an axial position, trans to the Co–Co bond. Such is generally the case with $(Q_2)Co_2(CO)_4L_2$ derivatives,[11] but this is the first $n = 1$ example. The stereochemistry at the asymmetric C1 and C2 centers is seen to be (S,R)[12] with the large Ph group on C1 directed away from the bulky PPh_3 ligand. The same stereochemistry is assigned to the major (or exclusive) isomers **2a,c** and **2d,e** on the basis of their chromatographic elution behavior.

In the course of characterizing complexes **2a–e** the minor isomers **2a′,b′,d′** were found to isomerize and disproportionate very slowly in solution at 20 °C ($t_{1/2}$ = ca. 50–200 h) to produce mixtures containing the major isomer, the bis(phosphine)complexes **4a,b,d**, and the starting hexacarbonyl complexes **1a,b,d** (eq 2). Formation of the disproportionated products in eq 2 suggests that PPh_3 dissociation/readdition may be involved in both the isomerization and the disproportionation mechanisms. This hypothesis was further supported by the results of a crossover experiment involving isomerization of **2b′** in the presence of $(Me_3SiC{\equiv}CH)Co_2(CO)_6$ monitored by ^1H NMR. Thus, formation of the major isomer **2b** was found to be accompanied by a substantial amount of the crossover product $(Me_3SiC{\equiv}CH)Co_2(CO)_5(PPh_3)$[13] as well as the disproportionation products (eq 3). An alternative isomerization pathway involving racemization at C1 via OH^- (or H_2O) dissociation/reassociation (facilitated by the considerable stability of the $(propynyl)Co_2(CO)_5(PPh_3)^+$ species[14]) is less likely because the isomerization of **2b′** in MeOH failed to produce any of the corresponding methyl ether(s) and its rate of isomerization was similar in solvents a differing polarity, i.e. benzene, THF, MeOH, ether, and hexane. Other *intramolecular* isomerization mechanisms such as an "acetylene twist"[15] or other cluster skeletal rearrangements[1,2] cannot be excluded at present and await future investigations.

$$\mathbf{2a',b',d'} \rightarrow \mathbf{2a,b,d} + \mathbf{4a,b,d} + \mathbf{1a,b,d} + \text{decomposition} \quad (2)$$

$$\mathbf{2b'} + (Me_3SiC{\equiv}CH)Co_2(CO)_6 \rightarrow \mathbf{2b} + (Me_3SiC{\equiv}CH)Co_2(CO)_5(PPh_3) \quad (3)$$

The configurational stability of **2a–e** was unexpected given the facile racemization of the related tetrahedral cluster compounds[16] $(PhC{\equiv}CCO_2Pr^i)[CpNiML_n]$ (ML_n = $Co(CO)_3$, $CpMo(CO)_2$),[2] and $Pr^iO_2CCo_3(CO)_7L_2$[2,3]). The magnitude of the diastereoselectivity observed in the **1** → **2** conversion is is also surprising, and its origin is not apparent. There is some correlation with the steric demand of the R^2 group (Table I), the isopropyl and *tert*-butyl derivatives giving only one isomer. Control experiments (at 50 °C) indicate that *partial* isomerization occurs under the reaction conditions so that the observed % de's are neither truly kinetic nor thermodynamic in origin. Nonetheless, exploitation of this novel type of asymmetric induction in effecting stereocontrolled coupling reactions of the extremely stable propargylium complexes derived from protonation of **2a–e**[14] appears very promising. Results toward this end will be reported in forthcoming publications.[17]

Acknowledgment. We are grateful for support provided by the National Institutes of Health (GM 34799) and for a gift of cobalt carbonyl from Pressure Chemical Co.

Supplementary Material Available: Tables of atomic coordinates, thermal parameters, and bond lengths and bond angles (8 pages); a listing of observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

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[11] Bonnett, J.-J.; Mathieu, R. *Inorg. Chem.* **1978**, *17*, 1973. Bianchini, C.; Dapporto, P.; Meli, A. *J. Organomet. Chem.* **1979**, *174*, 205. Bird, P. H.; Fraser, A. R.; Hall, D. N. *Inorg. Chem.* **1977**, *16*, 1923.

[12] Other enantiomer, (R,S), present in unit cell is not shown.

[13] ^1H NMR (300 MHz, C_6D_6) of $(Me_3SiC{\equiv}CH)Co_2(CO)_5(PPh_3)$: δ 7.19–7.32 (m, 15 H), 5.30 (d, 1 H, J = 7 Hz), 0.01 (s, 9 H); verified by independent synthesis from $(Me_3SiC{\equiv}CH)Co_2(CO)_6$ + PPh_3.

[14] Bradley/Nicholas unpublished results.

[15] These cluster complexes racemize between ca. 250 and 380 K *on the NMR time scale* with estimated ΔG = 13–21 kcal/mol. Assuming typical rate dependency on T and a first-order process for isomerization, complexes **2** are crudely estimated to racemize ca. 10^{-5} times more slowly that the former.

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[17] **Note Added in Proof.** After submission of this paper, the preparation of diastereomeric $(PhC{\equiv}CH)Co_2(CO)_5(^*PR_3)$ containing an optically active phosphine was reported. Isomerization of this complex occurs in ca. 3 h at 60 °C. Bladon, P.; Pauson, P. L.; Brunner, H.; Eder, R. *J. Organomet. Chem.* **1988**, *355*, 499.

Photochemical Conversion of (η^1-Butadienyl)iron Complexes to Hydroxyferrocenes[1]

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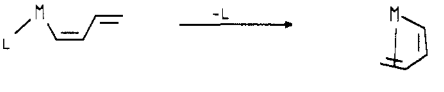
Summary: The photolysis of $(\eta^5\text{-}C_5H_5)(CO)_2Fe(\eta^1\text{-buta-1,3-dienyl})$ complexes gave substituted hydroxyferrocenes in high yields. Low-temperature ^1H NMR and IR studies implicate loss of CO as the sole photochemical process with an η^3-butadienyl complex and an η^5-pentadienoyl complex as key intermediates in this rearrangement.

We have recently been interested in utilizing η^1-butadienyl complexes as potential synthons of transition metallacycles.[2] The corresponding η^3-butadienyl complexes **1**, which may be approached with loss of a ligand from η^1-butadienyl complexes (eq 1), are of further interest due to their intrinsically novel bonding and reactivity.[3,4] We here report a detailed study of the synthesis and conversion of $(\eta^5\text{-}C_5H_5)(CO)_2Fe(\eta^1\text{-buta-1,3-dienyl})$ complexes to thermodynamically unstable η^3-butadienyl complexes. These complexes undergo nearly quantitative conversion



(1)

1

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[1] (a) Initial work was presented at the 192nd National Meeting of the American Chemical Society, Anaheim, CA, Sept 1986; paper INOR 263 (Neil T. Allison, Warunee Yongkulrote, H. D. Frame III, C. Mike, and B. Durham). (b) Initial results: Yongskulrote, W. Doctoral Dissertation, University of Arkansas, 1985.

[2] (a) Ferede, R.; Allison, N. T. *Organometallics* **1983**, *2*, 463. (b) Ferede, R.; Hinton, J. F.; Korfmacher, W. A.; Freeman, J. P.; Allison, N. T. *Organometallics* **1985**, *3*, 614. (c) Ferede, R.; Noble, M.; Cordes, A. W.; Lay, J. O.; Allison, N. T. *J. Organomet. Chem.* **1988**, *339*, 1. (d) Mike, C. A.; Ferede, R.; Allison, N. T. *Organometallics* **1988**, *7*, 1457.

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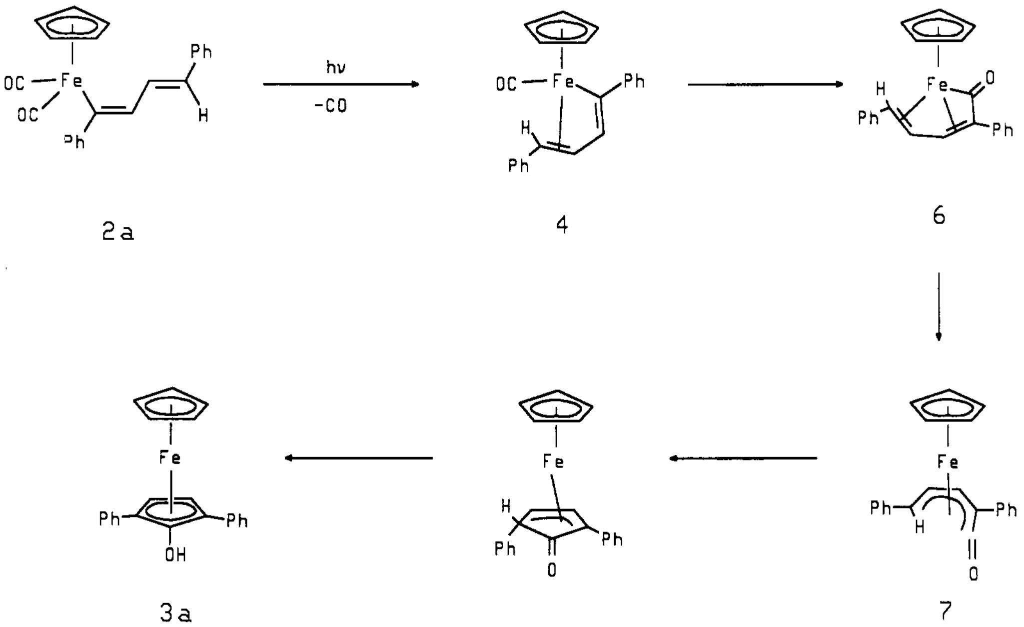
0276-7333/89/2308-0556$01.50/0

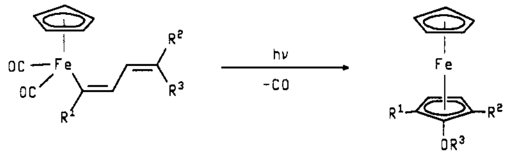
Scheme I



to the rarely accessible class of substituted hydroxyferrocenes.[5]

Our initial studies followed by a systematic approach for preparing η^3-butadienyl complexes by the photolysis of photoactive η^1-butadienyl transition-metal complexes. Most accessible are η^1-butadienyl complexes of $(\eta^5\text{-}C_5H_5)Fe(CO)_2$. The η^1-butadienyl complexes **2** were prepared following similar procedures of introducing selected 1-lithio-1,3-butadienes[6] to THF solutions of $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ followed by column chromatography (neutral alumina/pentane).

Experiments aimed at preparing η^3-butadienyl complexes by irradiation of solutions of **2**[7] gave instead the hydroxyferrocenes **3** in excellent yields (eq 2).[8]



(2)

2a	R^1,R^2 = Ph; R^3 = H	3a	R^1,R^2 = Ph; R^3 = H.	100%
2b	R^2 = Ph; R^1,R^3 = H	3b	R^2 = Ph; R^1,R^3 = H.	98%
2c	R^2 = CH_3; R^1,R^3 = H	3c	R^2 = CH_3; R^1,R^3 = H.	95%
2ad$_1$	R^1,R^2 = Ph; R^3 = D			

To investigate the mechanism of this transformation, photolysis of **2a** with intermittent monitoring by ^{1}H NMR and IR was undertaken. At room temperature, this reaction proceeds directly to the above observed products with no indication of intermediates. However, low-temperature irradiation (methylcyclohexane glass, −196 °C) and IR monitoring (−196 °C) indicated loss of intensity of the starting material carbonyl stretching frequencies at 1964 and 2003 cm^{-1} concomitant to absorptions appearing at 1944 and 2140 cm^{-1}. This is consistent with loss of one terminal carbonyl and formation of η^3-butadienyl complex **4** and free CO (Scheme I). Warming from −196 to +25 °C results in the disappearance of the 1944 cm^{-1} absorption.

Trapping experiments also establish this photochemical process. Irradiation of a degassed solution of **2a** with a 10-fold excess of $Ph(CH_3)_2P$ at +25 °C in a sealed NMR tube affects the disappearance of the cyclopentadienyl resonance of **2a** (δ 5.0 ppm (s, Cp)) with the appearance of a new cyclopentadienyl resonance for $(\eta^5\text{-}C_5H_5)(CO)(PPh_3)FeC(Ph){=}CHCH{=}CH(Ph)$ (**5**) (δ 4.66 ppm (d, Cp)). This trapping completely quenched conversion to the hydroxyferrocene product **3a**. Preparative scale photolysis led to isolation and characterization of **5**. Thus, these data are in full accord with loss of CO and formation of an η^3-butadienyl complex, **4**, as being the sole observable photochemical process.

Attempts at generating other kinetic intermediates from **2a** were undertaken at higher temperatures. Photolysis

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(7) Typical experimental for generation of **3**: Compound **2a** (0.125 g, 0.327 mmol) was dissolved in 1 mL of CD_2Cl_2 in a 5-mm NMR tube. The solution was freeze/pump/thaw degassed and the tube sealed. After the solution was cooled to −78 °C (dry ice/2-propanol) in a non-silvered Pyrex Dewar flask, photolysis with a 150-W high pressure Xenon arc lamp (a 450-W Hanovia medium pressure Hg lamp was also used under similar conditions with equal success) and intermittent warming to monitor the reaction by ^{1}H NMR (times indicated below) gave **3a**. Typical photolysis times and temperatures were as follows: **2a**, −78 °C, 107 min, CD_2Cl_2; **2b**, 0 °C, 90 min, Et_2O; **2c**, −15 °C, 90 min, $CDCl_3$. In each case, removal of the indicated solvent gave the product as an air and thermally unstable viscous red oil.

(8) Product yields determined by ^{1}H NMR. Spectroscopic data for **3a**: ^{1}H NMR ($(CD_3)_2CO$, 25 °C, 60 MHz) δ 8.05–7.48 (m, 10, Ph), 6.78 (br s, 1, OH), 4.51 (s, 2, subst Cp), 4.05 (s, 5, C_5H_5); $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$, 25 °C, 22.6 MHz) δ 139.1, 128.8, 128.8, 126.7 (Ph), 117.5 (C–OH), 77.2 (C–Ph), 72.6 (C_5H_5), 62.5 (CH on subst Cp). **3b**: ^{1}H NMR ($CDCl_3$, 25 °C, 90 MHz) δ 7.7–7.2 (m, 5, Ph), 4.24–3.90 (m, 3, subst Cp), 4.08 (s, 5, C_5H_5), 3.67 (s, 1, OH); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C, 22.6 MHz) δ 137.5, 128.4, 127.8, 126.2 (Ph), 119.5 (C–OH), 74.6 (C–Ph), 70.4 (C_5H_5), 62.5, 60.7, 58.2 (CH on subst. Cp). **3c**: ^{1}H NMR ($CDCl_3$, 25 °C, 60 MHz) δ 4.07 (s, 5, C_5H_5), 3.85–3.60 (m, 3, CH on subst Cp), 3.40 (br s, 1, OH), 2.00 (s, 3, CH_3); $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$, 25 °C, 22.6 MHz) δ 121.9 (C–OH), 86.4 (C–CH_3), 69.9 (C_5H_5), 64.1, 59.4, 56.9 (CH on subst Cp), 11.8 (CH_3). (H–D hydroxyl ^{1}H NMR exchange experiments for **3a**, **3b**, and **3c** with D_2O were performed.) Elemental analysis for **3a**, **3b**, and **3c** were not obtained due to their thermal and air sensitivity. All three compounds decomposed upon attempted sublimation or chromatography (silica gel and C18 reverse phase), thereby thwarting efforts for suitable elemental analysis.

of **2a** at −78 °C in a sealed degassed solution of CD_2Cl_2 gave a thermally unstable intermediate identified as the η^5-pentadienoyl complex **7** (Scheme I) from low-temperature ^{1}H NMR and IR data.[9,10] Warming of **7** gave the hydroxyferrocene **3a** quantitatively.

The structure of **7** is proposed from the following data. After photolysis of a solution of **3a** (CD_2Cl_2, −78 °C) in a sealed degassed NMR tube, the low-temperature (−40 °C) NMR spectra contained new vinyl absorptions centered at δ 6.54 ppm (2 H, m), a cyclopentadienyl absorption at δ 4.29 ppm (5 H, s), a high-field multiplet centered at δ 0.2 ppm (1 H, m), and changes in the complex aromatic resonances. The vinyl and high-field multiplets can be attributed to an ABX spectrum (H_A, δ 6.53 ppm; H_B, δ 6.55 ppm; H_X, δ 0.20 ppm; J_{AB} = 5.6 Hz, J_{AX} = −0.7 Hz, J_{BX} = 8.2 Hz). In order to assign a specific hydrogen to the high-field absorption (and in turn assign the vinyl absorptions), we prepared the labeled butadienyl complex **2a**-d_1 (eq 2). Photolysis of a solution (CD_2Cl_2) of **2a**-d_1 at −78 °C and low-temperature ^{1}H NMR experiments gave a spectrum consistent with that observed for **7** including the absence of the high-field absorption (H_X). This labeling experiment clearly indicates that the terminal hydrogen of **2a** converts to the terminal hydrogen in the η^5-pentadienoyl complex **7**. In addition, low-temperature IR experiments were also helpful in identifying a second structural feature of **7**. Photolysis of **2a** at −78 °C in CH_2Cl_2 resulted in the disappearance of the terminal carbonyl stretching absorptions with concomitant appearance of a strong 1720 cm^{-1} stretch consistent with the ketene-like moiety present in **7**.[11] In accord with the above NMR data, warming of this solution resulted in loss of the 1720 cm^{-1} stretch with no appearance of new carbonyl absorptions.

A mechanism for the conversion of **2a** to **3a** which incorporates these above observed intermediates is summarized in Scheme I. The sole photochemical process is loss of a terminal carbonyl. Coordination of the terminal alkene moiety generates the η^3-butadienyl intermediate **4**. Carbonyl insertion gives **6**. Rearrangment of **6** gives the η^5-pentadienoyl complex **7**. Formation of a C–C bond via electrocyclic ring closure from **7** followed by keto–enol tautomerization gives product **3a**.

In conclusion, the high-yield conversion of η^1-butadienyl complexes to hydroxyferrocenes appears to be general. Trapping experiments and low temperature spectroscopic data implicate an η^3-butadienyl complex and a pentadienoyl complex as intermediates in the conversion. Further work concerning mechanistic studies and synthetic applications of this cyclization reaction are currently underway.

Acknowledgment. We thank Dr. J. Lay, Jr., at the National Center for Toxicological Research, Jefferson, AR, for the high-resolution mass spectroscopic data. N.T.A. would like to thank the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for funding of this research.

Supplementary Material Available: Experimental descriptions and ^{1}H NMR, ^{13}C NMR, and high-resolution MS data for **2a**, **2b**, **2c**, and **5** and high-resolution MS data for **3a**, **3b**, and **3c** (4 pages). Ordering information given on any current masthead page.

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[9] Approximately 60% conversion to **7** at −78 °C was accomplished with a photolysis time of 4 h. This is indicative of **7** quenching the initial photoreaction. As the hydroxyferrocene product **3a** does not effectively quench the photoreaction, shorter times are needed (cf. ref 8) if the solution is warmed to room temperature occasionally during the reaction. At −40 °C slow conversion of **7** to **3a** is observed in the ^{1}H NMR. Solubility problems have thwarted our efforts for low-temperature NMR observation of intermediates from photolysis of **2b** and **2c**.

[10] An alkylvinylketene complex would constitute one canonical resonance form for **7**. We thank one reviewer for pointing out that form **7** could better represent the structure of the observed intermediate. Vinylketene complexes have been postulated as intermediates in the Dötz–Wulff cyclization reaction: cf. Fischer, H.; Muhlemeier, J.; Markl, R.; Dötz, K. H. *Chem. Ber.* **1982**, *115*, 1355. Dötz, K. H.; Muhlemeier, J. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 929.

[11] Herrmann, W. A. *Chem. Ber.* **1975**, 486.

Benzyltitanium and -zirconium Cobalt Carbonyls. Preparation and Spectroscopic Characterization

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Summary: Tetrabenzyltitanium (**1a**) and -zirconium (**1b**) react with equimolar $HCo(CO)_4$ (**2**) to give the corresponding tribenzylmetal–cobalt tetracarbonyl (M = Ti, **5a**; M = Zr, **5b**) derivatives. Compounds **5** also can be obtained from $(PhCH_2)_3MX$ (X = Cl, Br) compounds and $[Co(CO)_4]^-$ salts, while complexes **6** are formed from equimolar **5** and **2**. Compounds **5** react with PPh_3 to give the substitution products $(PhCH_2)_3M[Co(CO)_3(PPh_3)]$ (M = Ti, **7a**; M = Zr, **7b**), which also can be obtained from **1a** or **1b** and $HCo(CO)_3(PPh_3)$. The new, very unstable bimetallic complexes **5**, **6**, and **7** were characterized by IR and ^{1}H NMR spectroscopy.

Transition-metal-assisted or -catalyzed reactions often display a characteristic pattern of products which is typical for the metal. Bimetallic compounds are hoped, believed, or even proved to unify the advantages of the metal components.[2] This goal has been of great interest in the last

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[2] Early/late-transition-metal combination in organic synthesis: (a) Negishi, E.; Van Horn, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 3168. (b) Negishi, E.; Okukado, N.; King, A. O.; Van Horn, D. E.; Spiegel, B. I. *J. Am. Chem. Soc.* **1978**, *100*, 2254. (c) Schwartz, J.; Loots, M. J.; Kosugi, H. *J. Am. Chem. Soc.* **1980**, *102*, 1333. (d) LaCroce, S. J.; Cutler, A. R. *J. Am. Chem. Soc.* **1982**, *104*, 2312. (e) Bodnar, T. W.; Cutler, A. R. *Organometallics* **1985**, *4*, 1558. Early suggestions about the importance of these combinations in catalysis: (f) Muetterties, E. L. *Bull. Soc. Chim. Belg.* **1975**, *84*, 959; **1976**, *85*, 451. (g) Demitras, G. C.; Muetterties, E. L. *J. Am. Chem. Soc.* **1977**, *99*, 2796. (h) Masters, C. *Adv. Organomet. Chem.* **1979**, *17*, 61. (i) Wong, K. S.; Labinger, J. A. *J. Am. Chem. Soc.* **1980**, *102*, 3652. (j) Casey, C. P.; Jordan, R. F.; Rheingold, A. L. *J. Am. Chem. Soc.* **1983**, *105*, 665.