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# Synthesis and crystal structure of a new binuclear iron carbonyl cluster containing the triphos and $\mu,\eta^2$-$OCC_6H_5$ ligands

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The new bimetallic cluster $[Fe_2(CO)_4(\mu,\eta^2\text{-}OCC_6H_5)(\mu_4,\eta^3\text{-}CH_3C(CH_2PPh_2)_2CH_2PPh)]$ **3** has been synthesised from reaction between $Fe_3(CO)_{12}$ **1** and the tripodal polyphosphine compound $CH_3C(CH_2PPh_2)_3$ (1,1,1-tris(diphenylphosphinomethyl)ethane: triphos) **2**. The structure of cluster **3** has been established by single-crystal X-ray diffraction method.

**Keywords:** binuclear iron carbonyl cluster, triphos, X-ray structure

Transition metal carbonyl cluster compounds have attracted significant interest for a variety of reasons including, *inter alia*, the transition from molecular to bulk metallic properties which should ensue upon increasing cluster size,[1-3] as models for metal surfaces in chemisorption and catalysis,[4-9] and as precursors for metal particles active in heterogeneous catalysis.[4,5,7,8] The chemistry of polyphosphines, such as $CH_3C(CH_2PPh_2)_3$ [1,1,1-tris(diphenyl phosphinomethyl)ethane: triphos], has received a great deal of attention in recent years since it is an efficient ligand in a wide range of catalytic reactions such as hydrogenation and hydroformylation of olefins.[10-12] We report here the synthesis and crystal structure of the new cluster $[Fe_2(CO)_4(\mu,\eta^2\text{-}OCC_6H_5)(\mu_4,\eta^3\text{-}CH_3C\ (CH_2PPh_2)_2CH_2PPh)]$ **3** obtained by the reaction of $CH_3C(CH_2PPh_2)_3$ **2** with $Fe_3(CO)_{12}$ **1** in benzene at 60 °C (Scheme 1). The cluster **3** is stable in air in solid state and soluble in common organic solvents. Satisfactory C, H analysis was obtained for **3.**

The IR spectrum of **3** shows a weak absorption band around 3054 $cm^{-1}$ and intense absorption bands in the range 2048–1889 $cm^{-1}$, characteristic of the benzene rings and the terminal carbonyl ligand, respectively. The $^1H$ NMR spectrum of cluster **3** shows the presence of the tripodal polyphosphine ligand. The broad singlet at about δ 7.48 reveals the protons of the benzene ring. The signals at δ 2.28, 1.43 and 1.27 can be assigned to the protons of the $CH_2$ groups of the triphos and the singlet at δ 0.87 reveals the protons of the methyl.

The structural features of cluster **3** have been established by X-ray diffraction analysis of a suitable crystal. As seen in Fig. 1, three phosphorus atoms of the triphos ligand substituted the carbonyls of the iron atoms, respectively, and the average bond distance between the iron atom and phosphorus atom is 2.214 Å, which is shorter than corresponding distances that of $Re(CO)_3(\eta^2\text{-triphos})Br$.[12] Note that the structure of **3** contains an unusual coordination model, *i.e.*, $\mu,\eta^2$-$OCC_6H_5$, and the Fe(2), C(34), O(5) and Fe(1) atoms are located approximately in a plane due to the sum of the four internal angles (359.98°) and the torsion angles (Fe(2)–C(34)–O(5)–Fe(1) –0.35(15)°; Fe(2)–Fe(1)–O(5)–C(34) 0.5(2)°). The π system of the C(34)O(5) is conjugated with the benzene ring

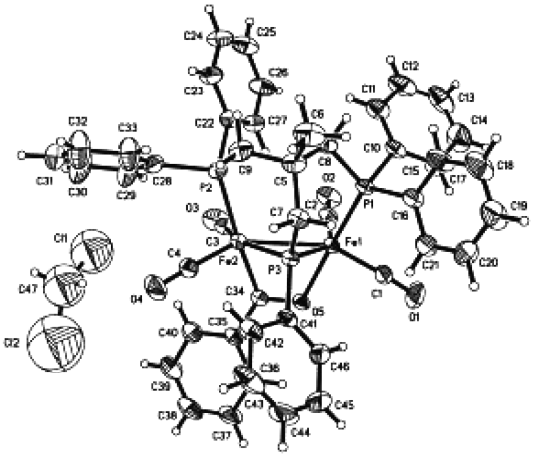
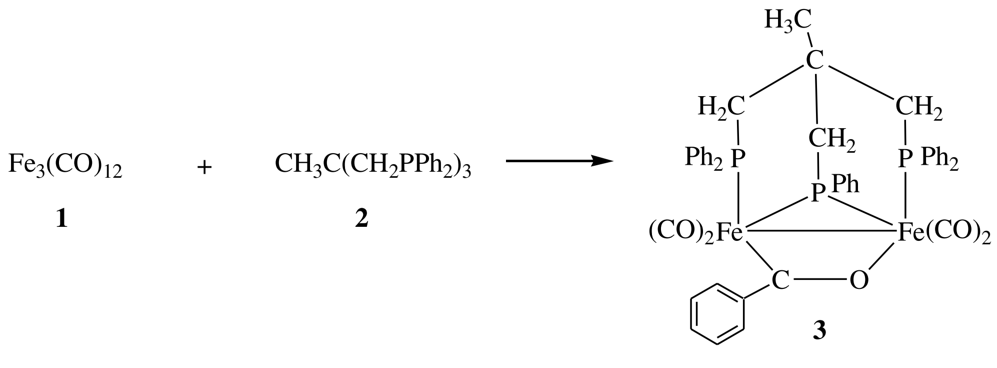


**Fig.1** Molecule structure of the cluster **3**·$CH_2Cl_2$. Selected bond distances (Å) and angles (°): Fe(1)–O(5) 1.989(3); Fe(1)–P(1) 2.1846(11); Fe(1)–P(3) 2.1935(11); Fe(1)–Fe(2) 2.7271(8); Fe(2)–P(3) 2.2066(11); Fe(2)–P(2) 2.2703(12); Fe(2)–C(34) 1.927(4); C(34)–C(35) 1.500(5); O(5)–C(34) 1.243(5); O(5)–Fe(1)–P(1) 170.78(9); O(5)–Fe(1)–P(3) 84.44(8); P(1)–Fe(1)–P(3) 87.79(4); O(5)–Fe(1)–Fe(2) 68.29(8); P(1)–Fe(1)–Fe(2) 110.43(4); P(3)–Fe(1)–Fe(2) 51.92(3); C(34)–Fe(2)–P(3) 83.76(12); C(34)–Fe(2)–P(2) 175.69(12); P(3)–Fe(2)–P(2) 94.94(4); C(34)–Fe(2)–Fe(1) 67.09(12); P(3)–Fe(2)–Fe(1) 51.49(3); P(2)–Fe(2)–Fe(1) 108.91(4); Fe(1)–P(3)–Fe(2) 76.60(4); C(34)–O(5)–Fe(1) 108.3(2); Fe(2)–C(34)–O(5)–Fe(1) -0.35(15).



**Scheme 1**

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π system (Fe(1)–O(5)–C(34)–C(35) 178.2(2)°; C(34)–C(35)–C(36)–C(37) –179.6(5)°), therefore in the bond length of C(34)-C(35) [1.500(5) Å] shows double-bond character and is shorter than the normal C–C distance (1.54 Å). It is not clear how the benzene group transfers from phosphorus atom to the carbon atom, further studies concerning the mechanism are currently underway.

## Experimental

All preparative work was carried out under an atmosphere of pure nitrogen by using standard Schlenk or vacuum-line techniques. Column chromatography was carried out by using silica gel columns of 160–200 mesh. [$Fe_3(CO)_{12}$] and $CH_3C(CH_2PPh_2)_3$ were used as received from a commercial source. IR spectra were recorded on a Nicolet NEXUS 670 FT-IR spectrophotometer. $^1H$ NMR spectra were measured on a Bruker AM-300 MHz spectrometer. Elemental analyses (C, H) were performed on a Perkin-Elmer 2400 type analyser.

*Synthesis of cluster* [$Fe_2(CO)_4(\mu,\eta^2\text{-}OCC_6H_5)(\mu_4,\eta 3\text{-}CH_3C(CH_2PPh_2)_2CH_2PPh)$] **3**: To a solution of **1** (504 mg, 1.0 mmol) in THF (20 ml) at room temperature was added dropwise a solution of **2** (312 mg, 0.5 mmol) in THF (5 ml) under dinitrogen. The mixture was stirred at 60°C for 18 h. During the stirring the colour of the solution gradually changed from black-green to brown-red and monitoring by TLC showed the disappearance of the starting material. After the THF was removed, the residue was extracted by a small amount of $CH_2Cl_2$ and transferred to the silica gel chromatography column. Elution with THF/petroleum ether (1:1) afforded the brown-red band. Condensing the solvent and crystallisation at –20°C gave red crystals of **3** (99.8 mg, 20.8%, based on 2). IR (KBr disc): ν (Ar–H) 3054w; ν (CO) 2048s, 1980s, 1943vs, 1913s, 1889s cm$^{-1}$; $^1H$ NMR($CDCl_3$, 300MHz): δ 7.48 (s, br, 30H, $6C_6H_5$), 2.28 (s, 2H, $CH_2$), 1.43 (s, 2H, $CH_2$), 1.27 (s, 2H, $CH_2$), 0.87 (s, 3H, $CH_3$) ppm.

*Crystal data of cluster 3·$CH_2Cl_2$*: Suitable crystals of cluster **3**·$CH_2Cl_2$ ($C_{47}H_{41}Cl_2Fe_2O_5P_3$) ($M_r$ = 961.31) were obtained from $CH_2Cl_2$-hexane at –20°C. The crystal system and space group was triclinic and $P_1$, respectively. The cell parameters were determined on a Bruke APEX CCD diffractometer with graphite-monochromated Mo-$K_\alpha$ radiation: $a$ = 9.4548(7), $b$ = 15.4195(12), $c$ = 16.1775(13) Å, $\alpha$ = 82.8340(10)˚, $\beta$ = 84.892(2)˚, $\gamma$ = 75.3160(10)°, $V$ = 2259.6(3) Å$^3$, $Z$ = 2, $D_c$ = 1.413g/cm$^3$, $\mu$ = 0.911 mm$^{-1}$, $\theta_{max}$ = 27.00° and $F(000)$ = 988. A total of 13341 reflections were collected with 9578 unique reflections ($R_{int}$ = 0.0346). The structure was solved by direct method and expanded using the Fourier technique. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were added according to the geometrical method. The final cycle of full-matrix least-squares refinement was based on 9578 observed reflections [$I>2\sigma(I)$] and 518 variable parameters and converged with unweighted and weighted agreement factors of $R$ = 0.0599, $R_w$ = 0.1981. The minimum and maximum final electron densities were –0.884 and 1.643 e Å$^{-3}$. All the calculations were performed using the SHELXL-97 crystallographic program package.

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