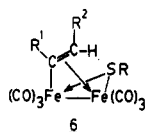


is comparable to other diiron μ - σ , π -vinyl systems. The parent compound of this class, **5**, $R^1 = R^2 = H$, had been prepared by Hoffmann and Weiss⁹ some years ago by the reaction of thiomaleic anhydride with $\text{Fe}(\text{CO})_5$, and its structure was determined by means of X-ray crystallography.

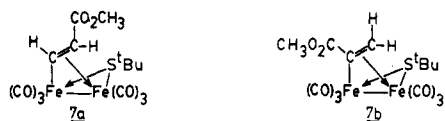
A plausible mechanism for the formation of **5** is shown in Scheme II starting with the anionic intermediate **4**, postulated in Scheme I. Reaction with $\text{CF}_3\text{CO}_2\text{H}$ presumably yields the neutral O-protonated product that may then spontaneously undergo acid-catalyzed, metal-assisted intramolecular oxidation to give the observed product. In analogy with the known acid-catalyzed oxidation of organic hemimercaptals,⁹ further protonation at sulfur would take place, yielding an unstable metallasulfonium species. Unable to eliminate RSH (as occurs in the acid-catalyzed oxidation of hemimercaptals), this intermediate undergoes a metal-assisted oxidation to a protonated oxonium species with concomitant formation of an Fe-S bond and elimination of RH . Subsequent loss of a proton then gives the neutral product **5**. This complex is only a minor (6-9%) product in such reactions of $[(\mu\text{-C}_2\text{H}_5\text{S})(\mu\text{-CO})\text{Fe}_2(\text{CO})_6]^-$ and $[(\mu\text{-C}_6\text{H}_5\text{CH}_2\text{S})(\mu\text{-CO})\text{Fe}_2(\text{CO})_6]^-$ and is not formed at all in the analogous reaction of $[(\mu\text{-C}_6\text{H}_5\text{S})(\mu\text{-CO})\text{Fe}_2(\text{CO})_6]^-$. In these cases, the major products (obtained in ca. 40% yield) are complexes of type **6**. The provenance



($R^1, R^2 = \text{CO}_2\text{CH}_3$ when $\text{CH}_3\text{O}_2\text{C}\equiv\text{CCO}_2\text{CH}_3$

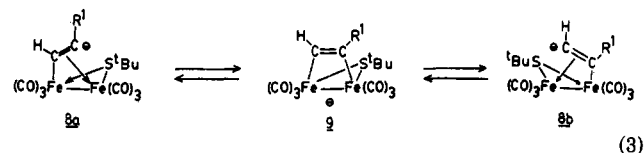
is the acetylene used)

of these products is, at this time, obscure. In any case, it appears that this complicated chemistry of Schemes I and II is much slower at low temperatures since even when R in RS is $t\text{-Bu}$, at -78°C products of type **6** are formed, presumably via direct protonation of the intermediate vinyl anion. Thus, when the $\text{Li}[(\mu\text{-}(\text{CH}_3)_3\text{CS})(\mu\text{-CO})\text{Fe}_2(\text{CO})_6]/\text{CH}_3\text{O}_2\text{C}\equiv\text{CCO}_2\text{CH}_3$ reaction mixture (reaction for 1 h at -78°C) was protonated, also at -78°C , **6** ($\text{R} = t\text{-Bu}$) was formed in 71% yield and **5** in only 10% yield. In the case of the reaction of methyl propiolate with $\text{Li}[(\mu\text{-}(\text{CH}_3)_3\text{CS})(\mu\text{-CO})\text{Fe}_2(\text{CO})_6]$ at -78°C , followed by addition of $\text{CF}_3\text{CO}_2\text{H}$ and warming to room temperature, a major (30%) product was **5a**, but *two* μ -vinyl products, **7a** and **7b**, also were formed, each in 23% yield. Formation



of **7b** was unexpected since **7a**, the expected Michael addition product, was the only product of the reaction of $\text{HC}\equiv\text{CCO}_2\text{CH}_3$ with $[\text{Et}_3\text{NH}][(\mu\text{-}(\text{CH}_3)_3\text{CS})(\mu\text{-CO})\text{Fe}_2(\text{CO})_6]$ at room temperature or at -78°C .² It may be that at low temperature in the absence of a proton source, the initially formed anion **8a** has a chance to undergo isomerization to **8b**, possibly via **9** (eq 3). Similar results were obtained for the corresponding reactions of 3-butyne-2-one.

The action of the $[(\mu\text{-RS})(\mu\text{-CO})\text{Fe}_2(\text{CO})_6]^-$ anions on acetylenes, a reaction which we originally thought was



simple and straightforward, thus turns out to be quite complicated. Its course, according to our studies thus far, is dependent on the counterion (Et_3NH^+ vs. Li^+), on the substituents on the acetylenic carbon atoms, on the organic group of the RS ligand, on the reaction temperature, and on the electrophile added to react with the anionic intermediate. We are continuing our studies using other types of acetylenes.

All new compounds have been characterized by analysis and NMR and IR spectroscopy. Characterizing data are provided as supplementary material.

Acknowledgment. We are grateful to the National Science Foundation for generous support of this work. We thank the Biomedical Research Support Shared Instrumentation Grant Program, Division of Research Resources, for funds to purchase the X-ray diffraction equipment, NIH Grant S1ORRO2243-01, and Mr. David R. Wheeler, an undergraduate research participant, for technical assistance.

Supplementary Material Available: Tables of final positional and thermal parameters for **3g** and **5b** and characterization data for compounds **3a-g** and **5a-c** (12 pages); tables of observed and calculated structure factors for **3g** and **5b** (26 pages). Ordering information is given on any current masthead page.

Synthesis of a Diamagnetic Fulvalene Zirconium(III) Derivative. The Crystal Structure of $(\eta^5\text{-}\eta^5\text{-C}_{10}\text{H}_8)[(\eta^5\text{-C}_5\text{H}_5)\text{Zr}(\mu\text{-Cl})_2]$

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Summary: The comproportionation reaction between $\text{Cp}_2\text{Zr}^{\text{IV}}\text{Cl}_2$ and $\text{Cp}_2\text{Zr}^{\text{II}}[\text{P}(\text{CH}_3)_3]_2$ leads to $(\eta^5\text{-}\eta^5\text{-C}_{10}\text{H}_8)[(\eta^5\text{-C}_5\text{H}_5)\text{Zr}(\mu\text{-Cl})_2]$ (**1**) in good yields. Its structure has been determined by X-ray diffraction methods. It crystallizes in a monoclinic space group of $P2_1/n$ symmetry with $a = 8.234$ (4) Å, $b = 15.199$ (5) Å, $c = 14.096$ (5) Å, $\beta = 93.65$ (3)°, and $Z = 4$. Its diamagnetism and the Zr-Zr distance of 3.233 (1) Å are consistent with the presence of a metal-metal bond.

The reduction of zirconocene dichloride is a fascinating topic that for a long time has attracted the attention of chemists. This interest has been stimulated by several features displayed by the low-valent zirconium(II, III) organometallic compounds, like dinitrogen fixation,¹ for-

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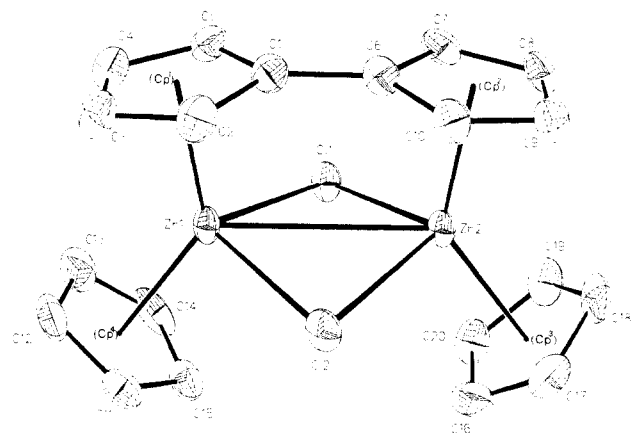


Figure 1. Molecular structure of $(\eta^5\text{-}\eta^5\text{-C}_{10}\text{H}_8)[(\eta^5\text{-C}_5\text{H}_5)\text{Zr}(\mu\text{-Cl})]_2$. Selected bond lengths (Å) and angles (deg) (estimated standard deviations in parentheses): Zr1-Cl1 = 2.591 (2), Zr1-Cl2 = 2.583 (2), Zr2-Cl1 = 2.568 (2), Zr2-Cl2 = 2.571 (2), Zr1-Zr2 = 3.233 (1), Cl1-Zr1-Cl2 = 99.5 (1), Cl1-Zr2-Cl2 = 100.5 (1), Zr1-Cl1-Zr2 = 77.6(1), Zr1-Cl2-Zr2 = 77.7 (1), torsion angle Cl1-Zr1-Zr2-Cl2 = 159.0 (1), Zr1-(Cp1) = 2.163 (9), Zr2-(Cp2) = 2.162 (7), Zr2-(Cp3) = 2.200 (9), Zr1-(Cp4) = 2.208 (10), (Cp1)-Zr1-(Cp4) = 135.1 (4), (Cp2)-Zr2-(Cp3) = 135.4 (3), torsion angle (Cp2)-Zr2-Zr1-(Cp1) = 0.4 (3) [(Cp) = centroids of the Cp rings and fulvalene ligand]; C1-C6 = 1.451 (10), Cl1...Cl2 = 3.950 (3).

mation of hydrides,² reactivity with alkynes,³ and the possibility of M-M bond occurrence.⁴ Our current interest in synthesis and reactivity of Zr(III) systems has led to a preliminary characterization of some bis(cyclopentadienyl)zirconium (III) derivatives. Well-identified Zr(III) species are rare,⁵⁻⁷ and only in one case has the structure of a Zr(III) inorganic complex been determined by an X-ray diffraction analysis.⁷ For reactions leading to Z(III) derivatives, either the maintenance of the Cp ring in its intact form,^{5a,b} its rearrangement to the bridging $\eta^1\text{:}\eta^5\text{-C}_5\text{H}_4$,^{5f} or its transformation into fulvalene^{2b,5f} has been claimed. Sometimes different products have been suggested even for the same reaction;^{2c,8,9} therefore, further

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Table I. Selected Bond Distances in Some Dinuclear Molecules Containing Bridging Fulvalene (C_{10}H_8)

compd	M-M, Å	ref	M-M bond
$\text{Cp}_2\text{Ti}_2(\text{C}_{10}\text{H}_8)(\text{H})(\text{Cl})$	3.125	18b	
$\text{Cp}_2\text{Ti}_2(\text{C}_{10}\text{H}_8)(\text{H})(\text{H}_2\text{AlEt}_2)$	3.374	15a	no
$\text{Cp}_2\text{Ti}_2(\text{HAlEt}_2)_2(\text{C}_{10}\text{H}_8)$	2.910	15a	yes
$\text{Cp}_2\text{Ti}_2(\text{C}_{10}\text{H}_8)(\text{Cl})_2$	3.638	15b	no
$\text{Cp}_2\text{Ti}_2(\text{C}_{10}\text{H}_8)(\text{OH})_2$	3.195	17	no
$\text{Cp}_2\text{Nb}_2(\text{C}_{10}\text{H}_8)(\text{Cl})$	3.270	18a	yes
$\text{Cp}_2\text{Nb}_2(\text{C}_{10}\text{H}_8)(\text{H})(\text{OEt})$	3.136	18b	
$\text{Cp}_2\text{Nb}_2(\text{C}_{10}\text{H}_8)(\text{NC}_6\text{H}_4\text{OMe})_2$	2.834	19	yes
$[\text{Cp}_2\text{Nb}_2(\text{C}_{10}\text{H}_8)(\text{NC}_6\text{H}_4\text{OMe})_2]^+$	2.921	19	yes
$[\text{Cp}_2\text{Mo}_2(\text{C}_{10}\text{H}_8)(\text{H})(\text{OH})]^{2+}$	3.053	20	yes
<i>cis</i> - $[\text{Rh}_2(\text{CO})_2(\text{PPh}_3)_2(\text{C}_{10}\text{H}_8)]$	2.930	21	yes
$[(\text{C}_{10}\text{H}_8)_2(\text{CH}_3\text{CN})_2\text{V}_2][\text{PF}_6]_2$	3.329	22	yes
$(\text{C}_{10}\text{H}_8)(\text{CO})_4\text{Ru}_2$	2.821	23	yes
$\text{Cp}_2\text{Zr}_2(\text{C}_{10}\text{H}_8)(\text{Cl})_2$	3.233	a	yes
$\text{W}_2(\text{CO})_6(\text{C}_{10}\text{H}_8)$	3.347	23	yes

^a This work.

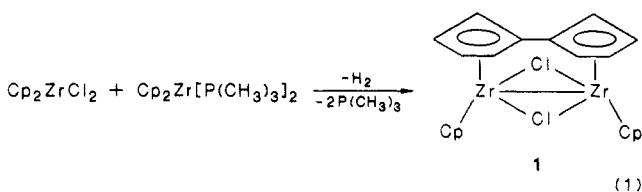
Table II. Zr-Zr Bond Distances

compd	M-M, Å	ref
$\beta\text{-Zr}$	3.1789	24
$\beta\text{-ZrCl}_3$	3.07 ^a	25
ZrBr_3	3.16 ^a	25
ZrI_3	3.32 ^a	25
$[\text{ZrCl}_3(\text{PBu}_3)_2]_2$	3.182	7
$(\text{C}_{10}\text{H}_8)(\text{C}_5\text{H}_5)_2\text{Zr}_2\text{Cl}_2$	3.233	b

^a From X-ray powder diffraction patterns. ^b This work.

clarifying work is necessary.

We wish to describe in this paper, which is the first structural report of a dinuclear organometallic Zr(III) compound, the synthesis and X-ray structure of $(\eta^5\text{:}\eta^5\text{-C}_{10}\text{H}_8)[(\eta^5\text{-C}_5\text{H}_5)\text{Zr}(\mu\text{-Cl})]_2$ obtained by using comproportionation reaction (1).¹⁰⁻¹² The spectroscopic and ana-



lytical data¹³ are consistent with the solid-state structure as solved by X-ray analysis.¹⁴ The structure reveals that

(10) Comproportionation reaction using $\text{Cp}_2\text{Zr}(\text{CO})_2$ or "zirconocene" has been reported to lead to the formation of $(\text{Cp}_2\text{ZrCl})_2$ as a green diamagnetic solid. (a) Fochi, G.; Guidi, G.; Floriani, C. *J. Chem. Soc., Dalton Trans.* **1984**, 1253. (b) Wailes, P. C.; Weigold, H. *J. Organomet. Chem.* **1971**, *28*, 91.

(11) In a standard experiment, a deep red solution of 1 g of $\text{Cp}_2\text{Zr}[\text{P}(\text{CH}_3)_3]_2$ and 0.8 g of Cp_2ZrCl_2 in toluene (100 mL) was heated until the boiling point of the solvent was reached. A little darkening of the color was observed during the heating. After partial removal of the solvent and standing 2 days at -30°C , large-size, air-sensitive, deep red crystals (see ref 12) separated in 57% yield. Another crop of crystals could be obtained after *n*-hexane addition.

(12) The color of the crystalline **1** appeared as shiny green. When ground under inert atmosphere, the color of the solid is actually deep red as well as its toluene, THF, and pyridine solutions.

(13) Spectra: EI-MS, m/e 508 [$^{12}\text{C}_{20}\text{H}_{18}\text{^{35}Cl}_2$], 288 [$\text{C}_{10}\text{H}_8\text{ZrCl}_2$], 253 [$\text{C}_{10}\text{H}_8\text{ZrCl}$], 225 [$\text{C}_5\text{H}_5\text{ZrCl}$], isotopic pattern typical for Zr-containing ions; IR [KBr, (rings C-H), Nujol mull, cm^{-1}] 1525 (w), 1430 (m), 1295 (w), 1115 (w), 1047 (w), 1045 (w), 1020 (m), 1005 (s), 840 (w), 800 (vs), 782 (vs). NMR (350 MHz, C_6D_6 , 31°C): ^1H , δ 5.57 (s, 10 H, C_5H_5), 4.92 (pseudotriplet, 4 H, C_{10}H_8), 3.98 (pseudotriplet, 4 H, C_{10}H_8), consistent with an AA'BB' spin system, $J(\text{exptl}) = 2.9$ Hz; ^{13}C , δ 104.8 (C_5H_5), 104.6, 101.1, 106.2 (C_{10}H_8). Anal. Calcd for $\text{C}_{20}\text{H}_{18}\text{Cl}_2\text{Zr}_2$: C, 46.90; H, 3.52; Cl, 13.87; Zr, 35.36. Found: C, 46.65; H, 3.88; Cl, 12.75; Zr, 35.46. Elemental hydrogen has been identified and measured by GC analysis of the gas phase.

the crystal is composed of discrete molecules of $(\eta^5\text{-}\eta^5\text{-C}_{10}\text{H}_8)[(\eta^5\text{-C}_5\text{H}_5)\text{Zr}(\mu\text{-Cl})_2]$ (Figure 1), containing two Zr atoms bonded to two bridging chlorines and η^5 -bonded to the cyclopentadienyl rings and bridging fulvalene ligand.

The Zr-Zr distance [3.233 (1) Å] is consistent with the formation of a M-M bond. The coordination around each Zr atom can be described as a distorted tetrahedron if we consider the Cp ring centroid as each occupying one coordination site around the metal.

The fulvalene ligand is folded, forming a dihedral angle of 166.7 (1)° between the two ring planes. The inter-ring bond distance C1-C6 is 1.451 (10) Å, and an almost negligible twist is observed along this bond [dihedral angles C5-C1-C6-C7 = 1.2 (1)°, C2-C1-C6-C10 = 1.4 (1)°]. The angles subtended at the Zr by the centroids of the two staggered individual Cp and fulvalene [(Cp1)-Zr1-(Cp4) = 135.1 (2)°, (Cp2)-Zr2-(Cp3) = 135.4 (4)°; (Cp) = ring centroid], are in the region expected for a normal bent η^5 -Cp metal system. Probably as a result of the M-M interaction, the plane containing the Zr_2Cl_2 fragment is symmetrically folded along the Zr-Zr vector [torsion angle Cl1-Zr1-Zr2-C12 = 159.0 (1)°], assuming a butterfly configuration with the two bridging chlorine atoms symmetrically placed on the wings. The Zr-Cl-Zr [77.7 (1)-77.6(1)°] and Cl-Zr-Cl [100.5 (1)-99.5 (1)°] angles are comparable to those observed by Schrock for a similar molecular frame.⁷ The little increase in Zr-Cl [Zr1-Cl1 = 2.591 (2) Å, Zr2-Cl1 = 2.568 (2) Å, Zr1-Cl2 = 2.583 (2) Å, Zr2-Cl2 = 2.571 (2) Å] and Zr-Zr bond lengths, in this case, can be ascribed to a distortion caused by the fulvalene ligand. The Cl1...Cl2 nonbonded distance [3.950 (3) Å] is just 0.35 Å larger than the van der Waals diameter for Cl. All the other bond lengths and angles are as expected.

The absence of any hydride signal in both the IR and ¹H NMR spectra, down to a δ value of -30 ppm, rules out the presence of bridging hydrogen atoms undetected by the X-ray diffraction. The diamagnetism of 1, containing two Zr(III) atoms, can be rationalized either by a direct M-M interaction (bond) or by ligand-propagated superexchange.¹⁵ In the present case, the Zr-Zr distance falls within the range observed for other transition metals with similar arrangement (Table I). Since only few structures

of Zr(III) species have been clarified by X-ray analysis (Table II), the evaluation of the significance of a Zr-Zr distance in the complex 1 is difficult and any extensive comparison with other Zr(III) organometallic derivatives is impossible. It is unclear whether Zr(II) or Zr(III) is responsible for the unexpected formation of fulvalene in reaction 1. Further work to clarify this point is presently in progress together with a broad investigation of the reactivity of complex 1.

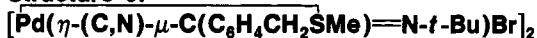
Acknowledgment. We are indebted to the generosity of Columbia University Chemistry Department for supporting this work.

Supplementary Material Available: Tables of crystal data, anisotropic thermal parameters, atomic coordinates, interatomic distances, bond lengths, bond angles, and torsion angles and a stereoview and a lateral view of the molecule (18 pages); a listing of observed and calculated structure factors (13 pages). Ordering information is given on any current masthead page.

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Influence of the Donor Atom in Metallo-cyclic Rings on the Insertion of *tert*-Butyl Isocyanide and Carbon Monoxide into Their Pd-C Bonds.¹ X-ray Molecular Structure of



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Summary: The insertion of CO and *tert*-butyl isocyanide (*t*-BuNC) into the Pd-C bonds of metallo-cyclic complexes occurs much more readily with cyclopalladated benzyl methyl sulfide or methyl 1-naphthyl sulfide derivatives than with the corresponding compounds in which the SMe unit is replaced by an NMe₂ group. These reactions afford new compounds containing six-membered organopalladium rings, in both cases the reaction with CO being reversible.

The reaction of nucleophiles and electrophiles with cyclopalladated compounds is well-known to produce new organopalladium compounds or/and organic products.^{3a}

(1) Reactivity of Cyclopalladated Compounds. 17. Part 16: see ref 3i.

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(14) X-ray diffraction data: crystal size (mm), 0.40 × 0.45 × 0.80, deep red prism; monoclinic, space group $P2_1/n$; $a = 8.234$ (4) Å, $b = 15.199$ (5) Å, $c = 14.096$ (5) Å, $\beta = 93.65$ (3)°, $Z = 4$, $V = 1761$ Å³, $d(\text{calcd}) = 1.93$ g/cm³, $\mu(\text{Cu}) = 131.0$ cm⁻¹ (absorption coefficient); $F(000) = 1008$; data were collected on a Nicolet R3m diffractometer; Cu radiation, $\lambda = 1.54178$ Å; scan mode = $\theta/2\theta$, scan speed = 3.91 -29.3 deg·min⁻¹, scan width = 2.01 -2.44; $T = 298$ K; measured reflections 2693, range of $hkl = (+h, +k, \pm l)$; $(\sin \theta)/\lambda$ limit (Å⁻¹) = 0.544 ($2\theta_{\text{max}} = 114^\circ$); no. of unique reflections, 2379; no. of reflections used in analysis, 2182 [$I > 3\sigma(I)$]; structure solved by direct method; all the non-hydrogen atoms were located and refined anisotropically; hydrogen atom positions were calculated; number of variables, 217; $R = 0.053$; $R_w = 0.068$, $w = 1/[\sigma^2(F_o) + g(F_o)^2]$ with $g = 0.0005$; GOF = 2.522; largest remaining peak, 1.12 e/Å; largest shift/esd, final cycle, 0.057.

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