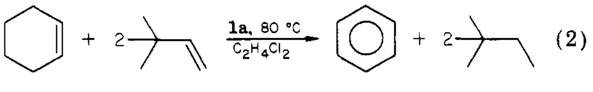
side reactions; **1a** catalyzes the disproportionation of cyclohexene to benzene and cyclohexane at 80 °C. In this reaction the desired arene is accompanied by 2 mol equiv of alkane. The addition of tbe, however, leads to the selective formation of benzene (eq 2). At a substrate:catalyst ratio of 100:1, the initial rate is 3 turnovers/h and the conversion is complete in 48 h at 80 °C. Essentially no cyclohexane is formed, showing how selective[5] is **1a** in hydrogenating tbe in preference to cyclohexene. Methylcyclohexene is also catalytically dehydrogenated at 130 °C in $C_2H_4Cl_2$ (sealed tube).



Initial experiments on the effect of base show that catalytic alkane dehydrogenation can occur. For example, cyclooctane gives $[Ir(cod)L_2]A$ (75%, cod = 1,5-cyclooctadiene) with **1c** at 125 °C for 18 h but gives 8 turnovers of free cyclooctene and a trace of cyclooctadienes after 24 h at 140 °C (tbe:Ir = 100:1) with 1.1 mol equiv of 1,8-bis(dimethylamino)naphthalene. The base deprotonates the metal (the protonated amine can be isolated at the end of the reaction), and olefin binding may be weaker to the resulting neutral species and therefore may be released.[10] Cyclohexane gives cyclohexene and benzene (0.4 turnovers each). The deprotonated system is alkane soluble.

While some of the reactions reported above are heterogeneous in the sense that two phases are present, the similarity between this chemistry and that previously reported by us[2d] makes it probable that all these systems are mechanistically alike and in particular do not involve metallic iridium.[12] The salts may well be slightly soluble in the reaction mixture under the reaction conditions.

The degree of dehydrogenation achieved in alkane activation appears to depend on the electron count of the metal species and the binding strength for olefins. The 12-electron strongly binding fragment "IrL_2^+" gives benzene, neutral 12–14-electron fragments tend to give olefins,[10] and 16-electron fragments[4] give the alkyl hydride.

Acknowledgment. We thank the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support and Johnson Matthey for a loan of iridium.

Registry No. **1a**, 72414-17-6; **1b**, 89509-77-3; **1c**, 89529-62-4; **2** (R = Me), 89509-81-9; **2** (R = Et), 89509-83-1; **3**, 89509-84-2; **4**, 89509-85-3; $[IrCp[P(p\text{-}FC_6H_4)_3]_2]SbF_6$, 89509-79-5; $[Ir(MeC_6H_6)H[P(p\text{-}FC_6H_4)_3]_2]^+$, 89509-86-4; $[Ir(cod)[P(p\text{-}FC_6H_4)_3]_2]SbF_6$, 89509-87-5; ±-BuCH=CH$_2$, 558-37-2; ethylcyclopentane, 1640-89-7; cyclohexane, 110-82-7; methylcyclohexane, 108-87-2; cyclopentane, 287-92-3; methylcyclopentane, 96-37-7; cyclohexene, 110-83-8; methylcyclohexene, 1335-86-0; cyclooctane, 292-64-8; 1,8-bis(dimethylamino)naphthalene, 20734-58-1; benzene, 71-43-2; chlorobenzene, 108-90-7; toluene, 108-88-3; cyclooctene, 931-88-4.

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(10) One equivalent of base is required for full activity, but up to 10 equiv did not inhibit the dehydrogenation reaction. These simple dehydrogenations of alkanes to olefins by neutral highly coordinatively unsaturated species and tbe seem to be quite general.[3] Hugh Felkin informs us (personal communication, 1983) that $RuH_4(PPh_3)_3$ and $IrH_5(PPh_3)_2$ are active, and we have more recently found $OsH_4(p\text{-}FC_6H_4)_3P)_3$ is also effective.[11]

(11) Crabtree, R. H.; Davis, M. W., unpublished observations, 1983.

(12) The reactions described proceed even in the presence of metallic mercury, a poison for heterogeneous catalysts,[13] suggesting that metallic iridium is not involved in these dehydrogenations.

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Electron Transfer vs. Hydride Transfer in the Reduction of $[C_5R_5Fe(dppe)(CO)]^+PF_6^-$ (R = H or CH_3) by $LiAlH_4$[1]

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Received November 22, 1983

Summary: $LiAlH_4$ reacts with $[C_5Me_5Fe^{II}(dppe)(CO)]^+PF_6^-$, **4**, at −80 °C to give $C_5Me_5Fe^{II}(dppe)(CO)(H)$, **5**, via an electron-transfer mechanism and subsequent H atom abstraction by the 17-electron intermediate $[C_5Me_5Fe^{I}(dppe)(CO)]$; this highly unstable and reactive species can also be generated by one-electron reduction of **4** (K mirror or Na/Hg) and gives **5** on Na/Hg/OH$^-$.

Intermolecular reduction by main-group hydrides of CO activated in transition-metal complexes is a widely recognized model for the important Fischer–Tropsch process.[2–6] Yet the site of hydride transfer to the transition-metal carbonyl complex is not always the carbonyl carbon; it may in some instances be an ancillary organic ligand or the metal itself. The rules of Green et al. have proposed priorities in this respect, based on the principle that nucleophilic attack on organotransition-metal cations is charge controlled.[7] A possible alternative that we wish to illustrate here is the electron-transfer (ET) pathway, followed by H atom abstraction from the hydride or the medium (Scheme I). Recently, we showed that the ET mechanism may occur in the reduction of d^6 and d^7 organoiron complexes by $NaBH_4$ and $LiAlH_4$,[8] but this study was limited to sandwich complexes.

It is already known from the recent work by Davies et al. that $LiAlH_4$ reduction of $[C_5H_5Fe^{II}(dppe)(CO)]^+PF_6^-$, **1**, in THF yields the formyl complex $C_5H_5Fe^{II}(dppe)(CHO)$, **2**, at −80 °C. We have verified this finding and noticed that **2** is stable up to 0 °C (by ^1H and ^{31}P NMR), giving then *inter alia* $C_5H_5Fe^{II}(dppe)(CO)(H)$,[9] **3**. Reduction of $[C_5Me_5Fe^{II}(dppe)(CO)]^+PF_6^-$, **4**,[10] under identical conditions at −80 °C immediately gives the new, pale yellow hydride complex $C_5Me_5Fe^{II}(dppe)(CO)(H)$, **5**.[11] No

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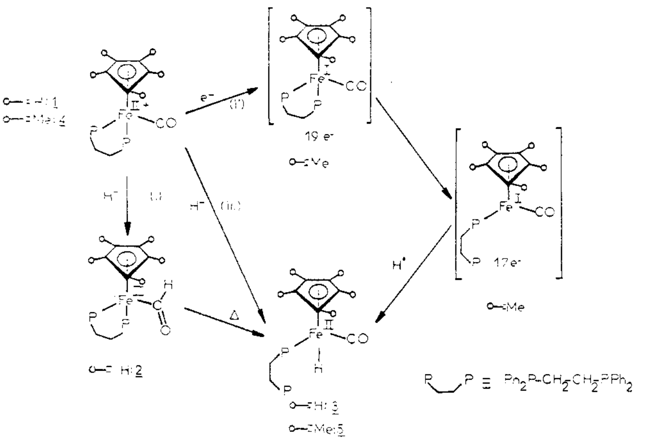
Scheme I. Possible Pathways for Hydride Reduction of 1 and 4



(i) H^- transfer to CO (-o = H); (ii) electron transfer (-o = CH_3); (iii) H^- attack at the iron center (reported in ref 12 for $CpFe^+$triphos).

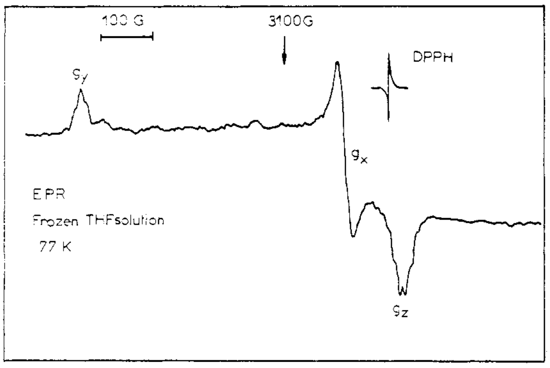


Figure 1. EPR spectrum (77 K) of the reaction medium: 4 + $LiAlH_4$ in THF at -80 °C.

trace of the formyl complex is found (^1H and ^{31}P NMR) in THF-d_8 at -80 °C. The $LiAlH_4$ reduction of $[(C_5H_5Fe^{II}tripod)]^+PF_6^-$ has been reported by Davies et al. to give $C_5H_5Fe^{II}(tripod)(H)$ by direct hydride attack at the metal.[12] In view of the facile, low-temperature decomplexation of one phosphorous donor in these diphos and triphos complexes and knowing that monoelectronic reduction of transition-metal complexes containing both CO and phosphine ligands always induces removal of the phosphine rather than CO,[13] we have investigated the possibility of an ET path. Indeed, mixing $LiAlH_4$ and 4 in the solid state followed by introduction of THF at -80 °C results in the appearance of a green color often encountered for Fe^I complexes.[14] The EPR spectrum of the reaction medium at 77 K (Figure 1) displays three signals close to $g = 2$, indicating a rhombic distortion ($g_x = 2.05$, $g_y = 2.43$, $g_z = 1.98$) characteristic of Fe^I monomers.[15] The Mössbauer spectrum of the frozen green reaction medium indicates that the Fe^I intermediate is only present as a small proportion of the iron species, a quadrupole doublet for Fe^I not being observed ($Fe^I < 2\%$). Thus, as expected, this Fe^I species is extremely reactive. Indeed, from the EPR spectrum, the steady-state concentration is around 5×10^{-4} mol L^{-1} starting from an amount of 4 leading to a 1.0 M solution. The Fe^I intermediate can also be generated on a K mirror in THF at -60 °C. In the absence of a H atom donor, decomposition rapidly occurs at this temperature, leaving inorganic iron, free dppe (80%), and small amounts of $[C_5Me_5Fe(CO)_2]_2$. Good sources of H atom are OH^- and AlH_4^-;[8] (i) when Na/Hg reduction of 4 is effected at 20 °C in the presence of NaOH in THF or toluene, a 40% yield of 5 is obtained together with 60% of free dppe; in the presence of NaOD, d^1 5 is obtained, as indicated by the mass spectrum $[(M - CO) - d_1]^+$; (ii) when $LiAlH_4$ is added to a green solution of the Fe^I complex generated by one-electron reduction (K or Na/Hg), the solution immediately turns yellow (and 5 is extracted). When Na/Hg reduction is carried out for 1 min at -20 °C in THF, freezing to 77 K also allows the observation of EPR signals characteristic of Fe^I complexes, although the exact spectrum of Figure 1 is not obtained because of the presence of Na/Hg. Thus, whether a 17-electron or 19-electron intermediate or both are present remains open to question. For comparison, we have studied the reduction of $[C_5H_5Fe^{II}(tripod)]^+PF_6^-$ by either $LiAlH_4$ or K mirror in THF at -80 °C. Again, we find that the EPR spectra obtained at 77 K are typical of Fe^I species, identical spectra being observed for either type of reduction.[16] The great reactivity of the light green Fe^I species formed by $LiAlH_4$ or Na/Hg reduction of 4 suggests the intermediacy of the 17-electron Fe^I complex in which the diphos ligand is bound in a monodentate fashion. In 19-electron complexes, H atom transfer from $LiAlH_4$ or AlH_3 proceeds at a ligand,[8] but, in the present case, no formyl complex is formed in this way. The possibility that this path be operative in the reduction of 1 is not yet rigorously excluded.

Nonetheless, the mechanisms of reduction of 1 and 4 are probably different. A strong argument for this point of view is that the reactions of $LiAlH_4$ with the Cp and permethyl Cp carbonyl complexes 1 and 4 lead quantitatively to the formyl complex 2 and to the hydride complex 5, respectively, at -80 °C. Since no byproducts are observed in the hydride reduction of 4, the ET path must give rise to hydride 5, and the low concentration of the Fe^I intermediate probably indicates its steady-state conversion to this product. The permethylation of the Cp ring would have stabilized the formyl complex 2 if it were formed, but instead it disfavors H^- attack by decreasing the positive charge on the carbonyl carbon.

Recently, an interesting radical chain mechanism has been reported by Kochi[17,18] for the decomposition of a

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(11) ^1H NMR (C_6D_6): δ (from Me_4Si) -13.56 (d, 1 H, FeH, $J_{PH} = 75$ Hz), 1.39 (s, 15 H, CH_3), 2.0 (m, 4 H, CH_2). ^{31}P NMR (THF, external lock; CD_3COCD_3): δ (from external H_3PO_4) -14.4 (d, 1 P, P–C, $J_{PP} = 39$ Hz), +84.2 (d, 18, Fe–P–C, $J_{PP} = 39$ Hz). ^{13}C NMR (C_6D_6): δ (from Me_4Si) 10.8 (s, CH_3), 90.8 (s, $C_5(CH_3)_5$), 24.7 (m, CH_2), 128.2 (m, $(C_6H_5)P$–Fe), 133.2 (m, $(C_6H_5)P$), 223.5 (d, CO, $J_{PC} = 26$ Hz). Mass spectrum: $[M - CO]^+$, calcd 590. 185, found 590.197; $[M - CO - H]^+$, calcd 589.188, found 589.190. Anal. Calcd: C, 73.41; H, 6.46; P, 10.53. Found: C, 73.77; H, 6.38; P, 10.46.

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bimetallic rhenium formyl to a hydride. Such a mechanism is not operative in the present case since (i) no iron formyl complex is detected at −80 °C and (ii) its radical chain decomposition would suppose the reduction of this neutral formyl complex to an anionic intermediate, a process that would require an extremely negative reduction potential (probably around −2.5 to −2.8 V vs. SCE).

Finally, note that coordinated CO is not reduced in the present ET mechanism. On the other hand, hydridocarbonyl species are currently postulated to form surface-bound formyl species in heterogeneous catalysis. An ET path for the hydride reduction of coordinated CO in the Fischer–Tropsch process may be significant insofar as ET through a metal surface should be facile.

Acknowledgment. We are grateful to Professor Louis Nadjo for EPR facilities (University of Paris VI) and to BASF (Ludwighafen, West Germany) for a generous gift of iron carbonyl.

Registry No. 1, 55904-75-1; 2, 84749-11-1; 3, 84365-32-2; 4, 88251-02-9; 5, 89530-20-1; CpFe(tripod)$^+PF_6^-$, 32843-42-8; [$C_5Me_5Fe^I$(dppe)(CO)], 89530-21-2.

Manipulation of Organoactinide Coordinative Unsaturation and Stereochemistry. Properties of Chelating Bis(polymethylcyclopentadienyl) Hydrocarbyls and Hydrides

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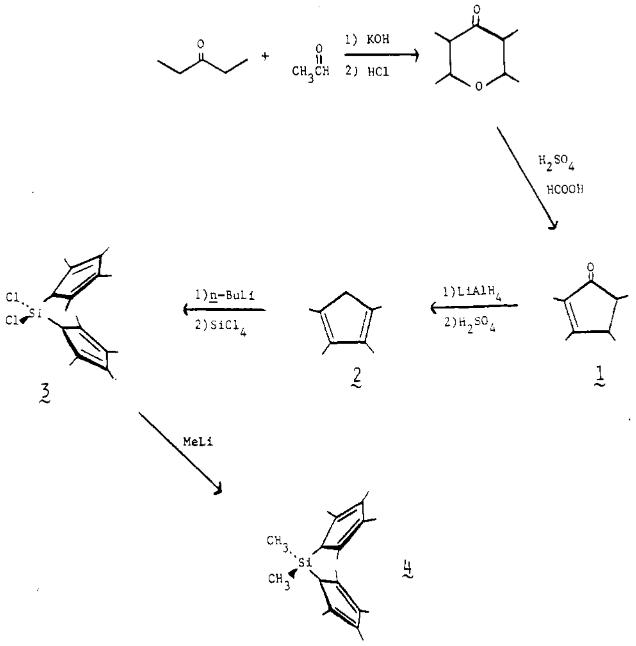
Received February 29, 1984

Summary: The synthesis of the chelating polymethylcyclopentadienyl ligand $(CH_3)_2Si[(CH_3)_4C_5]_2^{2-}$ is reported. Reaction with $ThCl_4$ followed by alkylation yields the new, thermally stable thorium hydrocarbyls $(CH_3)_2Si[(CH_3)_4C_5]_2ThR_2$, R = n-C_4H_9, $CH_2C(CH_3)_3$, $CH_2Si(CH_3)_3$, $CH_2C_6H_5$, and C_6H_5. The R = $CH_2Si(CH_3)_3$ complex has also been characterized by single-crystal X-ray diffraction. The most unusual feature of the molecular structure is the rather small (ring center of gravity)–Th–(ring center of gravity) angle of 118.4° and the rather large ring–ring dihedral angle of 105.4°. The hydrocarbyls undergo facile hydrogenolysis to yield the new thorium hydride $\{(CH_3)_2Si[(CH_3)_4C_5]_2ThH_2\}_x$. The infrared spectrum of this hydride lacks terminal Th–H stretching transitions. The new hydride catalyzes olefin hydrogenation at turnover frequencies significantly in excess of those for $\{Th[(CH_3)_5C_5]_2H_2\}_2$.

The advantageous characteristics of bis(pentamethylcyclopentadienyl) ligation (solubility, crystallizability, electron donation, and probable resistance to redistribution and certain thermal decomposition modes) have afforded major advances in organo f-element chemistry over bis(cyclopentadienyls).[1,2] However, as indicated by considerable structural data,[1-3] these improvements are realized at the expense of congesting the metal coordination sphere and possibly depressing reactivity. It would clearly be of interest to "open" the Cp'_2M < (Cp' = η^5-$(CH_3)_5C_5$) geometry, and we report here[4] a chelating polymethylcyclopentadienyl ligand which, as illustrated by a new class of actinide hydrocarbyls and hydrides, offers one such approach to modifying coordinative saturation and reactivity. The unusual molecular structure of one member of the new series is also reported.

Scheme I



2,3,4,5-Tetramethylcyclopent-2-enone (1) was prepared by a modification of the Burger, Delay, and Mazenod procedure[5,6] (Scheme I) and converted straightforwardly to tetramethylcyclopentadiene (2). Reaction of the anion with $SiCl_4$ followed by methylation and workup afforded $(CH_3)_2Si[(CH_3)_4C_5H]_2$ (4, $Me_2Si(Cp''H)_2$) in good yield.[7a,b] The dilithio derivative of 4 (via n-C_4H_9Li metalation) can then be converted to thorium precursor complex 5 (eq 1).

$$\mathrm{Me_2SiCp''_2}^{2-} + \mathrm{ThCl_4} \xrightarrow{\mathrm{DME}} \text{“}\underset{\mathbf{5}}{\mathrm{Me_2SiCp''_2ThCl_2}}\text{”} + 2\mathrm{Cl}^- \tag{1}$$

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(7) (a) All new compounds gave expected spectral and analytical data; see supplementary material for details. (b) Yields in the ligand synthesis: 54% (2), 80% (3), 57% (4). (c) Flame tests indicate negligible Li in compounds 6–10.

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