Pyridine-Based Oligonitriles as Pincer Ligands for Palladium(II), Copper(II), Cobalt(II), and Nickel(II) Ions[‡]

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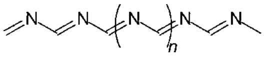
Nucleophilic ring opening of the 1-oxa-3,5-diazinium salts **2** and **3** by propylamine furnishes the new polydentate, branched, pincer-type ligands **4** and **5**, respectively, in 34 and 57 % yield. The 1-oxa-3,5-diazinium salts **2** and **3** were prepared from pyridine-2,6-dicarbonyl dichloride (**1**) by treatment with dimethylcyanamide and diisopropylcyanamide in the presence of antimony pentachloride and tin tetrachloride, respectively. The structure of **4**, which is characterised by a strongly twisted *N*-acyloligonitrile arm, was determined by X-ray crystallography. The ligand **4**, with its short and long arms, forms chelate complexes **4⁻·Pd(OAc)⁺** and **4·CuCl₂** when treated with palladium(II) acetate and copper(II) chloride, respectively. **4⁻·Pd(OAc)⁺** shows remarkable catalytic activity in Suzuki–Miyaura cross-coupling reactions. The pincer-type ligand **5** gives the chelate complexes **5·Co(ClO₄)₂·DMF**, **5·CoCl₂** and **5·Ni(ClO₄)₂·DMF** upon treatment with the respective metal salts. These three complexes show octahedral configuration, with DMF or chloride occuping the sixth coordination site. For the Co^{II} complexes a *cis* configuration is oberserved for **5·CoCl₂** and a *trans* configuration for **5·Co(ClO₄)₂·DMF**. In all cases **5** acts as a pentadentate ligand. All metal complexes were characterised by X-ray diffraction.

Introduction

Oligonitriles may be considered as formal analogues of polyacetylenes (polyenes) in which an isoelectronic nitrogen atom replaces every second CH unit. As oligomers with an unsaturated backbone they have been investigated with respect to their special electronic and molecular structure, and also with regard to their redox and NLO properties.[1]



Oligonitriles

Recently, we were able to show that 1-oxa-3,5,7,9-tetraazadecapentaenes have the potential to act as chelating ligands with Pd^{II} ions in metal coordination reactions.[2] Similarly, a peramino derivative [2,4,6,8,8-pentakis(dimethylamino)-1-oxa-3,5,7-triazaoctatetraene] forms a complex with $ZnCl_2$ by chelating through the oxygen atom O1 and the nitrogen atom N5. Other known examples are *N*-acylamidine complexes of Cu^{II}, which show chelating monomeric 1:1, 2:1 and tetrameric 1:1 moieties.[3,4] In contrast, Pd^{II} forms 2:1 complexes with *N*-acylamidines where the ligand acts in a monodentate fashion. Such compounds have been found to be highly active as precatalysts in cross-coupling reactions of the Suzuki–Miyaura type.[5] Triazapentadienes may also be considered to be short examples of oligonitriles. These compounds also form six-membered chelate complexes, for example with Co^{II}, Ni^{II}, Cu^{II}, Pd^{II} and Zn^{II} ions.[6]

As oligonitriles are not available in a well-defined composition by polymerisation reactions,[7] and since the step-by-step chain elongation affords a multi-step synthesis,[8] we thought of another synthetic route to prepare longer, unsaturated systems. Ring-opening reactions of 1-oxa-3,5-diazinium salts by nucleophiles present a general and convenient access to oligonitriles.[9,10] As such salts are easily prepared by the Lewis acid promoted ring formation from 2 equiv. of nitrile and 1 equiv. of acid chloride,[11] we chose pyridine-2,6-dicarbonyl dichloride as the starting material for the synthesis of two-armed oligonitriles incorporating a central pyridine unit, which offers an additional site for metal coordination. The resulting products form a new class of ligands resembling those of other 2,6-bis(imino)pyridine systems of the pincer type.[12–17] In this article we describe the synthesis of such ligands and report on their coordination chemistry with various metal ions.

Results and Discussion

The synthesis of the two-armed ligands **4** and **5** was achieved in a one-pot procedure consisting of the in situ preparation of the 1-oxa-3,5-diazinium salts **2** and **3** from

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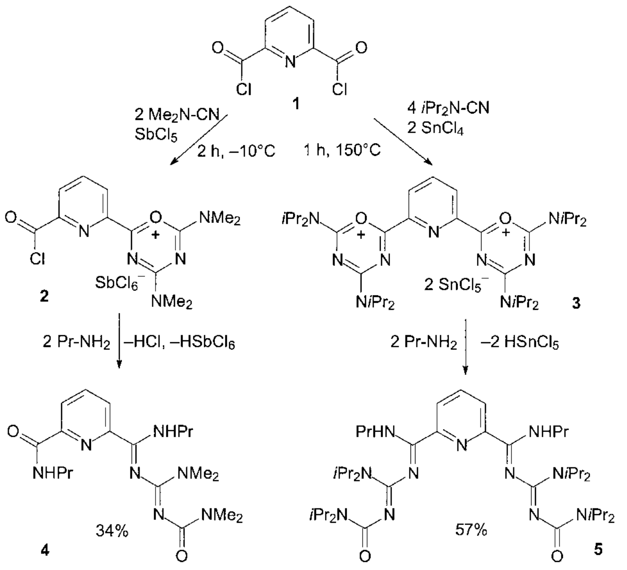
pyridine-2,6-dicarbonyl dichloride (**1**), dimethyl- or diisopropylcyanamide and a Lewis acid (antimony pentachloride in dichloromethane as solvent or neat tin tetrachloride), and subsequent nucleophilic ring opening by treatment with *n*-propylamine. Depending on the reaction conditions (Lewis acid, stoichiometry, reaction time) either one or both chlorocarbonyl functions of **1** can be converted into the 1-oxa-3,5-diazinium ring. Thus, treatment of a mixture of 1 equiv. of **1** with 2 equiv. of dimethylcyanamide at –10 °C with antimony pentachloride in dichloromethane for 2 h, and subsequent treatment with propylamine, yields compound **4** with one short and one long arm (34% yield), whereas the reaction of 1 equiv. of **1** with 4 equiv. of diisopropylcyanamide with tin tetrachloride (heating to 150 °C for 1 h), and subsequent treatment with propylamine, results in the formation of **5** with its two equivalent long arms in 57% yield.



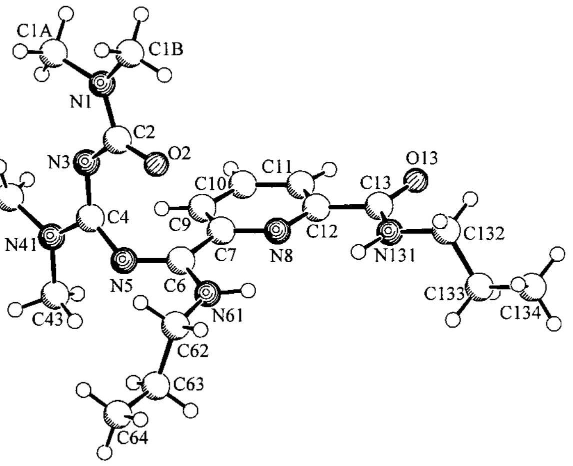
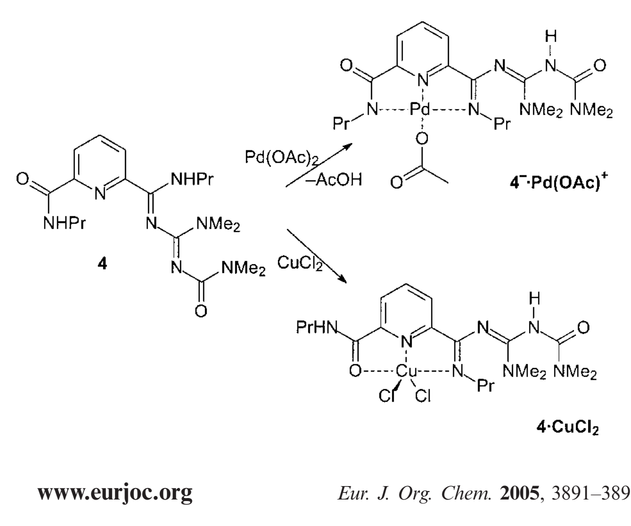


Figure 1. Molecular structure of **4** in the solid state. Selected bond lengths [Å], bond angles [°] and torsional angles [°]: N(1)–C(2) 1.363(3), C(2)–O(2) 1.251(3), C(2)–N(3) 1.373(3), N(3)–C(4) 1.325(3), C(4)–N(41) 1.360(3), C(4)–N(5) 1.363(3), N(5)–C(6) 1.302(3), C(6)–N(61) 1.334(3), C(6)–C(7) 1.503(3), C(7)–N(8) 1.343(3), C(7)–C(9) 1.387(3), N(8)–C(12) 1.342(3), C(9)–C(10) 1.388(4), C(10)–C(11) 1.378(4), C(11)–C(12) 1.379(4), C(12)–C(13) 1.507(4), C(13)–O(13) 1.237(3), C(13)–N(131) 1.329(3); O(2)–C(2)–N(1) 119.1(2), O(2)–C(2)–N(3) 127.7(2), N(1)–C(2)–N(3) 113.2(2), C(4)–N(3)–C(2) 122.0(2), N(3)–C(4)–N(41) 116.0(2), N(3)–C(4)–N(5) 128.6(2), N(41)–C(4)–N(5) 115.0(2), C(6)–N(5)–C(4) 126.1(2), N(5)–C(6)–N(61) 120.1(2), N(5)–C(6)–C(7) 124.7(2), N(8)–C(7)–C(9) 121.9(2), N(8)–C(7)–C(6) 115.1(2), N(8)–C(12)–C(13) 117.3(2), C(11)–C(12)–C(13) 120.0(2), O(13)–C(13)–N(131) 125.1(3), O(13)–C(13)–C(12) 120.1(3); N(1)–C(2)–N(3)–C(4) –172.2(2), O(2)–C(2)–N(3)–C(4) 8.1(4), C(2)–N(3)–C(4)–N5 –1.7(4), N(3)–C(4)–N(5)–C(6) –59.8(4), C(4)–N(5)–C(6)–C(7) –28.9(4), N(5)–C(6)–C(7)–N(8) 173.2(2), C(7)–C(6)–N(61)–C(62) 179.6(2), N(8)–C(12)–C(13)–O(13) –173.4(2), N(8)–C(12)–C(13)–N(131) 4.9(3), N(41)–C(4)–N(5)–C(6) 127.3(3).

We were able to grow suitable crystals of **4** for X-ray crystallography (Figure 1). Whereas the propylamide group is located in the plane of the pyridine ring, only carbon atom C6 and its neighbours N61 and N5 of the *N*-carbamoyl-1,3-diazabutadiene subunit are situated in the pyridine plane. The rest of the subunit is strongly twisted about the N5–C4 bond, whereas the part from N5 to O2 is more or less planar (torsional angles: C6–N5–C4–N3 = –59.93°, N5–C4–N3–C2 = –1.56°, C4–N3–C2–O2 = 8.03°). Such three-dimensional structures are characteristic of *N*-acyloligonitriles.[18]

Complexation Reactions

Upon treatment of ligand **4** with palladium(II) acetate in acetonitrile and subsequent precipitation by slow addition of diethyl ether, small, yellow crystals of the corresponding Pd^{II} complex **4^{-}·Pd(OAc)$^{+}$** were obtained in 93% yield. The X-ray structure determination revealed that **4^{-}·Pd(OAc)$^{+}$** is a 1:1 complex consisting of a deprotonated ligand **4** (the amide proton has been abstracted) and a Pd^{II} acetate cation. **4^{-}·Pd(OAc)$^{+}$** is a bicyclic chelate complex with two five-membered rings with the amide function, the nitrogen atom of the pyridine ring and the imine function of the longer arm acting as coordination sites. Although the oligonitrile arm offers additional coordination sites, they are not involved in metal bonding. Thus, acetic acid is split off during the reaction and the mobile proton of the longer arm has undergone a 1,5-shift (Figure 2).



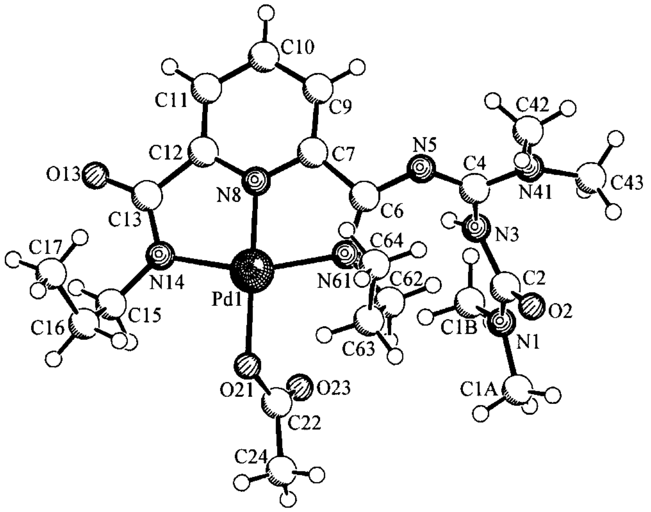


Figure 2. Molecular structure of complex **4^{-}·Pd(OAc)$^{+}$** in the solid state. Selected bond lengths [Å], bond angles [°] and torsional angles [°]: Pd(1)–N(8) 1.920(2), Pd(1)–N(14) 2.025(2), Pd(1)–O(21) 2.032(2), Pd(1)–N(61) 2.056(3), N(1)–C(2) 1.347(4), C(2)–O(2) 1.232(3), C(2)–N(3) 1.387(4), N(3)–C(4) 1.405(4), C(4)–N(5) 1.304(4), C(4)–N(41) 1.334(4), N(5)–C(6) 1.349(4), C(6)–N(61) 1.307(4), C(6)–C(7) 1.495(4), C(7)–N(8) 1.337(4), C(12)–C(13) 1.504(4), C(13)–O(13) 1.249(3), C(13)–N(14) 1.337(4), O(21)–C(22) 1.289(4), C(22)–O(23), 1.211(4); N(8)–Pd(1)–N(14) 80.71(10), N(8)–Pd(1)–O(21) 179.17(9), N(14)–Pd(1)–N(61) 160.85(10), O(2)–C(2)–N(1) 122.6(3), O(2)–C(2)–N(3) 120.5(3), N(1)–C(2)–N(3) 116.9(3), C(2)–N(3)–C(4) 121.8(2), N(5)–C(4)–N(41) 119.9(3), N(5)–C(4)–N(3) 122.2(3), C(4)–N(5)–C(6) 124.7(3), N(61)–C(6)–N(5) 129.8(3), N(5)–C(6)–C(7) 115.2(3), N(8)–C(7)–C(6) 113.0(3), C(9)–C(7)–C(6) 127.2(3), C(7)–N(8)–C(12) 123.3(3), N(8)–C(12)–C(13) 113.0(3), C(11)–C(12)–C(13) 128.0(3), O(13)–C(13)–N(14) 127.2(3), C(22)–O(21)–Pd(1) 116.7(2); N(1)–C(2)–N(3)–C(4) 176.8(3), C(2)–N(3)–C(4)–N(5) –121.9(4), N(3)–C(4)–N(5)–C(6) 20.9(5), C(4)–N(5)–C(6)–C(7) –129.8(3), N(5)–C(6)–C(7)–N(8) –175.5(2), C(6)–C(7)–N(8)–Pd(1) –2.2(3), N(8)–C(12)–C(13)–N(14) 0.7(3), N(8)–Pd(1)–N(14)–C(13) 2.22(19).

The coordination sphere around Pd^{II}, which is essentially square-planar (sum of angles: 358°), is characterised by a short contact (1.919 Å) to the pyridine nitrogen atom and two longer distances to the amide nitrogen atom (short arm: 2.019 Å) and to the oligonitrile chain (2.059 Å). A comparison between the free ligand **4** and this complex **4^{-}·Pd(OAc)$^{+}$** reveals surprisingly small differences in the amide and pyridine part of the complex, but significant changes in the oligonitrile arm due to the proton shift. Hence, in the complex the C7–N7, N8–C9 and C11–O12 bonds are shorter and the C6–N8, C9–N10 and N10–C11 bonds are longer than those of the free ligand, which is well in line with the Lewis structure given.

Complex **4^{-}·Pd(OAc)$^{+}$** displays remarkable catalytic activity in cross-coupling reactions of the Suzuki–Miyaura type (Table 1). For the basic coupling reaction of phenylboronic acid with bromobenzene to give biphenyl, catalyst loadings as low as 10^{-3} and 10^{-4} mol-% at 110 °C are possible with respectable turnover numbers. Interestingly, in comparison to palladium(II) acetate and mixtures of palladium(II) acetate and the free ligand, an induction period of about 10 min is observed before the catalytic process starts (Table 2). Complex **4^{-}·Pd(OAc)$^{+}$** serves here as a pre-catalyst, the active form will be a Pd^{0} species, possibly as an "ate"-type complex.[19] An advantage of this catalytic system is the chemical stability of solutions of the complex under the reaction conditions (no formation of palladium black even after prolonged reaction times). We have used this complex **4^{-}·Pd(OAc)$^{+}$** successfully in a series of Suzuki–Miyaura couplings of various *p*-bromophenyl-substituted *N*-acyloligonitrile derivatives to obtain the corresponding biphenyl compounds.[5,20]

Table 1. Suzuki–Miyaura reactions of bromobenzene with phenylboronic acid to give biphenyl, catalysed by **4^{-}·Pd(OAc)$^{+}$**.

Entry	Concentration of catalyst [mol-%]	Base	Reaction temp. [°C]	Reaction time [h]	Yield [%]	Turnover number
1	1.0	K_2CO_3	85	4	99	99
2	0.1	K_2CO_3	85	4	99	990
3	0.01	K_2CO_3	85	4	33	3300
4	0.001	K_2CO_3	85	4	12	12000
5	0.01	K_2CO_3	110	4	95	9500
6	0.001	K_2CO_3	110	4	83	83000
7	0.0001	K_2CO_3	110	4	14	140000

Table 2. Comparison of various catalytic systems in the Suzuki–Miyaura coupling of bromobenzene and phenylboronic acid.

Entry	Catalytic system	Base	Reaction temp. [°C]	Time [h]	Yield [%]
1	Pd(OAc)$_2$ (0.1 mol-%)	K_2CO_3	85	4	52
2	Pd(OAc)$_2$ (0.1 mol-%)	K_2CO_3	110	4	71
3	Pd(OAc)$_2$ (0.1 mol-%) + ligand **4**	K_2CO_3	85	4	61
4	Pd(OAc)$_2$ (0.1 mol-%) + ligand **4**	K_2CO_3	110	4	71
5	**4^{-}·Pd(OAc)$^{+}$** (0.1 mol-%)	K_2CO_3	85	4	99
6	**4^{-}·Pd(OAc)$^{+}$** (0.01 mol-%)	K_2CO_3	110	4	95

Similar to Pd$^{\mathrm{II}}$, copper(II) chloride also forms a 1:1 bis(chelate) complex **4·CuCl$_2$**, containing now the *neutral* ligand **4**, if **4** is treated with copper(II) chloride in acetonitrile followed by subsequent slow diffusion with diethyl ether. The small, green crystals are formed in 85% yield. The X-ray structure of **4·CuCl$_2$** is similar to that of **4$^-$·Pd(OAc)$^+$** in many respects (e.g. the 1,5-proton shift), but the main difference is that the oxygen atom of the amide function (short arm) acts as a coordination site rather than the nitrogen atom as in **4$^-$·Pd(OAc)$^+$**. This observation is well in line with the "harder" character of Cu$^{\mathrm{II}}$ in comparison to Pd$^{\mathrm{II}}$. The copper(II) ion is pentacoordinate in an approximate square-pyramidal fashion with the two chloride ions bound quite differently to the copper ion (2.216 and 2.428 Å). Again, the many coordination sites of the long arm are not used for metal coordination (Figure 3).

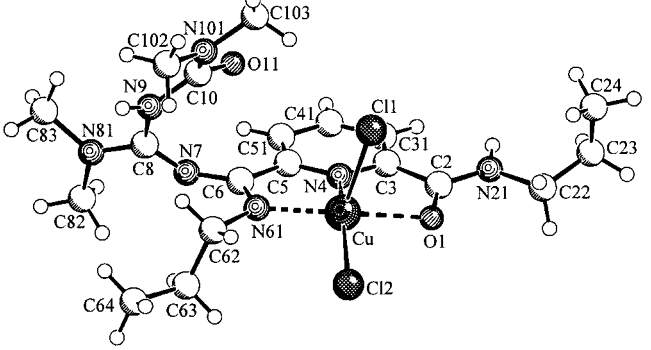


Figure 3. Molecular structure of **4·CuCl$_2$** in the solid state. Selected bond lengths [Å], bond angles [°] and torsional angles [°]: Cu–N(4) 1.947(3), Cu–N(61) 2.030(3), Cu–Cl(2) 2.2156(11), Cu–O(1) 2.222(3), Cu–Cl(1) 2.4292(11), O(1)–C(2) 1.248(5), C(2)–N(21) 1.323(5),C(2)–C(3) 1.503(6), C(3)–N(4) 1.341(5), C(5)–C(6) 1.499(5), C(6)–N(61) 1.300(5), C(6)–N(7) 1.358(5), N(7)–C(8) 1.297(5), C(8)–N(81) 1.341(5), C(8)–N(9) 1.392(5), N(9)–C(10) 1.389(5), C(10)–O(11) 1.240(4), C(10)–N(101) 1.341(5); N(4)–Cu–N(61) 80.52(13), N(4)–Cu–Cl(2) 157.09(9), N(4)–Cu–O(1) 75.52(12), N(4)–Cu–Cl(1) 98.18(9), Cl(2)–Cu–Cl(1) 103.45(4), O(1)–C(2)–N(21) 123.0(4), O(1)–C(2)–C(3) 117.8(4), N(21)–C(2)–C(3) 119.2(4), N(4)–C(3)–C(2) 110.1(3), C(5)–N(4)–C(3) 120.6(3), N(4)–C(5)–C(6) 113.1(3), N(61)–C(6)–N(7) 129.6(4), N(7)–C(6)–C(5) 114.9(3),C(8)–N(7)–C(6) 127.8(3), N(7)–C(8)–N(81) 118.5(4), N(7)–C(8)–N(9) 125.3(4), N(81)–C(8)–N(9) 116.2(3), C(10)–N(9)–C(8) 123.9(3), O(11)–C(10)–N(101) 122.3(4), O(11)–C(10)–N(9) 120.5(4), N(101)–C(10)–N(9) 117.2(4); N(4)–Cu–O(1)–C(2) 15.1(3), Cl(2)–Cu–O(1)–C(2) 172.9(2), Cl(1)–Cu–O(1)–C(2) –83.8(3), O(1)–C(2)–C(3)–N(4) 11.3(5), N(21)–C(2)–C(3)–N(4) –169.8(3), C(2)–C(3)–N(4)–C(5) –176.8(3), C(3)–N(4)–C(5)–C(6) 179.6(3), N(4)–C(5)–C(6)–N(61) –3.2(4), N(4)–C(5)–C(6)–N(7) –175.3(3), N(61)–C(6)–N(7)–C(8) 63.5(6), C(5)–C(6)–N(7)–C(8) –125.8(4), C(6)–N(7)–C(8)–N(81) –164.2(4), C(6)–N(7)–C(8)–N(9) 14.6(6), N(7)–C(8)–N(9)–C(10) 32.6(6), C(8)–N(9)–C(10)–O(11) 18.2(6), C(8)–N(9)–C(10)–N(101) –161.9(3).

Ligand **5**, with its two long arms, forms two different chelate complexes to cobalt(II). If Co$^{\mathrm{II}}$ perchlorate is used in dimethylformamide (DMF) as solvent, pink prismatic crystals of an approximate octahedral complex **5·Co(ClO$_4$)$_2$·DMF** are formed, which incorporate two five-membered and two six-membered chelate rings. The sixth coordination site is occupied by the oxygen atom of one DMF molecule (Figure 4). As seen in the X-ray structure, the pyridine nitrogen atom and the Co$^{\mathrm{II}}$ ion lie on a twofold axis with a split position for DMF. Thus, the oligonitrile ligand **5** offers five coordination sides, and a *trans* arrangement of the oxygen and nitrogen donors of the arms is achieved. The coordinating bonds to the pyridine nitrogen atom have a length of 2.058 Å, those to nitrogen atoms of the side arms 2.229 Å, and those to the oxygen atoms 2.041 Å. The bonds of the side arms display strongly alternating lengths.

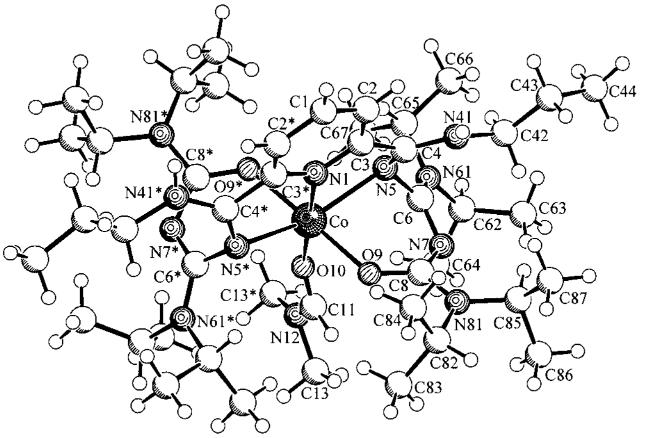
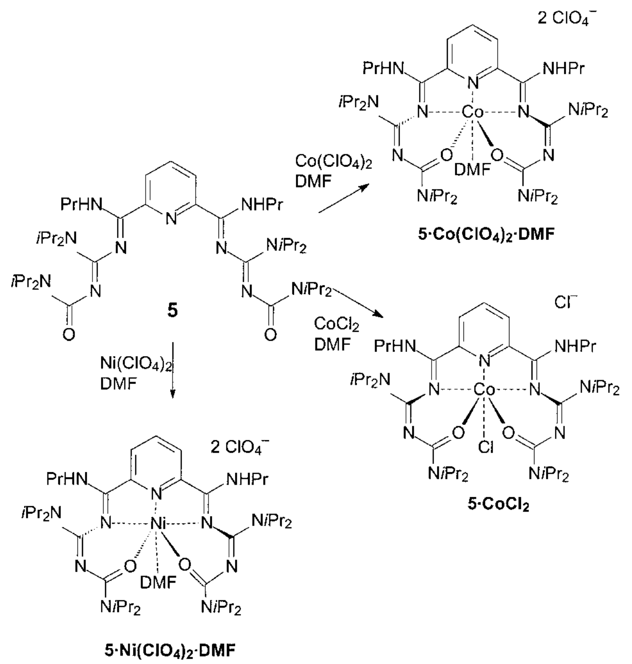


Figure 4. Molecular structure of **5·Co(ClO$_4$)$_2$·DMF** in the solid state. Selected bond lengths [Å], bond angles [°] and torsional angles [°]: Co–O(9) 2.0420(12), Co–O(10) 2.051(2), Co–N(1) 2.058(2), Co–N(5) 2.2285(13), N(1)–C(3) 1.3338(19), C(3)–C(4) 1.500(2), C(4)–N(5) 1.309(2), C(4)–N(41) 1.333(2), N(5)–C(6) 1.413(2), C(6)–N(7) 1.307(2), C(6)–N(61) 1.341(2), N(7)–C(8) 1.374(2), C(8)–O(9) 1.271(2), C(8)–N(81) 1.342(2); O(9)#1–Co–O(9) 177.00(9), O(9)–Co–O(10) 88.50(4), O(9)–Co–N(1) 91.50(4), O(10)–Co–N(1) 180.0, O(9)#1–Co–N(5) 101.62(5), O(9)–Co–N(5) 79.16(5), C(3)–N(1)–Co 119.47(10), N(1)–C(3)–C(4) 112.91(15), N(5)–C(4)–N(41) 128.83(16), N(5)–C(4)–C(3) 115.34(14), N(41)–C(4)–C(3) 115.82(15), C(4)–N(5)–C(6) 120.71(14), N(7)–C(6)–N(61) 121.58(16), N(7)–C(6)–N(5) 120.41(15), N(61)–C(6)–N(5) 117.90(15), C(6)–N(7)–C(8) 119.50(15), O(9)–C(8)–N(81) 118.55(16), O(9)–C(8)–N(7) 124.32(16); O(9)–Co–N(1)–C(3) –109.90(9), O(9)–Co–N(1)–C(3) 70.10(9), N(5)–Co–N(1)–C(3) 171.72(9), N(5)–Co–N(1)–C(3) –8.28(9), O(9)–Co–N(1)–C(3) 70.10(9), N(1)–C(3)–C(4)–N(5) 21.7(2), N(1)–C(3)–C(4)–N(41) –157.41(14), N(5)–C(4)–N(41)–C(42) 9.3(3), N(41)–C(4)–N(5)–C(6) 26.2(3), C(4)–N(5)–C(6)–N(7) 62.1(2), C(4)–N(5)–C(6)–N(61) –121.48(17), N(61)–C(6)–N(7)–C(8) –162.61(16), N(5)–C(6)–N(7)–C(8) 13.7(2), C(6)–N(7)–C(8)–O(9) 38.4(3), C(6)–N(7)–C(8)–N(81) –146.95(18), N(7)–C(8)–O(9)–Co –20.4(3), O(10)–C(11)–N(12)–C(13) 3.1(7).

Interestingly, if cobalt(II) chloride in DMF is used for the complexation reaction, small purple crystals of **5·CoCl$_2$** are formed in 32% yield. As seen in Figure 5, **5** again acts as a pentadentate ligand and a chloride ion occupies the sixth, apical position. Much to our surprise, the oxygen and nitrogen donors are now in a *cis* arrangement to each other, giving approximate mirror symmetry to the whole complex. The environment around Co$^{\mathrm{II}}$ is best described as a highly distorted octahedron (Figure 6) with large deviation from octahedral symmetry in the apical positions. Here, the coordination to the oxygen donors is significantly stronger than



the coordination to the oligonitrile nitrogen atoms, as seen in the bond lengths (2.050 and 2.064 Å vs. 2.413 and 2.466 Å). The reason for this *cis*/*trans* isomerism of the Co^{II} complexes is not yet clear, although crystal packing forces may be responsible.[21]

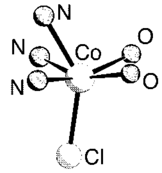


Figure 6. Coordination sphere of **5·CoCl$_2$** around the Co^{II} ion. Selected angles [°]: N(1)–Co–Cl 142.49(6), N(1)–Co–O(9) 99.01(8), N(1)–Co–O(109) 100.83(8), N(1)–Co–N(5) 92.84(5).

We were also able to isolate a nickel(II) complex **5·Ni(ClO$_4$)$_2$·DMF** from ligand **5** and nickel(II) perchlorate in dimethylformamide after precipitation with diethyl ether. **5·Ni(ClO$_4$)$_2$·DMF** forms long, green needles. After a week of crystallisation, the yield amounted to 49%. The X-ray structure determination shows many similarities between

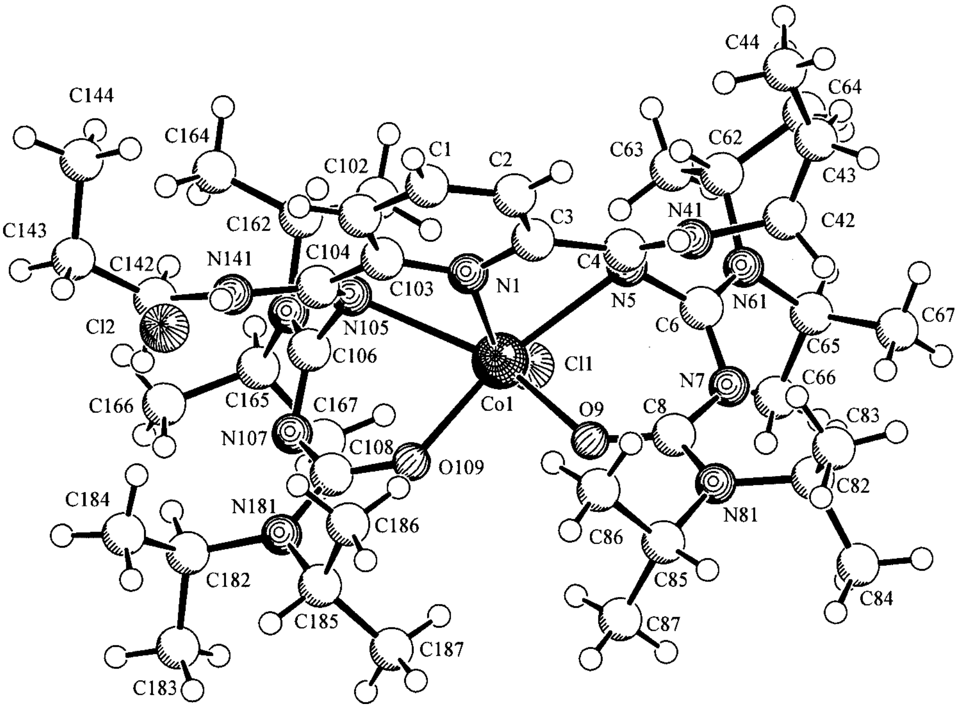


Figure 5. Molecular structure of **5·CoCl$_2$** in the solid state Selected bond lengths [Å], bond angles [°] and torsional angles [°]: C(3)–N(1) 1.343(3), C(3)–C(4) 1.502(4), N(1)–Co 2.084(2), C(4)–N(5) 1.305(3), C(4)–N(41) 1.333(3), N(5)–C(6) 1.398(3), N(5)–Co 2.413(2), C(6)–N(7) 1.317(3), C(6)–N(61) 1.345(3), N(7)–C(8) 1.370(3), C(8)–O(9) 1.263(3), C(8)–N(81) 1.360(3), O(9)–Co 2.0647(18), O(109)–Co 2.0499(19), Co–Cl 2.2838(7); N(1)–C(3)–C(4) 113.8(2), C(3)–N(1)–C(103) 119.6(2), C(3)–N(1)–Co 119.67(18), N(5)–C(4)–N(41) 129.0(3), N(5)–C(4)–C(3) 115.1(2), C(4)–N(5)–C(6) 119.9(2), C(4)–N(5)–Co 105.91(17), N(7)–C(6)–N(61) 120.3(2), N(7)–C(6)–N(5) 121.4(2), C(6)–N(7)–C(8) 118.6(2), O(9)–C(8)–N(81) 119.2(2), O(9)–C(8)–N(7) 124.8(2), C(8)–O(9)–Co 131.34(17); C(4)–C(3)–N(1)–C(103) –171.8(2), C(4)–C(3)–N(1)–Co 15.7(3), N(1)–C(3)–C(4)–N(5) 18.3(3), N(1)–C(3)–C(4)–N(41) –163.6(2), N(41)–C(4)–N(5)–C(6) 25.0(4), C(3)–C(4)–N(5)–C(6) –157.1(2), N(41)–C(4)–N(5)–Co 146.0(3), C(3)–C(4)–N(5)–Co –36.1(3), C(4)–N(5)–C(6)–N(7) 57.8(4), Co–N(5)–C(6)–N(7) –62.7(3), C(4)–N(5)–C(6)–N(61) –124.6(3), N(61)–C(6)–N(7)–C(8) –165.6(2), N(5)–C(6)–N(7)–C(8) 12.0(4), C(6)–N(7)–C(8)–O(9) 39.5(4), C(6)–N(7)–C(8)–N(81) –144.0(3), O9 C8 N81, N(7)–C(8)–O(9)–Co –19.0(4), C(3)–N(1)–Co–O(9) 44.49(19), C(3)–N(1)–Co–Cl(1) –94.4(2).

5·Co(ClO$_4$)$_2$·DMF and **5·Ni(ClO$_4$)$_2$·DMF**: the ligand acts in a pentadentate fashion in both complexes, forming a *trans* arrangement with respect to the chelating oxygen and nitrogen atoms. Again, DMF occupies the sixth coordination site (Figure 7).

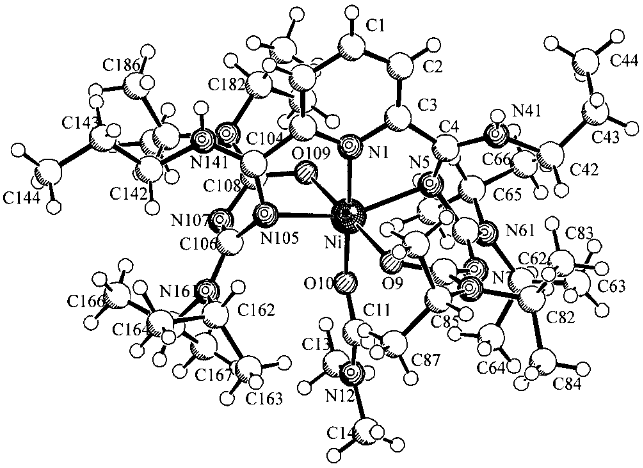


Figure 7. Molecular structure of **5·Ni(ClO$_4$)$_2$·DMF** in the solid state. Selected bond lengths [Å], bond angles [°] and torsional angles [°]: Ni–N(1) 1.9905(17), Ni–O(109) 2.0320(15), Ni–O(10) 2.0328(15), Ni–O(9) 2.0515(15), Ni–N(5) 2.1421(19), Ni–N(105) 2.1726(18), N(1)–C(3) 1.336(3), C(3)–C(4) 1.501(3), C(4)–N(5) 1.311(3), C(4)–N(41) 1.326(3), N(5)–C(6) 1.419(3), C(6)–N(7) 1.302(3), C(6)–N(61) 1.342(3), N(7)–C(8) 1.380(3), C(8)–O(9) 1.270(3), C(8)–N(81) 1.342(3), O(10)–C(11) 1.233(3), C(11)–N(12) 1.321(3); N(1)–Ni–O(109) 89.34(7), N(1)–Ni–O(10) 175.59(7), N(1)–Ni–O(9) 92.57(7), N(1)–Ni–N(5) 77.67(7), N(1)–Ni–N(105) 77.00(7), N(1)–C(3)–C(4) 111.97(18), N(5)–C(4)–N(41) 129.1(2), N(5)–C(4)–C(3) 114.61(19), N(41)–C(4)–C(3) 116.32(19), C(4)–N(5)–C(6) 121.11(18), N(7)–C(6)–N(61) 122.28(19), N(7)–C(6)–N(5) 120.47(19), N(61)–C(6)–N(5) 117.21(19), C(6)–N(7)–C(8) 119.17(18), O(9)–C(8)–N(81) 118.9(2), O(9)–C(8)–N(7) 124.4(2), N(81)–C(8)–N(7) 116.5(2), O(10)–C(11)–N(12) 124.1(3); O(109)–Ni–N(1)–C(103) 70.17(16), O(10)–Ni–N(1)–C(103) 93.5(10), O(9)–Ni–N(1)–C(103) –110.42(16), N(5)–Ni–N(1)–C(103) 169.77(17), N(105)–Ni–N(1)–C(103) –10.18(15), N(1)–C(3)–C(4)–N(5) 23.3(3), N(1)–C(3)–C(4)–N(41) –155.6(2), N(41)–C(4)–N(5)–C(6) 24.2(4), C(3)–C(4)–N(5)–C(6) –154.47(19), C(4)–N(5)–C(6)–N(7) 64.9(3), C(4)–N(5)–C(6)–N(61) –117.5(2), N(61)–C(6)–N(7)–C(8) –165.3(2), N(5)–C(6)–N(7)–C(8) 12.1(3), C(6)–N(7)–C(8)–O(9) 39.3(3), C(6)–N(7)–C(8)–N(81) –145.5(2).

Various other experiments involving [PdCl$_2$(PhCN)$_2$] as well as various Zn^{II}, Ag^{I}, Cu^{I}, Fe^{II} and Fe^{III} salts in different solvents were performed. However, crystalline material for thorough characterisation was not obtained in these cases.

Conclusions

The easily accessible new pincer-type ligands **4** and **5**, obtained from ring-opening reactions of 1,3,5-oxatriazinium salts **2** and **3**, respectively, form chelate complexes with various metal salts. These complexes demonstrate the use of branched *N*-acyloligonitrile ligands in coordination chemistry. The Pd^{II} and Cu^{II} complexes of ligand **4**, with its short and long arm, are characterised by two five-membered chelate rings involving the pyridine nitrogen atom. **4$^–$·Pd(OAc)$^+$** displays high catalytic activity in Suzuki–Miyaura cross-coupling reactions. The pincer ligand **5** acts as a pentadentate ligand to form octahedral complexes with Co^{II} and Ni^{II} ions featuring two five-membered and two six-membered chelate rings. Either DMF or a chloride ion occupies the sixth coordination site. Interestingly, depending on the counterion (Cl$^–$ vs. ClO$_4$$^–$) used for the coordination reaction, *cis*/*trans* isomerism is observed in the case of the Co^{II} complexes.

Experimental Section

Materials and Methods: IR: Nicolet 5DXC. ^{1}H NMR: Bruker WM 300 (300.13 MHz), internal reference tetramethylsilane. ^{13}C NMR: Bruker WM 300 (75.47 MHz), internal reference solvent. CHN elemental analysis: Elementar Vario El III. Melting points are uncorrected. All solvents were rigorously dried by standard methods. When necessary, the experiments were carried out with complete exclusion of moisture (argon, septum-syringe technique) in glassware that had been thoroughly dried by repeated heating under argon and subsequent evacuation.

6-[3,5-Bis(dimethylamino)-1-propylamino-6-oxa-2,4-diaza-1,3,5-hexatrienyl]-*N*-propylpyridine-2-carboxamide (4): A solution of antimony pentachloride (3.2 mL, 25 mmol) in dry dichloromethane (100 mL) followed by a solution of dimethylcyanamide (4.0 mL, 50 mmol) in dry dichloromethane (100 mL) was added dropwise at –10 °C to 2,6-pyridinedicarbonyl dichloride (**1**; 5.10 g, 25 mmol) in dry dichloromethane (100 mL). The reaction mixture was allowed to warm slowly to room temperature and was stirred for 2 h. To the resulting suspension of **2** propylamine (8.2 mL, 100 mmol) was added slowly at 0 °C. The reaction mixture was again allowed to warm slowly to room temperature and was then stirred overnight. The resulting solution was washed with sodium hydroxide solution (200 mL, 2 M) and the aqueous layer was extracted three times with dichloromethane. The combined organic layers were dried with sodium sulfate and the solvent was removed in vacuo. The crude product **4** was purified by recrystallisation from chloroform and pentane. Yield: 3.33 g (34 %), colourless solid; m.p. 147 °C. IR (KBr): $\tilde{\nu}$ = 3307 cm^{-1} (vs, NH), 3276 (vs, NH), 3020 (sh, CH$_{\text{arom.}}$), 2962 (s, CH$_{\text{aliph.}}$), 2933 (s, CH$_{\text{aliph.}}$), 2873 (s, CH$_{\text{aliph.}}$), 1676 (vs, C=O), 1637 (vs, C=N), 1587 (vs, C=C), 1537 (s), 1483 (s), 1450 (s), 1394 (s), 1359 (s), 1315 (s), 1292 (m), 1259 (m), 1184 (m), 1157 (m), 1137 (m), 1082 (w), 1037 (m), 983 (w), 914 (w), 887 (w), 835 (w), 786 (w), 738 (w), 661 (w), 644 (w), 543 (w). ^{1}H NMR (300.13 MHz, CDCl$_3$): δ = 0.79–0.90 (m, 6 H, NCH$_2$CH$_2$C*H*$_3$), 1.47–1.57 (m, 4 H, NCH$_2$C*H*$_2$CH$_3$), 2.83–2.90 (br., 12 H, NCH$_3$), 3.12–3.26 (m, 4 H, NC*H*$_2$CH$_2$CH$_3$), 7.66 (m, 1 H, CH$_{\text{arom.}}$), 7.73–7.88 (br., 1 H, NH), 7.89 (m, 2 H, CH$_{\text{arom.}}$), 8.57 (br., 1 H, NH) ppm. ^{13}C NMR (75.47 MHz, CDCl$_3$): δ = 11.4, 11.5, 22.6, 22.7, 36.7, 41.2, 43.4 (CH$_{\text{aliph.}}$), 123.1, 124.4 (CH$_{\text{arom.}}$), 137.5 (*i*-C$_{\text{arom.}}$), 148.9, 150.5 (C=N), 160.9, 163.5 (C=O) ppm. MS (EI, 70 eV): *m*/*z* (%) = 389 (1) [M$^+$], 344 (100) [M$^+$ – NMe$_2$], 315 (52) [M$^+$ – Me$_2$NCO], 288 (12), 272 (27), 232 (8), 216 (20), 190 (25), 139 (11), 131 (15), 83 (12), 70 (33). C$_{19}$H$_{31}$N$_7$O$_2$ (389.50): calcd. C 58.59, H 8.02, N 25.17; found C 58.40, H 8.03, N 25.00.

X-ray Crystal Structure Analysis of 4:[22] C$_{19}$H$_{21}$N$_7$O$_2$, M = 389.51, colourless crystal 0.15 × 0.15 × 0.05 mm, a = 9.911(1), b = 10.330(1), c = 11.658(1) Å, α = 109.64(1)°, β = 108.34(1)°, γ = 94.36(1)°, V = 1044.7(2) Å^3, $\rho_{\text{calcd.}}$ = 1.238 g cm^{-3}, μ = 6.79 cm^{-1}, no absorption correction ($0.905 \le T \le 0.967$), $Z = 2$, triclinic, space group $P\bar{1}$ (no. 2), $\lambda = 1.54178$ Å, $T = 198$ K, ω and φ scans, 6994 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.61$ Å^{-1}, 3508 independent ($R_{int} = 0.045$) and 2497 observed reflections [$I \ge 2\sigma(I)$], 268 refined parameters, $R = 0.050$, $wR_2 = 0.107$, max. residual electron density 0.18 (–0.21) eÅ^{-3}, hydrogen atoms at N61 and N131 from difference Fourier calculations; others calculated and all refined as riding atoms.

2,6-Bis[3,5-bis(diisopropylamino)-1-propylamino-6-oxa-2,4-diaza-1,3,5-hexatrienyl]pyridine (5): Tin tetrachloride (5.4 mL, 44 mmol) was added slowly at 0 °C to a mixture of 2,6-pyridinedicarbonyl dichloride (**1**; 4.48 g, 22 mmol) and diisopropylcyanamide (11.10 g, 88 mmol). After complete addition, the reaction mixture was heated to 150 °C and stirred for 1 h. A black precipitate of **3** was formed after cooling to room temperature. The precipitate was crushed in a mortar, washed with pentane and suspended in dry dichloromethane (100 mL). Propylamine (7.4 mL, 88 mmol) was added slowly at 0 °C to this suspension. The reaction mixture was allowed to warm slowly to room temperature and was stirred overnight. It was then washed with sodium hydroxide solution (200 mL, 2 M) and the aqueous layer was extracted three times with dichloromethane. The combined organic layers were dried with sodium sulfate and the solvent was removed in vacuo. The crude product **5** was purified by recrystallisation from *tert*-butyl methyl ether. Yield: 9.37 g (57 %), colourless solid; m.p. 206 °C. IR (KBr): $\tilde{\nu}$ = 3292 cm^{-1} (m, NH), 3062 (w, CH$_{arom.}$), 2964 (s, CH$_{aliph.}$), 2929 (s, CH$_{aliph.}$), 2871 (m, CH$_{aliph.}$), 1637 (vs, C=O), 1591 (vs, C=N), 1577 (vs, C=C), 1542 (vs), 1506 (s), 1446 (s), 1423 (s), 1371 (s), 1319 (s), 1215 (s), 1155 (s), 1132 (s), 1066 (w), 1033 (m), 970 (w), 964 (w), 921 (w), 844 (w), 831 (w), 752 (w), 721 (w), 698 (w), 669 (w). ^{1}H NMR (300.13 MHz, CDCl$_3$): δ = 1.00 (m, 6 H, NCH$_2$CH$_2$CH_3), 1.11–1.31 (br., 48 H, NCHCH_3), 1.66 (m, 4 H, NCH$_2$CH_2CH$_3$), 3.51 (br., 8 H, NCHCH$_3$), 3.87–4.19 (br., 4 H, NCH_2CH$_2$CH$_3$), 6.69 (br., 2 H, NH), 7.75 (m, 1 H, H$_{para}$), 8.18 (m, 2 H, H$_{meta}$) ppm. ^{13}C NMR (75.47 MHz, CDCl$_3$): δ = 11.5, 20.4, 21.0, 21.5, 22.7, 43.3, 44.1, 46.0, 46.6 (CH$_{aliph.}$), 124.2, 137.2, 149.4 (CH$_{arom.}$), 149.7, 157.2 (C=N), 162.8 (C=O) ppm. MS (EI, 70 eV): *m*/*z* (%) = 652 (4) [M$^+$ – N*i*Pr$_2$], 552 (68) [M$^+$ – 2 N*i*Pr$_2$], 508 (37), 452 (11) [M$^+$ – 3 N*i*Pr$_2$], 341 (47), 299 (8), 255 (9), 172 (18), 116 (80), 86 (100), 58 (20) [NHPr$^+$]. $C_{41}H_{75}N_{11}O_2$ (754.11): calcd. C 65.30, H 10.02, N 20.43; found C 65.04, H 9.98, N 20.30.

Complexes 4$^-$·Pd(OAc)$^+$ and 4·CuCl$_2$. General Procedure: Ligand **4** (38 mg, 0.10 mmol) and the metal salt (0.10 mmol) were dissolved in acetonitrile (2 mL). After centrifugation to remove undissolved residues, diethyl ether was allowed to diffuse into the solution. Coloured crystals were formed overnight. After one week, they were collected, washed with diethyl ether, and dried under reduced pressure.

4$^-$·Pd(OAc)$^+$: According to the general procedure, **4$^-$·Pd(OAc)$^+$** was prepared from **4** (38 mg, 0.10 mmol) and palladium(II) acetate (23 mg, 0.10 mmol). Yield: 27 mg (93 %), yellow crystals; m.p. 192 °C (decomposition). IR (KBr): $\tilde{\nu}$ = 3153 cm^{-1} (m, NH), 3089 (m, CH$_{arom.}$), 2960 (s, CH$_{aliph.}$), 2933 (s, CH$_{aliph.}$), 2871 (m, CH$_{aliph.}$), 1685 (vs, C=O), 1633 (vs, C=N), 1598 (vs, C=C), 1552 (vs), 1506 (s), 1454 (s), 1442 (s), 1404 (s), 1373 (s), 1334 (s), 1315 (s), 1265 (m), 1218 (m), 1172 (m), 1091 (w), 1060 (w), 1039 (w), 1001 (w), 983 (sh), 945 (w), 923 (w), 831 (w), 767 (w), 713 (w), 678 (w), 640 (w), 615 (w). MS (Maldi, Matrix DHB): *m*/*z* (%) = 494 (59) [M$^+$ – OAc – Et], 411 (100) [M$^+$ + Na – PdOAc]. UV/Vis (acetonitrile): λ_{max} (ε) = 419 nm (sh, 2061 M^{-1}cm^{-1}), 331 (sh, 11384), 219 (sh, 49953). $C_{21}H_{33}N_7O_4Pd$ (553.95): calcd. C 45.53, H 6.00, N 17.70; found C 44.75, H 5.68, N 18.27.

X-ray Crystal Structure Analysis of 4$^-$·Pd(OAc)$^+$:[22] $C_{21}H_{33}N_7O_4Pd$, $M = 553.94$, yellow crystal $0.20 \times 0.20 \times 0.10$ mm, $a = 9.661(1)$, $b = 14.179(1)$, $c = 18.999(1)$ Å, $\alpha = 85.65(1)°$, $\beta = 86.43(1)°$, $\gamma = 75.99(1)°$, $V = 2515.3(3)$ Å^3, $\rho_{calcd.} = 1.463$ g cm^{-3}, $\mu = 7.78$ cm^{-1}, empirical absorption correction ($0.860 \le T \le 0.926$), $Z = 4$, triclinic, space group $P\bar{1}$ (no. 2), $\lambda = 0.71073$ Å, $T = 198$ K, ω and φ scans, 31538 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.66$ Å^{-1}, 11909 independent ($R_{int} = 0.050$) and 8703 observed reflections [$I \ge 2\sigma(I)$], 617 refined parameters, $R = 0.041$, $wR_2 = 0.081$, max. residual electron density 0.58 (–0.94) eÅ^{-3}, hydrogen atom at N3 from difference Fourier calculations, others calculated and all refined as riding atoms.

4·CuCl$_2$: According to the general procedure, **4·CuCl$_2$** was prepared from **4** (38 mg, 0.10 mmol) and copper(II) chloride (17 mg, 0.10 mmol). Yield: 43 mg (82 %), green crystals; m.p. 153 °C (decomposition). IR (KBr): $\tilde{\nu}$ = 3147 cm^{-1} (m, NH), 3088 (m, CH$_{arom.}$), 2953 (s, CH$_{aliph.}$), 2934 (s, CH$_{aliph.}$), 2888 (m, CH$_{aliph.}$), 1681 (vs, C=O), 1629 (vs, C=N), 1592 (vs, C=C), 1557 (vs), 1512 (s), 1457 (s), 1439 (s), 1389 (s), 1331 (s), 1317 (s), 1222 (m), 1179 (m), 1099 (w), 1066 (w), 1028 (w), 1007 (w), 988 (sh), 938 (w), 833 (w), 769 (w), 711 (w), 675 (w), 633 (w), 615 (w). MS (Maldi, Matrix DHB): *m*/*z* (%) = 486 (45) [M$^+$ – Cl], 451 (35) [M$^+$ – CuCl], 390 (100) [M$^+$ – CuCl$_2$]. UV/Vis (acetonitrile): λ_{max} (ε) = 462 nm (375 M^{-1}cm^{-1}), 238 (sh, 20209), 219 (sh, 22482), 202 (33015). $C_{19}H_{31}Cl_2CuN_7O_2$ (523.95): calcd. C 43.56, H 5.96, N 18.71; found C 43.03, H 5.74, N 19.39.

X-ray Crystal Structure Analysis of 4·CuCl$_2$:[22] $C_{19}H_{31}Cl_2CuN_7O_2 \cdot CH_3CN$, $M = 544.48$, green crystal $0.10 \times 0.10 \times 0.05$ mm, $a = 21.590(1)$, $b = 14.389(1)$, $c = 18.753(1)$ Å, $\beta = 117.97(1)°$, $V = 5145.3(5)$ Å^3, $\rho_{calcd.} = 1.406$ g cm^{-3}, $\mu = 10.88$ cm^{-1}, empirical absorption correction ($0.899 \le T \le 0.948$), $Z = 8$, monoclinic, space group $C2/c$ (no. 15), $\lambda = 0.71073$ Å, $T = 198$ K, ω and φ scans, 2ß743 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.60$ Å^{-1}, 4537 independent ($R_{int} = 0.087$) and 2970 observed reflections [$I \ge 2\sigma(I)$], 330 refined parameters, $R = 0.047$ $wR_2 = 0.100$, max. residual electron density 0.61 (–0.46) eÅ^{-3}. Hydrogen atoms at N9 and N21 from difference Fourier calculations; others calculated and all refined as riding atoms.

Complexes 5·Co(ClO$_4$)$_2$·DMF, 5·CoCl$_2$, and 5·Ni(ClO$_4$)$_2$·DMF. General Procedure: Ligand **5** (38 mg, 0.05 mmol) and the metal salt (0.05 mmol) were dissolved in DMF (2 mL). After centrifugation to remove any precipitate, diethyl ether was allowed to diffuse into the solution. Coloured crystals were formed overnight. After one week, they were collected, washed with diethyl ether, and dried under reduced pressure.

5·Co(ClO$_4$)$_2$·DMF: According to the general procedure, **5·Co(ClO$_4$)$_2$·DMF** was prepared from **5** (38 mg, 0.05 mmol) and cobalt(II) perchlorate hexahydrate (18 mg, 0.05 mmol). Yield: 23 mg (42 %), pink crystals; m.p. 213 °C (decomposition). IR (KBr): $\tilde{\nu}$ = 3274 cm^{-1} (s, NH), 3093 (m, CH$_{arom.}$), 2970 (s, CH$_{aliph.}$), 2935 (s, CH$_{aliph.}$), 2879 (s, CH$_{aliph.}$), 1664 (s, C=O), 1622 (s, C=N), 1566 (s, C=C), 1531 (s), 1465 (s), 1429 (s), 1363 (s), 1338 (s), 1249 (w), 1211 (m), 1151 (s), 1130 (s), 1110 (s), 1062 (s), 975 (w), 929 (w), 883 (w), 860 (w), 844 (w), 829 (w), 754 (w), 688 (w), 669 (w), 622 (m), 603 (w), 576 (w), 543 (w). MS (Maldi, Matrix DHB): *m*/*z* (%) = 813 (80) [M$^+$ – DMF – 2 ClO$_4$], 770 (10) [M$^+$ – DMF – 2 ClO$_4$ – NHPr], 753 (20) [M$^+$ – DMF – Co(ClO$_4$)$_2$], 725 (25) [M$^+$ – DMF – Co(ClO$_4$)$_2$ – Et], 710 (20) [M$^+$ – DMF – Co(ClO$_4$)$_2$ – Pr], 653 (100) [M$^+$ – DMF – Co(ClO$_4$)$_2$ – N*i*Pr$_2$], 609 (30) [M$^+$ – DMF – Co(ClO$_4$)$_2$ – N*i*Pr$_2$ – Pr], 552 (80) [M$^+$ – DMF – Co(ClO$_4$)$_2$ – 2 N*i*Pr$_2$]. UV/Vis (acetonitrile): λ_{max} (ε) = 565 nm (44 M^{-1}cm^{-1}), 490

(51), 246 (39082), 201 (49246). $C_{44}H_{82}Cl_2CoN_{12}O_{11}$ (1085.04): calcd. C 48.71, H 7.62, N 15.49; found C 48.54, H 7.52, N 15.41.

X-ray Crystal Structure Analysis of 5·Co(ClO$_4$)$_2$·DMF:[22] $C_{41}H_{75}N_{11}O_2Co{\cdot}C_3H_7NO{\cdot}2ClO_4$, M = 1085.05, light pink crystal 0.50 × 0.40 × 0.30 mm, a = 25.932(1), b = 13.770(1), c = 16.507(1) Å, β = 97.16(1)°, V = 5848.4(6) Å^3, $\rho_{calcd.}$ = 1.232 g cm^{-3}, μ = 4.46 cm^{-1}, empirical absorption correction ($0.808 \leq T \leq 0.878$), Z = 4, monoclinic, space group $C2/c$ (no. 15), λ = 0.71073 Å, T = 198 K, ω and φ scans, 23269 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda]$ = 0.66 Å^{-1}, 6926 independent (R_{int} = 0.038) and 5854 observed reflections [$I \geq 2\sigma(I)$], 337 refined parameters, R = 0.044, wR_2 = 0.110, max. residual electron density 0.60 (–0.46) e Å^{-3}. Hydrogen atom at N41 from difference Fourier calculations; others calculated and all refined as riding atoms.

5·CoCl$_2$: According to the general procedure, **5·CoCl$_2$** was prepared from **5** (38 mg, 0.05 mmol) and cobalt(II) chloride hexahydrate (12 mg, 0.05 mmol). Yield: 14 mg (32%), purple crystals; m.p. 161 °C (decomposition). IR (KBr): $\tilde{\nu}$ = 3189 cm^{-1} (w, NH), 3023 (sh, CH$_{arom.}$), 2952 (s, CH$_{aliph.}$), 2938 (s, CH$_{aliph.}$), 2869 (m, CH$_{aliph.}$), 1658 (s, C=O), 1623 (s, C=N), 1606 (C=N), 1579 (s, C=C), 1544 (vs, C=C), 1508 (s), 1423 (s), 1355 (s), 1332 (s), 1205 (s), 1141 (s), 1126 (s), 1060 (m), 1033 (m), 1012 (w), 971 (w), 919 (w), 877 (w), 838 (w), 817 (w), 752 (m), 736 (m), 655 (w), 603 (w), 574 (w), 511 (w), 466 (w). MS (Maldi, Matrix DHB): m/z (%) = 813 (10) [M$^+$ – 2 Cl], 776 (40) [M$^+$ + Na – CoCl$_2$], 653 (95) [M$^+$ – CoCl$_2$ – N*i*Pr$_2$], 552 (100) [M$^+$ – CoCl$_2$ – 2 N*i*Pr$_2$]. UV/Vis (acetonitrile): λ_{max} (ε) = 684 nm (35 M^{-1} cm^{-1}), 666 (32), 588 (99), 248 (38394), 201 (54929). $C_{41}H_{75}Cl_2CoN_{11}O_2$ (883.95): calcd. C 55.71, H 8.55, N 17.43; found C 55.19, H 8.39, N 17.56.

X-ray Crystal Structure Analysis of 5·CoCl$_2$:[22] $C_{41}H_{75}Cl_2CoN_{11}O_2{\cdot}C_3H_7NO$, M = 957.05, pink crystal 0.20 × 0.20 × 0.07 mm, a = 14.223(1), b = 19.042(1), c = 19.980(1) Å, β = 102.42(1)°, V = 5284.6(5) Å^3, $\rho_{calcd.}$ = 1.203 g cm^{-3}, μ = 4.74 cm^{-1}, empirical absorption correction ($0.911 \leq T \leq 0.968$), Z = 4, monoclinic, space group $P2_1/c$ (no. 14), λ = 0.71073 Å, T = 198 K, ω and φ scans, 34062 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda]$ = 0.66 Å^{-1}, 12565 independent (R_{int} = 0.077) and 6668 observed reflections [$I \geq 2\sigma(I)$], 587 refined parameters, R = 0.060, wR_2 = 0.116, max. residual electron density 0.88 (–0.91) e Å^{-3}. Hydrogen atoms at N41 and N141 from difference Fourier calculations; others calculated and all refined as riding atoms.

5·Ni(ClO$_4$)$_2$·DMF: According to the general procedure, **5·Ni(ClO$_4$)$_2$·DMF** was prepared from **5** (38 mg, 0.05 mmol) and nickel(II) perchlorate hexahydrate (18 mg, 0.05 mmol). Yield: 27 mg (49%), green crystals; m.p. 211 °C. IR (KBr): $\tilde{\nu}$ = 3273 cm^{-1} (s, NH), 3091 (m, CH$_{arom.}$), 2970 (s, CH$_{aliph.}$), 2935 (s, CH$_{aliph.}$), 2877 (s, CH$_{aliph.}$), 1640 (s, C=O), 1622 (s, C=N), 1573 (s, C=C), 1542 (s), 1467 (s), 1429 (s), 1369 (s), 1336 (s), 1249 (w), 1211 (m), 1145 (s), 1130 (s), 1110 (s), 1064 (s), 975 (w), 927 (w), 885 (w), 862 (w), 842 (w), 829 (w), 756 (w), 707 (w), 673 (w), 622 (m), 605 (w), 588 (w), 543 (w). MS (Maldi, Matrix DHB): m/z (%) = 910 (20) [M$^+$ – DMF – ClO$_4$ – Et], 810 (30) [M$^+$ – DMF – 2 ClO$_4$ – Et], 709 (100) [M$^+$ – DMF – 2 ClO$_4$ – Et – N*i*Pr$_2$]. UV/Vis (acetonitrile): λ_{max} (ε) = 586 nm (13 M^{-1} cm^{-1}), 243 (43186), 203 (51760). $C_{44}H_{82}Cl_2N_{12}NiO_{11}$ (1084.8): calcd. C 48.72, H 7.62, N 15.49; found C 48.31, H 7.46, N 15.29.

X-ray Crystal Structure Analysis of 5·Ni(ClO$_4$)$_2$·DMF:[22] $C_{41}H_{75}N_{11}NiO_2{\cdot}C_3H_7NO{\cdot}2ClO_4$, M = 1084.83, green crystal 0.35 × 0.20 × 0.10 mm, a = 13.672(1), b = 14.683(1), c = 16.423(1) Å, α = 91.87(1)°, β = 98.20(1)°, γ = 117.47(1)°, V = 2877.0(3) Å^3, $\rho_{calcd.}$ = 1.252 g cm^{-3}, μ = 4.92 cm^{-1}, empirical absorption correction ($0.847 \leq T \leq 0.953$), Z = 2, triclinic, space group $P\bar{1}$ (no. 2), λ = 0.71073 Å, T = 198 K, ω and φ scans, 34021 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda]$ = 0.66 Å^{-1}, 13604 independent (R_{int} = 0.051) and 9708 observed reflections [$I \geq 2\sigma(I)$], 657 refined parameters, R = 0.051, wR_2 = 0.113, max. residual electron density 0.53 (–0.53) e Å^{-3}. Hydrogen atoms at N41 and N141 from difference Fourier calculations; others calculated and all refined as riding atoms.

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A **1990**, *46*, 467–473), structure refinement SHELXL-97 (G. M. Sheldrick, University of Göttingen, **1997**), graphics SCHAKAL (E. Keller, Universität Freiburg, **1997**). CCDC-266377 (**4**), -266376 [**4^{-}·Pd(OAc)$^{+}$**], -266381 (**4·$CuCl_2$**), -266378 [**5·$Co(ClO_4)_2$·DMF**], -266379 (**5·$CoCl_2$**) and -266380 [**5·$Ni(ClO_4)_2$·DMF**] 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.

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