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Reactivity of (1-methoxycarbonylpentadienyl)iron(1+) cations with hydride, methyl, and nitrogen nucleophiles

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ABSTRACT

The reaction of tricarbonyl and (dicarbonyl)triphenylphosphine (1-methoxycarbonyl-pentadientyl) iron(1+) cations **7** and **8** with methyl lithium, $NaBH_3CN$, or potassium phthalimide affords (pentenediyl) iron complexes **9a-c** and **11a-b**, while reaction with dimethylcuprate, gave (*E,Z*-diene)iron complexes **10** and **12**. Oxidatively induced-reductive elimination of **9a-c** gave vinylcyclopropanecarboxylates **17a-c**. The optically active vinylcyclopropane (+)-**17a**, prepared from (1*S*)-**7**, undergoes olefin cross-metathesis with excess (+)-**18** to yield (+)-**19**, a C9–C16 synthon for the antifungal agent ambruticin. Alternatively reaction of **7** with methanesulfonamide or trimethylsilylazide gave (*E,E*-diene)iron complexes **14d** and **e**. Huisgen [3 + 2] cyclization of the (azidodienyl)iron complex **14e** with alkynes afforded triazoles **25a-e**.

1. Introduction

Acyclic (pentadienyl)iron(1+) cations are versatile precursors for organic synthesis, due to the wide variety of structural motifs which may be produced upon nucleophilic addition (Scheme 1).[1] While NMR spectra for most cations **1** are indicative of the "U" or cisoid structure in solution, it is generally believed that the "S" or transoid form does exist in an equilibrium with the more stable "U" form (Scheme 1).[1] The spectroscopic detection of a transoid structure has only been reported for a single sterically biased case.[2] Nucleophilic attack on the "U" structure may proceed via attack at one of the pentadienyl termini to afford *cis*-diene complexes **2** (path A), or with weak nucleophiles such as water, amines and electron-rich aromatics, via the less-stable but more reactive "S" form to generate *trans*-diene complexes (path B). For certain combinations of nucleophiles and cations, attack occurs at an internal carbon of the dienyl ligand to afford (3-pentene-1,5-diyl)iron complexes **4** (path C). Stable complexes **4**, which possess an electron withdrawing substituent at the σ-bound (C1) carbon, may be decomposed under oxidative conditions to afford vinylcyclopropanes. Alternatively, unstable complexes **4** are known to afford 5-substituted-2-cyclohexenones **6** via cyclocarbonylation.

The reactivity of (1-methoxycarbonylpentadienyl)iron(1+) cations **7** and **8** with *carbon* nucleophiles is observed to proceed via all three pathways.[3–5] This reactivity has been utilized in the synthesis of methyl 5-hydroxyeicosatetraenoate (5-HETE),[3a] iron containing HETE analogs,[3c] and the C7–C24 segments of macrolactin A,[3b] (path A), and 2-(2'-carboxycyclopropyl)-glycines,[5c] bicyclopropanes,[5h] and dysibetaine CPa[5i] (path C). There are fewer examples of the reaction of (dienyl)iron cations.

2. Results and discussion[8]

The (1-methoxycarbonylpentadienyl)iron(1+) cations (±)-**7** and (±)-**8** were prepared by literature methods.[3a,5b] Cationic complex (±)-**8** was isolated as an amorphous solid. Recrystallization from acetone/diethyl ether gave yellow block crystals that were characterized by X-ray diffraction analysis (Fig. 1).[9] The structure of **8** revealed that the triphenylphosphine ligand occupies the basal site *anti* to the methoxycarbonyl substitutent on the pentadienyl ligand. This relative orientation of the PPh_3 ligand, in solution, was previously proposed on the basis of the upfield shifts of H-7 and H-8exo (numbering in Fig. 1) compared to those for **7**.[5b] As anticipated, the Fe–CO bond distances (Table 1) are shorter (1.784–1.812 Å) and the carbonyl C–O distances (1.133–1.142 Å) for **8** compared to those observed in the crystal structure of **7**

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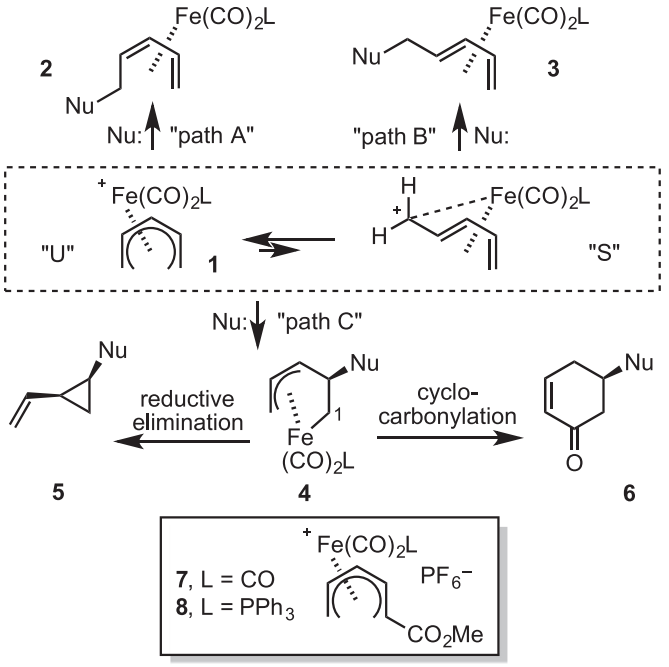


Scheme 1. **7** and **8** with non-carbon nucleophiles.[6] We herein report on the reactivity of these cations with hydride, methyl,[7] and nitrogen nucleophiles, and their subsequent reactions.

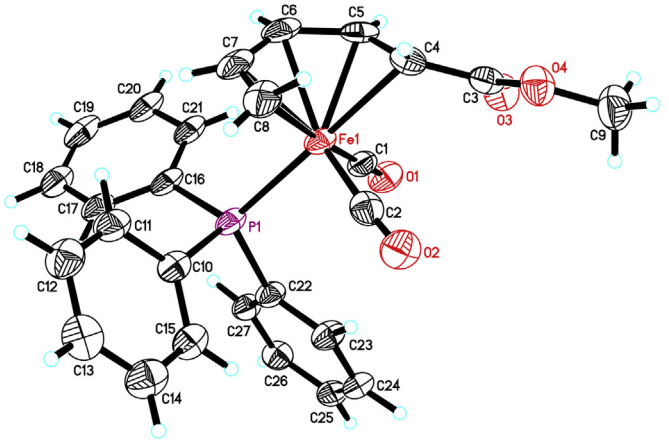


Fig. 1. ORTEP of **8** (PF_6^- counterion and solvent molecule omitted for clarity).

(Fe–CO = 1.835–1.837 Å; FeC–O = 1.121–1.137 Å).[3c] *In contrast*, the C4–C5, C5–C6 and C6–C7 distances within the pentadienyl ligand and the iron-to-pentadienyl distances Fe–C4, Fe–C5 and.

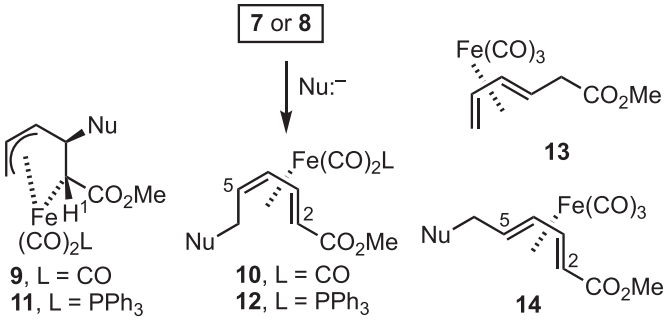
Fe–C6 for **7** and **8** are relatively similar, while the C-7-C8, Fe–C7 and Fe–C8 distances (1.395 Å, 2.102 Å and 2.165 Å) are slightly shorter for **8**, compared to those for **7** (1.419 Å, 2.141 Å and 2.207 Å).

We have previously reported[7] that addition of a solution of methyllithium in ether to a solution of **7** in dichloromethane gave predominantly the pentendiyl complex **9a** along with variable amounts of the known[10] complex **13**, while reaction of **7** with Me_2CuLi (formed from MeLi/CuBr) gave primarily the *E,Z*-diene complexes **10a** (Scheme 2, Table 2). The reactions of **7** with Me_3Al or MeTi(*i*-PrO)$_3$ were less selective and gave mixtures of **9a** and **10a**. Reaction of **8** with MeLi or with Me_2CuLi gave predominantly pentenediyl complex **11a** or diene complex **12a**. The reaction of **7** with $NaBH_3CN$ gave a separable mixture of pentenediyl complex **9b** and *E,Z*-diene complex **10b**. Use of LiAlH(*t*-BuO)$_3$ instead of $NaBH_3CN$ gave lower yields of **9b**. In a similar fashion, reaction of **8** with $NaBH_3CN$ gave predominantly pentenediyl complex **11b**. Finally, reaction of **7** with KNPhth, $MeSO_2NH_2$ or $TMSN_3$ gave pentendiyl complex **9c** or *E,E*-diene complexes **14d** or **14e**.

The structures of the products were assigned on the basis of their NMR spectral data. In particular for **9a-c** the presence of three

Table 1
Bond lengths (Å) for (pentadienyl)iron cations **7** and **8** (atom numbering corresponds to structure in Fig. 1).

Bond	**7** (ref. 3c)	**8** (this work)
Fe–C1	1.835(7)	1.812(5)
Fe–C2	1.837(6)	1.784(5)
C1–O1	1.137(8)	1.133(6)
C2–O2	1.121(7)	1.142(6)
Fe–C4	2.168(7)	2.177(5)
Fe–C5	2.114(7)	2.101(5)
Fe–C6	2.129(7)	2.128(5)
Fe–C7	2.141(6)	2.102(5)
Fe–C8	2.207(7)	2.165(5)
C4–C5	1.402(9)	1.404(7)
C5–C6	1.418(9)	1.408(8)
C6–C7	1.417(9)	1.417(8)
C7–C8	1.419(10)	1.395(8)



a, Nu = Me; **b**, Nu = H; **c**, Nu = NPhth; **d**, Nu = $NHSO_2Me$; **e**, Nu = N_3

Scheme 2. Nucleophilic addition to (1-methoxypentadienyl)iron cations.

Table 2
Nucleophilic addition to (1-methoxycarbonylpenta-dienyl)iron cations.

	Reagents	Nu	Product(s)
7	MeLi[c]	Me	**9a** (46–71%) + **13** (0–25%)[a]
7	MeLi/CuBr–SMe_2[d]	Me	**10a** + **9a** (14:1, 58%)[a]
7	Me_3Al[e]	Me	**10a** + **9a** (3:1, 59%)[b]
7	MeLi/TiCl(*i*-PrO)$_3$[c]	Me	**10a** + **9a** (2:1, 37%)[b]
8	MeLi[c]	Me	**11a** (66%) + **12a** (2%)[b]
8	MeLi/CuBr–SMe_2[d]	Me	**12a** (56%)[b]
7	$NaBH_3CN$[f]	H	**9b** (78%) + **10b** (12%)[b]
7	LiI/LiAlH(*t*-BuO)$_3$[f]	H	**9b** (31%)[b]
8	$NaBH_3CN$[f]	H	**11b** (87%) + **12b** (5%)[b]
7	K^+ $^-$NPhth[g]	NPhth	**9c** (62%)[b]
7	H_2NSO_2Me[h]	NHMs	**14d** (98%)[b]
7	$TMSN_3$[h]	N_3	**14e** (56%)[b]

[a] Reported in preliminary communication (ref. 7).
[b] This work.
[c] CH_2Cl_2/−78 °C.
[d] THF–Et_2O (3:1)/−78 °C.
[e] CH_2Cl_2/−30 °C.
[f] THF/0 °C.
[g] CH_3NO_2/23 °C.
[h] CH_2Cl_2/23 °C.