Table VII. Summary of the Crystal Structure Data

	10	12
formula	$C_{34}H_{43}F_{10}N_5Pd$	$C_{34}H_{43}F_{10}N_5Pt$
recryst solvent	CH_2Cl_2/hexane	CH_2Cl_2/hexane
fw	818.1	906.83
cryst size, mm	0.1 × 0.1 × 0.1	0.4 × 0.2 × 0.15
cryst syst	tetragonal	tetragonal
space group	$P4_32_12$	$P4_32_12$
Z	4	4
a, b, Å	17.022 (2)	17.008 (2)
c, Å	12.466 (3)	12.466 (4)
V, Å^3	3612	3607
D_{exptl}, g cm^{-3}	1.50	1.66
λ(Mo Kα), Å	0.710 69	0.710 69
abs corr	none	DIFABS;[47] max 1.118, min 0.896
μ, cm^{-1}	20.4	40.1
2θ range, deg	4–50	4–50
hkl range	h, 0–20; k, 0–20; l, 0–14	h, 0–20; k, 0–20; l, 0–14
no. of measd rflns	3756	3572
no. of unique rflns	3196	3192
no. of obsd rflns	2146 ($\lvert F^2\rvert > 2\sigma(F^2)$)	2540 ($\lvert F^2\rvert > 2\sigma(F^2)$)
no. of variables	229	227
temp factors	C, F, N, Pd aniso	C, F, N, Pt aniso
w	$\sigma^2(F)$	$\sigma^2(F)$
R	0.045	0.029
R_w	0.050	0.033
s	1.15	0.94
$\Delta/\sigma_{\max}$	0.02	0.02
$(\Delta p)_{\max,\min}$ e Å^{-1}	+0.97, −1.59	0.56, 0.47
$F(000)$	1672	1800

programs from the Enraf-Nonius SDP package[46] with non-hydrogen atoms anisotropic. The hydrogen atom attached to N2 was located and freely refined with an isotropic thermal parameter, while the other hydrogen atoms were fixed at calculated positions with U_{iso} = 1.3 times the U_{eq} value for the parent atom; $w = 1/\sigma^2(F)$, and $\sum w(|F_o| - |F_c|)^2$ was minimized.

Data for 12 were collected using a prismatic crystal (0.4 × 0.2 × 0.15 mm). Unit cell parameters for 12 were obtained by a least-squares fit of 25 reflections with $8 < \theta < 12°$. The space group was assigned as $P4_32_12$ from the systematic absence of $h00$ for h odd and $00l$ for $l = 4n$ and successful refinement. Original refinement in the enantiomorphous space group $P4_12_12$ (No. 92) gave a final R = 0.047 and R_w = 0.065, which were improved on refinement in $P4_32_12$. Non-hydrogen positions were taken from the isomorphous palladium complex and were refined by full-matrix least squares on F using programs from the SDS-Plus package.[46] Non-hydrogen atoms were refined anisotropically; $w = 1/\sigma^2(F)$, and $\sum w(|F_o| - |F_c|)^2$ was minimized. Hydrogen atoms were placed in calculated positions, except for the hydrogen atom involved in H-bonding. This could not be located on a difference map.

Acknowledgment. Financial support from the DGICYT (Project PB91-0574) of Spain is gratefully acknowledged. C.V. and J.M.M. thank the Dirección Regional de Educación y Universidad de Murcia and the Fundación ONCE of Spain, respectively, for a research grant. P.A.C. thanks the CIBA foundation for an Award for Collaboration in Europe, and R.M.H. thanks the SERC for a maintenance grant.

Registry No. 1, 143858-10-0; 2, 143858-11-1; 3, 143858-12-2; 4, 143858-13-3; 5, 143858-14-4; 6, 143858-15-5; 7, 143886-85-5; 8, 143858-17-7; 9, 143858-19-9; 10, 143886-99-1; 11, 143858-21-3; 12, 143858-23-5; 13, 143858-25-7; 14, 143858-27-9; *cis*-$Pd(C_6F_5)_2(PhCN)_2$, 110900-60-2; *cis*-$Pd(C_6Cl_5)_2(PhCN)_2$, 136314-36-8; *cis*-$Pt(C_6F_5)_2(PhCN)_2$, 139912-62-2; *cis*-$Pt(C_6Cl_5)_2(PhCN)_2$, 139912-63-3; $(NBu_4)_2[\{(C_6F_5)_2Pd\}_2(\mu\text{-}Cl)_2]$, 74436-08-1; $(NBu_4)_2[\{(C_6F_5)_2Pt\}_2(\mu\text{-}Cl)_2]$, 90590-30-0; Hpz, 288-13-1; Hdmpz, 67-51-6.

Supplementary Material Available: Tables of hydrogen coordinates, anisotropic temperature factors, and least-squares planes for 10 and 12 and of torsion angles for 12 and plots of the NBu_4^+ cation and the unit cell packing diagram for 10 (14 pages). Ordering information is given on any current masthead page.

OM920219P

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(46) Frenz, B. A. Enraf-Nonius Structure Determination Package; Enraf-Nonius: Delft, The Netherlands, and College Station, TX, 1984.

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Iron Carbonyl Promoted Conversion of α,ω-Diynes to (Cyclopentadienone)iron Complexes

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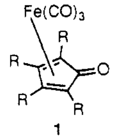
Received July 8, 1992

An efficient high-yielding procedure is described for the intramolecular carbonylative coupling of α,ω-diynes to give cyclopentadienone–$Fe(CO)_3$ complexes. Exchanging one CO ligand with PPh_3 affords control over the manipulation of α,α′-trimethylsilyl-substituted cyclopentadienone complexes. The preparation of α,ω-diynes with a hydroxy group adjacent to one alkyne unit leads to modest stereocontrol upon cyclization forming the $Fe(CO)_3$ complex. The hydroxy-substituted complex was oxidized to ketone. Borohydride reduction and Grignard addition to the ketone proceed anti to the $Fe(CO)_3$ moiety. The X-ray crystal structure of $C_{40}H_{31}FeO_3P$ shows that it crystallizes in the monoclinic space group $P2_1/n$ in a unit cell of dimensions a = 12.0595 (24), b = 13.3926 (30), c = 19.0682 (38) Å, β = 93.98 (2)°, with Z = 4.

Introduction

We have developed a procedure for the synthesis of tricarbonyl(cyclopentadienone)iron complexes 1 in high yield via the intramolecular coupling of two alkyne moieties accompanied by the insertion of carbon monoxide.[1] Historically, the iron carbonyl mediated cyclization of acetylenes to form cyclopentadienone (CPD) complexes has been, with few exceptions, an inefficient process. Early reports cite the preparation of CPD tricarbonyliron complexes from phenyl- and diphenylacetylene in very low yields (<15%).[2] Only in cases where the R group is



1

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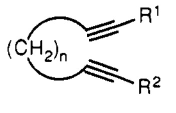
(1) Pearson, A. J.; Dubbert, R. A. *J. Chem. Soc., Chem. Commun.* 1991, 202–203.

Table I. Preparation of Symmetrically Substituted Diynes



2 - 8

	$R^1 = R^2$	*n*	method	yield, %
2	Ph	3	1	97
3	Ph	4	1	74
4	Ph	5	1	nd[a]
5	Np–OMe	3	1	13
6	$SiMe_3$	3	1	82
7	$SiMe_3$	4	2	nd[a]
8	Me	3	2	66

[a] These compounds were not purified. See Experimental Section.

electron withdrawing, for example, ${}^tBuO$,[3] Cl,[4] or CF_3,[5] does this reaction proceed in good yields. Intramolecular iron-mediated alkyne cyclizations were first described by Dickson and co-workers,[6] but low yields were again obtained, likely due to their reaction conditions. Moderate CO pressure has been shown to be beneficial for reactions where a carbonyl ligand undergoes migratory insertion.[7] Other researchers have studied similar inter- and intramolecular cyclization reactions, using $CpCo(CO)_2$, with good results.[8]

Interest in making the cyclopentadienone complexes stems from studies in our laboratory on the iron-mediated analog to the Pauson–Khand reaction.[1] The Pauson–Khand reaction has been increasingly used in organic synthesis as a means of stereoselectively forming cyclopentenone rings.[9] The development of this chemistry based on iron, instead of cobalt, has profound financial benefits.

The cyclopentadienone moiety is anti-aromatic, hence quite reactive. In fact, cyclopentadienones have been shown to dimerize upon standing, unless stabilized by bulky substituents.[10] Coordination to a metal also affords temporary stabilization of the reactive anti-aromatic system.[8a,10] Without the necessity of substitution of the cyclopentadienone moiety to prevent dimerization, synthetically more useful molecules may be targeted. Toward this end, the cyclopentadienone ligand can be manipulated while coordinated to the metal and then decomplexed. Furthermore, the reactivity of the cyclopentadienone moiety is, in some cases, controlled by the electronic influences of the metal. Therefore, changing the ligand environment of the metal may give greater control over the reactivity of the cyclopentadienone. The coordinated metal also provides a strong stereodirecting effect by blocking one face of the cyclopentadienone molecule. These effects are currently being explored in our laboratory, and the present paper describes our progress to date.

Scheme I

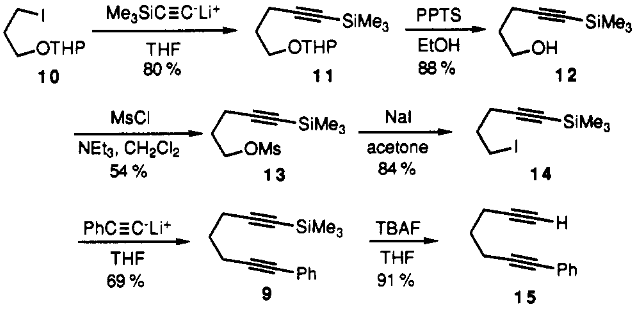


Table II. Data for Eq 1

	R^1, R^2	*n*	yield, %
16	Ph	3	81
17	Ph	4	52
18	Ph	5	18
19	Np–OMe	3	82
20	$SiMe_3$	3	81
21	$SiMe_3$	4	57
22	Me	3	87
23	Ph, $SiMe_3$	3	78
24	Ph, H	3	84

Results and Discussion

Symmetrically substituted diynes **2**–**8** were prepared by one of two standard methods: (1) treatment of a monosubstituted acetylene with butyllithium to generate the acetylide anion, followed by S_N2 substitution of both iodide ions on the diiodoalkane; (2) starting from 1,7-octadiyne, the acetylide dianion was prepared, then quenched with either trimethylsilyl chloride[11] or iodomethane (Table I).[7]

The unsymmetrically substituted diyne **9** was similarly prepared using the nucleophilic substitution of iodide by substituted acetylides with the added complication of substituting one iodide at a time (see Scheme I). A Finkelstein halide exchange reaction on 3-bromo-1-propanol, using NaI in acetone, afforded 3-iodo-1-propanol which was protected as the tetrahydropyranyl (THP) ether, **10**.[12] The iodide was then substituted with trimethylsilyl acetylide, generated from the treatment of the acetylene with BuLi, giving **11**. Deprotection of the alkynol was effected under mildly acidic conditions, using pyridinium *p*-toluenesulfonate (PPTS).[12] The alkynol, **12**, was converted via the mesylate, **13**, to the iodide, **14**,[13] and this was converted to the diyne as above by reaction with lithium phenyl acetylide. The unsymmetrical diyne **9** was isolated as a yellow oil in 20% overall yield. Desilylation of **9** using tetra-*n*-butylammonium fluoride (TBAF) in THF gave the terminal diyne **15** in 91% yield.

Our procedure for conversion of diynes to CPD–$Fe(CO)_3$ complexes involves the intramolecular alkyne cyclizations, with carbonyl insertion, assisted by performing the reaction sealed in a CO atmosphere (eq 1). Other work has shown that in the absence of CO pressure, carbonyl will not insert prior to reductive elimination of the metal, as evidenced by the formation of cyclobutadiene rings.[7] Decomposition

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(2) (a) Schrauzer, G. N. *Chem. Ind.* **1958**, 1403. (b) Schrauzer, G. N. *Chem. Ind.* **1958**, 1404. (c) Hübel, W.; Braye, E. H. *J. Inorg. Nucl. Chem.* **1959**, *10*, 250–268.

(3) Formals, D.; Pericas, M. A.; Serratosa, F.; Vinaixa, J.; Font-Altaba, M.; Solans, X. *J. Chem. Soc., Perkin Trans. 1* **1987**, 2749–2752.

(4) Krespan, C. G. *J. Org. Chem.* **1975**, *40*, 261–262.

(5) Boston, J. L.; Sharp, D. W. A.; Wilkinson, G. *J. Chem. Soc.* **1962**, 3488–3494.

(6) Dickson, R. S.; Mok, C.; Connor, G. *Aust. J. Chem.* **1977**, *30*, 2143–2151.

(7) McDonnell Bushnell, L. P.; Evitt, E. R.; Bergman, R. G. *J. Organomet. Chem.* **1978**, *157*, 445–456.

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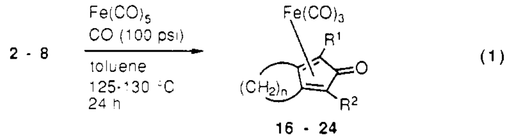
(9) (a) Rowley, E. G.; Schore, N. E. *J. Organomet. Chem.* **1991**, *413*, C5–C9. (b) Castro, J.; Sorenson, H.; Riera, A.; Morin, C.; Moyano, A.; Pericas, M. A.; Greene, A. E. *J. Am. Chem. Soc.* **1990**, *112*, 9388–9389. (c) Exon, C.; Magnus, P. *J. Am. Chem. Soc.* **1983**, *105*, 2477–2478.

(10) Ogliaruso, M. A.; Romanelli, M. G.; Becker, E. I. *Chem. Rev.* **1965**, *65*, 261–368.

(11) Hillard, R. L., III; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1977**, *99*, 4058 (using BuLi) Auderset, P. C.; Dreiding, A. S.; Gesing, E. R. F. *Synth. Commun.* **1983**, *13*, 881–7 (using Mg).

(12) Miyashita, M.; Yoshikoshi, A.; Grieco, P. A. *J. Org. Chem.* **1977**, *42*, 3772–3774.

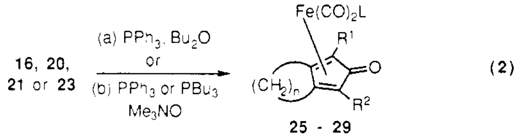
(13) A similar reaction scheme for the conversion of **12** to **14** was reported, however, no experimental detail was given. Smith, R.; Livinghouse, T. *Tetrahedron* **1985**, *41*, 3559.



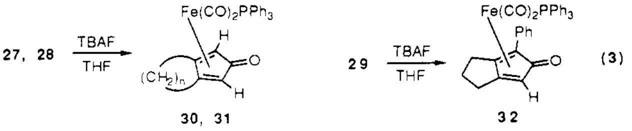
of $Fe(CO)_5$ occurs during the cyclization; therefore, for convenience, a large excess is used.

The yields of the bicyclic cyclopentadienone complexes are related to the size of the methylene ring being formed and not the R group attached to the acetylene moiety (Table II), unless $R^1 = R^2 = H$. Ease of formation of the aliphatic rings follows the expected trend: 5-ring > 6-ring > 7-ring; we were unable to form a complex with an eight-membered second ring. A similar relationship between yield and ring size has also been noted in work on bicyclic titanocyclopentadienes.[14]

One of the carbonyl ligands on the tricarbonyl iron complexes was readily replaced with triphenyl- or tri-*n*-butylphosphine to give complexes **25–29** (eq 2). As discussed later, this tactic proved to be essential for manipulating the trimethylsilyl-substituted complexes. This reaction was done in refluxing di-*n*-butyl ether; however, better yields were obtained when 1.5 equiv of Me_3NO was used (Table III). The reactions using Me_3NO were faster and were carried out under milder conditions, refluxing with either acetone or benzene.



Treatment of the $Fe(CO)_3$ complexes **20** and **22** with TBAF did not produce the desilylated complex. However, treatment of the analogous PPh_3 complexes **27** and **28** with TBAF under identical conditions gave the parent cyclopentadienone complexes **30** and **31** in high yields. Since attempts to cyclize 1,7-octadiyne failed, this represents the best approach for preparing α,α′-unsubstituted CPD complexes. We were successful in forming complex **24** from 1-phenyl-1,7-heptadiyne; however, desilylation of the $Fe(CO)_3$ complex **23** also proved to be problematic. It appears that fluoride demetalates the $Fe(CO)_3$ complexes based on the ^1H NMR and IR of the crude reaction mixture which indicated the presence of uncomplexed cyclopentadienone derivatives.[8a] However, we were unable to isolate and fully characterize them. This observation is consistent with the need for using the $Fe(CO)_2(PPh_3)$ analogs, since the demetalation probably proceeds via fluoride addition on the carbonyl ligands. The carbonyls are made less electrophilic by exchanging one carbonyl ligand with the more strongly σ-donating phosphine ligand, thus suppressing nucleophilic attack by fluoride. (An alternate, but less likely, explanation is that the carbonyls are sterically hindered on introduction of the PPh_3 group.) The ensuing reactivity difference gives a measure of control in manipulating the trimethylsilyl-substituted complexes (eq 3, Table IV).



The stability of the tricarbonyl complexes is attested to by the difficulty we have experienced in trying to oxidatively decomplex them. For example, treatment with ceric ammonium nitrate, a reagent that is normally used for demetalation of diene–$Fe(CO)_3$ complexes, gave only recovered starting material. The ketone moiety itself is very unreactive as shown by its failure to react with 2,4-dinitrophenylhydrazine, MeMgBr, and in the presence of $TiCl_4$. Similar lack of reactivity has also been observed for the tricarbonyl[tetrakis(trifluoromethyl)cyclopentadienone]iron complex.[5]

Table III. Data for Eq 2

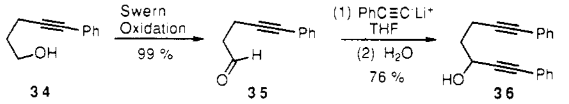
product complex	$Fe(CO)_3$ complex	phosphine	method[a]	yield, %
25	16	PPh_3	a	56
26	16	PBu_3	b	81
27	20	PPh_3	b	82
28	21	PPh_3	b	80
29	23	PPh_3	b	98

[a] See Eq 2 for description of methods.

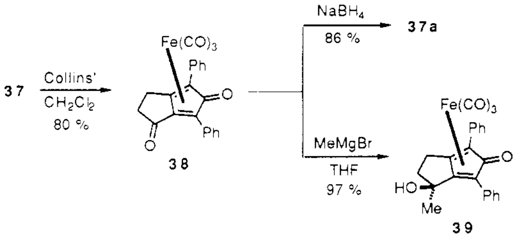
Table IV. Data for Eq 3

	$Fe(CO)_2(PPh_3)$ complex	yield, %
30	27	68
31	28	58
32	29	77

Scheme II

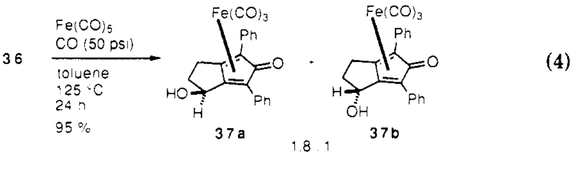


Scheme III



To produce diquinane derivatives[15] of potential value for future synthetic applications, we sought a way to introduce functionality into the aliphatic portion of the bicyclic system. To achieve this, an α-hydroxy-substituted diyne was prepared as shown in Scheme II. The phenyl alkynol **34** was prepared from 3-bromo-1-propanol as described above for **9**. Oxidation of the alkynol using Swern's procedure[16] gave the aldehyde **35**, which was treated with 1 equiv of phenyl acetylide to yield the α-hydroxy diyne **36** in 47% overall yield (from 3-bromo-1-propanol).

Cyclization of the diyne **36** was carried out as previously described (eq 4), the hydroxy substituted cyclopentadienone complex **37** being obtained in higher yield than the analogous unsubstituted complex. On the basis



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[14] Parshall, G. W.; Nugent, W. A.; Chan, D. M.-T.; Tam, W. *Pure Appl. Chem.* **1985**, *57*, 1809–1818.

[15] Diquinane and triquinanes ring systems occur in the structures of a wide range of biologically active terpenoid molecules. For examples, see: Groweiss, A.; Fenical, W.; He, C.; Clardy, J.; Wu, Z.; Yiao, Z.; Long, K. *Tetrahedron Lett.* **1985**, *26*, 2379. Set, H.; Yonehara, H. *J. Antibiot.* **1980**, *33*, 92. For reviews on cyclopentanoid and polyquinane synthesis, see: Paquette, L. A. *Top. Curr. Chem.* **1984**, *119*, 1; *Tetrahedron*, **1981**, *37*, 4359.

[16] Mancuso, A. J.; Huang, S.-L.; Swern, D. *J. Org. Chem.* **1978**, *43*, 2480–2482.

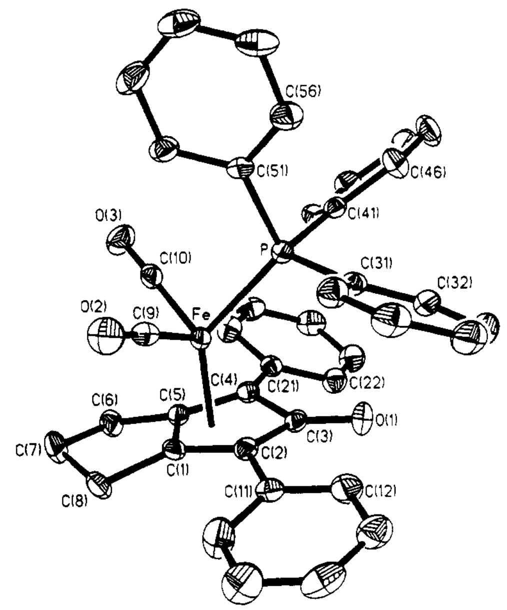

Figure 1. Thermal ellipsoid plot of **25**. Ellipsoids are drawn at 30% probability.

of literature reports of hydroxy- and alkoxy-directed complexation of cyclohexadienes,[17] we expected to see a stereodirecting effect during the cyclization favoring the complex with the hydroxy group syn to the metal. Unfortunately, the best ratio of syn:anti was 1.8:1, which was obtained at a CO pressure of 50 psi. We felt a lower temperature would improve the stereoselectivity, but little reaction occurred.

To confirm the stereochemistry of the product obtained from the cyclization, the syn diastereomer was prepared unambiguously (Scheme III). Oxidation of the mixture of diastereomers using Collins' reagent gave the ketone **38**. Reduction of **38** using $NaBH_4$ gives exclusively one diastereomer, according to ^1H and ^{13}C NMR spectra. Previous work on ketones adjacent to diene–$Fe(CO)_3$ moieties has shown that the approach of borohydride is anti to the metal due to steric hindrance.[18] MeMgBr added to the ketone **38** to give the tertiary alcohol **39**, the stereochemistry of which was assigned based on this steric approach control model.

We have developed methods for efficient construction of cyclopentadienone complexes that are expected to provide a framework for the construction of di- and triquinanes.[15] From the synthetic standpoint, the incorporation of hydroxy and ketone functionality as in complexes **37–39** is expected to provide an important lynchpin for further manipulation of this ring system.

Description of Structure

The X-ray structure of **25** (Figure 1) compares well with other CPD–$Fe(CO)_3$ complexes,[3,5,19] with the exception of the effect of the bulky PPh_3 ligand. As was previously observed, the ketone is bent away from the metal, out of the plane formed by the diene, by 12.2°. Also unique to this structure is the aliphatic ring. The β-position on the aliphatic ring is bent *toward* the metal. The bonding of the $Fe(CO)_2L$ moiety is typical of diene complexes.[20] The C(1)–C(5) is shorter than either the C(1)–C(2) or C(4)–C(5) bond,[21] as are the bonds C(1)–Fe and C(5)–Fe. The shorter bond from C(1)–C(5) is indicative of greater alkene character resulting from the increased population of the diene LUMO, which is enhanced by the σ-donation of the PPh_3. Concomitantly, bond C(1)–C(2) and C(4)–C(5) are longer because they are antibonding in the diene LUMO. There is no Fe–C(3) interaction as is confirmed by the considerably longer interatomic distance, also C(3)–O(1) distance is as expected for an sp^2 C–O bond.

Experimental Section

General Methods. All synthetic operations were performed under a dry nitrogen atmosphere, unless otherwise noted. All cyclization reactions were done in a CO atmosphere. The CO was used as purchased, without further purification. THF, benzene, and toluene were distilled from Na/benzophenone. Diethyl ether and CH_2Cl_2 were distilled from CaH_2. Acetone, ethyl acetate, and hexane were distilled from 4-Å molecular sieves. All other solvents were used as purchased. All nonvolatile compounds were dried overnight by exposure to a high vacuum (2×10^{-3} mmHg) prior to analysis. Compounds **10–14**, **34**, and **35** were previously reported in the literature, prepared via alternative synthetic routes and without complete characterization. Therefore, we record herein the complete details of our own syntheses and spectroscopic data.

Infrared spectra were recorded on a Perkin-Elmer Series 1600 FT-IR. All solutions were run in a NaCl chamber, while all Nujol mulls and neat samples were run on KBr plates. A Varian Gemini 300-MHz spectrometer was used to record all ^1H, ^{13}C, and ^{31}P NMR spectra. The ^1H NMR spectra were referenced either to TMS, C_6H_6, or $CHCl_3$. The ^{13}C NMR spectra were referenced to $CDCl_3$, and the ^{31}P NMR were externally referenced to H_3PO_4. Assignment of the phenyl regions of the ^1H and ^{13}C NMR spectra were based on chemical shift correlation tables.[22] Mass spectra were recorded, in house, on a Kratos MS25A instrument. Combustion analyses were performed by Galbraith Laboratories, Knoxville, TN.

General Procedure for the Preparation of Symmetrical Diaryl Diynes. To a degassed THF solution of the appropriate arylacetylene, cooled to −78 °C, 1.1 equiv of a hexane solution of butyllithium was added dropwise. The resultant mixture was warmed slowly to room temperature and then stirred for an additional 30–60 min. Alternatively, a 1.0 M solution of lithium phenyl acetylide was used, as purchased. Slightly less than 0.5 equiv of the appropriate diiodoalkane was then added. The solution was refluxed for 3 days. After cooling to room temperature, the reaction mixture was diluted with Et_2O and quenched with water. The organic layer was the washed with NaCl solution and dried with $MgSO_4$. Rotary evaporation of the solvent leaves the product as a yellow/brown oil. Any residual phenylacetylene was removed by exposure to vacuum overnight. The oils were used without further purification.

1,7-Diphenyl-1,6-heptadiyne (2). 1,3-Diiodopropane (1.03 mL, 9.0 mmol) was added to a solution of lithium phenylacetylide (19 mL; 19 mmol) in THF at room temperature. Reflux for 3 days followed by aqueous workup and ether extraction yielded the yellow oil (2.12 g, 97%). $R_f = 0.32$ (20% $CHCl_3$/hexane). IR (neat)

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[17] Pearson, A. J.; Gelormini, A. M.; Pinkerton, A. A. *Organometallics* **1992**, *11*, 936–8. Howard, P. W.; Stephenson, G. R.; Taylor, S. C. *J. Organomet. Chem.* **1989**, *370*, 97. Stephenson, G. R.; Howard, P. W.; Taylor, S. C. *J. Chem. Soc., Chem. Commun.* **1991**, 127. Howard, P. W.; Stephenson, G. R.; Taylor, S. C. *J. Chem. Soc., Chem. Commun.* **1990**, 1182; **1988**, 1603.

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2249 (w) CC, 2933 (m), 1958, 1878, 1804, 1753 (w) Ph. ^{1}H NMR ($CDCl_3$) δ 7.42–7.24 (m, 10 H, Ph), 2.57 (t, J = 7.0 Hz, 4 H, H3, H5), 1.88 (p, J = 7.0 Hz, 2 H, H4). ^{13}C NMR ($CDCl_3$) δ 131.5 (*o*-Ph), 128.1 (*m*-Ph), 127.5 (*p*-Ph), 123.8 (*ipso*-Ph), 89.1 (C1, C8), 81.2 (C2, C7), 27.9 (C4), 18.6 (C3, C5). HRMS calculated for $C_{19}H_{16}$ (M): 244.1252. Found: 224.1257; *m/e* (%) 244 (100), 228 (60), 216 (24).

1,8-Diphenyl-1,7-octadiyne (3). 1,4-Diiodobutane (0.65 mL, 4.9 mmol) was added to a solution of lithium phenylacetylide (10.0 mL, 10.0 mmol) in THF at room temperature. Reflux for 3 days followed by the usual workup and chromatography yielded the yellow oil (0.94 g, 74%). R_f = 0.23 (20% $CHCl_3$/hexane). IR (neat) 2230 (w) 2943 (m) CH_2. ^{1}H NMR ($CDCl_3$) δ 7.43–7.38 (m, 4 H, *o*-Ph), 7.30–7.23 (m, 6H, *m,p*-Ph), 2.48 (t, J = 6.2 Hz, 4 H, H3, H6), 1.79 (q, J = 6.2 Hz, 4 H, H4, H5). ^{13}C NMR ($CDCl_3$) δ 131.5 (*o*-Ph), 128.2 (*m*-Ph), 127.5 (*p*-Ph), 123.9 (*ipso*-Ph), 89.8 (C1, C8), 80.9 (C2, C7), 27.8 (C4, C5), 19.0 (C3, C6). HRMS calculated for $C_{20}H_{18}$ (M): 258.1409. Found: 258.1404; *m/e* (%) 258 (45), 185 (22), 115 (92).

1,9-Diphenyl-1,8-nonadiyne (4). 1,5-Diiodopentane (1.0 mL, 6.7 mmol) was added to a solution of lithium phenylacetylide prepared from phenylacetylene (1.50 mL, 13.7 mmol) and BuLi (15 mmol) in THF at room temperature. Reflux for 3 days followed by aqueous workup yielded a yellow oil which was not further purified. ^{1}H NMR ($CDCl_3$) δ 7.40–7.37 (m, 4 H, *o*-Ph), 7.28–7.24 (m, 6 H, *m,p*-Ph), 2.45 (t, J = 6.4 Hz, 4 H, H3, H7), 1.69–1.65 (m, 6 H, H4, H5, H6). ^{13}C NMR ($CDCl_3$) δ 131.4 (*o*-Ph), 128.1 (*m*-Ph), 127.4 (*p*-Ph), 123.9 (*ipso*-Ph), 90.0 (C1, C9), 80.8 (C2, C8), 28.1 (C3, C7), 27.9 (C5), 19.0 (C4, C6). HRMS calculated for $C_{21}H_{20}$ (M): 272.1565. Found: 272.1572; *m/e* (%) 272 (79), 243 (32), 229 (20), 215 (18), 202 (45).

1,7-Bis(6-methoxy-2-naphthyl)-1,6-heptadiyne (5). 6-Methoxy-2-naphthylacetylene (1.00 g, 5.50 mmol) was treated with BuLi (3.4 mL, 5.4 mmol). To this solution, 1,3-diiodopropane (0.35 mL, 3.1 mmol) was added followed by reflux and usual workup. Flash chromatography, R_f = 0.15 (10% EtOAc/hexane), followed by precipitation from CH_2Cl_2 gave the pure diyne (290 mg, 13%). Mp 145–6 °C. IR (CCl_4) 2937 CH_2, 2230 (w) CC, 1246 (s), 1036 (s) C–O–C. ^{1}H NMR ($CDCl_3$) δ 7.85 (s, 2 H), 7.65 (dd, J = 8.7, 3.01 Hz, 4 H), 7.44 (d, J = 8.5 Hz, 2 H), 7.17–7.10 (m, 4 H), 3.92 (s, 6 H, OMe), 2.67 (t, J = 6.9 Hz, 4 H, H3, H5), 1.96 (p, J = 6.9 Hz, 2 H, H4) ^{13}C NMR ($CDCl_3$) δ 158.0 (Np6), 133.7 (Np10), 131.0 (Np1), 129.3 (Np3), 129.1 (Np8), 128.5 (Np4), 126.6 (Np9), 119.2 (Np2), 118.7 (Np5), 105.7 (Np7), 88.8 (C1, C7), 81.6 (C2, C6), 55.3 (OMe), 28.1 (C4), 18.8 (C3, C5). HRMS calculated for $C_{29}H_{24}O_2$ (M): 404.1776. Found: 404.1775; *m/e* (%) 404 (100), 247 (5).

1-(Trimethylsilyl)-7-phenyl-1,6-heptadiyne (9). A THF solution of lithium phenylacetylide (4.0 mL, 4.0 mmol) and **14** (0.922 g, 3.46 mmol) was refluxed for 3 days followed by aqueous workup. Flash chromatography, R_f = 0.15 (hexane), yielded the diyne (0.576 g, 69%). IR (neat) 2174 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 7.36–7.33 (m, 2 H, *o*-Ph), 7.23–7.21 (m, 3 H, *m,p*-Ph), 2.47 (t, J = 7.1 Hz, 2 H, H5), 2.36 (t, J = 7.1 Hz, 2 H, H3), 1.77 (p, J = 7.1 Hz, 2 H, H4), 0.11 (s, 9 H, $SiMe_3$). ^{13}C NMR ($CDCl_3$) δ 131.5 (*ipso*-Ph), 128.2 (*m*-Ph), 127.6 (*p*-Ph), 123.8 (*o*-Ph), 106.3 (C1), 89.1 (C2), 85.1 (C7), 81.1 (C6), 27.8 (C4), 19.1 (C3), 18.5 (C5), 0.1 ($SiMe_3$). HRMS calculated for $C_{16}H_{20}Si$ (M): 240.1334. Found: 240.1340; *m/e* (%) 240 (38).

Trimethyl[5-[(tetrahydro-2*H*-pyran-2-yl)oxy]-1-pentynyl]silane (11). A 1.6 M solution of BuLi (13.5 mL, 21.6 mmol) was added to a solution of (trimethylsilyl)acetylene (2.77 mL, 19.6 mmol) in 15 mL of THF, cooled to −78 °C. The solution was stirred for 1 h, during which time it was allowed to warm to room temperature. A solution of **10** (5.00 g, 18.5 mmol) in 15 mL of THF was added. The solution was refluxed for 1.5 days, quenched with water, and worked up as usual. The pure yellow oil (3.76 g, 80%) was obtained by flash chromatography. R_f = 0.22 (5% EtOAc/hexane). ^{1}H NMR[23] ($CDCl_3$) δ 4.54 (s, 1 H), 3.80–3.74 (m, 2 H), 3.45–3.35 (m, 2 H), 2.28 (t, J = 7.1 Hz, 2 H), 1.74 (p, J = 7.1 Hz, 2 H), 1.64–1.46 (m, 6 H), 0.07 (s, 9 H). ^{13}C NMR ($CDCl_3$) δ 106.7, 98.5, 84.5, 65.6, 61.9, 30.5, 28.7, 25.4, 25.4, 19.3, 16.6, 0.0.

5-(Trimethylsilyl)-4-pentyn-1-ol (12). PPTS (1.23 g, 4.89 mmol) was added to a solution of **11** (7.84 g, 32.6 mmol) in 40 mL of EtOH. The solution was refluxed for 8 h, until ^{1}H NMR on a sample shows complete loss of **11**. The EtOH was removed by rotary evaporation. The crude product was dissolved in $CHCl_3$ followed by usual workup giving a yellow oil (4.47 g, 88%) which was used without further purification. IR[24] (neat) 3362 (br), 2176 (s) cm^{-1}. ^{1}H NMR[24] ($CDCl_3$) δ 3.63 (t, J = 6.6 Hz, 2 H, H1), 2.63 (br s, 1 H, –OH), 2.25 (t, J = 6.6 Hz, 2 H, H3), 1.67 (p, J = 6.6 Hz, 2 H, H2), 0.15 (s, 9 H, $SiMe_3$). ^{13}C NMR ($CDCl_3$) δ 106.7 (C4), 85.0 (C5), 61.5 (C1), 31.1 (C2), 16.4 (C3), 0.0 ($SiMe_3$). HRMS[24c] calculated for $C_8H_{16}OSi$: 156.0770. Found: 156.0969; *m/e* (%) 156 (3).

5-(Trimethylsilyl)-4-pentynyl Methanesulfonate (13). A solution of **12** (508 mg, 3.25 mmol) and NEt_3 (0.25 mL, 3.2 mmol) in CH_2Cl_2 (25 mL) was cooled to −30 °C. Methanesulfonyl chloride was added dropwise. The solution was warmed to room temperature slowly followed by stirring for 6 h. The CH_2Cl_2 was removed, and the product was redissolved in Et_2O. The solution was washed once with 10% $NaHCO_3$ solution and then twice with NaCl solution and dried with $MgSO_4$. The pure oil (410 mg, 54%) was obtained by flash chromatography. R_f = 0.13 (10% EtOAc/hexane). IR (neat) 2176 (CC), 1360 (S=O, asymmetric stretch), 1176 (S=O, symmetric stretch) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 4.28 (t, J = 6.5 Hz, 2 H, H5), 2.96 (s, 3 H, –OMs), 2.33 (t, J = 6.5 Hz, 2 H, H3), 1.88 (p, J = 6.5 Hz, 2 H, H4), 0.09 (s, 9 H, $SiMe_3$). ^{13}C NMR ($CDCl_3$) δ 104.5, 85.8, 68.3, 36.8, 27.5, 15.7, −0.3.

(5-Iodo-1-pentynyl)trimethylsilane (14). A solution of **13** (1.85 g, 7.89 mmol) and NaI (1.32 g, 8.84 mmol) in 50 mL of acetone was refluxed for 16 h. The acetone was removed in vacuo. The crude product was dissolved in Et_2O followed by usual aqueous workup. The pure yellow oil (2.10 g, 84%) was obtained by flash chromatography. R_f = 0.67 (10% EtOAc/hexane). IR (neat) 2176 (CC) cm^{-1}. ^{1}H NMR[25] ($CDCl_3$) δ 3.27 (t, J = 6.8 Hz, 2 H, H5), 2.34 (t, J = 6.8 Hz, 2 H, H3), 1.98 (p, J = 6.8 Hz, 2 H, H4), 0.12 (s, 9 H, –$SiMe_3$). ^{13}C NMR ($CDCl_3$) δ 104.7, 85.7, 32.0, 20.8, 5.1 (C5), 0.1 ($SiMe_3$).

Tetrahydro-2-[(5-phenyl-4-pentynyl)oxy]-2*H*-pyran (33). A 2.5 M solution of BuLi (2.5 mL, 5.9 mmol) was added to a solution of phenylacetylene (0.65 mL, 5.9 mmol) in 20 mL of THF, cooled to −78 °C. The solution as stirred for 20 min, then warmed to room temperature. A solution of **10** (1.50 g; 5.6 mmol) in 10 mL of THF was added. The solution was refluxed for 1 day, quenched with water, and worked up as usual. The product (1.31 g, 96%) was used without further purification. R_f = 0.28 (10% EtOAc/hexane). IR (neat) 2234 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 7.40–7.24 (m, 5 H), 4.62 (t, J = 3.3 Hz, 1 H), 3.93–3.85 (m, 2 H), 3.75–3.71 (m, 2 H), 2.53 (t, J = 6.6 Hz, 2 H), 1.89 (p, J = 6.6 Hz, 2 H), 1.83–1.49 (m, 7 H). ^{13}C NMR ($CDCl_3$) δ 131.4, 128.1, 127.4, 123.9, 98.7, 89.5, 80.8, 65.9, 62.0, 30.6, 28.9, 25.4, 19.4, 16.2. HRMS calculated for $C_{16}H_{20}O_2$ (M): 244.1463. Found: 244.1455; *m/e* (%) 244 (16), 160 (86), 142 (80), 128 (61).

5-Phenyl-4-pentyn-1-ol (34). PPTS (0.16 g, 0.62 mmol) was added to a solution of **33** (1.30 g, 5.3 mmol) in 100 mL of EtOH. The solution was refluxed for 18 h. The EtOH was removed by rotary evaporation. The crude product was dissolved in CH_2Cl_2 followed by the usual workup giving a yellow oil. Pure product (0.69 g, 74%) was obtained by flash chromatography. R_f = 0.04 (10% EtOAc/hexane). IR[26] (neat) 3340 (br), 2233 (w) cm^{-1}. ^{1}H NMR[26] ($CDCl_3$) δ 7.37–7.32 (m, 2 H, *o*-Ph), 7.23–7.20 (m, 3 H, *m,p*-Ph), 3.74 (t, J = 6.6 Hz, 2 H, H1), 2.47 (t, J = 6.6 Hz, 2 H, H3), 2.35 (br s, 1 H, –OH), 1.79 (p, J = 6.6 Hz, 2 H, H2). ^{13}C NMR ($CDCl_3$) δ 131.4, 128.1, 127.6, 123.6, 89.3, 81.0, 61.5, 31.3, 15.8. HRMS calculated for $C_{11}H_{12}O$ (M): 160.0888. Found: 160.0891; *m/e* (%) 160 (67), 129 (31), 115 (100).

5-Phenyl-4-pentynal (35). DMSO (0.23 mL, 3.2 mmol) was added, dropwise, to a solution of oxalyl chloride (0.14 mL, 1.6 mmol) in 10 mL of CH_2Cl_2 cooled to −60 °C and was stirred for

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2 min. A solution of **34** (256 mg, 1.45 mmol) in 5 mL of CH_2Cl_2 was added over 12 min. While stirring for 20 min, the solution was warmed to −45 °C. After cooling back to −60 °C, NEt_3 (1.0 mL; 7.2 mmol) was added. Stirring was continued for 5 min, and the solution was warmed to room temperature and worked up as usual. The product (249 mg, 99%) was used without further purification. R_f = 0.22 (10% EtOAc/hexane). IR (neat) 2234 (w), 1727 (s) cm^{-1}. ^1H NMR ($CDCl_3$) δ 9.80 (s, 1 H), 7.33–7.21 (m, 5 H), 2.70 (br s, 4 H). ^{13}C NMR ($CDCl_3$) δ 200.2 (C1), 131.3 (*ipso*-Ph), 128.0 (*m*-Ph), 127.6 (*p*-Ph), 123.2 (*o*-Ph), 87.7, 81.1, 42.3 (C2), 12.4 (C3). HRMS calculated for $C_{11}H_{10}O$ (M): 158.0732. Found: C, 158.0727; *m/e* (%) 158 (27%), 141 (22), 129 (54), 115 (100).

1-Phenyl-1,6-heptadiyne (15). To a solution of **9** (0.222 g, 0.92 mmol) in THF, 1.2 mL of a 1.0 M solution of TBAF was added. The solution was stirred for 10 min at room temperature. Aqueous workup followed by filtration through a short column of silica gel gave the diyne (140 mg, 91%). R_f = 0.47 (10% EtOAc/hexanes). ^1H NMR ($CDCl_3$) δ 7.40–7.36 (m, 2 H, *o*-Ph), 7.29–7.25 (m, 3 H, *m,p*-Ph), 2.54 (t, *J* = 7.0 Hz, 2 H, H3), 2.38 (dt, *J* = 7.0, 2.6 Hz, 2 H, H5), 1.99 (t, *J* = 2.6 Hz, 1 H, H7), 1.83 (p, *J* = 7.0 Hz, 2 H, H4). ^{13}C NMR ($CDCl_3$) δ 131.5 (*ipso*-Ph), 128.2 (*m*-Ph), 127.6 (*p*-Ph), 123.7 (*o*-Ph), 88.9, 83.5, 81.2, 68.9 (C7), 27.6 (C4), 18.4 (C3), 17.6 (C5).

General Procedure for the Preparation of Tricarbonyl(cyclopentadienone)iron Complexes. A solution of the appropriate diyne in 8–10 mL of toluene was injected into a 60-mL quartz, Griffen-Worden pressure vessel (Kontes Glassware). To this solution, a 5-fold excess of freshly filtered $Fe(CO)_5$ was added. The solution was degassed by the freeze–pump–thaw method. After warming to room temperature, the vessel was charged with CO (100 psi). The vessel was held in an oil bath at 125–130 °C for 24 h. After cooling and releasing the pressure, the reaction mixture was diluted in CH_2Cl_2 then filtered through Celite. The solvent was removed by rotary evaporation. The solid was dried further on a vacuum line to ensure complete removal of any residual $Fe(CO)_5$, and the complexes were purified by flash chromatography.

Tricarbonyl(2,4-diphenylbicyclo[3.3.0]octa-1,4-dien-3-one)iron (16). 1,7-Diphenyl-1,6-heptadiyne (1.07 g, 4.38 mmol) and $Fe(CO)_5$ (7.0 mL, 25 mmol) were heated as described in the general procedure. Flash chromatography, R_f = 0.29 (25% EtOAc/hexane), afforded the product as yellow/orange crystals (1.47 g, 81%). Mp 208 °C. IR (CCl_4) 2064, 2010, 1991, 1646 cm^{-1}. ^1H NMR (C_6D_6) δ 8.21 (d, *J* = 8.1 Hz, 4 H, *o*-Ph), 7.26–7.05 (m, 6 H, *m,p*-Ph), 2.39 (dd, *J* = 15.7, 7.6 Hz, 2 H), 2.05 (ddd, *J* = 15.7, 10.6 7.6 Hz, 2 H), 1.63 (dt, *J* = 14, 7.6 Hz, 1 H), 1.49–1.30 (m, 1 H). ^{13}C NMR ($CDCl_3$) δ 208.5 ($Fe(CO)_3$), 170.2 (C3), 132.2 (*ipso*-Ph), 128.6 (*m*-Ph), 128.1 (*p*-Ph), 127.9 (*o*-Ph), 105.5 (C1), 79.3 (C2), 28.1 (C6,C8), 26.3 (C7). HRMS calculated for $C_{23}H_{16}O_4Fe$ (M): 412.0398. Found: 412.0349; *m/e* (%) 412 (2), 384 (5), 328 (52), 272 (100). Anal. Calcd: C, 66.98; H, 3.91. Found: C, 66.96; H, 3.98.

Tricarbonyl(2,4-diphenylbicyclo[4.3.0]nona-1,4-dien-3-one)iron (17). 1,8-Diphenylocta-1,7-diyne (0.507 g, 1.96 mmol) and $Fe(CO)_5$ (2.5 mL, 19 mmol) were heated as described in the general procedure. Flash chromatography, R_f = 0.20 (25% EtOAc/hexane), afforded the product as yellow/orange crystals (0.434 g, 52%). Mp 166–8 °C (dec). IR (CCl_4) 2065, 2010, 1986, 1646 cm^{-1}. ^1H NMR (C_6D_6) δ 7.99 (d, *J* = 7.1 Hz, 4 H, *o*-Ph), 7.22–7.03 (m, 6 H, *m,p*-Ph), 2.39 (dt, *J* = 17.6, 6.1 Hz, 2 H), 2.04 (dt, *J* = 17.6, 6.1 Hz, 2 H), 1.37–1.05 (m, 4 H, H7, H8). ^{13}C NMR ($CDCl_3$) δ 208.9 ($Fe(CO)_3$), 169.4 (C3), 131.3 (*ipso*-Ph), 129.6 (*m*-Ph), 128.4 (*p*-Ph), 127.9 (*o*-Ph), 100.4 (C1, C5), 81.9 (C2, C4), 23.7 (C6, C9), 22.3 (C7, C8). HRMS calculated for $C_{24}H_{18}O_4Fe$ (M): 426.0554. Found: 426.0531; *m/e* (%) 398 (6), 370 (9), 342 (48), 286 (100). Anal. Calcd: C, 67.60; H, 4.26. Found: C, 67.35; H, 4.24.

Tricarbonyl(2,4-diphenylbicyclo[5.3.0]deca-1,4-dien-3-one)iron (18). 1,9-Diphenylnona-1,8-diyne (0.874 g, 3.21 mmol) and $Fe(CO)_5$ (5.0 mL, 18 mmol) were heated as described in the general procedure. Flash chromatography, R_f = 0.28 (40% EtOAc/hexane), afforded the product as an orange/yellow solid (0.234 g, 18%). Mp 174–5 °C. IR (CCl_4) 2065, 2010, 1987, 1649 cm^{-1}. ^1H NMR (C_6D_6) δ 7.64–7.61 (m, 4 H, *o*-Ph), 7.18–7.03 (m, *m,p*-Ph), 2.21 (br s, 4 H, H6, H10), 1.39–1.15 (m, 6 H, H7, H8, H9). ^{13}C NMR (C_6D_6) δ 209.8 ($Fe(CO)_3$), 170.8 (C3), 131.7 (*ipso*-Ph), 131.5 (*m*-Ph), 128.6 (*p*-Ph), 128.1 (*o*-Ph), 104.9 (C1, C5), 86.2 (C2, C4), 31.2 (C6, C10), 28.7 (C7, C9), 27.4 (C8). HRMS calculated for $C_{25}H_{20}FeO_4$ (M): 440.0711. Found: 440.0703; *m/e* (%) 440 (1), 412 (2), 384 (6), 300 (100).

Tricarbonyl(2,4-bis(6-methoxy-2-naphthyl)bicyclo[3.3.0]octa-1,4-dien-3-one)iron (19). 1,7-Bis(6-methoxy-2-naphthyl)-1,6-heptadiyne (87 mg, 0.22 mmol) and $Fe(CO)_5$ (0.35 mL, 2.6 mmol) were heated as described in the general procedure. Flash chromatography, R_f = 0.36 (50% EtOAc/hexane), afforded the yellow crystalline product (0.102 g, 82%). Mp 218 °C (dec). IR (CCl_4) 2060, 2007, 1989, 1630 cm^{-1}. ^1H NMR (C_6D_6) δ 8.88 (d, *J* = 1.2 Hz, 2 H), 8.41 (dd, *J* = 8.6, 1.9 Hz, 2 H), 7.65 (t, *J* = 8.9 Hz, 6 H), 6.91 (d, *J* = 2.4 Hz, 2 H), 3.38 (s, 6 H, –OMe), 2.61 (dd, *J* = 15.7, 7.5 Hz, 2 H), 2.23 (ddd, *J* = 17.6, 10.5, 7.5 Hz, 2 H), 1.86–1.50 (m, 2 H). ^{13}C NMR ($CDCl_3$) δ 208.7 ($Fe(CO)_3$), 170.2 (C3), 158.2, 134.1, 129.9, 128.8, 127.5, 127.0, 125.8, 119.1, 105.7, 105.2 (C1, C5), 78.7 (C2, C4), 55.3 (–OMe), 24.8 (C6, C8), 22.4 (C7). Anal. Calcd: C, 69.22; H, 4.23. Found: C, 68.65; H, 4.26.

Tricarbonyl(2,4-bis(trimethylsilyl)bicyclo[3.3.0]octa-1,4-dien-3-one)iron (20). 1,7-Bis(trimethylsilyl)-1,6-heptadiyne (0.482 g, 2.04 mmol) and $Fe(CO)_5$ (5.0 mL, 18 mmol) were heated as described in the general procedure. Flash chromatography, R_f = 0.32 (10% EtOAc/hexane), afforded of the product as yellow crystals (0.418 g, 51%). Mp 147–8 °C. IR (CCl_4) 2064, 2006, 1984, 1624 cm^{-1}. ^1H NMR (C_6D_6) δ 2.10 (dd, *J* = 16.4, 7.9 Hz, 2 H, H6, H8), 1.91 (ddd, *J* = 16.4, 9.7, 7.2 Hz, 2 H, H6, H8), 1.67–1.58 (m, 1 H, H7), 1.43–1.27 (m, 1 H, H7), 0.32 (s, 18 H, $SiMe_3$). ^{13}C NMR (C_6D_6) δ 210.1 ($Fe(CO)_3$), 184.4 (C3), 118.1 (C1, C5), 71.2 (C2, C4), 27.6 (C6, C8), 26.0 (C7), −0.1 ($SiMe_3$). HRMS calculated for $C_{17}H_{24}FeO_4Si_2$ (M): 404.0562. Found: 404.0678, *m/e* (%) 404 (3), 376 (35), 320 (53), 264 (91).

Tricarbonyl(2,4-bis(trimethylsilyl)bicyclo[4.3.0]nona-1,4-dien-3-one)iron (21). 1,8-Bis(trimethylsilyl)-1,7-octadiyne (0.248 g, 0.99 mmol) and $Fe(CO)_5$ (4.0 mL, 14 mmol) were heated as described in the general procedure. Flash chromatography, R_f = 0.23 (10% EtOAc/hexane), afforded the product as yellow crystals (0.233 g, 57%). Mp 135 °C. IR (CCl_4) 2064, 2008, 1985, 1630 cm^{-1}. ^1H NMR (C_6D_6) δ 2.26 (dt, *J* = 17.1, 5.8 Hz, 2 H), 2.04 (dt, *J* = 17.1, 5.8 Hz, 2 H), 1.30–1.11 (m, 4 H, H7, H8), 0.34 (s, 9 H, $SiMe_3$). ^{13}C NMR ($CDCl_3$) δ 209.1 (CO), 181.0 (C3), 111.0 (C1, C5), 71.7 (C2, C4), 24.8 (C6, C9), 22.4 (C7, C8), −0.3 ($SiMe_3$). HRMS calculated for $C_{18}H_{26}FeO_4Si_2$ (M): 418.0719. Found: 418.0685; *m/e* (%) 418 (9), 390 (40), 334 (59), 278 (77). Anal. Calcd: C, 51.67; H, 6.26. Found: C, 51.43; H, 6.16.

Tricarbonyl(2,4-dimethylbicyclo[3.3.0]octa-1,4-dien-3-one)iron (22). 2,7-Nonadiyne (85.2 mg, 0.71 mmol) and $Fe(CO)_5$ (2.0 ml, 7.1 mmol) were heated at 135 °C under 75 psi of CO for 24 h. The reaction mixture was concentrated, redissolved in $CHCl_3$, and filtered through a column packed with neutral Al_2O_3 to isolate the product as yellow crystals (0.178 g, 87%). Mp 114–5 °C. IR ($CDCl_3$) 2064, 2010, 1990, 1630 cm^{-1}. ^1H NMR ($CDCl_3$) δ 2.60–1.45 (m, 4 H), 2.43–2.32 (m, 1 H), 1.97–1.84 (m, 1 H), 1.77 (s, 6 H). ^{13}C NMR ($CDCl_3$) δ 209.1 ($Fe(CO)_3$), 173.8 (C3), 107.3 (C1, C5), 25.7 (C7), 25.6 (C6, C8), 9.5 (Me); (C2, C4) not observed. Anal. Calcd: C, 50.6; H, 5.95. Found: C, 50.3; H, 6.02.

Tricarbonyl(2-(trimethylsilyl)-4-phenylbicyclo[3.3.0]octa-1,4-dien-3-one)iron (23). 1-Trimethylsilyl-7-phenylhepta-1,6-diyne (0.360 g, 1.50 mmol) and $Fe(CO)_5$ (6.3 mL, 22 mmol) were heated as described in the general procedure. Flash chromatography, R_f = 0.43 (20% EtOAc/hexane), afforded the product as yellow/orange crystals (0.476 g, 78%). Mp 124.5–126 °C. IR (CCl_4) 2063, 2008, 1986, 1634 cm^{-1}. ^1H NMR (C_6D_6) δ 8.17 (d, *J* = 8.4 Hz, 2 H, *o*-Ph), 7.12–7.04 (m, 3 H, *m,p*-Ph), 2.37 (dd, *J* = 15.8, 7.8 Hz, 1 H), 2.04 (dd, *J* = 15.8, 7.8 Hz, 1 H), 1.95 (dd, *J* = 10.6, 7.8 Hz, 1 H), 1.85 (dd, *J* = 10.6, 7.8 Hz, 1 H), 1.64–1.55 (m, 1 H), 1.41–1.29 (m, 1 H), 0.39 (s, 9 H, $SiMe_3$). ^{13}C NMR ($CDCl_3$) δ 208.6 (CO), 176.6 (C3), 132.2 (*ipso*-Ph), 128.4 (*m*-Ph), 127.8 (*p*-Ph), 127.5 (*o*-Ph), 113.6 (C1), 109.1 (C5), 80.7 (C4), 67.5 (C2), 28.1, 27.1, 26.0, −0.8 ($SiMe_3$). HRMS calculated for $C_{20}H_{20}FeO_4Si$ (M): 408.0480. Found: 408.0470; *m/e* (%) 408 (3), 380 (15), 352 (36), 268 (100). Anal. Calcd: C, 58.83; H, 4.94. Found: C, 58.17; H, 4.91.

Tricarbonyl(2-phenylbicyclo[3.3.0]octa-1,4-dien-3-one)iron (24). 1-Phenyl-1,6-heptadiyne (0.123 g, 0.73 mmol) and $Fe(CO)_5$ (1.1 mL, 3.9 mmol) were heated as described in the general procedure. Flash chromatography, R_f = 0.31 (70% EtOAc/hexane), afforded the product as yellow/orange crystals (0.203 g, 84%). Mp 164 °C (d). IR (CCl_4) 2068, 2012, 1991, 1653 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 7.91 (d, J = 6.8 Hz, 2 H, *o*-Ph), 7.38–7.27 (m, 3 H, *m,p*-Ph), 4.23 (s, 1 H, H 4), 2.95 (dd, J = 8.9, 6.9 Hz, 2 H), 2.73–2.44 (m, 3 H), 2.08–1.94 (m, 1 H). ^{13}C NMR ($CDCl_3$) δ 208.2 ($Fe(CO)_3$), 172.5 (C3), 132.0 (*ipso*-Ph), 128.6 (*m*-Ph), 128.1 (*p*-Ph), 127.6 (*o*-Ph), 107.7 (C1), 107.2 (C5), 80.4 (C2), 60.2 (C4), 28.4, 26.5, 26.2. HRMS calculated for $C_{17}H_{12}O_4Fe$ (M): 336.0085. Found: 336.0082; *m/e* (%) 336 (1), 308 (14), 280 (21), 252 (100), 196 (92).

Dicarbonyl(triphenylphosphine)(2,4-diphenylbicyclo[3.3.0]octa-1,4-dien-3-one)iron (25). To a solution of **16** (1.032 g, 2.50 mmol) in Bu_2O (50 mL), PPh_3 (0.780 g, 2.97 mmol) was added. Reflux for 16 h followed filtration through celite and flash chromatography yielded the pure product (1.072 g, 66%). R_f = 0.39 (25% EtOAc/hexane). Mp 204–5 °C. IR (CCl_4) 1991, 1937, 1599. ^{1}H NMR (C_6D_6) δ 8.21–8.17 (m, 4 H), 7.43–7.33 (m, 6 H), 7.12–7.07 (m, 6 H), 7.03–6.76 (m, 9 H), 2.80–2.70 (m, 2 H), 2.08–1.79 (m, 4 H). ^{13}C NMR ($CDCl_3$) (Ph region contains undiscernible doublets due to ^{31}P coupling in PPh_3) δ 216.1 (d, J_P = 12.8 Hz, $Fe(CO)_2$), 167.4 (C3), 134.6, 133.2, 133.0, 132.6, 131.8, 129.4, 128.0, 127.9, 127.7, 126.2, 101.4 (C1, C5), 80.6 (C2, C4), 27.4 (C6, C8), 25.7 (C7). ^{31}P NMR ($CDCl_3$) δ 57.4. HRMS calculated for $C_{40}H_{31}FeO_3P$ (M): 646.1360. Found: 646.1344; *m/e* (%) 646 (1), 618 (2), 590 (9), 328 (3), 272 (99). Anal. Calcd: C, 74.29; H, 4.84. Found: C, 74.23; H, 4.83.

Dicarbonyl(tributylphosphine)(2,4-diphenylbicyclo[3.3.0]octa-1,4-dien-3-one)iron (26). To a solution of **16** (150 mg, 0.36 mmol) in acetone (15 mL), PBu_3 (0.19 mL, 0.76 mmol) and Me_3NO (40 mg, 0.53 mmol) were added. Reflux for 19 h followed by aqueous workup and flash chromatography yielded the pure product (172 mg, 81%). R_f = 0.39 (10% EtOAc/hexane). Mp 150.5–152 °C. IR (CCl_4) 1986, 1933, 1584 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 8.25 (d, J = 7.4 Hz, 4 H, *m*-Ph), 7.33–7.19 (m, 6 H, *o,p*-Ph), 3.09 (dd, J = 15.4, 7.9 Hz, 2 H), 2.68–2.58 (m, 2 H), 2.45–2.41 (m, 1 H, H7), 2.32–2.18 (m, 1 H, H7), 1.64–1.59 (m, 6 H, C1–PBu_3), 0.86 (s, br, 12 H, C2, C3–PBu_3), 0.63 (t, J = 6.2 Hz, 9 H, C4). ^{13}C NMR ($CDCl_3$) δ 216.0 (d, J_P = 14.0 Hz, ($Fe(CO)_2$), 164.8 (C3), 135.5 (*ipso*-Ph), 128.2 (*m*-Ph), 127.3 (*p*-Ph), 126.4 (*o*-Ph), 100.9 (C1, C5), (C2, C4 obscured by $CDCl_3$), 27.5 (C6, C8), 26.0 (C7), 25.0 (C3–PBu_3), 24.0 (d, J_P = 13.5 Hz, C2–PBu_3), 22.7 (d, J_P = 25.4 Hz, C1–PBu_3), 13.6 (C4–PBu_3). ^{31}P NMR (C_6D_6) δ 38.6. HRMS calculated for $C_{34}H_{43}FeO_3P$ (M): 586.2299. Found: 586.2291; *m/e* (%) 586 (2), 558 (4), 530 (100), 328 (27), 272 (80).

Dicarbonyl(triphenylphosphine)(2,4-bis(trimethylsilyl)bicyclo[3.3.0]octa-1,4-dien-3-one)iron (27). To a solution of **20** (103 mg, 0.26 mmol) in benzene (25 mL), PPh_3 (109 mg, 0.42 mmol) and Me_3NO (32 mg, 0.43 mmol) were added. Reflux for 1 h followed by aqueous workup and flash chromatography yielded 135 mg of the product (82%). R_f = 0.21 (20% EtOAc/hexane). Mp = 200 °C (dec). IR (CCl_4) 1992, 1938, 1585 cm^{-1}. ^{1}H NMR (C_6D_6) δ 2.10 (dd, J = 16.4, 7.9 Hz, 2 H), 1.91 (ddd, J = 16.4, 9.6, 7.2 Hz, 2 H), 1.67–1.58 (m, 1 H), 1.43–1.27 (m, 1 H). ^{13}C NMR ($CDCl_3$) δ 215.6 (d, J_P = 15.8 Hz, ($Fe(CO)_2$), 181.9 (C3), 134.4 (d, J_P = 40.4 Hz, *ipso*-PPh_3), 133.6 (d, J_P = 10.2 Hz, *m*-PPh_3), 130.0 (*p*-PPh_3), 128.2 (d, J_P = 9.6 Hz, *o*-PPh_3), 113.4 (C1, C5), 69.4 (C2, C4), 27.0 (C6, C8), 25.1 (C7), −0.3 ($SiMe_3$). HRMS calculated for $C_{32}H_{39}FeOPSi_2$ (M − 2CO): 582.1626. Found: 582.1618; *m/e* (%) 582 (4).

Dicarbonyl(triphenylphosphine)(2,4-bis(trimethylsilyl)bicyclo[4.3.0]nona-1,4-dien-3-one)iron (28). To a solution of **21** (113 mg, 0.27 mmol) in acetone (15 mL), PPh_3 (87 mg, 0.33 mmol) and Me_3NO (25 mg, 0.33 mmol) were added. Reflux for 20 h followed by aqueous workup and flash chromatography yielded of the pure product (140 mg, 80%). R_f = 0.28 (20% EtOAc/hexane). Mp 192–193 °C. IR (CCl_4) 1991, 1937, 1581 cm^{-1}. ^{1}H NMR δ 7.72 (t, J = 8.7 Hz, 6 H, *o*-PPh_3), 7.06–6.96 (m, 9 H *m,p*-PPh_3), 2.21 (br s, 4 H, H7, H8), 1.38 (br, s, 4 H, H6, H9), 0.31 (s, 18 H, $SiMe_3$). ^{13}C NMR ($CDCl_3$) δ 216.2 (d, J_P = 17.6 Hz, CO), 179.3 (C3), 134.8 (d, J_P = 40.3 Hz, *ipso*-PPh_3), 133.7 (d, J_P = 9.7 Hz, *m*-PPh_3), 130.1 (*p*-PPh_3), 128.2 (d, J_P = 9.7 Hz, *o*-PPh_3), 106.5 (C1, C5), 70.9 (C2, C4), 23.9 (C6, C9), 22.2 (C7, C8), 0.3 ($SiMe_3$). ^{31}P NMR (C_6D_6) δ 54.29. HRMS calculated for $C_{33}H_{41}FeOPSi_2$ (M − 2CO): 596.1782. Found: 596.1779; *m/e* (%) 596 (9).

Dicarbonyl(triphenylphosphine)(2-(trimethylsilyl)-4-phenylbicyclo[3.3.0]octa-1,4-dien-3-one)iron (29). To a solution of **23** (99 mg, 0.24 mmol) in acetone (15 mL), PPh_3 (95 mg, 0.36 mmol) and Me_3NO (27 mg, 0.36 mmol) were added. Reflux for 90 min followed by aqueous workup and flash chromatography yielded the pure product (151 mg, 98%). R_f = 0.35 (20% EtOAc/hexane). Mp 202 °C (dec). IR (CCl_4) 1991, 1938, 1586 cm^{-1}. ^{1}H NMR (C_6D_6) δ 7.71–7.67 (m, 2 H), 7.29–7.15 (m, 14 H), 6.99–6.89 (m, 4 H), 2.58 (dd, J = 15.9, 7.5 Hz, 1 H), 2.49–2.06, m, 3 H), 1.82–1.56 (m, 2 H), 0.22 (s, 9 H). ^{13}C NMR ($CDCl_3$) δ 216.0 (d, J_P = 8.2 Hz, ($Fe(CO)_2$)), 174.4 (C3), 134.5 (*ipso*-Ph), 133.3 (d, J_P = 42.3 Hz, *ipso*-PPh_3), 133.2 (d, J_P = 10.5 Hz, *m*-PPh_3), 129.9 (*p*-PPh_3), 128.1 (d, J_P = 10.0 Hz, *o*-PPh_3), 127.9 (*m*-Ph), 127.7 (*p*-Ph), 126.3 (*o*-Ph), 110.2 (C2), 105.6 (C4), 82.0 (C1), 64.5 (C5), 27.3, 27.2, 25.4, −0.2 ($SiMe_3$). ^{31}P NMR δ ($CDCl_3$) 61.86. HRMS calculated for $C_{37}H_{35}FeO_3PSi$ (M): 642.1442. Found: 642.1442; *m/e* (%) 642 (1).

Dicarbonyl(triphenylphosphine)(bicyclo[3.3.0]octa-1,4-dien-3-one)iron (30). To a solution of **27** (33 mg, 0.052 mmol) in 5 mL of THF was added 0.12 mL of a 1.0 M solution of TBAF (0.12 mmol). The reaction mixture was stirred for 20 min at room temperature. The reaction mixture was diluted with $CHCl_3$ and washed five times with water. The organic layer was dried with $MgSO_4$, concentrated, and filtered through silica gel using EtOAc as the eluent (15 mg, 58%), R_f = 0.32 (EtOAc). IR (CCl_4) 2000, 1943, 1624 cm^{-1}. ^{1}H NMR (C_6D_6) δ 7.76–7.33 (m, 15 H, PPh_3), 3.63 (s, 2 H), 2.35–1.60 (m, 6 H). ^{13}C NMR ($CDCl_3$) δ 214.8 (d, J_P = 13.5 Hz, ($Fe(CO)_2$), 170.7 (C3), 134.1 (d, J_P = 44.0 Hz, *ipso*-PPh_3), 133.3 (d, J_P = 10.2 Hz, *m*-PPh_3), 130.3 (*p*-PPh_3), 128.3 (d, J_P = 9.4 Hz, *o*-PPh_3), 105.3 (C1, C5), 64.4 (C2, C4), 26.6 (C6, C8), 25.9 (C7).

Dicarbonyl(triphenylphosphine)(bicyclo[4.3.0]nona-1,4-dien-3-one)iron (31). To a solution of **28** (0.846 g, 1.30 mmol) in 20 mL of THF was added 2.8 mL of a 1.0 M solution of TBAF (2.8 mL, 2.8 mmol). The yellow solution immediately changes to dark red. The reaction mixture was stirred for 30 min at room temperature. The THF was removed in vacuo. The remaining solid was dissolved in CH_2Cl_2 and washed twice with water. The organic layer was dried with $MgSO_4$ and concentrated. The complex was crystallized from the concentrated CH_2Cl_2 solution with cold hexanes as a yellow powder (555 mg, 84%). Mp 241 °C (d). IR (CCl_4) 1989, 1940, 1937, 1617 cm^{-1}. ^{1}H NMR (C_6D_6) δ 7.78 (t, J = 8.75 Hz, 6 H, *o*-PPh_3), 7.07 (m, 9 H, *m,p*-PPh_3), 3.39 (s, 2 H, H2, H4), 2.21–2.14 (m, 2 H), 1.88–1.83 (m, 2 H), 1.44–1.22 (m, 4 H). ^{13}C NMR ($CDCl_3$) δ 215.2 ($Fe(CO)_3$), 133.9 (d, J_P = 44.5 Hz, *ipso*-PPh_3), 133.4 (d, J_P = 9.9 Hz, *m*-PPh_3), 130.3 (*p*-PPh_3), 128.3 (d, J_P = 10.2 Hz, *o*-PPh_3), 98.9 (C1, C5), 67.2 (C2, C4), 23.0 (C6, C9), 22.4 (C7, C8), C(3) not observed. ^{31}P NMR (C_6D_6) δ 63.6. HRMS calculated for $C_{29}H_{25}FeO_3P$ (M): 508.0891. Found: 508.0881; *m/e* (%) 508 (1), 480 (3), 452 (13).

Dicarbonyl(triphenylphosphine)(2-phenylbicyclo[3.3.0]-octa-1,4-dien-3-one)iron (32). To a solution of **29** (47 mg, 0.073 mmol) in 5 mL of THF was added a 1.0 M solution of TBAF (0.10 mL, 0.10 mmol). The reaction mixture was stirred for 18 h at room temperature, then diluted with $CHCl_3$ and washed twice with saturated NaCl solution. The organic layer was dried with $MgSO_4$ and concentrated. The complex was isolated by flash chromatography (32 mg, 77%). R_f = 0.35 (70% EtOAc/hexane). ^{1}H NMR (C_6D_6) δ 8.23 (dd, J = 8.1, 1.6 Hz, 2 H), 7.63–7.56 (m, 6 H), 7.11–6.89 (m, 12 H), 3.50 (d, J_P = 2.2 Hz, 1 H), 2.68 (dd, J = 16.0, 5.7 Hz, 1 H), 2.09–1.98 (m, 2 H), 1.83–1.67 (m, 2 H). ^{13}C NMR ($CDCl_3$) (Ph region contains undiscernible doublets due to ^{31}P coupling in PPh_3) δ 215.4 (d, J_P = 14.3 Hz), 169.2, 134.6, 133.9, 133.3, 133.2, 130.0, 128.3, 128.2, 127.6, 126.4, 103.8, 103.1, 79.7, 64.4, 27.9, 25.9.

1,7-Diphenyl-3-hydroxy-1,6-heptadiyne (36). A 2.5 M solution of BuLi (2.3 mL; 5.9 mmol) was added to a solution of phenylacetylene (0.58 mL, 5.3 mmol) in THF, as above. A THF solution of **35** (0.83 g, 4.8 mmol) was added and was refluxed for 15 min. The reaction mixture was cooled and quenched with water, diluted with Et_2O, and worked up as usual. The pure oil (0.94 g, 76%) was obtained by flash chromatography. R_f = 0.40 (30% EtOAc/hexanes). IR (neat) 3356 (br), 2231 (w) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 7.46–7.22 (m, 10 H), 4.84 (q, J = 6.3 Hz, 1 H, H3), 2.68 (AB quartet of triplets, J_{AB} = 13.1, 6.3 Hz, 2 H, diastereotopic, H5), 2.11 (q, J = 6.3 Hz, 2 H, H4), 2.10 (d, J = 6.3 Hz, 1 H, –OH). ^{13}C NMR ($CDCl_3$) δ 131.6, 131.5, 128.4, 128.2, 128.1, 127.7, 123.6, 122.4, 89.3, 88.8, 85.3, 81.3, 61.7 (C3), 36.5 (C4),

Table V. Summary of X-ray Data Collection and Structural Analysis

	Crystal Data
empirical formula	$C_{40}H_{31}FeO_3P$
color; habit	red/brown; parallelepiped
cryst size (mm)	0.35 × 0.29 × 0.27
cryst syst	monoclinic
space group	$P2_1/n$
unit cell dimensions	a = 12.059 (2), b = 13.393 (3), c = 19.068 (4) Å; β = 93.980 (16)°
vol (Å^3)	3072.2 (11)
Z	4
formula wt	646.5
density(calcd) (Mg/m^3)	1.398
abs coeff (mm^{-1})	0.578
F(000)	1344
	Data Collection
diffractometer	Nicolet R3m/V
radiation	Mo Kα (λ = 0.71073 Å)
temp (K)	293
monochromator	highly oriented graphite crystal
2θ range	3.5–45.0°
scan type	ω
scan speed	variable; 3.50–15.00°/min in ω
scan range (ω)	1.20°
background measurement	stationary crystal and stationary counter at beginning and end of scan, each for 25.0% of total scan time
std rflns	3 measd every 100 reflns
index ranges	$0 \le h \le 12$, $0 \le k \le 14$, $-20 \le l \le 20$
reflns coll	4463
indep reflns	4015 (R_{int} = 1.64%)
obs reflns	2627 ($F > 6.0\sigma(F)$)
abs correction	face-indexed numerical
min/max transmission	0.8165/0.8704
	Solution and Refinement
system used	Nicolet SHELXTL PLUS (Micro VAX II)
solution	direct methods
refinement method	full-matrix least-squares
quantity minimized	$\sum\omega(F_o - F_c)^2$
absolute configuration	N/A
extinction correction	χ = 0.00060 (6), where $F^* = F[1 + 0.002\chi F^2/\sin(2\theta)]^{-1/4}$
hydrogen atoms	riding model, fixed isotropic U
weighting scheme	$\omega^{-1} = \sigma^2(F) + 0.0003F^2$
final R indexes (obs data)	R = 3.61%, wR = 3.84%
R indexes (all data)	R = 6.88%, wR = 4.56%
goodness-of-fit	1.29
largest and mean Δ/σ	0.009, 0.000
data-to-parameter ratio	6.5:1
largest difference peak (e Å^{-3})	0.28
largest difference hole (e Å^{-3})	−0.24

Table VI. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3)

	x	y	z	U(eq)^a
Fe	2038 (1)	1873 (1)	6476 (1)	29 (1)
P	3371 (1)	2855 (1)	6067 (1)	29 (1)
O(1)	933 (2)	2564 (2)	4868 (2)	45 (1)
O(2)	3585 (3)	246 (3)	6834 (2)	65 (1)
O(3)	2021 (3)	2861 (2)	7836 (2)	55 (1)
C(1)	849 (3)	790 (3)	6241 (2)	31 (1)
C(2)	1261 (3)	1060 (3)	5581 (2)	32 (1)
C(3)	857 (3)	2092 (3)	5416 (2)	32 (2)
C(4)	419 (3)	2461 (3)	6084 (2)	31 (1)
C(5)	356 (3)	1627 (3)	6536 (2)	30 (1)
C(6)	−215 (4)	1338 (3)	7183 (2)	42 (2)
C(7)	267 (4)	296 (3)	7361 (2)	52 (2)
C(8)	646 (4)	−139 (3)	6665 (2)	44 (2)
C(9)	2999 (4)	913 (3)	6705 (2)	40 (2)
C(10)	2070 (3)	2463 (3)	5069 (2)	36 (2)
C(12)	2065 (4)	713 (4)	4433 (2)	49 (2)
C(13)	2480 (4)	66 (4)	3952 (3)	59 (2)
C(14)	2561 (4)	−923 (5)	4082 (3)	63 (2)
C(15)	2202 (5)	−1284 (4)	4701 (3)	78 (3)
C(16)	1789 (5)	−642 (4)	5186 (3)	65 (2)
C(21)	−142 (3)	3426 (3)	6167 (2)	30 (1)
C(22)	−558 (4)	3969 (3)	5583 (2)	42 (2)
C(23)	−1094 (4)	4864 (4)	5668 (3)	51 (2)
C(24)	1226 (4)	5252 (3)	6322 (3)	52 (2)
C(25)	−829 (4)	4722 (4)	6907 (3)	47 (2)
C(26)	−302 (3)	3817 (3)	6832 (2)	41 (2)
C(31)	3847 (3)	2497 (3)	5215 (2)	34 (2)
C(32)	3491 (4)	2984 (3)	4600 (2)	44 (2)
C(33)	3872 (4)	2688 (4)	3958 (3)	59 (2)
C(34)	4592 (4)	1906 (5)	3936 (3)	65 (2)
C(35)	4940 (4)	1391 (4)	4535 (3)	58 (2)
C(36)	4565 (4)	1685 (3)	5175 (2)	45 (2)
C(41)	3099 (3)	4197 (3)	5989 (2)	30 (1)
C(42)	2229 (3)	4602 (3)	6318 (2)	36 (2)
C(43)	2007 (4)	5618 (3)	6292 (2)	45 (2)
C(44)	2674 (4)	6249 (3)	5941 (2)	49 (2)
C(45)	3569 (5)	5859 (4)	5623 (3)	54 (2)
C(46)	3776 (4)	4851 (3)	5639 (2)	46 (2)
C(51)	4702 (3)	2870 (3)	6614 (2)	31 (2)
C(52)	4758 (4)	2597 (3)	7318 (2)	44 (2)
C(53)	5759 (5)	2673 (4)	7730 (3)	59 (2)
C(54)	6690 (4)	3020 (4)	7439 (3)	60 (2)
C(55)	6650 (4)	3278 (4)	6742 (3)	59 (2)
C(56)	5668 (3)	3207 (3)	6336 (2)	48 (2)
cent^b	721	1484	6111	

^{a} Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor. ^{b} Cent is the calculated geometric center of C(1), C(2), C(4), and C(5).

15.5 (C5). HRMS calculated for $C_{19}H_{15}O$ (M − H): 259.1123. Found: 259.1116; *m/e* (%) 259 (25).

Tricarbonyl(2,4-diphenyl-6-hydroxybicyclo[3.3.0]octa-1,4-dien-3-one)iron (37). 1,7-Diphenyl-3-hydroxy-1,6-heptadiyne (0.357 g, 1.37 mmol) and $Fe(CO)_5$ (2.0 mL, 7.0 mmol) were heated for 23 h, under 50 psi of CO, and worked up as previously. TLC (40% EtOAc/hexanes) indicated the presence of two diastereomers, R_f(anti) = 0.22, R_f(syn) = 0.15. Flash chromatography afforded 0.223 g (38%) of the anti isomer and 0.335 g (57%) of the syn isomer. Total yield of the complex was 95%. *Data for the syn isomer* (*37a*): Mp 214 °C (dec). IR (CCl_4) 2072, 2017, 2003, 1629 cm^{-1}. ^1H NMR ($CDCl_3$) δ 8.00–7.94 (m, 4 H, *o*-Ph), 7.42–7.30 (m, 6 H, *m,p*-Ph), 5.56–5.51 (m, 1 H, H6), 3.08 (dd, J = 15.5, 7.9 Hz, 1 H), 2.97–2.78 (m, 2 H), 2.52 (br s, 1 H, -OH), 2.09–1.97 (m, 1 H). ^{13}C NMR ($CDCl_3$) δ 208.0 (CO), 169.6 (C3), 131.9, 131.1 (*ipso*-Ph), 129.2, 128.7 (*m*-Ph), 128.5, 128.2 (*p*-Ph), 128.1, 127.9 (*o*-Ph), 106.9 (C5), 106.1 (C1), 78.0 (C2), 71.2 (C4), 35.6 (C7), 25.2 (C8). HRMS calculated for $C_{23}H_{16}FeO_5$ (M): 428.0347. Found: 428.0342; *m/e* (%) 428 (1), 400 (4), 372 (14), 344 (45), 272 (100). *Data for the anti isomer* (*37b*): Mp 193.5–195 °C (dec). IR (CCl_4) 3341 (br), 2065, 2014, 2001, 1610 cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.80–7.64 (m, 4 H, *o*-Ph), 7.37–7.06 (m, 6 H, *m,p*-Ph), 5.34 (d, J = 9.1 Hz, 1 H), 5.08 (dd, J = 9.1, 5.4 Hz, 1 H), 3.12 (ddd, J = 16.7, 9.6, 7.5 Hz, 1 H), 2.67 (dd, J = 15.9, 7.5 Hz, 1 H), 2.48 (dd, J = 13.9, 7.2 Hz, 1 H), 2.31–2.19 (m, 1 H). ^{13}C NMR ($CDCl_3$) δ 207.5 ($Fe(CO)_3$), 170.1 (C3), 131.5, 130.6 (*ipso*-Ph), 128.7, 128.5 (*m*-Ph), 128.2, 127.9 (*p*-Ph), 127.7, 127.0 (*o*-Ph), 107.4 (C5), 101.6 (C1), 77.7 (C2), 71.3 (C4), 37.0 (C7), 26.3 (C8). HRMS calculated for $C_{23}H_{16}O_5Fe$ (M): 428.0347. Found: 428.0348; *m/e* (%) 428 (1), 400 (1), 372 (12), 344 (54), 272 (100).

Tricarbonyl(2,4-diphenylbicyclo[3.3.0]octa-1,4-diene-3,6-dione)iron (38). To a suspension of Collins' reagent (463 mg, 1.89 mmol) in 10 mL of CH_2Cl_2, a solution of **37** (202 mg, 0.47 mmol) in CH_2Cl_2 (10 mL) was added dropwise. The suspension was stirred overnight, and then additional Collins reagent (243 mg, 1.00 mmol) was added. Stirring was continued for 6 h until TLC indicated complete loss of **37**. The reaction mixture was diluted with $CHCl_3$ and filtered through Celite followed by standard aqueous workup. The product was isolated by flash chromatography (160 mg, 80%). R_f = 0.36 (40% EtOAc/hexanes). Mp 209 °C (dec). IR (CCl_4) 2074, 2027, 2006, 1725, 1653 cm^{-1}. ^1H NMR ($CDCl_3$) δ 8.43 (dd, J = 8.4, 1.6 Hz, 2 H), 8.05 (dd, J = 7.7, 1.7 Hz, 2 H), 7.48–7.26 (m, 6 H), 3.48–3.41 (m, 2 H), 3.06–3.00 (m, 2 H). ^{13}C NMR ($CDCl_3$) δ 206.5 ($Fe(CO)_3$), 202.9 (C6), 170.9 (C3), 130.8, 130.3 (*ipso*-Ph), 129.2, 129.1 (*m*-Ph), 129.0, 129.0 (*p*-Ph), 128.6, 127.8 (*o*-Ph), 117.2, 84.8, 84.5, 37.4 (C7), 23.3 (C8). HRMS calculated for $C_{23}H_{14}FeO_5$ (M): 426.0190. Found: 426.0195; *m/e* (%) 426 (3), 398 (5), 370 (24), 286 (100).

Procedure for the Borohydride Reduction of 38. To a suspension of **38** (8.3 mg, 0.020 mmol) in 2 mL of EtOH, $NaBH_4$ (1.0 mg, 0.026 mmol) was added. After stirring for 2 min, the reaction mixture became clear and TLC indicated complete loss of **38**. Aqueous workup, followed by flash chromatography gave pure **37a** (7.2 mg, 86%).

Table VII. Selected Distances (Å) and Angles (deg)

Fe-P	2.258 (1)	Fe-cent[a]	1.768
Fe-C(1)	2.067 (4)	O(1)-C(3)	1.231 (5)
Fe-C(2)	2.181 (4)	C(1)-C(2)	1.431 (6)
Fe-C(4)	2.188 (4)	C(1)-C(5)	1.406 (6)
Fe-C(5)	2.066 (4)	C(2)-C(3)	1.492 (6)
Fe-C(9)	1.765 (5)	C(3)-C(4)	1.496 (6)
Fe-C(10)	1.757 (5)	C(4)-C(5)	1.416 (6)
P-Fe-C(9)	92.2 (2)	C(5)-C(6)-C(7)	103.1 (4)
P-Fe-C(10)	94.3 (1)	C(1)-C(8)-C(7)	102.6 (3)
C(1)-C(2)-C(3)	106.9 (3)	O(1)-C(3)-C(2)	127.7 (4)
C(2)-C(3)-C(4)	104.8 (3)	C(1)-C(2)-C(11)	126.3 (4)
C(3)-C(4)-C(5)	107.2 (3)	C(3)-C(4)-C(21)	124.9 (4)
C(1)-C(5)-C(4)	110.1 (4)	Cent-Fe-P[a]	132.6
C(2)-C(1)-C(5)	109.4 (3)	Cent-Fe-C(9)[a]	116.9

[a] Cent is the calculated geometric center of C(1), C(2), C(4), and C(5).

Tricarbonyl(2,4-diphenyl-6-*syn*-hydroxy-6-*anti*-methylbicyclo[3.3.0]octa-1,4-dien-3-one)iron (39). To a solution of 38 (38 mg, 0.090 mmol) in 5 mL of THF cooled to −78 °C, 3.0 M MeMgBr (0.30 mL, 0.90 mmol) was added. The solution was stirred for 4 h, then quenched with saturated NH_4Cl solution, diluted with Et_2O, and washed twice with NaCl solution. The product was purified by flash chromatography giving 39 (39 mg, 97%). $R_f = 0.29$ (40% EtOAc/hexanes). Mp 210–1 °C. IR (CCl_4) 3363 (br), 2067, 2017, 1999, 1648 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 8.34 (d, *J* = 1.6 Hz, 2 H), 8.31 (d, *J* = 1.1 Hz, 2 H), 7.99–7.29 (m, 6 H), 3.07 (dd, *J* 16.5, 7.7 Hz, 1 H), 2.92 (ddd, *J* = 16.5, 10.1, 6.8 Hz, 1 H), 2.50–2.31 (m, 2 H, H7), 2.44 (s, 1 H, −OH), 1.66 (s, 3 H, −Me) ^{13}C NMR ($CDCl_3$) δ 208.2 ($Fe(CO)_3$), 171.1 (C3), 131.8, 129.2, 128.7, 128.4, 128.2, 127.9, 109.3, 104.4, 103.3, 78.5, 77.7 (C7), 43.0 (MeO), 26.4 (C7), 25.4 (C8). HRMS calculated for $C_{24}H_{18}O_5Fe$ (M): 442.0504. Found: 442.0500; *m/e* (%) 442 (1), 358 (37), 286 (100).

X-ray Diffraction Analysis of 25. Crystals formed in a concentrated solution of 25 in CH_2Cl_2, to which hexane was added, after storage at −20 °C for 1 day. A single crystal was mounted on the end of a glass fiber using epoxy. Details of the crystal data collection, solution, and refinement[27] of the structure are summarized in Table V. The refined atomic coordinates are listed in Table VI. Atomic scattering factors and corrections for anomolous dispersion were taken from the usual source.[28]

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Supplementary Material Available: Tables of anisotropic thermal parameters (U_{ij}), bond lengths, bond angles, and calculated hydrogen atom positions (7 pages). Ordering information is given on any current masthead page.

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Coordination and Reactivity of 3,3-Dimethylthietane in Dimanganese Carbonyl Cluster Complexes

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The complex $Mn_2(CO)_9(\overline{SCH_2CMe_2C}H_2)$ (1) was obtained from the reaction of $Mn_2(CO)_9(NCMe)$ with 3,3-dimethylthietane (3,3-DMT) at 40 °C. Reaction of 1 with Me_3NO resulted in decarbonylation and the formation of the complex $Mn_2(CO)_8[\mu\text{-}\overline{SCH_2CMe_2C}H_2]$ (**2**). Complex **2** was characterized by single-crystal X-ray diffraction analyses and was found to contain a 3,3-DMT ligand bridging the two mutually bonded manganese metal atoms by using both lone pairs of electrons on the sulfur atom, Mn–Mn = 2.8243 (9) Å. Complex **2** reacted with HCl at 25 °C to yield the complex $[Mn(CO)_3(\overline{SCH_2CMe_2C}H_2)(\mu\text{-Cl})]_2$ (**3**) in 84% yield and $HMn(CO)_5$. The structure of complex **3** was determined by single-crystal X-ray diffraction analyses. In the solid state the molecule contains two manganese atoms bridged by two chlorine atoms, Mn···Mn = 3.578 (1) Å. There are two 3,3-DMT ligands terminally coordinated in axial sites one on each metal atom with an overall trans geometry. IR and ^{1}H NMR spectra of **3** indicate that it exists in solution as a mixture of isomers. For 1: space group = *Pbca*, *a* = 12.018 (2) Å, *b* = 17.135 (2) Å, *c* = 16.669 (2) Å, *Z* = 8, 1432 reflections, *R* = 0.026. For **2**: space group = $P2_1/c$, *a* = 10.984 (2) Å, *b* = 9.052 (2) Å, *c* = 11.884 (2) Å, β = 90.94 (1)°, *Z* = 2, 1298 reflections, *R* = 0.023.

Introduction

Recently we have been studying the ring-opening transformations of thietane ligands on metal cluster carbonyl complexes. A number of ring-opening processes have now been identified.[1-8]

Thermal transformations result in the insertion of a metal atom into one of the carbon–sulfur bonds to yield the formation of a thiametallacycle (e.g., eq 1).[1-3] Similar results are achieved by photochemical stimulation (e.g. eq 2).[4,5]

We have also shown that the bridging thietane ligands undergo facile ring opening by nucleophilic addition in the

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