The Synthesis of Metal Organic Compounds of Calcium, Strontium and Barium by Ammonia Gas-saturated Ethereal Solvents

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The activation of the alkaline earth metals Ca, Sr and Ba in ammonia gas-saturated ethereal solvents at room temperature leads to rapid reaction with hexamethyldisilazide, pentamethylcyclopentadiene, triphenylsilanol, phenylacetylene, and triphenylmethane to yield the corresponding silamide, metallocene, siloxide, phenylacetylide and triphenylmethyl derivatives; ESR spectroscopic studies of the reaction system have detected the presence of solvated electrons.

The chemistry of the heavier alkaline earth metals (Ca, Sr and Ba) is dominated by the predominately ionic character of their compounds. Research in this area of main group chemistry is currently undergoing a renaissance. Previous workers have used a wide range of techniques to activate these metals. Notably, the reduction of the metal iodides in tetrahydrofuran with potassium has had reasonable success yielding reactive finely divided metal powders,[1] whilst other workers have used metal vapourisation techniques,[2a] metal halide metathesis,[2b] and the activation of the metals with either iodine or by amalgamation.[2c]

Until recently few organic derivatives of these elements had been prepared, let alone structurally characterised, this being largely due to the insolubility of such compounds in organic solvents (presumably this arises from their polymeric nature). The metal–cyclopentadienyl complexes $[M(\eta\text{-}C_5Me_5)_2]$ (M = Ca,[3] Sr[4] and Ba[5]) have been characterised in the gas phase,

and in the solid state the complexes $[Ba(C_5Me_5)_2]$,[6] $[Sr\{(\eta\text{-}C_5Me_3(SiMe_3)_2\text{-}1,3\}_2(thf)]$,[7] and $[Ca(OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4)_2\text{-}(thf)_3]$ (thf = tetrahydrofuran).[2a] These complexes are all monomeric and may be contrasted with oligomeric species $[\{Ca(C_5H_5)_2\}_\infty]$,[8] $[Sr_4(OPh)_8(HOPh)_2(thf)_6]$,[9] $[Ba_6H_4(\mu_6\text{-}O)\text{-}(OCH_2CH_2OMe)_{14}]$[10] and $[Ba_5H(\mu_5\text{-}O)(OPh)_9(thf)_8]$.[11]

We now report that activation of the metals Ca, Sr and Ba in ammonia gas-saturated ethereal solvents with the appropriate ligands *in situ* leads to a rapid reaction in high yield at room temperature (see Table 1). It is well known that the alkali metals dissolve in liquid ammonia to yield solvated metal ions and electrons; less well known and indeed poorly described in the literature is the corresponding chemistry of the alkaline earth metals with ammonia.[12] In dilute ammonia solutions, evidence suggests that solvated M^{2+} ions (M = Ca, Sr and Ba) and electrons are formed, whilst at higher concentrations the metal ammoniates, *e.g.* $Ba(NH_3)_6$, may be obtained.[12]

Table 1 Products obtained from the reaction of metal granules[a] with suitable organic ligands in the presence of NH_3 gas saturated THF[b]

Metal	Reagent	Time/h	Product	Yield (%)	Ref.
Ca	$(Me_3Si)_2NH$	20	$[Ca(N\{SiMe_3\}_2)_2(thf)_2]$	69	c
Ca	Ph_3SiOH	16	$[Ca_3(OSiPh_3)_6(thf)_2]$	73	d
Ca	C_5Me_5H	17	$[Ca(C_5Me_5)_2(thf)_2]$	75	e
Sr	$(Me_3Si)_2NH$	11	$[Sr\{N(SiMe_3)\}_2(thf)_2]$	90	d
Sr	PhCCH	10.5	$[Sr(CCPh)_2(thf)_4]$	76	d
Sr	Ph_3SiOH	10	$[Sr_3(OSiPh_3)_6(thf)_2]$	100	d
Sr	Ph_3CH	15	$[Sr(CPh_3)_2(thf)_4]$	78	f
Ba	C_5Me_5H	5.5	$[Ba(C_5Me_5)_2(thf)_2]$	84	g
Ba	Ph_3SiOH	5	$[Ba_3(OSiPh_3)_6(thf)]$	86	h
Ba	PhCCH	8	$[Ba(CCPh)_2(thf)_4]$	82	d
Ba	Ph_3CH	8.5	$[Ba(CPh_3)_2(thf)_4]$	80	f

[a] Obtained from Alfa Chemicals and not pretreated. [b] Typical reaction conditions involve the use of 10 mmol of metal and 20 mmol of ligand in 25 ml of THF, with the NH_3 gas bubbled into the solution for ca. 10–15 min at room temperature. [c] See refs. 2. [d] New compound with satisfactory spectroscopic and analytical data. [e] See ref. 3. [f] See ref. 14. [g] See refs. 5 and 6. [h] See ref. 16.

Solutions of these metals in liquid ammonia have previously been used in reactions with organic ligands containing acidic protons, and have generally resulted in moderate yields at best, owing to the eventual formation of insoluble '$M(NH_2)_2$' on work-up. It is known that NH_3 gas dissolves in ethereal solvents (diethyl ether, tetrahydrofuran etc.), toluene and benzene at room temperature to yield saturated solutions containing $\geqslant 25\%$ ammonia.[13] To date this phenomenon has found little synthetic utility, but an application is presented herein.

A preliminary survey of some reactions has shown that the ammonia gas-assisted reactions are generally more rapid than those based on other techniques previously described[1–4] with these metals (see Table 1). Barium metal (as granules) was found to react smoothly with C_5Me_5H at room temperature in high yield, using ammonia gas-saturated tetrahydrofuran, to yield $[Ba(C_5Me_5)_2(thf)_2]$. This may be contrasted with the observation that bulk Ba does not react with C_5Me_5H.[1] Comparable reactions and yields are also obtained for the corresponding calcium and strontium metallocenes.

The reaction of triphenylsilanol with either strontium or calcium metals was found to be very fast, with 10 mmol of metal consumed in <20 h at room temperature to yield the trimeric species $[M_3(OSiPh_3)_6(thf)_2]$. It should be noted that there is no reaction with this ligand using either thermal activation or by using a high energy ultrasonic gun. The alternative use of iodine or $HgCl_2$ catalysts which are known to activate metal surfaces were also found to be unsuccessful.

These colourless, air- and moisture-sensitive solids are the first hydrocarbon-soluble calcium and strontium siloxides to be reported. On sublimation they yield polymeric siloxide $[\{M(OSiPh_3)_2\}_\infty]$ species which may be converted back to the thf adducts on dissolution in this solvent.

The synthesis of the bis-triphenylmethyl metal complexes $[M(CPh_3)_2(thf)_4]$ (M = Ca, Sr or Ba) is 5–10 times more rapid than the corresponding synthesis using metal amalgams.[14] These organometallic products may be obtained with variable amounts of thf and have been characterised as the tetrakis-thf adducts.[14]

The formation of other complexes containing sterically hindered ligands such as hexamethylsilamide produces high yields of the monomeric complexes $[M(N\{SiMe_3\}_2)_2(thf)_2]$ (where M = Ca and Sr) under very mild conditions. This process alleviates the use of hydrocarbyl exchange reactions used extensively by Lappert and coworkers.[2a] This reaction may be contrasted with the previous route to the Ca derivative involving either metal vaporization techniques or refluxing the reactive calcium powder with the ligand in thf.[2a]

All three metals react vigorously with phenylacetylene at room temperature to yield the acetylides $[M_2(CCPh)_2(thf)_4]$ (where M = Ca, Sr and Ba) in high yield. These complexes have previously been prepared in low yield by using the metal

dissolved in liquid ammonia (ca. 200 ml) to form the metal amide, which was subsequently treated with phenylacetylene to yield the unsolvated species $M(CCPh)_2$.[15] The calcium adduct was previously noted to have a low solubility in thf; preliminary observations show that its solubility in hydrocarbon solvents is enhanced by the use of stronger Lewis bases such as tmeda ($Me_2NCH_2CH_2NMe_2$) or HMPA $[(Me_2N)_3P=O]$.
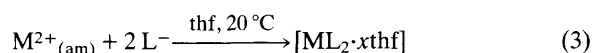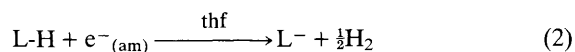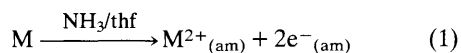
The overall reactivity sequence follows the sequence Ba > Sr > Ca, which is not altogether surprising given the fact that barium is more electropositive than Ca by 0.2 eV. This may be contrasted with the reverse behaviour of these metals using the Rieke method to form activated metal powders.[1] This may be due to incomplete reduction of the barium halides to the activated metal powders and or presence of unreacted barium iodide which may lower their effective reactivity.

Finally, we have studied the mechanism of the reactions discussed here. We postulated that the ammonia gas would react in ethereal solutions with the alkaline earth metals to yield solvated dications and electrons as occurs in bulk liquid ammonia.[12] Experiments with barium metal granules in ammonia gas-saturated tetrahydrofuran at 0 °C revealed a pale blue coloured solution stable from 77 to 300 K. ESR spectra were obtained on frozen solutions over the temperature range 77–200 K, and were entirely reproducible after thawing and then refreezing. Only one signal is apparent, with no hyperfine coupling being observed between the unpaired spin and the nuclear spin of any nuclei. The signal is observed at $g = 2.0024 \pm 0.0005$ (regardless of metal used and is relative to a diphenylpicrylhydrazyl standard). The line widths and line shapes are found to be temperature dependent over the range 77–200 K, and to diminish slowly in intensity with progressive warming. Such result imply that one or more radical-based species are present in this reaction. Microwave power-saturation studies at 77 K showed in fact that there was only one type of radical present.[18]

As to the nature of the species present, one strong possibility is that we are observing solvated electrons, since both g factors and linewidths (ΔH_{pp}) are in close agreement with those in the literature [eqn. (1)].[17,19] Alkali metals (e.g. sodium) are also known to dissolve in mixed ether–NH_3 solvent systems, with formation of solvated electrons.[17] No signals due to electron–cation pairs were observed, and this may be attributed to the high dilutions ($<10^{-4}$ mol l^{-1} of metal dissolved at any one time) used in the above system and is in accord with previous results for alkali metals.[18,20]

We have further investigated the reaction mechanism operating for these metal–ligand systems in ammonia-saturated tetrahydrofuran and observed similar ESR spectra, further strengthening the case for the presence of solvated electrons. When the reaction is carried out in the presence of a ligand LH, a mechanism involving reduction by the ammonia-

cal electrons [$e^-_{(am)}$] to yield L^- may be proposed [as shown in eqn. (2)]. This may be followed by the interaction of the ammoniacal dication [$M^{2+}_{(am)}$] and the anion L^- to yield the product [$ML_2 \cdot x$THF] [eqn. (3)].

$$M \xrightarrow{\text{NH}_3/\text{thf}} M^{2+}_{(am)} + 2e^-_{(am)} \qquad (1)$$

$$L\text{-}H + e^-_{(am)} \xrightarrow{\text{thf}} L^- + \tfrac{1}{2}H_2 \qquad (2)$$

$$M^{2+}_{(am)} + 2\,L^- \xrightarrow{\text{thf, 20 °C}} [ML_2 \cdot x\text{thf}] \qquad (3)$$

It may be noted that the bulk metals fail to react with any of the organic ligands used in this study either on prolonged reflux or by the use of an ultrasonic gun as mentioned earlier. Thus, ammonia gas-saturated ethereal solutions of the alkaline earth elements Ca, Sr and Ba may be considered the method of choice when preparing organometallic compounds of these elements. This is especially true when usii , sterically hindered ligands such as Ph₃SiOH and (Me₃ .

The extension of this technique to other metals k ɔ dissolve in liquid ammonia, such as europium and ytterbium is currently being explored. Further studies into the effects of the solvent and Lewis bases on the above reaction especially with regard to increases in reaction rate are presently being investigated.

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