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Preliminary communication

Preparation and properties of dimethyltris(triphenylphosphine)iron(II) and ethyl(acetylacetonato)tris(triphenylphosphine)iron(II)

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Tertiary phosphines are well known as stabilizing ligands for transition metal alkyls,[1,2] but very few iron alkyl complexes have been described which have tertiary phosphine ligands without other stabilizing ligands such as cyclopentadienyl and carbonyl. We describe below the preparation and properties of methyl- and ethyl-iron complexes containing tertiary phosphine ligands.

(1) Ethyl(acetylacetonato)tris(triphenylphosphine)iron(II) (I)

The reaction of iron(III) acetylacetonate, triphenylphosphine (PPh_3) and triethylaluminum in a molar ratio of 1/4/3.5 in diethyl ether under nitrogen or argon at −30° gave a bright light brown complex of a composition $Fe(C_2H_5)(acac)(PPh_3)_3$[★][3] (I). Purification of (I) was not feasible because of the lack of a suitable solvent and the complex was analyzed

$$Fe(acac)_3 + PPh_3 + Al(C_2H_5)_3 \longrightarrow \underset{\text{(I)}}{Fe(C_2H_5)(acac)(PPh_3)_3}$$

after the repeated washing with ether and hexane and vacuum drying below −5°. (Found: C, 74.7; H, 6.0; Fe, 6.0, PPh_3/Fe[★★], 2.9; $C_{61}H_{58}O_2P_3Fe$ calcd.: C, 75.7; H, 6.0; Fe, 5.8%, PPh_3/Fe 3.0); yield 65%. Complex (I) is paramagnetic, thermally unstable above 0° and rapidly oxidized in air.

On hydrolysis (I) released 84% of the ethane expected from $Fe(C_2H_5)(acac)(PPh_3)_3$, on pyrolysis 70% of the ethane, and on alcoholysis 82% of the ethane. Iodolysis of (I) gave a trace of butane. The IR spectrum of (I) showed the presence of triphenylphosphine and

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[★] Similar nickel complexes containing alkyls, tertiaryphosphine and acetylacetonato ligands have been prepared.[2,3]

[★★] The triphenylphosphine content was determined by a spectroscopic method after hydrolysis with sulfuric acid and extraction of triphenylphosphine with hexane.

acetylacetonato ligands, and there are also bands due to ν(C—H) and δ(C—H) of the ethyl group bonded to iron at 2830, 1450 and 1350 cm⁻¹.

Complex (I) initiates the polymerization of styrene, acrylonitrile and methacrylonitrile. It is inert to non-polar solvents, but polar solvents such as acetone and tetrahydrofuran cause disproportionation of the complex and evolution of ethane. Very air-sensitive orange needles were isolated from the homogeneous reaction mixture and were identified as $Fe(acac)_2$ after recrystallization from tetrahydrofuran. (Found: C, 47.5; H, 5.6; $C_{10}H_{14}O_4Fe$ calcd: C, 47.3; H, 5.6%).

The similar reaction of $Fe(acac)_3$, triphenylphosphine and tri-n-propylaluminum in a molar ratio of 1/3/3 in diethyl ether under nitrogen or argon at −25° gave a yellow complex analogous to (I) but containing a propyl group.

(2) Dimethyltris(triphenylphosphine)iron(II) (II)

In contrast to the behaviour of the ethyl iron complex, $Fe(acac)_3$ reacted with triphenylphosphine and trimethylaluminum in a molar ratio of 1/3.5/3 in diethyl ether under nitrogen or argon at −40° for 2 h to give a light green crystalline complex, with the composition $Fe(CH_3)_2(PPh_3)_3$(II). The complex was characterized after careful

$$Fe(acac)_3 + PPh_3 + Al(CH_3)_3 \longrightarrow \underset{(II)}{Fe(CH_3)_2(PPh_3)_3}$$

washing with ether and hexane. (Found: Fe, 6.6; PPh_3/Fe, 2.8; $C_{56}H_{51}P_3Fe$ calcd: Fe, 6.4; PPh_3/Fe, 3.0); Yield 35%.

Complex (II) is unstable above −10° and burns in air, and attempts of microanalysis failed. It is not soluble in common organic solvents, and decomposed in an excess of ether in spite of the fact that it was prepared in that solvent. Addition of pyridine caused the decomposition of (II) with evolution of methane. Alcoholysis gave 95% of the methane calculated for $Fe(CH_3)_2(PPh_3)_3$, while pyrolysis gave 92% of the expected methane, and hydrolysis 80%. Iodolysis gave traces of ethane and ethylene. The IR spectrum of (II) shows ν(C—H) of the methyl groups bonded to iron at 2850 and 2770 cm⁻¹, and other absorptions at 1510, 1270 and 1180 cm⁻¹, in addition to the bands due to the coordinated triphenylphosphine ligands.

Complex (II) initiates the polymerization of methyl methacrylate, acrylonitrile and methacrylonitrile.

Use of diethylaluminum and dimethylaluminum monoethoxides in place of trialkylaluminums did not give the alkyl iron complexes.

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