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Further iminopyrrolyl complexes of nickel, cobalt, iron and copper: Synthesis and structural characterisation☆

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The reaction between two equivalents of 2-(*N*-arylformimino)pyrrolyl sodium salts ($NaNC_4H_3C(H) = N$-Ar), with Ar = C_6H_5 (**I**), 2,6-*i*Pr_2-C_6H_3 (**II**) or 2-(*N*-arylformimino)phenanthro[9,10-*c*]pyrrolyl sodium salts ($NaNC_{16}H_{10}C(H){=}N$-Ar), with Ar=C_6H_5 (**III**), 2,6-*i*Pr_2-C_6H_3 (**IV**) and one equivalent of nickel(II), cobalt(II), iron(II) and copper(I) halides, in THF, at low temperatures, afforded bis(iminopyrrolyl) or bis(iminophenanthro[9,10-*c*]pyrrolyl) complexes with different geometries around the metal centres. Nickel(II) derivatives displayed distorted square planar geometries, whereas for cobalt a tetrahedral complex is proposed. The reactions with $FeCl_2$ resulted in very unstable products, giving rise to dimers with pentacoordinated Fe(III) centres. The addition of two equivalents of pyridine to the reaction medium improved the stability of the resulting compound, enabling the formation of a 16-electron Fe(II) complex, which contained simultaneously two iminopyrrolyls and also a pyridine ligand. In the reaction of CuBr with 2-(*N*-2,6-diisopropylphenylformimino)pyrrolyl sodium salt, a complex with the general formulation $[Cu(iminopyrrolyl)]_x$ was obtained. When exposed to the air, this complex gives rise to the corresponding bis(iminopyrrolyl) Cu(II) complex.

1. Introduction

Monoanionic bidentate nitrogen ligands are of particular interest in the stabilisation of a vast number of metal complexes. Among such type of ligands is the 2-iminopyrrolyl bidentate chelating ligand, containing an anionic pyrrolyl ring substituted in position 2 by a neutral imine donor moiety, which may be considered structurally similar to salicylaldiminate, anilidoimine or 2-(2-pyridyl)indolyl ligands. The 2-iminopyrrolyls are appealing ligands because they are readily accessible and easy to modify, either sterically or electronically, via straightforward Schiff-base condensation procedures [1]. The first examples of homoleptic 2-iminopyrrolyl metal complexes of Co(II), Ni(II), Pd(II), Cu(II) and Zn(II) have been described in the 1960s [2]. However, only recently this class of ligands has been commonly employed in the synthesis of several transition-metal compounds [3]. Another important feature is that they provide high stability to their complexes, being versatile spectator ligands in catalytic species, namely in post-metallocene catalysts for olefin polymerisation [3,4].

Our group has been interested in the synthesis and structural characterisation of a series of Na [5], Co(II) [6], Co(III) [7], Ni(II) [8], Zn(II) [9], and B(III) [10] complexes containing 2-(*N*-arylimino)pyrrolyl ligands or 2-(*N*-arylimino)phenanthro[9,10-*c*]pyrrolyl ligands (Chart 1). The bis-chelate Zn(II) and B(III) complexes showed tetrahedral geometries around the metal centres (Chart 1, D–F), some of the species exhibiting interesting luminescent properties [9,10]. In the case of Co(II) bis-chelate derivatives, the geometry around the metal centre was dependent upon the bulkiness of the substituents at the iminopyrrolyl ligand. Only the Co(II) derivative bearing the bulkiest 2-iminopyrrolyl ligand (Chart 1, B) showed a square-planar geometry, the remaining complexes being tetrahedral (Chart 1, A) [6a]. Attempts to obtain Co(II) tris-chelate derivatives were unfruitful, except for the less sterically demanding 2-(*N*-phenylformimino)pyrrolyl-type ligands, their formation occurring though with the concomitant oxidation of Co(II) to Co(III) (Chart 1, C). The B(III) and Zn(II) compounds were prepared by acid–base reaction between the parent neutral iminopyrrole precursors and aryl or alkyl derivatives of boron and zinc. The latter homoleptic bis(2-(*N*-arylformimino)pyrrolyl) complexes of Zn(II)

☆ Dedicated to Professor Maria José Calhorda on the occasion of her 65th birthday.

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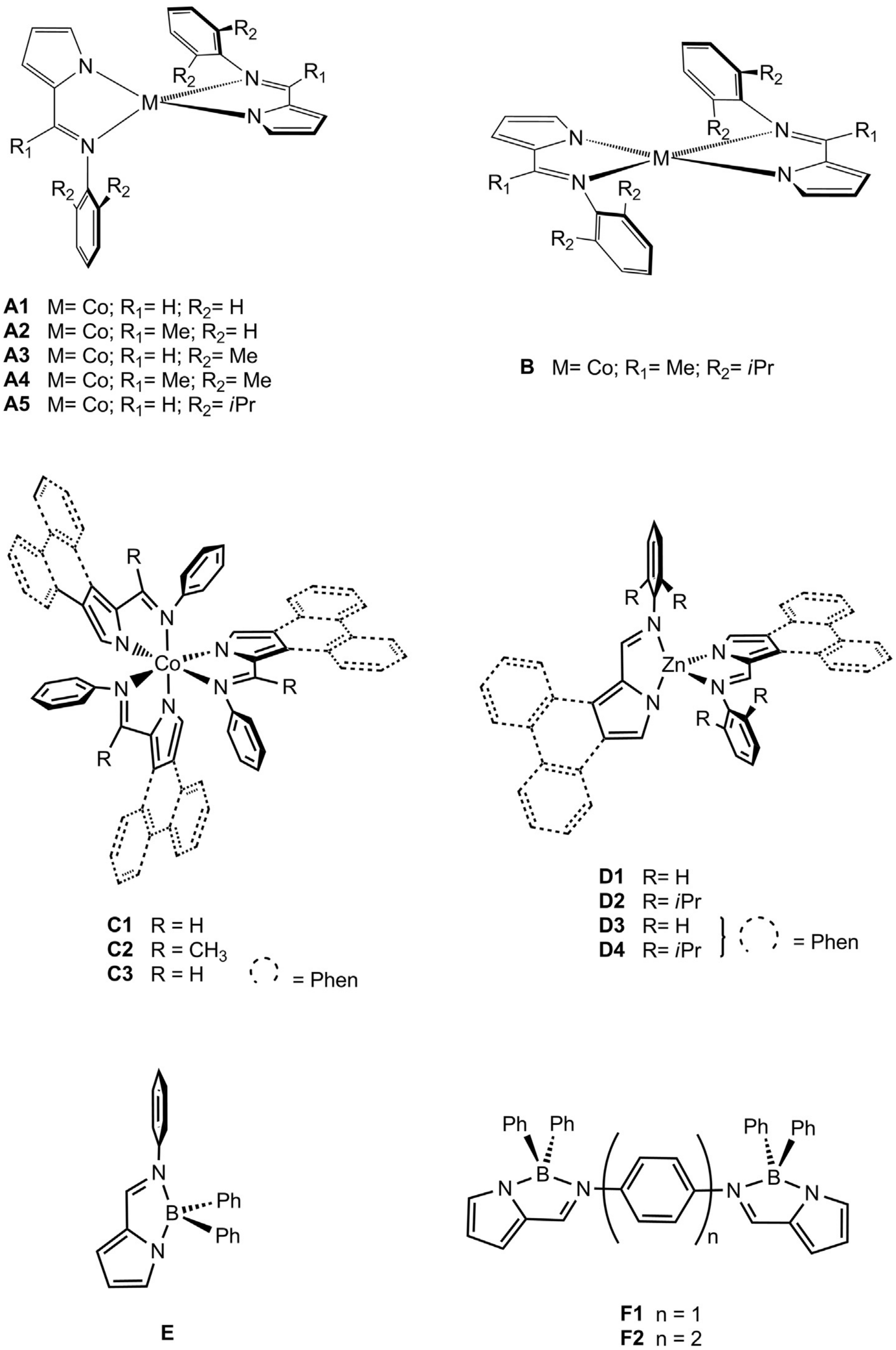


Chart 1. Examples of other 2-(*N*-arylformimino)pyrrolyl complexes synthesised by the authors.

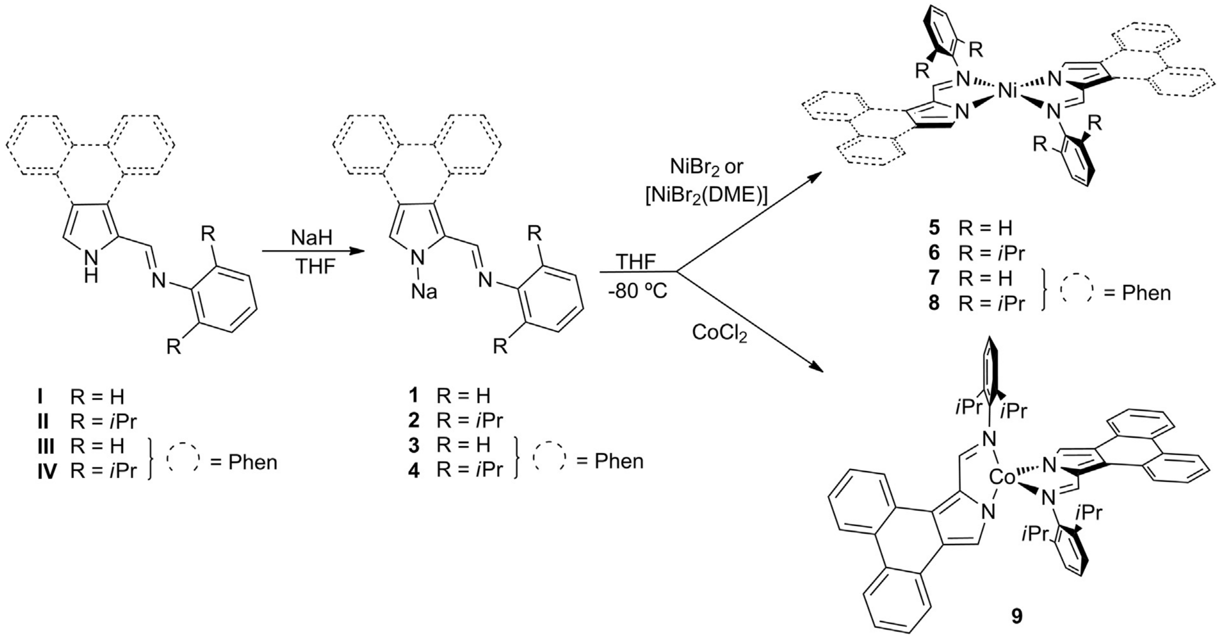
were obtained alternatively by reaction of the corresponding metal dichloride with two equivalents of the corresponding 2-(*N*-arylimino)pyrrolyl sodium salt or of its fused derivatives, this method being also employed for the synthesis of Co(II) and Co(III) homoleptic compounds.

In the present paper, in order to extend the scope of bis(iminopyrrolyl) and bis(iminophenanthro[9,10-*c*]pyrrolyl) complexes to transition-metals such as nickel, cobalt, iron and copper, we report the preparation of a series of new bis(2-(*N*-arylformimino) pyrrolyl) and bis(2-(*N*-arylformimino)phenanthro[9,10-*c*]pyrrolyl) chelates of the above mentioned metals and its characterisation by NMR spectroscopy, Mass Spectrometry and, whenever possible, X-ray Diffraction.

2. Results and discussion

2.1. Synthesis of metal complexes

The four ligand precursors derived from 2-arylformimino pyrrole (**I**–**IV**) used in this work (Scheme 1) were prepared by condensation of 2-formylpyrrole or 2-formylphenanthro[9,10-*c*]



Scheme 1. Synthesis of complexes **5**–**9**.

pyrrole with aniline or 2,6-diisopropylaniline, employing standard conditions, according to the method described previously [5–10].

In previous publications [6,9], metal halides were used as starting materials for the synthesis of homoleptic bis(iminopyrrolyl) Zn(II) and Co(II) complexes. Therefore, in a first approach, anhydrous $NiBr_2$ was employed as starting material in the preparation of Ni(II) derivatives. The synthetic procedure consisted in the treatment of ligand precursors **I**–**IV** with one equivalent of sodium hydride in THF, at −20 °C, which resulted in the deprotonation of the pyrrole NH proton, giving rise to the *in situ* formation of the 2-(*N*-arylformimino)pyrrolyl or 2-(*N*-arylformimino)phenanthro[9,10-*c*]pyrrolyl sodium salts **1**–**4** (Scheme 1). The addition of compound **1** to a suspension of $NiBr_2$ in THF, at −80 °C, followed by warming up and stirring overnight, at room temperature, afforded red crystals of Ni(II) complex **5** (Scheme 1), although in a low yield (15%). These crystals were suitable enough for X-ray diffraction (see below, Section 2.2). However, for ligand precursors **II**–**IV**, the reaction was not successful, being possible to recover a significant amount of reprotonated ligand. As a result, we decided to investigate an alternative procedure that could enable the preparation of the remaining Ni(II) complexes. Bochmann et al. [11] had already reported the synthesis of bis(aryliminopyrrolyl)nickel complex (aryl = 2,6-$iPr_2C_6H_3$) **6** (Scheme 1), in 15% yield from the reaction of the corresponding iminopyrrolyl lithium salt with [$NiBr_2$(DME)] (DME = 1, 2-dimethoxyethane), in Et_2O. Nevertheless, we decided to carry out the preparation of this compound using our synthetic methodology described above. The reaction of sodium salt **2** with [$NiBr_2$(DME)] in THF, led to complex **6** in 80% yield (Scheme 1). This significant increase in the reaction yield, when compared with that reported by Bochmann et al. [11], can be attributed to the higher solubility of the reagents in THF than in Et_2O. In fact, Flores et al. [12] have also prepared complex **6** in a very high yield (92%), using a procedure very similar to ours, but employing acetonitrile as the reaction solvent.

The use of the 2-(*N*-arylformimino)phenanthro[9,10-*c*]pyrrole ligand precursors **III** and **IV**, in the same reaction conditions, gave rise to complexes **7** and **8** as bronze crystals and a dark brown solid, in 74 and 37% yield, respectively. The discrepancy in the yields obtained for this type of complexes can be attributed to the instability of the iminopyrrolyl and iminophenanthro[9,10-*c*]pyrrolyl ligands, which are prone to reprotonation of the pyrrolyl moiety [13].

As referred above, our group reported recently the syntheses and characterisation of a series of cobalt complexes containing bis(iminopyrrolyl) ligands, which were prepared in high yields [6a]. In the light of these results, we have investigated the preparation of Co(II) complexes bearing the new 2-(*N*-arylformimino)phenanthro[9,10-*c*]pyrrolyl ligands. Ligand precursor **IV**, containing a 2,6-diisopropylphenyl group as the *N*-aryl substituent of the iminic moiety, was reacted with one equivalent of sodium hydride, in THF. The resulting sodium salt **4** was then slowly added to $CoCl_2$ in the same solvent, affording the paramagnetic Co(II) complex **9**, in 91% yield, as a brown-reddish solid. Several recrystallisations were tried, but it was impossible to obtain crystals suitable for X-ray diffraction. Despite the paramagnetic nature of this complex, its ^1H NMR spectrum was recorded in CD_2Cl_2, showing sharp resonances between *ca.* 20 and −26 ppm. The work developed in our group concerning the synthesis of a series of four-coordinate Co(II) complexes showed that all, except one, exhibited tetrahedral geometries; the most hindered derivative (bis(2-(*N*-2,6-diisopropylphenylacetimino)pyrrolyl)cobalt(II)) displaying a square planar geometry [6a]. Taking these facts into account, a tetrahedral geometry is proposed for the present formiminophenanthro[9,10-*c*]pyrrolyl derivative **9**. However, when ligand precursor **III** was employed under the same reaction conditions, a diamagnetic octahedral tris(2-(*N*-phenylformimino)phenanthro[9,10-*c*]pyrrolyl)cobalt(III) complex was obtained, in 58% yield [7].

We have also evaluated the use of $FeCl_2$ to prepare bis(iminopyrrolyl) complexes. We have attempted the preparation of homoleptic iron complexes using “simple” iminopyrrolyl ligand precursors **I** and **II**, under the same reaction conditions as those employed above for Zn, Ni and Co. The reaction products were extracted with Et_2O and *n*-hexane, for ligand precursors **I** and **II**, respectively. However, these products were highly thermally unstable, their crystals decomposing easily into brownish powders. Nevertheless, it was still possible to isolate from the mixtures very few crystals of both reactions. The structures of the Fe(III) complexes **10** and **11**, were determined by X-ray diffraction (Section

2.2), and are represented in Fig. 1 (a) and (b), respectively. Both compounds are dimers containing bis(iminopyrrolyl)iron moieties and bridging oxygen atoms but, while in compound **10** the μ-oxo ligand is bonded to two bridging Na atoms, which are each of them further bonded to an Et_2O molecule, in **11** only a single μ-oxo ligand is connecting the two bis(iminopyrrolyl)iron moieties. The formation of these Fe(III) complexes **10** and **11** containing μ-oxo ligands can be explained by the fact that bis(iminopyrrolyl)Fe(II) complexes, formed by substitution of the two chlorine atoms by two iminopyrrolyl ligands, are highly unsaturated (15-electron species). As a consequence, they are highly reactive towards adventitious water molecules (or less probably towards oxygen or THF) present in the solvent, leading to oxidised products, which are more saturated and thus more stable than the parent Fe(II) complexes. The difference between the two complexes can be rationalised in terms of their workup. In fact, the absence of the isopropyl groups in the *N*-aryl substituent confers insolubility to **10** in nonpolar solvents, such as *n*-hexane, and required the use of a more polar solvent such as Et_2O in the reaction workup. This solvent has an oxygen atom that can be easily coordinated to Na ions present in solution [14], whereas in the case of complex **11**, the use of *n*-hexane (a non-coordinating solvent) did not allow the formation of a compound similar to **10**, giving rise instead to a dimer bearing only a single bridging μ-oxo ligand.

In order to prevent the formation of these dimeric complexes, and the simultaneous oxidation from Fe(II) to Fe(III), we have investigated the same type of reaction in the presence of a neutral ligand, such as pyridine (Py), that could coordinate to the metal centre and improve the stability of the resulting compound. The deprotonation of two equivalents of ligand precursor **I** with NaH, followed by reaction with $FeCl_2$, in the presence of two equivalents of Py, afforded complex **12** as highly sensitive orange-red paramagnetic crystals, in 44% yield (Scheme 2), which structure was determined by X-ray diffraction (see Section 2.2). This compound was also characterised by ^1H NMR spectroscopy, in CD_2Cl_2, displaying resonances belonging to a paramagnetic species with chemical shifts spread between *ca.* 47 and −2 ppm. In fact, despite the increased stabilisation of Fe(II) centres introduced by the coordination of Py, compound **12**, a 16-electron species, is still thermally sensitive. Therefore, in an attempt to obtain the corresponding octahedral Fe(II) complex containing two iminopyrrolyl ligands and two coordinated Py molecules, we decided to repeat this synthesis now increasing the amount of Py from 2 to 12 equivalents. However, this procedure only gave rise to the same reaction product, complex **12**, although in higher yields (64%).

The last metal to be investigated in this work was copper, in the oxidation state +1. The synthetic methodology used was the general procedure described previously, consisting in the reaction of the deprotonated ligand precursor **II** with CuBr, affording complex **13**, as an off-white solid, in 57% yield. The elemental analyses showed that this compound had an iminopyrrolyl ligand:Cu composition of 1:1. On the other hand, the Electron-Spray Ionisation (ESI) mass spectrum indicated an *m*/*z* of 633, in agreement with the formulation $[Cu(iminopyrrolyl)]_2$. The ^1H NMR spectrum, obtained at room temperature, exhibited a pattern that pointed to a mixture of isomers, present in a ratio of 1:2, or alternatively to an intramolecular fluxional process occurring in a species containing non-equivalent iminopyrrolyl ligands, in a ratio of 1:2. Variable-temperature (VT) ^1H NMR experiments in toluene-d_8, from room temperature to 100 °C, have demonstrated that resonances belonging to equivalent groups tend to coalesce in one, but only above 100 °C (see Fig. S1 of Supplementary material and Experimental section). Unfortunately, no crystals suitable for X-ray diffraction were so far obtained. In the absence of further evidence, the only conclusion that can be drawn is that **13** is a polynuclear copper(I) species with the general formulation $[Cu(iminopyrrolyl)]_x$ (Scheme 3).

During the workup of the latter reaction, after removal of the solvent under vacuum, the residue was washed with *n*-hexane, and a pale yellow/almost colourless solution was filtered into a beaker exposed to air. The solvent of this solution was evaporated under vacuum and the obtained greenish precipitate was recrystallised from *n*-hexane, at −20 °C, giving black crystals, suitable for X-ray diffraction (see Section 2.2) of the bis(iminopyrrolyl)-Cu(II) complex **14** (Scheme 3).

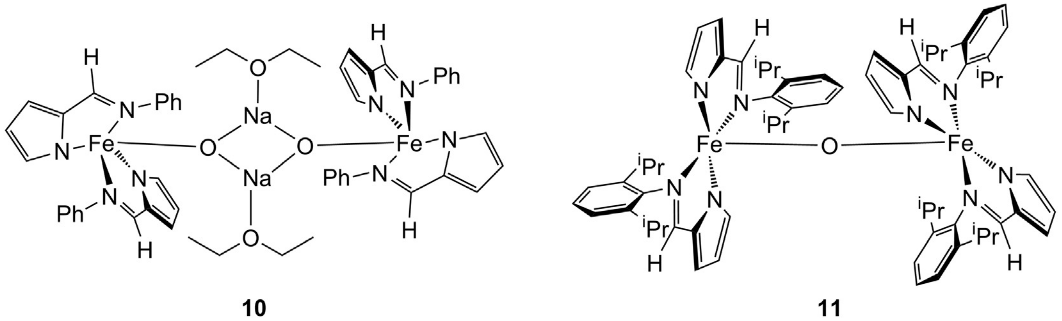
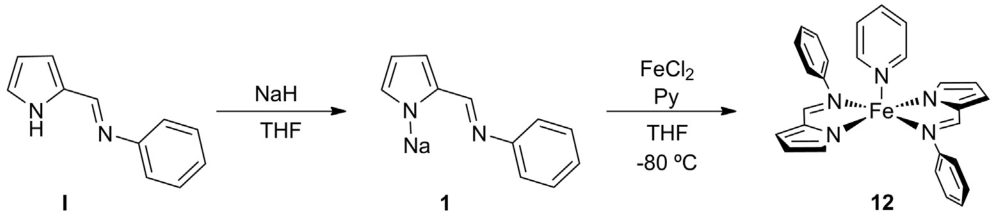
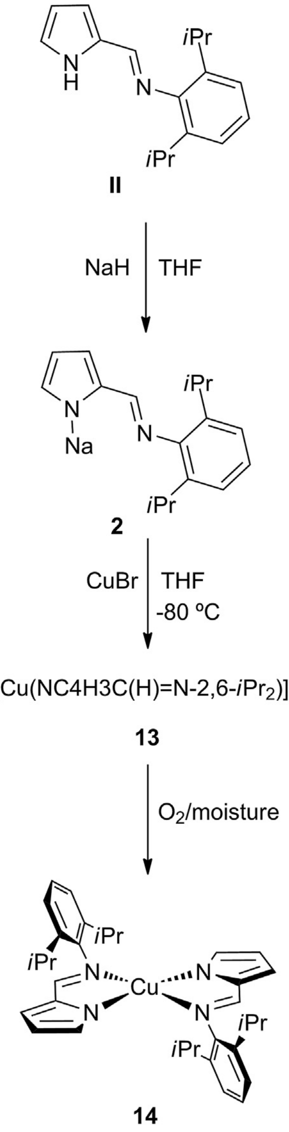


Fig. 1. Fe(III) compounds **10** and **11** formed by oxidation of the corresponding bis(iminopyrrolyl) Fe(II) derivatives.



Scheme 2. Synthesis of bis(iminopyrrolyl) Fe(II) pyridine complex **12**.



Scheme 3. Synthesis of Cu(I) and Cu(II) complexes **13** and **14**, respectively.

2.2. X-ray diffraction studies

Crystals suitable for X-ray diffraction were obtained for compounds **5**, **7**, **10**–**12**, and **14**, enabling the determination of their molecular and crystal structures. Perspective views of the molecular structures of these bis(iminopyrrolyl) complexes are shown in Fig. 2 and the corresponding selected bond distances and angles are given in Tables 1 and 2.

The crystal structures of complexes **5** and **7** (Fig. 2 and Table 1) are very similar, revealing a four-coordinate nickel centre, with distorted square planar geometry, where the two iminopyrrolyl ligands are coordinated in a transoid conformation. The dihedral angle α, defined in Table 1, measures the degree of distortion observed for this imaginary square plane. The values are small (1.48–19.19°), the higher and smaller distortions being observed for molecules 2 and 3 of complex **5**, respectively. In complexes **5** and **7**, the chelate bite angles of both ligands, N1–Ni1–N2, are *ca.* 83°. Despite the similarity of the Ni–$N_{pyrrolyl}$ and Ni–N_{imine} bond lengths, the Ni–$N_{pyrrolyl}$ ones are slightly shorter. As observed in a previous publication for a bis(iminophenanthro[9,10-*c*]pyrrolyl) Zn(II) complex [9], the imine bond distances N2–C6, which lie in the range 1.300(12)–1.346(12) Å, exhibit longer bond lengths than the corresponding distance in the free ligand **I** (*ca.* 1.281(2) Å) [5], showing a certain extent of steric congestion around the Ni centre and π–π* back-bonding from the metal to the iminic fragment. The features exhibited for ligand precursor **I** [5] only change slightly upon coordination to Ni, being comparable to those observed for similar compounds in earlier publications of our group [5–9].

Complex **10** (Fig. 2) crystallised as a dimer with pentacoordinated Fe(III) metal centres, where the geometry around these atoms, generated by two iminopyrrolyl ligands and one oxygen atom, can be described as distorted trigonal bipyramidal (τ value of 0.76). In a pentacoordinated structure, the τ parameter, $\tau = (\beta - \alpha)/60$, measures the degree of distortion within the structural continuum between trigonal bipyramidal and square pyramidal geometries ($\tau = 1$ for an ideal trigonal bipyramid and $\tau = 0$ for an ideal square pyramid) [15]. The axial positions are occupied by the neutral imine groups of both bidentate ligands, that are *trans* to each other, with an almost linear N2–Fe1–N2′ axis (175.8(2)°), being the Fe1–N_{imine} bonds (2.274(7) and 2.311(7) Å), the longest distances to the metal centre (Table 2). On the other hand, the pyrrolyl rings and the oxygen atom occupy the remaining equatorial positions. Moreover, this oxygen atom is bonded to two sodium atoms that are also bridging the oxygen atom of the other Fe trigonal bipyramid. A further Et_2O molecule is coordinated to each of these sodium atoms, giving rise to a trigonal planar geometry around each Na. Although the features exhibited for the ligand precursor **I** only change slightly upon coordination to Fe, being similar to those observed for the Ni(II) complexes **5** and **7**, the chelate bite angles N1–Fe1–N2 are *ca.* 75°, being smaller than those observed for the referred compounds.

In the case of compound **11**, which also crystallised as a dimer (Fig. 2), its structure can be described as two bis(iminopyrrolyl) iron fragments connected by a bridging oxygen atom, where the geometry around each Fe(III) atom is that of a distorted trigonal bipyramid (τ parameters of 0.69 and 0.60, respectively; Table 2). In this complex, the anionic pyrrolyl rings are closer to the axial positions, with angles N1–Fe1–N3 of *ca.* 156°, whereas the two N_{imine} groups and the oxygen atom occupy the equatorial positions. The shortest bond distances to the metal centre are those between the bridging oxygen and the Fe(III) atoms (1.779(4) and 1.773(4) Å, respectively). All the remaining features regarding the iminopyrrolyl ligand are in agreement with those described previously (see above). The Fe(II) compound studied, complex **12**, is formed by two iminopyrrolyl ligands and a pyridine molecule coordinated to the metal centre, showing an intermediate geometry in between a distorted trigonal bipyramid and a square pyramid (Fig. 2 and Table 2). The N_{imine} groups occupy the distorted axial positions (N–Fe–N *ca.* 165°), while the anionic pyrrolyl rings and the pyridine molecule fill the equatorial positions. The degree of distortion exhibited in this compound (τ parameter of 0.48) is higher than those observed for complexes **10** or **11**. The shortest bond around the metal centre is Fe1–$N_{pyrrolyl}$, whereas Fe–$N_{pyridine}$ has an intermediate length between the former Fe1–$N_{pyrrolyl}$ and that of Fe1–N_{imine}.

Complex **14** (Fig. 2) shows a four-coordinate copper centre with distorted square planar geometry, where the two iminopyrrolyl ligands appear in a transoid conformation. The dihedral angle α (defined in Table 2), which measures the degree of distortion observed for this imaginary square plane, has a small value of 15.38°. The chelate bite angle, N1–Cu1–N2, is *ca.* 82°, and the Cu–$N_{pyrrolyl}$ bond lengths, despite being very similar to those of the

Table 1
Selected bond distances (Å) and angles (°) for complexes **5** and **7**.

	5						**7**	
	Molecule 1		Molecule 2		Molecule 3		Molecule 1	
	Ligand 1	Ligand 2	Ligand 1	Ligand 2	Ligand 1	Ligand 2	Ligand 1	Ligand 2
Distances (Å)								
N1–C2	1.384(12)	1.371(12)	1.361(12)	1.378(12)	1.353(11)	1.415(12)	1.390(5)	1.388(5)
N1–C5	1.349(12)	1.354(12)	1.330(12)	1.344(12)	1.381(12)	1.348(12)	1.342(5)	1.346(5)
C3–C2	1.376(13)	1.404(13)	1.417(12)	1.424(12)	1.418(13)	1.408(14)	1.427(6)	1.415(6)
C3–C4	1.382(13)	1.355(13)	1.362(13)	1.397(12)	1.372(13)	1.397(14)	1.398(6)	1.398(6)
C5–C4	1.400(13)	1.403(13)	1.413(14)	1.418(13)	1.403(14)	1.436(14)	1.412(6)	1.409(6)
C6–C2	1.438(13)	1.411(14)	1.404(13)	1.406(13)	1.399(13)	1.403(14)	1.391(6)	1.399(5)
N2–C6	1.300(12)	1.328(12)	1.321(12)	1.313(12)	1.346(12)	1.320(12)	1.323(5)	1.325(5)
N2–C7	1.423(12)	1.436(12)	1.459(12)	1.429(12)	1.447(12)	1.472(11)	1.436(5)	1.429(5)
Ni1–N1	1.891(8)	1.902(8)	1.907(8)	1.897(8)	1.913(8)	1.908(8)	1.891(3)	1.899(3)
Ni1–N2	1.917(8)	1.914(7)	1.914(7)	1.928(7)	1.942(7)	1.934(8)	1.904(4)	1.911(4)
Angles (°)								
C6–N2–C7	119.9(8)	117.9(8)	117.5(7)	119.9(8)	115.3(8)	115.5(8)	118.1(4)	117.4(4)
N1–C2–C6	112.2(9)	113.9(9)	114.9(9)	114.8(8)	113.0(9)	115.6(9)	112.6(4)	112.5(4)
N2–C6–C2	116.2(9)	115.1(10)	115.6(9)	115.9(9)	117.4(9)	114.1(9)	117.4(4)	117.4(4)
C3–C2–C6	137.1(10)	135.8(10)	135.5(10)	135.0(10)	134.9(10)	133.7(10)	138.9(4)	138.6(4)
N1–C2–C3	110.7(8)	110.1(9)	109.6(8)	110.1(8)	111.4(8)	109.9(9)	108.4(4)	108.8(4)
C2–C3–C4	106.4(9)	106.3(9)	105.4(9)	104.8(8)	104.5(9)	106.4(9)	106.6(4)	106.2(4)
C5–C4–C3	105.7(8)	107.6(9)	108.1(10)	108.0(9)	109.3(10)	107.0(9)	106.6(4)	107.4(4)
N1–C5–C4	110.3(9)	109.8(10)	109.0(9)	109.4(9)	108.2(9)	110.2(9)	110.6(4)	109.6(4)
C5–N1–C2	105.5(8)	105.9(8)	108.0(9)	107.7(8)	106.5(8)	106.5(8)	107.9(4)	108.0(3)
N1–Ni1–N2	83.6(3)	83.2(4)	83.7(3)	84.0(4)	82.7(4)	83.3(4)	83.77(15)	83.82(15)
Dihedral α[a]	17.00		19.19		1.48		17.45	

[a] Dihedral α = angle between planes [(N1, Ni1, N2), ligand 1] and [(N1, Ni1, N2), ligand 2].

Cu–N$_{imine}$ groups, are slightly shorter. The features exhibited for ligand precursor **II** [5] only change slightly upon coordination to Cu, as it can be seen in Table 1, and are comparable to those observed for similar compounds in earlier publications of our group [5–9].

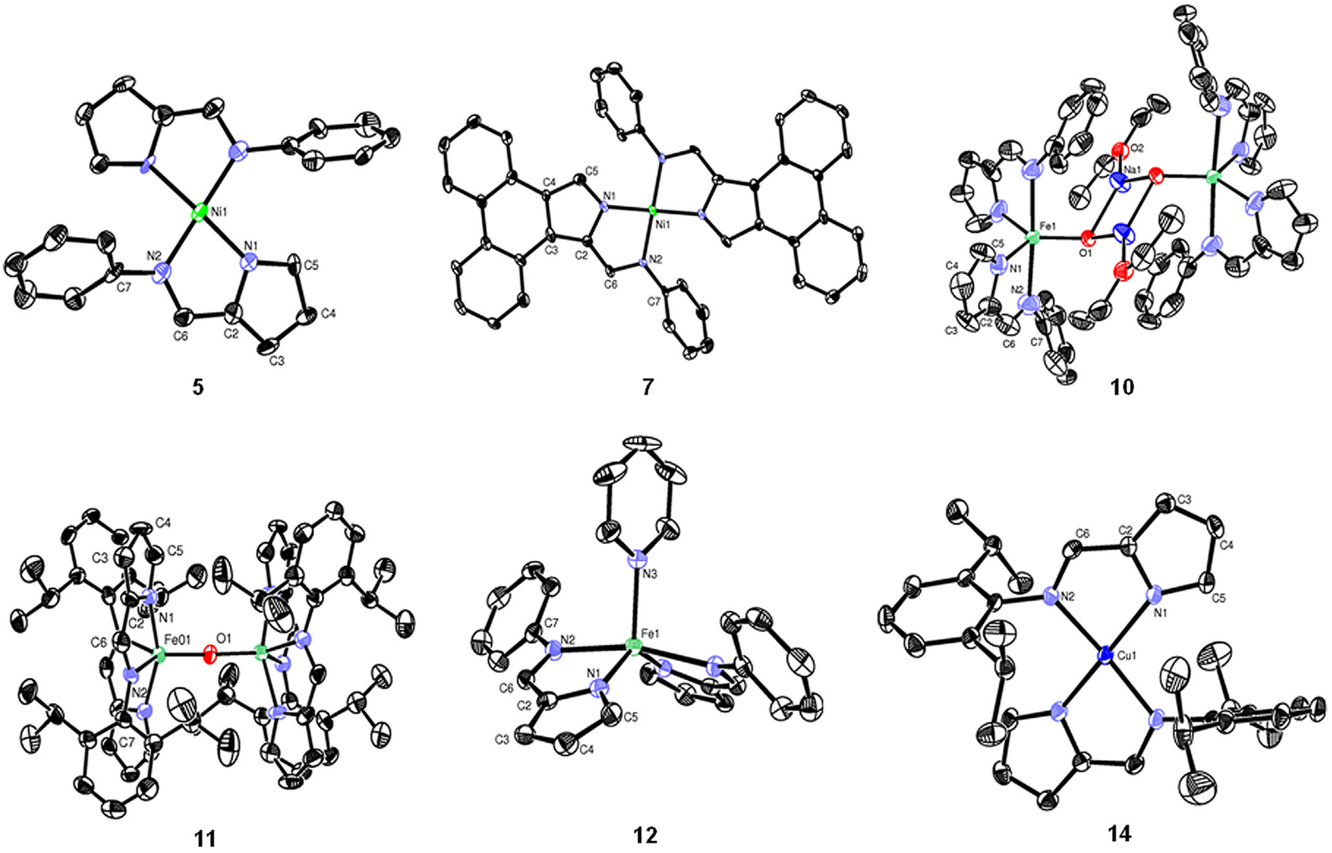
3. Conclusions

Several nickel, cobalt, iron and copper complexes containing two iminopyrrolyl or two iminophenanthro[9,10-*c*]pyrrolyl ligands were synthesised and characterised by multiple methods. X-ray crystallography studies revealed chelation of these ligands to the

Table 2
Selected bond distances (Å) and angles (°) for complexes **10**–**12**, and **14**.

	10[a]		**11**				**12**[b]	**14**	
	Ligand 1	Ligand 2	Ligand 1	Ligand 2	Ligand 3	Ligand 4		Ligand 1	Ligand 2
Distances (Å)									
N1–C2	1.387(11)	1.360(10)	1.383(8)	1.377(9)	1.388(8)	1.381(9)	1.365(3)	1.381(3)	1.373(3)
N1–C5	1.359(11)	1.323(11)	1.338(9)	1.358(9)	1.311(9)	1.330(9)	1.352(3)	1.354(3)	1.352(3)
C3–C2	1.373(10)	1.371(12)	1.374(10)	1.409(10)	1.404(10)	1.401(10)	1.394(3)	1.393(4)	1.394(4)
C3–C4	1.385(11)	1.397(12)	1.397(10)	1.386(10)	1.362(11)	1.381(11)	1.379(3)	1.378(4)	1.389(4)
C5–C4	1.363(11)	1.400(12)	1.387(10)	1.388(10)	1.422(10)	1.406(10)	1.384(3)	1.395(4)	1.387(4)
C6–C2	1.373(11)	1.386(13)	1.407(10)	1.433(10)	1.371(9)	1.435(10)	1.412(3)	1.407(4)	1.411(4)
N2–C6	1.333(11)	1.333(12)	1.295(9)	1.296(9)	1.308(8)	1.268(8)	1.295(3)	1.301(3)	1.296(3)
N2–C7	1.424(10)	1.376(11)	1.424(8)	1.432(9)	1.415(9)	1.410(9)	1.411(2)	1.432(3)	1.434(3)
Fe1–N1	2.054(6)	2.047(7)	2.057(6)	2.058(6)	2.078(5)	2.048(6)	2.0543(18)		
Fe1–N2	2.274(7)	2.311(7)	2.148(5)	2.172(6)	2.142(6)	2.167(6)	2.2158(18)		
Fe1–O1	1.973(5)		1.779(4)		1.773(4)		–		
Na1–O1	2.263(6)		–	–	–	–	–		
Na1–O2	2.289(6)		–	–	–	–	–		
Fe1–N3	–	–	–	–	–	–	2.110(3)		
Cu1–N1								1.957(2)	1.957(2)
Cu1–N2								2.029(2)	2.021(2)
Angles (°)									
N1–Fe1–N2	75.3(3)	75.7(3)	79.0(2)	77.7(2)	78.8(2)	77.0(2)	78.31(7)		
N1–Fe1–O1	130.1(2)	121.0(2)	100.3(2)	102.8(2)	102.6(2)	101.5(2)	–		
N2–Fe1–O1	90.4(2)	93.4(2)	119.3(2)	125.0(2)	117.6(2)	121.9(2)	–		
N1–Fe1–N3	–	–	–	–	–	–	111.76(5)		
N2–Fe1–N3	–	–	–	–	–	–	97.38(5)		
N1–Cu1–N2								82.32(9)	82.45(9)
τ parameter [15]	0.76		0.69		0.60		0.48		
Dihedral α[c]								15.38	

[a] In complex **10**, half molecule is generated by the symmetry operation $-x + 2, -y, -z$.
[b] In complex **12**, half molecule is generated by the symmetry operation $-x + 1, y, -z + 1/2$.
[c] Dihedral α = angle between planes [(N1, Cu1, N2), ligand 1] and [(N1, Cu1, N2), ligand 2].



5 7 10

11 12 14

Fig. 2. Perspective views of the molecular structures of bis(iminopyrrolyl) complexes **5**, **7**, **10**–**12**, and **14**, with 50% probability level ellipsoids. All hydrogen atoms were omitted for clarity. In the case of compound **7**, two co-crystallised CH_2Cl_2 molecules were also omitted.

metal centres, resulting in complexes with different geometries. Nickel(II) compounds presented distorted square planar geometries around the metal centre, whereas for cobalt, a tetrahedral complex is proposed.

In an attempt to prepare homoleptic bis(iminopyrrolyl)iron complexes, from the reaction of $FeCl_2$ with the corresponding iminopyrrolyl sodium salts, only complexes **10** and **11** were identified by X-ray diffraction. The resulting structure of **10** is a dimer with pentacoordinated Fe(III) metal centres, where the geometry around these atoms, generated by two iminopyrrolyl ligands and a μ-oxo ligand, can be described as distorted trigonal bipyramidal. The oxygen atom is bonded to two sodium atoms that are also bridging the μ-oxo ligand of the other trigonal bipyramidal Fe centre. To each of these sodium atoms, a further Et_2O molecule is coordinated, giving rise to a trigonal planar geometry around each Na. Conversely, compound **11** crystallised as a dimer, composed by two bis(iminopyrrolyl)iron fragments connected by a single bridging oxygen atom, where a distorted trigonal bipyramidal geometry around each Fe(III) is also exhibited. In order to prevent the formation of these dimeric complexes, and the simultaneous oxidation of Fe(II) to Fe(III), we performed the same type of reaction in the presence of a neutral ligand, pyridine (Py), that coordinated to the metal centre and improved the stability of the resulting compound. In fact, a 16-electron Fe(II) complex was isolated showing an intermediate geometry in between a distorted trigonal bipyramid and a square pyramid.

The reaction of CuBr with 2,6-diisopropylphenylformimino pyrrolyl sodium salt afforded a complex, whose proposed structure is that of a dimer with the general formulation $[Cu(\text{iminopyrrolyl})]_x$. When exposed to air, this complex gives rise to the corresponding bis(iminopyrrolyl) Cu(II) complex, whose molecular structure was determined by X-ray diffraction.

4. Experimental section

4.1. General considerations

All experiments dealing with air- and/or moisture-sensitive materials were carried out under inert atmosphere using a dual vacuum/nitrogen line and standard Schlenk techniques. Nitrogen gas was supplied in cylinders (Air Liquide) and purified by passage through 4 Å molecular sieves. Unless otherwise stated, all reagents were purchased from commercial suppliers (e.g., Acrös, Aldrich, Fluka) and used without further purification. All solvents to be used under inert atmosphere were thoroughly deoxygenated and dehydrated before use. They were dried and purified by refluxing over a suitable drying agent followed by distillation under nitrogen. The following drying agents were used: sodium (for toluene, diethyl ether, and tetrahydrofuran (THF)) and calcium hydride (for *n*-hexane and dichloromethane). Solvents and solutions were transferred using a positive pressure of nitrogen through stainless steel cannulae and mixtures were filtered in a similar way using modified cannulae that could be fitted with glass fibre filter disks.

Nuclear magnetic resonance (NMR) spectra were recorded on Bruker Avance III 300 or Bruker Avance III 400 (^1H and ^{13}C) spectrometers. Deuterated solvents were dried by storage over 4 Å molecular sieves and degassed by the freeze-pump-thaw method. Spectra were referenced internally to residual protio-solvent (^1H) or solvent (^{13}C) resonances and are reported relative to tetramethylsilane ($\delta = 0$). All chemical shifts are quoted in δ (ppm) and coupling constants given in Hz. Multiplicities were abbreviated as follows: broad (br), singlet (s), doublet (d), triplet (t), quartet (q), heptet (sep), and multiplet (m). For air- and/or moisture sensitive materials, samples were prepared in J. Young NMR tubes in a glovebox.

Elemental analyses were obtained from the IST elemental analysis services. The ESI mass spectra were obtained in a 500-MS Ion Trap mass spectrometer, Varian Inc. The operating parameters were as follows: the spray needle voltage was set at +5 kV, nitrogen was used both as nebulising and drying gas (25 psi and 10 psi, respectively), drying gas temperature 350 °C; the capillary voltage and the RF loading were optimised for each ion under study.

$NiBr_2$, $CoCl_2$, $FeCl_2$ and CuBr were available in the laboratory, dried under vacuum, at 100 °C, for several hours to constant weight and stored under nitrogen atmosphere. Ligand precursors **I**–**IV** were prepared according to literature procedures [5–9].

4.2. Syntheses

4.2.1. [Ni(κ^2N,N′-$NC_4H_3C(H){=}N{-}C_6H_5)_2$] (**5**)

Anhydrous nickel bromide (0.11 g, 0.5 mmol) was suspended in tetrahydrofuran and cooled to −80 °C. A solution of sodium salt **1** prepared *in situ* (0.19 g, 1.0 mmol) was filtered and directly added dropwise to the suspension, which was then stirred for 1 h. The mixture was allowed to warm to room temperature and further stirred overnight. All volatiles were evaporated and the resulting residue was washed with *n*-hexane and extracted with diethyl ether until extracts were colourless. The resulting orange-yellowish solution was concentrated and cooled to −20 °C, yielding a brownish-orange powder of **5**. Yield: 0.033 g (15%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 8.27 (s, 2H, N=C*H*), 7.36 (*br*, 4H, Ph-H_{ortho}), 7.17 (*br*, 6H, Ph-H_{meta} and Ph-H_{para}), 7.00 (s, 2H, H5), 6.67 (m, 2H, H3), 6.30 (m, 2H, H4).

4.2.2. [Ni(κ^2N,N′-$NC_4H_3C(H){=}N$-2,6-$iPr_2C_6H_3)_2$] (**6**)

This compound was already reported in the literature, although synthesised by slightly different methods (deprotonation with LiBu and Et_2O as solvent [11]; deprotonation with NaH and acetonitrile as solvent [12]). [$NiBr_2$(DME)] (0.14 g, 0.5 mmol) was suspended in tetrahydrofuran and cooled to −80 °C. A solution of sodium salt **2** prepared *in situ* (0.27 g, 1.0 mmol) was filtered and directly added dropwise to the suspension, which was then stirred for 1 h. The mixture was allowed to warm to room temperature and further stirred overnight. All volatiles were evaporated and the resulting residue was extracted with *n*-hexane until extracts were colourless. The resulting orange-brownish solution was concentrated and cooled to −20 °C, yielding a brown microcrystalline solid of **6**. Yield: 0.24 g (84%). ^{1}H NMR (300 MHz, C_6D_6): δ 7.31–7.13 (m, 6H, Ph-H_{meta} and Ph-H_{para}), 6.69 (s, 2H, N=C*H*), 6.66 (dd, 2H, $^3J_{HH} = 3.7$ Hz and $^4J_{HH} = 0.9$ Hz, H5), 6.06 (dd, 2H, $^3J_{HH} = 3.8$ Hz and $^4J_{HH} = 2.0$ Hz, H3), 5.22–5.21 (m, 2H, H4), 4.60 (sep, 4H, $^3J_{HH} = 6.9$ Hz, C*H*(CH_3)$_2$), 1.38 (d, 12H, $^3J_{HH} = 6.6$ Hz, CH(C*H*$_3$)$_2$), 1.3 (d, 12H, $^3J_{HH} = 6.9$ Hz, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6): δ 161.8 (N=*C*H), 145.7 (Ph-C_{ipso}), 143.9 (Ph-C_{ortho}), 140.6 (C2), 138.4 (C4), 127.5 (Ph-C_{para}), 124.0 (Ph-C_{meta}), 119.2 (C5), 113.1 (C3), 29.2 (*C*H(CH_3)$_2$), 24.6 (CH(*C*H$_3$)$_2$), 22.8 (CH(*C*H$_3$)$_2$).

4.2.3. [Ni(κ^2N,N′-$NC_{16}H_9C(H){=}N{-}C_6H_5)_2$] (**7**)

The same procedure described for the synthesis of **6** was followed, but a solution of sodium salt **3** prepared *in situ* (0.17 g, 0.5 mmol) was employed. Extraction of the reaction products with toluene, until extracts remained colourless, and removal of the solvent by vacuum evaporation, afforded a brown powder, which was recrystallised in CH_2Cl_2 and double-layered with *n*-hexane, at −20 °C, giving bronze crystals of **7b**, which were suitable for X-ray diffraction. Yield: 0.13 g (74%). Anal. Calcd. for $C_{46}H_{30}N_4Ni \cdot 0.7CH_2Cl_2$, obtained (*calculated*): C, 78.09 (*78.10*); H, 4.04 (*4.30*); N, 7.90 (*7.90*). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 8.97 (*br*, 2H, H15 or H12), 8.76 (d, 2H, $^3J_{HH} = 8.0$ Hz, H18 or H9), 8.65 (*br*, 2H, H12 or H15), 8.54 (*br*, 2H, H11 or H16), 8.47 (d, 2H, $^3J_{HH} = 7.4$ Hz, H16 or H11), 8.29 (d, 2H, $^3J_{HH} = 7.6$ Hz, H18 or H9), 8.19–8.07 (m, 6H, N=C*H*, H10 and H17), 7.75–7.59 (m, 4H, Ph-H_{ortho}), 7.57–7.43 (m, 6H, Ph-H_{meta} and Ph-H_{para}), 6.19 (s, 2H, H5). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ 159.1 (N=CH), 150.6 (Ph-C_{ipso}), 135.2 (Ph-C_{ortho}), 130.6 (C14 or C13), 130.3 (C13 or C14), 129.6 (Ph-C_{meta}), 128.2 (C8 or C19), 127.9 (C8 or C19), 127.5 (C9 or C18), 127.4 (C4 or C3), 127.3 (C3 or C4), 127.1 (C18 or C9), 126.5 (C16 or C11), 125.6 (Ph-C_{para}), 125.1 (C17 and C10), 125.0 (C11 or C16), 124.2 (C12 or C15), 123.6 (C15 or C12), 122.7 (C5), 119.4 (C2).

4.2.4. [Ni(κ^2N,N′-$NC_{16}H_9C(H){=}N$-2,6-$iPr_2C_6H_3)_2$] (**8**)

The same procedure described for the synthesis of **6** was followed, but a solution of sodium salt **4** prepared *in situ* (0.21 g, 0.5 mmol) was employed. After extraction of the reaction products with toluene, the resulting solution was concentrated and stored at −20 °C, giving a dark brown solid of **8**. Yield: 0.080 g (37%). Anal. Calcd. for $C_{58}H_{54}N_4Ni \cdot 2H_2O$, obtained (*calculated*): C, 76.91 (*77.25*); H, 6.25 (*6.48*); N, 5.74 (*6.21*). ESI-MS: *m*/*z* 865 $[M + H]^+$ (*calculated* for $C_{58}H_{55}N_4Ni$ $[M + H]^+$, *865*). ^{1}H NMR (300 MHz, C_6D_6): δ 8.37 (dd, 2H, $^3J_{HH} = 7.8$ Hz and $^4J_{HH} = 1.6$ Hz, H15 or H12), 8.33 (d, 2H, $^3J_{HH} = 8.3$ Hz, H9 or H18), 8.84 (dd, 2H, $^3J_{HH} = 7.4$ Hz and $^4J_{HH} = 1.6$ Hz, H12 or H15), 7.79 (dd, 2H, $^3J_{HH} = 8.0$ Hz and $^4J_{HH} = 0.8$ Hz, H18 or H9), 7.76 (s, 2H, N=C*H*), 7.49–7.39 (m, 4H, H16 and H11), 7.31–6.99 (m, 10 H, H10, H17, Ph-H_{meta} and Ph-H_{para}), 6.16 (s, 2H, H5), 4.66 (sep, 4H, $^3J_{HH} = 6.8$ Hz, C*H*(CH_3)$_2$), 1.24 (d, 24H, $^3J_{HH} = 6.8$ Hz, CH(C*H*$_3$)$_2$). ^{1}H NMR (400 MHz, toluene-d_8): δ 8.29 (d, 2H, $^3J_{HH} = 7.8$ Hz, H15 or H12), 8.24 (d, 2H, $^3J_{HH} = 8.2$ Hz, H9 or H18), 7.84 (dd, 2H, $^3J_{HH} = 7.8$ Hz and $^4J_{HH} = 1.3$ Hz, H12 or H15), 7.74 (s, 2H, N=C*H*), 7.55 (dd, 2H, $^3J_{HH} = 8.0$ Hz and $^4J_{HH} = 0.8$ Hz, H18 or H9), 7.40–7.34 (m, 4H, H16 and H11), 7.27–7.16 (m, 10 H, H10, H17, Ph-H_{meta} and Ph-H_{para}), 5.94 (s, 2H, H5), 4.58 (sep, 4H, $^3J_{HH} = 6.9$ Hz, C*H*(CH_3)$_2$), 1.23 (d, 12H, $^3J_{HH} = 6.9$ Hz, CH(C*H*$_3$)$_2$), 1.20 (d, 12H, $^3J_{HH} = 6.8$ Hz, CH(C*H*$_3$)$_2$). ^{13}C {^{1}H} NMR (100 MHz, C_6D_6): δ 160.4 (N=CH), 146.1 (Ph-C_{ipso}), 145.0 (Ph-C_{ortho}), 135.2 (C13 or C14), 134.2 (C14 or C13), 130.8 (C9 and C18), 129.3 (C4 or C3), 129.0 (C3 or C4), 128.7 (C19 or C8), 127.9 (Ph-C_{meta}), 127.5 (C8 or C19), 127.2 (C17 or C10), 126.2 (C10 or C17), 125.0 (C2), 124.8 (C16 or C11), 124.7 (C11 or C16), 124.6 (Ph-C_{para}), 124.4 (C15 and C12), 123.9 (C12 or C15), 122.6 (C5), 29.4 (*C*H(CH_3)$_2$), 24.8 (CH(*C*H$_3$)$_2$), 23.0 (CH(*C*H$_3$)$_2$).

4.2.5. [Co(κ^2N,N′-$NC_{16}H_9C(H){=}N$-2,6-$iPr_2C_6H_3)_2$] (**9**)

The same procedure described for the synthesis of **6** was followed, but a solution of sodium salt **4** prepared *in situ* (0.32 g, 0.75 mmol) was employed, and added to $CoCl_2$ (40 mg, 0.31 mmol). After extraction of the reaction products with toluene, the resulting solution was concentrated and stored at −20 °C, giving a brown-reddish paramagnetic solid of **9**. Attempts to obtain crystals suitable for X-ray diffraction were carried out by recrystallisation of the obtained powder from Et_2O, but no single crystals were obtained. Yield: 0.25 g (91% based on $CoCl_2$). Anal. Calcd. for $C_{58}H_{54}N_4Co \cdot C_4H_{10}O$, obtained (*calculated*): C, 78.65 (*79.21*); H, 6.79 (*6.86*); N, 6.19 (*5.96*). ESI-MS: *m*/*z* 866 $[M + H]^+$ (*calculated* for $C_{58}H_{55}N_4Co$ $[M + H]^+$, *866*). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 20.52 (s, 2H), 14.65 (s, 2H), 13.96 (s, 2H), 12.52 (s, 2H), 5.01 (s, 2H), 3.99 (*br*, 10H), 3.42 (q, 4H, $^3J_{HH} = 6.9$ Hz, (CH_3C*H*$_2$)O), 3.22 (s, 2H), 1.14 (t, 6H, $^3J_{HH} = 6.9$ Hz, (C*H*$_3$$CH_2$)O), 0.09 (s, 16H), −3.26 (s, 4H), −6.54 (s, 2H), −25.97 (*br*, 10H).

4.2.6. Attempt to synthesise [Fe(κ^2N,N′-$NC_4H_3C(H){=}N{-}C_6H_5)_2$]

The same procedure described for the synthesis of **8** was followed, but a solution of sodium salt **1** prepared *in situ* (0.19 g, 1.0 mmol) was employed, and added to $FeCl_2$ (65 mg, 0.5 mmol).

After extraction of the reaction products with Et_2O, the resulting solution was concentrated, double-layered with *n*-hexane and stored at −20 °C. However, the reaction product was highly unstable, easily decomposing from red crystals to a brownish powder. Nevertheless, it was still possible to isolate from the mixture very few crystals of **10**, which were suitable enough for X-ray diffraction, allowing the determination of its crystal structure.

4.2.7. Attempt to synthesise $[Fe(\kappa^2N, N'\text{-}NC_4H_3C(H){=}N\text{-}iPr_2C_6H_3)_2]$

The same procedure described for the synthesis of **6** was followed, but a solution of sodium salt **2** prepared *in situ* (0.27 g, 1.0 mmol) was employed, and added to $FeCl_2$ (65 mg, 0.5 mmol). After extraction of the reaction products with *n*-hexane, the resulting solution was concentrated and stored at −80 °C. However, the reaction product was highly unstable, easily decomposing from black crystals to a brownish powder. Nevertheless, it was still possible to isolate from the mixture very few crystals of **11**, which were suitable enough for X-ray diffraction, allowing the determination of its crystal structure.

4.2.8. $[Fe(\kappa^2N,N'\text{-}NC_4H_3C(H){=}N{-}C_6H_5)_2(NC_5H_5)]$ *(**12**)*

The same procedure described for **6** was followed, but a solution of sodium salt **1** prepared *in situ* (0.20 g, 1.03 mmol) was employed, and added to a suspension of $FeCl_2$ (65 mg, 0.5 mmol) and pyridine (1 mL, 12.34 mmol). The residue was washed with *n*-hexane, Et_2O and toluene. After extraction of the reaction products with THF, the resulting solution was concentrated and stored at −20 °C, giving highly sensitive orange-red paramagnetic crystals of **12**, suitable for X-ray diffraction. Yield: 0.15 g (64%). Anal. Calcd. for $C_{27}H_{23}N_5Fe$, obtained (*calculated*): C, 67.80 (*68.51*); H, 4.54 (*4.90*); N, 11.02 (*14.79*). ^1H NMR (300 MHz, CD_2Cl_2): 47.07 (s, 1H), 32.61 (*br*, 1H), 26.83 (s, 1H), 19.85 (s, 2H), 3.02 (s, 7H), 1.65 (s, 3H), −0.24 (s, 5H), −2.04 (*br*, 7H).

4.2.9. $[Cu(\kappa^2N,N'\text{-}NC_4H_3C(H){=}N\text{-}2,6\text{-}iPr_2C_6H_3)]_x$ *(**13**)*

The same procedure described for **6** was followed, but a solution of sodium salt **2** prepared *in situ* (0.27 g, 1.0 mmol) was employed, and added to CuBr (0.14 g, 1.0 mmol). The residue was washed with *n*-hexane. The remaining product was extracted with toluene, and the resulting solution was concentrated, double layered with *n*-hexane (1:3), and stored at −20 °C, giving an off-white solid of **13**. Yield: 0.18 g (57%). Anal. Calcd. for $C_{34}H_{42}N_4Cu_2$, obtained (*calculated*): C, 63.78 (*64.43*); H, 6.83 (*6.68*); N, 8.73 (*8.84*). ESI-MS: *m/z* 633 $[M + H]^+$ (*calculated* for $C_{34}H_{43}N_4Cu_2$ $[M + H]^+$, *633*). ^1H NMR (400 MHz, C_6D_6): Admitting that two isomers (**13A** and **13B**) were observed at room temperature in a ratio 2:1 (**13A**:**13B**), which was invariant with temperature, their NMR spectra are reported as follows: **13A** δ 7.52–6.82 (m, 6H, N=C*H*, Ph-H_{meta}, Ph-H_{para}, H5 and H3), 6.51 (dd, 1H, $^3J_{HH}$ = 3.6 Hz and $^4J_{HH}$ = 1.7 Hz, H4), 3.20 (sep, 2H, $^3J_{HH}$ = 6.8 Hz, C*H*$(CH_3)_2$), 1.0 (d, 6H, $^3J_{HH}$ = 6.8 Hz, $CH(CH_3)_2$), 0.80 (d, 6H, $^3J_{HH}$ = 6.8 Hz, $CH(CH_3)_2$). **13B** δ 7.52–6.82 (m, 6H, N=C*H*, Ph-H_{meta}, Ph-H_{para}, H5 and H3), 6.43 (dd, 1H, $^3J_{HH}$ = 3.5 Hz and $^4J_{HH}$ = 1.7 Hz, H4), 3.48 (sep, 2H, $^3J_{HH}$ = 6.8 Hz, C*H*$(CH_3)_2$), 1.20 (d, 6H, $^3J_{HH}$ = 6.8 Hz, $CH(CH_3)_2$), 1.06 (d, 6H, $^3J_{HH}$ = 6.8 Hz, $CH(CH_3)_2$). ^1H NMR (300 MHz, toluene-d_8): **13A** δ 7.52–6.88 (m, 6H, N=C*H*, Ph-H_{meta}, Ph-H_{para}, H5 and H3), 6.46 (*br*, 1H, H4), 3.18 (sep, 2H, $^3J_{HH}$ = 6.8 Hz, C*H*$(CH_3)_2$), 1.0 (d, 6H, $^3J_{HH}$ = 6.8 Hz, $CH(CH_3)_2$), 0.79 (d, 6H, $^3J_{HH}$ = 6.8 Hz, $CH(CH_3)_2$). **13B** δ 7.52–6.88 (m, 6H, N=C*H*, Ph-H_{meta}, Ph-H_{para}, H5 and H3), 6.46 (*br*, 1H, H4), 3.47 (sep, 2H, $^3J_{HH}$ = 6.8 Hz, C*H*$(CH_3)_2$), 1.21 (d, 6H, $^3J_{HH}$ = 6.8 Hz, $CH(CH_3)_2$), 1.01 (d, 6H, $^3J_{HH}$ = 6.8 Hz, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (300 MHz, C_6D_6): **13A** δ 161.9 (N=*C*H), 146.3 (Ph-C_{ipso}), 141.8 (Ph-C_{ortho}), 141.3 (C4), 135.1 (C2), 129.3 (C5), 126.6 (Ph-C_{para}), 123.9 (Ph-C_{meta}), 113.9 (C3), 28.6 (*C*H$(CH_3)_2$), 23.8 $(CH(CH_3)_2)$, 22.8 $(CH(CH_3)_2)$. **13B** δ 161.8 (N=*C*H), 146.2 (Ph-C_{ipso}), 142.1 (Ph-C_{ortho}), 141.0 (C4), 134.8 (C2), 126.9 (C5), 125.7 (Ph-C_{para}), 124.2 (Ph-C_{meta}), 113.8 (C3), 28.7 (*C*H$(CH_3)_2$), 24.0 $(CH(CH_3)_2)$, 23.6 $(CH(CH_3)_2)$.

4.2.10. Isolation of $[Cu(\kappa^2N,N'\text{-}NC_4H_3C(H){=}N\text{-}2,6\text{-}iPr_2C_6H_3)_2]$ *(**14**)*

The pale yellow solutions resulting from the *n*-hexane washings of compound **13** in the previous reaction were filtered into a beaker under O_2/moisture atmosphere. The solvent was evaporated under vacuum and recrystallised from *n*-hexane at −20 °C, giving black crystals of **14**. Yield: 0.097 g (17%). Anal. Calcd. for $C_{34}H_{42}N_4Cu{\cdot}H_2O$, obtained (*calculated*): C, 70.02 (*69.42*); H, 7.82 (*7.54*); N, 9.49 (*9.52*).

Table 3
Crystallographic data for **5**, **7**, **10**–**12** and **14**.

	5	**7**	**10**	**11**	**12**	**14**
Formula	$C_{22}H_{18}N_4Ni$	$C_{48}H_{34}Cl_4N_4Ni$	$C_{26}H_{28}FeN_4NaO_2$	$C_{68}H_{84}Fe_2N_8O$	$C_{27}H_{23}FeN_5$	$C_{34}H_{42}CuN_4$
M	397.09	867.30	507.36	1141.13	473.35	570.26
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
T (K)	150	150	150	150	150	150
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1$	$P2_1/c$	$P2_1/n$	$P2_1/c$	$C2/c$	$P\,2_1/c$
a (Å)	9.5447(11)	14.580(4)	11.717(4)	13.1660(17)	19.548(6)	8.3010(8)
b (Å)	20.320(2)	13.199(4)	11.947(5)	24.591(4)	8.689(2)	32.295(3)
c (Å)	14.2252(16)	20.730(6)	18.090(7)	22.747(3)	14.885(5)	11.4000(10)
α (°)	90	90	90	90	90	90
β (°)	101.047(6)	99.55(2)	96.84(2)	103.743(9)	116.398(14)	97.283(5)
γ (°)	90	90	90	90	90	90
V (Å^3)	2707.9(5)	3934(2)	2514.4(15)	7153.8(17)	2264.6(12)	3031.5(5)
Z	6	4	4	4	4	4
ρ_{calc} (g.cm^{-3})	1.461	1.464	1.340	1.180	1.388	1.249
μ (mm^{-1})	1.089	0.807	0.647	0.454	0.691	0.749
Crystal size	0.24 × 0.14 × 0.04	0.10 × 0.04 × 0.01	0.28 × 0.24 × 0.08	0.60 × 0.40 × 0.08	0.18 × 0.09 × 0.05	0.15 × 0.10 × 0.03
θ_{max} (°)	25.68	25.22	25.83	25.25	27.60	25.08
Total data	42737	30841	34090	128460	10229	45786
Unique data	4962	3295	2625	6115	1927	3927
R_{int}	0.1710	0.1582	0.1956	0.2422	0.0532	0.0768
R $[I > 2\sigma(I)]$	0.0720	0.0583	0.0908	0.0979	0.0392	0.0425
R_w	0.1395	0.0925	0.2463	0.2132	0.0865	0.0850
Goodness of fit	0.926	0.915	1.010	0.989	1.065	1.030
ρ_{min}	−1.140	−0.481	−1.049	−0.534	−0.390	−0.379
ρ_{max}	1.018	0.435	1.845	0.536	0.445	0.294

ESI-MS: m/z 570 $[M + H]^+$ (*calculated* for $C_{34}H_{43}N_4Cu$ $[M + H]^+$, *570*).

4.3. *X-ray diffraction studies*

Crystallographic and experimental details of crystal structure determinations are listed in Table 3. The crystals were selected under an inert atmosphere, covered with polyfluoroether oil, and mounted on a nylon loop. Crystallographic data for compounds **5**, **7**, **10**–**12**, and **14** were collected using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) on a Bruker AXS-KAPPA APEX II diffractometer equipped with an Oxford Cryosystem open-flow nitrogen cryostat, at 150 K. Cell parameters were retrieved using Bruker SMART [16] software and refined using Bruker SAINT [17] on all observed reflections. Absorption corrections were applied using SADABS [18]. Structure solution and refinement were performed using direct methods with the programs SIR92 [19], SIR97 [20] and SIR2004 [21] included in the package of programs WINGX-Version 1.80.05 [22]. All hydrogen atoms were inserted in idealised positions and allowed to refine riding on the parent carbon atom. All the structures refined to a perfect convergence, even though some of the crystals were of poorer quality, such as **5**, **7**, **10** and **11**, which presented high R_{int} and relatively low ratio of observed/unique reflections. Crystal **11** showed the presence of disordered solvent molecules, the PLATON/SQUEEZE [23] routine being applied, since a good disorder model was impossible to attain. Graphic presentations were prepared with ORTEP-III [24]. Data was deposited in CCDC under the deposit numbers 963691 for **5**, 963692 for **7**, 963693 for **10**, 963694 for **11**, 963695 for **12**, and 963696 for **14**.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2013.10.053.

References

[1] J.-S. Mu, Y.-X. Wang, B.-X. Lia, Y.-S. Li, Dalton Trans. 40 (2011) 3490–3497.

[2] R.H. Holm, A. Chakravorty, L.J. Theriot, Inorg. Chem. 5 (1966) 625–635 and references cited therein.

[3] K. Mashima, H. Tsurugi, J. Organomet. Chem. 690 (2005) 4414–4423 and references cited therein.

[4] (a) V.C. Gibson, S.K. Spitzmesser, Chem. Rev. 103 (2003) 283–315;
(b) Y. Yoshida, S. Matsui, T. Fujita, J. Organomet. Chem. 690 (2005) 4382–4397.

[5] C.S.B. Gomes, D. Suresh, P.T. Gomes, L.F. Veiros, M.T. Duarte, T.G. Nunes, M.C. Oliveira, Dalton Trans. 39 (2010) 736–748.

[6] (a) S.A. Carabineiro, L.C. Silva, P.T. Gomes, L.C.J. Pereira, L.F. Veiros, S.I. Pascu, M.T. Duarte, S. Namorado, R.T. Henriques, Inorg. Chem. 46 (2007) 6880–6890;
(b) S.A. Carabineiro, R.M. Bellabarba, P.T. Gomes, S.I. Pascu, L.F. Veiros, C. Freire, L.C.J. Pereira, R.T. Henriques, M.C. Oliveira, J.E. Warren, Inorg. Chem. 47 (2008) 8896–8911.

[7] C.S.B. Gomes, S.A. Carabineiro, P.T. Gomes, M.T. Duarte, Inorg. Chim. Acta 367 (2011) 151–157.

[8] R.M. Bellabarba, P.T. Gomes, S.I. Pascu, Dalton Trans. (2003) 4431–4436.

[9] C.S.B. Gomes, P.T. Gomes, R.E. Di Paolo, A.L. Maçanita, M.T. Duarte, M.J. Calhorda, Inorg. Chem. 48 (2009) 11176–11186.

[10] (a) D. Suresh, C.S.B. Gomes, P.T. Gomes, R.E. Di Paolo, A.L. Maçanita, M.J. Calhorda, A. Charas, J. Morgado, M.T. Duarte, Dalton Trans. 41 (2012) 8502–8505;
(b) D. Suresh, C.S.B. Gomes, P.T. Gomes, R.E. Di Paolo, A.L. Maçanita, M.J. Calhorda, A. Charas, J. Morgado, M.T. Duarte, Dalton Trans. 41 (2012) 14713.

[11] D.M. Dawson, D.A. Walker, M. Thornton-Pett, M. Bochmann, J. Chem. Soc. Dalton Trans. (2000) 459–466.

[12] P. Pérez-Puente, E. de Jésus, J.C. Flores, P. Gómez-Sal, J. Organomet. Chem. 693 (2008) 3902–3906.

[13] A.R. Dias, L.F. Veiros, J. Organomet. Chem. 690 (2005) 1840–1844.

[14] Q. Su, W. Gao, Q.-L. Wu, L. Ye, G.-H. Li, Y. Mu, Eur. J. Inorg. Chem. (2007) 4168–4175.

[15] (a) A.W. Addison, T.N. Rao, J. Reedijk, J. van Rijn, G.C. Verschoor, J. Chem. Soc. Dalton Trans. (1984) 1349–1356;
(b) C. O'Sullivan, G. Murphy, B. Murphy, B. Hathaway, J. Chem. Soc. Dalton Trans. (1999) 1835–1844.

[16] SMART Software for the CCD Detector System Version 5.625, Bruker AXS Inc., Madison, WI, USA, 2001.

[17] SAINT Software for the CCD Detector System, Version 7.03, Bruker AXS Inc., Madison, WI, USA, 2004.

[18] G.M. Sheldrick, SADABS, Program for Empirical Absorption Correction, University of Göttingen, Göttingen, 1996.

[19] A. Altomare, G.L. Cascarano, C. Giacovazzo, A. Guagliardi, J. Appl. Crystallogr. 26 (1993) 343–350.

[20] A. Altomare, M.C. Burla, M. Camalli, G.L. Cascarano, C. Giacovazzo, A. Guagliardi, A.G.C. Moliterni, G. Polidori, R. Spagna, J. Appl. Crystallogr. 32 (1999) 115–119.

[21] M.C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G.L. Cascarano, L. De Caro, C. Giacovazzo, G. Polidori, R. Spagna, J. Appl. Crystallogr. 38 (2005) 381–388.

[22] L.J. Farrugia, J. Appl. Crystallogr. 32 (1999) 837–838.

[23] A.L. Spek, J. Appl. Crystallogr. 36 (2003) 7–13.

[24] M.N. Burnett, C.K. Johnson, ORTEP-III: Oak Ridge Thermal Ellipsoid Plot Program for Crystal Structure Illustration, Oak Ridge National Laboratory, 1996. Report ORNL-6895.