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Metal Atom Synthesis of Iron 1,3,5,7-Cyclononatetraene Complexes

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The isolation of the unstable polyolefin 1,3,5,7-cyclononatetraene (CNT) has been reported in 1969 [1]. The first well characterised complex $\mathrm{Fe(1\text{-}4\eta^4\text{-}CNT)(CO)_3}$, was prepared by thermal reaction of bicyclo[6.1.0]-nona-2,4,6-triene (BCNT) with $\mathrm{Fe_2(CO)_9}$ [2, 3] or by photochemical reaction of BCNT with $\mathrm{Fe(CO)_5}$ [3]. Low yields of $\mathrm{Fe(1\text{-}4\eta^4\text{-}CNT)(CO)_3}$ have been obtained by reaction of BCNT with $\mathrm{Fe(BDA)(CO)_3}$ [4] and more recently the symmetrical isomer $\mathrm{Fe(3\text{-}6\eta^4\text{-}CNT)(CO)_3}$ has been prepared [5, 6].

We report here the metal atom synthesis of an "allene' iron complex of CNT which can be used as a route to $\mathrm{Fe(1\text{-}4\eta^4\text{-}CNT)L_3}$ complexes, as well as the characterisation of $\mathrm{Fe(1\text{-}4\eta^4\text{-}CNT)[P(OMe)_3]_3}$. A large number of iron diene phosphite complexes have been prepared recently [7] by cocondensation of iron atoms with olefins in a vertical fixed reactor. The metal evaporation technique used here is that developed by Timms [8].

The same CNT complex (1) is obtained by direct reaction of Fe atoms with RCNT at –120 °C in methylcyclohexane or by reaction of $\mathrm{Fe(1,5\text{-}COD)_2}$ [9] with BCNT at –78 °C in n-hexane (Scheme 1).

$$\mathrm{Fe_{at}} \xrightarrow{[9]} \mathrm{Fe(1,5\text{-}COD)_2}$$

(i) (ii) (iv)

$$\mathrm{Fe(\eta^6\text{-}CNT)(2\text{-}5\eta^4BCNT)} \xrightarrow{(iii)} \mathrm{Fe(1\text{-}4\eta^4\text{-}CNT)[P(OMe)_3]_3}$$

1 2

Scheme 1.

(i) The reaction was carried out in a stainless steel rotatory reactor [10]. The pumping system consisted of an Edwards 63-150 m oil diffusion pump backed by a two-stage Alcatel M-2012 primary pump, with two liquid nitrogen cooled traps between the pumping system and a pyrex reaction flask immersed in a petroleum ether/liquid nitrogen slush. The flask was connected to the rotating stainless steel head of the reactor by a 4.5 cm glass flange and a Teflon seal. A 3 ml alumina crucible with Mo filaments coated with Degussit 5010 cement (Degussa AG) was suspended in the center of the flask by two ethanol-cooled Cu electrodes. The two electrodes were insulated from the metal head of the reactor by Vespel SP1 connectors and Vito fluorocarbon rubber ring seals and powered by a transformer with regulating unit (Gutor AG) capable of delivering 100 A at 100 V. The head of the reactor was rotated at 40 r.p.m. inside a coaxial fixed stainless steel cylinder separated by Quad '0' ring seals X SEL (Busak-Luyken GMBH). The fixed cylinder was connected through Leybold vacuum valves to the vacuum system, to an auxiliary ligand introduction system and to a source of argon for flushing the entire apparatus. Typically, iron pellets (1.6 g; 28.6 mmol) were evaporated (45 A, 4V. 2×10^{-3} torr; 90 min.) towards the upper rotating liquid film coating the surface of a 6 liter pyrex reaction flask containing a mixture of BCNT [11] (6.5 g; 55.1 mmol) and methylcyclohexane (150 ml) at –120 °C. The filtered brown solution was reduced to a small volume at –40 °C/0.1 torr and the residue taken up in n-hexane. Chromatography under argon on a 15 × 1 cm column packed with alumina grade II using n-hexane at 10 °C as eluent brought down a brown band giving complex 1 (0.61 g) after recrystallisation from n-hexane at –80 °C. Yield: 7.3% based on invested iron.

$\mathrm{Fe(\eta^6\text{-}CNT)(2\text{-}5\eta^4\text{-}BCNT)}$ (1): black crystals unstable in air and in chloroalkane solutions. MS (70 eV): 292 ($\mathrm{M^+}$; 40), 176 (42), 174 ($\mathrm{M^+\text{-}C_9H_{10}}$; 55), 172 (65), 148 (66), 134 (97), 117 (68), 115 (100), 91 ($\mathrm{C_7H_7^+}$; 60), 56 ($\mathrm{Fe^+}$). ^{13}C-FT NMR (90.55 MHz) in d^8-toluene at room temperature; BCNT signals (δ in ppm relative to TMS; ^1J in Hz): C(6,7) 128.1 (d; 159), 125.6 (d; 160); C(3,4) 79.5 (d; 160), 78.6 (d; 156); C(2,5) 51.9 (d; 146), 42.3 (d; 150); C(1.8) 25.0 (d; 165), 24.5 (d; 161); C(9) 11.2 (t; 160); CNT signals: C(7.8) 135.1 (d; 159), 129.4 (d; 160); C(2,3,4,5) 98.0 (d; 161), 97.9 (d; 160), 94.0 (d; 161; ^3J 9.8), 93.1 (d; 161; ^3J 9.8); C(1,6) 64.5 (d; 153), 61.1 (d; 157); C(9) 30.5 (t; 125). One of the two ^{13}C triplets has a ^1J coupling constant identical to that of free BCNT (C(9) 14.2 (t; 160)). The other triplet has a much smaller coupling constant indicative of a C(1)–C(8) bond breaking of BCNT and is thus attributed to C(9) of CNT.

Complex 1 is completely asymmetric and non fluxional in toluene solution since 18 ^{13}C signals are observed up to +40 °C (decomposition occurs at

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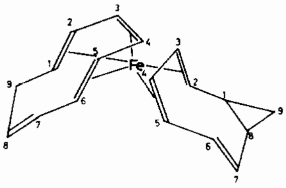
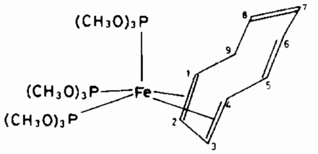
higher temperatures). Two C–C double bonds are uncoordinated as four ^{13}C doublets are observed in the region of olefinic carbon atoms (>125 ppm). Thus, complex 1 is the isomer which has its iron atom bonded to a 2–5 tetrahapto BCNT and a 1–6 hexahapto CNT.

(ii) Complex 1 was also obtained by the reaction of excess $Fe(1,5\text{-}COD)_2$ [9] with BCNT (17 mmol) in n-hexane (300 ml) at –78 °C under argon. The green solution turned brown and the unreacted $Fe(1,5\text{-}COD)_2$ was decomposed by warming the solution up to 0 °C. Similar workup as in (i) gave 1 (1 g; 3.4 mmol) in 20% yield.

The BCNT ligand is easily displaced from 1 by neutral ligands such as phosphites. A typical procedure is given below.



1



2

(iii) $P(OMe)_3$ (42 mmol) was added to a solution of 1 (1.71 mmol) in n-hexane (100 ml) at –30 °C under argon. The resulting solution turned orange and stirring was continued at r.t. for 30 min. The mixture was filtered over neutral alumina and reduced to a small volume. Chromatography under argon on a 20 × 2 cm column packed with alumina grade II using ether as eluent brought down free BCNT, then complex 2 (1.37 mmol) after recrystallisation from n-hexane/ether (1:1) at –70 °C. Yield 80%. Complex 2 may also be obtained from $Fe(1,5\text{-}COD)_2$ as in (ii), where excess $P(OMe)_3$ is introduced before the workup. Yield 16%.

$Fe(1\text{-}4\eta^4\text{-}CNT)[P(OMe)_3]_3$ (2); yellow crystals unstable in air. *Anal.* Calcd. for $C_{18}H_{37}P_3O_9Fe$: C, 39.58; H, 6.83. Found: C, 39.42; H, 6.71%. MS (70 eV); 546 (M^+; 5), 428 (12), 422 (13), 420 (9), 391 (9), 335 (6), 304 (100), 296 (18), 289 (9), 211 (61), 181 (30), 165 (14), 151 (5), 124 (21), 117 (26), 56 (Fe^+). ^{13}C-FT NMR (90.55 MHz) in C_6D_6 at r.t.: C(5,6,7,8) 124.4 (d; 160), 116.6 (d; 153), 134.8 (d; 154), 132.9 (d; 154); C(2, 3) 87.0 (d; 167), 82.2 (d; 161); OCH_3 52.2 (q; 144); C(1,4) 51.8 (d; 150), 50.0 (d; 150); C(9) 28.9 (t; 131). $^{31}P\{^1H\}$FT NMR (36.43 MHz) in d_6-acetone; at r.t.: 184.3 s (coalescence at –30 °C); at –70 °C: ABC spin system with δ_A 189.7, δ_B 183.6, δ_C 179.5 ppm (relative to H_3PO_4 62.5%), J_{AB} 46, J_{AC} 36 and J_{BC} 126 Hz. The temperature dependence of the ^{31}P NMR spectrum of 2 is similar to that reported by Ittel *et al.* [7] for iron diene phosphite complexes, indicating that the free double bonds of CNT do not take part in the phosphorus exchange process.

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