Crystal Structure of a Vinylidene Iron Complex, *Cis*-[(η -Cp)₂Fe₂(μ -CO)(CO)₂-(μ -C=C(COOCH₃)₂)], Formed by 1,2-Acyl Shift of Dimethylacetylenedicarboxylate

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The compound crystallized in a monoclinic system, and was characterized thus: $P2_1/n$; $a = 8.821(5)\text{\AA}$, $b = 14.971(5)\text{\AA}$, $c = 14.473(5)\text{\AA}$, $\beta = 101.306(5)^\circ$, $Z = 4$, $V = 1874.20(24)\text{\AA}^3$. The crystal structure was solved by direct methods and refined by full-matrix least-squares on F^2 to final values of $R_1 = 0.0528$ and $wR_2 = 0.1574$. An acyl-group of the dimethylacetylene dicarboxylate ligand underwent a 1,2-acyl shift, while forming a vinylidene dianion, which newly bridged to the *cis*-dicyclopentadienyldiiron-group by the ($\mu, \eta^1: \eta^1$)-bond fashion with atomic distances of Fe1-Fe2 2.5028(15) $\text{\AA}$, C1-C2 1.342(4) $\text{\AA}$, and Fe1-C1 1.917(3) $\text{\AA}$, Fe2-C1 1.901(3) $\text{\AA}$, respectively.

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The rearrangement of alkyne by its 1,2-substituent shift mediated by transition-metal complexes is known to afford its tautomeric vinylidene complexes.¹ 1,2-H, SiMe₃- and acyl-migration of alkyne converting to bridging vinylidene complexes have been well established in dinuclear Ru complexes, such as [(η -Cp)₂Ru₂(CO)₂(μ -CO)(μ -C=CH₂)]₂² and [(η -Cp)(η -Cp*)Ru₂(CO)₂(μ -CO){ μ -C=C(COOCH₃)₂}],³ which have been prepared by methodical syntheses: the initial alkyne exchange reaction of diruthenacyclopentenone structure by ethyne or dimethylacetylenedicarboxylate, followed by 1,2-H and acyl-shift *via* their *intra*-molecular C-H or C-C bond cleavages. Recently, by using a sequence of the ¹³C-labelling alkyne, its transformation to vinylidene-mononuclear ruthenium complexes is reported, suggesting that the acyl group exhibits the migratory aptitude.⁴ There are still only a few reports concerning the bridging vinylidene complexes of dinuclear iron. In our recent studies

for introducing alkyne into *trans*-[(η -Cp)₂Fe₂(CO)₄],⁵ a vinylidenediiron complex of dimethylacetylenedicarboxylate (dmd), *cis*-[(η -Cp)₂Fe₂(μ -CO)(CO)₂{ μ -C=C(COOCH₃)₂}], was newly prepared, although only in 8% yield. This title complex is given by a 1,2-acyl shift of dimethylacetylenedicarboxylate through an intramolecular C-C bond cleavage reaction, while the reaction is also accompanied by the cyclotrimerization of

Fig. 1 Chemical structure diagram of the title compound.

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Table 1 Crystal and experimental data

Chemical Formula: C ₁₉ H ₁₆ O ₇ Fe ₂
Formula weight: 742.00
$T = 293\text{ K}$
Crystal system: monoclinic
Space group: $P2_1/n$ $Z = 4$
$a = 8.821(5)\text{\AA}$
$b = 14.971(5)\text{\AA}$ $\beta = 101.306(5)^\circ$
$c = 14.473(5)\text{\AA}$
$V = 1874.20(24)\text{\AA}^3$
$D_x = 1.70\text{ g/cm}^3$
Radiation: Mo $K\alpha$ ($\lambda = 0.71073\text{ \AA}$)
$F(0\ 0\ 0) = 975.8$
Crystal size = $0.12 \times 0.12 \times 0.12\text{ mm}$
No. of reflections collected = 19008
No. of independent reflections = 4302
θ range for data collection: 1.4 to 27.5°
Data/Restraints/Parameters = 4302/0/254
Goodness-of-fit on $F^2 = 1.077$
R indices [$F_o > 4\sigma(F_o)$]: $R_1 = 0.0528$
R indices (all data): $R_1 = 0.0617$, $wR_2 = 0.1574$
$(\Delta/\sigma) = 0.000$
$(\Delta\rho)_{\max} = 1.19\text{ e\AA}^{-3}$
$(\Delta\rho)_{\min} = -0.690\text{ e\AA}^{-3}$
Measurement: Crystal Clear-SM Expert 2.0 r1 (Rigaku, 2009), Rigaku AFC7s
Refinement: full-matrix least-squares, SHELXL97
Program system: WinAFC, WinGX2013.3
Structure determination: SHELXS-97
CCDC deposit number: 922389

Fig. 2 ORTEP structure of *cis*-[(η -Cp) $_2$ Fe $_2$ (μ -CO)(CO) $_2$ { μ -C=C(COOCH $_3$) $_2$ }] showing 50% probability ellipsoids.

alkynes, affording hexamethybenzenehexacarboxylate.

By reacting *trans*-dicyclopentadienyldiiron tetracarbonyl with dimethylacetylenedicarboxylate (dmad) under reflux in toluene for 38 h, an extraordinary 1,2-migration of the acyl-group in dmad occurred, leading to the isolation of a bridging vinylidene complex,

[(η -Cp) $_2$ Fe $_2$ (μ -CO)(CO) $_2$ { μ -C=C(COOCH $_3$) $_2$ }], although its yield was only by 8%. Although, an excess amount of dmad (6-times molar quantity) was used for the reactions, alkyne-cyclotrimerization parallelly underwent to afford hexamethybenzenehexacarboxylate in a 23% isolated yield/dmad, and ferrocene was obtained in a 6% yield/Fe atom.

Crystal and experimental data of [(η -Cp) $_2$ Fe $_2$ (CO) $_3$ {=C=C(COOCH $_3$) $_2$ }] are given in Table 1. Intensity data were collected by $2\theta/\omega$ scans at 293 K using a Rigaku AFC-7S four circle diffractometer with Mo- K_α radiation ($\lambda = 0.7103$ Å), and were collected for Lorenz and Polarization effects. Structure solutions were performed by a direct method using SHELXS97 and by full-matrix least squares on F_o^2 with SHELXL97, using DIRDIF99 and WinGX32 software. All non hydrogen atoms were refined anisotropically with H atoms at the calculated positions riding on C atoms with C-H being fixed at 0.98 Å. A chemical structure diagram is shown in Fig. 1 and an Ortep plot in Fig. 2. The dmad ligand newly underwent a 1,2-acyl-shift, forming a vinylidene dianion, {=C=C(COOCH $_3$) $_2$ }, which cross-links to iron nuclei of *cis*-(η -Cp) $_2$ Fe $_2$ (μ -CO)(CO) $_2$ -groups {an atomic distance Fe1-Fe2 2.5028(15)Å} by Fe-C σ bonds with atomic distances of Fe1-C1 1.917(3)Å, Fe2-C1 1.901(3)Å, and C1-C2 1.342(4)Å, respectively. The terminal carbonyl carbons, C8 and C9, are *equi*-disistant from two iron nuclei {atomic distance Fe1-C8 is 1.767(3)Å, Fe2-C9 1.766(4)Å}. Although, the vinyl group leans toward one iron nucleus, and the bond angle Fe2-C1-C2 is

141.9(2)°, and Fe1-C1-C2 135.7(2)°. The 'lean' coordination of the bridging vinylidene may not be unusual, since the corresponding angles of [(η -Cp)(η -Cp*)Ru $_2$ (μ -CO)(CO) $_2$ { μ -C=C(COOCH $_3$) $_2$ }]⁴ are 141.0(3)° and 134.1(2)°, while those of [(η -Cp) $_2$ Ru $_2$ (μ -CO)(CO) $_2$ { μ -C=CH $_2$ }]⁵ 140.7(7)° and 135.9(7)°. The 'lean' coordination of the vinylidene ligand in the present case may not only be due to an unfavourable steric interaction between the bulky acyl-groups, but also involves electronic reasons, so that all atoms of one acyl-group {dihedral angle C6, O4, O2, C2 1.2(5)°}, including the C5 atom, are arranged approximately in the same plane to that formed by Fe1, Fe2, C1, including C2 atoms {dihedral angle 172.2(4)°}, indicating a relatively large electron delocalization through the Fe1, Fe2, C1, C2, C6, O4, and O2 atoms.

[(η -Cp) $_2$ Fe $_2$ (μ -CO)(CO) $_2$ { μ -C=C(COOCH $_3$) $_2$ }] was directly synthesized by reacting *trans*-[Cp $_2$ Fe $_2$ (μ -CO) $_2$ (CO) $_2$] with dmad under reflux in toluene for 38 h, although its isolated yield was low, down below 10%, possibly due to decomposition, since the reaction also produced ferrocene in 6% isolated yield. 1,2-Acyl shift of dmad observed at the present diiron complex apparently exhibit a C-C bond cleavage of dmad. We could not, however, have obtained the corresponding vinylidene complex in the *trans*-geometry. Instead, by using an excess amount of dmad (6-times molar quantity/Fe atom), the dmad cyclotrimerized product, hexamethylmellitic acid, was obtained in a 138% isolated yield/Fe atom. The present vinylidene complex may be given by an intramolecular C-C bond cleavage of the alkyne, while the cyclotrimerized compound by intermolecular C-C bond formation. These products may be formed *via* a preliminal intermediate having a dimetallacyclobutene or dimetallacyclobutenone structure.³ Yet, from the pyrolytic or photo-reactions of *trans*-[(η -Cp) $_2$ Fe $_2$ (μ -CO) $_2$ (CO) $_2$] with dmad for a duration within 1 day, we still have not succeeded to isolate it.

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