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Preliminary communication

CHEMICAL SYNTHESIS WITH METAL ATOMS: THE REACTION OF IRON WITH SOME CONJUGATED DIENES

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Summary

Complexes have been obtained by the reaction of iron atoms with butadiene or styrene at −196°C followed by treatment with ligands such as CO or $(MeO)_3P$.

The recently reported 16 electron compound, di-1,5-cyclooctadieneiron [1], prompted us to investigate the reactions of iron atoms produced by laser evaporation of iron [2,3] with conjugated diene systems which might involve 16 electron systems as low temperature intermediates preceding rearrangement to more stable 18 electron systems at higher temperatures.

The cocondensation of butadiene with iron at −196°C and subsequent warm-up in an atmosphere of CO or PF_3 [2] yields only dibutadieneiron carbonyl or trifluorophosphine as isolable products. Substitution of one of the butadiene moieties can be accomplished by warming up the reaction mixture in an atmosphere of trimethylphosphite; we have found this leads to a mixture of dibutadieneiron trimethylphosphite and butadieneiron tris(trimethylphosphite). Attempts to isolate a tris(2,3-dimethylbutadiene)iron complex failed; thus the cocondensation of 2,3-dimethylbutadiene with iron at −196°C followed by warm-up to −20°C in an atmosphere of nitrogen produced a brown material (after filtration and evaporation of all liquid) with erratic analysis. This material was kept at 0°C for three days and trimethylphosphite was introduced. The only identifiable product was 2,3-dimethylbutadieneiron tris(trimethylphosphite).

The cocondensation of styrene or phenylacetylene with iron atoms produces polystyrene and triphenylbenzene, respectively, as the only identifiable products (in low yields ~1%), but the cocondensation of styrene and iron at −196°C and subsequent warm-up to −20°C in an atmosphere of CO produces styreneiron tricarbonyl, styreneiron tetracarbonyl and iron pentacarbonyl.

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It appears, therefore, that no carbon—hydrogen bond activation and subsequent rearrangement to form stable organometallics occurs in these systems and no stable complexes are produced in the absence of stabilising ligands.

Experimental

Metal evaporation and ligand cocondensation procedures are reported elsewhere [2]. All procedures reported were run under an atmosphere of argon unless stated otherwise.

Butadiene (10 ml) was cocondensed on a matrix of pentane with iron (0.5 g), over a 1 h period at −196°C; $P(OMe)_3$ (10 ml) was distilled into the reactor which was then filled with argon and warmed to room temperature. The resulting solution was filtered, evaporated to dryness and the resulting yellow solid recrystallised from pentane. The resulting two crystalline products (a mixture of $(C_4H_6)_2FeP(OMe)_3$ and $(C_4H_6)Fe[P(OMe)_3]_3$) could not be separated by chromatography, recrystallisation or sublimation, but by recording the mass spectrum every degree and plotting temperature against ion current for four distinct characteristic ions, we were able to establish the amounts of each compound present and the sublimation temperature for the unknown source pressure ($\sim 10^{-5}$ mmHg/25 and 50°C, respectively) the ratio of the parent ion concentrations was found to be almost exactly the same as that determined from a ^1H NMR spectrum of the mixture. $(C_4H_6)_2FeP(OMe)_3$ Mass spectrum: 288 (M), 234 ($M - C_4H_6$), 180 ($M - 2C_4H_6$), 135, 93. ^1H NMR spectrum: τ (ppm) 10.6 (4), 8.92 (4), 6.4 (9), 5.5 (4); $^3J(H—P)$ 15.0 Hz. $(C_4H_6)Fe[P(OMe)_3]_3$ Mass spectrum: 482 (M), 428 ($M - C_4H_6$), 304 ($M - C_4H_6 - P(OMe)_3$), 211, 181, 124, 109, 93, 63. ^1H NMR spectrum: τ (ppm) 10.6 (2), 8.92 (2), 6.4 (27), 5.5 (2), $^3J(H—P)$ 15.0 Hz. $(CH_3)_2C_4H_4Fe[P(OMe)_3]_3$ Mass spectrum: 510 (M), 479 ($M - OMe$), 428 ($M - (CH_3)_2C_4H_4$), 386 ($M - P(OMe)_3$), 355, 344, 304 ($M - P(OMe)_3 - (CH_3)_2C_4H_4$) 262, 211.

Styrene 30 g was cocondensed with iron atoms 3 g over a 1 h period at −196°C. The matrix was allowed to warm up to −25°C in an atmosphere of CO. The resulting liquid was filtered and all excess styrene evaporated. The remaining solid was eluted from a SiO_2 column (Merck 7734) with pentane. The 1st orange band was a mixture of $Fe(CO)_5$ and $C_8H_8Fe(CO)_3$ (separated by sublimation at 0°C). $C_8H_8Fe(CO)_3$ was recrystallised from pentane at −80°C (yield 10% from iron evaporated). The 2nd slow moving red-brown band was subsequently removed from the column with pentane/diethyl ether (90:10) and the resulting solid after solvent evaporation was recrystallised from pentane. $C_8H_8Fe(CO)_3$ Found: C, 54.6; H, 3.25; Fe, 24.1; mol. wt. (benzene), 248. $C_{11}H_8FeO_3$ calcd.: C, 54.18; H, 3.28; Fe, 22.9%. IR spectrum: ν(CO) 2048, 1983, 1973 cm^{-1} Mass spectrum: 244 (M), 216 ($M - CO$), 180, 160 ($M - 3CO$) [4]. $C_8H_8Fe(CO)_4$ Mass spectrum: 272 (M), 244 ($M - CO$), 216 ($M - 2CO$), 188 ($M - 3CO$), 160 ($M - 4CO$), 104, 78, 56. IR spectrum: ν(CO) 2086, 2014, 2008, 1984 cm^{-1} [5]. $Fe(CO)_5$ IR spectrum: ν(CO) 2024, 2005 cm^{-1}.

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