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Preliminary communication

Perfluorophenyl derivatives of the elements

XXIV*. Lithium bis(pentafluorophenyl)silver, $LiAg(C_6F_5)_2$

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To our knowledge there are no stable organometallic derivatives of silver which contain anionic silver as AgR_2, although the polymeric compound $[C_6H_5C{\equiv}CAgP(CH_3)_3]_n$ does contain $C_6H_5C{\equiv}C{-}Ag{-}C{\equiv}CC_6H_5$ units[2]. It appears well established[3] that most of the highly fluorinated aromatic derivatives of metallic and metalloidal elements have an enhanced stability relative to their hydrogen analogues; when the reverse is true and the perfluoroaromatic derivative has the lower thermal stability (*e.g.* for Li and Mg) the decomposition normally occurs via an intramolecular fluorine shift from carbon to metal and not via simple cleavage of the M–C σ-bond. Since phenylsilver decomposes[4] into silver and biphenyl at temperatures only slightly below room temperature we assumed that pentafluorophenyl derivatives of silver would be capable of isolation by virtue of the expected enhancement in thermal stability. In this note we describe the synthesis and properties of the first anionic organo complex of silver, lithium bis(pentafluorophenyl)silver.

The slow addition of cooled silver chloride (one mole) to an ether solution of pentafluorophenyllithium (one mole) held at -78° under dry nitrogen, resulted in a clear solution. The solution was allowed to warm up slowly and at about -9° a black solid, which contained no free silver, was precipitated; when the mixture attained room temperature it was filtered under nitrogen to leave a very pale pink solution. Evaporation of the solvent under a vacuum gave crystalline, chloride-free lithium bis(pentafluorophenyl)silver, $LiAg(C_6F_5)_2$, in 76% yield. Lithium bis(pentafluorophenyl)silver is moisture sensitive, melts at 68–74° and appears stable at 80° under dry nitrogen [Found: Ag, as AgCl, 23.6; 23.8; C, 31.9; F, 41.6; Li, 1.1; $C_{12}F_{10}AgLi$ calcd.: Ag, 24.0; C, 32.1; F, 42.3; Li, 1.5%]. Treatment of $LiAg(C_6F_5)_2$ with mercuric chloride in ether solution gave bis(pentafluorophenyl)-mercury; lithium bis(pentafluorophenyl)silver was also formed when the $LiC_6F_5/AgCl$ reaction ratio was 2/1.

Iodine and $LiAg(C_6F_5)_2$ react in ether at 20° to give lithium iodide, silver iodide and iodopentafluorobenzene; dilute acid reacts with the salt to produce

* For part XXIII see ref. 1.

pentafluorobenzene. Exposure of lithium bis(pentafluorophenyl)silver to small quantities of water, either in the form of wet air or as damp solvents, results in the formation of the light sensitive pentafluorophenylsilver[5] as a white solid; larger quantities of water produce only pentafluorobenzene. The thermal decomposition of $LiAg(C_6F_5)_2$ in a sealed, evacuated tube gives mainly decafluorobiphenyl together with small amounts of *ortho*-linked polyfluoropolyphenyls which suggest that tetrafluorobenzyne may be one of the intermediates in the decomposition[3].

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