Registry No. 1, 78823-94-6; 2, 79161-14-1; 3, 84432-84-8; 4, 86022-50-6; 5, 37035-38-4; 6, 85976-72-3; 7, 85976-73-4; PhC(S)-SCH_3, 2168-78-7; $Co_2(CO)_8$, 10210-68-1; (*R*)-(+)-α-methylbenzylamine, 3886-69-9; styrene, 100-42-5.

Supplementary Material Available: Listing or positional and thermal atomic parameters and experimental and calculated structure factors (26 pages). Ordering information is given on any current masthead page.

Iron Complexes of Homocycloheptatrienylidene

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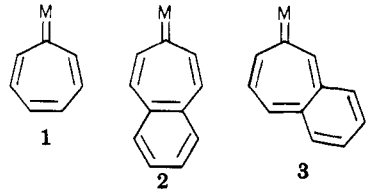
Received September 7, 1982

Summary: Protonation of FpCOT and FppCOT (Fp = η^5-cyclopentadienyl)iron dicarbonyl, COT= cyclooctatetraene, Fpp = (η^5 - cyclopentadienyl)iron carbonyl tri-R-phosphine) with strong acid produces homoaroamtic carbene complexes **7**, **8**, and **9**. Although all three complexes are clearly homoaromatic, ^1H and ^{13}C NMR spectra suggest that $d\pi$–$p\pi$ back-bonding reduces the homoaromaticity relative to the parent homotropylium ion.

In previous papers[1-3] we have reported the preparation and properties of some transition-metal complexes of cycloheptatrienylidenes **1–3**. As a continuation of our efforts



1 2 3

directed toward the synthesis and properties of complexes of cyclic conjugated carbenes that are stabilied by incorporation of the carbene p orbital in an aromatic $p\pi$ orbital system,[4] we have now prepared three iron complexes of homocycloheptatrienylidene. In this communication we report the synthesis of **7–9** (Scheme I) and spectral properties that both elucidate their structures and show that while considerable homoaromaticity is retained in the organic ligands of each complex, there is also significant back-bonding from iron into the π system.

The method of synthesis of the three complexes is outlined in Scheme I.[6] Neither of the two methods used to prepare FpCOT (**4**) gave very high yields (ca. 15–29%). However, of the two, we found the high dilution addition of Fp^- to BrCOT at 21 °C to be generally more satisfactory because it not only gave somewhat better yields but was easier to workup. σ complexes **5**[9] and **6**[10] were made in high yield by photoinduced replacement of CO by R_3P. The carbene complexes were made by protonation of the corresponding σ complexes (−40 °C) with either excess dry HCl, 2 equiv of FSO_3H, or 2 equiv of CF_3CO_2H in dry CH_2Cl_2,[11] Addition of 1.1 equiv of $Ph_2C^+PF_6^-$ followed by dilution with cold, dry ether gave the carbene complexes as their PF_6^- salts.[12]

The hexafluorophosphate salt **7**[13] crystallized as orange needles which are stable in air below −10 °C but which rapidly react with oxygen in solution. Above −10 °C it

(1) Allison, N. T.; Kawada, Y.; Jones, W. M. *J. Am. Chem. Soc.* **1978**, *100*, 5224.
(2) Riley, P. E.; Davis, R. E.; Allison, N. T.; Jones, W. M. *J. Am. Chem. Soc.* **1980**, *102*, 2452.
(3) Riley, P. E.; Davis, R. E.; Allison, N. T.; Jones, W. M. *J. Am. Chem. Soc.* **1982**, *21*, 1321.
(4) The first complexes stabilized by aromaticity were cyclopropenylidene complexes, first synthesized by Ofele and his co-workers.[5]
(5) (a) Ofele, K. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 950. (b) Ofele, K. *J. Organomet. Chem.* **1970**, *22*, C9.
(6) Bromocycloctatetraene was prepared by the method of; Gasteiger, J.; Gleam, G. E.; Huisgen, R.; Konz, W. E.; Schneeg, U. *Chem. Ber.* **1971**, *104*, 2412. KFp was prepared by the method of Gladysz.[7]
(7) Gladysz, J. A.; Williams, G. M.; Tam, W.; Johnson, D. L. *J. Organomet. Chem.* **1977**, *140*, C1.

(8) (a) **4** has been previously prepared via the cyclooctatetraenyllithium route. Cooke, M.; Russ, C. R.; Stone, F. . A. *J. Chem. Soc., Dalton Trans.* **1975**, 256. For example of displacement of a vinyl fluoride by Fp^-, see: King, R. B.; Bisnette, M. B., *J. Organomet. Chem.* **1964**, *2*, 38. (b) **4** is a yellow air-sensitive oil (best stored refrigerated in solvent other than $CHCl_3$): ^1H NMR (300 mHz, CD_2Cl_2, δ) 4.81 (s, Cp) 5.22 (dd, H7, $J_{7,8}$ = 11.1 Hz, $J_{2,3}$ = 3.4 Hz), 5.51 (dd, H5, $J_{5,6}$ = 10.9 Hz, $J_{4,5}$ = 3.2 Hz), 5.68 (d, H2, $J_{2,3}$ = 2.8 Hz), 5.75 (dd, H6), 5.77–5.85 (m, H3 and H4), 6.16 (d, H8); ^{13}C NMR (CD_3COCD_3, δ) 87.2 (Cp), 119.3, 129.2, 132.6 (2 C), 136.7, 139.3, 147.7, 151.7 (C1), 217.2 (CO), 217.7 (CO); IR (film, cm^{-1}) 2960, 1990, 1925, 1560, 1400, 1005, 909, 827, 702, 714; high-resolution mass spectrum, *m/e*(calcd) 280.018 50, *m/e*(measd) 280.019 84; Anal. Calcd for $C_{15}H_{13}FeO$: C, 64.31; H, 4.32. Found: C, 64.07; H, 4.40. The isodynamic interconversions of the COT moiety in **4** were observed. Exchange of diastereotopic CO ligand signals (^{13}C NMR) allowed calculation of ΔG^*(ring inversion) = 16.6 kcal/mol; broadening and coalescence of the COT ^1H NMR signals due to bond shift processes was consistent with a ΔG^*(bond shift) ~18 kcal/mol.
(9) FppCOT's were prepared by photolysis of **4** in THF (overnight) with the appropriate phosphine using a 450-W Hanovial Hg lamp. **5** was isolated by short column chromatography (neutral alumina, hexane) and is an air-stable orange glass: ^1H NMR (300 mHz, CD_2Cl_2, δ) 4.45 (d, Cp of one diastereoisomer, J_{PH} = 1.1 Hz) 4.49 (d, Cp of other diastereoisomers, J_{PH} = 1.1 Hz) 4.91 (dd, H7, $J_{7,8}$ = 11.1 Hz, $J_{6,7}$ = 3.2 Hz), 4.95 (dd, H7', $J_{7',8'}$ = 11.0 Hz, $J_{6',7'}$ = 3.2 Hz), 5.30–5.84 (complex multiplet H2, H5, H6, H4, H3), 6.10 (dd, H8), 6.29 (dd, H8'), 7.37 (br s, phenyls); ^{13}C NMR (CD_2Cl_2, δ) 85.4 (pseudo d, Cp diastereoisomers) 116.6 (pseudo d), 130–140 (phenyl and COT), 149.5 (s) 164.4 (pseudo dd, C-1 of COT) 222.3 (pseudo dd, CO); IR ($CHCl_3$, cm^{-1}) 2995, 1920; mass spectrum, *m/e* 486 (M^+ − CO), 383, 262 (100%), 224, 121, 56; *Anal.* Calcd for $C_{32}H_{27}FeOP$: C, 74.72; H, 5.29. Found: C 74.49; H, 5.35. The isodynamic interconversions of the COT moiety in **5** were observed. Exchange of diastereotopic Cp signals (^1H NMR) allowed calculation of ΔG^* (ring inversion) = 17.3 kcal/mol; broadening and coalescence of the COT H NMR signals due to bond shift processes produced a ΔG^* ~ 18 kcal/mol.
(10) **6** is a yellow-orange air-sensitive oil: ^1H NMR (300 mHz, CD_3COCD_3, δ) 0.9–1.9 (complex m, butyl), 4.4 and 4.5 (d's, Cp diastereoisomers, J_{PH} = 1.1 Hz), 4.9 (m, H7), 5.3 (m, H5), 5.6 (complex m, H2, H6, H3, H4), 6.3 (m, H8); ^{13}C NMR (CD_3COCD_3, δ) 24–32 (butyl) 3.6 (pseudo d, Cp diastereoisomers), 115.7 (pseudo d), 132.0 (s), 133.3 pseudo d), 137.0 (2 C, separated below 0 °C), 149.9 (pseudo d) 167.1 (pseudo dd, C1 of COT), 221.9 (pseudo dd, CO); IR[1] ($CHCl_3$, cm^{-1}) 2995, 1925. The isodynamic interconversions of the COT moiety in **6** were observed. Exchange of diastereoisomeric Cp signals (^1H NMR) allowed calculation of ΔG^*(ring inversion) = 17.0 kcal/mol; broadening and coalescence of the COT ^1H NMR signals due to bond shift processes produced a ΔG^* ~ 18 kcal/mol.
(11) Both **5** and **6** showed NMR spectra indicative of mixtures of slowly interconverting diasteroisomers.[9,10] It was therefore quite a surprise that in neither case did the protonated products appear as diastereomers. For instance, in the ^{13}C NMR spectra, in each case the carbonyl resonance appeared as simple doublets (coupled with phosphorus), in the ^1H spectra the exo and endo hydrogens appeared as simple doublets, etc. This surprising result is probably due to thermodynamic preference for one diastereoisomer which is rapidly formed (by a ring-flipping process) from a mixture of initially produced diastereoisomers. neither **8** nor **9** showed any significant change in their NMR spectra with changes in temperature.
(12) We have found metathesis with $Ph_3C^+PF_6^-$ to be a convenient technique for exchanging anions in relatively nonpolar solvents due to the solubility of the resulting Ph_3CX.
(13) **7**: ^1H NMR (300 mHz, CD_2Cl_2, −20 °C, δ) 1.27 (t, $H8_{endo}$ $J_{8_{endo},8_{exo}}$ = 8.9 Hz, $J_{7,8_{endo}}$ = 0.0 Hz), 5.26 (s, Cp), 5.57 (t, $H8_{exo}$ = 7.3 Hz), 5.78 (t, H7, $J_{6,7}$ = 9.0 hZ), 7.34 and 7.35 (m, H4 and H3, $J_{3,4}$ = 9.1 Hz), 7.47 (t, H6, $J_{5,6}$ = 6.9 Hz), 7.83 (m, H5, $J_{4,5}$ = 11.4 Hz), 8.86 (d, H2, $J_{2,3}$ = 9.7 Hz, $J_{2,5}$ = 0.9 Hz); ^{13}C NMR (CD_2Cl_2, −20 °C δ) 210.4 (CO), 211.5 (CO), 269.0 (C1); IR (KBr, cm^{-1}) 2002, 1970, 1440, 1300, 1275, 1070, 980, 840 cm^{-1}; mp (rapid heating), orange to brown at 70 °C melts at ca. 80 °, effervesces at 100–105 °C.

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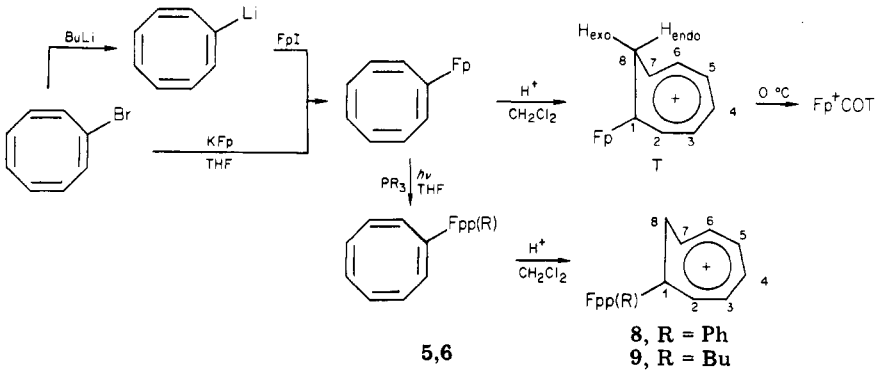
Scheme I



Fp = (η^5-cyclopentadienyl)iron dicarbonyl; Fpp(R) = (η^5-cyclopentadienyl)iron carbonyl tri-R-phosphine

rapidly decomposes both in the solid state and in solution. For example, a solution 7 in CD_2Cl_2 kept at 0 °C for 1 h led to 40% decomposition to the Fp^+ π complex of cyclooctatetraene. Complex 8[14] was isolated as an amorphous purple solid. It is the most thermally stable of the three. For instance, brief exposure in CD_2Cl_2 solution to temperatures as high as 50 °C was tolerated with no detectable decomposition. When dry this complex could be stored indefinetly at −10 °C. Complex 9[15] showed intermediate thermal stablity but is more sensitive to oxygen than 7, decomposing both in solution and as the solid.

Two parameters[16] that have been frequently used to evaluate the extent of homoaromatic delocalization in cyclooctatrienyl cations are the chemical shift separations of $H8_{exo}$ and $H8_{endo}$[17-19] and the coupling constants between $H8_{exo}$ and $H8_{endo}$. On both counts, complexes 7–9 are clearly homoaromatic. The chemical shift separations of $H8_{exo}$ and $H8_{endo}$ are 4.30, 3.12, and 3.00 ppm for the three complexes, respectively. These are less than has been reported for the parent homotropylium ion (5.8 ppm)[19a] but are similar to separations reported for other 1-substituted homotropylium ions.[17,19] The origin of the variations in chemical shift differences in 7–9 is discussed below. The coupling constants between $H8_{exo}$ and $H8_{endo}$ for all three complexes are also similar to those of other homotropylium ions. This is considered to be evidence against significant cyclopropane character in the ion[20] (i.e., σ bonding between C1 and C7).

At the same time that these complexes show homoaromatic delocalization, they also show a number of properties that would be expected if there were significant $d\pi$–$p\pi$ back-bonding from iron into the π system. Perhaps the most distinctive of these are the ^{13}C chemical shifts of C1. In all three complexes these resonances appear at very low fields as is characteristic of carbene complexes. These shifts are believed to be related to, among other things, the $d\pi$–$p\pi$ bonding between the metal and the carbene carbon (in a homologous series, the greater the back-bonding, the greater the downfield shift).[21,22] In the case at hand, it would be reasonable to expect backbonding into the homotropylium ring to be more favorable than into the more aromatic tropylium ion and, indeed, the shift of C1 in 7 (269.0 ppm) appears at much lower field relative to C1 in the homotropylium ion (122.2 ppm)[24,25] than is the case for the corresponding Fp- and H-substituted tropylium systems (242.3[1] vs. 160.6 ppm[26]). Furthermore, back-bonding should increase if a carbonyl ligand is replaced with a phosphine and the chemical shifts of the carbene carbons of 8 and 9 are at 311.1 and 315.7 ppm, respectively, significantly further downfield than observed in 7.

A second property of these complexes that suggests significant back-bonding is the separation of the NMR resonances of the endo and exo hydrogens. Thus, even though these separations clearly indicate homoaromaticity, their magnitude (4.30, 3.12, and 3.00 ppm for 7, 8, and 9, respectively) is significantly less than for the parent homotropylium ion (5.8 ppm)[19a,27] which suggests conjugation of Fp with the homotropylium ion. For comparison the shift difference for 1-methoxyhomotropylium is 3.1 ppm.[17] Finally, the vinyl H–C–C–H coupling constants of 7[13] 8[14] and 9[15] clearly require some degree of bond alternation.[28]

(14) 8: ^1H NMR (300 mHz, CD_2Cl_2, −20 °C, δ) 1.67 (t, $H8_{endo}$, $J_{endo,exo}$ = 8.9 Hz, $J_{7,8_{endo}}$ = 8.9 Hz), 4.79 (t, $H8_{exo}$, $J_{7,8}$ = 7.7 Hz), 4.87 (d, Cp, J_{PH} = 1.2 Hz), 5.42 (q, H7, $J_{6,7}$ = 8.5 Hz), 6.51 (t, H3, $J_{3,4}$ = 8.9 Hz), 6.66 (t, H4, $J_{4,5}$ = 11.6 Hz), 6.78 (t, H6), 7.07 (dd, H5, $J_{5,6}$ = 6.4 Hz), 7.37–7.77 (m, Ph's), 8.51 (d, H2, $J_{2,3}$ = 11.5 Hz); ^{13}C NMR (of trifluoroacetate salt, CD_2Cl_2, −20 °C, δ) 61.7 (C8), 90.8 (Cp), 124–138 (ring C's and Ph's, 161.5 (C2), 216.4 (d, CO, J_{CP} = 29.3 Hz), 311.4 (d, C1, J_{CP} = 22.0 Hz); IR (KBr, cm^{-1}) 1975.

(15) 9: ^1H NMR (300 mHz, CD_2Cl_2, −20 °C, δ) 0.9–2.0 (m, butyl), 2.48, t, $H8_{endo}$, $J_{8_{endo},8_{exo}}$ = 8.3 Hz, $J_{7,8_{endo}}$ = 8.1 Hz), 4.97 (d, Cp, J_{PH} = 1.2 Hz), 5.48 (m, $H8_{exo}$ and H7, $J_{7,8_{exo}}$ = 7.7 Hz), 6.45 (t, H3, $J_{3,4}$ = 8.9 Hz), 6.62 (t, H4, $J_{4,5}$ = 11.5 Hz), 6.73 (t, H6, $J_{6,7}$ = 8.7 Hz, 7.04 (dd, H5, $J_{5,6}$ = 5.7 Hz), 8.48 (d, H2, $J_{2,3}$ = 11.7 Hz); ^{13}C NMR (trifluoroacetate) (CD_2Cl_2, −20 °C, δ) 13.6–29.9 (butyl), 62.7 (C8), 90.3 (Cp), 123.2, 130.1, 134.3, 135.4, 137.4 (C3–C7), 161.5 (C2), 217.1 (d, CO, J_{CP} = 28.1 Hz), 315.7 (d, Cl, J_{CP} = 22.0 Hz); IR (KBr, cm^{-1}) 1960.

(16) A third parameter that has been used to assess homoaromaticity is the activation barrier to bridge flipping.[17] Unfortunately, deuterationof 7 was not sufficiently selective even at −100 °C to permit use of this technique.

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(22) We recognize the dangers inherent in attempting to overinterpret ^{13}C chemical shifts in metal complexes. Nonetheless we have found that this qualitative generality holds in every (η^5-cyclopentadienyl)iron complex that we have prepared. On the other hand, we note at least one reported exception.[23] We have also found that some ruthenium complexes that we have prepared show resonances at *higher* field than their iron analogues.

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(25) Some of the difference may be due to back-bonding induced reduction in cyclopropane character at C1. However, from comparison of shifts of remote carbons in 2 and their counterparts in the homotropylium ion, this cannot be the whole explanation for these differences.

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(28) Cf.: Gunter, H.; Schmickler, H.; Gunther, M. E.; Cremer, D. *Org. Magn. Reson.* **1977**, *9*, 420.

This alternation is as expected of $d\pi$–$p\pi$ back-bonding.

Acknowledgment. We gratefully acknowledge financial support for this research from the National Science Foundation. The 300-mHz spectra were obtained on a Nicolet NT-300 NMR spectrometer which was purchased with funds provided by the National Science Foundation.

Registry No. 5, 85957-15-9; 6, 85957-16-0; 7, 85957-10-4; 8, 85957-12-6; 9, 85957-14-8; FpCOT, 55672-79-2.

Exceedingly Mild, Selective and Stereospecific Phase-Transfer-Catalyzed Hydrogenation of Arenes

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Received April 29, 1983

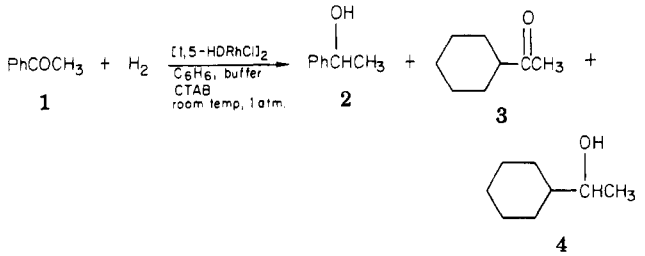
Summary: Arenes and heterocyclic compounds react with hydrogen, a catalytic amount of the dimer of chloro(1,5-hexadiene)rhodium (100:1 ratio of substrate/catalyst), benzene or hexane as the organic phase, a buffer solution, and a quaternary ammonium salt as the phase-transfer catalyst, to give reduced products in good to excellent yields. This very mild process (room temperature, 1 atm) is applicable to a variety of functionalized arenes, and the stereospecificity of the reaction was demonstrated with naphthalene and *p*-methylanisole.

Phase-transfer catalysis is a valuable method for effecting metal-catalyzed reactions under very gentle conditions.[1] Examples include the cobalt carbonyl catalyzed regiospecific acylation of dienes and trienes[2] and the palladium(0)-catalyzed carbonylation of vinylic dibromides to diacids, monoacids, or diynes.[3]

There has been considerable interest in asymmetric synthesis, under phase-transfer catalysis, using optically active quaternary ammonium salts. However, a number of claims in this area have been found to be incorrect.[4] Besides ammonium salts, bovine serum albumin (BSA) has been used in the two-phase asymmetric oxidation of dithioacetals with aqueous sodium metaperiodate.[5]

We reasoned that BSA might coordinate to a metal atom giving a complex capable of catalyzing reactions so as to give products in good optical, as well as chemical, yields. The metal-catalyzed and phase-transfer-catalyzed hydrogenation of acetophenone to 1-phenylethanol, in the presence of the protein, was chosen as a model reaction for this investigation. The homogeneous hydrogenation of acetophenone has been reported to occur in up to 51% optical yield using the dimer of chloro(1,5-hexadiene)-rhodium [1,5-HDRhCl]$_2$ as the catalyst with added optically active phosphine.[6]

Treatment of acetophenone (1) with hydrogen, [1,5-HDRhCl]$_2$ (100:1 ratio of 1/Rh complex), buffer of pH 9.2, benzene, BSA, and cetyltrimethylammonium bromide (CTAB) as the phase-transfer agent afforded racemic 1-phenylethanol (2) in 21% yield. However, the major and unexpected pathway was reduction of the benzene ring of 1, giving methyl cyclohexyl ketone (3) in 28% yield and 1-cyclohexylethanol (4) in 3% yield. Since 2 was optically



inactive, it seemed conceivable that BSA was not participating in the reaction. The mixture of BSA and the buffer of pH 9.2 gave a solution of pH 7.6. Therefore, the hydrogenation reaction was repeated by using a buffer of pH 7.6, but no BSA. In this case, the yield of methyl cyclohexyl ketone (3) improved significantly (to 53%—Table I). Use of hexane as the organic phase gave 3 and 4, products of reduction of the arene ring, in a total yield of 90%.

Application of the reaction to other aromatic ketones (phenylacetone, benzylacetone) gave saturated ketones in good yields. The selectivity of the arene reduction reaction was further demonstrated with benzamide, methyl benzoate, and phenyl acetate, all of which experienced reduction of only the benzene ring. Even phenol can be hydrogenated to form either cyclohexanol or cyclohexanone as the predominant product, depending on the reaction conditions.

Simple aromatic compounds are also hydrogenated. Naphthalene can be partially reduced to tetralin or completely and stereospecifically converted to *cis*-decalin. *cis*-4-Methylcyclohexyl methyl ether was obtained as the only product, in 92% yield, from *p*-methylanisole. Reasonable quantities of hydrogenated products were also formed from *n*-butylbenzene from *o*-xylene.

Several classes of heterocycles were also easily reduced, including 2-ethylfuran, 2-methylpyridine, and quinoline, the latter undergoing hydrogenation of the heterocyclic ring only. Surprisingly, isoquinoline was inert under identical reaction conditions.

Qualitatively, electron-donating substituents activate the arene ring toward hydrogenation while the presence of electron-withdrawing groups ($CONH_2$, $COOCH_3$) slows down or inhibits [NO_2] reduction.

The constituents which make up the buffer are not important. It is the pH of the buffer that is critical—i.e., pH 7.4–7.6. As noted in Table I, $C_6H_{11}CH_2CH_2COCH_3$ was isolated in 97% yield from the reaction of benzyl acetone with hydrogen, tetrabutylammonium hydrogen sulfate (THS) as the phase-transfer catalyst, hexane, and the buffer solution of pH 7.6 (prepared from boric acid, citric acid, and sodium phosphate).[7] Substitution of a pH 7.4 buffer, prepared from KH_2PO_4 and NaOH, in the latter reaction gave the saturated ketone in 100% yield. Likewise, $C_6H_{11}CH_2CH_2COCH$ was formed in 96% yield using a buffer of the same pH (7.4) but prepared by using tris(hydroxymethyl)aminomethane and HCl.

Several other points are noteworthy. First, the rhodium(III) catalyst, hydrated rhodium chloride ($RhCl_3 \cdot 3H_2O$), is inert under these conditions, as is rhodium acetate and chlorodicarbonylrhodium(I) dimer. Second, the reaction is an authentic phase-transfer process, since produce yields in the absence of the quaternary ammonium salt are much

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