Polymer Supported 'Magnesium(anthracene)': Effective in Forming Benzylic Grignard Reagents (*via* Electron Transfer Reactions)

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A polymer supported 'magnesium(anthracene)' (**4**) has been prepared from the reaction in tetrahydrofuran (thf) of [Mg(anthracene)(thf)$_3$] (**1**) with polystyrene bearing –9-CH$_2$SiMe$_2$(C$_{14}$H$_9$) groups (**3**); the green paramagnetic solid, containing dianion and radical anion anthracene sites, yields Grignard reagents (>90%) with benzylic halides in thf *via* electron transfer reactions, as does the model compound for the dianion sites, *viz.* [Mg{9-PhCH$_2$SiMe$_2$(C$_{14}$H$_9$)}(thf)$_2$] (**6**).

[Mg(anthracene)(thf)$_3$] (**1**) (thf = tetrahydrofuran),[1] affords Grignard reagents in high yield when treated with benzylic halides.[2] The solutions of these Grignard reagents, however, are loaded with anthracene, discouraging the use of this method despite the frequent failure of the classical method of Grignard formation, and even the use of highly activated magnesium,[3] for benzylic halides. We report the synthesis of a polymer supported 'magnesium(anthracene)' complex and its utility in forming Grignard reagents with benzylic halides in thf, *via* electron transfer reactions, which can be separated from the spent polymer by filtration.

The anthracene functionalized polymer (**3**) (Scheme 1) was prepared by treating the Grignard reagent of chloromethylated polystyrene[4] (microreticular BIO-RAD S-X1, 1.38 mequiv. g^{-1}, *ca.* 1.0% cross linked; swollen in thf) with 9-(chlorodimethylsilyl)anthracene‡ at 0 °C (>95% yield from weight gain; residual chlorine $\leqslant$0.12 mequiv. g^{-1}). The Grignard reagent was prepared using (**1**) as a soluble source of magnesium, as recently reported by independent workers.[4] Treatment of (**3**) with (**1**) results in uptake of magnesium and formation of a dark green paramagnetic solid, (**4**) (g = 2.0030). The electron transfer from (**1**) to the anthracene groups in the polymer is consistent with the expected higher electron affinity of anthracene bearing a polarizing, electropositive silicon atom.[5] No reaction was evident between (**3**) and highly activated magnesium prepared using both Rieke's method,[6] and the equilibration of magnesium with a catalytic amount of anthracene, where the intermediate implied is (**1**).[7] Compound (**5**),§ used to model the reaction of polymer (**3**), with (**1**) (or magnesium) yields a diamagnetic solid (**6**)¶ consisting of dianions which presumably bind to the metal

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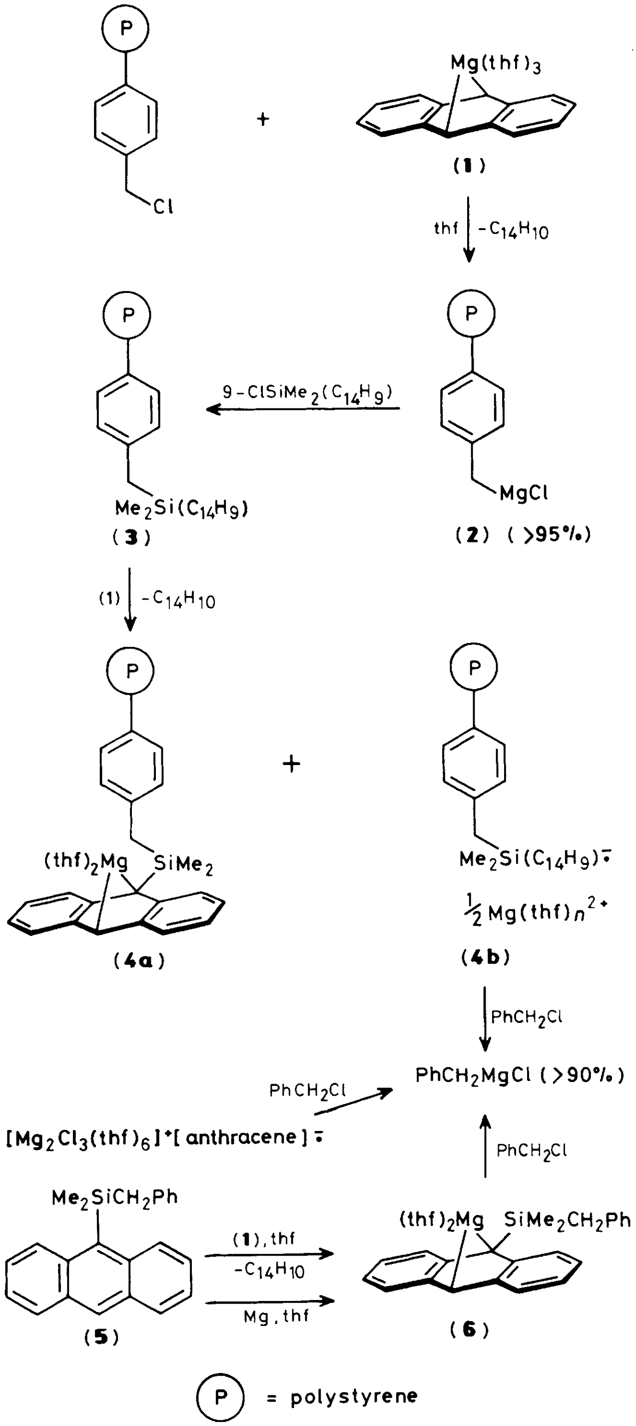
‡ 9-(Chlorodimethylsilyl)anthracene was prepared from 9-lithioanthracene and dichlorodimethylsilane in 80% yield (m.p. 62—64 °C, satisfactory spectroscopic data obtained).

§ Compound (**5**) was prepared from 9-(chlorodimethylsilyl)anthracene and benzyl magnesium chloride in 73% yield (m.p. 56—58 °C, satisfactory spectroscopic data obtained).

¶ (**6**): Yield 93% using magnesium, or 87% using (**1**). *Characterization*: C, H, Mg analysis, and protonolysis in CCl$_4$ to confirm the ratio of Mg to thf.



Scheme 1

centres through C-9 and C-10 as in (**1**)[8] and other substituted anthracene compounds.[1d,9]

Polymer (**4**) appears to contain dianion (**4a**) and radical anion (**4b**) anthracene groups in the ratio *ca.* 1 : 1. This follows from (i) the quantity of (**1**) consumed, (ii) analytical data and the weight increase of the polymer, assuming that the dianions are bound to $[Mg(thf)_2]^{2+}$ and that the radical anions are associated with the authenticated species $[Mg(thf)_6]^{2+}$ (ref. 10) {*cf.* $[Mg(thf)_6]^{2+}(\text{fluoranthene}^{\cdot-})_2$ (ref. 1d)}, and (iii) the activity of the polymer, determined by the quantity of (**4**) required for Grignard reagent formation (see below). The fact that radical centres are present in (**4**) but not in (**6**) may arise from the close proximity of the anthracene groups in (**4**), blocking electron transfer and magnesium uptake because of space limitations and/or electrostatic constraints in building up two negative charges per anthracene moiety.

Polymer (**4**) affords Grignard reagents with benzylic halides, >90% at *ca.* 0.1 mol dm^{-3}, *e.g.* with benzyl chloride and 1,2-bis(chloromethyl)benzene. The latter was used as a test for the synthesis of Grignard reagents using 'magnesium-(arene)' compounds because of the difficulty in preparing the di-Grignard reagent using elemental magnesium.[11] The high yields obtained (determined by the method of ref. 2) show that (**4a**) and (**4b**) are effective in the formation of Grignard reagents, suggesting that electron transfer reactions prevail, *e.g.* $RX \rightarrow RX^{\cdot-}$. (The accepted mechanism of classical syntheses of Grignard reagents involves electron transfer processes.[12]) Further support for this comes from the reaction of benzylic halides with (**1**) in thf to give deep green solutions containing radicals (most likely anthracene$^{\cdot-}$) that persist until Grignard reagent formation is complete,[2] and with $[Mg_2Cl_3(thf)_6]^+[\text{anthracene}^{\cdot-}]$,[9a] based exclusively on radical anions, to give Grignard reagents (Scheme 1). Radical anion–alkali metal compounds also yield organometallic reagents with certain organic halides *via* electron transfer reactions.[13] While (**4**) yields Grignard reagents, we note that the uptake of magnesium by polymer (**3**) diminishes by *ca.* 10% after each successive use.

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