Synthesis and Ready Metallation of (η-Benzene)-(η-pentafluorobenzene)chromium

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Summary $[(C_6H_6)Cr(C_6F_5H)]$, prepared by metal atom cocondensation, is readily lithiated at −78 °C and converted into $[(C_6H_6)Cr(C_6F_5X)]$, where X is $SiMe_3$, CO_2Li, CMe_2OH, $(\eta\text{-}C_5H_5)Fe(CO)_2$, or $(\eta\text{-}C_5H_5)Fe(\eta\text{-}C_5H_4CHOH)$.

Only a few substituted bis(arene)chromium compounds have been prepared by metallation procedures.[1] We now report that cocondensation of chromium vapour with a mixture of C_6F_5H and C_6H_6 (60:40) produced $[(C_6F_5H)Cr\text{-}C_6H_6)]$, (**1**) (22%), entirely analogous to the synthesis of $[(C_6F_6)Cr(C_6H_6)]$.[2] Sublimation of (**1**) at 35 °C and 0·2 mmHg followed by recrystallisation from aqueous ethanol gave air-stable, orange needles, m.p. 117 °C, whose ^{19}F n.m.r. spectrum in C_6D_6 showed multiplets at 185·0 (*ortho*), 194·9 (*meta*), and 196·8 (*para*) p.p.m. upfield of $CFCl_3$. The ^1H n.m.r. spectrum exhibited a triplet (9 Hz) of triplets (6 Hz) of doublets (2 Hz) at δ 4·97 (1H), and a multiplet (6H) at δ 4·43. The acidic proton of the complexed C_6F_5H ring is readily displaced to yield the lithio derivative $[(C_6H_6)Cr(C_6F_5X)]$ (**2**; X = Li) which reacts with $ClSiMe_3$, CO_2, Me_2CO, $[(\eta\text{-}C_5H_5)Fe(CO)_2I]$, and $[(\eta\text{-}C_5H_5)Fe(\eta\text{-}C_5H_4\text{-}CHO)]$ to form the complexes (**2**) with X = $SiMe_3$, CO_2Li, CMe_2OH, $(\eta\text{-}C_5H_5)Fe(CO)_2$ [ν_{CO} at 2006 and 1963 cm^{-1}; *cf.* $(\eta\text{-}C_5H_5)Fe(CO)_2C_6F_5$,[3] ν_{CO} at 2045 and 1997 cm^{-1}], and $(\eta\text{-}C_5H_5)Fe(\eta\text{-}C_5H_4CHOH)$ respectively.

In a typical experiment, 2 ml of a 0·135 M ethereal solution of Bu^tLi were added to (**1**) (78 mg) in 120 ml of Et_2O at −78 °C under N_2. The initially pale yellow solution became dark red-brown but, upon addition of excess of Me_3SiCl, soon became yellow again. Filtration at room temperature, removal of solvent *in vacuo*, and sublimation at 32 °C and 0·2 mmHg gave orange, air-stable $[(C_6H_6)Cr(C_6F_5\cdot SiMe_3)]$ (75 mg, 78%), m.p. 93·5 °C.

The possibility that (**2**; X = Li) might eliminate LiF to produce the tetrafluorobenzyne complex, which (by analogy with the formation of C_6F_4 from C_6F_5Li[4]) would be trappable as a Diels–Alder adduct, was investigated by allowing an ethereal solution of (**2**; X = Li) to warm to room temperature in the presence of furan. The Diels–Alder adduct was not observed, but the binuclear complex $[(C_6H_6)Cr(C_6F_5\text{-}\cdot C_6F_4H)Cr(C_6H_6)]$ (**3**) sublimed out of the residue at 55—60 °C and 0·2 mmHg. Apparently, (**3**) is produced by nucleophilic displacement of fluoride, and the accompanying tarry residue suggests that we have merely isolated the lowest homologue of a polymeric species.

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