

# Cross-coupling of alkyl halides with aryl or alkyl Grignards catalyzed by dinuclear Ni(II) complexes containing functionalized tripodal amine-pyrazolyl ligands†

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Structurally distinctive dinuclear Ni(II) complexes with furan or thiophene tethered amine-pyrazolyl tripodal hybrid ligands have been synthesized and crystallographically characterized. All complexes are catalytically active towards cross-coupling of aryl/alkyl Grignard reagents with  $\beta$ -H containing alkyl halides at room temperature in the presence of *N,N,N',N'*-tetramethylethylenediamine (TMEDA). The catalytic efficacy of the complexes is dependent on the tether substituent at the central amine. Two species, Ni(II) TMEDA and Mg(II) TMEDA complexes, have been isolated from the catalytic reaction mixtures under different conditions. Some ligand-stabilized Ni(II) and Mg(II) bimetallic species have also been identified in the ESI-MS spectra.

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## Introduction

Transition metal-catalyzed cross-coupling reactions have become an indispensable tool for the formation of new C–C bonds in organic synthesis.<sup>1</sup> Recently, rapid progress has been made on the cross coupling of non-activated and  $\beta$ -H containing alkyl halides with aryl or alkyl Grignards.<sup>2</sup> Among the many catalytic systems reported, iron compounds have been proven to be highly active and selective towards the cross coupling of aryl Grignards with a wide range of alkyl halides under ambient conditions.<sup>3</sup> The application of these iron complexes in  $sp^3$ – $sp^3$  cross-coupling of alkyl halides with alkyl Grignards is, however, less developed.<sup>4</sup> Recently, a few Ni(II) systems have actively challenged both  $sp^3$ – $sp^2$  and  $sp^3$ – $sp^3$  types of cross coupling reactions.<sup>5</sup> For example, NiCl<sub>2</sub>, Ni(acac)<sub>2</sub> and Ni(COD)<sub>2</sub> show excellent performance in the r.t. cross coupling of alkyl halides and alkyl tosylates with an alkyl Grignard reagent (*n*-BuMgCl) in the presence of 1,3-butadienes.<sup>5a</sup> In the presence of Cp\*CH<sub>2</sub>PPh<sub>2</sub> (Cp\* = 1,2,3,4,5-pentamethyl-2,4-cyclopentadienyl), NiCl<sub>2</sub> can catalyze the cross coupling of alkyl halides with an aryl Grignard reagent (PhMgBr) at r.t.<sup>5b</sup>

Hu *et al.* reported the low temperature (–20 °C to –35 °C) cross coupling of alkyl halides with an alkyl Grignard reagent catalyzed by a Ni(II) complex with a pincer amidobis(amine) ligand, [(<sup>Me</sup>NN<sub>2</sub>)NiCl]<sub>5c-e</sub>. The same catalyst can also be applied in the presence of an appropriate amine additive, such as TMEDA (*N,N,N',N'*-tetramethylethylenediamine), to the coupling of a wide range of alkyl halides with aryl and hetero-aryl Grignard reagents.<sup>2g</sup> Recently, Ni(II)/NHC (NHC = N-heterocyclic carbene) systems were also found to be active in the cross-coupling of aryl electrophiles and tertiary alkylmagnesium nucleophiles.<sup>5f,g</sup> Encouraged by the earlier success of Fe(II) complexes with functional amine-pyrazolyl tripodal ligand in the cross coupling of aryl Grignard reagents with alkyl halides,<sup>6</sup> we studied the use of these hybrid ligands in Ni(II) and the application of the Ni(II) complexes in the cross coupling of aryl or alkyl Grignard reagents with non-activated alkyl halides. We herein describe the structural features of these new complexes and their catalytic efficacy together with spectroscopically identified species in the catalytic reaction mixtures under different conditions.

## Results and discussions

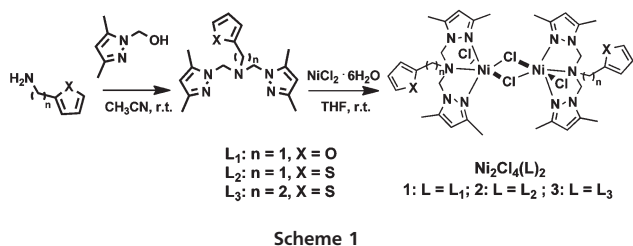
### Synthesis and characterization of nickel(II) complexes 1–3

The amine-pyrazolyl tripodal NNN ligands tethered by thiophene and furan L<sub>1</sub>–L<sub>3</sub> have been prepared in high yield from the reactions between (3,5-dimethyl-1*H*-pyrazol-1-yl)methanol with the corresponding amine based on adapted literature methods.<sup>6,7</sup> Treatment of L<sub>1</sub>–L<sub>3</sub> with NiCl<sub>2</sub>·6H<sub>2</sub>O in THF at r.t.

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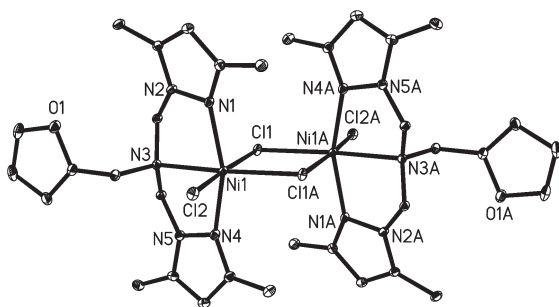


afforded the corresponding dinuclear Ni(II) complexes  $[\text{Ni}_2\text{Cl}_4(\text{L})_2]$  (**1–3**) in high yield (83–89%) (Scheme 1).

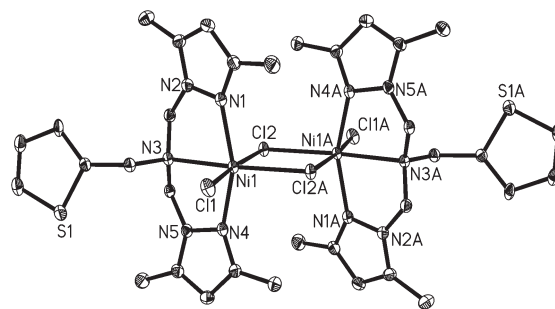
Complexes **1–3** can be handled in the laboratory atmosphere without decomposition. They have been characterized by IR, ESI-MS, single-crystal X-ray diffraction and elemental analysis. They invariably give the characteristic molecular ion peaks of  $[\text{Ni}_2\text{Cl}_3(\text{L})_2]^+$  and the fragment peaks of  $[\text{NiClL}]^+$  in the positive mode of their ESI-MS spectra.

### Molecular structure of compounds **1–3** determined by single-crystal X-ray diffraction

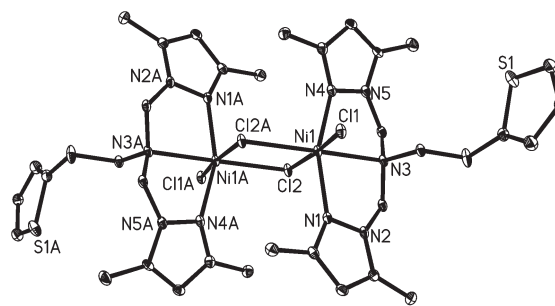
Diffusion of  $\text{Et}_2\text{O}$  into  $\text{CH}_3\text{CN}$  or  $\text{CH}_2\text{Cl}_2$  solutions of **1**, **2** or **3** at r.t. gives green crystals of  $1 \cdot 2\text{CH}_3\text{CN}$ ,  $2 \cdot 2\text{CH}_3\text{CN}$  or  $3 \cdot 2\text{CH}_2\text{Cl}_2$  which are suitable for X-ray crystallographic analysis. Crystallographic analysis reveals that **1–3** are invariably dinuclear complexes (Fig. 1–3). Two Ni(II) moieties carry the chloro and tridentate imine–amine–imine (NNN) ligands ( $\text{Ni}-\text{N}_{\text{amine}} = \text{ave. } 2.23 \text{ \AA}$ ;  $\text{Ni}-\text{N}_{\text{pyrazole}} = \text{ave. } 2.07 \text{ \AA}$ ). They are bridged by two chloro ligands across a non-bonding Ni–Ni separation ( $3.7067(4) \text{ \AA}$ ,  $3.6870(4) \text{ \AA}$  and  $3.6014(8) \text{ \AA}$  in **1**, **2** and **3**, respectively). Both Ni(II) centres adopt a *mer*-octahedral geometry with the central amine *trans* to one of the chloride bridges. The bond distances are comparable to those observed in other chloro-bridged dinickel(II) complexes.<sup>8</sup> A notable feature is that the amine substituent (thiophene or furan) remains pendant despite its proximity to the metal centre and



**Fig. 1** ORTEP diagram of **1** (30% probability ellipsoids). Hydrogen atoms and the lattice solvent molecule  $\text{CH}_3\text{CN}$  are omitted for clarity. Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ): Ni1–N1 2.0718(16), Ni1–N3 2.2282(16), Ni1–N4 2.0670(17), Ni1–Cl1 2.5345(5), Ni1–Cl1A 2.4011(5), Ni1–Cl2 2.3642(5), N1–Ni1–N3 79.17(6), N1–Ni1–Cl1 88.21(5), N1–Ni1–Cl2 92.30(5), N1–Ni1–Cl1A 99.95(5), N1–Ni1–N4 157.95(6), N3–Ni1–Cl2 95.79(4), N3–Ni1–Cl1 88.54(4), N3–Ni1–Cl1A 171.21(4), N3–Ni1–N4 79.06(6), N4–Ni1–Cl1 87.79(5), N4–Ni1–Cl2 93.31(5), N4–Ni1–Cl1A 101.02(5), Cl1–Ni1–Cl2 175.656(18), Cl1–Ni1–Cl1A 82.683(19), Cl2–Ni1–Cl1A 92.980(19), Ni1–Cl1–Ni1A 97.319(19).



**Fig. 2** ORTEP diagram of **2** (30% probability ellipsoids). Hydrogen atoms and lattice solvent molecule  $\text{CH}_3\text{CN}$  are omitted for clarity. Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ): Ni1–N1 2.0685(17), Ni1–N3 2.2308(15), Ni1–N4 2.0630(17), Ni1–Cl1 2.3722(5), Ni1–Cl2 2.5306(5), Ni1–Cl2A 2.3822(5), N1–Ni1–N3 77.67(6), N1–Ni1–Cl1 93.72(5), N1–Ni1–Cl2 88.39(5), N1–Ni1–Cl2A 101.36(5), N1–Ni1–N4 157.09(6), N3–Ni1–Cl2 86.92(4), N3–Ni1–Cl1 98.14(4), N3–Ni1–Cl2A 169.68(4), N3–Ni1–N4 79.53(6), N4–Ni1–Cl1 91.71(5), N4–Ni1–Cl2 88.15(5), N4–Ni1–Cl2A 100.65(5), Cl1–Ni1–Cl2 174.828(18), Cl1–Ni1–Cl2A 92.166(19), Cl2–Ni1–Cl2A 82.782(17), Ni1–Cl2–Ni1A 97.218(17).



**Fig. 3** ORTEP diagram of **3** (30% probability ellipsoids). Hydrogen atoms and the lattice solvent molecule  $\text{CH}_2\text{Cl}_2$  are omitted for clarity. Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ): Ni1–N1 2.071(3), Ni1–N3 2.235(3), Ni1–N4 2.063(3), Ni1–Cl1 2.3865(9), Ni1–Cl2 2.4617(9), Ni1–Cl2A 2.3923(9), Ni1–Ni1A 3.6014(8); N1–Ni1–N3 79.28(10), N1–Ni1–Cl1 91.30(8), N1–Ni1–Cl2 88.68(8), N1–Ni1–Cl2A 102.06(8), N1–Ni1–N4 157.45(11), N3–Ni1–Cl2 88.71(7), N3–Ni1–Cl1 98.06(7), N3–Ni1–Cl2A 172.75(7), N3–Ni1–N4 78.20(11), N4–Ni1–Cl1 92.92(8), N4–Ni1–Cl2 89.71(8), N4–Ni1–Cl2A 100.15(8), Cl1–Ni1–Cl2 173.12(3), Cl1–Ni1–Cl2A 89.06(3), Cl2–Ni1–Cl2A 84.22(3), Ni1–Cl2–Ni1A 95.78(3).

potential replacement of the terminal chloride to act as a tetradentate hybrid ligand.

### Cross-coupling of aryl Grignard reagents with non-activated alkyl halides

A preliminary screening was carried out on r.t. coupling of 1-bromooctane with  $\text{PhMgBr}$  as a representative of aryl Grignard–non-activated alkyl halide reaction catalyzed by **1–3**.  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Ni}(\text{tmeda})(\text{acac})_2$  were included for comparison (Table 1).

In the presence of 5 mol% of **1**, coupling of 1-bromooctane with  $\text{PhMgBr}$  produces only 16% of octylbenzene (entry 1). The elimination product (octene), the hydrodehalogenated product (1-octane) and the homo-coupling product (hexadecane) are observed in GC-MS. However, addition of TMEDA leads to significantly higher yield of the cross coupling product (70%) with 90% conversion of 1-bromooctane (entry 2). Only 1-octane

**Table 1** Cross coupling of 1-bromooctane with PhMgBr catalyzed by **1–3**<sup>a</sup>

Octyl-Br + PhMgBr		catalyst conditions	Octyl-Ph	
A			B	
Entry	Catalyst	Additive	Yield <sup>b</sup> of B (%)	Conv. <sup>b</sup> of A (%)
1	<b>1</b>	None	16	75
2	<b>1</b>	TMEDA	70	90
3	<b>2</b>	TMEDA	21	30
4	<b>3</b>	TMEDA	36	93
5	<b>1</b> <sup>c</sup>	TMEDA	50	80
6	<b>1</b> <sup>d</sup>	TMEDA	59	100
7	<b>1</b> <sup>e</sup>	TMEDA	23	100
8	<b>1</b> <sup>f</sup>	TMEDA	83	100
9	NiCl <sub>2</sub> ·6H <sub>2</sub> O	TMEDA	40/44 <sup>g</sup>	42/49 <sup>g</sup>
10	Ni(tmeda)(acac) <sub>2</sub>	None	36	100
11	Ni(tmeda)(acac) <sub>2</sub>	TMEDA	58	95
12	<b>1</b>	Triethylamine	20	80
13	<b>1</b>	TMPDA	42	76
14	<b>1</b>	DMEDA	0	0
15	<b>1</b>	DMCyDA	0	0
16	<b>1</b>	L <sub>1</sub>	25	87

<sup>a</sup> Reaction conditions: 0.6 mmol of PhMgBr and 0.3 mmol additive in 3 mL THF were added dropwise to the mixture of **1**, **2** or **3** (5 mol% based on metal) and octyl-Br (0.5 mmol) in 1 mL THF and stirred at r.t. for 1 h. <sup>b</sup> Conversion and yield were determined by <sup>1</sup>H NMR (mesitylene as the internal standard). <sup>c</sup> 0.15 mmol of TMEDA. <sup>d</sup> 50 °C. <sup>e</sup> THF-Et<sub>2</sub>O (1 : 1) used as a solvent. <sup>f</sup> 2 equiv. PhMgBr was added. <sup>g</sup> 5 h reaction time.

and hexadecane were detected as by-products, indicating that TMEDA suppresses the formation of the elimination product. Other amines, such as NEt<sub>3</sub>, TMPDA (*N,N,N',N'*-tetramethylpropane-1,3-diamine) and L<sub>1</sub>, do not give significant promotion effects (entries 12, 13 and 16). The addition of DMEDA (*N,N'*-dimethylethane-1,2-diamine) or DMCyDA (*trans-N,N'*-dimethylcyclohexane-1,2-diamine), however, inhibits the catalytic activity of **1** completely (entries 14 and 15).

When the amount of TMEDA is reduced from 0.3 to 0.15 equiv. (relative to the alkyl halide), the conversion of octyl bromide slightly improves, but the yield of octylbenzene drops to 50% (entry 5). Changing the solvent to Et<sub>2</sub>O/THF or raising the temperature (to 50 °C) results in poor cross coupling selectivity although the conversion was quantitative (entries 6 and 7). Increasing the amount of Grignard reagent from 1.2 equiv. to 2 equiv. (relative to octyl bromide) increases both the conversion and yield (entry 8).

Under similar conditions, in the presence of TMEDA, complexes **2** and **3** give only 21% and 36% yield of octylbenzene, respectively (entries 3 and 4). When Ni(tmeda)(acac)<sub>2</sub> was used as a catalyst the promotion effect of TMEDA was also observed (entries 10 and 11). In comparison with **1**, NiCl<sub>2</sub>·6H<sub>2</sub>O shows lower catalytic activity in the presence of TMEDA even with a prolonged reaction time (entry 9). These results indicate the advantage of the furan-bearing tripodal ligand L<sub>1</sub>.

Compound **1** was also applied in the coupling between other alkyl halides and aromatic Grignard reagents in THF in the presence of TMEDA (Table 2).

For the primary alkyl halides, **1** is similarly active as the Ni<sup>II</sup> pincer complex, [(<sup>Me</sup>NN<sub>2</sub>)NiCl]<sub>2</sub><sup>2g</sup> and more active than the Fe(II) complexes<sup>6</sup> with the same ligand under similar reaction conditions. These couplings are tolerant to a range of functional groups. Aryl Grignard reagents containing methyl or methoxy group give a similarly high yield of cross coupling products; functional alkyls such as ethers, acetals, olefins and phenol rings do not interfere with the cross-coupling reaction, giving rise to similar yields of the cross-coupling products (entries 1–18). However, **1** is less selective, in comparison with the [(<sup>Me</sup>NN<sub>2</sub>)NiCl] system,<sup>2g</sup> towards the secondary alkyl halide cross-coupling product (entry 19). It is also ineffective towards electron-poor Grignard reagents (entry 20).

### Cross-coupling of alkyl Grignard and alkyl halide

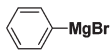

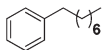

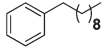
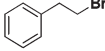
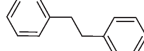

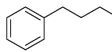
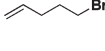
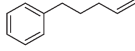
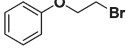
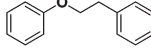
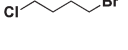
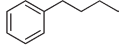
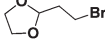
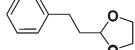

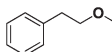
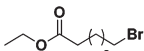
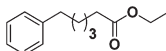
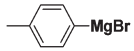

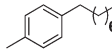
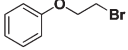
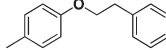
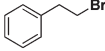
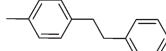
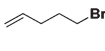
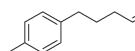
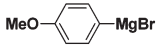

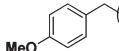

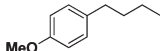
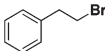
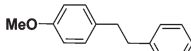

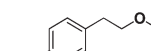
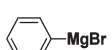

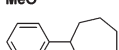
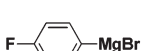

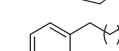
Under similar conditions, **1** has been applied to sp<sup>3</sup>–sp<sup>3</sup> coupling of alkyl Grignard reagents and alkyl halides as shown in Table 3.

[(<sup>Me</sup>NN<sub>2</sub>)NiCl] has been reported to be an efficient catalyst for this type of reaction at low temperature (–20 °C to –35 °C).<sup>5c</sup> However, **1** shows poor activities both at low temperature and r.t. in the coupling between EtMgBr and 1-bromooctane without any additive (entry 1). Upon the introduction of TMEDA, the product yield increases significantly (from 8% to 65%) at r.t. (entry 2), suggesting the promotion value of TMEDA in catalytic sp<sup>3</sup>–sp<sup>3</sup> cross coupling. At r.t., with 5 mol% of catalyst load, in the presence of TMEDA, **1** shows similarly good catalytic activity to [(<sup>Me</sup>NN<sub>2</sub>)NiCl] (obtained at –20 °C with 9 mol% of catalyst) for the cross coupling of primary alkyl halides and primary alkyl Grignards with 70–90% yield of coupling products (entries 3–13). Similar to [(<sup>Me</sup>NN<sub>2</sub>)NiCl], when using a benzyl Grignard reagent, **1** gives a low yield (entry 14).

These results suggest that **1** is effective for both sp<sup>2</sup>–sp<sup>3</sup> and sp<sup>3</sup>–sp<sup>3</sup> types of coupling in the presence of TMEDA. In order to understand the role of additives in the catalytic reactions, ESI-MS was used to monitor the species present in the catalytic reaction mixtures under different conditions.

Neither Ni nor Mg species is observed in the –ve mode ESI-MS spectra. Table 4 lists the intensities of some main Ni- and Mg-fragments observed in the positive mode of ESI-MS spectra of the mixtures of 1-bromooctane (0.5 mmol) and 5 mol% of **1** in 1 mL THF at r.t. after PhMgBr (with or without additive) was added for 1 min up to 20 min (also see Fig. 1–3 in the ESI†). The changes of the intensities of the fragments [L<sub>1</sub>NiCl]<sup>+</sup>, [L<sub>1</sub>NiBr]<sup>+</sup> and [L<sub>1</sub>MgBr]<sup>+</sup> show that TMEDA promotes the formation of Mg–L<sub>1</sub> species and the decomposition of Ni–L<sub>1</sub> species. However, when DMEDA is used as an additive (which inhibits the catalytic activity completely, see Table 1, entry 14), the +ve mode ESI-MS spectra show a similar trend of change to that observed in the case of TMEDA after 5, 10 and 20 min addition time of PhMgBr. In the [(<sup>Me</sup>NN<sub>2</sub>)NiCl] catalyzed coupling reaction system with PhMgCl, it was found that TMEDA suppresses the formation of [(<sup>Me</sup>NN<sub>2</sub>)(THF)MgCl] and stabilizes the catalytically active [(<sup>Me</sup>NN<sub>2</sub>)NiPh].<sup>2g</sup> However, the observations in this work show that both TMEDA (promoter) and DMEDA (inhibitor) can promote the formation of Ligand–

**Table 2** Cross-coupling of ArMgBr with alkyl halides catalyzed by **1**<sup>a</sup>

Entry	ArMgBr	Alkyl-X + Aryl-MgBr $\xrightarrow[0.3\text{mmol TMEDA, r.t., THF}]{5\text{ mol\% } 1}$ Alkyl-Aryl		Yield <sup>b</sup> %
		Alkyl halide	Product	
1				83
2				81
3				96
4				78
5				97
6				98
7				98
8				83
9				99
10				77
11				85
12				99
13				91
14				99
15				86
16				89
17				95
18				87
19				13
20				18

<sup>a</sup> Reaction conditions: 1.0 mmol of Grignard reagent and 0.3 mmol TMEDA in 3 mL THF were added dropwise to the mixture of **1** (5 mol% based on metal) and alkyl halide (0.5 mmol) in 1 mL THF and stirred at r.t., for 1 h. <sup>b</sup> Yield and conversion were determined by <sup>1</sup>H NMR (mesitylene as the internal standard). The conversion of alkyl halide for all reactions is 100% except in entry 20 which is 20%.

MgX complexes. Therefore, it seems that the presence of [L<sub>1</sub>MgBr]<sup>+</sup> and [L<sub>1</sub>NiBr]<sup>+</sup> provides no direct information on the role of amine additives.

Although no TMEDA species is observed in the ESI spectra discussed above, compound **4**, MgBr<sub>2</sub>(tmeda)(THF), was isolated from the above catalytic reaction mixture as colourless

**Table 3** Cross-coupling of alkyl-MgX with alkyl halides catalyzed by **1**<sup>a</sup>

Entry	Alkyl-MgBr	Alkyl-X + Alkyl-MgBr	5 mol% <b>1</b> Conditions	Alkyl-Alkyl	Yield <sup>b</sup> %
1	Et-MgCl				8*
2					65/70 <sup>c,d</sup> /72 <sup>d</sup>
3					90 <sup>d,e</sup>
4	<sup>i</sup> Bu-MgBr				73 <sup>d</sup>
5					96 <sup>g</sup>
6	<sup>n</sup> Bu-MgCl				77
7					72 <sup>d</sup>
8					72 <sup>d,f</sup>
9					77 <sup>d</sup>
10					78 <sup>d</sup>
11					74 <sup>d</sup>
12					81 <sup>e</sup>
13					86 <sup>e</sup>
14	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> MgCl				46 <sup>g</sup>

<sup>a</sup> Reaction conditions: 1.2 equiv. alkyl-MgX in 3 mL THF was added dropwise for 40 min to the mixture of 5 mol% of **1** and 0.5 mmol of alkyl-Br with 0.3 mmol TMEDA (\*for entry 1 without TMEDA) in 1 mL THF. <sup>b</sup> Yield and conversion were determined by GC-MS (*n*-nonane as the internal standard). The conversion of alkyl halide for all reactions is 100% except in entry 1 which is 83%. <sup>c</sup> DMA was used. <sup>d</sup> 1.5 equiv. alkyl-MgX was used. <sup>e</sup> Isolated yield. <sup>f</sup> 0.25 mmol 1,4-dibromobutane was used. <sup>g</sup> Yield and conversion were determined by <sup>1</sup>H NMR (mesitylene as the internal standard).

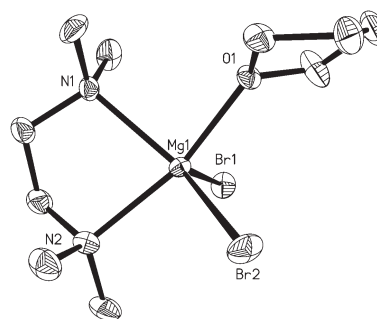
**Table 4** The intensities (%) of the main fragments observed in the positive mode of ESI-MS of the catalytic reaction mixture

Main fragments	[L <sub>1</sub> NiCl] <sup>+</sup> (406 <i>m/z</i> )	[L <sub>1</sub> MgBr] <sup>+</sup> (418 <i>m/z</i> )	[L <sub>1</sub> NiBr] <sup>+</sup> (452 <i>m/z</i> )
Without amine	100	0	48
additive	12	55	100
TMEDA as additive	0	25	100
	1 min	55	100
	5 min	10	48
	15 min	0	29
DMEDA as additive	10	90	32
	10 min	100	0
	20 min	100	0

Reaction conditions: PhMgBr (1.0 mmol) with or without an additive in 3 mL THF was added dropwise to the mixture of 1-bromooctane (0.5 mmol) and 5 mol% of **1** in 1 mL THF at r.t. for 40 min. The ESI-MS spectra were recorded after PhMgBr (with or without an additive) was added for 1 min up to 20 min.

single crystals. The structure is revealed by X-ray crystallographic analysis (Fig. 4).

Some Grignard compounds with different O- and N-donors have been structurally characterized by Steinborn *et al.*,<sup>9</sup> such



**Fig. 4** ORTEP diagram of **4** (30% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Mg(1)–O(1) 2.091(4), Mg(1)–N(2) 2.239(5), Mg(1)–N(1) 2.250(5), Mg(1)–Br(1) 2.5191(18), Mg(1)–Br(2) 2.5197(17); O(1)–Mg(1)–N(2) 164.29(19), O(1)–Mg(1)–N(1) 88.12(17), N(2)–Mg(1)–N(1) 79.46(19), O(1)–Mg(1)–Br(1) 95.59(12), N(2)–Mg(1)–Br(1) 96.85(14), N(1)–Mg(1)–Br(1) 104.81(13), O(1)–Mg(1)–Br(2) 90.82(12), N(2)–Mg(1)–Br(2) 92.46(14), N(1)–Mg(1)–Br(2) 139.63(14), Br(1)–Mg(1)–Br(2) 115.44(7), C(10)–O(1)–Mg(1) 123.6(4), C(7)–O(1)–Mg(1) 121.0(3).

as MgMeBr(tmeda)(THF), MgMe<sub>2</sub>(pmeda) and MgBr<sub>2</sub>(pmeda) (pmeda = *N,N,N',N''*-pentamethyl-diethylenetriamine). Complex **4** has a similar structure to the MgMeBr(tmeda)-



(THF)<sup>9</sup> but without an alkyl/aryl ligand. It is not an organo-metallic Grignard reagent, however, it could provide a driver for the Grignard reaction through stabilisation of the resultant magnesium halide. The Mg(II) is a distorted trigonal bipyramid with one amine nitrogen and two bromides (N<sub>1</sub>, Br<sub>1</sub> and Br<sub>2</sub>) on the basal plane. The Mg–Br bonds in **4** are slightly longer than those in MgMeBr(tmeda)(THF) (Mg–Br = 2.485(1) Å).<sup>9</sup> It has been proposed that TMEDA can coordinate to Mg(II) and reduce the Lewis acidity of the Mg center.<sup>2g,3a</sup> Some TMEDA–Mg species, such as a mixture of PhMgBr(tmeda), Ph<sub>2</sub>Mg(tmeda) and MgBr(tmeda)<sub>n</sub>(THF)<sub>2–n</sub> (n = 1, 2), have been observed in the mixture of PhMgBr and TMEDA in d<sup>8</sup>-THF.<sup>3a</sup> It is also found that the treatment of cycloheptyl bromide with Ph<sub>2</sub>Mg(tmeda) (by slow-addition of the Grignard reagent) in the presence of a catalytic amount of FeCl<sub>3</sub> gives good selectivity to the cross-coupling product.<sup>3a</sup> However, when **4** was used as an additive to replace TMEDA, no product was obtained in the coupling between octyl bromide and PhMgBr in the presence of **1**. This prompted us to turn our attention to the search for bimetallic Mg–Ni–TMEDA species.

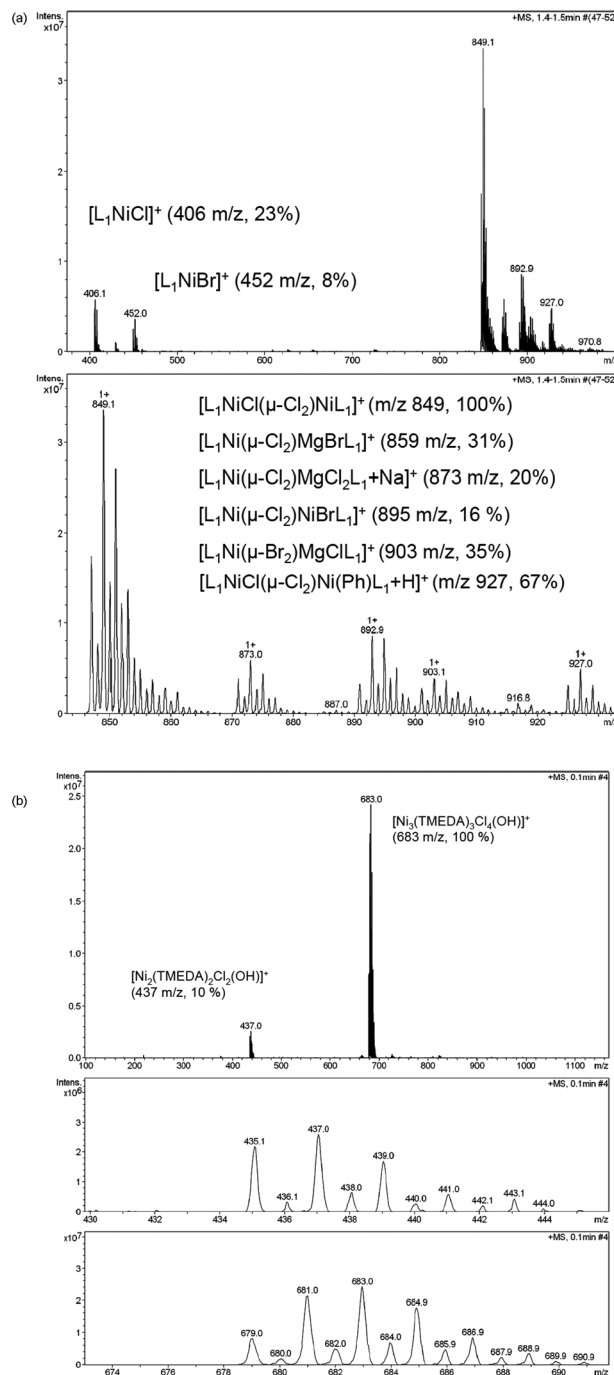
The ESI-MS spectra of the reaction mixtures of PhMgBr and **1** (2 : 1) with or without TMEDA were studied (Fig. 5).

Without TMEDA, the addition of PhMgBr to **1** leads to a color change of the reaction mixture from pale green to dark brown in THF. The +ve mode ESI-MS (Fig. 5a) shows one major peak at 849 *m/z* corresponding to [L<sub>1</sub>NiCl(μ-Cl<sub>2</sub>)NiL<sub>1</sub>]<sup>+</sup> and other minor peaks such as [L<sub>1</sub>NiCl]<sup>+</sup> (406 *m/z*), [L<sub>1</sub>NiBr]<sup>+</sup> (452 *m/z*) and [L<sub>1</sub>NiCl(μ-Cl<sub>2</sub>)Ni(Ph)L<sub>1</sub> + H]<sup>+</sup> (927 *m/z*). The latter is formed by replacement of a chloro with a phenyl ligand. Transmetalation species obtained by exchanging one Ni atom with one Mg atom, and/or halide replacement of Cl with Br can also be observed, as evident in [L<sub>1</sub>Ni(μ-Cl<sub>2</sub>)MgBrL<sub>1</sub>]<sup>+</sup> (859 *m/z*), [L<sub>1</sub>Ni(μ-Br<sub>2</sub>)MgClL<sub>1</sub>]<sup>+</sup> (903 *m/z*) and [L<sub>1</sub>Ni(μ-Cl<sub>2</sub>)NiBrL<sub>1</sub>]<sup>+</sup> (895 *m/z*).

The positive mode ESI-MS spectrum (Fig. 5b) of the reaction mixture of PhMgBr and TMEDA (2 equiv. to **1**) and **1** in THF dominated by one major peak at *m/z* 683 and a minor peak 437 *m/z* and no species corresponding to Ni–L<sub>1</sub> complexes can be obtained. The mixture of **1** and TMEDA in THF also gives the same peaks. Green crystals were obtained from this reaction mixture which allowed us to identify the peaks in the ESI spectra. The X-ray crystallographic analysis reveals the crystals to be [Ni<sub>3</sub>(tmeda)<sub>3</sub>Cl<sub>4</sub>(OH)]Cl (**5**) with a [Ni<sub>3</sub>Cl<sub>4</sub>(OH)] core (see Fig. 6).

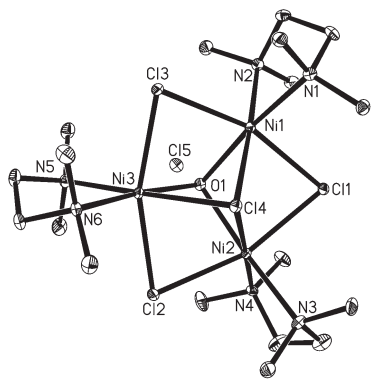
The same compound has been isolated from the reaction between TMEDA and NiCl<sub>2</sub>·6H<sub>2</sub>O in ethanol at 50 °C and the molecular structure has been reported by Horn *et al.*<sup>10</sup> The peak at 683 *m/z* is assigned to the fragment [Ni<sub>3</sub>(tmeda)<sub>3</sub>Cl<sub>4</sub>(OH)]<sup>+</sup> based on both the *m/z* value and the isotopic pattern, while the peak at 437 *m/z* corresponds to the fragment [Ni<sub>2</sub>(tmeda)<sub>2</sub>Cl<sub>2</sub>(OH)]<sup>+</sup>.

When using **5** as a catalyst (5 mol%) for the reaction between PhMgBr and 1-bromooctane, after one hour reaction time, the cross-coupling product yield is 38% and 23% with or without TMEDA, respectively. In both cases, the alkyl halide conversion is 100% (Table 5, entries 1–2). When **5** was used as



**Fig. 5** (a) The positive mode ESI-MS spectra of the reaction mixture of PhMgBr, TMEDA and complex **1** (2 : 2 : 1). (b) The positive mode ESI-MS spectra of the reaction mixture of PhMgBr and complex **1** (2 : 1).

a catalyst in the presence of free ligand L<sub>1</sub>, L<sub>2</sub> or L<sub>3</sub>, comparing the catalytic data in Table 1 (entries 2–4) and those in Table 5 (entries 3–5), it is indicated that the 5/free ligand L<sub>1</sub>, L<sub>2</sub> or L<sub>3</sub> system cannot represent the catalyst generated from the **1**/TMEDA system. Thus, it cannot be deduced that the higher performance of **1**/TMEDA in comparison with **2** or **3**/TMEDA is due to a better association of Mg with L<sub>1</sub> compared with L<sub>2</sub>, L<sub>3</sub> and TMEDA.



**Fig. 6** ORTEP diagram of **5** (30% probability ellipsoids). Hydrogen atoms were omitted for clarity.

**Table 5** Cross coupling of 1-bromooctane with PhMgBr catalyzed by **5**<sup>a</sup>

Entry	Octyl-Br + PhMgBr		catalyst conditions	Octyl-Ph	
	A	B		B (%)	A (%)
1	<b>5</b>	None	23	100	
2	<b>5</b>	TMEDA	38	100	
3	<b>5</b>	L1	23	100	
4	<b>5</b>	L2	8	25	
5	<b>5</b>	L3	26	59	

<sup>a</sup> Reaction conditions: 1.0 mmol of PhMgBr and 0.3 mmol additive in 3 mL THF were added dropwise to **5** (5 mol% based on metal) and octyl-Br (0.5 mmol) in 1 mL THF and stirred at r.t. for 1 h.

<sup>b</sup> Conversion and yield were determined by <sup>1</sup>H NMR (mesitylene as the internal standard).

## Experimental

### Materials and physical measurements

All chemicals were obtained from Sigma-Aldrich or Stem-Chemicals unless stated otherwise. Ligands **L**<sub>1</sub>–**L**<sub>3</sub> were synthesized using a similar procedure as described in the literature.<sup>6,7</sup> The complex Ni(tmEDA)(acac)<sub>2</sub> was prepared according to the literature method.<sup>11</sup> Dinuclear Ni(II) complexes **1**–**3** formation reactions were carried out using conventional Schlenk techniques under an inert atmosphere of nitrogen. NMR spectra were measured at 25 °C using a Bruker ACF 500 MHz NMR spectrometer. Electrospray ionization mass spectrometry (ESI-MS) was recorded using a thermo Finnigan LCQ spectrometer and Bruker AmaZon-X. Elemental analyses were performed on the vario MICRO Elementar system. Infrared spectra were obtained on a Varian 3100 FT-IR spectrometer. GC-MS analyses were recorded on an Agilent 6890N/5973N system.

### Synthesis of complexes **1**–**3**

Complexes **1**–**3** were synthesized by a common procedure as follows: to a THF solution (5 mL) of NiCl<sub>2</sub>·6H<sub>2</sub>O (118 mg, 0.5 mmol) was added a THF solution (5 mL) of **L**<sub>1</sub> (157 mg,

0.5 mmol), **L**<sub>2</sub> (165 mg, 0.5 mmol) or **L**<sub>3</sub> (171 mg, 0.5 mmol), and the mixture was stirred at r.t. for ~12 h, and then the solvent was removed under reduced pressure. The resulting green solid residue was washed with Et<sub>2</sub>O (3 × 20 mL) to afford complexes **1**–**3** as green solids.

For [NiCl<sub>2</sub>(**L**<sub>1</sub>)<sub>2</sub>] (**1**), Yield: 193 mg, 87%. IR (KBr, cm<sup>-1</sup>): 3458s, 3264w, 3167m, 2986w, 2919w, 2850w, 2360w, 2093w, 1620s, 1555s, 1490w, 1467m, 1444w, 1393m, 1320w, 1273m, 1238w, 1149m, 1104w, 1051s, 1006m, 980w, 946w, 910w, 855w, 821s, 748m and 697w, 599w. ESI-MS (*m/z*, 100%): [NiCl(**L**<sub>1</sub>)<sub>2</sub>]<sup>+</sup> (406.1), (*m/z*, 40%): [Ni<sub>2</sub>Cl<sub>3</sub>(**L**<sub>1</sub>)<sub>2</sub>]<sup>+</sup> (849.9). Anal. calcd for C<sub>34</sub>H<sub>46</sub>N<sub>10</sub>O<sub>2</sub>Ni<sub>2</sub>Cl<sub>4</sub>·2CH<sub>3</sub>CN: C, 47.14; H, 5.41; N, 17.36. Found: C, 46.79; H, 5.46; N, 17.29%.

For [NiCl<sub>2</sub>(**L**<sub>1</sub>)<sub>2</sub>] (**2**), Yield: 191 mg, 83%. IR (KBr, cm<sup>-1</sup>): 3462s, 3286w, 3163m, 3053w, 2987w, 2917w, 2850w, 2088w, 1748w, 1616s, 1554s, 1488m, 1466m, 1422w, 1394w, 1300w, 1273m, 1223w, 1175w, 1145w, 1123w, 1101w, 1052s, 980m, 937m, 852m, 818s, 740s, 707w, 629w, 597w. ESI-MS (*m/z*, 100%): [NiCl(**L**<sub>2</sub>)<sub>2</sub>]<sup>+</sup> (422.1), (*m/z*, 83%): [Ni<sub>2</sub>Cl<sub>3</sub>(**L**<sub>2</sub>)<sub>2</sub>]<sup>+</sup> (880.9). Anal. calcd for C<sub>34</sub>H<sub>46</sub>N<sub>10</sub>S<sub>2</sub>Ni<sub>2</sub>Cl<sub>4</sub>·2CH<sub>3</sub>CN: C, 45.63; H, 5.24; N, 16.80. Found: C, 45.12; H, 5.01; N, 16.37%.

For [NiCl<sub>2</sub>(**L**<sub>1</sub>)<sub>2</sub>] (**3**), Yield: 210 mg, 89%. IR (KBr, cm<sup>-1</sup>): 3360s, 2962w, 2919w, 2851w, 2737w, 2677w, 2086w, 1632s, 1557s, 1469s, 1471m, 1421w, 1392w, 1305w, 1269w, 1218w, 1126w, 1055m, 988m, 889w, 849w, 792w, 699m, 628w, 571w. ESI-MS (*m/z*, 50%): [NiCl(**L**<sub>3</sub>)<sub>2</sub>]<sup>+</sup> (436.0), (*m/z*, 85%): [Ni<sub>2</sub>Cl<sub>3</sub>(**L**<sub>3</sub>)<sub>2</sub>]<sup>+</sup> (908.8). Anal. calcd for C<sub>34</sub>H<sub>46</sub>N<sub>10</sub>S<sub>2</sub>Ni<sub>2</sub>Cl<sub>4</sub>·2CH<sub>2</sub>Cl<sub>2</sub>: C, 40.90; H, 4.88; N, 12.55. Found: C, 40.68; H, 5.15; N, 12.22%.

### General method for sp<sup>2</sup>–sp<sup>3</sup> cross-coupling catalysis runs

After standard cycles of evacuation and back-filling with pure N<sub>2</sub>, a catalyst (0.05 mmol, 5.0 mol% based on nickel) was introduced into a 25 mL Schlenk tube equipped with a magnetic stir bar. To the catalyst were added THF (1 mL) and alkyl halide (0.5 mmol) and the solution was stirred at r.t. Aryl Grignard (0.6 or 1.0 mmol) and additive (such as TMEDA) (0.3 mmol) were added dropwise within 1 h and the resulting mixture was stirred for another 20 min. The reaction was quenched with HCl (aq., 2 M, 5 mL). The organic phase was extracted with Et<sub>2</sub>O (3 × 5 mL) and dried over MgSO<sub>4</sub>. Mesitylene was added as an internal standard (0.5 mmol, 0.069 mL) and then the solvent was carefully removed on a rotary evaporator. The conversions and yield of the cross coupling reactions were determined by <sup>1</sup>H-NMR analysis.

### General method for sp<sup>3</sup>–sp<sup>3</sup> cross-coupling catalysis runs

After standard cycles of evacuation and back-fill with pure N<sub>2</sub>, a catalyst (0.05 mmol, 5.0 mol% based on nickel) was introduced into a 25 mL Schlenk tube equipped with a magnetic stir bar. To the catalyst were added THF (1 mL), alkyl halide (0.5 mmol), TMEDA (0.3 mmol) and the solution was stirred at r.t. Alkyl Grignard (0.6 or 0.75 mmol) was added dropwise within 40 min, and the resulting mixture was stirred for another 20 min. The reaction was quenched with HCl (aq., 2 M, 5 mL). The organic phase was extracted with Et<sub>2</sub>O

(3 × 5 mL) and dried over MgSO<sub>4</sub>. Nonane was added as an internal standard (0.06 mL). The conversion and yield of the cross coupling reactions were determined by GC-MS.

### X-ray crystallography

Diffraction measurements were conducted at 100(2)–293(2) K on a Bruker AXS APEX CCD diffractometer using Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The data were corrected for Lorentz and polarization effects with the SMART suite of programs and for absorption effects with SADABS.<sup>12</sup> Structure solutions and refinements were performed by using the programs SHELXS-97<sup>13a</sup> and SHELXL-97.<sup>13b</sup> The structures were solved by direct methods to locate the heavy atoms, followed by difference maps for the light non-hydrogen atoms. Anisotropic thermal parameters were refined for the rest of the non-hydrogen atoms. Hydrogen atoms were placed geometrically and refined isotropically.

### Conclusions

We have demonstrated the catalytic activity of dinuclear Ni(II) amine-pyrazolyl complexes towards aryl/alkyl Grignard reagents coupling with alkyl halides. The nature of the tether function on the central amine moiety of the hybrid ligand strongly affects the cross coupling selectivity and activity. Complex **1**, which contains the ligand with a pendant furan arm, gives the best catalytic efficacy. Compared with other catalyst systems,<sup>5</sup> **1** is efficient for both sp<sup>3</sup>–sp<sup>3</sup> and sp<sup>3</sup>–sp<sup>2</sup> types of cross coupling in the presence of TMEDA under milder reaction conditions (r.t.) with lower catalyst loading. The TMEDA-Mg compound (**4**) isolated from the catalytic reaction mixture cannot replace TMEDA's role in the catalysis. The TMEDA-Ni compound (**5**) obtained from the mixture of **1**, PhMgBr and TMEDA shows low selectivity towards the cross coupling product. Furthermore, the 5/free ligand L<sub>1</sub>, L<sub>2</sub> or L<sub>3</sub> system cannot represent the catalyst generated from the 1/TMEDA system. Nevertheless, the current catalytic data clearly show both the promoting nature of the TMEDA and the role of the tripodal ligand. ESI-MS has been used to detect the possible catalytic active species related to TMEDA and the tripodal ligand, a conclusive result cannot yet be obtained. However, it is noteworthy that the ESI-MS spectra of the mixture of Grignard reagent and **1** showed the presence of the Ni(II) and Mg(II) bimetallic species supported by the tripodal hybrid ligand L<sub>1</sub>, thus suggesting the intermetallic coordination effect of a hybrid ligand. Together with the X-ray crystallographic data, these point to a stabilising role of an additive donor such as TMEDA towards the Grignard reagent, the Ni(II) catalyst, as well as the possible bimetallic intermediate that holds the key to the aryl/alkyl transfer across the metals.

Current research in our laboratory is directed at the design of suitable intermetallic complexes supported by suitable hybrid ligands that can serve as single-site catalysts for cross-coupling reactions.

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