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Single-Electron-Transfer Reactions of α-Diimine dpp-BIAN and Its Magnesium Complex $(dpp\text{-}BIAN)^{2-}Mg^{2+}(THF)_3$

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The reactions of (dpp-BIAN)$Mg(THF)_3$ (**1**) {dpp-BIAN = 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene} with ethyl halides EtX (X = Cl, Br, I) in hexane proceed by single-electron transfer (SET) from the metal complex to the organic halide. Complexes $[(dpp\text{-}BIAN)(Et)]MgX(THF)_n$ [X = Cl, n = 0 (**2**); X = Br, n = 2 (**3**); X = I, n = 1 (**4**)] are the products of ethyl transfer to an imine carbon atom of a coordinated diimine ligand. The compound [(dpp-BIAN)(Et)]MgBr (**3a**) was obtained from the reaction of free dpp-BIAN with ethylmagnesiumbromide in hexane. In this case SET from the Grignard reagent to the neutral diimine takes place. Compounds **2**–**4** and **3a** were isolated as crystals and characterized by ^1H NMR spectroscopy. The molecular structure of **3** was determined by single-crystal X-ray analysis.

Introduction

Among the organometallic and coordination compounds of magnesium, only Grignard reagents are widely used in organic synthesis.[1] Despite the fact that magnesium amides, R_2NMgX (X = halide), so-called Hauser bases, were found to be excellent deprotonating reagents for nitriles,[2] enolizable ketones,[3] and C–H acids,[4] they have not yet become regular reagents in organic synthesis. Reactions of Grignard reagents with organic substrates may proceed by two different mechanisms: concerted polar addition or single-electron transfer (SET) from RMgX to the organic compound.[5] The second mechanism implies oxidation of RMgX and reduction of the substrate by SET. During this process, an R–Mg bonding electron leaves the HOMO of RMgX. This leads to cleavage of this bond and formation of a radical R and an MgX cation, which then attack the respective centers of the substrate. Some time ago, we started our search for new electron transfer reagents based on main-group metals. Our original concept involved the preparation of metal complexes in which a complex HOMO is mainly ligand-localized and the ligand has further functionalities to bind the metal (e.g. heteroatom lone pairs). In these cases, the SET from the HOMO to the organic substrate should not cause cleavage of a metal–ligand bond. Long-known alkali metal naphthalenides or magnesium anthracenide are strong reducing agents, which are able to transfer electrons to different substrates. However, since the π-systems of these arenes are very weak bases, an electron transfer from these species causes not only oxidation of the ligand but also its release from the metal. α-Diimines have a low-lying LUMO (π*), which can be populated with electrons from the metal, and basic nitrogen atoms. The 1,2-bis[(2,6-diisopropylphenyl)imino]-acenaphthene (dpp-BIAN) ligand has an extended π system that is formed from diimine and naphthalene. Four-step reduction of this diimine with alkali metals produces its tetraanion.[6] Metallic magnesium easily reduces dpp-BIAN to a dianion and provides the monomeric solvated complex (dpp-BIAN)$Mg(THF)_3$ (**1**).[7] To some extent, this complex is related to Hauser bases because it readily deprotonates C–H acids,[8] ketones,[9] and nitriles.[10] Reaction of **1** with diphenylketone provides, by SET, the pinacolate complex $[(dpp\text{-}BIAN)^{-}\cdot Mg]_2(\mu\text{-}O_2C_2Ph_4)$.[11] Note that, during oxidation from dianion to radical-anion, the dpp-BIAN ligand still remains on magnesium. Iodine and some organic halides (e.g. Ph_3SnCl, $BrCH_2CH_2Br$) oxidize complex **1** to give radical-anionic species of the type $(dpp\text{-}BIAN)^{-}\cdot MgX$ (X = Cl, Br, I).[12] Recently we have reported the reverse process; the reduction of a magnesium-bound radical-anion to the corresponding dianion by reductive elimination of an alkyl radical from (dpp-BIAN)Mg(*i*Pr)(Et_2O).[13] In this particular case, the SET occurred intramolecularly. Thus, the concept we wish to develop concerns the preparation of main-group metal complexes with ligands, which may vary their "oxidation state" while they are bound to the metal. This ap-

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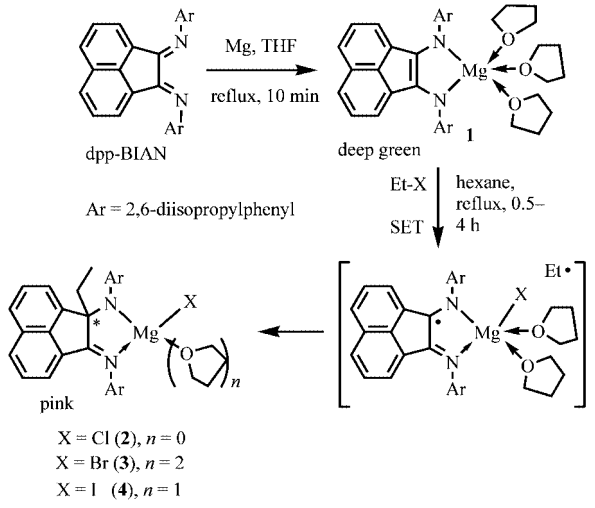
proach should provide redox-active complexes of redox-inactive metals (e.g. magnesium). In this paper, we report on the reactivity of **1** towards organic halides.

Results and Discussion

Treatment of complex **1** with ethyl halides EtX (X = Cl, Br, I) in THF causes a color change from deep green to red within a few minutes at room temperature. Evaporation of the solvent affords a red oily residue, which solidifies only after repeated treatment with hexane and storage of the solution formed at ambient temperature for several days. Because **1** is insoluble in hexane, its reaction with EtX (X = Cl, Br, I) in this solvent proceeds only at reflux and takes up to 30 min in the case of EtI, one hour for EtBr, and several hours for EtCl. However, the use of hexane as solvent allows simple isolation of the products because the products crystallize from the reaction mixture during the reaction. Use of an excess of organic halide increases the reaction rates in hexane. Thus, when a fivefold excess of EtCl is used, the reaction in hexane is complete within 3 hours. Completion of the reaction may be seen by the disappearance of the green crystals of **1** and the precipitation of the red crystalline product.

According to the results of ^{1}H NMR spectroscopy, the reaction of complex **1** with ethyl halides EtX (X = Cl, Br, I) yields the products of ethyl transfer to an imine carbon atom of the dpp-BIAN ligand coordinated to the magnesium atom (Scheme 1). The ethyl radical formed under SET from **1** to EtX attacks the radical-anion of dpp-BIAN, resulting in the formation of compounds **2**–**4** in good yields.



Scheme 1.

Molecular Structure of 3

The molecular structure of **3** (Figure 1) was determined by single-crystal X-ray analysis. Free dpp-BIAN as well as the dpp-BIAN dianion in complex **1** possess two planes of symmetry, one is orthogonal to the acenaphthene plane and crosses the middle C–C bond of the naphthalene moiety, whereas the other coincides with the diimine plane. Attachment of the ethyl group to the imino carbon atom destroys this symmetry and causes the appearance of a chiral carbon atom [C(1)] in the molecule. In the unit cell *R* and *S* isomers are present. In **3** the magnesium atom is five-coordinate. The amido and imino Mg–N distances [Mg–N(1) 2.015(2) and Mg–N(2) 2.3320(19) Å, respectively] differ significantly. Asymmetric chelation of magnesium metal has already been observed in the products of addition of enolizable ketones to **1**.[9] Addition of ketones to **1** occurs with protonation of one of the nitrogen atoms of the dpp-BIAN ligand and results in an asymmetric amido/amino structure. For instance, in the addition product of 1,1-diphenylacetone, the amido and amino bond lengths are 2.051(2) and 2.410(2) Å, respectively. The N(2)–C(2) double bond in **3** [1.281(3) Å] is nearly the same as those in free dpp-BIAN (both N–C 1.28 Å).[12] The distance N(1)–C(2) [1.471(3) Å] corresponds well to a single N–C bond. The Mg–O distances [2.092(2) and 2.1286(17) Å] fall into the range of the respective distances in **1** (2.070, 2.084 and 2.224 Å).[7]

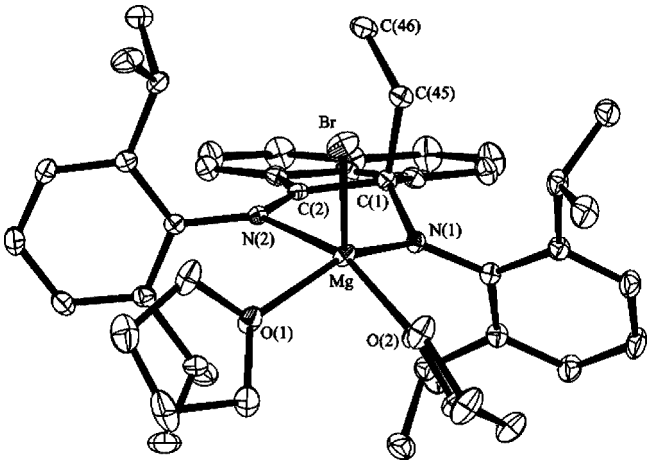


Figure 1. Molecular structure of **3** (*S* isomer). The hydrogen atoms are omitted. Thermal ellipsoids are drawn at 30% probability. Selected bond lengths [Å] and angles [°]: Mg–N(1) 2.015(2), Mg–N(2) 2.3320(19), Mg–O(1) 2.092(2), Mg–O(2) 2.1286(17), Mg–Br 2.5119(8), N(1)–C(1) 1.471(3), C(1)–C(2) 1.543(3), C(1)–C(45) 1.561(3), N(2)–C(2) 1.281(3); N(1)–Mg–O(1) 143.44(9), N(1)–Mg–O(2) 98.33(7), O(1)–Mg–O(2) 85.20(7), N(1)–Mg–N(2) 77.88(7), O(1)–Mg–N(2) 84.75(7), O(2)–Mg–N(2) 156.73(8), N(1)–Mg–Br 116.82(6), O(1)–Mg–Br 98.54(6), O(2)–Mg–Br 97.52(6), N(2)–Mg–Br 104.70(5).

NMR Spectroscopy of 2–4

Selected ^{1}H NMR spectroscopic data for **2**–**4** are given in Table 1. All three compounds reveal a similar spectral picture. The asymmetric amido/imino structure causes the twelve aromatic protons to be nonequivalent. The four methine protons of the isopropyl substituents give rise to four signals ranging from 4.85 to 2.97 ppm for **2** and **3** in [D_8]THF and from 5.25 to 3.06 ppm for **4** in C_6D_6. Because

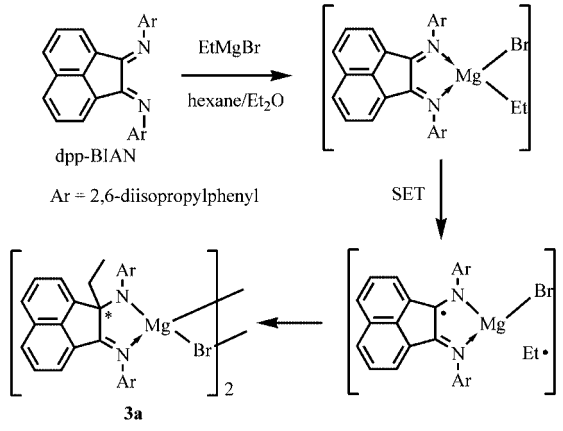
of restricted rotation around the N–C(*ipso*-Ph) bond, all eight methyl groups become unique and appear as eight doublets in the range from 1.40 to –0.15 ppm. The presence of the chiral carbon atom C(1) next to the methylene protons of the ethyl group causes them to be nonequivalent (**2**: 2.75, 2.54; **3**: 2.97, 2.51; **4**: 3.23, 2.88 ppm).

Table 1. Selected ^{1}H NMR spectroscopic data for **2** and **3** in [D_8]-THF and **4** in C_6D_6 (200 MHz, 293 K).

	2	**3**	**4**
H–C(CH_3)$_2$, septuplet[a]	4.82 3.63 3.09 2.97	4.85 3.68 3.05 3.00	5.25 3.93 3.23 3.06
C*H*$_2$–CH_3, multiplet[a]	2.75 2.54	2.97 2.51	3.23 2.88
H–C(C*H*$_3$)$_2$, doublet[b]	1.39 1.37 1.28 1.24 1.13 0.87 0.46 –0.18	1.40 1.37 1.27 1.23 1.13 0.87 0.44 –0.15	1.74 1.72 1.66 1.23 1.16 0.98 0.81 0.14
CH_2–C*H*$_3$, triplet[b]	–0.05	–0.07	0.23

[a] Integral intensity corresponds to one proton. [b] Integral intensity corresponds to three protons.

Compound **3a** was prepared by the reaction of dpp-BIAN with EtMgBr (Scheme 2). Only its coordinating solvent differs from that of **3**.



Scheme 2.

Addition of an equimolar amount of EtMgBr (1.9 M in Et_2O) to a stirred suspension of dpp-BIAN in hexane at room temperature causes immediate dissolution of the diimine (and provides a clear red solution). Evaporation of the solvent in vacuo leads to rapid precipitation of a microcrystalline solid, which does not dissolve in hexane again, but readily dissolves in Et_2O and toluene. Although the molecular structure of this product was not confirmed by X-ray crystallography, its identity was definitely established by ^{1}H NMR spectroscopy. The ^{1}H NMR spectroscopic data for the product obtained, together with those acquired for **2**–**4**, indicate that in the reaction of dpp-BIAN with EtMgBr a reverse process of SET – from Grignard reagent to neutral diimine ligand – takes place. Transfer of the alkyl radical formed to the imino carbon atom of dpp-BIAN follows this SET process. The ^{1}H NMR spectrum of **3a** is shown in Figure 2. According to the ^{1}H NMR data, the isolated compound **3a** does not contain coordinating solvent, e.g. diethyl ether. Therefore, we suggest that compound **3a** is dimeric in the solid state. This is supported by the recently reported dimeric structure of a closely related magnesium compound formed in the reaction of **1** with Me_3SiCl.[12] In this case, the SET from **1** to Me_3SiCl causes the formation of Me_3Si radicals, which attack THF molecules to form $Me_3SiO(CH_2)_3CH_2$ radicals. Transfer of these radicals to the imino carbon atom provided a compound that is an analog of **2**–**4**.

As in the case of compound **3**, the ^{1}H NMR spectrum of **3a** (Figure 2) reveals the nonequivalence of all 12 aromatic protons, whose signals range from 7.84 to 6.10 ppm. Signals of four different methine protons are positioned at 4.85, 3.70, 3.05, and 2.96 ppm. Eight different methyl groups give rise to eight doublets centered at 1.39, 1.36, 1.26, 1.22, 1.12, 0.86, 0.44, and –0.15 ppm. The ethyl group provides three signals: two multiplets at 2.97 and 2.49 (1 H each) and a triplet at –0.07 (3 H) ppm.

The reduction of α-diimines to radical-anions with main-group organometallic compounds followed either by alkyl radical transfer to a radical-anionic ligand or by an alkyl radical release has been reported. Van Koten and coworkers have studied reactions of 1,4-diazabutadienes with different dialkylzinc compounds. Tertiary, benzylic, and some secondary organozinc compounds give C-alkylation products (sometimes accompanied with 1,3-prototropic shift), whereas primary dialkylzinc compounds give N-alkylation products.[14] Recently, Bailey and coworkers reported on the reactivity of Me_2Mg towards dpp-BIAN and diacetal-bis(2,6-diisopropylphenylimine) (Ar′-DAD).[15] In both cases, the reactions occur with release of a methyl radical and afford complexes of radical-anionic ligands, e.g. (L$^{-\cdot}$)-MgMe (L = dpp-BIAN or Ar′-DAD). In the case of Ar′-DAD, the methyl transfer product was isolated in low yield when the reaction was carried out at low temperature. The formation of radical-anionic products in the above-mentioned reactions of organomagnesium compounds with diimines indicates clearly that these reactions occur by SET from the magnesium compound to the diimines. In order to find confirmation for the SET process in the course of the reaction of complex **1** with ethyl bromide, we have monitored this reaction by ESR spectroscopy. Addition of EtBr to a THF solution of complex **1** at –100 °C followed by slow warming of the reaction mixture to ambient temperature resulted in the appearance of the ESR signal of the dpp-BIAN radical-anion (g = 2.0045, A_N = 0.44, A_{Br} = 0.2 mT).[12] In the course of several minutes this signal disappeared completely, indicating the recombination of the radical-anion and the ethyl radical.

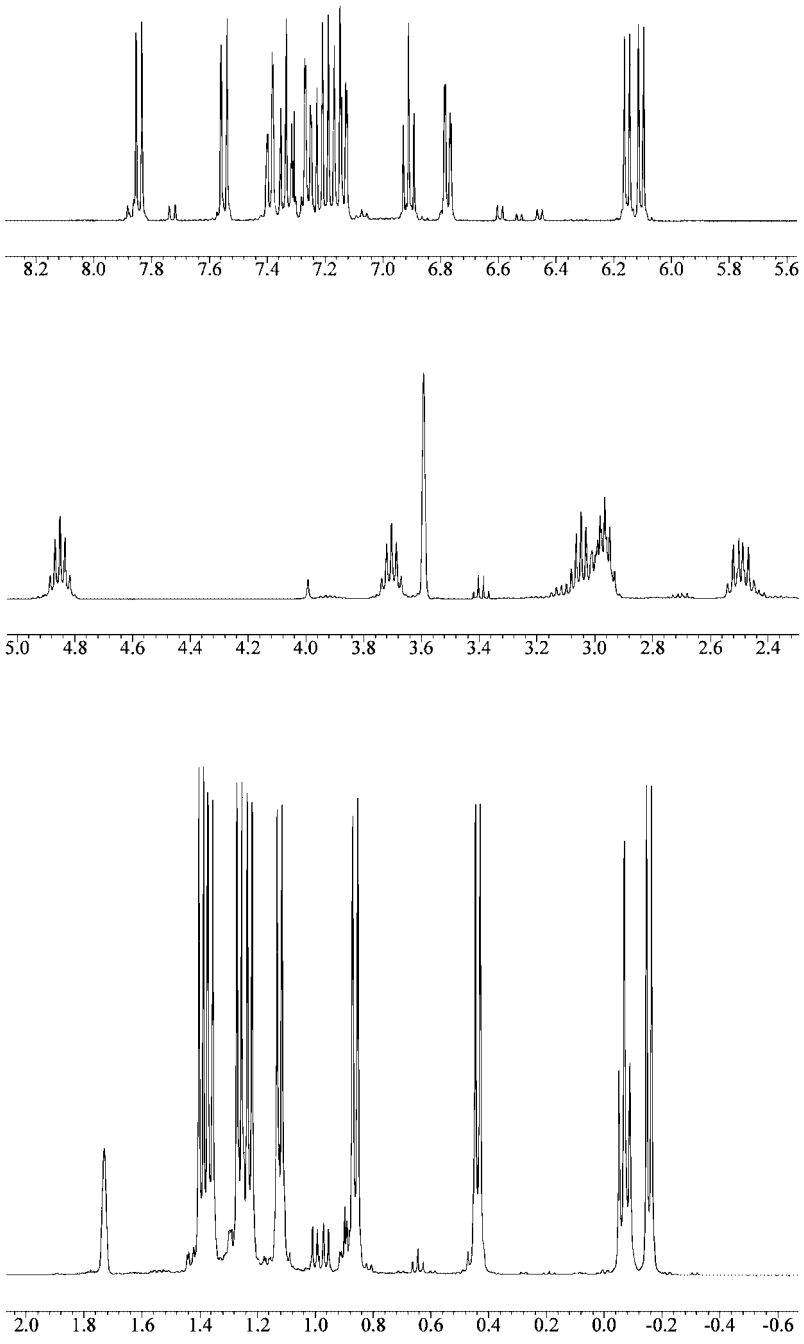


Figure 2. The ^{1}H NMR spectrum of **3** divided in three sections ([D_8]THF, 400 MHz, 20 °C).

Conclusions

In conclusion, we have demonstrated that diimine dpp-BIAN as well as its dianion may be involved in SET reactions. Thus, reagents having a low ionization potential, such as organometallic species, may reduce neutral dpp-BIAN. In contrast, the magnesium complex of the dpp-BIAN dianion acts as reducing agent towards organic halides. Taking into account the identity of the products isolated in both oxidation and reduction reactions one can suggest that both processes occur by the formation of the radical-anion of dpp-BIAN and an alkyl radical, which recombine to afford the final C–C coupling product.

Experimental Section

General Remarks: All manipulations were carried out under vacuum using Schlenk ampoules. Tetrahydrofuran and diethyl ether were dried by distillation from sodium/benzophenone. [D_8]THF and C_6D_6 (both from Aldrich) used for NMR experiments 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. Melting points were measured in sealed capillaries. IR spectra were recorded with an FTIR FSM-1201 spectrometer ("Monitoring Ltd."), ^{1}H NMR spectra with Bruker DPX-200 and Bruker DRX-400 NMR spectrometers.

(dpp-BIAN)Mg(THF)$_3$ (1): Magnesium shavings (2.4 g, 100 mmol) and I_2 (0.5 g, 2.0 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 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 (20 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 because of the formation of **1**. The solution was then cooled to ambient temperature and decanted from the excess magnesium. The solvent was evaporated in vacuo affording compound **1** as deep green, almost black crystals. The solid was washed three times with hexane (15 mL) and then used in the reactions with ethyl halides. The yields of the products **2**–**4** were calculated on the basis of the amount of dpp-BIAN used in the preparation of **1**.

[(dpp-BIAN)(Et)]MgCl (2): To a suspension of compound **1** (prepared from 0.5 g of dpp-BIAN) in hexane, was added ethyl chloride (0.32 g, 5 mmol). The reaction ampoule was sealed off under vacuum. In the course of 4 h at 80 °C, the precipitate of **1** dissolved completely. Slow cooling of the red solution to ambient temperature produced red crystals of **2** (0.39 g, 67%). M.p. 147 °C. $C_{38}H_{45}ClMgN_2$ (589.55): calcd. C 77.42, H 7.69; found C 77.11, H 7.91%. IR (Nujol): $\tilde{\nu}$ = 1626 (s), 1590 (m), 1307 (m), 1246 (m), 1188 (w), 1161 (w), 1103 (w), 1024 (m), 1015 (m), 934 (m), 857 (w), 854 (w), 800 (m), 780 (vs), 753 (s), 719 (s), 642 (w), 630 (w), 611 (w), 596 (w), 576 (w), 534 (w), 449 (s), 430 (s), 407 (vs) cm^{-1}. ^{1}H NMR (200 MHz, [D$_8$]THF, 20 °C): δ = 7.84 (d, J = 8.0 Hz, 1 H, CH arom.), 7.55 (d, J = 8.3 Hz, 1 H, CH arom.), 7.39–7.15 (m, 5 H, CH arom.), 7.13 (dd, 1 H, J = 7.5 and 1.7 Hz, CH arom.), 6.91 (t, J = 7.5 Hz, 1 H, CH arom.), 6.77 (dd, 1 H, J = 7.3 and 1.5 Hz, CH arom.), 6.17 (d, J = 7.3 Hz, 1 H, CH arom.), 6.11 (d, J = 7.0 Hz, 1 H, CH arom.), 4.82 [sept, 1 H, J = 6.8 Hz, CH(CH$_3$)$_2$], 3.63 [sept, 1 H, J = 6.8 Hz, CH(CH$_3$)$_2$], 3.09 [sept, 1 H, J = 6.8 Hz, CH(CH$_3$)$_2$], 2.97 [sept, 1 H, J = 6.8 Hz, CH(CH$_3$)$_2$], 2.75 (m, 1 H, CH_2CH$_3$), 2.54 (m,1 H, CH_2CH$_3$), 1.39 [d, J = 6.8 Hz, 3 H, CH(CH_3)$_2$], 1.37 [d, J = 6.8 Hz, 3 H, CH(CH_3)$_2$], 1.28 [d, J = 6.8 Hz, 3 H, CH(CH_3)$_2$], 1.24 [d, J = 6.8 Hz, 3 H, CH(CH_3)$_2$], 1.13 [d, J = 6.8 Hz, 3 H, CH(CH_3)$_2$], 0.87 [d, J = 6.8 Hz, 3 H, CH(CH_3)$_2$], 0.46 [d, J = 6.8 Hz, 3 H, CH(CH_3)$_2$], –0.05 (t, J = 7.3 Hz, 3 H, CH$_2$CH_3), –0.18 [d, J = 6.8 Hz, 3 H, CH(CH_3)$_2$] ppm.

[(dpp-BIAN)(Et)]MgBr(THF)$_2$ (3): Red crystals of **3** were obtained by the procedure described for **2** using dpp-BIAN (0.5 g, 1.0 mmol) and EtBr (0.11 g, 1.0 mmol). Yield 0.5 g (63%). M.p. 76 °C. $C_{46}H_{61}BrMgN_2O_2{\cdot}0.5(C_2H_5)_2O$ (815.25): calcd. C 70.72, H 8.16; found C 70.68, H 8.09%. IR (Nujol): $\tilde{\nu}$ = 1638 (s), 1588 (w), 1315 (m), 1242 (s), 1184 (w), 1104 (w), 1073 (w), 1027 (vs), 946 (w), 919 (m), 865 (w), 854 (s), 846 (w), 834 (w), 800 (w), 784 (s), 750 (vs), 719 (m), 673 (w), 630 (w), 611 (w), 596 (w), 576 (w), 542 (w), 519 (w), 492 (w), 430 (s) cm^{-1}. ^{1}H NMR (200 MHz, [D$_8$]THF, 20 °C): δ = 7.85 (d, J = 8.2 Hz, 1 H, CH arom.), 7.55 (d, J = 8.2 Hz, 1 H, CH arom.), 7.40–7.10 (m, 6 H, CH arom.), 6.91 (t, J = 7.5 Hz, 1 H, CH arom.), 6.77 (dd, 1 H, J = 7.5 and 1.5 Hz, CH arom.), 6.16 (d, J = 7.3 Hz, 1 H, CH arom.), 6.11 (d, J = 7.0 Hz, 1 H, CH arom.), 4.85 [sept, 1 H, J = 6.8 Hz, CH(CH$_3$)$_2$], 3.68 [sept, 1 H, J = 6.8 Hz, CH(CH$_3$)$_2$], 3.05 [sept, 1 H, J = 6.8 Hz, CH(CH$_3$)$_2$], 3.00 [sept, 1 H, J = 6.8 Hz, CH(CH$_3$)$_2$], 2.97 (m, 1 H, CH_2CH$_3$), 2.51 (m,1 H, CH_2CH$_3$), 1.40 [d, J = 6.8 Hz, 3 H, CH(CH_3)$_2$], 1.37 [d, J = 6.8 Hz, 3 H, CH(CH_3)$_2$], 1.27 [d, J = 6.8 Hz, 3 H, CH(CH_3)$_2$], 1.23 [d, J = 6.8 Hz, 3 H, CH(CH_3)$_2$], 1.13 [d, J = 6.8 Hz, 3 H, CH(CH_3)$_2$], 0.87 [d, J = 6.8 Hz, 3 H, CH(CH_3)$_2$], 0.44 [d, J = 6.8 Hz, 3 H, CH(CH_3)$_2$], –0.07 (t, J = 7.3 Hz, 3 H, CH$_2$CH_3), –0.15 [d, J = 6.8 Hz, 3 H, CH(CH_3)$_2$] ppm.

[(dpp-BIAN)(Et)]MgBr (3a): Dropwise addition of an ether solution of EtMgBr (1.9 M, 0.6 mL) by syringe to a stirred suspension of dpp-BIAN (0.53 g, 1.06 mmol) in hexane (20 mL) at 25 °C caused instant dissolution of the orange precipitate and resulted in a red solution. Evaporation of the solvent under vacuum led to quick precipitation of the red microcrystalline solid, which was then filtered off and dried in vacuo. Yield 0.58 g (87%). M.p. 205 °C. $C_{38}H_{45}BrMgN_2$: (634.00): calcd. C 71.99, H 7.15; found C 71.05, H 6.97%. IR (Nujol): $\tilde{\nu}$ = 1623 (s), 1588 (m), 1307 (m), 1246 (m), 1188 (w), 1161 (m), 1100 (w), 1038 (w), 1011 (m), 934 (w), 854 (w), 830 (w), 800 (w), 781 (s), 750 (s), 723 (s), 642 (w), 631 (w), 611 (w), 592 (w), 577 (w), 542 (w), 527 (w), 454 (s), 427 (s), 407 (s) cm^{-1}. ^{1}H NMR (400 MHz, [D$_8$]THF, 20 °C): δ = 7.84 (d, J = 8.2 Hz, 1 H, CH arom.), 7.55 (d, J = 8.2 Hz, 1 H, CH arom.), 7.39 (dd, 1 H, J = 7.7 and 1.5 Hz, CH arom.), 7.33 (t, J = 7.5 Hz, 1 H, CH arom.), 7.26 (dd, 1 H, J = 7.7 Hz and 1.5, CH arom.), 7.21 (t, J = 7.5 Hz, 1 H, CH arom.), 7.17 (dd, 1 H, J = 7.5 and 7.5 Hz, CH arom.), 7.13 (dd, 1 H, J = 7.7 and 1.7 Hz, CH arom.), 6.91 (t, J = 7.7 Hz, 1 H, CH arom.), 6.77 (dd, 1 H, J = 7.5 and 1.7 Hz, CH arom.), 6.15 (d, J = 7.3 Hz, 1 H, CH arom.), 6.10 (d, J = 7.1 Hz, 1 H, CH arom.), 4.85 [sept, 1 H, J = 6.8 Hz, CH(CH$_3$)$_2$], 3.70 [sept, 1 H, J = 6.8 Hz, CH(CH$_3$)$_2$], 3.05 [sept, 1 H, J = 6.8 Hz, CH(CH$_3$)$_2$], 2.97 (dq, 1 H, J = 14.8 and 7.3 Hz, CH_2CH$_3$), 2.96 [sept, 1 H, J = 6.8 Hz, CH(CH$_3$)$_2$], 2.49 (dq, 1 H, J = 14.8 and 7.3 Hz, CH_2CH$_3$), 1.39 [d, J = 6.8 Hz, 3 H, CH(CH_3)$_2$], 136 [d, J = 6.8 Hz, 3 H, CH(CH_3)$_2$], 1.26 [d, J = 6.8 Hz, 3 H, CH(CH_3)$_2$], 1.22 [d, J = 6.8 Hz, 3 H, CH(CH_3)$_2$], 1.12 [d, J = 6.8 Hz, 3 H, CH(CH_3)$_2$], 0.86 [d, J = 6.8 Hz, 3 H, CH(CH_3)$_2$], 0.44 [d, J = 6.8 Hz, 3 H, CH(CH_3)$_2$], –0.07 (t, J = 7.3 Hz, 3 H, CH$_2$CH_3), –0.15 [d, J = 6.8 Hz, 3 H, CH(CH_3)$_2$] ppm.

[(dpp-BIAN)(Et)]MgI(THF)$_2$ (4): Red crystals of **4** were obtained by the procedure described for **2** using 0.5 g (1.0 mmol) of dpp-BIAN and 0.15 g (1.0 mmol) of ethyl iodide. The reaction completed within 30 min. Yield 0.42 g (56%). M.p. 188 °C. $C_{42}H_{53}IMgN_2O$ (753.11): calcd. C 66.98, H 7.09; found C 70.68, H 8.09%. IR (Nujol): $\tilde{\nu}$ = 1623 (s), 1584 (m), 1307 (m), 1250 (s), 1181 (m), 1100 (w), 1038 (m), 1011 (s), 949 (w), 919 (w), 869 (s), 854 (m), 834 (w), 800 (m), 784 (s), 754 (s), 723 (m), 673 (w), 630 (w), 611 (w), 596 (w), 576 (w), 542 (w), 515 (w), 496 (w), 450 (m), 427 (s) cm^{-1}. ^{1}H NMR (200 MHz, C$_6$D$_6$, 20 °C): δ = 7.53–7.04 (m, 9 H, CH arom.), 6.89 (t, J = 7.8 Hz, 1 H, CH arom.), 6.51 (d, J = 7.3 Hz, 1 H, CH arom.), 6.46 (d, J = 7.0 Hz, 1 H, CH arom.), 5.25 [sept, 1 H, J = 6.8 Hz, CH(CH$_3$)$_2$], 3.93 [sept, 1 H, J = 6.8 Hz, CH(CH$_3$)$_2$], 3.23 [sept, 1 H, J = 6.8 Hz, CH(CH$_3$)$_2$], 3.22 (m, 1 H, CH_2CH$_3$), 3.06 [sept, 1 H, J = 6.8 Hz, CH(CH$_3$)$_2$], 2.88 (m,1 H, CH_2CH$_3$), 1.74 [d, J = 6.8 Hz, 3 H, CH(CH_3)$_2$], 1.72 [d, J = 6.8 Hz, 3 H, CH(CH_3)$_2$], 1.66 [d, J = 6.8 Hz, 3 H, CH(CH_3)$_2$], 1.23 [d, J = 6.8 Hz, 3 H, CH(CH_3)$_2$], 1.16 [d, J = 6.8 Hz, 3 H, CH(CH_3)$_2$], 0.98 [d, J = 6.8 Hz, 3 H, CH(CH_3)$_2$], 0.81 [d, J = 6.8 Hz, 3 H, CH(CH_3)$_2$], 0.23 (t, J = 7.3 Hz, 3 H, CH$_2$CH_3), 0.14 [d, J = 6.8 Hz, 3 H, CH(CH_3)$_2$] ppm.

X-ray Crystallographic Study of 3: Crystals of **3** suitable for X-ray structure determination were obtained from hexane. Crystal data: $C_{46}H_{61}BrMgN_2O_2{\cdot}0.5Et_2O$, M = 815.25, triclinic, a = 10.8322(6), b = 12.3710(6), c = 17.8518(9) Å, U = 2210.7(2) Å^3, T = 100(2) K,

space group $P\bar{1}$, $Z = 2$, $\mu = 0.984\ mm^{-1}$, 12387 reflections measured, 7760 unique ($R_{int} = 0.0180$) which were used in all calculations. $R_1[I > 2\sigma(I)] = 0.526$, w$R_1$(all data) = 0.0635. The structures were solved by direct methods using SHELXS-97[16] and were refined on F^2 using SHELXL-97.[17] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were found from Fourier synthesis except those at C(38) and C(39) in the THF molecule. The hydrogen atoms at C(38) and C(39) as well as hydrogen atoms in the lattice Et_2O molecule were placed in calculated positions and refined in the riding model. SADABS[18] was used to perform area-detector scaling and absorption corrections. CCDC-282656 (**3**) contains 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.

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