Structure of (2,2'-Biallylene)hexacarbonyldiiron

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Received October 11, 1994[®]

The crystal structures of the title compound $[C_{12}H_8Fe_2O_6, \text{ orthorhombic}, Iba2 (No. 45), a$ = 22.762(15) Å, b = 12.229(11) Å, c = 9.615(8) Å, Z = 8] and its triphenylphosphine substitution product $[C_{29}H_{13}Fe_2O_5P, triclinic, P1 (No. 2), a = 10.7506(20) \text{ Å}, b = 13.3657(23)$ Å, c = 9.5827(16) Å, $\alpha = 92.803(11)$, $\beta = 94.022(11)$, $\gamma = 73.444(14)^\circ$, Z = 2] are reported. They show systematic deviations from C_{2v} symmetry, with the biallylene ligand being nonplanar due to pyramidalization and internal rotation about its central C-C bond; also, the Fe-Fe and central C-C axes are not parallel, being twisted by 11° relative to each other. Low-temperature NMR studies at -95° indicate similar distortions in solution, with very low activation energy for interconversion of equivalent lower-symmetry forms. In the crystal structures, these distortions of the biallylene ligand are accompanied by relief of eclipsing interactions among the equatorial carbonyl ligands of the Fe₂(CO)₅L fragment. Pyramidalization is found in all published (2,2'-biallylene)diiron structures, but the twisting and rotation are not, consistent with the small energy change which accompanies these latter deformations.

The unstable organic fragment 2,2'-biallylene¹ [sometimes called tetramethyleneethane; systematic name; 2,3-bis(methylene)-1,4-butanediyl] should constitute an excellent ligand for formation of bimetallic complexes, on the basis of the ready formation of stable allyl complexes of many metals and the proximity of the two allyl groups. Current interest in bimetallic complexes, especially fulvalene complexes, as potential exemplars of cooperative reactivity² would lead one to expect many studies of (biallylene)bimetallics, but there have been surprisingly few.

In fact, the only known metal-metal-bonded biallylene complexes are the diiron complexes, first reported in 1965.³ These complexes have most commonly been prepared by *in situ* dimerization of allenes during reaction with various iron carbonyls.³⁻⁹ The parent

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0276-7333/95/2314-2002\$09.00/0

 $(C_6H_8)Fe_2(CO)_6$, 1, has also been prepared by reaction of 2,3-bis(bromomethyl)-1,3-butadiene or 2,3-bis(bromomethyl)-1,4-dibromo-2-butene with diiron nonacarbonyl.⁹ Derivatives having the biallylene moiety incorporated in rings have also been formed in o-xylylenederived systems^{10,11} and from polycyclic hydrocarbons such as anthracene¹² and naphthacene.¹³

Early discussion³ of parallel vs perpendicular isomers of 1 (Scheme 1) was effectively resolved by means of extended Hückel calculations by Thorn and Hoffmann,¹⁴ which indicated a substantial energetic preference (1.7)eV) for the parallel, C_{2v} form, and by a partial crystal structure (R = 0.12, the result of "multiple twinning") of the product, 2, from reaction of 1,2-cyclononadiene with $Fe_2(CO)_{9.5}$ However, the crystal structure showed only C_2 symmetry for 2, which, together with reduced



symmetry apparent in low-temperature NMR studies of 1 and 2, led to a further suggestion of equilibrating

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^{*} Abstract published in Advance ACS Abstracts, March 15, 1995.

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nonequivalent σ,π structures in solution (Scheme 2). Attempts to secure a crystal structure of **1** were apparently unsuccessful.^{3d} Crystal structures of some di- or tetrasubstituted derivatives of $1^{7,8,11,12}$ have been published more recently, and all show more or less parallel structures; however, the possible effects of reduced symmetry due to substituents or of structural rigidity imposed by polycyclic frameworks make unclear to what extent these may reflect the structure of the unperturbed parent complex, **1**. We therefore sought to establish the structures of complexes of unsubstituted 2,2-biallylene, which we report here.

Experimental Section

(2,2'-Biallylene)hexacarbonyldiiron, 1.³ Allene was condensed into a dry ice-cooled graduated cylinder (4.0 mL, ca. 90 mmol), diluted with 60 mL of hexane, and transferred to a small stainless steel autoclave. Nonacarbonyldiiron (28.56 g, 73 mmol) was added to the hexane solution, and the autoclave was sealed and heated in an oil bath at 60–70 °C for 23 h. The apparatus was cooled to room temperature, the autoclave was opened, and the mixture was filtered. Evaporation of the filtrate left 4.18 g of dark green-brown oil. Chromatography on silica, eluting with hexane, gave 66 mg (2%) of a product identified by IR and NMR spectra as $(C_3H_4)Fe_2(CO)_7$, 3,^{6,16}



followed by 2.38 g (18%) of 1. Pure 1 was obtained by slow cooling of hexane solutions to -80 °C, giving red crystals, mp 84–6 °C (lit.^{3,9} mp 88–9 °C). IR: (hexane, cm⁻¹) 2066 s, 2046 w, 2025 s, 1998 s, 1976 m, 1952 w (¹³CO?); (CCl₄) 2064 s, 2046 w, 2024 s, 1995 s, 1972 m. Room-temperature 300 MHz ¹H NMR: (CDCl₃) δ 1.68 (s), 1.75 (s); (acetone- d_6) δ 1.91 (s), 2.03 (s). Variable-temperature NMR spectra were measured at 250 MHz. The crystal structure of 1 is described below. Also produced, but not fully purified and identified, was a product which appeared by mass spectrometry to have the composition (C₃H₄)₃Fe₃(CO)₇; its proton NMR spectrum showed peaks at δ 2.26, 2.44, 6.21, and 6.43 in a ratio of 2:2:1:1. The ¹³C NMR

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Table 1. Crystallographic Data for $(\eta^6-C_6H_8)Fe_2(CO)_6$, 1, and $(\eta^6-C_6H_8)Fe_2(CO)_5PPh_3$, 5

	Crystal Data	
formula	$C_{12}H_8Fe_2O_6$	C29H23Fe2O5P
formula wt	359.9	594.1
cryst color and habit	orange plate	brown prism
cryst size, mm	$0.04 \times 0.48 \times 0.68$	$0.2 \times 0.3 \times 0.35$
cryst syst	orthorhombic	triclinic
space group	Iba2 (No. 45)	P1 (No. 2)
a, Å	22.762(15)	10.751(2)
<i>b</i> , Å	12.229(11)	13.366(2)
c, Å	9.615(8)	9.583(2)
α, deg	90	92.80(1)
β , deg	90	94.02(1)
γ, deg	90	73.44(1)
V, Å ³	2676(3)	1315.9(4)
Ζ	8	2
$D(\text{calcd}), \text{g cm}^{-3}$	1.786	1.499
μ (Mo K α), cm ⁻¹	21.9	11.975
	Data Collection	
diffractometer	Siemens P4	Enraf-Nonius CAD4
rflns collected	$1575 (\max 2\theta = 50^{\circ})$	6671 (max $2\theta = 54^{\circ}$)
independent rflns	1378	6339
obsd rflns	$1222 (4.5\sigma(F))$	3855 $(3\sigma(F))$
min/max transmission	0.53/0.94	0.92/1.03
	Refinement	
R(F), R(wF), %	3.12, 3.47	3.29, 3.62
data/param	6.7	11.5
$\Delta(\max)$, e Å ⁻³	0.36	0.25
goodness of fit	0.89	1.25
•		

showed peaks at δ 212.6, 149.3, 112.5, 38.0, 31.9, and 19.4. Attempted reaction of allene with pentacarbonyliron in the autoclave at 120° gave predominantly oligo(allene) products rather than iron carbonyl products.

2,3-Dibromopropene (10.7 mL, 20.7 g, 0.103 mol) was stirred for 2.5 h at 40 °C under a nitrogen atmosphere with 36.5 g (0.10 mol) of nonacarbonyldiiron in 50 mL of hexanes. The solution was filtered, and the solid was washed with hexane; evaporation of the filtrate left a yellow-brown solid product, which was predominantly (2-bromoallyl)tricarbonyliron bromide, 4; recrystallization from hexanes yielded 2.31 g of 4.¹⁵ A similar reaction run under reflux conditions produced predominantly **3** and small amounts of **1**, as indicated by NMR.

Stirring 0.633 g (1.87 mmol) of 4 with 0.152 g (2.32 mmol) of zinc powder in 25 mL of ether under nitrogen for 15 h gave a complex mixture of products, in which little or no 1 was detectable by NMR.

X-ray Crystallographic Structure Determination of 1. Crystallographic data are collected in Table 1. Structural studies were done on very brittle crystals with an extremely thin plate-like habit. Most cements distorted and cracked specimens as they hardened, and immobilization within a capillary was impossible due to the extreme fragility. Crystals were ultimately affixed to a fine glass fiber with a very small amount of an alkyd varnish. High esd's associated with the unit cell parameters are likely the result of crystal flexing due to air currents within the diffractometer chamber. A laminar correction for absorption was applied to the diffraction data, with data making a glancing angle $\leq 3^{\circ}$ discarded.

Systematic absences in the diffraction data indicated either of the orthorhombic space groups Iba2 or Ibam. Since Z = 8and the molecule does not possess mirror-plane symmetry, processing was confined to the noncentrosymmetric alternative. The Fe atoms were located from a Patterson synthesis. All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were located and successfully refined isotropically. All computations used SHELXTL software (version 4.2, G. Sheldrick, Siemens XRD, Madison, WI).

(2,2'-Biallylene)pentacarbonyl(triphenylphosphine)diiron, 5. Triphenylphosphine (291 mg, 1.11 mmol) and 1 (200 mg, 0.556 mmol) were refluxed for 16 h under nitrogen in 10 mL of benzene. Filtration and evaporation of the filtrate left a solid residue, which was chromatographed on silica.

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Elution with hexanes yielded some unreacted 1. Elution with 10% ethyl acetate/hexanes yielded 235 mg of substitution product 5, contaminated by some unreacted triphenylphos-

$$L = CO$$

$$6 L = PPh_3$$

phine. Pure **5** (100 mg, 37%) was obtained by recrystallization from ethyl acetate/hexanes or ethyl acetate/methanol as brown-black crystals, mp 150 °C dec. IR (KBr, cm⁻¹): 2026 s, 1977 s, 1961 s, 1948 m sh, 1911 m. ¹H NMR (CDCl₃): δ 7.5– 7.3 (complex m, 15H), 1.72 (s, 2H), 1.51 (s, 2H), 1.35 (s, 2H), 0.60 (d, 2H, ³J_{PH} = 10.5 Hz). MS (direct inlet) (*m/z*, intensity, assignment): 594, 0.2, P; 566, 1.0, P–CO; 538, 0.7, P–2CO; 510, 3.2, P–3CO; 482, 2.6, P–4CO; 454, 14, P–5CO; 398, 6.0, P–Fe(CO)₅; 318, 6.5, FePPh₃; 262, 100, PPh₃; 183, 93, C₁₂H₈P; 108, 42, PPh; 56, 31, Fe. Anal. Found: C, 59.30; H, 4.32; Fe, 18.22; P, 5.10. Calcd for C₂₉H₂₃Fe₂O₅P: C, 58.62; H, 3.90; Fe, 18.80; P, 5.21.

Repetition of the reaction using the same quantities of reactants, but refluxing for 45 h, gave 476 mg of crude product. Chromatography of the hexane-soluble portion of this material gave some recovered 1, triphenylphosphine, and an unidentified product, not completely separable from 5, which showed two multiplets of equal size in the ¹H NMR at δ 1.3 and 0.9, along with phenyl absorptions at δ 7.6-7.2, and infrared absorptions at 2033, 1975, and 1968 $\rm cm^{-1}.~Recrystallization$ of the hexane-insoluble portion of the crude product (226 mg) from ethyl acetate left a ruby-red product, mp 160 °C dec, which appeared to be a bis(triphenylphosphine) substitution product, $(C_6H_8)Fe_2(CO)_4(PPh_3)_2$, 6. IR (KBr, cm⁻¹): 1984 s, 1940 s, 1901 m. ¹H NMR (CD₂Cl₂): δ 7.6-7.3 (complex m, 30H), 1.70 (s, 4H), 0.43 (d, 4H, ${}^{3}J_{PH} = 11.4$ Hz). MS (direct inlet) (m/z, intensity, assignment): 482, 0.5, (C₆H₈)Fe₂(CO)PPh₃; 454, 3.1, (C₆H₈)Fe₂PPh₃; 400, 8.8; 398, 8.0, (C₆H₈)FePPh₃; 318, 11.5, FePPh₃; 262, 45, PPh₃; 183, 81, C₁₂H₈P; 108, 54, PPh; 107, 47, C₆H₄P; 77, 46, C₆H₅; 51, 100, C₄H₃. The mother liquor contained principally 5.

X-ray Crystallographic Structure Determination of 5. Suitable crystals of 5 were obtained by slow cooling of a toluene solution to -80 °C, using an insulating container. A dark brown crystal (ca. $0.2 \times 0.3 \times 0.35 \text{ mm}^3$) was mounted on a glass fiber using epoxy resin. Data were collected at 23 °C on an Enraf-Nonius CAD-4 diffractometer and processed using the TEXSAN suite of programs. A random search at low Θ yielded 25 reflections, which were indexed to give an initial cell. An accurate cell was obtained using higher angle (Θ = $10-12^{\circ}$) reflections. The structure was solved by direct methods using the SHELXS program, which revealed the irons, phosphorus, and most of the carbons and oxygens. A difference Fourier map then yielded the remaining heavy atoms. After partial refinement, hydrogen atom positions were calculated assuming sp² hybridization, and the structure was subject to full anisotropic refinement of the heavy atoms and isotropic refinement of the hydrogen atoms, after applying an absorption correction using the program DIFABS.

Extended Hitckel Calculations. Calculations were run on a VAX cluster using program FORTICON 8 (No. 517 from the Quantum Chemistry Program Exchange, Bloomington IN), slightly modified for more convenient data input and output. The atomic parameters used were identical to those of Thorn and Hoffman.¹⁴ For modeling the biallylene fragment, C-C, C-CH₂, and C-H distances used were 1.47, 1.41, and 1.07 Å, respectively. The Fe-Fe bond distance used was 3.00 Å, and the OC_{eq}-Fe-CO_{eq} angle was 100°. All Fe-CO bond distances were set at 1.77 Å, and all C-O at 1.16 Å. Pyramidalization of the biallylene ligand, keeping Fe-C distances of 2.04 Å while leaving the C_3H_4 fragments planar, did not result in stabilization of the structure, even though the Fe-CH₂ distances became more realistic as they decreased from 2.25 to 2.09 Å. It was necessary to rotate the CH_2 groups of the pyramidalized ligand so that the axial (anti) hydrogens moved away from the irons and the equatorial (syn) hydrogens moved toward the irons in order to observe stabilization relative to the planar combination. The best such structure had 0.15 Å pyramidalization (i.e., the central C's lay 0.15 Å above the plane of the four CH₂ carbons) and 26° rotation of the CH₂ groups; its energy was 0.63 eV lower than the all-planar model. Extended Hückel calculations using the actual coordinates of 1, 5 (with the triphenylphosphine replaced by a CO), and 9 (with the phenylthio groups replaced by hydrogens) gave still lower energies, however. The energies of 1 and modified 5 were almost identical, indicating net bonding of 6.99 and 7.00 eV relative to the separated C_6H_8 and $Fe_2(CO)_6$ fragments. The corresponding bonding energy using modified 9 was 7.51 eV. The HOMO-LUMO gap was greatest (1.83 eV) for 1. Most of the energy differences arose from changes in the levels of the three highest filled MO's, which in C_{2v} symmetry have a_2 , b_1 , and b_2 symmetry. These have been pictured and discussed by Thorn and Hoffmann.¹⁴

Results

Compound 1 was conveniently prepared by reaction of allene with $Fe_2(CO)_9$ in hexane at 70 °C.¹ It was also produced, but only in trace amounts, by reaction of 2,3dibromopropene with $Fe_2(CO)_9$; the major product of the latter reaction was (2-bromoallyl)tricarbonyliron bromide, 4.¹⁵ Reaction of this dibromo product with zinc dust did not produce 1 in significant amounts, although such a coupling reaction was claimed for the corresponding dichloride.¹⁶

The infrared spectrum of 1 in hexane or carbon tetrachloride solution shows four strong carbonyl peaks rather than the five allowed for a $Fe_2(CO)_6$ species with $C_{2\nu}$ symmetry or the six allowed with C_2 symmetry. In the absence of a total vibrational analysis, including isotopic labeling studies, vibrational degeneracies in 1 will apparently prevent assignment of the symmetry of the species present in solution.

The proton NMR spectrum of 1 at room temperature showed two closely spaced resonances,^{3c,6} whose chemical shifts were unusually solvent sensitive, ranging from δ 1.68 and 1.75 in CDCl₃ to 1.91 and 2.03 in acetone d_6 . Nakamura^{3c} reported that, on cooling a carbon tetrachloride solution of 1, the two peaks coalesced into a singlet at -10 °C; three broad peaks were reported at -55 °C in chloroform. We also find gradual merger of the two room-temperature proton resonances upon cooling a CD_2Cl_2 solution of 1, the result of the highfield peak (δ 1.73 at 25 °C) drifting downfield to merge with the low-field peak (δ 1.79 at 25 °C) to form a single, slightly broad peak at δ 1.80 at -80 °C. No evidence of decoalescence was observed at 250 MHz and -85 °C. In toluene- d_8 , the two proton resonances (δ 1.18 and 1.10 at 25 °C) merged upon cooling by moving upfield (δ 0.79 at -63 °C). The merger of the peaks upon cooling was solvent dependent, however, and therefore does not seem to correspond to any process resulting in chemical equivalence. In 1:1 acetone- d_6 -chloroformd, both peaks drifted downfield and broadened at comparable rates upon cooling. At -98 °C, two broad peaks, at δ 1.98 and 2.13, were seen. Decoalescence into

Table 2. Atomic Coordinates (×10⁴) and U(eq) (Å² × 10³) for 1

atom	<i>x</i>	у	z	$U(eq)^a$
Fe1	1444.6(6)	2029.6(9)	0	32(1)
Fe2	1061.8(5)	2578.5(9)	2821.2(5)	33(1)
O 1	2580(3)	1176(6)	931(10)	74(3)
02	1685(4)	1427(8)	-2871(10)	72(4)
O3	699(3)	97(6)	313(10)	69(3)
O4	-32(4)	1331(5)	2548(11)	68(3)
O5	837(4)	3182(8)	5711(9)	79(4)
O6	1878(3)	844(6)	3636(10)	56(2)
C1	2133(4)	1484(8)	656(11)	44(3)
C2	1590(5)	1682(8)	-1759(12)	46(4)
C3	979(4)	856(7)	242(11)	44(3)
C4	398(4)	1769(7)	2621(11)	41(3)
C5	922(5)	2934(9)	4600(11)	52(4)
C6	1576(5)	1516(8)	3258(10)	40(3)
C7	808(5)	3186(9)	-597(12)	49(4)
C8	1256(4)	3651(7)	210(12)	41(3)
C9	1827(5)	3588(7)	-371(12)	50(4)
C10	630(4)	4060(7)	2256(12)	46(3)
C11	1183(4)	3957(6)	1672(10)	36(3)
C12	1656(4)	3897(8)	2645(14)	48(4)

^{*a*} Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

the four peaks expected of a species of C_2 symmetry was not observed at this lowest obtainable temperature.

The room-temperature ¹³C NMR spectrum of 1 showed four carbon resonances, two for the equatorial and axial carbonyl groups and two for the biallylene ligand, at δ 38.6 and 87.9. On cooling, the high-field methylene resonance (¹J_{CH} = 158.3 Hz) broadened somewhat relative to the others, but did not decoalesce even at -98 °C. Similarly, in toluene- d_8 at -79 °C, the width of the methylene carbon resonance was five times that of the central carbons, which was essentially the same as that of TMS.

The low-temperature line broadening observed for the methylene groups in the ¹H and ¹³C NMR spectra is consistent with equilibration of unsymmetrical forms, but limiting spectra which would allow more complete characterization of those forms could not be obtained. No broadening of the equatorial carbonyl resonance was discernible, even at the lowest accessible temperatures.

Heating 1 with triphenylphosphine in benzene solution resulted in formation of the displacement product 5, $(C_6H_8)Fe_2(CO)_5PPh_3$. The proton NMR data showed four equally intense sets of proton resonances, indicating maintenance of a plane of symmetry. This requires the phosphine to occupy an axial position in the Fe₂-(CO)₅L "sawhorse" moiety. Only the most highly shielded pair of hydrogens, at δ 0.60, showed coupling to the phosphorus ($J_{\rm PH} = 11$ Hz); both the shielding and the coupling suggest that these are the axial hydrogens syn to the phosphine group. The crystal structure (vide infra) clearly shows these hydrogens in the face of a phenyl ring of the triphenylphosphine. Further reaction with triphenylphosphine gave a disubstitution product 6, $(C_6H_8)Fe_2(CO)_4(PPh_3)_2$, whose spectroscopic data likewise indicated a diaxial substitution pattern. The preference for axial orientation of the bulky triphenylphosphine substituents is probably steric in origin.

Crystal structures have been obtained for both 1 and 5. Details of data collection are given in Table 1; coordinates for 1 and 5 are given in Tables 2 and 3, respectively. Significant bond distances and angles for both compounds are given in Tables 4 and 5. Pictures of the structures of 1 and 5 are shown in Figures 1 and

Table 3. Atomic Coordinates (×10⁴) and U(eq) (Å² × 10³) for 5

		101 5		
atom	x	у	z	U(eq) ^a
Fel	230.8(4)	7024.8(3)	2920.4(4)	31.0(2)
Fe2	2920.0(4)	5575.9(3)	2737.8(5)	40.8(2)
P 1	-1726.2(7)	8212.1(6)	3116.3(7)	32.0(5)
01	1472(2)	8702(2)	3106(3)	70(2)
O2	4016(3)	7171(2)	4086(3)	86(2)
03	-236(2)	6892(2)	-109(2)	71(2)
04	5486(2)	4100(2)	2464(3)	82(2)
05	2607(3)	6049(3)	-223(3)	95(2)
C1	-2377(3)	8403(2)	4847(3)	34(1)
C2	-1651(3)	8717(3)	5969(3)	46(2)
C3	-2075(4)	8826(3)	7306(3)	56(2)
C4	-3211(4)	8607(3)	7559(4)	60(2)
C5	-3939(3)	8297(3)	6477(4)	57(2)
C6	-3534(3)	8192(2)	5122(3)	44(2)
C7	-3106(3)	8036(2)	1985(3)	37(1)
C8	-3092(3)	7078(2)	1355(3)	46(2)
C9	-4161(3)	6952(3)	550(4)	58(2)
C10	-5253(3)	7789(3)	371(4)	60(2)
C11	-5280(3)	8735(3)	970(4)	62(2)
C12	-4212(3)	8870(3)	1780(4)	52(2)
C13	-1755(3)	9536(2)	2662(3)	35(1)
C14	-2113(3)	10403(2)	3556(3)	49(2)
C15	-2087(4)	11375(3)	3141(4)	62(2)
C16	-1716(3)	11499(3)	1835(4)	56(2)
C17	-1397(3)	10654(3)	930(4)	58(2)
C18	-1406(3)	9672(2)	1329(3)	48(2)
C19	1018(3)	8024(2)	3048(3)	43(2)
C20	-24(3)	6938(3)	1074(3)	43(2)
C21	4479(3)	4682(3)	2553(4)	56(2)
C22	2670(3)	5914(3)	950(4)	58(2)
C23	3537(3)	6588(3)	3539(4)	57(2)
C24	556(3)	5748(2)	4121(3)	38(1)
C25	1770(3)	4953(2)	3809(3)	42(2)
C26	-595(3)	5803(2)	3298(3)	46(2)
C27	514(3)	6606(3)	5033(3)	46(2)
C28	2909(3)	4863(3)	4681(4)	52(2)
C29	1961(3)	4400(2)	2508(4)	51(2)

^{*a*} Equivalent isotropic U (Å² × 10³) defined as one-third of the trace of the orthogonalized U_{ij} tensor.

2, respectively. The phosphine substitution in 5 does increase the Fe-Fe bond length by 0.07 Å, but it does not induce qualitatively significant changes in the metrics or conformation of the biallylene ligand, and so the structures of both will be discussed together in this section. Comparisons will also be made to the reported structures of related compounds 7-10. (The reported



structure of 2^{5} while qualitatively consistent with the others, is of too low precision to justify discussion.)

 Table 4. Important Intramolecular Bond Distances (Å) in Biallylene Complexes 1 and 5

	1		5	
type	atoms	distance	atoms	distance
Fe-Fe	Fe1-Fe2	2.927(3)	Fe1-Fe2	2.998(1)
Fe-CH ₂	Fe1-C7	2.104(11)	Fe1-C27	2.105(3)
(short)	Fe2-C12	2.112(10)	Fe2-C29	2.108(3)
Fe-CH ₂	Fe1-C9	2.125(10)	Fe1-C26	2.125(3)
(long)	Fe2-C10	2.131(10)	Fe2-C28	2.135(3)
Fe-C	Fe1-C8	2.039(8)	Fe1-C24	2.038(3)
	Fe2-C11	2.035(9)	Fe2-C25	2.031(3)
C-CH ₂	C7-C8	1.402(15)	C24-C27	1.399(4)
	C8-C9	1.417(15)	C24-C26	1.406(4)
	C10-C11	1.385(14)	C25-C28	1.412(4)
	C11-C12	1.428(15)	C25-C29	1.416(4)
C-C	C8-C11	1.464(15)	C24-C25	1.468(4)
Fe-CO (ax)	Fe1-C2	1.775(11)	Fe2-C21	1.775(4)
	Fe2-C5	1.793(11)		
Fe-CO (eq)	Fe1-C1	1.817(10)	Fe1-C19	1.769(3)
	Fe1-C3	1.800(9)	Fe1-C20	1.775(3)
	Fe2-C4	1.818(9)	Fe2-C23	1.788(4)
	Fe2-C6	1.798(11)	Fe2-C22	1.776(4)
C-O (ax)	average	1.131(14)	C21-O4	1.144(4)
C-O (eq)	average	1.123(13)	average	1.142(4)
Fe-P	5		Fe1-P1	2.259(1)

The iron-iron bond lengths in these biallylene complexes are very long; only the (allyl)tricarbonyliron dimer, with Fe-Fe distance 3.138(3) Å,¹⁷ shows a longer Fe-Fe bond. Compounds 7^{12} 9^{7} and 10^{11} show similarly long bonds, the range being from 2.872(1) to 2.977-(1) Å. In the cluster compound $\mathbf{8}$,⁸ the iron-iron bond distance is only 2.566(1) Å, but bonding to the 2,2'biallylene unit remains intact. A normal, unbridged Fe-Fe single-bond length has been estimated to be 2.76 Å,¹⁸ and the range of values in several salts of $Fe_2(CO)_8^{2-}$ is 2.787(2)-2.841(1) Å.¹⁹ From this perspective, the bond length in the biallylene complexes appears to be increased from a normal value by the constraints imposed by the ligand. Indeed, the metal-metal distance which would result from normal metal-allyl bonding to the two ends of a fully coplanar 2,2'biallylene ligand would be well in excess of 3 Å. In the actual structures of 1 and 5, the $Fe-CH_2$ and Fe-Cdistances average 2.12 and 2.04 Å, similar to those in many allyliron complexes.²⁰ Given the Fe-Fe bond distance of almost 3 Å, these distances can only be achieved by systematic distortion of the biallylene ligand from coplanarity. The distortions seen involve (1) pyramidalization of the central carbons, and (2) rotation about the central C-C bond of the ligand such that one transoid C_4 portion of the unit (C9-C8-C11-C10 in 1, C26-C24-C25-C28 in 5) is nearly coplanar, with the remaining two CH₂ groups bent down toward the irons.

 Table 5.
 Important Intramolecular Bond Angles (deg) in Biallylene Complexes 1 and 5

	1		5	
type	atoms	distance	atoms	distance
CH ₂ -C-CH ₂	C7-C8-C9	115(1)	C26-C24-C27	115.3(3)
	C10-C11-C12	115(1)	C28-C25-C29	115.1(3)
$CH_2 - C - C$	C7-C8-C11	123.5(9)	C27-C24-C25	123.0(3)
	C8-C11-C10	121.1(9)	C24-C25-C28	120.5(3)
	C9-C8-C11	119.8(9)	C26-C24-C25	120.6(3)
	C8-C11-C12	122.0(9)	C24-C25-C29	123.0(3)
CH ₂ -Fe-CH ₂	C7-Fe1-C9	68.5(4)	C26-Fe1-C27	68.1(1)
-	C10-Fe2-C11	68.0(4)	C28-Fe2-C29	68.4(1)
Fe-Fe-CH ₂	Fe2-Fe1-C7	93.9(3)	Fe2-Fe1-C27	83.1(1)
	Fe2-Fe1-C9	94.1(3)	Fe2-Fe1-C26	93.5(1)
	Fe1-Fe2-C10	95.5(3)	Fe1-Fe2-C28	94.5(1)
	Fe1-Fe2-C12	84.8(4)	Fe1-Fe2-C29	84.3(1)
CH ₂ -Fe-ax	C7-Fe1-C2	91.7(5)	C27-Fe1-P1	96.4(1)
-	C9-Fe1-C2	88.8(4)	C26-Fe1-P1	90.3(1)
	C10-Fe2-C5	87.4(5)	C28-Fe2-C21	86.7(1)
	C12-Fe2-C5	90.3(5)	C29-Fe2-C21	93.4(1)
OC _{eq} -Fe-ax	C1-Fe1-C2	94.7(5)	C19-Fe1-P1	91.0(1)
	C3-Fe1-C2	92.4(5)	C20-Fe1-P1	91.6(1)
	C4-Fe2-P5	94.9(5)	C23-Fe2-C21	94.5(2)
	C6-Fe2-C5	93.9(5)	C22-Fe2-C21	95.1(2)
OC _{eq} -Fe-CO _{eq}	C1-Fe1-C3	99.8(4)	C19-Fe1-C20	99.4(1)
-1 -4	C4-Fe2-C6	99.9(4)	C22-Fe2-C23	102.9(2)

This results in diagonally opposed Fe-CH₂ distances averaging 2.129(6) Å to the coplanar CH₂ groups and 2.107(5) Å to the downward-bent CH_2 groups. The relative twisting of the two pyramidalized allyl units is accompanied by a comparable twisting of the Fe-Fe axis relative to the C-C axis, giving Fe-Fe-C-C torsion angles of $11-12^{\circ}$ in 1 and 5; the twisting motion is equivalent to rotation of the two iron octahedra (each composed of the three CO groups, the two CH₂ groups, and the other iron) about the Fe-Fe bond, and is illustrated in Figure 3. This rotation results in loss of the eclipsing of the equatorial carbonyl groups, which necessarily occurs when a "sawhorse" $Fe_2(CO)_6$ unit is bound to an untwisted 2,2'-biallylene unit. The torsion angles between neighboring equatorial CO groups in 1 and 5 average $21(3)^{\circ}$. This pyramidal-twist distortion reduces the symmetry of the $(C_6H_8)Fe_2(CO)_6$ complex from the idealized C_{2v} to C_2 and is consistent with the line broadening of the CH₂ groups observed in the lowtemperature NMR spectra of 1.

To what extent are analogous distortions found in the previously studied compounds 7-10? In 7 and 10, four carbons of the biallylene units are incorporated into benzenoid rings, whose tendency to maintain coplanarity tends to resist pyramidalization and (especially) twisting. The least pyramidalized structure is accordingly that of the tricyclic 7,¹² in which the central carbons of the biallylene unit lie only 0.11 Å above the mean plane of the four peripheral carbons. The most highly pyramidalized is $8,^8$ with the central carbons 0.19 Å out of the plane, clearly the result of accommodation of the biallylene unit to the much shorter Fe-Fe bond distance in 8. Compounds 9 and 10 show intermediate degrees of pyramidalization, the central carbons being 0.15 and 0.14 Å out of the plane, respectively. It thus appears that significant pyramidalization is the norm for these biallylene complexes, being observed in all six known examples.

There is, however, little twisting in 7-10, with the torsion angles Fe-Fe-C-C and OC_{eq} -Fe-Fe-CO_{eq} being less than 5° in all cases. The relationship between these distortions is indicated in Table 6. It will be seen

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Figure 1. ORTEP drawing of 1 showing the labeling scheme. Atoms are represented by thermal ellipsoids at the 50% level. Hydrogen atoms are omitted.



Figure 2. ORTEP drawing of 5 showing the labeling scheme. Atoms are represented by thermal ellipsoids at the 50% level.



Figure 3. PLUTO drawing of 1 showing the effects of intramolecular rotation about the Fe-Fe bond, with concomitant twisting of the biallylene ligand.

that in **7-10** the pairs of trans $CH_2-C-C-CH_2$ torsion angles within the biallylene ligand are similar. The value around 166° indicates the pyramidalization of the two central carbons, and the similarity of the two values indicates the lack of rotation around the central C-C bond. Similarly in these compounds, the very small Fe-Fe-C-C torsion angles indicate the parallelism of the Fe-Fe and central C-C axes, and the equatorial carbonyl groups are nearly eclipsed. In 1 and 5, the degree of pyramidalization is very similar to the other compounds, but in addition rotation and twisting generate substantial inequality in the $CH_2-C-C-CH_2$ torsion angles, large Fe-Fe-C-C torsion angles, and reduced equatorial carbonyl eclipsing. While structural constraints in 7, 8, and 10 would clearly hinder rotation and twisting, it remains unclear why the unconstrained 9 does not manifest these distortions to a greater extent. Its nearly idealized C_{2v} structure (except for the phenylthio substituents) is consistent, however, with the low barrier indicated in the variable-temperature NMR studies of 1 for interconversion of the two C_2 forms through the C_{2v} intermediate. Given the low energy difference between the C_2 and C_{2v} forms, the packing energies of the crystals may play a decisive role in defining which is observed.

High-level theoretical studies of free 2,2'-biallylene, as either the singlet or triplet, show no preference for the planar form, rotation about the central C-C bond being favored.¹ Extended Hückel calculations give the same result. Pyramidalization of the central carbons in the free ligand is not favored, costing 0.22 eV (extended Hückel result) for removal of the central C's 0.2 Å out of plane, leaving the individual C_3H_4 allyl units coplanar. However, binding of a planar 2,2'biallylene unit to a $Fe_2(CO)_6$ "sawhorse", even one having a Fe–Fe bond distance as long as 3.0 Å, results in rather long $Fe-CH_2$ distances of 2.25 Å. Most of the ligand-metal bonding in these complexes results from interaction of the a_2 and b_1 orbitals of the $Fe_2(CO)_6$ and 2,2'-biallylene moieties,¹⁴ the ligand orbitals involving only the CH_2 carbons. Hence, optimum bonding appears to require pyramidalization of the ligand in order to achieve satisfactory overlap. The range of Fe-CH₂ bond lengths observed in 1, 5, 7, 9, and 10 is 2.10-2.15A, achieved in all cases by pyramidalization. Unless prevented by a cyclic structure, rotation of the two pyramidalized allyl units, with concomitant twisting of the "sawhorse," appears to require little energy, being found in 1 and 5, but not in 9. Twisting appears to be favored by the reduced eclipsing of the equatorial carbonyl groups. [Note that unconstrained $Fe_2(CO)_8^{2-}$ is found only in the staggered, D_{3d} , form in the crystal

		$CH_2-C-C-CH_2$			
compd	Fe-Fe-C-C	trans	cis	OC_{eq} -Fe-Fe- CO_{eq}	ref no.
7	0.1	169.3, 169.8	0.2, 0.7	3.5, 3.7	12
10	0.4	165.6, 167.6	0.5, 1.6	1.8, 3.7	11
8	1.7	159.7, 164.2	1.1, 3.4	4.9	8
9	2.2	162.4, 168.3	2.4, 3.5	1.8, 3.8	7
5	11.2	149.3, 176.6	16.7, 17.5	17.2, 21.0	this paper
1	11.5	148, 178	16, 18	23.8, 23.9	this paper

structures of four different salts;¹⁹ the staggered form is favored by molecular mechanics calculations²¹ and by extended Hückel calculations.] Twisting may be opposed, however, by the loss of δ -bonding interactions between the two iron atoms. In the balance, there appears to be little energy difference between twisted C_2 and untwisted C_{2v} structures.

Given that all extant (2,2'-biallylene)Fe₂(CO)₆-derived structures show pyramidalization, we were initially somewhat perplexed when extended Hückel calculations on model structures having planar C₃H₄ units and Fe-Fe and Fe-C bond lengths of 3.00 and 2.04 A failed to indicate stabilization upon pyramidalization, even though the $Fe-CH_2$ distances went from 2.25 Å down to 2.09 Å in the process. In order to manifest such stabilization, it is necessary also to rotate the CH₂ groups within the pyramidal structure so that the axial (anti) H's move away from the iron and the equatorial (syn) H's toward the iron. With a degree of pyramidalization of 0.15 Å (typical for these structures), the amount of such CH_2 group rotation necessary to achieve optimum stabilization is about $20-30^{\circ}$. Seyferth et al.⁷ have previously noted this curious positioning of the axial substituents in discussing the structure of 9, attributing it to steric interactions with the axial carbonyl groups; the calculations suggest that optimum orbital alignment is also significant.

At the extended Hückel level, the structure of 9 (with hydrogens replacing the phenylthio substituents), which had its C-C and Fe-Fe axes nearly parallel, was slightly more stable than the twisted structures of 1 and 5 (with a CO replacing the phosphine); the latter were almost identical energetically despite the 0.07 Å difference in Fe-Fe bond lengths.

Finally, we may note that a recent structure of a related "sawhorse" complex, $(\mu, \eta^5: \eta^5-C_5H_4-C_5H_4)Mo_2-(CO)_4(PMe_3)_2$, showed distortions very analogous to those of 1 and 5: pyramidalization of the carbons joining the two rings and twisting about the metal-metal axis.^{2a,22} The corresponding hexacarbonyl showed similar pyramidalization but no twisting,²³ as was also the

case for the fulvalene– $W_2(CO)_6^{24}$ and $-Ru_2(CO)_4^{25}$ complexes. Some twisting was observed, however, in the bimetallic $(\mu,\eta^5:\eta^5$ -fulvalene)RhW(CO)_4(COMe)^{26} and in a carbenoid derivative of (fulvalene)Mo₂(CO)₆.²³ The presence of lengthened metal–metal bonds and analogous distortions from planarity (consistent pyramidalization and variable twisting) in these fulvalene-based systems and in the 2,2'-biallylene-based systems described here confirms the similarities between them. One difference which may deserve note is that bis-(trimethylphosphine) substitution into the (fulvalene)-Mo₂(CO)₆ system resulted in shortening of the Mo–Mo bond by 0.15 Å,^{2a,22,23} whereas our introduction of a triphenylphosphine substituent into 1 resulted in the Fe–Fe bond lengthening by 0.07 Å.

We expect to undertake studies of the chemical consequences of the long and presumably weak Fe-Fe bonds in the 2,2'-biallylene species in the near future. Preparation of biallylene complexes with a wider range of metals will also be a goal of future work.

Acknowledgment. We wish to thank Mr. Ian Becker for running some of the extended Hückel calculations during his tenure as a Simons Fellow during Summer 1994 and Mr. David Nellis for crystallographic assistance with 5. We are also grateful to Dr. Luc Girard and Prof. M. J. McGlinchey for supplying crystallographic coordinates for 10.

Supplementary Material Available: Tables of hydrogen parameters and anisotropic temperature factors for compounds 1 and 5 (3 pages). Ordering information is given on any current masthead page.

OM940785F

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