Acid-Catalyzed Trans to Cis Isomerization of $[C_5H_5(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CH_2)$

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Received June 5, 1989

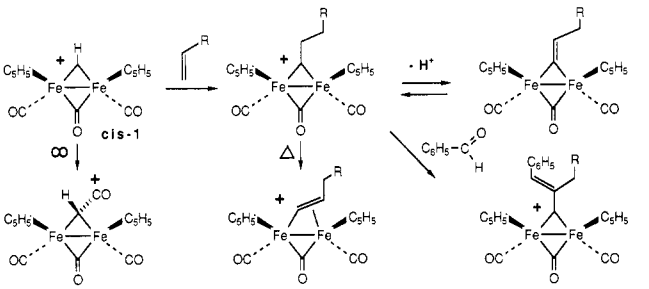
The isomerization of *trans*-$[C_5H_5(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CH_2)$ (*trans*-**2**) to an equilibrium mixture of *cis*- and *trans*-**2** occurs prior to hydride abstraction by $(C_6H_5)_3C^+PF_6^-$, which produces $[C_5H_5(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CH)^+PF_6^-$ (**1**). The isomerization of **2** was shown to be an acid-catalyzed process. Second-order kinetics were observed for isomerization of **2** by $HBF_4\cdot Et_2O$ and by CF_3CO_2H in CD_2Cl_2. An extremely large kinetic deuterium isotope effect (k_H/k_D = 70–105) was observed for the isomerization of **2** by CF_3CO_2D. A mechanism involving protonation at iron followed by bridge opening and rotation is proposed to explain the isomerization of **2**.

The diiron methylidyne complex $[C_5H_5(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CH)^+PF_6^-$ (**1**) (Scheme I) was the first compound synthesized that contained a CH group bridging between two metal atoms[1,2] and is interesting in its relation to CH groups bound to metal surfaces. It is also an important intermediate in the synthesis of a wide range of hydrocarbyl-bridged diiron compounds.[3] **1** adds its CH bond across the carbon–carbon double bond of simple alkenes in a hydrocarbation reaction to produce new (μ-alkylidyne)diiron complexes.[2,4–6] The μ-alkylidyne complexes can be converted into μ-alkenylidene complexes by deprotonation,[2] can be condensed with aldehydes to form μ-vinylcarbyne complexes,[7] and can be converted to μ-alkenyl complexes by thermal rearrangement.[8] **1** reacts with some more highly substituted alkenes such as 1-methylcyclohexene to produce new μ-alkenyl complexes directly in a reaction that involves electrophilic addition of the μ-CH carbon to the alkene followed by carbon migration.[5,6,9] Organocuprates,[10] carbon monoxide,[11,12] and isonitriles[13] all add to the methylidyne carbon of **1** to produce μ-alkylidene, μ-acylium, and μ-nitrilium complexes, respectively. A variety of heteroatom nucleophiles such as NEt_3, Me_3CO^-, and Br^- also add to the methylidyne carbon of **1**.[12]

Because of the central importance of **1** to the chemistry we are studying, we sought to learn as much as possible about the mechanism of its formation. We first prepared **1** from the bridging methylene complex $[C_5H_5(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CH_2)$ (**2**) (Scheme II) by treatment with the hydride abstracting reagent trityl hexafluorophosphate, $(C_6H_5)_3C^+PF_6^-$, in CH_2Cl_2 at low temperature. We were somewhat surprised that a 75:25 equilibrium mixture of *cis*-**2** and *trans*-**2** led to the formation of a 95:5 mixture of *cis*-**1** and *trans*-**1** in nearly quantitative yield.[1,2]

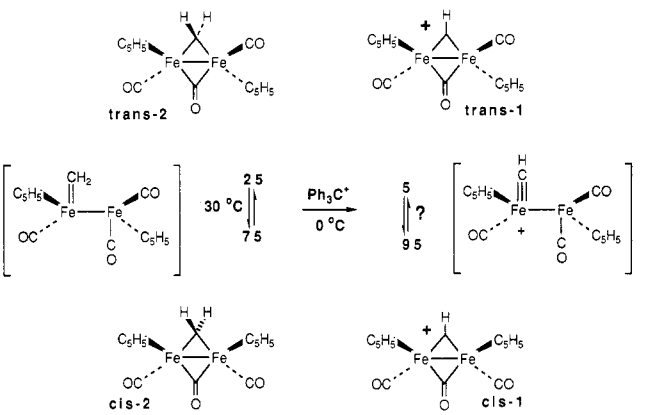
To explain the increase in cis:trans ratio on going from **2** to **1**, we initially considered the possiblity that hydride abstraction might occur stereospecifically and that the methylidyne complex **1** might then isomerize to the more stable cis isomer by a mechanism involving bridge opening, rotation, and rebridging. However, the idea that the cationic methylidyne complex **1** might open up more easily than the corresponding neutral methylene complex **2** at first seemed intuitively implausible. In going from a

Scheme I[a]



[a] Only the cation of *cis*-**1** is shown.

Scheme II[a]



[a] Only the cations of *cis*- and *trans*-**1** are shown.

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0276-7333/90/2309-0221$02.50/0

Table I. Thermal Equilibration of *trans*-2

T, °C	k_{eq}, s^{-1} [a]	K_{eq} [b]	k_{tc}, s^{-1} [c]
3	$(3.35 \pm 0.07) \times 10^{-5}$	4.81	2.77×10^{-5}
17	$(2.50 \pm 0.03) \times 10^{-4}$	4.11	2.01×10^{-4}
23	$(4.31 \pm 0.23) \times 10^{-4}$	3.86	4.22×10^{-4}
34	$(3.41 \pm 0.87) \times 10^{-3}$	3.46	2.65×10^{-3}

[a] Rate of approach to equilibrium, $k_{eq} = k_{tc} + k_{ct}$; k_{tc} = rate constant for conversion of *trans*-2 to *cis*-2; k_{ct} = rate constant for conversion of *cis*-2 to *trans*-2. [b] K_{eq} = [*cis*-2]/[*trans*-2] calculated from data in Table II involving measurements of K_{eq} over a wide temperature range. [c] $k_{tc} = k_{eq}[K_{eq}/(1 + K_{eq})]$.

terminal to a bridging position, a ligand is able to accept more electron density from the metal. A methylidyne ligand is more electron deficient than a methylene ligand and might be more stabilized in a bridging site, where more effective electron donation from iron is possible. On the other hand, the iron centers in the methylidyne complex 1 are more electron deficient than in the neutral methylene complex 2 and might be less prone to act as electron donors to the bridging ligands. It was clear that the factors that control the energy difference between isomers with bridging or terminal ligands are not well understood.

We therefore set out to generate the trans methylidyne complex at low temperature and to experimentally determine its rate of trans to cis isomerization. Here we report that treatment of the trans methylene complex *trans*-2 with $(C_6H_5)_3C^+PF_6^-$ in CD_2Cl_2 at −50 °C leads to rapid trans to cis isomerization of 2 *prior* to hydride abstraction, which occurs only at higher temperature. Our attempts to measure the trans to cis isomerization rate for μ-methylidyne complex 1 were therefore frustrated.

The detailed studies of the catalyzed isomerization of methylene complex 2 outlined here are intriguing and lead us to propose a mechanism for isomerization involving protonation at iron in 2, followed by bridge opening and rotation.

Results

Thermal Isomerization of 2. *trans*-2 was obtained as a purple solid in >95% isomeric purity by chromatography on alumina at 0 °C. No trans to cis isomerization was observed when the solid was stored at −25 °C for 2 months. The kinetics of the trans to cis isomerization of 2 were readily measured in CD_2Cl_2 by ^1H NMR spectroscopy since the μ-CH_2 group of *trans*-2 gives rise to a single resonance at δ 9.49 and the μ-CH_2 group of *cis*-2 gives rise to two resonances at δ 8.27 and 10.21. The half-life for thermal isomerization of *trans*-2 to an equilibrium mixture of *cis*- and *trans*-2 was 60 min at 17 °C. The rate of isomerization of *trans*-2 to an equilibrium mixture of *cis*- and *trans*-2 was measured between 3 and 34 °C (Table I); at 25 °C, $\Delta G^\ddagger = 21.8 \pm 0.2$ kcal mol^{-1}, $\Delta H^\ddagger = 23.8 \pm 0.2$ kcal mol^{-1}, and $\Delta S^\ddagger = 6.9 \pm 4.1$ eu. These rates of isomerization are similar to those in other solvents reported earlier by Ziegler[13] and indicate that thermal isomerization of *trans*-2 is negligible at the low temperatures (−20 to 0 °C) at which the hydride abstraction reaction is carried out.

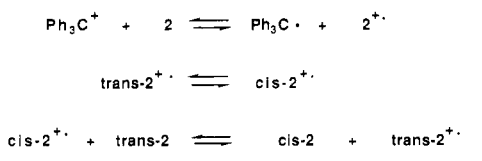
Trityl Cation Catalyzed Isomerization of 2. The reaction of *trans*-2 with $(C_6H_5)_3C^+PF_6^-$ in CD_2Cl_2 was carried out at low temperature in an effort to selectively generate the trans methylidyne complex *trans*-1. A solution of *trans*-2 in CD_2Cl_2 in an NMR tube was frozen at liquid-nitrogen temperature, and 1 equiv of a solution of $(C_6H_5)_3C^+PF_6^-$ was added by syringe. The tube was sealed under vacuum and monitored by low temperature ^1H NMR spectroscopy. At −78 °C, *trans*-2 and $(C_6H_5)_3C^+$ were the major species observed. When warmed to −50 °C, *trans*-2 isomerized to a 93:7 mixture of *cis*- and *trans*-2 with a half-life of less than 5 min; no formation of methylidyne complex 1 (δ 22.8) was observed. When the solution was warmed to −30 °C, slow formation of a >95:5 mixture of *cis*- and *trans*-1 was observed with a time for half-reaction of about 30 min. This clearly demonstrates that trans to cis isomerization is much more rapid than hydride abstraction from 1.

Table II. Temperature Dependence of the Equilibrium Constant for *trans*-2 ⇌ *cis*-2

T, °C	equilibration method	K_{eq} = [*cis*-2]/[*trans*-2]	K_{calc} [a]
34	thermal	3.4 ± 0.3	3.5
23	thermal	4.1 ± 0.4	3.9
−29	CPh_3^+ catal	6.9 ± 0.7	7.4
−39	CPh_3^+ catal	7.9 ± 0.8	8.7
−49	CPh_3^+ catal	11.5 ± 1.1	10.3
−59	CPh_3^+ catal	12.6 ± 1.2	12.5

[a] K_{calc} is calculated from $\Delta H = -1.8 \pm 0.1$ kcal mol^{-1} and $\Delta S = -3.4 \pm 0.5$ eu mol^{-1} obtained from plotting values of observed ln K_{eq} vs $(1/T)$.

Scheme III



The rapid $(C_6H_5)_3C^+PF_6^-$-catalyzed isomerization of 2 at low temperature allowed the measurement of the equilibrium constant for *trans*-2 ⇌ *cis*-2 over a wide temperature range. From the data in Table II, we have calculated $\Delta H = -1.8 \pm 0.1$ kcal mol^{-1} and $\Delta S = -3.4 \pm 0.5$ eu for this equilibrium.

Methylidyne Complex 1 Does Not Catalyze Isomerization of Methylene Complex 2. If both trans to cis isomerization of methylidyne complex 1 and degenerate intermolecular hydride transfer from methylene complex 2 to methylidyne complex 1 were rapid, this would provide a mechanism for trans to cis isomerization of 2 catalyzed by 1. However, a solution of *trans*-2 containing 10 mol % methylidyne complex 1 did not show detectable isomerization after 2 h at −50 °C.

Isomerization of 2 Is Not Catalyzed by Electron Transfer. In several cases, hydride abstraction from metal alkyls by the trityl cation has been shown to occur by one-electron oxidation followed by hydrogen atom transfer.[14] If trityl cation reacted with 2 by an electron-transfer pathway, then isomerization of 2 might be explained by rapid bridge cleavage of the radical cation $2^{\cdot+}$ (Scheme III). Once again, it is not at all clear why radical cation $2^{\cdot+}$ might undergo trans to cis isomerization more rapidly than 2. To investigate this possible mechanism, we studied the oxidation of 2 by cyclic voltammetry and the kinetics of trityl-catalyzed isomerization of *trans*-2.

At room temperature, the cyclic voltammogram of 2 (Pt working electrode) shows a one-electron-oxidation peak at 860 mV vs SCE but no return peak. However, at −78 °C, a return peak was observed (Figure 1). The separation between peaks increased with increasing scan rate: ΔE_p was 240 mV at a scan rate of 200 mV/s, and ΔE_p was 125 mV at 50 mV/s. Since these peak separations are substantially greater than the 58-mV separation expected for

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Table III. Acid-Catalyzed Isomerization of *trans*-2

acid	T, °C	$[H^+]$, mM	k_{eq}, s^{-1} [a]	K_{eq} [b]	k_{tc}, s^{-1} [c]	k_{2tc}, $M^{-1}\ s^{-1}$ [d]
$HBF_4 \cdot Et_2O$	−49	2.2	$(4.1 \pm 0.1) \times 10^{-4}$	10.3	3.8×10^{-4}	0.17
$HBF_4 \cdot Et_2O$	−49	4.2	$(9.8 \pm 0.2) \times 10^{-4}$	10.3	9.0×10^{-4}	0.21
CF_3CO_2H	−38	2.0	$(6.6 \pm 0.1) \times 10^{-3}$	8.5	5.9×10^{-3}	3.6
CF_3CO_2H	−44	2.0	$(3.0 \pm 0.5) \times 10^{-3}$	9.5	2.7×10^{-3}	1.4
CF_3CO_2H	−58	2.0	$(4.5 \pm 0.6) \times 10^{-4}$	12.2	4.2×10^{-4}	0.20
CF_3CO_2H	−66	6.5	$(7.6 \pm 0.6) \times 10^{-4}$	14.4	7.1×10^{-4}	0.11
CF_3CO_2D	−37	2.0	$(5.9 \pm 0.4) \times 10^{-5}$	8.4	5.3×10^{-5}	0.026
CF_3CO_2D	−40	2.0	$(6.9 \pm 0.1) \times 10^{-5}$	8.8	6.2×10^{-5}	0.031
CF_3CO_2D	−66	6.5	$(1.1 \pm 0.3) \times 10^{-5}$	14.4	1.0×10^{-5}	0.0016

[a] Rate of approach to equilibrium. [b] K_{eq} calculated from ΔH and ΔS. [c] Pseudo-first-order rate constant for trans to cis isomerization, $k_{tc} = k_{eq}[K_{eq}/(1 + K_{eq})]$. [d] Second-order rate constant for trans to cis isomerization.

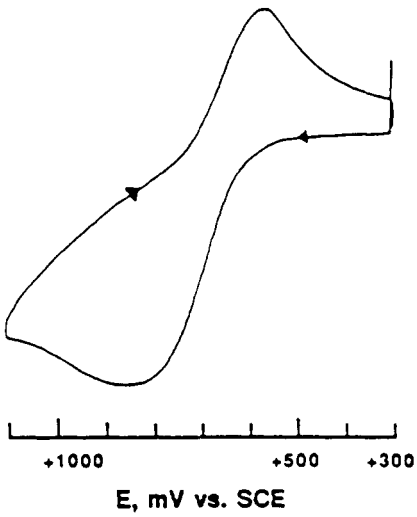

Figure 1. Cyclic voltammogram of $[CpFe(CO)]_2(\mu\text{-}CO)(\mu\text{-}CH_2)$ at −78 °C.

reversible single-electron transfer,[15] our system can be classified as quasi-reversible. The return peaks were always smaller than the oxidation peaks (i_{ox}/i_{red} = 1.3–1.7), indicating that a following chemical reaction was occurring. The $E_{1/2}$ value for oxidation of **2** was taken as $(E_p^{ox} + E_p^{red})/2$ and was 710 mV. The $E_{1/2}$ value for trityl cation at −78 °C was found to be 280 mV under similar conditions, in the good agreement with reported potentials.[16] This indicates that electron transfer from **2** to the trityl cation is *endothermic by 430 mV*; $\Delta G°$ = 9.9 kcal mol^{-1} at −78 °C for step 1 in Scheme III.

The kinetics of the trityl cation catalyzed isomerization of **2** could not be accurately reproduced and did not fit either a simple first- or second-order kinetic model. When plotted as a pseudo-first-order reaction, the rate fell off with time. The rate of isomerization increased at higher trityl cation concentrations, but the kinetic order of the reaction could not be accurately determined. The time for isomerization of *trans*-**2** half-way to equilibrium was about 70 min at −48 °C with use of 2.9 mM $(C_6H_5)_3C^+PF_6^-$. Assuming second-order kinetics of $k_{obs} = k_2[(C_6H_5)_3C^+]$, a crude estimate of $\Delta G^‡$ of about 14 kcal mol^{-1} was made. If an electron-transfer mechanism is operating, then the 9.9-kcal endothermic electron transfer from **2** to $(C_6H_5)_3C^+$ must be a major contributor to the activation barrier.

If the slow step in trans to cis isomerization is electron-transfer oxidation of **2**, or if the slow step involves an equilibrium amount of the μ-CH_2 radical cation $\mathbf{2}^{\bullet+}$, then more powerful oxidants should accelerate the isomerization. However, while the more powerful oxidants ferrocenium ion $((C_5H_5)_2Fe^{\bullet+}BF_4^-$, $E_{1/2}$ = 500 mV) and triarylaminium ion $(N(C_6H_4\text{-}p\text{-}Br)_3^{\bullet+}SbF_6^-$, $E_{1/2}$ = 1200 mV)[17] also catalyzed the isomerization of **2**, the rates of isomerization were not significantly faster than in the presence of the less powerful oxidant trityl cation, and the kinetic order of the isomerizations was not clean. Under similar reaction conditions in CD_2Cl_2 at −48 °C, the time for half-isomerization of 0.02 M *trans*-**2** by 3 mM trityl cation was 70 min while that by 0.9 mM ferrocenium cation, a more powerful oxidant, was 75 min. Even the very powerful oxidant $N(C_6H_4\text{-}p\text{-}Br)_3^{\bullet+}SbF_6^-$ (0.9 mM) brought about only 5% isomerization over 30 min. This insensitivity of isomerization rate to the oxidizing power of the catalyst argues against an electron-transfer mechanism.

Catalysis by Protic Acids. Because of our difficulties in accurately reproducing the kinetics of the trityl-catalyzed isomerization and because of the insensitivity of the isomerization rates to the oxidizing power of the isomerization catalysts, we began to suspect that all of the oxidants might react with trace impurities in our system or with our glassware to produce variable amounts of acid and that acid might be the actual catalyst. Consequently, we investigated the catalysis of the isomerization of *trans*-**2** by CF_3CO_2H and by $HBF_4 \cdot OEt_2$.

The isomerization of *trans*-**2** to *cis*-**2** in CD_2Cl_2 was greatly accelerated by added $HBF_4 \cdot Et_2O$ at −49 °C. Excellent pseudo-first-order plots were obtained for the isomerization of *trans*-**2** to an equilibrium mixture of *cis*- and *trans*-**2**. The pseudo-first-order rate constant for approach to equilibrium depended linearly on the acid concentration. The half-life for equilibration with 2.2 mM $HBF_4 \cdot Et_2O$ was 28 min, while that with 4.2 mM $HBF_4 \cdot Et_2O$ was 12 min (Table III). This establishes a second-order rate law for the isomerizations, rate = $k_1[H^+]\{[trans\text{-}2] - [trans\text{-}2]_{eq}\}$. Qualitatively, $HBF_4 \cdot Et_2O$ is a more efficient catalyst than $Ph_3C^+PF_6^-$ and is kinetically well behaved in contrast to $Ph_3C^+PF_6^-$.

The isomerization of *trans*-**2** to an equilibrium mixture of *cis*- and *trans*-**2** was also catalyzed by CF_3CO_2H in CD_2Cl_2. The rate of isomerization catalyzed by CF_3CO_2H was measured between −66 and −38 °C. The estimated activation parameters were $\Delta G^‡$ = 13.3 ± 0.2 kcal mol^{-1}, $\Delta H^‡$ = 11.0 ± 1.0 kcal mol^{-1}, and $\Delta S^‡$ = −9.5 ± 0.5 eu at −38 °C. Acid catalysis therefore lowers $\Delta G^‡$ by 8.9 kcal mol^{-1} and $\Delta H^‡$ by 12.8 kcal mol^{-1} compared with the thermal isomerization of **2**.

The isotope effect for the equilibration of *trans*-**2** was measured by using CF_3CO_2H and CF_3CO_2D. The isomerization of *trans*-**2** catalyzed by CF_3CO_2D was pseudo first

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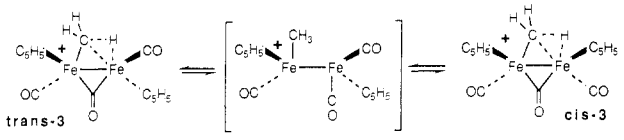
Scheme IV[a]



[a] Only the cations of *cis*- and *trans*-3 are shown.

order at up to 25–50% reaction but accelerated at longer times. Exchange of the μ-CH_2 protons with CF_3CO_2D generated the more efficient catalyst CF_3CO_2H; this exchange process involves an intermediate μ-CH_3 species and will be described in detail below. At −38 °C with 2 mM acid, a remarkably large isotope effect, $k_H/k_D = 105 \pm 20$, was observed. Similarly at −67 °C with 6.5 mM acid, a very large isotope effect, $k_H/k_D = 71 \pm 20$, was measured. We do not believe that the unusual apparent increase in k_H/k_D from 70 ± 20 to 105 ± 20 as the temperature is increased from −66 to −38 °C is significant due to our large experimental errors and to the difficulty of measuring rates with deuterated acid. As will be pointed out in detail in the Discussion, large isotope effects have been observed previously in reactions suggested to occur by protonation at a metal center.

Bridging Methyl Complex $[C_5H_5(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CH_3)^+$ Is Not an Intermediate in the Isomerization of 2. Since protonation of **2** led to the isolation of the bridging methyl complex $[C_5H_5(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CH_3)^+BF_4^-$ (**3**),[1] we considered the possibility that **3** might be an intermediate in the acid-catalyzed isomerization of *trans*-**2** (Scheme IV). Trans to cis isomerization of **3** might be particularly facile due to the ease of breaking a bridge to a methyl group. Therefore, we carefully examined ^1H NMR spectra taken during the acid-catalyzed isomerization of *trans*-**2**. In a sample of **2** (0.02 M) in CD_2Cl_2 with 0.5 equiv of HBF_4·OEt_2, *trans*- and *cis*-**2** had reached equilibrium after 10 min at −49 °C, but only 6% of the material had been converted to the bridging methyl complex **3** as determined by measuring the peak at δ −1.9 ppm. At longer times more **3** was formed. This demonstrates that the bridging methyl compound **3** is not an intermediate in the interconversion of *trans*- and *cis*-**2**.

Additional evidence against the intermediacy of **3** in the isomerization of *trans*-**2** was obtained by performing a crossover experiment with **2** and the μ-CD_2 derivative $[C_5H_5(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CD_2)$ (**2**-d_2). A 1:1 mixture of **2** and **2**-d_2 was allowed to cis–trans equilibrate at −50 °C with 0.5 equiv of HBF_4·Et_2O for 10 min and then quenched with triethylamine. Mass spectral analysis indicated that the isotopic composition of **2** was 56% d_2, 6% d_1, and 38% d_0. The maximum amount of crossover possible is therefore 6%. This matches closely the amount of bridging methyl compound **3** observed under similar conditions.

It should also be noted that deuterium exchange of the cyclopentadienyl protons of **2** does not occur during CF_3CO_2D-catalyzed isomerization. Thus, the ratio of cyclopentadienyl to μ-CH_2 resonances does not change during CF_3CO_2D-catalyzed isomerization.

Discussion

To explain the conversion of a 75:25 mixture of μ-CH_2 compounds *cis*- and *trans*-**2** to a 95:5 mixture of μ-CH complexes *cis*- and *trans*-**1**, we considered the hypothesis that hydride abstraction by trityl cation from *trans*-**2** might generate *trans*-**1**, which then rapidly equilibrated to 95:5 *cis*- and *trans*-**1**. In an attempt to determine how fast *trans*-**1** might isomerize, we attempted to synthesize *trans*-**1** by hydride abstraction from *trans*-**2** at low temperature. However, we found that treatment of *trans*-**2** with trityl cation at low temperature brought about much more rapid trans–cis equilibration of **2** than hydride abstraction to form the methylidyne complex **1**. Therefore, our attempts to determine the rate of trans–cis equilibration of **1** frustrated and we still do not know whether or not methylidyne complex **1** isomerizes rapidly. In addition, we were presented with the additional problem of explaining the rapid trans to cis isomerization of methylene complex **2** catalyzed by trityl cation.

Initially, we explored the hypothesis that trityl cation might reversibly oxidize *trans*-**2** to its radical cation, which might isomerize rapidly. This electron-transfer mechanism now appears unlikely on three grounds: (1) electron transfer from **2** to trityl was shown to be 430 mV endothermic by cyclic voltammetry, (2) the more powerful oxidants ferrocenium cation and tris(*p*-bromophenyl)-aminium radical cation were not better isomerization catalysts than trityl cation, and (3) the kinetics of trityl-catalyzed isomerization were not cleanly first or second order and were not easily reproduced.

Our next hypothesis was that all three oxidizing agents generated some protic acid in solution that was the active catalyst for isomerization of *trans*-**2**; this hypothesis is supported by our observation that both HBF_4·Et_2O and CF_3CO_2H were very active catalysts for isomerization. These acid catalysts gave well-behaved pseudo-first-order kinetics and showed a first-order dependence on the concentration of acid.

How does protonation of **2** promote trans–cis equilibration? Apparently protonation of **2** produces an intermediate that can undergo rapid bridge cleavage and rotation. Several possible sites of protonation of **2** will each be considered in turn.

Of the two types of carbonyl oxygen in the compound, the sp^2-hybridized bridging carbonyl oxygen should be more basic than the sp-hybridized terminal carbonyl oxygen.[18] Bridging carbonyl groups are known to interact with Lewis acids; indeed, for $[Cp(CO)Fe]_2(\mu\text{-}CO)_2$ several Lewis acid complexes have been isolated.[19] The second highest MO for **2** has a substantial (13%) contribution from an oxygen lone pair on the bridging carbonyl group.[20] However, protonation would be expected to make the carbonyl *more* likely to bridge and thus *less* likely to isomerize. The tendency of Lewis acids to promote bridging carbonyl formation is exemplified by $Ru_3(CO)_{12}$, which has only terminal CO ligands but forms an adduct with $AlBr_3$ that has aluminum bound to a bridging CO.[19,21] While protonation of the bridging CO of **2** may be occurring reversibly, it is probably unproductive.

Protonation of the bridging methylene group of **2** to produce bridging methyl compound **3** occurs but is too slow to account for cis–trans isomerization of **2**. The rate of trans to cis isomerization of **2** occurred much more rapidly than formation of **3**. In addition, crossover between μ-CH_2 compound **2** and μ-CD_2 compound **2**-d_2 was much slower than trans to cis isomerization of **2**.

Protonation at the cyclopentadienyl ring seems unlikely to lead to isomerization. Moreover, deuterium incorpo-

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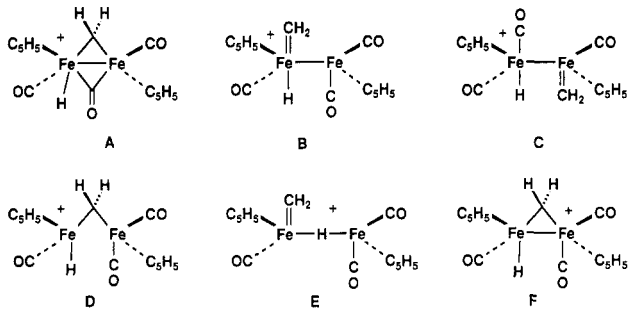
Chart I



ration into the cyclopentadienyl groups did not occur upon treatment with CF_3CO_2D. However, if ring protonation and deprotonation can occur stereoselectively on only one face of the ring, then H–D exchange would not occur.

Partly by default, we believe that protonation at iron is the key step in the isomerization of *trans*-**2**. Molecular orbital calculations on **2** indicate that the highest occupied molecular orbital is a π-antibonding combination of d orbitals on iron.[20] This makes protonation at iron appear reasonable. Protonation at the metal center has been seen for other dinuclear metal complexes such as $[Cp(CO)Rh]_2(\mu\text{-}CO)$ and $[C_5Me_5(CO)Ir]_2(\mu\text{-}CH_2)$.[22]

The huge deuterium isotope effect k_H/k_D of 70–105 seen for the trans to cis isomerization of **2** is also consistent with rate-determining protonation at iron. Such extremely large deuterium isotope effects are invariably ascribed to proton tunneling[23] and have been observed before for protonation at a metal center. Whitesides and Neilan[24] reported k_H/k_D = 27 for the acid-catalyzed cis–trans isomerization of diene–iron tricarbonyl complexes, which they suggested occurred via rate-determining protonation at iron. Knight and Mays reported isotope effects of 16 for protonation of mixed-metal clusters.[25] Pribich and Rosenberg[26] have reported a deuterium isotope effect of over 47 for protonation of a ruthenium cluster. They observe initial protonation of a bridging carbonyl followed by rearrangement to a bridging metal hydride and propose an intramolecular transfer of hydrogen from oxygen to a metal center.[26] However, their data are also consistent with reversible protonation of a bridging carbonyl and protonation at the metal center by intermolecular hydrogen transfer from an oxygen acid. Similarly, in our work, we cannot distinguish between direct protonation at iron and hydrogen migration from an initially protonated bridging carbonyl.

In considering how protonation at iron might promote isomerization by a bridge-opening mechanism, it is important to recall that a bridging ligand is more effective than a terminal ligand in accepting electron density from a metal center. For example, Fenske–Hall MO calculations on **2** indicate that the μ-CO ligand bears a negative charge of −0.20 while the terminal CO ligands each bear a slight positive charge of +0.03.[20] Protonation at a metal center increases electron demand at the positive metal center and decreases the need to transfer electron density onto the ligand system. For a metal-protonated complex, a structure with bridging ligands should be less favored over a structure with only terminal ligands than in the case of the unprotonated precursor. Consequently, the protonated iron complex A should undergo bridge opening more easily than its neutral precursor **2** (Chart I).

There are two possible ways to open both bridges of the protonated complex A. The open complex can have the proton on the iron bearing the methylene ligand as shown in B or on the iron bearing only CO ligands as shown in C. Other formulations for an iron methylene hydride intermediate capable of isomerization include D, in which the iron centers are linked only by the μ-methylene ligand, E, in which a μ-hydride is the only link, and F, in which the iron centers are linked by a metal–metal bond and a μ-methylene ligand. Isomerization via F could involve rearrangement of the iron center having a four-legged piano-stool geometry. We are exploring the plausibility of such intermediates using Fenske–Hall MO calculations.

In summary, we have found that the trans to cis isomerization of **2** is catalyzed by acid and we suggest that isomerization occurs by protonation at iron. The protonated complex is more prone to bridge cleavage and rotation, which eventually leads to isomerization.

Experimental Section

Materials. $[C_5H_5nCO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CH_2)$ (**2**) was prepared as described by Ziegler.[13] Separation of *trans*-**2** and *cis*-**2** was achieved by column chromatography (alumina, hexane) at 0 °C. $[C_5H_5(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CH)^+PF_6^-$ (**1**),[2] $(C_6H_5)_3C^+PF_6^-$,[27] and $(C_5H_5)_2Fe^+BF_4^-$[28] were prepared as described. $HBF_4{\cdot}Et_2O$ and $N(C_6H_4\text{-}p\text{-}Br)_3{}^{\cdot+}SbF_6^-$ were used as received from Aldrich. CF_3CO_2H and CF_3CO_2D (Aldrich) were vacuum-distilled prior to use. CD_2Cl_2 was vacuum-distilled from P_2O_5 prior to use.

NMR Kinetics. ^1H NMR spectra were obtained on a Bruker WP-270 spectrometer. Probe temperatures under operating conditions were measured with a thermocouple inserted into an NMR tube containing solvent.

NMR samples for kinetic studies were all prepared in a similar fashion. Solid *trans*-**2** (3–6 mg) was placed in a 5-mm NMR tube fused to a 14/20 ground-glass joint with a sidearm capped by a rubber septum. The assembly was attached to a high-vacuum line, and 0.2 mL of CD_2Cl_2 was condensed into the tube at liquid-nitrogen temperature. The vacuum line was placed under 1 atm of N_2, and a solution of the catalyst ($(C_6H_5)_3C^+PF_6^-$, CF_3CO_2H, etc., typically 5–15 μL of a 0.18 M CD_2Cl_2 solution) was injected into the tube through the sidearm by syringe. The tube was reevacuated, an additional 0.2 mL of CD_2Cl_2 was condensed in, and the tube was sealed under vacuum.

For kinetic studies, samples were warmed from liquid-nitrogen temperature to −78 °C, mixed, and immediately placed in a precooled NMR probe. Spectra were recorded periodically, and the amounts of *cis*- and *trans*-**2** were determined by measuring the integrals for the μ-CH_2 resonances with the assumption of a 100% material balance. A 30° pulse width was used, with no relaxation delay between scans. Measurement of the relaxation times of the three types of μ-CH_2 protons indicated they were almost equal; *trans*-**2** had T_1 = 3.27 s, while the two different protons in *cis*-**2** had T_1 = 3.60 and 2.96 s. A pseudo-first-order model for approach to equilibrium was used to fit the kinetic data with use of the equation $\ln\{[trans\text{-}2]_t - [trans\text{-}2]_{eq}\} = -k_{eq}t$. The observed rate constant for approach to equilibrium, k_{eq}, is equal to the sum of the rate constants for trans to cis isomerization, k_{tc}, and for cis to trans isomerization, k_{ct}.

Cyclic Voltammetry Experiments. Cyclic voltammograms were run with use of a three-electrode cell with a platinum-disk

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working electrode, a platinum-wire counter electrode, and a saturated calomel reference electrode; the reference electrode was in contact through a cracked bead well filled with electrolyte solution. The sample was weighed into the cell, the cell was flushed with nitrogen, and a known volume of the electrolyte solution (CH_2Cl_2, 0.1 M tetrabutylammonium perchlorate) was introduced via syringe. The voltammogram was run with use of a PAR Model 175 programmer hooked up to a PAR Model 173 potentiostat and a PAR Model 197 coulometer and I/V converter. The working electrode was polished after each run. Cyclic voltammograms at low temperature were run by cooling the cell in a dry-ice–acetone bath and allowing temperature equilibration for at least 15 min.

Acknowledgment. Financial support from the National Science Foundation is gratefully acknowledged.

Tripodal Polyphosphine Ligands in Homogeneous Catalysis. 1. Hydrogenation and Hydroformylation of Alkynes and Alkenes Assisted by Organorhodium Complexes with $MeC(CH_2PPh_2)_3$

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Received April 3, 1989

The crystal structure of the complex [(triphos)RhCl(C_2H_4)] (1) has been determined by X-ray methods (triphos = $MeC(CH_2PPh_2)_3$). The rhodium atom is coordinated to an ethylene molecule, a chlorine atom, and the triphos ligand, which occupies three *fac* positions of an octahedron. The Rh–C_2H_4 coordination exhibits a C–C distance that is among the longest found in metal–ethylene structures (1.49 (4) Å). Compound 1 is the starting point to synthesize a number of ethylene complexes of rhodium containing hydride or σ-organyl coligands: [(triphos)RhH(C_2H_4)], [(triphos)Rh(C_2H_5)(C_2H_4)], [(triphos)Rh(CH_3)(C_2H_4)], [(triphos)Rh(C_6H_5)(C_2H_4)]. All of the ethylene complexes but 1 react with CO, forming σ-acyl carbonyls of general formula [(triphos)Rh(COR)(CO)] via the σ-organyl carbonyls [(triphos)Rh(R)(CO)] (R = CH_3, C_2H_5, C_6H_5). Compound 1 reacts with CO, yielding the carbonyl [(triphos)RhCl(CO)]. The hydrogenolysis reactions of the σ-organyl ethylene complexes invariably give the trihydride [(triphos)Rh(H_3)] and the corresponding hydrocarbon. In contrast, the σ-acyl carbonyls and the σ-organyl carbonyls react with H_2 to form the hydride carbonyl [(triphos)RhH(CO)] and the corresponding hydrocarbon or aldehyde. Another excellent synthetic entry to organorhodium complexes of triphos is the η^2-alkyne complex [(triphos)Rh(η^2-DMAD)]BPh_4 (DMAD = dimethyl acetylenedicarboxylate). This reacts with H_2 to give the tetrahydride [(triphos)RhH(μ-H)$_2$HRh(triphos)](BPh_4)$_2$ and dimethyl succinate. Reaction of the η^2-alkyne complex with CO affords the dicarbonyl [(triphos)Rh($CO)_2$]BPh_4 which is converted into the ethylene carbonyl [(triphos)Rh(CO)(C_2H_4)]BPh_4 by treatment with Me_3NO under a C_2H_4 atmosphere. The ethylene carbonyl is much better synthesized by protonation of [(triphos)RhH(CO)] under C_2H_4. In the absence of ethylene, the reaction gives [(triphos)Rh($H)_2$(CO)]BPh_4. The hydrogenolysis and carbonylation reactions have been carried out at room temperature and 1 atm of H_2 or CO. All of the compounds have been properly characterized by spectroscopic technique, including the computer simulation of the second-order ^1H and ^{31}P NMR spectra. The activities of all of the compounds as catalyst precursors for the homogeneous hydrogenation, isomerization, and hydroformylation reactons of alkenes and alkynes have been studied in detail. Particular attention has been focused on the substrates 1-hexene, *cis*-stilbene, diphenylacetylene, dimethyl maleate, and dimethyl acetylenedicarboxylate.

Introduction

Over the past decade, tripodal polyphosphines have proven to be useful and versatile ligands in inorganic and organometallic chemistry.[1] Recently, transition-metal complexes of tripodal polyphosphines have begun to attract interest because of their potential as catalysts in several homogeneous reactions, including (i) hydrogenation of alkynes, alkenes,[2] and organic nitriles,[2d,3] (ii) hydroformylation and isomerization of alkenes,[2b-h] (iii) acetalization of aldehydes and ketones,[2d,4] (iv) functionalizaton, oligomerization, and polymerization of alkynes,[5] (v) oxidation of inorganic and organic substrates,[6] and (vi) synthesis of vinyl ethers from terminal alkynes and carboxylic acids.[7] The principal reasons tripodal polyphosphine ligands participate in such a wide range of catalyst systems can be summarized under six main headings:[8] excellent bonding ability, strong trans influence, formation of stable complexes in a variety of metal oxidation states, great control on the stereochemistry and stoichiometry, adaptability to many different coordination numbers, and high nucleophilicity of the metal centers.

The majority of studies have involved the triphosphine triphos, $MeC(CH_2PPh_2)_3$ (I), which can form stable com-

0276-7333/90/2309-0226$02.50/0