Dalton Transactions

PAPER

Dynamic Article Links ▶

Ni(II) and Pd(II) pyridinyloxazolidine-compounds: synthesis, X-ray characterisation and catalytic activities in the aza-Michael reaction†

G. Attilio Ardizzoia,[a] Stefano Brenna*[a] and Bruno Therrien[b]

The 3-phenyl-2-(pyridin-2-yl)oxazolidine ligand (**ppo**) was synthesised and its coordination behaviour regarding Ni(II) and Pd(II) centres was studied. The reaction with K_2PdCl_4 affords $[Pd(N,N'\text{-}\mathbf{ppo})Cl_2]$ (**1**), in which **ppo** binds to palladium *via* the pyridyl nitrogen and the oxazolyl nitrogen atoms. On the contrary, reaction with $NiCl_2 \cdot 6H_2O$ produces $[Ni(N,O\text{-}\mathbf{ppo})_2Cl_2]$ (**2**), in which two **ppo** ligands are coordinated *via* the pyridyl nitrogen and the oxygen atom of the oxazolidine ring. The X-ray diffraction analysis of the complexes confirms a square planar geometry for Pd(II) in **1** and an octahedral configuration around Ni(II) in **2**, which, to the best of our knowledge, represents the first reported example of a structurally characterised nickel-oxazolidine compound. In addition, both complexes prove to be active catalysts under mild conditions in the aza-Michael reaction of (*E*)-4-phenylbut-3-en-2-one (benzalacetone) with aliphatic amines.

Introduction

The rational design of coordination compounds can often be achieved by the use of suitable heteropolydentate ligands.[1] Among others, nitrogen-containing heterocyclic ligands have been very purposeful in the synthesis of diverse types of complexes showing mixed structures and bonding.[2] In this field, despite the large use of oxazoline-based compounds,[3] little has been reported on their saturated counterpart, oxazolidines. The interest in the use of these derivatives in coordination chemistry is mostly related to the presence of two potential donor sites (N and O) together with the ease of ring-functionalisation by varying the starting materials. For instance, oxazolidines are conveniently prepared by condensation of aldehydes with β-amino alcohols and the large accessibility of the latter in enantiopure form (*e.g.* ephedrine derivatives) facilitates the synthesis of a wide variety of chiral oxazolidine-based ligands.[4]

Examples of the use of oxazolidine-containing compounds in catalytic reactions are the enantioselective addition of Et_2Zn to aldehydes,[5] the Ru-catalysed epoxidation of olefins[6] and the allylic substitution mediated by palladium.[7] Importantly, the majority of these catalysts are prepared *in situ*, and only a few papers report the isolation and crystallographic characterisation of oxazolidine-complexes. The first structure of a compound containing an *NH* coordinated oxazolidine dates back to 1992,[8]

whereas some more recent reports on the structural description of phosphinoxazolidine-palladium[9] and rhodium[10] species appeared. Finally, a paper by Jones[11] and co-workers has described the only two known crystalline structures of transition metal complexes bearing pyridinyl-oxazolidine derivatives: these examples being summarised in Chart 1.
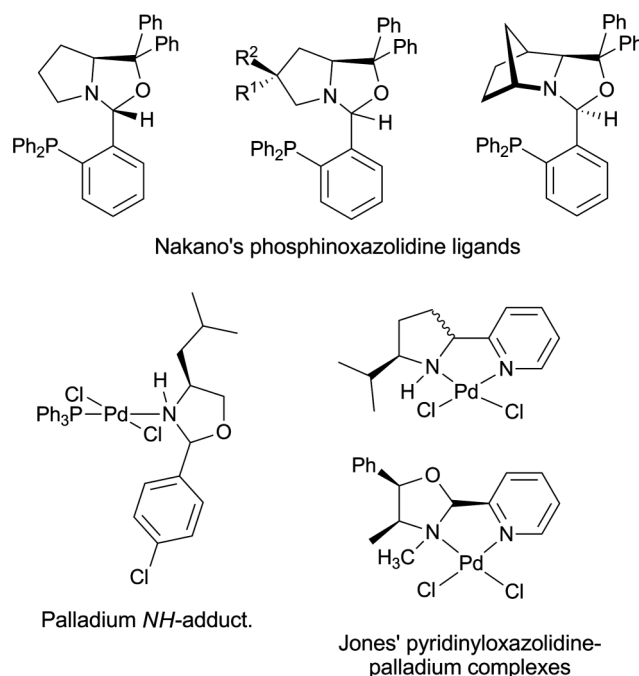

Chart 1 Structurally characterised oxazolidine-based ligands or complexes.

[a]*Dipartimento di Scienze Chimiche e Ambientali, Università degli Studi dell'Insubria, Via Valleggio, 11-22100, Como, Italy*
[b]*Service Analytique Facultaire, Université de Neuchâtel, Ave de Bellevaux 51, CH-2000, Neuchâtel, Switzerland*

We recently initiated a study on the coordination chemistry of fully saturated N-containing heterocylces and we have already reported on the coordination chemistry of dihydrobenzoxazine-type ligands towards copper[12] and group-12 metals.[13] To continue this study, we have now tested the coordination chemistry of ligands based on five-membered rings, specifically those containing an oxazolidine skeleton. Herein we report the coordination chemistry of 3-phenyl-2-(pyridin-2-yl)oxazolidine (**ppo**) towards Pd(II) and Ni(II) centres. The versatility displayed by the ligand, which coordinates in a different chelating mode depending on the metal centre is presented (Chart 2).[14] The X-ray structure analysis of these complexes includes what, to the best of our knowledge, is the first example of a crystallographic description of a nickel-oxazolidine compound. Finally, the synthesised species have been tested as catalysts in the conjugate addition of aliphatic amines to (*E*)-4-phenyl-but-3-en-2-one (benzalacetone) under mild conditions.
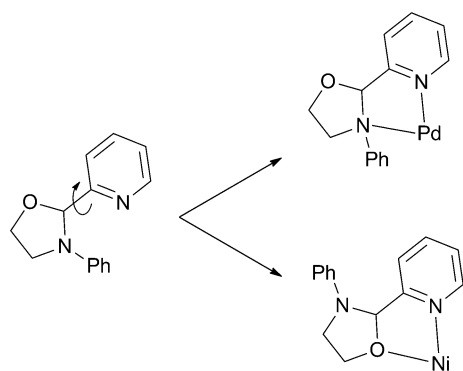

Chart 2 Schematic representation of the different chelating coordination modes displayed by 3-phenyl-2-(pyridin-2-yl)oxazolidine (**ppo**).

Results and discussion

Synthesis of 3-phenyl-2-(pyridin-2-yl)oxazolidine (ppo)

The ligand **ppo** is prepared following a reported procedure[15] by heating at 70 °C in ethanol an equimolar mixture of 2-anilino ethanol and 2-pyridinecarboxaldehyde (Scheme 1). The analysis of the ^{1}H and ^{13}C{^{1}H} NMR spectra (CD$_3$CN, 25 °C) confirms the formation of the desired product (see Scheme 1 for atom numbering). Specifically, the singlet at 5.87 ppm is easily attributed to H-2, while the diastereotopic CH$_2$ groups in position 4 and 5 of the strained oxazolidine ring appear as multiplets centred at 3.72 and 4.23 ppm, respectively. The related ^{13}C resonances are observed at 93.3 ppm (C-2), 66.7 ppm (C-5) and 48.5 ppm (C4). The ring-chain tautomerism typical of *N-H*-1,3-oxazolidines[16] is in this case forbidden by the presence of the phenyl substituent
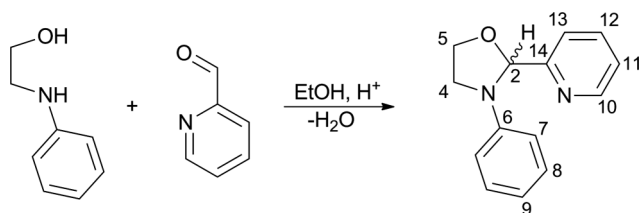
Scheme 1 Synthesis of **ppo** and relative atom numbering.

on the starting β-amino alcohol. As a consequence, the closed heterocyclic form is the only one present in solution, and signals due to the corresponding iminic form are not detected in the NMR spectra.

It should be stressed that **ppo** possesses a stereogenic centre in position 2 of the oxazolidine ring. However, no efforts were made to isolate the ligand in an enantiomerically pure form, and **ppo** was always used as a racemic mixture.

Synthesis and characterisation of the complexes

The reaction of **ppo** with K$_2$PdCl$_4$ in a 1 : 1 molar ratio, in methanol at room temperature, gives a yellow-to-orange suspension, from which a yellow solid is isolated in good yields after filtration. Together with the singlet at 5.80 ppm attributed to H-2, the ^{1}H NMR spectrum of **1** shows three aliphatic resonances corresponding to the protons of the CH$_2$ groups at 3.25 (H$_a$-4), 4.46 (H$_a$-5) and 5.03 (H$_b$-4/5) ppm, respectively (see ESI† for signals attribution). The diastereotopic protons in positions 4 and 5 are markedly split with respect to the free ligand: H$_a$-4 and H$_b$-4 being respectively at 3.58 and 3.84 ppm, and H$_a$-5 and H$_b$-5 being both at 4.26 ppm in free **ppo**. In the ^{13}C{^{1}H} NMR spectrum the signals relative to C-2, C-4 and C-5 are shifted downfield as compared to the free ligand (100.7, 58.0 and 66.9 ppm, in that order). The slightly higher splitting associated to H-4 with respect to H-5 suggests that **ppo** coordinates to palladium *via* the N-atom of the oxazolidine ring, thus assuming an *N,N′* chelation mode (Fig. 1). Accordingly, the complex can be described as [Pd(*N,N′*-**ppo**)Cl$_2$] (**1**). This finding was further confirmed by the X-ray crystal structure analysis of **1** (Fig. 2).

Complex **1** crystallises in the centrosymmetric space group *P* 2$_1$/*c* and crystals of **1** are found as racemates. The palladium atom adopts a square-planar geometry in which two chlorides and the two nitrogen atoms of the **ppo** ligand occupy the four coordination sites. Coordination of **ppo** in a *N,N′* chelating mode imposes distortion to the square-planar geometry, the N1–Pd1–N2 angle being acute at 82.23(13)°. The Pd–N distances are non-equivalent, the Pd N-pyridyl bond (2.031(3) Å) is shorter than the Pd N-oxazolidine bond (2.095(3) Å), which is consistent with those observed in the analogous complexes [Pd$_2$(*N,N′*-L)$_2$Cl$_2$] (*N,N′*-L = 3,4-dimethyl-5-phenyl-2(pyridine-2-yl)oxazolidine)[11] and [Pd$_2$(*N,N′*-L′)$_2$Cl$_2$] (*N,N′*-L′ = 3-benzyl-4-methyl-5-phenyl-2(pyridine-2-yl)oxazolidine).[17]

This first outcome encouraged us to investigate as well the behaviour of **ppo** towards nickel(II). Treatment of a solution of NiCl$_2$·6H$_2$O in acetonitrile at 60 °C with an equimolar amount of **ppo** affords a suspension from which a green solid could be easily recovered. The yield of the reaction is quite low (48%) and the mother liquors remain green, most probably due to the presence of unreacted nickel chloride. This could only be explained by a stoichiometry different from 1 : 1 between **ppo** and the metal centre in the final nickel compound, as confirmed by the elemental analysis which gave a 1 : 2 nickel : **ppo** ratio. To further confirm this hypothesis, a second reaction with double the amount of ligand has been performed, resulting in the formation of the green compound in quantitative yield. This complex is then formulated as [Ni(**ppo**)$_2$Cl$_2$] (**2**).

The configuration at the metal centre is determined by the X-ray structure analysis of [Ni(**ppo**)$_2$Cl$_2$]. The crystals are obtained
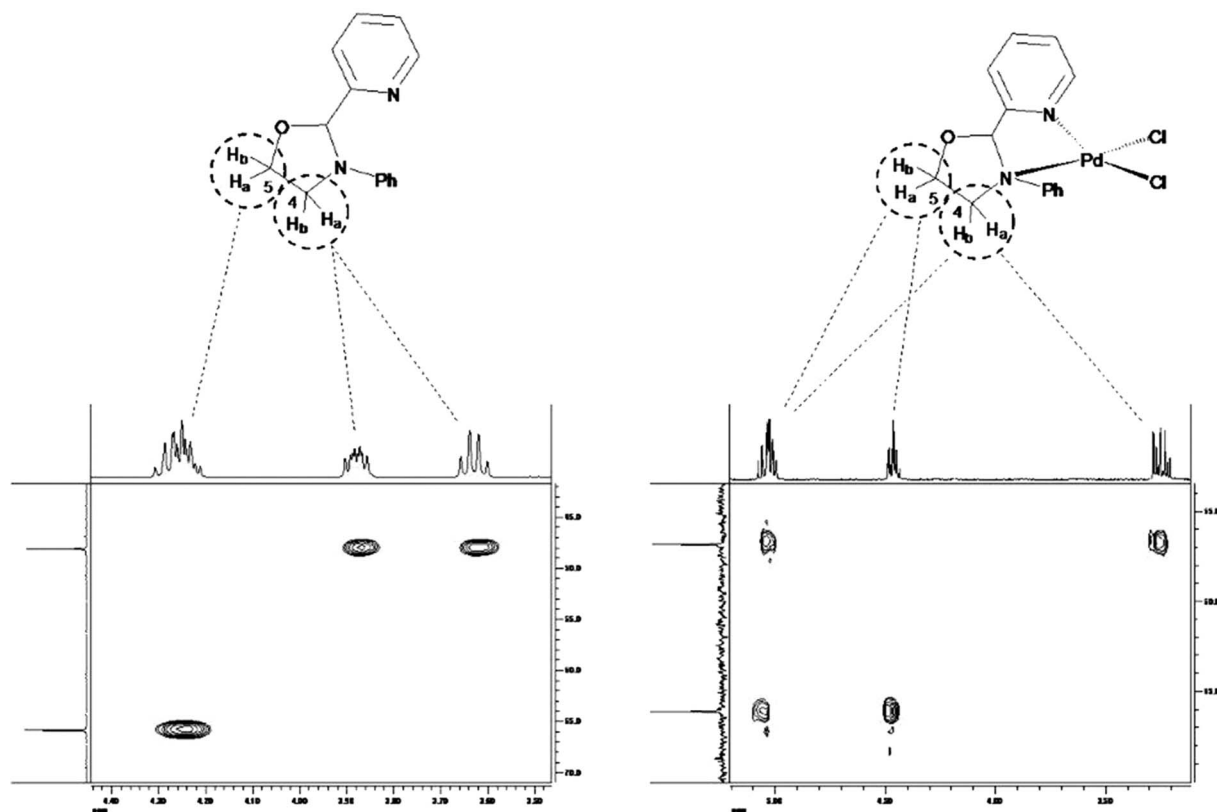
Fig. 1 ¹H-¹³C HETCOR spectra of **ppo** (left) and **1** (right) in the aliphatic region. Dashed lines indicate H-4$_{a/b}$ and H-5$_{a/b}$ splitting in the free ligand and after coordination to palladium.
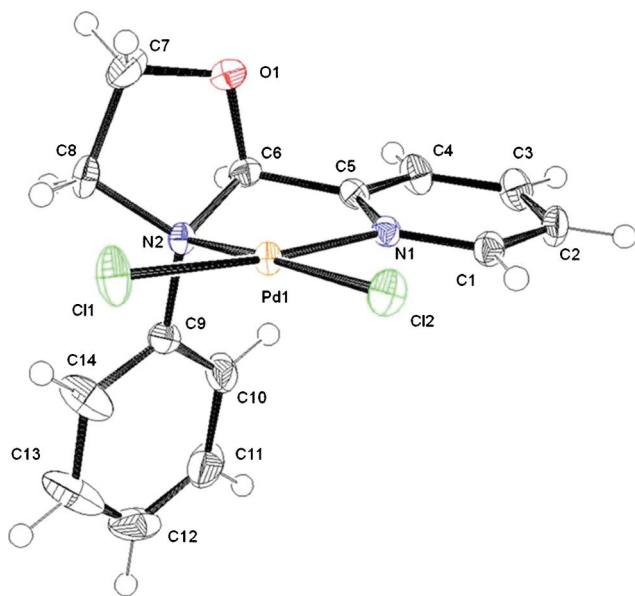

Fig. 2 ORTEP drawing of **1** (50% probability level ellipsoids) with selected bond lengths (Å) and angles (°): Pd1–Cl1 2.2982(11), Pd1–Cl2 2.2899(10), Pd1–N1 2.031(3), Pd1–N2 2.095(3); Cl1–Pd1–Cl2 90.22(4), Cl1–Pd1–N2 94.41(10), Cl2–Pd1–N1 93.40(10), N1–Pd1–N2 82.23(13).

by slow diffusion of diethylether into a DMF solution of **2**. In the crystal, the central Ni(II) atom is positioned on an inversion centre and the metal is surrounded by two **ppo** ligands and two chlorides (Fig. 3). Each molecule of **ppo** chelates the metal ion *via*

the aromatic nitrogen of the pyridyl group and the oxygen of the oxazolidine part, thus being better described as chelating *N,O*-**ppo** ligands. Therefore, complex **2** is best formulated as [Ni(*N,O*-**ppo**)$_2$Cl$_2$]. To the best of our knowledge, this represents the sole example reported in the literature of a crystallographic investigation of a nickel-oxazolidine complex. Despite analogous systems previously described by us[12,13] showing the *N,N′* coordination towards hard ions such as Zn²⁺ and Cu²⁺ (absolute hardness (eV): Zn²⁺: 10.8; Cu²⁺: 8.3, respectively), in the case of **ppo** the *N,N′* coordination is encountered for the *soft* Pd²⁺ (6.8 eV), the *hard* Ni²⁺ centre (8.5 eV) inducing *N,O* coordination to **ppo**. This apparently conflicting conduct has presumably to be ascribed to the intrinsic electronic features of the oxazolidine and the oxazine ligands.

The different coordination modes of **ppo** towards Pd(II) and Ni(II) are summarised in Scheme 2.

Semi-empirical calculations (PM6 model) on the energetic levels of the five possible isomers deriving from the N,O-coordination of two **ppo** ligands to a 'NiCl₂' framework show that the isomer characterised *via* X-ray analysis is effectively the lowest in energy. Optimisation with the COSMO[18] model in acetonitrile shows that all other possible isomers are separated by more than 40 kJ mol⁻¹ from **2** (Fig. 4), reasonably ensuring that crystals used in the X-ray study are representative of the isolated bulk. A similar trend was also found from an *in vacuo* geometry optimisation (ESI†).

Octahedral complexes of nickel(II) are typically high spin paramagnetic species (S = 1), hence their NMR spectra are often either not reported[19] or recorded by opening the spectral window to remedy by signals broadening and downfield shift.[20] In complex [Ni(*N,O*-**ppo**)$_2$Cl$_2$], the Ni–N and Ni–O distances (2.055(4) Å
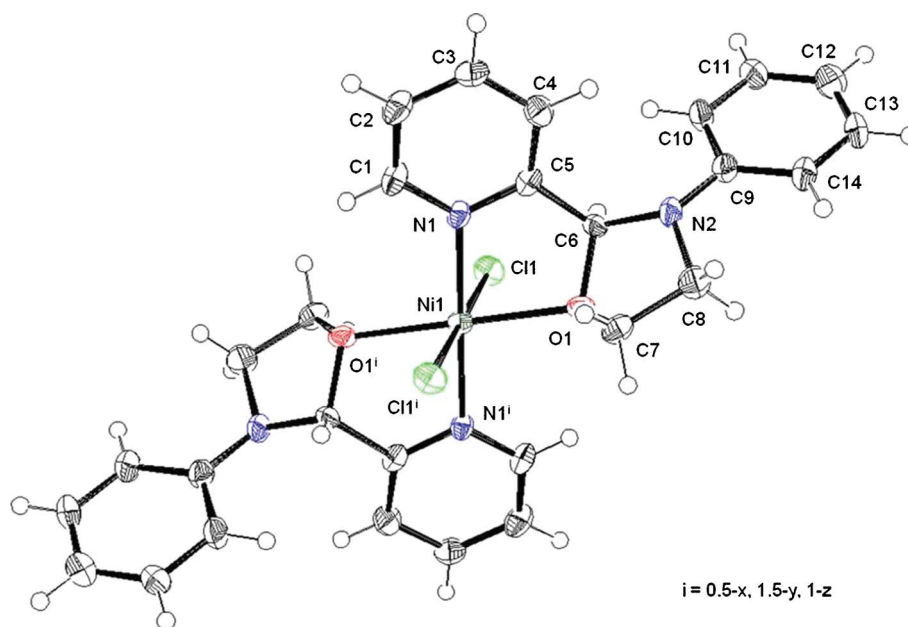
Fig. 3 ORTEP drawing of **2** (50% probability level ellipsoids) with selected bond lengths (Å) and angles (°): Ni1–Cl1 2.3857(14), Ni1–N1 2.055(4), Ni1–O1 2.167(3); Cl1–Ni1–N1 91.17(12), Cl1–Ni1–N1^i 88.83(12), Cl1–Ni1–O1 87.13(10), Cl1–Ni1–O1^i 92.87(10), N1–Ni1–O1 78.82(15), N1–Ni1–O1^i 101.18(15).
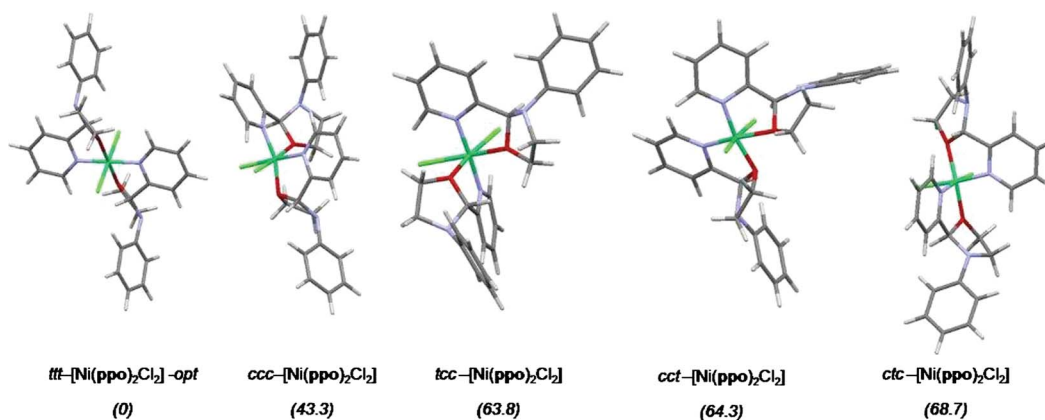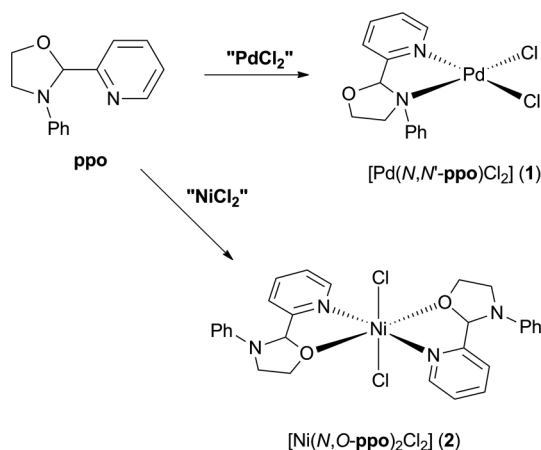

Fig. 4 Optimised geometries of possible isomers of **2** and relative energy (kJ mol^{-1}) with respect to **2**-*opt*.

Scheme 2 Coordination of **ppo** towards PdCl$_2$ and NiCl$_2$ fragments.

and 2.167(3) Å, respectively, Fig. 3) are in the range expected for high-spin Ni(II) compounds.[21] Accordingly, the ^{1}H NMR spectrum registered at room temperature in CD$_2$Cl$_2$ gives very broad undefined signals, thus confirming the octahedral high-spin nature of complex **2** in solution. Variable temperature magnetic moment measurements using solution ^{1}H NMR (Evans method) do not show any marked changes in the magnetic moment in the range –45 °C to 35 °C, μ_{eff} being comprised between 2.87 and 3.05 μ_B (ESI†). The spin-only theoretical value for an octahedral Ni(II) centre having two unpaired electrons is 2.83 μ_B, very close to the experimental data obtained with **2** (the methodology for magnetic moment measurement is summarised in the Experimental). Accordingly, we can conclude that the octahedral species is predominant over the whole range of temperatures. This finding is somehow corroborated by the lesser catalytic performances of crowded [Ni(N,O-**ppo**)$_2$Cl$_2$] species in aza-Michael reactions, when compared to the higher activity of the square planar [Pd(N,N'-**ppo**)Cl$_2$] at low temperatures (*vide infra*).
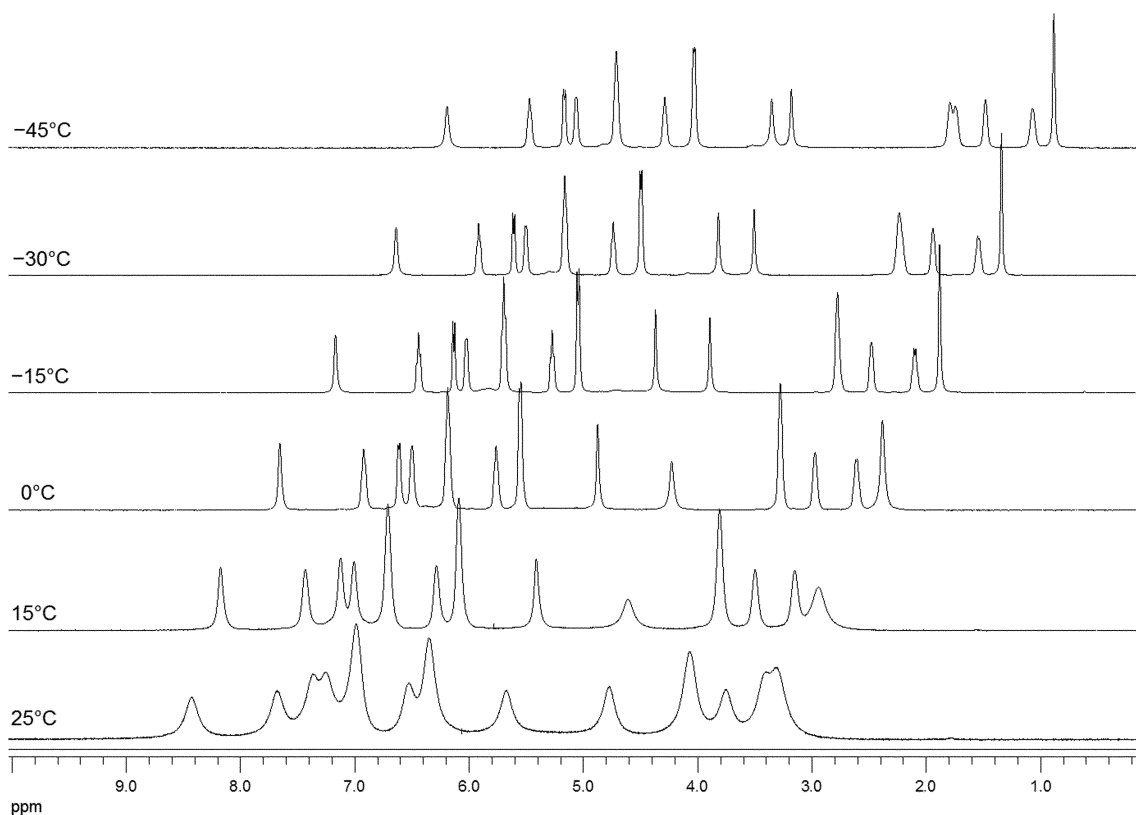
Fig. 5 ^{1}H VT NMR (CD$_3$OD) of compound **2** (the spectra are shifted by 0.5 ppm).

Differently, the ^{1}H NMR of **2** registered in CD$_3$OD at room temperature shows a pattern of resonances attributable to **ppo**. Even though the signals are not well-resolved, we tentatively carried out an interpretation of the spectrum by a comparison with the free ligand and consequently the signal at 5.67 ppm is attributed to H-2, whereas the three resonances at 3.40 (1H), 3.76 (1H) and 4.07 (2H) ppm are assigned to H$_a$-4, H$_a$-5 and H$_b$-4/5, respectively (ESI†). Afterwards, a variable temperature NMR experiment has been performed, lowering the temperature from 25 °C to –45 °C by 10-to-15-degree intervals (Fig. 5). Couplings in the aromatic region firstly appear at 0 °C, but a better resolution is obtained at –15 °C, where nearly all the multiplicities emerge. Moreover, on further lowering the temperature to –45 °C the separation of the signal centred at 4.07 ppm occurs, thus allowing discrimination between H$_b$-4 (4.18 ppm) and H$_b$-5 (4.23 ppm). The sharpening of the signals at low temperature does not derive from the conversion of [Ni(N,O-**ppo**)$_2$Cl$_2$] into a diamagnetic species. Indeed, the magnetic moment of **2** measured in CD$_3$OD at 25 °C, 0 °C and –45 °C spoke for a nickel atom with two unpaired electrons over the whole range of temperatures, μ_{eff} being 2.73, 2.81 and 2.94 μ_B, respectively (ESI†). Narrow line widths in ^{1}H NMR of paramagnetic nickel(II) complexes are rationalised in terms of fast relaxation times involving electron-spin relaxation.[22] Moreover, the value of line widths for complex **2** is very close to that observed for free **ppo** (8–9 Hz), then it is supposed that the unpaired electrons flip so rapidly with respect to the molecular motion that their effect on the nuclear relaxation time is partially averaged out.[23] Further studies will hopefully help to better elucidate this feature in the case of compound **2**, especially with regards to the solvent effect on this mechanism.

Aza-Michael catalytic reactions

Complexes **1** and **2** have been tested as catalysts in the conjugate addition of aliphatic amines to α,β-unsaturated ketones. This reaction, known as aza-Michael addition, is one of the most efficient methods to access β-amino carbonyl compounds, among which β-amino acids and β-lactams constitute an important target due to their pharmacological and synthetic importance.[24] Thus, many efforts have been devoted in the last decades to develop new catalysts for this reaction,[25] with special attention to its asymmetric variation.[26]
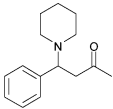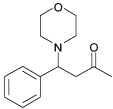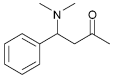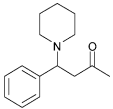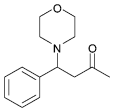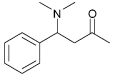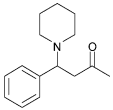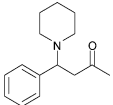
In this context, we decided to explore the catalytic activity of complexes [Pd(N,N'-**ppo**)Cl$_2$] and [Ni(N,O**ppo**)$_2$Cl$_2$] in the conjugate addition of aliphatic secondary amines (Me$_2$NH, piperidine, morpholine) to α,β-unsaturated ketones. In this specific case, (*E*)-4-phenylbut-3-en-2-one (benzalacetone) was used as a reference substrate (Scheme 3).

R$_2$NH = Me$_2$NH, piperidine, morpholine
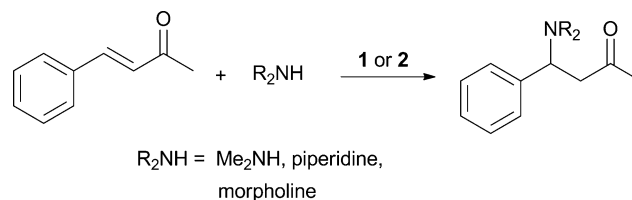
Scheme 3 Aza-Michael reactions catalysed by complexes **1** and **2**.

The catalyst was dissolved in anhydrous THF in the presence of benzalacetone (1 : 100 to the metal) and the reaction temperature was kept at 20 °C; then, the aliphatic amine was added (1 : 100 to

Table 1 Conjugate addition of secondary aliphatic amines to benzalacetone catalysed by [Pd(N,N′-**ppo**)Cl$_2$] (**1**) and [Ni(N,O-**ppo**)$_2$Cl$_2$] (**2**)[a]

Entry	Catalyst	Amine	Product	Yield[b] (%)
1	**1**	piperidine		92
2	**1**	morpholine		86
3	**1**	dimethylamine		83
4	**2**	piperidine		88
5	**2**	morpholine		81
6	**2**	dimethylamine		79
7[c]	**1**	piperidine		77
8[c]	**2**	piperidine		26

[a] Catalyst (0.025 mmol) : ketone : amine = 1 : 100 : 100; THF (8 ml), 20 °C. Internal standard: C$_6$(CH$_3$)$_6$, 50 mg. [b] Recorded after 24 h (GC-MS). [c] Reaction temperature: −30 °C.

the metal), monitoring the evolution of the reaction *via* GC-MS. The results are reported in Table 1.

Compounds **1** and **2** give both good to high yields of conversion of benzalacetone into the corresponding substituted amines, at 20 °C (entry 1–6). They also demonstrate activity even at low temperatures (−30 °C, entry 7–8), albeit the conversion of benzalacetone into the corresponding adduct with piperidine remains minor with **2** as compared to **1** in these conditions. This last behaviour can be ascribed to steric effects: the square planar Pd(II) centre in **1** is less hindered than the octahedral Ni(II) atom in **2**, where a chloride dissociation is required to generate an active catalytic species. The extent of this dissociation, and consequently the nickel-based catalyst activity, is reduced at low temperature.

Conclusions

In this study, the pyridinyloxazolidine ligand 3-phenyl-2-(pyridin-2-yl)oxazolidine (**ppo**) has been prepared and coordination to

palladium(II) and nickel(II) studied. The derived complexes have been characterised by X-ray single crystal analysis, showing different chelating modes of **ppo** depending on the metal. A N,N′-coordination in the square planar palladium species [Pd(N,N′-**ppo**)Cl$_2$] and a N,O-coordination towards nickel in [Ni(N,O-**ppo**)$_2$Cl$_2$] have been observed. In this latter compound, together with the two chloride ions, the nickel centre is surrounded by two **ppo** ligands, presenting an octahedral environment. These complexes have been tested as catalyst in the conjugate addition of aliphatic amines to benzalacetone, giving moderate-to-high yields of conversion under mild conditions.

Experimental

Materials

All reactions were carried out under nitrogen using standard Schlenk techniques. The solvents were dried and distilled according to standard procedures prior to use. NiCl$_2$·6H$_2$O, K$_2$PdCl$_4$, 2-anilino ethanol, 2-pyridinecarboxaldehyde and (E)-4-phenylbut-3-en-2-one (Aldrich) were used as purchased. All amines employed in the catalytic runs were taken from sealed bottles.

NMR spectra were recorded with an AVANCE 400 Bruker spectrometer at 400 MHz for ^{1}H NMR and 100 MHz for ^{13}C{^{1}H} NMR. Chemical shifts are given as δ values in ppm relative to residual solvent peaks as the internal reference. J values are given in Hz. ^{13}C NMR spectra are ^{1}H-decoupled and the determination of the multiplicities was achieved by the APT pulse sequence. Elemental analyses were obtained with a Perkin-Elmer CHN Analyser 2400 Series II. Quantitative analyses of products were performed on a Finningan Trace GC with a DB-5MS UI capillary column (30 m, 0.25 mm) equipped with a Finningan Trace MS.

Synthesis of 3-phenyl-2-(pyridin-2-yl)oxazolidine (ppo)

To a solution of 2-pyridinecarboxaldehyde (1 ml, d = 1.126 g ml^{-1}, 10.51 mmol) and 2-anilino ethanol (1.32 ml, d = 1.094 g ml^{-1}, 10.53 mmol) in ethanol (20 ml), 2–3 drops of glacial acetic acid were added and the mixture was heated at 70 °C for 24 h. Then the solvent was removed under reduced pressure, the residue dissolved in CH$_2$Cl$_2$ (20 ml) and washed with aqueous NaHCO$_3$. The organic phase was dried over Na$_2$SO$_4$, filtered and the solvent evaporated to dryness. The crude oil was crystallised from pentane giving a light yellow solid (1.90 g, 80%, mp 77 °C). Found: C, 74.12; H, 6.51; N, 12.10%. Calc. for C$_{14}$H$_{14}$N$_2$O: C, 74.31; H, 6.24; N, 12.38%. δ$_H$ (400 MHz, CDCl$_3$, 25 °C): 3.63 (1H, dd, $^2J_{HH}$ = 15.0, $^3J_{HH}$ = 7.5, H$_a$-4), 3.88 (1H, m, $^2J_{HH}$ = 8.1, $^3J_{HH}$ = 6.3, $^3J_{HH}$ = 4.3 H$_b$-4), 4.26 (2H, m, $^2J_{HH}$ = 8.3, $^3J_{HH}$ = 6.9, $^3J_{HH}$ = 4.7, H$_{a/b}$-5), 5.96 (1H, s, H-2), 6.58 (2H, dd, $^3J_{HH}$ = 4.1, $^4J_{HH}$ = 0.9, H-7), 6.77 (1H, td, $^3J_{HH}$ = 7.1, $^4J_{HH}$ = 0.7, H-9), 7.20 (2H, dt, $^3J_{HH}$ = 8.0, $^4J_{HH}$ = 1.2, H-8), 7.27 (1H, m, $^3J_{HH}$ = 7.5, $^3J_{HH}$ = 4.9, $^4J_{HH}$ = 1.0, H-11), 7.44 (1H, d, $^3J_{HH}$ = 7.8, H-13), 7.68 (1H, dt, $^3J_{HH}$ = 7.8, $^4J_{HH}$ = 1.7, H-12), 8.69 (1H, td, $^3J_{HH}$ = 4.8, $^4J_{HH}$ = 0.8, H-10). δ$_C$ (100 MHz, CDCl$_3$, 25 °C): 48.1 (C-4), 65.9 (C-5), 92.6 (C-2), 113.3 (C-7), 118.0 (C-9), 121.2 (C-13), 123.7 (C-11), 129.2 (C-8), 137.0 (C-12), 145.5 (C-6), 149.7 (C-10), 159.1 (C-14).

Synthesis of [Pd(N,N′-ppo)Cl$_2$] (1)

To a solution of K$_2$PdCl$_4$ (250 mg, 0.766 mmol) in methanol (20 ml), **ppo** (180 mg, 0.795 mmol) was added and the yellow-to-orange suspension was stirred for 4 h at room temperature. Then the solid was filtered, washed with water, methanol and finally with diethylether and dried *in vacuo* (284 mg, 92%). Found: C, 41.39; H, 3.71; N, 7.03%. Calc. for C$_{14}$H$_{14}$Cl$_2$N$_2$OPd: C, 41.66; H, 3.50; N, 6.94%. δ_H (400 MHz, CD$_3$CN, 25 °C): 3.25 (1H, m, $^2J_{HH}$ = 17.3, $^3J_{HH}$ = 8.8, $^3J_{HH}$ = 5.0, H$_a$-4), 4.46 (1H, m, $^2J_{HH}$ = 11.2, $^3J_{HH}$ = 6.4, $^3J_{HH}$ = 3.5, H$_a$-5), 5.03 (2H, m, H$_b$-4 and H$_b$-5), 5.80 (1H, s, H-2), 7.26 (2H, dd, $^3J_{HH}$ = 8.5, $^4J_{HH}$ = 1.3, H-7), 7.31 (1H, td, $^3J_{HH}$ = 7.0, $^4J_{HH}$ = 1.3, H-9), 7.36 (2H, dt, $^3J_{HH}$ = 8.0, $^4J_{HH}$ = 1.8, H-8), 7.63 (1H, m, $^3J_{HH}$ = 7.5, $^3J_{HH}$ = 5.9, $^4J_{HH}$ = 1.5 H-11), 7.92 (1H, dd, $^3J_{HH}$ = 8.0, $^4J_{HH}$ = 1.8, H-13), 8.19 (1H, dt, $^3J_{HH}$ = 7.9, $^4J_{HH}$ = 1.5, H-12).8.95 (1H, dd, $^3J_{HH}$ = 5.8, $^4J_{HH}$ = 0.8, H-10). δ_C (100 MHz, CD$_3$CN, 25 °C): 58.5 (C-4), 67.8 (C-5), 101.9 (C-2), 121.6 (C-7), 125.2 (C-13), 127.6 (C-11), 128.0 (C-9), 130.6 (C-8), 142.4 (C-12), 146.6 (C-6), 151.4 (C-10), 160.6 (C-14).

Yellow crystals suitable for X-ray investigation were obtained by slow diffusion of water into a CH$_3$CN solution of **1**.

Synthesis of [Ni(N,O-ppo)$_2$Cl$_2$] (2)

A solution of NiCl$_2$·6H$_2$O (300 mg, 1.26 mmol) in acetonitrile (15 ml) was treated with **ppo** (580 mg, 2.56 mmol) and the resulting suspension was stirred at 60 °C for 8 h. Then the solid was filtered, washed with acetonitrile, with diethylether and dried *in vacuo* (690 mg, 94%). Found: C, 57.24; H, 4.61; N, 9.29%. Calc. for C$_{28}$H$_{28}$Cl$_2$N$_4$O$_2$Ni: C, 57.77; H, 4.85; N, 9.62%.

Light green crystals suitable for X-ray investigation were obtained by slow diffusion of diethylether at 25 °C into a DMF saturated solution of **2**.

Magnetic moment measurements in solution

According to the NMR method described by Evans,[27] a solution of compound **2** (5–6 mg) in a mixture of CD$_2$Cl$_2$/toluene (or CD$_3$OD/toluene) (95/5 *v/v*) was prepared. A portion of this solution was transferred into a melting point capillary tube, which was then sealed with PTFE-tape and dropped into an NMR tube containing the CD$_2$Cl$_2$/toluene mixture. The chemical shift difference of the signal relative to the methyl on toluene between the inner and the outer tubes was measured at different temperatures. The following equations were used to calculate the molar susceptibility (χ_M) and the magnetic moment μ_{eff} (given in S.I. units):

$$\chi_M = \frac{3 \cdot D}{1000 \cdot f \cdot c}$$

$$\mu_{eff} = 798 \cdot \sqrt{T \cdot \chi_M}$$

where χ_M is the molar susceptibility of the sample in m^3 mol^{-1}, D is the difference in the chemical shift of toluene methyl in Hz, f is the frequency of operation of the spectrometer in Hz, c is the sample concentration in mol dm^{-3}, T is the temperature in K.

Computational details

All of the calculations have been performed with the MOPAC2009 program package.[28] The PM6 semiempirical method[29] was used to optimise the geometry (vacuum and acetonitrile) of the [Ni(**ppo**)$_2$Cl$_2$] species. For the sake of comparison, the geometry of complex **2** was optimised (**2**-*opt*) starting from the experimental Cartesian coordinates obtained by the X-ray diffraction study. Geometry optimisations in acetonitrile were performed using the COSMO dielectric continuum model as implemented in MOPAC2009[19] (MOPAC keywords: ESP = 37.5, RSOLV = 1.3, NSPA = 122). Graphics were obtained by the Jmol program package.[30]

Aza-Michael reactions

In a typical experiment, to a solution of the catalyst (0.025 mmol) and benzalacetone (2.5 mmol) in anhydrous THF (8 ml) kept at 20 °C, the amine (2.5 mmol) was added and the proceeding reaction was monitored *via* GC-MS. All of the products are known compounds and were easily identified by comparison of their spectroscopic data with those reported in the literature (see ESI† for mass spectra).

Single-crystal X-ray structure analysis

Crystals of **1** and **2** were mounted on a Stoe Image Plate Diffraction system equipped with a ϕ circle goniometer, using Mo-Kα graphite monochromated radiation (λ = 0.71073 Å) with ϕ range 0–200°. The structures were solved by direct methods using the program SHELXS-97, while the refinement and all further calculations were carried out using SHELXL-97.[31] The H-atoms were included in calculated positions and treated as riding atoms using the SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-square on F^2.

Table 2 Crystallographic and structure refinement parameters for complexes **1** and **2**

	1	2
Chemical formula	C$_{14}$H$_{14}$Cl$_2$N$_2$OPd	C$_{28}$H$_{28}$Cl$_2$N$_4$O$_2$Ni
Formula weight	403.57	582.15
Crystal system	Monoclinic	Monoclinic
Space group	P 2$_1$/c (no. 14)	C 2/c (no. 15)
Crystal colour and shape	Yellow block	Green block
Crystal size	0.23 × 0.18 × 0.15	0.22 × 0.17 × 0.16
a/Å	8.6308(6)	23.437(5)
b/Å	12.3692(6)	6.6280(10)
c/Å	15.1831(10)	17.741(4)
β (°)	114.683(5)	98.67(3)
V/Å^3	1472.79(16)	2724.4(9)
Z	4	4
T/K	173(2)	173(2)
D$_c$/g cm^{-3}	1.820	1.419
μ/mm^{-1}	1.618	0.941
Scan range (°)	2.21 < θ < 29.18	1.76 < θ < 29.19
Unique reflections	3971	3659
Observed refls [I > 2σ(I)]	3546	1812
R$_{int}$	0.0902	0.2128
Final R indices [I > 2σ(I)]^a	0.0424, wR$_2$ 0.0985	0.0890, wR$_2$ 0.1166
R indices (all data)	0.0496, wR$_2$ 0.1005	0.1891, wR$_2$ 0.1412
Goodness-of-fit	1.312	0.988
Max, Min $\Delta\rho$/e (Å^{-3})	0.856, −1.168	0.453, −0.616

^{a} Structures were refined on F_0^2: $wR_2 = [\Sigma[w (F_0^2 - F_c^2)^2]/\Sigma w (F_0^2)^2]^{1/2}$, where $w^{-1} = [\Sigma(F_0^2) + (aP)^2 + bP]$ and $P = [\max(F_0^2, 0) + 2F_c^2]/3$.

Crystallographic details are summarised in Table 2. Fig. 2 and 3 were drawn with ORTEP.[32]

Acknowledgements

Notes and references

1 D. Aguilà, E. Escribano, S. Speed, D. Talancón, L. Yermán and S. Alvarez, *Dalton Trans.*, 2009, 6610–6625 and references therein.
2 C. A. Caputo and N. D. Jones, *Dalton Trans.*, 2007, 4627–4640.
3 For recent reviews on catalytic applications of oxazoline-based complexes see: (*a*) G. C. Hargaden and P. J. Guiry, *Chem. Rev.*, 2009, **109**, 2505–2550; (*b*) R. Rasappan, D. Laventine and O. Reiser, *Coord. Chem. Rev.*, 2008, **252**, 702–714.
4 L. Neelakantan, *J. Org. Chem.*, 1971, **36**, 2256–2260.
5 E. Błocka, M. Jaworska, A. Kozakiewicz, M. Wełnak and A. Wojtczak, *Tetrahedron: Asymmetry*, 2010, **21**, 571–577; R. W. Parrot and S. R. Hitchcock, *Tetrahedron: Asymmetry*, 2007, **18**, 377–382.
6 C. Augier, L. Malara, V. Lazzeri and B. Waegell, *Tetrahedron Lett.*, 1995, **36**, 8775–8778.
7 Y. Okuyama, H. Nakano and H. Hongo, *Tetrahedron: Asymmetry*, 2000, **11**, 1193–1198; M-J. Jin, J-A. Jung and S-H. Kim, *Tetrahedron Lett.*, 1999, **40**, 5197–5198.
8 A. Albinati, F. Lianza, H. Berger, C. Arz and P. S. Pregosin, *Inorg. Chim. Acta*, 1992, **198-200**, 771–780.
9 H. Nakano, H. Takahashi, Y. Okuyama, C. Senoo, N. Tsugawa, Y. Suzuki, R. Fujita, K. Sasaki and C. Kabuto, *J. Org. Chem.*, 2004, **69**, 7092–7100; H. Nakano, Y. Okuyama, Y. Suzuki, R. Fujita and C. Kabuto, *Chem. Commun.*, 2002, 1146–1147.
10 G. Ríos-Moreno, R. A. Toscano, R. Redón, H. Nakano, Y. Okuyama and D. Morales-Morales, *Inorg. Chim. Acta*, 2005, **358**, 303–309.
11 S. A. Cardile, M. C. Jennings and N. D. Jones, *Dalton Trans.*, 2006, 4672–4678.
12 G. A. Ardizzoia, S. Brenna, F. Castelli, S. Galli and N. Masciocchi, *Inorg. Chim. Acta*, 2010, **363**, 324–329.
13 G. A. Ardizzoia, S. Brenna and B. Therrien, *Eur. J. Inorg. Chem.*, 2010, 3365–3371.
14 The monodentate coordination *via* the *N*- or *O*- atoms of the oxazolidine moiety or *via* the sp^2 nitrogen of the pyridine ring should not be excluded, but are considered less probable due to chelation effects.
15 M. Soliman, H. Abdine and S. El-Nanaey, *Aust. J. Chem.*, 1975, **28**, 49–56.
16 K. Pihlaja, M. Juhàsz, H. Kivelä and F. Fülöp, *Rapid Commun. Mass Spectrom.*, 2008, **22**, 1510–1518.
17 E. T. J. Strong, S. A. Cardile, A. L. Brazeau, M. C. Jennings, R. McDonald and N. D. Jones, *Inorg. Chem.*, 2008, **47**, 10575–10586.
18 A. Klamt and G. Schümann, *J. Chem. Soc., Perkin Trans. 2*, 1993, 799–805.
19 L. Li, C. S. B. Gomes, P. T. Gomes, M. T. Duarte and Z. Fan, *Dalton Trans.*, 2011, **40**, 3365–3380; H. Liu, L. Zhang, L. Chen, C. Redshaw, Y. Li and W.-H. Sun, *Dalton Trans.*, 2011, **40**, 2614–2621; N. Andrade-López, T. A. Hanna, J. G. Alvarado-Rodríguez, A. Luqueño-Reyes, B. A. Martínez-Ortega and D. Mendoza-Espinosa, *Polyhedron*, 2010, **29**, 2304–2310; C. Ochs, F. E. Hahn and T. Lügger, *Eur. J. Inorg. Chem.*, 2001, 1279–1285; B. Korybut-Daszkiewicz, J. Gluziński, J. Krajewski, A. Kemme and A. Mishnev, *Eur. J. Inorg. Chem.*, 1999, 263–268.
20 L. López-Banet, M. D. Santana, G. García, L. García, L. Lezama and J-P. Costes, *Inorg. Chem.*, 2011, **50**, 437–443; T. S. Lobana, P. Kumari,
R. Sharma, A. Castineiras, R. J. Butcher, T. Akitsu and Y. Aritake, *Dalton Trans.*, 2011, **40**, 3219–3228; K. Rudzka, A. M. Arif and L. M. Berreau, *Inorg. Chem.*, 2008, **47**, 10832–10840; M. D. Santana, L. López-Banet, G. García, L. García, J. Pérez and M. Liu, *Eur. J. Inorg. Chem.*, 2008, 4012–4018; O. Rotthaus, V. Labet, C. Philouze, O. Jarjayes and F. Thomas, *Eur. J. Inorg. Chem.*, 2008, 4215–4224; H. M. Alvarez, M. Krawiec, B. T. Donovan-Merkert, M. Fouzi and D. Rabinovich, *Inorg. Chem.*, 2001, **40**, 5736–5737; T. Yoshida and S. Kaizaki, *Inorg. Chem.*, 1999, **38**, 1054–1058; C. Dietz, F. W. Heinemann, J. Kuhnigk, C. Krüger, M. Gerdan, A. X. Trautwein and A. Grohmann, *Eur. J. Inorg. Chem.*, 1998, 1041–1049.
21 O. Rotthaus, F. Thomas, C. Philouze, O. Jarjayes, E. Saint-Aman and J-L. Pierre, *Chem.–Eur. J.*, 2006, **12**, 6953–6962; S. Mukhopadhyay, D. Mandal, D. Ghosh, I. Goldberg and M. Chaudhury, *Inorg. Chem.*, 2003, **42**, 8439–8445; G. Psomas, A. J. Stemmler, C. Dendrinou-Samara, J. J. Bodwin, M. Schneider, M. Alexiou, J. W. Kampf, D. P. Kessissoglou and V. L. Pecoraro, *Inorg. Chem.*, 2001, **40**, 1562–1570; H. Duval, V. Bulach, J. Fischer and R. Weiss, *Inorg. Chem.*, 1999, **38**, 5495–5501; J. C. Jeffrey and M. D. Ward, *J. Chem. Soc., Dalton Trans.*, 1992, 2119–2120.
22 D. Forster, *Inorg. Chim. Acta*, 1968, **2**, 116–118; G. N. La Mar, *J. Am. Chem. Soc.*, 1965, **87**, 3567–3571.
23 R. E. Richards, *Discuss. Faraday Soc.*, 1962, **34**, 74–76; D. R. Eaton, A. D. Josey, W. D. Phillips and R. E. Benson, *J. Chem. Phys.*, 1963, **39**, 3513–3518 and references therein.
24 E. Juaristi and V. A. Soloshonok, *Enantioselective Synthesis of* β-*Amino Acids*, 2nd Edn, John Wiley & Sons, Inc, Hoboken, New Jersey, 2005; I. Reboule, R. Gil and J. Collin, *Tetrahedron Lett.*, 2005, **46**, 7761–7764; P. A. Magriotis, *Angew. Chem., Int. Ed.*, 2001, **40**, 4377–4379.
25 See for example: X. Ai, X. Wang, J-M. Liu, Z-M. Ge, T.-M. Cheng and R.-T. Li, *Tetrahedron*, 2010, **66**, 5373–5377 and references cited therein; N. Azizi, R. Baghi, H. Ghafuri, M. Bolourtchian and M. Hashemi, *Synlett*, 2010, **3**, 379–382; K. De, J. Legros, B. Crousse and D. Bonnet-Delpon, *J. Org. Chem.*, 2009, **74**, 6260–6265; A-G. Ying, L. Liu, G-F. Wu, G. Chen, X-Z. Chen and W-D. Ye, *Tetrahedron Lett.*, 2009, **50**, 1653–1657; M. L. Kantam, M. Roy, S. Roy, B. Sreedhar and R. L. De, *Catal. Commun.*, 2008, **9**, 2226–2230; R. Varala, N. Sreelatha and S. R. Adapa, *Synlett*, 2006, **10**, 1549–1553; A. T. Khan, T. Parvin, S. Gazi and L. H. Choudhury, *Tetrahedron Lett.*, 2007, **48**, 3805–3808; K. Surendra, N. S. Krishnaveni, R. Sridhar and K. R. Rao, *Tetrahedron Lett.*, 2006, **47**, 2125–2127; H. Firouzabadi, N. Iranpoor and F. Nowrouzi, *Chem. Commun.*, 2005, 789–791; H. Firouzabadi, N. Iranpoor and A. A. Jafari, *Adv. Synth. Catal.*, 2005, **347**, 655–661; M. K. Chaudhuri, S. Hussain, M. L. Kantam and B. Neelima, *Tetrahedron Lett.*, 2005, **46**, 8329–8331; M. Pérez and R. Pleixats, *Tetrahedron*, 1995, **51**, 8355–8362; G. Jenner, *Tetrahedron Lett.*, 1995, **36**, 233–236.
26 See for example: J. Jiang, Y. Cai, W. Chen, L. Lin, X. Liu and X. Feng, *Chem. Commun.*, 2011, **47**, 4016–4018; L. Lykke, D. Monge, M. Nielsen and K. A. Jørgensen, *Chem.–Eur. J.*, 2010, **16**, 13330–13334; D. Enders, C. Wang and J. X. Liebich, *Chem.–Eur. J.*, 2009, **15**, 11058–11076; P. R. Krishna, A. Sreeshailam and R. Srinivas, *Tetrahedron*, 2009, **65**, 9657–9672; X. Lu and L. Deng, *Angew. Chem., Int. Ed.*, 2008, **47**, 7710–7713; A. Scettri, A. Massa, L. Palombi, R. Villano and M. R. Acocella, *Tetrahedron: Asymmetry*, 2008, **19**, 2149–2152; N. Yamagiwa, H. Qin, S. Matsunaga and M. Shibasaki, *J. Am. Chem. Soc.*, 2005, **127**, 13419–13427.
27 D. F. Evans, *J. Chem. Soc.*, 1959, 2003–2005.
28 J. J. P. Stewart, *MOPAC2009*, Stewart Computational Chemistry, Colorado Springs, CO, USA 2009, http://OpenMOPAC.net.
29 J. J. P. Stewart, *J. Mol. Model.*, 2007, **13**, 1173–1213.
30 Jmol: an open-source Java viewer for chemical structures in 3D, http://www.jmol.org/.
31 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **64**, 112–122.
32 L. J. Farrugia, *J. Appl. Crystallogr.*, 1997, **30**, 565.