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Carbene adducts of magnesium and zinc [*,**]

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Abstract

The syntheses and characterizations of adducts of dialkylmagnesium and dialkylzinc with nucleophilic carbenes are described. These carbene adducts are available directly from the reaction of the stable nucleophilic carbenes 1,3-dimesitylimidazol-2-ylidene or 1,3-di(1-adamantyl)imidazol-2-ylidene and the dialkylmetal compounds. The X-ray crystal structures of the 1,3-di(1-adamantyl)imidazol-2-ylidene · diethylzinc adduct and 1,3-dimesitylimidazol-2-ylidene · diethylmagnesium are reported. The adamantyl substituted carbene gave a monomeric metal adduct whereas the mesityl substituted carbene shows a structure with bridging alkyl groups.

1. Introduction

Carbene complexes of the Main Group II (Be, Mg, Ca, Sr, Ba) and Transition Group II (Zn, Cd, Hg) metals are rare except for a few mercury adducts [1–4]. Simple adducts with the dialkyl derivatives of these metals are unknown. We now report the synthesis and characterization of carbene complexes derived from diethylzinc and diethylmagnesium. The isolation of stable nucleophilic carbenes in the imidazol-2-ylidene series (**1**) enables the easy synthesis of a variety of carbene derivatives that previously have been inaccessible [5–9]. The recent report of a stable carbene-alane adduct **4** is an example [8].

2. Results and discussion

Imidazol-2-ylidenes **1a,b** react smoothly with diethyl zinc or diethyl magnesium to afford the corresponding carbene-metal complexes in good yields (eqn. (1)). The melting ranges of three of the adducts are narrow and in a moderate temperature range (**2a** 145–148°C, **3a** 169–170°C, **3b** 150–151°C). The melting range for adduct **2b** (diethyl magnesium and the dimesityl substituted carbene, **1b**) is also narrow but rather high (360–363°C). The reason for this dramatically higher melting point may be the dimeric nature of this particular adduct (*vide infra*). In the ^{13}C NMR spectra, the C_2 carbons of the imidazole nuclei are shifted substantially upfield by 25–30 ppm (Table 1) in the complexes. These upfield shifts are consistent with that reported for the alane adduct **4** [8], although the magnitude is smaller (*cf.* $\Delta\delta$ 44.4 for **4** relative to **1a**). The ^{13}C resonances in **2a**, **2b**, **3a** and **3b** for $C_{4,5}$ shift downfield by 2–3 ppm relative to the free carbenes, similar to the behavior of **4**. The ^{15}N NMR shift for **3a** was slightly upfield of the free carbene by about 2 ppm, again consistent with **4**. The ^{1}H NMR spectra, which usually provide a good indication of complex formation, showed directional shifts that are solvent dependent. The chemical shifts of the $H_{4,5}$ protons are downfield of the corresponding carbenes when the spectra are taken in thf-d_8 and upfield when the spectra are taken in benzene-d_6. This variation in shift direction may result from coordination of tetrahydrofuran (thf) to the coordinatively unsaturated metal centers. The downfield shifts for $H_{4,5}$ in the complexes relative to the free carbenes in thf-d_8 are reminisent of **4**. The methylene protons adjacent to the metal centers are sensitive to the substituents on the nitrogens of the imidazole nucleus. When the imidazole nucleus bears adamantyl substituents, the methylenes in the complexes resonate at δ 0.24 for magnesium and δ 0.80 for zinc. When the imidazole substituents are mesityl rings, the methylene

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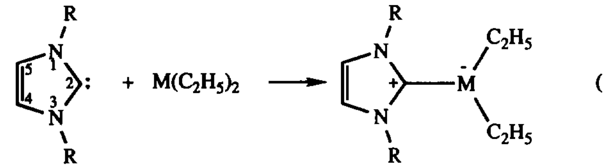
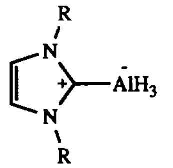


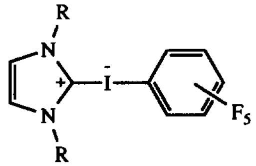
(1)

1a R = 1-adamantyl
1b R = mesityl

2a R = 1-adamantyl, M = Mg
2b R = mesityl, M = Mg
3a R = 1-adamantyl, M = Zn
3b R = mesityl, M = Zn



4 R = 1-adamantyl



5 R = 1-adamantyl

resonances shift upfield to δ −0.78 and −0.43, respectively. These substantial upfield shifts are likely to be the result of placement of the methylenes in the shielding cone above the plane of the mesityl rings. Another interesting observation of the ^1H resonances for the ethyl groups is that the typical $^3J/HH$ values of ~ 8 Hz are absent in the benzene-d_6 spectrum of **2b** (the spectrum shows only broad resonances for the two types of protons) but they reappear when the spectrum is taken in thf-d_8. This may be indication of the persistence of a bridged structure (as in the solid state, *vide infra*) in non-coordinating solvents such as benzene. A nucleophilic solvent such as thf probably coordinates to the magnesium center and destroys the dimeric structure.

The diethyl zinc–carbene adduct **3a** was crystallized from toluene to afford plate-like crystals suitable for X-ray diffraction studies. Selected bond distances and angles are given in Table 2 along with comparisons for some reference compounds. The ring-internal angle at the former carbene center is 104.2°. This value is slightly larger than that in the corresponding carbene but not as large as those in 2H-imidazolium ions which show a more relaxed angle of ~ 108° [10*]. The alane

TABLE 1. Selected NMR chemical shifts (ppm δ) in **1**, **2**, **3**, and **4** [a]

Nucleus	**1a** [b]	**1b** [c]	**2a** [b]	**2b** [b]	**3a** [b]	**3b** [c]	**4** [c]
$^{13}C_2$	211.4	219.7	180.1	194.8	185.0 (185.0) [c]	192.0	175.3
$^{13}C_{4(5)}$	113.9	121.3	116.8	123.0	116.0 (117.2) [c]	123.2	124.3
$^1H_{4(5)}$	6.91 (7.02) [c]	7.04 (6.48) [b]	6.66	6.07 (7.16) [c]	6.63 (7.36) [c]	7.32	7.42
$^{15}N_{1(3)}$	−160.5	−178.9	–	–	−162.3 [c]	–	−179.3
$C^1H_2C^1H_3$	–	–	0.24, 1.91	−0.78, 1.12, −1.19 [c], 0.91 [c]	0.80, 1.85, 0.04 [c], 1.12 [c]	−0.43, 0.85	–

[a] The numbering scheme for all compounds is as indicated for **1**. [b] In benzene-d_6 solution. References are tetramethylsilane or $NH_4^+NO_3^-$. [c] In thf-d_8 solution.

TABLE 2. Selected bond lengths (pm) and angles (°) in **1**, **2b**, **3a** and **4** [a]

Property	**1a**	**1b**	**2b**	**3a**	**4**
$r(C_2–N_{1(3)})$	136.7 (2), 137.3 (2)	136.5 (4), 137.1 (4)	136.3 (4), 135.6 (4)	135.6 (4), 136.0 (5)	135.5 (3), 135.0 (3)
$r(C_4–C_5)$	133.8 (3)	133.1 (5)	132.4 (5)	133.2 (6)	131.3 (4)
$r(N_{1(3)}–C_{5(4)})$	138.2 (2), 138.6 (2)	138.1 (4), 137.8 (4)	138.2 (5), 137.1 (4)	137.8 (5), 138.8 (5)	138.2 (4), 138.4 (4)
$r(N_{1(3)}$–Subst)	148.2 (2), 148.5 (2)	144.1 (4), 144.2 (4)	144.1 (4), 144.7 (4)	149.5 (5), 148.8 (5)	143.6 (3), 144.2 (3)
$r(C_2$–M)	–	–	227.9 (3)	209.6 (3)	203.4 (3)
r(M–Subst)	–	–	225.8 (3), 233.8 (4) (Et-bridge) 213.3 (4) (Et-term) 216.4 (H-bridge)	199.4 (4), 200.9 (4) (Et-term)	156.6 (H-avg.)
$\theta(N_1–C_2–N_3)$	102.2 (2)	101.4 (2)	102.1 (3)	104.2 (3)	104.2 (2)
$\theta(C_{5(4)}–N_{1(3)}–C_2)$	112.1 (2), 112.3 (2)	112.8 (3), 112.8 (3)	112.6 (3), 111.9 (3)	111.4 (3), 110.4 (3)	110.5 (3), 110.8 (3)
$\theta(N_{1(3)}–C_{5(4)}–C_{4(5)})$	107.2 (2), 106.2 (2)	106.5 (3), 106.5 (3)	105.4 (4), 108.0 (4)	106.8 (3), 107.3 (3)	107.5 (3), 107.0 (3)
$\theta(C_2–N_{1(3)}$–Subst)	123.4 (2), 122.1 (2)	121.8 (2), 122.6 (2)	127.4 (3), 127.2 (3)	126.2 (3), 124.7 (3)	124.2 (2), 124.5 (2)
$\theta(M–C_2–N_{1(3)})$	–	–	129.2 (2), 128.6 (2)	127.9 (3), 127.0 (2)	127.9 (2), 127.9 (2)
$\theta(C_2$–M–Subst)	–	–	106.8 (1), 110.0 (1) (Et-bridge) 110.3 (2) (Et-term) 94.2 (H-bridge)	118.1 (1), 109.8 (1) (Et-term)	105.3 (H-avg.)

[a] The numbering scheme for all compounds is as indicated for **1**.

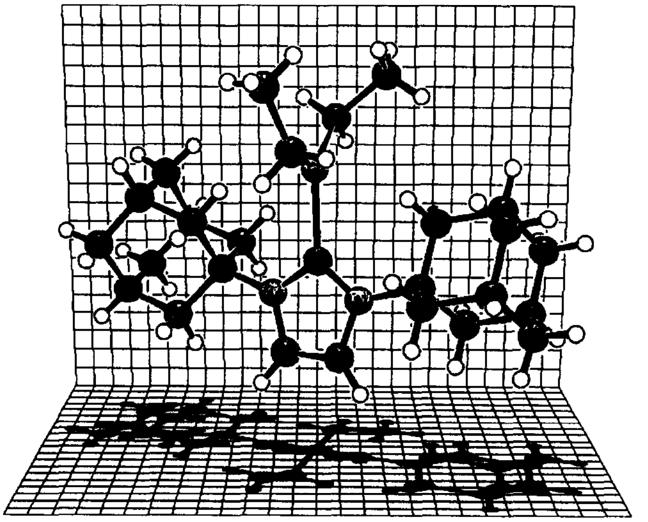


Fig. 1. KANVAS [12*] drawing of **3a**.

adduct **4** and a related reverse-polarized iodine ylide, **5** derived from **1a** also show a 104° ring-internal angles at the former carbene centers. The C–N bond distances ($r_{avg.}$ = 135.8 pm) at the former carbene center are shorter than those in the free carbene which seems to be typical of derivatives of these nucleophilic carbenes. The C–Zn distance to the imidazole substituent is 209.6 pm which is slightly longer than the other two zinc carbon distances ($r_{avg.}$ = 200.2 pm). The zinc atom is in a rather unusual trigonal planar (within 0.2 pm) arrangement [11]. The plane of the zinc coordination is twisted 81.6° with respect to the imidazole plane. This orientation, which is depicted clearly in the shadow of Fig. 1, creates a complication to the 3-coordination of the zinc center. There are close approaches of two hydrogens from the adamantyl substituents above and below the zinc plane (228 and 231 pm). Even though these hydrogens may not be considered to form formal bonds to the zinc center, they certainly protect the zinc from further coordination.

The diethyl magnesium–carbene adduct **2b** was crystallized from benzene to form irregular chunky crystals suitable for X-ray diffraction studies. Unlike the zinc adduct **3a**, **2b** is dimeric in the solid state (possibly also in solution *vide supra*). The dimeric structure is formed through bridging of one ethyl substituent from each magnesium center. The core of the dimeric structure is depicted in Fig. 2 [12]. Each magnesium bears both bridging and terminal ethyl groups. The 4-membered ring formed by the magnesium and bridging carbon centers resides on a crystallographic inversion center and is planar by symmetry. The bonds between magnesium and the bridging carbon centers are slightly asymmetrical with distances of 225.8 and 233.8 pm (Table 2). The longer bridging Mg–C bond involves an agostic hydrogen interaction (*vide infra*). These bridging distances are longer than the Mg–Et terminal bond at 213.3 pm. The Mg–C bond to the imidazole substituent is the longest at 227.9 pm. The magnesium centers seem to obtain additional coordination from an agostic hydrogen in the bridging ethyl groups (Mg–H = 216.4 pm). There is a 276.8 pm distance between the two magnesium centers, suggestive of a possible interaction. The structure of the complexes imidazole moiety in **2b** is quite similar to the free carbene **1b** with a ring-internal angle at the former carbene center of 102.1° and C–N bond distances of 136.3 and 135.6 pm. The mesityl substituents are twisted 86.2° and 83.6° with respect to the central imidazole ring and can thus provide steric protection above and below the imidzole ring due to the *ortho*-methyls. However, there is little steric hindrance in the imidazole plane at C_2.

The bridging structure of **2b** is clearly the result of the mesityl substituents inability to provide sufficient steric protection in the plane of the imidazole ring in the vicinity of C_2. The difference between **1a** and **1b** in this regard is evident in the space filling models of the two carbene structures [5,6]. Although we were not successful in obtaining high quality crystals of **2a**, a crude structure determination indicated a monomeric solid state structure like **3a** [13*].

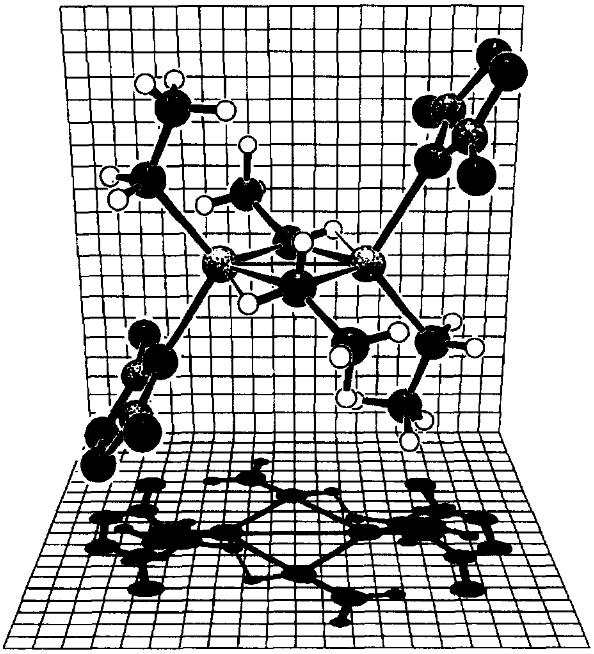


Fig. 2. KANVAS [12] drawing of **2b**.

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* Reference number with asterisk indicates a note in the list of references.

Easily handled stable nucleophilic carbenes such as **1a** and **1b** facilitate the synthesis of carbene adducts such as **2**, **3**, **4** and **5**. Nonetheless, metal adducts have been reported from other indirect routes for some imidazol-2-ylidenes and imidazolin-2-ylidenes (saturated analogs of the imidazole series in which the 4- and 5-position carbons bear additional hydrogen substituents). Lappert and co-workers have reported structures on several imidazolin-2-ylidene adducts of transition metals [14–23]. For comparison, a few examples of imidazol-2-ylidene-transition metal adduct structures are also available from indirect synthetic routes [1,24–27]. It is interesting to note that the imidazol-2-ylidene containing structures tend to retain what can be recognized as a carbene-like structure (small valence angle at the former carbene center and long C–N bonds to this center). The imidazolin-2-ylidene containing structures generally show valence angles and bond distances that are farther removed from the ideal structures of the corresponding carbenes. The persistence of a carbene-like structure in imidazol-2-ylidene metal adducts as compared to imidazolin-2-ylidene metal adducts may be indicative of superior stability for the parent imidazol-2-ylidenes compared to imidazolin-2-ylidenes (which have not yet been isolated or directly observed). The Group II metal adducts reported herein provide additional support for this trend.

3. Experimental details

Reactions and manipulations were carried out under an atmosphere of dry nitrogen, either in a Vacuum Atmospheres dry box or using standard Schlenk techniques. Solvents were dried (using standard procedures) [28], distilled, and deoxygenated prior to use, unless otherwise indicated. Glassware was oven-dried at 160°C overnight. The ^{1}H (300.75 MHz), ^{13}C (75.629 MHz) and ^{15}N (30.484 MHz) NMR spectra were recorded on a GE Omega 300WB spectrometer. NMR references are $(CH_3)_4Si$ (^{1}H, ^{13}C) and external NH_4+ NO_3-(^{15}N). The ^{15}N DEPT experiments were run using the standard DEPT sequence [29] assuming a $J(HN) \approx 7$ Hz with a θ pulse of 45° for the mesityl substituted compounds and 20° for the adamantyl substituted compounds. Melting points were obtained on a Thomas-Hoover capillary apparatus and were not corrected. Elemental analyses were performed by Oneida Research Services, Whitesboro, NY.

3.1. *Diethylmagnesium · 1,3-di(1-adamantyl)imidazol-2-ylidene adduct, 2a*

Diethylmagnesium (0.100 g, 1.21 mmol) and 1,3-di(1-adamantyl)imidazol-2-ylidene (**1a**) (0.390 g, 1.16 mmol) were mixed and toluene was added at room temperature. This mixture was stirred for 2 h to obtain a clear solution. The mixture was concentrated, diluted with hexane and cooled at −25°C to yield 0.385 g (79%) of **2a** as colorless crystals with m.p. 145–148°C. ^{1}H NMR (C_6D_6): δ 0.24 (q, $^3J(HH) = 8.15$ Hz, CH_2, 4H); 1.47 (m, $Ad_{4,6,10}$, 12H); 1.91 (t, $^3J(HH) = 8.15$ Hz, CH_3, 6H); 1.93 (m, $Ad_{3,5,7}$, 6H); 2.06 (m, $Ad_{2,8,9}$, 12H); 6.66 (s, NCH, 2H). ^{13}C {^{1}H} NMR (C_6D_6): δ 0.56 (s, CH_2); 15.13 (s, CH_3); 30.31 (s, $Ad_{3,5,7}$); 36.36 (s, $Ad_{4,6,10}$); 44.45 (s, $Ad_{2,8,9}$); 57.76 (s, Ad_1); 116.78 (s, N*C*H); 180.1 (br s, N*C*N). Anal. Found: C, 77.44; H, 9.84; N, 6.56. $C_{27}H_{42}N_2Mg$ calcd.: C, 77.41; H, 10.11; N, 6.69%.

3.2. *Diethylmagnesium · 1,3-dimesitylimidazol-2-ylidene adduct, 2b*

Diethylmagnesium (0.125 g, 1.51 mmol) and 1,3-dimesitylimidazol-2-ylidene (**1b**) (0.405 g, 1.33 mmol) were mixed and toluene was added at room temperature. The color slowly became pale yellow. This mixture was stirred for 3 h, concentrated, diluted with with some hexane and cooled at −25°C. Filtration afforded **2b** as white crystals, 0.320 g (62%), m.p. 360–363°C (dec.). X-Ray quality crystals were grown from concentrated benzene. ^{1}H NMR (C_6D_6): δ −0.78 (br s, CH_2, 4H); 1.12 (br s, CH_3, 6H); 2.10 (s, *o*-CH_3, 12H); 2.15 (s, *p*-CH_3, 6H); 6.07 (s, NCH, 2H); 6.78 (s, *m*-H, 4H). ^{1}H NMR (thf-d_8): δ −1.19 (q, $^3J(HH) = 8.14$ Hz, CH_2, 4H); 0.91 (t, $^3J(HH) = 8.14$ Hz, CH_3, 6H); 2.09 (s, *o*-CH_3, 12H); 2.31 (s, *p*-CH_3, 6H); 6.99 (s, *m*-H, 4H); 7.16 (s, NCH, 2H). ^{13}C NMR (thf-d_8): δ −0.08 (s, CH_2); 14.65 (s, CH_3); 17.98 (s, *o*-CH_3); 21.12 (s, *p*-CH_3); 123.00 (s, NC); 129.59 (s, Mes C-3,5); 136.26 (s, Mes C-2,6); 137.72 (s, Mes C-1); 138.96 (s, Mes C-4); 194.84 (s, NCN). Anal. Found: C, 78.00; H, 8.93; N, 6.81. $C_{25}H_{34}N_2Mg$ calcd.: C, 77.62; H, 8.86; N, 7.24%.

3.3. *Diethylzinc · 1,3-di(1-adamantyl)imidazol-2-ylidene adduct, 3a*

Carbene **1a** (0.670 g, 2 mmol) was dissolved in hexane (30 ml) and diethylzinc (2.00 ml, 1 M solution in hexane) was added at room temperature. A white precipitate formed slowly. This mixture was stirred for 3 h, filtered and the precipitate was collected. Yield 0.710 g (77%), m.p. 169–170°C. The complex was stable in thf and could be recrystallized from toluene. ^{1}H NMR (thf-d_8): δ 0.04 (q, $^3J(HH) = 8.08$ Hz, CH_2, 4H); 1.12 (t, $^3J(HH) = 8.08$ Hz, CH_3, 6H); 1.78 (s, $Ad_{4,6,10}$, 12H); 1.20 (s, $Ad_{2,3,5,7,8,9}$, 18H); 7.36 (s, NCH, 2H). ^{13}C {^{1}H} NMR (thf-d_8): δ 4.29 (s, CH_2); 15.11 (s, CH_3); 30.95 (s, $Ad_{3,5,7}$); 36.79 (s, $Ad_{4,6,10}$); 44.20 (s, $Ad_{2,8,9}$); 58.32 (s, Ad_1); 117.18 (s, N*C*H); 185 (br s, N*C*N). ^{15}N NMR: δ −162.3. ^{1}H NMR (C_6D_6): δ 0.80 (q, $^3J(HH) = 8.04$ Hz, CH_2, 4H); 1.48 (m, $Ad_{4,6,10}$, 12H); 1.85 (t, $^3J(HH) = 8.04$ Hz, CH_3, 6H); 1.93 (m, $Ad_{3,5,7}$, 6H); 2.07 (m, $Ad_{2,8,9}$, 12H); 6.63 (s, NCH, 2H). ^{13}C {^{1}H}

NMR (C_6D_6): δ 4.76 (s, CH_2); 15.57 (s, CH_3); 29.99 (s, $Ad_{3,5,7}$); 35.97 (s, $Ad_{4,6,10}$); 43.59 (s, $Ad_{2,8,9}$); 57.86 (s, Ad_1); 116.01 (s, NCH); 185.00 (br s, NCN). Anal. Found: C, 70.39; H, 9.03; N, 6.06. $C_{27}H_{42}N_2Zn$ calcd.: C, 70.50; H, 9.20; N, 6.09%.

*3.4. Diethylzinc · 1,3-dimesitylimidazol-2-ylidene adduct, **3b***

Carbene **1b** (0.610 g, 2.00 mmol) was dissolved in hexane (30 ml) and diethylzinc (2.00 ml, 1 M solution in hexane) was added at room temperature and stirred for 3 h. A slightly cloudy solution was obtained. This was filtered and concentrated and cooled at −25°C to obtain 0.78 g (91%) of **3b** as colorless crystals, m.p. 150–151°C. ^1H NMR (thf-d_8): δ −0.43 (q, ^3J(HH) = 8.08 Hz, CH_2, 4H); 0.85 (t, ^3J(HH) = 8.08 Hz, CH_3, 6H); 2.12 (s, *o*-CH_3, 12H); 2.34 (s, *p*-CH_3, 6H); 7.01 (s, *m*-H, 4H); 7.32 (s, NCH, 2H). ^{13}C NMR (thf-d_8): δ 4.62 (s, CH_2); 14.01 (s, CH_3); 17.84 (s, *o*-CH_3); 21.12 (s, *p*-CH_3); 123.20 (s, NCH); 129.78 (s, Mes, C-3,5); 135.88 (s, Mes C-2,6); 136.58 (s, Mes C-1); 139.55 (s, Mes C-4); 192.00 (s, NCN). Anal. Found: C, 70.14; H, 7.74; N, 6.12. $C_{25}H_{34}N_2Zn$ calcd.: C, 70.17; H, 8.01; N, 6.55%.

*3.5. X-Ray crystal structure of diethylzinc · 1,3-di(1-adamantyl)imidazol-2-ylidene adduct, **3a***

Formula: $C_{27}H_{42}N_2Zn \cdot C_7H_8$, monoclinic, space group *Cc* (No. 9), $a = 1665.7(3)$, $b = 1396.2(3)$, $c = 1300.6(2)$ pm, $\beta = 103.24(1)°$; $T = -125°C$, $Z = 4$, FW = 552.16, $D_c = 1.233$ g cm^{-3}, μ(Mo) = 8.68 cm^{-1}. Crystal description: amber plate (0.35 × 0.20 × 0.65 mm^3) grown by cooling a toluene solution of **3a**. A total of 7011 reflections were collected, $4.3° \leq 2\theta \leq 55.0°$, data octants: + + +, + + −, + − +, + − −, on a Syntex R3 diffractometer with graphite monochromator using Mo Kα radiation ($\lambda = 71.073$ pm). With 2813 unique reflections of intensity greater than 3.0σ, the structure was solved by automated Patterson analysis (PHASE) and standard difference Fourier techniques. Anomalous terms for zinc were included, biweight $\propto [\sigma^2(I) + 0.0009I^2]^{-1/2}$. There were 332 parameters with all non-hydrogen atoms anisotropic and all hydrogens in fixed positions. The final R factors were $R = 0.035$, $R_w = 0.036$. The final difference Fourier showed the largest residual density to be 0.44 e Å^{-3} near a hydrogen on one of the adamantyls. Further details of the crystal structure are available in the supplementary material deposited with the Cambridge Crystallographic Data Centre.

*3.6. X-Ray crystal structure of diethylmagnesium · 1,3-dimesitylimidazol-2-ylidene adduct, **2b***

Formula: $C_{25}H_{34}N_2Mg$, monoclinic, space group $P2_1/n$ (No. 14), $a = 1227.9(2)$, $b = 1392.7(3)$, $c = 1399.8(2)$ pm, $\beta = 90.55(1)°$; $T = -35°C$, $Z = 4$, FW = 386.87, $D_c = 1.073$ g cm^{-3}, μ(Mo) = 0.81 cm^{-1}. Crystal description: irregular sphere (0.44 × 0.38 × 0.45 mm^3) grown by cooling a benzene solution of **2b**. A total of 4629 reflections were collected, $4.1° \leq 2\theta \leq 50.0°$, data octants: + + +, + + −, on a Syntex R3 diffractometer with graphite monochromator using Mo Kα radiation ($\lambda = 71.073$ pm). With 2214 unique reflections of intensity greater than 3.0σ, the structure was solved by direct methods (SHELXS) and standard difference Fourier techniques. Anomalous terms for magnesium were included, biweight $\propto [\sigma^2(I) + 0.0009I^2]^{-1/2}$. There were 297 parameters with all non-hydrogen atoms anisotropic. All ring hydrogens and those associated with the bridging ethyl group were refined isotropically. The remaining hydrogens were calculated in ideal positions using peaks in the difference map to determine the orientations of methyl groups. The final R factors were $R = 0.051$, $R_w = 0.049$. The final difference Fourier showed the largest residual density to be 0.30 e Å^{-3} near a hydrogen on the terminal ethyl group. Further details of the crystal structure are available in the supplementary material deposited with the Cambridge Crystallographic Data Centre.

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10 For structures of representative imidazolium ions see: (a) 1,3-dimethylimidazolium chloride (ref. 6, supplementary material), (b) 1,3-di(1-adamantyl)imidazolium tetraphenylborate (ref. 5, supplementary material); (c) 1,3-diphenylimidazolium perchlorate: P. Luger and G. Ruban, *Z. Kristallogr., 142* (1975) 177; (d) V. Langer, K. Huml and G. Reck, *Acta Crystallogr., Sect. B, 38* (1982) 298; (e) A.K. Abdul-Sada, A.M. Greenway, P.B. Hitch-

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12 This drawing was made with the KANVAS computer graphics program. This program is based on the program SCHAKAL of E. Keller (Kristallographisches Institute der Universitat Freiburg, Germany), which was modified by A.J. Arduengo III (E.I. du Pont de Nemours & Co., Wilmington, DE) to produce the back and shadowed planes. The planes bear a 50-pm grid and the lighting source is at infinity so that shadow size is meaningful.

13 The best available crystal of **2a** contained a mixture of an ethylmagnesium bromide adduct along with the diethylmagnesium adduct (from ethylmagnesium bromide impurity in the starting material). The bromine content in the bulk was not sufficient to disturb the elemental analysis or NMR spectra but did preclude an accurate X-ray crystallographic structure determination on **2a** with the selected crystal. The crystal chosen for the diffraction experiment contained a bromine atom in a partial occupancy of the methylene position of one of the ethyl groups (i.e. an occasional coordination of CH_3CH_2MgBr rather than $(CH_3CH_2)_2$-Mg). The unit cell was monoclinic, space group $P2_1/n$ (No. 14), $a = 1364.3$, $b = 1384.3$, $c = 1597.0$ pm, $\beta = 105.7°$. There was also a benzene of crystallization. Although the structure could not be satisfactorily refined ($R = 9.21$, $R_w = 9.79$), the final structure obtained was monomeric and similar to **3a**.

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