Trimethylsilylmethylcopper, a Stable Copper(I) Alkyl

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Summary Interaction of Me_3SiCH_2Li with CuI gives $(Me_3SiCH_2Cu)_n$ a stable, volatile, petroleum-soluble copper-(I) alkyl (tetramer in C_6H_6, hexamer in n-C_6H_{14}), which shows a parent ion in the mass spectrum corresponding to the tetramer ($n = 4$); decomposition involves free radical pathways.

ALKYLCOPPER(I) complexes are unstable, decomposing at or below 0°,[1] and are soluble only in the presence of complexing agents.[2] Recent reports show that trimethylsilylmethyl (Me_3SiCH_2) and related ligands form a number of kinetically-stable, binary alkyls of the early transition metals,[3] *e.g.*, $(Me_3SiCH_2)_4Ti$[4] and $(Me_3SiCH_2)_4Cr$;[5] we now describe the preparation of trimethylsilylmethylcopper, a volatile alkylcopper(I) compound, stable at room temperature and readily soluble in non-polar media.

Treatment of copper(I) iodide in n-hexane–ether (1:1) with lithiomethyltrimethylsilane at *ca.* −10° gave $(Me_3SiCH_2Cu)_n$ as colourless prisms, m.p. 78—79° (dec.), from n-pentane. The crystals, or a solution in hydrocarbon solvent, are stable in the dark at room temperature, but decomposition occurs upon exposure to light. Cryoscopy of 10% *w/w* solutions showed that it is tetrameric in benzene and hexameric in cyclohexane. (The structure may resemble that of alkyl-lithium reagents.) The ^1H n.m.r. spectrum indicated that it is diamagnetic, the Me_3Si and CH_2 resonances appearing as singlets at τ 9·80 and 10·18 respectively. The mass spectrum showed a parent ion for the tetramer at *m/e* 600 for $(Me_3SiCH_2{}^{63}Cu)_4{}^+$ with the expected Cu_4 isotope pattern. Fragmentation occurs with loss of Me, Me_4Si, $Me_4Si + CH_4$, $(Me_3Si)_2CH_2$, and $2Me_4Si$. Pyrolysis *in vacuo* gave a copper mirror and a volatile, colourless liquid containing Me_4Si (major product), $(Me_3Si)_2CH_2$, $(Me_3SiCH_2)_2$, and three unidentified minor components. Photolysis or pyrolysis (at 80°) in toluene gave an unidentified, intensely red, copper-containing species, Me_4Si, $(Me_3Si)_2CH_2$ (only on pyrolysis), $(Me_3SiCH_2)_2$, $PhCH_2CH_2SiMe_3$, and $(PhCH_2)_2$, in accord with a free radical decomposition pathway.

The stability of $(Me_3SiCH_2Cu)_n$ is presumably associated with the preclusion of the olefin-elimination route to decomposition and the presence of a stable metal cluster (*X*-ray studies are in hand).

$(Me_3SiCH_2Cu)_n$ is an alkylating agent: reaction with Me_3SiCl, $CH_2{=}CHCH_2Br$, or PhI gave $(Me_3Si)_2CH_2$, $Me_3SiCH_2CH_2CH{=}CH_2$, or $PhCH_2SiMe_3$, respectively; with $PhCH_2Br$, $(PhCH_2)_2$ (presumably *via* halogen-metal exchange), as well as the expected $PhCH_2CH_2SiMe_3$ was formed. The copper–lithium reagent, $[(Me_3SiCH_2)_2CuLi]$, was obtained as a pale-violet, ethereal solution from CuI (1 mol) and Me_3SiCH_2Li (2 mol) and was unchanged after several days at room temperature.

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[1] K.-H. Thiele and J. Köhler, *J. Organometallic Chem.*, 1968, **12**, 225.

[2] H. O. House, W. L. Respass, and G. M. Whitesides, *J. Org. Chem.*, 1966, **31**, 3128; M. Tamura and J. K. Kochi, *J. Organometallic Chem.*, 1972, **42**, 205.

[3] *Cf.*, C. S. Cundy, B. M. Kingston, and M. F. Lappert, *Adv. Organometallic Chem.*, 1972, **11**, 253.

[4] M. R. Collier, M. F. Lappert, and M. M. Truelock, *J. Organometallic Chem.*, 1970, **25**, C36.

[5] W. Mowat, A. Shortland, N. J. Hill, M. Yagupsky, and G. Wilkinson, *J.C.S. Dalton*, 1972, 533.