Organometallics 1984, 3, 560–567

Synthesis, Reactivity, and Electronic Structure of (2-(Trimethylsilyl)-1,3-cyclohexadiene)iron Tricarbonyl Complexes[1]

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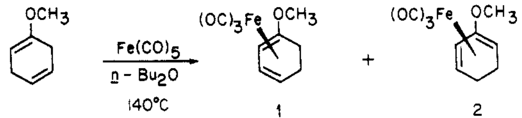
Received November 22, 1983

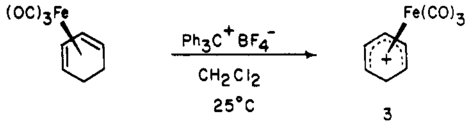
Reaction of several 2-(trimethylsilyl)-1,3-cyclohexadiene derivatives with excess iron pentacarbonyl in refluxing di-*n*-butyl ether produced the unrearranged $Fe(CO)_3$ complexes. Hydride abstraction from these organometallics with triphenylcarbenium tetrafluoroborate proved to be completely regiospecific in each instance, leading only to silyl-symmetric η^5 cations. These directive properties surfaced again during various nucleophilic additions [diethyl sodiomalonate, ethyl (phenylsulfonyl)sodioacetate, trimethyl[(4,5-dihydro-2-furanyl)oxy]silane]. Subsequent decomplexation with trimethylamine *N*-oxide gave the free ligands. The electronic structure and reactivity of the $Fe(CO)_3$ complexes was examined by tandem photoelectron spectroscopy and INDO calculations. Complete analysis of the first three bands, assignable to five transitions, was possible. The regiospecificity of hydride abstraction is analyzed in terms of electronic effects operating predominantly within the HOMO.

Following Hallam and Pauson's correct formulation in 1958 of the structure of dienyliron tricarbonyl complexes,[5] this class of substances became the focus of intense theoretical and physical–organic interest.[6] More recently, tricarbonyl(cyclohexadienyl)iron complexes have been systematically investigated and are finding their way into the arsenal of the synthetic organic chemist.[7,8] Various procedures are available for the preparation of these substrates. The methodology perhaps most frequently used, which is due to Cais and Maoz[9] as modified by Birch,[10] involves heating a cyclohexadiene with iron pentacarbonyl in di-*n*-butyl ether. Because 1,4-cyclohexadienes are readily available from the dissolving metal reduction of aromatic compounds in liquid ammonia, they have been most widely utilized as substrates. Mixtures of isomeric complexes such as **1** and **2** (ratio 2:1) often result and require separation.[10,11] The use of amine oxides as catalysts[12] or the more reactive diiron nonacarbonyl[13] and triiron dodecacarbonyl reagents,[11a,14] which permit lower reaction temperatures and shorter reaction times, does not often alleviate this complication. For dienes sensitive to heat and/or light, ligand transfer agents such as tricarbonyl(benzylideneacetone)iron,[15] tricarbonyl((*p*-methoxybenzylidene)acetone)iron,[13a] (benzylideneacetone)dicarbonyl(triphenylphosphine)iron,[16] and (benzylideneacetone)dicarbonyl(triphenyl phosphite)iron[16] are possible.



1 **2**

Tricarbonyl(cyclohexadienyl)iron complexes have seen broad application as protected dienes in chemical interconversions and natural product syntheses.[17] Their promise as reagents is based in large part upon the ease with which hydride abstraction occurs to produce (1–5-η-1,3-cyclohexadienylium)iron cations, as illustrated by Fischer and Fischer's pioneering preparation of the parent molecule **3** in 1960.[18] The Birch and Pearson groups have examined the regioselectivity of hydride abstraction from alkyl-, methoxy-, and carbomethoxy-substituted tricarbonyl(1–4-η-1,3-cyclohexadienyl)iron complexes.[7,8] Their varied results indicate that both steric and electronic factors must be operative. One postulate defines the transition state for hydride abstraction as productlike, with the site of abstraction (kinetically controlled since the process is irreversible) reflecting the magnitude of metal–dienyl bonding in the η^5-cationic complexes.[7] However, a detailed understanding of these observations is still lacking.



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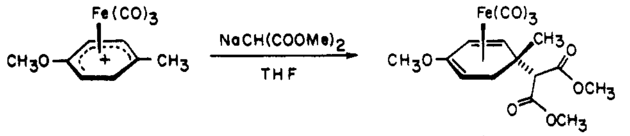
Customarily, cationic complexes of general formula **3** capture nucleophiles with high chemospecificity, regiospecificity, and stereospecificity (see **4**).[19] Proper eluci-



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[1] Silanes in Organic Synthesis. 24. For part 23, see Paquette, L. A.; Valpey, R. S.; Annis, G. D. *J. Org. Chem.* **1984**, in press.

[2] The Ohio State University.

[3] Presidential Fellow, 1981.

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[17] Pearson, A. J.; Rees, D. C.; Thornber, C. W. *J. Chem. Soc., Perkin Trans. 1* **1983**, 619 and references cited therein.

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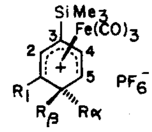
Table I. ^{13}C NMR Chemical Shifts for 11 and 12 (ppm, CD_3CN)



complex	R_1	$R_{6\alpha}$	$R_{6\beta}$	C_1	C_2	C_3	C_4	C_5	C_6
11a	H	CH_3	CH_3	79.5	101.7	99.5	101.7	79.5	*a*
11b	CH_3	H	H	95.4	102.6	*a*	100.5	65.1	23.9
11c	H	H	H	68.4	104.7	99.9	104.7	68.4	23.9
11d	H	CH_3	H	75.3	102.4	99.1	102.4	75.3	27.8
	H	H	CH_3	71.8	103.3	99.1	103.3	71.8	27.8
12	$(CH_2)_4$		H	102.8	109.6	*a*	96.0	78.1	*a*

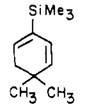
[a] Inadequate number of scans recorded to obtain shift of quaternary centers.

dation of those factors responsible for the relative reactivities of the two η^5-cyclohexadienylium termini have been complicated by charge delocalization over the orbitals of a three-dimensional system.

In an effort to heighten the tactical role that these cationic complexes might play in synthetic chemistry and to probe both types of electronic influences to an added extent, we have examined the directive role of the trimethylsilyl group in these reactions. Since the appearance of our preliminary communication on this subject,[20] Keil and Effenberger have disclosed the results of their independent investigation of this question without any attempt at theoretical interpretation.[21] Some preliminary calculations have, however, been carried out by Eisenstein.[22]

Results

Preparation of the Complexes. The 2-(trimethylsilyl)-1,3-cyclohexadienes required for this study were prepared from 2-cyclohexenone (phenylsulfonyl)hydrazones by application of the modified Shapiro procedure previously introduced.[23,24] As concerns 4,4-dimethylcyclohexenone, 3-methylcyclohexenone, and Δ^1-bicyclo[4.4.0]decen-3-one, direct derivatization was possible. Subsequent treatment with 4–5 equiv of *n*-butyllithium generated the corresponding 2-lithio-1,3-cycloalkadienes, which were trapped upon addition of chlorotrimethylsilane, affording 5–7.[25] Comparable handling of 2-cyclohexenone and its 4-methyl derivative resulted in facile Michael addition of the (arylsulfonyl)hydrazine.[26] In these examples, recourse was therefore made to the procedure of Dondoni[27] as modified by Lightner and coworkers[28] (Scheme I). The five dienylsilanes were chosen to allow determination of the effects, if any, of various alkyl-substitution patterns upon chemical behavior.



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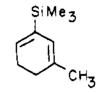

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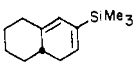

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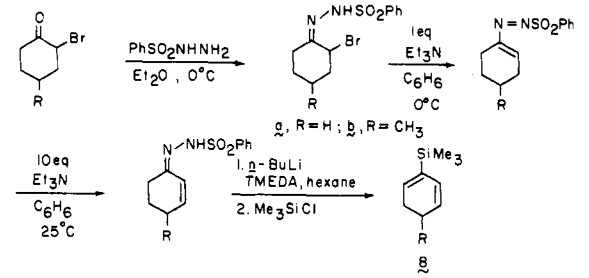
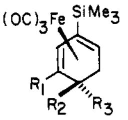
Scheme I



When 5 was heated with excess iron pentacarbonyl at the reflux temperature of di-*n*-butyl ether for 24 h, 65% conversion to **9a** was realized. More efficient was the reaction of 5 with 2 equiv of diiron nonacarbonyl in refluxing light petroleum ether. After 22 h, **9a** was produced to the extent of 91%. Treatment of the filtrate with additional $Fe_2(CO)_9$ resulted in complete consumption of the starting material. Application of this recycling procedure to each of the five dienylsilanes gave pure tricarbonyliron complexes in 54–87% isolated yield after chromatography.



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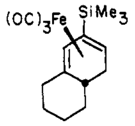

10

a, R_1 = H, R_2 = R_3 = CH_3
b, R_1 = CH_3, R_2 = R_3 = H
c, R_1 = R_2 = R_3 = H
d, R_1 = R_2 = H, R_3 = CH_3

In the case of 5, geminal dimethyl substitution at C-5 blocks potential isomerization of the 2-(trimethylsilyl)-1,3-cyclohexadienyl arrangement to the 1-(trimethylsilyl)-1,3-cyclohexadienyl isomer during the complexation process. Although such isomerizations are possible in the other four examples, they did not occur. Unexpectedly, **8b** gave rise to an 8:2 mixture of **9d** and its epimer, with coordination to tricarbonyliron occurring preferentially on the less hindered face of the 1,3-cyclohexadienyl ring. With 7, greater steric hindrance prevails and the single product

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(21) (a) Keil, M.; Effenberger, F. *Chem. Ber* **1982**, *115*, 1103. (b) Effenberger, F.; Keil, M. *Ibid.* **1982**, *115*, 1113.

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(24) (a) Chan, T. H.; Baldassarre, A.; Massuda, D. *Synthesis* **1976**, 801. (b) Chamberlin, A. R.; Stemke, J. E.; Bond, F. T. *J. Org. Chem.* **1978**, *43*, 147.

(25) Dienylsilane 5 and complex 9a have also been prepared in comparable fashion by M. Lotze (Dissertation, Philipps Universität, Marburg, West Germany). We thank Professor R. Hoffmann for informing us of these results.

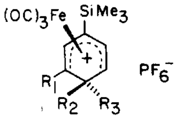
(26) (a) Kirmse, W.; Ruetz, L. *Justus Liebigs Ann. Chem.* **1969**, *726*, 30, 36. (b) Kirmse, W.; Munscher, G. *Ibid.* **1969**, *726*, 42.

(27) Dondoni, A.; Rossini, G.; Mossa, G.; Caglioti, L. *J. Chem. Soc. B* **1968**, 1404.

(28) Lightner, D. A.; Bouman, T. D.; Gawronski, J. K.; Gawronski, K.; Chappuis, J. L.; Crist, B. V.; Hansen, A. E. *J. Am. Chem. Soc.* **1981**, *103*, 5314.

10 was obtained. Assignment of stereochemistry to **10** was made by analogy to **9d**.

Hydride Abstraction Studies. Treatment of **9** and **10** with 1.2 equiv of triphenylcarbenium tetrafluoroborate in refluxing dichloromethane, followed by exposure of the unpurified tetrafluoroborate salts with aqueous ammonium hexafluorophosphate,[13b] afforded the respective tricarbonyl(1–5-η-3-(trimethylsilyl)-2,4-cyclohexadienylium)iron hexafluorophosphates **11** and **12**. Hydride abstraction proved invariably to be completely regiospecific, abstraction of a C-6 hydride generating only silyl-symmetric η^5 cations as determined by ^{1}H and ^{13}C NMR methods (Table I) irrespective of the position and level of additional alkyl substitution. This behavior contrasts with the moderate regioselectivity exhibited by alkyl, methoxy, and carbomethoxy analogues.[7,8]



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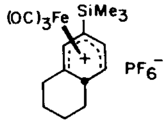
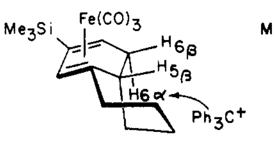


12

Clearly, **11a** has no alternative mode of hydride abstraction available to it. For **12**, one might argue that conformer **13** is its reactive form. If this is so, the β-hydrogen atoms at C-5 and C-6 are certainly less sterically accessible to the bulky triphenylcarbenium ion and improperly aligned stereoelectronically. Kinetically controlled $H_{6\alpha}$ abstraction in this example is seen to be the direct result of these factors. The boat form of a cyclohexene is utilized as the working model of the complexed six-membered ring in these systems in order to conform with X-ray structure data.[29]



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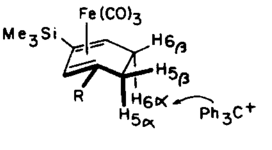

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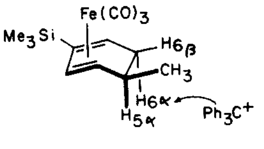

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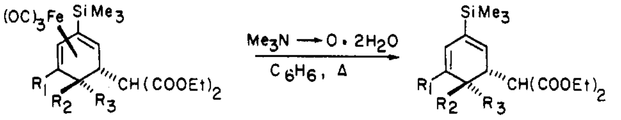
In contrast, two avenues of Ph_3C^+ attack are possible from the anti surface in **9b** and **9c** (see **14**, R = CH_3 or H), and molecular models suggest that no steric or stereoelectronic barriers operate at either site, especially when R = H. Notwithstanding, only $H_{6\alpha}$ is abstracted, much as in **13**. The situation becomes even more striking with *epi*-**11d** where a presumably more stable cation would result if the bond to $H_{5\alpha}$ were cleaved (**15**), but it is not. The trimethylsilyl substituent must therefore exert a major degree of regioelectronic control in these processes.

Nucleophilic Addition to the η^5 Cations. The directive properties of the trimethylsilyl group also carry over to the nucleophilic addition reactions of **11** and **12**. Thus, admixture of a tetrahydrofuran solution of diethyl sodiomalonate with a tetrahydrofuran suspension of each of the hexafluorophosphate salts resulted in the instantaneous consumption of starting material. Regioisomerically pure products were formed in high yield, delivery of the malonate also occurring stereospecifically on the α face of the η^5-cationic moiety. Subsequent removal of the tricarbonyliron group in **16** and **18** with trimethylamine *N*-oxide dihydrate in refluxing benzene proceeded readily to yield **17** and **19**, respectively.



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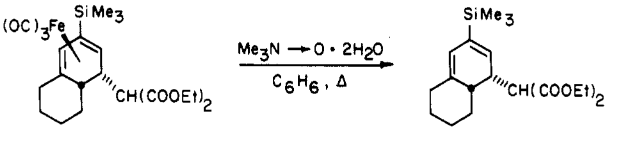

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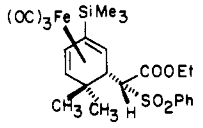
With **11a** and ethyl (phenylsulfonyl)sodioacetate,[30] an inseparable mixture of the diastereomers **20** and **21** was formed in 70% yield. Oxidative removal of the $Fe(CO)_3$ residue afforded **22** and **23**.



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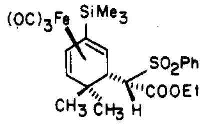

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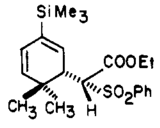

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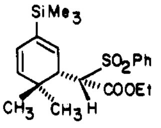
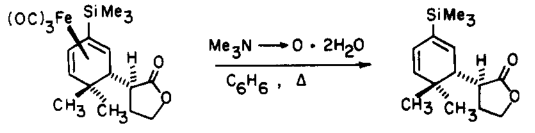


23

Comparable behavior was noted with trimethyl[(4,5-dihydro-2-furanyl)oxy]silane.[31] Where **11a** was concerned, it proved possible to separate diastereoisomers **24** and **26** and to subject them individually to decomplexation.



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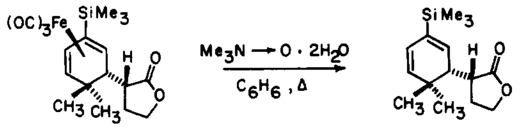

26 27

Photoelectron Spectroscopy, Theoretical Analysis, and Discussion. In an effort to gain deeper appreciation of the electronic structure and reactivity of **9a–d** and **10**, model calculations involving **3** and **28–30** have been carried out. The predicted orbital sequences were subsequently checked by appropriate comparison with He I photoelectron (PE) spectroscopic data derived from the neutral molecules. For the present purposes, recourse was made

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(29) See, for example: (a) Johnson, B. F. G.; Lewis, J.; Parker, D. G.; Raithby, P. G.; Sheldrick, G. M. *J. Organomet. Chem.* **1978**, *150*, 115. (b) Pearson, A. J.; Raithby, P. R. *J. Chem. Soc., Perkin Trans. 1* **1980**, 395.

(30) Huppartz, J. L. *Aust. J. Chem.* **1971**, *24*, 653.

(31) (a) Rasmussen, J. K.; Hassner, A. *J. Org. Chem.* **1974**, *39*, 2558. (b) Ainsworth, C.; Chen, F.; Kuo, Y.-N. *J. Organomet. Chem.* **1972**, *46*, 59. (c) Birch, A. J.; Kelly, L. F.; Narula, A. S. *Tetrahedron* **1982**, *38*, 1813.

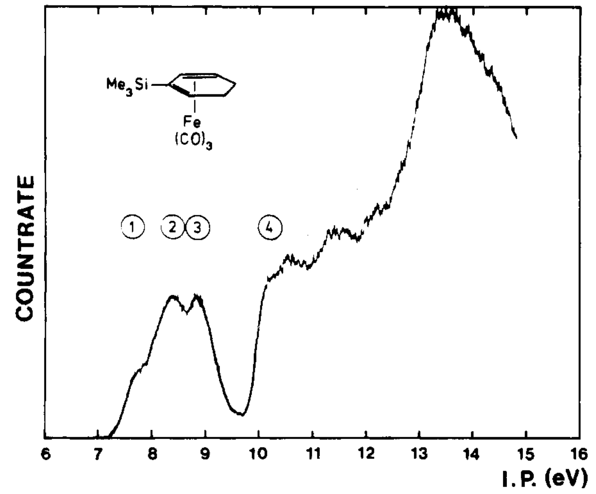


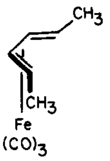
Figure 1. He(I) PE spectrum of **9c**.

Table II. First Ionization Potentials of 9a-d and 10[a]

compd/band	1	2	3	4
9c	7.8	8.45	8.9	10.25
9b	7.6	8.3	8.8	10.2
9d	7.7	8.4	8.8	10.2
9a	7.7	8.4	8.9	10.2
10	7.6	8.3	8.7	10.2

[a] All values in electron volts.

to a recently developed INDO procedure[32] that has proven to be remarkably reliable for the interpretation of PE results.[33] The geometrical parameters adopted for **28** and the cations were those of the butadienetricarbonyliron complex **31**.[34] Standard bond lengths have been employed for the C–Si and Si–H distances in **29** and **30**.[35]



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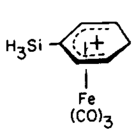

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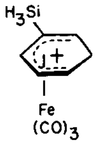

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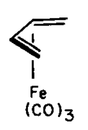


31

The recorded PE spectra of **9a–d** and **10** are very similar, particularly with respect to the shape and position of the first bands. A representative example is illustrated in Figure 1 for **9c**, where three overlapping bands at 7.7, 8.4, and 8.8 eV are seen to be well-separated from the envelope that appears above 10 eV. As can be seen from Table II, the position of the first four bands varies only slightly within the series. For the purpose of qualitative comparison, attention is called to the PE spectrum of **31**, which similarly features three bands (at 8.2, 8.8, and 9.1 eV) below 10 eV.[36]

Table III. Calculated Orbital Energies (ϵ_j), Iron 3d Contributions, MO Type, and Ionization Energies for 28

$-\epsilon_j$, eV	% Fe	type	IP, eV	band
8.35	35	$2b_1(\pi^*)$, $3d_{xz}$	7.1	①
10.17	21	$1a_2(\pi)$, $3d_{yz}$	9.5	③
10.54	63	$3d_{x^2-y^2}$	8.6	③
10.81	73	$3d_{xy}$	8.1	②
10.97	83	$3d_{z^2}$	8.0	②
11.29	10	$1b_1(\pi)$, $3d_{xz}$	10.8	④

[a] The Koopmans' defects adopted were those of **31**.[37]

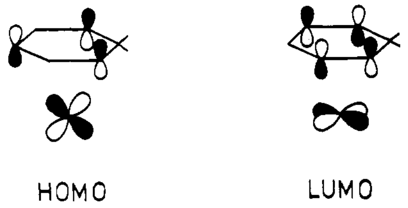


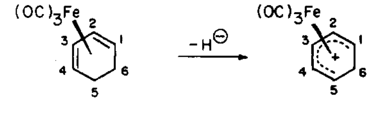
Figure 2. Schematic drawing of the highest occupied (HOMO) and lowest unoccupied (LUMO) of **3** as determined by INDO methods.

These bands have been assigned to five transitions, two originating from linear combinations involving $2b_1(\pi^*)$ and $1a_2(\pi)$ of the butadiene unit and $3d_{xz}$ and $3d_{yz}$ of the Fe$(CO)_3$ fragment, and three from MO's strongly localized at the metal. This analysis suggests that band 1 should be assigned to one transition and bands 2 and 3 to two transitions each, in line with intensity considerations.

The orbital sequence obtained by the INDO method of **28** (Table III) is very similar to that of **31**.[37] The calculated ionization potentials (IP's) correspond to a renormalized model potential for the self-energy part that has been widely used in our recent investigations.[38] The values derived are listed in the fourth column of Table III. The band position associated with these ionization energies in the PE spectra of **9a–d** and **10** is shown in the fifth column. As anticipated, the assignments parallel those given for **31**. The main difference is that the first band in the silyl complexes originates from a ligand orbital, while in **31** it is due to ionization from the $3d_{z^2}$ orbital. This difference is due to the very low orbital energy of the HOMO caused by the inductive effect of the alkyl groups in **9a–d** and **10**. Quite good agreement is seen between experiment (Table II) and model calculations (Table III).

With regard to the question of regiospecific hydride abstraction, the most interesting result is the low-lying HOMO of **3**, the frontier orbitals of which are depicted in Figure 2. Both can be derived from the fragment orbitals of the Fe$(CO)_3$ group[39] and the valence orbitals of a pentadienyl moiety. The corresponding interaction diagram has been published recently.[40]

The HOMO can be described as the bonding linear combination of the nonbonding $a_2(\pi)$ orbital of the pentadienyl fragment and the $3d_{xz}$ AO of the Fe$(CO)_3$ unit. Its nodal properties and high energy imply a stabilization by electron acceptors if the substituent is bonded to positions 1, 3, and 5 of the pentadienyl fragment. In other words, an acceptor group at position 1 or 3 of complex A should favor hydride abstraction at C(5), while an acceptor



A B

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situated at C(2) or C(4) should favor hydride abstraction at C(6). These predictions are in line with experimental observations.[7,8] For a donor substituent in position 2, hydride abstraction is anticipated at C(5), in agreement with earlier findings for 2-methoxy derivatives.[7,8] In this case, the destabilizing interaction between the HOMO of B and the lone pair of a donor will be a minimum since the nodal plane of the HOMO will be at the 2- and 4-positions.

In order to rationalize the regiospecificity observed for **13–15** in these terms, the trimethylsilyl group must act as an acceptor.[41] The preference of H_α over H_β can then be ascribed to stabilization of the developing positive charge in the transition state of the hydride abstraction by the electron-rich iron center. A similar effect has been encountered in the case of the hydride abstraction on methylferrocene derivatives[42] and rationalized by quantum chemical arguments.[43]

Experimental Section

4,4-Dimethyl-2-cyclohexenone (Phenylsulfonyl)hydrazone. A solution of 31.05 g (250 mmol) of 4,4-dimethyl-2-cyclohexenone,[44] 43.05 g (250 mmol) of (phenylsulfonyl)hydrazine, and 5 drops of concentrated hydrochloric acid in 100 mL of dry tetrahydrofuran was stirred at the reflux temperature for 5 h. Chilling of the reaction mixture (–20 °C) resulted in crystallization of the product, which was collected by suction filtration. Recrystallization from hot methanol with the aid of dichloromethane gave 46.83 g (67.3%) of white crystalline solid: mp 167–167.5 °C; ^{1}H NMR ($CDCl_3$) δ 8.08–7.79 (m, 2 H), 7.68–7.44 (m, 3 H), 5.98 (s, 2 H), 2.41 (t, J = 7 Hz, 2 H), 1.66 (t, J = 7 Hz, 2 H), 1.12 (s, 6 H); MS, m/e (M^+) calcd 278.1089, obsd 278.1096.

2-(Trimethylsilyl)-5,5-dimethyl-1,3-cyclohexadiene (5). To a cold (–45 °C) suspension of 8.35 g (30.0 mmol) of the preceding compound in 100 mL of 50% tetramethylethylenediamine (TMEDA)–hexane was added dropwise under nitrogen during 30 min 102 mL (137 mmol) of a 1.37 M solution of n-butyllithium in hexane. The reaction mixture was stirred at –45 °C for 30 min and at room temperature for 2 h and then chilled to 0 °C, whereupon 15.3 mL (120 mmol) of chlorotrimethylsilane was added dropwise during 15 min. The reaction mixture was stirred at room temperature for 1 h and then poured into 200 mL of water. The layers were separated, the aqueous layer was extracted twice with 100 mL of pentane, and the combined organic layers were washed twice with 200 mL of saturated copper(II) sulfate solution and 100 mL of brine, dried, and evaporated, yielding 10.57 g of a yellow-brown liquid. Distillation through a 10-cm Vigreux column gave 3.64 g (67.3%) of **5**, bp 75–76 °C (10 mm). Analytical purification was achieved by preparative VPC on 8% SE-30 (Chromosorb P) at 100 °C: IR (cm^{-1}, film) 2950, 1245, 1060, 830, 730; ^{1}H NMR ($CDCl_3$) δ 5.79 (t, J = 6 Hz, 1 H), 5.68 (d, J = 10 Hz, 1 H), 5.29 (d, J = 10 Hz, 1 H), 1.92 (d, J = 6 Hz, 2 H), 1.78 (s, 6 H), –0.12 (s, 9 H); MS, m/e (M^+) calcd 180.1334, obsd 180.1340.[25]

3-Methyl-2-cyclohexenone (Phenylsulfonyl)hydrazone. A solution of 50.0 g (454 mmol) of 3-methyl-2-cyclohexenone and 79.3 g (454 mmol) of (phenylsulfonyl)hydrazine was stirred at the reflux temperature and then allowed to cool. The product was collected by suction filtration and triturated with hot diethyl ether, affording 59 g (49%) of white solid, mp 128 °C. Recrystallization from hot methanol–hexane yielded fine white crystals: mp 130–130.5 °C; ^{1}H NMR ($CDCl_3$) δ 8.05–7.80 (m, 2 H), 7.64–7.40 (m, 3 H), 5.95–5.80 (br s, 1 H), 2.40–1.54 (overlapping s, m, 9 H); MS/m/e (M^+) calcd 264.0932, obsd 264.0924.

2-(Trimethylsilyl)-4-methyl-1,3-cyclohexadiene (6). Treatment of 7.93 g (30.0 mmol) of the preceding compound with 90 mL (140 mmol) of a 1.55 M solution of n-butyllithium in hexane, with quenching by 15.3 mL (120 mmol) of chlorotrimethylsilane, gave 12.02 g of a brown liquid. Distillation through a 10-cm Vigreux column yielded 3.09 g (61.9%) of **6**, bp 74–76 °C (15 mm). Analytical purification was achieved by preparative VPC as above (100 °C): IR (cm^{-1}, film 2950, 1430, 1245, 1090, 835, 740, 685, 615; ^{1}H NMR ($CDCl_3$) δ 5.78 (t, J = 4.5 Hz, 1 H), 2.09–1.80 (m, 4 H), 1.60 (s, 3 H), 1.57 (br s, 1 H), –0.08 (s, 9 H); MS, m/e (M^+) calcd 166.1178, obsd 166.1182.

Anal. Calcd for $C_{10}H_{18}Si$: C, 72.21; H, 10.91. Found: C, 71.97; H, 10.89.

Δ^1-Bicyclo[4.4.0]decen-3-one (Phenylsulfonyl)hydrazone. A solution of 37.56 g (250 mmol) of an 89:11 mixture of Δ^1- and $\Delta^{1(6)}$-bicyclo[4.4.0]decen-3-one,[45] 43.05 g (250 mmol) of (phenylsulfonyl)hydrazine, and 5 drops of concentrated hydrochloric acid was stirred at the reflux temperature for 5 h. Evaporation of the cooled reaction mixture and trituration of the residue with hexane yielded a yellow solid. Recrystallization from hot methanol with the aid of dichloromethane afforded 43.77 g (57.5%) of white crystalline solid: mp 143–143.5 °C; ^{1}H NMR ($CDCl_3$) δ 8.10–7.71 (m, 2 H), 7.62–7.29 (m, 3 H), 5.94 (br d, J = 12 Hz, 1 H), 2.82–0.72 (series of m, 13 H); MS, m/e (M^+) calcd 304.1245, obsd 304.1250.

3-(Trimethylsilyl)bicyclo[4.4.0]deca-1,3-diene (7). Treatment of 7.27 g (23.9 mmol) of the preceding compound with 80 mL (110 mmol) of a 1.37 M solution of n-butyllithium in hexane, with quenching by 12.2 mL (96 mmol) of chlorotrimethylsilane, gave 8.59 g of a yellow-brown liquid. Distillation through a 10-cm Vigreux column afforded 3.76 g (76.2%) of **7**, bp 90–92 °C (1.5 mm). Analytical purification was achieved by preparative VPC as above (125 °C): IR (cm^{-1}, film) 2920, 2850, 2810, 1445, 1425, 1245, 830, 745, 680, 625; ^{1}H NMR ($CDCl_3$) δ 5.73 (t, J = 3 Hz, 1 H), 5.47 (s, 1 H), 2.35–1.01 (series of m, 11 H), –0.09 (s, 9 H); MS, m/e (M^+) calcd 206.1491, obsd 206.1496.

2-Bromocyclohexanone (Phenylsulfonyl)hydrazone. A solution of 33.82 g (210 mmol) of freshly distilled 2-bromocyclohexanone[46] in 100 mL of diethyl ether was added to a cold (0 °C) rapidly stirred suspension of 34.44 g (200 mmol) of finely ground (phenylsulfonyl)hydrazine in 500 mL of diethyl ether. After 2 h at 0 °C, the reaction mixture was filtered and the collected pinkish solid was recrystallized from 900 mL of dichloromethane–900 mL of diethyl ether, providing 44.99 g (67.9%) of white crystalline solid: mp 117 °C; ^{1}H NMR ($CDCl_3$) δ 8.00–7.73 (m, 3 H), 7.63–7.40 (m, 3 H), 5.05–4.82 (br s, 1 H), 3.58–2.33 (m, 2 H), 2.05–1.45 (m, 6 H); MS, m/e (M^+ – HBr) 250.

2-Cyclohexenone (Phenylsulfonyl)hydrazone. A solution of 9.8 mL (70 mmol) of triethylamine in 50 mL of benzene was added dropwise during 1 h to a cold (0 °C) suspension of 23.19 g (700 mmol) of the above compound in 700 mL of the same solvent. The reaction mixture was stirred at 0 °C for 30 min and then suction filtered to remove precipitated triethylammonium bromide. The filtrate was stirred with an addition 98 mL (700 mmol) of triethylamine at room temperature for 20 h. Evaporation of the solvent yielded a yellow semisolid, which was triturated with 200 mL of hexanes and then filtered through silica gel (30 g, elution with ethyl acetate–hexane, 1:1). Evaporation and drying under high vacuum provided 9.87 g (56.3%) of product as a yellowish solid, mp 110–112 °C. Recrystallization from hot methanol afforded white crystals: mp 139.5–141 °C; ^{1}H NMR ($CDCl_3$) δ 8.01–7.70 (m, 3 H), 7.57–7.30 (m, 3 H), 6.18–6.03 (m, 2 H), 2.53–1.45 (m, 6 H); MS, m/e (M^+) calcd 250.0776, obsd 250.0783.

2-(Trimethylsilyl)-1,3-cyclohexadiene (8a). Treatment of 8.76 g (35.0 mmol) of the preceding compound with 102 mL (158

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[41] A trimethylsilyl group is known to be capable of behaving as an electron acceptor when directly linked to π systems [Bock, H.; Brähler, G.; Fritz, G.; Matern, E. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 699], especially when in the para position of anilines and phenols [Benkeser, R. A.; Krysiak, H. R. *J. Am. Chem. Soc.* **1953**, *75*, 2421]. Although comparable behavior toward a neighboring cation may appear unusual, the HOMO of **3** is seen at unusually high energy and thus donor characteristics might well be expected from the ring notwithstanding the positive charge. For considerations of a contrasting types, see: Cartledge, F. K.; Jones, J. P. *Tetrahedron Lett.* **1971**, 2193.

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mmol) of a 1.55 M solution of *n*-butyllithium in hexane, with quenching by 17.8 mL (140 mmol) of chlorotrimethylsilane, gave 10.57 g of a yellow-brown liquid. Distillation through a 10-cm Vigreux column yielded 2.06 g (25.8%) of **8a**, bp 71–72 °C (27 mm). Analytical purification was achieved by preparative VPC as above (100 °C): IR (cm^{-1}, film) 2950, 1245, 830, 745, 710; ^{1}H NMR (CDCl$_3$) δ 5.90 (m, 1 H), 5.77 (m, 1 H), 5.66 (m, 1 H), 2.02–1.91 (m, 4 H), –0.07 (s, 9 H); MS, m/e (M$^+$) calcd 152.1021, obsd. 152.1026.[23a]

2-Bromo-4-methylcyclohexanone (Phenylsulfonyl)-hydrazone. A solution of 40.12 g (210 mmol) of freshly distilled 2-bromo-4-methylcyclohexanone[47] in 100 mL of diethyl ether was added to a cold (0 °C) rapidly stirred suspension of 34.44 g (200 mmol) of (phenylsulfonyl)hydrazine in 500 mL of the same solvent. After 2 h, the solvent was evaporated, affording 66.57 g (96.4%) of crude product as a yellow oil, which was used directly in the next reaction.

4-Methyl-2-cyclohexenone (Phenylsulfonyl)hydrazone. Successive treatment of a benzene solution of 66.57 g (193 mmol) of the crude sulfonylhydrazone from above with 27.0 mL (194 mmol) and 270 mL (mol = 1.94) lots of triethylamine as described previously yielded a brown oil on evaporation of the solvent. Trituration of this oil with 250 mL of hexane and filtration through silica gel (75 g, elution with ethyl acetate–hexane, 1:1) yielded 38.60 g of partially purified product as a yellow-brown solid. Trituration with 400 mL of diethyl ether gave 16.95 g (33.3%) of a white crystalline solid: mp 140–141 °C; ^{1}H NMR (CDCl$_3$) δ 7.89–7.69 (m, 3 H), 7.53–7.24 (m, 3 H), 6.01 (s, 2 H), 2.70–1.60 (m, 5 H), 1.01 (d, J = 7 Hz, 3 H); MS, m/e (M$^+$) calcd 264.0932, obsd 264.0922.

2-(Trimethylsilyl)-5-methyl-1,3-cyclohexadiene (8b). Reaction of 7.93 g (30.0 mmol) of the preceding compound with 90 mL (140 mmol) of a 1.55 M solution of *n*-butyllithium in hexane and 15.3 mL (120 mmol) of chlorotrimethylsilane in the previously described manner gave 8.58 g of a yellow-brown liquid. Distillation through a 10-cm Vigreux column afforded 2.90 g (58.0%) of **8b**, bp 73–74 °C (12 mm). Analytical purification was achieved by preparative VPC as above (100 °C): IR (cm^{-1}, film) 2920, 1615, 1555, 1450, 1420, 1395, 1370, 1315, 1290, 1270, 1240, 1125, 1060, 1035, 1000, 945, 935, 830, 745, 715, 680, 625, 605; ^{1}H NMR (CDCl$_3$) δ 5.83 (m, 1 H), 5.68 (dt, J = 7.5 and 3 Hz, 1 H), 5.35 (dd, J = 7.5 and 3 Hz, 1 H), 2.01 (dd, J = 7.5 and 4.5 Hz, 2 H), 1.71 (dt, J = 18 and 4.5 Hz, 1 H), 0.76 (d, J = 3 Hz, 3 H), –0.17 (s, 9 H); MS, m/e (M$^+$) calcd 166.1178, obsd 166.1174.

Anal. Calcd for C$_{10}$H$_{18}$Si: C, 72.21; H, 10.91. Found: C, 71.86; H, 10.90.

Tricarbonyl[1-4-η-2-(trimethylsilyl)-1,3-cyclohexadiene]iron Complexes. General Procedure. A degassed solution of 1.00 g (ca. 5–6 mmol) of the dienylsilane in 75 mL of dry light petroleum ether was stirred under nitrogen at the reflux temperature with 2 equiv (ca. 3.4–4.5 g, 10–12 mmol) of diiron nonacarbonyl for 22 h while shielded from light. The cooled reaction mixture was suction filtered through Celite and the dark green filtrate was stirred at the reflux temperature with another 2 equiv of diiron nonacarbonyl for 22 h. The cooled reaction mixture was filtered through Celite and the filtrate was evaporated. Chromatography of the dark green residue on silica gel (100 g, elution with hexane) gave the pure tricarbonyliron complex.

Tricarbonyl[1-4-η-2-(trimethylsilyl)-5,5-dimethyl-1,3-cyclohexadiene]iron (9a). Reaction of 1.00 g (5.55 mmol) of **5** and 4.10 g (11.3 mmol) of diiron nonacarbonyl twice gave 1.54 g (86.7%) of **9a** as a clear yellow oil: IR (cm^{-1}, film) 2950, 2030, 1950, 1225, 1245, 835, 745; ^{1}H NMR (CDCl$_3$) δ 4.90 (d, J = 7 Hz, 1 H), 2.94 (overlapping m, d, J = 7 Hz, 2 H), 1.91 (s, 3 H), 1.75 (s, 3 H), 1.51 (dd, J = 8 and 4.5 Hz, 2 H), 0.08 (s, 9 H); MS, m/e 292 (M$^+$ – CO) and 264 (M$^+$ – 2CO).[25]

Tricarbonyl[1-4-η-2-(trimethylsilyl)-4-methyl-1,3-cyclohexadiene]iron (9b). Reaction of 1.00 g (6.02 mmol) of **6** and 4.40 g (12.1 mmol) of diiron nonacarbonyl twice provided 1.27 g (69.0%) of **9b** as a clear yellow oil: IR (cm^{-1}, film) 2950, 2840, 2020, 1950, 1245, 830; ^{1}H NMR (CDCl$_3$) δ 4.78 (s, 1 H), 3.01–2.88 (m, 1 H), 1.99–1.77 (m, 1 H), 1.72–1.58 (m, 1 H), 1.43 (s, 3 H), 1.27–1.22 (m, 2 H), 0.06 (s, 9 H); MS, m/e (M$^+$) calcd 306.0374, obsd 306.0379.

Tricarbonyl[1-4-η-3-(trimethylsilyl)bicyclo[4.4.0]deca-1,3-diene]iron (10). Reaction of 1.00 g (4.85 mmol) of **7** and 3.64 g (10.0 mmol) of diiron nonacarbonyl twice yielded 1.28 g (76.2%) of **10** as a clear yellow oil: IR (cm^{-1}, film) 2920, 2850, 2020, 1950, 1445, 830, 605, 565; ^{1}H NMR (CDCl$_3$) δ 4.77 (br s, 1 H), 2.92–2.72 (m, 1 H), 2.30–0.60 (m, 11 H), 0.11 (s, 9 H); MS, m/e (M$^+$) calcd 346.0687, obsd 346.0694.

Tricarbonyl[1-4-η-2-(trimethylsilyl)-1,3-cyclohexadiene]iron (9c). Reaction of 1.00 g (6.09 mmol) of **8a** and 4.43 g (12.2 mmol) of diiron nonacarbonyl twice afforded 1.37 g (78.9%) of **9c** as a clear yellow oil: IR (cm^{-1}, film) 2945, 2845, 2030, 1950, 1245, 1175, 1120, 830, 745; ^{1}H NMR (CDCl$_3$) δ 4.89 (d, J = 7.5 Hz, 1 H), 3.31–3.11 (m, 1 H), 3.04 (br s, 1 H), 1.83–1.18 (m, 4 H); MS, m/e (M$^+$) calcd 292.0218, obsd 292.0225.

Tricarbonyl[1-4-η-2-(trimethylsilyl)-5-methyl-1,3-cyclohexadiene]iron (9d). Reaction of 1.00 g (6.01 mmol) of **8b** and 4.40 g (12.1 mmol) of diiron nonacarbonyl twice furnished 1.00 g (54.3%) of **9d** as a clear yellow oil: IR (cm^{-1}, film) 2955, 2850, 2030, 1950, 1450, 1250, 1125, 975, 835, 750, 695, 610, 570; ^{1}H NMR (CDCl$_3$) δ 4.90 (t, J = 6 Hz, 1 H), 3.23–2.80 (m, 2 H), 2.20–1.15 (m, 3 H), 0.78 (t, J = 6 Hz, 3 H), 0.07 (s, 9 H); MS, m/e (M$^+$) calcd 306.0374, obsd 306.0381.

Tricarbonyl[1-5-η-3-(trimethylsilyl)-1,3-cyclohexadienylium]iron Hexafluorophosphates. General Procedure. A solution of 1.2 equiv of triphenylcarbenium tetrafluoroborate in 10 mL of dry dichloromethane was added under nitrogen via syringe to a rapidly stirred solution of 1.2–1.5 g (3.5–4.5 mmol) of the tricarbonyliron complex in 10 mL of the same solvent. The reaction mixture was stirred at the reflux temperature for 18–24 h, cooled, and poured into 50 mL of wet diethyl ether. The solvent was evaporated and the solid residue was triturated with 50 mL of diethyl ether, collected by suction filtration, washed with diethyl ether, and taken up in 75–125 mL of warm to hot water. Addition of a solution of 1.2 equiv of ammonium hexafluorophosphate in 5 mL of water gave immediate precipitation of the product hexafluorophosphate salt. This was collected by suction filtration, washed with a few milliliters of water, and dried under high vacuum. Analytical samples were reprecipitated twice from dichloromethane–diethyl ether.

Tricarbonyl[1-5-η-3-(trimethylsilyl)-6,6-dimethyl-1,3-cyclohexadienylium]iron Hexafluorophosphate (11a). Reaction of 1.45 g (4.53 mmol) of **9a** with 1.80 g (5.45 mmol) of triphenylcarbenium tetrafluoroborate and 0.90 g (5.5 mmol) of ammonium hexafluorophosphate gave 1.584 g (75.3%) of **11a** as a yellow powder: mp (sealed evacuated tube) 208–210 °C dec; IR (cm^{-1}, CH$_2$Cl$_2$) 2090, 2050, 1245, 830; ^{1}H NMR (CD$_3$CN) δ 5.32 (d, J = 7 Hz, 2 H), 4.15 (d, J = 7 Hz, 2 H), 1.32 (s, 3 H), 0.52 (s, 3 H), 0.35 (s, 9 H); ^{13}C NMR (ppm, CD$_3$CN) 203.44, 101.73, 99.49, 79.52, 37.83, 32.67, 28.12, 1.43.

Anal. Calcd for C$_{14}$H$_{19}$F$_6$FeO$_3$PSi: C, 36.22; H, 4.13. Found: C, 36.30; H, 4.12.

Tricarbonyl[1-5-η-1-methyl-3-(trimethylsilyl)-1,3-cyclohexadienylium]iron Hexafluorophosphate (11b). Reaction of 1.269 g (4.14 mmol) of **9b** with 1.65 g (5.00 mmol) of triphenylcarbenium tetrafluoroborate and 0.82 g (5.0 mmol) of ammonium hexafluorophosphate furnished 1.485 g (79.6%) of **11b** as a yellow powder: mp (sealed evacuated tube) 185–187 °C dec; IR (cm^{-1}, CH$_2$Cl$_2$) 2090, 2040, 1240, 1040, 830; ^{1}H NMR (CD$_3$CN) δ 5.48 (d, J = 7 Hz, 1 H), 5.18 (s, 1 H), 4.15 (t, J = 7 Hz, 1 H), 2.95 (br d, J = 7 Hz, 1 H), 2.68 (br d, J = 7 Hz, 1 H), 1.61 (s, 3 H), 0.34 (s, 9 H); ^{13}C NMR (ppm, CD$_3$CN) 102.58, 100.52, 95.42, 65.08, 29.82, 23.93, 1.92.

Anal. Calcd for C$_{13}$H$_{17}$F$_6$FeO$_3$PSi: C, 34.68; H, 3.81. Found: C, 34.67; H, 3.82.

Tricarbonyl[1-5-η-3-(trimethylsilyl)-1,3-cyclohexadienylium]iron Hexafluorophosphate (11c). Reaction of 1.250 g (4.279 mmol) of **9c** with 1.70 g (5.15 mmol) of triphenylcarbenium tetrafluoroborate and 0.85 g (5.2 mmol) of ammonium hexafluorophosphate yielded 1.236 g (66.2%) of **11c** as a yellow powder: mp (sealed evacuated tube) 194–195 °C dec; IR (cm^{-1}, CH$_2$Cl$_2$) 2100, 2050, 1240, 830; ^{1}H NMR (CD$_3$CN) δ 5.45 (d, J = 7 Hz, 2 H), 4.17 (t, J = 7 Hz, 2 H), 2.48 (t, J = 7 Hz, 1 H), 2.67 (t, J = 7 Hz, 1 H), 0.37 (s, 9 H); ^{13}C NMR (ppm, CD$_3$CN) 104.71, 99.87, 68.36, 23.93, 1.25.

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[47] Draper, A. L.; Heilman, W. J.; Schaeffer, W. E.; Shine, H. J.; Shoolery, J. N. *J. Org. Chem.* **1962**, *27*, 2727.

Anal. Calcd for $C_{12}H_{15}F_6FeO_3PSi$: C, 33.05; H, 3.47. Found: C, 33.21; H, 3.51.

Tricarbonyl[1-5-η-3-(trimethylsilyl)-6-methyl-1,3-cyclohexadienylium]iron Hexafluorophosphate (11d). Reaction of 970.8 mg (3.170 mmol) of **9d** with 1.25 g (3.79 mmol) of triphenylcarbenium tetrafluoroborate and 0.65 g (4.0 mmol) of ammonium hexafluorophosphate provided 635 mg (44.5%) of an 19:81 mixture (by ^{13}C NMR) of the *endo*- and *exo*-methyl isomers of **11d** as a yellow powder: mp (sealed evacuated tube) 190–191 °C dec; IR (cm^{-1}, CH_2Cl_2) 2090, 2040, 1020, 830; ^1H NMR (CD_3CN) δ 5.39 (d, J = 7.5 Hz, 2 H), 4.42 and 3.83 (d, J = 7.5 Hz and t, J = 7.5 Hz, 3 H), 1.78 (overlapping q, J = 7.5 Hz, 1 H), 1.33 and 0.44 (d, J = 7 Hz, and d, J = 7 Hz, 3 H), 0.33 (s, 9 H); ^{13}C NMR (ppm, CD_3CN) 103.31, 102.40, 99.13, 75.28, 71.82, 29.70, 27.76, 18.34, 2.46.

Anal. Calcd for $C_{13}H_{17}F_6FeO_3PSi$: C, 34.69; H, 3.81. Found: C, 34.63; H, 3.75.

Tricarbonyl[1-5-η-3-(trimethylsilyl)bicyclo[4.4.0]deca-1,3-dienylium]iron Hexafluorophosphate (12). Reaction of 1.226 g (3.541 mmol) of **10** with 1.40 g (4.24 mmol) of triphenylcarbenium tetrafluoroborate and 0.70 g (4.3 mmol) of ammonium hexafluorophosphate afforded 535.5 mg (30.9%) of **12** as a yellow powder: mp (evacuated sealed tube) 174–176 °C dec; IR (cm^{-1}, CH_2Cl_2) 2090, 2040, 835; ^1H NMR (CD_3CN) δ 5.47 (d, J = 8 Hz, 1 H), 5.12 (s, 1 H), 4.55 (d, J = 7 Hz, 1 H), 2.19–1.87 (m, 3 H), 1.67–1.38 (m, 6 H), 0.38 (s, 9 H); ^{13}C NMR (ppm, CD_3CN) 109.62, 102.83, 96.03, 78.13, 44.39, 41.90, 35.77, 32.31, 25.51, 2.10.

Anal. Calcd for $C_{16}H_{21}F_6FeO_3PSi$: C, 39.20; H, 4.32. Found: C, 39.08; H, 4.25.

Tricarbonyl[*anti*-diethyl (2–5-η-3-(trimethylsilyl)-2,4-cyclohexadienyl)malonate]iron (16c). A solution of 184 mg (1.15 mmol) of diethyl malonate in 5 mL of dry tetrahydrofuran was added dropwise under nitrogen via syringe to a rapidly stirred suspension of 55 mg (1.15 mmol) of 50% sodium hydride (mineral oil dispersion, prewashed three times with 4 mL of pentane). The resulting clear colorless diethyl sodiomalonate solution was stirred at room temperature for 5 min and then 2.2 mL of the solution was added dropwise under nitrogen via syringe to a rapidly stirred suspension of 100.5 mg (0.230 mmol) of **11c** in 5 mL of dry tetrahydrofuran. The clear yellow reaction mixture was stirred at room temperature for 30 min and poured into 5 mL of water. The layers were separated, the aqueous layer was extracted twice with 5 mL of light petroleum ether, and the combined organic layers were dried and evaporated. The residue was chromatographed on silica gel (10 g, elution with benzene), afforing 91 mg (87%) of **16c** as a clear yellow oil: IR (cm^{-1}, film) 2980, 2030, 1950, 1755, 1740, 1455, 1445, 1365, 1335, 1300, 1265, 1160, 1025, 835, 750, 610, 570; ^1H NMR ($CDCl_3$) δ 4.99 (d, J = 6 Hz, 1 H), 3.96 (dq, J = 7 and 3 Hz, 4 H), 3.17–2.97 (m, 1 H), 2.91–2.76 (m, 1 H), 2.73–2.53 (m, 1 H), 2.26–1.90 (br m, 1 H), 1.60–1.23 (br m, 2 H), 1.20 (dt, J = 7 and 3 Hz, 6 H), 0.08 (s, 9 H); MS, m/e 450 (M^+) 422 ($M^+ - CO$), 366 ($M^+ - 3CO$).

Diethyl [3-(Trimethylsilyl)-2,4-cyclohexadienyl]malonate (17c). A solution of 91 mg (0.20 mmol) of **16c** in 5 mL of dry benzene was stirred at the reflux temperature with 190 mg (1.6 mmol) of 98% trimethylamine *N*-oxide dihydrate for 24 h. The cooled reaction mixture was filtered through a plug of Celite and evaporated. The residue was chromatographed on silica gel (5 g, elution with benzene), yielding 35 mg (56%) of **17c** as a clear colorless liquid: IR (cm^{-1}, film) 2940, 1750, 1730, 1365, 1320, 1245, 1025, 830; ^1H NMR ($CDCl_3$) δ 5.87–5.35 (series of m, 3 H), 4.90 (q, J = 7.5 Hz, 4 H), 3.23 (d, J = 9 Hz, 1 H), 2.95–1.52 (m, 1 H), 2.07–1.77 (m, 2 H), 0.99 (t, J = 7.5 Hz, 6 H), –0.07 (s, 9 H); MS, m/e ($M^+ - H_2$) calcd 308.1444, obsd 308.1455.

Tricarbonyl[*anti*-diethyl (2–5-η-3-(trimethylsilyl)-6-methyl-2,4-cyclohexadienyl)malonate]iron (16d). Treatment of 100 mg (0.222 mmol) of **11d** with 2 mL of diethyl sodiomalonate solution [prepared from 178 mg (1.11 mmol) of diethyl malonate and 54 mg (1.1 mmol) of 50% sodium hydride in 10 mL of dry tetrahydrofuran] in the usual manner afforded 66 mg (64%) of **16d** as a clear yellow oil: IR (cm^{-1}, film) 2970, 2030, 1940, 1755, 1730, 1295, 1260, 1245, 1170, 835, 610, 570; ^1H NMR ($CDCl_3$) δ 4.90 (d, J = 7 Hz, 1 H), 3.97 (dq, J = 7 and 3 Hz, 4 H), 3.09 (dd, J = 6 and 3 Hz, 1 H), 2.97–2.75 (m, 1 H), 2.65–2.57 (m, 1 H), 2.35–2.10 (m, 1 H), 1.28 (s, 1 H), 1.13 (dt, J = 7 and 3 Hz, 6 H), 0.60 (d, J = 7 Hz, 0.07 (s, 9 H); MS, m/e 464 (M^+), 436 ($M^+ - CO$), 408 ($M^+ - 2CO$), 380 ($M^+ - 3CO$).

Diethyl [3-(Trimethylsilyl)-6-methyl-2,4-cyclohexadienyl]malonate (17d). Treatment of 65 mg (0.14 mmol) of **16d** with 135 mg (1.2 mmol) of 98% trimethylamine *N*-oxide dihydrate in the usual manner yielded 29 mg (64%) of **17d** as a clear yellow liquid: IR (cm^{-1}, film) 2950, 1755, 1735, 1245, 830; ^1H NMR ($CDCl_3$) δ 5.80–5.48 (series of m, 3 H), 4.03 (q, J = 7 Hz, 4 H), 3.31 (dd, J = 12 and 7 Hz, 1 H), 3.18–2.85 (m, 1 H), 2.81–2.50 (m, 1 H), 1.10 (t, J = 7 Hz, 6 H), 0.83 and 0.65 (d, J = 7 Hz, d, J = 7 Hz, 3 H), –0.09 (s, 9 H); MS, m/e ($M^+ - H_2$) calcd 324.1757, obsd 324.1762.

Tricarbonyl[*anti*-diethyl (2–5-η-3-(trimethylsilyl)-6,6-dimethyl-2,4-cyclohexadienyl)malonate]iron (16a). Treatment of 101 mg (0.217 mmol) of **11a** with 2 mL of diethyl sodiomalonate solution [prepared from 190 mg (1.19 mmol) of diethyl malonate and 57 mg (1.2 mmol) of 50% sodium hydride in 10 mL of dry tetrahydrofuran] in the usual manner afforded 98 mg (95%) of **16a** as a clear yellow oil: IR (cm^{-1}, film) 2970, 2030, 1950, 1750, 1725, 1415, 1300, 1255, 1245, 1190, 1050, 835, ^1H NMR ($CDCl_3$) δ 4.87 (d, J = 6 Hz, 1 H), 2.98 (dq, J = 7 and 3 Hz, 4 H), 2.98–2.43 (series of m, 3 H), 1.55–1.3 (m, 1 H), 1.10 (dt, J = 7 and 3 Hz, 6 H), 1.02 (s, 3 H), 0.61 (s, 3 H), 0.09 (s, 9 H); MS, m/e 478 (M^+), 450 ($M^+ - CO$), 422 ($M^+ - CO$), 422 ($M^+ - 2CO$), 394 ($M^+ - 3CO$).

Diethyl [3-(Trimethylsilyl)-6,6-dimethyl-2,4-cyclohexadienyl]malonate (17a). Treatment of 98 mg (0.20 mmol) of **16a** with 190 mg (1.63 mmol) of 98% trimethylamine *N*-oxide dihydrate in the usual manner yielded 54 mg (74%) of **17a** as a clear yellow liquid: IR (cm^{-1}, film) 2960, 1760, 1740, 1465, 1445, 1365, 1305, 1245, 1195, 1145, 1025, 835, 730; ^1H NMR ($CDCl_3$) δ 5.81 (br s, 1 H), 5.72 (d, J = 10 Hz, 1 H), 5.22 (d, J = 10 Hz, 1 H), 4.02 (q, J = 7 Hz, 4 H), 3.46 (d, J = 7 Hz, 1 H), 2.80 (d, J = 7 Hz, 1 H), 1.08 (t, J = 7 Hz, 6 H), 0.90 (s, 3 H), 0.76 (s, 3 H), –0.08 (s, 9 H); MS, m/e (M^+) calcd 338.1913, obsd 338.1920.

Tricarbonyl[*anti*-diethyl (2–5-η-3-(trimethylsilyl)-5-methyl-2,4-cyclohexadienyl)malonate]iron (16b). Treatment of 100 mg (0.223 mmol) of **11b** with 2.2 mL of diethyl sodiomalonate solution [prepared from 178 mg (1.11 mmol) of diethyl malonate and 54 mg (1.1 mmol) of 50% sodium hydride in 10 mL of dry tetrahydrofuran] in the usual manner afforded 84 mg (81%) of **16b** as a clear yellow oil: IR (cm^{-1}, film) 2950, 2890, 2840, 2030, 1950, 1755, 1740, 1475, 1445, 1390, 1375, 1365, 1300, 1245, 1185, 1150, 1090, 1060, 1030, 835, 785, 745, 685; ^1H NMR ($CDCl_3$) δ 4.84 (s, 1 H), 3.94 (dq, J = 7 and 3 Hz, 4 H), 2.79–2.58 (series of m, 3 H), 2.35–2.0 (br d, 2 H), 1.37 (s, 3 H), 1.11 (dt, J = 7 and 3 Hz, 6 H), 0.06 (s, 9 H); MS, m/e 464 (M^+), 436 ($M^+ - CO$), 408 ($M^+ - 2CO$), 380 ($M^+ - 3CO$).

Diethyl [3-(Trimethylsilyl)-5-methyl-2,4-cyclohexadienyl]malonate (17b). Treatment of 82 mg (0.18 mmol) of **16b** with 170 mg (1.46 mmol) of 98% trimethylamine *N*-oxide dihydrate in the usual manner yielded 37 mg (64%) of **17b** as a clear colorless liquid: IR (cm^{-1}, film) 2960, 1760, 1735, 1445, 1365, 1300, 1245, 1150, 1025, 830, 745; ^1H NMR ($CDCl_3$) δ 5.67 (d, J = 5 Hz, 1 H), 5.59 (s, 1 H), 4.03 (q, J = 7 Hz, 4 H), 3.26 (d, J = 10 Hz, 1 H), 3.05–2.66 (m, 1 H), 2.30–1.78 (m, 2 H), 1.63 (s, 3 H), 1.10 (t, J = 7 Hz, 6 H), –0.09 (s, 9 H); MS, m/e ($M^+ - H_2$) calcd 322.1606, obsd 322.1606.

Tricarbonyl[*anti*-diethyl 2-(3–6-η-4-(trimethylsilyl)bicyclo[4.4.0]deca-3,5-dienyl)malonate]iron (18). Treatment of 100 mg (0.205 mmol) of **12** with 2 mL of diethyl sodiomalonate solution [prepared from 163 mg (1.02 mmol) of diethyl malonate and 49 mg (1.0 mmol) of 50% sodium hydride in 10 mL of dry tetrahydrofuran] in the usual manner afforded 83 mg (80%) of **18** as a clear yellow oil: IR (cm^{-1}, film) 2930, 2850, 2020, 1950, 1755, 1730, 1475, 1445, 1385, 1365, 1315, 1295, 1265, 1245, 1215, 1190, 1155, 1090, 1030, 835, 750, 670, 605, 570; ^1H NMR ($CDCl_3$) δ 4.80 (s, 1 H), 3.79 (dq, J = 7 and 3 Hz, 4 H), 2.90–2.77 (br s, 1 H), 2.57–2.47 (s, 1 H), 2.35–2.1 (br s, 1 H), 1.89–1.37 (m, 9 H), 1.11 (dt, J = 7 and 3 Hz, 6 H), 0.07 (s, 9 H); MS, m/e 504 (M^+), 476 ($M^+ - CO$), 448 ($M^+ - 2CO$), 420 ($M^+ - 3CO$).

Diethyl 2-[4-(Trimethylsilyl)bicyclo[4.4.0]deca-3,5-dienyl]malonate (19). Treatment of 78 mg (0.15 mmol) of **17** with 145 mg (1.24 mmol) of 98% trimethylamine *N*-oxide dihydrate in the usual manner yielded 30 mg (53%) of **19** as a clear colorless liquid: IR (cm^{-1}, film) 2930, 1755, 1440, 1365, 1300, 1245, 1170, 1025, 860, 830, 745; ^{1}H NMR ($CDCl_3$) δ 5.51 (s, 1 H), 4.35 (d, J = 3 Hz, 1 H), 4.05 (q, J = 7 Hz, 4 H), 3.40 (d, J = 12 Hz, 1 H), 3.28–2.00 (m, 1 H), 2.80–1.33 (series of m, 9 H), 1.10 (t, J = 7 Hz, 6 H) –0.09 (s, 9 H); MS, *m/e* ($M^+ - H_2$) calcd 362.1913, obsd 362.1903.

Tricarbonyl[*anti*-ethyl (2–5-η-3-(trimethylsilyl)-6,6-dimethyl-2,4-cyclohexadienyl)(phenylsulfonyl)acetate]iron (20 and 21). A solution of 246 mg (1.08 mmol) of ethyl (phenylsulfonyl)acetate[29] in 5 mL of dry tetrahydrofuran was added dropwise under nitrogen via syringe to a rapidly stirred suspension of 52 mg (1.1 mmol) of 50% sodium hydride (mineral oil dispersion, prewashed three times with 4 mL of pentane). The clear colorless ethyl (phenylsulfonyl)sodioacetate solution was sitrred at room temperature for 5 min and then 2 mL thereof was added under nitrogen via syringe to a rapidly stirred suspension of 100 mg (0.216 mmol) of **11a** in 5 mL of dry tetrahydrofuran. The clear yellow reaction mixture was stirred at room temperature for 30 min and then processed as described above, giving 82 mg (69.5%) of a clear yellow oily mixture of diastereomers **20** and **21**, which crystallized on standing. Recrystallization of 69 mg of this material from 2 mL of hot hexanes afforded 33 mg of fine white needles (slightly enriched in the downfield silyl compound): mp 109–110 °C; IR (cm^{-1}, film), 2960, 2030, 1950, 1740, 1460, 1445, 1365, 1325, 1310, 1275, 1265, 1245, 1135, 835, 780, 750, 710, 680, 610, 590, 575; ^{1}H NMR ($CDCl_3$) δ 8.08–7.77 (m, 2 H), 7.75–7.42 (m, 3 H), 5.22–5.00 (m, 1 H), 4.13 (d, J = 7 Hz, 1 H), 3.73 (q, J = 7 Hz, 2 H), 3.02 (d, J = 7 Hz, 1 H), 2.77 (br s, 1 H), 1.58 (br s, 1 H), 1.22 (t, J =v 7 Hz, 3 H), 0.9 (d, J = 3 Hz, 3 H), 0.79 (d, J = 3 Hz, 3 H), 0.38, 0.15 (2 s, 9 H); MS, *m/e* 546 (M^+), 518 ($M^+ - CO$), 490 (M^+ – 2COe, 462 ($M^+ - 3CO$).

Ethyl [3-(Trimethylsilyl)-6,6-dimethyl-2,4-cyclohexadienyl](phenylsulfonyl)acetate (22 and 23). Treatment of 73.5 mg (0.13 mmol of **20**/**21** with 130 mg (1.12 mmol) of 98% trimethylamine *N*-oxide dihydrate in the usual manner (refluxed for 8 h) yielded 32 mg (59%) of **22**/**23** as a clear yellow oil: IR (cm^{-1}, $CHCl_3$) 2950, 1735, 1460, 1445, 1365, 1320, 1305, 1240, 1135, 1075, 1015, 830, 655, 575, 520; ^{1}H NMR ($CDCl_3$) δ 7.83–7.67 (m, 2 H), 7.50–7.20 (m, 3 H), 5.83 (d, J = 6 Hz, 1 H), 5.63 (d, J = 10 Hz, 1 H), 5.21 (d, J = 10 Hz, 1 H), 4.03 (d, J = 2 Hz, 1 H), 3.85 (q, J = 7 Hz, 2 H), 2.95 (dd, J = 2 and 2 Hz, 1 H), 0.98 (t, J = 7 Hz, 3 H), 0.80 (s, 3 H), 0.67 (s, 3 H), –0.18 (s, 9 H); MS, *m/e* 406 (M^+), 391 ($M^+ - CH_3$).

Tricarbonyl[*anti*-3-(2–5-η-3-(trimethylsilyl)-6,6-dimethyl-2,4-cyclohexadienyl)oxacyclopentan-2-one]iron (24 and 26). A solution of 100.5 mg (0.217 mmol) of **11a** and 170 mg (1.07 mmol) of trimethyl[(4,5-dihydro-2-furanyl)oxy]silane[30] in 5 mL of dry acetonitrile was stirred under nitrogen at room temperature for 22 h. Evaporation of the solvent and chromatography of the semisolid residue (220 mg) on silica gel (10 g, elution with benzene) gave 8.9 mg (10%) of **24** and 26 mg (29%) of **26**, both as white solids.

For **24**: IR (cm^{-1}, $CHCl_3$) 2950, 2030, 1960, 1765, 1365, 1245, 1020, 835, 605, 570; ^{1}H NMR ($CDCl_3$) δ 4.93 (dd, J = 6 and 2 Hz, 1 H), 4.05 (dt, J = 6 and 3 Hz, 2 H), 3.29 (s, 1 H), 2.86 (d, J = 6 Hz, 1 H), 2.05–1.96 (m, 4 H), 0.6 (s, 3 H), 0.75 (s, 3 H), 0.11 (s, 9 Hef MS, *m/e* (M^+) calcd 404.0742, obsd 404.0750.

For **26**: IR (cm^{-1}, $CHCl_3$) 2950, 2030, 1960, 1765, 1370, 1245, 1020, 830, 605, 570; ^{1}H NMR ($CDCl_3$) δ 4.93 (d, J = 7 Hz, 1 H), 3.99 (t, J = 7 Hz, 2 H), 2.29 (d, J = 7 Hz, 1 H), 2.57–2.37 (m, 2 H), 1.95 (overlapping t, J = 7 Hz and m, 3 H), 0.95 (s, 3 H), 0.65 (s, 3 H), 0.18 (s, 9 H); MS, *m/e* ($M^+ - CH_3$) calcd 389.0507, obsd 389.0515.

(*S*)-3-[3-(Trimethylsilyl)-6,6-dimethyl-2,4-cyclohexadienyl]oxacyclopentan-2-one (25). Reaction of 18 mg (0.045 mmole of **24** with 42 mg (0.36 mmole of 98% trimethylamine *N*-oxide dihydrate in the usual manner afforded 8.4 mg (71%) of **25** as a clear yellow oil: IR (cm^{-1}, $CHCl_3$) 2950, 1765, 1555, 1465, 1365, 1240, 1160, 1135, 1020, 965, 900, 830; ^{1}H NMR ($CDCl_3$) δ 5.73 (d, J = 6 Hz, 1 H), 5.65 (d, J = 10 Hz, 1 H), 5.27 (d, J = 10 Hz, 1 H), 4.23–3.80 (m, 2 H), 2.47–2.17 (m, 1 H), 2.13–1.87 (m, 2 H), 1.12 (d, J = 6 Hz, 1 H), 0.87 (s, 6 H), –0.08 (s, 9 H); MS, *m/e* (M^+) calcd 264.1545, obsd 264.1533.

(*R*)-3-[3-(Trimethylsilyl)-6,6-dimethyl-2,4-cyclohexadienyl]oxacyclopentan-2-one (27). Reaction of 51.5 mg (0.13 mmol) of **26** with 120 mg (1.03 mmol) of 98% trimethylamine *N*-oxide dihydrate in the usual manner yielded 23 mg (69%) of **27** as a clear yellow oil: IR (cm^{-1}, $CHCl_3$) 2950, 1765, 1555, 1465, 1370, 1240, 1205, 1160, 1020, 965, 900, 830; ^{1}H NMR ($CDCl_3$) δ 5.80–5.55 (m, 2 H), 5.25 (d, J = 10 Hz, 1 H), 4.18–3.82 (m, 2 H), 2.72–2.43 (m, 1 H), 2.20–1.73 (m, 2 H), 1.13 (d, J = 6 Hz, 1 H), 0.87 (s, 6 H), –0.10 (s, 9 H); ^{13}C NMR (ppm, $CDCl_3$) 137.15, 132.20, 123.70, 66.80, 43.50, 40.10, 32.72, 28.35, 24.42, 24.08, –1.99; MS, *m/e* (M^+) calcd 264.1545, obsd 264.1553.

Acknowledgment. We are grateful to Dr. M. C. Böhm for carrying out the model calculations, to Dr. Susan Hathaway for experimental assistance, and to the National Science Foundation, Deutsche Forschungsgemeinschaft, Fonds der Chemischen Industrie, and BASF Aktiengesellschaft in Ludwigshafen for financial support.

Registry No. **5**, 81044-36-2; **6**, 81044-35-1; **7**, 81044-37-3; **8a**, 63031-70-9; **8b**, 81064-06-4; **9a**, 81064-43-9; **9b**, 81064-42-8; **9c**, 81064-40-6; **9d**, 81064-41-7; **10**, 81064-33-7; **11a**, 81064-35-9; **11b**, 81064-39-3; **11c**, 81064-26-8; *endo*-**11d**, 81064-37-1; *exo*-**11d**, 81132-00-5; **12**, 81064-31-5; **16a**, 88996-43-4; **16b**, 88996-44-5; **16c**, 81064-32-6; **16d**, 88996-45-6; **17a**, 88996-46-7; **17b**, 88996-28-5; **17c**, 88996-29-6; **17d**, 88996-30-9; **18**, 81064-28-0; **19**, 88996-31-0; **20**, 88996-47-8; **21**, 89063-55-8; **22**, 88996-32-1; **23**, 88996-33-2; **24**, 81064-29-1; **25**, 88996-34-3; **26**, 81130-66-7; **27**, 88996-35-4; $Fe_2(CO)_9$, 15321-51-4; $PhSO_2NHNH_2$, 80-17-1; Me_3SiCl, 75-77-4; $Ph_3C^+BF_4^-$, 341-02-6; 4,4-dimethyl-2-cyclohexenone (phenylsulfonyl)hydrazone, 88996-36-5; 4,4-dimethyl-2-cyclohexenone, 1073-13-8; 3-methyl-2-cyclohexenone, 1193-18-6; Δ^1-bicyclo[4.4.0]decen-3-one, 1196-55-0; $\Delta^{1(6)}$-bicyclo[4.4.0]decen-3-one, 18631-96-4; Δ^1-bicyclo[4.4.0]decen-3-one (phenylsulfonyl)hydrazone, 88996-38-7; 3-methyl-2-cyclohexenone (phenylsulfonyl)hydrazone, 88996-37-6; 2-bromocyclohexanone (phenylsulfonyl)hydrazone, 88996-39-8; 2-bromocyclohexanone, 822-85-5; 2-cyclohexenone (phenylsulfonyl)hydrazone, 88996-40-1; 2-bromo-4-methylcyclohexanone (phenylsulfonyl)hydrazone, 88996-41-2; 2-bromo-4-methylcyclohexanone, 27579-55-1; 4-methyl-2-cyclohexenone (phenylsulfonyl)hydrazone, 88996-42-3; ammonium hexafluorophosphate, 16941-11-0; diethyl malonate, 105-53-3; trimethylamine *N*-oxide, 1184-78-7; ethyl (phenylsulfonyl)acetate, 7605-30-3; ethyl (phenylsulfonyl)sodioacetate, 75850-40-7; diethyl sodiomalonate, 996-82-7; trimethyl[(4,5-dihydro-2-furanyl)oxy]silane, 51425-66-2.