Notes

Aminium Salt Catalyzed Dimerization and Cross Additions of Vinylferrocene

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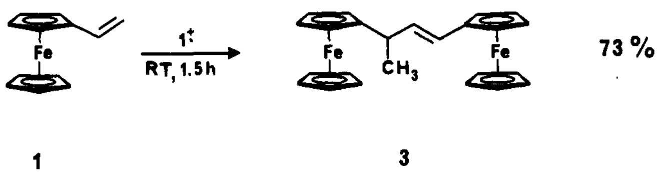
Summary: Tris(4-bromophenyl)aminium hexachloroantimonate, a stable cation-radical salt conventionally used as a hole catalyst, catalyzes the linear head to tail dimerization of vinylferrocene and the cross addition of the latter to 1,1-diphenylethene. A cation-radical (hole catalytic) addition mechanism is, however, not operative. The linear addition mode and the regiochemistry are consistent with a Brønsted acid catalyzed process, but surprisingly, this mechanistic possibility is also decisively excluded. Catalytic mechanisms involving iron-protonated vinylferrocene are also considered to be unlikely. A novel mechanism consistent with all of the pertinent observations is proposed.

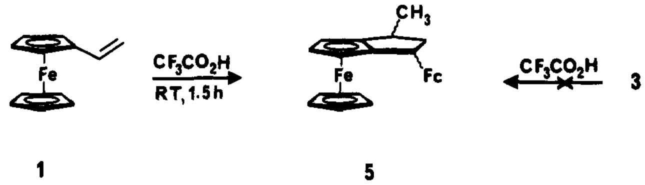
The acceleration of reactions by hole (i.e. single-electron deficit) transfer is of current interest in organic, organometallic, and bioorganic chemistry. Organic systems appear to be especially amenable to hole catalytic pericyclic reactions, and a wide range of extremely rapid, selective, and efficient chemistry of this type has recently emerged.[1,2] The reactions of hole-containing (e.g. 17 electron) organometallic systems are also being vigorously pursued.[3] The specific interest of this research group is in accelerating bimolecular reactions between organometallics and strictly organic molecules and eventually in developing a hybrid transition-metal/hole catalytic concept for organic synthesis. The present note describes novel catalytic acyclic addition chemistry in an organometallic and a mixed organic/organometallic system that is initiated by hole transfer.

Treatment of a dichloromethane solution of vinylferrocene (1) with a catalytic quantity (5 mol %) of tris(4-bromophenyl)aminium hexachloroantimonate ($2^{\bullet+}$) results in the immediate discharge of the aminium salt (λ_{max} 728 nm) and the production of neutral 2 (λ_{max} 306 nm) and the vinylferrocenium ion ($1^{\bullet+}$; λ_{max} 230, 483, 572 nm). The substrate 1 appears to be stable under these conditions for up to ca. 10 min, whereupon reaction rather abruptly commences and, after 1.5 h, produces a single acyclic dimer (3) in 73% yield (Scheme I). Neither the linear addition mode, its head to tail regiochemistry, nor the existence of a clearly defined induction period is consistent with the anticipated cation-radical/neutral ($1^{\bullet+}$/1) cycloaddition.[1,2] These characteristics are, however, compatible with a Brønsted acid catalyzed mechanism with the proviso that the induction period is required in order to generate the catalytic acid, presumably via decomposition of $1^{\bullet+}$. The operation of Brønsted acid catalyzed (cyclo)addition mechanisms under aminium salt conditions has been established.[4] Indeed, the dimerization of 1 to 3 has previously been observed on alumina and was plausibly suggested to occur via Brønsted acid catalysis.[5]

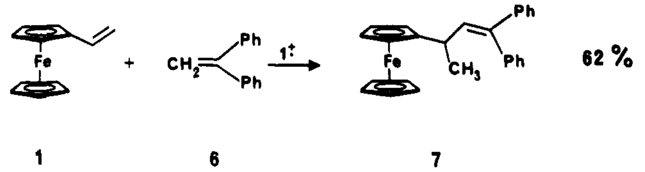
Scheme I



Scheme II



Scheme III



It therefore was surprising to observe that the dimerization of 1 catalyzed by $2^{\bullet+}$ occurs without loss of efficiency in the presence of an excess of 2,6-di-*tert*-butylpyridine (4), a hindered base that has been shown to efficiently suppress Brønsted acid catalyzed additions.[4] The unlikely possibility that the conjugate acid of 4, itself a weak Brønsted acid, could catalyze the dimerization was removed by testing both the hydrochloride and triflate salts of 4. In the presence of added stronger Brønsted acids (CF_3CO_2H, CF_3SO_3H), and under otherwise identical reaction conditions, 1 does in fact dimerize, but none of the four diastereoisomeric dimers (5) are identical with 3 (Scheme II), and both dimer types (3 and 5) are stable under both aminium salt and Brønsted acid conditions. The possibility that the dimerization route is qualitatively changed by a quantitative variation in the strength of the Brønsted acid is effectively removed by the observation

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(1) Bauld, N. L. *Advances in Electron Transfer Chemistry*; Mariano, P. S., Ed.; JAI Press: London, 1991; Vol. 2.

(2) Bauld, N. L. *Tetrahedron* **1989**, *45* (17), 5307–5363.

(3) Connelly, N. G. *Chem. Soc. Rev.* **1989**, *18*, 153–185.

(4) Gassman, P. G.; Singleton, D. A. *J. Am. Chem. Soc.* **1984**, *106*, 7993.

(5) Goldberg, S. I.; Loeble, W. D.; Tidwell, T. T. *J. Org. Chem.* **1967**, *32*, 4070.

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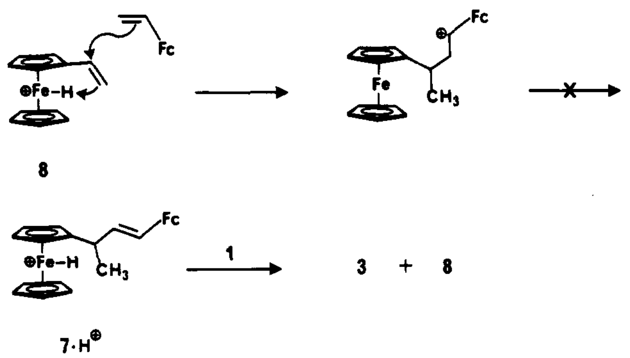
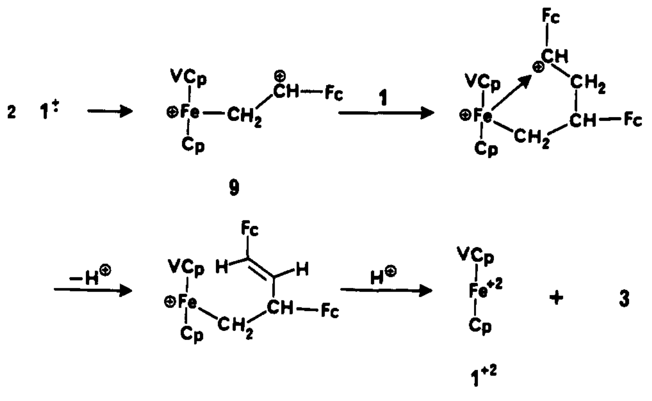
Scheme IV



Scheme V



$1^{+2} + 1 \longrightarrow 9$

Cp = Cyclopentadienyl

VCp = Vinylcyclopentadienyl

Fc = Ferrocenyl

that both triflic acid, an extremely strong Brønsted acid, and trifluoroacetic acid, an acid of only moderate strength, catalyze the formation of the same dimeric mixture (5).

Cross additions of organometallics with organics are of especial interest in this research and also serve as a mechanistic probe, since either component might potentially act as a hydrogen receptor. The reaction of 1 with 1,1-diphenylethene (6) catalyzed by $2^{\bullet+}$ (Scheme III) produces the single cross adduct 7 in 62% yield, along with the previously encountered dimer (3). The regiochemistry of this reaction reveals that 1 acts exclusively as the hydrogen receptor.

In view of the circumstance that both hole and conventional Brønsted acid catalyzed mechanisms have been negated, but that the acyclic addition mode and the regiochemistry are compatible with the formal protonation of the double bond of 1, a mechanism involving iron protonated vinylferrocene (8) was considered. Such an intermediate could potentially be formed by hydrogen abstraction from the solvent by $1^{\bullet+}$. However, the dimerization of 1 occurs at the same rate in CD_2Cl_2 as in CH_2Cl_2, and in the former solvent no detectable quantity of deuterium is incorporated into the product. Further, addition of large amounts of better hydrogen atom donors (e.g. toluene) also has no effect on the reaction rate. Consequently, hydrogen abstraction from the solvent appears unlikely, although other, more complex, mechanisms for the formation of 8 are more difficult to rule out decisively. The viability of the active intermediate in the presence of 2,6-di-*tert*-butylpyridine is noteworthy, however, as a property that would not necessarily be expected of 8. Further, if a mechanism involving 8 were operative, an intramolecular proton transfer from iron to the vinyl terminus of 8 would appear to be required to explain the regioselectivity of the protonation. To circumvent the necessity of invoking a 1-ferrocenylethyl carbocation (which is involved in the Brønsted acid reaction) a concerted proton transfer and electrophilic addition to a second molecule of 1 would then be required (Scheme IV). However, the resulting dimer carbocation center is then necessarily formed remote from the coordination sphere of iron and is, in effect, the same dimer carbocation that, in the authentic Brønsted acid catalyzed reactions, cyclizes to a cyclopentadienyl ring. The distinctly different outcomes of the two reactions argues that uniquely in the reaction promoted by $2^{\bullet+}$ the dimer carbocation is formed in or near the coordination sphere of iron. A mechanism that accounts for the high regioselectivity of the cross addition and for the unique dimer carbocation behavior, as well as all of the other observations mentioned above, is presented in Scheme V. The proposed mechanism invokes initial Fe–C coupling of two molecules of $1^{\bullet+}$, yielding a dication (9) that contains a carbocation site. Reaction of the latter with 1 yields a dimer carbocation in which the carbocation center can loosely coordinate with appropriate iron d orbitals. Subsequent deprotonation and reprotonation (either inter- or intramolecular) yields 3 and 1^{2+}, which reacts with 1 to re-form 9.

The use of a traditional hole catalyst to indirectly engender organometallic catalysis appears novel and may prove to have some generality.

Experimental Section

Analysis. Proton magnetic resonance (PMR) and high-field Cosy (2D NMR) spectra were recorded on a General Electric QE-300 or GN-500 spectrometer as solutions in $CDCl_3$. Chemical shifts are reported in parts per million (ppm) downfield from the reference, tetramethylsilane (TMS). Splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; q, quartet; p, pentet; m, multiplet. UV–visible spectra were recorded on a Hewlett-Packard 8450 A spectrophotometer. Low-resolution mass spectra (LRMS) were obtained on a Hewlett-Packard 5971A GC-MS spectrometer equipped with an HP-1 crosslinked methyl silicone GVM (12 m × 0.2 mm) capillary column. High-resolution mass spectra (HRMS) were recorded on a Du Pont (CEC) 21-110 B mass spectrometer.

Reagents. Methylene chloride was distilled from phosphorus pentoxide prior to use. Tris(4-bromophenyl)aminium hexachloroantimonate (Aldrich) was washed several times with cold anhydrous ether and dried in vacuo prior to use.

Preparation of Vinylferrocene Dimer 3 via Hole-Catalyzed Reaction. To a stirred solution of 50 mg (0.236 mmol) of vinylferrocene in 1.7 mL of methylene chloride under an inert nitrogen atmosphere was added 9.6 mg (0.0118 mmol, 5 mol %) of tris(*p*-bromophenyl)aminium hexachloroantimonate. The reaction was stirred at room temperature, and the progress of reaction was followed by TLC (silica gel plates, polyester, 254-nm fluorescent indicator, cyclohexane) and/or by the GC–MS spectrometer. After all the vinylferrocene was consumed (approximately 1–2 h), the reaction mixture was quenched with a saturated aqueous solution of potassium carbonate in methanol (1 mL). The product was separated from the aqueous layer by extraction with diethyl ether and the aid of brine solution. The ethereal solution was dried over anhydrous sodium sulfate. After filtration of sodium sulfate and removal of volatile material, the product was purified either by a preparative silica gel TLC plate (cyclohexane) or by a flash silica gel column with cyclohexane as eluent to give a red viscous oil upon removal of solvent. Yield: 36 mg, 72%. ^1H NMR ($CDCl_3$, 300 MHz): δ 6.08 (d, 1 H, 16 Hz), 5.93 (dd, 1 H, 15.8 Hz), 4.17 (s, 8 H), 4.11 (s, 10 H), 3.20 (p, 1 H, 7 Hz), 1.33 (d, 3 H, 6.6 Hz). λ_{max} (CH_2Cl_2) (nm): 230 (Soret band), 272 (shoulder). MS [*m/e* (relative intensity)]: 425 (30), 424 (100), 422 (14), 341 (12), 292 (6), 236 (28), 165 (24), 121 (60), 56 (26). HRMS (*m/e*): calcd for $C_{24}H_{24}Fe_2$, 424.057680; found, 424.057876.

TLC analysis (cyclohexane): R_f = 0.27.

Reaction of Vinylferrocene with 2,6-Di-*tert*-butylpyridine Hydrochloride. To a stirred solution of 50 mg (0.236 mmol) of vinylferrocene in 1.7 mL of methylene chloride under an inert nitrogen atmosphere at room temperature was added 26.8 mg (0.118 mmol, 50 mol %) of pyridine hydrochloride salt. GC–MS analysis after 2 h of reaction shows formation of *no* vinylferrocene dimer (**3**). The unreacted starting vinylferrocene was recovered.

Reaction of Vinylferrocene with 2,5-Di-*tert*-butylpyridinium Triflate. To a stirred solution of 50 mg (0.236 mmol) of vinylferrocene and 9.0 mg (0.047 mmol, 20 mol %) of 2,6-di-*tert*-butylpyridine in 1.7 mL of methylene chloride under an inert nitrogen atmosphere at room temperature was added 3.6 mg (0.024 mmol, 10 mol %) of triflic acid. GC–MS analysis after 2 h of reaction shows formation of *no* vinylferrocene dimer **3**. The unreacted starting vinylferrocene was recovered.

Preparation of Cross Adduct 7 via Hole-Catalyzed Reaction. To a stirred solution of 100 mg (0.472 mmol) of vinylferrocene, 19.4 mg (0.0236 mmol, 5 mol %) of tris(*p*-bromophenyl)aminium hexachloroantimonate, and 5.42 mg (0.0283 mmol, 6 mol %) of 2,6-di-*tert*-butylpyridine in 2.4 mL of methylene chloride at 0 °C under an inert nitrogen atmosphere was added via syringe a solution of 850 mg (4.72 mmol) of diphenylethene in 1.0 mL of methylene chloride. The reaction mixture was then allowed to warm to room temperature, and the progress of reaction was monitored by GC–MS. After all of the vinylferrocene was consumed (1–2 h), the reaction mixture was quenched with a saturated aqueous solution of potassium carbonate in methanol (2 mL). The products were separated from the aqueous layer by extraction with diethyl ether and the aid of brine solution. The ethereal solution was dried over anhydrous sodium sulfate. After removal of sodium sulfate and the volatile material, the product(s) was (were) purified by a preparative silica gel TLC plate (cyclohexane) to give 62% cross adduct (**7**) and 10% vinyl ferrocene dimer (**3**). Analysis of cross adduct **7** gave the following. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.42–7.24 (m, 10 H, Ph H), 6.16 (d, 1 H, 10 Hz), 4.12 (s, 9 H), 3.29 (p, 1 H), 1.33 (d, 3 H, 7 Hz). λ_{max} (CH_2Cl_2) (nm): 230. MS [*m/e* (relative intensity)]: 393 (29), 392 (100), 390 (7), 325 (40), 312 (18), 253 (8), 186 (59), 121 (40), 56 (31); HRMS (*m/e*): calcd for $C_{26}H_{24}Fe$; 392.122740; found, 392.121782. TLC analysis (cyclohexane): R_f = 0.43.

Preparation of Vinylferrocene Dimer 3 via Hole-Catalyzed Reaction in the Presence of 2,6-Di-*tert*-butylpyridine. To a stirred solution of 50 mg (0.236 mmol) of vinylferrocene and 27.2 mg (0.142 mmol, 60 mol %) of 2,6-di-*tert*-butylpyridine in 1.7 mL of methylene chloride under an inert nitrogen atmosphere was added 96.25 mg (0.118 mmol, 50 mol %) of tris(*p*-bromophenyl)aminium hexachloroantimonate. The reaction was stirred at room temperature, and the progress of reaction was followed by TLC (silica gel plates, polyester, 254-nm fluorescent indicator, cyclohexane) and/or by GC–MS spectrometer. After all the vinylferrocene was consumed (approximately 1–2 h), the reaction mixture was quenched with a saturated aqueous solution of potassium carbonate in methanol (1 mL). The product was separated from the aqueous layer by extraction with diethyl ether and the aid of brine solution. The ethereal solution was dried over anhydrous sodium sulfate. After filtration of sodium sulfate and removal of volatile material, the product was purified either by a preparative silica gel TLC plate (cyclohexane) or by a flash silica gel column with cyclohexane as eluent to give a red viscous oil upon removal of solvent. Yield: 36.5 mg, 73%. Analysis of this product (**3**) gave the same information as found in the absence of base.

Preparation of Vinylferrocene Dimer 5 via Acid-Catalyzed Reaction. To a stirred solution of 50 mg (0.236 mmol) of vinylferrocene in 1.7 mL of methylene chloride under an inert nitrogen atmosphere was added 13.5 mg (0.118 mmol, 50 mol %) of trifluoroacetic acid. The reaction was stirred at room temperature for a period of 2 h and then quenched with a saturated aqueous solution of potassium carbonate in methanol (2 mL). The product(s) was (were) separated from the aqueous layer by extraction with diethyl ether and the aid of brine solution. The ethereal solution was dried over anhydrous sodium sulfate. After removal of sodium sulfate and the volatile material, the product(s) was (were) purified by a preparative silica gel TLC plate (cyclohexane) to give a red viscous oil (**5**) upon removal of solvent (18 mg, 36%). Analysis of **5** gave the following data. GC–MS shows the presence of four diasterometric compounds. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 4.19–3.99 (m, 17 H, ferrocenyl hydrogens), 3.90–1.70 (complex), 1.34 (d, 3 H, 6.44 Hz), 1.31 (d, 3 H, 6.57 Hz), 1.07 (d, 3 H, 7.63 Hz), 0.98 (d, 3 H, 7.37 Hz). λ_{max} (CH_2Cl_2) (nm): 230. MS [*m/e* (relative intensity)]: 425 (31), 424 (100), 422 (15), 356 (76), 300 (12), 165 (28), 236 (12), 121 (50), 56 (33). HRMS (*m/e*): calcd for $C_{24}H_{24}Fe_2$, 424.057680; found, 424.057117.

MS [*m/e* (relative intensity)]: 425 (30), 424 (100), 422 (16), 356 (67), 291 (17), 236 (12), 165 (22), 121 (48), 56 (28). HRMS (*m/e*): calcd for $C_{24}H_{24}Fe_2$, 424.057680; found, 424.056267.

MS [*m/e* (relative intensity)]: 425 (29), 424 (100), 422 (16), 356 (70), 300 (12), 238 (13), 165 (24), 121 (52), 56 (29). HRMS (*m/e*): calcd for $C_{24}H_{24}Fe_2$, 424.057680; found, 424.056852.

MS [*m/e* (relative intensity)]: 425 (32), 424 (100), 422 (15), 356 (64), 291 (15), 236 (12), 165 (26), 121 (60), 56 (29). HRMS (*m/e*): calcd for $C_{24}H_{24}Fe_2$, 424.057680; found, 424.056541.

TLC analysis (cyclohexane): R_f = 0.36.

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