Direct Lithiation of (Cyclobutadiene)tricarbonyliron and ((Trimethylsilyl)cyclobutadiene)tricarbonyliron with *sec*-Butyllithium: Selective *para* Metalation

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(Cyclobutadiene)tricarbonyliron (**1a**) is metalated on treatment with *sec*-BuLi in THF, as could be shown by reaction of the product (lithiocyclobutadiene)tricarbonyliron (**1b**) with a variety of electrophiles (*inter alia* trimethylchlorosilane, methyl disulfide, methyl iodide, and diiodoethane); the respective adducts were obtained in good yields. Similarly, metalation of ((trimethylsilyl)cyclobutadiene)tricarbonyliron (**1c**) affords (3-lithio-1-(trimethylsilyl)cyclobutadiene)tricarbonyliron (**3a**), which has also been trapped with standard electrophiles. No products of *ortho* metalation were observed.

Introduction

The chemistry of cyclobutadiene[1] has challenged both experimentalists and theoreticians due to its importance with regard to the concept of (anti)aromaticity.[1b] The extreme reactivity of cyclobutadiene does not allow isolation of this compound under ordinary conditions.[2] Stabilization can be attained by capture through a macrocyclic host[2a] or complexation with an 14-electron organotransition-metal fragment to yield stable organometallic compounds,[2b] of which the most famous are (cyclobutadiene)tricarbonyliron (**1a**)[3] and cobalt complex **2**.[4] Free cyclobutadiene is liberated by oxidative decomposition of **1a**[2b] by cerium(IV) salts; **1a** can be considered a storage form of cyclobutadiene. Substituted cyclobutadiene complexes undergo this reaction as well.[2b]

The synthesis of substituted (cyclobutadiene)tricarbonyliron complexes has been achieved by preparation of suitable dihalocyclobutene precursors[5] in multistep sequences, by electrophilic substitution of **1a** under Lewis acid catalysis, thereby exploiting its metalloaromatic character,[5b,6] or most elegantly by dimerization of alkynes under the influence of a transition-metal fragment.[7]

Direct lithiation on the other hand is an important and often very efficient way of functionalization for organic and organometallic entities.[8] A prerequisite for the success of this reaction is the sufficient activation of the C–H bond involved and the stability of the substrate to strongly basic reaction conditions.

In contrast to the well-developed field of lithiated cyclopentadienyl complexes,[9] the chemistry of lithiated organotransition-metal-bonded cyclobutadienes has attracted much less attention. Early attempts to deprotonate **1a** by either MeLi or *n*-BuLi afforded the ketones **1j,k** instead.[10] Up to now there have been only three examples of lithiated cyclobutadiene complexes. One is prepared by metal halogen exchange of the iodide **1d**[10] (which itself is not easily available[6a]) with methyllithium. In the two other cases the organolithiums were obtained either by tin lithium exchange of a cobalt cyclobutadiene complex[11] or by direct deprotonation of **2** with *n*-butyllithium in tetramethylethylenediamine.[4] In the latter case the organolithiums were quenched by carbon dioxide. Metalation of both rings is a side reaction, and the yield of the desired mono acid (30%) is not satisfactory.

To find conditions for direct lithiation of **1a** would be a desirable process, considering the synthetic potential of organolithiums!

Results

Reaction of **1** with *sec*-butyllithium in tetrahydrofuran at −78 °C for 15 min (conditions described by Stille for lithiation of cyclopentadienylmanganese tricarbonyl[9]) afforded a dark brown but clear solution of **1b**. Reaction of **1b** with trimethylchlorosilane, 1,2-diiodoethane, methyl disulfide, trimethyltin chloride, methyl iodide, hexachloroethane, and diphenylchlorophosphane yielded the corresponding heterosubstituted (cyclobutadiene)tricarbonyliron complexes **1c–i** in yields between 58 and 67% (Table I). A notable exception is chloride **1h**, which was isolated in 26% yield only. Compounds **1d–g** have not been described in the literature.

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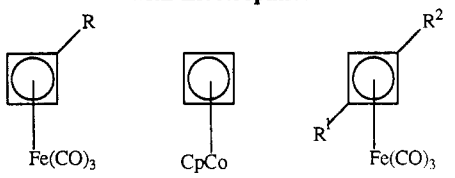
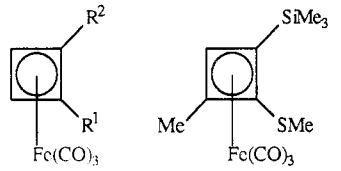
Table I. Substituent Key for 1, 3, and 4 and Yields of the Reaction of (Lithiocyclobutadiene)tricarbonyliron Complexes with Electrophiles



1 2 3



4 5

1	R	yield (%)	3, 4	R^1	R^2	yield (3, %)
a	H		a	$SiMe_3$	Li	
b	Li		b	$SiMe_3$	Me	63
c	$SiMe_3$	59	c	$SiMe_3$	I	56
d	I	67	d	$SiMe_3$	SMe	72
e	SMe	61	e	$SiMe_3$	$SiMe_3$	46
f	$SnMe_3$	60	f	$SiMe_3$	CH_2SMe	16
g	PPh_2	58	g	SMe	Me	
h	Cl	26				
i	Me	58				
j	C=OMe	*a*				
k	C=OBu	*a*				
l	$CH(SR)_2$	*a*				

[a] The entries for **1j–l** are only to list the substituents.

When silane **1c** was subjected to the same metalation conditions with *sec*-BuLi in THF, a clear yellow solution of **3a** formed. Functionalization of the organolithium compound with methyl iodide resulted in isolation of a yellow oil, whose proton NMR spectrum shows three singlets at δ 4.05, 1.79, and 0.10 in the ratio 2:3:9. The carbon NMR shows six signals at δ 215.1 (s), 93.9 (s), 69.4 (d), 61.2 (s), 13.7 (q), and −0.7 (q). The signal at δ 215.1 is attributed to the carbonyl groups, while three resonances at 93.9, 69.4, and 61.2 are assigned to the complexed cyclobutadienyl ring. The remaining two signals are due to the methyl and the trimethylsilyl group, respectively. These spectroscopic data strongly suggest that the two substituents are placed *para* to each other, leaving a plane of symmetry in **3b** intact. Reaction of **3a** with diiodoethane or methyl disulfide gives rise to the isolation of compounds **3c** and **3d**. Their NMR spectroscopic data are in full accordance with the above *para* assignment. In the case of (bis(trimethylsilyl)cyclobutadiene)tricarbonyliron (**3e**) (obtained by functionalization of **3a** with trimethylchlorosilane in 46% yield) the *para* substitution pattern can only be concluded from the other functionalization experiments. To strengthen the assumption of *para* metalation, **1e** was deprotonated and the corresponding metalated species were functionalized with trimethylchlorosilane. An inseparable mixture of the *ortho* and *para* isomers **3d** and **4d** is formed in the ratio of ca. 1:2:3. The major component has the same NMR spectroscopic characteristics as the independently prepared *para* compound **3d**. In the case of the *ortho*-substituted **4d** the two ring protons appear as two singlets at δ 4.16 and 4.64, respectively; for the cyclobutadiene ring of **4d** the carbon NMR spectrum shows also four different signals of correct multiplicity, in contrast to the spectrum for the *para*-substituted **3d**, where only three signals are observed.

When **3b** was subjected to the above-described metalation conditions and functionalized with methyl disulfide, a single compound was isolated in 16% yield after chromatography involving heavy losses. Its proton NMR spectrum shows four singlets at δ 4.17, 3.06, 2.22, and 0.10 in the ratio of 2:2:3:9. Moreover, the carbon NMR spectrum shows seven signals at δ 214.6 (s), 91.7 (s), 68.5 (d), 63.9 (s), 31.6 (t), 16.0 (q), and −0.8 (q). These spectral data rule out this compound being (1-(trimethylsilyl)-2-(methylthio)-3-methylcyclobutadiene)tricarbonyliron (**5**): the proton-coupled carbon NMR spectrum shows the presence of a methylene group and one instead of two methyl groups. The carbon NMR spectrum of **5** would be expected to show signals for three and not for only two quarternary carbon atoms as observed. Additionally, the integration of the proton NMR spectrum is at odds with the proposed structure. Instead, structure **3f** is in full accordance with the spectral data.

In order to make sure that the methyl position is not generally more acidic than the ring protons in compounds such as **1i**, we carried out a deprotonation reaction of this substrate under the above-described conditions and functionalized with methyl disulfide. We isolated an inseparable mixture which contained two main compounds, the *ortho*- and *para*-disubstituted complexes **3g** and **4g**, and a small (less than 5% by proton NMR integration) amount of other compounds which might have resulted by deprotonation of the methyl group. The selectivity of the *ortho* position over the *para* position is in this case ca. 2.5:1, corrected by the statistical bias.

Discussion

Attempts to deprotonate **1a** with *n*-alkyllithium reagents such as *n*-BuLi or MeLi resulted in the formation of ketones **1j** and **1k**.[10] The use of *sec*-BuLi at −78 °C in THF fortuitously suppresses this undesired side reaction. Instead, clean lithiation of the complexed cyclobutadiene ring is achieved. A wide variety of heterosubstituted complexes **1c–i** can be conveniently synthesized by this method. These compounds are otherwise not easily prepared. Especially, the hitherto unknown alkynyl-substituted (cyclobutadiene)tricarbonylirons should be accessible from iodide[6a] **1d**, which we can now obtain in gram quantities.

In the case of silane **1c** a pronounced *para* selectivity of the metalation reaction is observed. It is known that silicon substituents stabilize adjacent negative charges,[12] while at the β-position a positive charge is heavily stabilized[13] by the overlap of the carbon–silicon bond with the empty π orbital of the positive charge. The enhanced electron density of the carbon–silicon bond, on the other hand, destabilizes a negative charge β to the silicon substituent. This is probably more pronounced due to the forced *syn*-periplanar arrangement in the situation under consideration. The large steric demand of the trimethylsilyl group additionally enhances the *para* selectivity. 1,3-Heterodisubstituted (cyclobutadiene)tricarbonylirons are otherwise difficult to obtain;[2b,5b,6b] an exception is the low-yield dimerization of a 1-silyl-2-amino-

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substituted alkyne by iron pentacarbonyl.[14] Therefore, the method described here offers an access to *para*-trimethylsilyl-substituted (cyclobutadiene)tricarbonyl-irons (**3**).

In the case of the methyl- and the methylthio-substituted cyclobutadiene complexes **1i** and **1e**, deprotonation occurs at both *ortho* and *para* positions and the small differences in regioselectivity obtained render these reactions unattractive for preparation of disubstituted (cyclobutadiene)-tricarbonylirons. In **1i** we could not detect metalation of the methyl substituent.

However, the regioselectivity changes in the case of **3b**, whose most acidic proton is not located on the cyclobutadiene ring but at the attached methyl group. It is not unreasonable to assume that the increased steric bulk of the two substituents suppresses the ring metalation completely and instead leads to the metalation of the methyl protons. In a similar case, the attempted functionalization of **1l**[6b] with *n*-butyllithium merely leads to isolation of starting material. The reason for the difference in behavior of **1l** compared to that of **3b** is not clear.

Experimental Section

General Procedure. A flame-dried and nitrogen-flushed 100-mL Schlenk flask with magnetic stirbar is charged with 50 mL of anhydrous THF (freshly distilled from benzophenone–potassium) and the specified amount of (cyclobutadiene)-tricarbonyliron complex. After the mixture is cooled to −78 °C, 1.1 equiv of an 1.4 mol/L solution of *sec*-BuLi in pentane/cyclohexane is added by syringe. After 15 min of stirring at this temperature a dark clear solution has formed. An excess of the electrophile is added by syringe, and the cooling bath is removed. The reaction mixture is stirred for 1 h. After aqueous workup the residues are distilled at 0.001 mmHg and subsequently chromatographed over silica with pentane as eluent to give the desired compound as brown-yellow oils.

Tricarbonyl[(1–4-η)-(trimethylsilyl)-1,3-cyclobutadiene]-iron[10] **(1c).** **1a** (500 mg, 2.60 mmol), *sec*-BuLi (2.00 mL, 2.80 mmol), and trimethylchlorosilane (326 mg, 3.00 mmol) are treated according to the general procedure. Distillation at 20 °C/0.001 mmHg and chromatography yields 403 mg (59%) of the known **1c**.

Tricarbonyl[(1–4-η)-iodo-1,3-cyclobutadiene]iron[6a] **(1d).** **1a** (2.00 g, 10.4 mmol), *sec*-BuLi (8.20 mL, 11.5 mmol), and diiodoethane (3.24 g, 11.5 mmol), after distillation at 20 °C/0.001 mmHg, yield 2.23 g (67.3%) of the known **1d**.

Tricarbonyl[(1–4-η)-(methylthio)-1,3-cyclobutadiene]-iron (1e). **1a** (265 mg, 1.38 mmol), *sec*-BuLi (1.10 mL, 1.54 mmol), and methyl disulfide (1.00 g, 10.62 mmol), after distillation at 20 °C/0.005 mmHg, yield 201 mg (61%) of the analytically pure **1e**. IR (KBr, cm^{-1}): ν 2925, 2043 (CO), 1964 (CO), 1434, 1424, 1342, 1317. ^1H NMR ($CDCl_3$): δ 2.21 (s, 3 H), 4.13 (s, 1 H), 4.23 (s, 2 H). ^{13}C NMR ($CDCl_3$): δ 18.38 (q), 60.45 (d), 65.25 (d), 84.34 (s), 213.77 (s). Mass (EI; *m/z* (relative intensity, %)): 238 (M^+, 53), 210 (M^+ − CO, 100), 182 (M^+ − 2CO, 16), 154 (M^+ − 3CO), 121 (48). Anal. Calcd: C, 40.36; H, 2.54. Found: C, 40.00; H, 2.64.

Tricarbonyl[(1–4-η)-(trimethylstannyl)-1,3-cyclobutadiene]iron (1f). **1a** (312 mg, 1.63 mmol), *sec*-BuLi (1.28 mL, 1.80 mmol), and trimethyltin chloride (400 mg, 2.01 mmol), after distillation at 40 °C/0.005 mmHg, yield 346 mg (60%) of the sensitive **1f**. IR (KBr, cm^{-1}): ν 2986, 2919, 2040 (CO), 1960 (CO), 1256, 1193, 992, 927, 824. ^1H NMR ($CDCl_3$): δ 0.20 (s, 9 H), 3.97 (s, 2 H), 4.42 (s, 1 H). ^{13}C NMR ($CDCl_3$): δ −8.71 (q), 65.81 (s), 70.72 (d), 71.36 (d), 215.09 (s).

Tricarbonyl[(1–4-η)-(diphenylphosphino)-1,3-cyclobutadiene]iron (1g). **1a** (208 mg, 1.08 mmol), *sec*-BuLi (0.86 mL, 1.20 mmol), and chlorodiphenylphosphine (265 mg, 1.20 mmol), after chromatography (pentane/methylene chloride, 2:1), yield 237 mg (58%) of the analytically pure **1g**. IR (KBr, cm^{-1}): ν 3071, 3056, 2048 (CO), 1975 (CO), 1907, 1479, 1434, 1093. ^1H NMR ($CDCl_3$): δ 4.36 (d, J_{PH} = 0.64 Hz, 2 H), 4.49 (d, J_{PH} = 6.54 Hz, 1 H) 7.3–7.6 (m, 10 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 63.70, 68.86, 77.00, 77.43, 137.57, 133.10, 132.87, 128.90, 128.41, 213.11. Mass (EI; *m/z* (relative intensity, %)): 376 (M^+, 0.5), 348 (M^+ − CO, 58), 292 (M^+ − 3CO, 100), 291 (61), 188 (48), 183 (51). Anal. Calcd: C, 60.67; H, 3.48. Found: C, 60.44; H, 3.63.

Tricarbonyl[(1–4-η)-chloro-1,3-cyclobutadiene]iron[15] **(1h).** **1a** (500 mg, 2.61 mmol), *sec*-BuLi (1.90 mL, 2.66 mmol), and hexachloroethane (660 mg, 2.79 mmol), after distillation at 20 °C/0.01 mmHg, yield 152 mg (26%) of the known **1h**.

Tricarbonyl[(1–4-η)-methyl-1,3-cyclobutadiene]iron[16] **(1i).** **1a** (500 mg, 2.61 mmol), *sec*-BuLi (1.90 mL, 2.66 mmol), and methyl iodide (452 mg, 3.18 mmol), after distillation at 20 °C/0.001 mmHg, yield 309 mg (58%) of the known **1i**.

Tricarbonyl[(1–4-η)-3-methyl-1-(trimethylsilyl)-1,3-cyclobutadiene]iron (3b). **1c** (362 mg, 1.37 mmol), *sec*-BuLi (1.10 mL, 1.54 mmol), and iodomethane (1.00 g, 7.05 mmol), after distillation at 20 °C/0.05 mmHg and subsequent chromatography, yield 239 mg (63%) of analytically pure **3b**. IR (KBr, cm^{-1}): ν 3085, 2959, 2925, 2900, 2040 (CO), 1963 (CO), 1451, 1337, 1251, 1054, 1014, 841. ^1H NMR ($CDCl_3$): δ 0.10 (s, 9 H), 1.79 (s, 3 H), 4.05 (s, 2 H). ^{13}C NMR ($CDCl_3$): δ −0.70 (q), 13.66 (q), 61.20 (s), 93.91 (s), 69.38 (d), 215.14 (s). Mass (EI; *m/z* (relative intensity, %)): 278 (M^+, 9), 250 (M^+ − CO, 16), 222 (M^+ − 2CO, 24), 194 (M^+ − 3CO, 58), 154 (100). Anal. Calcd: C, 47.50; H, 5.07. Found: C, 47.47; H, 5.28.

Tricarbonyl[(1–4-η)-1-iodo-3-(trimethylsilyl)-1,3-cyclobutadiene]iron (3c). **1c** (507 mg, 1.92 mmol), *sec*-BuLi (1.57 mL, 2.20 mmol), and diiodoethane (620 mg, 2.20 mmol), after distillation at 40 °C/0.001 mmHg and subsequent chromatography, yield 422 mg (56%) of **3c**. IR (KBr, cm^{-1}): ν 3110, 2958, 2048 (CO), 1974 (CO), 1308, 1252, 1012, 843. ^1H NMR ($CDCl_3$): δ −0.05 (s, 9 H), 3.81 (s, 2 H). ^{13}C NMR (C_6D_6): δ −1.06 (q), 31.29 (s), 65.77 (s), 74.13 (d), 214.45 (s). Mass (EI; *m/z* (relative intensity, %)): 390 (M^+, 5), 362 (M^+ − CO, 16), 334 (M^+ − 2CO, 23), 306 (M^+ − 3CO, 15), 266 (12).

Tricarbonyl[(1–4-η)-1-(methylthio)-3-(trimethylsilyl)-1,3-cyclobutadiene]iron (3d). **1c** (236 mg, 0.893 mmol), *sec*-BuLi (0.650 mL, 0.910 mmol), and methyl disulfide (500 mg, 5.31 mmol) yield 199 mg (72%) of crude product and after chromatography yield 92 mg (33%) of analytically pure material. IR (KBr, cm^{-1}): ν 2957, 2926, 2039 (CO), 1965 (CO) 1962 (CO), 1435, 1425, 1251, 843. ^1H NMR ($CDCl_3$): δ 0.09 (s, 9 H), 2.20 (s, 3 H) 4.28 (s, 2 H). ^{13}C NMR ($CDCl_3$): δ −0.81 (q), 15.88 (q), 60.89 (s), 97.17 (s), 67.67 (d), 214.16 (s). Mass (EI; *m/z* (relative intensity, %)): 310 (M^+, 19), 282 (M^+ − CO, 84), 254 (M^+ − 2CO, 59), 226 (M^+ − 3CO, 49), 168 (77), 154 (100). Anal. Calcd: C, 42.59; H, 4.55. Found: C, 42.67; H, 4.53.

Tricarbonyl[(1–4-η)-1,3-bis(trimethylsilyl)-1,3-cyclobutadiene]iron (3e). **1c** (244 mg, 0.924 mmol), *sec*-BuLi (0.700 mL, 0.980 mmol), and trimethylchlorosilane (200 mg, 1.84 mmol), after distillation at 0.01 mmHg/30 °C and subsequent chromatography, yield 143 mg (46%) of **3e**. IR (KBr, cm^{-1}): ν 3120, 2960, 2038 (CO), 1966 (CO), 1251, 839. ^1H NMR ($CDCl_3$): δ 0.05 (s, 18 H), 3.74 (s, 2 H). ^{13}C NMR (C_6D_6): δ −1.12 (q), 73.39 (d), 77.96 (s), 215.81 (s). Mass (EI; *m/z* (relative intensity, %)): 336 (M^+, 23), 308 (M^+ − CO, 32), 280 (M^+ − 2CO, 43), 252 (M^+ − 3CO, 100), 154 (72). Anal. Calcd: C, 46.25; H, 5.99. Found: C, 46.35; H, 6.08.

Tricarbonyl[(1–4-η)-3-((methylthio)methyl)-1-(trimethylsilyl)-1,3-cyclobutadiene]iron (3f). **3b** (211 mg, 0.759 mmol), *sec*-BuLi (0.571 mL, 0.800 mmol), and methyl disulfide (200 mg, 2.12 mmol), after chromatography with a 1:1 methylene chloride/pentane mixture, yield 39 mg (16%) of analytically pure **3f**. IR

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(KBr, cm^{-1}): ν 2957, 2919, 2040 (CO), 1965 (CO), 1438, 1337, 1251, 1012. ^1H NMR ($CDCl_3$): δ 0.10 (s, 9 H), 2.22 (s, 3 H), 3.06 (s, 2 H), 4.17 (s, 2 H). ^{13}C NMR ($CDCl_3$): δ −0.83 (q), 16.04 (q), 31.60 (t), 63.94 (s), 68.52 (d), 91.66 (s), 214.60 (s). Mass (EI; *m/z* (relative intensity, %)): 324 (M^+, 3), 296 (M^+ − CO, 72), 277 (100), 268 (M^+ − 2CO, 44), 240 (M^+ − 3CO, 25), 224 (68). Anal. Calcd: C, 44.44; H, 4.97. Found: C, 44.62; H, 5.02.

Metalation of 1e. **1e** (113 mg, 0.475 mmol), *sec*-BuLi (0.360 mL, 0.504 mmol), and trimethylchlorosilane (105 mg, 0.966 mmol), after distillation at 30 °C/0.001 mmHg, yield 51 mg (35%) of a 2.3:1 mixture of **3d** and **tricarbonyl[(1–4-η)-1-(methylthio)-2-(trimethylsilyl)-1,3-cyclobutadiene]iron (4d)** as an inseparable mixture. **3d** was identified according to its known NMR data (*vide supra*). **4d**: ^1H NMR ($CDCl_3$) δ 0.18 (s, 9 H), 2.21 (s, 3 H), 4.16, 4.64 (2 s, 2 H); ^{13}C NMR ($CDCl_3$) δ −0.64 (q), 19.00 (q), 65.26 (s), 65.60 (d), 72.25 (d), 88.84 (s) 214.17 (s).

Metalation of 1i. **1i** (309 mg, 1.50 mmol), *sec*-BuLi (1.20 mL, 1.68 mmol), and methyl disulfide (212 mg, 2.25 mmol), after distillation at 40 °C/0.01 mmHg, yield 117 mg (31%) of an inseparable mixture of **tricarbonyl[(1–4-η)-2-methyl-1-(methylthio)-1,3-cyclobutadiene]iron (4g)** and **tricarbonyl-[(1–4-η)-3-methyl-1-(methylthio)-1,3-cyclobutadiene]iron (3g)** in a 5.1:1 ratio. **4g**: ^1H NMR ($CDCl_3$) δ 1.84 (s, 3 H), 2.23 (s, 3 H), 4.15, 4.19 (2 s, 2 H); ^{13}C NMR ($CDCl_3$) δ 11.63 (q), 19.26 (q), 61.52 (d), 63.01 (d), 63.90 (s), 88.18 (s), 214.11 (s). **3g**: ^1H NMR ($CDCl_3$) δ 1.79 (s, 3 H), 2.19 (s, 3 H), 4.30 (s, 2 H).

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