clarified on the basis of NMR and X-ray analyses coupled with theoretical treatments. These complexes are highly reactive toward aliphatic aldehydes and ketones and the 1:1 and/or 1:2 insertion reaction occurs selectively at the C(1) and/or C(4) atoms of the dienes to give unsaturated alcohol or glycols upon hydrolysis of the product. When the mixed-diene complex (**22**) is treated with an equivalent of a carbonyl compound, the insertion reaction takes place only at the butadiene ligand selectively. CpTa(diene)₂ is also reactive toward 1-alkynes such as 1-butyne and 1-hexyne. The addition of 3 equiv of 1-butyne to **9** or **10** results in the release of coordinated dienes at 60 °C and gives 1,3,5- and 1,2,4-triethylbenzene, a cyclic trimer of 1-butyne. Thus, Ta–diene complexes have unique chemical properties which promise a potential utility in organic synthesis and in homogeneous catalysis. Details of the reactions with these complexes will be given separately.

Acknowledgment. We thank Prof. N. Yasuoka of the Crystallographic Research Center for Protein Research, Osaka

University, for affording the facilities of X-ray data measurement. Support of this study by a Grant-in-Aid for Special Project Research (No. 57218014) from the Ministry of Education, Science and Culture, Japan, is acknowledged.

Registry No. 3, 95250-97-8; **4**, 95250-98-9; **5**, 95250-99-0; **6**, 95251-00-6; **7**, 95251-01-7; **8**, 95251-02-8; **9**, 95251-03-9; **10**, 95251-04-0; **11**, 95251-05-1; **12**, 95251-06-2; **13**, 95251-07-3; **22**, 95251-08-4; CpTaCl₄, 62927-98-4; Cp*TaCl₄, 71414-47-6; Fe(CO)₃(C₄H₆), 12078-32-9; Cp₂Zr(C₄H₆), 75374-50-4; (2-butene-1,4-diyl)magnisium, 70809-00-6; (2-methyl-2-butene-1,4-diyl)magnisium, 90823-62-4; (2,3-dimethyl-2-butene-1,4-diyl)magnisium, 95251-09-5.

Supplementary Material Available: Tables of fractional atomic coordinates, equivalent isotropic temperature factors, anisotropic temperature factors for non-hydrogen and hydrogen atoms, and observed and calculated structure factors for complexes **3, 10, 13** (20 °C), and **13** (−60 °C) (141 pages). Ordering information is given on any current masthead page.

Olefin Isomerization Catalysis by Heterobimetallic Hydrides, HFeM(CO)₈L⁻ (M = Cr, Mo, W; L = CO, PR₃)[†]

Patricia A. Tooley, Larry W. Arndt, and Marcetta Y. Darensbourg*

Contribution from the Department of Chemistry, Texas A&M University, College Station, Texas 77843. Received August 3, 1984

Abstract: The bis(triphenylphosphine)iminium (PPN⁺) salts of HFeM(CO)₉⁻ (M = Cr, Mo, W) were shown to be olefin isomerization catalysts under mild conditions (25 °C, fluorescent lighting) toward the conversion of allylbenzene to *cis*- and *trans*-propenylbenzenes and 1-hexene to internal olefins. When DFeM(CO)₉⁻ was used as catalyst, deuterium label was incorporated into the isomerized products. The olefin isomerization capability of HFe(CO)₄⁻ was reviewed. The HFe(CO)₄⁻ anion is *inactive* in THF solution with PPN⁺ as counterion, but activity may be generated in the presence of cocatalysts such as BF₃ and Ph₃C⁺ (via a 1,3-shift mechanism) or alkali cations, Na⁺ and Li⁺ (via a reversible Fe–H addition mechanism). Evidence is presented which supports the action of the group 6 metal carbonyl fragment, M(CO)₅⁰, to be similar to that of the alkali cations in promoting catalysis on the Fe–H⁻ center.

Although the use of metal co-catalysts or promoters is prevalent throughout the literature of catalysis, their precise mechanistic role is generally poorly understood if at all. Developing from the approach, most convincingly articulated by Earl L. Muetterties,[1] of using polynuclear metal compounds as catalysts or catalyst models, the chemistry of discrete heterobimetallic complexes as models for mixed-metal catalysts is a growing field in organometallic chemistry.[2,3] In this connection we report herein the use of simple mixed-metal carbonyl hydrides, HFeM(CO)₉⁻ (M = Cr, Mo, W),[4] as catalysts for olefin isomerization under mild conditions, of activity surpassing that of either parent homobimetallic hydride, HFe₂(CO)₈⁻ or HM₂(CO)₁₀⁻, or fragment components, HFe(CO)₄⁻ or M(CO)₅⁰.

The structure of HFeW(CO)₉⁻ has been determined by X-ray crystallography.[4] The hydrogen atom could not be located; however, the relatively short Fe–W distance of 2.989 (2) Å (well within bonding range), coupled with one wide (OC)ₑq–Fe–(CO)ₑq angle of 147.6 (8)⁰, suggested the hydrogen to have considerable Fe–H terminal character. On the other hand, the distinctive high-field position of the hydride resonance (−11.8 ppm) and a definite (albeit small, 15 Hz) W–H coupling is consistent with at least some bridging hydride character.[4,5] Thus the structure of the heterobimetallic is quite different from that of the homobimetallic parents,[6,7] as illustrated in Figure 1. In fact, the

extreme asymmetry of the "μ-H" ligand suggests the structure might be better visualized as a transition-metal Lewis acid, M(CO)₅⁰, interacting with HFe(CO)₄⁻ at electron density located on Feᵟ⁻ or at the Feᵟ⁻–H bond density site:

$$Fe \diagdown\!\!\overset{H}{\underset{}{\diagdown}}M$$

Another statement of this view is the HFe(CO)₄⁻ moiety serves as an "18-electron complex ligand",[8] in occupancy of the sixth coordination site of M(CO)₅⁰.

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[†] The group notation is being changed in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is being eliminated because of wide confusion. Group I becomes groups 1 and 11, group II becomes groups 2 and 12, group III becomes groups 3 and 13, etc.
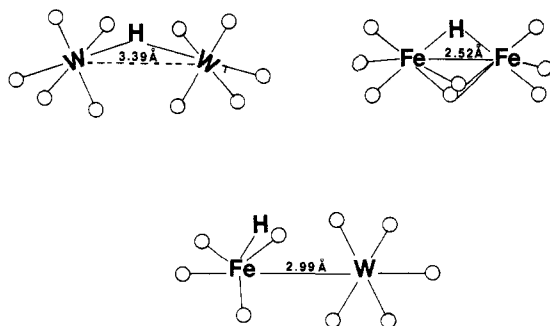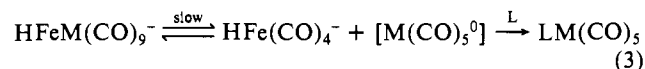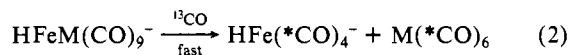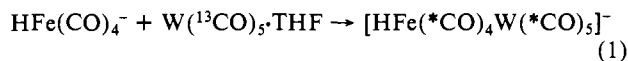
Figure 1. The molecular structures of the bimetallic anions, $HW_2(CO)_{10}^-$ (in its bent, staggered configuration),[5] $HFe_2(CO)_8^-$,[6] and $HFeW(CO)_9^-$,[4] as determined by X-ray crystallography on PPN⁺ salts. The hydrogen atom was not located for $HFeW(CO)_9^-$, and its representation as semibridging is based on spectroscopic data (see text).

The established chemistry associated with $HFeM(CO)_9^-$ includes extremely rapid CO exchange, both intra- and intermolecularly, as illustrated by 1 and 2 (here * represents a mixture of C-13 and C-12 labels and M = Cr or W).[4] Dimer disruption was rapid ($t_{1/2}$ = ca. 8 min) with CO as scavenging agent for $W(CO)_5^0$ but slow ($t_{1/2}$ = 5–6 hrs) with PPh_3 or $HW(CO)_5^-$ as trapping agents.[4] The latter results, eq 3, indicated the dimer

$$HFe(CO)_4^- + W(^{13}CO)_5 \cdot THF \rightarrow [HFe(^*CO)_4W(^*CO)_5]^- \quad (1)$$

$$HFeM(CO)_9^- \xrightarrow[\text{fast}]{^{13}CO} HFe(^*CO)_4^- + M(^*CO)_6 \quad (2)$$

$$HFeM(CO)_9^- \underset{\text{slow}}{\rightleftharpoons} HFe(CO)_4^- + [M(CO)_5^0] \xrightarrow{L} LM(CO)_5 \quad (3)$$

to be quite stable toward disruption, except in the presence of CO. Furthermore, addition of both CO and PPh_3 in equimolar amounts to $HFeW(CO)_9^-$ yielded a dimer cleavage reaction equal in rate to that of CO alone; however, the products were a mixture of $W(CO)_6$ and $W(CO)_5PPh_3$ in a 1:6 ratio, as well as $HFe(CO)_4^-$. The dimer disruption thus was promoted by CO, but the coordinatively unsaturated $W(CO)_5^0$ was not necessarily trapped by CO. That is, a $HFeW(CO)_9^-$ adduct of CO appeared to precede dimer disruption. The CO promoted dimer disruption was suggested to proceed via an associative mechanism. Similar results (eq 3) have been noted for M = Cr. Such behavior encouraged further study, and the mechanistically well-defined olefin isomerization reaction was chosen to probe the catalytic activation capabilities of this interesting bimetallic.

Experimental Section

All syntheses, reactions, and sample transfers were performed under O_2-free conditions with standard techniques (drybox, Schlenk-line (N_2)) or a high-vacuum line.

A. Materials. The solvents tetrahydrofuran (THF) and acetonitrile were distilled from the appropriate drying and oxygen-scavenging agents and stored in dry, N_2-filled flasks over activated 4A molecular sieves. Immediately prior to use these solvents were further purged with nitrogen and then transferred to reaction vessels via stainless steel cannula under a positive N_2 pressure.

Common reagents were obtained from standard vendors (Aldrich and Strem Chemical Co.), degassed, and otherwise used as received. Preparations of the following were as reported in the literature: PPN⁺-$HFeM(CO)_9^-$ (M = Cr, Mo, W; PPN⁺ = bis(triphenylphosphine)-iminium);[4] PPN⁺ $HFe(CO)_4^-$;[9] $Et_4N^+ HFe_2(CO)_8^-$;[7] PPN⁺ $HM(CO)_5^-$ (M = Cr, W);[10] PPN⁺ $H_2B(\mu\text{-}H)_2Cr(CO)_4^-$;[11] $Bu_4N^+ \mu\text{-}HCr_2(CO)_{10}^-$;[12] $Et_4N^+ \mu\text{-}HW_2(CO)_{10}^-$.[12] Salts of PPN⁺ $HFeM(CO)_8P^-$ (M = Cr, P = $P(OMe)_3$, PPh_3; M = W, P = $P(OMe)_3$) were made by aggregating a

Table I. Isomerization of Allylbenzene with PPN⁺ $HFeM(CO)_8L^-$ in THF Solution[a]

entry	catalyst	conditions[b]	mmol of product/ mmol of catalyst[c]
1	$HFeCr(CO)_9^-$	light, 25 °C, 17 h	10 (2.0)[d]
2	$HFeMo(CO)_9^-$	light, 25 °C, 17 h	9.8 (2.4)[d]
3	$HFeW(CO)_9^-$	light, 25 °C, 17 h	4.88[d]
4	$HFeCr(CO)_9^-$	dark, 25 °C, 17 h	0
5	$HFeMo(CO)_9^-$	dark, 25 °C, 17 h	1.6
6	$HFeW(CO)_9^-$	dark, 25 °C, 17 h	0.4
7	$HFeCr(CO)_9^-$	$h\nu$,[e] 0 °C, 15 min	2.0
8	$HFeMo(CO)_9^-$	$h\nu$,[e] 0 °C, 15 min	7.7
9	$HFeW(CO)_9^-$	$h\nu$,[e] 0 °C, 15 min	3.4
10	$H[Fe(CO)_3P(OMe)_3)]\text{-}[Cr(CO)_5]^-$	light, 25 °C, 72 h	4.0
11	$H[Fe(CO)_3PPh_3][Cr(CO)_5]^-$	light, 25 °C, 36 h	4.3[f]
12	$H[Fe(CO)_4][W(CO)_4\text{-}P(OMe)_3]^-$	light, 25 °C, 21 h	9.4

[a] Catalyst:allylbenzene ratio of 1:10. [b] "light" refers to fluorescent lighting; "dark" refers to foil wrapped tubes; "$h\nu$" refers to photolysis by a 450 W Hg vapor lamp, Pyrex tubes. [c] Average value of several repetitions. [d] 5 h reaction time. [e] 450 W mercury vapor lamp, Pyrex filter (>366 nm). [f] Catalyst:olefin = 1:7.

hydridoiron anion with the appropriate labile ligand group 6 complex, e.g., $HFe(CO)_4^-$ and $cis\text{-}THF\cdot W(CO)_4P(OMe)_3$ and $trans\text{-}HFe(CO)_3P(OMe)_3^-$ or $HFe(CO)_3PPh_3^-$ and $THF\cdot Cr(CO)_5^0$. The full characterization of the $HFeM(CO)_8P^-$ anions is the subject of a separate report.[13] The salt $Li^+ BPh_4^-$ was prepared according to the method of Szwarc et al.[14]

B. Instrumentation. Infrared spectra were obtained on a Perkin-Elmer 283B spectrophotometer or an IBM FTIR/85 spectrometer with 0.1 mm sealed NaCl solution cells. ^2H NMR spectra were collected on a Varian XL200 spectrometer. Olefinic product analysis was monitored by GLC on a Perkin-Elmer Sigma 2 gas chromatograph with flame ionization detector. Columns used in this analysis were as follows: 1-hexene, picric acid on graphpac, 80/100 mesh, 6 ft × $^1/_8$ in. stainless steel tubing; allylbenzene and isomerized products, 10% Carbowax on Chromosorb W H.P., 80/100 mesh, 2 m × $^1/_8$ in. stainless steel tubing. GC/MS data were collected at the Texas A&M Center for Trace Characterization Mass Spectrometric Analysis on a Hewlett Packard 5710A gas chromatograph in line with a Hewlett Packard 5980 mass spectrometer. GC/FTIR studies were performed on the combination of a Perkin-Elmer Sigma 3B gas chromatograph interfaced with an IBM IR/85 FTIR.

C. Reactions. 1. Olefin Isomerization with PPN⁺ [HFeM(CO)₈L⁻] Catalysts: Allylbenzene. In a typical reaction 50 mg (ca. 0.05 mmol) of the hydride catalyst was loaded into a 25-mL Schlenk tube equipped with magnetic stir bar and vacuum adapter in the drybox. Outside the glovebox the tube was evacuated and refilled with N_2 three times prior to addition of THF solvent (5 mL, via cannula). A 10-fold molar excess of allylbenzene was added and the reaction allowed to stir at room temperature (25 ± 2 °C) for 17 h, either in foil-wrapped Pyrex tubes ("dark") or exposed to the laboratory fluorescent lighting ("light" reactions). Volatiles were analyzed by GLC, Table I, and identification made by comparison of retention times of known compounds and by one additional spectroscopic method: GC-MS, ^1H or ^2H NMR, or GC-IR.

2. Isomerization of 1-Hexene. These studies were carried out identically with the above description by using CH_3CN as solvent instead of THF.

3. Olefin Isomerization with PPN⁺ $HFe(CO)_4^-$. In a typical experiment, 50 mg of PPN⁺ $HFe(CO)_4^-$ (0.070 mmol) along with any additive was loaded into a 25-mL pyrex Schlenk tube inside the drybox. Tetrahydrofuran and allylbenzene (10-fold molar excess) were added as described above and the reactions allowed to stir at room temperature for 17 h prior to product analysis (Table II). (The additive BF_3, obtained as the etherate, was syringed into the reaction vessel outside the drybox.)

4. Photolysis Reactions. The photolysis reactions employed the same 25-mL Pyrex Schlenk tubes (receiving radiation primarily at 366 nm), charged with catalyst, olefin, and solvent, as described above. The tubes

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Table II. Catalytic Isomerization of Allylbenzene[a] by
PPN⁺ HFe(CO)₄⁻ in THF Solution

entry	additive	[additive]/ [HFe(CO)₄⁻]	conditions	turn-overs[b]
1			light, 25 °C, 17 h	0.2
2			dark, 25 °C, 17 h	0.1
3			hν, 0 °C, 15 min	1.3
4	Ph₃C⁺ BF₄⁻	1:1	light, 25 °C, 17 h	7.1
5	BF₃	1:3	light, 25 °C, 17 h	2.7
6	Li⁺ BPh₄⁻	1:1	light, 25 °C, 17 h	4.3
7	PPN⁺ BPh₄⁻	1:1	light, 25 °C, 17 h	0
8	Na⁺ BPh₄⁻	1:1	light, 25 °C, 17 h	4.6
9	Na⁺ BPh₄⁻	4:1	light, 25 °C, 17 h	4.0
10	Na⁺ BPh₄⁻	4:1	dark, 25 °C, 17 h	4.5
11	Na⁺ BPh₄⁻/CO[c]	4:1	light, 25 °C, 17 h	1.6
12	Na⁺ BPh₄⁻/CO[c]	4:1	dark, 25 °C, 17 h	0.2
13	HOAc	2:1	light, 25 °C, 17 h	0.5

[a] HFe(CO)₄⁻:allylbenzene = 1:10 molar ratio. [b] Measured as mmol of isomerized product/mmol of catalyst over the period listed. [c] 1 atm % CO used.

and a 450 W Hanovia mercury vapor lamp (protected by a water-jacketed quartz well) were partially immersed in a 10-L Dewar flask filled with ice water. The top of this photolysis apparatus was covered with foil to protect against escaping radiation. As a further precaution, the photolysis was carried out inside a hood whose glass front was covered with a thick paper. The photolysis setup did not permit stirring of the reaction solution. At the end of the 15-min photolysis period products were analyzed by FTIR (organometallics) and GC (organics).

5, Control Experiments. (a) Addition of CO. PPN⁺ HFeW(CO)₉⁻ (50 mg, 0.048 mmol) was loaded into a Schlenk tube and THF (5 ml) and allybenzene (63.5 μl, 0.48 mmol) were added as described above. The system was evacuated and refilled with CO to 1 atm. After the mixture was stirred at room temperature for 17 h in the light, this solution displayed IR bands at 1980 cm⁻¹(s), characteristic of W(CO)₆, and also at 1910 (m) and 1880 cm⁻¹(s), characteristic of HFe(CO)₄⁻. GLC showed the only hydrocarbon present to be allylbenzene. A similar experiment was carried out with Na⁺ HFe(CO)₄⁻ (PPN⁺ HFe(CO)₄⁻ plus 4 equiv of Na⁺ BPh₄⁻ in THF) as isomerization catalyst. After 17 h some (ca. 10%) Fe(CO)₅ was observed by IR; however, most HFe(CO)₄⁻ remained, in both light and dark reactions. Results are in Table II.

(b) Addition of PMe₃. A similar experiment to that in 5a above was carried out with PMe₃ (20 μL, ca. 0.2 mmol) as additive to HFeCr(CO)₉⁻ (0.055 mmol) in 5 mL of THF instead of CO. After 5 h the infrared spectrum showed bands at 2053 (w) and 1932 (s), and 1930 (s), attributed to Cr(CO)₅PMe₃,[15] as well as the bands for HFe(CO)₄⁻ at 1995 (w), 1910 (m), and 1880 (s) cm⁻¹. There was no olefin isomerization.

(c) Addition of Octyl Bromide. Octyl bromide was added in 2-fold molar excess to the HFeW(CO)₉⁻ catalyst (in a typical olefin isomerization experiment). The solution was stirred for 17 h in the light and the volatiles analyzed. No octane was observed in the GLC trace; olefin isomerization products, cis- and trans-propenylbenzene, were present in ratios typical of the catalyst in the absence of additives.

(d) Addition of HCr(CO)₅⁻. PPN⁺HCr(CO)₅⁻ was added to PPN⁺-HFeW(CO)₉⁻ and the catalysis attempted as above. At the end of 17 h in the light no products of olefin isomerization were observed. The IR spectrum showed bands due to HFe(CO)₄⁻ and μ-HCr(CO)₅W(CO)₅⁻ as major products. Some (ca. 25%) W(CO)₆ or Cr(CO)₆ was also present.

(e) Other Control Experiments. Other metal carbonyl complexes were checked for potential catalysis of the isomerization of allylbenzene with the same procedure as described above, i.e., a 10-fold molar excess of olefin to complex in THF solution, 25 °C (except where noted), and 17 h reaction time, under laboratory lighting.

6. Deuterium-Labeling Studies. (a) DFeCr(CO)₉⁻. To 1.5 g (1.6 mmol) PPN⁺HFeCr(CO)₉⁻ in 10 mL of THF was added 0.43 mL (7.5 mmol) of CH₃COOD (98% d_1, Aldrich Chemical Co.). The solution was allowed to stir for 1 h after which it was examined by NMR. No resonance was observed in the hydride region of the ¹H NMR. The ²H NMR spectrum showed the DFeCr(CO)₉⁻ resonance at -14.75 ppm. The solvent was removed in vacuo and the oily residue triturated with several portions of hexane until a yellow-orange microcrystalline solid was obtained (1.45 g). To 1.2 g (1.33 mmol) of PPN⁺ DFeCr(CO)₉⁻ was

added 2.75 mL of THF and 165 μL (1.33 mmol) of allylbenzene. An additional 76 μL of CH₃COOD was also added. The solution was stirred in the light under N₂ for 17 h at 25 °C following which the volatiles were separated in a trap-to-trap distillation. Examination by ²H NMR showed strong resonances at δ 1.79, 6.22, and 6.37, corresponding to the three allylic positions of trans-propenylbenzene. (N.B.: The Sadtler Index reports the ¹H resonances at δ 1.79, 6.08, and 6.37.)

This solution was also analyzed by GC/mass spectroscopy. The isomerized products, cis- and trans-propenylbenzene, contained deuterium at the following levels: d_1, 18%; d_2, 30%; d_3, 6%.

(b) DFe(CO)₄⁻. To 900 mg (1.27 mmol) of PPN⁺ HFe(CO)₄⁻ in 10 mL of THF was added a 0.33-mL portion of CH₃COOD (5.8 mmol).[16] This solution was stirred for 2.5 h and examined by ¹H and ²H NMR to ascertain complete H/D exchange. The solvent was removed in vacuo, and the PPN⁺ DFe(CO)₄⁻ (>95% d labeled) was recrystallized from THF/hexane.

(c) DFe(CO)₄⁻ with BF₃. A 250-mg (0.35 mmol) portion of PPN⁺-DFe(CO)₄⁻ was dissolved in 2.5 mL of THF. To this was added 47 μL of allylbenzene (0.35 mmol) and 14 μL of BF₃ etherate (0.11 mmol). The solution was stirred at 25 °C for 17 h in the light following which time the olefinic products were separated from the catalyst by trap-to-trap distillation. GLC analysis showed >90% conversion to trans-propenylbenzene. Deuterium NMR showed no d-label incorporation in the olefinic product. Deuterium NMR indicated that d-label had been substantially retained in the remaining catalyst precursor, DFe(CO)₄⁻, δ = -8.41. A low-intensity hydride resonance was observed in the ¹H NMR, presumably due to exchange of deuterium for hydrogen from adventitious H⁺ sources (glass walls).[16]

(d) DFe(CO)₄⁻ with Na⁺ BPh₄⁻. A sample identical with that described in section 6c was prepared. Instead of BF₃, 120 mg of NaBPh₄ (0.35 mmol) was added. After the 17 h reaction period, the olefinic products were separated from the catalyst. GLC showed trans-propenylbenzene as the major product. The ²H NMR of the product had resonances at the expected olefinic positions (see section 6a, above). By GC/MS analysis the remaining allylbenzene as well as the cis- and trans-propenylbenzene had deuterium incorporation at the levels 17-19% d_1, 18-22% d_2, and 3-4% d_3.

Results

HFeM(CO)₉⁻ Anions. The HFeM(CO)₉⁻ anions (M = Cr, Mo, W) are found to be photocatalysts or catalyst precursors in the isomerization of external olefins into the thermodynamically favored internal olefins. Both 1-hexene and allylbenzene are catalytically isomerized in the presence of light. Difficulties in obtaining clean GC separations of the 3-hexenes and 1-hexene precluded extensive work with the linear alkenes, and the results of Table I were obtained for the isomerization of allylbenzene (eq 4). The hydrogenated products, propylbenzene or hexane, were not observed under the conditions of isomerization catalysis. Neither did addition of acetic acid equimolar to the HFeM(CO)₉⁻ or 5 atm of H₂ produce hydrogenated products.

(4)
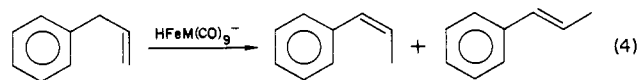
The results of Table I show that in the presence of ordinary laboratory fluorescent lighting all of the allylbenzene has been converted into cis- and trans-propenylbenzene (1:10 ratio of cis to trans) within 17 h for the HFeCr(CO)₉⁻ and HFeMo(CO)₉⁻ catalysts (entries 1 and 2). The tungsten analogue is less active for the all-carbonyl anion (entry 3, Table I).

The HFeCr(CO)₉⁻ catalyst is inactive in the dark, and the Mo and W analogues are of much lower activity as compared to catalytic activity in the presence of fluorescent light. Photolysis (450 W Hg vapor lamp, Pyrex filter) at 0 °C generates isomerized products; however, a different dependence of catalyst activity on M is observed in the fluorescent light reactions (Cr ≳ Mo > W) compared to the photolysis reactions (Mo > W > Cr).

The mixed-metal hydrides decompose under the photolysis conditions. In all cases a considerable amount of HFe(CO)₄⁻ and M(CO)₆ built up within the 15 min reaction period. In addition, bands at 1922 and 1917 cm⁻¹ (for the HFeMo(CO)₉⁻ and HFeCr(CO)₉⁻ decomposition products, respectively) indicate the presence of other, unidentified, species. Under the laboratory light some degradation of the HFeM(CO)₉⁻ anions into HFe(CO)₄⁻ and M(CO)₆ also occurs during catalysis for M = Cr (15%) and

(15) Cotton, F. A.; Darensbourg, D. J.; Kolthammer, B. W. S. *Inorg. Chem.* **1981**, *20*, 4440. This reference reports W(CO)₅PMe₃. The Cr analogue was prepared and purified in the same manner: IR ν(CO) (cm⁻¹) 2054 (w), 1934 (vs), THF solution, and 2059 (m), 1984 (w), 1936 (s), hexane.

Olefin Isomerization Catalysis by HFeM(CO)₈L⁻

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M = Mo (25%). A quantitative study of the decomposition indicated a 1:1 conversion of $HFeM(CO)_9^-$ to $HFe(CO)_4^-$, and less than 1 equiv of $M(CO)_6$ per reactant dimer was produced. The $M(CO)_6$ is thus produced from $M(CO)_5$ fragments. The W analogue shows no decomposition.

As was shown earlier,[4] addition of CO causes rapid fragmentation of the dimeric hydride and addition of PR_3 or $HM(CO)_5^-$ also effects Fe–M bond cleavage. Thus in the presence of added CO the $HFeCr(CO)_9^-$ catalyst is rendered inactive toward olefin isomerization, yielding $HFe(CO)_4^-$ and $Cr(CO)_6$. Interestingly, olefin isomerization was also completely quenched upon addition of PMe_3 or $HCr(CO)_5^-$, even though the $HFeCr(CO)_9^-$ species persisted in solution in the presence of the olefin for several hours.

Entries 10, 11, and 12 demonstrate the effect of P-donor ligand substituent. If P substitution is on the iron side, trans to the Fe–M bond, the catalyst is rendered less active than the all-CO analogue. If P substitution is on the group 6 metal side, cis to the M–Fe bond, the catalyst activity is enhanced. It should be noted that the catalysts of entries 10 and 11 are in general much less reactive (with respect to CO exchange, eq 1 and 2, or dimer disruption, eq 3) than are their all-CO analogues.[13]

The following hydrides were inactive as olefin isomerization catalysts under the same conditions of laboratory light and the same (or more rigorous) thermal conditions as used for the $HFeM(CO)_9^-$ catalysts: PPN^+ salts of $HCr(CO)_5^-$, $HW(CO)_5^-$, μ-$HCr_2(CO)_{10}^-$ (70 °C), μ-$HW_2(CO)_{10}^-$ (70 °C), and H_2B (μ-$H)_2Cr(CO)_4^-$. The complex THF·$Cr(CO)_5$ was generated by photolysis of a THF solution of $Cr(CO)_6$ (IR: $\nu(CO)$ 2075 (w), 1936 (s), 1895 (m) cm⁻¹) and stirred with allylbenzene for 17 h at 25 °C under ordinary laboratory light. No isomerized products were observed.

For further comparison the iron dimer, μ-$HFe_2(CO)_8^-$ as its Et_4N^+ salt, was generated by HOAc protonation of $Fe_2(CO)_8^{2-}$ at 0 °C[7b] and maintained at 0 °C to prevent decomposition. Used in situ at 0 °C under ordinary light the compound showed low catalytic activity (a conversion of 0.5 mmol of isomerized products out of 10 mmol of allylbenzene) over the 17-h period. If allowed to warm to 25 °C olefin isomerization activity increased substantially (to 9.4 mmol for the 17-h period). In the latter case the principal remaining organometallic species was $HFe_3(CO)_{11}^-$ (2070 (vw), 2004 (s), 1980 (m), 1950 (w) cm⁻¹).[17] Neutral $Fe(CO)_5$ is a poorer catalyst. Over a 24 hr period at 100°C in the light only 4.6 mol of allylbenzene per mol of $Fe(CO)_5$ was converted into propenylbenzenes.

The presence of a radical species was observed by EPR spectroscopy on solutions containing the $HFe_2(CO)_8^-$ and $Fe_2(CO)_8^{2-}$ anions.[7a,18] A similar signal was generated upon producing $HFeCr(CO)_9^-$ in situ from its EPR silent components $HFe(CO)_4^-$ and $Cr(CO)_5$·THF and on solutions of preformed and recrystallized PPN^+ $HFeCr(CO)_9^-$. This signal (g = 2.0385) was identified as the iron carbonyl radical anion, $Fe_2(CO)_8^-\cdot$,[18] present at low (<1% of total complex anion) concentrations.[19] The radical was destroyed upon addition of O_2. Addition of a 10-fold excess of allylbenzene did not change the EPR spectrum, monitored over a 17-h period. The $Fe_2(CO)_8^-\cdot$ is a ubiquitous impurity in samples of iron carbonylates.[19]

As its PPN^+ salt the anion $HFe(CO)_4^-$ showed low catalytic activity under the conditions used for these studies (0.014 M in $HFe(CO)_4^-$, 0.14 M in allylbenzene, 25 °C, THF solution). Additives such as the trityl cation, BF_3, Li^+, or Na^+ greatly enhanced catalysis, cf. Table II. Upon adding 1 equiv of Ph_3C^+ BF_4^- the yellow solution of $HFe(CO)_4^-$ was observed to immediately change to the red plum color characteristic of
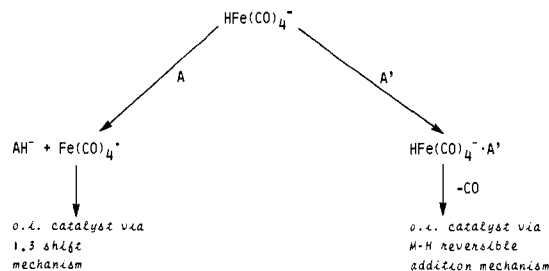
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(19) (a) EPR spectra on THF solutions of PPN^+ $HCrFe(CO)_9^-$ were measured both in these laboratories and by Dr. Paul Krusic, E. I. du Pont de Nemours and Co., Wilmington, DE. (b) Private communication, Dr. Krusic.
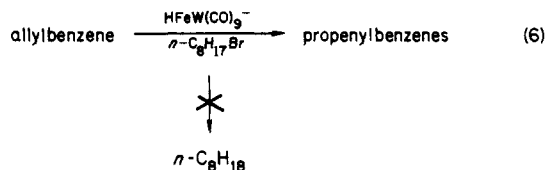
Scheme I

$HFe_3(CO)_{11}^-$, whose presence (>50%) was verified by IR. With BF_3 as additive the $HFe_3(CO)_{11}^-$ decomposition product was detected at ca. 10% levels. The solution of PPN^+ $HFe(CO)_4^-$ to which $Na^+BPh_4^-$ was added showed IR spectral changes indicative of contact ion pairing of the form $HFe(CO)_3CO^-\cdots Na^+$.[9] (These changes were reversed upon adding small amounts of the good donor solvent Me_2SO.) After the catalytic run there were no IR detectable decomposition products, although a pale pink color indicated the presence of minor amounts of $HFe_3(CO)_{11}^-$. No IR spectral changes indicative of contact ion pairing were observed with $Li^+BPh_4^-$ as additive; however, a pale pink color again developed as described for Na^+. To check whether the BPh_4^- counterion (or possible BPh_3 impurity) could affect the isomerization, a PPN^+ BPh_4^- salt, produced in situ by mixing the THF solution of $Na^+BPh_4^-$ and PPN^+Cl^-, was added to PPN^+ $HFe(CO)_4^-$ and the olefin isomerization was attempted as usual. None was observed (entry 7, Table II). Addition of CO to the catalytically active $Na^+HFe(CO)_4^-$ solutions resulted in a suppression of catalytic activity, entries 11 and 12.

The transfer of deuterium label from the olefin isomerization catalysts $PPN^+DFeW(CO)_9^-$, $PPN^+DFe(CO)_4^-/BF_3$, and $Na^+DFe(CO)_4^-$ into the isomerized olefins was monitored by ²H NMR and GC/MS. For D-Cat⁻ = $PPN^+DFeW(CO)_9^-$ and $Na^+DFe(CO)_4^-$, label was incorporated into the isomerized olefin as indicated by eq 5. In contrast, no label transfer was observed for the catalyst $DFe(CO)_4^-/BF_3$, although considerable isomerization was verified by GC.

major product   minor product

(5)
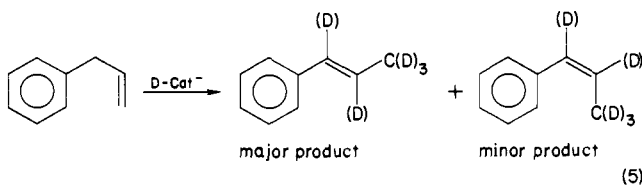
Discussion

The experiments described above established the reactivity of $HFeM(CO)_9^-$ anions as catalysts or catalyst precursors toward isomerization of olefins, specifically allylbenzene. In addition, other experiments were designed to contrast the reactivity of fragment components of $HFeM(CO)_9^-$ and to compare with homobimetallic parents. A discussion of those results follows.

The Parent Homobimetallic Anions. The μ-$HM_2(CO)_{10}^-$ anions do not isomerize olefins at 25 °C (or 70 °C) over extended periods under fluorescent lighting conditions. The $HFe_2(CO)_8^-$ anions are, in the presence of HOAc, stoichiometric reducing agents for activated olefins.[7a] The proposed mechanism for olefin hydrogenation suggests interaction of the intact $HFe_2(CO)_8^-$ dimer with the olefin, i.e., an olefin·$HFe_2(CO)_8^-$ adduct is the first-formed species, prior to hydrogen transfer to the olefin. Reversible hydrogen transfer can lead to olefin isomerization at this point, and the $HFe_2(CO)_8^-$ anion, generated in situ, was reported to isomerize olefins such as 1-hexene.[7a] Our experiments with this dimer indicated substantial decomposition at 25 °C, and the major product, $HFe_3(CO)_{11}^-$, was inactive as an olefin isomerization

Scheme II

$$HFe(CO)_4^-$$

A   A'

$$AH^- + Fe(CO)_4{}^{\cdot}$$ $$HFe(CO)_4{}^- \cdot A'$$

↓   ↓ -CO

o.i. catalyst via 1,3 shift mechanism   *o.i. catalyst via M-H reversible addition mechanism*

catalyst. Hence the lifetime of $HFe_2(CO)_8^-$ as a catalyst is short at room temperature.

Catalytic Activity of Fragment Components of $HFeM(CO)_9^-$. The thermal fragmentation pattern of the dimer was established earlier (eq 3) to yield $HFe(CO)_4^-$ and $[M(CO)_5^0]$.[4] The catalytic activity of these plus other possible (but not probable) fragments of $HFeM(CO)_9^-$, summarized in Scheme I, was studied.

The $HM(CO)_5^-$ anions are inactive as olefin isomerization catalysts under conditions where $HFeM(CO)_9^-$ is active. Furthermore, there is no indication that $HM(CO)_5^-$ anions are ever present during the olefin isomerization with $HFeM(CO)_9^-$ catalysts. To further check this the experiment represented by eq 6 was carried out. Were $HM(CO)_5^-$ units present, the added octyl bromide would have been converted to octane.[18] None was detected by gas chromatography.
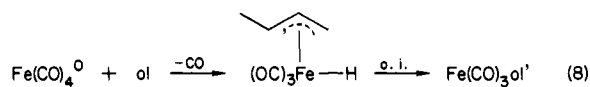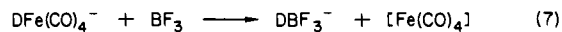
$$allylbenzene \xrightarrow[\substack{n-C_8H_{17}Br}]{HFeW(CO)_9^-} propenylbenzenes \quad (6)$$

$$\cancel{\downarrow}$$

$$n\text{-}C_8H_{18}$$

The $[M(CO)_5^0]$ coordinate unsaturates are established photoassisted catalysts for olefin isomerization, following the order $W > Mo \gg Cr$ (N.R.).[21] Our additional studies showed that photochemically generated $Cr(CO)_5 \cdot THF$ in THF solutions to be inactive as a thermal olefin isomerization catalyst for allylbenzene. In contrast, the $HFeCr(CO)_9^-$ is a better catalyst (or catalyst precursor) than is $HFeW(CO)_9^-$.
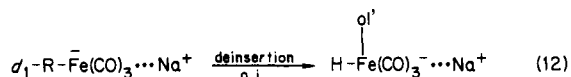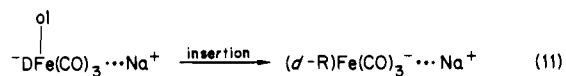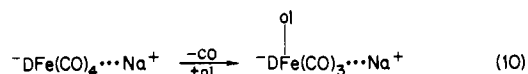
The $[Fe(CO)_4^0]$ moiety is a known isomerization catalyst. Wrighton et al. reports activity for 1-pentene in benzene of 3.27 turnovers per h with $Fe(CO)_4^0$ photogenerated from $Fe(CO)_5$ (continual photolysis, 450 W Hg-vapor lamp).[22] Casey and Cyr demonstrated $Fe(CO)_4^0$, thermally (80–100 °C) generated from $Fe_3(CO)_{12}$, to be the prototypical catalyst for the 1,3 hydrogen shift mechanism.[23] Those workers assumed a π-allyl hydride intermediate of Fe^{II}, i.e., $(OC)_3Fe(\pi\text{-allyl})(H)$, while others[24] have suggested the 1,3 shift to result from H^- abstraction by $Fe(CO)_4^0$, yielding $HFe(CO)_4^-$ intimately ion paired with a cationic allyl group. The activity of the $Fe(CO)_4^0$ catalyst is observed to be olefin dependent and, in some cases, is quite sluggish.

The $HFe(CO)_4^-$ anion is a well-known olefin isomerization catalyst;[25] however, it is of very low activity in the absence of additives (Table II, entries 1, 2, 3). Additives affect the catalytic activity of $HFe(CO)_4^-$ in one of the two ways presented in Scheme II. The trityl cation or the Lewis acid BF_3 are effective H^-

abstracting agents, represented by A in Scheme II, and generate an active $Fe(CO)_4^0$ unit.[26] Consistent with this view, no deuterium label was incorporated into the isomerized olefin when $DFe(CO)_4^-/BF_3$ was used as catalyst or catalyst precursor (a catalyst system similar to entry 5 of Table II). The 1,3 shift or the π-allyl hydride mechanism (eq 7 and 8) is most likely operative for this system.[27] In contrast, when an experiment analogous to entry

$$DFe(CO)_4^- + BF_3 \longrightarrow DBF_3^- + [Fe(CO)_4] \quad (7)$$

$$Fe(CO)_4{}^0 + ol \xrightarrow{-CO} (OC)_3Fe\text{—}H \xrightarrow{o.i.} Fe(CO)_3ol' \quad (8)$$

$$Fe(CO)_3ol' + ol \xrightarrow{-ol'} Fe(CO)_3ol \quad (9)$$
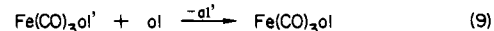
9 of Table II was carried out with $DFe(CO)_4^-$ in the presence of Na^+ ion, D label was incorporated into the isomerized olefin, indicative of a reversible Fe–D addition to the olefin.[25e] The presence of added CO inhibits the catalytic activity of Na^+-$HFe(CO)_4^-$ either in the dark or in the light (entries 11 and 12, Table II). Hence we propose that the major effect of the additives Na^+ or Li^+ lies in CO labilization, a cation-promoted phenomenon noted earlier for $HFe(CO)_4^-$[9] and apparently general for anionic organometallics.[28] The open coordination site thus generated becomes the olefin binding site according to eq 10–12.

$$^-DFe(CO)_4 \cdots Na^+ \xrightarrow[+ol]{-CO} {}^-DFe(CO)_3 \cdots Na^+ \quad (10)$$

$$^-DFe(CO)_3 \cdots Na^+ \xrightarrow{insertion} (d\text{-}R)Fe(CO)_3{}^- \cdots Na^+ \quad (11)$$

$$d_1\text{-}R\text{-}\bar{Fe}(CO)_3 \cdots Na^+ \xrightarrow[o.i.]{deinsertion} H\text{-}\bar{Fe}(CO)_3{}^- \cdots Na^+ \quad (12)$$

where ol' = d_1-isomerized olefin

The $HFeM(CO)_9^-$ Anions. A basic requirement for activity of a transition-metal complex toward catalytic olefin isomerization is that of an open coordination site for the reversible binding of olefin.[29] Succeeding steps depend on the presence and activity of a metal–hydrogen bond. In the absence of a M–H bond in the catalyst or catalyst precursor, the 1,3 hydrogen shift mechanism apparently prevails. In its presence, reversible addition of M–H across the olefinic bond readily accounts for the observed isomerization. The preponderance of evidence suggests the M–H addition/elimination mechanism is favored whenever possible.[30] There are examples of circuituous routes taken by a catalyst precursor to generate metal hydrides in order to avoid the 1,3 shift mode.[31] There is only one example of a hydride-containing metal complex which acts as an olefin isomerization catalyst without using the activity of the M–H bond.[32]

The $HFeM(CO)_9^-$ anions are CO labile and a M–H bond exists. The compounds are catalytically active toward olefin isomerization. When $DFeM(CO)_9^-$ is used as catalyst (precursor), a scrambling of label into the isomerized olefin is observed. The dimeric anions are relatively easily cleaved into two fragments, neither of which, $HFe(CO)_4^-$ or $M(CO)_5^0$, is catalytically active toward olefin

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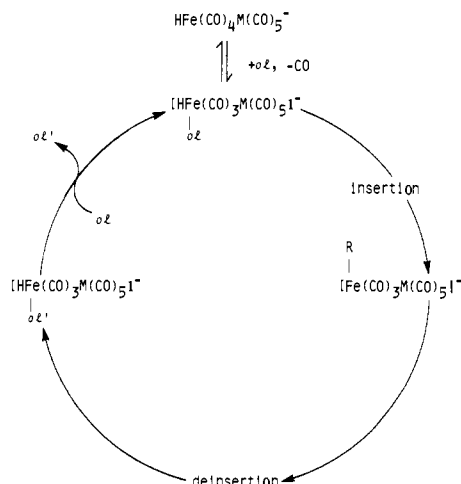
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Scheme III

isomerization *under the conditions of our experiments: fluorescent lighting and PPN⁺ counterion.* The $HFe(CO)_4^-$ anion becomes both CO labile[9] and catalytically active when subjected to alkali counterion additives. It also becomes catalytically active when subjected to agents which remove the hydride. The $M(CO)_5^0$ Lewis acids cannot remove hydride from $HFe(CO)_4^-$;[4] however, the CO lability of the dimeric hydrides is exceptional with ^{13}CO as ligand exchange reagent.[4] Interestingly, added phosphine ligands do *not* replace CO in a direct substitution process on the dimer even though such $HFeM(CO)_8P^-$ species are preparable via an alternate route.[13] The phosphorus–ligand substituent may be attached to either Fe or the group 6 metal, and both types of anions are catalytically active toward olefin isomerization.

We have been unable to establish the site of CO lability in $HFeM(CO)_9^-$. In view, however, of the much greater catalytic activity of the alkali cation promoted $HFe(CO)_4^-$ species as compared to the $M(CO)_5^0$ species, we are most comfortable with the suggestion that olefin isomerization is localized on the iron center of the intact heterobimetallic hydride anion, as demonstrated in Scheme III. The express nature of the CO/ol displacement reaction is not indicated in the scheme; however, the possibility of an associative mechanism, involving an olefin/ $HFeM(CO)_9^-$ adduct, can be supported. Such an adduct has precedent[7a] and is possible because the dimeric complex is overall electron poor. Such an adduct is attractive because of the observed total inhibition of catalysis by other interactive ligands such as phosphines. That is, even though the dimer cleavage by P-donor ligands is slow, *no* olefin isomerization is seen in the presence of such ligands, suggesting that the P ligands block some binding site which precedes active site binding. According to our view the latter requires CO loss and is the entry into the catalytic cycle, Scheme III. No role is assigned to the $M(CO)_5$ unit other than to promote CO loss and to disperse negative charge. We have no evidence for a more intricate involvement of the second metal as has been proposed for other systems.[24b,33]

Repeated attempts to observe the intermediate, $[RFeM(CO)_8]$, or $RFeM(CO)_9^-$ as derived from the insertion of allyl benzene into the Fe–H bond have been unsuccessful. However, we have observed that anions analogous to the proposed $RFeM(CO)_8^-$ intermediates can be synthesized. Salts of $MeFeM(CO)_9^-$ (M = Cr, W) have recently been prepared either by methylation of the dianion $FeM(CO)_9^{2-}$ or by aggregation of $MeFe(CO)_4^-$ with $THF·M(CO)_5$.[34] The $PPN^+MeFeW(CO)_9^-$ salt give satisfactory elemental analyses, and its spectral characteristics (IR and ^1H and ^{13}C NMR) is similar to those of $HFeW(CO)_9^-$, suggesting a similar structure.

Finally, the possibility that some radical species is responsible for the isomerization catalysis must be considered, in view of the observation of radical species by EPR. Note, however, that the major species $Fe_2(CO)_8^-·$ contains no hydride and the deuterium-labeling experiment suggests a reversible M–H addition/ elimination to lie at the heart of the catalytic process. Attempts to enhance the concentration of radical species included the 1-electron oxidation of $HFeCr(CO)_9^-$ by ferricenium ion at room temperature in the presence of allylbenzene. The catalyst decomposed, and no olefin isomerization was observed. At this time we have no convincing evidence that radical species are involved in the olefin isomerization reaction.

Summary

The heterobimetallic hydride anions $HFeM(CO)_9^-$ were identified as olefin isomerization catalysts whose activity is based in a reversible metal hydride addition/elimination process. The activity of a possible catalytically active fragment component, $HFe(CO)_4^-$, was reviewed and the profound influence of additives established. With PPN^+ as counterion, THF solutions of $HFe(CO)_4^-$ are inactive toward olefin isomerization. The previously noted catalytic activity of $HFe(CO)_4^-$ depends on the presence of hydride abstracting agents or the presence of interacting alkali cations. The role of the latter would appear to be to promote CO loss, thus creating an open coordination site for the binding of the olefin. Although evidence is incomplete, the possibility of the $M(CO)_5^0$ unit performing a similar role as the alkali cations, i.e., that of a highly interacting, associated Lewis acid co-catalyst, is an appealing rationale for the catalytic activity of $HFeM(CO)_9^-$.

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