Metal Vapour Synthesis of Complexes of Methylphenylsiloxane Polymers

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Summary Vapours of Ti, V, Cr, and Mo react with liquid methylphenylsiloxane polymers at 0 °C to give high yields of thermally stable bis(π-arene)metal complexes of the polymers.

ONLY a few methods are known for forming transition-metal complexes of polymeric ligands[1,2] although such complexes are of growing interest because of their potential catalytic and electrical properties.[2,3] We now report the use of metal vapours to form complexes from liquid methylphenylsiloxane polymers; the reactions are carried out at 0 °C, a higher temperature than is common in work with metal atoms.[4] Complexes in which two phenyl rings in the polymer are co-ordinated to each metal atom are formed with Ti, V, Cr, and Mo vapours. In a typical experiment with chromium, 30 mmol of the metal is vaporized by resistance heating over 1·5 h inside a rotating 2 dm^3 flask[5] containing 150 cm^3 of Dow Corning 510 (viscosity 0·5 cm^2 s^{-1}), a mobile liquid methylphenylsiloxane polymer with a methyl:phenyl ratio of *ca.* 17:1 and $OSiMe_3$ end groups. The flask is cooled by a bath at 0 to -10 °C so that a vacuum of *ca.* 10^{-3} Torr can be maintained while the metal evaporates. The crude reaction product contains traces of chromium metal but filtration yields a clear, brown-red fluid only slightly more viscous than the original DC 510. The ^1H n.m.r. spectrum of the liquid shows a multiplet at δ 4·73 [*cf.* bis(trimethylsilylbenzene)chromium, δ 4·42[6]] in addition to the multiplet at δ 7·67 and singlet at δ 0·36 of the free DC 510. Integration indicates a ratio of unco-ordinated:co-ordinated phenyl groups of 2.4:1. In the absence of air, the liquid is unchanged on heating at 300 °C. On bubbling air through the liquid, it initially becomes clear yellow and shows an e.s.r. spectrum typical for $[(\text{arene})_2Cr]^+$ (single line with hyperfine splitting, $g = 1{\cdot}988$, $a_H = 3{\cdot}45$ G). Extended air oxidation gives a fine, yellow, water-soluble precipitate which, on treatment with NH_4PF_6, yields $(C_6H_6)_2CrPF_6$. The residual silicone fluid then shows a strong i.r. band at 3660 cm^{-1} indicative of SiOH. The phenyl–silicon bond seems to be activated towards hydrolysis following oxidation of the co-ordinated chromium Oxidation of the DC 510–chromium product with 7,7,8,8-tetracyanoquinodimethane (TCNQ) gives a bright green, paramagnetic solution. Chemical analysis and the u.v.–visible, e.s.r., and i.r. spectra of the solution are consistent with the formula $(\text{arene})_2Cr(TCNQ)_2$ for the complex.[7] The electrical properties of this material are being investigated.

Reaction between chromium vapour and DC 510 proceeds efficiently until at least 50% of the available phenyl groups have become co-ordinated to chromium. Other methylphenylsiloxanes, *e.g.* Silicone 704, a tetramethyltetraphenyltrisiloxane, react in a similar way to DC 510 with chromium vapour.

A bright pink liquid is obtained from titanium vapour and DC 510, which shows a ^{1}H n.m.r. signal at δ 5·39, a shift of $-2{\cdot}28$ p.p.m. from the unco-ordinated phenyl groups [*cf.* $(C_6H_6)_2Ti$, $-2{\cdot}23$ p.p.m. from C_6H_6[8]]. The liquid is stable to 200 °C but it is rapidly oxidised by air depositing TiO_2. Vanadium vapour and DC 510 yield a dark brown, paramagnetic liquid which shows an eight-line e.s.r. spectrum ($g = 1{\cdot}987$, $a_V = 63{\cdot}5$ G) typical of $(arene)_2V$. The golden-brown liquid from molybdenum vapour and DC 510 shows a ^{1}H n.m.r. signal shifted $-2{\cdot}83$ p.p.m. from the uncoordinated phenyl groups, appropriate for an $(arene)_2Mo$ complex. Some solid siloxane polymer is also formed in the DC 510–Mo vapour reaction, probably because of the high light flux accompanying metal evaporation.

The result of condensing manganese, iron, or nickel, vapours into DC 510 is to form metal slurries which can be readily oxidised. Treatment of the DC 150–nickel slurry with hydrogen at 100 atm and 50 °C causes aggregation of the metal accompanied by partial hydrogenation of the phenyl to cyclohexyl groups. Slurries formed by condensing iron atoms into DC 510 or into polymethylsiloxane fluids, *e.g.* DC 200, show similar e.s.r. spectra and line broadening of the ^{1}H n.m.r. signal of the methyl protons.

The work with siloxane polymers shows that it is practicable to carry out metal atom reactions with compounds of low volatility without the expensive refrigeration required when using more volatile reactants.

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