The vinylstannanes **4c** were purified by flash chromatography (petroleum ether). Benzaldehyde gave 2-(tri-*n*-butylstannyl)-1-phenylethene (**4c**, R^2, R^3 = H, Ph) (1.37 g, 35%) as a mixture of the *E*- and *Z* isomers (ca. 55:45 by NMR):[12] R_f (petroleum ether) 0.4; IR ν_{max} ($CHCl_3$) 1590 cm^{-1} (ArC=C); NMR δ 7.61 (ca. 0.5 H, d, J = 13 Hz (*Z*)-C*H*Ph), 7.5–7.1 (5 H, m, Ph), 6.87 (ca. 1 H, br s, (*E*)-C*H*=C*H*), 6.12 (ca. 0.5 H, d, J = 13 Hz (*Z*)-CHSn), 1.7–0.7 (27 H, m, $SnBu_3$).

Acknowledgment. The financial support of the Research Corp. and a University of Toledo FRAF award are gratefully acknowledged.

Registry No. **2a**, 79409-19-1; **2b**, 98830-88-7; **2c**, 77425-85-5; **4a** (R^1 = SPh, R^2 = Ph, R^3 = H), 103533-68-2; **4a** (R^1 = SPh, R^2 = R^3 = Ph), 103533-69-3; **4b** (R^1 = CO_2-*t*-Bu, R^2 = Ph, R^3 = H), 98830-92-3; **4b** (R^1 = CO_2-*t*-Bu, R^2 = R^3 = Ph), 103533-70-6; **4c** (R^1 = R^2= H, R^3 = Ph), 66680-88-4; **4c** (R^1 = R^3 = H, R^2 = Ph), 66680-87-3; tri-*n*-butyltin chloride, 1461-22-9; (phenylthio)(trimethylsilyl)methane, 17873-08-4; *tert*-butyl (trimethylsilyl)acetate, 41108-81-0; (trimethylsilyl)methyl chloride, 2344-80-1; *tert*-butyl acetate, 540-88-5; chlorotrimethylsilane, 75-77-4; benzaldehyde, 100-52-7; benzophenone, 119-61-9.

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(12) Leusink, A. J.; Budding, H. A.; Marsma, J. W. *J. Organomet. Chem.* **1967**, *9*, 285. Hibino, J. I.; Matsubara, S.; Morizawa, Y.; Oshima, K.; Nozaki, H. *Tetrahedron Lett.* **1984**, *25*, 2151. Labadie, J. W.; Stille, J. K. *J. Am. Chem. Soc.* **1983**, *105*, 6129.

Communications

Synthesis of $(C_5H_5)Fe(CO)_2(\eta^1\text{-}C_5H_7)$, $(C_5H_5)Fe(CO)(\eta^3\text{-}C_5H_7)$, and $(C_5H_5)Fe(\eta^5\text{-}C_5H_7)$ Involving the $\eta^1 \rightarrow$ Syn-$\eta^3 \rightarrow \eta^5$ Route

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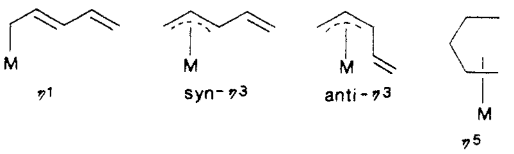
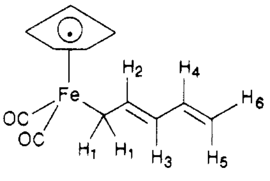
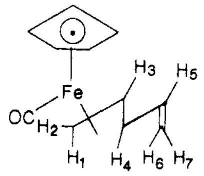
Summary: Reaction of $(C_5H_5)Fe(CO)_2Na$ with *trans*-1-chloropenta-2,4-diene in tetrahydrofuran at −78 °C gives $(C_5H_5)Fe(CO)_2(\eta^1$-2,4-pentadienyl) (**1**) in good yields. Photolysis of **1** in ether at −20 °C yields a mixture of $(C_5H_5)Fe(CO)(\eta^3$-pentadienyl) (**2**) and $(C_5H_5)Fe(\eta^5$-pentadienyl) (**3**). Compound **2** exists as two stereoisomers characterized as endo syn-η^3 and exo syn-η^3 by its ^1H NMR and IR spectra. The endo form undergoes facile isomerism to exo form at ambient temperatures. The conversion of **2** to **3** is effected by photolysis. A half-open-sandwich structure is assigned to **3** as inferred from its ^1H and ^{13}C NMR spectra.

In recent years, there is growing interest in the chemistry of acyclic pentadienylmetal complexes.[1] One of the intriguing features of these complexes is a variety of geometries for the pentadienyl group bound to a metal center as represented below. Although many recent papers[2] have described the structures of transition-metal pentadienyl compounds of the syn-η^3, anti-η^3, and η^5 configurations, the transition-metal η^1-pentadienyl compounds are rare.[3] In this communication, in addition to the report on the iron η^1-pentadienyl complex Fp–(η^1-2,4-pentadienyl) (Fp = $(C_5H_5)Fe(CO)_2$ (**1**), we also describe the conversion of **1** to $Fe(C_5H_5)(CO)(syn\text{-}\eta^3$-pentadienyl) (**2**) and further to $Fe(C_5H_5)(\eta^5$-pentadienyl) (**3**).

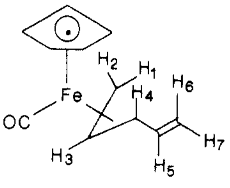




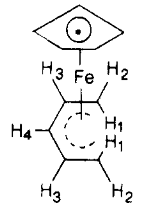
1



2 (exo isomer)



2 (endo isomer)



3

When a tetrahydrofuran solution of *trans*-1-chloropenta-2,4-diene was stirred with $(C_5H_5)Fe(CO)_2Na$[4] at −78 °C for 3 h, an air-sensitive, orange oil of **1** was obtained in higher yields after workup.[5] Analytical and spectroscopic data[6] indicate the structure of **1** as shown.

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(1) For recent reviews of acyclic pentadienyl metal complexes see: (a) Ernst, R. D. *Acc. Chem. Res.* **1985**, *18*, 56. (b) Yasuda, H.; Nakamura, A. *J. Organomet. Chem.* **1985**, *285*, 15.

(2) Bleeke, J. R.; Kotyk, J. J. *Organometallics* **1985**, *4*, 194. and references therein.

(3) Only one compound is known $Cp_2Zr(\eta^1$-2,4-pentadienyl$)_2$: see Yasuda, H.; Nagasuna, K.; Asami, K.; Nakamura, A. *Chem. Lett.* **1983**, 955.

(4) $(C_5H_5)Fe(CO)_2Na$ was prepared by reduction of $(C_5H_5)_2Fe_2(CO)_4$ (1.5 g, 4.2 mmol) with sodium amalgam (55 g, 5% sodium contents) in 50 mL of tetrahydrofuran.

(5) In a typical preparation, *trans*-1-chloropenta-2,4-diene (1.2 g, 11.6 mmol) was added dropwise to 50 mL of tetrahydrofuran solution containing $(C_5H_5)_2Fe(CO)_2Na$ (8.4 mmol) at −78 °C and stirred for 3 h. After the insoluble sodium amalgam was filtered out at −78 °C, the solution was warmed to 0 °C and evaporated to dryness to yield dark green residues. The residues were extracted with 20 mL of pentane three times, filtered, and evaporated to dryness. Using pentane as eluting solvent, the residues were chromatographed through neutral alumina column (60 g, Merck) at 23 °C. In addition to an immobile band of $(C_5H_5)_2Fe_2(CO)_4$, a gold-yellow band was eluted rapidly and collected. After the solution was removed, followed by vacuum distillation (7.0 × 10^{-3} torr, 28 °C) of the residue, an orange oil of **1** (1.39 g, 5.70 mmol) was obtained.

(6) Anal. Calcd for $C_{12}H_{12}FeO_2$: C, 59.05; H, 4.95. Found: C. 59.14; H, 5.07. Mass spectrum (12 eV): *m/e* 244 (M^+), 216 $(M - CO)^+$, 188 $(M - 2CO)^+$, 177 $(M - C_5H_7)^+$, 149 $(M - C_5H_7 - CO)^+$, 121 $(M - C_5H_7 - 2CO)^+$. IR (pentane): ν(CO) 2010 (s) and 1956 (s) cm^{-1}; ν(C=C) 1625 (w) cm^{-1}. ^1H NMR (100 MHz, C_6D_6): δ 2.16 (2 H, d, H_1, J_{12} = 6 Hz), 3.95 (5 H, s, C_5H_5), 5.05 (1 H, dd, H_6, J_{46} = 11 Hz, J_{56} = 1 Hz), 5.20 (1 H, dd, H_5, J_{45} = 16 Hz, J_{56} = 1 Hz), 5.60–6.70 (3 H, complex m, H_2, H_3, and H_4). ^{13}C NMR (C_6D_6, 25.14 MHz): δ32.4 (CH_1H_1), 68.2 (CH_2), 79.6 (C_5H_5), 115.1 (CH_5H_6), 124.7, 146.63 (CH_3 and CH_4), and 217.3 (CO).

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Photolysis of an ether solution of **1** at −20 °C for 2 h yielded a mixture of **2** and **3** in ca. 3:2 molar ratio. After separation of the mixture by column chromatography, followed by vacuum sublimation, orange crystals of **2** were obtained in moderate yields.[7] The elemental analysis and mass spectrum[8] conform to the expected formula $Fe(C_5H_5)(CO)(C_5H_7)$. The IR and ^1H NMR spectra[9] reveal that compound **2** exists as two stereoisomers which are designated as the exo syn-η^3 and endo syn-η^3 isomers as inferred from the stereochemistry of the related compounds $Fe(C_5H_5)(CO)(\eta^3\text{-}1\text{-}C_3H_4R)$.[10] The assignment of syn configuration to both isomers is based on their observed coupling constants $J_{13} \simeq J_{34} \simeq 11$ Hz and $J_{23} \simeq 7$ Hz which indicate that the proton H_3 is trans to H_1 and H_4 and cis to H_2. The exo isomer is characterized by a greater shielding of anti protons (H_1 and H_4) and a larger geminal coupling constant of syn and anti protons J_{12} than the endo form in the ^1H NMR resonances.[10] The endo isomer undergoes facile isomerism to the exo isomer at ambient temperatures. If a NMR sample (endo:exo = 3:7) was allowed to stand at 23 °C, with the progress monitored by NMR spectroscopy, less than 1% of the endo isomer remained in the solution after 12 h. For the conceivable syn–anti isomerism, no evidence was obtained for such a process from the NMR spectrum taken at 120 °C in $CD_3C_6D_5$. No anti isomer was observed even after reflux of the syn isomer in toluene for 12 h. In the latter case, *exo*-$Fe(C_5H_5)(CO)$(*syn*-η^3-pentadienyl) was recovered exclusively. Rosenblum et al.[10] have studied the isomerism of complexes of the types $Fe(C_5H_5)(CO)(\eta^3\text{-}1\text{-}C_3H_4R)$ and concluded that the endo–exo isomerism of these complexes is best described by the π–σ–π mechanism as for the syn–anti isomerism, and thus these two isomerisms have similar activation energies. In this manner, the absence of the anti isomer for **2** appears to arise from its thermodynamic instability.

Although thermal activation appears formidable, photolytical conversion of *exo*-$(C_5H_5)Fe(CO)$(*syn*-η^3-pentadienyl) to $(C_5H_5)Fe(\eta^5\text{-pentadienyl})$ (**3**) is feasible at room temperature.[11] The C, H analyses and mass spectrum[12] were consistent with the given formula. The compound **3** possesses a half-open sandwich structure as shown by its ^1H and ^{13}C NMR spectroscopic data.[13] Like its close analogue, ferrocene, compound **3** was obtained as orange-red crystals which readily sublimed under vacuum at room temperature. Ernst and co-workers[14] recently have reported a similar half-open compound, $Fe(C_5H_5)(2,4\text{-}(CH_3)_2C_5H_5)$, prepared from the following reaction.

$$\begin{aligned}4FeCl_2 + 2NaC_5H_5 + 2K(2,4\text{-}(CH_3)_2C_5H_5) \xrightarrow[-78\ ^\circ C]{THF} \\ 2Fe(C_5H_5)(2,4\text{-}(CH_3)_2C_5H_5) + Fe(C_5H_5)_2 + \\ Fe(2,4\text{-}(CH_3)_2C_5H_5))_2 + 2NaCl + 2KCl\end{aligned}$$

By comparison, our alterative method for synthesis of **3** appears to be more selective. In particular, the route in the preparation of **3** involves the successive change in configuration $\eta^1 \rightarrow \text{syn-}\eta^3 \rightarrow \eta^5$, which is intriguing in both synthetic and mechanistic aspects. Previously, the syn-$\eta^3 \rightarrow \eta^5$ process was achievable only with thermolysis, as known for the compound $Mn(CO)_4(\eta^3\text{-pentadienyl})$.[15] In contrast, the conversion of **2** to **3**, made possible only by photolysis, is of interest even though the nature of the mechanism is not clear at the present stage. Moreover, the presence of **1** and **3** represents considerable significance in both practical and theoretical aspects because of the close resemblances to Fp–allyl and ferrocene, respectively. Fp–ally[16] is a good example of the use of the allyl ligand in many organic reactions. For instance, it undergoes 3 + 2 cycloaddition with many electrophiles. The reaction of **1** with organic molecules certainly deserves exploration. In the near furture, we will present more data which would enable one to look into the reactivity and bonding of these iron–pentadienyl complexes.

Acknowledgment. We wish to thank the National Science Council, R. O. C. for the financial support of this work.

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[7] A 20-mL ether solution of **1** (1.0 g, 4.1 mmol) in a vacuum-sealed tube was irradiated by a 400-W mercury lamp at −20 °C for 2 h. After removal of the solvent under reduced pressure, the residue was chromatographed through a neutral alumina column (150 g, Merck) at 0 °C with pentane as eluting solvent. An orange band which was eluted first was identified as **3** and collected. A second band was collected, and the solvent was removed under reduced pressure. A yellow band of unknown species and a purple band of $(C_5H_5)_2Fe_2(CO)_4$ remained on the top portion of the column, and these were not collected. The orange solids from the second band were further purified by vacuum sublimation (5×10^{-3} torr, 28 °C) to yield orange crystals of **2** (0.35 g, 1.6 mmol) with a melting point of 21 °C. The purification of **3** from the first orange band was conducted in a similar procedure, and orange crystals (0.18 g, 1.0 mmol) of **3** were obtained.

[8] Anal. Calcd for $C_{11}H_{12}FeO$: C, 61.12; H, 5.59. Found: C, 61.04; H, 5.54. Mass spectrm (12 eV): *m/e* 216 (M^+), 188 $(M - CO)^+$.

[9] IR spectrum (pentane): $\nu(C{=}C)$ 1618 (w) cm^{-1}; $\nu(C{=}O)$ 1965 (s) (endo isomer) and 1954 (s) cm^{-1} (exo isomer). ^1H NMR (400 MHz, $CD_3C_5D_5$): exo isomer, δ 0.59 (dd, 1 H, H_1), 2.00 (t, 1 H, H_4), 2.49 (dd, 1 H, H_2) 3.96 (s, 5 H, C_5H_5), 4.21 (ddd, 1 H, H_3), 4.88 (dd, 1 H, H_7), 5.11 (dd, 1 H, H_6), 5.80 (ddd, 1 H, H_5), $J_{13} = 11.1$ Hz, $J_{12} = 1.5$ Hz, $J_{34} = J_{45} = 10.8$ Hz, $J_{23} = 7.0$ Hz, $J_{57} = 10.1$ Hz, $J_{67} = 1.5$ Hz, $J_{56} = 16.9$ Hz; endo isomer, δ 1.29 (dd, 1 H, H_1), 2.64 (dd, 1 H, H_2), 2.76 (t, 1 H, H_4), 3.62 (ddd, 1 H, H_3), 4.10 (s, 5 H, C_5H_5), 4.81 (dd, 1 H, H_7), 5.05 (dd, 1 H, H_6), 5.92 (ddd, 1 H, H_5), $J_{13} = 11.4$ Hz, $J_{12} = 0.7$ Hz, $J_{23} = 6.8$ Hz, $J_{34} = J_{45} = 10.5$ Hz, $J_{57} = 10.2$ Hz, $J_{56} = 17.0$ Hz, $J_{67} = 1.4$ Hz. ^{13}C NMR (101 MHz, C_6D_6): exo isomer, δ 30.9 (CH_1H_2), 56.6 (CH_3), 74.5 (CH_4), 79.6 (C_5H_5), 110.0 (CH_6H_7), 143.4 (CH_5), 222.56 (CO).

[10] Fish, R. W.; Giering, W. P.; Marten, D.; Rosenblum, M. *J. Organomet. Chem.* **1976**, *105*, 101.

[11] In a typical reaction, a 20-mL benzene solution of compound **2** (0.45 g, 2.0 mmol) in a vacuum-sealed Pyrex tube was irradiated by a 400-W mercury lamp at room temperature, for 24 h. After the solvent was removed under reduced pressure, the remaining orange solids were sublimated (5.2×10^{-3} torr) at 28 °C into a −25 °C cold trap to yield orange crystals of **3** (0.35 g, 1.9 mmol).

[12] Anal. Calcd for $C_{10}H_{12}Fe$: C, 63.87; H, 6.43. Found: C, 63.54, H, 6.25. Mass spectrum (12 eV): *m/e* 188 (M^+).

[13] ^1H NMR (100 MHz, C_6D_6): δ −0.52 (dd, 2 H, H_1), 2.60 (dd, 2 H, H_2), 4.02 (s, 5 H, C_5H_5), 4.42 (ddd, 2 H, H_3), 5.36 (t, 1 H, H_4), $J_{12} = 1$ Hz, $J_{13} = 10$ Hz, $J_{23} = 9$ Hz, $J_{34} = 6$ Hz; ^{13}C NMR (25.14 MHz, C_6D_6): δ 42.9 (CH_1H_2), 74.8 (C_5H_5), 81.6 (CH_4), 91.5 (CH_3).

[14] An X-ray crystallographic structure of $Fe(C_5H_5)(2,4\text{-}(CH_3)_2C_5H_5)$ was published in a recent review paper of metal pentadienyl complexes by R. D. Ernst.[1]

[15] (a) Kreiter, C. G.; Leyendecker, M. *J. Organomet. Chem.* **1985**, *280*, 225. (b) Lee, D. W.; Liu, R. S., unpublished results.

[16] (a) Williams, J. P.; Wojcicki, A. *Inorg. Chem.* **1977**, *16*, 3116. (b) Cutler, A.; Ehntholt, D.; Gierinin, W. P.; Lennon, P.; Raghu, S.; Rosan, A.; Rosenblum, M.; Tancrede, J.; Wells, D. *J. Am. Chem. Soc.* **1976**, *98*, 3495. (c) Wright, M. E. *Organometallics* **1983**, *2*, 558.

β-Cyclodextrin-Promoted, Rhodium(I)-Catalyzed Conversion of Carbonyl Compounds to Hydrocarbons under Remarkably Mild Conditions

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Summary: Aryl alkyl ketones and aromatic aldehydes react with hydrogen in the presence of catalytic quantities of the dimer of chloro(1,5-hexadiene)rhodium(I) and β-cyclodextrin to give hydrocarbons in high yields; this re-

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