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Synthesis and Electrochemistry of Iron-Pyrylium Complexes

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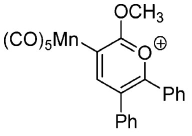
The syntheses and characterization of three cationic iron-pyrylium complexes (**2**$^+$, [2-OMe-3-Fp-5,6-Ph$_2$(C$_5$HO)]$^+$; **3**$^+$, [2-OMe-3-Fp-6-Ph(C$_5$H$_2$O)]$^+$; **4**$^+$, [2-OMe-3-Fp′-6-Ph (C$_5$H$_2$O)]$^+$) that result from the sequential addition of methyl propiolate and PhC≡CR (R = Ph, H) to FpBF$_4$ (Fp = η^5-C$_5$H$_5$(CO)$_2$Fe) or Fp′PF$_6$ (Fp′ = η^5-(C$_5$H$_4$Me)(CO)$_2$Fe) are presented. The initially formed cationic Fp-methyl propiolate complex is shown to convert into a complicated mixture that includes the corresponding vinylidene and alkynyl complexes. The iron-pyrylium complexes have been characterized by ^{1}H NMR and IR spectroscopy, elemental analysis, FAB-MS, electrochemical, and fiber-optic-IR and ESR spectroelectrochemical techniques. These metal-pyrylium complexes undergo electron transfer at the pyrylium ring rather than at the metal center. The subsequent chemistry of the neutral species **2**$^\bullet$, **3**$^\bullet$, and **4**$^\bullet$ is strongly influenced by the nature of the substituents on the ring. The sterically protected complex **2**$^+$ undergoes chemically and electrochemically reversible reductions. The complexes **3**$^+$ and **4**$^+$ undergo dimerization reactions after reduction presumably through the 4-position of the pyrylium ring.

Introduction

Pyrylium salts are important intermediates in the regiospecific synthesis of many organic compounds such as nitrobenzenes, pyridines, thiopyryliums, phosphabenzenes, and 2,4-pentadienones.[1] Despite the large number of pyrylium compounds known, few σ-bonded organometallic pyrylium complexes have been prepared and investigated.[2,3] This oversight is surprising in light of the utility of purely organic pyrylium ions in organic synthesis and their applications as dyes, laser dyes, photosensitizers, and corrosion-inhibiting additives in paints.[1] Pyrylium ions have a rich redox chemistry and can undergo reduction to form stable radicals, dimers, or pyran compounds, depending on steric factors and on the reducing agent. The coupling of this redox chemistry to the recognized properties of a transition metal has the potential to yield systems with useful physical and chemical properties.



1$^\oplus$

Cationic hydrocarbyl groups such as pyridinium or pyrylium bound to the metal via a M−C σ-bond are very rare.[2,4] Recently, we prepared an example of a cationic Mn(CO)$_5$-pyrylium σ-complex, **1**$^+$, and explored its reactivity.[5] The ligand turned out to be less electron-rich than neutral hydrocarbyl ligands because of the delocalization of the positive charge around the heterocyclic ring. Consistent with this relative lack of electron density,[6] the Mn−pyrylium σ-bond resisted electrophilic cleavage by H$^+$ and did not undergo migratory insertion reactions to coordinated CO.[5] Reduction occurred at the ligand, but the metal's reactivity was increased,[7] thereby resulting in a rapid electrocatalytic ligand substitution reaction involving the initial loss of CO. Ligand-based reactivity in the form of dimerization reactions and H-atom abstraction reactions were also observed. In this contribution, we outline the preparation of several iron-based pyrylium complexes and explore their redox chemistry by using fiber-optic-based IR spectroelectrochemistry.[8]

Results and Discussion

(1) Synthesis of Dicarbonylcyclopentadienyl-3-(2-methoxy-5,6-diphenylpyrylium)iron(II) Tetra-

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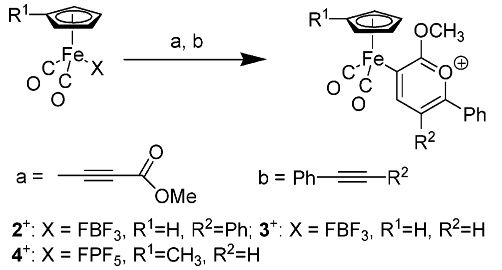
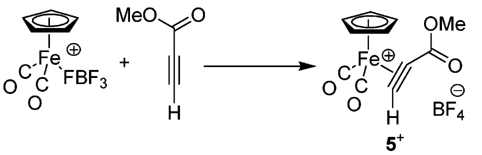
Scheme 1: Synthesis of Cationic Fp-Pyrylium Complexes



fluoroborate (2^+BF_4), Dicarbonylcyclopentadienyl-3-(2-methoxy-6-phenylpyrylium)iron(II) Tetrafluoroborate (3^+BF_4), and Dicarbonyl(methylcyclopentadienyl)-3-(2-methoxy-6-phenylpyrylium)iron(II)-Hexafluorophosphate (4^+PF_6). The ability of metal cations to condense organic compounds into cyclic structures is well-documented.[9] In particular, the ability of Fp^+ ($Fp = \eta^5\text{-}C_5H_5(CO)_2Fe$) to condense acetylenic esters with alkenes to form cyclic lactones[10] prompted Legzdins to verify that $[CpM(NO)_2]^+$ salts ($Cp' = Cp$, Cp^*; M = Cr, Mo, W) also form corresponding lactones.[11] With a second, more electron-rich alkyne instead of an alkene, the nitrosyl salts mediated the formation of pyrylium complexes. We have found that other electrophilic transition metal cations, specifically $[Mn(CO)_5]^+$, Fp^+, and Fp'^+ ($Fp' = \eta^5\text{-}(C_5H_4Me)(CO)_2Fe$), can also mediate the condensation of methyl propiolate and certain alkynes to form organometallic pyrylium complexes as in Scheme 1.[5,12,13]

It seems reasonable to suggest that the first step of the reaction involves η^2-coordination of the methyl propiolate to the metal center (eq 1), as originally proposed by Rosenblum for the preparation of Fp-lactone complexes.[10]

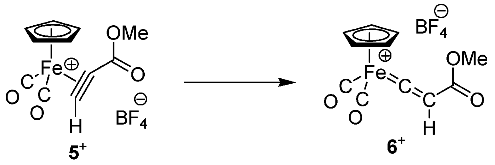


(1)

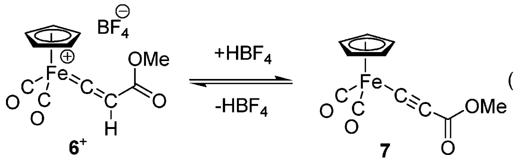
This alkyne complex 5^+ has been identified for the first time in CH_2Cl_2 by using in-situ fiber-optic IR techniques and in CD_2Cl_2 by ^1H NMR. Addition of 3 equiv of methyl propiolate to a 0.03 M solution of $FpBF_4$ in CH_2Cl_2 results in the loss of IR intensity due to the starting $FpBF_4$ complex (2081, 2037 cm^{-1}) and the growth of bands at 2073, 2027, and 1631 cm^{-1}, the latter bands being more clearly revealed when the starting materials' bands are subtracted out. The two product carbonyl bands are appropriate for a cationic Fp complex,[14] and the band at 1631 cm^{-1} represents the ester ν(CO), which has been shifted considerably from the free ligand's value of 1718 cm^{-1}. In a pseudo-octahedral d^6-transition metal complex such as Fp^+, there are antibonding interactions between the filled d orbitals on the metal and the $\pi_\perp$ orbital on the alkyne.[15] This interaction should result in more electron density being delocalized to the ester C═O, thereby accounting for the considerable shift in its IR band. The metal-bound alkyne C≡C band has not been observed, either because it is under the carbonyl bands or because it is too broad.

In CD_2Cl_2 solution, $FpBF_4$ also reacts with a 2-fold excess of methylpropiolate to form the bright red 5^+ complex. The alkyne complex is characterized by three peaks in the expected 5:3:1 integration ratio. A C_5H_5 peak is observed at 5.73 ppm, a value consistent with a cationic Fp complex. The bound alkyne's OCH_3 and H groups display signals at 4.02 and 6.29 ppm, respectively. These values are shifted considerably downfield of the free ligand's value of 3.77 and 2.98 ppm, respectively. The large shift in the terminal alkyne hydrogen signal is particularly indicative of side-on bonding of the methylpropiolate ligand through the C≡C triple bond.[16,17]

The methylpropiolate complex 5^+ is unstable in solution with respect to vinylidene complex formation (eq 2).[18] The vinylidene complex 6^+ (2097, 2063 cm^{-1}, Cp at 5.22 ppm, OCH_3 at 4.44 ppm) is acidic and is in equilibrium with the corresponding deprotonated Fp-alkynyl complex **7** (2028, 1984 cm^{-1}, Cp at 5.09 ppm, OCH_3 at 3.90 ppm). Efforts to observe the vinylidene terminal H signal were unsuccessful. Two other minor, as-yet unidentified signals are also observed in the Cp region of the ^1H spectrum at 5.15 and 5.41 ppm. Their corresponding IR bands are likely hidden by the bands due to Fp^+, 5^+, 6^+, and **7**. The overall result is that solutions of 5^+ spontaneously develop into a mixture of other species within a few minutes of preparation.



(2)



(3)

Equivalent studies in $CDCl_3$ were complicated because the equilibration appears to be more rapid in this solvent and because of problems of solubility of the various cationic species. However, within a few minutes of mixing the $CDCl_3$ solutions display a similar set of five Cp peaks as the CD_2Cl_2 solutions display after a day of equilibration.

Complex **7** was isolated by treating an equilibrated solution of $FpBF_4$ and methylpropiolate with solid

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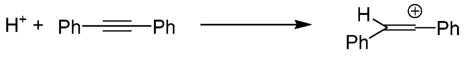
$NaHCO_3$ overnight, followed by filtration and crystallization from CH_2Cl_2/toluene. Addition of >10 equiv of excess HBF_4 to a $CDCl_3$ solution of **7** resulted in an equilibrium mixture of **6**$^+$ and **7**, as judged by the ^{1}H NMR and IR signals, which match those described above. The fact that **7** resists full protonation, even in the presence of excess strong acid, suggests that the electron-withdrawing ester group on the terminal vinylidene carbon atom increases the acidity of this site in **6**$^+$.

The proposed mechanism of the formation of the pyrylium complex **2**$^+$ is shown in eqs 4 and 5.



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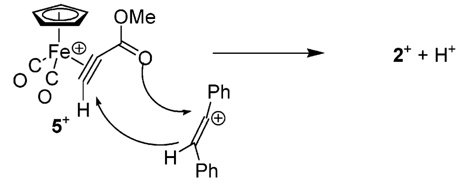

(5)

Protonation of diphenylacetylene forms a resonance-stabilized carbocation. The H$^+$ comes from the vinylidene/alkynyl equilibrium in eq 3. Attack by the nucleophilic C═O of the ester functionality begins the ring formation, which is completed after loss of H$^+$ and attack on the CH group of metal-bound alkyne as shown. This mechanism is supported by the following observations:

(1) Addition of both methyl propiolate and diphenylacetylene at the same time to a solution that contains $FpBF_4$[19] results in a mixture of [Fp(η^2-PhC≡CPh)]BF_4[20] and the pyrylium complex **2**$^+$. No [Fp(η^2-PhC≡CPh)] is detected when diphenylacetylene is added 30 min after the methyl propiolate, conditions that favor the complete conversion of $FpBF_4$ into **5**$^+$ but minimize the amount of **6**$^+$ and **7** present. This evidence also suggests that attack by **5**$^+$ on [Fp(η^2-PhC≡CPh)] is not a significant pathway, otherwise the whole solution would be expected to be converted to **2**$^+$.

(2) FpOTf, when combined first with methyl propiolate followed by diphenylacetylene, yields Fp(η^2-PhC≡CPh)]OTf as the only detectable product. This evidence suggests that methyl propiolate is not a strong enough ligand to displace the triflate anion from the metal's coordination sphere, thereby underscoring the importance of the coordination of methyl propiolate to the metal center in the overall cyclization reaction.

(3) H$^+$, BF_3, and $Cp_2Zr(BF_4)_2$ were used as Lewis acids in three separate NMR tube experiments. No detectable pyrylium ions were formed when the Lewis acids were combined with methyl propiolate and diphenylacetylene. This result contrasts with recently reported intramolecular cyclizations of acetylenic carbonyl compounds by H$^+$ to form pyrylium compounds.[21] Since these Lewis acids lack d electrons, they could coordinate to the O atom of methyl propiolate, but not to the triple bond. This evidence suggests two conclusions. First, Lewis acid binding to the ester group is not the initial step of the pyrylium-formation sequence. Second, since carbocations are presumably formed when H$^+$ reacts with phenylacetylene, it shows that binding of methyl propiolate to the metal center enhances the nucleophilicity of the carbonyl oxygen relative to the unreactive free alkyne.

(4) Only aromatic alkynes were observed to undergo cyclization with $FpBF_4$. No pyrylium-containing products were isolated or detected in NMR experiments when 1-hexyne, 3-hexyne, trimethylsilylacetylene, or bis(trimethylsilyl)acetylene was used in place of phenylacetylene or diphenylacetylene. The C_5H_5 regions of these NMR solutions show only the mixture of five signals discussed above. Since aliphatic alkynes are less likely to form resonance-stabilized carbonations (eq 4), they are not attacked by the nucleophilic ester group of **5**$^+$. These alkynes are also less likely than aromatic alkynes to coordinate to Fp$^+$.[22] Interestingly, the $[Cp'M(NO)_2]^+$ (Cp′ = Cp, Cp*; M = Cr, Mo, W) systems are known to cyclize both aliphatic and aromatic alkynes with methylpropiolate,[4] a capability that may indicate a different mechanism than in the present case.

While the pyrylium complexes are the only products observed when diphenylacetylene or phenylacetylene is reacted with a metal cation and methyl propiolate after several days under NMR conditions, isolation of samples of compounds that are pure enough for electrochemical characterization has only been accomplished in fairly low yields (15−20%) to date, probably due to the interference of **6**$^+$ and **7**. It is noteworthy that the preparation of the electrophilic metal cation may be accomplished in situ by halide abstraction without ill effects upon the overall reaction.

These iron complexes appear to be thermally sensitive, which may be another reason for their low preparative yields. While they persist for months when stored under argon at −30 °C, they decompose overnight when stored under argon at room temperature. Still, formation of the pyrylium complexes is more selective than the Fp$^+$-mediated formation of the lactone complexes, which form in refluxing THF as a mixture of five- and six-membered rings, [10] possibly from both **5**$^+$ and **6**$^+$. As was the case with **1**$^+$, the physical properties of **2**$^+$ to **4**$^+$ are consistent with the positive charge being distributed around the pyrylium ring. These compounds have CO bands in their IR spectra that appear at frequencies similar to those of neutral compounds. For example, the complex **2**$^+$ exhibits ν(CO) frequencies at 2038 and 1989 cm^{-1}, which are very similar to those displayed by the neutral complexes Fp−Cl (2040, 1999 cm^{-1}) and Fp−C≡CPh (2040, 2000 cm^{-1}).[23] The ^{1}H NMR spectra reveal signals assigned to the H atom on the 4-position of the pyrylium ring at 8.47 and 8.62 ppm (d, J = 7 Hz) in **2**$^+$ and **3**$^+$, respectively. In addition, **3**$^+$ displays a doublet at 7.37 ppm for the hydrogen at the 5-position, with a coupling constant consistent with H atoms on two adjacent positions on the ring.[24] Similar features are observed for **4**$^+$. Such highly deshielded

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[19] Although we used the method in ref 12 to prepare [Fp(THF)]-BF_4, the red substance we obtained did not show any trace of THF by NMR.

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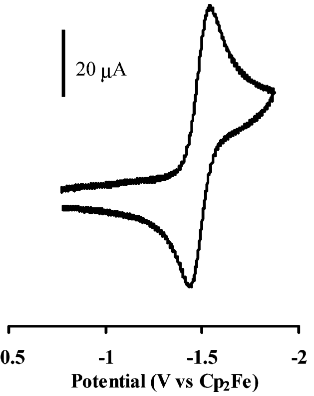

Figure 1. CV of $\mathbf{2}^+$ in THF/0.1 M NBu_4PF_6 at 800 mV/s.

signals indicate that the positive charge resides on the pyrylium ring, thereby leaving the metal center relatively uncharged.

The pyrylium ligand in both complexes seems to be the primary redox site. Since the only difference between the two pyrylium rings is the substituent metal complex *meta* to the O atom, it is surprising that $\mathbf{2}^+$ and $\mathbf{3}^+$ display such different electrochemical properties (vide infra).

Electrochemistry of Complex $\mathbf{2}^+$. Cyclic voltammograms (CV) of complex $\mathbf{2}^+$ measured in THF at 22 °C at scan rates larger than 400 mV/s reveal a chemically reversible reduction feature at -1.49 V versus Cp_2Fe, as shown in Figure 1. Pyrylium derivatives are known to undergo reduction in the range -0.5 to -1.5 V versus Cp_2Fe,[1b] so this derivative appears to be electron-rich, which is probably a result of the electron-donating ability of the methoxy group. In comparison, Fp-CH_3 is irreversibly reduced at considerably more negative potentials (-2.3 V versus Cp_2Fe).[25] The difference in potentials suggests that the pyrylium ring is reduced first. In-situ ESR spectroelectrochemistry reveals the presence of a sharp signal at $g = 2.018$ after reduction of the complex, but no hyperfine couplings were observed. However, fiber-optic IR spectroelectrochemistry reveals that upon reduction, the bands for $\mathbf{2}^+$ are consumed and replaced by bands at 2015 and 1956 cm^{-1}, as shown in a series of difference spectra presented in Figure 2. The relatively small shifts in the IR bands (23 and 33 cm^{-1}) support the idea that the metal center is not the main site of electron transfer since otherwise a shift of about 100 cm^{-1} would be expected.[26]

The appearance of the reduction wave in CH_2Cl_2 is equally reversible. Controlled potential coulometry in this solvent confirms that this feature is due to the one-electron reduction of $\mathbf{2}^+$. Exhaustive electrolysis results in the passage of ca. 1 Faraday equivalent of charge but a solution devoid of any electrochemical features or infrared bands in the carbonyl region. This result indicates that on longer time scales the reduced complex $\mathbf{2}^\bullet$ is unstable and decomposes.

Addition of alcohols or water to solutions containing $\mathbf{2}^+$ results in no change in the reversibility of the reduction features, but does result in a slow diminishment in size of the CV waves due to $\mathbf{2}^+$ over the period of an hour, which ultimately precludes meaningful study by bulk electrolysis. It is unlikely that the M–C bond is cleaved under these conditions to form a free pyrylium ion, since such a species would be redox active in the potential range examined, and no new features were observed. The reversibility of the reduction of $\mathbf{2}^+$ is independent of whether $HSnPh_3$, alcohols, phenylacetic acid, or water has been added to the solution. On the CV time scale, these observations indicate that the reduced neutral radical **2** is not subject to attack by H^+ and does not participate in H-atom abstraction processes, in contrast to what was observed for the manganese analogue $\mathbf{1}^+$.[5]

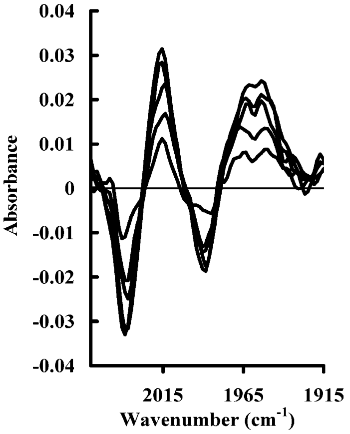

Figure 2. Fiber-optic spectroelectrochemistry of $\mathbf{2}^+$ in CH_2Cl_2/0.1 M NBu_4PF_6. Each subsequent difference spectrum was recorded at 5 s intervals after application of potential.

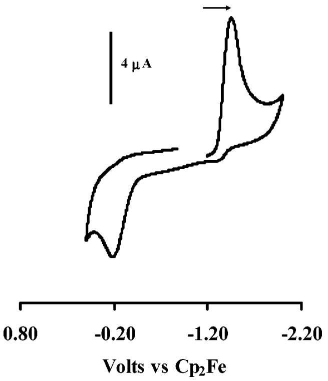

Figure 3. CV of $\mathbf{4}^+$ in CH_2Cl_2/0.1 M NBu_4PF_6 at 200 mV/s.

Electrochemistry of Complex $\mathbf{3}^+$ and $\mathbf{4}^+$. Cyclic voltammetry reveals electrochemically irreversible features for $\mathbf{3}^+$ and $\mathbf{4}^+$ in contrast to the reversible feature observed for $\mathbf{2}^+$. This observation is consistent with the fact that the 4-position on the pyrylium ring is more accessible on $\mathbf{3}^+$ and $\mathbf{4}^+$ than it is on $\mathbf{2}^+$, due to the absence of a second phenyl ring. For $\mathbf{3}^+$ in THF, these reductions are electrochemically irreversible at 3.2 V/s even at temperatures as low at -45 °C. However, in CH_2Cl_2 there are anodic features that manifest at -0.26 V versus Cp_2Fe that are only observed after the reduction waves are scanned, as shown for $\mathbf{4}^+$ in Figure 3. For $\mathbf{1}^+$ it was previously shown that a slow dimerization reaction occurs after electron transfer, consistent with known pyrylium chemistry.[5] The dimer, $\mathbf{4}_2$, was observed to give a similar electrochemical response. For $\mathbf{3}^+$ and $\mathbf{4}^+$, it is likely that a similar dimerization of the neutral organic radicals through the 4-position of the

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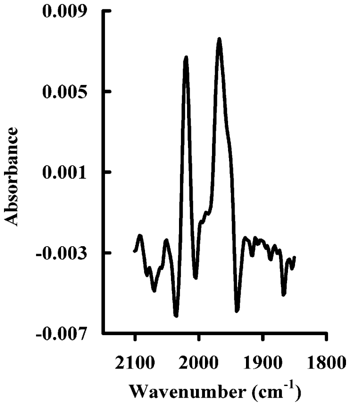

Figure 4. Spectrum of **4**$^{\bullet}$ obtained by subtraction from pulsed spectroelectrochemistry data.

pyrylium ring occurs. Accordingly, a fiber-optic spectroelectrochemical investigation of **4**$^+$ where the difference spectrum is recorded as the electrode is held at -1.5 V versus Cp_2Fe revealed the reductive conversion of the IR bands due to **4**$^+$ to bands at 2008 and 1943 cm^{-1}, a change of 27 and 40 cm^{-1}, respectively. These bands are consistent with the formation of a neutral Fp′-alkyl species, such as that expected when **4**$^{\bullet}$ dimerizes to form **4**$_2$. This conversion was found to be chemically reversible, in that reoxidation of **4**$_2$ resulted in the clean formation of **4**$^+$.

In an effort to provide more detail to this dimerization reaction, a modification of the fiber-optic spectroelectrochemical experiment was performed where the potential on the electrode was synchronized with the motion of the moving mirror in the IR spectrometer. Typically, a scan of the moving mirror lasted 420 ms. At the beginning of each scan, the potential was pulsed for 100 ms to -1.5 V versus Cp_2Fe. When the rest potential was insufficient to reoxidize the dimer, the aforementioned bands ascribed to the conversion of **4**$^+$ to its neutral dimer were observed with small shoulders at higher frequencies. Subtraction of the data from an experiment where the potential on the electrode was set to -1.5 V for 90 s resulted in the clear observation of another pair of bands at 2021 and 1969 cm^{-1}, as shown in Figure 4. These bands are intermediate between **4**$^+$ and those of **4**$_2$ and are consistent with the bands observed directly for **2**$^{\bullet}$. We therefore ascribe this low-concentration electrode product to be **4**$^{\bullet}$. When the rest potential was set to -0.05 V versus Cp_2Fe, these bands were seen more clearly since the spectral changes due to the conversion of **4**$^+$ to **4**$_2$ cancel out in the difference spectrum. The fact that these bands are not observed at longer electrolysis times is consistent with the speed with which **4**$^{\bullet}$ dimerizes.

To probe the reactivity of the electrochemically generated neutral radical, the reduction of **3**$^+$ in THF was studied in the presence of a hydrogen-atom donor. The cyclic voltammogram of **3**$^+$ undergoes no change upon the addition of up to 5 equiv of $HSnPh_3$ at any scan rate. However, when 2.5 equiv of phenylacetic acid is also added, a 10% enhancement in the cathodic current is observed at low scan rates (<200 mV/s). At higher scan rates (>800 mV/s) the current is the same as in the absence of phenylacetic acid. Thus, the current enhancement is due to a relatively slow process that regenerates the starting complex **3**$^+$ during the scan, since a plateau-shaped current feature is not observed and the process can be outpaced at faster scan rates. Similar chemistry was observed with **1**$^+$.[5]

Conclusions

The synthesis of metal-pyrylium complexes is complicated by various equilibria that result from the addition of methyl propiolate to a cationic transition metal complex. Initial coordination of methyl propiolate to Fp$^+$ results in an alkyne complex that isomerizes to a vinylidene complex within minutes. The vinylidene is strongly acidic and is in equilibrium with the corresponding alkynyl species. Cyclization occurs only when the second alkyne added to the reaction can form a resonance-stabilized carbocation. The resulting metal-pyrylium complexes undergo electron transfer at the pyrylium ring rather than at the metal center, and they display subsequent chemistry that is strongly influenced by the nature of the substituents on the ring. The sterically protected complex **2**$^+$ undergoes chemically and electrochemically reversible reductions, even in the presence of H-atom donors and fairly strong acids. The complexes **3**$^+$ and **4**$^+$ undergo dimerization reactions after reduction through the neutral radicals **3**$^{\bullet}$ and **4**$^{\bullet}$.

Experimental Section

All reactions and subsequent manipulations involving organometallic reagents were performed under anaerobic and anhydrous conditions in an atmosphere of prepurified dinitrogen or argon. Diethyl ether, hexanes, dichloromethane, and chloroform-*d* were purified by distillation from CaH_2 into 500 mL rotoflow vessels charged with additional CaH_2. THF was distilled from sodium-benzophenone ketyl into a 500 mL rotoflow vessel charged with fresh benzophenone ketyl. All solvents were vacuum transferred directly into reaction vessels when needed. Methyl propiolate (Acros), diphenylacetylene (Acros), tetrafluoroboric acid (Acros), and cyclopentadienyldicarbonyliron dimer (Aldrich) were used as received. $FpBF_4$,[12] and Fp′I[27] were prepared as described in the literature. NMR spectra were obtained with a 300 MHz Varian 300 Unity Plus spectrometer. IR spectra were obtained using a Mattson Research Series IR spectrophotometer.

General procedures used for electrochemistry[5] and fiber-optic IR spectroelectrochemistry[8] in these laboratories have been described previously. CV experiments were performed at 0 °C. Electrochemical measurements were performed using an EG&G PAR 263 potentiostat interfaced to a computer running EG&G PAR Model 270 software. Pulsed-potential spectroelectrochemistry experiments were performed by directing the signal from the IR detector to the computer interfaced to the potentiostat via a National Instruments analogue input board. A program written in LabView was designed to detect the centerburst from the IR detector, wait until the start of the next IR scan, and then send a command to the potentiostat to change the electrode potential. The potential was held for typically 100 ms and then returned to the resting value. The synchronization was checked and adjusted empirically with the aid of an HP-7090 digital plotter. Copies of this program are available on request. Pt-disk working electrodes were obtained from BAS, and a vacuum cell was custom-built by ChemGlass with metal-to-glass seals obtained from Wilmad. Bulk electrolyses were performed using

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[27] Fp′I was prepared in a fashion analogous to Fp-I. King, R. B. *Organometallic Synthesis*; Academic Press: New York, 1965; Vol. 1, p 175.

a BAS bulk electrolysis cell contained within the vacuum cell. Simulations were performed using DIGISIM[28] software or ESP 2.4.[29]

Synthesis of 2BF$_4$. FpBF$_4$ (0.26 g, 1.0 mmol) was dissolved in CH_2Cl_2 (20 mL), and methyl propiolate (200 μL g, 2.2 mmol) was added by syringe. The mixture was stirred for 30 min, and the diphenylacetylene (0.18 g, 1.0 mmol) was added. The solution was stirred overnight and filtered through Celite supported on a medium porous glass frit, and then the solvent was removed under reduced pressure. THF (10 mL) was vacuum transferred onto the residue and then concentrated under reduced pressure until incipient precipitation had been reached. The solution was cooled to −30 °C overnight, and reddish-black crystals of **2**BF$_4$ (0.13 g, 19%) were isolated by filter cannulation followed by washing with diethyl ether (2 × 5 mL). No further crops were obtained from this solution. Anal. Calcd for $C_{25}H_{19}O_4FeBF_4$: C, 57.08; H, 3.64. Found: C, 57.28; H, 3.73. ^{1}H NMR ($CDCl_3$) δ: 8.47 (s, 1H, $C_5H(OCH_3)$-Ph_2), 7.7−7.2 (m, 10H, *Ph*), 5.18 (s, 5H, C_5H_5) 4.54 (s, 3H, OCH_3). IR: ν(CO) 2038, 1989 cm^{-1}, ν(pyrylium CO) 1631 cm^{-1}. ESI-MS (*m*/*z*): 439 ($P^+ - BF_4$), 383 ($P^+ - BF_4 - 2CO$). $E°'$(THF): −1.49 V vs Cp_2Fe. UV−vis (CH_2Cl_2) λ_{max}: 278 nm (ϵ = 5700 M^{-1} cm^{-1}), λ_{max}: 381 nm (ϵ = 3800 M^{-1} cm^{-1}).

Synthesis of 3BF$_4$. FpBF$_4$ (0.26 g, 1.0 mmol) was dissolved in CH_2Cl_2 (20 mL), and methyl propiolate (200 μL, 2.2 mmol) was added by syringe. The mixture was stirred for 30 min, and the phenylacetylene (200 μL, 1.8 mmol) was added. The solution was stirred overnight and filtered through Celite supported on a medium porous glass frit, and then the solvent was removed under reduced pressure. THF (10 mL) was vacuum transferred onto the residue and then concentrated under reduced pressure until incipient precipitation had been reached. The solution was cooled to −30 °C overnight, and reddish-black crystals of **3**BF$_4$ (0.10 g, 19%) were isolated by filter cannulation followed by washing with diethyl ether (2 × 5 mL). No further crops were obtained from this solution. Anal. Calcd for $C_{19}H_{15}O_4FeBF_4$: C, 50.71; H, 3.35. Found: C, 51.04; H, 3.45. ^{1}H NMR ($CDCl_3$) δ: 8.62 (d, 1H, 4-C_5H_2 (OMe)-Ph, $^3J_{H-H}$ = 7.0 Hz), 7.89 (s, 1H, Ph para H) 7.55, (s, 2H, Ph ortho H's) 7.38 (d, 1H, 5-C_5H_2 (OMe)Ph, $^3J_{H-H}$ = 7.0 Hz), 7.26 (s, 2H, Ph meta H's), 5.15 (s, 5H, C_5H_5), 4.59 (s, 3H, OCH_3). IR (CH_2Cl_2): ν(CO) 2039, 1988 cm^{-1}, ν(pyrylium CO) 1630 cm^{-1}. ESI-MS (*m*/*z*): 363 ($P^+ - BF_4$), 307 ($P^+ - BF_4 - 2CO$). E_{pc}(THF): −1.42 V vs Cp_2Fe.

Synthesis of 4PF$_6$. FpI (0.45 g, 1.4 mmol) was dissolved in CH_2Cl_2 (15 mL), and $AgPF_6$ (0.35 g, 1.4 mmol) was added. The dark brown solution brightened to red, and a voluminous white precipitate formed. The mixture was stirred for an hour, whereupon methyl propiolate (200 μL, 2.2 mmol) was added by syringe. The mixture was stirred for a further 30 min, and phenylacetylene (200 μL, 1.8 mmol) was added. The solution was stirred overnight and filtered through Celite supported on a medium porous glass frit, toluene (2 mL) was added, and then the mixture was concentrated under reduced pressure. The solution was cooled to −30 °C overnight, and reddish-black crystals of **4**PF$_6$ (0.15 g, 20%) were isolated by filter cannulation followed by washing with toluene (2 × 5 mL). Anal. Calcd for $C_{20}H_{17}O_4FePF_6$: C, 46.00; H, 3.28. Found: C, 46.24; H, 3.36. ^{1}H NMR ($CDCl_3$) δ: 8.58 (d, 1H, 4-C_5H_2 (OMe)Ph, $^3J_{H-H}$ = 7.3 Hz), 7.89−7.50, (m, 5H, Ph) 7.38 (d, 1H, 5-C_5H_2 (OMe)Ph, $^3J_{H-H}$ = 7.3 Hz), 5.04 (d, 2H, C_5H_4Me), 4.95 (d, 2H, C_5H_4Me), 4.57 (s, 3H, OCH_3), 2.02 (s, 3H, C_5H_4*Me*). IR (CH_2Cl_2): ν(CO) 2030, 1980 cm^{-1}, ν(pyrylium CO) 1641 cm^{-1}. ESI-MS (*m*/*z*): 377 ($P^+ - BF_4$), 321 ($P^+ - BF_4 - 2CO$). E_{pc}(CH_2Cl_2): −1.47 V vs Cp_2Fe.

Synthesis of 7. FpBF$_4$ (0.15 g, 0.56 mmol) was dissolved in CH_2Cl_2 (40 mL), and methyl propiolate (300 μL, 3.5 mmol) was added. The solution was monitored by in-situ IR spectroscopy and was stirred overnight. Excess $NaHCO_3$ was added (0.5 g), and the solution was stirred for a further 24 h. The mixture was filtered through Celite supported on a medium porous glass frit, toluene (2 mL) was added, and then the mixture was concentrated under reduced pressure. The solution was cooled to −30 °C overnight, and reddish-black crystals of **7** (0.04 g, 27%) were isolated by filter cannulation followed by washing with toluene (2 × 5 mL) and drying in vacuo. Anal. Calcd for $C_{11}H_8O_4Fe$: C, 50.81; H, 3.10. Found: C, 51.01; H, 3.15. ^{1}H NMR ($CDCl_3$) δ: 5.09 (s, 5H, C_5H_5), 3.90 (s, 3H, OCH_3). IR (CH_2Cl_2): ν(CO), 2028, 1984 cm^{-1}, ν(ester CO) 1720 cm^{-1}. ESI-MS (*m*/*z*): 260 (P^+).

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(28) CV simulations were performed using Digisim 3.1 (Bioanalytical Systems).

(29) SWV simulations were performed using ESP version 2.4 (written by Carlo Nervi), available at http://lem.ch.unito.it/