Preparation and Reactivity of Acyclic (Pentadienyl)iron(1+) Cations: Applications to Organic Synthesis

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Nucleophilic attack on coordinated polyenes is one of the paradigms of π-organometallic chemistry.[1] Where reactions of this type occur with predictable regioselectivity they can be of synthetic utility. For example, the tricarbonyl(cyclohexadienyl)iron(1+) cation (**1**, **Scheme 1**)[2] is known to undergo nucleophilic attack at the dienyl terminus to afford substituted (cyclohexadiene)Fe(CO)$_3$ complexes. Cation **1** may be prepared via hydride abstraction from the parent (cyclohexadiene)Fe(CO)$_3$ complex, which is in turn prepared by complexation of cyclohexadiene with Fe(CO)$_5$. Liberation of the substituted cyclohexadiene ligand can be effected by oxidation with Ce(NH$_4$)$_2$(NO$_3$)$_6$ or Me$_3$NO, and this sequence of steps serves as a regio- and stereoselective method for the functionalization of cyclohexadiene (**Scheme 1**).[2] The application of this methodology to natural product synthesis has been used in the preparation of carbazole,[3] limaspermine,[4] and *O*-methyljoubertiamine[5] alkaloids and trichothecenes.[6] The preparation and reactivity of the corresponding *acyclic* (pentadienyl)iron(1+) cations (**2**) have been the subject of intense recent investigations in a number of laboratories (**Figure 1**).[7]

A. Preparation

The hydride abstraction method for the preparation of cationic organometallic complexes has been applied to the preparation of *acyclic* (pentadienyl)Fe(CO)$_3$$^+$ cations. However, in spite of what is indicated in a popular organometallic chemistry text, there are only a few examples since the success of this reaction requires the presence of a *cis*-alkyl substituent on the diene (Method A, **Scheme 2**).[8,9] The most common method for the preparation of cations **2** is the protonation of (pentadienol)- or (pentadienyl ether)Fe(CO)$_3$ complexes (Method B, **Scheme 2**).[8] Lillya and co-workers have demonstrated that ionization of the hydroxyl

substituent occurs with anchimeric assistance from iron, and that isomerization of the initially generated transoid pentadienyl cation (**3**) to the more stable cisoid cation occurs with retention of configuration about the C1-C2 bond.[10] A third method of preparation involves protonation of (triene)Fe(CO)$_3$ complexes with HBF$_4$ or HPF$_6$ (Method C, **Scheme 2**).[11] To date, a wide variety of (pentadienyl)iron(1+) cations have been prepared and *isolated* (**Figure 1**), including stereoselectively labeled cations **2ii** and **2jj**. Cations **2b**, **2l**, **2q**, **2r**, **2s**, **2z**, **2ee**, **2gg**, and **2ii** have been prepared in both optically enriched and optically pure form.

B. Structure, Spectral Characterization and Electronic Distribution

The *first* crystal structure of a (pentadienyl)Fe(CO)$_3$$^+$ cation, **2x**, has recently been reported.[12] This structure indicates that the distance between the terminal pentadienyl carbons (C1/C5) and Fe (ca. 2.177 Å) is longer than that between Fe and C2/C4 (ca. 2.145 Å) or between Fe and C3 (2.109 Å). In addition, the angle about the C3 carbon in the ligand (ca. 129°) is greater than that about the C2/C4 carbons (ca. 122°), and the methyl substituents at C2/C4 are tilted *toward* the iron atom (ca. 8.7° below the

plane of the pentadienyl ligand). Extensive NMR spectral analysis indicates that all of the *isolated* cations **2** (**Figure 1**) exhibit the "U" or cisoid structure in solution. In the parent cation **2a**, the signals due to protons attached to the ligand appear at δ 7.22 (C$_3$-H), δ 6.26 (C$_{2/4}$-H), δ 3.75 (C$_{1/5}$-H$_{exo}$), and δ 2.17 ppm (C$_{1/5}$-H$_{endo}$), with couplings $J_{1exo-1endo}$ 3.5 Hz, J_{1exo-2} 9.8 Hz, $J_{1-endo-2}$ 13 Hz, J_{2-3} 6.8 Hz.[8a] The signals for these protons in the substituted cations appear in the same general order with variations due to substituent effects. The spectroscopic detection of an

Scheme 1
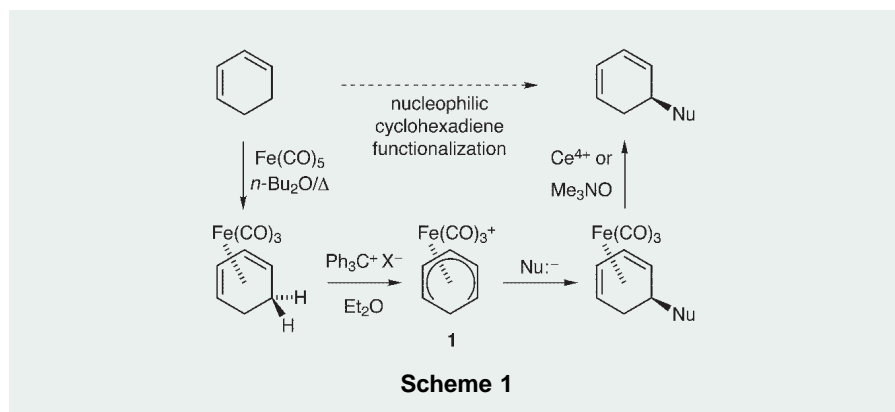
"S" or transoid (pentadienyl)iron cation has only been reported for a single sterically biased case (**eq 1**).[13] While NMR spectra for most cations **2** reveal only the cisoid conformer, it is generally believed that the cisoid (pentadienyl)Fe$^+$ cations **2** exist, in solution, in an equilibrium with the less stable transoid form.

Extended Hückel molecular orbital calculations have indicated that the greatest portion of the positive charge in **2a** is located at C2/C4, followed by C3, and that C1/C5 bear the least partial positive charge.[10b] While it is not always valid to correlate ^{13}C NMR chemical shifts with the charge on coordinated atoms, it is instructive to note that the signals for C2/C4 of a variety of cations **2** appear farthest downfield.[10b,14-20] An empirical set of substituent effects on chemical shifts has been reported.[10b] The ^{57}Fe NMR spectrum of **2b** exhibits a signal at δ 1017.9ppm.[21] On the basis of ^{1}H, ^{13}C, and variable temperature ^{31}P NMR spectroscopy, it has been proposed that phosphine-substituted (pentadienyl)Fe(CO)$_2$PR$_3^+$ cations, **2q-2w**, exist predominantly in the conformer which has the phosphine

ligand in the basal position which is opposite to the C1 substituent (B^1, **Figure 2**).[16,22,23]

C. Reactivity of Pentadienyl Cations

The acyclic (pentadienyl)iron(1+) cations **2** can act as excellent organometallic electrophiles toward a wide variety of nucleophiles. A priori, the reactivity of cations **2** might be anticipated to be similar to that of the corresponding (cyclohexadienyl)iron cation **1**. While this is true for a number of cases, *there exist significant differences between the reactivity of cyclic cation 1 and that of the acyclic cations 2*. Nucleophilic attack can take place on the cisoid form of the pentadienyl cation at either terminus to afford the *E,Z*-diene complexes **4** or **5**, or on the internal atoms of the ligand (C2/C3/C4) to afford complexes **6**, **7** or **8** (**Scheme 3**). Alternatively, since the transoid form exists in equilibrium with the cisoid form, nucleophilic attack on the transoid pentadienyl cation generates *E,E*-diene complexes **9** or **10**. Nucleophilic
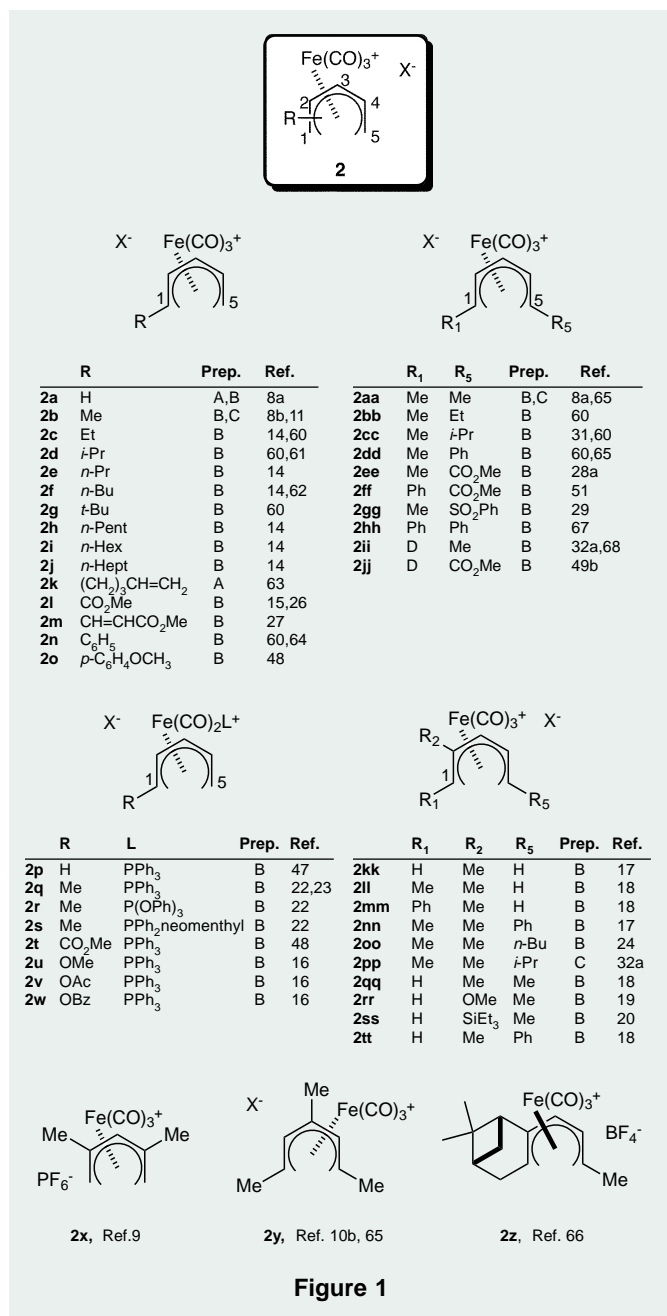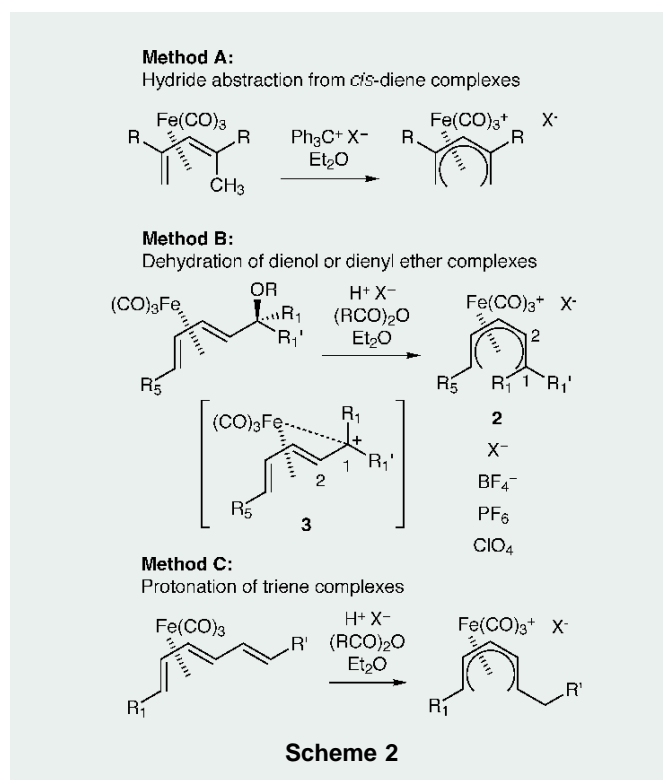
	R	Prep.	Ref.
2a	H	A,B	8a
2b	Me	B,C	8b,11
2c	Et	B	14,60
2d	*i*-Pr	B	60,61
2e	*n*-Pr	B	14
2f	*n*-Bu	B	14,62
2g	*t*-Bu	B	60
2h	*n*-Pent	B	14
2i	*n*-Hex	B	14
2j	*n*-Hept	B	14
2k	(CH$_2$)$_3$CH=CH$_2$	A	63
2l	CO$_2$Me	B	15,26
2m	CH=CHCO$_2$Me	B	27
2n	C$_6$H$_5$	B	60,64
2o	*p*-C$_6$H$_4$OCH$_3$	B	48

	R$_1$	R$_5$	Prep.	Ref.
2aa	Me	Me	B,C	8a,65
2bb	Me	Et	B	60
2cc	Me	*i*-Pr	B	31,60
2dd	Me	Ph	B	60,65
2ee	Me	CO$_2$Me	B	28a
2ff	Ph	CO$_2$Me	B	51
2gg	Me	SO$_2$Ph	B	29
2hh	Ph	Ph	B	67
2ii	D	Me	B	32a,68
2jj	D	CO$_2$Me	B	49b

	R	L	Prep.	Ref.
2p	H	PPh$_3$	B	47
2q	Me	PPh$_3$	B	22,23
2r	Me	P(OPh)$_3$	B	22
2s	Me	PPh$_2$neomenthyl	B	22
2t	CO$_2$Me	PPh$_3$	B	48
2u	OMe	PPh$_3$	B	16
2v	OAc	PPh$_3$	B	16
2w	OBz	PPh$_3$	B	16

	R$_1$	R$_2$	R$_5$	Prep.	Ref.
2kk	H	Me	H	B	17
2ll	Me	Me	H	B	18
2mm	Ph	Me	H	B	18
2nn	Me	Me	Ph	B	17
2oo	Me	Me	*n*-Bu	B	24
2pp	Me	Me	*i*-Pr	C	32a
2qq	H	Me	Me	B	18
2rr	H	OMe	Me	B	19
2ss	H	SiEt$_3$	Me	B	20
2tt	H	Me	Ph	B	18

2x, Ref.9   **2y**, Ref. 10b, 65   **2z**, Ref. 66

Figure 1

Method A:
Hydride abstraction from *cis*-diene complexes

Method B:
Dehydration of dienol or dienyl ether complexes

Method C:
Protonation of triene complexes

Scheme 2

K$_{eq}$ = 3.0 + 0.3 (-50°C)
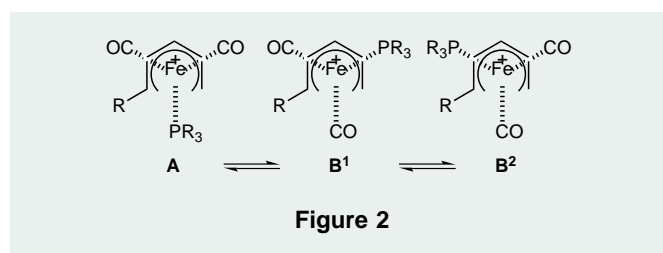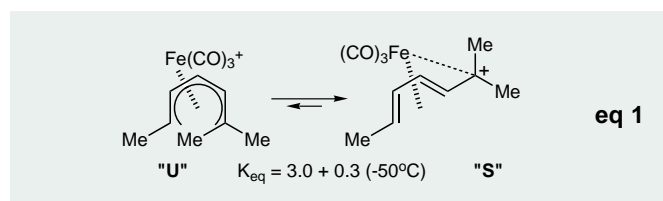
eq 1

A ⇌ B^1 ⇌ B^2

Figure 2

attack at the metal, with concomitant loss of a ligand, is a final possibility (**Scheme 3**). Except for attack at C3, all of these possibilities have been observed.

1. Reaction with Heteroatom Nucleophiles

In general, the reaction of cations **2** with water and alcohol nucleophiles leads to the formation of (*E,E*-dienol)- and (*E,E*-dienyl

Scheme 3

eq 2

Figure 3

ether)Fe(CO)$_3$ complexes in excellent yields (**eq 2**).[8,10,11,17-20,24] The stereochemistry at the alcohol methine carbon, relative to the (diene)Fe(CO)$_3$ fragment, was established as "Ψ-exo" on the basis of X-ray diffraction analysis.[25] The formation of the Ψ-exo-*E,E*-dienol products is rationalized on the basis of reaction of the weak oxygen nucleophiles with the less stable, but more reactive, transoid pentadienyl form of the cations on the face opposite to Fe(CO)$_3$. In contrast, the reaction of water or alcohols with pentadienyl cations bearing an electron-withdrawing substituent (e.g., **2l**, **2m**, and **2ee**) gives the corresponding *Z,E*-diene complexes (e.g., **11**, **Figure 3**).[26-28] This may be due to the increased reactivity of these cations in the "U" form. Grée et al. have utilized the optically active *Z,E*-diene complex (2S)-**11** in the preparation of intermediates **12** and **13** (**Figure 3**) for the synthesis of AF/AK toxins.[28b]

Reaction of cations **2** with Group 15 neutral nucleophiles (1°/2°amines,[29,30] phosphines,[31,32] and arsines[33]) affords the cationic complexes **14/15** (**Scheme 4**). Deprotonation of the ammonium salts generates the correspondingly substituted amine complexes. Reaction of cations **2** with phosphites proceeds via an Arbuzov-type reaction to give dienyl phosphonates.[34] It has recently been demonstrated that the addition of amines[35] and phosphines[18,32,36] is reversible in certain cases (**Scheme 4**). Thus, kinetic nucleophilic attack occurs on the more abundant cisoid form of the cation to generate *E,Z*-diene complexes **14**. Where there are significant steric interactions between the amine/phosphine and other substituents present on the pentadienyl ligand, nucleophilic attack may be reversible. At higher temperatures and longer reaction times, the thermodynamically more stable *E,E*-diene complex **15** is formed via nucleophilic attack on the much less abundant transoid form of the pentadienyl cation. It is worth noting that nucleophilic attack of phosphines on the (*cyclohexadienyl*)Fe(CO)$_3^+$ cations is not reversible.[37]

Deprotonation of either the *E,Z*- or the *E,E*-dienyltriphenylphosphonium salts **14** or **15** (R$_3$A = PPh$_3$) leads to the formation of the corresponding *E,E*-dienyl ylides. Uncomplexed dienyl ylides participate in Wittig olefination with low *E/Z*-selectivity (ca. 1:1). In contrast, the complexed ylide **16** undergoes olefination with greater *Z*-selectivity (1:4, *E:Z*, **Scheme 5**).[34a,38] The perfumery component 1,3*E*,5*Z*-undecatriene has been prepared by this methodology.[34a]

Reaction of pentadienyl cations **2** with halide ions proceeds via attack at the metal followed by loss of a ligand; in the case of **2x** loss
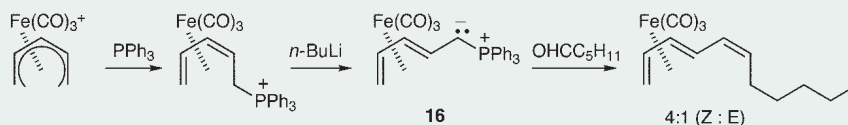

Scheme 4
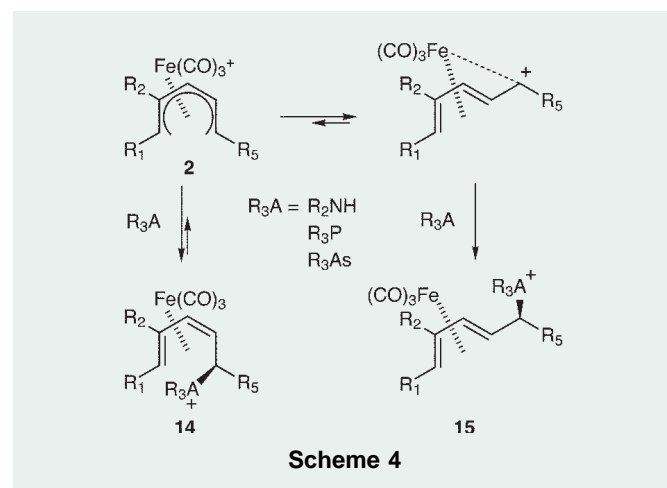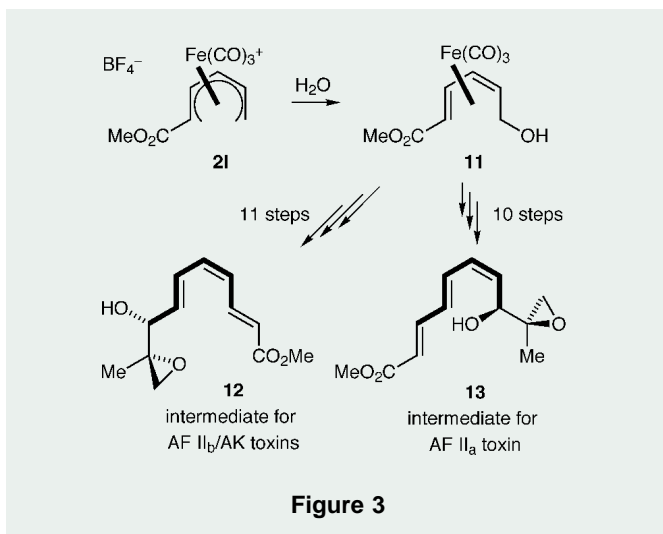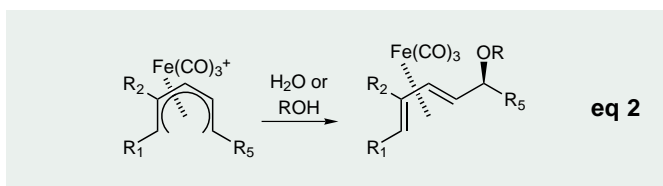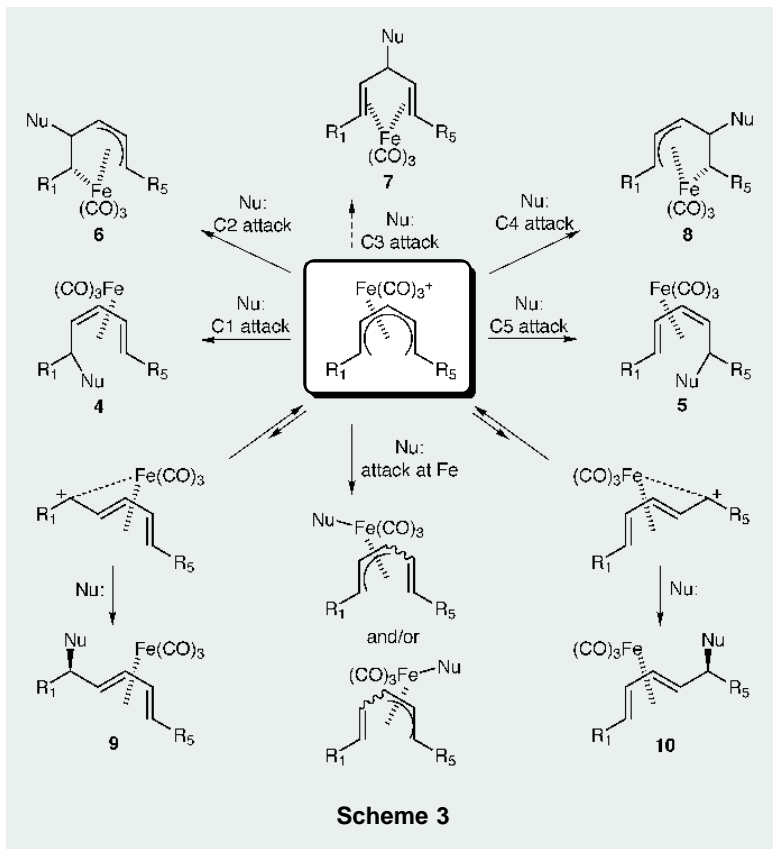
of coordinated CO gives a (pentadienyl)Fe(CO) for **2aa** this entails decomplexation of two atoms of the pentadienyl ligand to afford the (allyl)-Fe(CO)$_3$X complexes **18** (**eq 3**).[39] By comparison, reaction of **2ee** with tetrabutyl-ammonium fluoride (TBAF) affords a "very complex mixture" of unidentified products.[40]
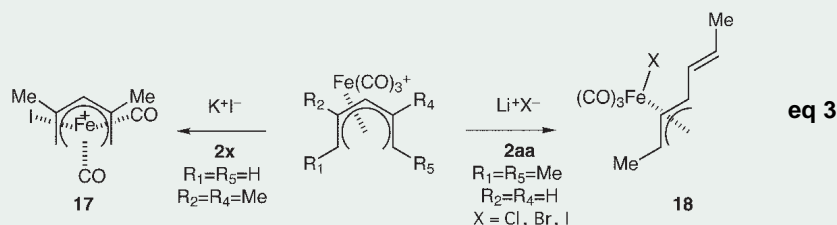
2. Reaction with Carbon Nucleophiles

The reaction of cations **2** with simple organocadmium reagents[41] or organo-cuprates[17,20,42] gives *E,Z*-diene complexes (**Scheme 6**). Likewise, the reaction of func-tionalized organozinc reagents in the pres-ence of CuCN ("Knochel reagents")[43] with cations **2** affords the diene complexes **19**.[44] Even alkynyl cuprates, usually considered to be the least reactive of organocuprate ligands,[45] react with cations **2** to give 1*E*,3*Z*,6-dienyne complexes **20**.[15,46] For 1- or 2-substituted or 1,2-disubstituted pentadienyl cations (e.g., **2b**, **2l**, **2n**, **2kk**, **2ll**, and **2mm**) nucleophilic attack occurs at the less steri-cally hindered terminus of the pentadienyl ligand with excellent regioselectivity; however, for 1,4-disubstituted pentadienyl cations (e.g., **2qq** and **2tt**), mixtures of regio-isomeric products are formed. Yeh et al. have further utilized dienes **19** in intra-molecular cyclocarbonylation reactions to produce [3.3.0]- and [3.4.0]bicyclo-alkanones.[44b] The optically active (methyl 2*E*,4*Z*-hexadecadiene-7,10-diynoate)-Fe(CO)$_3$ complex **20** (R = CH$_2$C≡CC$_5$H$_{11}$) prepared from (2*R*)-**2l** was utilized in the enantioselective synthesis of (5*R*)-HETE methyl ester (**Scheme 6**).[15]
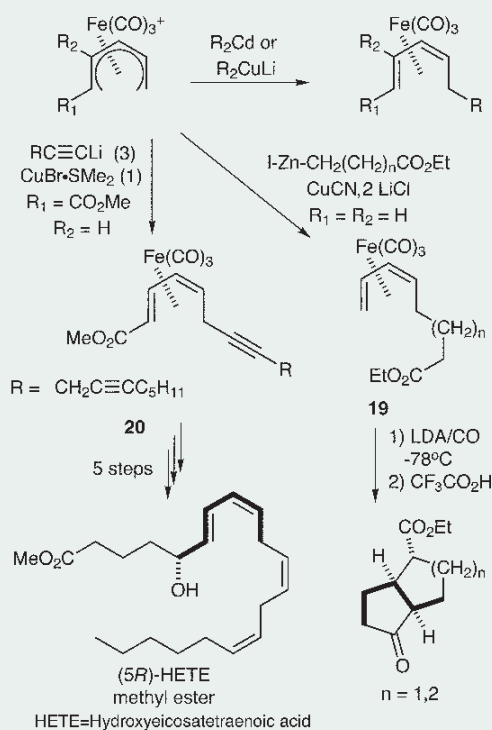
The reaction of (pentadienyl)-Fe(CO)$_2$PPh$_3$$^+$ cations **2p**, **2v**, or **2w** with alkyl or aryl lithium compounds proceeds via attack at C2 to afford complexes **21** (**Scheme 7**).[16,47] For the parent system (R = H), the resulting σ,π-allyl complex **21** is unstable and decomposes in solution over a period of time in the presence of air via carbonyl insertion and reductive elimina-tion to afford cyclohexenone products.[47] Similarly, malonate nucleophiles react with (methoxycarbonylpentadienyl)iron cation **2l** at C2 to afford predominantly **22** (**Scheme 8**).[48,49] The substituted σ,π-allyl complexes **21** (R = OAc, OBz)[16] and **22**[48] are consider-ably more stable than the parent system **21** (R = H), and after isolation may be structur-ally characterized by X-ray diffraction. In contrast to **21**, oxidation of **22** (R = H; Ce^{4+}) results in the formation of a vinylcyclopropanecarboxylate in good yields (**Scheme 8**).[49] The difference in stability of **21** and **22**, and their divergent paths for the loss of the iron atom, may be
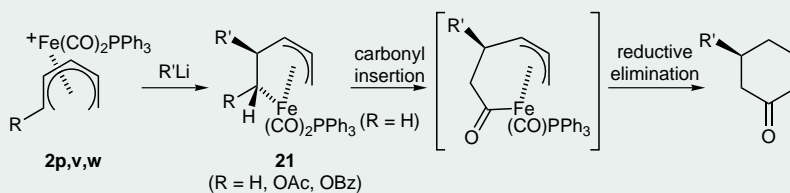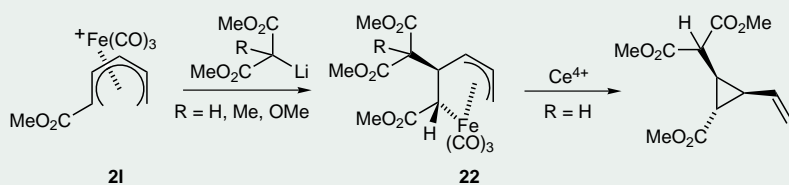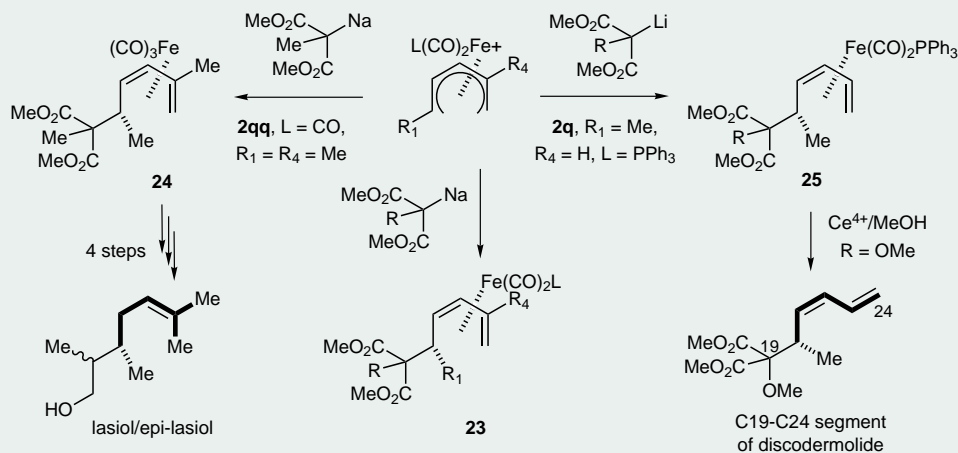

Scheme 5

eq 3

(5*R*)-HETE
methyl ester
HETE=Hydroxyeicosatetraenoic acid
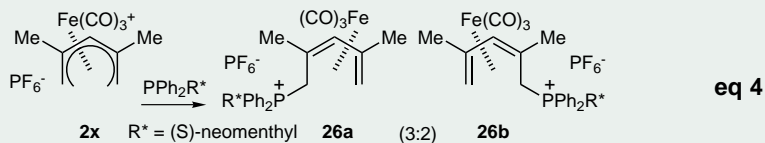
Scheme 6

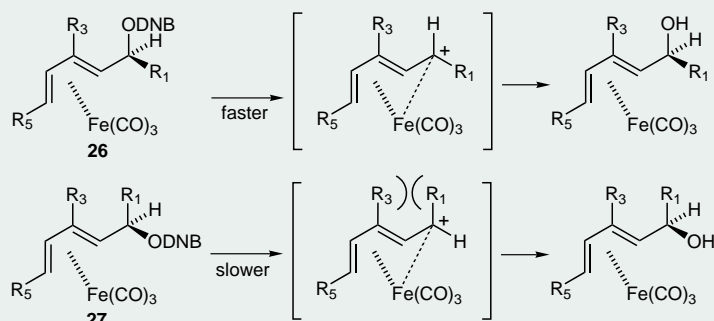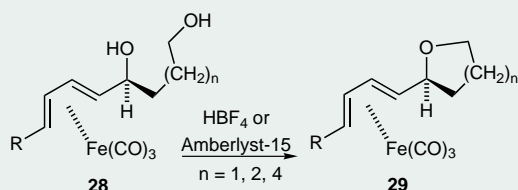**Scheme 7**

Scheme 8

Scheme 9

eq 4

Scheme 10

eq 5

attributed to the retarding effect of an electron withdrawing substituent on the rate of carbonyl insertion.[50] The reaction of cations **2l**, **2ee**, or **2ff** with alkynyl cerium reagents,[51] or the reaction of cations **2b**, **2m**, or **2n** with dimethylmalonate anion,[27,48] gives mixtures of diene complexes resulting from attack at C5 and unstable σ,π-allyl complexes resulting from attack at C2. In comparison, the reactions of disubstituted (pentadienyl)Fe(CO)$_3$$^+$ cations **2x**,[9] **2qq**,[42] **2ss**,[20] and **2tt**[42] or Fe(CO)$_2$PPh$_3$$^+$ cation **2q**[23] with malonate anions proceeds via attack at C1 to afford Z-1,3-diene complexes **23** (**Scheme 9**). The synthesis of the rearranged terpenes lasiol/epi-lasiol from **24**,[42] and the preparation of the C19-C24 segment of the immune response suppressant discodermolide from **25**[23] have been reported (**Scheme 9**).

The regioselectivity of nucleophilic attack by carbon nucleophiles at the pentadienyl termini versus attack at an internal carbon appears to depend upon both the nucleophile and the substituents present on the pentadienyl ligand. The general trends can be summarized as follows: Nucleophilic attack by organocuprates occurs at the sterically less hindered terminus. Nucleophilic attack by malonate anions on Fe(CO)$_3$-complexed 1-*substituted* pentadienyl cations occurs with little regioselectivity unless there is either a strongly electron-withdrawing or strongly electron-donating substituent present at the terminal position of the ligand. The presence of a 2-*substituent* has a pronounced directing effect for malonate attack at C5. Regioselectivity of nucleophilic attack on Fe(CO)$_2$PPh$_3$-complexed pentadienyl cations is generally improved over that of the corresponding Fe(CO)$_3$ complexed cations due to the increased stability/decreased reactivity of the Fe(CO)$_2$PPh$_3$ cations. Finally, the steric bulk of the malonate nucleophile has only a minor effect on the regioselectivity of nucleophilic attack on the pentadienyl ligand.
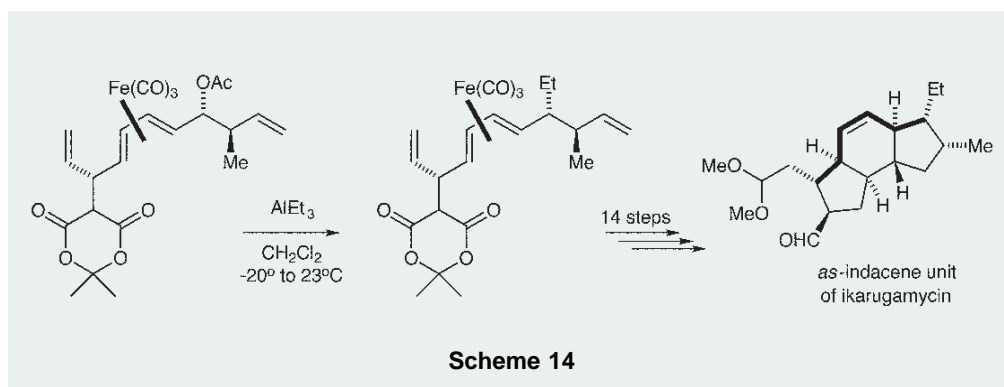
3. Resolution via Pentadienyl Cations

The desymmetrization of C$_2$-symmetrical (pentadienyl)Fe(CO)$_3$ cations has been reported. Thus the reaction of **2x** with (S)-neomenthyldiphenylphosphine gives a mixture of the two optically active diastereomeric phosphonium salts **26a** and **26b** (20% de). Slow recrystallization of this mixture gives a *single* diastereomer **26a** with >80% mass recovery via an asymmetric

transformation of the second kind (**eq 4**).[32] The reaction of the symmetrical cation **2aa** with (–)-sparteine (-78 °C) led to the formation of (3,4,5,6-η⁴-1,3E,5E-heptatriene)-Fe(CO)₃ in an optically enriched fashion, albeit with low enantiomeric excess (ca. 6% ee).[52] Recently, Käser and Salzer reported the kinetic resolution of racemic α-methylbenzylamine by reaction with the optically pure cation **2z** (38% de).[35]

D. In Situ Generation and Reactivity of Transoid Pentadienyl Cations

In the early 1970s, Lillya reported that Ψ-exo dienyl dinitrobenzoates **27a** undergo solvolysis (acetone/H₂O) at rates which were ca. 10-60 times faster than those of the free ligands while the corresponding Ψ-endo dienyl dinitrobenzoates **27b** undergo solvolysis slower than the free ligands.[53] These reactions take place with net retention of configuration at the center undergoing substitution (**Scheme 10**). These results are rationalized on the basis of ionization of the leaving group with anchimeric assistance from the iron atom, followed by attack of the external nucleophile on the face of the cation opposite to iron (i.e., double inversion). The Ψ-exo dinitrobenzoates have the leaving group oriented favorably for this ionization, while the Ψ-endo dinitrobenzoates must undergo rotation about the diene-to-Cα bond which would bring the remaining substituent at the α-carbon into steric congestion with the dienyl portion of the molecule. In a similar fashion, cyclodehydration of dienyldiols **28** under acidic conditions affords 5-, 6-, or 8-membered-ring ethers **29** (**eq 5**).[54] An unusual rearrangement of dienyldiol **30**, in the presence of Amberlyst® resin (acidic form), gave dienyl-1,4-dioxane **31** (**Scheme 11**).[55] This transformation is believed to involve the generation of the transoid pentadienyl cation **32** followed by rearrangement to the transoid pentadienyl cation **33** and eventual intramolecular nucleophilic capture. Good yields for cyclization (50-91%) are only observed for the Ψ-endo glycol ethers **30**. A similar 1,2-transposition of the Fe(CO)₃ group was observed in the reaction of cyanophosphonates with weak nucleophiles in the presence of Lewis acids.[56] The stereoselective substitution of dienol complexes using (diethylamino)-sulfur trifluoride (DAST) and proceeding via the transoid pentadienyl cations has been reported.[40]

Scheme 11

Scheme 12

C11-C24 segment of macrolactin A

Scheme 13

as-indacene unit of ikarugamycin

Scheme 14
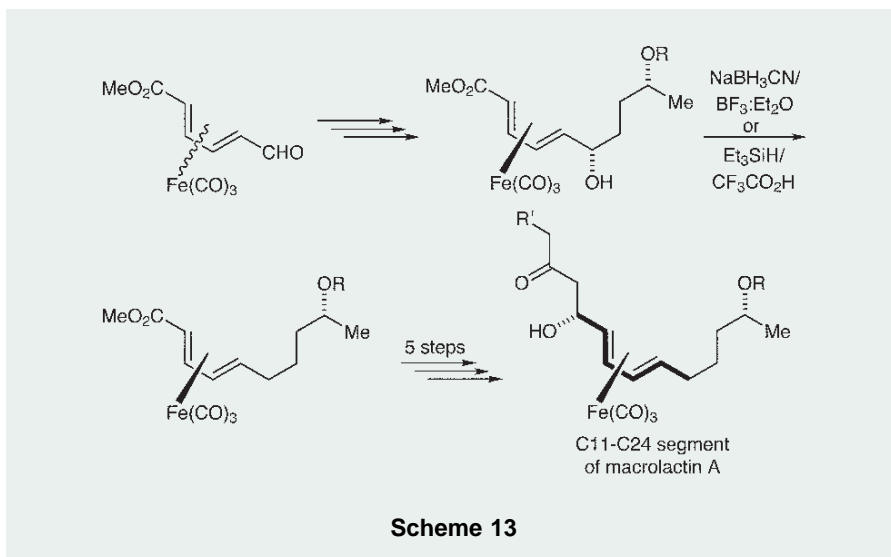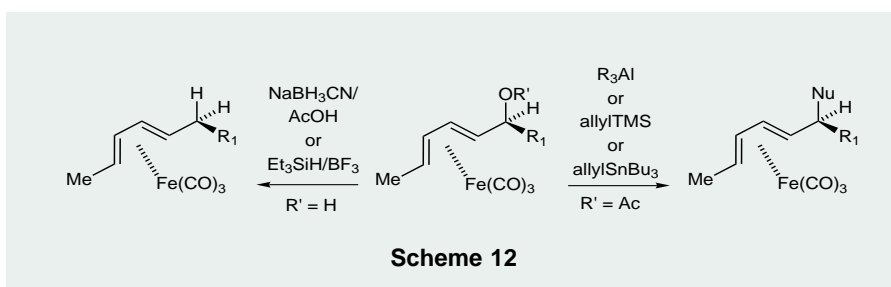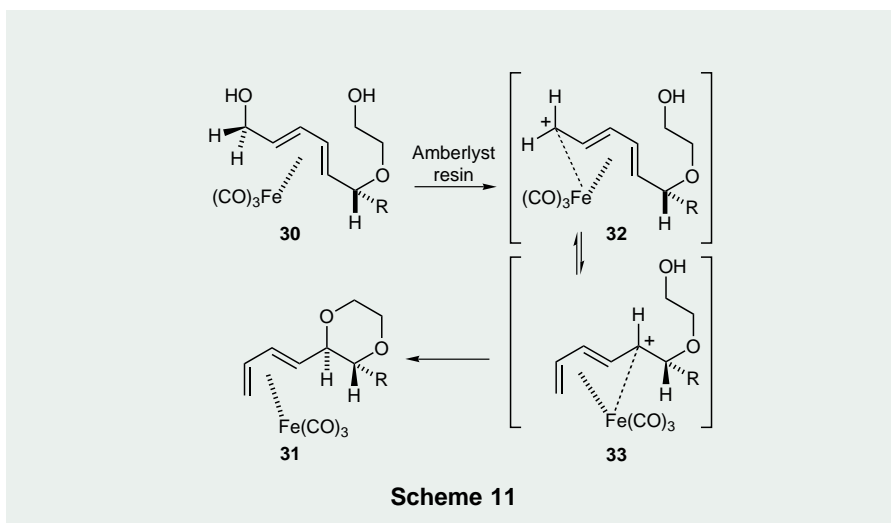
The in situ generated transoid pentadienyl cations may also undergo reaction with hydride and carbon nucleophiles. Under acidic conditions, the selective ionic reduction of hydroxyl functionalities adjacent to (diene)Fe(CO)$_3$ may be accomplished (**Scheme 12**).[57] This methodology has been utilized in syntheses of the Fe(CO)$_3$ complexed segments of the polyene macrolactin A (**Scheme 13**).[57a,b] Likewise, substitution of dienyl acetate complexes with weak carbon nucleophiles (allyltrimethylsilane, trialkylaluminums) occurs with retention of configuration.[58] This type of diastereoselective C-C bond formation has been utilized as a key step in the synthesis of the *as*-indacene unit (**34**) of ikarugamycin (**Scheme 14**).[59]

Acknowledgments

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William Donaldson received his B.A. degree in Chemistry with Honors from Wesleyan University (1977), having done undergraduate research with Prof. Al Fry, and a Ph.D. degree in Organometallic Chemistry at Dartmouth College (1981) under the direction of Prof. Russell Hughes. After a postdoctoral fellowship with Prof. Myron Rosenblum at Brandeis University (1981-82), he returned to Wesleyan University as a Visiting Assistant Professor (1982-83), before coming to Marquette University as Assistant Professor in August 1983. He was promoted to Associate Professor in 1990 and Full Professor in 1996. Prof. Donaldson is the recipient of the Edward D. Simmons Award for Junior Faculty Excellence (1988) and the Rev. John P. Raynor Award for Teaching Excellence (1995) both from Marquette University, and held an Alexander von Humboldt Fellowship at Philipps Universitaet-Marburg (1990-91). His hobbies revolve around his family, particularly spending time with his wife, Pam, and his two sons, Scott and Jimmy.

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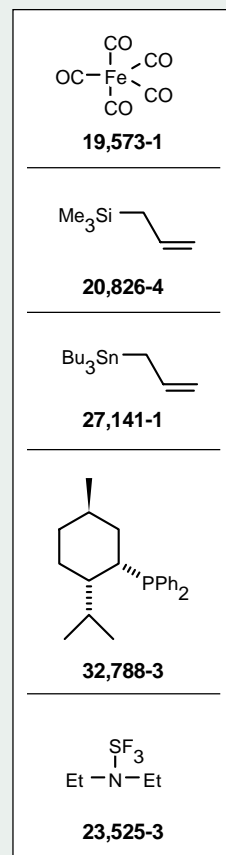
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