

Preparation and reactions of tricarbonyl-(3-trimethylstannylcycloheptadienyl)iron hexafluorophosphate and tricarbonyl(3-trimethylsilylcycloheptadienyl)iron hexafluorophosphate

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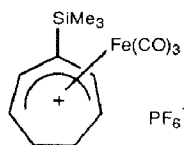
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Abstract

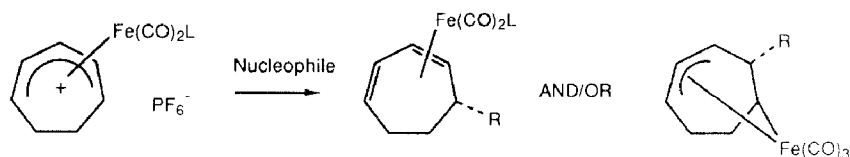
The preparation of tricarbonyl(2-trimethylstannylcycloheptadiene)iron and tricarbonyl(2-trimethylsilylcycloheptadiene)iron is described. Hydride abstraction from these complexes, using triphenylmethyl hexafluorophosphate, leads to tricarbonyl-(3-trimethyl-stannyl- and -silyl-cycloheptadienyl)iron complexes. Reaction of the trimethylstannyl-substituted dienyl complex with enolate nucleophiles gives the expected addition products, together with almost equal amounts of diene-Fe(CO)₃ complexes resulting from a nucleophile addition/protiodestannylation reaction. The trimethylsilylcycloheptadienyl complex is better behaved, giving good yields of nucleophile addition products. Cyanide anion adds to this complex to give exclusively the C(1) addition product, in contrast to tricarbonylcycloheptadienyliron cation, which gives mixtures of C(1) and C(2) addition products. Treatment of tricarbonyl(5-methyl-3-trimethylsilylcyclohepta-1,3-diene)iron with triphenylmethyl hexafluorophosphate resulted in loss of a methyl group to give tricarbonyl(3-trimethylsilylcycloheptadienyl)iron hexafluorophosphate, a highly unusual reaction.

Introduction

As part of an ongoing effort to utilize the stereochemical directing power of a transition metal moiety to accomplish stereocontrolled multiple functionalization of seven-membered carbocyclic rings, we have investigated the chemistry of cycloheptadienyliron complexes **1** which carry a silyl or stannyl group at C(3) of the dienyl ligand. The reasons for undertaking this study are that the parent cycloheptadienyl-Fe(CO)₃ complex **2a** is ill-behaved during its reactions with certain carbon nucleophiles [1]. While this has been partly remedied by using the triphenylphosphite derivative **2b**, there are still a few problems with regiocontrol [2]. Some examples are given here to illustrate these shortcomings.



- 1 (a) X = SnMe₃
(b) X = SiMe₃



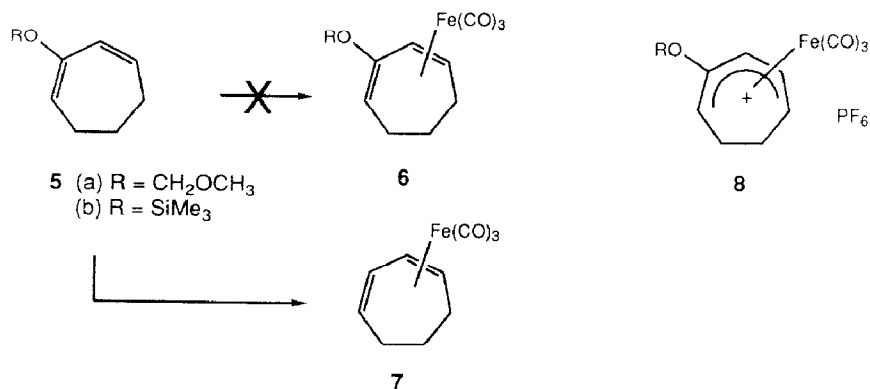
- 2 (a) L = CO
(b) L = P(OPh)₃

- 3 (a) L = CO, R = CH(CO₂Me)₂
(b) L = CO, R = Me
(c) L = P(OPh)₃, R = CH(CO₂Me)₂
(d) L = P(OPh)₃, R = Me
(e) L = CO, R = CN

- 4 (a) L = CO, R = CN
(b) L = P(OPh)₃, R = CN

Complex **2a** reacts with dimethyl sodiomalonate to give **3a** in good yield, but reaction with lithium dimethylcuprate gives **3b** in only 15–20% yield; complex **2b** gives both **3c** and **3d** in excellent (> 95%) yield, under the same reaction conditions; however, addition of cyanide to **2b** gives exclusively the σ,π -allyl derivative **4b**, while the same reaction on **2a** gives a mixture of **3e** and **4a** [2]. While complexes such as **4b** may be intrinsically interesting, from the standpoint of organic synthesis they are problematic, since there are currently no known methods to effect high yield decomplexation [1] to give organic products.

A substituted complex of type **1** might allow regiocontrolled addition of, e.g., cyanide to the dienyl terminus, due to either steric hindrance to attack at C(2) or C(4) or to changes in electron density and/or Frontier Molecular Orbital energies and coefficients at the dienyl carbon atoms [3]. We also anticipated that significant



- 5 (a) R = CH₂OCH₃
(b) R = SiMe₃

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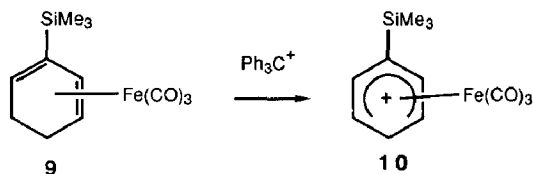
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changes in overall reactivity of the complexes might result from incorporation of substituents, leading to cleaner reactions with carbon nucleophiles compared with complex **2a**.

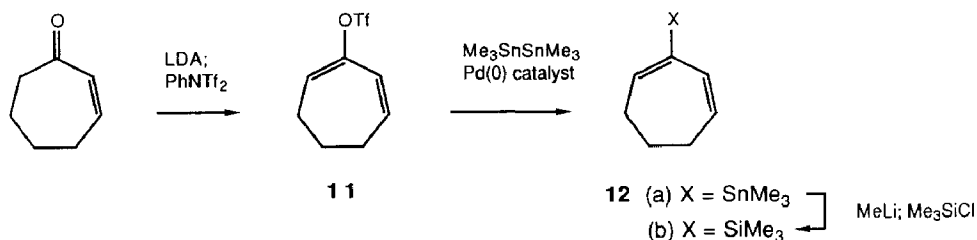
Prior to embarking on the preparation of complexes **1a** and **1b**, we had attempted the synthesis of alkoxy-substituted complexes, since we felt that electron-donating substituents would lead to better control of reactivity and would also allow facile conversion to cycloheptenone derivatives. While a variety 2-alkoxycycloheptadienes **5** were readily prepared, none of these could be converted to complexes **6** using a variety of known procedures [4]. In several cases, treatment with iron carbonyls resulted in an unusual deoxygenation reaction to give complex **7** (in low yield). This contrasts with the corresponding alkoxy-cyclohexadienes, which may be converted to the corresponding alkoxy-Fe(CO)₃ complexes without problem [5]. Since access to dienyliron systems **8** was thus denied, our attention was directed toward complex **1**.

Results and discussion

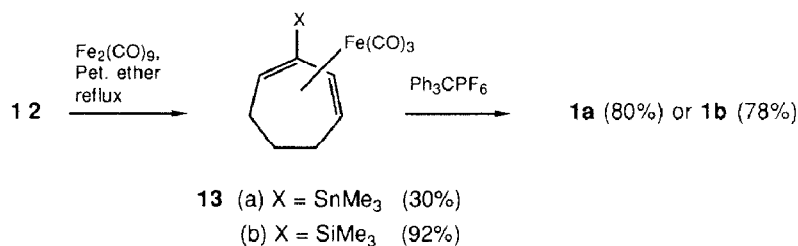
Paquette et al. [6] have reported the preparation and reactions of a range of trimethylsilyl-substituted cyclohexadiene-Fe(CO)₃ complexes such as **9**, which undergo regiospecific hydride abstraction on treatment with triphenylmethyl cation to generate complexes of type **10**. A modified Shapiro reaction was used to generate the required cyclohexadienes, but attempts to prepare the analogous cycloheptadiene by identical methods in our laboratory failed. Accordingly, we turned our attention to the palladium-catalyzed coupling of vinyl triflates with organotin compounds developed by Stille and co-workers [7] and modified by Wulff et al. [8].



Conversion of cycloheptenone to the corresponding dienol triflate **11** was readily accomplished in 74% yield by sequential treatment with lithium diisopropylamide and commercially available *N*-phenyltrifluoromethanesulfonimide, following a modification of the procedure of McMurry and Scott [9]. It may be noted that this procedure is superior to that originally reported for the preparation of **11**, which used triflic anhydride, sodium carbonate and cycloheptenone in dichloromethane as solvent, and which gives only 42% yield [10]. Treatment of **11** with hexamethylditin in the presence of lithium chloride and a catalytic amount (2 mole%) of tetrakis(triphenylphosphine)palladium(0) in refluxing tetrahydrofuran gave 2-trimethylstannylcyclohepta-1,3-diene (**12a**) in 71% yield. This compound was readily converted to 2-trimethylsilylcyclohepta-1,3-diene (**12b**) in 75% yield, by sequential treatment with methyllithium and chlorotrimethylsilane [11].

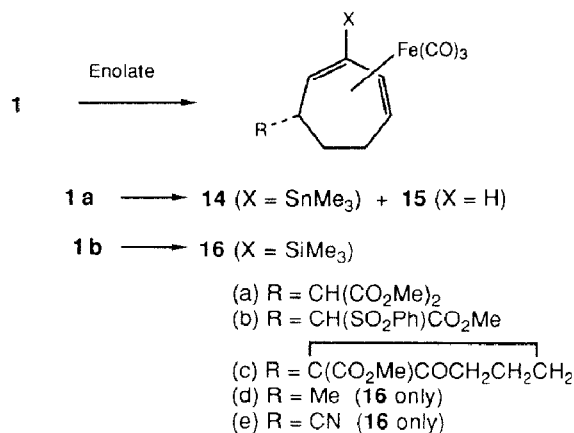


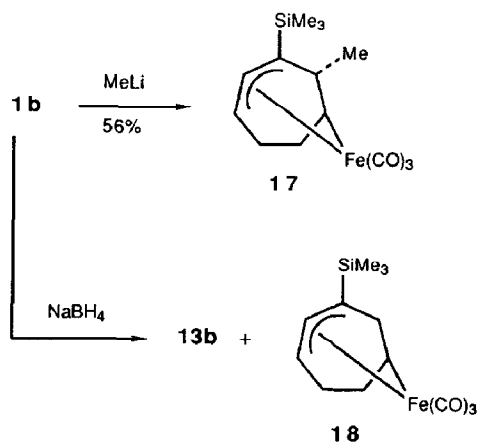
Conversion of **12a** to complex **13a** proceeded in low yield under a variety of conditions. In many cases considerable decomposition was noted, and destannylation to give complex **7** accompanied the formation of **13a**. The best conditions were the use of $\text{Fe}_2(\text{CO})_9$ in petroleum ether at reflux (ca. 50°C), which gave **13a** in 30% yield after purification by chromatography. In contrast, diene **12b** was converted to complex **13b** in 92% yield without problem, consistent with the fact that the C–Si bond is much stronger than the C–Sn bond [12]. Hydride abstraction from **13a** and **13b** proceeded cleanly to furnish complexes **1a** and **1b** in 80 and 78% yield, respectively, free from regioisomeric dienyl complexes according to ^1H NMR spectroscopy.



Next, the reactions of complexes **1a** and **1b** with a range of carbon nucleophiles was studied. Again, the trimethyltin derivative was problematic, generally giving mixtures of complexes **14** and **15**, corresponding to simple nucleophile addition and destannylation, respectively. These reactions are summarized below.

In contrast, the trimethylsilylcycloheptadienyl- $\text{Fe}(\text{CO})_3$ complex (**1b**) was well-behaved toward nucleophile addition, giving good yields of complexes **16**. Of particular significance, addition of cyanide gave the diene complex **16e** in 75% yield. Thus, different regiocontrol may be obtained by incorporation of the trimethylsilyl group (compare with the results for complexes **2a** and **2b** discussed earlier). However, this behavior is not exclusive, since methyllithium reacted with **1b** at C(2) to give complex **17** in 56% yield, while sodium borohydride gave an equimolar mixture of **13b** and **18**. The formation of **17** does not present a problem, since the reaction of **1b** with lithium dimethylcuprate gave adduct **16d**, albeit in only

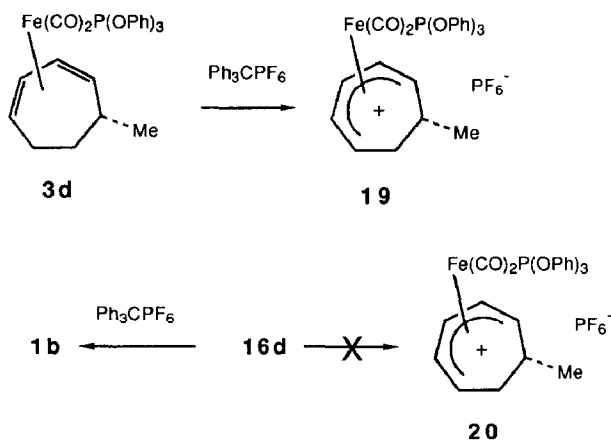




moderate yield (39%). Better results were obtained using the higher order cuprate $\text{Me}_2\text{Cu}(\text{CN})\text{Li}_2$ [13], which gave **16d** in 62% yield.

We have previously noted [2] that the regiochemistry of nucleophile additions to complex **2b** appears to be a function of nucleophile hardness. In general soft nucleophiles, such as stabilized enolates, cuprates, thiolates, etc., add to the dienyl terminus, while harder nucleophiles, such as alkylolithiums, hydride, etc., add to C(2) to give complexes of general structure **4**. Cyanide appears to be near the borderline in terms of hardness/softness [4], but is more commonly referred to as a soft nucleophile. Clearly, the relationship between electrophile LUMO and nucleophile HOMO energies is of considerable importance in this respect. The crossover that occurs on going from complex **2b** to complex **1b** most likely reflects a significant lowering of the LUMO energy of the complex, so that the reaction of cyanide with these complexes changes from being charge controlled (addition to C(2)) to orbital controlled (addition to C(1)) [2,3].

Our earlier studies demonstrated that the products of nucleophile addition, such as **3d**, could be subjected to a second hydride abstraction to generate substituted



dienyl complexes, in this case **19**. The chemistry of these systems is significantly altered by attachment of the trimethylsilyl group, and complex **16d** undergoes methyl group abstraction on treatment with triphenylmethyl hexafluorophosphate, to generate **1b** as the only isolable dienyl complex. This is fully consistent with the strong directing power of the Me_3Si group observed during the conversion of **9** to **10** and of **13b** to **1b**, and reflects a strong preference for electron accepting substituents to occupy C(3) or C(1) of the complexed dienyl ligand, a phenomenon also noted for the methoxycarbonyl group [15]. The *endo*-C(7)-hydride is not removed because stereoelectronic effects dictate elimination of groups having antiperiplanar alignment with the carbon-metal bond of the diene- $\text{Fe}(\text{CO})_3$ system [16]. Abstraction of the C(5)-hydride would lead to complex **20**, which is highly unstable relative to **1b**. Thus, the trimethylsilyl group exerts a profound effect, sufficient to lead to scission of the C- CH_3 bond, which is unprecedented for these complexes.

Experimental

General

Infrared spectra were recorded on a Perkin-Elmer 1420 Ratio Recording Spectrophotometer, and NMR spectra were obtained using a Varian XL-200 instrument, employing tetramethylsilane as an internal standard. Mass spectra were obtained through the Midwest Center for Mass Spectrometry, at the University of Nebraska, Lincoln, an NSF Regional Facility. Combustion analyses were performed by Galbraith, Inc., Knoxville, Tennessee. All compounds that were purified by preparative TLC were shown to be homogeneous on TLC subsequent to their purification. Melting points were obtained on a Fisher-Johns Melting Point Apparatus and are uncorrected. All glassware used in reactions performed under a dry argon atmosphere was oven- or flame-dried prior to use.

Materials

Tetrahydrofuran (THF) was distilled from sodium/benzophenone, methylene chloride (CH_2Cl_2) was distilled from calcium hydride, and diethyl ether was distilled from lithium tetrahydroaluminate, all immediately prior to use. Petroleum ether (b.p. 35–60°C), and toluene were dried with magnesium sulfate prior to use. Acetone was stored over 4A Molecular Sieves under a nitrogen atmosphere. Argon was purified by passing through 1 m columns of, in order, Rid-Ox oxygen scavenger, activated silica and 4A Molecular Sieves. Cycloheptenone was prepared by the procedure of Garbisch [17]. Other materials were purchased from commercial sources and used as obtained.

Cyclohepta-1,3-dien-2-yl-trifluoromethanesulfonate (11)

A solution of lithium diisopropyl amide was prepared by adding 18.5 ml of a 2.5 *M* (hexanes) solution of *n*-butyllithium (46.2 mmol) to a stirred solution of diisopropylamine (4.66 g, 6.60 ml, 46.2 mmol) in 100 ml of THF, under an argon atmosphere at 0°C. The mixture was stirred at 0°C for 45 min, then cooled to –78°C, and cycloheptenone (4.63 g, 4.68 ml, 42.0 mmol) was added dropwise via syringe.

The clear, yellow solution was stirred at –78°C for 2 h, then a solution of *N*-phenyltrifluoromethanesulfonimide (15.0 g, 42.0 mmol) in 40 ml of THF was

added to the cooled solution over 10 min. The orange, cloudy solution was stirred at 0 °C overnight, during which time the solution turned clear and orange. The solvent was removed under reduced pressure, the resulting semi-solid was washed repeatedly with hexanes, and the slurry was filtered through a glass sinter until the solid was nearly white. The orange hexanes washings were combined, and the solvent removed under reduced pressure to yield the crude product as an orange oil. The product was purified by column chromatography (hexanes, SiO₂), yielding the triflate as a bright yellow, air-stable liquid (7.52 g, 75%). This material was spectroscopically identical to that reported in the literature (lit. yield, 42%) [10].

Cyclohepta-1,3-dien-2-yl-trimethylstannane (12a)

Under an atmosphere of argon, a mixture of **11** (4.54 g, 18.75 mmol), hexamethylditin (5.58 g, 17.05 mmol), lithium chloride (5.06 g, 119.3 mmol), tetrakis(triphenylphosphine)palladium(0) (0.394 g, 0.34 mmol) in 100 ml of THF was heated at reflux for 3.5 h, until thin layer chromatography showed the complete consumption of hexamethylditin. The reaction mixture was partitioned between pH 7 buffer and ether. The organic layer was dried (MgSO₄), filtered, and the solvent removed under reduced pressure. Chromatography (hexanes, SiO₂) gave **12a** as a clear, colorless oil (3.09 g, 71%). ¹H NMR (200 MHz, CDCl₃): δ 0.13 (s, 9H, Sn-CH₃), 1.87–1.92 (m, 2H), 2.24–2.36 (m, 4H), 5.81–5.90 (m, 1H, =C-H), 5.92 (t, *J* 11.3 Hz, 1H, =C-H), 6.06 (t, *J* 5.6 Hz, 1H, =C-H). IR (hexanes): 1585, 1185, 1035, 850, 755 cm⁻¹.

Tricarbonyl(1-4-η-2)-trimethylstannyl-cyclohepta-1,3-diene)iron (13a)

Method A. Under an atmosphere of argon, a solution of **12a** (42 mg, 0.164 mmol), diiron nonacarbonyl (119 mg, 0.327 mmol), and 10 ml of petroleum ether was heated at reflux for 24 h. The cooled reaction mixture was filtered through a plug of Celite 545, and the solvent was removed under reduced pressure. Chromatography (hexanes, SiO₂) yielded the product as a yellow oil (19 mg, 30%). ¹H NMR (200 MHz, CDCl₃): δ 0.26 (s, 9H, Sn-CH₃), 1.2–1.5 (m, 2H), 1.8–2.1 (m, 4H), 2.95–3.05 (m, 1H, =C-H), 3.1–3.2 (m, 1H, =C-H), 4.91 (d, *J* 7.4 Hz, 1H, =C-H). IR (hexanes): 2015, 1965, 505 cm⁻¹. HRMS: Found: 397.9610. C₁₃H₁₈FeSnO₃ (*M*⁺) calcd.: 397.9653.

Method B. Same as above, except that the solvent system was acetone heated at 40 °C for 24 h. Yield: 18%.

Method C. Same as above, except that the solvent system was toluene heated at reflux for 24 h. Yield: 22%.

Method D. Under an atmosphere of argon, a solution of **12a** (600 mg, 2.33 mmol), iron pentacarbonyl (1142 mg, 0.766 ml, 5.83 mmol), in 15 ml of di-*n*-butyl ether was heated at reflux for 24 h. Workup as above gave the product. Yield: 185 mg (20%).

Tricarbonyl(1-5-η-3-trimethylstannylcyclohepta-1,3-dienylium)iron hexafluorophosphate (1a)

Under an atmosphere of argon, triphenylmethyl hexafluorophosphate (393 mg, 1.01 mmol) was added to a stirred solution of **13a** (393 mg, 0.990 mmol) in 15 ml of methylene chloride at room temperature. The mixture was stirred for 20 h, then poured into 100 ml of wet ether. The precipitated solid was collected by filtration,

and washed with ether. Drying under vacuum gave the product as a yellow solid (430 mg, 80%). ^1H NMR (200 MHz, CD_3CN): δ 0.56 (s, 9H, $\text{Sn}-\text{CH}_3$), 1.7–2.1 (m, 2H), 2.6–2.8 (m, 2H), 4.85–5.05 (m, 2H, H(1), H(5)), 5.74 (d, J 8 Hz, 2H, H(2), H(4)). IR (CH_2Cl_2): 2080, 2030, 835 cm^{-1} . Anal. Found: C, 29.08 H, 3.09. $\text{C}_{13}\text{H}_{17}\text{FeO}_3\text{SnPF}_6$ calcd.: C, 28.87; H, 3.17%.

Addition of enolate nucleophiles to complex 1a

General procedure. Under an argon atmosphere, the indicated amount of nucleophile precursor was added to a stirred suspension of sodium hydride (60% dispersion, 4.4 mg, 0.11 mmol) in 2 ml of THF at room temperature. The mixture was stirred for 30 min, then complex **1a** (54 mg, 0.10 mmol) was added in one portion. Stirring was continued for another 30 min, after which time the reaction solution was diluted with ether, then washed with water, brine, then dried (MgSO_4), filtered, and the solvent was removed under reduced pressure. Preparative TLC (8/1 hexanes/ethyl acetate; SiO_2 , 1 mm layer) yielded two bands. The band with the higher R_f was the desired product, and the band with the lower R_f was the protio-destannylated product.

*Tricarbonyl[methyl(2–5- η -3-trimethylstannylcyclohepta-2,4-dienyl)phenylsulfonyl acetate]iron (**14b**)*

The reaction employing methyl phenylsulfonyl acetate (24 mg, 18.4 μl , 0.11 mmol) gave the product (33 mg, 54%) as a yellow oil, a 1.47/1 mixture of diastereomers. ^1H NMR (200 MHz, CDCl_3): δ 0.20, 0.29 (2s, 9H, $\text{Sn}-\text{CH}_3$), 1.1–1.3 (m, 1H), 1.4–1.6 (m, 1H), 1.8–2.1 (m, 1H), 2.6–2.8 (m, 1H), 2.8–3.0 (m, 1H), 3.1–3.3 (m, 1H), 3.62, 3.64 (2s, 3H, CO_2CH_3), 3.72, 3.80 (2d, J 10 Hz, 1H, SO_2CH), 4.84, 4.92 (2d, J 8 Hz, 1H), 7.5–7.8 (m, 3H, Ar–H), 7.93 (t, J 8 Hz, 2H, Ar–H), IR (hexanes): 2020, 1965, 1735, 1220, 1150, 1135, 1075 cm^{-1} . HRMS Found: 553.9864. $\text{C}_{20}\text{H}_{26}\text{O}_5\text{FeS}^{120}\text{Sn}$ ($M - 2\text{CO}$) calcd.: 553.9879. Found: 525.9934; for $\text{C}_{19}\text{H}_{26}\text{O}_4\text{FeS}^{120}\text{Sn}$ ($M - 3\text{CO}$) calcd.: 525.9913.

The second band was the protio-destannylated product tricarbonyl[methyl(2–5- η -cyclohepta-2,4-dienyl)phenylsulfonyl acetate]iron (**15b**), obtained as a yellow oil (16 mg, 36%), a 1.56/1 mixture of diastereomers. ^1H NMR (200 MHz, CDCl_3): δ 1.0–1.3 (m, 1H), 2.0–2.3 (m, 1H), 2.8–3.1 (m, 2H), 3.71, 4.13 (2s, and m, 4H, CO_2CH_3 , SO_2CH), 5.2–5.5 (m, 2H), 7.4–7.7 (m, 3H), 7.95 (d, J 7.3 Hz, 2H). IR (hexanes): 2025, 1970, 1745, 1265, 1150, 1080 cm^{-1} . HRMS: Found: 390.0214. $\text{C}_{17}\text{H}_{18}\text{FeO}_5\text{S}$ ($M - 2\text{CO}$) calcd.: 390.0241. Found: 362.0286. $\text{C}_{16}\text{H}_{18}\text{FeO}_4\text{S}$ ($M - 3\text{CO}$) calcd.: 362.0257.

*Tricarbonyl[methyl-1-(2–5- η -3-trimethylstannylcyclohepta-2,4-dienyl)-2-oxocyclopentane carboxylate]iron (**14c**)*

The reaction employing methyl 2-oxocyclopentane carboxylate (15.6 mg, 13.7 μl , 0.11 mmol) gave the product (30 mg, 56%) as a yellow oil, a 1.37/1 mixture of diastereomers. ^1H NMR (200 MHz, CDCl_3): δ 0.27 (s, 9H, $\text{Sn}-\text{CH}_3$), 0.8–1.1 (m, 2H), 1.2–1.4 (m, 2H), 1.8–2.2 (m, 4H), 2.3–2.6 (m, 3H), 2.9–3.3 (m, 2H), 3.67, 3.75 (2s, 3H, CO_2CH_3), 4.85 (t, J 8 Hz, 1H). IR (hexanes): 2020, 1960, 1745, 1715, 1245, 1210, 1190, 1120, 1095 cm^{-1} . HRMS: Found: 482.0218. $\text{C}_{18}\text{H}_{26}\text{FeO}_4\text{Sn}$ ($M - 2\text{CO}$) calcd.: 482.0185. Found: 454.0227. $\text{C}_{17}\text{H}_{26}\text{FeO}_3\text{Sn}$ ($M - 3\text{CO}$) calcd.: 454.0285.

The second band was the protio-destannylated product tricarbonyl[methyl-1-(2-5- η -cyclohepta-2,4-dienyl)-2-oxo-cyclopentane carboxylate]iron (**15c**), obtained as a yellow oil (12 mg, 32%), a 1.23/1 mixture of diastereomers. ^1H NMR (200 MHz, CDCl_3): δ 0.8–1.4 (m, 2H), 1.8–2.6 (m, 9H), 2.9–3.2 (m, 2H), 3.64, 3.76 (2s, 3H, CO_2CH_3), 5.2–5.4 (m, 2H). IR (hexanes): 2020, 1965, 1748, 1715, 1215, 1140, 1130, 1100 cm^{-1} .

*Tricarbonyl[dimethyl(2-5- η -3-trimethylstannylcyclohepta-2,4-dienyl)malonate]iron (**14a**)*

The reaction employing dimethyl malonate (14.5 mg, 12 μl , 0.11 mmol) gave the product (22 mg, 42%) as a yellow oil. ^1H NMR (200 MHz, CDCl_3): δ 0.26 (s, 9H, $\text{Sn}-\text{CH}_3$), 0.95–1.2 (m, 1H), 1.25–1.45 (m, 1H), 1.9–2.2 (m, 2H), 2.7–2.9 (m, 2H), 3.1–3.3 (m, 1H), 3.21 (d, J 6.3 Hz, 1H), 3.72 (s, 6H, CO_2CH_3), 4.89 (d, J 7.4 Hz, 1H). IR (hexanes): 2015, 1960, 1745, 1730, 1315, 1245, 1200, 1140, 750 cm^{-1} . HRMS Found: 471.9975. $\text{C}_{16}\text{H}_{24}\text{FeO}_5\text{Sn}$ ($M - 2\text{CO}$) calcd.: 472.0017.

The second band was the protio-destannylated product tricarbonyl[dimethyl(2-5- η -cyclohepta-2,4-dienyl)malonate]iron [**15a**], obtained as a yellow oil (12 mg, 33%). ^1H NMR (200 MHz, CDCl_3): δ 1.1–1.5 (m, 2H), 1.9–2.2 (m, 2H), 2.6–2.9 (m, 2H), 3.0–3.1 (m, 1H), 3.26 (d, J 6.4 Hz, 1H), 3.66, 3.82 (2d, J 3.0 Hz, 1H), 3.74, 3.75 (2s, 6H, CO_2CH_3), 5.15–5.35 (m, 1H). IR (hexanes): 2020, 1965, 1750 (sh), 1735 cm^{-1} . HRMS Found: 308.0347. $\text{C}_{13}\text{H}_{16}\text{O}_5\text{Fe}$ ($M - 2\text{CO}$) calcd.: 308.0347. Found: 280.0400. $\text{C}_{12}\text{H}_{16}\text{O}_4\text{Fe}$ ($M - 3\text{CO}$) calcd.: 280.0394.

*Cyclohepta-1,3-dien-2-yl-trimethylsilane (**12b**)*

Under an argon atmosphere, methylolithium (7.93 ml of a 1.4 M solution in ether, 11.1 mmol) was added dropwise, over 10 min, to a stirred solution of **12a** (2.83 g, 11.0 mmol) in 75 ml of THF at -78°C . The solution was stirred at -78°C for an additional 30 min, then chlorotrimethylsilane (1.79 g, 2.09 ml, 16.5 mmol) was added via syringe. The system was allowed to warm slowly to room temperature over 3.5 h, the reaction mixture was partitioned between ether and water. The organic layer was washed with brine, dried (MgSO_4), filtered, and the solvent was removed under reduced pressure. Distillation ($65\text{--}66^\circ\text{C}/26\text{ mmHg}$) gave the product as a clear, colorless oil (1.37 g, 75%). ^1H NMR (200 MHz, CDCl_3): δ 0.06 (s, 9H, $\text{Si}-\text{CH}_3$), 1.8–2.0 (m, 2H), 2.2–2.4 (m, 4H), 5.8–6.0 (m, 2H, H(1), H(3), 6.18 (t, J 5.6 Hz, 1H, H(4)). IR (hexanes): 1575, 1325, 1305, 1240, 1060, 990, 835 cm^{-1} . HRMS Found: 166.1183. $\text{C}_{10}\text{H}_{18}\text{Si}$ calcd.: 166.1152.

*Tricarbonyl(1-4- η -2-trimethylsilylcyclohepta-1,3-diene)iron (**13b**)*

Under an argon atmosphere, and protected from light by a layer of aluminium foil, a mixture of the diene **12b** (1.83 g, 11.0 mmol), and diiron nonacarbonyl (8.0 g, 22 mmol), in 125 ml of petroleum ether was heated at reflux for 24 h. The solution was allowed to cool to room temperature, then another 8.0 g of diiron nonacarbonyl was added, and the solution was heated at reflux for another 24 h. The reaction mixture was allowed to cool, then filtered through a plug of Celite 545, and the solvent was removed under reduced pressure to yield a dark green oil. Column chromatography (hexanes, basic alumina, activity I) gave the product as a yellow oil (3.09 g, 92%). ^1H NMR (200 MHz, CDCl_3): δ 0.22 (s, 9H, $\text{Si}-\text{CH}_3$), 1.1–1.2 (m,

1H, H(6_{exo})), 1.3–1.4 (m, 1H, H(6_{endo})), 1.8–2.1 (m, 4H, H(5), H(7)). 3.1–3.2 (m, 1H), 3.2–3.3 (m, 1H) (H(1), H(4)), 5.00 (d, *J* 7.7 Hz, 1H, H(3)). IR (hexanes): 2030, 1965, 1245, 835 cm⁻¹.

Tricarbonyl(1-5-η-3-trimethylsilylcyclohepta-1,3-dienylium)iron hexafluorophosphate (1b)

Under an argon atmosphere, a solution containing **13b** (900 mg, 2.94 mmol), triphenylmethyl hexafluorophosphate (1.253 g, 3.23 mmol), and 50 ml of methylene chloride was stirred at room temperature for 27 h. The mixture was poured into 300 ml of wet ether, and the precipitated solid was collected by filtration and washed with ether. Drying under vacuum gave the product as a yellow solid (1.034 g, 78%). ¹H NMR (200 MHz, CD₃CN): δ 0.52 (s, 9H, Si-CH₃), 1.85 (d, *J* 10.3 Hz, 2H, H(6_{exo}), H(7_{exo})), 2.64–2.73 (m, 2H, H(6_{endo}), H(7_{endo})), 4.95–5.02 (m, 2H, H(1), H(5)), 5.83 (d, *J* 9.2 Hz, 2H, H(2), H(4)). IR (CH₂Cl₂): 2060, 2010, 835 cm⁻¹. Anal. Found: C, 34.59; H, 3.83. C₁₃H₁₇FeO₃SiPF₆ calcd.: C, 34.69; H, 3.87%.

Addition of stabilized enolate nucleophiles to the salt 1b

General procedures. Under an argon atmosphere, the indicated amount of nucleophile precursor was added to a stirred suspension of sodium hydride (60% dispersion, 9.8 mg, 0.244 mmol) in 3 ml of the THF at room temperature. The mixture was stirred for 30 min, then the dienyl iron salt **1b** (100 mg, 0.222 mmol) was added in one portion. Stirring was continued for another 30 min, after which time the reaction solution was diluted with ether, then washed with water, brine, dried (MgSO₄), filtered, and the solvent removed under reduced pressure. The product was isolated by preparative TLC (4/1 hexanes/ethyl acetate; SiO₂; 1 mm layer).

Tricarbonyl[dimethyl(2-5-η-3-trimethylsilylcyclohepta-2,4-dienyl)malonate]iron (16a)

The reaction employing dimethyl malonate (32.3 mg, 28 μl, 0.244 mmol) gave the product (86 mg, 89%) as a yellow oil. ¹H NMR (200 MHz, CDCl₃): δ 0.20 (s, 9H, Si-CH₃), 0.85–1.1 (m, 1H, H(7_{exo})), 1.2–1.4 (m, 1H, H(7_{endo})), 1.9–2.1 (m, 2H, H(6)), 2.64 (s, 1H, H(2)), 2.6–2.8 (m, 1H, H(1)), 3.09 (d, *J* 8.2 Hz, 1H, C-H), 3.15–3.30 (m, 1H, H(5)), 3.67 (s, 3H, CH₃), 3.71 (s, 3H, CH₃), 4.99 (d, *J* 7.4 Hz, 1H, H(4)). IR (hexanes): 2030, 1965, 1755, 1745 cm⁻¹. HRMS Found: 380.0733. C₁₆H₂₄FeO₅Si (*M* - 2CO) calcd.: 380.0757. Found: 352.0791. C₁₅H₂₄FeO₄S (*M* - 3CO) calcd.: 352.0797.

Tricarbonyl[methyl(2-5-η-3-trimethylsilylcyclohepta-2,4-dienyl)-2-oxocyclopentane carboxylate]iron (16c)

The reaction employing methyl 2-oxocyclopentane carboxylate (34.7 mg, 30 μl, 0.244 mmol) gave the product (78 mg, 79%) as a yellow oil. ¹H NMR (200 MHz, CDCl₃): δ 0.25 (s, 9H, Si-CH₃), 0.7–1.2 (m, 2H, H(7)), 1.7–2.2 (m), 2.2–2.6 (m, 9H), 2.9–3.1 (m), 3.1–3.2 (m), (2H, H(2), H(5)), 3.66, 3.75 (2s, 3H, CO₂CH₃), 5.02 (d, *J* 7.1 Hz, 1H, H(4)). IR (hexanes): 2030, 1970, 1750, 1720 cm⁻¹. HRMS Found 390.0949. C₁₈H₂₆FeO₄Si (*M* - 2CO) calcd.: 390.0950. Found: 362.0999. C₁₇H₂₆FeO₃Si (*M* - 3CO) calcd.: 362.1003.

Tricarbonyl[methyl(2-5-η-3-trimethylsilylcyclohepta-2,4-dienyl)phenylsulfonyl acetate]-iron (16b)

The reaction employing methyl phenylsulfonyl acetate (52 mg, 41 μ l, 0.244 mmol) gave the product (78 mg, 68%) as a yellow oil, a 1.48/1 mixture of diastereomers. ^1H NMR (200 MHz, CDCl_3): δ 0.161, 0.267 (2s, 9H, Si-CH₃), 0.9–1.1 (m, 1H, H(7_{exo})), 1.4–2.2 (m, 3H, H(7_{endo})), 2.58 (m, 1H, H(1)), 3.05 (br s, 1H, H(2)), 3.1–3.2 (m, 1H, H(5)), 3.60, 3.63 (2s, 3H, CO₂CH₃), 3.68, 3.78 (2d, J 7.6, 6.0 Hz, 1H), 5.02 (dd, J 11.4, 7.6 Hz, 1H, H(4)), 7.5–7.8 (m, 3H, Ar-H), 7.9–8.0 (m, 2H, Ar-H). IR (hexanes): 2020, 1965, 1735, 1320, 1240, 1150, 730, 605 cm^{-1} . HRMS Found: 462.0612. $\text{C}_{20}\text{H}_{26}\text{FeO}_5\text{SSi}$ ($M - 2\text{CO}$) calcd.: 462.0640. Found: 434.0644. $\text{C}_{19}\text{H}_{26}\text{FeO}_4\text{SSi}$ ($M - 3\text{CO}$) calcd.: 434.0705.

Tricarbonyl(1-4-η-5-cyano-3-trimethylsilylcyclohepta-1,3-diene)iron (16e)

With stirring, the dienyl iron salt **1b** (332 mg, 0.738 mmol) was taken up in 30 ml of THF/3 ml of H₂O, and the solution was cooled to 0 °C. Sodium cyanide (43 mg, 0.885 mmol) was added in one portion, and the system was allowed to come to room temperature over 4 h. After this time, the mixture was partitioned between ether and water, and the organic layer washed with brine, dried (MgSO₄), filtered, and the solvent removed under reduced pressure. Column chromatography (4/1 hexanes/ethyl acetate; SiO₂) yielded the product as a yellow solid, m.p. 78–80 °C (195 mg, 75%). ^1H NMR (200 MHz, CDCl_3): δ 0.24 (s, 9H, Si-CH₃), 0.90–1.2 (m, 1H, H(6_{exo})), 1.6–1.8 (m, 1H, H(6_{endo})), 2.15–2.40 (m, 2H, H(7)), 2.79 (app s, 1H, H(4)), 3.15–3.25 (m, 1H, H(1)), 4.05–4.20 (m, 1H, H(3)), 5.01 (d, J 7.8 Hz, 1H, H(2)). IR (hexanes): 2035, 1970, 1245, 995, 830 cm^{-1} . HRMS: Molecular ion not observed. Found: 305.0286. $\text{C}_{13}\text{H}_{17}\text{FeO}_3\text{Si}$ ($M - \text{CN}$) calcd.: 305.0318. Found: 247.0477. $\text{C}_{11}\text{H}_{17}\text{FeSi}$ ($M - 3\text{CO}$) calcd.: 247.0486.

Tricarbonyl(1-4-η-5-methyl-3-trimethylsilylcyclohepta-1,3-diene)iron (16d)

Method A. Dimethylolithium cuprate was made by adding methylolithium (approx. 317 μ l of a 1.4 M /Et₂O solution, approx 0.44 mmol) to a stirred suspension of cuprous iodide (42 mg, 0.22 mmol) in 5 ml of ether at 0 °C under an argon atmosphere, just until the solution clears. The dienyl iron salt **1b** (50 mg, 0.11 mmol) was added in one portion, and the solution was stirred at 0 °C for 1 h. The solution was then poured into 10 ml of saturated aqueous NH₄Cl, and stirred for 15 min. The mixture was poured into ether, and the organic layer dried (MgSO₄), filtered, and the solvent removed under reduced pressure. Preparative TLC (hexanes; SiO₂; 1 mm layer) yielded the product as a yellow oil (14 mg, 39%). ^1H NMR (200 MHz, CDCl_3): δ 0.23 (s, 9H, Si-CH₃), 0.60–0.80 (m, 1H, H(6_{exo})), 0.91 (d, J 6.7 Hz, 3H, CH₃), 1.2–1.3 (m, 1H, H(6_{endo})), 1.8–2.1 (m, 3H, H(5), H(7)), 2.77 (s, 1H, H(4)), 3.1–3.2 (m, 1H, H(1)), 4.99 (d, J 7.3 Hz, 1H, H(2)). IR (hexanes): 2025, 1965, 1240, 830, 605 cm^{-1} . HRMS: No molecular ion observed. Found: 292.0580. $\text{C}_{13}\text{H}_{20}\text{FeO}_2\text{Si}$ ($M - \text{CO}$) calcd.: 292.0585. Found: 264.0640. $\text{C}_{12}\text{H}_{20}\text{FeOSi}$ ($M - 2\text{CO}$) calcd.: 264.0612. Found: 234.0527. $\text{C}_{11}\text{H}_{18}\text{FeSi}$ ($M - 3\text{CO} - \text{H}_2$) calcd.: 234.0529.

Method B. Cuprous cyanide (118 mg, 1.32 mmol) was added to a previously flame-dried flask under a stream of argon, then taken up in 35 ml of THF. The solution was cooled to –78 °C, then methylolithium (1.88 ml, 1.4 M /Et₂O, 2.63 mmol) was added. The solution was warmed to 0 °C for 5 min, then recooled to –78 °C. The iron salt **1b** (296 mg, 0.658 mmol) was added in one portion, and the

reaction mixture turned orange and clear. The solution was stirred at -78°C for 1 h, then allowed to warm to room temperature, then poured into a mixture of 90 ml saturated aqueous NH_4Cl /10 ml conc. NH_4OH and stirred for 15 min. The biphasic solution was extracted with ether, and the organic layers washed with brine, dried (MgSO_4), filtered, and the solvent removed under reduced pressure. The product was purified by preparative TLC as before (132 mg, 63%), and was identical to the material obtained by the use of lithium dimethyl cuprate.

Tricarbonyl[3-5- η -1- σ -(2-methyl-3-trimethylsilylcyclohept-3-enyl)]iron (17)

Under an atmosphere of argon, a solution of the dienyl iron salt **1b** (100 mg, 0.222 mmol) in 10 ml of methylene chloride was cooled to -78°C . Methyllithium (175 μl of a 1.4 *M*/ Et_2O solution, 0.244 mmol) was added, and the solution was stirred for 2 h at -78°C . The reaction mixture was warmed to room temperature, diluted with methylene chloride, washed with water, dried (MgSO_4), filtered, and the solvent removed under reduced pressure. Preparative TLC (8/1 hexanes/ethyl acetate; SiO_2 ; 1 mm layer) yielded the product as a yellow oil (40 mg, 56%). ^1H NMR (200 MHz, CDCl_3): δ 0.19 (s, 9H, Si- CH_3), 0.72 (d, *J* 7.0 Hz, 3H, CH_3) 1.2–1.3 (m, 1H, $\text{H}(7_{\text{exo}})$), 1.6–2.0 (m, 3H, $\text{H}(6)$, $\text{H}(7_{\text{endo}})$), 2.2–2.4 (m, 1H, $\text{H}(1)$), 2.7–2.9 (m, 1H, $\text{H}(2)$), 4.21 (d, *J* 8.4 Hz, 1H, $\text{H}(4)$), 4.87 (s, *J* 8.4 Hz, 1H, $\text{H}(5)$). IR (hexanes): 2020, 1960, 1240, 825 cm^{-1} . HRMS Found: 292.0588. $\text{C}_{13}\text{H}_{20}\text{O}_2\text{FeSi}$ (*M* – CO) calcd.: 292.0567. Found: 264.0621. $\text{C}_{12}\text{H}_{20}\text{OFesi}$ (*M* – 2CO) calcd.: 264.0664.

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