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Synthesis, Structure, and Methyl Methacrylate Polymerization Activity of a Mixed π-Ferrocene π-Toluene Complex of Potassium Tris(hexamethyldisilazide)magnesiate

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Summary: Treating a toluene solution of mixed potassium−magnesium tris(hexamethyldisilazide) with ferrocene yields a surprising complex exhibiting simultaneous arene and metallocene π-coordination of K^+, which when prepared in situ initiates the polymerization of MMA to give syndio-rich PMMA.

Our recent studies of the reactivity of heterobimetallic (alkali-metal−magnesium) amides toward the most important metallocene, ferrocene, have uncovered some remarkable examples of synergistic deprotonative metalation. The most spectacular example to date has been sodium−magnesium tris(diisopropylamide) "NaMg(N^iPr_2)$_3$"-promoted regioselective 4-fold deprotonation, which transforms ferrocene to an unprecedented 1,1′,3,3′-tetrayl form, stabilized and encapsulated by an azapolymetallic $[(NaNMgN)_4]^{4+}$ cationic ring.[1] Illustrating the profound effect that the identity of the amide can have on the outcome of the reaction, in contrast, switching to 2,2,6,6-tetramethylpiperidide ($Me_2C(CH_2CH_2CH_2)C(Me)_2N^-$; TMP) in "NaMg(TMP)$_3$" promotes 2-fold 1,1′-deprotonation, manifested in the unusual trinuclear ferrocenophane $[\{Fe(C_5H_4)_2\}_3\{Na_2Mg_3(TMP)_2\cdot(TMPH)_2\}]$.[2] A lithium−magnesium partnership has been found to effect the same reactivity to produce the structurally similar $[\{Fe(C_5H_4)_2\}_3\{Li_2Mg_3(TMP)_2\cdot(L)_2\}]$ (L = TMPH, pyridine).[2] While one would not anticipate such deprotonative metalation of ferrocene using the weaker base 1,1,1,3,3,3-hexamethyldisilazide ($(Me_3Si)_2N^-$; HMDS) in a conventional homometallic reaction, the recent intriguing finding that the mixed potassium−zinc system "KZn(HMDS)$_3$" can smoothly convert toluene to a benzyl group in $[\{KZn(HMDS)_2(CH_2Ph)\}_\infty]$[3] stimulated us to check whether the magnesium analogue "KMg(HMDS)$_3$" is active toward ferrocene. As reported here, the outcome is surprising. Thus, the product turns out to be the unprecedented mixed π-metallocene/π-arene ion-separated complex $[\{K(\eta^5\text{-ferrocene})_2(\eta^3\text{-toluene})_2\}^+\{Mg(HMDS)_3\}^-]$ (**1**). We report here its synthesis, crystal structure, and promising preliminary results of its application as an initiator for the anionic polymerization of methyl methacrylate (MMA).

With an inert-atmosphere protocol employed throughout, the synthesis of **1** (Scheme 1) involved first diamination of the commercially available reagent $^{n,s}Bu_2Mg$ with 2 molar equiv of the silylamine HMDS(H) and second an addition reaction with KHMDS to generate in situ the tris(amide) "KMg(HMDS)$_3$". Finally ferrocene (1 molar equiv) and then toluene (in a large excess) were introduced into the hydrocarbon solution to complete the synthesis of orange-yellow crystalline **1**.[4] The good yield obtained with respect to ferrocene consumption (76.1%) could not be significantly improved upon by using 2 molar equiv of the metallocene in the reaction mixture, commensurate with the stoichiometry of **1**. As in the original synthesis the yield of **1** with respect to "KMg(HMDS)$_3$" consumption is only 38.05%, it can be deduced that more than half of the available tris(amide) starting material remains in solution. This is almost certainly due to solvation by toluene, as we have previously crystallized $[\{KMg(HMDS)_3\cdot 2(\text{toluene})\}_\infty]$ (**2**) from ferrocene-free solutions containing concentrations of toluene much lower than that used in the synthesis of **1**.[5] It is also worth noting that the peroxide variant $[\{K_2Mg_2(O_2)(HMDS)_4\}_\infty]$,[6] a member of the inverse crown ether family,[7] has also been previously isolated

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(2) Henderson, K. W.; Kennedy, A. R.; Mulvey, R. E.; O'Hara, C. T.; Rowlings, R. B. *Chem. Commun.* **2001**, 1678.

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(4) Yield: 2.09 g, 76.1% (with respect to ferrocene). Melting point: 190−192 °C. Anal. Found: C, 52.02; H, 7.85; N, 3.75. Calcd for $[\{K(Cp_2Fe)_2\cdot 2(\text{toluene})\}^+\{Mg(N\{Si(Me)_3\}_2)_3\}^-]$: C, 56.78; H, 8.19; N, 3.82. The elemental analysis may be affected by loss of solvent upon isolation of the solid.

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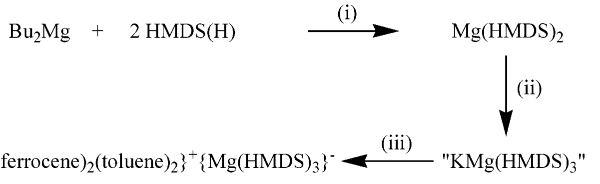
Scheme 1 [a]



(**1**)

[a] Legend: (i) heptane/hexane, 25 °C, −2BuH; (ii) added KHMDS in toluene; (iii) added ferrocene and more toluene, heated orange solution to reflux.

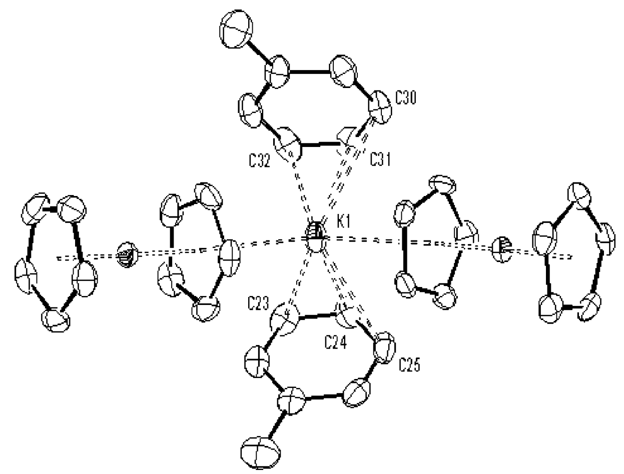


Figure 1. Molecular structure of the cationic moiety of **1**. Thermal ellipsoids are drawn at the 40% probability level; hydrogen atoms are omitted for clarity. Selected bond lengths (Å): K(1)−C(6), 3.195; K(1)−C(7), 3.248(4); K(1)−C(8), 3.236(4); K(1)−C(9), 3.193(4); K(1)−C(10), 3.168(4); K(1)−C(11), 3.144(4); K(1)−C(12), 3.141(4); K(1)−C(13), 3.202(4); K(1)−C(14), 3.224(4); K(1)−C(15), 3.197(4); K(1)−C(24), 3.252(5); K(1)−C(23), 3.317(4); K(1)−C(25), 3.359(4); K(1)−C(31), 3.241(4); K(1)−C(30), 3.385(4); K(1)−C(32), 3.263(4).

from oxygen- and moisture-contaminated hydrocarbon solutions of the tris(amide).

X-ray crystallographic studies of **1** revealed a discrete ion-pair (potassium−magnesiate) structure.[8] The cationic moiety (Figure 1) is mononuclear, with K^+ surrounded by two ferrocene and two toluene ligands. When the ligands are counted as single coordination sites, K^+ occupies a distorted-tetrahedral geometry (mean centroid−K−centroid angle of 109.04°), the smallest and largest such angles being associated with ferrocene−K−ferrocene (106.08°) and toluene−K−toluene (115.03°) contacts, respectively. The greater electron-donating ability of ferrocene (formally through a Cp^- anion) and closer steric approach can also be seen in its shorter K···centroid distances (mean 2.964 Å; cf. 3.143 Å for toluene). Each ferrocene molecule forms five nearly equivalent K−C bonds spanning a narrow range (0.080 and 0.083 Å for the Fe1 and Fe2 molecules, respectively); thus, the interactions are unequivocally both η^5 in character. Both toluene molecules bind more asymmetrically to K^+, with the closest approaches at the unsubstituted end of the aryl ring, suggesting that steric factors (Me > H) outweigh electronic ones (i.e., the electron-donating effect of the Me substituent). The shortest such contacts are to para C atoms (mean 3.247 Å) and the next shortest to both meta C atoms within each toluene molecule (mean 3.331 Å). Progressively longer contacts are found for the ortho, ipso, and methyl C atoms (mean values 3.517, 3.635, and 4.627 Å, respectively). While defining the hapticity of $K^+{-}\pi$ interactions can sometimes be an arbitrary decision, the pattern of K−C lengths exhibited here suggests that the toluene ligands coordinate in a limited η^3 manner, reflecting the high degree of steric crowding about K^+. The anionic moiety of **1** $[Mg(HMDS)_3{}^-]$ (not shown) is well-known.[5] It adopts its usual near-perfect trigonal-planar Mg geometry (N−Mg−N bond angles 120.08(12), 120.51(12), 119.41(12)°) with noneclipsed $Me_3SiNSiMe_3$ branches. The Mg−N bond lengths (2.024(3), 2.025(3), 2.029(3) Å) are unremarkable.

To the best of our knowledge, there is no precedent for the cationic arrangement within **1**. It represents the first complex with a crystallographically characterized K−ferrocene bond (of any type) and the first mixed π-metallocene/π-arene complex of K^+ (or indeed of any alkali-metal cation). Also, examples of ferrocene acting as a π-donor to main-group metals are, surprisingly, extremely rare, though one was recently reported for gallium.[9] For an analogy to **1**, one has to look to monocyclopentadienylpotassium $[(CpK)_\infty]$ (**3**).[10] Although **3** has a markedly different polymeric zigzag chain arrangement, the interconnections between the chains produce a distorted-tetrahedral K^+ center comprising two η^5- and two η^2-bonded Cp rings, not unlike the situation in **1**. However, the K^+−toluene π coordinations in the aforementioned **2** bear little resemblance to those in **1**, being η^6 in character (as opposed to η^3) with lengths in the range 3.124−3.345 Å. In the absence of ferrocene ligands, the K^+ cation in **2** supplements its coordinative requirements by interacting agostically with Me groups of HMDS (range of lengths 3.128(2)−3.399(2) Å). There are no corresponding K^+···Me contacts in **1** (all such contacts exceed 3.9 Å in length).

Preliminary studies on the use of solutions of **1** as an initiator for the anionic polymerization of methyl methacrylate (MMA) have revealed some intriguing results. Thus, making **1** in situ exclusively in toluene solution and then adding an aliquot of this solution to a 100-fold excess of MMA in bulk THF solvent produces PMMA quantitatively. The syndiotacticity content of this PMMA is found to be unusually high (84%) for a quantitative polymerization run at ambient temperature, as side reactions are expected to be pronounced

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(7) Mulvey, R. E. *Chem. Commun.* **2001**, 1049.

(8) Crystallographic data for **1**: $C_{52}H_{90}Fe_2KMgN_3Si_6$, orange block of approximate dimensions 0.25 × 0.12 × 0.06 mm, monoclinic, space group $P2_1/c$, $a = 12.0176(2)$ Å, $b = 22.4722(3)$ Å, $c = 23.2871(4)$ Å, $\beta = 99.293(1)°$, $V = 6206.4(2)$ Å^3, $T = 150$ K, $Z = 4$, $\rho_{calcd} = 1.178$ Mg m^{-3}, $2\theta_{max} = 53.5°$, λ(Mo Kα) = 0.710 73 Å. The structure was solved, and refined on F^2, using programs of the Shelx family (Sheldrick, G. M. Shelx; University of Göttingen, Göttingen, Germany, 1997) to convergence at R1 = 0.0693 (for 6963 reflections with $I > 2\sigma(I)$), wR2 = 0.1651, and $S = 1.023$ for 726 parameters and 12 844 unique reflections. The highest residual electron density was 0.394 e Å^{-3}. H atoms of the aryl rings were refined isotropically, but all other H atoms were placed in calculated positions and in riding modes. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC 226147. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax (+44) 1223-336-033; e-mail deposit@ccdc.cam.ac.uk).

(9) Scholz, S.; Green, J. C.; Lerner, H.-W.; Bolte, M.; Wagner, M. *Chem. Commun.* **2002**, 36.

(10) Dinnebier, R. E.; Behrens, U.; Olbrich, F. *Organometallics* **1997**, *16*, 3885.

under such comparatively warm conditions. This performance betters that of ethyl α-lithioisobutyrate at 0 °C used in toluene in the presence of activating organoaluminum amide additives (up to 75% syndiotacticity).[11] This result is also comparable with the excellent syndiotacticities (89−90%) noted recently for a samarium phenoxide initiator at −78 °C.[12] However, the promise of the solution of **1** as an initiator is severely tempered by the high average molecular weight (565 200; cf. the theoretical value of 10 000) and broad polydispersity (1.49) of the syndio-rich PMMA, as determined by SEC analysis. This is consistent with a slow rate of initiation coupled with a fast rate of propagation or perhaps some decomposition process, both of which would lead to longer than (theoretically) expected, but fewer polymeric chains. That notwithstanding, it is of interest to ponder the nature of the initiating species within solutions of **1**. Formally, the anion is [Mg(HMDS)$_3$$^-$], which could be viewed as a HMDS$^-$ nucleophile with a Mg(HMDS)$_2$ additive.[13] However, control polymerizations using KMg(HMDS)$_3$ and KHMDS, carried out under the same conditions as for **1** but in the absence of ferrocene, show much reduced syndiotactic contents of 44% and 31%, respectively, though the yields are similar.[14] Hence, it can be concluded that the countercation in **1** (or more accurately the presence of ferrocene) has a direct and major bearing on the observed high syndiotacticity. Furthermore, the different results obtained for the three HMDS-based initiators mean that this counterion is not simply [K$^+$·xTHF], as might have been anticipated when the bulk solvent is medium-polarity THF. Accordingly, studies are being undertaken to pair the cation in **1**, [K(η^5-ferrocene)$_2$(η^3-toluene)$_2$]$^+$, with a more nucleophilic anion, to generate an initiator that will maintain the high syndiotacticity of **1** but facilitate faster initiation.

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Supporting Information Available: Text giving full experimental details and polymerization data and tables giving atomic coordinates, anisotropic displacement parameters, and bond lengths and angles for **1**: crystallographic data are also available as a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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[11] Péron, G. L.; Peace, R. J.; Holmes, A. B. *J. Mater. Chem.* **2001**, *11*, 2915.

[12] Nodono, M.; Tokimitsu, T.; Makino, T. *Macromol. Chem. Phys.* **2003**, *204*, 877.

[13] For a relevant paper on lithium HMDS and other amide initiators, see: Couper, S. A.; Mulvey, R. E.; Sherrington, D. C. *Eur. Polym. J.* **1998**, *34*, 1877.

[14] Yield of polymer using **1**: 2.8 g (100%). Tacticity: isotactic, 0.9%; heterotactic, 15.4%; syndiotactic, 83.7%. SEC data: M_n, 379 100; M_w, 565 200; M_w/M_n, 1.491. Corresponding values for KMg(HMDS)$_3$ and KHMDS initiation, respectively, are as follows. Yield of polymer: 2.8 g (100%) and 2.6 g (91.8%). Tacticity: isotactic, 8.2 and 11.5%; heterotactic, 47.5 and 57.4%; syndiotactic, 44.3 and 31.1.