The Preparation and Structure of $[Fe_3(CO)_9(PMe_2Ph)_3]$

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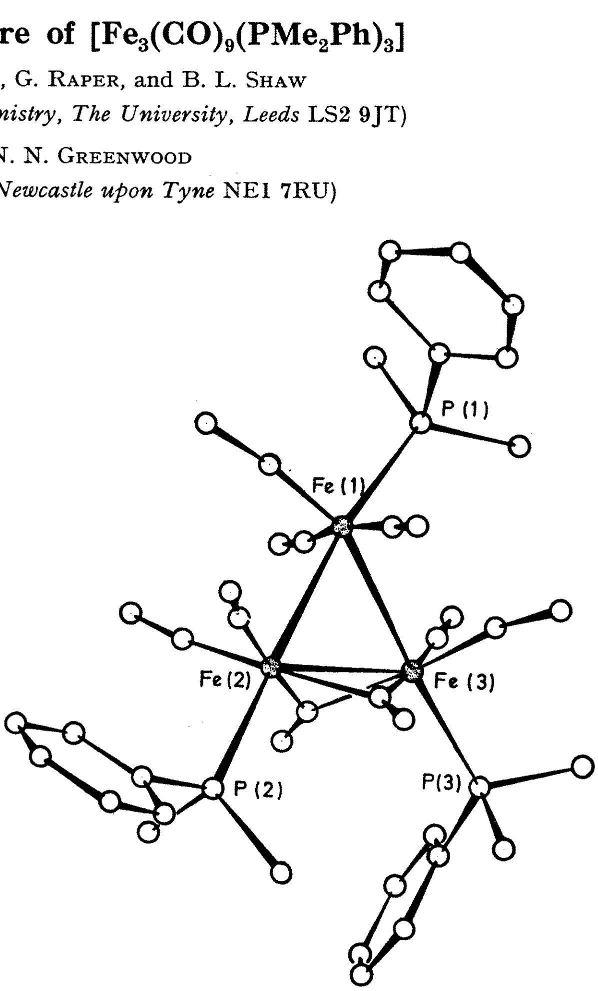
Summary The structure of $[Fe_3(CO)_9(PMe_2Ph)_3]$, prepared from $[Fe_3(CO)_{12}]$ and dimethylphenylphosphine, has been established by i.r. and Mössbauer spectroscopy and by *X*-ray crystal structure analysis.

TREATMENT of tri-iron dodecacarbonyl with dimethylphenylphosphine in boiling tetrahydrofuran for 1 hr. gives $[Fe_3(CO)_9(PMe_2Ph)_3]$ as glistening black needles. Osmometry suggests that the compound dissociates in solution; variable molecular weights such as 720 (C_6H_6), 700 ($CHCl_3$), 768 (Me_2CO) were found (calculated 834). The i.r. spectrum of the solid or its solution shows the presence of bridging carbonyls, *e.g.* in $CHCl_3$ $\nu(C{\equiv}O)$ are 2045w, 2019s, 1947 vs, 1792s, and 1745s cm.$^{-1}$, in contrast with the compounds $[M_3(CO)_9(PPh_3)_3]$, (M = Ru^{1-3} or Os^4) where ν (C=O) are $\geqslant$ 1920 cm.$^{-1}$, and no bridging carbonyls are present.

The Mössbauer spectrum of the compound comprises a pair of quadrupole split doublets with intensity ratio *ca.* 2 : 1, suggesting that the trinuclear framework of $Fe_3(CO)_{12}$ is retained. The chemical isomer shifts change from $0{\cdot}31 \pm 0{\cdot}01$ and $0{\cdot}37 \pm 0{\cdot}01$ in $[Fe_3(CO)_{12}]^5$ to $0{\cdot}28 \pm 0{\cdot}02$ and $0{\cdot}35 \pm 0{\cdot}02$ mm. sec.$^{-1}$ in $[Fe_3(CO)_9(PMe_2Ph)_3]$, indicating that the three iron atoms are affected about equally by the trisubstitution. In addition the unique iron atom suffers a large change in quadrupole splitting ($0{\cdot}13 \pm 0{\cdot}02$ to $0{\cdot}57 \pm 0{\cdot}02$ mm. sec.$^{-1}$) indicating that its charge cloud is more easily distorted tnan that of the basal iron atoms.

Crystals of $[Fe_3(CO)_9(PMe_2Ph)_3]$ are orthorhombic, space group *Pbca*, with $a = 16{\cdot}76$, $b = 18{\cdot}75$, $c = 23{\cdot}43$ Å, $Z = 8$. The structure, based on 1394 independent reflections, and refined by isotopic least squares to $R = 11{\cdot}4\%$, is shown in the Figure. Some bond lengths and their e.s.d.'s are given in the Table. The positions of phosphorus substitution are those found[6] in the two isomers of $[Fe_3(CO)_{11}PPh_3]$, and the phosphorus atoms lie within 0·1 Å of the plane passing through the three iron atoms.



FIGURE

Bond lengths (*Å*) *and e.s.d.'s in* $[Fe_3(CO)_9(PMe_2Ph)_3]$

Fe(1)–Fe(2)	2·688(7)	Fe(1)–P(1)	2·242(9)
Fe(1)–Fe(3)	2·689(7)	Fe(2)–P(2)	2·232(9)
Fe(2)–Fe(3)	2·540(7)	Fe(3)–P(3)	2·236(9)
Fe–C(O) bridging	1·97 to 2·04(3)		
Fe–C(O) non-bridging	1·70 to 1·86(3)		

Although the *X*-ray structure shows the three phosphorus ligands to be non-equivalent, the ^{1}H(methyl) n.m.r. pattern shows only a sharp 1 : 1 doublet in either $CHCl_3$ or C_6H_6 solution, suggesting that some rapid rate process is making the methyls equivalent. With iodine at −70° $[Fe_3(CO)_9(PMe_2Ph)_3]$ gives $[FeI_2(CO)_3(PMe_2Ph)]$ in 85% yield.

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