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PAPER

Neutral and cationic chiral NCN pincer nickel(II) complexes with 1,3-bis(2′-imidazolinyl)benzenes: synthesis and characterization†

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Chiral 1,3-bis(2′-imidazolinyl)benzenes **1a–e** easily undergo direct nickelation at the C2 position of the central benzene ring *via* the C–H bond activation in the reaction with anhydrous $NiCl_2$ giving neutral NCN pincer nickel(II) complexes **2a–e** in 40–87% yields. Treatment of the nickel pincers **2a** or **2c** with $AgBF_4$ in CH_3CN–CH_2Cl_2 afforded the cationic nickel pincers **3a** or **3c** in good yields. All the complexes were characterized by elemental analysis, ^1H, ^{13}C NMR, and IR spectra. Molecular structures of the neutral complexes **2a**, **2b** and **2c** as well as the cationic complex **3c** have been determined by X-ray single-crystal diffraction. The cationic nickel pincers **3** are found to be effective catalysts for the Michael addition of ethyl 2-cyanopropionate to methyl vinyl ketone in the presence of *i*-Pr_2NEt base with a catalyst loading of 5 mol% even at −78 °C, producing the adduct in >99% yield after 24 h albeit with no ee.

Introduction

Aryl-based pincer metal complexes with anionic terdentate ligands have been widely applied in organic synthesis, organometallic catalysis, materials science and the related areas since the pioneering work of Shaw,[1] van Koten and Noltes[2] on so-called PCP and NCN type complexes in the 1970s. Among them, the complexes with anionic tridentate 1,3-bis(2′-oxazolinyl)phenyl (abbreviated as Phebox, Chart 1) ligands have emerged as one versatile chiral pincer complex family due to the ample opportunities to introduce chirality in the oxazoline rings by using readily available, optically active aminoalcohols.[3] Numerous metal-Phebox complexes including Rh,[4] Ir,[4c] Pd,[5] Pt,[6] Ru,[7] Ni[8] and even Fe[9] have been reported and some show high performance in asymmetric catalytic reactions. For example, the Rh(Phebox) complexes are efficient catalysts for conjugate reduction of α,β-unsaturated esters with hydrosilanes (up to 98% ee),[4a,c] and for asymmetric reductive aldol reaction of acrylates and aldehydes with hydrosilanes (up to 96% ee for *anti*-products).[4b,c] The Pt(Phebox)s have been used in alkylation of aldimines (up to 82% ee)[6a] and Ru(Phebox)s in hydrogenation (up to 98% ee) and transfer hydrogenation of ketones (up to 97% ee).[7a,b] On the other hand, replacing an oxazoline oxygen atom by a NR group gives an imidazoline, which is a structural analogue of oxazoline and has demonstrated unique advantages of further tuning electronic and conformational properties of the ligand by the proper choice of the group on the additional nitrogen atom. This N-substitution can also serve as a linker for attaching the ligand to a solid support. Moreover, similar to the oxazolines, the chirality in the imidazolines can be easily introduced and tuned through using different chiral aminoalcohols.[10] Consequently, we have studied the synthesis and characterization of a series of Pt(II) and Pd(II) pincer complexes with anionic tridentate 1,3-bis(2′-imidazolinyl)phenyl (abbreviated as Phebim, Chart 2) ligands.[11] In the preparation of these complexes, it was found that the Phebim-H ligands showed different reactivities from Phebox-H

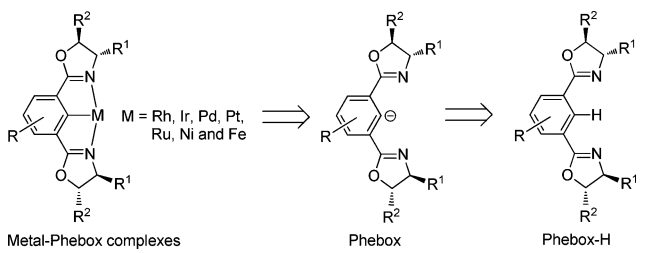

Chart 1 Phebox-H, Phebox and the corresponding metal-Phebox complexes.

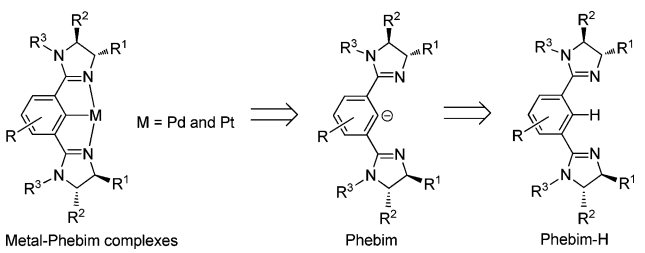

Chart 2 Phebim-H, Phebim and the corresponding Pt- and Pd-Phebim complexes.

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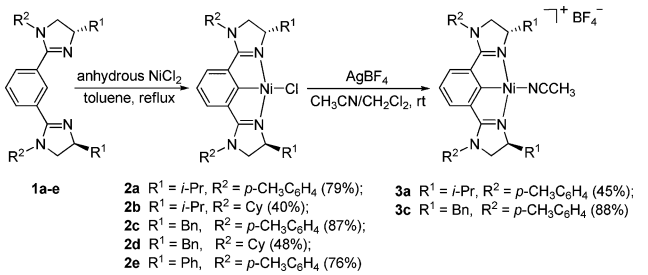
ligands towards direct C–H activation of the ligand's central benzene ring in the reaction with Pd(II) or Pt(II) precursors, where the activation of the Phebim-H ligands was more facile. For instance, the Pd(Phebim)s could be prepared by this aryl C–H activation method (mostly in 28–54% yields),[11b] while such process did not seem to be applicable to the Phebox-H ligands[5,8c] and a Pd(Phebox) complex was isolated in only 3% yield by this method.[6c] Additionally, the yields of Pt(Phebim)s were obviously higher (51–84%)[11] than those of the related Pt(Phebox)s (9–49%)[6c,d] when this direct metalation methodology was used. In the meanwhile, we noticed that up to now the reported Ni(Phebox) complexes could only be prepared by oxidative addition reaction of 2-halo-1,3-bis(oxazolinyl)benzenes with $Ni(COD)_2$ or by lithiation–transmetalation also starting from the appropriate 2-halo derivatives.[8] From a synthetic point of view, the direct metal-induced C_{aryl}–H bond activation should be the most simple and convenient method for the construction of aryl-based pincer metal complexes since it is unnecessary to prepare appropriate 1,2,3-trisubstituted benzenes (in the oxidative addition and transmetalation methods) and the synthetic procedures are thus simplified. On the basis of the above findings and also considering that examples on the chiral pincer nickel(II) complexes are rather limited,[12] we have investigated the synthesis and preliminary application of pincer Ni(Phebim) complexes. Herein, we report the convenient preparation of neutral Ni(Phebim) complexes **2a–e** by direct C–H activation of the related Phebim-H ligands **1a–e** and their cationic pincers **3a** and **3c** as well as the catalytic activity of the cationic complexes **3** in Michael addition.

Results and discusssion

Synthesis and spectroscopic characterization of pincer Ni(Phebim) complexes

The needed 1,3-bis(2′-imidazolinyl)benzene namely Phebim-H ligands **1** can be readily prepared from isophthalyl chloride, chiral amino alcohol and amine in two steps using the published procedure.[11] Three known Phebim-H ligands **1a–c** and two new ones **1d–e** were thus synthesized by treatment of isophthalyl chloride with L-valinol, L-phenylalaninol or L-phenylglycinol, respectively, to give the corresponding bis(amido alcohol)s, which reacted with excess thionyl chloride, followed by the addition of *p*-toluidine or cyclohexylamine and basic workup with 10% NaOH solution. The direct nickelation of the Phebim-H ligands **1** for preparation of the NCN pincer nickel(II) complexes *via* the C–H activation was then attempted. Accordingly, **1** reacted with easily available, cheap $NiCl_2$ in dry toluene at reflux for 40–48 h. We were delighted to find that the new chiral Ni(Phebim)Cl pincers **2a–e** could be isolated in 40–87% yields after chromatography on silica gel (Scheme 1). It should be mentioned that $NiCl_2$ is an often-used metallating reagent in the preparation of achiral PCP pincer Ni(II) complexes *via* the C–H activation.[1,13] Focusing our initial attention on the Lewis acid-catalyzed reactions,[11b] we wish to replace the chloride ligand in **2** by an exchangeable neutral ligand, and generate the corresponding cationic pincer metal complexes. Thus, treatment of **2a** or **2c** with 2.0 eq. of $AgBF_4$ in CH_3CN/CH_2Cl_2 (v/v 1 : 1) at room temperature for 12 h easily removed the chloride and resulted in the formation of the cationic [Ni(Phebim)·$NCCH_3$][BF_4] complexes **3a** or **3c** in 45% and 88% yields, respectively (Scheme 1). It should be noted that the result was in contrast to that of the neutral Pt(Phebim)Cl complexes, from which pure samples of the cationic Pt complexes could not be isolated by the reaction with commonly used Ag(I) salts such as $AgBF_4$ or AgOTf or $AgSbF_6$ under various conditions.[11b]



Scheme 1 Synthesis of the neutral and cationic chiral pincer Ni(Phebim) complexes.

All of the neutral complexes **2a–e** are air- and moisture-stable both in the solid state and in solution. While it seems that the cationic complexes **3**, particularly **3a** have a tendency to partially exchange their CH_3CN ligand for H_2O existing in trace amounts in the wet air or the undried solvent including deuterium solvent and solvent used during work-up. The exchange was somewhat confirmed by the ^1H NMR spectra of complex **3a**. It was found that sometimes the signal at δ 2.57 ppm corresponding to the CH_3CN protons became very small and a new broad singlet at δ 3.59 ppm possibly due to the metal-coordinated water protons was observed. For this reason, satisfactory elemental analysis data could not be obtained for complex **3a**. In addition, the possibility of generating water-coordinated cationic species from **3** was briefly investigated. Thus, the cationic complex **3c** was treated with more than quantitative water in CH_2Cl_2/H_2O (10 : 1, v/v) at room temperature for 0.5 h. After evaporation of solvent under reduced pressure, the ^1H and ^{13}C NMR spectra of the obtained solids were determined. Although the signal of coordinated water protons could not be identified undoubtedly from the ^1H NMR spectrum, it could be clearly seen that the signal at δ 2.56 ppm (^1H NMR) and δ 2.9 ppm (^{13}C NMR) corresponding to the protons and carbon atom of the CH_3- group, respectively in coordinated CH_3CN for complex **3c** disappeared almost completely. The related NMR spectra are collected in the ESI.† All the other complexes including the cationic **3c** were well characterized by elemental analysis, ^1H NMR, ^{13}C NMR, and IR spectra. The formation of the pincer Ni(II) complexes **2a–e** was confirmed by the disappearance of the signal at δ 7.50–8.09 ppm corresponding to the central aryl proton located *ortho* to both imidazoline rings in the ^1H NMR spectra. Similar to the M(Phebim)Cl (M = Pd and Pt) complexes, the signals of central aryl protons for the Ni(Phebim)Cl complexes were strongly shifted upfield relative to those in the corresponding free ligands **1a–e**, and signals of the *N*-aryl protons as well as those of the Cy-proton directly attached to imidazoline-*N* shifted downfield due to the N–M coordinations and C–M bond formation in the complexes. The protons of the imidazoline ring in **2a–e** appeared in three different positions, of which the multiplet or doublet of doublets at δ 4.00–5.14 ppm was for the CH proton and the signals for the CH_2 protons were observed at δ 3.56–4.42 and 3.45–3.92 ppm, respectively as one apparent triplet and one doublet of doublets in a 2 : 2 ratio. Among them,

Table 1 Selected bond lengths (Å) and angles (°) for the neutral complexes **2a**, **2b**·CH_2Cl_2·0.5H_2O, **2c** and the cationic complex **3c**

	2a	**2b**·CH_2Cl_2·0.5H_2O	**2c**	**3c**
Ni(1)–C(1)	1.846(4)	1.848(4)	1.836(4)	1.831(6)
Ni(1)–N(1)	1.912(3)	1.878(4)	1.914(3)	1.902(5)
Ni(1)–N(3)	1.894(3)	1.891(4)	1.920(3)	1.894(4)
Ni(1)–Cl(1)/Ni–N(5)	2.2408(14)	2.2462(12)	2.2249(11)	1.904(6)
C(1)–Ni(1)–N(1)	81.19(19)	81.55(19)	81.65(14)	81.8(2)
C(1)–Ni(1)–N(3)	81.56(17)	81.93(18)	81.10(14)	81.7(2)
N(1)–Ni(1)–N(3)	162.67(17)	163.48(17)	162.75(12)	163.3(2)
C(1)–Ni(1)–Cl(1)/C(1)–Ni(1)–N(5)	177.91(13)	177.76(19)	179.45(12)	176.2(3)
N(1)–Ni(1)–Cl(1)/N(1)–Ni(1)–N(5)	100.39(14)	96.98(13)	97.83(10)	96.4(2)
N(3)–Ni(1)–Cl(1)/N(3)–Ni(1)–N(5)	96.82(12)	99.51(12)	99.42(10)	100.2(2)

the doublet of doublets at δ 3.45–3.92 ppm corresponding to one of the CH_2 protons (*trans* to R^1 substituent) were also significantly shifted downfield compared to the parent ligands. Comparison of the ^{1}H NMR spectra of the cationic [Ni(Phebim)·$NCCH_3$][BF_4] complexes **3a** and **3c** with those of their corresponding Phebim-H ligands revealed the similar phenomena. Some evidence for the coordination of CH_3CN to the Ni center in **3a** and **3c** were obtained from NMR spectra in which the singlet arising from the CH_3CN protons was observed at δ 2.55 and 2.56 ppm, respectively, together with the resonance due to the carbon atom of CH_3 appearing at δ 2.9 ppm in the ^{13}C NMR spectra. Also, the downfield shift of the CH_3CN protons in the complexes relative to free CH_3CN (2.10 ppm) can be seen. It was thought that relative Lewis acidity of pincer complexes could be indirectly measured by the downfield shift that occurred to methyl protons of the CH_3CN compared to free CH_3CN.[8c] Therefore, the bigger downfield shift of the CH_3 protons (0.45 and 0.46, respectively) in [Ni(Phebim)·$NCCH_3$][BF_4] complexes **3a** and **3c** may mean that they should be more acidic than the related [Ni(Phebox)][ClO_4] complexes (values of downfield shift: 0.25–0.31).[8c]

Molecular structures of 2a–c and 3c

The molecular structures of the neutral Ni(Phebim)Cl complexes **2a–c** and the cationic one **3c** were determined by X-ray single crystal analysis. The molecules are shown in Fig. 1–4, respectively. Selected bond lengths and angles are collected in Table 1.

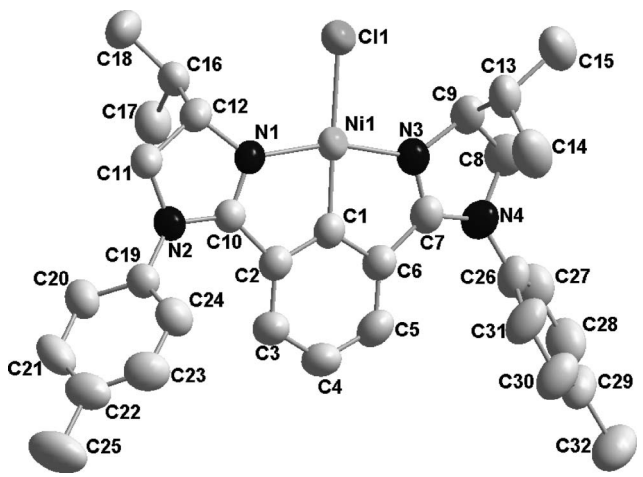


Fig. 1 Molecular structure of complex **2a**. Hydrogen atoms are omitted for clarity.

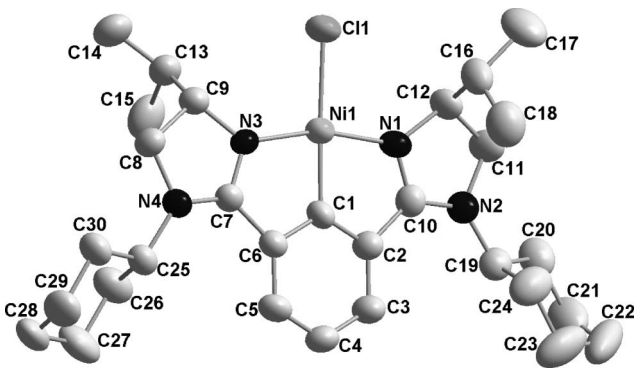


Fig. 2 Molecular structure of complex **2b**·CH_2Cl_2·0.5H_2O. Hydrogen atoms and noncoordinated molecules (CH_2Cl_2 and H_2O) are omitted for clarity.

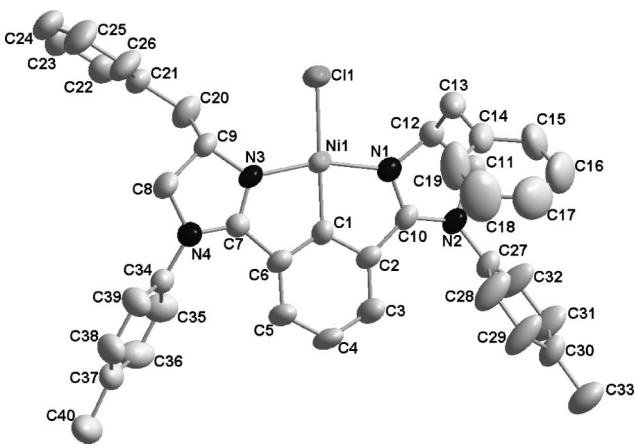


Fig. 3 Molecular structure of complex **2c**. Hydrogen atoms are omitted for clarity.

The structural features of **2a–c** and **3c** are directly related to the Pt(Phebim) and Pd(Phebim) complexes.[11] Phebim ligand in each complex is coordinated to the Ni(II) center in a tridentate manner, and the formed two five-membered-ring metallacycles as well as two imidazoline rings are approximately coplanar with the central aryl ring. The metal center adopts a typical distorted square-planar geometry with bond angles of N–Ni–N being around 163° and C–Ni–Cl(C–Ni–N) being around 178°. All of the bond lengths and angles around the Ni(II) center in complexes **2a–c** are similar, which are also comparable to those in the related Ni(Phebox) complexes.[8a–c] A comparison of **2c** and

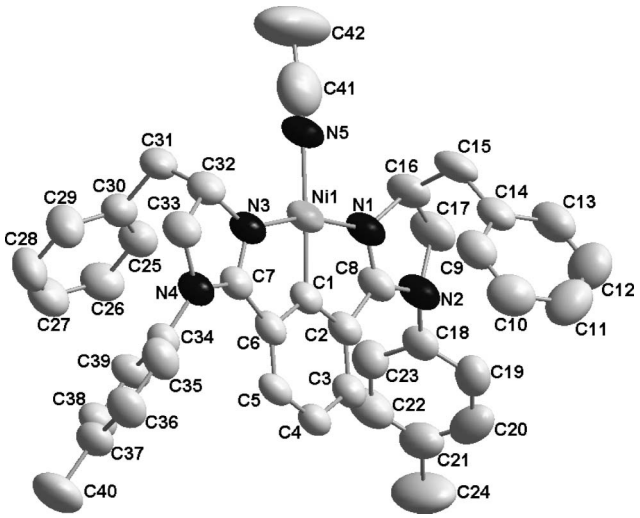


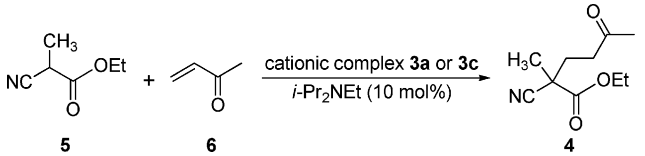
Fig. 4 Molecular structure of the cationic complex **3c**. Hydrogen atoms and the anion are omitted for clarity.

its Pt(Phebim)Cl complex reveals that the metal–tridentate ligand bond lengths in the two complexes follow the expected pattern of Ni < Pt. For example, the Ni complex **2c** has a Ni–C bond length of 1.836(4) Å, Ni–N bond lengths of 1.914(3) [1.920(3)] Å, and a Ni–Cl bond length of 2.2249(11) Å. The corresponding values in the Pt(Phebim)Cl complex are 1.907(10), 2.031(8) [2.039(9)], and 2.454(2) Å, respectively.[11b] The two phenyl groups of the Phebim ligand in **2c** reside either side of the metallacyclic plane and are thus *trans* orientated due to the free rotation of carbon-carbon single bond. A striking structural difference in Phebim ligand between **3c** and **2c** is the arrangement of the two phenyl groups, which are mutually *cis* in **3c**. The metal–tridentate ligand bond lengths in the cationic complex **3c** are slightly shorter than that seen in the corresponding neutral complex **2c**, which can be explained by the reduced *trans* influence of the $NCCH_3$ ligand.

Catalytic studies

Chiral NCN pincer metal complexes have been applied as Lewis acid catalysts in the asymmetric Michael addition of activated nitriles to Michael acceptors, which has received increasing attention since the products bear a quaternary carbon center with various functionalities.[14] For example, the *in situ* generated cationic chiral bis-aldimine NCN pincer Pd(II) and Pt(II) complexes only gave racemic products in the Michael reaction between methyl vinyl ketones and methyl 2-cyanopropionate.[15] While the cationic Pd(Phebox) complexes showed catalytic activity for the reaction of 2-cyanocarboxylates and various Michael acceptors to form the adducts with up to 34% ee.[5d] Remarkably, the reaction could be efficiently catalyzed by the chiral pyrroloimidazolone-based NCN pincer Pd(II) complexes with high levels of enantioselectivities (up to 83% ee).[16] Additionally, the addition of 2-cyanocarboxylates to acrolein proceeded in the presence of the *in situ* generated Rh(III)(Phebox)-($SnMe_3$)Cl complex under mild and neutral conditions to afford high yields of the products with up to 86% ee.[17] It was reported that there was a correlation between Lewis acidity and reactivity of the cationic pincer complexes in the Michael reaction,[6c] and the palladium pincer complexes showed less Lewis acidity than the Ni(II) complexes due to the greater inherent electronegativity of Ni(II) *vs.* Pd(II).[8c] In fact, catalysis of the Michael addition of ethyl 2-cyanopropionate to methyl vinyl ketone in THF at room temperature with 5 mol% of an achiral cationic [Ni(Phebox)·$NCCH_3$][BF_4] complex, in which the nickel center seemed to be electron deficient enough to work as an efficient Lewis acid from the cyclic voltammetry study, resulted in the formation of racemic product in 99% yield after 4.5 h.[8d] As a preliminary investigation, the activity and the stereocontrolling potential of the cationic Ni(Phebim) complexes **3a** and **3c** in the Michael addition were evaluated, and the addition of ethyl 2-cyanopropionate (**5**) to methyl vinyl ketone (**6**) was chosen as the model reaction. As shown in Table 2, the results indicated that the cationic nickel pincers **3** gave highly effective but not stereoselective catalysts for the Michael addition, and in all cases the racemic product **4** was obtained. In the presence of 5 mol% of **3a**, the reaction proceeded in THF at room temperature to afford product **4** in a 92% isolated yield after 5 h (entry 1), and the yield increased to > 99% yield by employing toluene as solvent (entry 2). When the reaction temperature was lowered to –30 °C, the yield dropped to 81% after 24 h, partially due to the poor solubility of **3a** in THF at lower temperature (entry 3). The cationic complex **3c** was also found to be active for this reaction with a catalyst loading of 2 mol%, affording the Michael adduct **4** in a 89% yield in THF at room temperature after 5 h (entry 4). Furthermore, the Michael addition smoothly proceeded with 5 mol% of **3c** in CH_2Cl_2 at temperatures as low as –78 °C, affording the product in a nearly quantitative yield (> 99% yield, entry 5). As a control reaction, the Michael reaction was also conducted in THF or toluene at room temperature for 5 h in the absence of the cationic pincer Ni(II) complex. It was found that only trace amount of the expected adduct was detected by GC analysis.

Table 2 Asymmetric Michael addition of ethyl 2-cyanopropionate to methyl vinyl ketone catalyzed by the cationic Ni(Phebim) complexes **3**[a]



5 6 4

Entry	Cat.	Temp. (°C)	Solvent	Time (h)	Yield (%)[b]
1	**3a**	rt	THF	5	92
2	**3a**	rt	Toluene	5	> 99
3	**3a**	–30	THF	24	81
4[c]	**3c**	rt	THF	5	89
5	**3c**	–78	CH_2Cl_2	24	> 99

[a] Reactions were performed with 5 mol% of the cationic pincer Ni(II) complex, 0.2 mmol of **5**, 0.3 mmol of **6**, and 0.02 mmol of *i*-Pr_2NEt in 2 mL solvent. [b] Isolated yield. [c] 2 mol% of **3c**.

Conclusions

In summary, reaction of chiral 1,3-bis(2′-imidazolinyl)benzenes with anhydrous $NiCl_2$ provided direct access to the neutral NCN pincer nickel(II) complexes *via* C–H activation. These complexes could be readily transformed into analytically pure cationic complexes containing CH_3CN in the exchangeable coordination site. The identity of neutral and cationic complexes was confirmed by X-ray crystal structure analysis. The cationic complexes proved

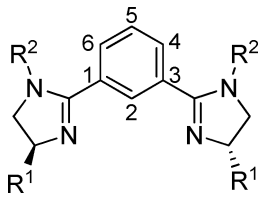
to be effective Lewis acid catalysts for the Michael addition of ethyl 2-cyanopropionate to methyl vinyl ketone even at temperature as low as −78 °C. Although they show the lack of stereocontrol in the model reaction, their facile synthesis offers the benefits of simple procedure and low cost. Additionally, it is reasonable to assume that a combination of isophthalyl chloride or substituted isophthalyl chloride, chiral aminoalcohols and amines provides a high diversification of chiral NCN pincer Ni(Phebim) complexes and some assistance in extending the scope of pincer-Ni(II) catalyzed reactions.

Experimental

General

Reactions involving air-sensitive reagents were performed under a nitrogen atmosphere. Solvents were dried with standard methods and freshly distilled prior to use if needed. The 1,3-bis(2′-imidazolinyl)benzene ligands **1a–e** were prepared according to the literature method reported by us.[11b] All other chemicals were used as purchased. Melting points were measured on an XT4A melting point apparatus and are uncorrected. Infrared spectra were obtained with a Bruker VECTOR 22 spectrophotometer in KBr pellets. NMR spectra were recorded on a Bruker DPX 400 instrument using TMS as an internal standard. HRMS were determined on a *Waters* Q-Tof Micro MS/MS System ESI spectrometer. Elemental analyses were measured on a Thermo Flash EA 1112 elemental analyzer. Optical rotations were recorded on a Perkin Elmer 341 polarimeter.

Characterization of new ligands 1d and 1e

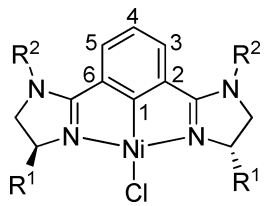


1,3-Bis((*S*)-4-benzyl-1-cyclohexyl-4,5-dihydro-1*H*-imidazol-2-yl)benzene (1d). Yellow oil in 45% isolated yield. $[\alpha]_D^{20}$ −13 (*c* 0.2 in CH_2Cl_2). IR (KBr): ν_{max}/cm^{-1} 3420, 3028, 2930, 2855, 2365, 1707, 1569, 1492, 1447, 1400, 1276, 1085, 996, 888, 815, 749, 703. ^1H NMR (400 MHz, $CDCl_3$): δ 7.50 (s, 1H, central Ar(2)), 7.43 (d, J = 6.7 Hz, 2H, central Ar(4,6)), 7.36 (t, J = 6.7 Hz, 1H, central Ar(5)), 7.25–7.14 (m, 10H, Ph-H), 4.34–4.27 (m, 2H, NCH), 3.35 (app t, J = 10.0 Hz, 2H, NC*H*H), 3.14–3.06 (m, 6H, NCH*H*, C*H*HPh and N-Cy), 2.69 (dd, J = 8.5, 13.6 Hz, 2H, CH*H*Ph), 1.61–1.55 (m, 6H, Cy), 1.46–1.43 (m, 2H, Cy), 1.29–1.13 (m, 6H, Cy), 1.06–0.83 (m, 6H, Cy). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.0, 138.5, 132.2, 129.4, 129.0, 128.1, 128.0, 127.6, 125.9, 64.8, 54.5, 48.3, 42.1, 31.0, 30.0, 25.3, 25.2, 25.1. MS (*m*/*z*, ESI$^+$): 559.5 (M+H), HRMS (*m*/*z*, ESI$^+$), found for M + H = 559.3801, $C_{38}H_{47}N_4$ requires 559.3801.

1,3-Bis((*S*)-4-phenyl-1-*p*-tolyl-4,5-dihydro-1*H*-imidazol-2-yl) benzene (1e). Yellow solid in 76% isolated yield. mp: 81–83 °C. $[\alpha]_D^{20}$ −10 (*c* 0.12 in CH_2Cl_2). IR (KBr): ν_{max}/cm^{-1} 3027, 2922, 2864, 1608, 1568, 1512, 1380, 1300, 815, 759, 701. ^1H NMR (400 MHz, $CDCl_3$): δ 8.09 (s, 1H, central Ar(2)), 7.43 (dd, J = 1.6, 7.6 Hz, 2H, central Ar(4,6)), 7.34–7.23 (m, 10H, Ph), 7.14 (t, J = 7.8 Hz, 1H, central Ar(5)), 6.97 (d, J = 8.4 Hz, 4H, NAr), 6.69 (d, J = 8.4 Hz, 4H, NAr), 5.30 (dd, J = 8.0, 10.8 Hz, 2H, NCH), 4.47 (dd, J = 9.4, 10.8 Hz, 2H, NCH*H*), 3.78 (dd, J = 8.0, 9.4 Hz, 2H, NC*H*H), 2.25 (s, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.3, 143.8, 140.3, 133.7, 131.4, 130.4, 129.7, 129.4, 128.7, 127.8, 127.3, 126.8, 123.3, 67.6, 62.1, 20.9. HRMS (*m*/*z*, ESI$^+$), found for M + H = 547.2858, $C_{38}H_{35}N_4$ requires 547.2862.

General procedure for the synthesis of Ni(Phebim)Cl complexes 2a–e

To a well-stirred solution of bis(imidazoline)benzene **1** (0.3 mmol) in anhydrous toluene (30 mL) was added Et_3N (65 μL, 0.45 mmol) and anhydrous $NiCl_2$ (58 mg, 0.45 mmol). The reaction mixture was then refluxed for 40–48 h. After cooling and concentrating *in vacuo*, the residue was purified by silica gel flash chromatography using ethyl acetate (for **2a–d**) or CH_2Cl_2/MeOH 10 : 1 (for **2e**) as the eluent.



2,6-Bis((*S*)-4-isopropyl-1-*p*-tolyl-4,5-dihydro-1*H*-imidazol-2-yl) phenylchloronickel(II) (2a). Orange solid in 79% isolated yield. mp: > 260 °C. $[\alpha]_D^{20}$ +289 (*c* 0.144 in CH_2Cl_2). IR (KBr): ν_{max}/cm^{-1} 2956, 2868, 1574, 1536, 1512, 1429, 1298, 1158, 1040, 821, 723. ^1H NMR (400 MHz, $CDCl_3$): δ 7.20 (d, J = 8.1 Hz, 4H, NAr), 7.09 (d, J = 8.1 Hz, 4H, NAr), 6.51 (t, J = 7.7 Hz, 1H, central Ar (4)), 6.34 (d, J = 7.7 Hz, 2H, central Ar (3,5)), 4.10–4.00 (m, 4H, NCH and NC*H*H), 3.79 (dd, J = 2.8, 8.9 Hz, 2H, NCH*H*), 2.81–2.74 (m, 2H, C*H*(CH_3)$_2$), 2.39 (s, 6H, CH_3), 0.88 (d, J = 7.0 Hz, 12H, CH(C*H*$_3$)$_2$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.4, 167.0, 137.2, 137.0, 132.7, 130.0, 125.5, 124.2, 121.6, 64.7, 55.3, 30.3, 21.1, 18.7, 14.3. Anal. calcd for $C_{32}H_{37}ClN_4Ni$: C, 67.22; H, 6.52; N, 9.80. Found: C, 67.00; H, 6.78; N, 9.51%.

2,6-Bis((*S*)-1-cyclohexyl-4-isopropyl-4,5-dihydro-1*H*-imidazol-2-yl)phenylchloronickel(II) (2b). Orange solid in 40% isolated yield. mp: 257–258 °C. $[\alpha]_D^{20}$ +283 (*c* 0.146 in CH_2Cl_2). IR (KBr): ν_{max}/cm^{-1} 2925, 2854, 1569, 1532, 1509, 1459, 1379, 1269, 1070, 1011, 720. ^1H NMR (400 MHz, $CDCl_3$): δ 7.19 (d, J = 7.7 Hz, 2H, central Ar (3,5)), 6.97 (t, J = 7.7 Hz, 1H, central Ar (4)), 4.05–4.00 (m, 2H, NCH), 3.88–3.84 (m, 2H, N-Cy), 3.57 (app t, J = 10.5 Hz, 2H, NC*H*H), 3.45 (dd, J = 4.1, 9.8 Hz, 2H, NCH*H*), 2.70–2.58 (m, 2H, C*H*(CH_3)$_2$), 1.92–1.78 (m, 10H, Cy), 1.61–1.50 (m, 4H, Cy), 1.41–1.34 (m, 4H, Cy), 1.19–1.08 (m, 2H, Cy), 0.82 (d, J = 7.0 Hz, 6H, C*H*$_3$CHCH$_3$), 0.72 (d, J = 6.8 Hz, 6H, CH$_3$CHC*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.6, 167.9, 133.6, 122.7, 122.4, 63.3, 54.7, 45.6, 31.9, 30.74, 30.65, 25.6, 25.4, 25.3, 18.6, 14.2. Anal. calcd for $C_{30}H_{45}ClN_4Ni{\cdot}0.2CH_2Cl_2$: C, 63.32; H, 7.99; N, 9.78. Found: C, 63.39; H, 8.40; N, 9.73%.

2,6-Bis((*S*)-4-benzyl-1-*p*-tolyl-4,5-dihydro-1*H*-imidazol-2-yl)-phenylchloronickel(II) (2c). Orange solid in 87% isolated yield. mp: 239–241 °C. $[\alpha]_D^{20}$ +297 (*c* 0.181 in CH_2Cl_2). IR (KBr): ν_{max}/cm^{-1} 3025, 2918, 1573, 1533, 1511, 1430, 1302, 1262, 1158, 1090, 1018, 817, 724, 699, ^1H NMR (400 MHz, $CDCl_3$): δ 7.48

(d, J = 7.0 Hz, 4H, Ph), 7.26–7.17 (m, 6H, Ph), 7.13 (d, J = 8.1 Hz, 4H, NAr), 6.81 (d, J = 7.8 Hz, 4H, NAr), 6.46 (t, J = 7.7 Hz, 1H, central Ar (4)), 6.24 (d, J = 7.7 Hz, 2H, central Ar (3,5)), 4.44–4.39 (m, 2H, NCH), 4.10 (app t, J = 10.0 Hz, 2H, NC*H*H), 3.78 (dd, J = 3.1, 9.9 Hz, 2H, NCH*H*), 3.40 (dd, J = 3.0, 13.3 Hz, 2H, C*H*HPh), 3.07 (dd, J = 7.9, 13.3 Hz, 2H, CH*H*Ph), 2.36 (s, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.9, 167.5, 137.9, 137.3, 136.5, 132.8, 130.1, 129.9, 128.2, 126.2, 125.5, 124.3, 121.7, 60.9, 58.9, 41.1, 21.1. Anal. calcd for $C_{40}H_{37}ClN_4Ni$: C, 71.93; H, 5.58; N, 8.39. Found: C, 71.79; H, 5.80; N, 8.27%.

2,6-Bis((*S*)-4-benzyl-1-cyclohexyl-4,5-dihydro-1*H*-imidazol-2-yl)phenylchloronickel(II) (2d). Orange solid in 48% isolated yield. mp: 210–211 °C. $[\alpha]_D^{20}$ +191 (c 0.112 in CH_2Cl_2). IR (KBr): ν_{max}/cm^{-1} 3057, 3023, 2930, 2853, 1600, 1568, 1527, 1434, 1326, 1259, 1188, 1165, 1088, 1054, 996, 891, 789, 742, 720, 700. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, J = 7.2 Hz, 4H, Ph), 7.27–7.16 (m, 8H, Ph and central Ar (3,5)), 6.99 (t, J = 7.7 Hz, 1H, central Ar (4)), 4.21–4.15 (m, 2H, NCH), 3.98–3.91 (m, 2H, N-Cy), 3.56 (app t, J = 10.0 Hz, 2H, NC*H*H), 3.50 (dd, J = 3.2, 13.1 Hz, 2H, C*H*HPh), 3.45 (dd, J = 3.2, 9.9 Hz, 2H, NCH*H*), 2.65 (dd, J = 9.4, 13.1 Hz, 2H, CH*H*Ph), 1.85–1.67 (m, 10H, Cy), 1.44–1.25 (m, 8H, Cy), 1.13–1.08 (m, 2H, Cy). ^{13}C NMR (100 MHz, $CDCl_3$): δ 179.1, 168.4, 138.5, 133.8, 129.9, 128.2, 126.1, 123.0, 122.6, 60.2, 54.6, 49.6, 41.0, 31.8, 30.6, 25.6, 25.4, 25.2. Anal. calcd for $C_{38}H_{45}ClN_4Ni{\cdot}2.5CH_2Cl_2$: C, 56.28; H, 5.83; N, 6.48. Found: C, 56.03; H, 5.75; N, 6.46%.

2,6-Bis((*S*)-4-phenyl-1-*p*-tolyl-4,5-dihydro-1*H*-imidazol-2-yl)-phenylchloronickel(II) (2e). Orange solid in 76% isolated yield. mp: 190–191 °C. $[\alpha]_D^{20}$ +200 (c 0.096 in CH_2Cl_2). IR (KBr): ν_{max}/cm^{-1} 3028, 2921, 1570, 1511, 1426, 1299, 1157, 821, 761, 697. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (d, J = 7.4 Hz, 4H, Ph), 7.33 (t, J = 7.6 Hz, 4H, Ph), 7.22 (t, J = 8.0 Hz, 2H, Ph, partially overlapped with NAr), 7.20 (d, J = 8.2 Hz, 4H, NAr, partially overlapped with Ph), 7.14 (d, J = 8.2 Hz, 4H, NAr), 6.60 (t, J = 7.6 Hz, 1H, central Ar (4)), 6.46 (d, J = 7.6 Hz, 2H, central Ar (3,5)), 5.14 (dd, J = 3.5, 10.6 Hz, 2H, NCH), 4.42 (app t, J = 10.3 Hz, 2H, NC*H*H), 3.92 (dd, J = 3.5, 9.7 Hz, 2H, NCH*H*), 2.39 (s, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 179.3, 168.1, 143.8, 137.6, 136.8, 132.7, 130.1, 128.5, 127.2, 126.7, 125.7, 124.7, 121.8, 64.2, 62.8, 21.1. Anal. calcd for $C_{38}H_{33}ClN_4Ni$: C, 71.33; H, 5.20; N, 8.76. Found: C, 70.99; H, 5.51; N, 8.45%.

General procedure for the synthesis of the cationic Ni(Phebim) complexes 3a and 3c

In a flask protected from light, Ni(Phebim)Cl (0.35 mmol) and $AgBF_4$ (136 mg, 0.7 mmol) were stirred in CH_3CN/CH_2Cl_2 (20 mL, v/v 1 : 1) at room temperature for 12 h. After the solvent was removed under reduced pressure, the residue redissolved in CH_2Cl_2 and filtered through Celite. The resulting solution was evaporated to dryness and the residue washed with Et_2O, yielding pure **3** as a yellow solid.

Cationic Ni(Phebim) complex 3a

45% isolated yield. mp: 188 °C (dec.). $[\alpha]_D^{20}$ +306 (c 0.066 in CH_2Cl_2). IR(KBr): ν_{max}/cm^{-1} 3031, 2925, 2866, 1575, 1537, 1512, 1430, 1297, 1158, 1107, 1039, 820, 764, 722, 670, 647, 580, 519. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22 (d, J = 8.1 Hz, 4H, NAr), 7.09 (d, J = 8.1 Hz, 4H, NAr), 6.52 (t, J = 7.7 Hz, 1H, central Ar (4)), 6.25 (d, J = 7.7 Hz, 2H, central Ar (3,5)), 4.10 (app t, J = 10.2 Hz, 2H, NC*H*H), 4.03–4.00 (m, 2H, NCH), 3.81 (dd, J = 3.4, 9.7 Hz, 2H, NCH*H*), 2.55 (br s, 3H, CH_3CN), 2.40 (s, 6H, CH_3), 2.10 (br s, 2H, C*H*(CH_3)$_2$), 0.95 (d, J = 5.2 Hz, 12H, CH(C*H*$_3$)$_2$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.7, 167.1, 137.9, 136.3, 132.8, 130.2, 125.7, 124.8, 122.6, 63.6, 55.4, 31.1, 21.2, 18.2, 14.6, 2.9.

Cationic Ni(Phebim) complex 3c

88% isolated yield. mp: 191–193 °C. $[\alpha]_D^{20}$ +234 (c 0.09 in CH_2Cl_2). IR(KBr): ν_{max}/cm^{-1} 3026, 2938, 2679, 2490, 1577, 1539, 1511, 1430, 1302, 1158, 1088, 1055, 823, 706, 517. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, J = 6.9 Hz, 4H, Ph), 7.29–7.24 (m, 6H, Ph), 7.10 (d, J = 8.2 Hz, 4H, NAr), 6.66 (br s, 4H, NAr), 6.47 (t, J = 7.6 Hz, 1H, central Ar (4)), 6.11 (d, J = 8.0 Hz, 2H, central Ar (3,5)), 4.35–4.33 (m, 2H, NCH), 4.27 (app t, 2H, J = 10.0 Hz, NC*H*H), 3.79 (dd, J = 2.6, 9.7 Hz, 2H, NCH*H*), 2.95 (d, 4H, J = 4.6 Hz, CH_2Ph), 2.56 (s, 3H, CH_3CN), 2.35 (s, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.2, 168.5, 138.2, 136.2, 135.2, 132.8, 130.1, 130.0, 128.4, 126.8, 125.6, 125.1, 123.3, 60.0, 58.9, 41.0, 21.1, 2.9. Anal. calcd for $C_{42}H_{40}BF_4N_5Ni$: C, 66.35; H, 5.30; N, 9.21. Found: C, 66.53; H, 5.51; N, 9.21%.

General procedure for the asymmetric Michael addition of ethyl 2-cyanopropionate to methyl vinyl ketone

Under a nitrogen atmosphere, the catalyst (0.01 mmol, 5.0 mol%) was dissolved in 2 mL of solvent. *N*-ethyldiisopropylamine (0.02 mmol, 3.5 μL) was added, followed by methyl vinyl ketone (0.3 mmol, 24 μL), and finally ethyl 2-cyanopropionate (0.2 mmol, 25.5 μL). The resulting solution mixture was stirred for the allotted times and temperatures (Table 2). The solvent was removed, and the residue was purified by flash column chromatography to give the product **4** (ethyl ether/petroleum ether, 1 : 1). The enantiomeric excess was determined by chiral-phase HPLC (Daicel Chiralpak AD-H column).

Ethyl 2-cyano-2-methyl-5-oxohexanoate 4[5d]

Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.27 (q, J = 7.1 Hz, 2H, OCH_2), 2.75–2.61 (m, 2H, CH_2), 2.19 (s, 3H, $COCH_3$), 2.02–2.24 (m, 2H, CH_2), 1.62 (s, 3H, C(CN)CH_3), 1.29 (t, J = 7.1 Hz, 3H, CH_3).

Crystal structure determination and data collection

Crystals of **2a** and **2c** were obtained by recrystallization from ethyl acetate and those of **2b** and **3c** from CH_2Cl_2/n-hexane at ambient temperature. The data of **2a–c** were collected with Rigaku-IV imaging plate area detector with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) and those of **3c** were collected on a Oxford diffraction Gemini E diffractometer with graphite-monochromated Cu-Kα radiation (λ = 1.54184 Å) at ambient temperature. The diffraction data were corrected for Lorentz and polarization factors. The structures were solved by direct methods and expanded using Fourier techniques and refined by full-matrix least-squares methods. The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were

Table 3 Summary of crystal structure determination for complexes **2a**, **2b**·CH_2Cl_2·0.5H_2O, **2c** and **3c**

	2a	**2b**·CH_2Cl_2·0.5H_2O	**2c**	**3c**
Empirical formula	$C_{32}H_{37}ClN_4Ni$	$C_{31}H_{48}Cl_3N_4NiO_{0.5}$	$C_{40}H_{37}ClN_4Ni$	$C_{42}H_{40}BF_4N_5Ni$
M_r	571.82	649.79	667.90	760.31
T/K	291(2)	291(2)	291(2)	293(2)
λ/Å	0.71073	0.71073	0.71073	1.54184
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Crystal size/mm	0.20 × 0.18 × 0.16	0.20 × 0.20 × 0.18	0.20 × 0.18 × 0.17	0.20 × 0.13 × 0.10
a/Å	28.671(6)	13.976(3)	6.5204(13)	11.0806(2)
b/Å	9.971(2)	22.955(5)	22.603(5)	12.41579(19)
c/Å	10.646(2)	10.551(2)	11.813(2)	13.7889(3)
α (°)	90	90	90	90
β (°)	100.00(3)	90	95.40(3)	101.4050(18)
γ (°)	90	90	90	90
V/Å^3	2997.3(10)	3384.7(12)	1733.3(6)	1859.54(6)
Z	4	4	2	2
Space group	C2	$P2_12_12$	$P2_1$	$P2_1$
D_c/g cm^{-3}	1.267	1.275	1.280	1.358
μ/mm^{-1}	0.763	0.837	0.670	1.233
θ range (°)	1.44–27.52	1.71–25.00	1.73–27.53	3.27–61.08
F(000)	1208	1380	700	792
No. of data collected	6073	10501	7082	5855
No. of unique data	6044	5709	6777	4030
R_{int}	0.0279	0.0533	0.0185	0.0264
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0486$	$R_1 = 0.0614$	$R_1 = 0.0426$	$R_1 = 0.0509$
	w$R_2 = 0.1143$	w$R_2 = 0.1476$	w$R_2 = 0.1066$	w$R_2 = 0.1355$
R indices (all data)	$R_1 = 0.0632$	$R_1 = 0.0668$	$R_1 = 0.0540$	$R_1 = 0.0584$
	w$R_2 = 0.1271$	w$R_2 = 0.1511$	w$R_2 = 0.1183$	w$R_2 = 0.1479$
Largest diff. peak and hole/e Å^{-3}	0.473 and –0.253	0.446 and –0.512	0.279 and –0.478	0.335 and –0.436
Flack parameter	0.508(19)	0.0(6)	0.481(16)	0.02(5)

included but not refined. Their raw data were corrected and the structures were solved using the SHELXS-97 program.[18] Details of crystal structure determination are summarized in Table 3. CCDCs 810478, 810120, 809675 and 811901 contain the crystallographic data for complexes **2a**, **2b**·CH_2Cl_2·0.5H_2O, **2c** and **3c**, respectively.†

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