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# Addition of phenylacetylene to a magnesium complex of monoiminoacenaphtheneone (dpp-mian)†‡

D. A. Razborov, A. N. Lukoyanov, E. V. Baranov and I. L. Fedushkin*

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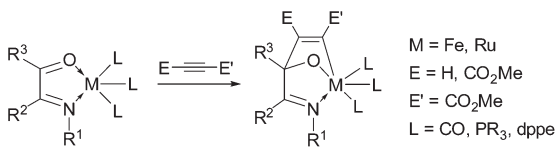
In the presence of formic acid, acenaphthenequinone (AQ) reacts with one molar equivalent of 2,6-diisopropylaniline in toluene to give monoiminoacenaphtheneone (**3**, dpp-mian) in good yield. Reduction of compound **3** with an excess of magnesium in thf results in green crystalline amido-alcoholate [(dpp-mian)Mg(thf)$_2$]$_2$ (**4**). Crystallization of complex **4** from toluene affords a blue tetramer [(dpp-mian)Mg-(thf)]$_4$ (**5**). Reactions of compounds **4** and **5** with phenylacetylene proceed with C–C bond formation between the alkyne and the dpp-mian ligand to give the monomeric alkynyl-magnesium derivative [(dpp-mian)(PhC=CH$_2$)Mg(C≡CPh)$_2$(thf)]$_2$ (**7**). Hydrolysis of complex **5** gives metal-free dpp-mian(PhC=CH$_2$)H (**8**). Reaction of **7** with acetylacetone yields [{dpp-mian(PhC=CH$_2$)}Mg(acac)]$_2$ (**9**). Compounds **3–5** and **7–9** have been characterized by IR and NMR spectroscopy; molecular structures of **3**, **5**, **7**, **8** and **9** have been determined by single crystal X-ray analysis.

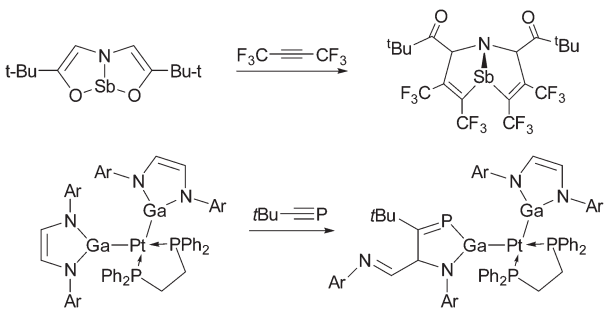
## Introduction

From 1983 to 2002 Frühauf *et al.* reported in a series of papers[1] on cycloaddition reactions between unsaturated substances and transition metal complexes of neutral 1,4-diaza-1,3-diene (dad) or 1,4-dihetero-1,3-diene ligands. Iron and ruthenium complexes with ketoimino ligands react for instance with activated alkynes to form stable cycloadducts (Scheme 1).




**Scheme 1** Frühauf's cycloaddition reactions.

A notable feature of these reactions is the addition of the substrate not only to the metal centre but also to the ligand resulting in a carbon–carbon bond. Similar cycloadducts have been obtained reacting aromatic ketones with zirconium[2a] and samarium[2b] complexes of the dad dianion. Comparable addition reactions involving main group metal complexes are limited to a few examples. Among them are reactions of antimony amido-alkoxide with $CF_3$–C≡C–$CF_3$ [3a] and of a platinum gallyl complex with *t*Bu–C≡P[3b] (Scheme 2).



**Scheme 2** Addition of $CF_3$–C≡C–$CF_3$ and *t*Bu–C≡P to antimony and gallium derivatives respectively.

In 2010 we have found that (dpp-bian)Ga–Ga(dpp-bian) (**1**) (dpp-bian = 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene) easily reacts even with non-activated alkynes affording cycloadducts[4] (Scheme 3).

*G. A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences, Tropinina str. 49, 603137 Nizhny Novgorod, Russian Federation.*
*E-mail: igorfed@iomc.ras.ru; Fax: +7 831 4627495; Tel: +7 831 4629631*

† Dedicated to Prof. A. L. Buchachenko on the occasion of his 80th birthday.

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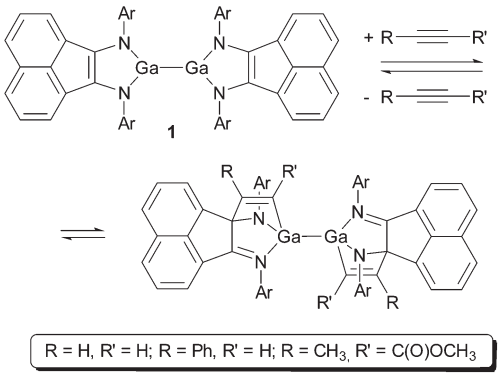
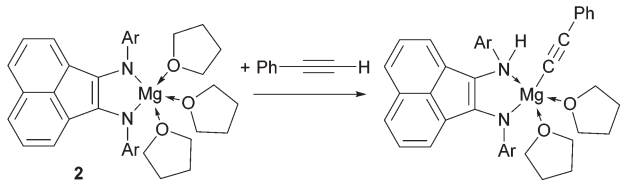
Remarkable for this dpp-bian gallium metal–organic system is the reversibility of the alkyne addition. It can be compared with the π coordination of organic molecules by transition metals. Dialanes (L)Al–Al(L) (L = dpp-bian,[5a] or dad[5b]) are even more active in the cycloaddition of alkynes. The mononuclear (dpp-bian)AlEt(Et$_2$O)[6a] and (dpp-bian)Ga(S$_2$-




**Scheme 3** Reversible addition of alkynes to digallane **1**.




**Scheme 4** Addition of PhC≡CH to (dpp-bian)Mg(thf)$_3$ (**2**).

$CNMe_2$)[6b] also react with alkynes to produce cycloadducts. Furthermore, the latter complex reversibly adds to conjugated methylvinylketone.[6b] Alteration of the main group metal coordinated by the dpp-bian dianion changes the reactivity of the complex. For instance, the magnesium complex (dpp-bian)Mg(thf)$_3$ (**2**) behaves in contrast to digallane **1** like a frustrated Lewis pair[7] when reacted with PhC≡CH. The reaction affords a magnesium alkynyl derivative supported with an amido–amino chelating ligand (Scheme 4).[8]

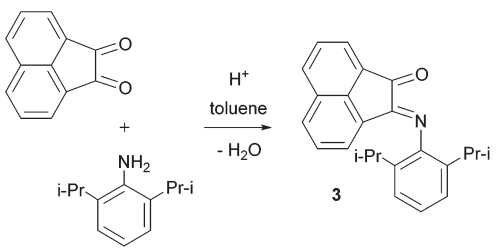
The ability of complex **1** to "coordinate" PhC≡CH allows hydroamination and hydroarylation of the latter with anilines and 1-naphthol in the presence of **1** as the catalyst.[4b,6b] Moreover, complex **1** catalyses the addition of anilines to carbodiimides.[9] In its turn the magnesium complex **2** serves well as the catalyst for ROP of lactide[10] and hydroamination/cyclization of amino-olefins.[11] But, the wide usage of compounds **1** and **2** as catalysts is limited by their instability in air. Searching for more robust metal complexes with redox-active ligands we studied the reactions of (2,6-diisopropylphenylimino)acenaphtheneone[12] (**3**, dpp-mian) with different metals and metal-containing reagents. While transition metal complexes with neutral dpp-mian,[12b,c,d] and related Ar-mian[13] ligands have been reported, crystallographically authenticated main group metal complexes with these ligands are unknown. It should be noted that reactions of dpp-mian with Grignard reagents have been reported[14] recently but no metal containing derivative of dpp-mian could be isolated. Here we report: (i) the modified synthesis of dpp-mian; (ii) preparation of the first metal complexes containing dpp-mian in the form of a dianion; and (iii) the reactivity of magnesium dpp-mian complexes towards phenylacetylene.

## Results and discussion

### (2,6-Diisopropylphenylimino)acenaphtheneone (3, dpp-mian): synthesis and characterisation

In dpp-bian bulky 2,6-i$Pr_2C_6H_3$ groups ensure efficient shielding of the nitrogen atoms. Thus, only in the bian plane enough space is left for interaction with the metal. This prevents formation of complexes, in which dpp-bian acts as a bridging ligand. Further, it provides the unique reactivity of dpp-bian metal complexes. Hence, we started the synthesis of dpp-substituted monoiminoacenaphtheneone **3** (dpp-mian). In contrast to the reported procedure[12a] we mixed acenaphthenequinone (AQ), 2,6-diisopropylaniline and formic acid (catalytic amount) in toluene at once and refluxed the mixture. After complete dissolution of AQ the mixture was cooled to ambient temperature. Unreacted AQ and dpp-bian formed were filtered off. From the filtrate the solvent was removed in a vacuum and the crude product was extracted with diethyl ether. Orange crystalline **3** was isolated in 80% yield (Scheme 5). As impurity it contains 5 mol% of dpp-bian. Analytically pure **3** can be prepared by repeated extraction with diethyl ether. Although Kim's procedure[12a] for the preparation of **3** resulted in compound **3** in high yield (84%) the reported method is both solvent and time consuming compared to our approach. Thus, we used only 150 mL of toluene as a solvent to react 10 g of AQ with aniline, while in the reported synthesis[12a] 600 mL of methanol were used to prepare **3** starting from 3.2 g of acenaphthenequinone.

The strongest absorptions in the IR spectrum of dpp-bian are the C=N stretching vibrations at 1671, 1652, and 1642 $cm^{-1}$.[15] In compound **3** they are shifted to lower wavenumbers (1658, 1602, and 1589 $cm^{-1}$). The stretching vibrations of C=O cause absorption at 1726 $cm^{-1}$, which is the most intensive one in the IR spectrum. Compound **3** is moderately soluble in organic media. Crystals of **3** obtained from toluene have been studied by X-ray single crystal analysis. The key bond distances and angles in **3** are within the range of those values reported earlier.[12b] However, in contrast to the structure reported[12b] crystals of **3** obtained by us are free of any lattice content. It is worth noting that in **3** due to the




**Scheme 5** Synthesis of dpp-mian (**3**).

restricted rotation around the N–C(*ipso* Ph) bond the 2,6-$iPr_2C_6H_3$ ring stands orthogonal to the heterodiene moiety.

### Reduction of dpp-mian with magnesium

Reaction of dpp-mian with magnesium proceeds in thf at reflux. The reaction rate strongly depends on whether the metal was activated or not. Thus, addition of a catalytic amount of iodine to magnesium allows reduction of dpp-mian to its dianion within 30 minutes. In the course of the reaction the colour of the solution turned from red-orange to dark green. The product (dpp-mian)$Mg(thf)_2$ (**4**) is poorly soluble in thf and precipitates as a green microcrystalline solid from the reaction mixture. Complex **4** has been separated from the metal by extraction with hot thf. Dissolution of crude **4** in toluene at 110 °C led to a blue solution. The solvent was evaporated and the residue was dissolved in toluene again. This evaporation/dissolution process was repeated three times. The compound $[(dpp\text{-}mian)Mg(thf)]_4$ (**5**) was isolated in the form of blue crystals from the concentrated toluene solution (Scheme 6).

Complexes **4** and **5** have been characterized by IR and NMR spectroscopy. The X-ray analysis of the crystals of **4** has been attempted several times. Unfortunately, they do not diffract satisfactorily. Taking into account the composition of compound **4** we suggest that in the solid state it has a dimeric structure with $\mu^2$-O-bridges and a five-coordinated magnesium atom. Crystals of compound **5** suitable for X-ray analysis have been obtained from toluene. According to the X-ray data complex **5** is a tetramer with a slightly distorted cuboid core $Mg_4O_4$ (Fig. 1). The latter is assembled *via* $\mu^3$-bridging oxygen atoms of the dpp-mian ligand. Each magnesium atom in **5** has a coordination number of five. For comparison, the magnesium atom in complex **2**[15] is also five-coordinated. The bond lengths in the ketoiminate fragment point to the dianionic state of dpp-mian. Compared to neutral dpp-mian the C–O and C–N bonds in **5** are significantly elongated (average C–O and C–N bonds are 1.399 and 1.383 Å), but very close to C–N bond lengths in **2**[15] (1.401(6) and 1.378(7) Å), which contains a dpp-bian dianion. The $^1H$ NMR spectrum of compound **2** in thf-$d_8$ consists of two doublet signals that arise from non-equivalent methyl groups (in pairs in each isopropyl substituent).[15] This non-equivalence is caused by restricted rotation of fragments around N–C(*ipso*) and C(iPr)–C(*ipso*) bonds. The four methine protons in compound **2** produce only one septet signal. According to the $^1H$ NMR spectra dissolution of **4** and **5** in thf-$d_8$ results in only one and the same species: the $^1H$ NMR spectra of **4** and **5** consist of two doublets and one septet (see the ESI‡). In contrast, the $^1H$ NMR spectrum of compound **5** in $C_6D_6$ reveals four doublets ($\delta$ 1.37, 1.04, 0.89 and 0.34 ppm) and two septets ($\delta$ 3.99 and 3.64 ppm) (see the ESI‡). This indicates that complex **5** retains its tetrameric structure in benzene.

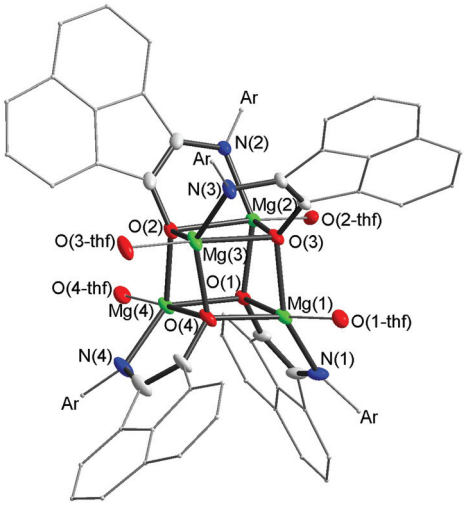
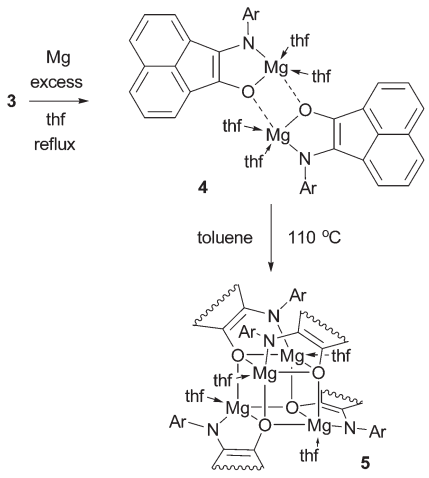



**Fig. 1** Molecular structure of compound **5** (thermal ellipsoids are drawn at 30% probability; hydrogen as well as carbon atoms of 2,6-diisopropyl groups and thf molecules are omitted for clarity).

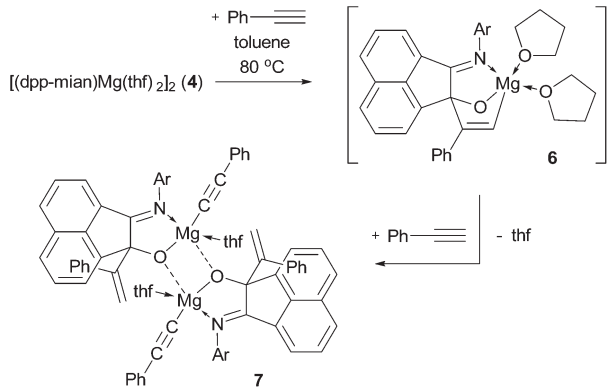



**Scheme 6** Synthesis of complexes **4** and **5**. The acenaphthene part of the ligand in the formula of **5** is omitted.

### Reactions of complexes 4 and 5 with phenylacetylene: synthesis, molecular structure and solution behaviour of $[(dpp\text{-}mian)(PhC{=}CH_2)Mg(C{\equiv}CPh)_2(thf)]_2$ (7)

Both **4** and **5** readily react with PhC≡CH in thf or toluene at 80 °C. The NMR monitoring has shown that **4** and **5** reacted completely within 8 h to give at least two products in each case. Workup of the reaction mixture formed in toluene using **4** as the starting material gives compound $[(dpp\text{-}mian)(PhC{=}CH_2)Mg(C{\equiv}CPh)_2(thf)]_2$ (**7**) as pink crystals in 38% yield when crystallised from toluene.

We suggest that complex **7** is a result of protonation of the Mg–C bond with an alkyne followed by the formation of the cycloadduct [(dpp-mian)(PhC=$CH_2$)Mg(thf)] (**6**) (Scheme 7). This suggestion is supported by the fact that the reaction of $[(dpp\text{-}mian)GaI]_2$ with PhC≡CH resulted in a cycloaddition product, which was isolated and crystallographically characterized. These data will be published elsewhere. The reaction




**Scheme 7** Formation of [(dpp-mian)(PhC═$CH_2$)Mg(thf)] (**6**) and [(dpp-mian)(PhC═$CH_2$)Mg(C≡$CPh)_2$(thf)]$_2$ (**7**).

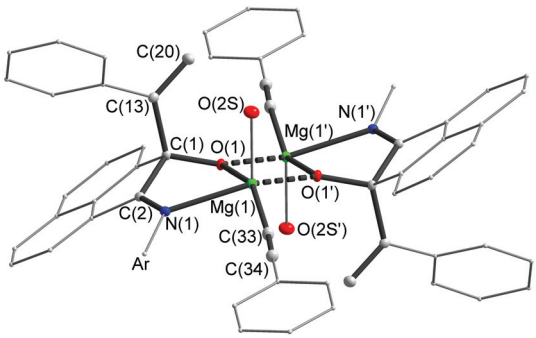



**Fig. 2** Molecular structure of compound **7** (thermal ellipsoids are drawn at 30% probability; hydrogen as well as carbon atoms of 2,6-di-isopropyl groups and thf molecules are omitted for clarity).

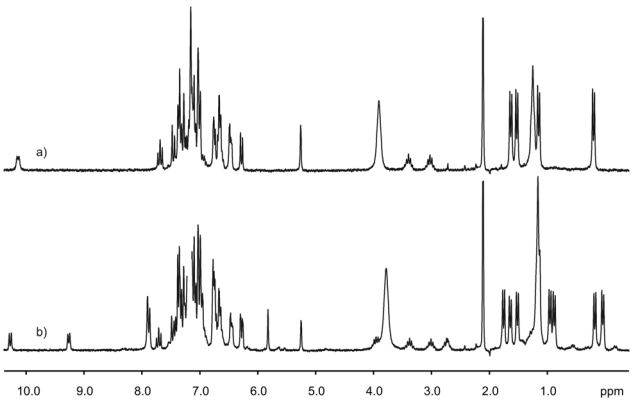



**Fig. 3** The $^1$H NMR spectra of complex **7** in $C_6D_6$ (200 MHz, 293 K): (a) dissolved at 293 K and stored at ambient temperature for 7 days; (b) after heating at 80 °C for 8 hours.

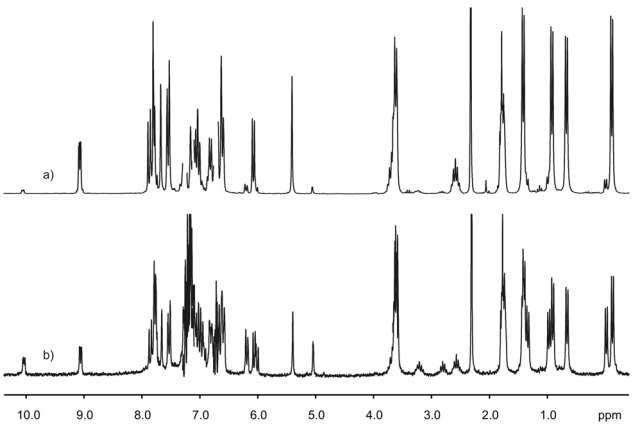
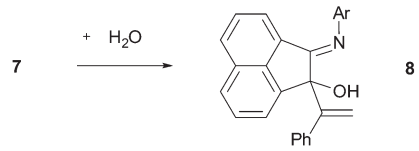



**Fig. 4** The $^1$H NMR spectra of complex **7** in thf-$d_8$ (200 MHz, 293 K): (a) dissolved at 293 K and stored at ambient temperature for 7 days; (b) after heating at 80 °C for 8 hours.

between **5** and PhC≡CH in thf also produces **7**, which has been isolated from thf. According to single crystal X-ray analysis complex **7** is a centrosymmetric dimer with a planar $Mg_2O_2$ core (Fig. 2). The only difference between the crystals of compound **7** obtained from toluene or from thf is the solvent molecules present in the unit cells (toluene and thf correspondingly).

Owing to the asymmetry of the formed ligand all its protons should be different. Thus, four non-equivalent methyl groups and two non-equivalent methine protons give rise to four doublets and to two septets respectively in the $^1$H NMR spectrum of complex **7** (Fig. 3a). For 7 days at 20 °C the spectrum remains unchanged. But, heating of the sample to 80 °C results in an additional set of NMR signals (Fig. 3b).

As evident from the integration of the signals two species are present in solution in nearly equal amounts. In thf-$d_8$ complex **7** behaves similarly (Fig. 4). Both samples ($C_6D_6$ and thf-$d_8$) attain the steady-state after 8 h of heating (80 °C). The spectra shown in Fig. 3a and 4a both consist of signals above 9 ppm. In order to assign a corresponding signal in the spectrum shown in Fig. 4a we have carried out the COSY NMR experiments (see the ESI‡). Based on the spectroscopy data we conclude that the signal at $\delta$ 9.07 ppm (dd, 1H) belongs to the proton of the naphthalene ring in the position next to the chiral centre C(13). Its multiplicity reflects coupling to two neighbouring protons in the six-membered ring, whereas its low-field shift is caused by the close proximity to the chiral centre C(1). Several hypotheses have been considered in order to understand the solution behaviour of compound **7**. Elimination of PhC≡CH from complex **7** to give compound **6** in the course of heating should be probably excluded since the signals of free phenylacetylene (*e.g.* singlet at $\delta$ 2.77 ppm) are absent in the spectra (Fig. 3b and 4b). The next hypothesis is based on the observation that one form of compound **7** present in both $C_6D_6$ and thf-$d_8$ shows remarkable differences of the chemical shifts of the NMR signals that correspond to methine protons of the iPr groups ($C_6D_6$: septets $\delta$ 3.96 and 2.74 ppm; thf-$d_8$: septets $\delta$ 3.69 and 2.59 ppm). This splitting




**Scheme 8** Formation of metal-free compound **8**.

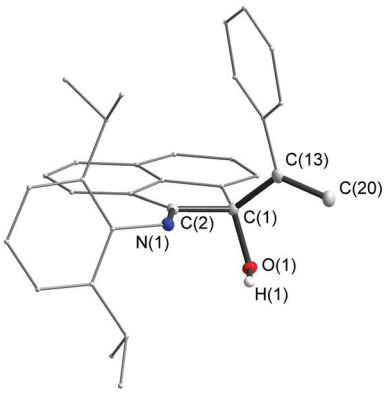


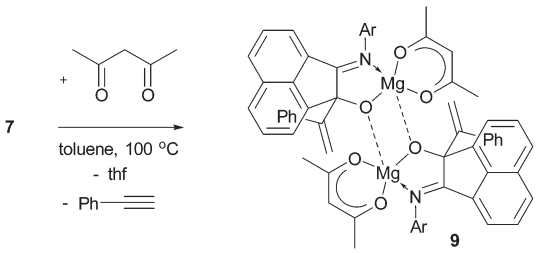

**Fig. 5** Molecular structure of compound **8** (thermal ellipsoids are drawn at 30% probability; hydrogen atoms except for H(1) are omitted for clarity).

may indicate the close proximity of a chiral centre to the above-mentioned protons. This might be the case when PhC≡CH adds across the C–N–Mg fragment in **4** or **5**, thus making the carbon atom bound to the chiral nitrogen.

In order to detect such a species we hydrolysed the NMR samples of complex **7** in $C_6D_6$ and thf-$d_8$. In both cases the NMR spectra indicate the presence of the only product – metal-free compound (dpp-mian)(PhC═$CH_2$)H (**8**), which has also been obtained in a bench experiment and isolated in the form of yellow crystals (22%) from hexane (Scheme 8).

In the $^1$H NMR spectrum of **8** in $CDCl_3$ (see the ESI‡) the $CH_2$ protons appear as two doublets (each 1H) at $\delta$ 6.20 and 5.66 ppm ($J$ = 1.0 Hz). Most probably the proton of the OH group results in a singlet signal at $\delta$ 3.42 ppm. The structure of compound **8** (Fig. 5) has been determined by single crystal X-ray analysis. The unit cell ($Z$ = 4) consists of two pairs of enantiomers. The structure of **8** corresponds to that of **7**: the vinyl group is connected to the carbon atom bound to oxygen. The N(1)–C(1) bond is 1.2730(16) Å and corresponds to a C–N double bond. Taking into account the solid state structure and the NMR spectroscopy data we suggest that in solution complex **7** may exist as two diastereomers: *R*,*S*-diastereomer (heterochiral dimer, **7-hetero**), which is also present in the solid state (Fig. 2) and the 1 to 1 mixture of *R*,*R*- + *S*,*S*-diastereomers (homochiral dimers, **7-homo**), which exists only in solution.

Diastereotopic protons in the $H_2C$═CPh fragment in the $^1$H NMR spectrum of **7-hetero** in $C_6D_6$ (Fig. 3a) give rise to two




**Scheme 9** Synthesis of the acetylacetonate derivative **9**.

signals (each 1H) centred at $\delta$ 6.77 and 5.25 ppm. In the spectrum of **7-homo** in $C_6D_6$ these protons produce the signals (1H) at $\delta$ 7.90 and 5.82 ppm (Fig. 3b). Formation and stability of homo- and heterochiral dimers of methylzinc alkoxides have been studied in detail by Noyori and co-workers.[16] They found that in solution as well as in the solid state, the heterochiral dimers are more stable than the homochiral isomers. In the case of compound **7** inter-conversion between diastereomers requires dissociation of the dimers into monomers. As mentioned above the reaction of [(dpp-mian)GaI]$_2$ with phenylacetylene resulted in a cycloaddition product. It is worth mentioning that this product is present in the crystal as a homochiral dimer.

In order to gain more insight into the diastereomerisation process we attempted substitution of the phenylethynyl ligand in complex **7** by an acetylacetonate-anion. The reaction between complex **7** and acetylacetone (acacH) proceeds in toluene at 100 °C and is completed within 1 h. The colourless compound (dpp-mian)(PhC═$CH_2$)Mg(acac)$_2$ (**9**) has been isolated from the mother liquor in 39% yield (Scheme 9). According to single crystal X-ray analysis complex **9** is a centrosymmetric dimer with a planar $Mg_2O_2$ core (Fig. 6). Due to the constraints caused by the chelating ligands the coordination environment of the metal atoms in **9** is somewhat different from that found in compound **7**. It is more like a

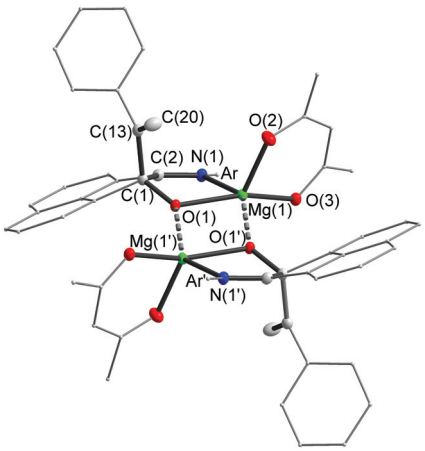



**Fig. 6** Molecular structure of compound **9** (thermal ellipsoids are drawn at 30% probability; hydrogen atoms are omitted for clarity).

trigonal bipyramid: atoms O(1) and O(3) are located in the axial positions, O(1′), O(2) and N(1) are situated in an equatorial plane.

Another difference between **7** and **9** concerns the angle N(1)–Mg–O(1′): in the latter this angle (139°) is nine degrees smaller compared to that in compound **7** (148°). Furthermore, the difference between Mg–N(1) bond lengths in **7** (2.308(1) Å) and **9** (2.255(1) Å) is remarkable. On the other hand, Mg–O(1) bonds in **7** and **9** are similar (**7**: 2.049(1) Å; **9**: 2.025(1) Å). Bearing in mind the features of the molecular structure of **9** we studied its solution behaviour. We have found that complex **9** does not possess any dynamics neither in $C_6D_6$ nor in thf-$d_8$. The diastereotopic protons of the $H_2C{=}CPh$ fragment in the $^1H$ NMR spectrum of **9** in $C_6D_6$ give rise to two signals (each 1H) centred at $\delta$ 6.98 and 5.50 ppm. The acetylacetonate ligand results in two singlets at $\delta$ 5.16 (1H) and 1.54 ppm (6H). As in the case of compound **7** the isopropyl groups in complex **9** give rise to two septets ($\delta$ 3.38 and 3.09 ppm) and to four doublets ($\delta$ 1.77, 1.35, 1.02 and 0.61 ppm). Finally, hydrolysis of complex **9** yields compound **8**.

## Conclusions

We have modified Kim's procedure[12a] for the synthesis of monoiminoacenaphtheneone **3** (dpp-mian). Our method allows preparation of **3** with a yield comparable to that reported by the Korean team but using lower amounts of the solvent. In our case the reaction proceeds faster due to the higher boiling temperature of toluene compared to methanol and gave compound **3** in 80% yield already in a couple of hours. Reduction of **3** in thf with magnesium and crystallisation of the product either from thf or toluene allowed the synthesis of the first metal complexes with dpp-mian dianions – compounds $[(dpp\text{-}mian)Mg(thf)_2]_2$ (**4**) and $[(dpp\text{-}mian)Mg(thf)]_4$ (**5**), respectively. As other main group metal complexes with dpp-bian ligand compounds **4** and **5** are reactive towards phenylacetylene. However, in contrast to $(dpp\text{-}bian)Mg(thf)_3$ reactions of **4** and **5** with phenylacetylene proceed *via* cycloaddition but not as acid–base interactions. On the other hand, cycloadducts have been obtained recently in the reactions of alkynes with dpp-bian gallium complexes.[3] These data demonstrate a variety of chemical properties of the main group metal complexes of non-innocent ligands. Owing to the high reactivity of the magnesium–carbon bond the cycloadduct **6** reacts with a second equivalent of phenylacetylene to give acetylenide $[(dpp\text{-}mian)(PhC{=}CH_2)Mg(C{\equiv}CPh)_2(thf)]_2$ (**7**). An interesting finding here is the diastereomerisation of **7** in solution. Thus, crystallisation of compound **7** from solution makes preferences for the heterochiral dimer **7-hetero**, which structure has been determined by single crystal X-ray analysis. Being dissolved in benzene or thf **7-hetero** isomerizes partially to the homochiral dimer **7-homo**. Obviously, inter-conversion between **7-hetero** and **7-homo** requires dissociation of the dimers into monomers. Interestingly, the cycloaddition product obtained by reacting a dpp-mian gallium derivative with phenylacetylene represents a homochiral dimer in the crystalline state. These recent results will be published elsewhere. As shown by the synthesis of compound **9** the acac spectator ligand affects not only the coordination environment of the central atom but also the ability of the dimer to dissociate in solution into monomers. In conclusion, two other research projects involving dpp-mian as the ligand have been conducted in our group. These involve preparation of main group metal complexes with neutral dpp-mian ligands (Ga, Sb, Sn, Ti, and Co derivatives) as well as a detailed study of the reduction of dpp-mian with alkali metals to produce dpp-mian polyanions. The results of these projects will be published elsewhere. In the future we intend to study the catalytic activity of compounds **4** and **5** in organic synthetic reactions involving phenylacetylene and some other unsaturated substrates.

## Experimental

### General procedures

All manipulations were carried out in a vacuum or under nitrogen by using Schlenk techniques. The solvents were distilled from sodium benzophenone prior to use. The deuterated solvents used for the NMR measurements were dried with sodium benzophenone at ambient temperature and were, just prior to use, condensed under vacuum into the NMR tubes already containing the respective compounds. Acenaphthenequinone and 2,6-diisopropylaniline were purchased from Aldrich. Melting points were measured in sealed capillaries. The $^1H$ NMR spectra were recorded on Bruker DPX-200 NMR and Bruker Advance III 400 spectrometers; IR spectra – on a FSM-1201 spectrometer. The yields of compounds **4**, **5**, **7**, **8** and **9** were calculated on the amount of the dpp-mian used in the syntheses.

**(*E*)-2-(2,6-Diisopropylphenylimino)acenaphthylene-1(2*H*)-one (3, dpp-mian).** A mixture of acenaphthenequinone (10.0 g, 55 mmol), 2,6-diisopropylaniline (9.75 g, 55 mmol) and formic acid (0.6 g, 13 mmol) was refluxed in toluene (150 mL) for 2 h. After cooling to ambient temperature the solution was filtered. From the filtrate all volatiles were removed under vacuum and the residue was extracted with diethyl ether. Compound **3** precipitated from diethyl ether as a crystalline orange solid. Yield 15.7 g (80%). According to NMR data product **3** contains as impurity dpp-bian (5%), which can be removed by further extraction. M.p. 177 °C. Anal. calcd for $C_{24}H_{23}NO$: C 84.42, H 6.79; Found: C 84.52, H 6.76. $^1H$ NMR (200 MHz, $CDCl_3$, ppm): 8.19 (dd, 2H, arom, 7.1 and 8.2 Hz), 7.99 (d, 1H, arom, 8.2 Hz), 7.83 (dd, 1H, arom, 7.1 and 8.2 Hz), 7.41 (dd, 1H, arom, 7.1 and 8.2 Hz), 7.27 (s, 3H, arom), 6.62 (d, 1H, arom, 7.1 Hz), 2.84 (sept, 2H, $C\underline{H}(CH_3)_2$, 6.8 Hz), 1.17 (d, 6H, $CH(C\underline{H}_3)_2$, 6.8 Hz), 0.90 (d, 6H, $CH(C\underline{H}_3)_2$, 6.9 Hz). $^{13}C$ NMR (50.32 MHz, $CDCl_3$, ppm): 189.52, 160.55, 146.52, 143.05, 135.18, 132.26, 131.04, 130.84, 129.48, 129.00, 128.29, 128.13, 127.63, 125.07, 123.55, 123.33, 122.14, 28.39, 23.40. IR (Nujol, $cm^{-1}$): $\nu$ = 1986 w, 1905 w, 1852 w, 1726 s, 1658 s, 1623 w,

1602 m, 1589 m, 1488 w, 1436 m, 1420 m, 1362 m, 1348 w, 1329 w, 1273 s, 1218 w, 1196 w, 1178 w, 1150 w, 1123 w, 1067 m, 1049 w, 1027 s, 939 w, 912 m, 832 m, 812 w, 782 s, 753 s, 698 w, 671 w, 645 w, 606 w, 577 w, 551 w, 525 m, 505 w, 463 m, 453 w. UV-VIS (toluene, 293 K): 365 (sh), 395 (sh), 460 nm.

**[(dpp-mian)Mg(thf)$_2$]$_2$ (4).** A solution of dpp-mian (0.34 g, 1.0 mmol) in thf (30 mL) was added to magnesium shavings (5 g) activated prior to use with iodine (10 mg). In the course of reflux (30 min) the reaction mixture turned green. The solution was cooled to ambient temperature and decanted from an excess of magnesium. Crude product **4** was obtained as a green crystalline solid on removal of the volatiles from thf solution in a vacuum. Yield 0.43 g (84%). M.p. 179 °C. Anal. calcd for $C_{32}H_{39}MgNO_3$: C 75.37, H 7.71; Found: C 73.09, H 7.84. $^1$H NMR (200 MHz, thf-d$_8$, ppm): $\delta$ 7.31–6.92 (m, 9H, arom), 6.87 (d, 1H, arom, 8.1 Hz), 6.80 (dd, 1H, arom, 6.9 and 8.1 Hz), 6.66–6.53 (m, 2H, arom), 6.37 (d, 1H, arom, 6.7 Hz), 5.62 (d, 1H, arom, 6.7 Hz), 3.69 (sept, 2H, C$\underline{H}$(CH$_3$)$_2$, 6.8), 2.29 (s, 3H, C$_6$H$_5$C$\underline{H}_3$), 1.19 (d, 6H, CH(C$\underline{H}_3$)$_2$, 6.8 Hz), 0.91 (d, 6H, CH(C$\underline{H}_3$)$_2$, 6.8 Hz). $^{13}$C NMR (50.32 MHz, CDCl$_3$, ppm): 153.23, 145.66, 145.02, 140.21, 138.21, 135.78, 129.72, 128.94, 128.03, 127.16, 126.69, 126.37, 126.08, 124.89, 123.61, 122.76, 121.03, 118.69, 109.89, 68.26, 28.71, 26.43, 26.00, 24.31, 21.51. IR (Nujol, cm$^{-1}$): $\nu$ = 3055 w, 3023 w, 2726 w, 2676 w, 1800 w, 1734 w, 1693 w, 1657 m, 1602 w, 1587 w, 1552 w, 1515 w, 1422 w, 1341 m, 1246 m, 1214 m, 1188 w, 1173 m, 1144 w, 1128 m, 1103 w, 1072 m, 1026 m, 999 w, 954 w, 937 w, 911 m, 888 w, 877 w, 830 w, 805 m, 780 w, 767 m, 754 w, 728 m, 695 m, 670 w, 622 w, 604 m, 569 m, 523 m, 499 m, 465 m. UV-VIS (THF, 293 K): 320, 345 (sh), 445, 730 nm.

**[(dpp-mian)Mg(thf)]$_4$ (5).** Complex **4** (prepared from 0.34 g (1.0 mmol) of dpp-mian as described above) was dissolved in toluene (30 mL) at 110 °C. In 30 min the mixture was cooled to ambient temperature and the solvent was removed completely under vacuum. Dissolution of the residue and evaporation of the solvent were repeated three times. Crystallization from toluene (10 mL) at ambient temperature gave product **5** as blue crystals. Yield 0.41 g (78%). M.p. >250 °C (dec.). Anal. calcd for $C_{140}H_{156}Mg_4N_4O_8$: C 79.32, H 7.42; Found: C 78.38, H 7.29. $^1$H NMR (200 MHz, $C_6D_6$, ppm): 7.30–6.93 (m, 12H, arom), 6.90–6.75 (2H, arom), 6.28 (d, 1H, 6.7 Hz), 3.99 (sept, 1H, C$\underline{H}$(CH$_3$)$_2$, 6.7 Hz), 3.65 (br s, thf), 3.64 (sept, 1H, C$\underline{H}$(CH$_3$)$_2$, 6.7 Hz), 2.11 (s, 6H, C$_6$H$_5$C$\underline{H}_3$), 1.37 (d, 3H, CH(C$\underline{H}_3$)$_2$, 6.7 Hz), 1.04 (d, 3H, CH(C$\underline{H}_3$)$_2$, 6.7 Hz), 1.03 (br s, 4H, thf), 0.89 (d, 3H, CH(C$\underline{H}_3$)$_2$, 6.7 Hz), 0.34 (d, 3H, CH(C$\underline{H}_3$)$_2$, 6.7 Hz). $^{13}$C NMR (50.32 MHz, CDCl$_3$, ppm):149.74, 147.56, 146.92, 144.19, 138.50, 137.54, 135.32, 128.98, 126.68, 126.43, 125.34, 124.35, 123.96, 123.50, 119.47, 110.05, 28.23, 27.94, 26.39, 26.33, 25.24, 24.77, 22.90, 21.06. IR (Nujol, cm$^{-1}$): $\nu$ = 3055 w, 3025 w, 1932 w, 1864 w, 1808 w, 1736 w, 1657 m, 1619 w, 1604 w, 1589 m, 1522 s, 1495 m, 1473 m, 1443 s, 1432 s, 1362 w, 1346 w, 1331 s, 1300 m, 1241 m, 1218 w, 1210 w, 1180 m, 1124 m, 1105 m, 1068 m, 1034 w, 1016 m, 1003 w, 957 w, 932 m, 913 m, 865 w, 813 m, 769 m, 744 w, 730 m, 695 m, 671 w, 626 m, 612 w, 597 m, 571 w, 544 w, 525 m, 499 m, 483 w, 464 w, 453 m. UV-VIS (toluene, 293 K): 310 (sh), 325, 340 (sh), 475, 570, 640 nm.

**[(dpp-mian)(PhC=CH$_2$)Mg(C≡CPh)$_2$(thf)]$_2$ (7).** Heating of a mixture of complex **4** (0.41 g, 0.78 mmol) and phenylacetylene (0.31 g, 3.0 mmol) in toluene (25 mL) at 80 °C for 8 h caused a change of the colour of the reaction mixture from blue to light-violet. After cooling to ambient temperature the volatiles were removed from the mixture under vacuum. The remaining solid was dissolved in toluene (10 mL) at heating. Crystallization at ambient temperature gave complex **7**·C$_7$H$_8$ as light-pink crystals. Yield 0.22 g (38%). M.p. 200–210 °C (dec.). Anal. calcd for $C_{102}H_{102}Mg_2N_2O_4$: C 83.42, H 7.00; Found: C 83.39, H 7.05. $^1$H NMR (200 MHz, $C_6D_6$, ppm): 10.25 (dd, 1H, arom, 6.8 and 1.0 Hz), 7.70 (t, 1H, arom, 7.1 Hz), 7.45 (d, 1H, arom, 8.3 Hz), 7.40–6.85 (m, 26H, arom), 6.77 (1, 1H, PhC=C$\underline{H}$(H)), 6.77–6.37 (m, 9H, arom), 6.26 (d, 1H, arom, 7.0 Hz), 5.25 (s, 1H, PhC=C$\underline{H}$(H)), 3.78 (s, 4H, thf), 3.37 (sept, 1H, C$\underline{H}$(CH$_3$)$_2$, 6.8 Hz), 3.00 (sept, 1H, C$\underline{H}$(CH$_3$)$_2$, 6.8 Hz), 2.10 (s, 12H, C$_6$H$_5$C$\underline{H}_3$), 1.63 (d, 3H, CH(C$\underline{H}_3$)$_2$, 6.8 Hz), 1.51 (d, 3H, CH(C$\underline{H}_3$)$_2$, 6.8 Hz), 1.31 (s, 4H, thf), 1.14 (d, 3H, CH(C$\underline{H}_3$)$_2$, 6.8 Hz), 0.19 (d, 3H, CH(C$\underline{H}_3$)$_2$, 6.8 Hz). IR (Nujol, cm$^{-1}$): $\nu$ = 3056 w, 2077 w, 1941 w, 1738 w, 1649 m, 1636 w, 1614 w, 1591 m, 1482 w, 1345 w, 1327 w, 1257 w, 1232 w, 1200 m, 1185 w, 1171 w, 1102 m, 1081 m, 1058 w, 1033 m, 1010 w, 993 w, 924 m, 910 m, 903 w, 885 m, 852 w, 833 m, 815 w, 803 w, 785 m, 755 m, 705 m, 692 m, 682 w, 672 w, 645 w, 610 w, 581 w, 560 w, 548 w, 533 m, 515 w, 505 w, 486 w, 468 w. $^1$H NMR (400 MHz, thf-d$_8$, ppm): 9.07 (dd, 1H, arom, 6.5 and 1.0 Hz), 7.88 (dd, 1H, arom, 8.2 Hz), 7.82–7.76 (m, 2H, arom), 7.67 (s, 1H), 7.61–7.48 (m, 2H, arom), 7.33–7.09 (m, 9H, arom), 7.09–6.97 (m, 2H, arom), 6.82 (d, 1H, arom, 7.3), 6.78–7.66 (m, 2H, arom), 6.66–6.54 (m, 2H, arom), 6.08 (d, 1H, arom, 7.0 Hz), 5.41 (s, 1H, PhC=C$\underline{H}$), 3.69 (sept, 1H, C$\underline{H}$(CH$_3$)$_2$, 6.8 Hz), 3.67–3.55 (m, 4H, thf), 2.59 (sept, 1H, C$\underline{H}$(CH$_3$)$_2$, 6.8 Hz), 2.32 (s, 3H, C$_6$H$_5$C$\underline{H}_3$), 1.85–1.71 (m, 4H, thf), 1.42 (d, 3H, CH(C$\underline{H}_3$)$_2$, 6.8 Hz), 0.92 (d, 3H, CH(C$\underline{H}_3$)$_2$, 6.8 Hz), 0.67 (d, 3H, CH(C$\underline{H}_3$)$_2$, 6.8 Hz), −0.11 (d, 3H, CH(C$\underline{H}_3$)$_2$, 6.8 Hz). $^{13}$C NMR (100.62 MHz, thf-d$_8$, ppm): 156.44, 155.84, 147/35, 146.47, 145.87, 143.47, 142.74, 142.67, 141.01, 140.84, 140.54, 139.77, 138.61, 137.70, 133.57, 132.95, 132.92, 132.73, 132.21, 132.14, 131.69, 131.55, 131.41, 131.05, 130.69, 130.45, 130.12, 130.00, 129.84, 129.72, 129.55, 129.30, 129.07, 128.95, 128.56, 128.14, 128.01, 127.77, 127.71, 126.97, 126.73, 126.61, 126.50, 126.21, 126.13, 125.63, 125.31, 125.26, 124.91, 124.80, 124.30, 124.15, 124.08, 123.92, 121.92, 117.4, 111.77, 110.85, 89.08, 88.62, 68.39, 29.74, 29.25, 28.95, 28.25, 26.66, 26.55, 24.53, 24.45, 21.65. Product **7**·C$_4$H$_8$O was obtained under the same conditions reacting complex **4** (0.43 g, 0.84 mmol) and phenylacetylene (0.31 g, 3.0 mmol) in thf (30 mL). Yield 0.29 g (48%). M.p. 185–190 °C. Anal. calcd for $C_{48}H_{51}MgNO_3$: C 80.72, H 7.20, N 1.96; Found: C 80.68, H 7.24, N 1.92. UV-VIS (toluene, 293 K): 305 (sh), 319, 340, 370 nm.

**dpp-mian(PhC=CH$_2$)H (8).** A mixture of complex **4** (prepared from 0.34 g dpp-mian) and phenylacetylene (0.51 g, 5.0 mmol) was heated in thf (35 mL) at 80 °C for 8 h in a sealed ampule. After addition of H$_2$O (0.1 mL) to the obtained

Table 1 Crystal data and structure refinement details for **3**, **5**, **7**·$C_7H_8$, **7**·$C_4H_8O$, **8** and **9**

| | **3** | **5** | **7**·$C_7H_8$ | **7**·$C_4H_8O$ | **8** | **9** |
|---|---|---|---|---|---|---|
| Formula | $C_{24}H_{23}NO$ | $C_{140}H_{156}Mg_4N_4O_8$ | $C_{102}H_{102}Mg_2N_2O_4$ | $C_{96}H_{102}Mg_2N_2O_6$ | $C_{32}H_{31}NO$ | $C_{74}H_{74}Mg_2N_2O_6$ |
| $M_r$ | 341.43 | 2119.93 | 1468.48 | 1428.41 | 445.58 | 1135.97 |
| $T$/K | 100(2) | 100(2) | 100(2) | 100(2) | 100(2) | 100(2) |
| Crystal size/mm$^3$ | 0.14 × 0.10 × 0.08 | 0.50 × 0.45 × 0.40 | 0.60 × 0.50 × 0.40 | 0.36 × 0.32 × 0.30 | 0.50 × 0.20 × 0.10 | 0.65 × 0.46 × 0.15 |
| Crystal system | Monoclinic | Triclinic | Triclinic | Triclinic | Monoclinic | Monoclinic |
| Space group | $P2(1)/c$ | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ | $P2(1)/n$ | $P2(1)/n$ |
| $a$/Å | 15.2395(11) | 15.3860(4) | 10.83521(13) | 10.5447(12) | 9.1993(2) | 11.2637(7) |
| $b$/Å | 14.3009(11) | 18.9900(5) | 13.2253(2) | 12.8512(15) | 18.5141(4) | 18.6717(11) |
| $c$/Å | 17.4321(12) | 20.3370(4) | 15.70481(19) | 15.2786(17) | 14.7826(4) | 15.0467(9) |
| $\alpha$/° | 90 | 85.228(2) | 97.5746(12) | 98.9945(19) | 90 | 90 |
| $\beta$/° | 96.931(2) | 84.9367(18) | 99.7585(10) | 94.5901(18) | 102.905(3) | 92.6400(10) |
| $\gamma$/° | 90 | 81.210(2) | 110.4065(14) | 109.5268(17) | 90 | 90 |
| $V$/Å$^3$ | 3771.4(5) | 5834.7(2) | 2033.83(5) | 1907.8(4) | 2454.15(11) | 3161.1(3) |
| $Z$ | 8 | 2 | 1 | 1 | 4 | 2 |
| $D_{calcd}$/g cm$^{-3}$ | 1.203 | 1.207 | 1.199 | 1.243 | 1.206 | 1.193 |
| $\mu$/mm$^{-1}$ | 0.073 | 0.093 | 0.085 | 0.091 | 0.072 | 0.092 |
| $F(000)$/e | 1456 | 2272 | 784 | 764 | 952 | 1208 |
| $hkl$ range | $-18 \le h \le 18$<br>$-17 \le k \le 17$<br>$-21 \le l \le 21$ | $-18 \le h \le 18$<br>$-22 \le k \le 22$<br>$-24 \le l \le 24$ | $-15 \le h \le 15$<br>$-18 \le k \le 18$<br>$-22 \le l \le 22$ | $-13 \le h \le 13$<br>$-15 \le k \le 15$<br>$-18 \le l \le 18$ | $-12 \le h \le 12$<br>$-24 \le k \le 24$<br>$-19 \le l \le 19$ | $-14 \le h \le 14$<br>$-23 \le k \le 23$<br>$-19 \le l \le 19$ |
| $\theta$ Range for data collection/° | 2.20 to 26.00 | 2.94 to 25.00 | 3.05 to 30.00 | 2.587 to 25.997 | 2.931 to 28.000 | 2.465 to 27.000 |
| Max. and min. transmission | 0.9942 and 0.9899 | 0.9638 and 0.9551 | 0.9667 and 0.9506 | 0.7457 and 0.6654 | 1.00000 and 0.68031 | 0.9697 and 0.8761 |
| Refl. measured | 32 162 | 82 508 | 41 431 | 17 520 | 43 719 | 34 803 |
| Refl. unique | 7403 | 20 491 | 11 810 | 7424 | 5906 | 6884 |
| $R_{int.}$ | 0.0910 | 0.0778 | 0.0232 | 0.0224 | 0.0720 | 0.0316 |
| Parameters refined | 477 | 1410 | 509 | 498 | 314 | 385 |
| $R(F^2)$/w$R(F^2)$ [$I > 2s(I)$] | 0.0585/0.1106 | 0.0828/0.1943 | 0.0381/0.1039 | 0.0554/0.1467 | 0.0458/0.0961 | 0.0437/0.1132 |
| $R(F^2)$/w$R(F^2)$ [all data] | 0.1147/0.1263 | 0.1281/0.2216 | 0.0440/0.1079 | 0.0665/0.1535 | 0.0732/0.1038 | 0.0536/0.1180 |
| GoF ($F^2$) | 0.962 | 1.080 | 1.051 | 1.045 | 1.032 | 1.055 |
| $\Delta\rho_{fin}$ (max/min)/e Å$^{-3}$ | 0.240/−0.172 | 0.778/−0.453 | 0.430/−0.316 | 0.764/−0.439 | 0.260/−0.204 | 0.360/−0.193 |

mixture at ambient temperature the colour of the solution turned brown. After evaporation of the volatiles under vacuum the residue was dissolved in hexane (20 mL). The solution was filtered off. From the concentrated solution compound **8** was isolated as light yellow crystals. Yield 0.10 g (22%). M.p. 104 °C. Anal. calcd for $C_{32}H_{31}NO$: C 86.25, H 7.01; Found: C 85.45, H 7.34. $^1$H NMR (400 MHz, $CDCl_3$, ppm): 7.92–7.88 (m, 2H, arom), 7.73(d, 1H, arom, 2.0 Hz), 7.71(s, 1H), 7.28 (pst, 1H, arom, 7.3 Hz), 7.17–7.06 (m, 4H, arom), 7.03–6.95 (m, 2H, arom), 6.78 (m, 2H, arom), 6.43 (d, 1H, arom, 7.0 Hz), 6.20 (d, 1H, PhC=C$\underline{H}_2$, 1 Hz), 5.66 (d, 1H, PhC=C$\underline{H}_2$, 1 Hz), 3.42 (s, 1H, OH), 2.81 (sept, 1H, C$\underline{H}$(CH$_3$)$_2$, 7.0 Hz), 2.00 (sept, 1H, 6.8 Hz), 1.12 (d, 3H, CH(C$\underline{H}_3$)$_2$, 7.0 Hz), 0.90 (d, CH(C$\underline{H}_3$)$_2$, 6.8 Hz), 0.78 (d, 3H, CH(C$\underline{H}_3$)$_2$, 7.0 Hz), 0.52 (d, 3H, CH(C$\underline{H}_3$)$_2$, 7.0 Hz). $^{13}$C NMR (50.32 MHz, $CDCl_3$, ppm): 174.55, 150.92, 146.00, 141.74, 140.32, 139.90, 137.10, 135.66, 131.22, 130.89, 128.99, 128.80, 128.03, 127.49, 125.76, 124.38, 123.89, 123.58, 123.30, 121.09, 116.49, 83.12, 28.70, 27.80, 27.64, 23.80, 23.72, 23.36, 23.09. IR (Nujol, cm$^{-1}$): $\nu$ = 3216 m, 3095 w, 3060 m, 3023 m, 1983 w, 1954 w, 1895 w, 1883 w, 1856 w, 1823 w, 1797 w, 1754 w, 1657 s, 1635 m, 1623 m, 1590 m, 1554 w, 1493 m, 1443 m, 1399 m, 1365 m, 1349 m, 1325 m, 1290 m, 1255 m, 1231 w, 1217 w, 1192 m, 1165 m, 1146 m, 1113 m, 1104 m, 1075 m, 1058 m, 1050 w, 1029 w, 997 m, 962 w, 940 m, 919 w, 904 w, 892 m, 836 m, 793 m, 776 w, 766 w, 731 m, 704 w, 650 m, 598 m, 545 w, 535 m, 503 w, 484 w, 472 w, 461 w. UV-VIS (toluene, 293 K): 305 (sh), 315, 345, 390 (sh) nm.

**[{dpp-mian(PhC=CH$_2$)}Mg(acac)]$_2$ (9).** A mixture of complex **4** (prepared from 0.34 g dpp-mian) and phenylacetylene (0.51 g, 5.0 mmol) was heated in thf (30 mL) at 80 °C for 8 h in a sealed ampule. After removal of all volatiles in a vacuum the residual solid was treated with a solution of 0.098 g (0.98 mmol) of acetylacetone in toluene (20 mL). The obtained solution was heated for 1 h at 100 °C. Concentration of the resulting solution gave the product **9** as colourless crystals. Yield 0.22 g (39%). M.p. 210–220 °C (dec.). Anal. calcd for $C_{74}H_{74}Mg_2N_2O_6$: C 78.24, H 6.57; Found: C 79.01, H 6.69. $^1$H NMR (400 MHz, $C_6D_6$, ppm): 7.93 (dd, 1H, arom, 6.5 and 1.0 Hz), 7.37–6.47 (m, 19H, arom), 5.49 (d, 1H, PhC=C$\underline{H}_2$, 1.8 Hz), 5.15 (s, 1H, CH acac), 3.58–3.54 (m, 4H, thf), 3.38 (sept, 1H, C$\underline{H}$(CH$_3$)$_2$, 6.8 Hz), 3.09 (sept, 1H, C$\underline{H}$(CH$_3$)$_2$, 6.8 Hz), 2.10 (s, 3H, C$_6$H$_5$C$\underline{H}_3$), 1.77 (d, 3H, CH(C$\underline{H}_3$)$_2$, 6.8 Hz), 1.53 (s, 6H, CH$_3$ acac), 1.42–1.38 (m, 4H, thf), 1.35 (d, 3H, CH(C$\underline{H}_3$)$_2$, 6.8 Hz), 1.02 (d, 3H, CH(C$\underline{H}_3$)$_2$, 6.8 Hz), 0.61 (d, 3H, CH(C$\underline{H}_3$)$_2$, 6.8 Hz). IR (Nujol, cm$^{-1}$): $\nu$ = 3112 w, 3083 w, 3056 m, 3024 w, 3010 w, 2363 w, 2341 w, 2274 w, 1934 w, 1865 w, 1826 w, 1803 w, 1745 w, 1661 s, 1599 s, 1542 w, 1516 s, 1490 w, 1456 w, 1440 w, 1429 w, 1407 s, 1361 m, 1348 w, 1326 m, 1263 m, 1247 w, 1236 w, 1220 w, 1198 m, 1188 m, 1168 m, 1144 m, 1107 w, 1099 m, 1080 m, 1055 w, 1033 m, 1014 m, 994 w, 964 w, 929 w, 912 m,

Table 2 Selected bond lengths (Å) for **3**, **5**, **7**·$C_7H_8$, **7**·$C_4H_8O$, **8** and **9**

| Compound | **3**[a] | **5**[b] | **7**·$C_7H_8$ | **7**·$C_4H_8O$ | **8** | **9** |
|---|---|---|---|---|---|---|
| O(1)–C(1) | 1.215(2) | 1.389(3)–1.409(3) | 1.3924(8) | 1.384(2) | 1.4420(15) | 1.382(1) |
| C(1)–C(2) | 1.552(3) | 1.375(3)–1.388(4) | 1.5626(9) | 1.548(2) | 1.5569(17) | 1.548(2) |
| C(2)–N(1) | 1.273(3) | 1.351(4)–1.382(3) | 1.2788(9) | 1.268(2) | 1.2730(16) | 1.272(2) |
| N(1)–Ar | 1.431(3) | 1.429(3)–1.445(4) | 1.4421(8) | 1.436(2) | 1.4290(16) | 1.440(2) |
| Mg–N(1) | — | 2.031(2)–2.065(2) | 2.3083(6) | 2.283(2) | — | 2.255(1) |
| Mg–O(1) | — | 2.022(2)–2.389(2) | 2.0492(5) | 2.035(1) | — | 2.025(1) |
| Mg–O(1′) | — | 2.022(2)–2.389(2) | 2.0035(5) | 2.000(1) | — | 1.960(1) |
| Mg–O(thf) | — | 2.073(2)–2.116(2) | 2.0740(5) | 2.058(1) | — | — |
| Mg–O(2) | — | — | — | — | — | 1.957(1) |
| Mg–O(3) | — | — | — | — | — | 1.987(1 |
| Mg–C | — | — | 2.1511(8) | 2.138(2) | — | — |

[a] The numbering scheme is that presented in the literature.[12b] [b] The range of bond lengths in four chemically equivalent units in tetramers.

894 w, 834 m, 815 w, 802 m, 797 w, 781 s, 774 w, 758 m, 709 w, 697 m, 669 m, 647 m, 612 m, 600 w, 586 w, 572 w, 558 m, 531 w, 521 m, 505 m, 481 m, 465 w.

### Single-crystal X-ray structure determination

The data were collected on Bruker SMART APEX (for **3**), Agilent Xcalibur E (for **5**, **7**·$C_4H_8O$ and **8**) and Bruker D8 Quest (for **7**·$C_7H_8$ and **9**) diffractometers using monochromated $MoK_\alpha$ radiation ($\omega$-scan technique, $\lambda$ = 0.71073 Å). The intensity data were integrated by using SAINT for **3**,[17] **7**·$C_7H_8$ [18] and **9**[18] and by using CrysAlisPro for **5**,[19] **7**·$C_4H_8O$[19] and **8**.[19] The structures were solved by direct[20] (**3**, **5**, **7**·$C_7H_8$ and **7**·$C_4H_8O$) and dual-space[21] (**8** and **9**) methods and were refined on $F^2$ using the SHELXTL package.[22] SADABS (for **3**, **7**·$C_7H_8$ and **6**)[23] and SCALE3 ABSPACK (for **5**, **7**·$C_4H_8O$ and **8**)[24] were used to perform area-detector scaling and absorption corrections. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in the calculated positions and refined in the "riding-model" ($U_{iso}$(H) = 1.5$U_{eq}$(C) in $CH_3$-groups and $U_{iso}$(H) = 1.2$U_{eq}$(C) in other ligands), except for those of $CH_2$ and OH groups in **7**·$C_4H_8O$ and **8** respectively, which were obtained from differential Fourier-synthesis and refined isotropically. In **5** and **7**·$C_7H_8$ solvate molecules of toluene were found in a common position. In the same position a disordered THF solvate molecule was located in the crystal of **7**·$C_4H_8O$. A part of the toluene molecules in **5** are also disordered. The crystal data and structure refinement details are collected in Table 1. Selected bond distances and angles are presented in Table 2. CCDC 1419025 (for **3**), 1419026 (for **5**), 1419027 (for **7**·$C_7H_8$), 1419028 (for **7**·$C_4H_8O$), 1419029 (for **8**) and 1419030 (for **9**) contain the supplementary crystallographic data for this paper.

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