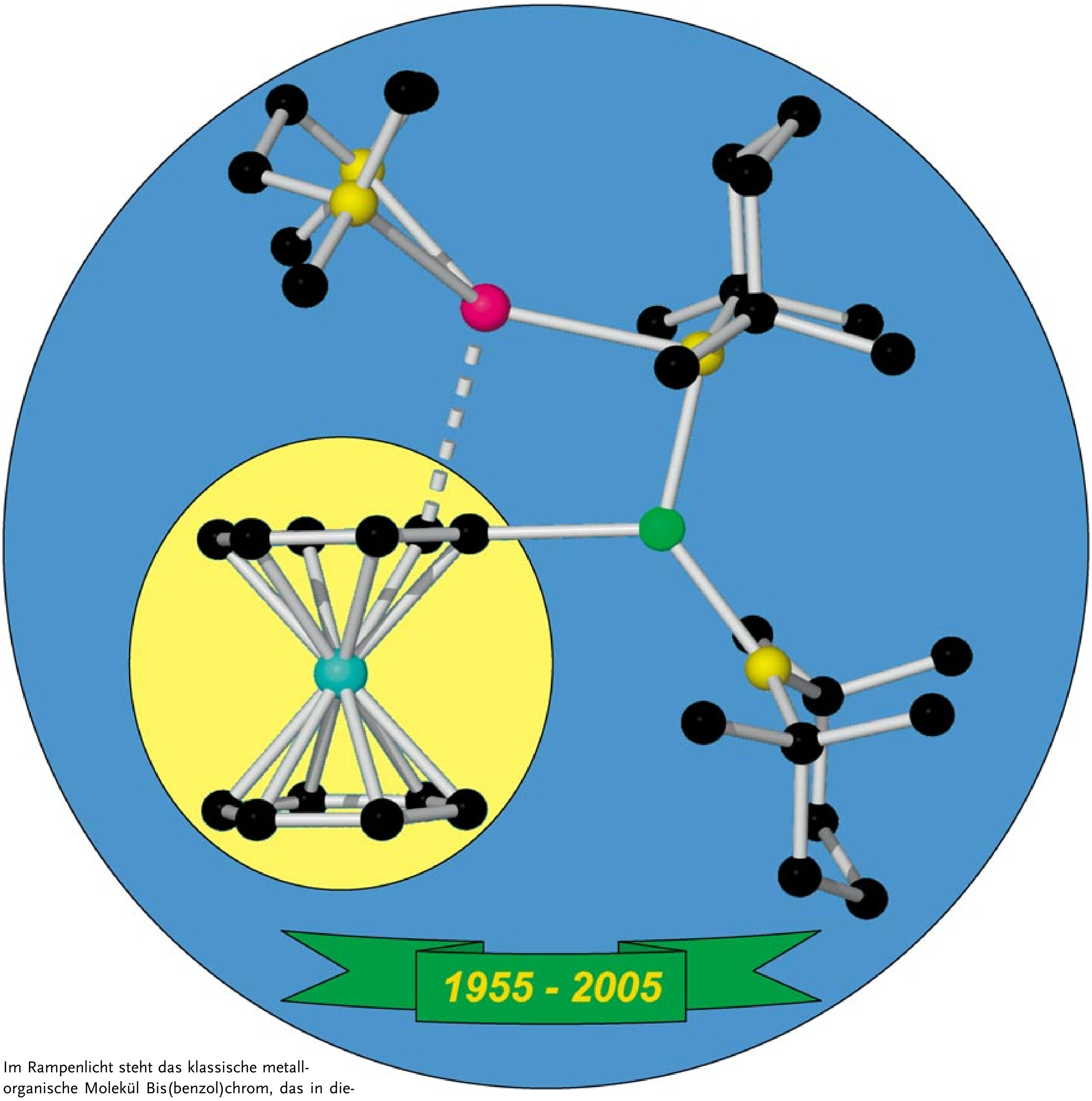
Zuschriften



Im Rampenlicht steht das klassische metallorganische Molekül Bis(benzol)chrom, das in diesem Jahr seinen 50. Geburtstag feiert. Es ist einfach zu dimetallieren, doch seine Monometallierung in präparativem Maßstab war bisher nicht gelungen. Die Verwendung von gemischten Na^+/Mg^{2+}- oder K^+/Mg^{2+}-Basen ermöglicht seine selektive Deprotonierung. Mehr dazu finden Sie in der Zuschrift von R. E. Mulvey et al. auf den folgenden Seiten.

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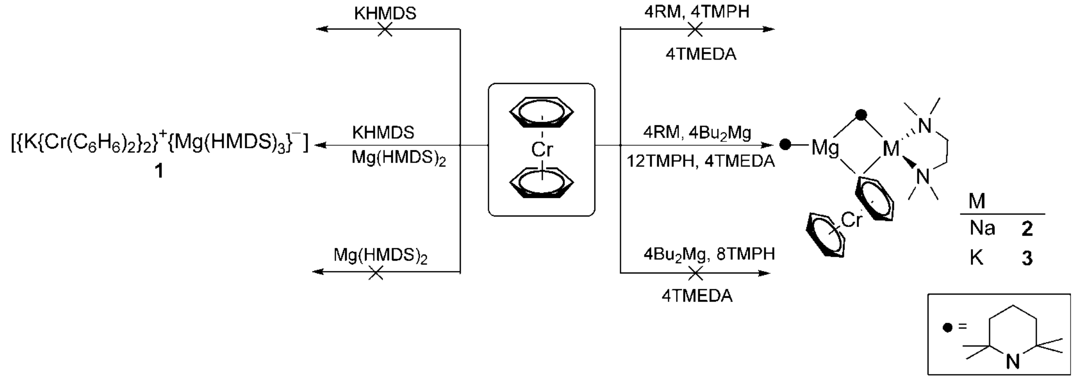
Metalation Reactions

Synergic Monodeprotonation of Bis(benzene)chromium by Using Mixed Alkali Metal–Magnesium Amide Bases and Structural Characterization of the Heterotrimetallic Products**

Eva Hevia, Gordon W. Honeyman, Alan R. Kennedy, Robert E. Mulvey, and David C. Sherrington*

Developed by Elschenbroich in the late 1960s,[1] the reaction of bis(benzene)chromium with TMEDA-activated *n*BuLi still represents today the standard method for metalating the sandwich complex (TMEDA is *N,N,N′,N′*-tetramethylethylenediamine). Metalation plays a pivotal part in the development of bis(benzene)chromium chemistry,[2] which celebrates its 50th anniversary in 2005,[3] as in transforming the parent neutral compound to a more reactive carbanionic form, it opens up a gateway to a plethora of selectively functionalized derivatives.[4] The original lithiation method, which employs a 5:1 molar excess of base, produces mainly the heteroannular dilithio derivative "$[Cr(C_6H_5Li)_2]$" in yields of about 50 % at best, as determined indirectly by mass spectrometric studies of D_2O-quenched reaction mixtures. Lithiation of one benzene ring strongly activates the molecule towards a second lithiation (on the other ring), hence the yield of the monolitho derivative "$[Cr(C_6H_5Li)(C_6H_6)]$" is always much poorer (typically 5–20 %). A lack of crystallographic evidence means that neither lithio reagent has been structurally authenticated, though an analogy with the TMEDA adduct of heteroannular dilithioferrocene $[\{Fe(C_5H_4)_2\}_3Li_6\cdot(TMEDA)_2]$[5] suggests both could be molecularly complex. Following our recent report[6] that ferrocene can be regioselectively tetrametalated by the synergic action of mixed sodium/magnesium tris(diisopropylamide), manifested in the sixteen-membered inverse crown complex $[\{Fe(C_5H_3)_2\}Na_4Mg_4(i\text{Pr}_2N)_8]$, we posed the question "how would such synergic base mixtures behave towards bis(benzene)chromium?". The surprising and contrasting answers to this question when the π-arene complex is subjected to synergic amide mixtures based on either 1,1,1,3,3,3-hexamethyldisilazide (HMDS) or 2,2,6,6-tetramethylpiperidide (TMP) provides the basis for this Communication. Moreover, all of the metal products synthesized in this study have been successfully characterized crystallographically, thus belatedly revealing the first crystal structures of polar metal complexes of bis(benzene)chromium.[7]

In the first synergic trial, treatment of bis(benzene)chromium with an equimolar mixture of potassium HMDS and magnesium bis(HMDS) afforded $[\{\{K\cdot[Cr(C_6H_6)_2]_2\}^+[Mg(HMDS)_3]^-\}_\infty]$ (**1**; Scheme 1). No metalation has taken place during the synthesis, thus reflecting the relatively weak basic character of HMDS, instead the bis(benzene)chromium acts as a π ligand to the K^+ cation, which forms an ion-pair "-ate" complex with the $[Mg(HMDS)_3]^-$ ion. However, this is still a synergic reaction in the sense that neither homometallic component KHMDS or $Mg(HMDS)_2$ reacts unilaterally with bis(benzene)chromium under similar conditions to those employed in the preparation of **1**. In the molecular structure of **1** (Figure 1)[8] two distinct bis(benzene)chromium molecules π bond to the K^+ ion, which, in turn, engages with the $[Mg(HMDS)_3]^-$ ion through $K\cdots CH_3Si(Me_2)$ agostic interactions. One of the bis(benzene)chromium molecules (labeled Cr2) bridges to the K^+ ion of a neighboring molecule, thus extending the structure through a metal-rich $\{K(C_6H_6)Cr(C_6H_6)K'\}$ sandwich and making the K^+ ion four-coordinate overall (counting both the anion and neutral ligands as single coordination points). Disorder in one of the bis(benzene)chromium molecules renders the dimensions in which it is involved meaningless, but other key dimensions are listed in the legend to Figure 1. To the best of our knowledge, the cationic moiety of **1** is unprecedented and as such represents with the other



Scheme 1. Comparative reactions of bis(benzene)chromium with homometallic and heterometallic base mixtures.

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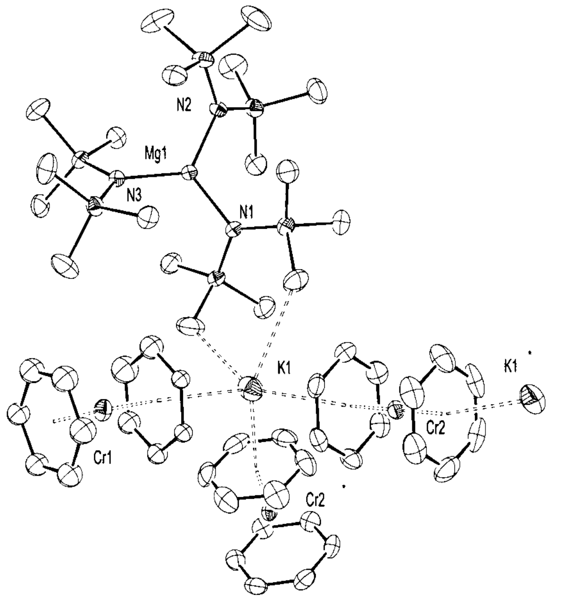

Figure 1. Extended structure of **1** showing the coordination geometry about K1. Hydrogen atoms and disorder components are omitted for clarity. Selected separations [Å] and angles [°]: K1-C33 3.356(3), K1-C34 3.330(3), K1-C38 3.424(3), K1-C39 3.169(4), K1-C40 3.161(3), K1-C41 3.411(3), K1-C1 3.688(3), K1-C4 3.356, C1-K1-Ct2 150.87, C4-K1-Ct2 90.54, Ct1-K1-Ct2 106.42, C1-K1-Ct1 80.03, C4-K1-Ct1 113.59. For the atom labeling scheme refer to cif file.

new complexes reported herein, the first characterized bis(benzene)chromium complexes of any alkali metal. An indirect comparison can be made with the recently reported ferrocene complex $[\{K\cdot[Fe(C_5H_5)_2]_2\cdot(toluene)_2\}^+\{Mg(HMDS)_3\}^-]$.[9]

A distinct change of the reaction solution from brown to deep red gave cause for optimism that metalation had occurred during the synergic trials of the stronger base TMP, as a similar color change accompanies lithiation of bis(benzene)chromium. Composed of butylsodium or benzylpotassium, dibutylmagnesium, TMPH, and TMEDA in a 1:1:3:1 stoichiometry, the synergic base mixture was employed in a 4:1 molar excess with respect to bis(benzene)chromium (Scheme 1). Each reaction afforded a red crystalline product, namely $[NaMg\{Cr(C_6H_5)(C_6H_6)\}(TMP)_2\cdot(TMEDA)]$ (**2**) or $[KMg\{Cr(C_6H_5)(C_6H_6)\}(TMP)_2\cdot(TMEDA)]$ (**3**). Thus, surprisingly, in contrast to the lithiation precedent, these sodium and potassium congeners show metalation (formally magnesiation) selectively on only one ring, leaving the second benzene ring untouched. Even when the molar excess of base is increased to 10:1, **2** and **3** are still the only isolable products, thus indicating that synergic monometalation deactivates the second benzene ring (and the remaining H sites of the phenyl ring) towards metalation. Moreover, the yields of **2** and **3** of the isolated solids (first batch 64 and 67 %, respectively), are unquestionably high for metallo compounds of bis(benzene)chromium, which are usually used in situ without isolation or characterization. Homometallic control reactions that employ the same TMPH/TMEDA mixtures but with only a single metallic reagent (butylsodium, benzylpotassium, or dibutylmagnesium) failed to similarly promote metalation of added bis(benzene)chromium, thus confirming that the selective metalation behind the syntheses of **2** and **3** is also synergic in origin.

The molecular structures of **2** (Figure 2)[10] and **3** (Figure 3)[11] share many common features. These include a central near-planar, four-element MNMgC ring [counting

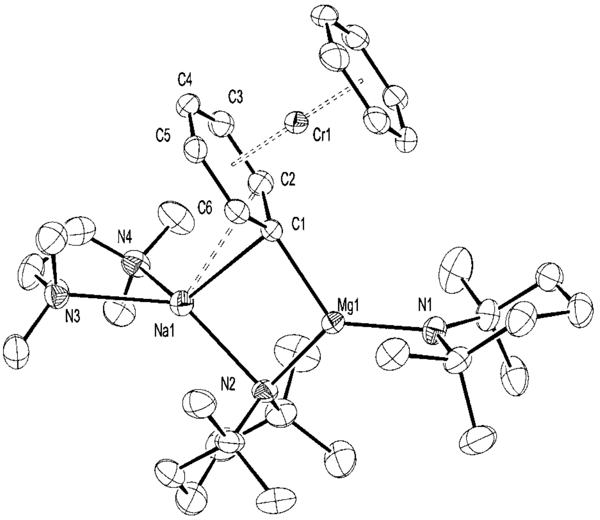

Figure 2. Molecular structure of **2** with hydrogen atoms omitted for clarity. Selected separations [Å] and angles [°]: Na1-N2 2.455(2), Na1-N3 2.515(2), Na1-N4 2.522(2), Na1-C1 2.705(2), Na1-C2 2.910(2), Mg1-N1 2.0032(9), Mg1-N2 2.0825(19), Mg1-C1 2.197(2), N1-Mg1-C1 124.57(8), N1-Mg1-N2 131.09(9), N2-Mg1-Na1 81.83(7), Mg1-N2-Na1 90.51(7), N3-Na1-N4 75.72(7), N2-Na1-N3 133.41(8), N2-Na1-N4 129.66(8), N2-Na1-C1 81.76(7), N3-Na1-C1 119.49(7), N3-Na1-C1 123.17(8).

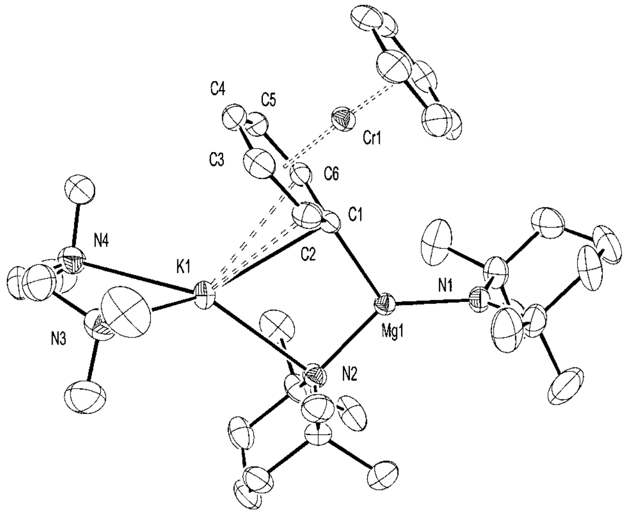

Figure 3. Molecular structure of **3** with hydrogen atoms omitted for clarity. Selected separations [Å] and angles [°]: K1-N2 2.9203(16), K1-N3 2.8313(18), K1-N4 2.8499(18), K1-C1 2.9171(18), K1-C2 3.018(2), K1-C6 3.2279(19) Mg1-N1 2.0018(16), Mg1-N2 2.0857(16), Mg1-C1 2.1720(19),N1-Mg1-N2 132.96(7), N1-Mg1-C1 123.43(7), N2-Mg1-C1 103.54(7), Mg1-N2-K1 94.12(6), Mg1-C1-K1 92.39(6), N3-K1-N4 64.12(5), N3-K1-C1 128.63(5), N4-K1-C1 134.22(5), N4-K1-N2 144.04(5), N3-K1-N2 127.28(5), C1-K1-N2 69.92(5).

bis(benzene)chromium as formally a ligand that coordinates through a single C atom]; a Mg-attached, terminal TMP ligand; and, bidentate TMEDA chelation of the alkali metal (Na or K). Another salient feature, which has become a distinguishing trademark of inverse crown chemistry[12] is the σ/π distinction of the s-block metal–arene bonding, which reflects the relative size, polarizability, and hardness or softness of the particular type of metal atoms involved. Refilling the position vacated by the H atom, the lower polarity Mg atom forms a stronger, more covalent bond with the anionic C center, the predominately σ character of which can be discerned from its near coplanarity with the plane of the phenyl ring [deviation of Mg from plane: 0.005(3) Å in **2**; 0.290(3) Å in **3**]. In contrast, the higher polarity (and softer) alkali-metal atoms occupy skewed positions above the Ph ring to engage electrostatically with its π face. The closest contact is to the anionic C1 center [2.705(2) Å in **2**; 2.917(2) Å in **3**], where charge is most concentrated, and there are other short contacts to proximate atoms, one for Na [2.910(2) Å to C(2)] and, reflecting the larger cation size and softer character, two for K [3.018(2) Å to C(2); 3.228(2) Å to C(6)]. All other M···C(Ph) distances exceed 3.38 Å and 3.44 Å in **2** and **3** respectively. Dimensions involving Mg atoms vary little between **2** and **3** [e.g., Mg–C1, 2.197(2) Å and 2.172(2) Å, respectively; C1-Mg-N2, 104.39(8)° and 103.54(7)°, respectively], which is consistent with Mg being the anchoring metal center that templates the anionic ligand set into a distorted trigonal planar, pseudoate arrangement about it. The TMEDA-chelated M atoms affix loosely to this template to form a contacted ion pair. Interestingly, the shortest interatomic distance for Na is with the μ-N(TMP) atom [2.455(2) Å; the distance to C1 is 0.250 Å longer], whereas for K the corresponding distances are equally short [to C1, 2.917(2) Å; to μ-N(TMP), 2.920(2) Å]. Furthermore, the K–μ-N(TMP) contact is significantly longer than the K–N(TMEDA) distances (mean, 2.841 Å), which is the reverse of that found for Na [mean Na–N(TMEDA) distance, 2.519 Å, compared with 2.455(2) Å for Na-C1]. Hence it can be deduced that the K center has a greater affinity for binding to the softer areneide than to the harder N anion. The close proximity between the terminal TMP ligand and the non-metalated benzene ring, coupled with the overhanging of the TMEDA molecule above the Ph ring, suggest that the simultaneous attachment of a second TMP-Mg-TMP-M-TMEDA coordination arc (concomitant with a second deprotonation) could possibly be ruled out on steric grounds (though electronic factors may also contribute to the inertness of **2** and **3** towards further deprotonation). It must also be stressed that the synergic Na–Mg/K–Mg bases will themselves be extremely sterically demanding, much more so than *n*BuLi. Thus, in the usual lithium reagent methodology there is no such steric control, hence the selectivity of monometalation is lost and dimetalation readily proceeds.

Further studies will address how different synergic bases will behave towards bis(benzene)chromium and, in view of their ready availability in pure crystalline form, whether **2** and **3** (in the mould of the lithio precedents) can be employed as access reagents to monofunctionalized bis(benzene)chromium derivatives.

Experimental Section

All reactions were carried out under a protective argon atmosphere.

Synthesis of **1**: K(HMDS) (2 mL of a 0.5 M solution in toluene, 2 mmol) was added to a solution of $Mg(HMDS)_2$ in heptane, which was prepared in situ by treating $n/s\mathrm{Bu}_2\mathrm{Mg}$ (1 mL of a solution in heptane, 1 mmol) with HMDS(H), (0.422 mL, 2 mmol) at reflux for two hours. The solution was heated at reflux for one hour then left to reach room temperature. Bis(benzene)chromium (0.208 g, 1 mmol) was added and the resulting solution was heated at reflux for another hour. Toluene was added (10 mL) to completely dissolve the dark green precipitate that had formed and the reaction mixture was then heated to reflux for a further hour. The resulting solution was left to cool overnight to facilitate crystallization. A large crop of green/black needle-shaped crystals was obtained. Yield: 34.4 % (0.33 g). M.p.: 228 °C. ^{1}H NMR (400.13 MHz, [D$_8$]toluene, 300 K): $\delta = 0.45$ (s, CH_3, $\mathrm{Mg[N\{Si(}CH_3)_3\}_2]_3$), 4.28 ppm (broad s, $\mathrm{Cr}(\eta^6\text{-}C_6H_6)_2$). ^{13}C{^{1}H} NMR (100.63 MHz, [D$_8$]toluene, 300 K): $\delta = 7.35$ (CH_3, $\mathrm{Mg[N\{Si(CH_3)_3\}_2]_2}$), 74.74 ppm ($\mathrm{Cr}(\eta^6\text{-}C_6H_6)_2$).

Synthesis of **2**: *n*BuNa (0.4 g, 5 mmol) was suspended in hexane (20 mL). $n/s\mathrm{Bu}_2\mathrm{Mg}$ (5 mL of a 1 M solution in heptane, 5 mmol) and TMPH (2.5 mL, 15 mmol) were added. The resulting pale yellow solution was stirred for 30 minutes and TMEDA (0.75 mL, 5 mmol) was introduced. The slightly cloudy pale yellow solution was filtered through Celite and $[\mathrm{Cr}(C_6H_6)_2]$ (0.26 g, 1.25 mmol) was added. The reaction mixture was heated at reflux for 45 minutes and a change from brown to red was observed. Allowing the solution to cool slowly to room temperature produced a crop of red crystals. Yield: 64 % (0.52 g). ^{1}H NMR (400.13 MHz, [D$_8$]thf, 300 K): $\delta = 4.61$ (d, 2H, H_{ortho}, C_6H_5), 4.16 (t, 2H, H_{meta}, C_6H_5), 4.10 (m, 1H, H_{para}, C_6H_5), 4.03 (s, 6H, C_6H_6), 2.30 (s, 4H, CH_2, TMEDA), 2.15 (s, 12H, CH_3, TMEDA), 1.62 (m, 4H, TMP), 1.30 (s, 24H, CH_3, TMP), 1.18 ppm (m, 8H, TMP). ^{13}C{^{1}H} (100.63 MHz, [D$_8$]thf, 300 K): $\delta = 105.4$ (C_{para}, C_6H_5), 88.7 (C_{ortho}, C_6H_5), 79.4 (C_{meta}, C_6H_5), 75.9 (C_{ipso}, C_6H_5), 72.2 (C_6H_6), 59.1 (CH_2, TMEDA), 53.2 (N-*C*, TMP), 46.6 (CH_3, TMEDA), 42.8 (TMP), 36.4 (CH_3, TMP), 21.6 ppm (TMP). An as-yet unidentified minor product with signals at 4.71 (d) 4.22 (m), 4.07 (s) was also present in the ^{1}H NMR spectrum.

Synthesis of **3**: BzK (0.65 g, 5 mmol) was suspended in hexane (20 mL). $n/s\mathrm{Bu}_2\mathrm{Mg}$ (5 mL of a 1 M solution in heptane, 5 mmol), TMPH (2.5 mL, 15 mmol) and TMEDA (0.75 mL, 5 mmol) were added and the resulting mixture was stirred for 1 h affording a slightly cloudy red solution which was filtered through Celite. $[\mathrm{Cr}(C_6H_6)_2]$ (0.26 g, 1.25 mmol) was subsequently added and the reaction mixture was heated under reflux for 45 minutes. Allowing the red solution to cool slowly to room temperature produced a crop of red crystals. Yield: 67 % (0.55 g). (400.13 MHz, [D$_8$]thf, 300 K): $\delta = 4.71$ (d, 2H, H_{ortho}, C_6H_5), 4.16 (t, 2H, H_{meta}, C_6H_5), 4.08 (m, 1H, H_{para}, C_6H_5), 3.98 (s, 6H, C_6H_6), 2.30 (s, 4H, CH_2, TMEDA), 2.15 (s, 12H, CH_3, TMEDA), 1.68 (m, 4H, TMP), 1.28 (s, 24H, CH_3, TMP), 1.23 ppm (m, 8H, TMP). ^{13}C{^{1}H} (100.63 MHz, [D$_8$]thf, 300 K): $\delta = 107.6$ (C_{para}, C_6H_5), 89.3 (C_{ortho}, C_6H_5), 79.6 (C_{meta}, C_6H_5), 76.2 (C_{ipso}, C_6H_5), 71.7 (C_6H_6), 59.3 (CH_2, TMEDA), 53.2 (N-*C*, TMP), 46.5 (CH_3, TMEDA), 42.8 (TMP), 36.5 (CH_3, TMP), 21.8 ppm (TMP).

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[8] Crystal data for **1**: $C_{42}H_{78}Cr_2KMgN_3Si_6$; A yellow tablet of approximate dimensions $0.25 \times 0.12 \times 0.05$ mm gave a monoclinic space group $P2_1/n$, $a = 16.4987(4)$ $b = 14.8080(3)$ $c = 22.7857(5)$ Å, $\beta = 109.571(1)°$, $V = 5245.2(2)$ Å^3, $T = 150$ K, $Z = 4$, $\rho_{calc} = 1.217$ Mg m^{-3}, $2\theta_{max} = 54.96°$, Mo$_{K\alpha}$ $\lambda = 0.71073$ Å. All structures were solved and refined to convergence on F^2 (SHELXS and SHELXL-97, G. M. Sheldrick, University of Göttingen, Germany, **1997**). $R1 = 0.0461$ (for 8234 reflections with $I > 2\sigma(I)$) $wR2 = 0.1107$ and $S = 1.020$ for 562 parameters and 12000 unique reflections. Minimum/maximum residual electron density $-0.509/0.624$ eÅ^{-3}. CCD-238576, 238577 and 238578 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 CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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[10] *Crystal Data* for **2**: $C_{36}H_{63}CrMgN_4Na$; A red fragment of approximate dimensions $0.30 \times 0.30 \times 0.06$ mm gave a triclinic space group $P\bar{1}$, $a = 11.8831(5)$, $b = 12.0196(3)$, $c = 14.7612(6)$ Å, $\alpha = 96.602(2)$, $\beta = 109.447(2)$, $\gamma = 108.630(2)°$, $V = 1825.18(12)$ Å^3, $T = 123$ K, $Z = 2$, $\rho_{calc} = 1.185$ Mg m^{-3}, $2\theta_{max} = 54.16°$, Mo$_{K\alpha}$ $\lambda = 0.71073$ Å. $R1 = 0.0476$ (for 5304 reflections with $I > 2\sigma(I)$) $wR2 = 0.1064$ and $S = 1.012$ for 466 parameters and 7991 unique reflections. Minimum/maximum residual electron density $-0.412/0.281$ e Å^{-3}.

[11] *Crystal Data* for **3**: $C_{36}H_{63}CrKMgN_4$; A red fragment of approximate dimensions $0.35 \times 0.27 \times 0.18$ mm gave a monoclinic space group $C2/c$, $a = 31.4001(7)$, $b = 12.5255(2)$, $c = 21.1754(4)$ Å, $\beta = 115.787(1)°$, $V = 7499.0(2)$ Å^3, $T = 123$ K, $Z = 8$, $\rho_{calc} = 1.182$ Mg m^{-3}, $2\theta_{max} = 54.96°$, Mo$_{K\alpha}$ $\lambda = 0.71073$ Å. $R1 = 0.0413$ (for 6373 reflections with $I > 2\sigma(I)$) $wR2 = 0.1034$ and $S = 1.035$ for 488 parameters and 8590 unique reflections. Minimum/maximum residual electron density $-0.388/0.437$ e Å^{-3}.

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