

Preparation of Activated Calcium, Strontium, and Barium Powders by Reduction of Alkaline Earth Di-iodides

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Reduction of heavy alkaline earth (Ca, Sr, Ba) di-iodides with metallic potassium in tetrahydrofuran precipitates finely divided metal powders which react rapidly with triphenylmethyl chloride, $\text{Me}_5\text{C}_5\text{H}$, fluorinated acetylacetonates, and phenols to generate the corresponding alkyl metal halides, metallocenes, acetylacetonates, and aryl oxides.

The use of finely divided metal powders as reagents in organic chemistry has received growing attention in recent years.¹ Alkali metal reduction in organic solvents of many main group and transition metal halides will produce powders which are substantially more reactive than bulk or amalgamated metals.

Although the first application of this method was to Mg,² no extension of the technique to the heavier alkaline earth metals (Ca, Sr, Ba) has been reported. Since the reduction potentials of the alkali metals differ by less than 0.2 eV from those of the heavy alkaline earths, chemical reduction of the latter is

Table 1. Products from the powders produced from potassium reduction of the alkaline earth di-iodides in thf. A typical reaction would involve 17 mmol of K, 10 mmol of the dihalide, and 45 ml of thf. Precipitated KI is removed after the reaction by filtration. Yields are the highest obtained so far.

Metal	Reagent	Time /h	Product	Yield /%
Ca	Ph ₃ CCl	0.5	Ph ₃ CCaCl(thf) ₂	Quantitative
Ca	H(tfa)	1	Ca(tfa) ₂	"
Ca	H(hfa)	1	Ca(hfa) ₂	35
Ca	HOC ₆ H ₂ Bu ^t ₂ -2,6-Me-4	24	(ArO) ₂ Ca(thf) ₂	37
Sr	Ph ₃ CCl	1	Ph ₃ CSrCl(thf) ₄	85
Ba	Ph ₃ CCl	3	Ph ₃ CBaCl(thf) ₂	71
Ba	C ₅ Me ₅ H	24	(C ₅ Me ₅) ₂ Ba(thf) ₂	48

usually difficult. Indeed, CaCl₂ is reduced by molten sodium at 750 °C to produce only a 15% yield of calcium powder.³ Reductions in organic solvents near room temperature might be substantially less efficient.

We have found, however, that stirring a mixture of potassium metal with a stoichiometric quantity of an anhydrous alkaline earth di-iodide in dry tetrahydrofuran (thf) or toluene under nitrogen at ambient or reflux temperatures produces suspensions of black or grey powders. Calcium di-iodide is the most reproducibly reduced, requiring 1 h at reflux or 4 h room temperature in thf to generate a black powder which undergoes no further visual change on prolonged stirring; a reaction time of 2 days in toluene is required to generate a solid of the same appearance.

Strontium di-iodide is reduced more slowly than CaI₂. Up to 3 days may be required to generate a grey powder from SrI₂ in thf at room temperature; a black powder is produced within 2 days at reflux temperatures. The reduction of BaI₂ is somewhat variable; production of a brownish-black powder in thf at room temperature is observed within 4–24 h, and a black solid can be observed after 1 h at reflux. The di-iodides are much more readily reduced than the dichlorides, probably because of their greater solubility. In refluxing thf, CaCl₂ only slowly becomes black (1 week) and BaCl₂ is not affected at all. We have found the powders produced by toluene-mediated reductions to be rather unreactive and unsuitable for synthetic purposes.

Isolation of the powders by filtration and subsequent drying yields agglomerates ranging in size from 4 μm–1 mm (determined by SEM). Grinding the powders in a mortar generated particles 50–100 nm in size, and they were too small for accurate analysis by SEM/EDX. Elemental analysis (Ca or Ba, K, I) on dried powders from calcium and barium iodide reductions with excess K (24 h reaction time) indicate essentially quantitative reduction of Ca²⁺, but a composition corresponding to a Ba⁰/BaI₂ ratio of 3.1:1, or ca. 76% reduction.

An initial survey of reactions revealed that in general the powders generated products in higher yield or more rapidly than standard procedures (Table 1). The formation of the Ph₃CMCl(thf)_x complexes from triphenylmethyl chloride, for example, is 12–16 times more rapid than the corresponding syntheses using metal amalgams.^{4,5}

The calcium salts of trifluoroacetylacetone (Htfa) and hexafluoroacetylacetone (Hhfa) have recently been used to produce thin films of CaF₂ by chemical vapour deposition methods.⁶ Their synthesis from bulk Ca and the parent acid requires 9 and 5 days, respectively. The formation of Ca(tfa)₂ and Ca(hfa)₂ from Ca powder in 1 h in thf represents more than a 100-fold increase in rate.

Reaction of 2,6-di-*t*-butyl-4-methylphenylphenol with Ca powder in thf forms the corresponding alkoxide Ca(OC₆H₂Bu^t₂-2,6-Me-4)₂(thf)₂ in moderate yield. This white, air-sensitive solid is the first hydrocarbon-soluble calcium aryl oxide to be described.† Although stable at room temperature, it decomposes on attempted sublimation at 95 °C and 10⁻³ Torr.

Ba powder reacts with Me₅C₅H to produce the (Me₅C₅)₂-Ba(thf)₂ metallocene.^{7,8} Although higher yields are available from the metathesis of KC₅Me₅ and BaI₂, it should be noted that bulk Ba does not react with Me₅C₅H.

The full scope of this method in the synthesis of organo-alkaline earth complexes is being explored.

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† Satisfactory elemental analyses were obtained. ¹H NMR data (300 MHz, C₆D₆): δ 1.19 (m, 8H, α-C₄H₈O), 1.64 (s, 18H, C₄H₆), 2.45 (s, 3H, CH₃), 3.54 (m, 8H, β-C₄H₈O), 7.29 (s, 2H, C₆H₂). ¹³C NMR data (50.3 MHz, C₆D₆): δ 21.7 (CH₃-4), 25.1 (β-C₄H₈O), 31.4 [C(CH₃)₃], 35.1 [C(CH₃)₃], 69.7 (α-C₄H₈O), 120.2 (C₆-4), 125.5 (C₆-3,5), 136.6 (C₆-1).