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Preliminary communication

THE INTERACTION OF $CF_3C{\equiv}CC(CF_3)(C_2F_5)_2$ AND METAL CARBONYL DERIVATIVES

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Summary

$CF_3{\equiv}CC(CF_3)(C_2F_5)_2$ (ac) forms $(C_5H_5Ni)_2$ac and $Co_2(CO)_6$ac on reaction with $[C_5H_5NiCO]_2$ or $Co_2(CO)_8$. There is no interaction with iron carbonyls.

Few reaction between acetylenes containing bulky electronegative substituents and transition metal derivatives have been reported to date [1, 2]. The acetylene $CF_3C{\equiv}CC(CF_3)(C_2F_5)_2$ (I) is readily prepared [3] and its reactions with a series of metal carbonyl derivatives have been examined.

Cyclopentadienylnickel carbonyl dimer and dicobalt octacarbonyl react with I at 330 K to give $(C_5H_5Ni)_2$ac (II) and $Co_2(CO)_6$ac (III) respectively (ac = $CF_3C{\equiv}C(CF_3)(C_2F_5)_2$). The complexes have physical and spectroscopic features similar to other acetylene complexes of similar stoichiometry and whose structures have been established by X-ray methods [4, 5] to have bridging acetylene residues perpendicular to a metal—metal bond. Complexes II and III do not react with excess of I at 380 K although they do react with hexafluoro-2-butyne, $CF_3C{\equiv}CCF_3$,to give $[C_5H_5NiC_4F_6]_4$ (IV) and $Co_2(CO)_4(C_4F_6)_3$ (V) respectively. IV and V are formed by the action of excess of hexafluoro-2-butyne on $(C_5H_5Ni)_2C_4F_6$ [6] and $Co_2(CO)_6C_4F_6$ [7] respectively suggesting that acetylene exchange occurs as the first step in the reaction. No reactions were observed between I and diiron enneacarbonyl, cyclopentadienylcobalt dicarbonyl, or tetrakis(trifluoro phosphine)nickel(0) although hexafluoro-2-butyne reacts readily with each of these derivatives [1, 2, 8].

Previous studies of reactions between various acetylenes and cobalt carbonyls [1, 2, 9] have suggested that substituents which are both bulky and electronegative reduce the tendency to cyclooligomerisation and the present results confirm this trend.

Experimental

Manipulation of materials was carried out under dry oxygen-free nitrogen in a Lintott inert atmosphere box. Hydrocarbon solvents were dried over sodium and deaerated before use. Analyses are by Bernhardt. ^{1}H and ^{19}F NMR spectra were taken at 60 MHz and 56.4 MHz respectively on Perkin–Elmer R10 and Jeol C-60HL spectrometers in $CDCl_3$ and CH_2Cl_2 solution with Me_4Si and CCl_3F as internal standards. IR spectra were recorded in cyclohexane solution on a Perkin–Elmer 225 spectrophotometer calibrated against water vapour and carbon monoxide. Mass spectra were recorded on an AEI MS 12 mass spectrometer at 70 eV with a probe inlet (temperature ~370 K). Melting points are uncorrected.

Preparation of $CF_3C{\equiv}CC(CF_3)(C_2F_5)_2$ *[3]*

Anhydrous sodium acetate (10 g), $C_{10}F_{20}$ (58 g, a gift from I.C.I. Mond Division) and dimethyl formamide (75 mol) were stirred for 1 hour and 11 g triethylamine was added to the mixture. The whole was heated under reflux for 10 hours. The lower layer was separated and fractionated. The fraction b.p. 368-383 K was collected.

Dicyclopentadienyldinickel acetylene complex

0.5 g Cyclopentadienylnickel carbonyl dimer (Strem Chemicals Inc.), 1.0 g acetylene, and 20 ml pentane were heated in a sealed tube at 333 K for 10 hours. Volatile products were removed under vacuum and the product extracted with methylene chloride and hexane to give green black crystals m.p. 438 K in 53% yield. Found: C, 34.9; H, 1.3; F, 47.1; Ni, 17.5. $C_{19}H_{10}F_{16}Ni_2$ calcd.: C, 34.5; H, 1.5, F, 46.9; Ni, 17.9%. IR spectrum (cm^{-1} in cyclohexane solution) 1570 w(br) (C–C mode), 1300w, 1246s, 1234s, 1220s, 1204m, 1198m(sh), 1182w, 1156(sh), 1143m (C–F modes). NMR spectrum ^{1}H τ 4.67. ^{19}F 50.3(3), 59.7(3), 75.2(6), 105.0(4) (integrated intensities in brackets) The mass spectrum showed a parent ion at *m/e* 658.

Hexacarbonyldicobalt acetylene complex

The reaction was carried out as for the nickel complex but the product was sublimed at 313 K to give the orange-red complex as a waxy solid (m.p. 340 K with decomposition) in 85% yield. Found, C, 24.6; Co, 17.2; F, 44.4. $C_{15}Co_2F_{16}O_6$ calcd.: C, 25.7; Co, 16.9; F, 43.4%. IR spectrum 2116m, 2085vs, 2061vs, 2058vs, 2050w(sh) (C–O modes), 1564w, 1558w(sh) (C–C mode), 1311w, 1291w, 1249m, 1236m, 1222m, 1206m, 1184m, 1159w, 1140m (C–F modes). ^{19}F NMR 53.8(3), 62.1(3), 77.2(6), 103.7(4). The mass spectrum showed *M* — CO as the peak of highest *m/e* and peaks corresponding to successive loss of CO groups.

Reaction between the acetylene and diiron enneacarbonyl, cyclopentadienylcobalt dicarbonyl, and tetrakis(trifluorophosphine)nickel(0) were attempted using similar reaction conditions to those described above, except that the experiments extended over four days. In each case starting materials (and $Fe(CO)_5$ and $Fe_3(CO)_{12}$ in the case of $Fe_2(CO)_9$) were the only products to be identified. In the case of the reaction involving $Fe_2(CO)_9$ the experiment was also carried out in Pyrex under irradiation from a Hanovia medium pressure mercury lamp but again no new products were observed.

The reactions between the acetylene complexes and hexafluoro-2-butyne were carried out in hexane using excess of hexafluoro-2-butyne at 390 K. The products were identified spectroscopically by comparison with authentic samples.

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