$BiPh_3$—A convenient synthon for heavy alkaline-earth metal amides†

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Received (in Cambridge, UK) 24th April 2008, Accepted 16th June 2008
First published as an Advance Article on the web 31st July 2008
DOI: 10.1039/b806948d

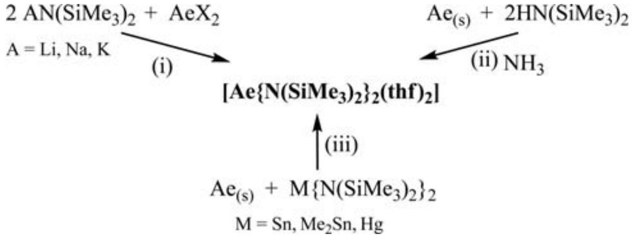
Environmentally friendly, commercially available $BiPh_3$ reacts with heavy alkaline-earth metals (Ae) and bulky trimethylsilylamines to give the corresponding amides $[Ae\{N(SiMe_3)(R)\}_2(thf)_n]$ (R = $SiMe_3$, 2,4,6-$Me_3C_6H_2$, 2,6-$^iPr_2C_6H_3$) in good yields, providing proof of concept for a general synthetic method.

Heavy alkaline-earth metal bis(bis(trimethylsilyl)amides), $[Ae\{N(SiMe_3)_2\}_2]_n$, are attractive synthetic reagents in protolysis reactions[1,2] owing to the high pK_a of $HN(SiMe_3)_2$.[3] Thus, they can provide an invaluable pathway to otherwise elusive heavy Group 2 metal–organic complexes.[1] However, the most common synthetic routes to the amides (Scheme 1)[2] are associated with several disadvantages. Metathesis (i) requires either expensive reagents or prior synthesis of air-sensitive reactants, and the incomplete precipitation of alkali metal halides can lead to their incorporation in the product. Synthesis by halide metathesis can also give rise to a product that is significantly contaminated with '-ate' impurities that are difficult to detect spectroscopically.[4] Method (ii) requires use of either liquid or gaseous ammonia, while (iii) requires prior synthesis of air-sensitive reactants.

An alternative is to use redox transmetallation/ligand exchange reactions (RTLE) between a metal, a diarylmercurial and a protic agent. This methodology, now well established in lanthanoid chemistry,[5] is effective in the synthesis of $Ln\{N(SiMe_3)_2\}_2$ (Ln = Sm, Yb)[6] complexes and has been successfully extended to the formation of pyrazolates and formamidinates of the heavy alkaline-earth metals (eqn (1)).[7]

$$2M + nHgAr_2 + 2nLH \rightarrow 2ML_n + 2nArH + nHg \qquad n = 2,\ M = Ln,\ Ae;\ n = 3,\ M = Ln \quad (1)$$

To establish the general applicability of this RTLE approach and to open up a new route to $Ae\{N(SiMe_3)_2\}_2$ complexes we conducted a series of NMR scale reactions using metal filings (Ca, Sr, Ba), diphenylmercury and two equivalents of $HN(SiMe_3)_2$ in D_8-thf. Under ultrasonication, all reactions showed clean and quantitative conversion to the respective amides in under 30 h. However, from a toxicological and environmental perspective it would be highly desirable to replace the diarylmercurial by a derivative of a less toxic metal. Successful transmetallation/ligand exchange reactions between highly electropositive metals and kinetically inert organometallic compounds (*e.g.* organomercurials and organotins) are thermodynamically driven, requiring a large overall difference in the free enthalpies of formation.[8,9] ΔH_f° values for organobismuth compounds are endothermic,[8,10] indicating analogous reactions to those of Hg should be feasible. This prompted us to investigate the use of $BiPh_3$ (ΔH_f° *ca.* 115 kcal mol^{-1}),[10] a reagent that has the advantages of being inexpensive, air and moisture stable, and of very low toxicity (LD_{50} $BiPh_3$, 180 g kg^{-1} {dog, oral})[11] (eqn (2)).



Scheme 1 Three of the most common synthetic routes to alkaline-earth metal amides (Ae = Ca, Sr, Ba); solvent thf.[2]

$$Ae_{(s)} + 2\,HN(SiMe_3)(R) \xrightarrow[thf]{{}^2/_3\,BiPh_3} [Ae\{N(SiMe_3)(R)\}_2(thf)_n] + 2\,C_6H_6 + {}^2/_3\,Bi_{(s)} \quad (2)$$

Whilst the target Ae amides are air sensitive, there is the convenience of using a starting material that can be handled and stored without special precautions. In addition, we estimate that RTLE reactions employing $BiPh_3$ cost around 4–8% (metal dependent) of corresponding metathesis syntheses.† It was anticipated that the more electropositive nature of the heavy alkaline-earth metals would mitigate the poorer performance of $BiPh_3$ relative to $HgAr_2$ observed in earlier redox transmetallation reactions with rare-earth metals.[12] Accordingly, we now report the excellent performance of $BiPh_3$ in the synthesis of the alkaline-earth amides $[Ae\{N(SiMe_3)_2\}_2(thf)_2]$ (Ae = Ca, Sr, Ba)[2] and $[Ae\{N(SiMe_3)(R)\}_2(thf)_n]$ (R = 2,4,6-$Me_3C_6H_2$ (Mes)[13] or 2,6-$^iPr_2C_6H_3$ (Dipp), n = 2,3).[14] This success with such sterically challenging systems means the method should be widely applicable.

Initial synthetic attempts using $BiPh_3$‡ with metal pieces and a series of amines under reflux conditions, only gave the heaviest alkaline-earth amides after extended reaction times despite the use

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† Electronic supplementary information (ESI) available: X-ray powder diffraction data confirming the identity of **1–3**, ^1H NMR data for **1–3** and **7–9**, ^1H NMR spectrum of the reaction mixture, calculations of the costs of RTLE *vs.* metathesis reactions, a graphical representation of compound **5**, as well as geometrical details for compounds **5** and **6**. CCDC 655775 and 655776. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b806948d

Table 1 Yields (%) of $[Ae\{N(SiMe_3)(R)\}_2{\cdot}(thf)_n]$ complexes

Compound	R	Ae	*n*	A	B	C
1	$SiMe_3$	Ca	2	70	75	70
2	$SiMe_3$	Sr	2	80	85	80
3	$SiMe_3$	Ba	2	85	90	85
4	Mes	Ca	2	80	75	70
5	Mes	Sr	2	85	80	75
6	Mes	Ba	3	89	85	80
7	Dipp	Ca	2	50	50	k
8	Dipp	Sr	2	55	55	k
9	Dipp	Ba	2	60	65	60, k

[l] A = reflux; 1 drop Hg; metal pieces, **1–3** (4–5 d), **4–6** (18–21 d), **7–9** (21–29 d); B & C = ultrasound; metal filings; B = 1 drop Hg, **1–3** (1.5 d), **4–6** (2.5–3 d), **9** (4–5 d); C = No Hg added **1–3** (2.5 d), **4–6** (4 d), **9** (6 d); k = quantitative yields (determined *in situ* by ^{1}H NMR spectroscopy in D_8-thf), **7** and **9** (4 d), **8** (7 d).

of mercury activation; five days for $HN(SiMe_3)_2$, 21 days using $HN(SiMe_3)(Mes)$ and 29 days for $HN(SiMe_3)(Dipp)$ (Table 1, Path A). Subsequent syntheses focused on increasing the metal surface area of the Ae metals and the use of sonication (Table 1, Path B). Path B led to excellent product yields and purity with significantly shortened reaction times but did not provide the sought after "less-toxic" synthetic strategy. In a major breakthrough, optimised reaction conditions, *using metal filings, sonication in the absence of Hg*, afforded the target compounds; $[Ae\{N(SiMe_3)(R)\}_2(thf)_n]$ (R = $SiMe_3$, Ae = Ca, **1**; Ae = Sr, **2**; Ae = Ba, **3**; R = Mes, Ae = Ca, **4**; Ae = Sr, **5**; Ae = Ba, **6**; and R = Dipp, Ae = Ca, **7**; Ae = Sr, **8**; Ae = Ba, **9**; $n = 2$ except **6**, $n = 3$) in only marginally reduced yields and with only a slight increase in reaction time (Table 1, Path C). Thus, we achieved our goal of developing a novel and effective environmentally benign synthetic route to alkaline-earth amides. A major advantage of the RTLE method is that the filtered final reaction solution is suitable to be used for reactions of the Ae amides without need for their isolation.

Data provided in Table 1, Path C, indicate a clear correlation between product yield and ligand bulk, with a need for longer reaction times to obtain comparable yields when using larger ligands. In the case of compounds **7**, **8** and **9** the syntheses were followed by ^{1}H NMR spectroscopy in D_8-thf to assess yields for possible use as *in situ* reagents, and quantitative conversions were observed each time (*e.g.* Fig. 1).§ As representative, **9**, was isolated in good yield from a preparative scale reaction.

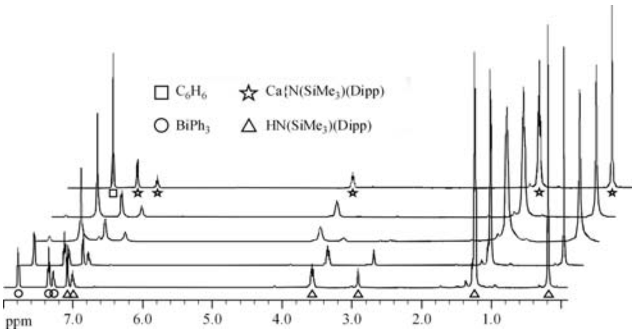

Fig. 1 ^{1}H NMR spectra in D_8-thf of the reaction of excess Ca with 2/3 $BiPh_3$ and 2 $HN(SiMe_3)(Dipp)$. Spectra recorded (from bottom to top) after 0, 2, 4, 6 and 8 days.

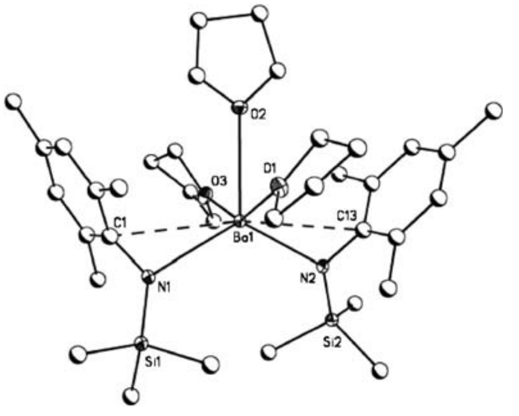

Fig. 2 Computer-generated plot of the structure of **6** with anisotropic displacement parameters depicting 30% probability for all non-carbon atoms and showing the agostic interactions. Bond lengths and angles are given in ESI.†

The necessity of $BiPh_3$ as a reactant was established from experiments between Ae metal pieces and two equivalents of $HN(SiMe_3)_2$ in thf under reflux conditions, or using metal filings under ultrasound. Both approaches gave no reaction. Adding one drop of Hg did not change this outcome, confirming that direct metallation does not proceed without pre-activation of the metal with NH_3 (Scheme 1, method (ii)).[2]

This novel route has now allowed for the clean preparation and structural characterisation of the hitherto elusive $[Ae\{N(SiMe_3)(Mes)\}_2(thf)_n]$ (Ae: Sr, $n = 2$, **5** (see graphical abstract); Ba, $n = 3$, **6**, see Fig. 2).¶ Their structures have four (**5**) and five (**6**) coordinate metal centres that achieve coordinative saturation by several secondary interactions. In **5**, one of the aryl substituents forms an η^2,π-interaction (Sr–C 2.884(2), 3.284(1) Å), and provides a weak agostic interaction from a methyl group (C7–Sr 3.447(2) Å). The second aryl ring shows one π-interaction (Sr–C 3.105(2) Å) and there is a weak agostic interaction originating from the $SiMe_3$ group (C24–Sr 3.573(2) Å). Compound **6** displays one significant π-interaction to each aryl ring (3.205(2) and 3.140(2) Å).

Actual mechanistic details have not yet been established. However, the reactions studied by NMR spectroscopy provide some evidence that highly reactive Ae(Ph)X species are formed which subsequently undergo protolysis to give the corresponding organoamides. All ^{1}H NMR spectra show benzene formation, and many display relatively small, transient aryl resonances suggestive of the formation of short-lived active intermediates.

There are literature precedents for the formation of Ae(Ar)X species at low temperatures *e.g.* Ca(Ph)H,[15] $CaPh_2$[16] and Ca(Ar)I,[17a] which then readily decompose, and the isolation, or stabilisation in solution, of complexes bearing bulky ligands; $[Ca(Ph)\{N(SiMe_3)_2\}(thf)_3]$,[17b] $[Ca\{2,4,6\text{-}Me_3C_6H_2\}_2(thf)_3]$[18] and $[Ae(C_6F_5)(2,6\text{-}Ar_2C_6H_3\text{–}N\text{–}N{=}N\text{–}C_6H_4\{2\text{-}Ar'\})]$ (Ae = Ca, Sr, Ba; Ar = $2,4,6\text{-}Me_3C_6H_2$, Ar′ = $2,4,6\text{-}{}^iPr_3C_6H_2$).[19] Supporting the proposal of reactive aryl metal intermediates, $[Eu(C_6F_5)_2(thf)_5]$,[20a] $[Yb(C_6F_5)_2(thf)_4]$[20b] and $[LnPh_3(thf)_3]$[12b,20b] (Ln = Er, Ho, Yb) have been isolated and characterised from corresponding redox transmetallation reactions between Ln metals and mercurials in the absence of protic agents. An obvious driving force for the RTLE reaction is the liberation of benzene as dictated by the relative acidities of $HN(SiMe_3)(R)$ (*ca.* 30)[3] *vs.* C_6H_6 (*ca.* 43).[21]

If the thermodynamic acidities are an important factor in driving the protolysis reactions then it should be possible to extend the application of the methodology to carbon-based ligand systems, thereby bypassing the need for the amides as reactive intermediates. The Hg-free reaction of Cp*H with Ba in the presence of $BiPh_3$ gives a good yield of the known[22] $[Ba(Cp^*)_2(thf)_2]$ **10** within 60 h providing a glimpse of the breadth of synthetic possibilities of the $BiPh_3$ system.

In summary, these studies establish redox transmetallation/ligand exchange as an exciting new synthetic route to alkaline-earth metal amides and cyclopentadienides. This can be achieved using either $BiPh_3$ or $HgPh_2$, both commercially available reagents, with excellent conversions under relatively mild and convenient conditions, in some cases outperforming previous syntheses. Whilst $HgPh_2$ offers reduced reaction times, $BiPh_3$ provides a significantly less toxic and more environmentally attractive approach for future RTLE reactions.[23]

We acknowledge funds from the Australian Research Council and the National Science Foundation.

Notes and references

‡ All manipulations were carried out under purified N_2 employing standard Schlenk and glovebox techniques. $HN(SiMe_3)R$ (R = Dipp, Mes) were synthesised using a previously reported method.[24] Ae metals were filed manually in the glovebox. Compounds **1–10** were prepared using RTLE involving $BiPh_3$. In addition **1–3** were prepared using $HgPh_2$. In a typical experiment 4.0 mmol of metal filings (Ca = 0.16 g; Sr = 0.35 g, Ba = 0.55 g) and 1.2 mmol (0.53 g) of $BiPh_3$ were stirred in thf (40 mL). 3.6 mmol of amine [$HN(SiMe_3)(R)$: R = $SiMe_3$, 0.58 g; R = Mes, 0.75 g; R = Dipp, 0.89 g] or HC_5Me_5 (0.49 g) was then added slowly followed by sonication for between 2.5 and 7 days (Table 1). All volatiles were then removed under vacuum and the residue treated with hexane (50 mL). Filtration through a Celite padded filter frit afforded a faint yellow solution. X-Ray quality crystals were obtained after storage at −23 °C for a few days. Compounds **1–4** and **7–10** were identified by comparison of spectra with those of samples from previous syntheses, in addition, **1–3** were identified by comparison with calculated X-ray powder patterns. Compound **5**: $[Sr\{N(SiMe_3)(Mes)\}_2(thf)_2]$ (0.93 g, 75%); mp 80–85 °C; ^1H NMR (300 MHz, $[D_6]$benzene, 25 °C): δ 0.41 (s, 18H, $SiMe_3$); 1.14 (s, 8H, thf); 2.23 (s, 6H, *p*-CH_3Ar); 2.38 (s, 12H, *o*-CH_3Ar); 3.08 (s, 8H, thf); 6.91 (s, 4H, Ar–H). IR (Nujol): ν_{max}/cm^{-1} 2923 (s), 2722 (s), 1461 (w), 1376 (w), 1302 (w), 963 (w). **6**: $[Ba\{N(SiMe_3)(Mes)\}_2(thf)_3]$ (1.11 g, 80%); mp 60–65 °C; ^1H NMR (300 MHz, C_6D_6, 25 °C): δ 0.42 (s, 18H, $SiMe_3$); 1.30 (s, 12H, thf); 2.23 (s, 6H, *p*-CH_3Ar); 2.32 (s, 12H, *o*-CH_3Ar); 3.30 (s, 12H, thf); 6.93 (s, 4H, Ar-H). IR (Nujol): ν_{max}/cm^{-1} 2936 (s), 2723 (s), 1461 (w), 1376 (w), 1302 (w), 1297 (w), 1260 (w), 963 (w). Compound **10**: $[Ba(Cp^*)_2(thf)_2]$ crystallized from thf (0.65 g, 65%).

§ *NMR studies*: 2.0 mmol of metal filings (Ca = 0.08 g; Sr = 0.18 g, Ba = 0.28 g) and either 0.50 mmol (0.18 g) of $HgPh_2$ and 1.00 mmol of $HN(SiMe_3)_2$ (0.16 g) or 0.33 mmol (0.15 g) of $BiPh_3$ and 1.00 mmol of $HN(SiMe_3)(Dipp)$, (0.25 g) were mixed in D_8-thf (0.75 mL) in a NMR tube sealed with a Young's tap and sonicated. ^1H NMR spectra were collected several times until the reactions were completed. All reactions showed quantitative conversions based on amine consumption and amide formation. For example, a ^1H NMR scale reaction in D_8-thf with Ba filings, $HN(SiMe_3)_2$ and $BiPh_3$ showed complete conversion of the $BiPh_3$ peaks (d, 7.65 ppm; t, 7.22 ppm; t, 7.27 ppm) to C_6H_6 (7.24 ppm); $Ba\{N(SiMe_3)_2\}_2$ was also identified (s, 0.017 ppm). The black residue from the reaction was washed 2–3 times with degassed toluene to eliminate unreacted $BiPh_3$ and then oxidized and shown to be Bi by EDAX.

¶ (a) *Crystal data* for **5**: $C_{32}H_{56}N_2O_2Si_2Sr$, $M = 644.59$, space group $P2_1/n$ (no. 14), $a = 12.191(2)$, $b = 15.350(2)$, $c = 19.413(2)$ Å, $\beta = 91.321(3)°$, $V = 3632.1(8)$ Å^3, $T = 95(2)$ K, $Z = 4$, 38 062 reflections collected, 9062 independent reflections ($R_{int} = 0.0439$), $R_1 = 0.0367$ (7320 observed data) and $wR_2 = 0.0884$ (all data). (b) *Crystal data* for **6**: $C_{36}H_{64}N_2O_3Si_2Ba$, $M = 766.41$, space group $C2/c$ (no. 15), $a = 17.1615(10)$, $b = 12.2957(7)$, $c = 38.200(2)$ Å, $\beta = 90.792(10)°$, $V = 8059.8(8)$ Å^3, $T = 104$ K, $Z = 8$, 41 841 reflections collected, 9999 independent reflections ($R_{int} = 0.0307$), $R_1 = 0.0318$ (9058 observed data) and $wR_2 = 0.0739$ (all data). Both structures were solved and refined using SHELXTL-Plus program package.[25] CCDC 655775 **6** and 655776 **5**.

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