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Reactivity of Tricarbonyl(pentadienyl)iron(1+) Cations: Preparation of an Optically Pure Tricarbonyl(diene)iron Complex via Second-Order Asymmetric Transformation

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Summary: Reactions of tricarbonyl(2,4-dimethylpentadienyl)iron(1+) hexafluorophosphate (1) with sodium methoxide/methanol and with phosphines are reported. Use of (S)-neomenthyldiphenylphosphine gives a 3:2 mixture of diastereomers. Slow diffusion-controlled recrystallization of the mixture gives the single, optically pure diastereomer ***6a*** *in >80% mass recovery via a second-order asymmetric transformation involving reversible addition of the phosphine. The stereochemistry of* ***6a*** *at C2 (S) was determined by single-crystal X-ray diffraction analysis.*

The use of acyclic dienes complexed to a tricarbonyliron moiety has found increasing application in organic synthesis.[2] In addition to protecting the diene functionality, the bulky $Fe(CO)_3$ adjunct serves to direct the approach of various reagents opposite to the metal, thus facilitating *highly* diasteroselective carbon–carbon[3] or carbon-oxygen[4] bond formation, in certain cases. If the diene complex utilized is optically pure, this diastereoselectivity can be translated into acyclic stereocontrol upon removal of the $Fe(CO)_3$ adjunct. Optically pure acyclic (diene)$Fe(CO)_3$ complexes have been obtained via separation of racemic mixtures by classical[5] and kinetic resolutions[6] and by chiral chromatography.[7] Diastereoselective complexation of optically active diene ligands have been reported recently.[8] In this communication, we report on a novel method for the preparation of optically active diene complexes via reversible nucleophilic addition to a symmetrical (pentadienyl)$Fe(CO)_3$ cation.[9]

The symmetrical tricarbonyl(2,4-dimethylpentadienyl)iron(1+) cation of **1** has been previously prepared and its reactions with sodium dimethylmalonate or with Zn examined.[10] A wide variety of substituted (pentadienyl)-$Fe(CO)_3$ cations are known to react readily with methanol to give the corresponding *trans*-dienyl ether complexes.[11] In comparison, **1** was found to react with methanol *only* in the presence of sodium methoxide to give the racemic (2*Z*)-dienyl ether complex **2** (Scheme 1). This underscores the stability of this cation relative to other (pentadienyl)-$Fe(CO)_3^+$ cations. The reaction of **1** with triphenylphosphine or tris(*p*-methoxyphenyl)phosphine gave the corresponding racemic phosponium salts **3** and **4** (91 and 88%, respectively). The triphenylphosphonium salt **3** is quantitatively recovered after heating at reflux in acetone (14 h); however, in the presence of $P(p\text{-}C_6H_4OMe)_3$, **3** is converted to **4** (88% isolated yield). This transformation occurs via reversible addition of PPh_3 to regenerate the cation **1**, which is captured by the more nucleophilic $P(p\text{-}C_6H_4OMe)_3$. We have previously observed reversible phosphine addition to only one other (pentadienyl)$Fe(CO)_3^+$ cation.[11c]

The reaction of **1** with (*S*)-neomenthyldiphenylphosphine (**5**) (CH_2Cl_2, 22 h) gave a mixture of two diastereomers, **6a** and **6b** (3:2, 82%),[12] resulting from attack of the optically active phosphine at each of the two pentadienyl termini. *Slow* (6 days), diffusion-controlled recrystallization of the mixture (CH_2Cl_2/ether) gave **6a** (*81% mass recovery*) as a single, optically active diastereomer.[13] Notably, if pure **6a** is allowed to stand in CD_3CN (16 h),

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(9) Diastereoselective, *irreversible* nucleophilic addition to (cyclohexadienyl)- and (cycloheptadienyl)$Fe(CO)_3$ cations has been reported. The selectivity in these additions varies from good (maximum 80% de) to nonexistent: (a) Maglio, G.; Musco, A.; Palumbo, R.; Sirigu, A. *J. Chem. Soc., Chem. Commun.* **1971**, 100. (b) Howell, J. A. S.; Thomas, M. J. *J. Chem. Soc., Dalton Trans.* **1983**, 1401. (c) Pearson, A. J.; Blystone, S. L.; Nar, H.; Pinkerton, A. A.; Roden, B. A.; Yoon, J. *J. Am. Chem. Soc.* **1989**, *111*, 134. (d) Pearson, A. J.; Khetani, V. D.; Roden, B. A. *J. Org. Chem.* **1989**, *54*, 5141.

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(12) The ratio **6a**:**6b** was determined by integration of the signals for H3 for each diastereomer (δ 4.17 and 4.26 ppm, respectively; $CDCl_3$).

(13) **6a**: mp 190–192 °C; ^1H NMR (CD_3CN, partial) δ 8.1–7.6 (m, Ar H), 4.31 (br s, H3), 3.87 (dd, $J = 11.1, 15.6$ Hz, H1), 2.33 (m, H1′), 2.26 (d, $J = 4.8$, $H5_{exo}$), 1.72 (s, Me-4), 1.38 (d, $J = 2.1$, Me-2), 1.25 (dd, $J = 0.9, 4.8$, $H5_{endo}$); ^{31}P NMR ($CDCl_3$, H_3PO_4 reference) δ 32.2, −143.2 $[\alpha]_D$ (CH_3CN, after 15 min) +119.1°.

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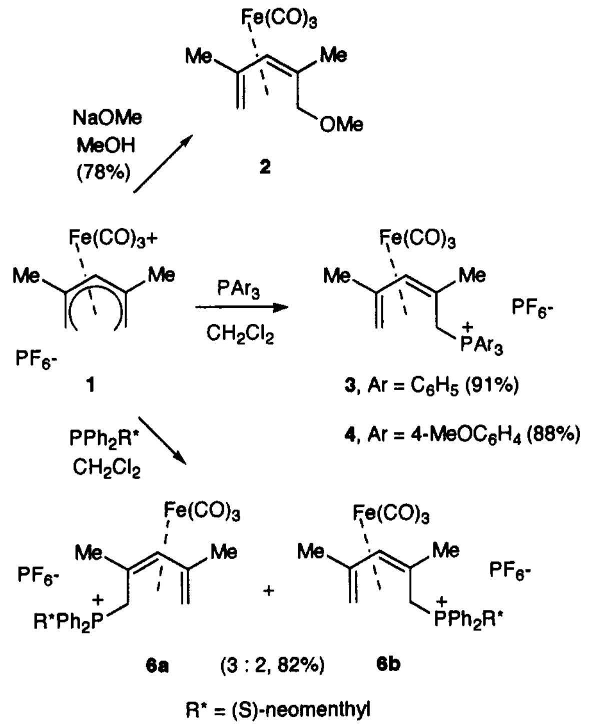
Scheme 1



the equilibrium mixture of **6a** and **6b** (3:2) is obtained. Thus, the diastereoselectivity observed for addition of **5** to **1** is the result of thermodynamic control. The relative configuration of **6a** was determined by single-crystal X-ray diffraction analysis (see Figure 1).[14] Since the absolute configuration of the phosphine is known, the absolute configuration at C2 of **6a** (Scheme 1) is assigned as *S*.

Isolation of greater than the equilibrium amount of **6a** is rationalized on the basis of interconversion of **6a** and **6b** in solution and preferential crystallization of the major diastereomer, i.e. a second-order asymmetric transformation.[15] There are two possible mechanisms for the interconversion of diastereomers of **6a** and **6b**: (i) migration of the $Fe(CO)_3$ group from one face of the diene to the other or (ii) reversible nucleophilic attack by **5** to regenerate the symmetrical cation **1**. While the former possibility has been demonstrated for other optically active (diene)$Fe(CO)_3$ complexes, in general this requires substantially higher temperatures (ca. 120 °C).[5a] Because reversible phosphine addition to **1** has been demonstrated (*vide supra*), we favor the latter possibility for the interconversion of **6a** and **6b**. The relative lability of the C–P bond toward dissociation may be due to stereoelectronic effects. Steric hindrance between the C2 diene methyl substituent and the bulky phosphine orients the C–P bond perpendicular to the plane of the diene. This orients the C–P bond anti to the $Fe(CO)_3$ adjunct which should facilitate phosphine dissociation.

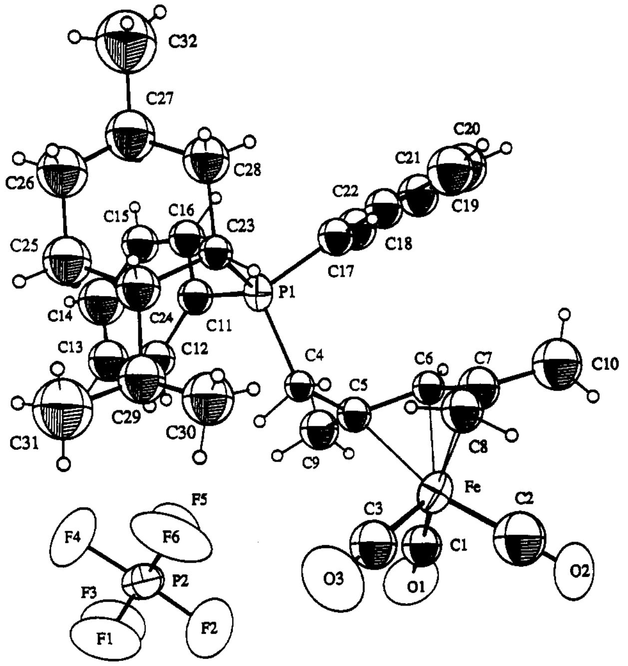


Figure 1. X-ray structure of complex **6a**, showing thermal ellipsoids (atom numbering is arbitrary). Selected bond lengths (Å): Fe–C(5), 2.16(2); Fe–C(6), 2.06(2); Fe–C(7), 2.04(2); Fe–C(8), 2.14(2); P(1)–C(4), 1.83(2); C(4)–C(5), 1.52(2); C(5)–C(6), 1.48(2); C(6)–C(7), 1.40(2), C(7)–C(8), 1.36(3).

In summation, we have shown that optically pure acyclic (diene)$Fe(CO)_3$ complexes can be prepared in good yield by second order asymmetric transformations of symmetrical (pentadienyl)$Fe(CO)_3^+$ cations. Attempts to convert **6a** into optically active (triene)$Fe(CO)_3$ complexes are in progress.

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Supplementary Material Available: Crystallographic data for **6a**, including tables of bond distances and angles, final fractional coordinates, and thermal parameters (6 pages). Ordering information is given on any current masthead page.

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[14] Compound **6a** crystallizes in the acentric space group $P2_12_12_1$ with the following unit cell dimensions: a = 10.513(5) Å, b = 16.928(6) Å, c = 19.218(6) Å, V = 3420.1 Å^3, and d_{calc} = 1.37 g cm^{-3}. Crystallographic data were collected with an Enraf-Nonius CAD-4/ω–2θ diffractometer using Mo K_α radiation. Reflections over a range of $2 \le 2\theta \le 50°$ were collected. Refinement to convergence of the 252 parameters on 1035 observed reflections with $F_o \ge 5\sigma(F_o)$ gave R = 0.058, R_w = 0.061, and GOF = 1.48.

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