hydrogen atoms in both structures, except those of the cyclohexane rings in the cis compound, which were given assumed positions calculated after each cycle of the refinement, were located from difference electron density calculations, and their positions were kept riding on the respective mother atoms.

In the last stage of the refinements, the positions of the non-hydrogen atoms together with their anisotropic thermal parameters and isotropic temperature factors for the hydrogen positions were refined. In the case of the cis compound, for which an empirical extinction correction factor was also included, two group and four individual isotropic temperature factors were refined for the H atoms. In the case of the trans complex, each hydrogen has its own temperature factor refined.

Final R values together with some details of the refinement calculations are shown in Table II. The atomic scattering factors for the C and Cl atoms were taken from Cromer and Mann,[26] those for the Pd^{2+} ion from Cromer and Waber,[27] and those for the H atoms from Stewart et al.[28] The correction terms for the anomalous dispersion of the non-hydrogen atoms were taken from Cromer and Liberman.[29] Weights of the structure factors were calculated as $w = \text{const}/[\sigma^2(F) + g(F^2)]$ with g estimated to be 0.000 79 and 0.001 26 for the cis and trans complexes, respectively.

Acknowledgment. We thank Dr. Ulla Jacobson and Dr. Krister Zetterberg for help with the NMR measurements and Dr. Jeff Martin for carrying out the 2D NMR experiments and for many helpful discussions. This work was supported by the Swedish Natural Science Research Council.

Supplementary Material Available: Fractional atomic coordinates of the H atoms (Table VII), bond distances and bond angles (Table VIII), bond distances and bond angles involving the hydrogen atoms (Table IX), and anisotropic thermal parameters of the non-hydrogen atoms (Table X) (5 pages); lists of structure factor amplitudes (22 pages). Ordering information is given on any current masthead page.

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(26) Cromer, D. T.; Mann, J. B. *Acta Crystallogr.* **1988**, *A24*, 321.

(27) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, 1974; Vol. IV, pp 99–101.

(28) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(29) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.

Synthesis of [μ-1,9,10,11-η:4,5,6,12-η-Tricyclo[7.1.1.$1^{4,6}$]dodeca-1(11),4,6-(12),9-tetraene]bis(tricarbonyliron): The Smallest Cyclophane with Metal-Stabilized Antiaromatic Decks[1]

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The synthesis and structure of [μ-1,9,10,11-η:4,5,6,12-η-tricyclo[7.1.1.$1^{4,6}$]dodeca-1(11),4,6(12),9-tetraene]bis(tricarbonyliron) (1), a small cyclophane containing iron-stabilized antiaromatic decks of cyclobutadiene, is reported. Complex 1 crystallizes in the monoclinic space group $P2_1/a$, a = 12.455 (6) Å, b = 9.769 (4) Å, c = 7.156 (2) Å, β = 92.88 (3)°, and d(calcd, Z = 2) = 1.665 g cm^{-3}. The structure was resolved by direct methods using MULTAN80 and refined by least squares to R_f = 4.2% (R_w = 5.2%). The physical properties of 1 were examined and compared to [2.2]paracyclophane. The cyclobutadiene ligands are parallel to and lie directly over each other with no ring distortion, and there is a 20.6° out-of-plane bending of the aliphatic bridges away from the metal. The intradeck distance of 2.7 Å is the smallest observed for the cyclophanes. The carbonyl moieties are in the staggered conformation.

Introduction

The theory of interaction of molecular orbitals has spurred the study of many synthetic methods and reactions, inter alia, Diels–Alder reactions and photochemical cycloaddition reactions.[2] Cyclophanes, the most famous being [2.2]paracyclophane, have occupied the thoughts of theorists and experimentalists for many years.[3] Cyclophanes containing benzene are among those most investigated and show considerable cofacial π–π repulsions which result in the distortion of the benzene ring from planarity and increased reactivity.[3,4] These distortions have been confirmed by X-ray determinations and charge-transfer complex formation, and these observations are explained by increased electron density on the outer faces of these cyclophane systems with rehybridization of

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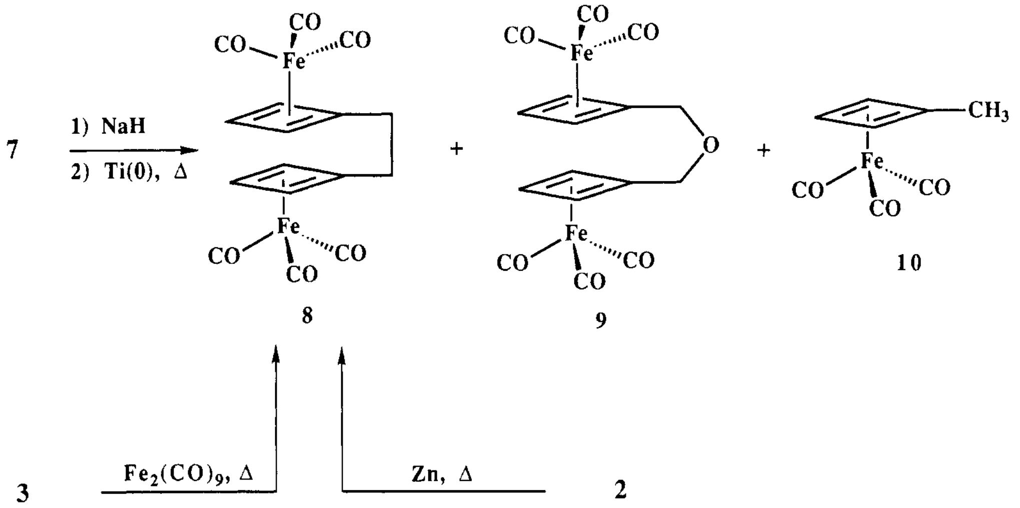
(1) (a) Preliminary results were presented at the 3rd Chemical Congress of North America and 195th National Meeting of the American Chemical Society, Toronto, Canada, June 5–10, 1988, ORGN 365, and the 197th National Meeting of the American Chemical Society, Dallas, TX, April 9–14, 1989, ORGN 186. (b) C.M.A. was an Alexander von Humboldt Research Fellow, 1984–1985.

(2) (a) Fleming, I., Ed. *Frontier Molecular Orbitals and Organic Chemical Reactions*; Wiley: New York, 1976. (b) Woodward, R. B., Hoffmann, R., Eds. *The Conservation of Orbital Symmetry*; Academic Press: New York, 1970.

(3) (a) Keehn, P. M., Rosenfield, S. M., Eds. *Cyclophanes*; Academic Press: New York, 1983; Vols. 1 and 2, and references therein. (b) Boschke, F. L., Ed. *Topics in Current Chemistry*; Springer-Verlag: New York, 1983; Vols. 113 and 115, and references therein. (c) Greenberg, A., Liebman, J. F., Eds. *Strained Organic Molecules*; Academic Press, New York, 1978; Vol. 38, and references therein.

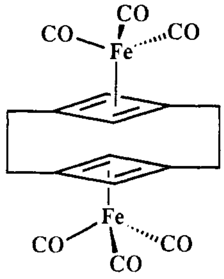
(4) (a) Cram, D. J.; Cram, J. M. *Acc. Chem. Res.* **1971**, *4*, 204–213, and references therein. (b) Boekelheide, V.; Hollins, R. A. *J. Am. Chem. Soc.* **1973**, *95*, 3201–3208, and references therein. (c) Hope, H.; Berstein, J.; Trueblood, K. N. *Acta Crystallogr., Sect. B* **1972**, *28*, 1733–1743.

Scheme I



orbitals in response to the distortions and strain.[5]

Recent investigation of metal-complexed[2.2]paracyclophanes and cyclopentadienyl metallocenes as components of crystals for ferroorganics has expanded,[6] and metal-stabilized ligands as components of small-ring cyclophanes have been reported.[7] Of primary interest are studies of the interdeck distances and bond angles as a result of the stability, geometry, distortions, and interactions in the complexes. The information gained in these studies contributes toward the use of small-ring metal-complexed cyclophanes as potential precursors for polymers containing desired electrical or magnetic properties.[5,6] Toward these goals we present here the synthesis and structure of [μ-1,9-11:4-6,12-η-tricyclo[7.1.1.1^{4,6}]dodeca-1-(11),4,6(12),9-tetraene]bis(tricarbonyliron) (1), the smallest cyclophane containing two metalloaromatic (cyclobutadiene)iron tricarbonyl components held cofacial by two ethylene bridges.

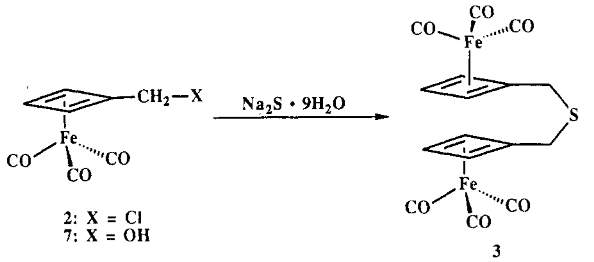


1

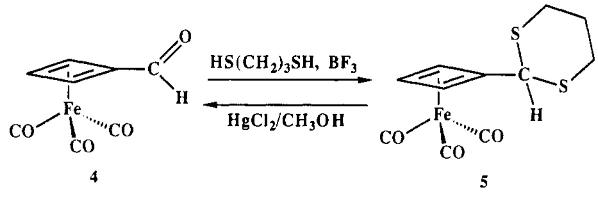
Results and Discussion

Cyclobutadienophane bis(tricarbonyliron) 1 precursors were readily available starting from cyclobutadienyliron tricarbonyl by utilizing its metalloaromatic properties.[1,8]

Procedures commonly used in the formation of [2.2]-paracyclophanes incorporating cyclobutadienophane bis-(tricarbonyliron) precursors met with limited success. The chloromethyl complex 2 readily yields sulfide 3, [μ-[bis-(η^4-1,3-cyclobutadien-1-ylmethyl)sulfide]]bis(tricarbonyliron), when treated with sodium sulfide (eq 1). When bisferrocenyl sulfide derivatives were reported to resist known Stevens rearrangement,[9] or radical sulfur extrusion pathways using trimethyl phosphite,[3] an attempt was made to explore the deprotonation of the thioketal derivatives of aldehyde 4. Treatment of 4 with propanedithiol in titanium tetrachloride produced the desired thioketal 5, tricarbony[2-(η^4-1,3-cyclobutadien-1-yl)-*m*-dithiane]iron (eq 2). Thioketal 5 can facilely release aldehyde 4 when stirred at room temperature in a mixture of mercuric(II) chloride in methanol. All attempts to deprotonate 5 using butyllithium or lithium diisopropylamine followed by alkylation with methyl iodide, allyl chloride, the chloromethyl complex 2, or deuterium oxide returned the unchanged starting material. Evidently the ability of the metalloaromatic (cyclobutadiene)tricarbonyliron complex to stabilize a carbonium ion dramatically opposes anion stabilization by the thioketal functionality.[10]



(1)



(2)

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(5) Cram. D. J.; Bauer, R. H. *J. Am. Chem. Soc.* **1959**, *81*, 5971–5977.

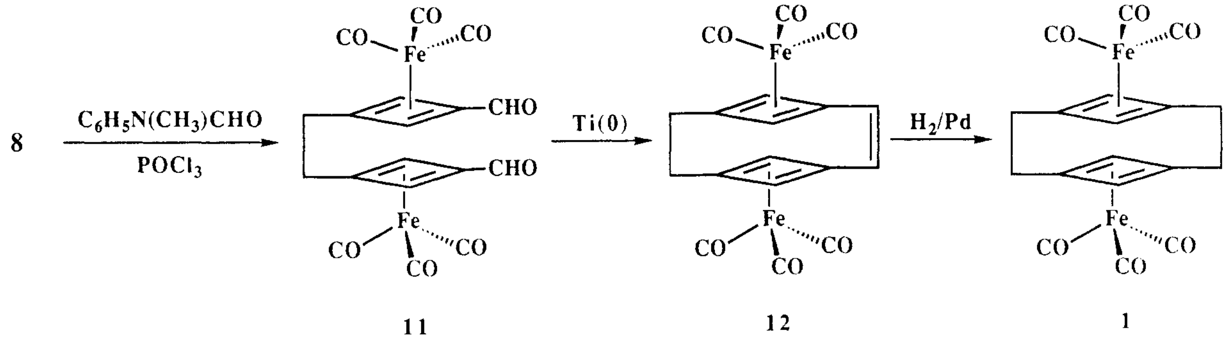
(6) (a) Boekelheide, V. *Pure Appl. Chem.* **1986**, *58*, 1–6, and references therein. (b) Plitzko, K. D.; Boekelheide, V. *Organometallics* **1988**, *7*, 1573–1582. (c) LePage, T. J.; Breslow, R. *J. Am. Chem. Soc.* **1987**, *109*, 6412–6421. (d) Miller, J. S.; Epstein, A. J. Reiff, W. M. *Science* **1988**, *240*, 40–47.

(7) Gleiter, R.; Karcher, M.; Ziegler, M. L.; Nuber, B. *Tetrahedron Lett.* **1987**, *28*, 195–198.

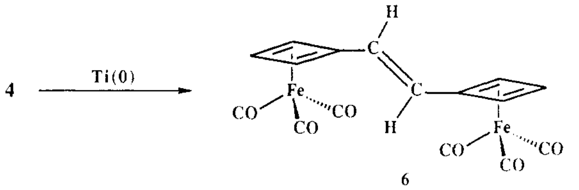
(8) (a) Watts, L.; Fitzpatrick, J. D.; Pettit, R. *J. Am. Chem. Soc.* **1965**, *87*, 3253–3254. (b) Efraty, A. *Chem. Rev.* **1977**, *77*, 691–744, and references therein. (c) Maitlis, P. M.; Eberius, K. W. In *Non-Benzenoid Aromatics*; Synder, J. B., Ed.; Acaemic Press, New York, 1971; Vol. 2, pp 359–409. (d) Pettit, R. In *Organometallic Chemistry, 3rd International Symposium*; IUPAC, Munich, 1967; pp 253–272. (e) Pettit, R. *J. Organomet. Chem.* **1975**, *100*, 205–217.

(9) (a) Van Tamelen, E. E.; Schwartz, M. A. *J. Am. Chem. Soc.* **1965**, *87*, 3277–3278. (b) Sharpless, K. B.; Hanzlik, R. P.; Van Tamelen, E. E. *J. Am. Chem. Soc.* **1968**, *90*, 209–210. (c) Hylton, T.; Boekelheide, V. *J. Am. Chem. Soc.* **1968**, *90*, 6887–6888. (d) Corey, E. J.; Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 1075–1077. (e) Corey, E. J.; Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 1077–1078.

Scheme II



While standard [2.2]paracyclophane methods utilizing anions have been fruitless, methods using modified McMurry radical coupling reactions were investigated.[11] Reductive coupling of aldehyde **4** with low-valent titanium gave the substituted ethylene **6**, [μ-(*E*)-1,2-η^4-1,3-cyclobutadien-1-ylethylene]bis(tricarbonyliron), as yellow crystals, in moderate yield (eq 3). Similiar reductive radical fragmentation and coupling of the alkoxide of ((hydroxymethyl)cyclobutadiene)tricarbonyliron (**7**) gave the monobridged complex **8**, [μ-1,2-di-η^4-1,3-cyclobutadien-1-ylethane]bis(tricarbonyliron), as pale yellow, air-stable crystals in 10% yield, along with ether **9**, [μ-[bis(η^4-1,3-cyclobutadien-1-ylmethyl)ether]]bis(tricarbonyliron), and the reduced (methylcyclobutadiene)tricarbonyliron **10** (Scheme I). Ether **9** and (methylcyclobutadiene)tricarbonyliron (**10**) were confirmed by independent synthesis.[12] Our direct entry into the monobridged **8** could also be achieved by radical sulfur extrusion from complex **3** using diiron nonacarbonyl in 26% yield. This method represents the first time sulfur could be extruded from phanes containing iron that did not have a benzyl group attached to the sulfur. One advantage of this method is to allow any decomplexed ligand to be trapped by the diiron nonacarbonyl used in the formation of (cyclobutadiene)tricarbonyliron. The method also precludes the use of triethyl phosphite, which substitutes for the carbon monoxide ligand upon photolysis, eliminates oxidative desulfurization, which destroys the iron complex, and prevents the Steven's rearrangement, which requires formation of an anion adjacent to sulfur.[9] The monobridged complex **8** can now be obtained in 52% yield from the chloromethyl derivative **2** by reductive zinc coupling.



(3)

Bis-Vilsmeier formylation of complex **8** gratifyingly led to the formation of only dialdehyde **11**, [μ-3,3'-ethylenebis[(1–4-η)-1,3-cyclobutadiene-1-carboxaldehyde]]bis(tricarbonyliron), as bright yellow crystals in 50% yield (Scheme II). Prior to this the only reaction of (ethylcyclobutadiene)tricarbonyliron has yielded a mixture of acylated derivatives, 1,3 and 1,2, in a ratio of 2:1, respectively.[12] The formation of the 1,3 isomer over the 1,2 isomer indicates that there is a 4-fold inductive effect of the alkyl group over just statistical substitution. Formation of only dialdehyde **11** indicates that interdeck electronic effects may significantly enhance the preference for one isomer.

Our success in the synthesis of the monobridged **8** allowed formation of [μ-1,9-11:4-6,12-η-tricyclo[7.1.1.1^{4,6}]dodeca-1(11),2,4,6(12),9-pentaene]bis(tricarbonyliron), **12**, via direct reductive coupling. Slow addition of dialdehyde **11** to Ti(0) formed **12**, incorporating a second unsaturated bridge, in 58% yield. Evidently, formation of the unsaturated bridge is assisted by Ti(0)-oriented oxygen binding and is not precluded by π-electron repulsions of the metalloaromatic species. In addition to the reduced or lack of repulsive interactions, the orientation of the carbonyls is assisted by a 2-fold additive, out-of-plane bending of the bridge and carbonyl substituents attached to each deck. Hydrogenation of **12** over Pd(C) gave (cyclobutadienophane)bis(tricarbonyliron) **1** as pale yellow, air-sensitive crystals in 72% yield.

The iron complexes **1**, **8**, and **12** were characterized by ^{1}H and ^{13}C NMR, IR, and MS. The symmetry and geometry of the compounds simplified their identification by NMR techniques. All compounds gave singlets in their ^{1}H NMR spectrum, owing to their symmetry and the ability of the iron to equate ring proton signals.[13] There is an observed upfield shift of the ring protons of (cyclobutadienophane)bis(tricarbonyliron), from δ 3.84 for **8** to δ 3.78 for **1**, due to the shielding by the opposite deck. This value is not as dramatic as that observed between biphenyl, δ 7.15, and [2.2]paracyclophane, δ 6.37.[3,14] Likewise, there is a deshielding of the ethylene bridge protons in **1** by the opposite deck, δ 2.10 for **8** to δ 2.52 for **1**, compared to the downfield shift between biphenyl, δ 3.05, and [2.2]paracyclophane, δ 2.89, which is in similar agreement when the rings are oriented face to face. The magnitude of the observed shifts in the (cyclobutadienophane)bis(tricarbonyliron) may be moderated by the ligand–metal binding in the complex. Mass spectroscopy of **1** resulted in patterns characteristic of sequential loss of six carbonyl groups (M – 28, CO) and metals (M – 56, Fe). The mass spectrum of the crude reaction mixture from the reductive coupling, to form **12**, showed no peaks above 434, which suggests that no dimeric products are formed during the conversion of **11** to **12**.

An X-ray determination of the monobridged complex **8** showed the expected connectivity with the iron atoms opposed and the ethylene system anti, 178.1°, with respect

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[10] (a) Davis, R. E.; Simpson, H. D.; Grice, N.; Pettit, R. *J. Am. Chem. Soc.* **1971**, *93*, 6688–6690. (b) Hill, E. A. *J. Organomet. Chem.* **1970**, *24*, 457–462. (c) Franch-Neumann, M. *Pure Appl. Chem.* **1983**, *55*, 1715–1732.

[11] McMurry, J. E.; Flemming, M. P.; Kees, K. L.; Krepski, L. R. *J. Org. Chem.* **1978**, *43*, 3255–3266.

[12] Marcinal, P.; Hannior-Guisez, N.; Cuingnet, E. *Trav. Soc. Pharm. Mont.* **1973**, *33*, 281–288.

[13] Breslow, R. *Chem. Eng. News* **1965**, *43*(26), 90–98.

[14] Rice, J. E.; Lee, T. J.; Remington, R. B.; Allen, W. D.; Clabo Jr., D. A.; Schaefer, H. F. *J. Am. Chem. Soc.* **1987**, *109*, 2902–2909.

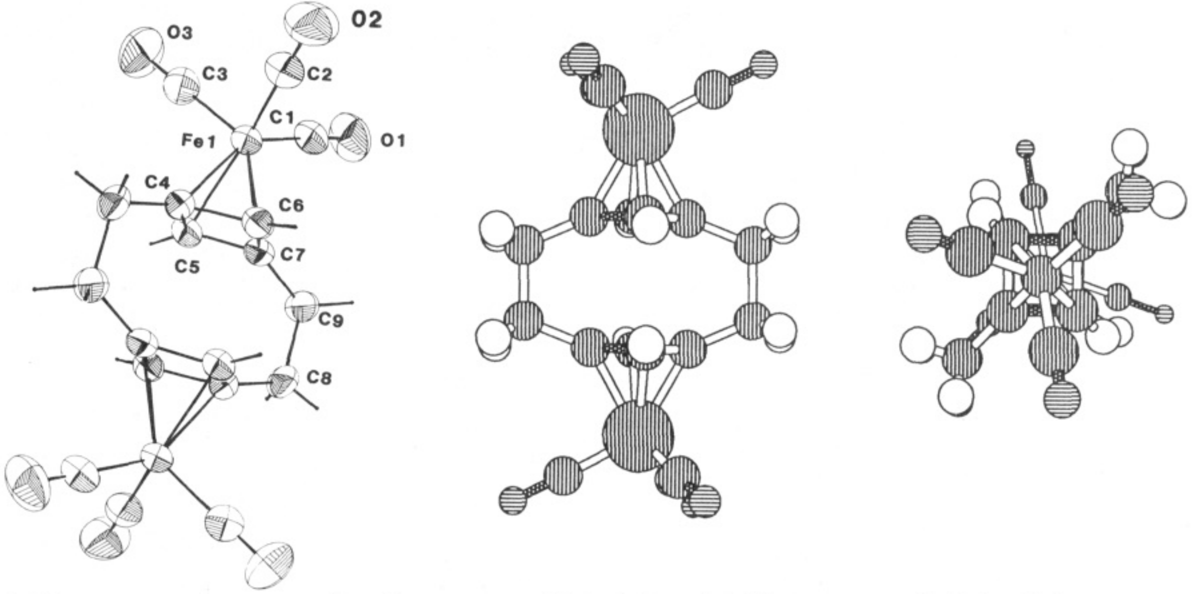

Figure 1. X-ray structure for compound 1 and computer graphic depictions of the X-ray structure displaying the important structural features.

Table I. Crystal Data for $Fe_2C_{18}H_{12}O_6$ (1)

formula	$Fe_2C_{18}H_{12}O_6$	μ(Mo Kα), cm^{-1}	16.95
MW	436.0	λ(Mo Kα), Å	0.71069
a, Å	12.455 (6)	D_{calc}, g cm^{-3}	1.665
b, Å	9.769 (4)	Z	2
c, Å	7.156 (2)	space group	$P2_1/a$
α, deg	90.0	abs	$h0l$, $h = 2n$; $0k0$, $k = 2n$
β, deg	92.88 (3)	obs refl	1272
γ, deg	90.0	octants meads	$\pm h,-k,l$
V, Å^3	869.6 (6)	R/R_w, %	4.2/5.2
F(000)	440	GOF	0.27

Table II. Positional Parameters for $Fe_2C_{18}H_{12}O_6$ (1)

atom	x ($\sigma(x)$)	y ($\sigma(y)$)	z ($\sigma(z)$)	U_{eq}, Å^2
Fe1	0.05138 (5)	0.25858 (6)	0.74811 (9)	38.2 (3)
O1	0.1711 (4)	0.2128 (5)	1.1044 (6)	49 (2)
O2	0.1817 (4)	0.4715 (4)	0.5896 (7)	73 (3)
O3	−0.1238 (4)	0.4260 (5)	0.8779 (7)	100 (3)
C1	0.1247 (4)	0.2330 (5)	0.9642 (7)	50 (2)
C2	0.1303 (4)	0.3909 (5)	0.6547 (8)	55 (3)
C3	−0.0551 (4)	0.3619 (6)	0.8273 (8)	58 (3)
C4	−0.0222 (3)	0.1726 (4)	0.5129 (6)	35 (2)
C5	−0.0448 (3)	0.0962 (4)	0.6793 (6)	38 (2)
C6	0.0887 (3)	0.1290 (4)	0.5378 (6)	37 (2)
C7	0.0635 (3)	0.0491 (4)	0.6980 (6)	35 (2)
C8	0.0900 (4)	−0.2039 (5)	0.6580 (7)	46 (2)
C9	0.1135 (4)	−0.0768 (5)	0.7819 (7)	48 (2)

to the complexed ligands.[15] The decks are nearly parallel to each other.

The X-ray determination for (cyclobutadienophane)bis(tricarbonyliron) 1 confirmed its structure. The struture is shown in Figure 1, and relevant parameters are given in Tables I–III. The complex has been redrawn to clearly show the important characteristics of the complex. The complex crystallizes as a clear, yellow solid from chloroform. The iron to carbonyl and iron to cyclobutadiene bond distances are nearly identical with those of tetraphenyl-substituted (cyclobutadiene)tricarbonyliron. The cyclobutadiene rings lie directly over each other. The interdeck distance is an average of 2.704 Å, which is considerably closer than that observed for the cobalt [3.3.3.3]superphane, 2.994 Å.[7] This value is also comparable to the 1,5-cyclooctadiyne distance of 2.60 Å.[16] The [2.2]paracyclophane has interdeck distances of 2.78 and 3.09 Å and shows considerable distortion from planarity.[3] There is considerable out-of-plane bending of the alkyl bonds of 20.6° away from the iron atoms, nearly double that observed for the (tetraphenylcyclobutadiene)tricarbonyliron, 10.8°.[17] In [2.2]paracyclophane the bending is 11.2°, in addition to ring distortion. The observed angles in the (cyclobutadienophane)bis(tricarbonyliron) 1 can be a 2-fold consequence of orbital rehybridization of the cyclobutadiene p orbitals when bound to iron and the strain energy of the face-to-face interactions in the metalloaromatic species. There is an inward bending of the ring hydrogens in 1 in response to orbital rehybridization. Similar evidence for this rehybridization in response to

Table III. Bond Distances (Å) and Angles (deg) for $Fe_2C_{18}H_{12}O_6$ (1)

Fe1–C1	1.774 (5)	C3–O3	1.134 (7)
Fe1–C2	1.774 (5)	C4–C5	1.445 (6)
Fe1–C3	1.782 (6)	C5–C7	1.426 (6)
Fe1–C4	2.056 (4)	C7–C6	1.435 (6)
Fe1–C5	2.034 (4)	C6–C4	1.448 (6)
Fe1–C6	2.038 (4)	C7–C9	1.491 (6)
Fe1–C7	2.084 (4)	C9–C8	1.545 (7)
C1–O1	1.149 (7)	C8–C4′	1.483 (6)
C2–O2	1.130 (7)		
C1–Fe1–C2	99.2 (2)	C3–Fe1–C6	142.0 (2)
C1–Fe1–C3	99.3 (2)	Fe1–C1–O1	178.1 (6)
C1–Fe1–C4	147.7 (2)	Fe1–C2–O2	177.2 (5)
C1–Fe1–C5	111.9 (2)	Fe1–C3–O3	179.0 (11)
C1–Fe1–C7	88.4 (2)	C6–C4–C5	88.3 (3)
C1–Fe1–C6	115.4 (2)	C4–C5–C7	91.2 (3)
C2–Fe1–C3	98.2 (2)	C5–C7–C6	89.6 (3)
C2–Fe1–C4	102.8 (2)	C7–C6–C4	90.7 (3)
C2–Fe1–C5	143.8 (2)	C5–C7–C9	132.6 (4)
C2–Fe1–C7	127.1 (2)	C6–C7–C9	131.8 (4)
C2–Fe1–C6	91.3 (2)	C7–C9–C8	111.6 (4)
C3–Fe1–C4	100.6 (2)	C9–C8–C4′	113.0 (4)
C3–Fe1–C5	94.6 (2)	C5–C4–C8′	131.3 (4)
C3–Fe1–C7	132.3 (2)	C6–C4–C8′	131.5 (4)

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[15] Crystals of 8 were of poor quality [a = 8.652 (3) Å, b = 8.108 (3) Å, c = 6.164 (5) Å, α = 109.95 (1)°, β = 106.48 (1)°, γ = 90.02 (1)°, space group $P1$, d(calcd, Z = 1) = 1.728 g cm^{-3}, R = 17.2%, 2548 observed reflections]. Refinement revealed the general connectivity of the atoms. However, disorder of the carbonyl groups inhibited further refinement.

[16] Kloster-Jensen, E.; Wirg, J. *Helv. Chem. Acta* **1975**, *58*, 162–177.

[17] Dodge, R. P.; Schomaker, V. *Acta Crystallogr.* **1965**, *18*, 614–617.

strain and p orbital interactions was observed in the [2.2]paracyclophanes, where it was postulated that there is increased p character in the σ bonds of benzene.[14] In the case of the [2.2]metacyclophane the bending results in a decreased carbon–carbon distance of 2.69 Å, and a bond is formed in the metacyclophane when the compound is subjected to electrophilic aromatic substitution reactions.[4,18] A very interesting structural feature of the (cyclobutadienophane)bis(tricarbonyliron) is that the carbonyls on each iron are staggered with respect to each other. Whether there is orbital communication across the π system or the result is an artifact of the crystal remains uncertain.

Experimental Section

General Comments. All reactions were carried out under an atmosphere of dry nitrogen or argon. Air- and/or moisture-sensitive reagents were handled by using standard syringe transfer techniques and flasks capped with rubber septa or under an inert atmosphere in a glovebag (Aldrich AtmosBag). Tetrahydrofuran, ether, and dimethoxyethane were freshly distilled from the potassium benzophenone ketyl just prior to use. Phosphorous oxychloride and *N*-methylformanilide (Aldrich) were distilled prior to use. Cyclooctatetraene was obtained from BASF or Aldrich and distilled prior to use. All other solvents and reagents were reagent grade and used without further purification. Reactions were monitored by thin-layer chromatography on silica gel plates (E. Merck Kieselgel 60 F254) and alumina (Aluminiumoxid 150 F254 neutral Type T) and column or filtration chromatography used silica gel (J.T. Baker, 80–200 mesh) and alumina (E.M. Science, 80–200 mesh). ((Chloromethyl)cyclobutadiene)tricarbonyliron (**2**), (cyclobutadienecarboxaldehyde)tricarbonyliron (**4**), and ((hydroxymethyl)cyclobutadiene)tricarbonyliron (**7**) were prepared as described in the literature.[8]

High-field NMR spectra were recorded on a Varian XL-300 spectrometer (NSF DMB-8603864). Carbon-13 and proton NMR spectra were recorded at 75.43 and 299.94 MHz, respectively. Chemical shifts are reported in δ units, part per million downfield, with $CDCl_3$ or TMS as the reference signal. Infrared spectra were obtained by using a Perkin-Elmer 681 IR spectrometer. EI mass spectra were recorded on a VG TS-250 mass spectrometer operating at 70 eV, and exact mass determinations were recorded on a VG ZAB-2SE HR-HM spectrometer. Melting points were determined by using a Fisher-John melting point apparatus and are reported uncorrected.

[μ-[Bis(η^4-1,3-cyclobutadien-1-ylmethyl) sulfide]]bis(tricarbonyliron) (3). A solution of 1.05 g (4.37 mmol) of $Na_2S{\cdot}9H_2O$ in 80 mL of ethanol and 8 mL of H_2O was placed in a round-bottomed flask, and 2.165 g of the ((chloromethyl)cyclobutadiene)tricarbonyliron (**2**) in 50 mL of benzene was added dropwise. This solution was stirred for 20 min at room temperature, filtered, and evaporated to leave an orange oil. The oil was dissolved in 150 mL of ether, extracted with 3 × 100 mL of water, 1 × 100 mL of 2 N HCl, 1 × 100 mL of 5% $NaHCO_3$, 1 × 100 mL of saturated NaCl, dried with $MgSO_4$, and reduced in volume to leave an orange solid. The solid was chromatographed on basic alumina using ether to give thioether **3** as an air-sensitive, yellow solid, 1.77 g (4.00 mmol, 89%); mp 59 °C; ^1H NMR ($CDCl_3$) 4.11 (s, 4 H), 4.07 (s, 2 H), 3.16 (s, 4 H); ^{13}C NMR ($CDCl_3$) 214.15, 82.07, 64.04, 61.61, 30.23; IR (neat, cm^{-1}) 2050 vs 1970 vs br, 1410 m, 1230 m, 1066 m, 913 m, 824 m, 738 m; MS for $C_{16}H_{10}O_6SFe$, $(M^+ - CO)_{calcd}$ 413.8947, $(M^+ - CO)_{obs}$ 413.8945, 272, 205 (100%), 177, 149, 121.

Tricarbonyl[2-(η^4-1,3-cyclobutadien-1-yl)-*m*-dithiane]iron (5). A solution of 0.668 g (3.0 mmol) of (cyclobutadienecarboxaldehyde)tricarbonyliron (**4**) and 0.337 g (3.4 mmol) of 1,3-dimercaptopropane was placed in a 10-mL round-bottomed flask. The system was cooled to 0 °C, and 0.483 g (3.4 mmol) of BF_3/etherate added dropwise. The resulting orange–brown solution was stirred for 30 min at room temperature and then quenched with 5 mL of methanol, followed by addition of 150 mL of water. The aqueous solution was extracted with ether, 3 × 150 mL, and the ether layers were combined. The organic layer was washed with 2 × 150 mL of water, 1 × 150 mL of 5% $NaHCO_3$, and 1 × 150 mL of saturated NaCl solution and dried over $MgSO_4$. Following concentration, the resulting oil was chromatographed on basic alumina by using ether. Concentration under reduced pressure gave **5** as an air-sensitive, orange–yellow oil, 0.921 g (2.96 mmol, 98%); ^1H NMR ($CDCl_3$) 4.47 (s, 1 H), 4.17 (s, 2 H), 4.15 (s, 1 H), 2.86 (m, 4 H), 1.93 (m, 2 H); ^{13}C NMR ($CDCl_3$) 213.84, 82.12, 62.93, 43.58, 30.96, 25.13; IR (neat, cm^{-1}) 2050 vs, 1975 vs br, 1426 m, 1280 m, 913 m, 738 m; MS calcd for $C_{11}H_{10}O_3S_2Fe$ 309.9421, obs 309.9573, 282 (100%), 270, 254, 226, 198.

Thioacetal Removal. Method 1. A solution of 1.72 g (9.66 mmol) of *N*-bromosuccinimide in 8 mL of acetonitrile and 2 mL of water was cooled to 0 °C in a 25-mL round-bottomed flask, and 0.50 g (1.61 mmol) of thioacetal **5** in 5 mL of acetonitrile was added dropwise. After the exothermic reaction was stirred for 10 min, 125 mL of dichloromethane was added. The organic layer was extracted with 2 × 100 mL of 5% $NaHCO_3$, 1 × 100 mL of H_2O, and 1 × 100 mL of saturated NaCl solution and dried with $MgSO_4$. Concentration under reduced pressure and chromatography on alumina with ether returned **4** 0.140 g (0.64 mmol, 40%).

Method 2. A solution of 0.95 g (3.06 mmol) of the thioacetal **5** and 30 mL of methanol was placed in a 50-mL round-bottomed flask. To this solution was added 2 g (7.37 mmol) of mercury(II) chloride, and the system stirred 1 h. The pasty white precipitate was transferred to a separatory funnel, and 150 mL of ether added, extracted with 1 × 100 mL of 0.5 N HCl, 1 × 100 mL of H_2O, 1 × 100 mL of saturated NaCl and dried with $MgSO_4$. Concentration followed by chromatography on alumina using ether yielded **4**, 0.54 g (2.45 mmol, 80%).

[μ-(*E*)-1,2-Di-η^4-1,3-cyclobutadien-1-ylethylene]bis(tricarbonyliron) (6). In a 100-mL round-bottomed flasked was placed 3.13 g (22.8 mmol) of a 4:1 mixture of $TiCl_3$:$LiAlH_4$ and 40 mL of dry THF. After the heterogeneous mixture was stirred for 10 min, 1 g (4.55 mmol) of (cyclobutadienecarboxaldehyde)tricarbonyliron (**4**) in 30 mL of dry THF was added, and the system refluxed for 4 h. The organic layer was cooled and filtered through a pad of silica gel, and the silica gel washed with ether. Concentration yielded a dark green-yellow oil. The oil was chromatographed on basic alumina by using ether and concentrated. Recrystallization from ethyl acetate/hexane gave the disubstituted ethene **6** as a yellow, air-sensitive solid, 0.568 g (1.39 mmol, 56%); mp 129 °C; ^1H NMR ($CDCl_3$) 4.16 (s, 2 H), 4.21 (s, 4 H), 5.60 (s, 2 H); ^{13}C NMR ($CDCl_3$) 213.92, 121.36, 80.82, 63.60, 62.12; IR (KBr, cm^{-1}) 2040, 1950; MS calcd for $C_{16}H_8O_6Fe_2$ 407.9019, obs 407.9023, 380, 352, 324, 296, 268, 239 (100%).

[μ-1,2-Di-η^4-1,3-cyclobutadien-1-ylethane]bis(tricarbonyliron) (8). Method A. To a suspension of 2.51 g of $TiCl_3$ (16.3 mmol) in 90 mL of dry dimethoxyethane was added 0.59 g of granular magnesium metal (20 mesh), and the system refluxed for 12 h or until all the metal had been consumed. This produced Ti(0) as a fine black suspension. In a separate flask was placed 6.5 g (29.3 mmol) of ((hydroxymethyl)cyclobutadiene)tricarbonyliron, 40 mL of dry DME, and after this was cooled to 0 °C under nitrogen, 1.25 g of NaH (41.6 mmol, 80% in oil) was added portionwise. After stirring 15 min at 0 °C, the system was warmed to room temperature and stirred an additional hour. This solution was cannulated into the hot Ti(0) reaction mixture, and the mixtured refluxed for 3 h. The solution was cooled, filtered through alumina, followed by an ether wash, and evaporated to give an orange oil. Chromatography on silica gel with hexane slowly eluted two fractions: the first gave ether **9**, 1.48 g (3.47 mmol, 24%), and the second gave monobridged **8**, 0.58 g (1.41 mmol, 9.6%). In some instances varying amounts of the reduced (methylcyclobutadiene)tricarbonyliron (**10**) were isolated.[12] **8**: mp 69–70 °C; ^1H NMR ($CDCl_3$) 3.95 (s, 4 H), 3.84 (s, 2 H), 2.10 (s, 4 H); ^{13}C NMR ($CDCl_3$) 214.63, 86.94, 63.78, 59.68, 27.68; IR (cm^{-1}, KBr) 3112 m, 2040 vs, 1950 vs, 1443 m, 955 m, 827 m, 790 m, 758 m; MS calcd for $C_{16}H_{10}O_6Fe$ 409.9176, obs 409.9163, 382, 354, 326, 298, 270, 242 (100%).

Method B. To 30 mL of dry dimethoxyethane under nitrogen was placed 0.58 g (1.31 mmol) of thioether **3**. To this was added 0.50 g (1.37 mmol) of diiron nonacarbonyl, $Fe_2(CO)_9$. The system was refluxed for 18 h, an additional 2 g (5.5 mmol) of $Fe_2(CO)_9$

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(18) Coulter, C. L.; Trueblood, K. N. *Acta Crystallogr.* **1963**, *16*, 667–676.

was added, and the reflux was continued another 18 h. After cooling, the reaction mixture was filtered through basic alumina, followed by an ether wash. Concentration under reduced pressure yielded an orange oil. Chromatography on silica gel using hexane gave a colorful column from which a yellow polymeric fraction slowly came first followed by a second, pale yellow solution which, upon solvent removal, gave monobridged **8** as a light yellow, air-sensitive solid, 0.14 g (0.34 mmol, 26%).

Method C. To a 250-mL round-bottomed flask containing 150 mL of dry THF and 2.876 g (44 mmol) of powdered zinc was added 10.567 g (43.9 mmol) of ((chloromethyl)cyclobutadiene)tricarbonyliron (**2**). After stirring 10 min at room temperature, the system was refluxed for 1 h. Filtration and concentration gave an orange oil, which was subsequently redissolved in 150 mL of ether, extracted with 2 × 100 mL of H_2O, 2 × 100 mL of 10% HCl, 1 × 100 mL of saturated $NaHCO_3$, 1 × 100 mL of saturated NaCl, dried with $MgSO_4$, and reduced in volume. Chromatography on silica using 3% chloroform/pentane, followed by concentration gave **8**, 4.728 g (11.5 mmol, 52%). Monobridged **8** prepared by this method was formylated without further purification.

[μ-[Bis(η^4-1,3-cyclobutadien-1-ylmethyl) ether]]bis(tricarbonyliron) (9). In a 50-mL round-bottomed flask was placed 85.7 mg (0.21 mmol) of alcohol **7**, 50 mL of dry benzene, and 94.3 mg of Amberlyst 15. This was stirred under argon for 3 h at 25 °C, filtered, and concentrated at reduced pressure. Chromatography on alumina using ether, followed by concentration at reduced pressure gave ether **9** as an orange oil, 80.1 mg (0.188 mmol, 90%); ^1H NMR ($CDCl_3$) 4.15 (s, 4 H), 4.11 (s, 2 H), 3.83 (s, 4 H); ^{13}C NMR ($CDCl_3$) 214.08, 79.78, 65.90, 64.58, 62.65; IR (neat, cm^{-1}) 2040 vs, 1960 vs, 1445 m, 1352 m, 1080 m, 1050 m; MS calcd for $C_{16}H_{10}O_7Fe_2$ 425.9125, obs 425.9120, 398, 370, 342, 286, 258 (100%), 206, 177.

[μ-3,3′-Ethylenebis[(1–4-η)-1,3-cyclobutadiene-1-carboxaldehyde]]bis(tricarbonyliron) (11). In a small round-bottomed flask was placed 1.18 g (8.73 mmol) of *N*-methylformanilide, and the system cooled to 0 °C. To this was added 1.4 g (9.13 mmol) of phosphorus oxychloride, and the system stirred 15 min. The resulting mixture was added to 0.64 g (1.56 mmol) of the monobridged **8**. The system was warmed to 50 °C and stirred for 12 hours. The dark oil was added slowly to 100 mL of ice/water with stirring, and then the entire solution transferred to a separatory funnel containing 150 mL of dichloromethane. The organic layer was removed, and the aqueous layer extracted a second time with 50 mL of dichloromethane. The organic layers were combined and extracted with 3 × 100 mL of H_2O, 3 × 100 mL of 1 N HCl, 2 × 100 mL of saturated $NaHCO_3$, and 1 × 100 mL of saturated NaCl, dried with $MgSO_4$, and reduced in volume. Chromatography on basic alumina using ether followed by recrystallization from ethyl acetate/hexane gave only the 1,3-substituted dialdehyde **11** as an orange, air-sensitive solid, 0.34 g (0.73 mmol, 50% yield); mp 152–153 °C; ^1H NMR ($CDCl_3$) 9.23 (s, 1 H), 4.69 (s, 2 H), 2.29 (s, 2 H); ^{13}C NMR ($CDCl_3$) 211.04, 187.78, 94.75, 64.97, 64.55, 27.08; IR (cm^{-1}, KBr) 3110 m, 2070 vs, 2000 vs, 1950 vs, 1555 m, 1378 m, 1088 m; MS calcd for $C_{18}H_{10}O_8Fe_2$ 466, obs 466, 438, 410, 382, 354, 326, 298 (100%).

[μ-1,9,10,11-η:4,5,6,12-η-Tricyclo[7.1.1.1^{4,6}]dodeca-1(11),2,4,6(12),9-pentaene]bis(tricarbonyliron) (12). In a 250-mL three-neck flask was placed 2.4814 g (16.1 mmol) of $TiCl_3$ and 200 mL of anhydrous dimethoxyethane, and to this added 3.00 g zinc powder (49.5 mmol). This mixture was refluxed for 1 h. Over approximately 16 h 0.8162 g (1.7 mmol) of dialdehyde **11** in 50 mL of anhydrous dimethoxyethane was then added under high dilution using a syringe pump. After refluxing 2 hours longer, the system was cooled, filtered, and reduced in volume. The system was dissolved in 150 mL of dichloromethane and extracted with 2 × 150 mL of 1 N HCl, 1 × 150 mL of saturated $NaHCO_3$, and 2 × 150 mL of saturated NaCl. After drying with $MgSO_4$, the solution was reduced in volume to give an orange–yellow oil. Chromatography on silica with 15% ethyl acetate/hexane, followed by solvent removal, gave the unsaturated cyclophane **12** as yellow, air-sensitive crystals, 0.4412 g (1.02 mmol, 58% yield); mp 153 °C (dec); ^1H NMR ($CDCl_3$) 6.43 (s, 1 H), 3.74 (s, 2 H), 2.67 (s, 2 H); ^{13}C NMR ($CDCl_3$) 214.18, 130.98, 93.65, 78.46, 64.52, 26.63; IR (cm^{-1}, KBr) 2020 vs, 1960 vs, 605 m; MS calcd for $C_{18}H_{10}O_6Fe_2$ 433.9176, obs 434, 406, 378, 350, 322, 294, 266 (100%).

[μ-1,9,10,11-η:4,5,6,12-η-Tricyclo[7.1.1.1^{4,6}]dodeca-1(11),4,6(12),9-tetraene]bis(tricarbonyliron) (1). In a 100-mL round-bottomed flask was placed 0.4412 g (1.02 mmol) of unsaturated cyclophane **12**, 50 mL of ethyl acetate and approximately 100 mg of Pd(C). The system was purged with hydrogen and then stirred for 24 h under a positive hydrogen atmosphere. The system was concentrated and chromatographed on alumina by using ether. Concentration gave cyclophane **1** as an air-sensitive, yellow solid, 0.3197 g (0.73 mmol, 72%); mp 187–189 °C (dec); ^1H NMR ($CDCl_3$) 3.78 (s, 4 H), 2.52 (s, 8 H); ^{13}C NMR ($CDCl_3$) 214.78, 86.67, 63.29, 25.78; IR (cm^{-1}, KBr) 2020 vs, 1985 vs, 1935 vs, 1017 m, 605 m; MS calcd for $C_{18}H_{10}O_6Fe_2$ 436, obs 436, 408, 380, 352, 324, 296, 268 (100%).

Structure Determination. A single crystal (0.1 × 0.2 × 0.2 mm) of **1** was grown from a saturated chloroform solution, sealed in a capillary, and mounted on a Syntex P3 automated diffractometer. Unit-cell dimensions (Table I) were determined by least-squares refinement of the best angular positions for 15 independent reflections ($2\theta > 15°$) during normal alignment procedures using molybdenum radiation (λ = 0.71069 Å). Data (1961 independent points after removal of space group forbidden and redundant data) were collected at room temperature by using a variable scan rate, a θ–2θ scan mode, and scan width of 1.2° below $K\alpha_1$ and 1.2° above $K\alpha_2$ to a maximum 2θ value of 50°. Backgrounds were measured at each side of the scan for a combined time equal to the total scan time. The intensities of three standard reflections were remeasured after every 97 reflections. As the intensities of these reflections showed less than 5% variation, corrections for decomposition were deemed unnecessary. Data were collected for Lorentz, polarization, and background effects. Observed reflections [1272 ($I > 3.0\sigma(I)$)] were used for solution of the structure by direct methods using MULTAN80.[19] Refinement of scale factor and positional and anisotropic thermal parameters for all non-hydrogen atoms was carried out to convergence.[20] Hydrogen positional parameters were determined from a difference Fourier synthesis. These hydrogen positional parameters and fixed isotropic thermal parameters (U = 0.03) were included in the final cycles of refinement but were held invariant. The final cycle of refinement [function minimized $\sum(|F_o| - |F_c|)^2$] led to a final agreement factor R = 4.2% [$R = 100(\sum||F_o| - |F_c||/\sum|F_o|)$]. Anomalous dispersion corrections were made for Fe.[21] Scattering factors were taken from Cromer and Mann.[22] In the final stages of refinement a weight of $1/\sigma(F)^2$ was used.

Chemical Abstracts Names

1 hexacarbonyl[μ-[(1,9,10,11-η:4,5,6,12-η)-tricyclo[7.1.1.1^{4,6}]dodeca-1(11),4,6(12),9-tetraene]]diiron
3 hexacarbonyl[μ-[(1,2,3,4-η:1′,2′,3′,4′-η)-1,1′-[thiobis(methylene)]bis[1,3-cyclobutadiene]]]diiron
5 tricarbonyl[2-(η^4-1,3-cyclobutadien-1-yl)-1,3-dithiane]iron
6 hexacarbonyl[μ-[(1,2,3,4-η:1′,2′,3′,4′-η)-1,1′-(1,2-ethenediyl)bis[1,3-cyclobutadiene]]]diiron stereoisomer
8 hexacarbonyl[μ-[(1,2,3,4-η:1′,2′,3′,4′-η)-1,1′-(1,2-ethanediyl)bis[1,3-cyclobutadiene]]]diiron
9 hexacarbonyl[μ-[(1,2,3,4-η:1′,2′,3′,4′-η)-1,1′-[oxybis(methylene)]bis[1,3-cyclobutadiene]]]diiron
11 hexacarbonyl[μ-[(1,2,3,4-η:1′,2′,3′,4′-η)-3,3′-(1,2-ethanediyl)bis[1,3-cyclobutadiene-1-carboxaldehyde]]]diiron
12 hexacarbonyl[μ-[(1,9,10,11-η:4,5,6,12-η)tricyclo[7.1.1.1^{4,6}]dodeca-1(11),2,4,6(12),9-pentaene]]diiron

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[19] Main, P.; Fiske, S. J.; Hull, S. E.; Lessinger, L.; Germain, G.; DeClerq, J. P.; Woolfson, M. M. University of York, England, 1980.

[20] Stewart, J. M., Ed. *The XRAY System—Version of 1980*, Technical Report TR446 of the Computer Center, University of Maryland, College Park, MD.

[21] Ibers, J.; Hamilton, W. C. *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, 1984; Vol. IV.

[22] Cromer, D. T.; Mann, I. B. *Acta Crystallogr.* **1968**, *A24*, 321.

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Registry No. 1, 125519-39-3; 2, 64121-49-9; 3, 125519-40-6; 4, 33056-62-1; 5, 125519-41-7; 6, 125519-42-8; 7, 58396-62-6; 8, 125519-43-9; 9, 125519-44-0; 10, 53407-14-0; 11, 125519-45-1; 12, 125519-46-2; $Fe_2(CO)_9$, 15321-51-4; 1,3-dimercaptopropane, 109-80-8.

Supplementary Material Available: Tables of anisotropic thermal parameters and least-squares planes for 1 and tables of crystal data, positional and anisotropic thermal parameters, and bond angles and distances for 8 (7 pages); listings of observed and calculated structure factor amplitudes for 1 and 8 (37 pages). Ordering information is given on any current masthead page.

Reactions of Binuclear Rhodium Hydrides with Imines: Factors Influencing the Insertion of Carbon–Nitrogen Double Bonds into Rhodium–Hydride Bonds

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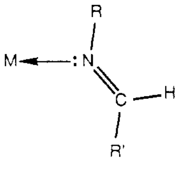
The reaction of the binuclear rhodium hydride complexes $[(R_2PCH_2CH_2PR_2)Rh]_2(\mu\text{-H})_2$ (R = Pr^i, **1a**, $[(\text{dippe})Rh]_2(\mu\text{-H})_2$; R = OPr^i, **1b**, $[(\text{dipope})Rh]_2(\mu\text{-H})_2$) with simple aldimines (RCH=NR′), the ketimine benzophenone imine ($Ph_2C{=}NH$), and the cyclic imine isoquinoline are described. Amido–hydride products of the general formula $[(R_2PCH_2CH_2PR_2)Rh]_2(\mu\text{-NR}'CH_2R)(\mu\text{-H})$ are produced. The mechanism of this reaction has been investigated by labeling studies and kinetic analysis. Intermediates have been detected and characterized spectroscopically that are consistent with the imine binding through the lone pair on nitrogen and through the π-system of the carbon–nitrogen double bond. On the basis of these studies it is proposed that a necessary condition for migratory insertion of a C=N double bond into a metal hydride is prior coordination through the C=N π-system. Iminium salts of the formula $[PhCH{=}NHR']^+BF_4^-$ react with the hydride dimer **1a** to generate cationic complexes of the formula $\{[(Pr^i_2PCH_2CH_2PPr^i_2)Rh]_2(\mu\text{-NR}'{=}CHPh)(\mu\text{-H})\}^+BF_4^-$ having the imine bound in the μ-η^2-σ-mode. Further reaction of this material with $LiAl(OBu^t)_3H$ generates the corresponding amido hydride. Attempts at using the hydride dimers **1a** and **1b** as catalyst precursors for the homogeneous hydrogenation of imines were only partially successful, resulting in at best seven turnovers (1 atm, 16 h).

Introduction

Many homogeneous mononuclear organotransition-metal systems mediate the reduction of carbon–carbon multiple bonds.[1] However there are very few examples of those that bring about the hydrogenation of carbon–nitrogen double (C=N) or triple (C≡N) bonds under ambient conditions.[2-6] This observation seems to parallel the known π-complexation chemistry of each type of functional group: for olefins and alkynes, this chemistry is vast,[7] but for imines and nitriles the tendency to σ-donate the lone pair on nitrogen to a metal almost always precludes π-coordination of the C=N or the C≡N group to the metal.[8] Since it is generally accepted that π-coordination of olefins or alkynes to the metal precedes its reduction via migratory insertion of a metal–hydride bond, the lack of homogeneous systems for the hydrogenation of imines or nitriles appears to stem from the fact that this key step is prevented in a cycle involving C=N or C≡N moieties, due to the stronger donating ability of the lone pair compared with that of the C=N or C≡N π-system.

The relatively few known imine transition-metal complexes exhibit σ-bonding through the nitrogen lone pair, i.e., type I. In fact, mononuclear complexes having side-on π-bonding imine ligands (type II) have only been reported for the early metals,[8] generally as a result of migratory insertion reactions of isonitriles and metal hydrocarbyls. In systems which hydrogenate imines under ambient conditions, it has been proposed that the nitrogen lone pair is occupied in some manner other than bonding to the metal. For example, this feature is included in the mechanistic proposal for the hydrogenation of aldimines by a cationic rhodium triphenylphosphine complex,[2a] wherein an intermediate in which the imine C=N bond is π-coordinated forms when the lone pair at nitrogen



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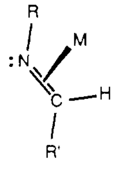
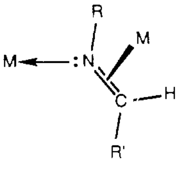


II



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(1) Parshall, G. W. *Homogeneous Catalysis*; Wiley-Interscience: New York, 1980; Chapters 3–5.

(2) (a) Longley, C. J.; Goodwin, T.; Wilkinson, G. *Polyhedron* **1986**, *5*, 1625. (b) Grigg, R.; Mitchell, T. R. B.; Tongpenyai, N. *Synthesis* **1981**, 442.

(3) (a) Vastag, S.; Bakos, J.; Torös, S.; Takach, N. E.; King, R. B.; Heil, B.; Marko, L. *J. Mol. Catal.* **1984**, *22*, 283. (b) Vastag, S.; Heil, B.; Torös, S.; Marko, L. *Transition Met. Chem.* **1977**, *2*, 58. (c) Levi, A.; Modena, G.; Scorrano, G. *J. Chem. Soc., Chem. Commun.* **1975**, 6. (d) Kang, G.-J.; Cullen, W. R.; Fryzuk, M. D.; James, B. R.; Kutney, J. P. *J. Chem. Soc., Chem. Commun.* **1988**, 1466.

(4) (a) Radhi, M. A.; Palyi, G.; Marko, L. *J. Mol. Catal.* **1983**, *22*, 195. (b) Radhi, M. A.; Marko, L. *J. Organomet. Chem.* **1984**, *262*, 359.

(5) Baranyai, A.; Ungvary, F.; Marko, L. *J. Mol. Catal.* **1985**, *32*, 343.

(6) Palagyi, J.; Nagy-Magos, Z.; Marko, L. *Transition Met. Chem.* **1985**, *10*, 336.

(7) Lewandos, G. S. In *The Chemistry of the Metal-Carbon Bond*; Hartley, F. R., Patai, S., Eds.; Wiley: New York, 1982; Vol. 1, Chapter 7.

(8) (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*, 2nd ed.; University Science Books: Mill Valley, CA, 1987; p 64. For examples of η^2-imines, see: (b) Chamberlain, L. R.; Steffey, B. D.; Rothwell, I. P.; Huffman, J. C. *Polyhedron* **1989**, *8*, 341. (c) Durfee, L. D.; Fanwick, P. E.; Rothwell, I. P.; Folting, K.; Huffman, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 4720 and ref 10 therein.