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MOLECULAR STRUCTURE OF η^3-[(trans-1,2-DIMETHOXYCARBONYLVINYL)-METHOXYCARBENE]TRICARBONYLIRON(0), A NOVEL COMPLEX CONTAINING THREE-CARBON FOUR-ELECTRON LIGAND, η^3-VINYLCARBENE

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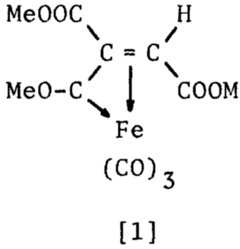
X-ray structure determination of the title complex, $[(OC)_3FeC(OMe)-C(COOMe)=CH(COOMe)]$, reveals that the η^3-vinylcarbene ligand coordinates to Fe with both the C=C group and the carbene C atom. The short Fe-C(carbene) length of 1.819(3) Å suggests some partial double bond character to its bond.

The methylation of 1:1 adduct of $[HFe(CO)_4]^-$ and dimethyl acetylenedicarboxylate gave yellow crystals of the composition $Fe(C_{11}H_{10}O_8)$, which was inferred to be η^3-[(trans-1,2-dimethoxycarbonylvinyl)methoxycarbene]tricarbonyliron(0)1) [1]. To elucidate the stereochemistry of [1] an X-ray crystallographic analysis has been carried out.



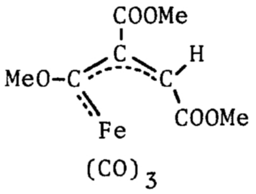
[1]

Single crystal specimens were grown from a light petroleum solution. Crystal data: Monoclinic, space group C2/c; a = 18.127(6), b = 9.713(2), c = 15.909(4) Å, β = 97.51(5)°; Z = 8. The intensity data were collected on a computer-controlled diffractometer with graphite-monochromated Mo $K\alpha$ radiation. On the basis of 2024 reflections with $|F_o| > 3\sigma(F)$ the structure was solved and refined by the least-squares method. Anisotropic thermal vibrations were assumed for the nonhydrogen atoms. All the H atoms were revealed from a difference Fourier map and refined isotropically. The conventional R value was 0.039.

The crystal structure consists of a packing of discrete complex molecules. Figure 1 shows the molecular structure. The coordination around the Fe atom is described as a greatly distorted trigonal bipyramid with the C(3)(carbene) and C(18)(carbonyl) atoms at the axial apices (C(3)-Fe-C(18) 143.9(2)°) and the other carbonyl C atoms, C(14) and C(16), and the C(4)=C(5) group on the equatorial plane, the latter being taken as a monodentate ligand. The two COOMe groups are trans to each other about the C(4)=C(5) bond as predicted in the previous study.1)

The Fe-C(3) length of 1.819(3) Å is considerably shorter than those ranging 1.926-2.03 Å2-6) so far reported for Fe-carbene complexes. Moreover, the present length is the shortest transition metal-C(carbene) length. The axial Fe-C(18) length of 1.837(4) Å is longer than the equatorial Fe-C(carbonyl) lengths (av 1.783(4) Å). These findings suggest that back-donation of electrons from Fe into C(3) is enhanced, while that into C(18) is weakened, to give some partial double-bond character to the Fe-C(3) bond: this is inconsistent with the result obtained for Cr-carbene complexes.[7]

The C(3) atom and the three atoms bonded to it are non-coplanar and the bond angles about C(3) deviate greatly from the trigonal(sp^2) angle. This finding is in contrast with those so far observed on the previously known carbene complexes and must be due to the coordination of C(4)=C(5) to Fe. The C(3)-O(2) length of 1.295(4) Å agrees well with the reported values ranging 1.26-1.33 Å. The coordination geometry of the Fe-olefin group is similar to those found in π-bonded olefin complexes. The C(3)-C(4) length of 1.420(4) Å is significantly shorter than the usual $C(sp^2)$-$C(sp^2)$ single-bond length.



[2]

In conclusion the bond-structure of the complex molecule is well represented by [2] on the basis of the present X-ray structure.

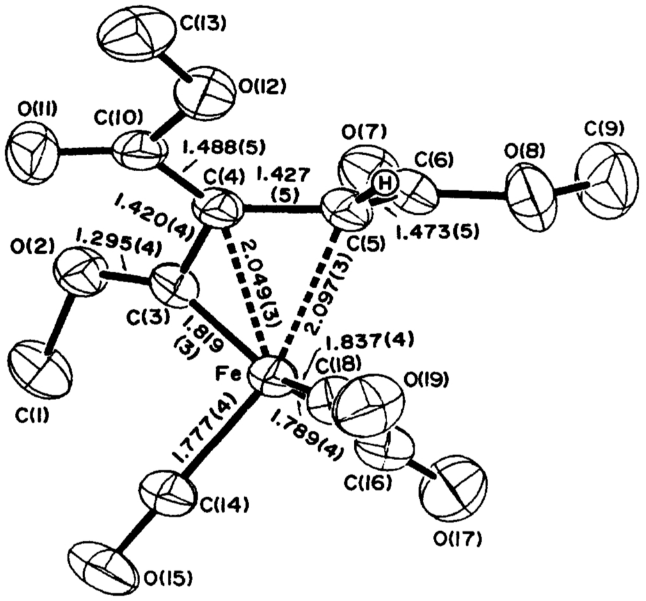


Fig. 1. Stereochemistry of and important bond lengths (in Å) in the complex. Methyl H atoms are omitted. Thermal ellipsoids are scaled to include 40% probability except for that of H, which is drawn by a sphere of an arbitrary radius. Relevant bond angles are: Fe-C(3)-O(2) 151.1(3)°, Fe-C(3)-C(4) 77.4(2)°, C(3)-C(4)-C(5) 109.3(3)°, O(2)-C(3)-C(4) 127.2(3)°, C(4)-C(5)-C(6) 119.6(3)°.

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