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Preliminary communication

Zinc and aluminium trimethylsilylmethyls and their use as alkylating agents

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SUMMARY

The trimethylsilylmethyl compounds $Zn(Me_3SiCH_2)_2$ and $Al(Me_3SiCH_2)_3(C_2H_5)_2O$ and some amine derivatives of the former are described. Action of the zinc alkyl on $NbCl_5$ and $TaCl_5$ differs from alkylation by lithium or magnesium reagents in giving the di- or trialkyl chloro species.

A number of stable transition metal binary trimethylsilylmethyls have recently been synthesised using lithium or magnesium reagents for the alkylation of halides[1,2].

We now report the preparation of zinc and aluminium trimethylsilylmethyls. These may prove to be useful alkylating agents and we have already shown, as noted below, that the transition metal products may be different from those obtained by use of lithium or magnesium reagents.

TABLE 1

Compound[a]	*Colour*	*m.p. (b.p.) (°C)*
$(Me_3SiCH_2)_2Zn$	Colourless	(44°/1.5 mm)
$(Me_3SiCH_2)_3Al{\cdot}OEt_2$	Colourless	(64°/0.02 mm)
$bipyZn(CH_2SiMe_3)_2$	Red-orange	91–92°
$phenZn(CH_2SiMe_3)_2$	Orange	166–167° (dec)
$TMEDZn(CH_2SiMe_3)_2$[b]	White	84–85°
$(quinoline)_2Zn(CH_2SiMe_3)_2$	Yellow	liq.
$(pyridine)_2Zn(CH_2SiMe_3)_2$	Yellow	liq.
$(Me_3SiCH_2)_3NbCl_2$	Orange	68–70°
$(Me_3SiCH_2)_2TaCl_3$	Pale yellow	68.5–70°
$(Me_3SiCH_2)_3TaCl_2$	Lemon yellow	64–67°

[a] Correct elemental analysis as well as IR and NMR spectra have been obtained.
[b] TMED = tetramethylethylenediamine.

The properties of the new alkyl compounds are given in Table 1.

Bis(trimethylsilylmethyl)zinc is obtained in 90% yield by the standard Grignard method and is a colourless liquid spontaneously flammable in air. It may also be obtained but in low yield (ca 50%) by interaction of iodomethyltrimethylsilane with zinc–copper couple. The infrared and Raman spectra are similar to those of other trimethylsilylmethyls[1] and confirm the expected linearity of the zinc to carbon bonds. The single Zn–C stretch occurs at 508 cm^{-1} (polarized) while ν(Si–C) is at 609 cm^{-1} (polarized).

Tris(trimethylsilylmethyl)aluminium as its diethyletherate is obtained in 60% yield by the Grignard method and is also a spontaneously flammable liquid.

The zinc alkyl readily forms adducts with amines that are much less oxygen sensitive than the parent. The 2,2′-bipyridyl (bipy) and 1,10-phenanthroline (phen) complexes are unaffected by air over several days.

The only products isolated from the interaction of niobium and tantalum pentahalides with magnesium or lithium reagents were the complexes[3] $(Me_3SiCH_2)_2M(\mu\text{-}CSiMe_3)_2M(CH_2SiMe_3)_2$, which have been found by X-ray diffraction[4] to have two carbene-like bridges and a four-membered Nb_2C_2 ring. By contrast, the interaction of $TaCl_5$ and $(Me_3SiCH_2)_2Zn$ gives a mixture of $(Me_3SiCH_2)_2TaCl_3$ and $(Me_3SiCH_2)_3TaCl_2$. Niobium pentachloride gives mainly $(Me_3SiCH_2)_3NbCl_2$. The reactions are complete in ca. 30 min at room temperature in diethyl ether. Extraction of the residue after removal of ether with pentane effectively removes zinc chloride and any unreacted metal chloride. In hydrocarbon solvents the reactions are slower due to insolubility of the pentachlorides.

The tantalum compounds can be readily separated by fractional crystallisation from pentane at −80°, the dialkyl being less soluble; they can be purified by vacuum sublimation at 50°/10^{-4} mm. There is no evidence for alkylation beyond the dichloride even with excess zinc alkyl at 80°. The trialkyl is best made by interaction of the dialkyl with a stoichiometric quantity of zinc alkyl.

The formation of the $CSiMe_3$ bridged species using lithium and magnesium reagents may be due to the metallation of the methylene group allowing the formation of species such as $(Me_3SiCH_2)_2MCl_2\bar{C}HSiMe_3$. This could act as a nucleophile to form the bridged species via proton and chloride abstraction.

The uses of the zinc and aluminium alkyls for alkylation of other metal halides, are under study.

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