Synthesis of new dipyridinylamine and dipyridinylmethane ligands and their coordination chemistry with Mg(II) and Zn(II)†

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Received (in Montpellier, France) 29th April 2008, Accepted 10th June 2008
First published as an Advance Article on the web 28th August 2008
DOI: 10.1039/b807258b

Sterically hindered, symmetrically 2,2′-substituted bispyridylamines **1a–c** and methylene-bispyridine **4** were prepared in a three-step procedure from commercially available 2,6-dibromopyridine, *via* a Cu-mediated alkylation followed by two consecutive Buchwald–Hartwig *N*-arylation reactions or two Negishi cross-coupling reactions, respectively, in the presence of Pd catalysts. Deprotonation of the NH and CH_2 bridge of **1a** and **4**, respectively, enables the formation of Zn(II) and Mg(II) complexes, whose structures have been determined by single-crystal diffraction studies and/or NMR spectroscopy. A magnesium–isopropyl complex stabilized by a bispyridyldiiminate ligand derived from **4** is shown to be an active catalyst for the isotactic polymerization of methyl methacrylate.

Introduction

Nitrogen ligands are able to bind strongly a large variety of metal centers and can stabilize both very low and high oxidation states.[1–6] Ubiquitous examples of *neutral* nitrogen ligands are diimines (including bipyridines),[7–11] which have been intensively studied in asymmetric catalysis with almost all transition metals.[2,12] Other neutral multidentate *N*-donor ligands have also found use in various processes. For instance, catalytic applications of mainly late transition metal complexes have been reported for tridentate bis(pyrazolyl)amine,[13] triazacyclononane,[14] and pyridine-2,6-diimine[15] ligands. A notable achievement in this line was reported by Gibson and Brookhart with the discovery of highly active iron and cobalt ethylene polymerization catalysts containing bulky pyridinediimine ligands.[16]

Other members of privileged nitrogen ligands that have emerged over the past several years are β-diiminate ligands **A** and bisoxazolines **B** (Chart 1).[17] The common feature of these ligands is that they usually act as three-electron chelates,

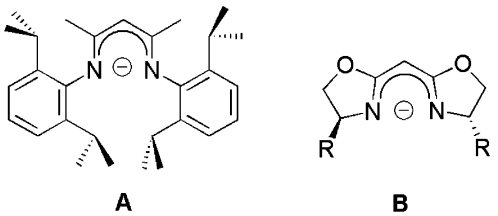

Chart 1

namely, *monoanionic* aza-acac ligands. Metal complexes of ligands **A** and **B** have been successfully applied to a broad range of industrially important catalytic reactions.[18,19] However, minor structural variations within substrate molecules may dramatically change the outcome of the catalytic reaction. Basically, each substrate needs its own optimized catalyst and ligand system. Hence, it is a significant advantage of a given ligand class if it allows easy steric and electronic tuning of the structure.

As recently pointed out by Chelucci and Thumel,[20] the chemistry of those *N*-donor ligands mostly relies on the formation of stable five- or (to a lesser extent) six-membered chelates upon metal binding. Only a few pyridine-based ligands with the potential to form six-membered chelates with metals have been introduced. Wright's di(pyridyl)silane,[21] Chelucci's dipyridylpropane,[22] Nájera's dihydropyridylmethane[23] and Kwong's dipyridyl ketone[24] are examples of such neutral ligands. Recently, the groups of Kempe,[25] Bolm[26] and Kim[27] showed the applicability of 2,2′-dipyridylamines as neutral ligands in transition metal-catalyzed polymerization, allylic oxidation and transesterification, respectively. Burns and Jordan also prepared olefin polymerization catalysts that contain neutral bidentate dipyridylmethane.[28] Despite these interesting examples, the chemistry and catalytic applications of 2,2′-dipyridylamines and 2,2′-dipyridylmethane remains limited, and, to our knowledge, no sterically hindered bispyridyl derivative has been described in the literature.

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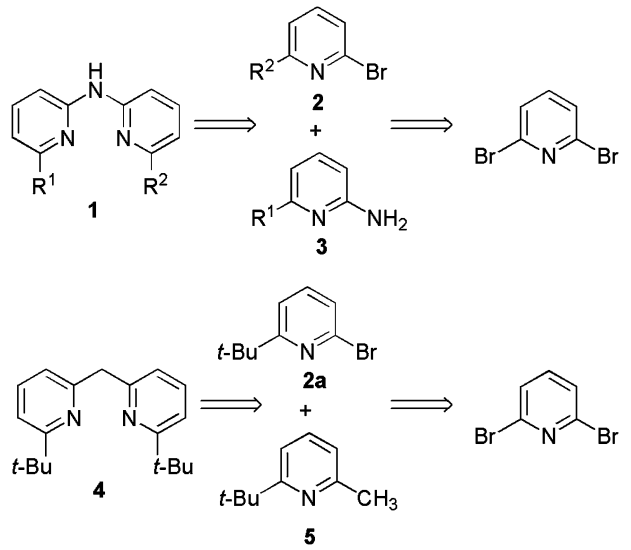
† CCDC reference numbers 682251–682253. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b807258b



Scheme 1 Strategy used for the synthesis of bispyridines **1** and **4**.

Based on our studies in allylic substitutions catalyzed by ruthenium complexes[8a–d] and in polymerization reactions catalyzed by rare earth complexes bearing nitrogen ligands,[19] we envisioned to prepare new modular dipyridylamines **1** and dipyridylmethane (pro)ligands **4**, starting from simple, commercially available 2,6-dibromopyridine (Scheme 1). Due to the formation of six-membered chelates, bulky and/or chiral substituents at the 2,2′-positions shall be closer to the metal center.

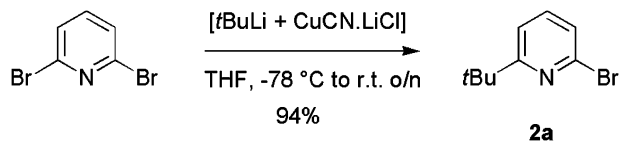
We report here the synthesis of 6-*tert*-butyl-2-bromopyridine **2** and of new symmetrically 2,2′-substituted-dipyridylamine **1** and 2,2′-dipyridylmethane derivatives **4** (Scheme 1). Preliminary studies on the coordination of those molecules as monoanionic ligands onto Zn(II) and Mg(II) centers, and on the reactivity of some of these complexes, are described as well.

Results and discussion

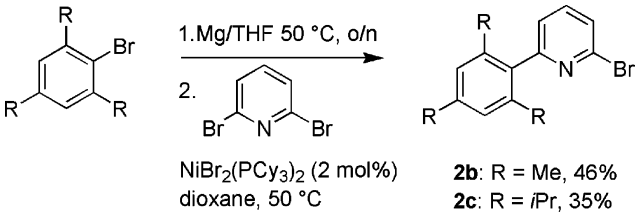
Synthesis of 6-substituted-2-bromopyridines

The first step of our strategy required the addition of a sterically hindered substituent onto 2,6-dibromopyridine. For this purpose, we chose a *tert*-butyl group and two differently substituted aryl derivatives as *ortho*-pyridine substituents. Two important issues have to be addressed: (i) this addition must proceed without any (or significant) reduction of the halopyridines, and (ii) no double addition of the nucleophile must occur.

With alkyl derivatives, palladium and nickel catalysts often led to elimination products from secondary and tertiary Grignard reagents.[29] As lithium reagents could also



Scheme 2 Synthesis of 2-bromo-6-*tert*-butylpyridine.



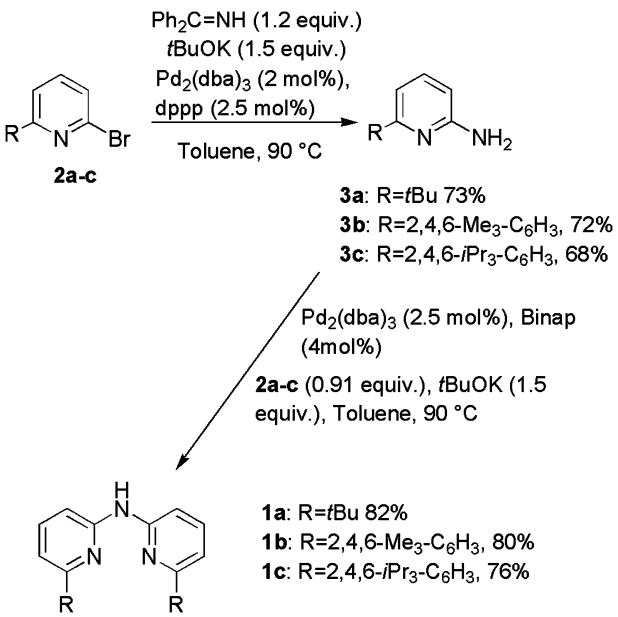
Scheme 3 Synthesis of 2-aryl-6-bromopyridines.

transmetallate aryl halides, we turned our attention to copper chemistry.[30] Among different copper sources, cuprates, and more specifically those arising from CuI and CuCN·2LiCl,[31] provided better yields than neutral organocopper reagents. Thus, treatment of 2,6-dibromopyridine with 1.5 equiv. of *in situ*-generated tBu_2CuLi or *t*BuCuCN·LiCl at −78 °C in THF led to **2a** in 66 and 94% yields, respectively (Scheme 2). Neither reduction of the bromopyridine nor bis addition of the alkyl substituent was observed. To the best of our knowledge, this is the shortest procedure to prepare efficiently **2a**.[32]

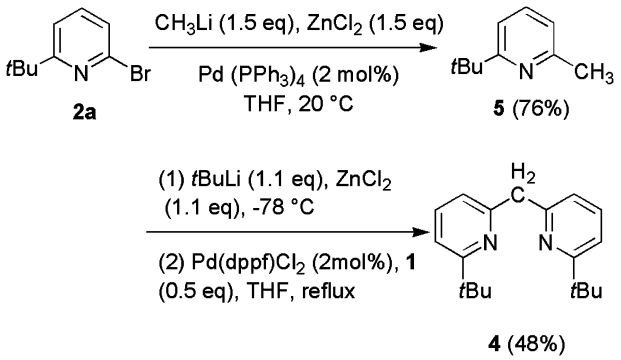
The introduction of aryl substituents was carried out *via* a nickel-catalyzed cross-coupling reaction between a sterically hindered aryl Grignard reagent and 2,6-dibromopyridine at 50 °C in dioxane.[33] The corresponding 2-aryl-6-bromopyridines **2b–c** were isolated in (non-optimized) yields of 46 and 35%, respectively (Scheme 3).

Synthesis of bispyridylamine 2 and methylene bispyridine 4

Primary arylamines are typically prepared from ammonia surrogate.[34] Thus, by using benzophenone imine as the ammonia source and bromopyridines **2a–c**, in the presence of a catalytic amount of palladium(0) and dppp, followed by hydrolysis, the amino derivatives **3a–c** were isolated in good yields (68–73%, Scheme 4). The last step in the synthesis of the new symmetrically-substituted 2,2′-dipyridylamines **1a–c** was a second *N*-arylation between the corresponding aminopyridine **3a–c** and bromopyridine **2a–c** *via* a palladium-catalyzed



Scheme 4 Synthesis of bispyridylamines **1a–c.**



Scheme 5 Synthesis of dipyridylmethane **4**.

Buchwald–Hartwig coupling reaction. In the presence of 2.5 mol% of $Pd_2(dba)_3$, 4 mol% of *rac*-BINAP[35] and 1.5 equiv. of *t*BuOK in toluene at 90 °C, compounds **1a–c** were isolated in high yields (74–98%, Scheme 4).[36,37] The crystal structure of the bulky derivative **1c** has been determined by an X-ray diffraction study (see ESI†).

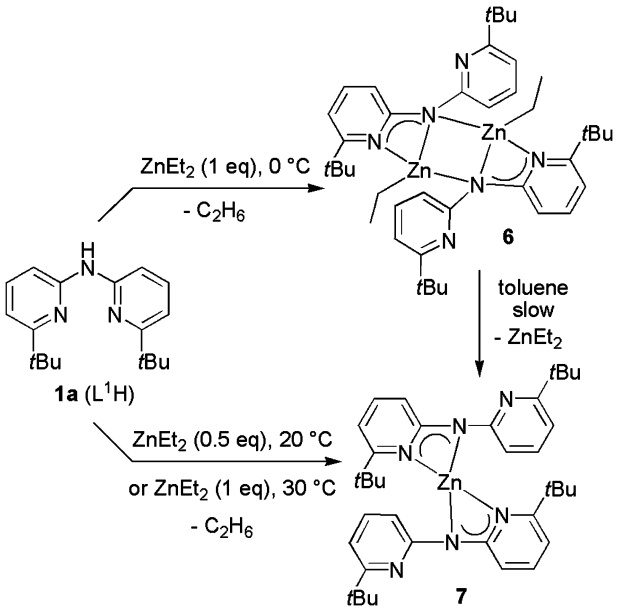
The 2,2′-*tert*-butyl-substituted dipyridylmethane **4** was prepared *via* two consecutive palladium-catalyzed Negishi cross-coupling reactions (Scheme 5). Thus, the reaction of *in situ*-generated methylzinc chloride and bromopyridine **2a**, in the presence of a catalytic amount of palladium(0) in THF at room temperature, led to the corresponding 2-*tert*-butyl-6-methylpyridine (**5**) in 76% isolated yield. Subsequent deprotonation, followed by a transmetallation step with zinc(II) chloride and a coupling reaction in the presence of palladium(II)–dppf in refluxing THF, provided the desired methylene-bridged dipyridine **4** in a moderate yield of 48% (overall yield of 36%).

Coordination chemistry of bispyridylamine 1a and methylene bispyridine 4

To explore the potential of these new dipyridines as monoanionic (pro)ligands, preliminary studies of their coordination chemistry onto Zn(II) and Mg(II) centers were conducted. The 2,2′-*tert*-butyl-substituted amino- and methylene-bridged derivatives **1a** (hereafter referred as L^1H) and **4** (L^2H) were selected for this purpose.

Reaction of the amino-bridged pro-ligand L^1H (**1a**) with 1 equiv. of $ZnEt_2$ at 0 °C in toluene affords *via* ethane elimination the ethyl-zinc complex $[L^1]ZnEt$ (**6**), which was isolated after recrystallization in low yield (20%) as colorless crystals (Scheme 6). Complex **6** is unstable in toluene solution and disproportionates slowly at room temperature to the bis(ligand) complex $[L^1]_2Zn$ (**7**) and $ZnEt_2$ (identified by ^1H NMR). When the alkane elimination reaction between $ZnEt_2$ and 1 equiv. of L^1H was performed at 30 °C, only **7** was isolated as colorless crystals in moderate yield (36% *vs.* Zn). As expected, reducing the amount of $ZnEt_2$ to 0.5 equiv. *vs.* L^1H (*i.e.*, using the exact stoichiometry) and carrying out the alkane elimination reaction at 20 °C led to **7** in higher isolated yield (60%).

Complexes **6** and **7** were authenticated by elemental analyses, ^1H and ^{13}C NMR spectroscopy, and single-crystal X-ray diffraction studies (see Experimental section). In both complexes, the Zn centers adopt four-coordinated, slightly distorted tetrahedral geometries. Complex **6** exists as a dimer



Scheme 6 Preparation of zinc complexes from L^1H (**1a**).

in the solid state with coordination of the ethyl residue, nitrogen of one of the two pyridyl groups and the central N atom which bridges between the two Zn centers; there is a crystallographically imposed twofold symmetry (Fig. 1). One pyridyl group of the ligand does not coordinate and its nitrogen and *tert*-butyl substituent point in the opposite direction to zinc, to minimize steric crowding. On the other hand, the bis(ligand) complex **7** is monomeric in the solid state (Fig. 2). Each ligand is coordinated to the zinc center *via* one pyridyl nitrogen atom and the central bridging nitrogen atom. As observed in **6**, the nitrogen atoms of the coordinated and free pyridine rings are arranged in a *trans* conformation, with

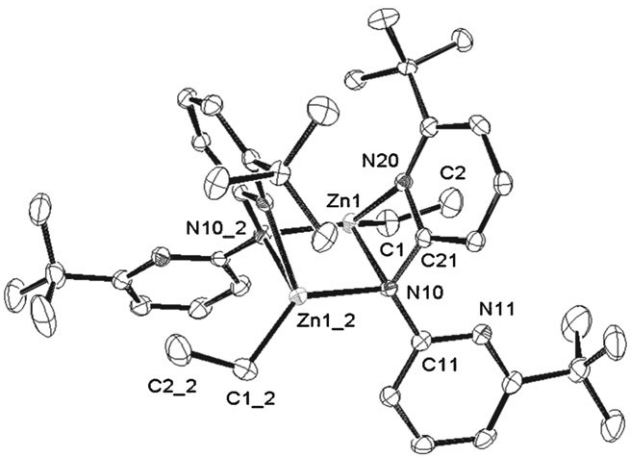


Fig. 1 Solid-state structure of complex **6** (ellipsoids drawn at the 60% probability, H atoms omitted for clarity) (the "_2" symbol in the atom labels indicates that these atoms are at equivalent position (1 − *x*, *y*, 1/2 − *z*)). Selected bond distances (Å) and angles (°): Zn(1)–C(1), 1.9703(19); Zn(1)–N(10), 2.2794(15); Zn(1)–N(10_2), 2.0386(16); Zn(1)–N(20), 2.1363(15); Zn(1)–Zn(1_2), 2.9951(4); N(10)–C(11), 1.406(2). C(1)–Zn(1)–N(10), 119.08(8); C(1)–Zn(1)–N(20), 115.98(7); C(1)–Zn(1)–N(10_2), 133.85(8); N(10)–Zn(1)–N(10_2), 92.25(6); N(20)–Zn(1)–N(10), 62.07(5), Zn(1)–N(10)–C(11), 120.78(12).

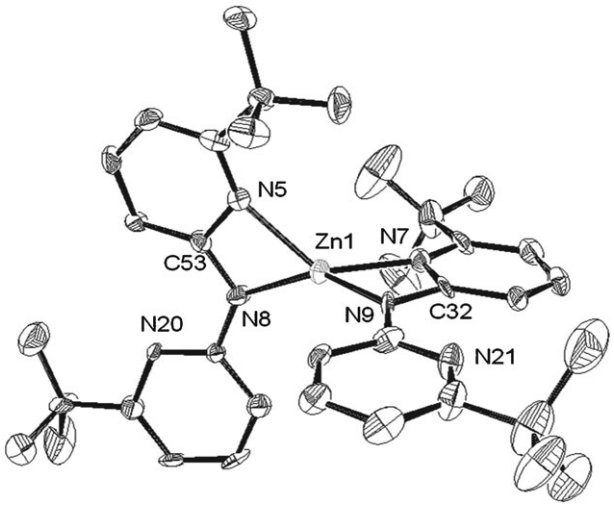
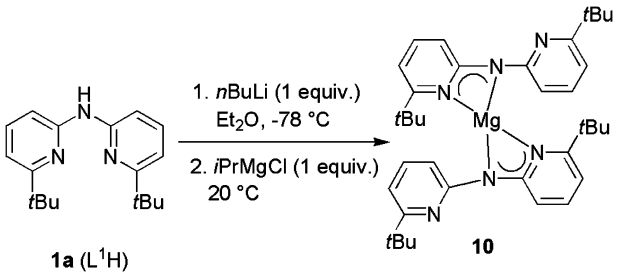


Fig. 2 Solid-state structure of complex **7** (ellipsoids drawn at the 50% probability, H atoms omitted for clarity; only one of the four independent molecules is depicted). Selected bond distances (Å) and angles (°) (data in parentheses refer to the range observed in the other three independent molecules, to illustrate the slight deviations): Zn(1)–N(5), 2.117(6) (2.110(6)–2.118(6)); Zn(1)–N(7), 2.086(6) (2.088(6)–2.102(6)); Zn(1)–N(8), 1.964(5) (1.947(6)–1.963(6)); Zn(1)–N(9), 1.943(5) (1.943(6)–1.951(6)); N(5)–C(53), 1.379(8); N(8)–C(53), 1.360(9); N(7)–C(32), 1.343(9); N(9)–C(32), 1.395(8); N(5)–Zn(1)–N(8), 66.0(2) (65.8(2)–66.4(2)); N(7)–Zn(1)–N(9), 66.2(2) (66.3(2)); Zn(1)–N(5)–C(53), 89.0(4); Zn(1)–N(8)–C(53), 96.2(4); N(8)–C(53)–N(5), 108.7(5); Zn(1)–N(7)–C(32), 95.6(4); Zn(1)–N(9)–C(32), 91.0(4); N(7)–C(32)–N(9), 107.1(5).

the *tert*-butyl substituents pointing in opposite directions. The Zn–N distances involving the central bridging N atom [Zn(1)–N(8), 1.964(5) Å; Zn(1)–N(9); 1.943(5) Å] compare well with those observed in related complexes, *e.g.* the tri-coordinated imidinate zinc complex [dipp-NacNac]ZnMe (dipp = 2,6-diisopropylphenyl) (N–Zn, 1.9480 and 1.9429 Å)[38a] and in the terminal imidinate ligand of the tetra-coordinated dinuclear complex bis(μ_2-*N*-(2-pyridyl)aniline-*N*,*N*′)-bis(*N*-(2-pyridyl)-aniline-*N*,*N*′)dizinc (N(Ph)–Zn, 2.010 Å).[38b] The N(pyr)-Zn–N(Ph) angle of 65.14° in the latter complex[38b] is very similar to that observed in **7** (66.0(2)°). Also, the Zn–N distances involving the pyridyl-N atom in **7** [Zn(1)–N(5), 2.117(6) Å; Zn(1)–N(7), 2.086(6) Å] compare well with that observed in the aforementioned imidinate dizinc complex (N(pyr)–Zn, 2.127 Å).[38b]

Coordination of the methylene-bridged pro-ligand **4** (L^2H) onto Zn was next attempted. When **4** was reacted with 1 equiv. of $ZnEt_2$ in toluene either at room temperature or up to 60 °C for 3 days, no reaction took place. This inertness most likely reflects the much weaker acidity of pro-ligand L^2H, as compared to that of NH-bridged ligand L^1H (**1a**) (Scheme 5). Direct metallation of L^2H with *n*BuLi (*vide infra*), followed by reaction with 1 equiv. of $ZnCl_2$ or MeZnCl, afforded crude materials that could not be purified sufficiently to establish their identity.

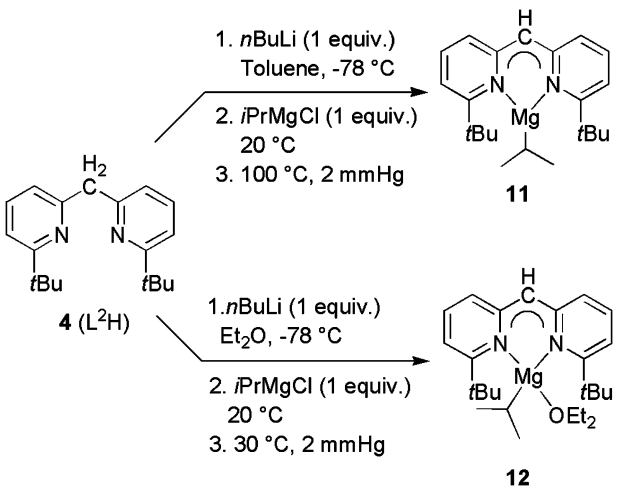
The synthesis of alkyl-magnesium complexes was carried out in a two-step procedure: (i) reaction of the bispyridines **1a** and **4** with 1 equiv. of *n*BuLi to generate the corresponding Li salts [L^n]Li (L^1, **8**; L^2, **9**), and (ii) reaction of the latter salts



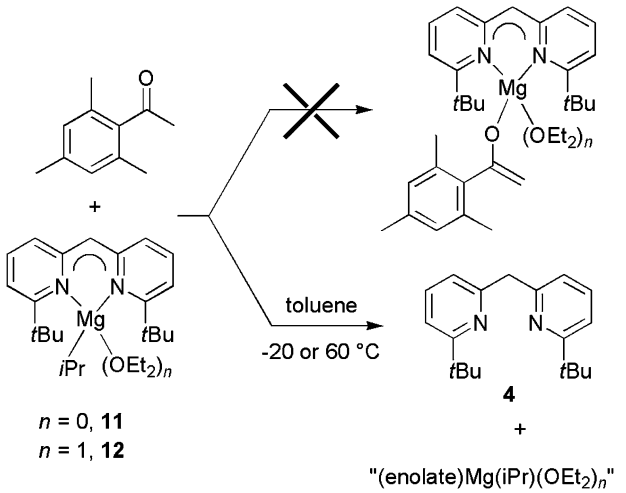
Scheme 7 Preparation of magnesium complex **8** from L^1H (**1a**).

with 1 equiv. of *i*PrMgCl to generate the corresponding low-coordinated magnesium complexes. Applying this procedure to the amino-bridged pro-ligand L^1H (**1a**) led systematically to the isolation of the bis(ligand) magnesium complex $[L^1]_2Mg$ (**10**) (Scheme 7). Modification of the reaction temperature and the sequential order of addition of reagents apparently had no influence on the reaction outcome. This suggests that "$[L^1]Mg(iPr)$" is not stable in solution and rapidly undergoes disproportionation to form **10** (and $Mg(iPr)_2$), an observation which can be related to the aforementioned disproportionation of the ethyl-zinc complex $[L^1]ZnEt$ (**6**) (Scheme 6).

More satisfactory results were obtained with the methylene-bridged pro-ligand **4**. When the reaction was carried out using toluene as the solvent, the base-free three-coordinated complex $[L^2]Mg(iPr)$ (**11**) was isolated in 20% yield. This complex is, however, quite unstable in solution, decomposing to unidentified products, as revealed by ^1H NMR monitoring. On the other hand, using diethyl ether as the solvent in the above procedure led to the stable ether-adduct $[L^2]Mg(iPr)(OEt_2)$ (**12**) in 31% yield (Scheme 8). Attempts to grow crystals suitable for X-ray diffraction studies have failed thus far, and complexes **11** and **12** were identified on the basis of ^1H and ^{13}C NMR spectroscopy. Key ^1H NMR data for **11** include a set of three resonances in the range δ 6.2–7.0 for the pyridine hydrogens, one singlet at δ 5.16 for the bridge CH hydrogen, and a doublet at δ 1.70 and a multiplet at δ 0.42 for the isopropyl group. Those isopropyl resonances are shifted upfield compared with those in Gibson's isopropylmagnesium



Scheme 8 Preparation of alkyl-magnesium complexes from L_2H (**4**).



Scheme 9 Enolysis reaction of isopropyl-magnesium complexes **11** and **12**.

imidinate (δ 0.86 and 0.13, respectively);[39] this is probably due to the anisotropic shielding effect of the pyridyl systems and the weaker ability of the latter rings to act as electron donors as compared with usual imidinate frameworks. The NMR data for **12** are similar to those of **11**, except an additional set of resonances for the diethyl ether molecule.

Preliminary investigations showed that **12** is an active catalyst for the polymerization of methyl methacrylate at low temperature (−78 °C) in toluene ([MMA]/[Mg] = 100; 65% conversion in 3 h). The PMMA formed had a unimodal distribution (M_w/M_n = 1.97, M_n = 27 000 g mol^{-1} *vs.* PS standards, as determined by GPC) and an isotactic-enriched microstructure (42% *mm*, 43% *mr*, as determined by ^{1}H NMR).

In this context, we were interested in preparing [L^2]Mg-enolate species. Indeed, Gibson and co-workers have reported that low-coordinate magnesium–enolate complexes supported by imidinate ligands polymerize MMA in a living manner to give highly syndiotactic PMMA under mild conditions (92% *rr* at −30 °C).[39] Following the procedure of Gibson, the alkyl Mg complexes **11** and **12** were reacted with 1 equiv. of the bulky enolizable ketone 2,4,6-Me$_3$C$_6$H$_2$COMe under a variety of conditions (toluene solvent, −20 °C for 24 h, 20 °C for 6 h, and 60 °C for 3 h) (Scheme 9); however, monitoring of these reactions by NMR revealed the rapid formation, in all cases, of an intense, sharp resonance at δ 4.50 ppm (in toluene-d_8), which was assigned unambiguously to free pro-ligand L^{2}H (**4**). These observations indicate that, surprisingly enough, enolysis of **11**/**12** by the bulky ketone takes place at the Mg-[L^2] rather than at Mg–C(*i*Pr) bond.

Conclusions

In conclusion, we have prepared efficiently, by using a combination of catalytic methods, a series of new dipyridylamines and dipyridylmethane that have bulky substituents at the 2,2′ positions. Preliminary investigations show that these molecules can be deprotonated at the amino and methylene bridge, respectively, to form monoanionic ligands capable to coordinate onto Zn(II) and/or Mg(II) centers. The dipyridylamines ligand acts as a bidentate ligand toward Zn(II) and Mg(II), leaving a pendant pyridine group, consistent with recent observations on related late transition metal complexes.[25–27] On the other hand, the methine-bridged dipyridine appears to adopt an diiminate-like coordination mode towards Mg(II). Further work is currently under way to explore the coordination abilities of these dipyridines onto diverse metal centers, as well as their performance in catalytic processes.

Experimental

General

All experiments involving metal complexes were carried out under purified argon using standard Schlenk techniques or in a glove box (<1 ppm O_2, 5 ppm H_2O). Hydrocarbon solvents, diethyl ether and tetrahydrofuran were distilled from Na/benzophenone, toluene and pentane were distilled from Na/K alloy under nitrogen and degassed by freeze–thaw–vacuum cycles prior to use. 2,6-dibromopyridine, benzophenone imine, *t*-BuLi (1.5 M in pentane), MeLi (1.6 M in diethyl ether), 1,3-bis(diphenylphosphine)propane (dppp), tricyclohexylphosphine (P(Cy)$_3$), *rac*-Binap, Pd$_2$(dba)$_3$, *t*-BuOK, Pd(dppf)Cl$_2$, CuCN, LiBr, 2,4,6-Me$_3$C$_6$H$_2$COMe, ZnCl$_2$, ZnEt$_2$ (15 wt% solution in hexane) and *i*-PrMgCl (2.0 M solution in diethyl ether) were purchased from Acros or Aldrich Co. and used as received. Methyl methacrylate (MMA, Acros) was distilled twice under argon over CaH_2 before use.

NMR spectra were recorded on Bruker AC-200, AC-300 and AM-500 spectrometers (in Teflon-valved NMR tubes for complexes) at 20 °C otherwise stated. ^{1}H and ^{13}C NMR chemical shifts were determined using residual solvent resonances and are reported *vs.* $SiMe_4$. Assignment of signals was made from 2D ^{1}H–^{1}H COSY and ^{1}H–^{13}C HMQC and HMBC NMR experiments. Elemental analyses (C, H, N) were performed using a Flash EA1112 CHNS Thermo Electron apparatus and are the average of two independent determinations. HRMS spectra were obtained on a high resolution MS/MS spectrometer Micromass ZABSpecTOF (EI, ESI-methods). Molecular weights of PMMA were determined by GPC at 20 °C on a Waters apparatus equipped with five PL gel columns and a differential refractometer Shimadzu RID 6A. THF was used as eluent at a flow rate of 1.0 mL min^{-1}; PS standards were used for molecular weight calibration. The microstructure of PMMA was determined by ^{1}H NMR in $CDCl_3$.

Syntheses

6-*tert*-Butyl-2-bromopyridine 2a. In a flame-dried Schlenk flask, CuCN (1.02 g, 12.0 mmol) was added to a solution of LiCl (dried under vacuum) (1.07 g, 24.0 mmol) in THF (80 mL). The resulting pale green solution was cooled to −78 °C and *t*BuLi in THF (8.0 mL of a 1.5 M solution, 12.0 mmol) was added. After an additional 30 min of stirring at −78 °C, 2,6-dibromopyridine (2.37 g, 10.0 mmol) was added. The mixture was slowly warmed up to room temperature and stirred overnight. Et_2O (180 mL) was added and the reaction mixture was filtered on Celite®. Organic layers were washed with aqueous ammonia solution (2 × 200 mL), brine

(2 × 200 mL), dried over Na_2SO_4, filtered and concentrated under vacuum. The crude product was used without purification to yield the 6-*tert*-butyl-2-bromopyridine (2.02 g, 94%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (dd, J = 7.7, 7.8 Hz, 1H, H_4), 7.25 (dd, J = 0.8, 7.8 Hz, 1H, H_3), 7.24 (dd, J = 0.8, 7.6 Hz, 1H, H_5), 1.34 (s, 9H, *t*Bu). ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) δ 171.2 (pyr-C_6), 141.2 (pyr-C_2) 138.5 (pyr-C_4), 124.9 (pyr-C_3), 117.8 (pyr-C_5) 37.6 (CMe_3), 29.9 (CMe_3). IR (neat) ν/cm^{-1} 3074, 2962, 2867, 1580, 1553, 1434, 1398, 1166, 1114, 983, 852, 794, 756, 742, 653 cm^{-1}. HRMS: m/z calc. for $C_9H_{12}BrN$ [M$^+$]: 213.0153; found: 213.0169.

Dipyridylamine 1a

To a 100 mL Schlenk flask were added successively $Pd_2(dba)_3$ (0.18 g, 0.20 mmol), dppp (0.10 g, 0.25 mmol), 2-bromo-6-*tert*-butylpyridine (**2a**, 1.07 g, 5.0 mmol), benzophenone imine (1.085 g, 6.0 mmol) and *t*BuOK (0.84 g, 7.5 mmol), and then toluene (80 mL). The mixture was heated under nitrogen at 90 °C for 24 h. The solution was cooled to room temperature, diluted with diethyl ether (*ca.* 80 mL) and filtered through Celite. Solvents were removed under vacuum to give an oily residue which was redissolved in aqueous 2 M HCl (30 mL), stirred for 1 h, and then diluted with 0.5 M HCl (30 mL). The aqueous phase was treated with a saturated aqueous solution of Na_2CO_3 and extracted with diethyl ether (100 mL). The organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography (heptane–ethyl acetate = 5 : 1) to give **3a** as a yellow liquid (0.55 g, 73%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.29 (s, 9H), 4.25–4.35 (br s, 2H), 6.30 (dd, J = 0.5, 7.8 Hz, 1H), 6.68 (dd, J = 0.5, 7.8 Hz, 1H), 7.35 (t, J = 7.8 Hz, 1H). ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) δ 30.1 (q × 3), 37.0 (s), 105.5 (d), 108.9 (d), 137.8 (d), 157.5 (s), 168.1 (s). IR (neat) ν/cm^{-1} 3475, 3378, 2956, 1577, 1457, 1257, 1043, 800, 665 cm^{-1}.

To a 100 mL Schlenk flask were added successively $Pd_2(dba)_3$ (0.080 g, 0.087 mmol), BINAP (0.064 g, 0.10 mmol), 2-bromo-6-*tert*-butylpyridine (**2a**, 0.34 g, 1.69 mmol), 2-amino-6-*tert*-butylpyridine (**3a**, 0.28 g, 1.86 mmol), and *t*BuOK (0.31 g, 2.76 mmol), and then toluene (30 mL). The mixture was heated under nitrogen at 90 °C for 12 h. The solution was cooled to room temperature, diluted with diethyl ether (*ca.* 30 mL) and filtered through celite. The residue was purified by flash chromatography (heptane–ethyl acetate = 5 : 1) to give **1a** as a yellow liquid (0.387 g, 82%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.58 (t, ^3J = 7.8, 2H, pyr-H, *p*), 7.45 (d, ^2J = 8.0, 2H, pyr-H, *m*), 7.18 (s, 1H, NH), 6.93 (d, ^2J = 7.4, 2 H, pyr-H, *m*), 1.38 (s, 18H, *t*Bu). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 167.74 (pyr-C6), 153.21 (pyr-C2), 137.65 (pyr-C4), 110.94 (pyr-C5), 108.29 (pyr-C3), 37.41 (CMe_3), 30.20 (CMe_3). HRMS: calc. for $C_{18}H_{25}N_3$ 283.2048, found 283.2034; [M − H]$^+$: found 282.1969, calc. 282.1970; [M − CH_3]$^+$: found 268.1821, calc. 268.1814.

Dipyridylamine 1b

To a 100 mL Schlenk flask were added successively $Pd_2(dba)_3$ (0.18 g, 0.20 mmol), dppp (103 mg, 0.25 mmol), **2b** (1.38 g, 5.0 mmol), benzophenone imine (1.085 g, 6.0 mmol), *t*BuOK (0.84 g, 7.5 mmol), and then toluene (80 mL). The mixture was heated at 90 °C for 24 h. The solution was cooled to room temperature, diluted with diethyl ether (80 mL) and filtered through Celite. Solvents were removed under vacuum to give an oily residue which was redissolved in aqueous 2 M HCl (30 mL), stirred for 1 h, then diluted with 0.5 M HCl (30 mL). The aqueous phase was treated with a saturated aqueous solution of Na_2CO_3 and extracted with diethyl ether. The organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The residue was washed with hexane–diethyl ether = 1 : 1 (100 mL) to give **3b** as a pale yellow solid (0.78 g, 72%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.52 (t, ^3J = 7.5, 1H, pyr-H, *p*), 6.93 (s, 2H, Ph-H, *m*), 6.61 (d, ^2J = 7.0, 1H, pyr-H, *m*), 6.47 (d, ^2J = 8.0, 1H, pyr-H, *m*), 4.48 (s, 2H, NH_2), 2.33 (s, 3H, Ph-Me, *p*), 2.09 (s, 6H, Ph-Me, *o*). ^{13}C{^{1}H} NMR (C_6D_6, 75 MHz): δ 158.46 (pyr-C2), 158.16 (pyr-C6), 137.97 (pyr-C4), 137.10 (Ph-C4), 135.58 (Ph-C2), 128.21 (Ph-C3,5), 114.78 (pyr-C5), 106.25 (pyr-C3), 21.07 (Me, Ph-*p*), 20.04 (Me, Ph-*o*).

Compound **1b** was prepared following the procedure described above for **1a** starting from $Pd_2(dba)_3$ (80 mg, 0.087 mmol), BINAP (64 mg, 0.10 mmol), **2b** (0.62 g, 2.24 mmol), **3b** (0.50 g, 2.40 mmol), and *t*BuOK (0.38 g, 3.36 mmol), and then toluene (30 mL). **1b** was isolated after purification by chromatography as a yellow liquid (0.74 g, 80%). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.75 (t, J = 15.6, 2H, pyr-H, *p*), 7.65 (s, 2H, Pyr-H, *m*), 7.42 (s, 1H, NH), 6.98 (s, 4H, Ph-H), 6.84 (d, J = 7.2, 2H, pyr-H, *m*), 2.37 (s, 6 H, Ph-CH_3, *p*), 2.12 (s, 12 H, Ph-CH_3), *m*). ^{13}C{^{1}H} NMR (C_6D_6, 300 MHz): δ 20.204 (phenyl-2,6-CH_3), 21.140 (phenyl-4-CH_3), 109.22 (pyr-5C), 117.06 (pyr-3C), 127.05, 128.30 (Ph-3,5 C), 135.79 (Ph-1C), 137.22 (Ph-4C), 137.88 (Ph-2,6-C), 138.03 (pyr-4C), 153.69 (pyr-6C), 157.94 (pyr-2C).

Dipyridylamine 1c

Compound **3c** was prepared following the procedure described above for **3a**, starting from $Pd_2(dba)_3$ (0.12 g, 0.13 mmol), dppp (70 mg, 0.17 mmol), **2c** (1.60 g, 4.4 mmol), benzophenone imine (0.87 g, 4.8 mmol) and *t*BuOK (0.74 g, 6.6 mmol), to give **3c** as a pale yellow solid (890 mg, 68%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.49 (t, ^3J = 7.9, 1H, pyr-H, *p*), 7.06 (s, 2H, Ph-H, *m*), 6.64 (d, ^2J = 7.0, 1H, pyr-H, *m*), 6.47 (d, ^2J = 8.3, 1H, pyr-H, *m*), 4.43 (s, 2H, NH_2), 2.94 (sept, 1 H, $CH(CH_3)_2$), 2.63 (sept, 2 H, $CH(CH_3)_2$), 1.00–1.30 (m, 18 H, $CH(CH_3)_2$).

Compound **1c** was prepared following the procedure described above for **1a**, starting from $Pd_2(dba)_3$ (0.070 g, 0.076 mmol), BINAP (0.056 g, 0.087 mmol), **2b** (0.62 g, 1.73 mmol), **3b** (0.54 g, 1.82 mmol), and *t*BuOK (0.29 g, 2.60 mmol), to give **1c** as a white solid (0.77 g, 76%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.59 (t, ^3J = 15.5, 2H, pyr-4H), 7.55 (d, ^2J = 9.2, 2H, pyr-5H), 7.42 (s, 1H, NH), 7.11 (s, 4H, Ph-H), 6.81 (d, ^2J = 7.8, 2H, pyr-3H), 2.94 (sept, 2 H, $CH(CH_3)_2$), 2.70 (sept, 4 H, $CH(CH_3)_2$), 1.10–1.40 (m, 36 H, $CH(CH_3)_2$). ^{13}C{^{1}H} NMR (C_6D_6, 300 MHz): δ 24.12 ($CH(CH_3)_2$), 24.22 ($CH(CH_3)_2$), 24.42 ($CH(CH_3)_2$), 30.29 (phenyl-*o*-$C(CH_3)_2$), 34.39 (phenyl-*p*-$C(CH_3)_2$), 109.17 (pyr-5C), 117.58 (pyr-3C), 120.68 (Ph-3,5C), 136.39 (Ph-1C), 137.38 (pyr-4C), 146.27 (Ph-2,6C), 148.44 (Ph-4C), 153.43 (pyr-6C), 158.13 (pyr-2C). HRMS: calc. for $C_{40}H_{53}N_3$ [M + H]$^+$: 576.4318, found: 576.4317.

Dipyridylmethane 4

To a 100 mL Schlenk flask was added a dried solution of $ZnCl_2$ (2.05 g, 15.0 mmol) in THF (40 mL). The solution was cooled to −78 °C, then CH_3Li (10 mL of 1.6 M solution in diethyl ether, 16.0 mmol) was slowly added. After stirring for 30 min at this temperature, 6-*tert*-butyl-2-bromopyridine (**2a**, 2.14 g, 10.0 mmol) and $Pd(PPh_3)_4$ (0.23 g, 0.20 mmol) were added. The mixture was warmed to room temperature and stirred overnight. The solution was diluted with Et_2O (150 mL), washed with a saturated solution of NH_4Cl and then with a saturated solution of NaCl. The organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated, and purified by chromatography (heptane–diethyl ether = 100 : 1) to give **5** as a yellow liquid (1.13 g, 76%). ^1H NMR ($CDCl_3$, 300 MHz): δ 7.49 (t, ^3J = 7.6, 1H, pyr-H, *p*), 7.15 (d, ^2J = 7.8, 1H, pyr-H, *m*), 6.96 (d, ^2J = 7.6, 1H, pyr-H, *m*), 2.56 (s, 2H, CH_3), 1.35 (s, 9H, *t*Bu). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 167.74 (pyr-C6), 153.2 (pyr-C2), 137.65 (pyr-C4), 110.94 (pyr-C5), 108.29 (pyr-C3), 37.41 (CMe_3), 30.20 (CMe_3).

Bis(6-*tert*-butyl-2-pyridyl)methane (4, L^2H). To a 100 mL Schlenk flask containing a solution of 2-methyl-6-*tert*-butylpyridine (**5**, 0.46 g, 3.00 mmol) in THF (20 mL) placed at −78 °C, *t*-BuLi (2.1 mL of a 1.5 M solution in hexane, 3.15 mmol) was added. The mixture was stirred at this temperature for 30 min, then warmed to room temperature for another 2 h, and again cooled to −78 °C. Then, a suspension of anhydrous $ZnCl_2$ (0.45 g, 3.3 mmol) in THF (10 mL) was added under argon. The mixture was warmed to room temperature for 1 h. $Pd(dppf)Cl_2$ (0.044 g, 0.060 mmol) and 2-bromo-6-*tert*-butylpyridine (**2a**, 0.32 g, 1.50 mmol) were added at −78 °C, the mixture was warmed to room temperature and heated to reflux with vigorous stirring for 15 h. Volatiles were removed under vacuum, the residue was suspended in $CHCl_3$, and an aqueous 5 M solution of NaOH (2 mL) and a saturated aqueous solution of Na_2S (2 mL) were added. The mixture was stirred for 1 h to give a white precipitate, which was removed by filtration and washed with $CHCl_3$. The filtrate and washings were transferred to a separatory funnel, and the $CHCl_3$ layer was separated and dried over anhydrous Na_2SO_4, and concentrated to dryness. The residue was purified by column chromatography on silica (EtOAc–CH_2Cl_2 first 1 : 10 and then 1 : 4) to give **4** as a light yellow liquid (0.203 g, yield: 48%). ^1H NMR ($CDCl_3$, 300 MHz): δ 7.50 (t, ^3J = 7.8, 2H, pyr-H, *p*), 7.15 (d, ^2J = 8, 2H, pyr-H, *m*), 7.06 (d, ^2J = 7.4, 2H, pyr-H, *m*), 4.30 (s, 2H, CH_2), 1.37 (s, 18H, *t*Bu). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 168.55 (pyr-C6), 158.60 (pyr-C2), 136.21 (pyr-C4), 120.13 (pyr-C3), 116.07 (pyr-C5), 47.79 (CH_2), 37.37 (CMe_3), 30.21 (CMe_3). HRMS: calc. for $C_{19}H_{26}N_2$ [M^+]: 282.2096, found 282.2104, calc. for [$M - CH_3$]$^+$: 267.1861, found 267.1875.

[L^1]ZnEt (6)

To a 50 mL Schlenk flask were added bis(6-*tert*-butyl-2-pyridyl)amine (**1a**, 0.200 g, 0.706 mmol) in toluene (10 mL), and $ZnEt_2$ (0.087 g of a 15 wt% solution in hexane, 0.706 mmol). The solution was stirred at room temperature overnight. After evaporation of volatiles under vacuum, the residue was recrystallized from pentane at −34 °C to give **6** as colorless crystals (0.055 g, 20%). ^1H NMR (C_6D_6, 300 MHz): δ 7.35 (m, 4H, pyr-H, *m* and *p*), 6.70 (d, ^2J = 7.2, 2H, pyr-H, *m*), 1.36 (m, 21H, *t*Bu and CH_3), 0.75 (q, ^4J = 1.4, 2H, CH_2CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6, 300 MHz): δ 166.84 (pyr-C6), 138.75 (pyr-C4), 128.14 (pyr-C5), 128.06 (pyr-C4), 112.20 (pyr-C2), 36.88 (CMe_3), 29.99 (CMe_3), 12.08 (Zn–CH_2CH_3), 2.21 (Zn–CH_2). Anal. Calc. for $C_{20}H_{29}N_3Zn$: C, 63.74; H, 7.76; N, 11.15. Found: C, 63.8; H, 7.8; N, 11.0%.

[L^1]$_2$Zn (7)

Procedure A. To a 50 mL Schlenk flask were added bis(6-*tert*-butyl-2-pyridyl)amine (**1a**, 0.200 g, 0.706 mmol) in toluene (10 mL), and $ZnEt_2$ (0.58 g of a 15 wt% solution in hexane, 0.706 mmol). The solution was stirred at 30 °C overnight. After evaporation of volatiles under vacuum, the residue was recrystallized from pentane at −34 °C to give **7** as colorless crystals (0.096 g, 36%).

Procedure B. To a 50 mL Schlenk flask were added bis(6-*tert*-butyl-2-pyridyl)amine (**1a**, 0.200 g, 0.706 mmol) in toluene (10 mL), and $ZnEt_2$ (0.290 g of a 15 wt% solution in hexane, 0.353 mmol). The solution was stirred at 20 °C overnight. After evaporation of volatiles under vacuum, the residue was recrystallized from pentane at −34 °C to give **7** as colorless crystals (0.080 g, 60%). ^1H NMR (C_6D_6, 500 MHz): δ 7.79 (d, ^2J = 8.2, 4H, pyr-H, *o*), 7.33 (t, ^3J = 15.8, 4H, pyr-H, *p*), 6.61 (d, ^2J = 8.2, 4H, pyr-H, *m*), 1.40 (s, 36H, *t*Bu). $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz): δ 166.32 (pyr-C6), 161.28 (pyr-C4), 139.34 (pyr-C5), 111.18 (pyr-C4), 108.92 (pyr-C2), 36.85 (CMe_3), 30.12 (CMe_3). Anal. Calc. for $C_{36}H_{48}N_6Zn$: C, 68.61; H, 7.68; N, 13.34. Found: C, 68.4; H, 7.7; N, 13.4%.

[L^1]$_2$Mg (10)

To a 50 mL Schlenk flask containing bis(6-*tert*-butyl-2-pyridyl)-amine (**1a**, 0.200 g, 0.706 mmol) in toluene (10 mL), *n*BuLi (0.57 mL of a 1.6 M solution in hexane, 0.920 mmol) was added slowly in at −78 °C. The solution was stirred and gently warmed to 20 °C. After 2 h stirring at 20 °C, volatiles were removed under vacuum and the resulting yellow solid residue was washed with pentane (*ca.* 3 mL) to afford the lithium salt [L^1]Li (**8**) as a white powder. ^1H NMR (C_6D_6, 200 MHz) of **8**: δ 7.7 (m, 4H, pyr-H, *m* and *p*), 7.0 (d, 2H, pyr-H, *m*), 1.52 (s, 18H, *t*Bu). This powder was dissolved in toluene (5 mL) and *i*PrMgCl (0.35 mL of a 2.0 M solution in diethyl ether, 0.70 mmol) was added. The resulting solution was stirred at 20 °C overnight and the solvent was removed under vacuum. Then, toluene (5 mL) was added to dissolve the residue, the solution was filtered, and the filtrate concentrated in vacuum to give **10** as a white solid (0.091 g, 22%). ^1H NMR (C_6D_6, 300 MHz): δ 7.20–7.32 (m, 8H, pyr-H, *m* and *p*), 6.79 (d, *J* = 8.3, 4H, pyr-H, *m*), 1.39 (s, 36H, *t*Bu). $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz): δ 30.21 ($C(CH_3)_3$), 37.32 ($C(Me)_3$), 108.59 (pyr-C3), 110.94 (pyr-C5), 128.14, 137.66 (pyr-C4), 153.35 (pyr-C2), 167.52 (pyr-C6). Anal. Calc. for $C_{36}H_{48}N_6Mg$: C, 73.40; H, 8.21; N, 14.27. Found: C, 73.4; H, 8.3; N, 14.4%.

[L^2]Mg(*i*Pr) (11)

To a 50 mL Schlenk flask containing bis(6-*tert*-butyl-2-pyridyl)-methane (**4**, 0.31 g, 1.10 mmol) in diethyl ether (15 mL), *n*BuLi (0.89 mL of a 1.6 M solution in hexane, 1.43 mmol) was added slowly in at −78 °C. The solution was stirred and gently warmed to 20 °C. After 2h stirring at 20 °C, volatiles were removed under vacuum and the resulting yellow solid was washed with pentane (*ca.* 3 mL) to afford the lithium salt [L^2]Li (**9**) as a yellow powder; ^{1}H NMR (C_6D_6, 500 MHz) of **9**: δ 6.81 (t, ^3J = 15.5, 2H, pyr-H, *p*), 6.21 (br s, 2H, pyr-H, *m*), 6.03 (d, ^2J = 6.8, 2H, pyr-H, *m*), 4.72 (s, 1H, CH), 1.38 (s, 1.36, 18H, *t*Bu). This powder was dissolved in diethyl ether (*ca.* 5 mL) and *i*PrMgCl (0.55 mL of a 2.0 M solution in diethyl ether, 1.10 mmol) was added. The resulting mixture was stirred at 20 °C overnight and volatiles were removed under vacuum. Then, toluene (5 mL) was added to dissolve the residue, the solution was filtered and concentrated in vacuum to give **11** as a dark red solid (0.077 g, 20%). ^{1}H NMR (C_6D_6, 500 MHz): δ 6.91 (t, ^3J = 15.7, 2H, pyr-H, *p*), 6.53 (d, ^2J = 8.4, 2H, pyr-H, *m*), 6.20 (d, ^2J = 7.9, 2H, pyr-H, *m*), 5.16 (s, 1H, CH), 1.70 (d, ^2J = 7.6, 6H, $C(CH_3)_2$, 1.38 (s, 18H, CMe_3), 0.42 (m, 1H, $CHMe_2$. Compound **11** was found to be too unstable in benzene or toluene solutions to run $^{13}C\{^1H\}$ NMR spectroscopy and also to obtain reliable elemental analyses.

[L^2]Mg(*i*Pr)(OEt$_2$) (12)

Complex **12** was prepared following the procedure described above for **11**, using diethyl ether instead of toluene as the solvent when Li-**2** was reacted with *i*PrMgCl. Complex **12** was recovered as a white solid (0.144 g, 31%). ^{1}H NMR (C_6D_6, 500 MHz): δ 6.91 (t, ^3J = 15.8, 2H, pyr-H, *p*), 6.53 (d, ^2J = 8.5, 2H, pyr-H, *m*), 6.20 (d, ^2J = 7.9, 2H, pyr-H, *m*), 5.16 (s, 1H, CH), 1.70 (d, ^2J = 7.8, 6H, $C(CH_3)_2$, 1.38 (s, 18H, *t*Bu), 0.42 (m, 1H, $CHMe_2$). $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz): δ 164.03 (pyr-C2), 158.30 (pyr-C6), 135.44 (pyr-C4), 119.16 (pyr-C5), 106.33 (pyr-C3), 84.27 (bridge-C), 36.23 (CMe_3), 30.40 (CMe_3), 24.44 ($CH(Me)_2$), 9.66 ($CH(Me)_2$). Anal. Calc. for $C_{26}H_{42}MgN_2O$: C, 73.84; H, 10.01; N, 6.62. Found: C, 73.5; H, 10.2; N, 6.6%.

X-Ray crystallography of bispyridine 1c and complexes 6 and 7

Suitable single crystals of **1c**, **6** and **7** were mounted onto a glass fiber using the "oil-drop" method. Diffraction data were collected at 100 K using an APEXII Bruker-AXS diffractometer with graphite monochromatized Mo-Kα radiation (λ = 0.71073 Å). The structure was solved by direct methods using the SIR97 program,[40] and then refined with full-matrix least-squares methods based on F^2 (SHELX-97)[41] with the aid of the WINGX[42] program. All carbon-bound hydrogen atoms were placed at calculated positions and forced to ride on the attached carbon atom. In ligand **1c**, the hydrogen atom at N(3) was found from Fourier difference maps analysis. All non-hydrogen atoms were refined with anisotropic displacement parameters.

For complex **7**, metric parameters and PLATON symmetry checks suggested that the structure should be described in the higher symmetry tetragonal $P\bar{4}$ space group, with two independent molecules. However, this appears to be a pseudo-symmetry: refinements in the $P\bar{4}$ space group led to a disordered structure, especially pronounced at the *tert*-butyl groups, with several non-positive-definite anisotropic displacement parameters. The structure is clearly best described in the *P*1 space group, with four independent molecules, which allows satisfactory refinements, with all atomic displacement parameters refined anisotropically.

CCDC reference numbers 682251–682253.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b807258b

Acknowledgements

The authors thank the Agence Nationale pour la Recherche (ANR) for a grant "Jeunes Chercheurs-Jeunes Chercheuses" (ANR-06-JCJC-0013). Z. Z. is grateful to Arkema Co. for a post-doctoral fellowship.

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