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 $(C_5H_5)Fe(\eta^5$-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.

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

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 $\eta^1 \rightarrow$ 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 $Mn(CO)_4(\eta^3$-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.

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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): ν(C=C) 1618 (w) cm^{-1}; ν(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).

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(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]

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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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action occurs in tetrahydrofuran at room temperature and 1 atm and can tolerate the presence of a variety of functional groups.

A reaction which has been extensively investigated in organic chemistry is the conversion of aldehydes and ketones to hydrocarbons. Few direct methods are available for effecting this transformation, the classical procedure being the Clemmenson and Wolff–Kishner reduction reactions.[2] The Clemmenson reduction is sluggish in some instances and does not usually proceed well for acid sensitive substrates. The Wolff–Kishner reaction normally requires strong base (e.g., potassium *tert*-butoxide) and is often effected as an indirect deoxygenation method (e.g., via a semicarbazone or hydrazone).

Gas-phase hydrogenation of ketones using nickel on alumina does afford hydrocarbons. However, high temperatures (190 °C) are required, and the method lacks selectivity.[3] Another heterogeneous process involves catlaytic transfer hydrogenation, with palladium on carbon as the catalyst, ferric chloride as a Lewis acid promoter, and (+)-limonene or cyclohexene as the donor.[4] Aryl ketones can be converted to aromatic hydrocarbons by means of palladium chloride and sodium borohydride, but 2 equiv of the palladium compound and 5 equiv of the hydride are needed for this reaction.[5] Triethylsilane and boron trifluoride in methylene chloride is capable of deoxygenating carbonyl compounds, but an excess of the silane is required in order to realize good product yields.[6] A variety of two-step reaction sequences exist including, among others, the intermediate formation of enol triflates,[7] tosylhydrazones,[8-11] and selenides or selenoacetals.[12]

Rhodium(I) complexes catalyze the hydrogenation of a variety of functionalities under homogeneous conditions. Several such complexes are also effective catalysts for the decarbonylation of aldehydes.[13] In 1983, one of us described the phase-transfer-catalyzed reduction of aromatic and heterocyclic compounds using the dimer of chloro(1,5-hexadiene)rhodium(I) $[1,5\text{-HDRhCl}]_2$ as the metal catalyst and a quaternary ammonium salt as the phase-transfer agent. Preferential or exclusive reduction of the benzene ring occurred in the case of ketones such as acetophenone and phenylacetone. When some carbonyl reduction did take place (e.g., acetophenone), then the alcohol was formed and not the hydrocarbon.[14] We now wish to report that use of the same rhodium(I) catalyst, under modified conditions, enables one to deoxygenate aromatic aldehydes and ketones to hydrocarbons.

Treatment of *p*-methoxyacetophenone with hydrogen in tetrahydrofuran, in the presence of a catalytic amount of $[1,5\text{-HDRhCl}]_2$ for 24 h at ambient temperature and pressure, afforded *p*-ethylanisole in 24% yield (73% recovered starting material).

$$RC(O)R' + H_2 \xrightarrow[\text{THF, room temp, 1 atm}]{[1,5\text{-HDRhCl}]_2} RCH_2R'$$

β-Cyclodextrin, an oligomer of D-glucose, is known to promote the palladium chloride catalyzed oxidation of olefins to carbonyl compounds,[15] and it seemed conceivable that the cycloamylose could provide rate enhancement of the deoxygenation reaction. If the reaction of *p*-methoxyacetophenone is repeated under identical conditions but in the presence of β-cyclodextrin, then the yield of the product increased appreciably indeed (to 88%). Similarly, while deoxygenation of *m*-anisaldehyde in the absence of β-cyclodextrin afforded *m*-methylanisole in 24% yield and *m*-methoxybenzyl alcohol in 40% yield (24 h, room temperature, 1 atm), the yield of *m*-methylanisole was 80% and that of the alcohol was 20% if β-cyclodextrin was present. Use of a longer reaction time (40 h) gave *m*-methylanisole in quantitative yield. The ratio of substrate:β-cyclodextrin:rhodium(I) catalyst used in these reactions was 50:5:1. Metal complexes which did not catalyze hydrogenation of acetophenone under these conditions include chlorotris(triphenylphosphine)rhodium(I), dichlorotris(triphenylphosphine)ruthenium(II), and molybdenum hexacarbonyl.

A series of aromatic ketones and aldehydes were hydrogenated to the corresponding hydrocarbon products using $[1,5\text{-HDRhCl}]_2$ and β-cyclodextrin. The results, listed in Table I, indicate that the reaction can tolerate a variety of functionalities including alkyl, ether, hydroxy, dimethylamino, and ester groups. The position of the substituent on the benzene ring has little influence on the product yields (e.g., isomers of methoxyacetophenone). With the exception of butyrophenone, hydrogenation of the benzene ring is not the major reaction pathway for ketones, and aldehydes do not undergo arene reduction.

It is interesting to note that the principal reaction of *p*-acetoxybenzaldehyde is reduction of the aldehydic function to a methyl group, with *p*-acetoxybenzyl alcohol obtained as the byproduct. The isomeric methyl *o*-formylbenzoate, however, affords the benzylic alcohol as the major product. Also, α-methoxyacetophenone gave methyl 2-phenylethyl ether as the minor product (29%), with 2-methoxy 1-phenylethanol isolated as the main product.

It does appear that the benzylic alcohol is the intermediate in the rhodium(I)–β-cyclodextrin system. For example, use of benzyl alcohol as the substrate gives toluene in 93% yield (18 h—78% in the absence of β-cyclodextrin) and 1-phenylethanol affords ethylbenzene in 81% yield and ethyl cyclohexane in 19% yield (22 h).

Nonaromatic carbonyl compounds such as *n*-decanol are inert under the above reaction conditions. In addition, phenylacetone, which has a methylene group between the benzene ring and carbonyl functionalities, does give *n*-propylbenzene but in only 18% yield, with 1-phenyl-2-propanol formed in 17% yield.

It is known that aryl ketones form 1:1 complexes with β-cyclodextrin.[16,17] In such a complex, the carbonyl group

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Table I. Reduction of Carbonyl Compounds by H_2/[1,5HDRhCl]$_2$/β-Cyclodextrin/THF

reactant	reaction time, h	product[a]	yield,[b] %
$PhCOCH_3$	8	PhC_2H_5	86[c]
		$C_6H_{11}C_2H_5$	14
$PhCOC_2H_5$	16	PhC_3H_7-*n*	75[d]
		$C_6H_{11}C_3H_7$-*n*	24
$PhCOC_3H_7$	24	$C_6H_{11}C_4H_9$-*n*	42
		$C_6H_{11}C_4H_9$-*n*	58
o-$CH_3C_6H_4COCH_3$	24	*o*-$CH_3C_6H_4C_2H_5$	92
m-$CH_3C_6H_4COCH_3$	24	*m*-$CH_3C_6H_4C_2H_5$	85
		1-ethyl-3-methylcyclohexane	15
o-$CH_3OC_6H_4COCH_3$	24	*o*-$CH_3OC_6H_4C_2H_5$	98
m-$CH_3OC_6H_4COCH_3$	24	*m*-$CH_3OC_6H_4C_2H_5$	96
p-$CH_3OC_6H_4COCH_3$	24	*p*-$CH_3OC_6H_4C_2H_5$	88
$PhCOCH_2OCH_3$	17	$PhCH_2CH_2OCH_3$	29
		$PhCH(OH)CH_2OCH_3$	71
1-tetralone	24	tetralin	93
		decalin	7
6-methoxy-1-tetralone	24	6-methoxytetralin	49
PhCHO	18	toluene	93[e]
o-$CH_3OC_6H_4CHO$	24	*o*-$CH_3OC_6H_4CH_3$	98
m-$CH_3OC_6H_4CHO$	24	*m*-$CH_3OC_6H_4CH_3$	80
		m-$CH_3OC_6H_4CH_2OH$	18
	40	*m*-$CH_3OC_6H_4CH_3$	99
o-$CH_3C_6H_4CHO$	24	*o*-xylene	92
		o-$CH_3C_6H_4CH_2OH$	8
p-$CH_3C_6H_4CHO$	48	*p*-xylene	84
		p-methylbenzyl alcohol	16
o-HOC_6H_4CHO	24	*o*-$HOC_6H_4CH_3$	98
m-HOC_6H_4CHO	24	*m*-$HOC_6H_4CH_3$	86
	36	*m*-$HOC_6H_4CH_3$	100
p-$(CH_3)_2NC_6H_4CHO$	36	*p*-$(CH_3)_2NC_6H_4CH_3$	95[d]
p-$CH_3OCOC_6H_4CHO$	48	*p*-$CH_3OCOC_6H_4CH_3$	18
		p-$CH_3OCOC_6H_4CH_2OH$	77
p-$CH_3COOC_6H_4CHO$	48	*p*-$CH_3COOC_6H_4CH_3$	54
		p-$CH_3COOC_6H_4CH_2OH$	36

[a] Products were identified by comparison of spectral data, as well as GC retention times, with authentic samples. [b] Yield determined by gas chromatography. [c] Use of 2:1 sulfolane/THF as the solvent afforded PhC_2H_5 in 48% yield. [d] Isolated yield. [e] No reaction in the absence of the metal catalyst.

is believed to be located in an exposed position and the arene ring is inside the cavity and thus protected from reaction. Consequently, the carbonyl function would be easily susceptible to attack by an in situ generated rhodium hydride intermediate. That the formation of a β-cyclodextrin–substrate inclusion complex is critical to the success of the reduction process was clearly demonstrated by comparison with the behavior of α-cyclodextrin under identical reaction conditions. α-Cyclodextrin does not form 1:1 complexes with the carbonyl substrates.[18] Reaction of *p*-methoxyacetophenone with H_2,[1,5-HDRhCl]$_2$, and α-cyclodextrin in THF afforded *p*-ethylanisole in only 14% yield (85% recovered starting material). The yield is much lower than that realized by using β-cyclodextrin (88%) and is even less than in the absence of a cyclodextrin (24%). The presence of a presumably "inert" additive such as α-cyclodextrin may have an unfavorable effect on the kinetics of the hydrogenation reaction. Irrespective of the mechanistic details,[19] the method described above for the reduction of aldehydes and ketones to hydrocarbons is simple in both execution and workup,[20] proceeds under exceptionally mild conditions and shows good functional group selectivity.

Acknowledgment. We are indebted to British Petroleum, and to the Natural Sciences and Engineering Research Council, for support of this research.

Registry No. $PhCOCH_3$, 98-86-2; $PhCOC_2H_5$, 93-55-0; $PhCOC_3H_7$, 495-40-9; *o*-$MeC_6H_4COCH_3$, 577-16-2; *m*-$MeC_6H_4COCH_3$, 585-74-0; *o*-$MeOC_6H_4Ac$, 579-74-8; *m*-$MeOC_6H_4Ac$, 586-37-8; *p*-$MeOC_6H_4Ac$, 100-06-1; $PhCOCH_2OCH_3$, 4079-52-1; PhCHO, 100-52-7; *o*-$MeOC_6H_4CHO$, 135-02-4; *m*-$MeOC_6H_4CHO$, 591-31-1; *o*-MeC_6H_4CHO, 529-20-4; *p*-MeC_6H_4CHO, 104-87-0; *o*-HOC_6H_4CHO, 90-02-8; *m*-HOC_6H_4CHO, 100-83-4; *p*-$Me_2NC_6H_4CHO$, 100-10-7; *p*-$MeOCOC_6H_4CHO$, 1571-08-0; *p*-$AcOC_6H_4CHO$, 878-00-2; PhEt, 100-41-4; $C_6H_{11}Et$, 1678-91-7; PhC_3H_7-*n*, 103-65-1; $C_6H_{11}C_3H_7$-*n*, 1678-92-8; $C_6H_{11}C_4H_9$-*n*, 1678-93-9; *o*-MeC_6H_4Et, 611-14-3; *m*-MeC_6H_4Et, 620-14-4; *o*-$MeOC_6H_4Et$, 14804-32-1; *m*-$MeOC_6H_4Et$, 10568-38-4; *p*-$MeOC_6H_4Et$, 1515-95-3; $Ph(CH_2)_2OMe$, 3558-60-9; $PhCH(OH)CH_2OMe$, 3587-84-6; MePh, 108-88-3; *o*-$MeOC_6h_4Me$, 578-58-5; *m*-$MeOC_6H_4Me$, 100-84-5; *m*-$MeOC_6H_4CH_2OH$, 6971-51-3; *o*-MeC_6H_4Me, 95-47-6; *o*-$MeC_6H_4CH_2OH$, 89-95-2; *p*-MeC_6H_4Me, 106-42-3; *p*-$MeC_6H_4CH_2OH$, 589-18-4; *o*-HOC_6H_4Me, 95-48-7; *m*-HOC_6H_4Me, 108-39-4; *p*-$Me_2NC_6H_4Me$, 99-97-8; *p*-$MeOCOC_6H_{Me}$, 99-75-2; *p*-$MeOCOC_6H_4CH_2OH$, 6908-41-4; *p*-$AcOC_6H_4Me$, 140-39-6; *p*-$AcOC_6H_4CH_1OH$, 6309-46-2; [1,5HDRhCl]$_2$, 32965-49-4; 1-tetralone, 529-34-0; 6-methoxy-1-tetralone, 1078-19-9; 1-ethyl-3-methylcyclohexane, 3728-55-0; tetralin, 119-64-2; decalin, 91-17-8; 6-methoxytetralin, 1730-48-9; β-cyclodextrin, 7585-39-9.

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(20) The following general procedure was used. Hydrogen is bubbled through a stirred THF solution (9 mL) of the substrate (3.2 mmol), [1,5-HDRhCl]$_2$ (0.065 mmol), and β-cyclodextrin (0.32 mmol) at room temperature and 1 atm. After 8–48 h (see Table I), the solvent was removed by rotary evaporation, and the product was purified either by distillation or by column chromatography.

Trapping of Silylenes by 9,10-Dimethylanthracene: 2,3:5,6-Dibenzo-7-silabicyclo[2.2.1]hepta-2,5-dienes

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Summary: Silylenes generated thermally from 7-silanorbornadienes **1a–c** react with 9,10-dimethylanthracene (DMA) to give 7-silabicyclo[2.2.1]hepta-2,5-dienes **3a–c**. For dimethylsilylene, a small amount of 2,3:5,6-dibenzo-1,4,7,7,8,8-hexamethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene (**4a**) is also obtained, arising via Diels–Alder reaction of tetramethyldisilene with DMA.

Although silylenes are known to add to alkenes, alkynes, dienes, and carbonyl compounds,[1] addition of silylenes to

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(1) Gaspar, P. P. In *Reactive Intermediates*; Jones, M., Jr., Moss, R. A., Eds.; Wiley: 1978; Vol. 1, p 229. *Ibid.*, Vol. 2, p 335, 1981. *Ibid.*, Vol. 3, p 333, 1985.

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