The Probable Molecular Configuration of $Fe_3(CO)_{12}$ based on the Structure of $Fe_3(CO)_{11}PPh_3$

By DONALD J. DAHM and ROBERT A. JACOBSON

(*Institute for Atomic Research and Department of Chemistry, Iowa State University, Ames, Iowa*)

SINCE 1930, when iron tetracarbonyl was found to be trimeric, the configuration of $Fe_3(CO)_{12}$ has been highly disputed. The i.r. spectra of solutions of $Fe_3(CO)_{12}$ contain strong terminal carbonyl absorption bands around 2000 cm.$^{-1}$, but only very weak bridging carbonyl bands[1,2] around 1800 cm.$^{-1}$. In 1957, work in this laboratory on the solid-state i.r. spectrum of $Fe_3(CO)_{12}$ strongly indicated the existence of the bridging carbonyls.[3] Most configurations proposed recently for $Fe_3(CO)_{12}$ have had both terminal and bridging carbonyls,[4–7] although some authors have suggested configurations containing no bridging carbonyls.[1,8] A crystal-structure determination attempted by earlier workers in this laboratory showed the iron atoms to be arranged triangularly,[9] but unfortunately disorder prevented a complete structural determination. Later, when Mössbauer-effect studies indicated that $Fe_3(CO)_{12}$ contains two iron atoms having identical electronic environments with the third having a more symmetrical environment, a linear model regained favour.[4–7]

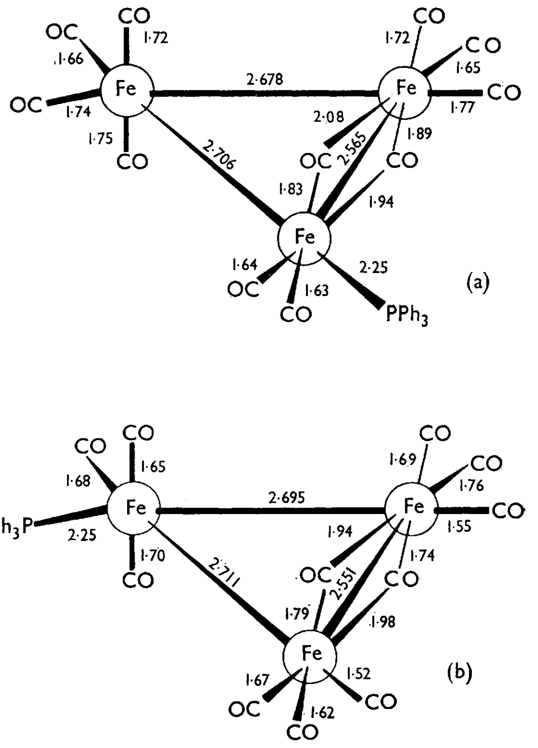
Recently, Dahl and Blount[10] suggested a configuration having the iron atoms arranged triangularly with two of them connected by bridging carbonyls, extrapolating from the structure of $[Et_3NH][HFe_3(CO)_{11}]$, and pointed out that this configuration is consistent with all the above mentioned facts. We now give evidence for a similar configuration but with improved Fe–Fe distances and an altered arrangement for the bridging carbonyls by reporting the molecular structures of two substitution products of $Fe_3(CO)_{12}$.

Recently, Angelici and Siefert[11] have prepared $Fe_3(CO)_{11}PPh_3$, a monosubstituted triphenylphosphine derivative of $Fe_3(CO)_{12}$ with properties very similar to those of the parent compound. Monoclinic crystals were obtained and the systematic absences are those of the space group C_2c. The unit-cell parameters are $a = 37{\cdot}14$, $b = 12{\cdot}26$, $c = 26{\cdot}05$ Å, and $\beta = 93{\cdot}96°$; with $\rho_{calc} = 1{\cdot}66$g./cm.^{3} for sixteen molecules per unit cell. There are two crystallographically independent molecules in the asymmetric unit. These two molecules are chemically similar, but, surprisingly, are structural isomers of one another, with the PPh_3 group attached to different iron atoms (Figure).

The agreement factor, R, is 0·10 for about 1800 observed reflections and further refinement is in progress. A difference electron-density map indicates no peaks greater than 0·7 $e/\text{Å}^3$. While more complete structural details will be published later, some of the more important bond distances are included in the Figure.

Of particular interest is the *asymmetric* location of the bridging carbonyls, with the longer Fe–C distances averaging 1·98 Å and the shorter 1·81 Å. At this stage of refinement, the estimated standard errors are $\pm 0{\cdot}03$ Å for Fe–C bonds and $\pm 0{\cdot}008$ Å for Fe–Fe bonds. Thus it appears that the bridging carbonyls occupy positions which differ significantly from being equidistant from the two iron atoms. To our knowledge, the isomer in the Figure (b) contains the first reported asymmetric carbonyl bridge in which the environment of a bridging carbonyl is substantially the same in the direction of each of the bridged metal atoms. This asymmetry is consistent with the fact that the bridged Fe–Fe distances are greater than the 2·49 Å found in $Fe_2(CO)_4(C_5H_5)_2$[12] or the 2·46 Å in $Fe_2(CO)_9$[13] in which the carbonyls form a nearly symmetric bridge. The Fe–Fe distances are similar to those found in $[Et_3NH][HFe_3(CO)_{11}]$[10] (2·577 Å for bridged; 2·685 and 2·696 for unbridged), but the reportedly symmetric bridge for that compound had only one bridging carbonyl and a bridging hydrogen.

Since both isomers of $Fe_3(CO)_{11}PPh_3$ show asymmetric bridging, it seems more likely that this is a property of the parent compound rather than an effect introduced by the PPh_3 group. Thus we suggest that the structure of $Fe_3(CO)_{12}$ is very similar to that shown in the Figure (b), but with the PPh_3 group replaced by a carbonyl. The replacement of this group would have little effect on the bridged portion of the molecule. The three iron atoms would be arranged in the form of an isosceles triangle, approximately 2·68 Å on a side and 2·55 Å across the base.[14,15] The only carbonyl bridges would be the two in the base, *asymmetrically* located.[15] On this basis, the symmetry of a $Fe_3(CO)_{12}$ molecule would be C_2 instead of C_{2v} as previously proposed.[10,15]



FIGURE

Molecular configurations of two isomers of $Fe(CO)_{11}PPh_3$.

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[14] Each of these distances was taken from a different isomer of $Fe_3(CO)_{11}PPh_3$ and is the Fe–Fe distance found between iron atoms, neither of which is bonded to a phosphorus atom.
[15] A recent private communication (see: C. H. Wei and L. F. Dahl, *J. Amer. Chem. Soc.*, 1966, **88**, 1821) indicates that these Fe–Fe distances are not inconsistent with those found in a redetermination of the structure of $Fe_3(CO)_{12}$. However, due to disorder and the resulting large standard errors, any asymmetric nature of the carbonyl bridges was undetected in that work.