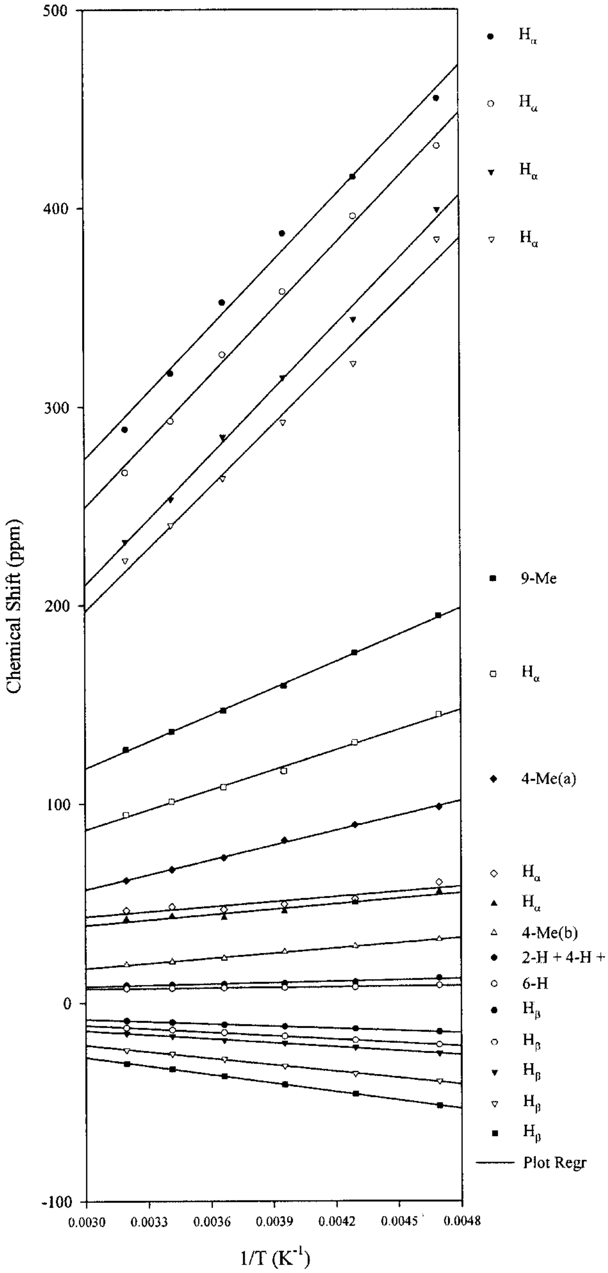


Figure 2. Curie plots of proton resonances of complex **4**.

frequent conformation in complexes having these macrocycles.[13] The Ni–O bond lengths in **4** are close to each other [2.085(2)–2.129(2) Å]. The carboxylate ligands are bonded in a symmetric (or almost) chelating mode with a ΔO = {[Ni–O(2)] – [Ni–O(1)]} value of 0.034 Å. There is a classical intermolecular hydrogen bonding between N(2)–H(2) and N(4) of a neighbor cation generated by (–*x* + 2, –*y* + 2, –*z*) symmetry operation, and a "non-classical" hydrogen bonding between C(16)–H(16) and O(2), generated by the same symmetry operation. The hydrogen bonds of complex **4** are summarised in Table 2 (see Figure 4). These bond lengths are comparable to those reported for other crystallographically characterized nickel carboxylate complexes with a distorted square-pyramidal[22] or octahedral[22–24] geometry. The bite angle of the carboxylate anion shows a value of 62.76(8)°. The torsion angle between the pyridine ring and the nickel-bound carboxylate group is 2.27(8)°. This is the first crystal structure of a pentacoordinate (nicotinato)nickel(II) complex (3D search using the Cambridge Structural Database, CSD version 5.25, July 2004 release).

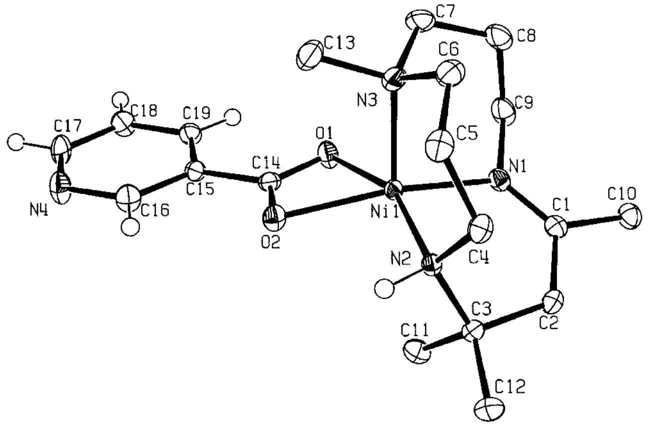


Figure 3. ORTEP drawing of complex **4** showing the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. For clarity hydrogen atoms of the macrocycle are omitted.

Table 1. Selected bond lengths [Å] and angles [°] for complex **4**.

Bond lengths		Bond angles	
Ni(1)–N(1)	1.988(2)	N(1)–Ni(1)–N(2)	92.37(10)
Ni(1)–N(2)	2.008(2)	N(1)–Ni(1)–N(3)	94.91(11)
Ni(1)–N(3)	2.044(3)	N(1)–Ni(1)–O(1)	100.87(9)
Ni(1)–O(1)	2.129(2)	N(1)–Ni(1)–O(2)	157.29(9)
Ni(1)–O(2)	2.085(2)	N(2)–Ni(1)–N(3)	102.68(10)
		N(2)–Ni(1)–O(1)	156.97(9)
		N(2)–Ni(1)–O(2)	98.73(9)
		N(3)–Ni(1)–O(1)	94.93(10)
		N(3)–Ni(1)–O(2)	101.82(10)
		O(2)–Ni(1)–O(1)	62.76(8)

Table 2. Hydrogen bonds for complex **4** [Å and °].

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	<(DHA)
N(2)–H(2)···N(4)#1	0.93	2.08	2.991(4)	166.3
C(16)–H(16)···O(2)#1	0.95	2.44	3.284(4)	147.6

Symmetry transformations used to generate equivalent atoms: #1: –*x* + 2, –*y* + 2, –*z*

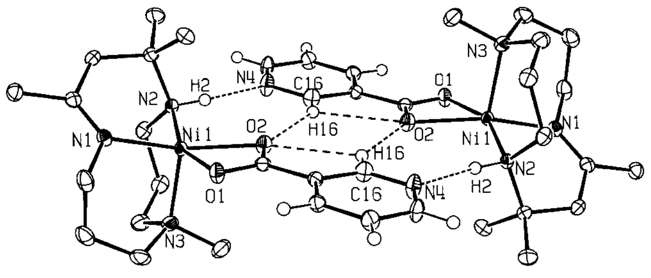


Figure 4. Hydrogen bonding in complex **4**. ORTEP drawing (ellipsoids at 50% probability level) with atom labeling scheme.

Synthesis and Characterization of Monomeric Pyridinecarboxylic Acid/Ester Complexes of Palladium(II)

The labile complex *cis*-[Pd(C_6F_5)$_2$(PhCN)$_2$] has been used as starting material for the preparation of several palladium complexes.[25–28] When *cis*-[Pd(C_6F_5)$_2$(PhCN)$_2$][29] was treated with the pyridinecarboxylic acids NC_5H_4-4-COOH (isonicotinic), NC_5H_4-3-COOH (nicotinic) or NC_5H_4-4-CH_2COOH (in methanol), complexes **5**–**7** were obtained in high yields (Scheme 2). Complexes **5**–**7** are all white, air-stable solids. Their IR spectra show the characteristic absorptions of the C_6F_5 group ($\tilde{\nu}$ = 1630 m, 1490 vs, 1050 s, 950 vs cm^{-1})[30] and a split band at $\tilde{\nu} \approx 800$ cm^{-1} assigned to the *cis*-Pd(C_6F_5)$_2$ moiety.[31,32] The IR spectra of **5** and **6** show the expected strong ν(C=O) band at $\tilde{\nu} \approx$ 1720 cm^{-1}, a frequency that is typical for aromatic carboxylic acids.[33,34] In complex **7** the ν(C=O) band is observed at $\tilde{\nu}$ = 1744 cm^{-1}. The ^{19}F NMR spectra of complexes **5**–**7** show the presence of two equivalent freely rotating C_6F_5 rings giving three resonances with relative intensities of 4:2:4 due to the *ortho*-, *para*-, and *meta*-F atoms, respectively. The ^{1}H NMR spectrum of complex **7** shows the methoxy resonance of the pyridinecarboxylic ester ligands at δ = 3.66 ppm.

Description of the Crystal Structure of Complex 7

Figure 5 depicts the structure of the neutral palladium complex. Selected bond lengths and angles are given in Table 3. The coordination around Pd is square-planar. The N1, N2, C1, and C7 atoms form a perfect plane with the Pd atom 0.0037(7) Å above this plane. The angle between the two C_6F_5 rings is 90.72(7)° and the angle between the two N-donor ligands is 90.16(5)°. The Pd–N distances lie within the range reported in complexes containing the {Pd(C_6F_5)$_2$N$_2$} moiety, such as [Pd(C_6F_5)$_2$-{NH=CMe$_2$}$_2$],[25] [Pd(C_6F_5)$_2${NH=C(OMe)Me}$_2$][35] and [Pd(C_6F_5)$_2$(pz···H···pz)] (pz = pyrazolate).[27] The Pd–C_6F_5 bond lengths are in the range found in the literature for (pentafluorophenyl)palladium complexes.[36–38] In addition, there are some interconnections by hydrogen bonds involv-

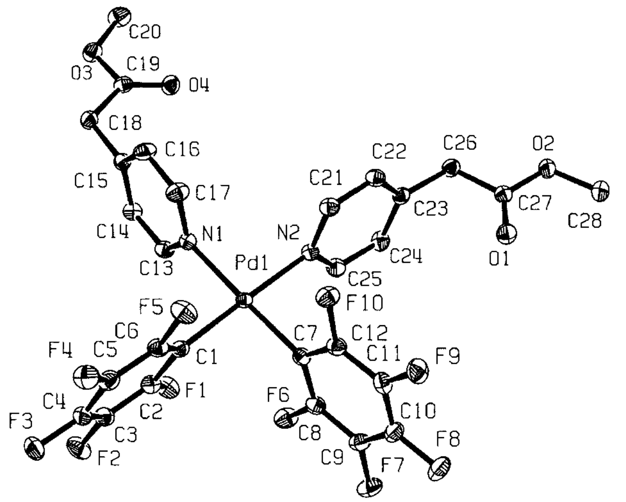
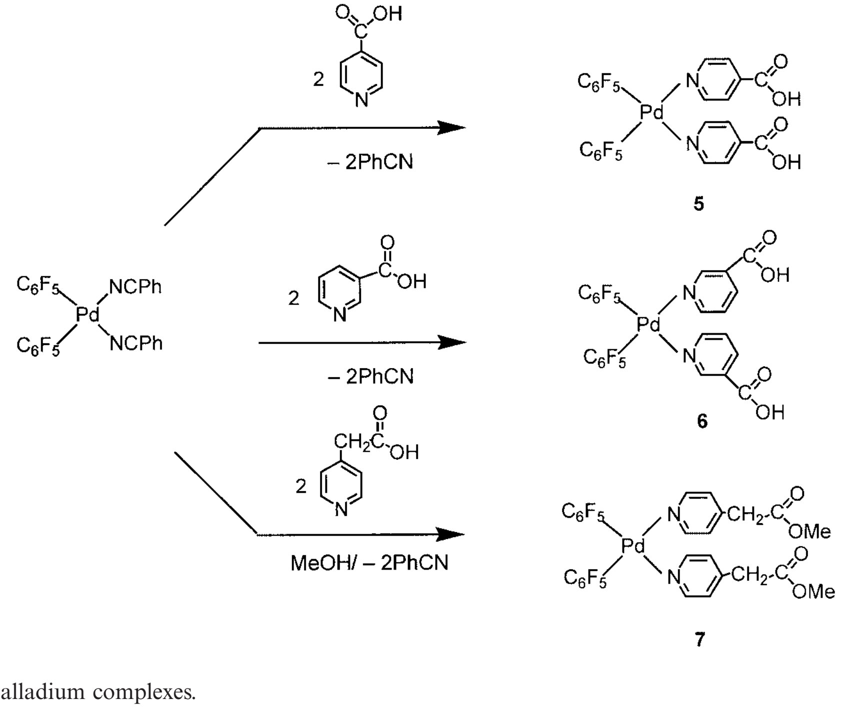


Figure 5. ORTEP drawing of complex **7** showing the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

Table 3. Selected bond lengths [Å] and angles [°] for complex **7**.

Bond lengths		Bond angles	
Pd(1)–C(1)	2.0012(17)	C(1)–Pd(1)–C(7)	90.72(7)
Pd(1)–C(7)	2.0031(17)	C(1)–Pd(1)–N(2)	178.78(6)
Pd(1)–N(2)	2.0866(14)	C(7)–Pd(1)–N(2)	88.08(6)
Pd(1)–N(1)	2.0897(14)	C(1)–Pd(1)–N(1)	91.04(6)
		C(7)–Pd(1)–N(1)	178.15(6)
		N(2)–Pd(1)–N(1)	90.16(5)



Scheme 2. Monomeric palladium complexes.

ing some of the *para*-, *meta*-, and *ortho*-fluorine atoms as proton acceptors, with short intermolecular C–H···F distances (Table 4).[25,39]

Table 4. Selection of the shorter intermolecular F···H distances [Å] in complex 7.

F_8H_{25}(i)	2.600
$F_{10}H_{13}$(iii)	2.568
F_9H_{28A}(ii)	2.565
F_6H_{17}(iv)	2.586
F_1H_{21}(iv)	2.546
F_2H_{22}(iv)	2.577

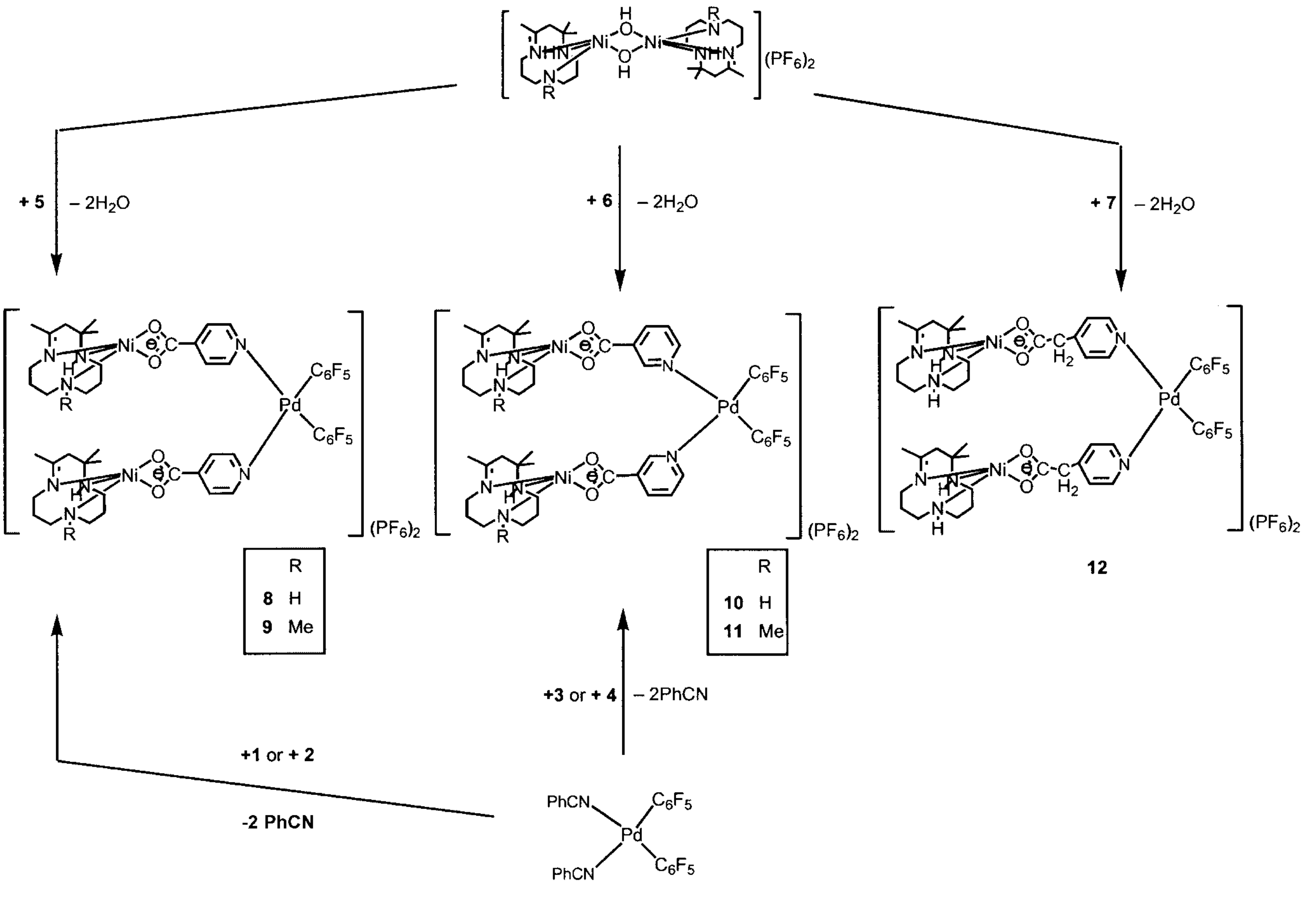
i: 2 – *x*, 2 – *y*, 2 – *z*; ii: 0.5 + *x*, 1.5 – *y*, –0.5 + *z*;
iii: 1.5 – *x*, –0.5 + *y*, 1.5 – *z*; iv: 1.5 – *x*, 0.5 + *y*, 1.5 – *z*

Synthesis and Characterization of Heterotrinuclear Pyridinecarboxylate Complexes of Nickel(II) and Palladium(II)

Heterotrinuclear pyridinecarboxylate complexes of nickel(II) and palladium(II) of the types [Ni(mcN$_3$)(pyridinecarboxylate)]$_2${μ-[Pd(C$_6$F$_5$)$_2$]}(PF$_6$)$_2$ (mcN$_3$ = Me$_3$-mcN$_3$ or Me$_4$-mcN$_3$) **8**–**12** have been prepared by two different routes (Scheme 3). The first method is based on the reaction of the monomeric pyridinecarboxylate complexes of nickel(II) [Ni(mcN$_3$)(A)](PF$_6$) **1**–**4** with the labile complex *cis*-[Pd(C$_6$F$_5$)$_2$(PhCN)$_2$], which takes place with the concomitant release of PhCN. The second method is based on the treatment of the monomeric pyridinecarboxylic derivatives of palladium(II) **5**–**7** with the hydroxo complex [Ni(mcN$_3$)(μ-OH)]$_2$(PF$_6$)$_2$ (mcN$_3$ = Me$_3$-mcN$_3$ or Me$_4$-mcN$_3$). Complexes **8**–**12** are air-stable both in the solid state and in solution. They were characterized by partial elemental analyses, FAB$^+$ mass spectrometry and spectroscopic (IR and ^{1}H NMR) methods. The IR spectra of complexes **8**–**12** show characteristic absorptions for the mcN$_3$ ligands,[12,14] the absorption of the pyridinecarboxylate ligands, the characteristic absorptions of the C$_6$F$_5$ group[30] and a split band at $\tilde{\nu} \approx 800\,\text{cm}^{-1}$ assigned to the *cis*-Pd(C$_6$F$_5$)$_2$ moiety.[31,32] Two strong bands as a result of the PF$_6^-$ ion at $\tilde{\nu}$ = 840 and 560 cm^{-1} are also observed.

NMR Study of Complexes 8–12

The ^{19}F NMR spectra of complexes **8**–**12** show the presence of two equivalent freely rotating C$_6$F$_5$ rings giving three resonances with relative intensities of 4:2:4 due to the *ortho*-, *para*-, and *meta*-F atoms, respectively. The ^{1}H NMR spectra of the complexes **8**–**12** also show relatively sharp and well-resolved resonances for the macrocyclic protons as well as the expected resonance line pattern. The magnitudes of these shifts are also similar to those observed for the



Scheme 3. Heterotrinuclear complexes.

corresponding monomeric pyridinecarboxylate derivatives of nickel (**1**–**4**). However, the coordination to the *cis*-Pd(C_6F_5)$_2$ moiety through the nitrogen atom of pyridinecarboxylate disturbs the spin density into the pyridine ring and the shifts of pyridinecarboxylate in heterotrinuclear derivatives are in general larger than in monomeric complexes. The temperature dependence of the shifts of **11** in Figure 6 follows the established pattern, with the shifts moving away from the diamagnetic position and increasing with T^{-1}.

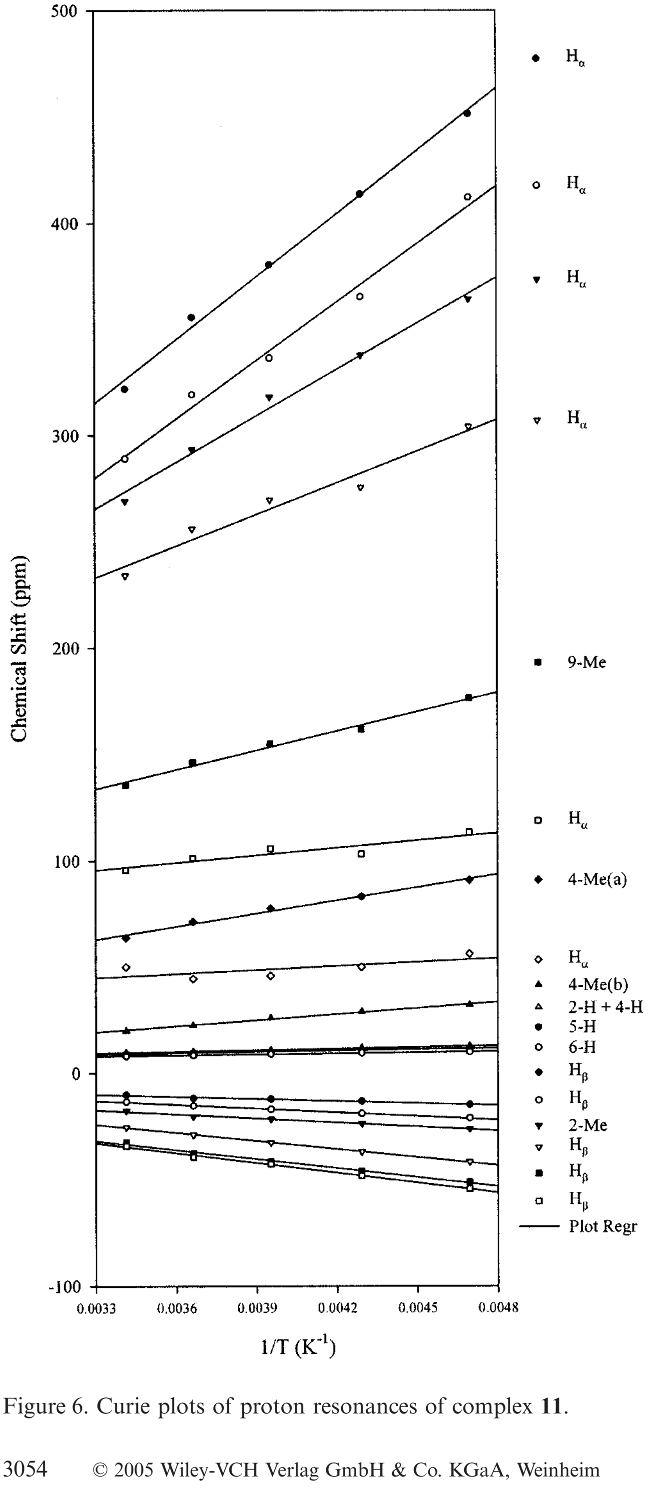


Figure 6. Curie plots of proton resonances of complex **11**.

Experimental Section

General Methods: The C, H, N analyses were performed with a Carlo Erba model EA 1108 microanalyzer. The ^{1}H and ^{19}F NMR spectra were recorded with a Bruker AC 200E, Bruker AC 300E or Bruker AV-400 spectrometer, using $SiMe_4$ or $CFCl_3$ as standards, respectively. IR spectra were recorded with a Perkin–Elmer 16F PC FT-IR spectrophotometer using Nujol mulls between polyethylene sheets. Fast-atom bombardment (FAB) mass spectra were run with a Fisons VG Autospec spectrometer operating in the FAB$^+$ mode. The UV/Vis spectra (in acetone) were recorded with a UNICAM 520 spectrophotometer equipped with matched quartz cells in the 300–800 nm range. The chemicals were purchased from Aldrich and were used without further purification. Solvents were dried and distilled by general methods before use. The starting compound [{Ni(Me$_3$-mcN$_3$)(μ-OH)}$_2$](PF$_6$)$_2$ and its 9-methyl derivative,[40,41] as well as *cis*-[Pd(C_6F_5)$_2$(PhCN)$_2$][29] were prepared by procedures described elsewhere.

Preparation of Complexes

Complexes 1 and 3: NC_5H_4-4-COOH or NC_5H_4-3-COOH (0.30 mmol) was added to a solution of [Ni(Me$_3$-mcN$_3$)(μ-OH)]$_2$-(PF$_6$)$_2$ (100 mg, 0.15 mmol) in acetone (25 mL). The mixture was stirred overnight at room temperature and the solvent was partially evaporated under reduced pressure. On addition of diethyl ether, the blue-green complexes precipitated and were filtered off, washed with diethyl ether and air-dried. **1:** Yield: 115 mg (92%). $C_{18}H_{29}F_6N_4NiO_2P$ (537): calcd. C 40.25, H 5.44, N 10.43; found C 39.96, H 5.71, N 10.14. MS (FAB$^+$): *m*/*z* (%) = 391 (100) [M$^+$]. IR (nujol): $\tilde{\nu}$ = 3286, 3268 (NH), 1650 (C=N), 1548 (OCO) cm^{-1}. ^{1}H NMR [(CD$_3$)$_2$CO, TMS]: δ = 290.8 (H$_\alpha$), 263.0 (H$_\alpha$), 192.3 (H$_\alpha$, 2 H), 161.4 (H$_\alpha$), 85.0 (H$_\alpha$, 2 H), 57.3 (H$_\alpha$), 38.7 (4-Me, 3 H), 22.7 (4-Me, 3 H), 9.6 (Hisonic, 4 H), –11.0 (H$_\beta$), –13.3 (H$_\beta$, 2 H), –15.2 (H$_\beta$), –17.3 (H$_\beta$), –20.3 (2-Me, 3 H), –33.0 (H$_\beta$) ppm. **3:** Yield: 117 mg (94%). $C_{18}H_{29}F_6N_4NiO_2P$ (537): calcd. C 40.25, H 5.44, N 10.43; found C 40.03, H 5.61, N 10.14. MS (FAB$^+$): *m*/*z* (%) = 391 (100) [M$^+$]. IR (nujol): $\tilde{\nu}$ = 3287, 3269 (NH), 1659 (C=N), 1552 (OCO) cm^{-1}. ^{1}H NMR [(CD$_3$)$_2$CO, TMS]: δ = 366.8 (H$_\alpha$), 321.9 (H$_\alpha$), 226.8 (H$_\alpha$, 2 H), 207.8 (H$_\alpha$), 99.7 (H$_\alpha$, 2 H), 65.5 (H$_\alpha$), 53.1 (4-Me, 3 H), 16.3 (4-Me, 3 H), 13.4 (2-H + 4-H, 2 H), 9.4 (5-H + 6-H, 2 H), –11.8 (H$_\beta$, 2 H), –13.2 (H$_\beta$), –16.8 (2-Me, 3 H), –24.0 (H$_\beta$), –27.9 (H$_\beta$), –30.2 (H$_\beta$) ppm.

Complexes 2 and 4: NC_5H_4-4-COOH or NC_5H_4-3-COOH (0.30 mmol) was added to a solution of [Ni(Me$_4$-mcN$_3$)(μ-OH)]$_2$(PF$_6$)$_2$ (100 mg, 0.12 mmol) in acetone (25 mL). The mixture was stirred overnight at room temperature and the solvent was partially evaporated under reduced pressure. On addition of diethyl ether, the blue-green complexes precipitated and were filtered off, washed with diethyl ether and air-dried. **2:** Yield: 103 mg (83%). $C_{19}H_{31}F_6N_4NiO_2P$ (551): calcd. C 41.41, H 5.67, N 10.17; found C 41.64, H 6.04, N 10.15. MS (FAB$^+$): *m*/*z* (%) = 405 (100) [M$^+$]. IR (nujol): $\tilde{\nu}$ = 3270 (NH), 1659 (C=N), 1552 (OCO) cm^{-1}. ^{1}H NMR [(CD$_3$)$_2$CO, TMS]: δ = 315.0 (H$_\alpha$), 290.7 (H$_\alpha$), 252.3 (H$_\alpha$), 236.9 (H$_\alpha$, 2 H), 135.6 (9-Me, 3 H), 98.3 (H$_\alpha$, 2 H), 65.0 (4-Me, 3 H), 48.5 (H$_\alpha$), 20.2 (4-Me, 3 H), 11.1 (3-H + 5-H, 2 H), 9.1 (2-H + 6-H, 2 H), –9.8 (H$_\beta$, 2 H), –13.4 (H$_\beta$), –16.9 (2-Me, 3 H), –25.2 (H$_\beta$), –32.7 (H$_\beta$, 2 H) ppm. **4:** Yield: 113 mg (91%). $C_{19}H_{31}F_6N_4NiO_2P$ (551): calcd. C 41.41, H 5.67, N 10.17; found C 41.27, H 5.94, N 9.97. MS (FAB$^+$): *m*/*z* (%) = 405 (100) [M$^+$]. IR (nujol): $\tilde{\nu}$ = 3121 (NH), 1661 (C=N), 1530 (OCO) cm^{-1}. ^{1}H NMR [(CD$_3$)$_2$CO, TMS]: δ = 320.0 (H$_\alpha$), 296.0 (H$_\alpha$), 257.1 (H$_\alpha$), 243.8 (H$_\alpha$), 136.8 (9-Me, 3 H), 101.9 (H$_\alpha$, 2 H), 67.4 (4-Me, 3 H), 46.7 (H$_\alpha$), 41.5 (H$_\alpha$), 20.8 (4-Me, 3 H), 9.2 (2-H + 4-H + 5-H, 3

H), 7.4 (6-H), –9.7 (H_β, 2 H), –13.7 (H_β), –16.5 (2-Me, 3 H), –25.7 (H_β), –32.7 (H_β), –33.7 (H_β) ppm.

Complexes 5–7: NC_5H_4-4-COOH, NC_5H_4-3-COOH, or NC_5H_4-4-CH_2COOH (0.31 mmol) was added to a solution of *cis*-[Pd(C_6F_5)$_2$(PhCN)$_2$] (100 mg, 0.15 mmol) in methanol (10 mL), the solution was stirred for 24 h, and the solvent was partially evaporated under reduced pressure. On addition of water, the white complexes precipitated and were filtered off and air-dried. **5:** Yield: 80 mg (75%). $C_{24}H_{10}F_{10}N_2O_4Pd$ (687): calcd. C 41.9, H 1.5, N 4.1; found C 41.6, H 1.4, N 4.1. MS (FAB$^+$): *m/z* (%) = 519 (100) [M$^+$ – C_6F_5]. IR (nujol): $\tilde{\nu}$ = 1720 (C=O), 798, 787 (Pd–C_6F_5) cm^{-1}. ^{1}H NMR [$(CD_3)_2CO$, TMS]: δ = 9.27 (d, J_{HH} = 6 Hz, 4 H, H^{2,6}), 8.34 (d, J_{HH} = 6 Hz, 4 H, H^{3,5}) ppm. ^{19}F NMR [$(CD_3)_2CO$, TMS]: δ = –117.2 (d, 4 F_o, J_{om} = 24.0 Hz), –163.5 (t, 2 F_p, J_{mp} = 19.0 Hz), –165.8 (m, 4 F_m) ppm. **6:** Yield: 85 mg (80%). $C_{24}H_{10}F_{10}N_2O_4Pd$ (687): C 41.9, H 1.5, N 4.1; found C 41.7, H 1.5, N 4.0. IR (nujol): $\tilde{\nu}$ = 1705 (C=O), 796, 784 (Pd–C_6F_5) cm^{-1}. ^{1}HNMR [$(CD_3)_2CO$, TMS]: δ = 9.21 (s, 2 H, 2-H), 8.99 (d, J_{HH} = 5 Hz, 2 H, 6-H), 8.48 (d, J_{HH} = 7 Hz, 2 H, 4-H), 7.72 (dd, J_{HH} = 5 Hz, 2 H, 5-H) ppm. ^{19}F NMR [$(CD_3)_2CO$, TMS]: δ = –117.0 (d, 4 F_o, J_{om} = 28.0 Hz), –163.2 (t, 2 F_p, J_{mp} = 17.0 Hz), –165.5 (m, 4 F_m). **7:** Yield: 85 mg (74%). $C_{28}H_{18}F_{10}N_2O_4Pd$ (743): C 45.3, H 2.4, N 3.8; found C 44.9, H 2.5, N 3.8. MS (FAB$^+$): *m/z* (%) = 575 (100) [M$^+$ – C_6F_5]. IR (nujol): $\tilde{\nu}$ = 1744 (C=O), 795, 783 (Pd–C_6F_5) cm^{-1}. ^{1}H NMR [$(CD_3)_2CO$, TMS]: δ = 8.64 (d, J_{HH} = 6 Hz, 4 H, 2,6-H), 7.47 (d, J_{HH} = 6 Hz, 4 H, 3,5-H), 3.79 (s, 4 H, PhCH$_2$), 3.66 (s, 6 H, CH$_3$) ppm. ^{19}F NMR [$(CD_3)_2CO$, TMS]: δ = –116.8 (d, 4 F_o, J_{om} = 28.0 Hz), –163.7 (t, 2 F_p, J_{mp} = 20.0 Hz), –165.8 (m, 4 F_m) ppm.

Complexes 8 and 10. Method 1: Pd(C_6F_5)$_2$(PhCN)$_2$ (45.3 mg, 0.07 mmol) was added to a solution of complex **1** or **3** (0.14 mmol) in acetone (25 mL). The mixture was stirred at room temperature for 24 h. The solution was concentrated under reduced pressure and the addition of diethyl ether caused the precipitation of a pale blue solid, which was collected by filtration, washed with diethyl ether and air-dried. Yields: 100 mg (94%) (for **8**) and 97 mg (91%) (for **10**). **Method 2:** [Ni(Me$_3$-mcN$_3$)(μ-OH)]$_2$(PF$_6$)$_2$ (63.1 mg, 0.073 mmol) was added to a solution of complex **5** or **6** (50.1 mg, 0.073 mmol) in acetone (15 mL) and the resulting solution was refluxed for 5 h. The solvent was partially evaporated under reduced pressure. On addition of Et$_2$O, the blue complexes precipitated and were filtered off and air-dried. Yields: 81 mg (73%) (for **8**) and 78 mg (70%) (for **10**). **8:** $C_{48}H_{58}F_{22}N_8Ni_2O_4P_2Pd$ (1515): calcd. C 38.1, H 3.9, N 7.4; found C 37.7, H 3.9, N 7.4. MS (FAB$^+$): *m/z* (%) = 391 (100) [Ni(Me$_3$-mcN$_3$)(isonic)]$^+$. IR (nujol): $\tilde{\nu}$ = 3285, 3271 (NH), 1658 (C=N), 1548 (OCO), 795, 778 (Pd–C_6F_5) cm^{-1}. ^{1}H NMR [$(CD_3)_2CO$, TMS]: δ = 254.0 (H_α), 236.3 (H_α, 2 H), 168.5 (H_α), 156.3 (H_α), 101.3 (H_α, 2 H), 72.8 (H_α), 54.5 (4-Me, 3 H), 16.3 (4-Me, 3 H), 10.7 (2-H + 6-H, 2 H), 8.8 (3-H + 5-H, 2 H), –12.3 (H_β, 2 H), –14.2 (H_β), –17.3 (H_β), –17.6 (2-Me, 3 H), –24.6 (H_β), 28.8 (H_β), –31.5 (H_β) ppm. ^{19}F NMR [$(CD_3)_2CO$, TMS]: δ = –72.0 (d, 12 F, PF$_6^-$, J_{FP} = 708 Hz), –116.8 (d, 4 F_o, J_{om} = 24.5 Hz), –163.5 (t, 2 F_p, J_{mp}= 20.7 Hz), –165.7 (m, 4 F_m) ppm. ^{31}P NMR ([D$_6$]acetone, H$_3$PO$_4$): δ = –143.5 (sept, 2 P, J_{PF} = 707 Hz) ppm. **10:** $C_{48}H_{58}F_{22}N_8Ni_2O_4P_2Pd$ (1515): calcd. C 38.1, H 3.9, N 7.4; found C 37.8, H 3.9, N 7.4. MS (FAB$^+$): *m/z* (%) = 391 (100) [Ni(Me$_3$-mcN$_3$)(nic)]$^+$, 1367 (2) [M$^+$]. IR (nujol): $\tilde{\nu}$ = 3288, 3275 (NH), 1658 (C=N), 1556 (OCO), 795, 778 (Pd–C_6F_5) cm^{-1}. ^{1}H NMR [$(CD_3)_2CO$, TMS]: δ = 224.1 (H_α, 2 H), 207.1 (H_α), 96.2 (H_α, 2 H), 73.8 (H_α), 52.1 (4-Me, 3 H), 22.8 (H_α), 16.4 (4-Me, 3 H), 12.3 (H_α), 9.7 (2-H + 4-H, 2 H), 9.4 (5-H), 8.6 (6-H), –11.9 (H_β, 2 H), –14.3 (H_β), –17.9 (2-Me, 3 H), –24.6 (H_β), –28.9 (H_β), –32.1 (H_β) ppm. ^{19}F NMR [$(CD_3)_2CO$, TMS]: δ = –71.9 (d, 12 F, PF$_6^-$, J_{FP} = 712 Hz), –116.2 (d, 4 F_o, J_{om} = 22.5 Hz), –162.7 (t, 2 F_p, J_{mp} = 25.4 Hz), –164.8 (m, 4 F_m) ppm. ^{31}P NMR ([D$_6$]acetone, H$_3$PO$_4$): δ = –143.6 (sept, 2 P, J_{PF} = 709 Hz) ppm.

Complexes 9 and 11. Method 1: Pd(C_6F_5)$_2$(PhCN)$_2$ (45.3 mg, 0.07 mmol) was added to a solution of complex **2** or **4** (0.14 mmol) in acetone (25 mL). The mixture was stirred at room temperature for 24 h. The solution was concentrated under reduced pressure and the addition of diethyl ether caused the precipitation of a pale blue solid, which was collected by filtration, washed with diethyl ether and air-dried. Yields: 105 mg (97%) (for **9**) and 96 mg (89%) (for **11**). **Method 2:** [Ni(Me$_4$-mcN$_3$)(μ-OH)]$_2$(PF$_6$)$_2$ (65.3 mg, 0.073 mmol) was added to a solution of complex **5** or **6** (50.1 mg, 0.073 mmol) in acetone (15 mL) and the resulting solution was refluxed for 5 h. The solvent was partially evaporated under reduced pressure. On addition of Et$_2$O, the blue complexes precipitated and were filtered off and air-dried. Yields: 79 mg (70%) (for **9**) and 86 mg (76%) (for **11**). **9:** $C_{50}H_{62}F_{22}N_8Ni_2O_4P_2Pd$ (1542): calcd. C 38.9, H 4.2, N 7.3; found C 38.5, H 4.4, N 7.3. MS (FAB$^+$): *m/z* (%) = 405 (100) [Ni(Me$_4$-mcN$_3$)(isonic)$^+$], 1395 (1) [M$^+$]. IR (nujol): $\tilde{\nu}$ = 3269 (N–H), 1657 (C=N), 1547 (OCO), 797, 780 (Pd–C_6F_5) cm^{-1}. ^{1}H NMR [$(CD_3)_2CO$, TMS]: δ = 317.7 (H_α), 259.8 (H_α), 242.9 (H_α), 210.5 (H_α, 2 H), 128.9 (9-Me, 3 H), 92.5 (H_α), 87.8 (H_α, 2 H), 56.9 (4-Me, 3 H), 19.0 (4-Me, 3 H), 11.4 (2-H + 6-H, 2 H), 10.4 (3-H + 5-H, 2 H), –10.4 (H_β, 2 H), –12.9 (H_β), –18.3 (2-Me, 3 H), –25.0 (H_β), –30.4 (H_β), –35.2 (H_β) ppm. ^{19}F NMR [$(CD_3)_2CO$, TMS]: δ = –71.6 (d, 12 F, PF$_6^-$, J_{FP} = 708 Hz), –116.7 (d, 4 F_o, J_{om} = 24.5 Hz), –163.4 (t, 2 F_p, J_{mp} = 20.7 Hz), –165.6 (m, 4 F_m) ppm. ^{31}P NMR ([D$_6$]acetone, H$_3$PO$_4$): δ = –143.3 (sept, 2 P, J_{PF} = 708 Hz) ppm. **11:** $C_{50}H_{64}F_{22}N_8Ni_2O_4P_2Pd$ (1542): calcd. C 38.9, H 4.2, N 7.3; found C 38.4, H 4.2, N 7.1. MS (FAB$^+$): *m/z* (%) = 405 (100) [Ni(Me$_4$-mcN$_3$)(nic)$^+$], 1394 (1) [M]$^+$. IR (nujol): $\tilde{\nu}$ = 3270 (NH), 1657 (C=N), 1547 (OCO), 797, 785 (Pd–C_6F_5) cm^{-1}. ^{1}H NMR [$(CD_3)_2CO$, TMS]: δ = 310.6 (H_α), 287.5 (H_α), 249.7 (H_α), 233.5 (H_α), 134.4 (9-Me, 3 H), 95.6 (H_α, 2 H), 63.5 (4-Me, 3 H), 48.8 (H_α, 2 H), 19.8 (4-Me, 3 H), 9.7 (2-H + 4-H, 2 H), 9.3 (5-H), 8.2 (6-H), –9.8 (H_β, 2 H), –13.3 (H_β), –17.1 (2-Me, 3 H), –25.0 (H_β), –32.2 (H_β), –33.4 (H_β) ppm. ^{19}F NMR [$(CD_3)_2CO$, TMS]: δ = –71.2 (d, 12 F, PF$_6^-$, J_{FP} = 712 Hz), –116.2 (d, 4 F_o, J_{om} = 26.4 Hz), –162.3 (t, 2 F_p, J_{mp} = 16.9 Hz), –164.6 (m, 4 F_m) ppm. ^{31}P NMR ([D$_6$]acetone, H$_3$PO$_4$): δ = –143.3 (sept, 2 P, J_{PF} = 691 Hz) ppm.

Complex 12: [Ni(Me$_3$-mcN$_3$)(μ-OH)]$_2$(PF$_6$)$_2$ (63.1 mg, 0.073 mmol) was added to a solution of complex **7** (54.2 mg, 0.073 mmol) in acetone (15 mL) and the resulting solution was refluxed for 5 h. The solvent was partially evaporated under reduced pressure. On addition of Et$_2$O, the blue complexes precipitated and were filtered off and air-dried. **12:** Yield: 96 mg (85%). $C_{50}H_{62}F_{22}N_8Ni_2O_4P_2Pd$ (1543): calcd. C 38.9, H 4.1, N 7.3; found C 38.5, H 4.3, N 7.0. MS (FAB$^+$): *m/z* (%) = 405 (100) [Ni(Me$_3$-mcN$_3$)(PyOAc)]$^+$, 1397 (15) [M$^+$ + 1 + PF$_6$]. IR (nujol): $\tilde{\nu}$ = 3289, 3266 (NH), 1661 (C=N), 1558 (OCO), 795, 783 (Pd–C_6F_5) cm^{-1}. ^{1}H NMR [$(CD_3)_2CO$, TMS]: δ = 230.2 (H_α, 2 H), 207.4 (H_α), 196.4 (H_α), 185.5 (H_α), 174.3 (H_α), 103.2 (H_α, 2 H), 56.3 (4-Me, 3 H), 19.7(–CH$_2$–, 2 H), 16.8 (4-Me, 3 H), 8.8 (2-H + 6-H, 2 H), 7.4 (3-H + 5-H, 2 H), –12.0 (H_β, 2 H), –15.1 (H_β), –16.4 (2-Me, 3 H), –23.9 (H_β), 28.8 (H_β, 2 H). ^{19}F NMR [$(CD_3)_2CO$, TMS]: δ = –72.0 (d, 12 F, PF$_6^-$, J_{FP} = 709 Hz), –116.2 (d, 4 F_o, J_{om} = 25.4 Hz), –163.1 (t, 2 F_p, J_{mp} = 16.9 Hz), –164.8 (m, 4 F_m) ppm. ^{31}P NMR ([D$_6$]acetone, H$_3$PO$_4$): δ = –143.6 (sept, 2 P, J_{PF} = 708 Hz) ppm.

X-ray Data Collection and Structure Determination: Data collection was performed with a Bruker Smart CCD diffractometer with a nominal crystal–detector distance of 4.5 cm. Diffraction data were collected based on an ω-scan. A total of 1371 (**7**) and 2524 (**4**) frames were collected at 0.3° intervals and 10 s per frame. The diffraction frames were integrated using the SAINT package[42] and corrected for absorption with SADABS.[43] The crystallographic data are shown in Table 5. The structures were solved by direct methods[44] and refined anisotropically on F^2.[44] Hydrogen atoms were introduced in calculated positions. CCDC-256615 (**4**) and -256616 (**7**) contain 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.

Table 5. Crystal data and summary of data collection and refinement for 4 and 7.

	4·MeCN	**7**
Empirical formula	$C_{21}H_{34}F_6N_5NiO_2P$	$C_{28}H_{18}F_{10}N_2O_4Pd$
Formula mass	592.21	742.84
Crystal system	triclinic	monoclinic
Unit cell dimensions:		
a [Å]	8.1682(5)	14.1830(6)
b [Å]	13.0538(8)	12.7318(6)
c [Å]	13.4683(8)	15.6193(7)
α [°]	110.329(1)	90
β [°]	98.568(1)	91.6980(10)
γ [°]	96.192(1)	90
Unit cell volume [Å^3]	1311.72(14)	2819.2(2)
Temperature [K]	100(2)	100(2)
Space group	$P\bar{1}$	$P2_1/n$
Z	2	4
μ [mm^{-1}]	0.871	0.763
Reflections collected	15437	17361
Independent reflections	5901	6309
R(int)	0.0233	0.0152
R_1 [$I > 2\sigma(I)$][a]	0.0626	0.0241
wR_2 (all data)[b]	0.1314	0.0609

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