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Preliminary communication

CHEMICAL SYNTHESIS WITH METAL ATOMS: THE REACTION OF CHROMIUM AND NICKEL ATOMS WITH STYRENE

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Summary

The preparation of $C_8H_8Cr(CO)_3$ (or $C_8H_8Cr(PF_3)_3$) and polystyrenechromium tricarbonyl (or polystyrenechromium tris(trifluorophosphine) from chromium atoms, styrene and carbon monoxide (or trifluorophosphine) is described; nickel atoms and styrene produce tristyrenenickel, which reacts with α, α' -bipyridyl to yield bipyridylstyrenenickel.

We have described the reaction of iron atoms with styrene and carbon monoxide [1], which yields $C_8H_8Fe(CO)_4$ and $C_8H_8Fe(CO)_3$ complexes; little polymerisation of the excess styrene present in the reaction system was observed. Activated chromium atoms, on the other hand, are known to polymerise ethylene [2], and we therefore expected that the reaction of chromium atoms with styrene might lead to polymeric products.

The cocondensation of chromium atoms (1 g) and styrene (40 ml) at $-196^\circ C$ on a pentane matrix (200 ml) does indeed produce polystyrene (IR) but intractable material is present in which chromium is bound to polystyrene (mass spectrum $((C_8H_8)_n H_m Cr)$ $n = 2, m = 0; n = 3$ to $5, m = 4$). The cocondensation of chromium atoms (2 g) and styrene (20 ml) at $-196^\circ C$ on a pentane matrix (200 ml) and subsequent warm-up to room temperature in an atmosphere of CO (20 l) produces a red material, which on elution on silica gel (Merck 9385) with pentane/benzene (80/20) yields an elongated red band. The band was collected in two fractions; the first fraction yielded small amounts of $C_8H_8Cr(CO)_3$ (I) as orange-red crystals [3] recrystallised from toluene/pentane at $-80^\circ C$. (Found: C, 55.0; H, 3.40; Cr, 21.7. $C_{11}H_8CrO_3$ calcd.: C, 55.1; H, 3.36; Cr, 21.65%. IR: $\nu(CO)$ 1975, 1930 cm^{-1}). The second fraction ($\sim 40\%$ by weight) on cooling to $-80^\circ C$ in pentane yielded a non-crystallisable oil (Ia). The 1H NMR spectrum of Ia showed signals at τ 2.4 ~ 2.7, 5.7, 8.5 ~ 9.0 ppm in the intensity ratio 4:1.2:3.2, assigned to phenyl, phenyl bonded to $CrCO_3$ (*hexahapto*), and methylene hydrogens respectively. IR: $\nu(CO)$ 1970, 1910 cm^{-1} ; mol. wt. 860 (benzene).

The mass spectrum of Ia indicated volatile ions corresponding to the formula $(C_8H_8)_nH_2Cr(CO)_3$ ($n = 3$ to 7).

A similar reaction using PF_3 (15 l) instead of CO was worked-up and chromatographed under the same conditions. A broad red band was eluted with pentane/benzene (80:20) from silica gel. Two fractions were collected; from the first $C_8H_8Cr(PF_3)_3$ (II) was isolated as crystals from a pentane solution at $-80^\circ C$. (Found: C, 22.83; H, 1.90; Cr, 12.17; P, 22.51; F, 40.93. $C_8H_8Cr(PF_3)_3$ calcd.: C, 22.85; H, 1.92; Cr, 12.38; P, 22.18; F, 40.70%; mol. wt. 405 (benzene).

The second fraction yielded an oily solid (IIa) with properties very similar to Ia. We believe Ia and IIa contain a mixture of polystyrenes to which a CrL_3 unit ($L = CO, PF_3$) is bonded *hexahapto* to a phenyl substituent.

The cocondensation of nickel [4] (1.5 g), on the other hand, with styrene (20 ml) on a toluene matrix (200 ml) at $-196^\circ C$ yields after work-up at $-40^\circ C$ and recrystallisation at $-80^\circ C$ from toluene, red-brown crystals of tristyrene-nickel (III). (Found: C, 77.95; H, 6.58; Ni, 15.7. $C_{24}H_{24}Ni$ calcd.: C, 77.68; H, 6.49; Ni, 15.82%). These crystals decompose above $-20^\circ C$. Introduction of α, α' -bipyridyl to a freshly prepared solution of III at $-30^\circ C$ yields bipyridylstyrene-nickel (IV) (Found: C, 67.48; H, 5.02; N, 8.64; Ni, 18.61. $C_{18}H_{16}N_2Ni$ calcd.: C, 67.69; H, 5.05; N, 8.77; Ni, 18.40%; mol. wt. 325 (benzene)) and styrene.

The usefulness of Ia and IIa as a basis for polymer-supported metal atoms will be discussed in a further publication.

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