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Preliminary communication

REACTION OF TETRAKIS(TRIFLUOROMETHYL)ALLENE WITH CARBONYLATE ANIONS. X-RAY STUDY OF THREE NOVEL FLUOROOLEFINIC COMPLEXES

A.N. NESMEYANOV, G.G. ALEKSANDROV, N.G. BOKII, I.B. ZLOTINA,
Yu.T. STRUCHKOV* and N.E. KOLOBOVA

Institute of Organo-Element Compounds, Academy of Sciences of the USSR, Vavilov Str. 28, Moscow, B-312 (U.S.S.R.)

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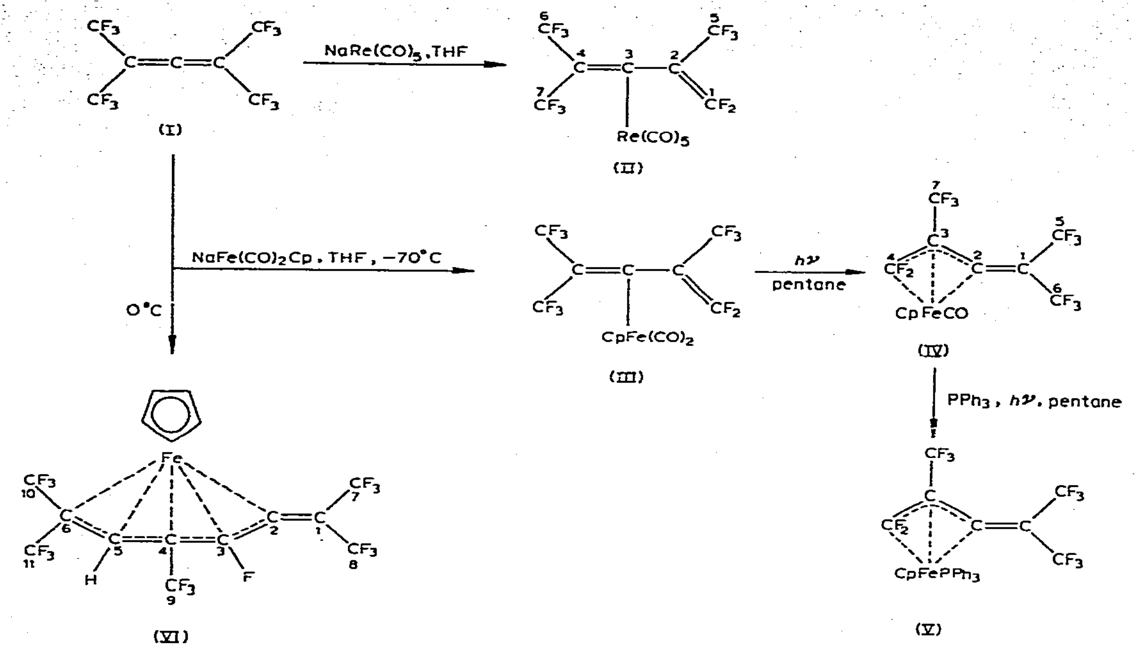
Summary

X-ray structure analysis is carried out for three new complexes prepared by interaction of tetrakis(trifluoromethyl)allene with carbonylate anions $[CpFe(CO)_2]^-$ and $[Re(CO)_5]^-$. In the molecule of $[\{(F_3C)_2C{=}C{-}C(CF_3){=}CF_2\}\text{-}Re(CO)_5]$ the η^1-butadienyl ligand is non-planar with a dihedral angle of 83° due to steric overcrowding and is bonded by the Re—C σ-bond (2.25 Å). In the complex $[\{(F_3C)_2C{=}C\overset{\cdots}{-}C(CF_3)\overset{\cdots}{-}CF_2\}Fe(\eta^5\text{-}Cp)PPh_3]$ the unusual η^3-allylidene ligand is found. One of its double bonds is not coordinated by metal. In the sandwich molecule $[\{(F_3C)_2C{=}C\overset{\cdots}{-}CF\overset{\cdots}{-}C(CF_3)\overset{\cdots}{-}CH\overset{\cdots}{-}C(CF_3)_2\}\text{-}Fe(\eta^5\text{-}Cp)]$ the dihedral angle between η^5-ligands is equal to 7°. One of them is a novel acyclic pentadienylidene ligand with a terminal double C=C bond not interacting with metal. The nature of the two latter complexes was revealed by the present X-ray study.

Recently it was reported [1] that tetrakis(trifluoromethyl)allene (I) reacted in THF at $-70°C$ with carbonylate anions $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^-$ and $[Re(CO)_5]^-$ cleaving-off one fluorine atom. As the most electron-deficient centre of allene is its central carbon atom, carbonylate anions probably attack this atom with migration of one of the allenic double bonds, cleaving-off of a fluorine atom which is in allylic position relative to the attacked site thus forming the σ-complexes II and III (Scheme 1) with 2,4,4-tris(trifluoromethyl)-1,1-difluorobuta-1,3-dien-3-yl ligand.

By heating or UV irradiation in solution complex III readily cleaves off a CO group turning into complex IV. In photochemical reactions of III with PPh_3 besides the cleaving-off of one CO group, replacement of the second CO ligand by PPh_3 takes place with formation of complex V. Results of elemental analysis, IR, PMR and ^{19}F NMR spectra are consistent with the proposed structures of compounds II—V [2].



In reactions of I with Na[(η^5-C_5H_5)Fe(CO)$_2$] in THF at 0°C we succeeded in isolating besides III, a small yield (4%) of another crystalline complex VI with composition $C_{16}H_6F_{16}Fe$ which was characterized by IR and mass spectra [3].

To elucidate transformations of perfluoroolefinic ligand I and to establish unequivocally structures of the complexes formed we undertook an X-ray study of II, V and VI (four-circle automatic Hilger & Watts diffractometer, Mo-radiation, graphite monochromator, heavy atom technique, block-diagonal anisotropic least squares refinement).

Crystal data. II, triclinic, a 8.842(3), b 11.950(5), c 8.817(3) Å, α 92.80(4)°, β 115.80(4)°, γ 90.70(4)°, D_m 2.44, D_c 2.46 g cm^{-3} for $Z = 2$, space group $P\bar{1}$, 2000 independent reflections, $R = 0.099$. V, monoclinic, a 10.423(3), b 19.375(4), c 15.202(4) Å, β 116.77(3)°, D_m 1.63, D_c 1.64 g cm^{-3} for $Z = 4$, space group $P2_1/c$, 2006 independent reflections, $R = 0.039$, all hydrogen atoms located and refined isotropically. VI, monoclinic, a 23.70(1), b 10.046(8), c 15.41(1) Å, β 98.32(5)°, D_m 2.05, D_c 2.05 g cm^{-3} for $Z = 8$, space group $C2/c$, 1500 independent reflections, $R = 0.080$.

For complex II the structure with octahedral coordination of the metal atom is confirmed (Fig. 1) : five CO groups (av. Re—C 1.98(2), C—O 1.16(2) Å, $\angle$ Re—C—O 175(1)°) and a σ-bonded η^1-butadienyl ligand with the usual [4] Re—C(2) bond length of 2.25(3) Å. In accordance with sp^2-hybridization of C(1), C(2), C(3) and C(4) four atomic fragments centered on these atoms are planar, however, the butadiene system as a whole is essentially non-planar with the dihedral angle C(1)=C(2)—C(3)=C(4) of 83(1)°. This distortion is due to steric hindrance because in planar conformations the non-bonded distances $CF_3 \cdots CF_3$ in the *trans*- and $CF_3 \cdots CF_2$ in the *cis*-form would be equal to ca. 2.3 Å, i.e. in-

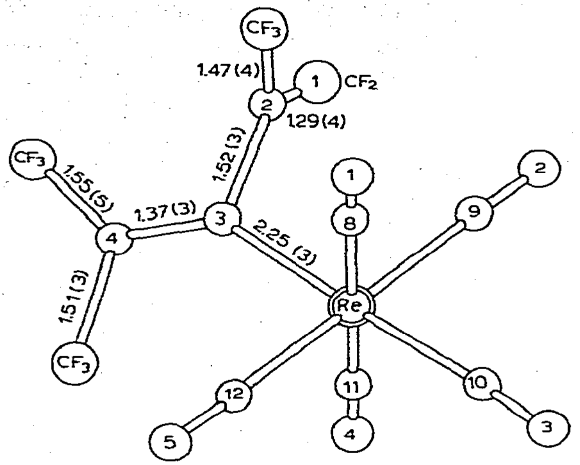


Fig. 1. Molecular geometry of II with main bond lengths and angles.

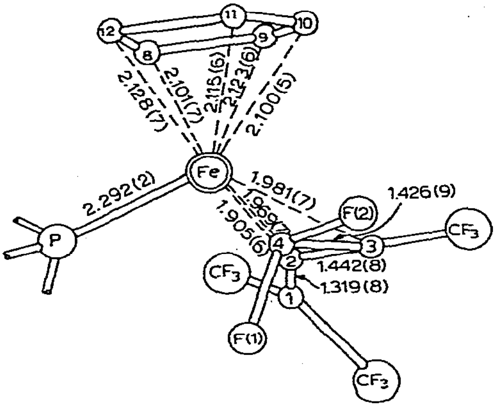


Fig. 2. Molecular geometry of V with main bond lengths and angles.

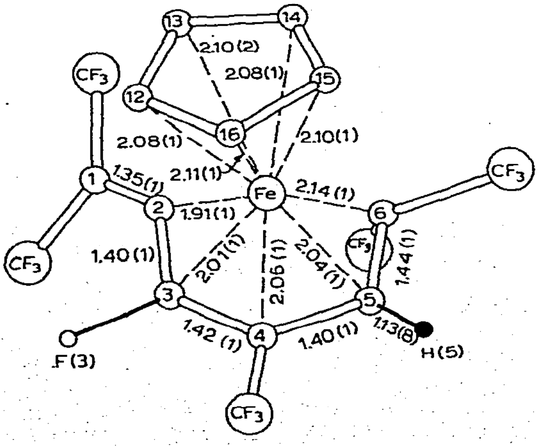


Fig. 3. Molecular geometry of VI with main bond lengths and angles.

admissibly short. Steric repulsion Re···F (3.28(1) Å) leads also to distortion of the planar-trigonal bond configuration around C(3): the Re—C(3)—C(4) angle is increased to 134(2)°.

In complex V (Fig. 2) the iron atom is coordinated by the η^5-Cp-ring (av. Fe—C 2.113(4), C—C 1.416(6) Å), the PPh_3 ligand (Fe—P 2.292(2) Å) and the π-allylic system of the η^3-butadienyl ligand. The double bond C(1)=C(2) of 1.319(8) Å length does not interact with the metal atom (Fe···C(1) 3.143(6) Å) and is inclined to the allylic plane at 28.3(9)°. Allylic and Cp ligands form a wedge-like "sandwich" (dihedral angle between their planes is 5(1)°) to accomodate the PPh_3 ligand. The novel allylidene ligand in V represents an isomeric form of butadienyl arising because of changes in electronic requirements of the metal caused by replacement of two CO groups by a single PPh_3 ligand.

The Fe—C(allyl) distances in V are shorter than in ordinary π-allyl complexes of iron [5]. The especially pronounced Fe—C(2) shortening to 1.905(6) Å and the opening of the C(1)—C(2)—C(3) angle to 134.5(7)° bring V near allene complexes [6].

The structure of VI turned out to be different from that expected (Fig. 3). In VI the iron atom is coordinated by the η^5-Cp ligand (av. Fe—C 2.09(1), C—C 1.42(2) Å) and the acyclic η^5-pentadienyl fragment of 1,1,4,6,6-pentakis(trifluoromethyl)-3-fluorohexa-1,3,5-trien-2-yl ligand, the two η^5-systems being almost parallel (dihedral angle 7(1)°). As in V one of the double bonds C(1)=C(2) of 1.35(1) Å length is not coordinated by the metal (Fe···C(1) 3.16(2) Å), i.e. this novel ligand is to be named pentadienylidene. It is bonded similarly to the allylidene ligand in V: average C$\overset{\dots}{-}$C 1.42(2) Å, the Fe—C(2) distance of 1.91(1) Å is considerably shorter than others (2.01—2.14 Å), the angle at C(2) is increased up to 134(1)°. With the exception of distortions brought about by the uncoordinated double bond the bonding of the η^5-pentadienyl system is similar to that found in the pentadienyl complex of tricarbonylmanganese [7]. The C(1)=C(2) bond is inclined to the mean least-squares plane C(2)···C(6) at 21(1)°, and C(5) is displaced from this plane by 0.10 Å, i.e. the five-atomic conjugated system is not quite planar. Both CF_3-groups at C(6) are also displaced from the mean plane mentioned (C(10) by 1.38 Å from the Fe atom, C(11) by 0.40 Å towards it).

Formation of a novel trienyl ligand by reaction of I does not seem unaccountably strange in view of recent data concerning fluorine migration [8] and carbon—carbon double bond cleavage [9] in reactions of fluoroolefins with transition metal complexes. However the mechanism of the corresponding process, namely formation of VI, is unclear at present and demands further investigation.

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