Addition of Enolisable Ketones to (dpp-bian)Mg(THF)$_3$ [dpp-bian = 1,2-Bis{(2,6-diisopropylphenyl)imino}acenaphthene]

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Dedicated to Prof. Dr. Alexei N. Egorochkin on the occasion of his 70th birthday

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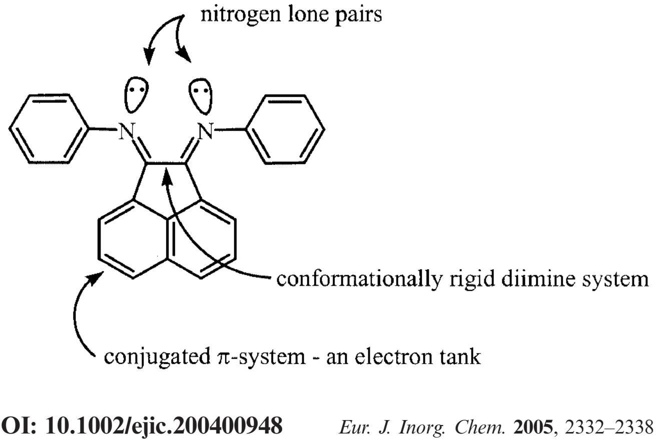
The enolates [(dpp-bian)(H)]Mg[OC(=CHPh)CH$_2$Ph](THF)$_2$ (**6**), [(dpp-bian)(H)]Mg[OC(=CPh$_2$)CH$_3$](THF)$_2$ (**7**) and [(dpp-bian)(H)]Mg(camphor)(py)$_2$ (**8**) were prepared by treating (dpp-bian)Mg(THF)$_3$ (**1**) with equimolar amounts of dibenzyl ketone, 1,1-diphenylacetone and camphor, respectively. Single-crystal X-ray structure analyses showed these enolates to be five-coordinate, trigonal bipyramidal magnesium complexes with terminal, nonbridging enolate ligands. In solutions of **6** and **7** the proton, which in the solid-state is attached to only one of the two nitrogen atoms of the dpp-bian ligand, is delocalised between both nitrogen atoms.

Introduction

Besides fundamental chemical knowledge, the chemistry of metal complexes prepares the way for applied material science, bioinorganic and synthetic organic chemistry. Traditionally, metal complexes have been widely used in organic synthesis[1] and, so far, this area of research has not lost its topical interest. Nowadays, it is difficult to find a complex organic molecule, the synthesis of which does not involve transition metal mediated key steps.[2] The electronic differences between transition and non-transition metal atoms cause the differences in the reactivity of their corresponding organic complexes. In general, the main group metals hold quite distinct oxidation states in their complexes, thus preventing oxidative addition and reductive elimination processes which play a very important role in transition metal chemistry. The application of organometallic compounds of the alkali, alkaline earth and group 13 metals in organic synthesis is primarily based on their ability to transfer organic groups, whereas transition metal complexes are mainly used in transformation reactions of various organic molecules including catalytic processes.

A short time ago, we became interested in the preparation of main group metal complexes which would be able to compete with the reactivity modes of transition metal complexes. The idea was to design a complex in which the central main group metal atom with all its advantages such as Lewis acidity, vacant coordination sites and ability to form thermodynamically stable but reactive metal-to-carbon bonds, is coordinated by a ligand which would adopt certain features of transition metals especially their oxidative and reductive power and their ability to add protons, Lewis acids and Lewis bases. Ligands which meet these requirements to a high degree are the 1,2-bis(arylimino)-acenaphthenes. These ligands possess (a) a conformationally rigid, chelating diimine fragment, (b) lone pairs of electrons at the nitrogen atoms capable of coordinating to metals or capturing protons, and (c) a conjugated π system acting as an electron tank.



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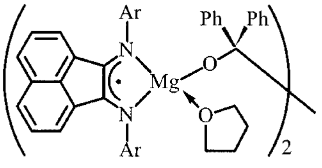
During the last decade, 1,2-bis(arylimino)acenaphthens have been used in transition metal chemistry as ancillary ligands. The corresponding nickel and palladium complexes show high catalytic activity in a number of important organic reactions including the polymerisation of olefins.[3] Very recently, we reported several alkali,[4a,4b] alkaline earth[4c–4e] and germanium(II) complexes[4f,4g] with different charged 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene (dpp-bian) anions as ligands. Following our initial idea that dpp-bian complexes of the main group metals might show unique reactivity, we began to study the reactions of (dpp-bian)Mg(THF)$_3$ (**1**), a complex which is easy to prepare from activated magnesium and dpp-bian in THF[4c] with organic substrates. We were able to demonstrate that **1** reduces diphenyl ketone with simultaneous oxidation of the dianionic dpp-bian ligand to a radical-anionic ligand, thus affording the pinacolate complex $[(\text{dpp-bian})^{\cdot-}\text{Mg(THF)}]_2[\mu\text{-}O_2C_2Ph_4]$ (**2**).[5a] On the other hand, the reaction of **1** with 9(10*H*)-anthracenone causes deprotonation of the respective phenolic tautomer yielding the 9-anthracenolato complex $[(\text{dpp-bian})^{\cdot-}\text{Mg}(OC_{14}H_9)(\text{THF})_2]$ (**3**).[5a]



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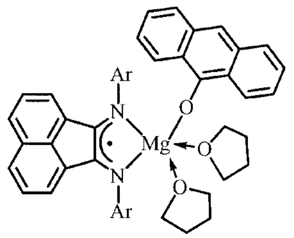

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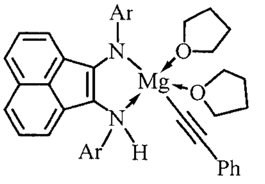
Owing to the Lewis basicity of **1**, it also adds phenylacetylene to give the phenylethynyl derivative [dpp-bian(H)]Mg(C≡CPh)(THF)$_2$ (**4**) which in turn reacts with diphenyl ketone with insertion into the magnesium carbon bond, elimination of the *N*-bonded hydrogen and oxidation of the dianionic dpp-bian ligand to the radical anion affording the carbonilate $(\text{dpp-bian})^{\cdot-}\text{Mg[OC(Ph}_2\text{)CCPh](THF)}$ (**5**).[5b]



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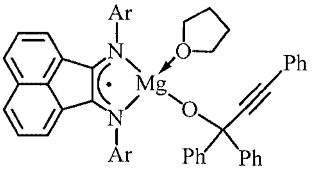

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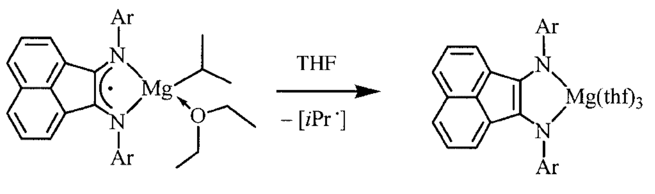
Recently we observed the unprecedented elimination of isopropyl radicals from $(\text{dpp-bian})^{\cdot-}(\text{MgPr-}i)(Et_2O)$ accompanied by the reduction of the radical anionic dpp-bian ligand to the dianion.[5c]

From the short survey of the reactivity of **1** given above the following two important conclusions can be drawn: (1) in all the reactions the dpp-bian ligand remains coordinated to the metal and (2) the reactions occur not only at the metal but also at the ligand.

Continuing our studies on the reactivity of **1** towards organic substrates, we report in this paper the reactions of **1** with aliphatic ketones containing C–H bonds in α-position to the carbonyl group.



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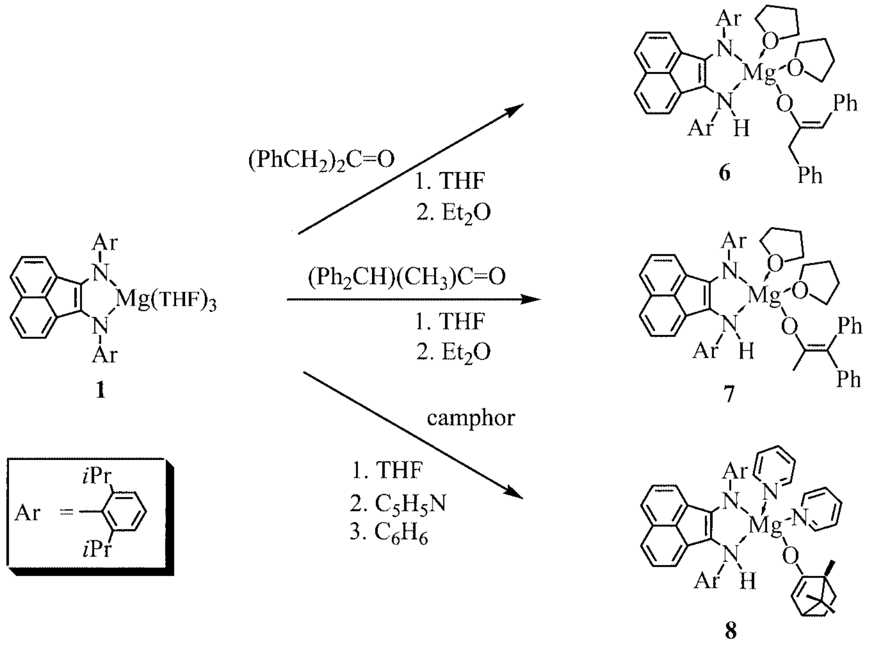
Results and Discussion

Reactions of Enolisable Ketones with (dpp-bian)Mg(THF)$_3$ (1)

Complex **1**, prepared by treating activated magnesium metal with dpp-bian in THF,[4c] was used in situ for the reactions with ketones. Addition of one equiv. of acetone, butan-2-one, or pentan-3-one to THF solutions of **1** caused a quick colour change from deep green to deep blue. Unfortunately, we did not succeed in isolating these products since they are highly soluble in THF and aromatic solvents and too little soluble in Et$_2$O and hexane. Attempts to isolate the products from THF/hexane or THF/Et$_2$O resulted in their decomposition into dpp-bian(H)$_2$ and colourless, insoluble solids. However, since a similar change in colour from green to blue was observed in the reaction of **1** with phenylacetylene yielding **4**, it can be suggested that the reactions proceed in a comparable way by protonation of one of the two nitrogen atoms of the dpp-bian ligand and attachment of the respective enolate anion to magnesium. Fortunately, the reactions of **1** with equimolar amounts of dibenzyl ketone, 1,1-diphenylacetone and camphor in THF allowed the successful isolation of the enolates [(dpp-bian)(H)]Mg[OC(=CHPh)CH$_2$Ph](THF)$_2$ (**6**), [(dpp-bian)(H)]Mg[OC(=CPh$_2$)CH$_3$](THF)$_2$ (**7**) and [(dpp-bian)(H)]Mg(camphor)(py)$_2$ (**8**), respectively (Scheme 1). In the case of the reaction of **1** with dibenzyl ketone and 1,1-diphenylacetone, the colour of the reaction mixture immediately changed from green to deep blue, whereas in the reaction with camphor the respective change in colour was not to observed until the mixture was heated to 60 °C for some minutes. Using two equiv. of the ketone caused a violet colour which might indicate double protonation of the ligand forming the diimine (dpp-bian)H$_2$.

Compounds **6** and **7** were crystallised from diethyl ether and isolated in yields of 72 and 79%, respectively, as deep blue, almost black crystals. The crude camphor derivative was treated first with pyridine and then crystallised from benzene affording **8** in 43% yield. In the solid-state as well as in solution **6**–**8** are extremely sensitive towards moisture and air but thermally quite stable. They decompose (**6**) or melt (**7**, **8**) above 115 °C and are stable in THF at reflux for several minutes. The single-crystal X-ray structure determinations indicated the formation of magnesium enolates each supported by a dpp-bian amido/amino ligand. The ^{1}H



Scheme 1.

NMR spectra of **6** and **7** discussed below indicate delocalisation of the amino hydrogen in solution between both nitrogen atoms.

Henderson and co-workers reported the formation of magnesium enolates by amine elimination from enolisable ketones and magnesium amides such as *i*Pr$_2$NMgBr, (*i*Pr$_2$N)$_2$Mg, and [(Me$_3$Si)$_2$N]$_2$Mg.[6] Since both nitrogen atoms of the dpp-bian ligand in **1** and **6**–**8** are part of a conformationally rigid chelating system, an amine elimination cannot take place. Despite the protonation of one of the nitrogen atoms of the dpp-bian system in **6**, **7** and **8**, the system still acts as a chelating ligand.

Molecular Structures of 6, 7 and 8

The molecular structures of **6**, **7** and **8** are depicted in Figures 1, 2 and 3, respectively. The crystallographic, collection and structure refinement data are listed in Table 1, selected bond lengths and bond angles are collected in Table 2.

The magnesium atoms in the molecules of the complexes **6**, **7** and **8** are five-coordinate with slightly distorted trigonal bipyramidal geometries. In **6** and **7** the axial positions of the bipyramids are occupied by the atoms N(2) and O(3) and in **8** by the atoms N(2) and N(4). The angles between the axially positioned atoms are 177.32(13)° in **6**, 176.09(7)° in **7**, and 172.22(8)° in **8**. The significant differences in the lengths of the two Mg–N bonds in **6**, **7** and **8** [**6**: Mg–N(1), 2.066(3) Å, Mg–N(2), 2.369(4) Å; **7**: Mg–N(1), 2.051(2) Å, Mg–N(2), 2.410(2) Å; **8**: Mg–N(1), 2.055(2) Å, Mg–N(2), 2.436(2) Å] reflect the different strengths of the metal coordination to the amido [N(1)] and the amino functions [N(2)]. The long Mg–N(2)(amino) bonds are always to the N atoms in the axial positions. The differences between the N(amido)–metal and the N(amino)–metal distances correspond well with those found for **4** (2.355 and 2.045 Å), obtained by addition of phenylacetylene to **1**.[5b] The short amido Mg–N(1) bonds in **6**, **7** and **8** are close to the Mg–N bond lengths in the starting complex **1** (2.045 and 2.105 Å).[4c] In **6** as well as in **7**, the Mg–O(2) bond of the equatorially positioned THF molecule is shorter than the Mg–O(3) bond to the THF molecule situated in the axial position [**6**: Mg–O(2) 2.075(3), Mg–O(3) 2.114(3) Å; **7**: Mg–O(2) 2.042(2), Mg–O(3) 2.137(2) Å]. The difference in the lengths of the Mg–N coordination bonds of the two equato-

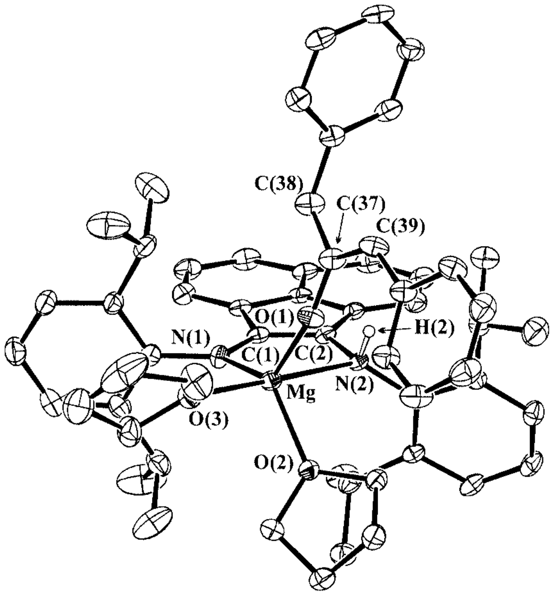


Figure 1. ORTEP drawing of **6** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms with the exception of H(2) are omitted for clarity.

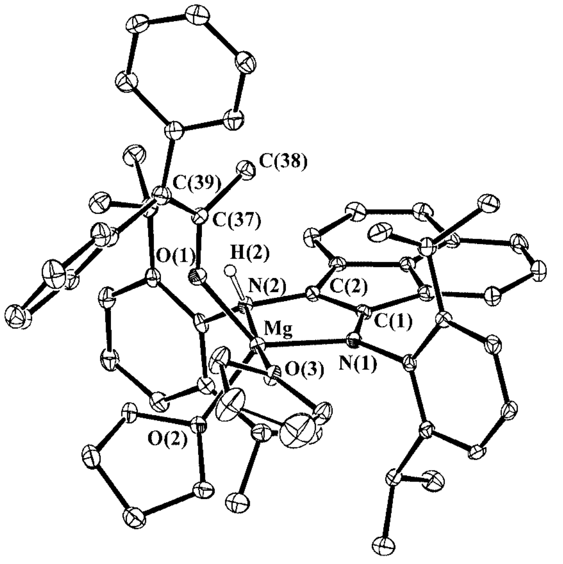


Figure 2. ORTEP drawing of **7** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms with the exception of H(2) are omitted for clarity.

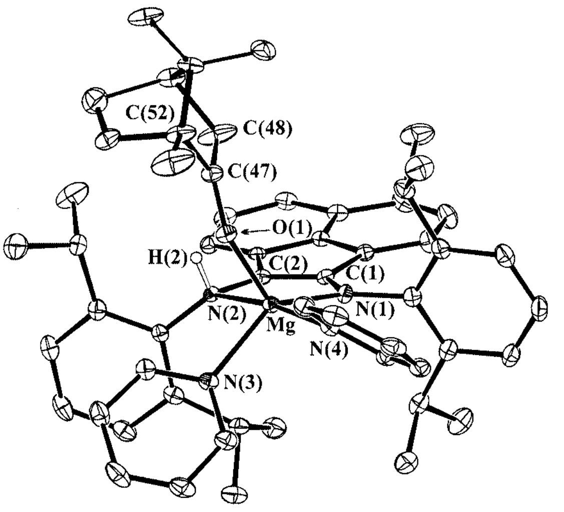


Figure 3. ORTEP drawing of **8** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms with the exception of H(2) are omitted for clarity.

rially and axially positioned pyridine molecules in **8** is far less pronounced [Mg–N(3) 2.151(2) and Mg–N(4) 2.195(2) Å]. In **6**, **7** and **8** the enolate ligand and the amine hydrogens H(2) are located on the same side of the plane formed by the metallacycle Mg–N(1)–C(1)–C(2)–N(2). The torsion angles H(2)–N(2)–Mg–O(1) are 7.0° (**6**), 17.2° (**7**) and 8.1° (**8**), respectively. Whereas the enolate group in the four magnesium enolates studied crystallographically up to now – [{*t*Bu(CH$_2$)CO}MgBr{(Me$_2$N)$_3$PO}]$_2$,[6a] [Mes(CH$_2$)CO]$_8$Mg$_4${OC(Mes)(Me)}$_2$,[6c] [{*t*Bu(CH$_3$CH)CO}MgBr(Et$_2$O)]$_2$[7a] and [{CH(CMeN-C$_6$H$_3$-2,6-*i*Pr$_2$)$_2$}Mg(μ-OC$_6$H$_9$)]$_2$[7b] – is acting as a μ$_2$-bridging ligand, the enolate group in **6**, **7** and **8** is a terminal group. This is clearly due to steric crowding imposed by the 2,6-diisopropylphenyl substituents on the nitrogen atoms of the ligand. The terminal Mg–O(1) bonds are 1.902(3), 1.921(2) and 1.890(2) Å for **6**, **7**, and **8**, respectively, and are somewhat shorter than the Mg–O(μ$_2$-enolate) bonds in two of the above mentioned magnesium enolates [{*t*Bu(CH$_2$)CO}MgBr{(Me$_2$N)$_3$PO}]$_2$ [1.956(4) and 1.981(4) Å][6a] and [{CH(CMeNC$_6$H$_3$-2,6-*i*Pr$_2$)$_2$}Mg(μ-OC$_6$H$_9$)]$_2$ [1.970(2) and 1.994(2) Å].[7b] The carbon-carbon double bonds formed as a consequence of the enolisation of the ketones are longer in **6** and **7** [C(37)–C(39): 1.368(6) (**6**), 1.373(3) Å (**7**)] than in **8** [C(47)–C(48) 1.333(4) Å] probably due to π conjugation of those double bonds in **6** and **7** with the phenyl rings of the dpp-bian unit. The conjugation is evident from the small dihedral angle of only 0.6° between the plane formed by the phenyl ring attached to C(39) and the plane formed by O(1)–C(37)–C(39).

^{1}H NMR Spectroscopic Studies on Solutions of 6 and 7

As indicated by the X-ray structural analyses, the molecules of **6**, **7** and **8** exhibit asymmetric amido/amino structures in the solid-state. Proceeding on the assumption that this general molecular structure will be maintained in solution, the ^{1}H NMR spectra of the compounds should reveal nonequivalence for all aromatic ring protons as well as for the four methine protons and the eight CH$_3$ groups of the isopropyl substituents at the phenyl groups of the dpp-bian ligand. It was expected, however, that in analogy to the ^{1}H NMR spectroscopic results obtained for the closely related compound [(dpp-bian)(H)]Mg(C≡CPh)(THF)$_2$ (**4**), the complexes **6** and **7** would adopt more symmetric structures in solution with the amino hydrogen not being fixed at one dpp-bian nitrogen atom but being delocalised between both nitrogen atoms of the ligand. Such a fast proton transfer (on the NMR time scale) between both nitrogen atoms results in a general structure with a plane of symmetry bisecting the N–Mg–N angle thus dividing the dpp-bian ligand into two equal parts. The ^{1}H NMR spectra of **6** and **7** are depicted in the supporting information.

According to our expectations, the ^{1}H NMR spectrum of **6** in [D$_8$]toluene revealed two septets for the methine protons centred at δ = 3.97 and 3.32 ppm. The low field signal overlaps with the THF signal at δ = 3.39 ppm but can be clearly assigned by means of the ^{1}H ^{1}H COSY spectrum. Each septet has cross peaks with two pairs of doublets in the range of δ = 1.4 to 1.0 ppm which can be assigned to the methyl protons and appear together with signals of THF and Et$_2$O. The signal of the delocalised N–H proton appears as a singlet at δ = 6.10 ppm and overlaps partially with a doublet signal of the aromatic protons at δ = 6.15 ppm. The protons of the CH and CH$_2$ groups of the enolate ligand give rise to singlets at δ = 5.31 and 3.53 ppm, respectively.

In agreement with the spectroscopic results obtained for **6**, the ^{1}H NMR spectrum of **7** in [D$_8$]THF shows two septets for the isopropyl methine protons at δ = 3.79 and 3.67 ppm, four doublets for the protons of the isopropyl methyl groups at δ = 1.30, 1.22, 0.98 and 0.92 ppm, a singlet for the protons of the CH_3 group of the enolate ligand at δ = 1.99 ppm and a singlet separated from other resonances for the delocalised NH proton at δ = 6.42 ppm. The ^1H NMR spectra of **6** and **7** indicate the presence of small amounts of (dpp-bian)H_2 probably due to partial hydrolysis of the compounds during sample preparation.

Conclusions

We have been able to demonstrate that the recently prepared magnesium complex (dpp-bian)Mg(THF)$_3$ containing the dianionic 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene ligand can serve as an enolising reagent towards aliphatic ketones such as dibenzyl ketone, 1,1-diphenylacetone or camphor. In contrast to the reactions of magnesium amides with enolisable ketones which proceed with amine elimination,[6] the above reactions proceed by addition of the enols with formation of magnesium enolate bonds and simultaneous protonation of one of the acenaphthene nitrogen atoms of the stabilising ligand. These reactions are the first examples of such a reaction pathway in transition as well as non-transition metal chemistry. The magnesium enolates [dpp-bian(H)]MgOR formed from dibenzyl ketone and 1,1-diphenylacetone are labile in solution. The proton attached only to one nitrogen atom of the dpp-bian ligand in the solid-state is delocalised between the two nitrogen atoms of the ligand in solution. We intend to investigate the potential of the compounds reported here as reagents for aldol reactions.

Experimental Section

General Remarks: All manipulations were carried out under vacuum using Schlenk ampoules. The solvents THF and diethyl ether were dried by distillation from sodium benzophenone. The deuterated solvents [D$_8$]THF (Aldrich) and [D$_8$]toluene (Aldrich) used for the NMR measurements were dried with sodium benzophenone at ambient temperature and, just prior to use, condensed under vacuum into the NMR tubes already containing the respective compound, the spectrum of which could then be recorded. Melting points were measured in sealed capillaries. 1,2-Bis[(2,6-diisopropylphenyl)imino]acenaphthene was prepared according to the published procedure.[8] The IR spectra were recorded on a Specord M80 spectrometer and the ^1H NMR spectra on a Bruker DPX-200 NMR spectrometer.

(dpp-bian)Mg(THF)$_3$ (1): Magnesium shavings (2.4 g, 100 mmol) and CH_2I_2 (0.8 g, 2.98 mmol) were placed in a Schlenk-like ampoule (ca. 100 mL volume) equipped with a Teflon stopcock. After evacuation of the ampoule (at 10^{-1} Torr for ca. 1 min), THF (40 mL) was added by condensation and the mixture was stirred for 2 h. The $MgI_2(THF)_n$ formed was decanted together with the

Table 1. Crystal data and structure refinement details for **6**, **7** and **8**.

	6	**7**	**8**
Empirical formula	$C_{61}H_{75}MgN_2O_{3.5}$	$C_{63}H_{80}MgN_2O_4$	$C_{59}H_{69}MgN_4O$
Formula mass	916.58	953.60	874.4
Temperature [K]	173(2)	100(2)	100(2)
Wavelength [Å]	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$C2/c$	$P2_1/n$
a [Å]	12.1786(2)	46.217(2)	12.8143(15)
b [Å]	23.4643(1)	14.4134(7)	21.868(3)
c [Å]	19.1081(3)	16.1226(8)	18.509(2)
β [°]	103.6480(10)	90.1870(10)	102.247(3)
Volume [Å^3]	5306.19(12)	10740.0(9)	5068.5(11)
Z	4	8	4
$\rho_{calcd.}$ [g cm^{-3}]	1.147	1.180	1.146
μ [mm^{-1}]	0.086	0.083	0.079
$F(000)$	2166	4128	1884
Crystal size [mm]	0.50 × 0.44 × 0.08	0.25 × 0.20 × 0.05	0.50 × 0.45 × 0.20
$\theta_{min}/\theta_{max}$	1.81/25.00	1.76/23.00	1.77/25.00
Index ranges	$-13 \le h \le 14$	$-50 \le h \le 50$	$-13 \le h \le 15$
	$-17 \le k \le 27$	$-15 \le k \le 15$	$-26 \le k \le 25$
	$-21 \le l \le 22$	$-17 \le l \le 14$	$-18 \le l \le 22$
Reflections collected	31042	24617	27335
Independent reflections	9326	7467	8900
R_{int}	0.1524	0.0584	0.0318
Completeness to θ_{max} [%]	99.8	99.9	99.7
Absorption correction	SADABS	SADABS	SADABS
Max./min. transmission	0.953674/0.611385	0.9959/0.9797	0.9844/0.9617
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	9327/2/623	7467/16/944	8900/24/638
GOF on F^2	0.956	0.965	1.218
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0798$	$R_1 = 0.0427$	$R_1 = 0.0835$
	$wR_2 = 0.1475$	$wR_2 = 0.0927$	$wR_2 = 0.1719$
R indices (all data)	$R_1 = 0.0798$	$R_1 = 0.0771$	$R_1 = 0.0929$
	$wR_2 = 0.1895$	$wR_2 = 0.1021$	$wR_2 = 0.1748$
Largest diff. peak/hole [e Å^{-3}]	0.530/–0.301	0.426/–0.321	0.639/–0.670

solvent and the residual metal was washed three times with THF (40 mL). A suspension of dpp-bian (0.5 g, 1.0 mmol) in THF (30 mL) was then added to the activated magnesium metal and the mixture was heated to reflux. Over the course of about 30 min, the reaction mixture turned deep green due to the formation of **1**. The solution was then cooled to ambient temperature, decanted from the excess magnesium and used in situ for the reactions with ketones.

[(dpp-bian)(H)]Mg[OC(=CHPh)CH$_2$Ph](THF)$_2$ (6): To a THF solution of **1** [prepared from 0.5 g (1.0 mmol) of dpp-bian in 30 mL THF] was added dibenzyl ketone (0.21 g, 1.0 mmol) with stirring. The solution immediately turned deep blue. Evaporation of the solvent and crystallisation of the crude product from diethyl ether (40 mL) at room temperature yielded 0.66 g (72%) of **6**$(Et_2O)_{0.5}$ as deep blue crystals. M.p. >115 °C (dec.). IR (Nujol): $\tilde{\nu}$ = 1580 (s), 1510 (s), 1405 (m), 1315 (m), 1290 (w), 1240 (m), 1180 (s), 1110 (w), 1080 (w), 1040 (w), 1012 (m), 935 (w), 920 (w), 905 (m), 895 (m), 870 (s), 825 (m), 805 (w), 770 (s), 745 (s), 695 (s), 660 (w), 620 (w), 565 (w), 515 (m), 465 (m), 420 (w) cm^{-1}. ^{1}H NMR (200 MHz, [D$_8$]toluene, 20 °C): δ = 7.56 (d, J = 6.8 Hz, 2 H, C–H Ar.), 7.33–6.76 (m, 18 H, C–H Ar.), 6.38 (d, J = 7.0 Hz, 1 H, C–H Ar.), 6.15 (d, J = 6.5 Hz, 1 H, C–H Ar.), 6.10 (s, 1 H, N–H), 5.31 (s, 1 H, C*H*Ph), 3.97 [sept, J = 6.8 Hz, 2 H, C*H*$(CH_3)_2$], 3.53 (s, 2 H, CH_2 Ph), 3.39 (m, 8 H, α-THF), 3.32 [sept, 2 H, C*H*$(CH_3)_2$], 3.23 (q, 4 H, Et_2O), 1.32 [d, J = 6.8 Hz, 6 H,CH(C$\mathit{H}_3)_2$], 1.24–1.09 (m, 8 H, β-THF; 12 H, CH(C$\mathit{H}_3)_2$; 6 H, Et_2O), 1.03 (d, J = 6.8 Hz, 6 H, CH(C$\mathit{H}_3)_2$). $C_{59}H_{70}MgN_2O_3\cdot(C_4H_{10}O)_{0.5}$ (916.58): calcd. C 79.94, H 8.25; found C 80.03, H 8.14.

[(dpp-bian)(H)]Mg[OC(=CPh$_2$)CH$_3$](THF)$_2$ (7): Diphenylacetone (0.21 g, 1.0 mmol) was added with stirring to a THF solution of **1** (prepared in situ from 0.5 g (1.0 mmol) of dpp-bian in 40 mL THF). The solution instantly turned deep blue. The residue remaining after removal of the solvent in vacuo was crystallised from diethyl ether (40 mL) affording 0.72 g (79%) of **7**(Et_2O) as deep blue crystals. M.p. 142–144 °C. IR (Nujol): $\tilde{\nu}$ = 1560 (s), 1515 (s), 1330 (m), 1290 (m), 1275 (m), 1240 (m), 1185 (s), 1170 (m), 1105 (s), 1080 (w), 1045 (w), 1030 (m), 1010 (s), 970 (m), 935 (w), 915 (w), 865 (s), 835 (m), 815 (w), 800 (w), 760 (s), 700 (vs), 660 (w), 615 (m), 570 (w), 525 (m), 500 (m), 485 (m) cm^{-1}. ^{1}H NMR (200 MHz, [D$_8$]THF, 20 °C): δ = 7.37–6.67 (m, 20 H, C–H Ar.), 6.42 (s, 1 H, N–H), 5.96 (d, J = 7.0 Hz, 1 H, C–H Ar.), 5.75 (d, J = 6.3 Hz, 1 H, C–H Ar.), 3.79 [sept, J = 6.8 Hz, 2 H, C*H*$(CH_3)_2$], 3.67 [sept, J = 6.8 Hz, 2 H, C*H*$(CH_3)_2$] 3.39 [q, J = 7.0 Hz, 4 H, (CH$_3$C$\mathit{H}_2)_2$O], 1.99 (s, 3 H, CH_3), 1.30 [d, J = 6.8 Hz, 6 H, CH(C$\mathit{H}_3)_2$], 1.22 [d, J = 6.8 Hz, 6 H, CH(C$\mathit{H}_3)_2$], 1.10 [t, J = 7.0 Hz, 6 H, (CH_3CH$_2)_2$O], 0.98 [d, J = 6.8 Hz, 6 H, CH(C$\mathit{H}_3)_2$], 0.92 [d, J = 6.8 Hz, 6 H, CH(C$\mathit{H}_3)_2$]. $C_{59}H_{70}MgN_2O_3\cdot(C_4H_{10}O)$ (953.60): calcd. C 79.35, H 8.46; found C 79.72, H 8.61.

[(dpp-bian)(H)]Mg(camphor)(py)$_2$ (8): Camphor (0.15 g, 1.0 mmol) was added with stirring to a THF solution of **1** [prepared in situ from 0.5 g (1.0 mmol) of dpp-bian in 40 mL THF]. The solution was heated to 60 °C for 1 h. During heating, the solution turned deep blue. The solvent was then removed in vacuo and the residue was dissolved in pyridine (10 mL). After removal of pyridine and all other volatiles in vacuo, a waxy residue remained which was dried in vacuo at room temperature for 1 h. Subsequently the solid was dissolved in benzene (20 mL). The resultant solution was concentrated to 10 mL in vacuo at 50 °C. Crystallisation at room temperature afforded 0.37 g (43%) of **8**$(C_6H_6)_{0.5}$ as deep blue crystals. M.p. 172–174 °C. $C_{56}H_{66}MgN_4O\cdot0.5(C_6H_6)$ (874.40): calcd. C 81.03, H 7.95; found C 81.38, H 8.09. IR (Nujol): $\tilde{\nu}$ = 1595 (vs), 1510 (s), 1325 (m), 1305 (w), 1240 (m), 1190 (s), 1135 (w), 1100 (m), 1060 (m), 1035 (m), 1005 (w), 970 (w), 930 (w), 905 (m), 880 (m), 860 (w), 830 (w), 815 (w), 800 (w), 770 (s), 745 (s), 700 (s), 675 (s), 455 (m) cm^{-1}.

Single Crystal X-ray Structure Determinations of 6, 7 and 8: The crystal data and details of data collection are given in Table 1, selected bond lengths and bond angles are collected in Table 2. The data for **6** were collected on a Siemens SMART CCD diffractometer (graphite-monochromated Mo-K_α radiation, ω-scan technique, λ = 0.71073 Å) at 173 K. The data for **7** and **8** were collected on a Bruker SMART APEX diffractometer (graphite-monochromated Mo-K_α radiation, ω- and Φ-scan technique, λ = 0.71073 Å) at 100 K. The structures were solved by direct methods using SHELXS-97[9] and were refined on F^2 using SHELXL-97.[10] All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were placed in calculated positions and assigned to an isotropic displacement parameter of 0.08 Å^2. SADABS[11] was used to perform area detector scaling and absorption corrections. The geometrical aspects of the structures were analysed by using the PLATON program.[12] CCDC-259974 (for **6**), -259975 (for **7**) and -259976 (for **8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information Available: ^{1}H NMR spectra of **6** and **7**.

Table 2. Selected bond lengths [Å] and angles [°] for **6**, **7** and **8**.

Compound	**6**	**7**	**8**
		Bond length	
Mg–N(1)	2.066(3)	2.051(2)	2.055(2)
Mg–N(2)	2.369(4)	2.410(2)	2.436(2)
Mg–O(1)	1.902(3)	1.9212(18)	1.8902(19)
Mg–O(2)	2.075(3)	2.0420(17)	
Mg–O(3)	2.114(3)	2.1370(17)	
Mg–N(3)			2.151(2)
Mg–N(4)			2.195(2)
N(1)–C(1)	1.359(5)	1.356(3)	1.352(3)
N(2)–C(2)	1.453(5)	1.449(3)	1.449(3)
C(1)–C(2)	1.391(5)	1.386(3)	1.384(3)
O(1)–C(37)	1.320(5)	1.321(3)	
O(1)–C(47)			1.307(3)
C(37)–C(38)	1.514(5)	1.501(3)	
C(37)–C(39)	1.368(6)	1.373(3)	
C(47)–C(48)			1.333(4)
C(47)–C(52)			1.540(3)
N(2)–H(2)	0.840	0.886	0.888
		Bond angles	
N(1)–Mg–N(2)	80.33(13)	79.16(7)	79.31(8)
N(1)–Mg–O(1)	123.48(13)	129.83(8)	122.43(8)
N(2)–Mg–O(1)	86.28(14)	84.96(7)	90.17(8)
N(1)–Mg–O(2)	128.49(14)	124.50(8)	
N(2)–Mg–O(3)	177.32(13)	176.09(7)	
N(1)–Mg–N(3)			135.32(9)
N(2)–Mg–N(4)			172.22(8)
Mg–O(1)–C(37)	156.1(3)	138.23(15)	
Mg–O(1)–C(47)			144.63(17)

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