Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

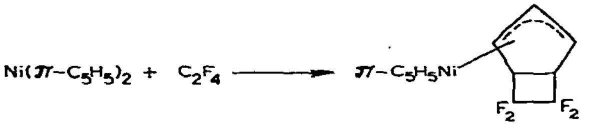
Preliminary communication

Perfluorophenyl derivatives of the elements XXIII★. Addition of tetrafluorobenzyne to nickelocene

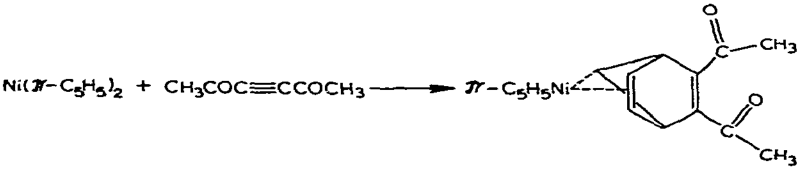
D.M. ROE and A.G. MASSEY
Department of Chemistry, Queen Mary College, London E.1 (Great Britain)

(Received Septe~~n~~ber 4th, 1969)

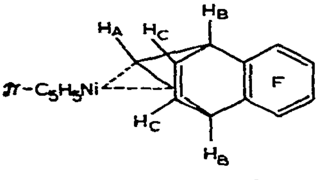
Nickelocene, Ni(π-C_5H_5)$_2$, behaves in some of its reactions as an unsaturated system and, for example, readily adds tetrafluoroethylene^2:



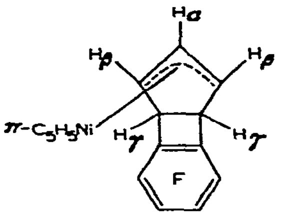
and dimethyl acetylenedicarboxylate^3:



By generating tetrafluorobenzyne in the presence of nickelocene we obtained a dark red mixture having the composition (C_5H_5)$_2$NiC_6F_4 and containing nearly equal amounts of two isomers. Their proton NMR spectra, recorded for deuterobenzene solutions at 100 MHz, indicate that these isomers have the structures:



(I) m.p. 150–152°



(II) air sensitive;
(conformation unknown)

For (I), the single NMR peak at 5.10 ppm (relative intensity 5) may be assigned to the protons in the cyclopentadienyl ring whilst the multiplets at 4.20 (rel. int. 2),

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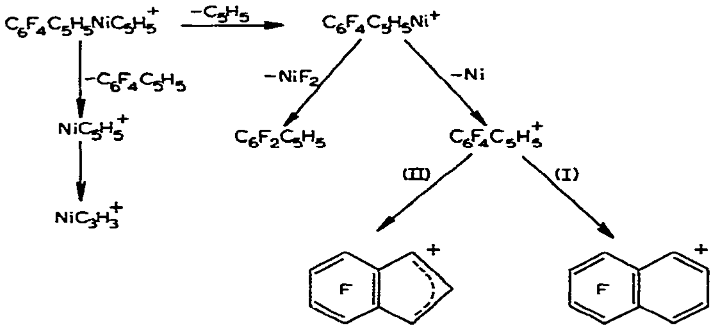
★For Part XXII, see ref. 1.

3.94 (rel. int. 2) and 1.45 ppm (rel. int. 1) are due to H_C, H_B and H_A. In the NMR spectrum of (II) the peak due to H_α cannot be located with certainty but appears to lie under the large peak at 5.02 ppm assigned to the cyclopentadienyl ring protons; the protons H_β and H_γ give rise to peaks at 3.85 (rel. int. 2) and 2.68 ppm (rel. int. 2).

Mass spectra show the compounds to be monomeric in the vapour state, the basic fragmentation patterns being:



EXPERIMENTAL

Pentafluorophenyl magnesium bromide was initially prepared in diethylether and then a higher-boiling ether was substituted for $(C_2H_5)_2O$. Freshly recrystallised nickelocene was added and the mixture refluxed under dry nitrogen for about one hour before the black solution was taken to dryness and the unreacted nickelocene removed by sublimation at 60°(10^{-4} mm). The two benzyne adducts sublimed from the reaction flask at 100–130° (10^{-4} mm) to yield a mass of dark red crystals; total yield of (I) and (II) was *ca.* 20% based on C_6F_5. Purification by thin layer chromatography and recrystallisation gave analytically pure products (Found for I: C, 56.75, 56.8; H, 2.85, 2.9%; found for II: C, 56.75; H, 2.85; $C_{16}H_{10}F_4Ni$ calcd.: C, 57.0; H, 3.0%). Molecular weight of both (I) and (II) as determined mass spectroscopically was 336 (calcd. 336 for ^{58}Ni).

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