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Benzylsamarium Complexes and their Reactivity*

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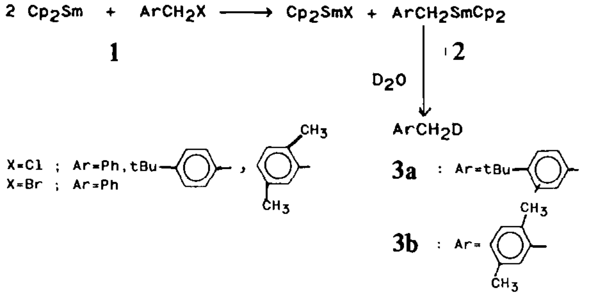
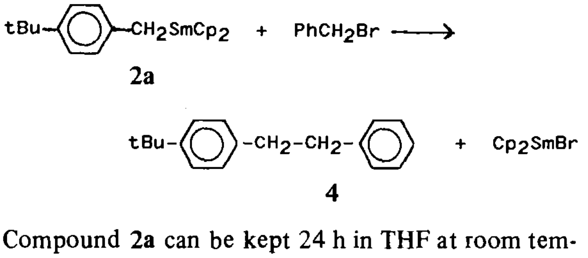
Reaction of benzylic halides with samarium dicyclopentadienide leads to samarium(III)benzyl complexes. Their reactivity towards benzyl bromide, aldehydes or a ketone, and acid chlorides is investigated.

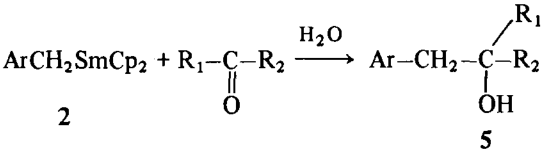
When benzylic halides (**1**) are added to purple samarium dicyclopentadienide (Cp_2Sm) (obtained from samarium diiodide and sodium cyclopentadienide) suspended in tetrahydrofuran (THF) at room temperature, the mixture turned dark brown and the precipitate disappeared. Formation of an organometallic species (**2**) was indicated by reaction with deuterated water, which led to 4-t-butyltoluene (**3a**) or xylene (**3b**), monodeuterated on the methyl group.



Reaction of **2a** with benzyl bromide gives 2-(4-t-butylphenyl)-1-phenylethane (**4**) as the main product, which is in agreement with the occurrence of a samarium–benzyl bond in **2a**.

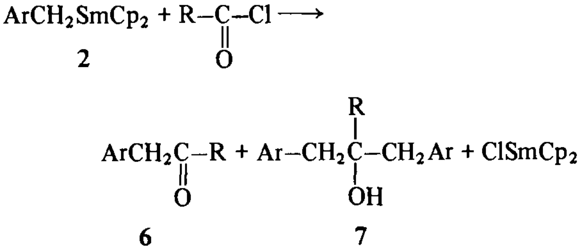


Compound **2a** can be kept 24 h in THF at room temperature without decomposition. Addition of aldehydes or a ketone to compounds **2** at room temperature leads to alcohols **5** in good yields (Table I).



$$\underset{\mathbf{2}}{\mathrm{ArCH_2SmCp_2}} + \mathrm{R_1{-}}\underset{\substack{\| \\ \mathrm{O}}}{\mathrm{C}}\mathrm{{-}R_2} \xrightarrow{\mathrm{H_2O}} \underset{\mathbf{5}}{\mathrm{Ar{-}CH_2{-}}\overset{\mathrm{R_1}}{\underset{\substack{| \\ \mathrm{OH}}}{\mathrm{C}}}\mathrm{{-}R_2}}$$

Acid chlorides are transformed into ketones (**6**) in moderate yield by reaction with **2** at low temperature (Table II). Formation of the tertiary alcohol **7** can be avoided by using bulky groups (R = t-Bu or Ar = 2,5-dimethylphenyl) or by lowering the temperature.



$$\underset{\mathbf{2}}{\mathrm{ArCH_2SmCp_2}} + \mathrm{R{-}}\underset{\substack{\| \\ \mathrm{O}}}{\mathrm{C}}\mathrm{{-}Cl} \longrightarrow$$

$$\underset{\mathbf{6}}{\mathrm{ArCH_2}\underset{\substack{\| \\ \mathrm{O}}}{\mathrm{C}}\mathrm{{-}R}} + \underset{\mathbf{7}}{\mathrm{Ar{-}CH_2}\overset{\substack{\mathrm{R} \\ |}}{\underset{\substack{| \\ \mathrm{OH}}}{\mathrm{C}}}\mathrm{{-}CH_2Ar}} + \mathrm{ClSmCp_2}$$

These results provide strong evidence for the occurrence of a samarium–benzyl bond in the compounds obtained by reaction between benzylic halides and samarium dicyclopentadienide. We are trying to extend this reaction to alkyl halides in order to obtain other organosamarium complexes.

TABLE I. Reaction of Benzyl Complexes ($ArCH_2SmCp_2$) with Aldehydes and a Ketone (R_1COR_2)

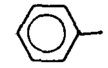
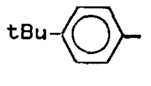
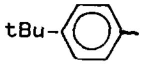
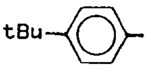
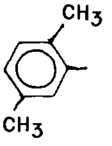
Ar	R_1	R_2	Yield (%)
	C_6H_{13}	H	80
	C_2H_5	H	80
	C_6H_{13}	H	60
	tBu	Me	92
	C_2H_5	H	76

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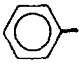
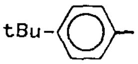
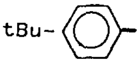
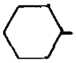
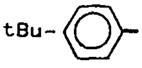
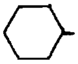
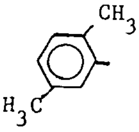
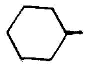
TABLE II. Addition Reactions of Benzyl Complexes ($ArCH_2SmCp_2$) with Acid Chlorides (RCOCl)

Ar	R	Temperature (°C)	6:7	Yield (%)
	tBu	−30	1:0.13	35
	tBu	−20	1:0.19	46
		−20	1:1.17	
		−70	1:0.5	39
		−30	1:0.05	38

Experimental

$SmCp_2$ (5 mmol) was prepared as previously described [1, 2] from SmI_2 (0.1 M in THF, 50 ml) and NaCp (0.4 M in THF, 25 ml) and washed twice with THF. In a typical experiment a solution of 2 mmol of 4-t-butylbenzyl chloride in 20 ml THF was added slowly at room temperature to $SmCp_2$ suspended in 75 ml THF. After 30 min the mixture turned dark brown and 2 mmol of propanol were then added. After a few minutes at room temperature the usual workup [3] gave the crude material which was purified by flash chromatography on a silica column and analysed with GC, GC/MS and ^1H NMR (1-(4-t-butylphenyl)butan-2-ol, 80% isolated yield).

References

1 J. L. Namy, P. Girard, H. B. Kagan and P. E. Caro, *Nouv. J. Chim., 5,* 479 (1981).
2 J. L. Namy, J. Collin, J. Zhang and H. B. Kagan, *J. Organomet. Chem.,* in press.
3 P. Girard, J. L. Namy and H. B. Kagan, *J. Am. Chem. Soc., 102,* 2693 (1980).