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# Photolysis of ($\eta^5$-$C_5H_5$)Fe$(CO)_2$(butadienyl) Complexes. Synthesis and Electrocyclic Ring Closure of ($\eta^5$-$C_5H_5$)Fe(pentadienoyl) Complexes to Hydroxyferrocenes

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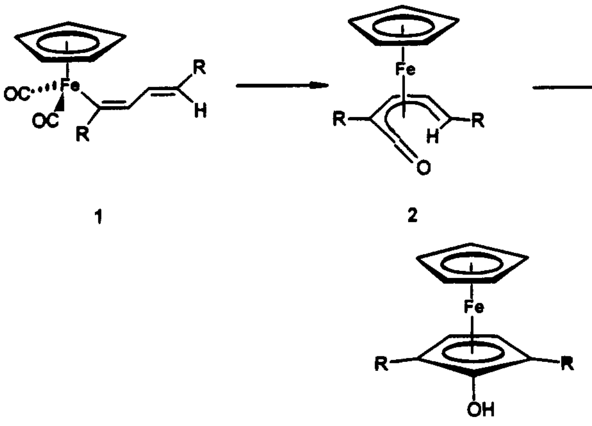
A study of the synthesis and photolysis of seven ($\eta^5$-$C_5H_5$)Fe$(CO)_2$($\eta^1$-1,3-butadienyl) complexes is reported. Photolysis of these complexes leads to the formation of the rarely accessible class of substituted hydroxyferrocenes in very high yields. Low-temperature experiments aimed at elucidating the mechanism of this conversion indicate that loss of a terminal carbonyl from ($\eta^5$-$C_5H_5$)Fe$(CO)_2$($\eta^1$-1,3-butadienyl) complexes is the only photochemical reaction and that ($\eta^5$-$C_5H_5$)Fe($\eta^5$-pentadienoyl) complexes are intermediates. Spectroscopic data for two kinetically unstable pentadienoyl intermediates are presented. Pentadienoyl ligands undergo electrocyclic ring closure followed by keto–enol tautomerization to give the hydroxycyclopentadienyl ligands. Acid catalyzes this ring-closure reaction with the rate of closure being linearly dependent on the concentration of acid. Ring strain and electronic effects also influence the rate of formation of substituted bicyclic hydroxyferrocenes.

## Introduction

Transition metals complexed to unsaturated organic compounds are intermediates in many catalytic and stoichiometric reactions. The study of the synthesis and chemistry of one such class of complexes, transition-metal pentadienyl complexes, has yielded extensive information regarding the bonding and chemistry of the $C_5H_7$ structural unit over the past decade.[1] Recently, we reported that photolysis of ($\eta^5$-$C_5H_5$)Fe$(CO)_2$($\eta^1$-1,3-butadiene) complexes **1** led to hydroxyferrocene products **3** and that pentadien*oyl* complexes **2**—complexes containing a pentadienyl ligand having a cumulative noncoordinated terminal carbonyl moiety—were key intermediates in the conversion (eq 1).[2–5]



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We here report the experimental details of work examined in our previous communication and a detailed study of the synthesis and electrocyclic ring closure of a class of ring-annelated ($\eta^5$-$C_5H_5$)$(CO)_2$Fe($\eta^1$-1,3-butadienes) which convert to bicyclic hydroxyferrocenes *via* ring-annelated ($\eta^5$-$C_5H_5$)Fe($\eta^5$-pentadienoyl) complexes.

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⊗ Abstract published in *Advance ACS Abstracts,* August 15, 1994.

(1) For review articles see: (a) Ernst, R. D. *Chem. Rev.* **1988**, *88*, 1255. (b) Ernst, R. D. *Struct. Bonding (Berlin)* **1984**, *57*, 1. (c) Ernst, R. D. *Acc. Chem. Res.* **1985**, *18*, 56. (d) Powell, P. In *Advances in Organometallic Chemistry*; West, R., Stone, F. G. A., Eds.; Academic: New York, 1986; Vol. 26, p 125. (e) Kreiter, C. G. In ref 1d, p 297. (f) Yasuda, H.; Tatsumi, K.; Nakamura, A. In *Recent Advances in Anionic Polymerization*; Hogen-Esch, T. E., Smid, J., Eds.; Elsevier: Lausanne, Switzerland, 1987; p 59. Lead references from the Ernst group: (g) Melendez, E.; Arif, A. M.; Ziegler, M. L.; Ernst, R. D. *Angew. Chem.* **1988**, *100*, 1132. (h) Gedridge, R. W.; Patton, A. T.; Ernst, R. D.; Ma, H. *J. Organomet. Chem.* **1987**, *331*, 73. (i) Stahl, L.; Ma, H.; Ernst, R. D.; Hyla-Kryspin, I.; Gleiter, R.; Ziegler, M. L. *J. Organomet. Chem.* **1987**, *326*, 257. (j) Han, J. C.; Hutchinson, J. P.; Ernst, R. D. *J. Organomet. Chem.* **1987**, *321*, 329. (k) Freeman, J. W.; Wilson, D. R.; Ernst, R. D.; Smith, P. D.; Klendworth, D. D.; McDaniel, M. P. *J. Polym. Sci., Part A: Polym. Chem.* **1987**, *25*, 2063. (l) Kralik, M. S.; Rheingold, A. L.; Ernst, R. D. *Organometallics* **1987**, *6*, 2612. (m) Newbound, T. D.; Freeman, J. W.; Wilson, D. R.; Kralik, M. S.; Patton, A. T.; Campana, C. F.; Ernst, R. D. *Organometallics* **1987**, *6*, 2432. (n) Newbound, T. D.; Ernst, R. D. *J. Organomet. Chem.* **1986**, *316*, 213. (o) Stahl, L.; Ernst, R. D. *J. Am. Chem. Soc.* **1987**, *109*, 5673. (p) Kowaleski, R. M.; Basolo, F.; Trogler, W. C.; Gedridge, R. W.; Newbound, T. D.; Ernst, R. D. *J. Am. Chem. Soc.* **1987**, *109*, 4860. (q) Ernst, R. D.; Ma, H.; Sergeson, G.; Zahn, T.; Ziegler, M. L. *Organometallics* **1987**, *6*, 848. (r) Ma, H.; Weber, P.; Ziegler, M. L.; Ernst, R. D. *Organometallics* **1987**, *6*, 854. (s) Ma, H.; Weber, P.; Ziegler, M. L.; Ernst, R. D. *Organometallics* **1986**, *5*, 2009. (t) Kowaleski, R. M.; Basolo, F.; Trogler, W. C.; Ernst, R. D. *J. Am. Chem. Soc.* **1986**, *108*, 6046–6048. Leading references from Bleeke's group: (u) Bleeke, J. R.; Rauscher, D. J. *Organometallics* **1988**, *7*, 2328–2339. (v) Bleeke, J. R.; Donaldson, A. J. *Organometallics* **1988**, *7*, 1588. (w) Bleeke, J. R.; Hays, M. K.; Wittenbrink, R. J. *Organometallics* **1988**, *7*, 1417. (x) Bleeke, J. R.; Rauscher, D. J.; Moore, D. A. *Organometallics* **1987**, *6*, 2614. (y) Bleeke, J. R.; Hays, M. K. *Organometallics* **1987**, *6*, 1367–1369. (z) Bleeke, J. R.; Hays, M. K. *Organometallics* **1987**, *6*, 486–491. (aa) Bleeke, J. R.; Kotyk, J. J.; Moore, D. A.; Rauscher, D. J. *J. Am. Chem. Soc.* **1987**, *109*, 417. (bb) Bleeke, J. R.; Donaldson, A. J. *Organometallics* **1986**, *5*, 2401. (cc) Bleeke, J. R.; Moore, D. A. *Inorg. Chem.* **1986**, *25*, 3522. (dd) Bleeke, J. R.; Stanley, G. G.; Kotyk, J. J. *Organometallics* **1986**, *5*, 1642. (ee) Bleeke, J. R.; Peng, W. J. *Organometallics* **1986**, *5*, 635. (ff) Bleeke, J. R.; Kotyk, J. J. *Organometallics* **1985**, *4*, 194.

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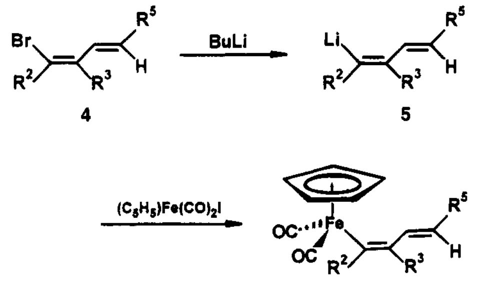
**Scheme 1**



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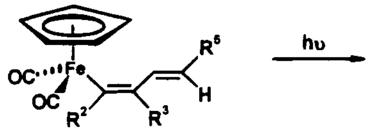
1a $R^2$=H, $R^3$=H, $R^5$=$CH_3$
1b $R^2$=H, $R^3$=H, $R^5$=Ph
1c $R^2$=Ph, $R^3$=H, $R^5$=Ph
1d $R^2$, $R^3$ = -$CH_2CH_2CH_2$-, $R^5$=H
1e $R^2$, $R^3$ = -$CH_2CH_2CH_2$-, $R^5$=Ph
1f $R^2$, $R^3$ = -$CH_2CH_2CH_2CH_2$-, $R^5$=H
1g $R^2$, $R^3$ = -$CH_2CH_2CH_2CH_2$-, $R^5$=Ph

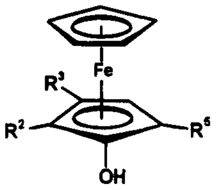
## Results

**Preparation and Structure of σ Complexes.** Starting ($\eta^5$-$C_5H_5$)Fe$(CO)_2$($\eta^1$-butadiene) complexes **1** (Scheme 1) were prepared in 25–35% yields by introduction of selected substituted butadienyllithiums to ($\eta^5$-$C_5H_5$)Fe$(CO)_2$I.[6] The butadienyllithium reactants **5** were prepared *in situ* from their respective bromobutadienes[7] **4** by low-temperature lithium–halogen exchange with either *n*-butyllithium or *tert*-butyllithium.[8] The transition-metal complexes **1** are air sensitive and were characterized as yellow to brown oils or solids.[9]

**Photochemistry of Butadienyl Complexes.** The extended photolysis of butadienyl complexes **1** led to the high-yield (≥95% based on starting material) generation of hydroxyferrocenes (eq 2). The yields of these conversions are not affected by the UV light source or solvent. $^1H$ NMR photolysis experiments in 5 mm sealed tubes were carried out using either a high-pressure 150 W Xe or 75 W Hg lamp in $CD_2Cl_2$ or THF-$d_8$, without significant differences in yield or reaction chemistry. Batch reactions in Pyrex vessels utilized either the above lamps or a 450 W medium-pressure Hg lamp in the solvents $CH_2Cl_2$, $CHCl_3$, $Et_2O$, and THF. In specific cases, the temperature did play a role in the observed product yield. For instance, whereas photolysis of the diphenyl complex **1c** did not show a temperature dependency on product yields at temperatures ranging from +25 to −78 °C, photolysis of **1b** was optimal at 0 °C. At very low temperatures (−78 °C) **1b** gave only [($\eta^5$-$C_5H_5$)Fe$(CO)_2$]$_2$ and unidentified organic products.



1a $R^2$=H, $R^3$=H, $R^5$=$CH_3$
1b $R^2$=H, $R^3$=H, $R^5$=Ph
1c $R^2$=Ph, $R^3$=H, $R^5$=Ph
1d $R^2$, $R^3$= -$CH_2CH_2CH_2$-, $R^5$=H
1e $R^2$, $R^3$= -$CH_2CH_2CH_2$-, $R^5$=Ph
1f $R^2$, $R^3$= -$CH_2CH_2CH_2CH_2$-, $R^5$=H
1g $R^2$, $R^3$= -$CH_2CH_2CH_2CH_2$-, $R^5$=Ph



(2)

| | | |
|---|---|---|
| 3a | $R^2$=H, $R^3$=H, $R^5$=$CH_3$ | 95% |
| 3b | $R^2$=H, $R^3$=H, $R^5$=Ph | 95% |
| 3c | $R^2$=Ph, $R^3$=H, $R^5$=Ph | 99% |
| 3d | $R^2$, $R^3$= -$CH_2CH_2CH_2$-, $R^5$=H | 99% |
| 3e | $R^2$, $R^3$= -$CH_2CH_2CH_2$-, $R^5$=Ph | 99% |
| 3f | $R^2$, $R^3$= -$CH_2CH_2CH_2CH_2$-, $R^5$=H | 99% |
| 3g | $R^2$, $R^3$= -$CH_2CH_2CH_2CH_2$-, $R^5$=Ph | 99% |

The yields given in eq 2 for the hydroxyferrocene products were determined in sealed NMR tubes by $^1H$ NMR integration using an internal standard. The yields of compounds **3a–c** represent overall yields, whereas compounds **3d–g** are percent conversion yields based on remaining starting butadienyl complex (overall yields ca. 50%). Further purification of these products were attempted but were unsuccessful in our hands. In most cases, removal of the solvent gave oils and attempted purifications by chromatography (silica gel, alumina, or preparatory reverse phase HPLC) were unsuccessful.

**Limits of Conversion.** Although these conversions are general for many ($\eta^5$-$C_5H_5$)Fe$(CO)_2$($\eta^1$-butadienyl) complexes, one class of compounds did not follow this reaction path. Specifically, when the butadienyl ligand is annelated with aromatic moieties (compounds **6–8**), the formation of hydroxyferrocenes is not observed.

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(2) Yongskulrote, W.; Bramlett, J. M.; Mike, C. A.; Durham, B.; Allison, N. T. *Organometallics* **1989**, *8*, 556.

(3) Oxapentadienyl complexes, homologs of pentadienoyl complexes, have been reported; cf.: Cheng, M. H.; Cheng, C. Y.; Wang, S. L.; Peng, S. M.; Liu, R. S. *Organometallics* **1990**, *9*, 1853.

(4) Pentadienoyl complex intermediates have been proposed in reactions with other transition-metal systems. For instance, pentadienoyl complexes of chromium were suggested as intermediates that give cyclopentenones; cf.: (a) Turner, S. U.; Herndon, J. W.; McMullen, L. A. *J. Am. Chem. Soc.* **1992**, *114*, 8394. (b) Harvey, D. F.; Lund, K. P.; Neil, D. A. *J. Am. Chem. Soc.* **1992**, *114*, 8424.

(5) Photolysis of ($\eta^1$-pentadienyl)Fe$(CO)_2$($\eta^5$-$C_5H_5$) complexes has been reported; cf.: Lee, G. H.; Peng, S. M.; Lush, S. F.; Liao, M. Y.; Liu, R. S. *Organometallics* **1987**, *6*(10), 2094–2099.

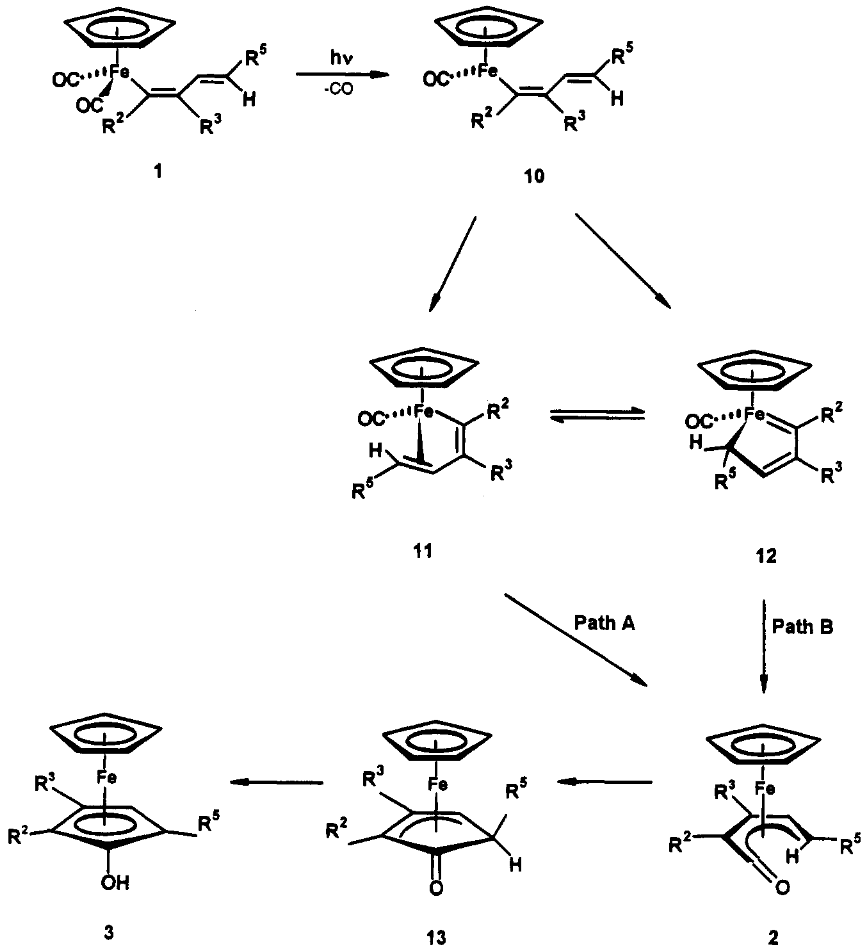
(6) King, R. B.; Stone, F. G. A. *Inorg. Synth.* **1963**, *3*, 110.

(7) Reaction of crotonaldehyde and cinnamaldehyde with $Ph_3P$=CHBr generates (1*Z*,3*E*)-1-bromopentadiene (**4a**) and (1*Z*,3*E*)-1-bromo-4-phenylbutadiene (**4b**), respectively; cf.: Matsumoto, M.; Kuroda, K. *Tetrahedron Lett.* **1980**, *21*, 4021. (1*Z*,3*E*)-1-Bromo-1,4-diphenylbutadiene was prepared by lithium halogen exchange of a single Br in (1*Z*,3*Z*)-1,4-dibromo-1,4-diphenylbutadiene (**4c**) (cf.: Weyenberg, D. R.; Toporcer, L. H.; Bey, A. E. *J. Org. Chem.* **1965**, *30*, 4096. Atwell, W. H.; Weyenberg, D. R.; Gilman, H. *J. Org. Chem.* **1967**, *32*, 885) followed by quenching with water. The cyclopentene- and cyclohexene-annelated bromobutadienes **4d–g** were prepared from reaction of selected $Ph_3P$=CHR reagents with the bromo-cyclopentene and cyclohexene aldehydes (Arnold, Z.; Holy, A. *Collect. Czech. Chem. Commun.* **1961**, *26*, 3059). Reference for the preparation of 1-bromo-2-(2-phenylethenyl)cyclopentene (**4e**): Sharp, J. T.; Robertson, I. R. *Tetrahedron* **1984**, *40*, 3095.

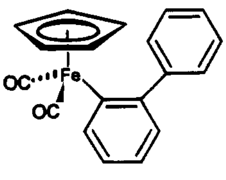
(8) (a) Neumann, H.; Seebach, D. *Chem. Ber.* **1978**, *111*, 2785. (b) Neumann, H.; Seebach, D. *Tetrahedron Lett.* **1976**, *18*, 4839–4842. (c) Kobrich, G.; Trapp, H. *Chem. Ber.* **1966**, *99*, 680.

(9) Where appropriate, the *cis* geometry of the alkene moiety **1** was determined by the coupling constants of vinylic hydrogens. For instance, in compound **1a** $J_{12}$ = 9 Hz (*Z* stereochemistry). In compounds **1d–g** $J_{34}$ = 17.5, 16, 18, and 16 Hz, respectively (*E* stereochemistry in the nonannelated double bond). For compound **1c**, where analysis of geometry by coupling constants could not be determined, the stereochemistry was analyzed by X-ray crystallography: Cordes, A. W.; Graham, J. University of Arkansas, private communication.

**Scheme 2**



Compound **6** was photoinactive and only [($\eta^5$-$C_5H_5$)Fe(CO)$_2$]$_2$ and unidentified organic products were produced, presumably via radical processes,[10] when compounds **7** and **8** were photolyzed.



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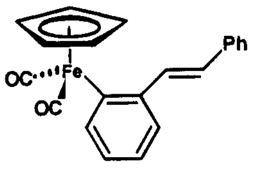

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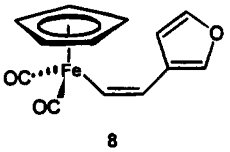

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## Discussion

**Mechanism of Reaction.** A mechanism for the conversion of **1** to **3** is shown in Scheme 2. Analogous loss of a terminal carbonyl and formation of the 16-electron unsaturated intermediate **10** is followed by formation of the $\eta^3$-butadienyl complex **11** or metallacyclopentadiene **12**. The incorporation of a CO moiety into the incipient pentadienoyl ligand can be viewed as occurring either by an alkyl migration/CO insertion mechanism (path A) or by a CO–carbene ligand coupling (path B)[11] from the metallacyclopentadiene **12**.[12] Electrocyclic ring closure of the pentadienoyl complex **2** to give **13**[13] followed by enol–keto tautomerization forms the hydroxyferrocene product **3**.[14–16]

**Detection of Intermediates.** In order to probe the mechanism of this process, we studied the photolysis of complex **1c**, which was determined by $^1$H NMR to quantitatively convert to **3c**. Key in this process is the

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[10] Bartz, J. A.; Barnhart, T. M.; Galloway, D. B.; Huey, L. G.; Glenewinkel-Meyer, T.; McMahon, R. J.; Crim, F. F. *J. Am. Chem. Soc.* **1993**, *115*, 8389 and references cited therein.

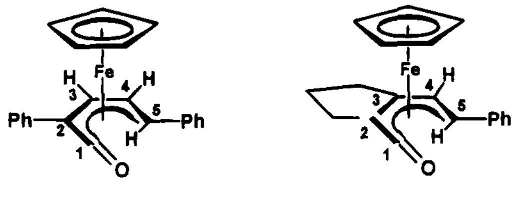
[11] Schore, N. E. *Chem. Rev.* **1988**, *88*, 1081–1119. See also ref 16.

[12] Metallacyclopentadienes have been observed in ($\eta^5$-$C_5H_5$)Fe(CO)$_2$ chemistry by Jones and co-workers; cf.: (a) Stenstrøm, Y.; Koziol, A. E.; Palenik, G. J.; Jones, W. M. *Organometallics* **1987**, *6*, 2079. (b) Stenstrøm, Y.; Klauck, G.; Koziol, A.; Palenik, G. J.; Jones, W. M. *Organometallics* **1986**, *5*, 2155.

[13] Precedent for intermediates similar to **13** is found in reactions reported as early as two decades ago by Heck. In his studies, reaction of Co(CO)$_4^-$ with sorbyl chloride followed by addition of PPh$_3$ gave a (CO)$_2$(PPh$_3$)Co(cyclopentenoyl) complex: (a) Heck, R. F.; Breslow, D. S. *J. Am. Chem. Soc.* **1961**, *83*, 1097. (b) Heck, R. F. *J. Am. Chem. Soc.* **1963**, *85*, 3387. (c) Heck, R. F. *Adv. Organomet. Chem.* **1966**, *4*, 243.

[14] Ring closures of parent pentadienyl complexes that do not incorporate a terminal carbonyl have been observed but are not common; cf.: (a) Mann, B. E.; Manning, P. W.; Spencer, C. M. *J. Organomet. Chem.* **1986**, *312*, C64. (b) Kirss, R. U. *Organometallics* **1992**, *11*, 497. Reaction of ($\eta^5$-$C_5H_5$)Fe(CO)$_2$CH$_3$ with 2 equiv of diphenylacetylene gives tetraphenylferrocene, presumably via a pentadienyl intermediate; cf.: (c) Heck, R. F. *Organotransition Metal Chemistry, A Mechanistic Approach*; Academic Press: New York, 1974; p 184. (d) Nakamura, A. *Mem. Inst. Sci. Ind. Res., Osaka Univ.* **1962**, *19*, 81. (e) Nakamura, A. *Chem. Abstr.* **1963**, *59*, 8786.

[15] For a discussion of transition-metal-mediated electrocyclic ring closures cf.: Pinhas, A. R.; Carpenter, B. K. *J. Chem. Soc., Chem. Commun.* **1980**, 15. Pinhas, A. R.; Carpenter, B. K. *J. Chem. Soc., Chem. Commun.* **1980**, 17.



2c 2e

**Figure 1.**

photochemical loss of a terminal carbonyl. Photolysis of **1c** at 77 K in a methylcyclohexane glass resulted in loss of the carbonyl absorptions of **1c** at 1964 and 2003 cm$^{-1}$ with concomitant appearance of an absorption at 1944 cm$^{-1}$.[17] This is consistent with loss of CO and formation of the 16-electron coordinatively unsaturated intermediate **10c**.[18] Compound **10c** was also effectively trapped by photolysis of **1c** in the presence of a 10-fold excess of phenyldimethylphosphine which gave ($\eta^1$-(1*Z*,3*E*)-1,4-diphenyl-1,3-butadienyl)($\eta^5$-$C_5H_5$)Fe(CO)-$PPhMe_2$ (**9**) in 62% yield.[19]

At higher temperatures, spectroscopic evidence for the pentadienoyl complex **2** was obtained. When **1c** was photolyzed in $CH_2Cl_2$ at −78 °C and the IR absorptions were monitored, a band at 1720 cm$^{-1}$, which is attributed to the carbonyl group in the pentadienoyl complex **2c** (Figure 1), was detected. In this same temperature range, the $^1$H NMR of **2c** was also investigated. Compound **1c** was sealed in an NMR tube ($CD_2Cl_2$) and photolyzed at −78 °C. At this temperature the absorptions of **2c** were broad due to viscosity effects; however, at −40 °C the resonances are reasonably sharp, although the pentadienoyl complex **2c** slowly converted to the hydroxyferrocene product **3c**. The pentadienoyl ligand proton absorptions of **2c** (Figure 1) at $\delta$ 6.54 ppm (2H, m, H(3), H(4)) and at $\delta$ 0.2 ppm (1H, m, H(5)) are attributed to an ABX pattern.[20]

Two pathways for pentadienoyl complex formation from the coordinatively unsaturated intermediate **10** are shown in Scheme 2. Path A depicts the pentadienoyl complex **2** being formed by a CO insertion reaction with concomitant geometric reorganization for the pentadienyl unit. Path B dictates that a metallacyclopentadiene complex is formed either directly from **10** or from **11**, followed by a carbene−carbonyl coupling reaction. Both paths have ample precedent.[11,16] Furthermore, interconversion between **11** and **12** is also possible as shown in this scheme.

It is interesting to note that, under our photolysis conditions at low temperature, complete conversion of **1c** to **2c** could not be obtained; however, at higher temperatures which allow the thermal conversion of **2c** to proceed to the product hydroxyferrocene **3c**, complete conversion is observed. These data indicate that the pentadienoyl intermediate **2c**, but not the product **3c**, efficiently quenches the photoreaction. The pentadienoyl complex **2c** was completely photostable at low temperatures.

The pentadienoyl intermediate **2e** (Figure 1), prepared from photolysis of butadienyl complex **1e**, was more robust (*vide supra*) and at room temperature allowed spectroscopic monitoring at ambient temperatures. $^1$H NMR (500 MHz, THF-$d_8$) of the pentadienoyl ligand in compound **2e** exhibits an AX splitting pattern for the protons at $\delta$ 6.605 ppm (1H, HC(4)) and $\delta$ −0.168 ppm (1H, H(5)), with $J_{45}$ = 8.3 Hz.[21] In the IR spectrum, a carbonyl absorption is observed at 1728 cm$^{-1}$ ($CH_2Cl_2$) which is similar to that observed for **2c**, discussed above, and similar to those found in some vinylketene complexes.[22,23] The $^{13}$C NMR (THF-$d_8$) was obtained at room temperature and gave a carbonyl carbon absorption at $\delta$ 238.9 ppm.[24]

As stated above, the disappearance of the pentadienyl complex with concomitant formation of hydroxyferrocene is observed at room temperature for **2e**. A mechanism consistent with this transformation is bond formation between the terminal pentadienoyl carbon atoms to give the cyclopentenoyl complex **13** followed

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[16] Reactions of chromium carbene complexes with acetylenes lead to cyclization giving phenols where keto−enol tautomerization is thought to follow C−C bond formation; cf.: (a) Boger, D. L.; Jacobson, I. C. *J. Org. Chem.* **1990**, *55*, 1919. (b) Yamashita, A. *J. Am. Chem. Soc.* **1988**, *107*, 5823. (c) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 644. (d) Dötz, K. H.; Dietz, R. *Chem. Ber.* **1978**, *111*, 2517. (e) Dötz, K. H.; Popall, M. *Tetrahedron* **1985**, *41*, 5797. (f) Padwa, A.; Xu, S. L. *J. Am. Chem. Soc.* **1992**, *114*, 5881. (g) Semmelhack, M. F.; Bozell, J. J.; Keller, L.; Sato, T.; Spiess, E. J.; Wu, W.; Zask, A. *Tetrahedron* **1985**, *41*, 5803. (h) Wulff, W. D.; Peterson, G. A.; Kunng, F.-A.; McCallum, J. S.; Wulff, W. D.; Xu, Y.-C. *Tetrahedron* **1987**, 1381. (i) Wulff, W. D. In *Advances in Metal-Organic Chemistry*; Liebeskind, L. S., Ed.; JAI Press: Greenwich, CT, 1989; Vol. 1. (j) Wulff, W. D.; McCallum, J. S.; Kunng, F.-A.; Gilbertson, S. R.; Wulff, W. D. *Organometallics* **1988**, *7*, 2346. (k) Wulff, W. D. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: New York, 1990; Vol. 5.

[17] Brinkman, K. C.; Blakeney, A. J.; Krone-Schmidt, W.; Gladysz, J. A. *Organometallics* **1984**, *3*(9), 1325−1332.

[18] The photolysis of $CpFe(CO)_2$benzyl gives a carbonyl absorption of 1938 cm$^{-1}$ from the 16-electron coordinatively unsaturated intermediate CpFe(CO)benzyl; cf.: Blaha, J. P.; Wrighton, M. S. *J. Am. Chem. Soc.* **1985**, *107*, 2694−2702. The possible metallacyclopentadiene intermediate may be ruled out from the carbonyl stretching frequency observed by Jones et al. for an ($\eta^5$-$C_5H_5$)(CO)aminoferracyclopentene at 1885 cm$^{-1}$.[12]

[19] In sealed-tube $^1$H NMR experiments, we determined that **9** was the only detected product.

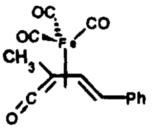
[20] Computer simulation of these data with the LAOCOON3 computer program gave the following coupling constant and shift data: $H_A$, $\delta$ 6.53 ppm; $H_B$, $\delta$ 6.55 ppm; $H_X$, $\delta$ 0.02 ppm; $J_{AB}$ = 5.6 Hz, $J_{AX}$ = −0.7 Hz, $J_{BX}$ = 8.2 Hz. For LAOCOON3 cf.: Bothner-By, A. A.; Castellano, S. In *Computer Programs for Chemistry*; DeTar, D. F., Ed.; Benjamin: New York, 1968; Vol. 1, Chapter 3; Program QCPE 111 from Quantum Chemistry Program Exchange, Bloomington, IN. The IBM-PC modified program by M. Clark and J. S. Thrasher (QCMP 013) was used.

[21] The high-field proton signal is similar to those found in pentadienyl complexes.[5]

[22] Mitsudo and co-workers have observed vinylketene complex absorptions for [$\eta^6$-O=C=C(OMe)C($CO_2$Me)=CHR]$Fe(CO)_3$ at 1740 cm$^{-1}$ ($CHCl_3$) and 1728 cm$^{-1}$ (KBr): Mitsudo, T.; Watanabe, H.; Sasaki, T.; Takegami, Y.; Watanabe, Y.; Kafuku, K.; Nakatsu, K. *Organometallics* **1989**, *8*, 368.

[23] A nonplanar acyl−butadiene complex, formed from **1** by migration of the butadienyl ligand to a terminal carbonyl, may represent an intermediate leading to the planar pentadienoyl complex. Evidence that the pentadienoyl ligands in **2** are indeed planar is given by the IR acyl absorptions at 1720 and 1728 cm$^{-1}$ for **2c** and **2e**, respectively. In contrast, $CpFe(CO)_2$(acyl) absorptions appear at 1650 cm$^{-1}$; cf.: (a) Green, M. L. H.; Hurley, C. R. *J. Organomet. Chem.* **1967**, *10*, 188. (b) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

[24] It is interesting to contrast this resonance with that of ($\eta^4$-4-phenylvinylketene)$Fe(CO)_3$, where the carbonyl carbon absorption is centered at $\delta$ 234.6 ppm. Also, similarity of the chemical shift of the phenyl ipso group in the vinylketene complex



at 138.0 ppm is comparable to that of compound **2e** at 145.4 ppm; cf.: Alcock, N. W.; Richards, C. J.; Thomas, S. E. *Organometallics* **1991**, *10*, 231−238.

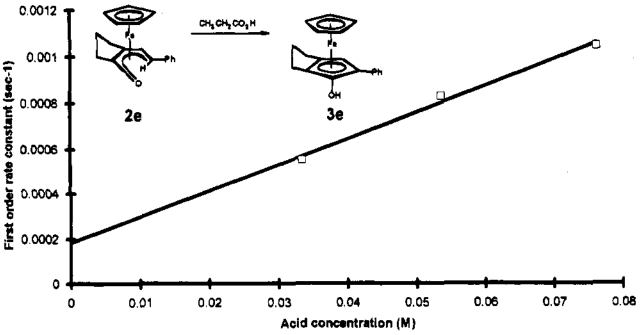
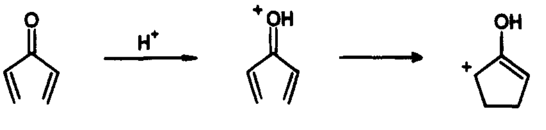


**Figure 2.** First-order rate dependency of the pentadienoyl complex ring closure **2e** to **3e** with propionic acid in THF-$d_8$. Rate constants are as follows: $[CH_3CH_2CO_2H] = 3.35 \times 10^{-2}$ M, $k = (5.51 \pm 0.09) \times 10^{-4}$ s$^{-1}$; $[CH_3CH_2CO_2H] = 5.36 \times 10^{-2}$ M, $k = (8.3 \pm 0.3) \times 10^{-4}$ s$^{-1}$; $[CH_3CH_2CO_2H] = 7.6 \times 10^{-2}$ M, $k = (10.4 \pm 0.2) \times 10^{-4}$ s$^{-1}$.

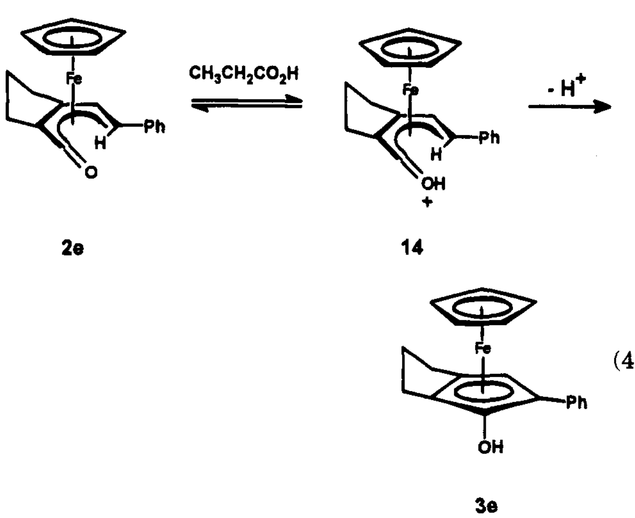
by keto–enol tautomerization as depicted in Scheme 2.[13,14]

**Electrocyclic Ring Closure Dependence on Acid Concentration.** The ring closure, which is dependent on a carbonyl at the terminal position in the pentadienyl chain, is similar to the Nazarov cyclization used in synthetic organic chemistry (eq 3).[25] Here dienones form five-membered rings via acid catalysis.



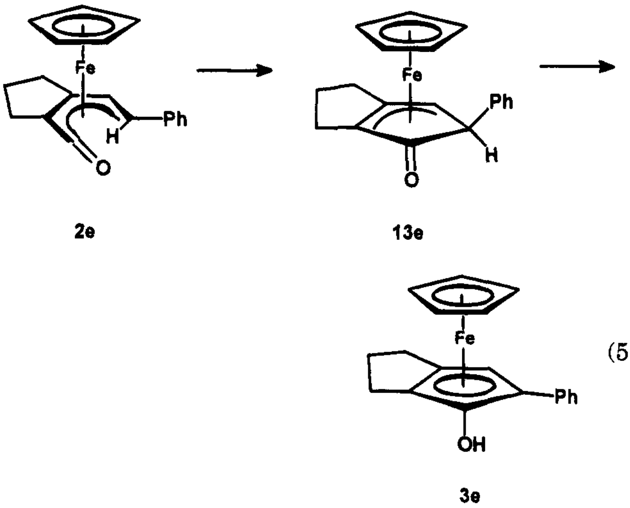
(3)

We have initiated a kinetic study of the ring closure of pentadienoyl complex **2e** and found that the rate of ring closure in our pentadienoyl complexes does follow a first-order rate law.[26] The addition of acid to pentadienoyl complex **2e** does catalyze the transition-metal-mediated pentadienoyl ring closure. The kinetic study, in which the disappearance of **2e** was monitored by $^1$H NMR, showed the first-order rate constant to be dependent on the acid concentration as indicated in Figure 2, which shows the linear correlation of added propionic acid with the rate of disappearance of the pentadienoyl complex **2e**. We conclude from this observation that ring cyclization in **2e** is accelerated via protonation of the carbonyl carbon to give intermediate **14** as shown in eq 4.

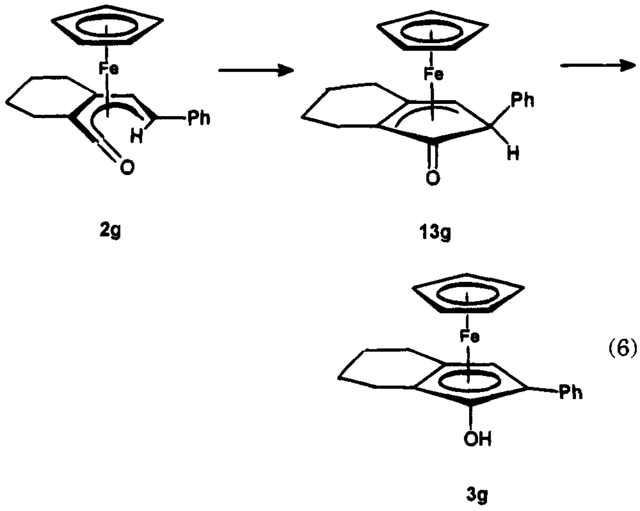


(4)

**Electronic and Structural Factors Influencing the Rate of Conversion of Ring-Annelated Pentadienoyl Complexes.** As noted above, pentadienoyl complex **2e** is kinetically more robust than the parent cyclopentene-annelated complex **2d** and the cyclohexene-annelated complexes **2f,g**. These last three complexes are not observed at room temperature. We suggest that a contributing factor in the kinetic stability difference between cyclopentene complex **2e** *vs* cyclohexene complex **2g** is a difference in increasing ring strain associated with each ring closure. Specifically, in the transition state, the cyclopentene-annelated pentadienoyl complex **2e** must convert to a bicyclo[3.3.0]-octenonyl system (**13e**) whereas the cyclohexene-annelated pentadienoyl complex **2g** must convert to a less strained bicyclo[3.4.0]nonenonyl system (**13g**), as shown in eqs 5 and 6, respectively.



(5)



(6)

In order to shed some light on these differences, we calculated using MM2 parameters the difference in

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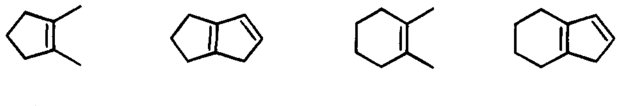
(25) For leading references, cf.: (a) Denmark, S. E. Nazarov and Related Reactions. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: New York, 1991; Vol. 5, Section 6.3, p 751. (b) Lavallee, J. F.; Spino, C.; Ruel, R.; Hogan, K. T.; Deslongchamps, P. *Can. J. Chem.* **1992**, *70*, 1406. (c) Michael, J. P.; Zwane, M. I. *Tetrahedron Lett.* **1992**, *33*, 4755. (d) Franck-Neumann, M.; Miesch, M.; Gross, L. *Tetrahedron Lett.* **1992**, *33*, 3879. (e) Kang, H. T.; Kim, S. S.; Lee, J. C.; U., J. S. *Tetrahedron Lett.* **1992**, *33*, 3495. (f) Pasto, D. J.; Yang, S. H.; Muellerliele, J. A. *J. Org. Chem.* **1992**, *57*, 2976.

(26) The rate constants were determined to be independent of the concentration of **2e**.



15 16 17 18

**Figure 3.**

strain energies in **15** and **16** vs that in **17** and **18** (Figure 3). This difference is 8 kcal/mol,[27] which is consistent with compound **2e** $^1H$ NMR being observed at ambient temperature vs compound **2g** at −50 °C.[28] Strain energy differences are not, however, solely responsible for the slow ring closure reaction in **2e**. If this were the case, **2d** would convert to product at a rate similar to that for **2e**, when, in fact **2d** is significantly faster. This rate difference can be explained in terms of the relative stabilities of the starting pentadienoyl complexes **2d** *vs* **2e**. The lack of conjugation of the phenyl group with the formally anionic pentadienoyl ligand in **2d** raises its energy level relative to **2e** concomitant with a lower activation energy in the conversion of **2d** to **3d** *vs* that of **2e** to **3e**.

## Conclusions

A systematic study of ($\eta^5$-$C_5H_5$)Fe(CO)$_2$(1,3-butadienyl) complexes shows that, with the exception of aromatic annelated butadienyl ligands, substituted hydroxyferrocenes are formed in high yields. A study of the mechanism of this conversion implicates photochemical loss of a terminal CO from the starting material, followed by thermal formation of an intermediate pentadienoyl complex. Subsequent transition-metal-mediated electrocyclic ring closure gives the hydroxyferrocene product. This electrocyclic closure is catalyzed by acid and the rate of ring closure is influenced by ring strain and electronic factors.

## Experimental Section

**General Information.** Reactions and workup procedures on organometallic compounds were performed using standard Schlenk techniques under a nitrogen atmosphere. The nitrogen was passed through an oxygen scrubber (Catalyst R3-11, Chemical Dynamics Corp.) and dried by a column of anhydrous calcium sulfate. Diethyl ether and tetrahydrofruan were distilled immediately before use from sodium benzophenone ketyl under an inert atmosphere. Pentane used in reaction mixtures was distilled from phosphorus pentoxide after washing sequentially with concentrated sulfuric acid, aqueous sodium bicarbonate, and water followed by predrying over calcium chloride.

Low-temperature reactions were performed at −78 °C in a 2-propanol/dry ice or a 2-propanol/liquid nitrogen bath and at −120 °C by a 4:1:1 petroleum ether (boiling range 60−90 °C)/acetone/pentane bath with liquid nitrogen. All reaction temperatures were monitored utilizing a Type J thermocouple thermometer (Omega Model 650).

Neutral alumina (95+%, 60 mesh; Alfa) and silica gel (60−200 mesh; Baker) were used as supplied. The alumina was used in different grades by the addition of 3%, 6%, or 10% water at least 24 h prior to chromatography, which was performed under an inert atmosphere.[29] Zinc silicate was added to the silica gel as an indicator (1 wt %) in order to visualize the colorless fractions by use of a ultraviolet lamp.

NMR spectra were collected on a Varian EM-360 spectrometer, a JEOL FX-90Q spectrometer, or a Varian XT-500 instrument. Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 283 or a Nicolet 205 spectrometer either in solution or as a thin film. Low-resolution mass spectra were obtained on a Hewlett-Packard 5980A mass spectrometer. High-resolution mass spectra (HREIMS) were obtained from the Midwest Center for Mass Spectrometry, University of Nebraska—Lincoln, Lincoln, NE 68588-0362. Elemental analysis was done by Atlantic Microlab, Inc., P.O. Box 2288, Norcross, GA 30091.

**($\eta^5$-Cyclopentadienyl)($\eta^1$-(1*Z*,3*E*)-penta-1,3-dienyl)dicarbonyliron (1a).** A Schlenk flask equipped with a septum, stirbar, and cold bath was charged with 1.56 g (10.6 mmol) of (1*Z*,3*E*)-1-bromo-1,3-pentadiene (**4a**)[7] and 90 mL of 4:1:1 THF/$Et_2O$/*n*-$C_5H_{12}$. The mixture was then cooled to −120 °C (4:1:1 petroleum ether/acetone/2-propanol in liquid nitrogen bath), and *tert*-butyllithium (12.4 mL, 21.2 mmol, 1.7 M in pentane)[8] was added dropwise over 25 min. After the mixture was stirred for 1.3 h, a solution of 3.22 g (10.6 mmol) of ($\eta^5$-$C_5H_5$)-Fe(CO)$_2$I in 90 mL of THF was added while the above cold solution's temperature was maintained lower than −110 °C. The solution was stirred cold for an additional 1 h. Removal of the solvent *in vacuo* and chromatography on neutral alumina (2.5 cm × 60 cm), eluting first with pentane and then gradually increasing the polarity of the eluent with diethyl ether, gave a second yellow band (8% diethyl ether) yielding 1.329 g (51%) of ($\eta^5$-cyclopentadienyl)($\eta^1$-(1*Z*,3*E*)-penta-1,3-dienyl)dicarbonyliron as a yellow oil. $^1H$ NMR (60 MHz, $CDCl_3$): $\delta$ 6.90 (dd, $J_{23}$ = 10 Hz, $J_{12}$ = 9 Hz, 1H, C(2)—H), 6.52 (d, $J$ = 9 Hz, 1H, C(1)—H), 6.23−5.07 (m, 2H, C(3)—H and C(4)—H), 4.80 (s, 5H, $\eta^5$-$C_5H_5$), 1.75 (d, $J_{45}$ = 6 Hz, 3H, $CH_3$). $^{13}C\{^1H\}$ NMR (22.5 MHz, $CDCl_3$): $\delta$ 215.8 (CO), 143.6, 133.6, 130.7, 128.1 (butadienyl carbons), 85.6 ($\eta^5$-$C_5H_5$), 18.5 ($CH_3$). IR ($CH_2Cl_2$): $\nu$ 1975, 2015 cm$^{-1}$ (CO). HREIMS: calcd for $C_{12}H_{12}FeO_2$ *m/z* 244.079, found 244.079.

**($\eta^5$-Cyclopentadienyl)($\eta^1$-(1*Z*,3*E*)-4-phenyl-1,3-butadienyl)dicarbonyliron (1b).** A Schlenk flask equipped with a rubber septum and stirbar was charged with 1.045 g (5.0 mmol) of (1*Z*,3*E*)-1-bromo-4-phenyl-1,3-butadiene (**4b**)[7] and 100 mL of a 4:1:1 mixture of THF/$Et_2O$/*n*-$C_5H_{12}$. The solution was then cooled to −120 °C (4:1:1 petroleum ether/acetone/2-propanol in liquid nitrogen bath), and *tert*-butyllithium (5.9 mL, 10.0 mmol, 1.7 M in pentane) was added over a period of 10 min. After it was stirred for 1 h, the mixture was warmed to −90 °C and a solution of 1.5 g (5.0 mmol) of ($\eta^5$-$C_5H_5$)Fe-(CO)$_2$I in 30 mL of diethyl ether was slowly added while the reaction mixture was maintained colder than −78 °C. The solution was stirred for 1 h at −90 °C and warmed to room temperature.

Removal of the solvent *in vacuo* and chromatography on neutral alumina (2.5 cm × 60 cm), eluting first with pentane and then gradually increasing the polarity of the eluent with deithyl ether and collecting the second yellow band (3% diethyl ether), gave 0.387 g (25%) of ($\eta^5$-cyclopentadienyl)($\eta^1$-(1*Z*,3*E*)-4-phenyl-1,3-butadienyl)dicarbonyliron as a yellow oil. $^1H$ NMR (90 MHz, $CDCl_3$): $\delta$ 7.42−6.59 (m, 8H, Ph, C(1)—H, C(2)—H, C(3)—H), 6.40 (d, $J_{34}$ = 15 Hz, 1H, C(4)—H), 4.89 (s, 5H, $C_5H_5$). $^{13}C\{^1H\}$ NMR (22.5 MHz, $CDCl_3$): $\delta$ 215.5 (CO), 143.8, 139.2, 138.6, 131.5, 131.1, 128.5, 126.5, 125.9 (phenyl and butadienyl carbons), 89.6 ($\eta^5$-$C_5H_5$). IR ($CH_2Cl_2$): $\nu$ 1975, 2025 cm$^{-1}$ (CO). HREIMS: calcd for $C_{17}H_{14}FeO_2$ *m/z* 306.034, found 306.034.

**($\eta^5$-Cyclopentadienyl)($\eta^1$-(1*Z*,3*E*)-1,4-diphenyl-1,3-butadienyl)dicarbonyliron (1c).** A Schlenk flask fitted with a septum and magnetic stirbar was charged with 0.598 g (2.10 mmol) of 1-bromo-1,4-diphenyl-1,3-butadiene (**4c**)[7] and 40 mL of diethyl ether. The solution was cooled to −10 °C, and *n*-butyllithium (1.0 mL, 2.6 mmol, 2.6 *M* in pentane) was added

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(27) Difference in SE = [(SE compound **16**) − (SE compound **15**)] − [(SE compound **18**) − (SE compound **17**)] with the strain energies being computed using the computer program PCMODEL (IBM PC version): Serena Software, P.O. Box 3076, Bloomington, IN 47402-3076.

(28) At this temperature **2g** slowly converts to product **3g**.

(29) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

dropwise. The mixture was stirred at −10 °C for an additional 15 min, warmed to room temperature, and then added to a cold (−78 °C) solution of 0.666 g (2.19 mmol) of ($\eta^5$-$C_5H_5$)Fe(CO)$_2$I in 50 mL of diethyl ether. The reaction mixture was stirred for an additional 30 min and warmed to room temperature. Chromatography on neutral alumina (60 mesh, 6% water, 1.2 × 40 cm), first eluting with pentane and then gradually increasing the polarity of the eluent with diethyl ether, gave a single yellow band (1% diethyl ether). Removal of the solvent *in vacuo* gave 0.43 g (1.12 mmol) of the title compound as a yellow solid in 54% yield. Mp: 134–136 °C. $^1$H NMR (60 MHz, acetone-$d_6$): $\delta$ 5.3 (s, 5H, $\eta^5$-$C_5H_5$), 6.62 (d, $J$ = 15 Hz, 1H, =CH−), 6.98 (d, $J$ = 9 Hz, 1H, =CH−), 7.25–7.65 (m, 6H, =CH−) and $C_6H_5$). $^{13}$C{$^1$H} NMR (22.6 MHz, acetone-$d_6$): $\delta$ 87.2 ($C_5H_5$), 125.2, 126.8, 127.0, 127.4, 128.4, 129.5, 132.2, 133.8, 139.6, 142.2, 156.5, 160.0 ($C_6H_5$ and =CH), 216.7 (CO). IR ($CH_2Cl_2$): $\nu$ 1970, 2003 cm$^{-1}$ (CO). HREIMS: calcd for $C_{17}H_{14}FeO_2$ *m/z* 382.066, found 382.058. MS (D/CI $NH_3$): *m/z* 382.9 (M + 1, $^{56}$Fe).

**($\eta^5$-Cyclopentadienyl)($\eta^1$-2-ethenyl-1-cyclopentenyl)dicarbonyliron (1d).** A Schlenk tube equipped with a stirbar, $N_2$ line, septum, and thermocouple was charged with 2.00 g (11.6 mmol) of 1-bromo-2-ethenylcyclopentene (**4d**)[7] in 50 mL of 4:1:1 THF/$Et_2O$/pentane. The solution was chilled to −120 °C, and *tert*-butyllithium (14.2 mL, 1.7 M in pentane, 24.2 mmol) was added slowly while the temperature was maintained below −110 °C. After the mixture was stirred for 80 min, during which time the solution turned from colorless to yellow, a solution of ($\eta^5$-$C_5H_5$)Fe(CO)$_2$I (3.67 g, 11.6 mmol) in 40 mL of the 4:1:1 solvent mixture was added over 5 min. The solution was maintained at −120 °C for 2 h. Chromatography was carried out on neutral alumina (6% water, 1.2 × 16 cm) by eluting with pentane and gradually increasing the polarity of the eluent with ethyl ether (5% ether). The second yellow band was collected, and removal of the solvent *in vacuo* gave an brown-red oil identified as the title compound (0.66 g, 2.4 mmol, 21% yield). $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 6.70 (dd, $J$ = 17.3 Hz, $J$ = 10.5 Hz, 2H, $H_x$), 4.98 (d, $J$ = 10.5 Hz, 1H, $H_a$), 4.97 (d, $J$ = 17.5 Hz, 1H, $H_b$) 4.8 (s, 5H, $\eta^5$-$C_5H_5$), 2.59 (m, 6H, cyclopentene). $^{13}$C{$^1$H} NMR (22.5 MHz, $CDCl_3$): $\delta$ 215.6 (CO), 149.8, 146.7, 137.5, 110.6 (vinyl), 85 ($\eta^5$-$C_5H_5$), 32.8, 52, 23.8 (cyclopentene). IR (film): $\nu$ 2021, 1967 cm$^{-1}$. LREIMS: *m/z* 270 (11, M$^+$), 242 (32, −1 CO), 215 (24), 214 (100, −2 CO), 213 (28), 212 (48), 199 (57), 148 (37), 122 (23), 121 (55), 86 (16), 84 (26), 56 (14). HREIMS; calcd for $C_{14}H_{14}FeO_2$ *m/z* 270.034 32, found 270.0329.

**($\eta^5$-Cyclopentadienyl)($\eta^1$-($E$)-2-(2-phenylethenyl)-1-cyclopentenyl)dicarbonyliron (1e).** A Schlenk tube equipped with a stirbar, $N_2$ line, septum, and thermocouple was charged with 1.0 g (4.0 mmol) of ($E$)-1-bromo-2-(2-phenylethenyl)cyclopentene (**4e**)[7] in 100 mL of THF. The solution was chilled to −78 °C, and *tert*-butyllithium (4.7 mL, 8.04 mmol, 1.7 M in pentane) was added. After the mixture was stirred for 1 h, a solution of ($\eta^5$-$C_5H_5$)Fe(CO)$_2$I (1.22 g, 4.02 mmol) in 40 mL of THF was added at a rate to maintain the reaction temperature below −70 °C. After this mixture was stirred for 5 h at low temperature and warmed to room temperature, the solvent was removed *in vacuo*. Grade 3 alumina was added and the solvent evaporated to coat the product on the alumina. Chromatography on neutral alumina (9% water, 1.2 × 16 cm), eluting with pentane and gradually increasing the polarity of the eluent with ether, gave a second yellow band (10% ether). Removal of the solvent *in vacuo* gave a yellow solid identified as the title compound (0.51 g, 1.5 mmol, 36% yield). Mp: 128–129 °C. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 7.41 (d, $J$ = 8 Hz, 2H, Ph), 7.29 (t, $J$ = 7.5 Hz, 2 H, Ph), 7.16 (d, $J$ = 16 Hz, 1H, vinyl), 7.12 (d, $J$ = 7.5 Hz, 1H, Ph), 6.33 (d, $J$ = 16 Hz, 1H, vinyl), 4.88 (s, 5H, $\eta^5$-$C_5H_5$), 2.64 (t, $J$ = 7.5 Hz, 2 H, cyclopentene), 2.56 (t, $J$ = 7.5 Hz, 2H, cyclopentene), 1.86 (quintet, $J$ = 7.5 Hz, 2H, cyclopentene). $^{13}$C{$^1$H} NMR (125 MHz, $CD_2Cl_2$): $\delta$ 215.5 (CO), 153.7, 146.4, 139.2, 130.2, 128.384, 126.0, 125.9, 125.6 (Ph and butadiene), 85.2 ($\eta^5$-$C_5H_5$), 52.7, 30.9, 24.0 (−$CH_2CH_2CH_2$−). IR (film): $\nu$ 2013, 1958 cm$^{-1}$ (CO). HREIMS: calcd for $C_{20}H_{18}FeO_2$ *m/z* 346.065 57, found 346.065 25. Anal. Calcd for $C_{20}H_{18}FeO_2$: C, 69.35; H, 5.24. Found: C, 69.29; H, 5.26.

**Table 1**

| complex | temp (°C) | time (min) | light source | yield (%) |
|---|---|---|---|---|
| **1a** | −10 | 90 | *a* | 95 |
| **1b** | 0 | 120 | *a* | 95 |
| **1c** | 0 | 90 | *a* | 95 |
| **1d** | 0 | 120 | *b* | 99 |
| **1e** | 0 | 120 | *b* | 99 |
| **1f** | 0 | 120 | *b* | 99 |
| **1g** | 0 | 120 | *b* | 99 |

[a] 150 W high-pressure Xe lamp. [b] 75 W high-pressure Hg lamp.

**($\eta^5$-Cyclopentadienyl)($\eta^1$-2-ethenyl-1-cyclohexenyl)dicarbonyliron (1f).** A Schlenk tube equipped with a stirbar, $N_2$ line, septum, thermocouple, and cold bath was charged with 0.76 g (4.1 mmol) of 1-bromo-2-ethenylcyclohexene (**4f**)[7] in 50 mL of THF and cooled to −78 °C. *tert*-Butyllithium (4.8 mL, 8.1 mmol, 1.7 M in pentane) was added dropwise, and the solution was then stirred for 1 h. A solution of ($\eta^5$-$C_5H_5$)Fe(CO)$_2$I (1.24 g, 4.07 mmol) in 40 mL of THF was added over 0.5 h followed by stirring for 5 h at −78 °C. Chromatography on neutral alumina (10% water, 0.6 × 38 cm), eluting with pentane and then gradually increasing the polarity of the eluent with ether, gave a second yellow band (10% ether). Collection of this band and removal of the solvent *in vacuo* gave a yellow oil (0.20 g, 0.70 mmol, 17% yield) identified as the title compound. $^1$H NMR (90 MHz, $CDCl_3$): $\delta$ 6.6 (dd, 1H, vinyl, $J$ = 18 Hz, $J$ = 10 Hz), 5.0–4.7 (m, 2H), 4.80 (s, 5H, $\eta^5$-$C_5H_5$), 2.56 (m, 2H, cyclohexene), 2.26 (m, 2H, cyclohexene), 1.60 (m, 4H, cyclohexene). $^{13}$C{$^1$H} NMR (125 MHz, $CD_2Cl_2$): $\delta$ 216.6 (CO), 150.0, 144.9, 140.4, 107.4 (vinyl), 86.3 ($\eta^5$-$C_5H_5$), 49.9, 29.7, 27.5, 23.8 (cyclohexene). LREIMS: *m/z* 284 (6), 283 (4), 256 (32), 255 (17), 228 (70), 227 (67), 226 (40), 199 (100), 198 (60), 162 (42), 160 (72), 159 (19), 121 (59). IR (film): $\nu$ 2005.7, 1949.8 cm$^{-1}$. HREIMS: calcd for $C_{15}H_{16}FeO_2$ *m/z* 284.049 97, found 284.049 19.

**($\eta^5$-Cyclopentadienyl)($\eta^1$-($E$)-2-(2-phenylethenyl)-1-cyclohexenyl)dicarbonyliron (1g).** A Schlenk tube equipped with a stirbar, septum, thermocouple, and cold bath was charged with 0.60 g (2.3 mmol) of ($E$)-1-bromo-2-(2-phenylethenyl)cyclohexene (**4g**)[7] and 50 mL of THF. The solution was cooled to −78 °C, and *tert*-butyllithium (2.7 mL, 4.6 mmol, 1.7 M in pentane) was added, followed by stirring for 1 h. To this solution was added over 30 min ($\eta^5$-$C_5H_5$)Fe(CO)$_2$I (0.69 g, 2.3 mmol) in 40 mL of THF. The solution was stirred for 5 h at −78 °C. Chromatography on alumina (10% water, 0.6 × 60 cm), eluting with pentane followed by gradually increasing the polarity of the eluent with ether, gave a second yellow band (15% ether). Removal of the solvent *in vacuo* gave **1g** as a yellow oil (0.71 g, 0.86 mmol, 38% yield). $^1$H NMR (90 MHz, acetone-$d_6$): $\delta$ 7.6–7.1 (m, 6H, Ph and vinyl), 6.43 (d, $J$ = 16 Hz, 1H, vinyl), 5.12 (s, 5H, $\eta^5$-$C_5H_5$), 2.72 (m, 2 H, cyclohexene), 2.40 (m, 2 H, cyclohexene), 1.66 (m, 4H, cyclohexene). $^{13}$C{$^1$H} (125 MHz, acetone-$d_6$): $\delta$ 217.1 (CO), 154, 140.5, 138, 128.8 (butadiene), 126, 122.9, 126.2, 128.6, 125.8 (Ph), 86.9 ($\eta^5$-$C_5H_5$) 49.9, 30.1, 27.3, 23.8 (cyclohexene). LREIMS: *m/z* 360 (2), 332 (21), 304 (47), 303 (100), 275 (18), 238 (17), 235 (19), 234 (65), 178 (25), 141 (20), 121 (33), 115 (21), 56 (31). IR (film): $\nu$ 2004.3, 1949.2 cm$^{-1}$. HREIMS: calcd for $C_{21}H_{20}FeO_2$ *m/z* 360.081 27, found 360.080 58.

**General Procedure for Photolysis of Butadienyl Complexes. Formation of Hydroxyferrocenes.** An oven-dried, $N_2$-purged 5 mm NMR tube was charged with compound **1** in $CD_2Cl_2$. The solution was freeze–pump–thaw-degassed thrice and then sealed with a flame under vacuum. The sample was placed in a non-silvered Dewar flask and was cooled to the temperature indicated in Table 1. With intermittent warming to room temperature to monitor NMR as well as to allow pentadienoyl intermediate **2** to convert, photolysis gave the desired hydroxyferrocene product **3**. For conversion of compounds **1a**−**c** to **3a**−**c**, respectively, the yields represent overall yields, compounds **1d**−**g** are percent conversion yields based on remaining starting butadienyl complex (overall yields ca. 50%).

**1-Hydroxy-2-methylferrocene (3a).** $^1$H NMR (60 MHz, $CD_2Cl_2$): $\delta$ 4.07 (s, 5H, $\eta^5$-$C_5H_5$), 3.85−3.60 (m, 3H, CH on substituted Cp), 3.40 (br s, 1H, OH), 2.00 (s, 3H, $CH_3$). $^{13}C\{^1H\}$ NMR (22.5 MHz, $CD_2Cl_2$): $\delta$ 121.9 (C−OH), 86.4 (C−$CH_3$), 69.9 ($\eta^5$-$C_5H_5$), 64.1, 59.4, 56.9 (CH on substituted Cp), 11.8 ($CH_3$). HREIMS: calcd for $C_{11}H_{12}FeO$ *m/z* 216.024, found 216.024.

**1-Hydroxy-2-phenylferrocene (3b).** $^1$H NMR (90 MHz, $CDCl_3$): $\delta$ 7.7−7.2 (m, 5H, $C_6H_5$), 4.24−3.90 (m, 3H, substituted Cp), 4.08 (s, 5H, $\eta^5$-$C_5H_5$), 3.67 (s, 1H, OH). $^{13}C\{^1H\}$ NMR (22.5 MHz, $CDCl_3$): $\delta$ 137.5, 128.4, 127.8, 126.2 ($C_6H_5$), 119.5 (C−OH), 74.6 (C−Ph), 70.4 ($C_5H_5$), 62.5, 60.7, 58.2 (CH on substituted Cp). HREIMS: calcd for $C_{16}H_{14}FeO$ *m/z* 278.039, found 278.039.

**1-Hydroxy-2,5-diphenylferrocene (3c).** $^1$H NMR (60 MHz, acetone-$d_6$): $\delta$ 8.05−7.48 (m, 10H, $C_6H_5$), 6.78 (br s, 1H, OH), 4.51 (s, 2H, −CH), 4.05 (s, 5H, $C_5H_5$). $^{13}C\{^1H\}$ NMR (22.6 MHz, acetone-$d_6$): $\delta$ 139.1, 128.8, 128.8, 126.7 ($C_6H_5$), 117.5 (C−OH), 77.2 (C−Ph), 72.6 ($\eta^5$-$C_5H_5$), 62.5 (CH on substituted Cp). HREIMS: calcd for $FeC_{22}H_{18}O$ *m/z* 354.070, found 354.064.

**2,3-(1,3-Propanediyl)-1-hydroxyferrocene (3d).** $^1$H NMR (90 MHz, $CD_2Cl_2$): $\delta$ 4.04 (s, 6H, substituted and unsubstituted Cp), 3.61 (s, 1H, substituted Cp), 3.52−3.26 (m, 1H, OH), 2.41−2.09 (m, 6H, cyclopentene). $^{13}C\{^1H\}$ NMR (125 MHz, $CD_2Cl_2$): $\delta$ 115.1 (C−OH), 89.2, 88.7, 82.2 (substituted Cp), 70.3 ($\eta^5$-$C_5H_5$) 58.8 (substituted Cp), 29.3, 26.4, 24.7 (cyclopentene $CH_2$). LREIMS: *m/z* 242 (100, M$^+$), 243 (24), 240 (19), 224 (16), 213 (14), 212 (21), 199 (15), 186 (23), 121 (65), 91 (16), 56 (25). HREIMS: calcd for $C_{13}H_{14}FeO$ *m/z* 242.039 36, found 242.038 83.

**2,3-(1,3-Propanediyl)-1-hydroxy-5-phenylferrocene (3e).** $^1$H NMR (90 MHz, $CDCl_2$): $\delta$ 7.8−7.68 (m, 5H, $C_6H_5$), 4.16 (s, 1H, substituted Cp), 3.97 (s, 5H, $\eta^5$-$C_5H_5$), 3.62 (br s, 1H, OH, verified by addition of $D_2O$ and peak disappearance), 2.52−2.2 (br m, 6H, cyclopentene $CH_2$). $^{13}C\{^1H\}$ NMR (22.5 MHz, $CD_2Cl_2$): $\delta$ 139.3 (*ipso* Ph), 128.5 (*ortho* Ph), 127.9 (*meta* Ph), 125.9 (*para* Ph), 113.4 (C−OH), 88.0, 83.3, 76.7, 54.8 (sub *m/z* Cp), 72.1 ($\eta^5$-$C_5H_5$), 29.2, 26.4, 25.0 (cyclopentene $CH_2$). LREIMS: *m/z* 318 (100, M$^+$), 319 (29), 290 (41), 289 (65), 287 (16), 262 (18), 223 (17), 222 (29), 166 (22), 165 (24), 121 (34), 56 (18). HREIMS: calcd for $C_{19}H_{18}FeO$ *m/z* 318.070 66, found 318.069 45.

**2,3-(1,4-Butanediyl)-1-hydroxyferrocene (3f).** $^1$H NMR (90 MHz, $CD_2Cl_2$): $\delta$ 4.21 (s, 7 H, substituted and unsubstituted Cp), 3.80 (s, 1H, OH), 2.80−1.25 (m, 8H, cyclohexane). $^{13}C\{^1H\}$ NMR (22.5 MHz, $CD_2Cl_2$): $\delta$ 118.4 (C−OH), 88.1, 80.1, 74, 57.5 (substituted Cp), 70.7 ($\eta^5$-$C_5H_5$), 24.9, 23.7, 23.5, 22.5 (cyclohexene $CH_2$). LREIMS: *m/z* 256 (100), 240 (29), 211 (27), 199 (37), 188 (25), 160 (30), 121 (88), 115 (37), 91 (37), 79 (34), 77 (32), 56 (59). HREIMS: calcd for $C_{14}H_{16}FeO$ *m/z* 256.055 01, found 256.0541.

**2,3-(1,4-Butanediyl)-5-phenyl-1-hydroxyferrocene (3g).** $^1$H NMR (90 MHz, $CD_2Cl_2$): $\delta$ 7.7−7.5 (multiplet, 2H, Ph), 7.4−7.1 (multiplet, 4H, Ph), 4.0 (s, 1H, substituted Cp), 3.8 (s, 5H, $\eta^5$-$C_5H_5$), 3.5 (s, 1H, OH), 2.8−2.2 and 1.8−1.3 (m, 4H, 4H, cyclohexene $CH_2$). $^{13}C\{^1H\}$ NMR (22.5 MHz, $CD_2Cl_2$): $\delta$ 138.9, 128.4, 127.8, 125.9 ($C_6H_5$), 116.4 (C−OH), 88.0, 79.4, 75.0, 58.6 (substituted Cp), 72.3 ($\eta^5$-$C_5H_5$), 24.6, 23.6, 23.4, 22.4 (cyclohexene $CH_2$). HREIMS: calcd for $C_{20}H_{20}FeO$ *m/z* 332.086 31, found 332.085 34.

**Photolysis of ($\eta^5$-Cyclopentadienyl)($\eta^1$-(*E*)-2-(2-phenylethenyl)-1-cyclopentyl)dicarbonyliron (1e). Observation of Pentadienoyl Intermediate 2e.** $\sigma$ complex **1e** was dissolved in $CD_2Cl_2$ and filtered through a plug of glass wool into a 5 mm NMR tube with a 2 in. extension of 8 mm glass tubing. After freeze−pump−thawing thrice, the tube was sealed and an initial spectrum taken. The solution was then photolyzed at 0 °C using a high-pressure 75 W Hg lamp, until approximately 50% conversion to the intermediate was observed (by $^1$H NMR). Absorptions assigned to the intermediate **2e** are as follows. $^1$H NMR (500 MHz, THF-$d_8$): $\delta$ 7.17 (d, $J$ = 7.69 Hz, 2H, *ortho* $C_6H_5$), 7.12 (t, $J$ = 7.41 Hz, 2H, *meta* $C_6H_5$), 6.98 (d, $J$ = 7.41 Hz, 1H, *para* $C_6H_5$), 6.61 (d, $J_{45}$ = 8.3 Hz, 1H, pentadienoyl ligand HC(4)), 4.18 (s, 5H, $\eta^5$-$C_5H_5$), 2.97 (m, 1H, saturated cyclopentene CH), 2.86 (m, 1H, saturated cyclopentene CH), 2.25 (m, 1H, saturated cyclopentene CH), 1.94 (m, 1H, saturated cyclopentene CH), 1.59 (m, 2H, saturated cyclopentene CH), −0.168 (d, $J_{45}$ = 8.3 Hz, 1H, pentadienoyl HC(5)). $^{13}C\{^1H\}$ NMR: $\delta$ 238.9 (C=O), 129.4, 126.9, 125.8 ($C_6H_5$), 83.6 ($\eta^5$-$C_5H_5$), 68 (C(2)), 98 (C(3)), 54, 50.6 (C(4) and C(5)), 33.2, 28.7, 24.6 ($CH_2$) ppm. IR (solution cell, $CH_2Cl_2$): $\nu$ 1728 cm$^{-1}$ (CO).

**Photolysis of ($\eta^1$-(1*Z*,3*E*)-1,4-Diphenyl-1,3-butadienyl)-($\eta^5$-cyclopentadienyl)dicarbonyliron (1c) in the Presence of Dimethylphenylphosphine. Preparation of ($\eta^5$-Cyclopentadienyl)($\eta^1$-(1*Z*,3*E*)-1,4-diphenyl-1,3-butadienyl)(dimethylphenylphosphine)carbonyliron (9).** A 100-mL Schlenk flask fitted with septum and magnetic stirbar was charged with 0.193 g (0.505 mmol) of ($\eta^1$-(1*Z*,3*E*)-1,4-diphenyl-1,3-butadienyl)($\eta^5$-cyclopentadienyl)dicarbonyliron, 20 mL of dichloromethane, and 1 mL (7 mmol) of dimethylphenylphosphine. The mixture was irradiated by a 450 W medium-pressure mercury lamp. The progress of the reaction was monitored by infrared spectroscopy. When the reaction was completed, the solvent was removed *in vacuo*. Chromatography on alumina (6% water, 0.6 × 53 cm), eluting with pentane and gradually increasing the polarity of the eluent with diethyl ether, gave a single orange band (5% ethyl ether). Removal of the solvent *in vacuo* gave 0.154 g (0.313 mmol) of an orange solid of the title compound in 62% yield. Mp: 68−70 °C. $^1$H NMR (90 MHz, acetone-$d_6$): $\delta$ 1.55, 1.65 (d, $CH_3$), 4.64 (d, $C_5H_5$), 6.2 (d, =CH), 6.9−7.3 (m, $C_6H_5$). $^{13}C\{^1H\}$ NMR (22.6 MHz, acetone-$d_6$): $\delta$ 17.4, 18.6, 18.9, 20.3 ($CH_3$), 84.4 ($C_5H_5$), 124.2, 126.3, 126.7, 127.3, 127.7, 128.9, 129.2, 129.4, 129.8, 130.1, 130.5, 136.0, 140.2, 142.4, 142.6, 162.7 ($C_6H_5$ and =CH), 231.325 (CO). IR ($CH_2Cl_2$): 1925 cm$^{-1}$ (CO). LREIMS: *m/z* 492 (M$^+$), 464 (M$^+$ − CO), 354 (M$^+$ − (P$(CH_3)_2$Ph)).

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