

Polymer supported alkali metal naphthalenides: application in the generation of lithium and sodium reagents

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Polymer supported lithium and sodium naphthalenide complexes are prepared from the reaction of THF solutions of lithium and sodium biphenylide with polystyrene bearing $-\text{CH}_2\text{SiMe}_2(1-\text{C}_{10}\text{H}_7)$ groups, generating highly coloured paramagnetic material, which afford lithium and sodium reagents in high yield when treated with organic halides, nitriles and phosphates.

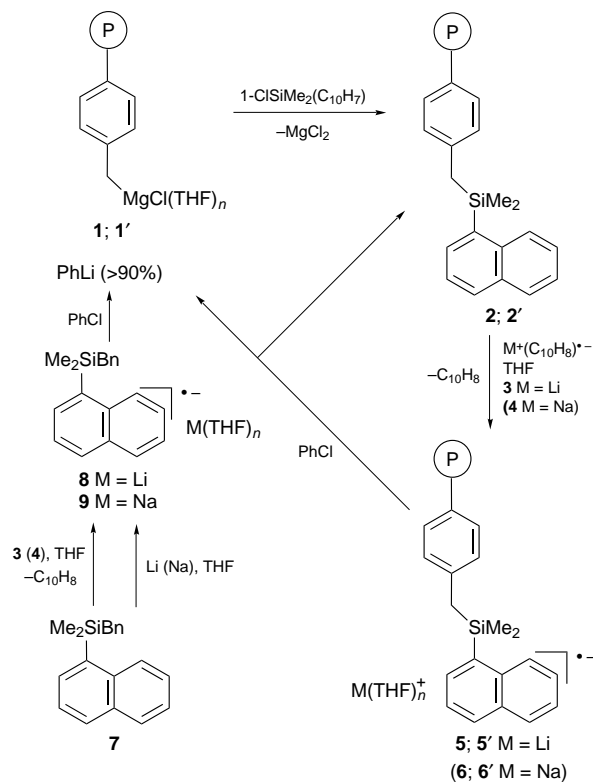
Lithium arene radical anion complexes afford organic lithium complexes in high yield;¹ the solutions of these reagents, however, are loaded with the arene by-product. Yus *et al.*² have developed a method for the preparation of lithium reagents by the reaction of lithium powder with catalytic amounts of arene (1–2%), resulting in a reduced amount of the by-product. A strategy that completely avoids generating solutions containing the arene is the use of supported lithium reagents. This is developed herein for polymer supported lithium reagents, along with analogous supported sodium reagents, due to their utility in generating lithium and sodium reagents which can be separated from the spent polymer by simple filtration. This work follows from our success in developing synthetically useful polymer^{3,4} and silica⁵ supported magnesium anthracene. These act as a source of magnesium in the generation of anthracene-free benzylic Grignard reagents.

The naphthalene functionalised polymer **2**; **2'** (Scheme 1) was prepared by the treatment of a THF slurry of the Grignard reagent of chloromethylated polystyrene^{3,6} (microporous BIO-RAD S-X1, 1.34 mmol g⁻¹ **1** and 4.11 mmol g⁻¹ **1'**, 1.0% crosslinked) with an excess of 1-(chlorodimethylsilyl)naphthalene[†] at 0 °C, in greater than 95% yield based on weight increase (assuming two THF molecules attached to the metal centre), IR studies and analysis for residual chlorine content of < 0.3 mmol g⁻¹. Solutions of lithium biphenylide **3** in THF (or DME) were added to THF (or DME) slurries of polymers **2**; **2'** resulting in the formation of a red–brown paramagnetic material ($g_{\text{av}} = 2.0034, 2.0035/\text{THF}$; $g_{\text{av}} = 2.0029, 2.0026/\text{DME}$) of polymer supported lithium naphthalenide **5**; **5'**. Similarly addition of a THF (or DME) solution of sodium biphenylide **4** to THF (or DME) slurries of polymers **2**; **2'** resulted in the formation of a red–brown paramagnetic material ($g_{\text{av}} = 2.0034, 2.0035/\text{THF}$; $g_{\text{av}} = 2.0029, 2.0100/\text{DME}$) of polymer supported sodium naphthalenide **6**; **6'**. Lithium and sodium biphenylide were chosen as the electron transfer reagents because of the lower reduction potential of biphenyl (–2.70 V *vs.* SCE) relative to that of naphthalene (–2.50 V *vs.* SCE), thus favouring transfer from the biphenyl to naphthalene;⁷ the presence of the silyl group on naphthalene in the polymer would further favour electron transfer since silicon stabilises charge by polarisation.⁹ No reaction was evident between **2**; **2'** and activated lithium powders.

In an attempt to model the reaction of the functionalised polymers, 1-(benzyl dimethylsilyl)naphthalene[‡] **7** was prepared. Reaction with lithium or sodium metal yielded a deep green paramagnetic solution of lithium[1-(benzyl dimethylsilyl)naphthalene](THF)_n **8**, ($g_{\text{av}} = 2.0028$) and sodium[1-(benzyl dimethylsilyl)naphthalene](THF)_n **9**,

($g_{\text{av}} = 2.0028$) respectively (Scheme 1). Complexes **8** and **9** were also prepared by the reaction of **7** with THF solutions of **3** and **4** respectively.

EPR spectra of the polymer supported alkali naphthalenides **5** and **6** were obtained at room temperature in THF. The EPR spectrum of **5** is shown in Fig. 1(a), the simulated spectra in Fig. 1(b). The spectrum appears as a multiplet ($g_{\text{av}} = 2.00275$) with hyperfine coupling. Extensive simulation using SOPHE¹⁰ indicated the multiplet arises from the coupling of two equivalent lithium atoms [$A(^7\text{Li}) = 2.327(4) \times 10^{-4} \text{ cm}^{-1}$], four equivalent protons [$A(^1\text{H}) = 1.310(4) \times 10^{-4} \text{ cm}^{-1}$] and two other equivalent protons [$A(^1\text{H}) = 2.424(4) \times 10^{-4} \text{ cm}^{-1}$] to a single unpaired electron. Consequently, the EPR spectrum arises from an unpaired electron delocalised over two lithium centres rather than a contact ion pair involving a lithium and a radical anion. Polymer supported magnesium anthracene has radical anion sites with the divalent magnesium accounting for a pair of radicals.^{3,4} The EPR spectrum of polymer supported sodium naphthalenide also gave a multiplet with hyperfine coupling, in this case there is a broadening of the signals, resulting in difficulty in the simulation. The broadening may arise from dipole–dipole interaction of the sodium atoms a phenomenon seen in sodium zeolite systems.¹¹



Scheme 1

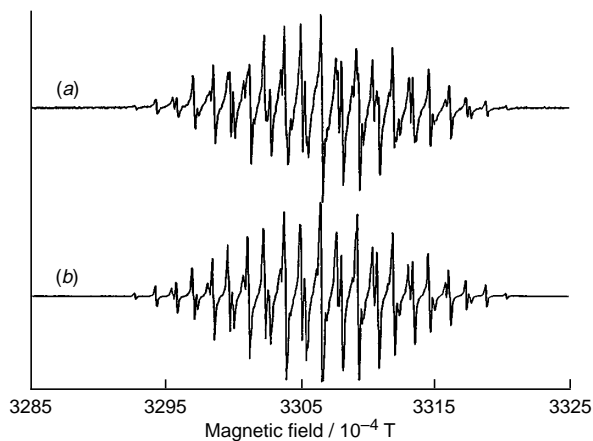


Fig. 1 EPR spectra of polymer supported lithium naphthalenide **5**: (a) experimental ($\nu = 9.2776$ GHz) and (b) simulated spectra

Polymer **5**; **5'** affords lithium reagents with a range of organic halides [e.g. chlorobenzene, 9-chloroanthracene, 2-(3'-chloropropyl)-2-methyl-1,3-dioxalane, 3-chloro-1-phenylpropan-1-ol], organo nitriles (acetonitrile, benzonitrile) and triorgano-phosphates [O=P(OR)₃, R = Et, Ph] in >75% yield at ca. 0.1 m. These reactions are based on two different methods. The first involves the formation of the organoalkali, which is then quenched to give the desired complex.[§] The second reaction involves the quenching of the organoalkali complex *in situ*, in a Barbier-type[¶] reaction. Reaction of **8** and **9** with 0.5 equiv. of chlorobenzene or 9-chloroanthracene both gave the corresponding lithium or sodium complexes, respectively.

The spent polymers **2**; **2'** were tested for recycling potential and overall the uptake of lithium from **3** and the yield of lithium reagents obtained differ only slightly over successive cycles. As an example, for three such cycles for **5** the uptake of lithium from **3** was successively 110, 100 and 100% with the corresponding yields of lithiobenzene at 93, 91 and 89% (based on titrations). Each cycle involved quenching **5** with chlorobenzene, separating the polymer and washing it with THF followed by treatment with **3** to regenerate a deep red polymer. Investigations into the use of the sodium naphthalene polymer to generate the sodium reagent of chlorobenzene were also undertaken, with yields of >80%. This work has also been extended to the use of metal oxide supported complexes.¹²

The main advantages in using polymers **5**; **5'** and **6**; **6'** in generating lithium and sodium reagents, which is possible for a variety of substrates, are that the reactions are high yielding, and the reaction mixtures are free of arene by-products. The ability to recycle the polymers is also noteworthy, as is the fact that the supported polymers offer a means of delivering a small amount of the equivalent of a Group 1 metal.

We thank the Australian Research Council for support of this work.

Footnotes

† 1-(Chlorodimethylsilyl)naphthalene was prepared by quenching 1-lithio-naphthalene with excess dichlorodimethylsilane.⁸

‡ 1-(benzylidimethylsilyl)naphthalene **8** was prepared by the treatment of benzylmagnesium chloride with **2**, in Et₂O in 66% yield (bp 137 °C, 0.5 mmHg, satisfactory spectroscopic and analytical data obtained).

§ In a typical experiment the organic halide in THF was slowly added over 20 min to a THF slurry of the polymer supported lithium naphthalenide at -78 °C. This resulted in the dissipation of the red colour of the polymer supported lithium naphthalenide and the formation of an orange solution. The solution was stirred for a further 1–3 h then filtered to give the arene free organoalkali. In all cases target concentrations of the resulting lithium reagent were close to 0.1 m. For example the lithium reagent of chlorobenzene was generated in >95% yield (by titration) with quenching by chlorotrimethylsilane affording trimethylsilylbenzene in 90% yield as the exclusive product.

¶ A mixture of the organic halide and electrophile in THF was slowly added over 45 min to a THF slurry of the polymer supported lithium naphthalenide at -30 or 0 °C. This resulted in the dissipation of the red colour and the formation of a pale yellow solution. The resulting solution was then stirred for 15 min, filtered, and the solution hydrolysed and the product extracted into Et₂O and purified by distillation. As an example, benzonitrile gave trimethylsilylbenzene in 75% yield as the only product.

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Received, 9th September 1996; Com. 6/06181H