σ-Bond Metathesis

Oxidative Addition of Phenylacetylene through C–H Bond Cleavage To Form the Mg^{II}–dpp-bian Complex: Molecular Structure of [Mg{dpp-bian(H)}(C≡CPh)(thf)$_2$] and Its Diphenylketone Insertion Product [Mg(dpp-bian)$^{\bullet-}$\{OC(Ph$_2$)C≡CPh\}(thf)] **

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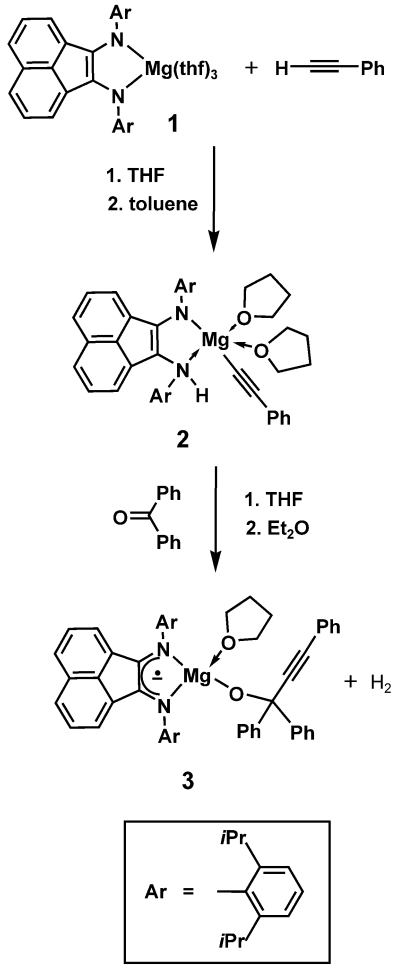
Dedicated to Professor Viktor A. Dodonov on the occasion of his 70th birthday

Over the past decade dpp-bian began to be used widely in coordination chemistry owing to a number of interesting chemical reactions, which include catalytic olefin polymerization,[1] shown by the metal complexes based on this ligand.[2] The rigidity and bulkiness of the ligand and its π-acceptor properties cause an electron deficiency at the coordinated metal and render these complexes highly reactive towards organic substrates. However, a huge number of publications and patents until now have been concerned with metal complexes of only neutral dpp-bian ligand. One might suggest that the presence of both extended π-system and Lewis basic nitrogen centers in dpp-bian may enable this ligand to act as an electron and proton reservoir. The ability of dpp-bian to accept up to four electrons to form a tetraanion $(dpp\text{-}bian)^{4-}$ upon reduction with sodium in ether was recently verified.[3] We also reported on the synthesis and characterization of the Mg and Ca complexes with dianionic dpp-bian ligand.[4] One of our objectives at present is to test whether these alkaline-earth-metal salts may serve as reducing agents towards organic substrates. It was shown that the magnesium complex [Mg(dpp-bian)(thf)$_3$] (**1**) serves well as a reducing agent towards aromatic ketones.[5] However, in contrast to the 1,3-dipolar cycloaddition of diphenylketone to dianionic 1,4-diaza-1,3-diene lanthanide or Group 4 metal complexes, the reduction of Ph_2CO with **1** affords the pinacol coupling product.[5] The reduction of 9-(10*H*)-anthracenone with **1** yields the aryloxy derivative as result of the deprotonation of 9-anthracenol (phenolic tautomer of 9-(10*H*)-anthracenone). Herein, we wish to report the unprecedented oxidative addition of phenylacetylene to **1** through acidic activation of a C–H bond to form the phenylethynyl derivative and the product of diphenylketone insertion thereof.

Complex **1** was prepared by treating an excess of magnesium metal with dpp-bian at reflux in THF for 30 min and was used in situ for the reactions with phenylacetylene. The addition of a five molar excess of the phenylacetylene to the THF solution of **1** causes a quick change in the solution from dark green to dark blue. Removal of the volatile fractions under vacuum and crystallization of the crude product from toluene afforded the alkynyl complex [Mg{dpp-bian(H)}(C≡CPh)(thf)$_2$] (**2**) in 63% yield as black prisms. As shown by X-ray crystal-structure determination and ^{1}H NMR spectroscopy, the reaction proceeds by oxidative addition with the formation of phenylethynylmagnesium amido/amino complex **2** (Scheme 1).



Scheme 1. Synthesis of complexes **2** and **3**.

Recently Chang and co-workers reported the formation of alkynyl magnesium amides [{Mg(RC≡C)(μ-N*i*Pr$_2$)(thf)}$_2$] (R = Ph, $SiMe_3$) through amine elimination within the stoichiometric reaction between [Mg(*i*Pr$_2$N)$_2$] and HC≡CR in THF.[6] As the dpp-bian acts as chelating ligand in the complexes **1** and **2**, the amine elimination from **2** cannot take place. The X-ray crystal structure of **2** shows that both the

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amido and the amino function of the dpp-bian ligand chelate the Mg atom. It is noteworthy that even an excess of the alkyne does not force complex **2** to eliminate 1,2-bisaminoacenaphthene. To test whether insertion reactions into alkynyl–Mg bond may be accomplished, we treated complex **2** with diphenylketone. The reaction between **2** and Ph_2CO in THF is completed within several minutes when the solution is heated at 50–60 °C and results in a change from deep blue to violet. Evaporation of the solvent and crystallization of the crude product from diethyl ether gave the corresponding carbinolate [Mg(dpp-bian)$^{\bullet-}${OC(Ph_2)C≡CPh}(thf)] (**3**) in 47 % yield. Surprisingly, an abstraction of a hydrogen atom from the amino functional group of the ligand takes place simultaneously with the insertion of the ketone into the Mg–C bond (Scheme 1). The formation of the radical anion of dpp-bian in the course of the reaction was confirmed by ESR spectroscopy.

The molecular structures of **2** (Figure 1) and **3** (Figure 2) were determined by single-crystal X-ray-diffraction studies on crystals obtained from toluene and diethyl ether, respectively.[7] Compound **2** is a five-coordinated magnesium complex in which the terminal alkynyl fits in the pocket formed by two isopropyl groups of the aryl groups bonded to the nitrogen atoms. The significant difference in Mg–N bond

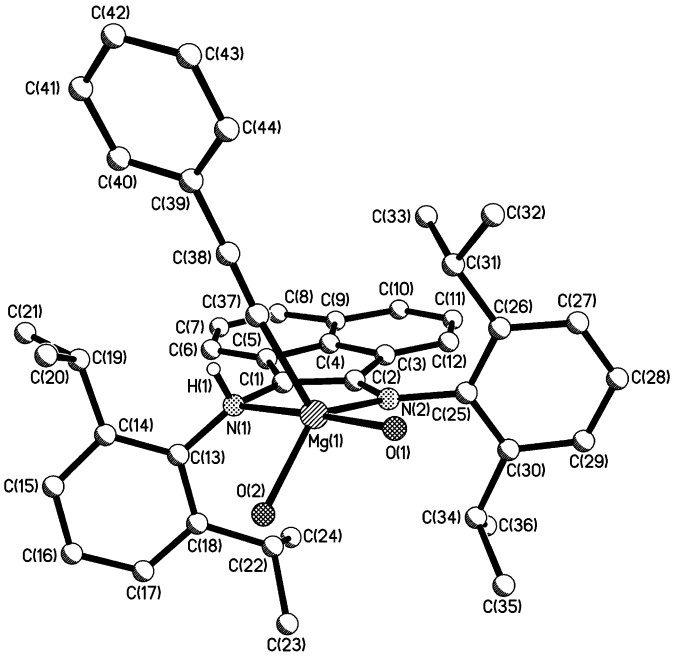


Figure 1. Molecular structure of **2**. The hydrogen atoms are omitted as well as the carbon atoms of the solvent molecules. Selected bond lengths [Å] and angles [°]: Mg(1)-N(1) 2.355(2), Mg(1)-N(2) 2.045(2), Mg(1)-O(1) 2.1233(17), Mg(1)-O(2) 2.0499(17), Mg(1)-C(37) 2.124(3), Mg(1)-C(2) 2.841(2), N(1)-C(13)1.438(3), N(1)-C(1) 1.444(3), N(1)-H(1) 0.889(19), N(2)-C(2) 1.350(3), N(2)-C(25) 1.430(3), C(1)-C(2) 1.378(3), C(1)-C(5) 1.443(3), C(37)-C(38) 1.209(3), C(38)-C(39) 1.435(3); N(2)-Mg(1)-N(1) 80.97(7), O(2)-Mg(1)-O(1) 85.94(7), N(2)-Mg(1)-O(1) 98.95(8), O(1)-Mg(1)-N(1) 177.79(7), O(2)-Mg(1)-N(1) 92.42(7), N(2)-Mg(1)-O(2) 130.06(8), O(1)-Mg(1)-C(37) 95.72(8), O(2)-Mg(1)-C(37) 110.98(9), C(37)-Mg(1)-N(1) 86.24(8), N(2)-Mg(1)-C(37) 117.79(9), C(13)-N(1)-H(1) 108.1(14), C(1)-N(1)-H(1) 114.3(12), Mg(1)-N(1)-H(1) 83.6(13).

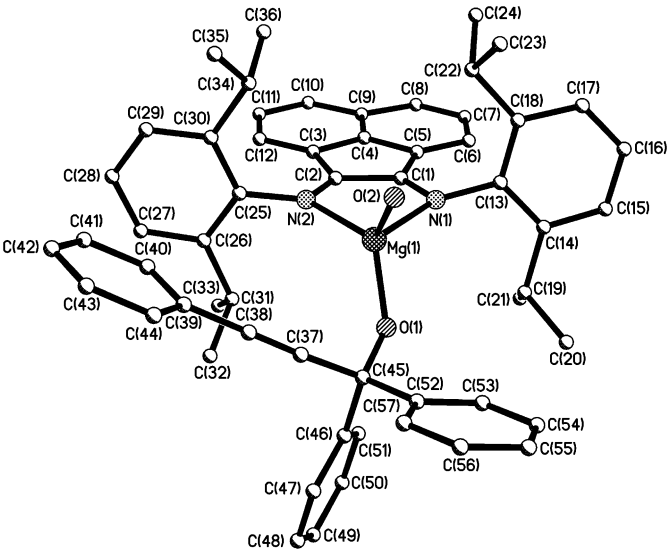


Figure 2. Molecular structure of **3**. The hydrogen atoms are omitted as well as the carbon atoms of the solvent molecules. Selected bond lengths [Å] and angles [°]: Mg(1)-O(1) 1.8529(15), Mg(1)-O(2) 2.0265(17), Mg(1)-N(1) 2.0844(18), Mg(1)-N(2) 2.0802(18), Mg(1)-C(1) 2.789(2), Mg(1)-C(2) 2.792(2), O(1)-C(45) 1.381(3), N(1)-C(1) 1.340(3), N(1)-C(13) 1.430(3), C(1)-C(2) 1.441(3), C(1)-C(5) 1.470(3), N(2)-C(2) 1.336(2), N(2)-C(25) 1.436(2), C(37)-C(38) 1.205(3), C(37)-C(45) 1.497(3), C(38)-C(39) 1.433(3); O(1)-Mg(1)-O(2) 105.67(7), O(1)-Mg(1)-N(2) 124.78(7), O(2)-Mg(1)-N(2) 118.97(6), O(1)-Mg(1)-N(1) 113.48(7), O(2)-Mg(1)-N(1) 106.82(8), N(2)-Mg(1)-N(1) 84.07(7).

length (Mg(1)–N(1), 2.355 Å and Mg(1)–N(2), 2.045 Å) reflects the difference in bond strengths between amino (N(1)) and amido (N(2)) functional groups with the Mg center. The latter bond length is close to Mg–N bond lengths in **1** (2.045 and 2.105 Å).[4] The Mg–O bonds in **2** also reveal a pronounced difference between Mg(1)–O(1), 2.123 Å, and Mg(1)–O(2), 2.050 Å. This may be explained by a difference in the coordination sites of oxygen atoms in the distorted trigonal-bipyramidal environment around magnesium. The angle between axially positioned atoms N(1) and O(1) is 177.8°. The hydrogen atom H(1) was found to be 0.889 Å from N(1). Both the alkynyl ligand and H(1) located on the same side of the plane formed with the metallacycle -Mg-N-C-C-N- and the torsion angle H(1)-N(1)-Mg-C(37) is small (4.4°). The angle H(1)-N(1)-N(2) is 107.8°. The terminal Mg–C(alkynyl) bond length (Mg(1)–C(37), 2.124 Å) is somewhat shorter than the respective bond in the six-coordinated complex [Mg(C≡CPh)$_2$(tmeda)$_2$] (tmeda = *N,N,N,N*-tetramethyl ethylene diamine) (2.176 and 2.200 Å)[8] but close to those in [Mg(RC≡C)(μ-N*i*Pr$_2$)(thf)]$_2$ (R = Ph, 2.134 Å; $SiMe_3$, 2.135 Å).[6] Compound **2** has a wider C≡C-Mg angle (174.6°) compared to [(RC≡C)Mg(μ-N*i*Pr$_2$)(thf)]$_2$ (R = Ph, 172.8°; $SiMe_3$, 167.8°).[6]

In contrast to **2** the magnesium atom in **3** is four-coordinated, and this is probably due to the steric factors imposed by diphenyl(phenylethynyl)carbinolato ligand. The Mg–N bond lengths in **3** are almost equal (Mg(1)-N(1), 2.084 Å and Mg(1)-N(2), 2.080 Å) and differ only slightly from those in the four-coordinated dpp-bian radical-anionic

pinacolato complex [{Mg(dpp-bian)(thf)}$_2${μ-$O_2C_2Ph_4$}] (2.079 Å and 2.107 Å).[5] The diimine moiety in **3** is rather symmetrical: the C–C and C–N distances (C(1)–N(1), 1.340; C(2)-N(2), 1.336; C(1)–C(2) 1.441 Å) fall in the range of related distances in [{(dpp-bian)Na}$_2$][3] and [{(dpp-bian)Mg(thf)}$_2${μ-$O_2C_2Ph_4$}][5] The Mg–O (carbinolato) bond in **3** is much shorter than Mg–O(thf) bond length (1.853 and 2.027 Å, respectively).

To determine whether the unsymmetrical amido/amino structure of **2** is maintained in solution, we recorded ^{1}H- and ^{13}C NMR spectra of **2** in C_6D_6. If the unsymmetrical structure were present in solution, one can expect a complicated spectral picture due to the non-equivalence of all the ring protons as well as a non-equivalence of the four methine protons and eight CH_3-groups. In contrast to this expectation the spectrum revealed a relatively simple pattern (Figure 3).

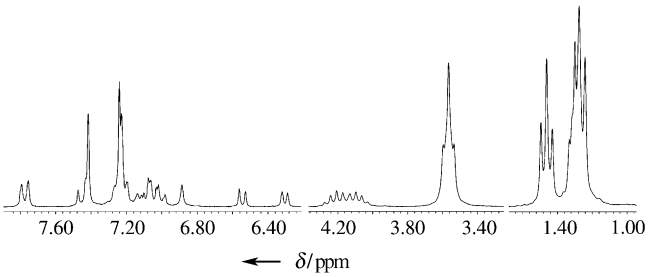
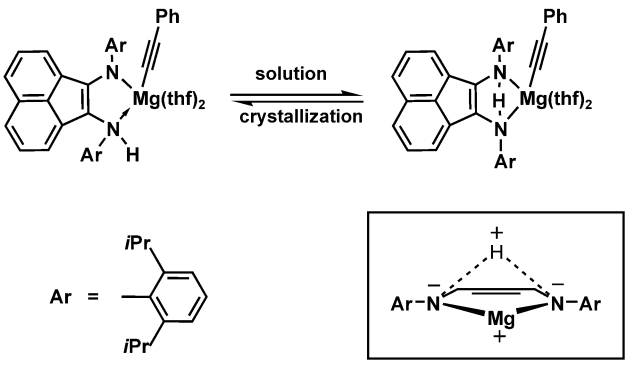


Figure 3. ^{1}H NMR spectrum of **2** in C_6D_6 (200 MHz, 293 K).

The appearance of two different signals that belong to the methine protons *H*-*i*Pr ($\delta = 4.13$ and 4.02 ppm) indicates that in complex **2** in solution the dpp-bian ligand is no longer in the plane of symmetry that runs within the acenaphthene portion of the ligand. However, the ^{1}H NMR data signify that in solution complex **2** still has a plane of symmetry that bisects the N-Mg-N angle and divides the ligand in two chemically equivalent portions. Occasionally, four signals, which correspond to the four different methyl group protons, appear as a "triplet" and a "doublet" (each of 12H) at $\delta = 1.38$ and 1.17 ppm, respectively. The latter overlaps with the signal of the coordinated THF molecules. Restricted rotation of the 2,6-*i*Pr$_2$C$_6$H$_3$ groups along the N–C(ipso) bonds causes a non-equivalence of the Me groups, one of which is turned towards and the other away from the magnesium atom. Although the signals of the ring protons were not unequivocally assigned, the spectrum in the aromatic region reveals the expected set of doublets and triplets. The only H resonance signal that is not coupled is that at δ 6.81 ppm. Though the integral intensity of this signal is somewhat higher than expected for one proton, we suppose that this signal presents the "amino" proton. The ^{13}C NMR spectrum of **2** consists of 24 signals of 25 anticipated (two signals of *C*(H)Me$_2$ appears as a single resonance at $\delta = 24.54$ ppm). The given spectroscopic data suggest that in solution the proton in complex **2**, which comes from phenylacetylene, is symmetrically localized between two N atoms (Scheme 2). In this case the bonding of the proton to the dpp-bian ligand may be described as an ionic interaction of cation H$^+$ with the planar conjugated dianionic system of



Scheme 2. Symmetrical occupation of the H atom of complex **2** in solution.

6 π electrons. An ionic character of the H-to-(ddp-bian) interaction may be responsible for the unusual down-field shift of the "amino" proton.

In conclusion, we have found that the magnesium complex with dianionic dpp-bian ligand [Mg(dpp-bian)] readily reacts with phenylacetylene in an oxidative addition manner through C–H bond cleavage to form alkynylmagnesium derivative [Mg{dpp-bian(H)}(C≡CPh)(thf)$_2$]. This for non-transition-metal complexes unprecedented reaction pathway became possible due to the high proton affinity of the dpp-bian ligand and its rigid bidentate bonding character. In the solid state the complex consists of a chelating amido/amino dpp-bian ligand. In solution the dpp-bian ligand in [Mg{dpp-bian(H)}(C≡CPh)(thf)$_2$] behaves as dianion (dpp-bian)$^{2-}$, thus bridging H$^+$ and [PhC≡CMg(thf)$_2$]$^+$ ions. We are going to investigate this phenomenon in more detail by low-temperature UV and NMR spectroscopy. The lability of the H$^+$ cation of complex **2** in solution is shown by easy abstraction of hydrogen upon insertion of diphenylketone into the Mg–C(alkynyl) bond. The abstraction of a H radical from **2** results in the oxidation of the dpp-bian dianion to a radical anion. We recently found that [Mg(dpp-bian)] reacts with acetonitrile and some halogen alkyls similar to the reaction with acetylene. Characterization of the products formed in these reactions is in progress.

Experimental Section

All manipulations were carried out under vacuum by using Schlenk ampoules. The solvents THF, benzene and toluene were distilled from sodium/benzophenone prior to use. The dpp-bian was prepared according to literature procedures.[9] The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX-200 NMR spectrometer. The IR spectra were recorded on a Specord M80 spectrometer.

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 (about 100 mL in volume) equipped with a Teflon stopcock. After the ampoule was evacuated (10^{-1} Torr within about 1 min), THF (40 mL) was added by condensation and the mixture was stirred for 2 h. The formed [$MgI_2(thf)_n$] 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 (30 mL) was then added to the activated Mg metal and the mixture was heated to reflux. In the course of about 10 min at reflux, the reaction mixture turned dark green. The solution was then cooled to ambient temperature and

decanted from the excess of Mg. The THF solution of **1** obtained was further used in situ for the reaction with phenylacetylene.

2: Phenyacetylene (0.51 g, 5.0 mmol) was added to a stirring THF solution of **1** (obtained from 0.5 g, 1.0 mmol of dpp-bian in 30 mL of THF). The solution turned quickly dark blue. Evaporation of the solvent and crystallization of the crude product from toluene (15 mL) yielded 0.54 g (63 %) of **2**·(C_7H_9) as red crystals. M.p.: 143 °C (decomposition). ^{1}H NMR (200 MHz, C_6D_6, 20 °C): $\delta = 7.69$ (d, 4H, $^3J = 7.3$ Hz), 7.37 (d, 2H, $^3J = 8.3$ Hz), 7.34 (s, 2H), 7.22–7.09 (m, 4H), (d, 2H, $^3J = 8.3$ Hz), 7.08–6.88 (m, 4H), (d, 2H, $^3J = 8.3$ Hz), 6.81 (s, 1H, H-N), 6.46 (d, 2H, $^3J = 7.0$ Hz), 6.22 (d, 2H, $^3J = 6.3$ Hz), 4.13 (septet, 2H, $^3J = 6.8$ Hz), 4.02 (septet, 2H, $^3J = 6.8$ Hz), 3.49 (m, 18H, thf), 1.38 (pst, 12H, $CH(CH_3)_2$, $^3J = 6.0$ Hz), 1.22 (m, 18H, thf), 1.17 ppm (d, 12H, $CH(CH_3)_2$, $^3J = 6.8$ Hz). ^{13}C NMR (200 MHz, C_6D_6, 20 °C): $\delta = 155.09, 149.75, 145.45, 142.67, 140.96, 140.19, 134.86, 132.16, 131.70, 126.76, 125.80, 124.16, 124.13, 124.06, 123.86, 123.66, 118.15, 121.10, 109.58, 99.60, 28.27, 28.05, 24.67, 24.55, 24.50$ ppm. IR (nujol): $\tilde{\nu} = 3272$ s, 3078 m, 3062 m, 3030 m, 1590 s, 1510 m, 1250 w, 1200 w, 1110 w, 1029 m, 890 s, 779 s, 760 s, 683 s, 625 w, 580 w, 535 cm^{-1} s. Elemental analysis calcd (%) for $C_{59}H_{70}MgN_2O_2$: C 82.12, H 8.18; found: C 80.20, H 8.21. Crystal data for **2**: $C_{59}H_{70}Mg\,N_2O_2$, $M_r = 862.9$, monoclinic, space group $P(2)1/n$, $a = 12.149(2)$, $b = 21.774(4)$, $c = 18.386(4)$ Å; $\beta = 108.780(4)°$, $V = 4604.8(15)$ Å^3, $Z = 4$, $T = 100(2)$ K, $F_{000} = 1762$, $\mu = 0.082$ mm^{-1}, $\theta = 1.78$–$24.00°$, reflection collected 22 529, independent reflections 7201 [$R_{int} = 0.0609$], $GOF = 0.996$, $R = 0.0646$, $wR^2 = 0.1599$, largest diff. peak and hole 0.629/−0.487 e Å^{-3}. Except for the disordered parts (lattice toluene) H atoms were located from the difference maps. Their positional and isotropic thermal parameters were refined without constraints.

3: Phenylacetylene (0.51 g, 5.0 mmol) was added to the THF solution of **1** (obtained from 0.5 g (1.0 mmol) of dpp-bian in 30 mL THF). Afer 10 min, the solvent and the excess of phenylacetylene were removed under vacuum. The residual solid was dried under vacuum at ambient temperature for 10 min and then dissolved in THF (20 mL). Diphenylketone (0.18 g, 1.0 mmol) was added to the resulting solution. The reaction mixture turned red-violet within 25 min upon heating to 60 °C. Removal of the solvent and crystallization of the crude product from diethyl ether gave 0.41 g (47 %) of compound **3** as deep-red crystals. M.p. 165 °C (decomposition). IR (Nujol): $\tilde{\nu} = 3050$ w, 1516 m, 1508 m, 1430 s, 1312 w, 1250 w, 1178 m, 760 s, 690 cm^{-1} m. ESR spectrum (Et_2O, 293 K): quintet, $A_N = 0.50$ mT (A_N is the coupling constant for the coupling between the unpaired electron and the N nuclei) ($2 \times {}^{14}$N), $g = 2.0028$ (g is the spectroscopic splitting factor). Elemental analysis calcd (%) for $C_{61}H_{64}MgN_2O_2$: C 83.12, H 7.32; found C 82.07, H 7.43. Crystal data for **3**: $C_{61}H_{64}MgN_2O_2$, $M_r = 881.45$, monoclinic, space group $P2(1)/c$, $a = 21.506(2)$, $b = 12.7536(13)$, $c = 18.7068(19)$ Å; $\beta = 101.232(2)°$, $V = 5032.7(9)$ Å^3, $Z = 4$, $T = 100(2)$ K, $F_{000} = 1888$, $\mu = 0.080$ mm^{-1}, $\theta = 1.87$–$22.00°$, reflection collected 25 058, independent reflections 6168 [$R_{int} = 0.0464$], $GOF = 1.046$, $R = 0.0457$, $wR^2 = 0.1192$, largest diffraction peak and hole 0.270/−0.228 e Å^{-3}. CCDC-212777 (**2**) and CCDC-212778 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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