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Chelate [2-(Iminoethyl)pyridine *N*-oxide]metal Complexes – Synthesis and Structural Comparison with Their Chemically Related 2-(Iminoethyl)pyridine-Derived Systems

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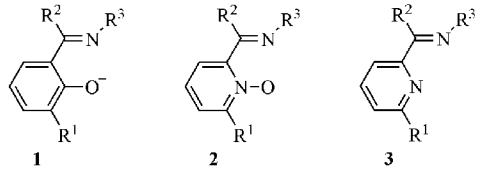
The N,O-chelate ligands 2-(iminoethyl)pyridine *N*-oxide (**2a**) and 2-(iminoethyl)-6-isopropylpyridine *N*-oxide (**2b**) were prepared by conventional synthetic routes, the latter involving a variant of the Reissert–Henze reaction. Treatment of **2a** with $FeCl_2$ resulted in a deoxygenation reaction of the ligand and formation of the salt [bis{2-(iminoethyl)-pyridine}FeCl]$^+$[$FeCl_4$]$^-$ (**18a**). In contrast, the reaction of **2a** with $PdCl_2$ or $CoCl_2$ cleanly furnished the six-membered chelate [κ*N*,*O*-2(iminoethyl)pyridine *N*-oxide]MCl_2 complexes (**19a**, M = Pd) or (**20a**, M = Co), respectively, which were both characterised by X-ray diffraction. Treatment of **2b** with [$NiBr_2$(dme)], followed by crystallisation from THF, gave the complex [(κ*N*,*O*-**2b**)$NiBr_2$(THF)] (**21b**), which features a distorted trigonal-bipyramidal coordination geometry of the central metal atom. The reaction of **2a** with [$NiBr_2$(dme)] gave the structurally related complex [(κ*N*,*O*-**2a**)$NiBr_2$(κ*O*-**2a**)] (**21a**). The N,O-chelate Pd complex **19a** was shown to be an active catalyst for the Suzuki coupling reaction. The ligand systems **2a**,**b** and their related 2-(iminoethyl)-pyridines **3a**,**b** and a variety of metal complexes of ligands **3** were also prepared and characterised for comparison by X-ray diffraction.

Introduction

Chelating ligand systems are of considerable importance in metal-catalysed organic reactions[1] and in polymerisation catalysis.[2] Among the various chelating ligand types, many salicylaldimine-derived bi- and multidentate ligands have been found to be very useful. The monoanionic bidentate systems **1**, which feature various types of substituent patterns at the central framework, have been employed extensively in homogeneous Ziegler–Natta-type polymerisation catalysis[3–5] as well as in asymmetric organic reactions,[6] and they form the basis of the many salen-type ligands whose metal complexes have found extensive catalytic uses.[7]

The neutral pyridine *N*-oxide aldimines or ketimines **2** (see Scheme 1) are the neutral analogues of the ubiquitous anionic ligand systems **1**. A variety of such examples and their metal complexes have been described so far[8–12] but overall much less is known about these interesting bidentate ligand systems than their phenolic counterparts, especially with a bulky alkyl substituent (R^1) in the 6-position. We have therefore prepared several examples of metal complexes of this class of neutral bidentate ligand systems **2** and compared their structural features with those of the related [2-(iminoethyl)pyridine]metal complex systems **3**.



Scheme 1.

Results and Discussion

Preparation of the Chelating Ligand Systems

For this study two general lines of acetylpyridine (R^2 = CH_3) derived ligands were employed, namely the parent systems (R^1 = H) and the 6-isopropyl analogue (R^1 = *i*Pr). We also briefly investigated the corresponding *tert*-butyl system (R^1 = *t*Bu), but encountered some difficulties that will be described below. All the imine systems of this study were derived from 2,6-diisopropylaniline as the coupling component of the Schiff-base synthesis. 2-Acetylpyridine (**4**) was, thus, condensed with 2,6-diisopropylaniline to yield the Schiff-base product **3a** (see Scheme 2).[13] Oxidation of **4** with *m*-chloroperbenzoic acid in chloroform gave the cor-

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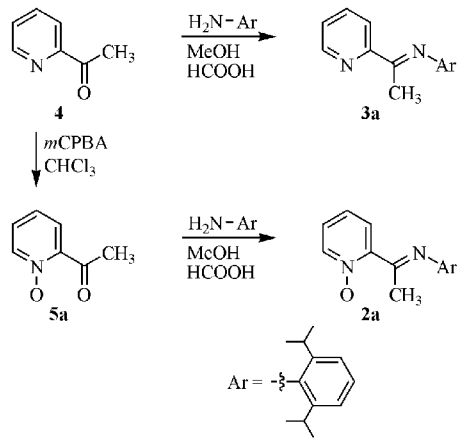
responding 2-acetylpyridine *N*-oxide (**5a**),[14] which was then treated with diisopropylaniline to yield **2a**.



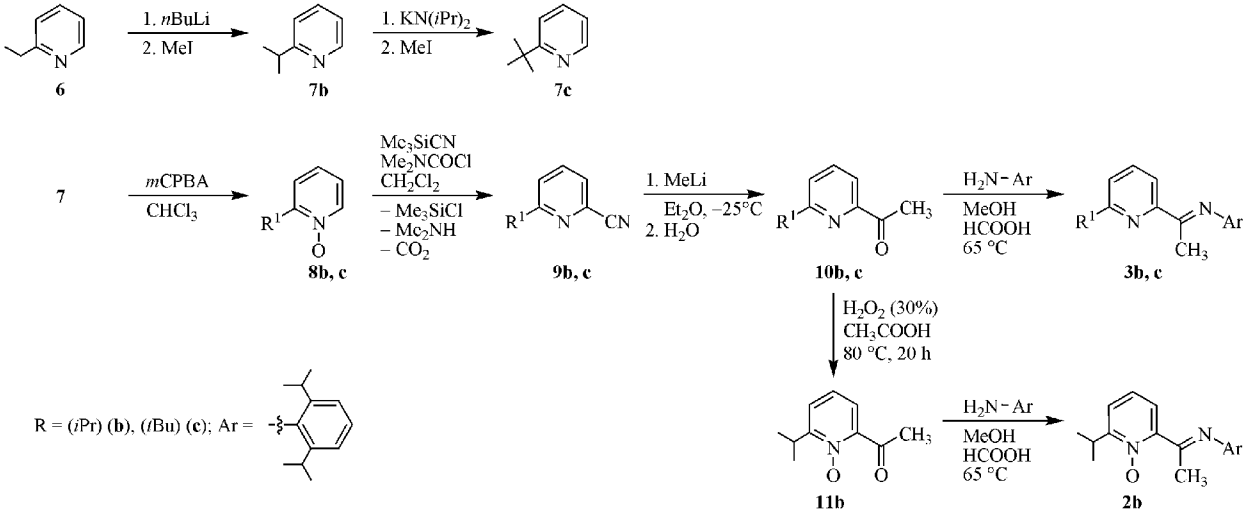
Scheme 2.

The synthesis of the 6-isopropyl and 6-*tert*-butyl derivatives of **2** and **3** started from 2-ethylpyridine (**6**, see Scheme 3). Deprotonation of **6** with *n*-butyllithium at –30 °C followed by treatment with methyl iodide at –50 °C furnished 2-isopropylpyridine (**7b**, 67%).[15] Subsequent α-deprotonation of **7b** was achieved by treatment with the stronger base potassium diisopropylamide (generated in situ from isopropylamine, KO*t*Bu and *n*BuLi) at –50 °C. Quenching with MeI at –75 °C then gave **7c** in 68% yield.[15] The 2-cyano substituent was introduced by a modified Reissert–Henze reaction.[16] For that purpose, compounds **7b** and **7c** were first converted into their respective pyridine *N*-oxides **8b** and **8c** by treatment with *m*-chloroperbenzoic acid in chloroform at 0 °C.[17] The selective CN introduction was achieved by treatment of compounds **8** with Me_3SiCN in the presence of dimethylcarbamoyl chloride in CH_2Cl_2 at ambient temperature. Distillation gave the products **9b** (61%) and **9c** (65%) in good yield. The products **9** were then converted into the corresponding 2-acetyl-6-alkyl-pyridines **10b** (25%) and **10c** (36%) by treatment with methyllithium in diethyl ether (–25 °C), followed by aqueous workup and distillation. Subsequent treatment of compounds **10** with 2,6-diisopropylaniline (MeOH, catalysed by formic acid) eventually gave the 6-alkyl-substituted 2-(iminoethyl)pyridine ligands **3b** (R = *i*Pr) and **3c** (R = *t*Bu), respectively.

2-Acetyl-6-isopropylpyridine (**10b**) was converted into the corresponding pyridine *N*-oxide product **11b**. First attempts to achieve the selective oxidation by treatment with *m*-chloroperbenzoic acid were unsuccessful, and stronger oxidation conditions, such as 30% H_2O_2 at 80 °C in acetic acid for 20 h, were required to achieve the conversion of **10b** into **11b** (61% isolated). The *tert*-butyl-substituted analogue **10c** even proved inert under these forcing oxidation conditions and could not be converted into the corresponding *N*-oxide under the applied reaction conditions. Eventually, condensation of **11b** with 2,6-diisopropylaniline gave the *N*-aryl-2-(iminoethyl)-6-isopropylpyridine *N*-oxide system **2b**, which was used as a sterically more hindered chelate ligand in this study.

The chelate ligands **3a**, **3b** and **3c** and the pyridine *N*-oxide systems **2a** and **2b** were characterised by X-ray diffraction. Details of **3c** are given in the Supporting Information. The structures of the chelate ligand pairs **3a/2a** and **3b/2b** are depicted for comparison in Figures 1 and 2, respectively.

In the crystal, the ligand system **3a** features a close to planar central (iminoethyl)pyridine framework with an *s-trans* arrangement of the pyridyl and the imino subunits [dihedral angle $\theta 1$ = –177.1(1)° (see Table 1)]. The C7–N9 bond length [1.280(2) Å] is in the typical C=N double bond range,[18] which is (*E*)-configured in **3a**, i.e. the bulky pyridyl and 2,6-diisopropylphenyl substituents are oriented *trans* to each other. The plane of the 2,6-diisopropylphenyl



Scheme 3.

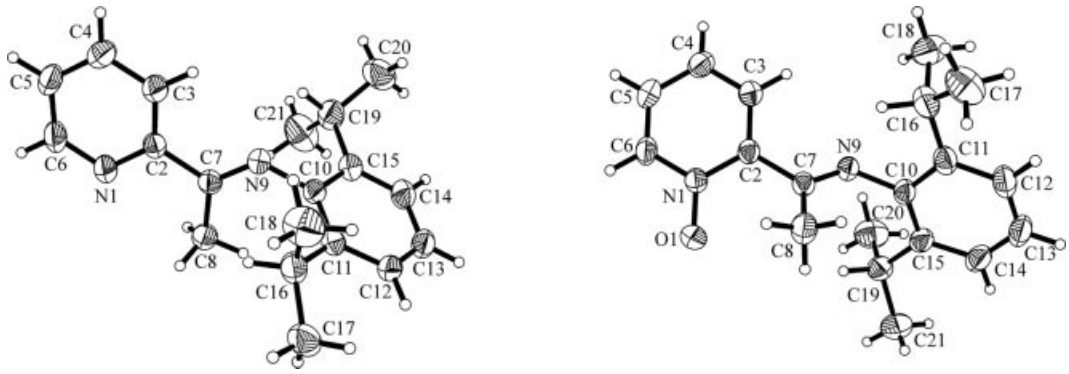


Figure 1. Comparison of the molecular structures of the ligand systems **3a** (left) and **2a** (right).

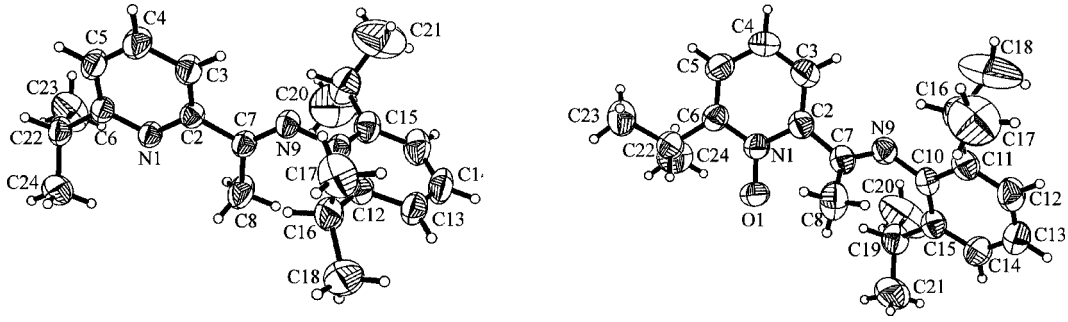


Figure 2. Comparison of the conformational arrangements of the chelating ligand systems **3b** (left) and **2b** (right).

Table 1. Selected structural parameters of the chelate ligands **2** and **3**.[a]

	3a	**2a**	**3b**	**2b**[b]	
C7–N9	1.280(2)	1.278(2)	1.274(2)	1.283(4)	1.276(4)
C2–C7–N9–C10 [θ1]	–177.1(1)	174.3(1)	–179.0(1)	177.4(3)	–177.7(2)
N1–C2–C7–N9 [θ2]	–177.9(1)	143.2(1)	173.0(1)	133.7(3)	–137.4(3)
C7–N9–C10–C15 (C11) [θ3]	104.0(2)	93.1(2)	98.0(2)	88.1(3)	97.2(4)
	–81.9(2)	–92.5(2)	–88.5(2)	–96.9(3)	–90.0(4)
pyridyl vs. aryl plane	74.2	128.8	91.0	143.1	135.6

[a] Bond lengths in Å and angles in °. [b] Two independent molecules.

ring is rotated close to normal from the central C=N plane [θ3 = 104.0(2)/–81.9(2)°].

The conformational arrangement of the corresponding *N*-aryl[2-(iminoethyl)]pyridine *N*-oxide system **2a** is related. The attachment of the oxygen atom to the pyridyl nitrogen atom [N1–O = 1.301(1) Å] causes the adjacent imino moiety to rotate away from the central plane by about 140° (θ2, see Table 1 and Figure 1). This conformational arrangement appears to be the best compromise between competing repulsive interactions between the bulky =*N*-aryl group attached at the (sp^2) carbonyl carbon atom C7 or its CH_3 group, respectively, with the newly introduced N–O functionality. Again, the 2,6-diisopropylphenyl plane is oriented close to normal [θ3 = 93.1(2)/–92.5(2)°] to the C=N plane in **2a**.

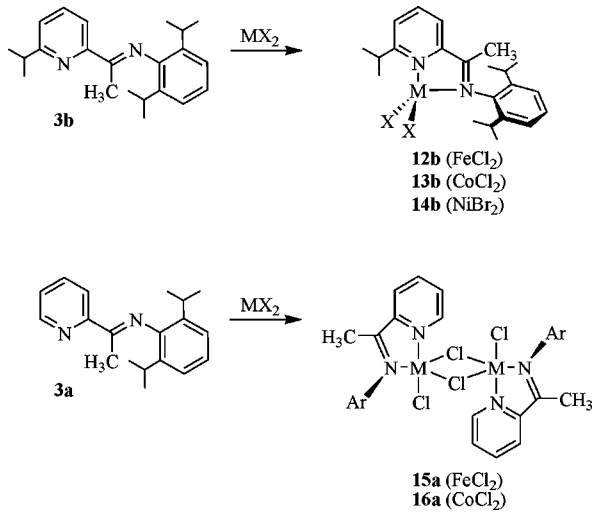
In the ligand system **3b** the bulky isopropyl substituent is attached to the pyridyl 6-position. The framework conformation in **3b** is *s-trans* [θ1 = –179.0(1)°; see Table 1]. The central trisubstituted imino C=N double bond [1.274(2) Å] remains (*E*)-configured and the 2,6-diisopropylphenyl plane is close to normal to the C=N plane [θ3 = 98.0(2)/–88.5(2)°; see Table 1].

In the pyridine *N*-oxide derivative **2b** the C=N double bond is again substantially rotated away from planarity. Actually, the observed dihedral angle θ2 in **2b** [averaged absolute value 135.6(3)°] is very close to that observed in **2a** (see above and Table 1). Thus, compound **2b** has almost the same optimal rotational angle around the C2–C7 vector, which probably leads to an optimal compensation of the N–O vs. C7–CH_3 and C7–N9(Ar) steric interactions. Again, the 2,6-diisopropylphenyl substituent plane is oriented close to normal to the C=N substituent plane [averaged θ3 = –93.1(4)°; see Table 1].

The ligand systems **2** and **3** seem to adopt similar conformational structures in solution. A perpendicular arrangement between the C=N and 2,6-diisopropylphenyl planes would create an axially prochiral subunit in all these compounds. This would be monitored by the occurrence of pairwise diastereotopic methyl groups of the isopropyl substituents of the *N*-aryl substituent. For **3b**, the *i*$Pr_2C_6H_3$

methyl resonances in the ^{1}H NMR spectrum are, by chance, isochronous in $CDCl_3$ at ambient temperature, but they split upon cooling of the sample to –65 °C {^{1}H NMR: δ = 2.74 [sept, 2 H, C*H*$(CH_3)_{2ar}$], 1.12 and 1.10 [each d, 6 H, CH(C*H*$_3)_{2ar}$] ppm; ^{13}C NMR: δ = 27.7 [*C*H$(CH_3)_{2ar}$], 23.1, 23.0 [CH(*C*H$_3)_2]_{ar}$ ppm}. The ^{1}H NMR resonances of the remaining isopropyl group at C6 of the pyridyl ring occur at δ = 3.08 [sept, 1 H, C*H*$(CH_3)_{2py}$] and 1.32 [d, 6 H, CH(*C*H$_3)_{2py}$] ppm {^{13}C NMR: δ = 36.2 [*C*H$(CH_3)_{2py}$], 22.7 [CH(*C*H$_3)_{2py}$] ppm}.

The corresponding pyridine *N*-oxide derivative **2b** also shows a single CH(C*H*$_3)_{2py}$ ^{1}H NMR resonance even at –60 °C in $CDCl_3$ [δ = 1.28 (d, 6 H) ppm; ^{13}C: δ = 20.5 (25 °C) ppm]. In contrast, the CH$(CH_3)_{2ar}$ methyl groups of **2b** are diastereotopic at room temperature [^{1}H: δ = 1.23, 1.16 (each d, each 6 H) ppm; ^{13}C: δ = 23.5, 22.9 ppm] which indicates that the rotation around the imino =N–C(aryl) vector is "frozen" on the NMR timescale under these conditions and that the *N*-aryl substituent plane is oriented substantially out of the N=C plane in solution, as was observed in this and the related systems in the crystal.



Scheme 4.

Metal Complex Formation and Structural Characterisation

First, we treated the ligand system **3b** (R = *i*Pr) with $FeCl_2$, $CoCl_2$, and $NiBr_2$(dme). In clean reactions the corresponding 1:1 chelate complexes [(**3b**)MX_2] were obtained in high yields. Single crystals were obtained from all the three complexes **12b** [(**3b**)$FeCl_2$], **13b** [(**3b**)$CoCl_2$] and **14b** [(**3b**)$NiBr_2$], and their molecular structures in the solid state determined (see Table 2 and Scheme 4). Since the three compounds are structurally analogous, we will briefly describe only the nickel system **14b** (see Figure 3 for the structure). The structural data of **12b**, **13b** and **14b** are listed in Table 2. For additional information see the Supporting Information.

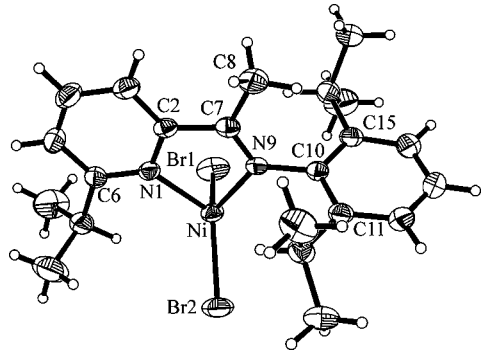


Figure 3. Molecular structure of the nickel chelate complex **14b**.

In complex **14b** the ligand system adopts a *cisoid* conformation [θ(N1–C2–C7–N9) = 2.8(3)°] that allows both the nitrogen centres N1 and N9 to coordinate to the nickel atom. The C7–N9 bond length in the ligand system is not affected by the coordination and retains its value of

Table 2. Selected structural data of the [2-(iminoethyl)pyridine]metal complexes **12**–**16**.[a]

	12b (Fe)[b]	**13b** (Co)[b]	**14b** (Ni)[c]	**15a** (Fe)[b]	**16a** (Co)[b]
C2–C7	1.497(5)	1.484(5)	1.474(4)	1.483(11)	1.482(2)
C7–N9	1.271(5)	1.288(4)	1.286(3)	1.294(10)	1.290(2)
M–N1	2.108(3)	2.034(3)	1.994(2)	2.126(7)	2.093(1)
M–N9	2.111(3)	2.044(3)	1.995(2)	2.201(6)	2.123(1)
M–Hal1	2.209(1)	2.200(1)	2.3577(5)	2.385(2)	2.3419(5)
M–Hal2	2.223(1)	2.209(1)	2.3169(5)	2.278(3)	2.2878(6)
M–Hal1*	–	–	–	2.484(2)	2.4589(5)
N1–M–N2	77.3(1)	81.1(1)	81.7(1)	74.8(2)	76.64(5)
Hal1–M–Hal2	118.68(5)	113.78(5)	123.64(2)	105.3(1)	103.42(2)
Hal1–M–Hal1*	–	–	–	84.9(1)	86.01(2)
C2–C7–N9–C10	–179.0(3)	–178.6(3)	–178.0(2)	–175.4(7)	175.2(1)
C7–N9–C10–C11 (C15)	–89.1(5)	–89.7(5)	97.7(3)	–89.0(9)	89.8(2)
	94.3(5)	94.5(4)	–84.0(3)	90.3(9)	–88.8(2)
pyridyl vs. aryl plane	93.1	85.9	99.7	98.6	97.9

[a] Bond lengths in Å; angles and dihedral angles in °. [b] Hal = Cl. [c] Hal = Br.

1.286(3) Å. The metal–nitrogen bond lengths amount to 1.994(2) Å (Ni–N1) and 1.995(2) Å (Ni–N9). In complex **14b** the nickel atom has a pseudo-tetrahedral coordination geometry with a small N1–Ni–N9 angle of 81.7(1)° inside the five-membered chelate ring and, consequently, a much larger complementary Br1–Ni–Br2 angle of 123.64(2) Å. Again, an (*E*)-trisubstituted C=N unit is found and the 2,6-diisopropylphenyl substituent at the imine nitrogen atom is rotated close to perpendicular to the plane of the central (iminoethyl)pyridine moiety (angle between the planes: 99.7°).

The less bulky parent ligand system **3a** also reacts readily with the metal dihalides $FeCl_2$ or $CoCl_2$. In both cases we were able to obtain single crystals and characterise the structures of the products (**15a** and **16a**, respectively) by X-ray diffraction. The coordination of the *cisoid* chelate ligand in **15a** and **16a** (see Scheme 4) is very similar to that in **12b** and **13b** (see Table 2). However, use of the less bulky ligand **3a** results in the formation of a chloro-bridged dimer.[19] In both **15a** and **16a** the coordination geometry of the central metal atom can best be described as distorted trigonal-bipyramidal with two equivalent half molecules in an overall C_2-symmetric framework. The pyridyl nitrogen atom (N1) and Cl1 mark the apical centres of the distorted trigonal bipyramid {**15a**: N1–Fe–Cl1 = 155.6(2)° [163.77(4)°]; the value in brackets is the corresponding value of the isostructural cobalt complex **16a**}. The angles between the three equatorial ligands amount to 126.0(2)° (N9–Fe–Cl1*) [122.86(4)°], 116.7(2)° (N9–Fe–Cl2) [114.03(4)°] and 115.5(1) (Cl1*–Fe–Cl2) [119.79(2)°], which amounts to a sum of the three bonding angles of 358.2° in the iron complex **15a** [356.68° in the cobalt complex **16a**]. Most angles between the apical and basal ligands are rather close to the expected value of 90° [Fe complex **15a**: between 84.1(2)° and 99.1(2)°; Co complex **16a**: between 83.18(4)° and 99.41(4)°] with the exception of the smaller chelate nitrogen angle [N1–Fe–N9 = 74.8(2)°; N1–Co–N9 = 76.64(5)°] and the correspondingly enlarged angle between the bridging halide ligands [Cl1–Fe–Cl2 = 105.3(1)°; Cl1–Co–Cl2 = 103.42(2)°]. The structure of the dimeric (chelate ligand) $FeCl_2$ complex **15a** is depicted in Figure 4 (for further details of the isostructural cobalt system **16a** see the Supporting Information).

The reaction of **3a** with [$NiBr_2$(dme)] in dichloromethane at room temperature takes a slightly different course. We isolated the 2:1 reaction product **17a** (see Scheme 5) of the composition $[(\mathbf{3a})_2NiBr]^+Br^-$ as a green-yellow solid.[20] The general trigonal-bipyramidal structural type of **17a** with the pyridyl nitrogen atoms was determined by X-ray diffraction but the quality of the X-ray crystal structure analysis of **17a** was too poor to allow for any detailed discussion.

Let us now turn to the reactions of the chelate pyridine *N*-oxide ligands with the metal halides. The reaction of **2a** with $FeCl_2$ did not give an (iminoethyl)pyridine *N*-oxide complex as one might have expected. Instead, it turned out that the *N*-oxide is reduced by part of the iron. Crystallisation of the crude reaction product furnished single crystals of the Fe^{II}/Fe^{III} salt of the deoxygenated (iminoethyl)pyridine ligand $[(\mathbf{3a})_2FeCl]^+[FeCl_4]^-$ (**18a**; see Scheme 6 and Figure 5). The X-ray crystal structure analysis of **18a**, although of a rather poor quality, shows a distorted trigonal-bipyramidal coordination geometry around the Fe^{II} centre in the cation (the Fe^{III} centre in the $[FeCl_4]^-$ ion is tetrahedrally coordinated) with the pyridine nitrogen atoms oriented *trans* to each other at the apical positions [N1A–Fe1–N1B = 159.5(3)°] and a sum of the basal ligand angles [Cl1–Fe1–N9A = 117.2(2)°; Cl1–Fe–N9B = 117.8(2)°; N9A–Fe–N9B = 124.9(3)°] of 359.9°.

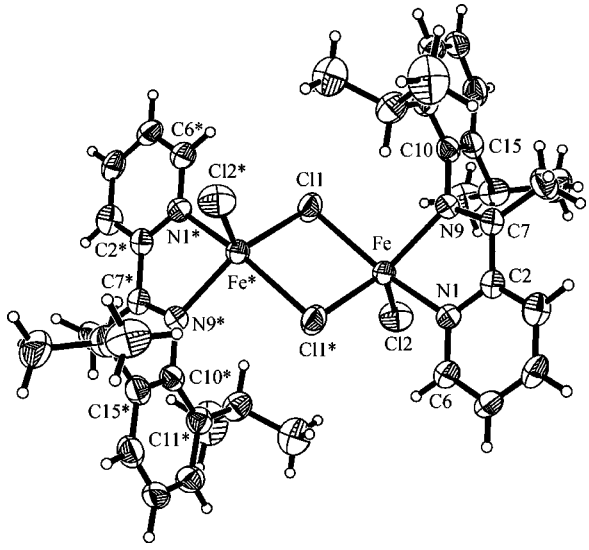
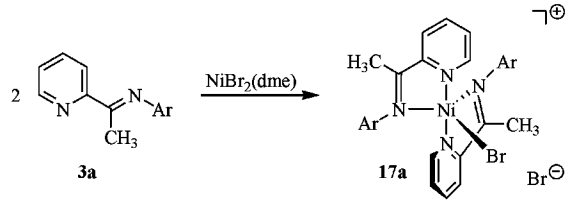
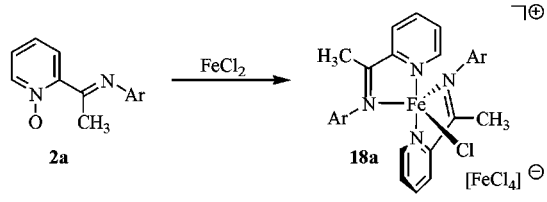


Figure 4. View of the molecular structure of the dimeric iron complex **15a**.



Scheme 5.



Scheme 6.

The reaction of the N,O-chelate ligand **2a** with $PdCl_2$ gave complex **19a** (see Scheme 7), which was isolated as a yellow solid in 75% yield. The X-ray crystal-structure analysis showed a six-membered chelate structure where both the pyridine *N*-oxide oxygen atom and the imino nitrogen atom are coordinated to the palladium atom [Pd–O1 = 2.029(1) Å; N9–Pd = 2.035(2) Å]. In complex **19a** both the N–O [1.343(2) Å] and the C7–N9 [1.284(2) Å] bond lengths are almost unchanged relative to the free ligand (see

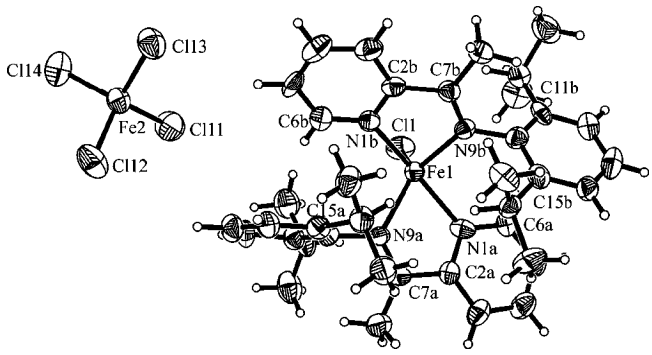


Figure 5. Molecular structure of the salt $[(\mathbf{3a})_2FeCl]^+[FeCl_4]^-$ (**18a**).

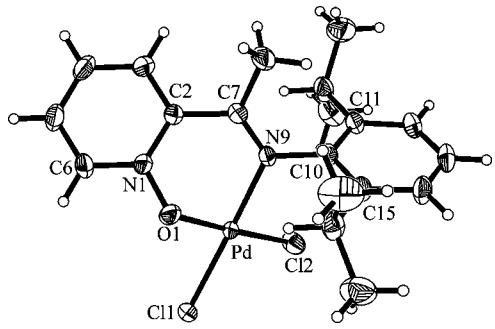
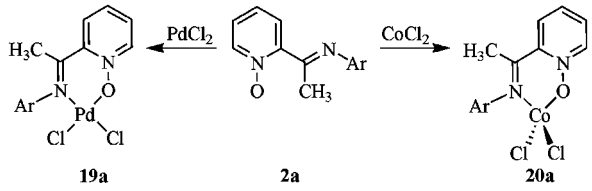


Figure 6. Molecular structure of palladium complex **19a**.

Table 3 and Table 1). The palladium atom in complex **19a** features a square-planar coordination geometry with Pd–Cl bond lengths of 2.2945(5) Å (Cl1) and 2.2678(5) Å (Cl2). The bond angles at Pd amount to 91.52(2)° (Cl1–Pd–Cl2), 90.46(4)° (Cl1–Pd–O1), 84.92(6)° (O1–Pd–N9) and 93.12(4)° (N9–Pd–Cl2) (sum of bonding angles at Pd: 360.02°). In contrast to the free ligand **2a**, the chelate core of complex **19a** is markedly rotated away from planarity, with central dihedral angles of 40.7(3)° (N9–C7–C2–N1) and –1.5(3)° (C7–C2–N1–O1). The six-membered core of complex **19a** features a twist-boat-like conformation (see Figure 6), and the 2,6-diisopropylphenyl substituent at the imine nitrogen centre N9 is rotated almost as far out of the adjacent imine C=N plane as in the free ligand **2a** [C7–N9–C10–C11 = –77.3(2)° in **19a** and –92.5(2)° in **2a**].



Scheme 7.

Complex **19a** is one of the few diamagnetic chelate systems obtained in this study, and could thus be characterised by NMR spectroscopy. Its most prominent feature is the observation of pair-wise diastereotopic methyl groups of the 2,6-diisopropylphenyl substituent at the C=N nitrogen atom [^{1}H NMR: δ = 1.59, 1.19 (each d, each 6 H) ppm; ^{13}C: δ = 24.9, 23.8 ppm].

The [2-(*N*-aryliminoethyl)pyridine *N*-oxide]cobalt complex **20a** was obtained from the reaction of **2a** with $CoCl_2$ (see Scheme 7). The X-ray crystal structure analysis of **20a** features a pseudo-tetrahedral coordination geometry of the central transition metal atom. The intact chelate ligand is again N,O-coordinated, with the 2,6-diisopropylphenyl substituent oriented close to normal to the C=N plane (see Table 3 and Figure 7). The complex framework also features a twist-boat-type six-membered ring conformation with dihedral angles of –22.6(4)° (N1–C2–C7–N9) and 2.2(4)° (C7–C2–N1–O1).

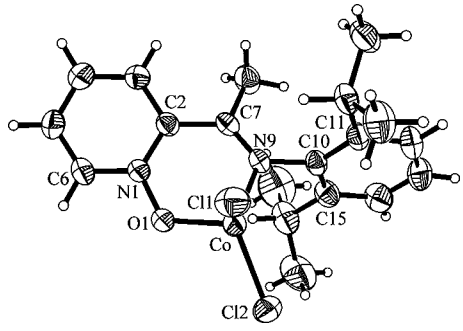


Figure 7. View of the molecular structure of the cobalt complex **20a**.

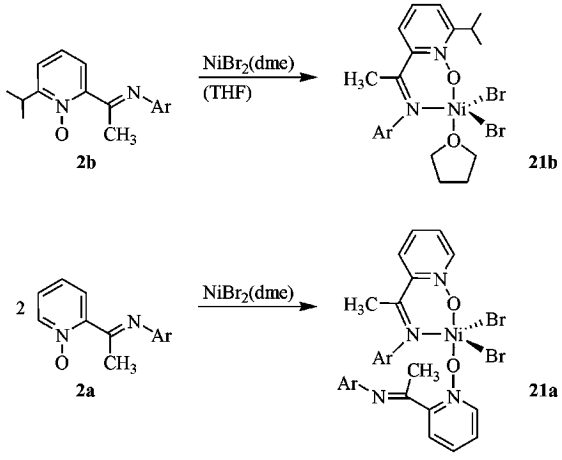
The reaction of the N,O-chelate ligand **2b** with $[NiBr_2(dme)]$ takes a different course. Again, a 1:1 addition product (**21b**, see Scheme 8) was obtained. Single crystals

Table 3. Selected structural data of the metal complexes **19**–**23**.[a]

	19a (Pd)	**20a** (Co)	**21b** (Ni)	**21a** (Ni)		**22a** (Zn)		**23a** (Cu)
C2–C7	1.489(3)	1.496(4)	1.486(4)	1.485(5)	1.491(5)[b]	1.499(6)	1.500(6)	1.490(4)
C7–N9	1.284(2)	1.291(4)	1.285(4)	1.284(4)	1.272(4)[b]	1.282(5)	1.285(6)	1.281(4)
N1–O1	1.343(2)	1.340(3)	1.336(3)	1.332(4)	1.337(3)[b]	1.340(5)	1.332(5)	1.340(3)
N9–M	2.035(2)	2.020(2)	2.041(3)	2.073(3)	–	2.072(4)	2.076(4)	1.985(2)
O1–M	2.029(1)	1.957(2)	2.005(2)	2.049(2)	2.055(2)[b]	1.976(3)	2.005(3)	1.919(2)
C7–N9–M	121.8(1)	123.7(2)	123.6(2)	123.8(2)	–	121.6(3)	121.6(3)	123.2(2)
N9–M–O1	84.92(6)	87.84(9)	82.9(1)	81.7(1)	–	84.3(1)	83.7(1)	87.07(9)
M–O1–N1	109.9(1)	118.2(2)	113.8(2)	113.6(2)	–	113.0(3)	113.2(3)	115.4(2)
C2–C7–N9–C10	175.9(2)	174.4(2)	–175.3(3)	–179.3(4)	–176.6(3)[b]	–174.1(4)	174.2(4)	–179.8(3)
C2–N1–O1–M	–54.9(2)	40.8(4)	57.6(3)	53.5(4)	–	–52.3(5)	50.4(5)	49.0(3)
N1–C2–C7–N9	40.7(3)	–22.6(4)	–32.0(4)	–32.4(6)	–126.8(4)[b]	26.8(7)	–26.9(7)	–29.7(4)

[a] Bond lengths in Å and angles and dihedral angles in °. [b] κO-coordinated ligand **2a**.

were obtained from THF solution. In **21b** (see Figure 8) the (iminoethyl)pyridine *N*-oxide ligand coordinates to the nickel atom through both the oxygen atom and the imino nitrogen atom to form a favoured six-membered chelate ring. The ring conformation is twisted, with the core atoms N1–C2–C7–N9 deviating from coplanarity by about –32° (see Table 3). The corresponding dihedral angles amount to 57.6(3)° (C2–N1–O1–Ni), 5.9(4)° (C2–C7–N9–Ni), 31.8(2)° (C7–N9–Ni–O1) and –62.2(2)° (N1–O1–Ni–N9). The N1–O1 bond length in complex **21b** is 1.336(3) Å, which is similar to that found in the free ligand **2b**. The nickel atom in complex **21b** features a distorted trigonal-bipyramidal coordination geometry, with the pyridine *N*-oxide oxygen atom O1 [Ni–O1 = 2.005(2) Å] and the oxygen atom of a coordinated THF ligand [Ni–O25 = 2.160(2) Å] being at the apical positions [O1–Ni–O25 = 174.1(1)]. The imino-nitrogen atom N9 [Ni–N9 = 2.041(3) Å] and the pair of bromide ions [Ni–Br1 = 2.4407(6) Å; Ni–Br2 = 2.4173(6) Å] are oriented in the central plane [N9–Ni–Br1 = 96.17(7)°; N9–Ni–Br2 = 126.67(8)°; Br1–Ni–Br2 = 136.84(3)°]. The 2,6-diisopropylphenyl substituent at N2 is rotated almost normal to the C=N imine plane [C7–N9–C10–C11 = –94.3(4)°] as is the bulky $CHMe_2$ group at the α-position of the pyridine *N*-oxide ring.



Scheme 8.

The reaction of the less bulky chelate pyridine *N*-oxide ligand **2a** with [$NiBr_2$(dme)] takes a similar course, except that a 2:1 adduct (**21a**, see Scheme 8 and Figure 9) was obtained after recrystallisation. The X-ray crystal-structure analysis of **21a** revealed the presence of a six-membered chelate ring that is very similar to the corresponding substructural unit in **21b** (see above and Table 3), but instead of the THF solvent the nickel atom in **21a** has picked up a second (iminoethyl)pyridine *N*-oxide ligand (**2a**) and is coordinated to it only through the N–O oxygen atom (κO) to complete its distorted trigonal-bipyramidal coordination sphere [Ni–O1a = 2.055(2) Å; N1a–O1a–Ni = 123.2(2)°]. The κO-coordinated ligand **2a** in **21a** features a conformation that is similar to that of the free ligand [N1a–C2a–C7a–N9a = –126.8(4)°].

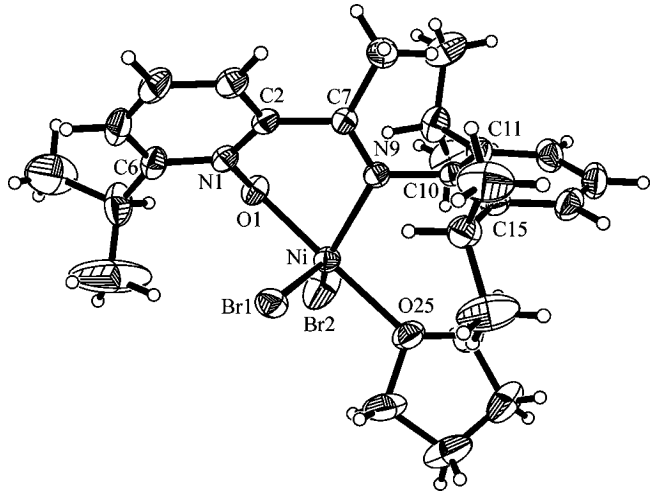


Figure 8. Molecular geometry of the nickel(II) complex **21b**.

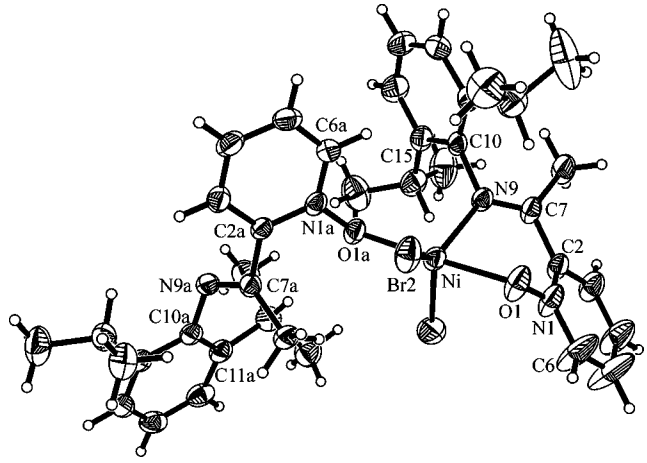
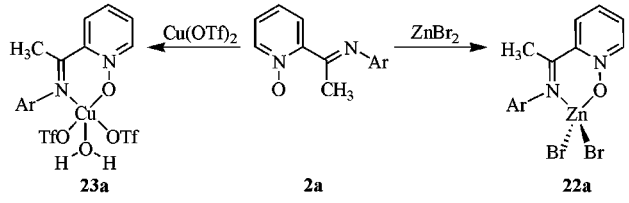


Figure 9. View of the molecular structure of complex **21a**.

In addition to the metal complexes described above, we also prepared a zinc and a copper complex of the unsubstituted N,O-ligand **2a** (see Scheme 9).



Scheme 9.

The reaction of ligand **2a** with $ZnBr_2$ in acetonitrile at room temperature yielded a bright yellow solid (**22a**). The molecular structure is depicted in Figure 10 and shows a monomeric complex with a four-coordinate zinc atom. The geometry around the metal centre can be described as distorted tetrahedral with an N9–Zn–O1 angle of 84.3(1)° and a Br1–Zn–Br2 angle of 121.60(4)°. Again, the six-membered metallacycle features a twist-boat-type conformation [dihedral angles C2–N1–O1–M = –52.3(5)° and N1–C2–C7–N9 = 26.8(7)°; all values for molecule A].

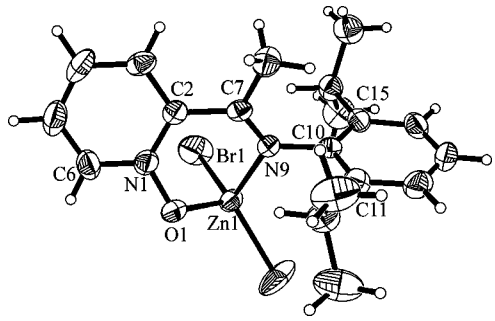


Figure 10. View of the molecular structure of complex **22a**.

Compound **23a** was obtained from the reaction of Cu(OTf)$_2$ with **2a** in dichloromethane (see Figure 11). In this case the metal centre is five-coordinate. The geometry can be regarded as distorted square-pyramidal, with the nitrogen atom of the imino bridge, the pyridine *N*-oxide oxygen atom, the oxygen atom of one triflate group and the oxygen atom of an additional water molecule as the four basal atoms [O2–Cu–N9 = 167.5(1)°; O1–Cu–O6 = 168.1(1)°]. The oxygen atom of the second triflate group occupies the axial coordination site.

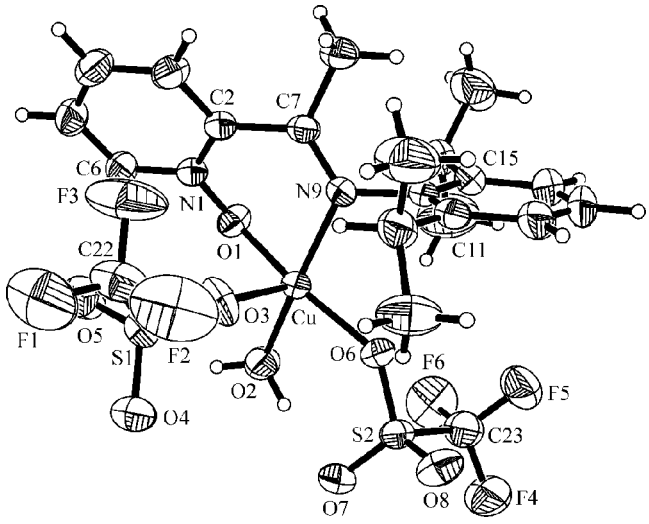


Figure 11. View of the molecular structure of complex **23a**.

We have only begun to investigate the chemistry of the (iminoethyl)pyridine *N*-oxide chelate metal complexes. In a first experiment, the (N,O-chelate)PdCl$_2$ system **19a** was employed as a catalyst in the Suzuki coupling reaction of bromobenzene with phenylboronic acid to yield biphenyl. With 3 mol-% of **19a** in the presence of the base K_2CO_3 (toluene, 80 °C, 8 h) a practically quantitative yield of the Ph-Ph coupling product was obtained, which is superior to the reaction catalysed by PdCl$_2$ alone in the absence of a supporting ligand, which gives only a 62% yield of biphenyl under these general reaction conditions. This makes it probably worthwhile to explore the catalytic potential of the [(iminoalkyl)pyridine *N*-oxide]metal complexes described in this article and related systems.

Conclusion

We have shown that pyridine *N*-oxide systems can readily be obtained in a straightforward synthetic way. The systems **2a** and **2b** in many cases serve as rather stable chelate ligands, cleanly forming the respective κN,O-coordinated complexes with a variety of metal systems. Only in an exceptional case did we observe a redox reaction that resulted in loss of the pyridine *N*-oxide oxygen atom with concurrent formation of a corresponding (iminoethyl)pyridine chelate metal complex. The (iminoethyl)pyridine *N*-oxide complexes are structural analogues of the ubiquitous (salicylimino)metal complexes. However, the (iminoethyl)pyridine *N*-oxides are neutral ligands in contrast to their negatively charged salicylimino ligand analogues. Therefore, one might envision a variety of complementary use of these chelating ligand systems, both in coordination chemistry and catalysis.

Experimental Section

General: All reactions involving air- or moisture-sensitive compounds were carried out under an inert gas using Schlenk-type glassware or in a glovebox. Solvents were dried and distilled prior to use. The following instruments were used for physical characterisation of the compounds: melting points: DSC 2010 TA-instruments; elemental analyses: Foss–Heraeus CHNO-Rapid; MS: Micromass Quattro LC-Z electrospray mass spectrometer; NMR: Bruker AC 200 P (^{1}H: 200 MHz; ^{13}C: 50 MHz), ARX 300 (^{1}H: 300 MHz; ^{13}C: 75 MHz), Varian UNITY plus NMR spectrometer (^{1}H: 600 MHz; ^{13}C: 151 MHz). 2-Isopropylpyridine (**7b**),[15] 2-*tert*-butylpyridine (**7c**),[15] 2-acetylpyridine *N*-oxide (**5a**)[14] and (2,6-diisopropylphenyl)(1-pyridin-2-ylethylidene)amine (**3a**)[13] were synthesised according to methods published elsewhere. Compounds **8b** and **8c** were synthesised by a general procedure for the preparation of amine *N*-oxides.[17] Compounds **9b** and **9c** were synthesised according to a modified Reissert–Henze reaction.[16]

X-ray Crystal Structure Determinations: Data sets were collected with Enraf Nonius CAD4 and Nonius KappaCCD diffractometers, with Mo-K_α radiation, equipped with a rotating anode generator. Programs used: data collection EXPRESS (Nonius B.V., 1994) and COLLECT (Nonius B.V., 1998); data reduction MolEN (K. Fair, Enraf–Nonius B.V., 1990) and Denzo-SMN;[21] absorption correction for CCD data SORTAV[22] and Denzo;[23] structure solution SHELXS-97;[24] structure refinement SHELXL-97;[25] graphics XP (BrukerAXS, 2000). CCDC-277028 to -277044 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.

2-Isopropylpyridine *N*-Oxide (8b): A solution of **7b** (70.0 g, 578 mmol) in chloroform (700 mL) was cooled to 0 °C and *m*-chloroperbenzoic acid (143 g, 578 mmol), dissolved in chloroform (400 mL), was added dropwise. The resulting mixture was warmed to ambient temperature within 3 h, then passed through a column of alkaline alumina. Evaporation of the solvent yielded the product as a yellow oil (63.0 g, 79%). ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 8.19 (d, ^3J = 6.4 Hz, 1 H, 6-H), 7.18 (m, 2 H, 3-H/5-H), 7.12–7.01 (m, 1 H, 4-H), 3.74 [sept, ^3J = 6.8 Hz, 1 H, C*H*(CH$_3$)$_2$], 1.24 [d, ^3J = 6.9 Hz, 6 H, CH(C*H*$_3$)$_2$] ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 °C): δ = 157.7 (C-2), 139.6 (C-6), 125.5 (C-5), 122.9 (C-4), 122.6 (C-3), 27.4 [*C*H(CH$_3$)$_2$], 20.1 [CH(*C*H$_3$)$_2$] ppm.

2-*tert*-Butylpyridine *N*-Oxide (8c): In an analogous procedure, reaction of **7c** (33.0 g, 244 mmol) in chloroform (750 mL) with *m*-chloroperbenzoic acid (60.2 g, 244 mmol) yielded **8c** as a yellow oil (29.0 g, 79%). ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 8.15 (dd, ^3J = 6.1, ^4J = 1.8 Hz, 1 H, 6-H), 7.29 (dd, ^3J = 7.9, ^4J = 2.4 Hz, 1 H, 3-H), 7.15 (dt, ^3J = 7.9, ^4J = 1.8 Hz, 1 H, 4-H), 7.11–7.02 (m, 1 H, 5-H), 1.48 [s, 9 H, C(CH_3)$_3$] ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 °C): δ = 157.9 (C-2), 141.6 (C-6), 125.3 (C-5), 123.5 (C-4), 123.4 (C-3), 36.1 [*C*(CH$_3$)$_3$], 26.8 [C(*C*H$_3$)$_3$] ppm.

6-Isopropylpyridine-2-carbonitrile (9b): Dimethylcarbamoyl chloride (52.7 mL, 574 mmol) was added dropwise to a solution of **8b** (62.3 g, 454 mmol) and trimethylsilyl cyanide (71.8 mL, 574 mmol) in dichloromethane (400 mL). The resulting mixture was stirred at room temperature for 2 d and the progress of the reaction was monitored by TLC (pentane/chloroform/triethylamine, 20:5:1). Then, a 10% aqueous K_2CO_3 solution was added and stirring continued for 15 min. The organic phase was separated and the aqueous layer extracted with dichloromethane. The combined organic layers were dried ($MgSO_4$), the solvent was evaporated and the crude product distilled to give the **9b** as a bright-yellow oil (40.2 g, 61%). ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 7.71 (t, ^3J = 7.9 Hz, 1 H, 4-H), 7.47 (dd, ^3J = 7.9, ^4J = 1.0 Hz, 1 H, 3-H), 7.36 (dd, ^3J = 7.9, ^4J = 1.0 Hz, 1 H, 5-H), 3.06 [sept, ^3J = 7.0 Hz, 1 H, C*H*(CH$_3$)$_2$], 1.25 [d, ^3J = 7.0 Hz, 6 H, CH(CH_3)$_2$] ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 °C): δ = 169.3 (C-6), 137.1 (C-4), 133.0 (C-2), 125.8 (C-3), 124.3 (C-5), 117.5 (*C*N), 36.2 [*C*H(CH$_3$)$_2$], 22.1 [CH(*C*H$_3$)$_2$] ppm.

6-*tert*-Butylpyridine-2-carbonitrile (9c):[26] Analogously to the preparation of **9b**, reaction of **8c** (29.0 g, 192 mmol), trimethylsilyl cyanide (30.4 mL, 243 mmol) and dimethylcarbamoyl chloride (22.3 mL, 243 mmol) in dichloromethane (200 mL) yielded **9c** as a bright-yellow oil (20.0 g, 65%). ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 7.72 (t, ^3J = 7.9 Hz, 1 H, 4-H), 7.53 (dd, ^3J = 7.9, ^4J = 1.1 Hz, 1 H, 3-H), 7.46 (dd, ^3J = 7.9, ^4J = 1.1 Hz, 1 H, 5-H), 1.32 [s, 9 H, C(CH_3)$_3$] ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 °C): δ = 171.4 (C-6), 137.0 (C-4), 132.7 (C-2), 125.3 (C-3), 122.7 (C-5), 117.7 (*C*N), 37.9 [*C*(CH$_3$)$_3$], 29.8 [C(*C*H$_3$)$_2$] ppm.

2-Acetyl-6-isopropylpyridine (10b): A solution of **9b** (38.0 g, 260 mmol) in diethyl ether (400 mL) was cooled to –25 °C and methyllithium (179 mL, 286 mmol, 1.6 M solution in diethyl ether) was added dropwise. The reaction mixture was warmed to ambient temperature within 2 h and then quenched with a mixture of aqueous ammonium chloride solution and hydrochloric acid. The organic phase was separated and the aqueous phase extracted with diethyl ether. The ethereal solution was dried (Na_2SO_4) and the solvent evaporated. Distillation yielded the product as a colourless oil (10.6 g, 25%). ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 7.79 (dd, ^3J = 7.7, ^4J = 1.2 Hz, 1 H, 5-H), 7.67 (t, ^3J = 7.7 Hz, 1 H, 4-H), 7.28 (dd, ^3J = 7.7, ^4J = 1.2 Hz, 1 H, 3-H), 3.07 [sept, ^3J = 7.0 Hz, 1 H, C*H*(CH$_3$)$_2$], 2.68 (s, 3 H, COCH_3), 1.29 [d, ^3J = 7.0 Hz, 6 H, CH(CH_3)$_2$] ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 °C): δ = 200.8 (*C*O), 166.6 (C-6), 153.0 (C-2), 136.8 (C-4), 124.2 (C-3), 118.6 (C-5), 36.0 [*C*H(CH$_3$)$_2$], 25.5 (CO*C*H$_3$), 22.4 [CH(*C*H$_3$)$_2$] ppm. $C_{10}H_{13}NO$ (163.22): calcd. C 73.59, H 8.03, N 8.58, found C 73.30, H 8.21, N 8.94.

2-Acetyl-6-*tert*-butylpyridine (10c): Analogously to the preparation of **10b**, **10c** was prepared from the reaction of **9c** (18.4 g, 115 mmol) with methyllithium (79.4 mL, 127 mmol, 1.6 M solution in diethyl ether) in diethyl ether (180 mL). After aqueous workup and distillation, the product was obtained as a colourless oil (7.33 g, 36%). ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 7.79 (dd, ^3J = 7.7, ^4J = 1.3 Hz, 1 H, 3-H), 7.69 (t, ^3J = 7.7 Hz, 1 H, 4-H), 7.46 (dd, ^3J = 7.7, ^4J = 1.3 Hz, 1 H, 5-H), 2.69 (s, 3 H, COCH_3), 1.36 [s, 9 H, C(CH_3)$_3$] ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 °C): δ = 201.0 (*C*O), 168.7 (C-6), 152.4 (C-2), 136.8 (C-4), 122.4 (C-5), 118.1 (C-3), 37.6 [*C*(CH$_3$)$_3$], 30.5 [C(*C*H$_3$)$_3$], 25.6 (CO*C*H$_3$) ppm. $C_{11}H_{15}NO$ (177.24): calcd. C 74.54, H 8.53, N 7.90; found C 74.30, H 8.64, N 7.85.

2-Acetyl-6-isopropylpyridine *N*-Oxide (11b): Compound **10b** (6.00 g, 36.8 mmol), dissolved in glacial acetic acid (25 mL), was treated with hydrogen peroxide solution (5.6 mL, 30%). The mixture was allowed to react at 70–80 °C for 10 h. Additional hydrogen peroxide solution (4.6 mL, 30%) was then added and the mixture was heated for another 10 h. After cooling to room temperature, the solvent was evaporated and the crude residue was treated with sodium carbonate solution. The aqueous phase was extracted with dichloromethane, the combined organic layers dried (Na_2SO_4) and the solvent evaporated. The product was obtained as a yellow oil (3.99 g, 61%). ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 7.40 (dd, ^3J = 7.8, ^4J = 2.2 Hz, 1 H, 3-H), 7.30 (dd, ^3J = 7.8, ^4J = 2.2 Hz, 1 H, 5-H), 7.21 (t, ^3J = 7.8 Hz, 1 H, 4-H), 3.72 [sept, ^3J = 7.1 Hz, 1 H, C*H*(CH$_3$)$_2$], 2.71 (s, 3 H, COCH_3), 1.26 [d, ^3J = 7.1 Hz, 6 H, CH(CH_3)$_2$] ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 °C): δ = 196.1 (*C*O), 158.6 (C-6), 147.5 (C-2), 124.9 (C-4), 124.3 (C-5), 123.4 (C-3), 30.2 (CO*C*H$_3$), 27.2 [*C*H(CH$_3$)$_2$], 20.1 [CH(*C*H$_3$)$_2$] ppm. $C_{10}H_{13}NO_2$ (179.22): calcd. C 67.02, H 7.31, N 7.82; found C 66.63, H 7.49, N 8.11.

General Procedure for the Preparation of the Ketimines 3a, 3b, 2a, 2b: A mixture of the appropriate 2-acetylpyridine compound (12 mmol), 2,6-diisopropylaniline (16 mmol), a catalytic amount of formic acid and sodium sulfate in methanol was refluxed for several hours. The progress of the reaction was monitored by TLC. After cooling to room temperature, the precipitate was removed by filtration, the solvent was evaporated and the crude product purified by column chromatography on silica gel. In most cases crystals suitable for the X-ray crystal structure analysis were grown from pentane at room temperature by means of solvent evaporation.

(2,6-Diisopropylphenyl)[1-(pyridin-2-yl)ethylidene]amine (3a): Formula $C_{19}H_{24}N_2$, M = 280.40, light yellow crystal 0.50 × 0.30 × 0.10 mm, a = 8.469(1), b = 9.503(1), c = 11.790(1) Å, α = 108.47(1), β = 103.82(1), γ = 100.68(1)°, V = 838.1(2) Å^3, $\rho_{calcd.}$ = 1.111 g cm^{-3}, μ = 0.65 cm^{-1}, no absorption correction (0.968 ≤ T ≤ 0.994), Z = 2, triclinic, space group $P\bar{1}$ (no. 2), λ = 0.71073 Å, T = 198 K, ω and φ scans, 5134 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.62 Å^{-1}, 3372 independent (R_{int} = 0.019) and 2651 observed reflections [$I \geq 2\sigma(I)$], 195 refined parameters, R = 0.047, wR^2 = 0.124, max. residual electron density 0.18 (–0.16) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

(2,6-Diisopropylphenyl)[1-(6-isopropylpyridin-2-yl)ethylidene]amine (3b): Reaction of 2-acetyl-6-isopropylpyridine (**10b**; 3.51 g, 21.5 mmol) with 2,6-diisopropylaniline (5.4 mL, 28.7 mmol) yielded a yellow solid (5.87 g, 85%) after column chromatography (SiO_2; pentane/ethyl acetate, 20:1). M.p. 81 °C. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 8.18 (br. d, 1 H, 3-H$_{py}$), 7.71 (t, ^3J = 7.7 Hz, 1 H, 4-H$_{py}$), 7.25 (d, ^3J = 7.7 Hz, 1 H, 5-H$_{py}$), 7.16 (m, 2 H, 3-/5-H$_{ar}$), 7.09 (m, 1 H, 4-H$_{ar}$), 3.12 [sept, ^3J = 6.9 Hz, 1 H, C*H*(CH$_3$)$_{2py}$], 2.77 [sept, ^3J = 6.9 Hz, 2 H, C*H*(CH$_3$)$_{2ar}$], 2.22 (s, 3 H, CNCH_3), 1.35 [d, ^3J = 6.9 Hz, 6 H, CH(CH_3)$_{2py}$], 1.15 [d, ^3J = 6.9 Hz, 12 H, CH(CH_3)$_{2ar}$] ppm. ^{1}H NMR (600 MHz, $CDCl_3$, –65 °C): δ = 8.14 (d, ^3J = 7.6 Hz, 1 H, 3-H$_{py}$), 7.75 (t, ^3J = 7.6 Hz, 1 H, 4-H$_{py}$), 7.29 (d, ^3J = 7.6 Hz, 1 H, 5-H$_{py}$), 7.19 (m, 2 H, 3-/5-H$_{ar}$), 7.14 (m, 1 H, 4-H$_{ar}$), 3.08 [sept, ^3J = 6.7 Hz, 1 H, C*H*-(CH$_3$)$_{2py}$], 2.74 [sept, ^3J = 6.7 Hz, 2 H, C*H*(CH$_3$)$_{2ar}$], 2.22 (s, 3 H, CNCH_3), 1.32 [d, ^3J = 6.7 Hz, 6 H, CH(CH_3)$_{2py}$], 1.12 [d, ^3J =

6.7 Hz, 6 H, CH(CH_3^ACH_3^B)$_{ar}$], 1.10 [d, ^3J = 6.7 Hz, 6 H, CH(CH_3^ACH_3^B)$_{ar}$] ppm. ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, –65 °C): δ = 167.7 (*C*N), 165.9 (C-6$_{py}$), 154.7 (C-2$_{py}$), 145.9 (C-1$_{ar}$), 136.7 (C-4$_{py}$), 135.8 (C-2/–6$_{ar}$), 123.1 (C-4$_{ar}$), 122.7 (C-3/–5$_{ar}$), 121.7 (C-5$_{py}$), 118.2 (C-3$_{py}$), 36.2 [*C*H(CH$_3$)$_{2py}$], 27.7 [*C*H(CH$_3$)$_{2ar}$], 23.1 [CH(CH$_3^A$*C*H$_3^B$)$_{ar}$], 23.0 [CH(*C*H$_3^A$CH$_3^B$)$_{ar}$], 22.7 [CH(*C*H$_3$)$_{2py}$], 17.5 (CN*C*H$_3$) ppm. MS (ESI): *m*/*z* (%) = 345.3 (100) [M + Na]$^+$, 323 (12) [M + H]$^+$. $C_{22}H_{30}N_2$ (322.49): calcd. C 81.94, H 9.38, N 8.69; found C 81.75, H 9.32, N, 8.64.

X-ray Crystal Structure Analysis of 3b: Formula $C_{22}H_{30}N_2$, M = 322.48, colourless crystal 0.45 × 0.30 × 0.20 mm, a = 11.486(1), b = 17.360(1), c = 11.529(1) Å, β = 117.34(1)°, V = 2042.1(3) Å^3, $\rho_{calcd.}$ = 1.049 g cm^{-3}, μ = 4.59 cm^{-1}, no absorption correction (0.820 ≤ T ≤ 0.914), Z = 4, monoclinic, space group $P2_1/c$ (no. 14), λ = 1.54178 Å, T = 223 K, ω and φ scans, 11145 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.59 Å^{-1}, 3444 independent (R_{int} = 0.022) and 2708 observed reflections [$I \geq 2\sigma(I)$], 225 refined parameters, R = 0.046, wR^2 = 0.133, max. residual electron density 0.28 (–0.18) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

2-[1-(2,6-Diisopropylphenylimino)ethyl]pyridine *N*-Oxide (2a): Reaction of 2-acetylpyridine *N*-oxide (5.77 g, 42.1 mmol) with 2,6-diisopropylaniline (10.6 mL, 56.0 mmol) yielded a yellow solid (8.36 g, 67%) after column chromatography (SiO_2; pentane/chloroform/triethylamine/methanol, 4:1:1:1). M.p. 80 °C. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 8.23 (m, ^3J = 6.4 Hz, 1 H, 6-H$_{py}$), 7.62 (dd, ^3J = 7.6, ^4J = 2.3 Hz, 1 H, 3-H$_{py}$), 7.35 (dt, ^3J = 7.6, ^4J = 1.3 Hz, 1 H, 4-H$_{py}$), 7.32 (ddd, ^3J = 7.6, ^3J = 6.4, ^4J = 2.3 Hz, 1 H, 5-H$_{py}$), 7.16 (m, 2 H, 3-/5-H$_{ar}$), 7.10 (m, 1 H, 4-H$_{ar}$), 2.88 [sept, ^3J = 6.8 Hz, 2 H, C*H*(CH$_3$)$_{2ar}$], 2.19 (s, 3 H, CNC*H*$_3$), 1.22 [d, ^3J = 6.8 Hz, 6 H, CH(CH_3^ACH$_3^B$)$_{ar}$], 1.16 [d, ^3J = 6.8 Hz, 6 H, CH(CH$_3^A$CH_3^B)$_{ar}$] ppm. ^{1}H NMR (600 MHz, $CDCl_3$, –60 °C): δ = 8.27 (d, ^3J = 6.3 Hz, 1 H, 6-H$_{py}$), 7.66 (d, ^3J = 7.6 Hz, 1 H, 3-H$_{py}$), 7.46 (t, ^3J = 7.6 Hz, 1 H, 4-H$_{py}$), 7.41 (m, 1 H, 5-H$_{py}$), 7.19 (m, 2 H, 3-/5-H$_{ar}$), 7.16 (m, 1 H, 4-H$_{ar}$), 2.82 [sept, ^3J = 6.8 Hz, 2 H, C*H*(CH$_3$)$_{2ar}$], 2.17 (s, 3 H, CNC*H*$_3$), 1.19 [d, ^3J = 6.8 Hz, 6 H, CH(CH_3^ACH$_3^B$)$_{ar}$], 1.13 [d, ^3J = 6.8 Hz, 6 H, CH(CH$_3^A$CH_3^B)$_{ar}$] ppm. ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, 25 °C): δ = 164.9 (*C*N), 149.4 (C-2$_{py}$), 144.4 (C-1$_{ar}$), 140.1 (C-6$_{py}$), 136.1 (C-2/–6$_{ar}$), 128.0 (C-4$_{py}$), 126.9 (C-5$_{py}$), 126.1 (C-3$_{py}$), 124.3 (C-4$_{ar}$), 123.1 (C-3/–5$_{ar}$), 28.1 [*C*H(CH$_3$)$_{2ar}$], 23.4 [CH(CH$_3^A$*C*H$_3^B$)$_{ar}$], 22.9 [CH(*C*H$_3^A$CH$_3^B$)$_{ar}$], 19.8 (CN*C*H$_3$) ppm. MS (ESI): *m*/*z* (%) = 319 (100) [M + Na]$^+$, 297 (85) [M + H]$^+$. $C_{19}H_{24}N_2O$ (296.41): calcd. C 76.99, H 8.16, N 9.45; found C 76.87, H 8.10, N 9.37.

X-ray Crystal Structure Analysis of 2a: Formula $C_{19}H_{24}N_2O$, M = 296.40, yellow crystal 0.35 × 0.25 × 0.15 mm, a = 8.698(1), b = 8.800(1), c = 11.502(1) Å, α = 103.05(1), β = 95.07(1), γ = 97.15(1)°, V = 844.8(2) Å^3, $\rho_{calcd.}$ = 1.165 g cm^{-3}, μ = 5.62 cm^{-1}, empirical absorption correction (0.828 ≤ T ≤ 0.920), Z = 2, triclinic, space group $P\bar{1}$ (no. 2), λ = 1.54178 Å, T = 223 K, $\omega/2\theta$ scans, 3610 reflections collected (±h, ±k, -l), [(sinθ)/λ] = 0.62 Å^{-1}, 3433 independent (R_{int} = 0.023) and 2840 observed reflections [$I \geq 2\sigma(I)$], 205 refined parameters, R = 0.043, wR^2 = 0.126, max. residual electron density 0.20 (–0.20) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

2-[1-(2,6-Diisopropylphenylimino)ethyl]-6-isopropylpyridine *N*-Oxide (2b): Reaction of 2-acetyl-6-isopropylpyridine *N*-oxide (3.21 g, 17.9 mmol) with 2,6-diisopropylaniline (4.5 mL, 23.9 mmol) yielded, after column chromatography (SiO_2; pentane/chloroform/methanol, 20:3:1), 2.47 g (41%) of a yellow solid. M.p. 117 °C. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 7.46 (br. m, 1 H, 3-H$_{py}$), 7.31 (m, 2 H, 4-/5-H$_{py}$), 7.16 (m, 2 H, 3-/5-H$_{ar}$), 7.10 (m, 1 H, 4-H$_{ar}$), 3.85 [sept, ^3J = 6.9 Hz, 1 H, C*H*(CH$_3$)$_{2py}$], 2.92 [sept, ^3J = 6.9 Hz, 2 H, C*H*(CH$_3$)$_{2ar}$], 2.17 (s, 3 H, CNC*H*$_3$), 1.31 [d, ^3J = 6.9 Hz, 6 H, CH(C*H*$_3$)$_{2py}$], 1.23 [d, ^3J = 6.9 Hz, 6 H, CH(CH_3^ACH$_3^B$)$_{ar}$], 1.16 [d, ^3J = 6.9 Hz, 6 H, CH(CH$_3^A$CH_3^B)$_{ar}$] ppm. ^{1}H NMR (600 MHz, $CDCl_3$, –60 °C): δ = 7.46 (dd, ^3J = 7.7, ^4J = 2.1 Hz, 1 H, 3-H$_{py}$), 7.41 (t, ^3J = 7.7 Hz, 1 H, 4-H$_{py}$), 7.37 (dd, ^3J = 7.7, ^4J = 2.1 Hz, 1 H, 5-H$_{py}$), 7.19 (m, 2 H, 3-/5-H$_{ar}$), 7.15 (m, 1 H, 4-H$_{ar}$), 3.84 [sept, ^3J = 6.8 Hz, 1 H, C*H*(CH$_3$)$_{2py}$], 2.87 [sept, ^3J = 6.8 Hz, 2 H, C*H*(CH$_3$)$_{2ar}$], 2.15 (s, 3 H, CNC*H*$_3$), 1.28 [d, ^3J = 6.8 Hz, 6 H, CH(C*H*$_3$)$_{2py}$], 1.19 [d, ^3J = 6.8 Hz, 6 H, CH(CH_3^ACH$_3^B$)$_{ar}$], 1.14 [d, ^3J = 6.8 Hz, 6 H, CH(CH$_3^A$CH_3^B)$_{ar}$] ppm. ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, 25 °C): δ = 165.8 (*C*N), 158.3 (C-6$_{py}$), 149.5 (C-2$_{py}$), 144.2 (C-1$_{ar}$), 136.3 (C-2/–6$_{ar}$), 125.4 (C-4$_{py}$), 124.2 (C-4$_{ar}$), 123.2 (C-3$_{py}$), 123.1 (C-3/–5$_{ar}$, C-5$_{py}$), 28.0 [*C*H(CH$_3$)$_{2ar}$], 27.2 [*C*H(CH$_3$)$_{2py}$], 23.5 [CH(CH$_3^A$*C*H$_3^B$)$_{ar}$], 22.9 [CH(*C*H$_3^A$CH$_3^B$)$_{ar}$], 20.5 [CH(*C*H$_3$)$_{2py}$], 19.9 (CN*C*H$_3$) ppm. MS (ESI): *m*/*z* (%) = 361 (45) [M + Na]$^+$, 339 (100) [M + H]$^+$. $C_{22}H_{30}N_2O$ (338.49): calcd. C 78.06, H 8.93, N 8.28; found C 77.92, H 9.05, N 8.16.

X-ray Crystal Structure Analysis of 2b: Formula $C_{22}H_{30}N_2O$, M = 338.48, colourless crystal 0.40 × 0.25 × 0.20 mm, a = 8.534(1), b = 14.593(1), c = 16.546(1) Å, β = 92.64(1)°, V = 2058.4(3) Å^3, $\rho_{calcd.}$ = 1.092 g cm^{-3}, μ = 5.14 cm^{-1}, empirical absorption correction (0.821 ≤ T ≤ 0.904), Z = 4, monoclinic, space group $P2_1$ (no. 4), λ = 1.54178 Å, T = 293 K, $\omega/2\theta$ scans, 4517 reflections collected (±h, –k, +l), [(sinθ)/λ] = 0.62 Å^{-1}, 4369 independent (R_{int} = 0.035) and 3210 observed reflections [$I \geq 2\sigma(I)$], 466 refined parameters, R = 0.045, wR^2 = 0.136, Flack parameter 0.0(4), max. residual electron density 0.21 (–0.16) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

General Procedure for the Preparation of Metal Complexes: The metal precursor (1 mmol) was suspended in the appropriate solvent (20 mL), stirred, and a solution of the ligand (1 mmol) in the same solvent (10 mL) was added. The resulting mixture was stirred for several hours. For workup, the mixture was filtered, the solvent evaporated, the crude product washed with pentane and dried in vacuo. In most cases crystals suitable for X-ray analyses were grown from a concentrated solution of the complex in a mixture of acetonitrile/dichloromethane/THF layered with pentane.

Reaction of Ligand 3b with $FeCl_2$; Synthesis of Compound 12b: A suspension of anhydrous $FeCl_2$ (393 mg, 3.1 mmol) in THF was heated to 70 °C and a solution of **3b** (1.00 g, 3.1 mmol) in THF was added. The resulting mixture was stirred for 2 h. After workup and drying, the product was obtained as brown powder (1.22 g, 87%). MS (ESI): *m*/*z* (%) = 535.3 (100) [$FeCl_2$(**3b**) + BF_4]$^-$. $C_{22}H_{30}Cl_2FeN_2$ (449.24): calcd. C 58.82, H 6.73, N 6.24; found C 57.01, H 6.67, N, 5.71.

X-ray Crystal Structure Analysis of 12b: Formula $C_{22}H_{30}Cl_2FeN_2 \cdot C_4H_8O$, M = 521.33, red crystal 0.30 × 0.25 × 0.15 mm, a = 8.701(1), b = 15.738(1), c = 20.229(1) Å, β = 97.33(1)°, V = 2747.4(4) Å^3, $\rho_{calcd.}$ = 1.260 g cm^{-3}, μ = 7.63 cm^{-1}, empirical absorption correction (0.803 ≤ T ≤ 0.894), Z = 4, monoclinic, space group $P2_1/c$ (no. 14), λ = 0.71073 Å, T = 198 K, ω and φ scans, 16643 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.66 Å^{-1}, 6533 independent (R_{int} = 0.047) and 4332 observed reflections [$I \geq 2\sigma(I)$], 282 refined parameters, R = 0.069, wR^2 = 0.226, max. residual electron density 1.19 (–0.74) e Å^{-3}, solvent molecule disordered, refined with split positions, geometrical restraints, fixed occupancies (0.67:0.33) and one common isotropic displacement parameter, hydrogen atoms calculated and refined as riding atoms.

Reaction of Ligand 3b with $CoCl_2$; Synthesis of Compound 13b: Complex **13b** was prepared in an analogous procedure. Reaction

of $CoCl_2$ (402 mg, 3.1 mmol) and **3b** (1.00 g, 3.1 mmol) in THF yielded a green-blue powder (1.05 g, 74%). MS (ESI): *m*/*z* (%) = 451.1 (100) $[CoCl_2(\mathbf{3b})]^+$. $C_{22}H_{30}Cl_2CoN_2$ (452.33): calcd. C 58.42, H 6.69, N 6.19; found C 58.63, H 7.00, N 5.25.

X-ray Crystal Structure Analysis of 13b: Formula $C_{22}H_{30}Cl_2CoN_2{\cdot}0.5CH_2Cl_2{\cdot}0.5C_4H_8O$, M = 530.83, turquoise crystal 0.40 × 0.05 × 0.05 mm, a = 8.679(1), b = 15.655(1), c = 20.196(1) Å, β = 97.93(1)°, V = 2717.8(4) Å^3, $\rho_{calcd.}$ = 1.297 g cm^{-3}, μ = 9.42 cm^{-1}, empirical absorption correction (0.704 ≤ T ≤ 0.954), Z = 4, monoclinic, space group $P2_1/c$ (no. 14), λ = 0.71073 Å, T = 198 K, ω and φ scans, 15372 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.59 Å^{-1}, 4789 independent (R_{int} = 0.091) and 2800 observed reflections [$I \geq 2\sigma(I)$], 323 refined parameters, R = 0.056, wR^2 = 0.116, max. residual electron density 0.33 (–0.45) e Å^{-3}, solvent molecules sharing same side refined with split positons and fixed occupancies (0.5), hydrogen atoms calculated and refined as riding atoms.

Reaction of Ligand 3b with $[NiBr_2(dme)]$; Synthesis of Compound 14b: A suspension of $[NiBr_2(dme)]$ (948 mg, 3.1 mmol) in dichloromethane was treated with a solution of **3b** (1.0 g, 3.1 mmol) in dichloromethane. The resulting mixture was stirred at room temperature for 24 h. After workup, the product was isolated as a light-brown powder (1.19 g, 71%). MS (ESI) *m*/*z* (%) = 461.3 (83) $[NiBr(\mathbf{3b})]^+$, 323.4 (25) $[\mathbf{3b} + H]^+$, 189.1 (100). $C_{22}H_{30}Br_2N_2Ni$ (540.99): calcd. C 48.84, H 5.59, N 5.18; found C 48.81, H 5.51, N 5.04.

X-ray Crystal Structure Analysis of 14b: Formula $C_{22}H_{30}Br_2N_2Ni$, M = 541.01, yellow crystal 0.50 × 0.30 × 0.08 mm, a = 8.685(1), b = 19.351(1), c = 27.866(1) Å, V = 4683.3(6) Å^3, $\rho_{calcd.}$ = 1.535 g cm^{-3}, μ = 42.50 cm^{-1}, empirical absorption correction (0.225 ≤ T ≤ 0.727), Z = 8, orthorhombic, space group $Pbca$ (no. 61), λ = 0.71073 Å, T = 198 K, ω and φ scans, 10395 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.66 Å^{-1}, 5573 independent (R_{int} = 0.036) and 4039 observed reflections [$I \geq 2\sigma(I)$], 251 refined parameters, R = 0.038, wR^2 = 0.079, max. residual electron density 0.91 (–0.89) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Reaction of Ligand 3a with $FeCl_2$; Synthesis of Compound 15a: Reaction of $FeCl_2$ (1.00 g, 7.89 mmol) in THF with **3a** (2.21 g, 7.89 mmol) at 80 °C yielded a black solid (1.99 g, 62%).

X-ray Crystal Structure Analysis of 15a: Formula $C_{19}H_{24}Cl_2FeN_2$, M = 407.15, red crystal 0.30 × 0.25 × 0.15 mm, a = 14.151(1), b = 10.073(1), c = 14.431(1) Å, β = 109.97(1)°, V = 1933.4(3) Å^3, $\rho_{calcd.}$ = 1.399 g cm^{-3}, μ = 10.59 cm^{-1}, empirical absorption correction (0.742 ≤ T ≤ 0.857), Z = 4, monoclinic, space group $P2_1/n$ (no. 14), λ = 0.71073 Å, T = 198 K, ω and φ scans, 6709 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.62 Å^{-1}, 3913 independent (R_{int} = 0.043) and 2907 observed reflections [$I \geq 2\sigma(I)$], 222 refined parameters, R = 0.096, wR^2 = 0.291, max. residual electron density 1.97 (–0.62) e Å^{-3}, the remaining electron density is located around x,0,z, all attempts to refine these in a chemically meaningful way failed, analysis only done to confirm the geometry of the complex, hydrogen atoms calculated and refined as riding atoms.

Reaction of Ligand 3a with $CoCl_2$; Synthesis of Compound 16a: In an analogous procedure, complex **16a** was obtained by treating $CoCl_2$ (1.0 g, 7.70 mmol) with compound **3a** (2.16 g, 7.70 mmol) in THF and collected as a green powder (2.10 g, 66%). MS (ESI): *m*/*z* (%) = 496.1 (100) $[CoCl_2(\mathbf{3a}) + BF_4]^-$. $C_{19}H_{24}Cl_2CoN_2$ (410.25): calcd. C 55.63, H 5.90, N 6.83; found C 56.96, H 6.90, N 5.10.

X-ray Crystal Structure Analysis of 16a: Formula $C_{19}H_{24}Cl_2CoN_2$, M = 410.23, pink crystal 0.30 × 0.25 × 0.10 mm, a = 14.132(1), b = 10.132(1), c = 14.308(1) Å, β = 110.48(1)°, V = 1919.2(3) Å^3, $\rho_{calcd.}$ = 1.420 g cm^{-3}, μ = 11.75 cm^{-1}, empirical absorption correction (0.719 ≤ T ≤ 0.892), Z = 4, monoclinic, space group $P2_1/n$ (no. 14), λ = 0.71073 Å, T = 198 K, ω and φ scans, 21540 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.66 Å^{-1}, 4559 independent (R_{int} = 0.044) and 3700 observed reflections [$I \geq 2\sigma(I)$], 222 refined parameters, R = 0.031, wR^2 = 0.070, max. residual electron density 0.30 (–0.32) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Reaction of Ligand 3a with $[NiBr_2(dme)]$; Synthesis of Compound 17a: A suspension of $[NiBr_2(dme)]$ (680 mg, 2.22 mmol) in dichloromethane was treated with a solution of **3a** (622 mg, 2.22 mmol) in dichloromethane. The resulting mixture was stirred at room temperature for 2 d, then another 300 mg of **3a** (1.07 mmol) was added, and stirring was continued for 2 d. After workup, compound **17a** was isolated as a green solid (1.46 g, 84%). MS (ESI): *m*/*z* (%) = 699.4 (100) $[NiBr(\mathbf{3a})_2]^+$. $C_{38}H_{48}Br_2N_4Ni$ (779.32): calcd. C 58.57, H 6.21, N 7.19; found C 57.46, H 6.48, N 6.82.

Reaction of Ligand 2a with $FeCl_2$; Synthesis of Compound 18a: The reaction of $FeCl_2$ (107 mg, 0.84 mmol) with **2a** (500 mg, 1.69 mmol) in THF at room temperature yielded a black powder (0.52 mmol, 62%). MS (ESI): *m*/*z* (%) = 651.4 (100) $[FeCl(\mathbf{3a})]^+$, 102.0 (45). $C_{38}H_{48}Cl_5Fe_2N_4$ (849.77): calcd. C 53.71, H 5.69, N 6.59; found C 53.02, H 5.78, N 6.58.

X-ray Crystal Structure Analysis of 18a: Formula $C_{38}H_{48}ClFeN_4{\cdot}FeCl_4$, M = 849.76, red crystal 0.30 × 0.30 × 0.10 mm, a = 8.835(1), b = 15.414(1), c = 15.138(1) Å, β = 95.31(1)°, V = 2052.7(3) Å^3, ρ_{calc} = 1.375 g cm^{-3}, μ = 10.64 cm^{-1}, empirical absorption correction (0.741 ≤ T ≤ 0.901), Z = 2, monoclinic, space group $P2_1$ (no. 4), λ = 0.71073 Å, T = 198 K, ω and φ scans, 17177 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.59 Å^{-1}, 6886 independent (R_{int} = 0.064) and 6040 observed reflections [$I \geq 2\sigma(I)$], 452 refined parameters, R = 0.099, wR^2 = 0.267, Flack parameter 0.01(4), max. residual electron density 2.42 (–0.56) e Å^{-3}, very poor, partly amorphous crystal leads to an analysis of limited accuracy, hydrogen atoms calculated and refined as riding atoms.

Reaction of Ligand 2a with $PdCl_2$; Synthesis of Compound 19a: A suspension of $PdCl_2$ (500 mg, 2.82 mmol) in acetonitrile was treated with a solution of **2a** (836 mg, 2.82 mmol) in acetonitrile. After workup, the product was obtained as an orange solid (1.0 g, 75%). ^{1}H NMR (600 MHz, CH_3CN, 25 °C): δ = 8.68 (dd, ^3J = 6.5, ^4J = 1.3 Hz, 1 H, 6-H_{py}), 8.18 (dd, ^3J = 8.0, ^4J = 1.8 Hz, 1 H, 3-H_{py}), 8.08 (dt, ^3J = 8.0, ^4J = 1.3 Hz, 1 H, 4-H_{py}), 7.82 (ddd, ^3J = 8.0, ^3J = 6.5, ^4J = 1.8 Hz, 1 H, 5-H_{py}), 7.33 (m, 2 H, 3-/5-H_{ar}), 7.28 (m, 1 H, 4-H_{ar}), 3.32 [sept, ^3J = 6.8 Hz, 2 H, CH(CH$_3$)$_{2ar}$], 2.23 (s, 3 H, CNCH_3), 1.59 [d, ^3J = 6.8 Hz, 6 H, CH(CH_3^ACH$_3^B$)$_{ar}$], 1.19 [d, ^3J = 6.8 Hz, 6 H, CH(CH$_3^A$CH_3^B)$_{ar}$] ppm. MS (ESI): *m*/*z* (%) = 561.0 (100) $[PdCl_2(\mathbf{2a}) + BF_4]^-$. $C_{19}H_{24}Cl_2N_2OPd$ (473.73): calcd. C 48.17, H 5.11, N 5.91; found C 47.94, H 5.49, N 5.97.

X-ray Crystal Structure Analysis of 19a: Formula $C_{19}H_{24}Cl_2N_2OPd{\cdot}C_2H_3N$, M = 514.76, red crystal 0.50 × 0.40 × 0.30 mm, a = 9.307(1), b = 17.942(1), c = 13.611(1) Å, β = 97.51(1)°, V = 2253.4(3) Å^3, $\rho_{calcd.}$ = 1.517 g cm^{-3}, μ = 10.77 cm^{-1}, empirical absorption correction (0.615 ≤ T ≤ 0.738), Z = 4, monoclinic, space group $P2_1/n$ (no. 14), λ = 0.71073 Å, T = 198 K, ω and φ scans, 14417 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.66 Å^{-1}, 5323 independent (R_{int} = 0.034) and 5074 observed reflections [$I \geq 2\sigma(I)$], 259 refined parameters, R = 0.026, wR^2 = 0.068, max. residual electron density 1.04 (–0.83) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Reaction of Ligand 2a with $CoCl_2$; Synthesis of Compound 20a: Reaction of $CoCl_2$ (1.0 g, 77 mol) with **2a** (2.28 g, 77 mmol) in THF yielded a blue powder (3.12 g, 95%). $C_{19}H_{24}Cl_2CoN_2O$ (426,25): calcd. C 53.54, H 5.68, N 6.57; found C 54.79, H 6.65, N 5.95.

X-ray Crystal Structure Analysis of 20a: Formula $C_{19}H_{24}Cl_2CoN_2O{\cdot}C_5H_{12}$, M = 498.38, green crystal 0.60 × 0.10 × 0.05 mm, a = 32.646(1), b = 10.395(1), c = 13.788(1) Å, β = 93.73(1)°, V = 4669.1(6) Å^3, $\rho_{calcd.}$ = 1.418 g cm^{-3}, μ = 9.83 cm^{-1}, empirical absorption correction (0.590 ≤ T ≤ 0.953), Z = 8, monoclinic, space group $C2/c$ (no. 15), λ = 0.71073 Å, T = 198 K, ω and φ scans, 24564 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.67 Å^{-1}, 5836 independent (R_{int} = 0.054) and 3644 observed reflections [$I \geq 2\sigma(I)$], 251 refined parameters, R = 0.052, wR^2 = 0.166, max. residual electron density 0.48 (–0.41) e Å^{-3}, solvent molecule refined as pentane with geometrical restraints, hydrogen atoms calculated and refined as riding atoms.

Reaction of Ligand 2a with [$NiBr_2$(dme)]; Synthesis of Compound 21a: A solution of the ligand **2a** (0.77 g, 26 mmol) in dichloromethane was added to a suspension of [$NiBr_2$(dme)] (1.0 g, 26 mmol) in dichloromethane. The resulting mixture was refluxed for 2 h. After workup, compound **21a** was obtained as a brown solid (1.17 g, 54%). MS (ESI): m/z (%) = 731.3 (40) [NiBr(**2a**)$_2$]$^+$, 325.2 (80), 297.2 (100), 178.0 (70), 101.9 (70).

X-ray Crystal Structure Analysis of 21a: Formula $C_{38}H_{48}Br_2N_4NiO_2$, M = 811.33, red crystal 0.35 × 0.30 × 0.20 mm, a = 11.156(1), b = 30.146(1), c = 12.011(1) Å, β = 109.81(1)°, V = 3800.4(5) Å^3, $\rho_{calcd.}$ = 1.418 g cm^{-3}, μ = 26.50 cm^{-1}, empirical absorption correction (0.457 ≤ T ≤ 0.619), Z = 4, monoclinic, space group $P2_1/c$ (no. 14), λ = 0.71073 Å, T = 198 K, ω and φ scans, 22711 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.62 Å^{-1}, 7688 independent (R_{int} = 0.059) and 4718 observed reflections [$I \geq 2\sigma(I)$], 434 refined parameters, R = 0.047, wR^2 = 0.103, max. residual electron density 0.63 (–0.52) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Reaction of Ligand 2b with [$NiBr_2$(dme)]; Synthesis of Compound 21b: [$NiBr_2$(dme)] (453 mg, 1.48 mmol) was suspended in dichloromethane and **2b** (500 mg, 1.48 mmol) in dichloromethane was added. After workup compound **21b** was isolated as dark-brown solid (610 mg, 74%). MS (ESI) m/z (%) = 477.3 (100) [NiBr(**2b**)]$^+$, 339.4 (61) [**2b** + H]$^+$. $C_{22}H_{30}Br_2N_2NiO$ (556.99): calcd. C 47.44, H 5.43, N 5.03; found C 48.02, H 5.40, N 4.83.

X-ray Crystal Structure Analysis of 21b: Formula $C_{26}H_{38}Br_2N_2NiO_2$, M = 629.11, red crystal 0.75 × 0.15 × 0.10 mm, a = 8.744(1), b = 33.910(1), c = 9.367(1) Å, β = 95.39(1)°, V = 2765.1(4) Å^3, $\rho_{calcd.}$ = 1.511 g cm^{-3}, μ = 36.16 cm^{-1}, empirical absorption correction (0.172 ≤ T ≤ 0.714), Z = 4, monoclinic, space group $P2_1/n$ (no. 14), λ = 0.71073 Å, T = 198 K, ω and φ scans, 19041 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.68 Å^{-1}, 6690 independent (R_{int} = 0.054) and 5100 observed reflections [$I \geq 2\sigma(I)$], 305 refined parameters, R = 0.045, wR^2 = 0.115, max. residual electron density 1.20 (–1.30) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Reaction of Ligand 2a with $ZnBr_2$; Synthesis of Compound 22a: Reaction of $ZnBr_2$ (0.76 g, 3.37 mmol) with ligand **2a** (1.0 g, 3.37 mmol) in acetonitrile yielded after workup a bright yellow powder (1.70 g, 97%).

X-ray Crystal Structure Analysis of 22a: Formula $C_{19}H_{24}Br_2N_2OZn{\cdot}0.5C_4H_8O$ M = 557.64, colourless crystal 0.30 × 0.12 × 0.08 mm, a = 15.943(1), b = 10.254(1), c = 28.396(1) Å, β = 97.36(1)°, V = 4603.9(6) Å^3, $\rho_{calcd.}$ = 1.609 g cm^{-3}, μ = 45.54 cm^{-1}, empirical absorption correction (0.342 ≤ T ≤ 0.712), Z = 8, monoclinic, space group $P2_1/c$ (no. 14), λ = 0.71073 Å, T = 198 K, ω and φ scans, 29515 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.68 Å^{-1}, 11531 independent (R_{int} = 0.075) and 5668 observed reflections [$I \geq 2\sigma(I)$], 506 refined parameters, R = 0.062, wR^2 = 0.144, max. residual electron density 1.34 (–1.25) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Reaction of Ligand 2a with $Cu(OTf)_2$; Synthesis of Compound 23a: $Cu(OTf)_2$ (1.0 g, 2.76 mmol) was treated with ligand **2a** (0.82 g, 2.76 mmol) at room temperature in dichloromethane. After workup a green powder was isolated (1.38 g, 76%).

X-ray Crystal Structure Analysis of 23a: Formula $C_{19}H_{24}CuN_2O(H_2O)(CF_3SO_3)_2{\cdot}CH_2Cl_2$, M = 761.02, green crystal 0.40 × 0.15 × 0.05 mm, a = 8.881(1), b = 19.970(1), c = 18.480(1) Å, β = 97.77(1)°, V = 3247.4(4) Å^3, $\rho_{calcd.}$ = 1.557 g cm^{-3}, μ = 10.44 cm^{-1}, empirical absorption correction (0.680 ≤ T ≤ 0.950), Z = 4, monoclinic, space group $P2_1/n$ (no. 14), λ = 0.71073 Å, T = 198 K, ω and φ scans, 22468 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.68 Å^{-1}, 8157 independent (R_{int} = 0.052) and 5356 observed reflections [$I \geq 2\sigma(I)$], 399 refined parameters, R = 0.052, wR^2 = 0.132, max. residual electron density 0.71 (–0.51) e Å^{-3}, hydrogen atoms at water from difference Fourier calculations, other calculated and all refined as riding atoms.

Supporting Information (see footnote on the first page of this article): X-ray crystal structure analyses of **3c**, **12b**, **13b** and **16a**, and additional spectroscopic information for **2a**,**b**, **3b**,**c** and **19a**.

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