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Generation and Trapping of Radicals Derived from Cyclobutadieneiron Tricarbonyl

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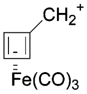
Summary: Trapping products consistent with the formation of radical intermediates α *to and on the ring carbon of cyclobutadieneiron tricarbonyl have been synthesized. These examples constitute the first strong experimental evidence for the formation of radicals derived from cyclobutadieneiron tricarbonyl.*

Introduction

Cyclobutadiene has long been a molecule of interest to organic chemists,[1] but has been directly observed only under the most stringent conditions.[2] Due to its exceptional instability, it has usually been incorporated into more complex organic structures as its $Fe(CO)_3$ derivative, cyclobutadieneiron tricarbonyl[3] (henceforth, CBIT), which can undergo further transformations under a wide variety of conditions. Free cyclobutadiene or cyclobutadiene derivatives for subsequent trapping experiments are commonly generated upon oxidation of these $Fe(CO)_3$ complexes, most commonly with ceric ammonium nitrate.[3]

Recently, there has been a modest, but significant resurgence of interest in the reactivity of derivatives of CBIT. CBIT-stabilized cation **1**[4] has recently been studied extensively by the Snapper group,[5] who have demonstrated the synthetic utility of this interesting intermediate, which reacts as an electrophilic partner in a variety of transformations. These reactions have been used to append olefinic substituents to CBIT, allowing for the syntheses of a wide variety of novel polycyclic systems through intramolecular Diels−Alder reactions, which in turn have proven to be useful precursors to interesting ring systems found in natural products.[5e]



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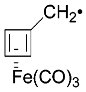

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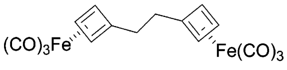

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Given our general interest in radical reactions, and more specifically in the radical reactions of transition metal polyene complexes, we became interested in the generation and trapping of the α-methylene CBIT radical (**2**). The ways in which a modest number of common transition metal complexes interact with adjacent radicals have been studied. For example, experimental[6] and theoretical[7] studies have indicated a significant radical stabilizing effect by ferrocene. Radicals stabilized by iron-diene complexes, formally pentadienyl radicals, have been implicated in electrochemical studies,[8] as well as in radical additions to the uncomplexed alkene in iron-triene complexes.[9] Cyclizations of radicals mediated by $(alkyne)Co_2(CO)_6$[10] and reductive dimerizations of radicals derived from $(alkyne)Co_2(CO)_6$-stabilized cations[11] have also been studied. Given the paucity of data on radicals stabilized by transition metal−olefin complexes, we felt that examining the reactivity of radical **2** would be intrinsically interesting and might lead to useful methodology.

Very little published work has appeared concerning reactive intermediate **2**. Most notably, Creary[7] has carried out calculations at the B3LYP/LANL2DZ level on the isodesmic reaction between radical **2** and toluene, generating the benzylic radical and methyl CBIT, showing a ΔE of +7.7 kcal/mol, indicating that radical **2** should possess exceptional stability. This computational study also predicted a short exocyclic C−C bond length (1.361 Å), indicative of a double bond and implying a η^3-complex with significant spin delocalization onto the Fe. On the basis of this study, we reasoned that formation of radical **2** should be straightforward, but the question loomed whether it could be rendered reactive enough to add to olefins. There has

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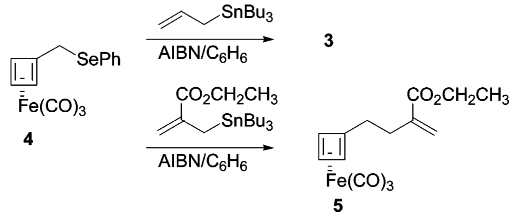
Scheme 1



been scant experimental evidence for radicals of this type. Reductive McMurry radical coupling of the sodium salt of hydroxymethyl CBIT has been shown to form dimer **3**.[12] The reductive pinacol coupling of acetyl CBIT by aluminum amalgam, possibly proceeding through a ketyl intermediate, has also been reported.[13]

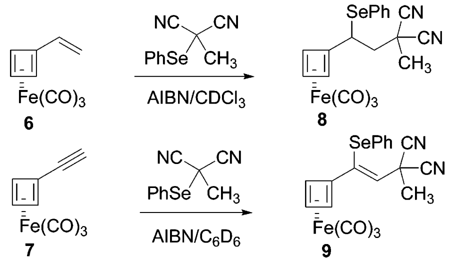
Results and Discussion

Our initial studies focused on the direct generation and trapping of radical **2**, with the assumption that this radical would prove highly nucleophilic, and relatively unreactive. Since phenyl selenides have proven to be useful radical precursors in substrates where solvolysis might be otherwise problematic,[14] we chose to generate phenylselenide **4** as a precursor to radical **2.** This was accomplished by treatment of hydroxymethyl CBIT[15] with PhSeH and catalytic H_2SO_4, leading to formation of **4** in 87% yield. The attempted trapping of radical **2** by allyltributylstannane,[16] generated from **4** under standard AIBN conditions, yielded only minute traces of the desired allylated product, as evidenced by a minor component in the GC/MS exhibiting an ion at 245 *m*/*z* ($M^+ - 1$). The only isolable product of this reaction (Scheme 1) was dimer **3**, as evidenced by its molecular ion at 410 *m*/*z*, and NMR data, which matched literature values.[12] The dimer presumably arose from radical−radical coupling, characteristic of radicals too unreactive to add to olefins at synthetically useful rates.[17]

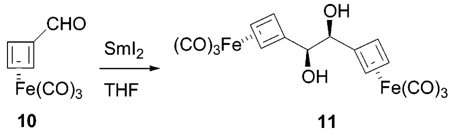
We reasoned that the rate of radical−olefin reactions arising from **2** might be enhanced if a more electron-deficient allylstannane was employed. When **4** was allowed to react with 2-carboethoxyallyltributylstannane[18] in the presence of AIBN, the desired allylated product was obtained in 42% yield (Scheme 1). The successful trapping of this electron-deficient olefin not only confirmed our thesis that **2** should be a highly nucleophilic radical but also diminished any outstanding concerns that allylation might arise through allylstannane nucleophilicity, rather than through a radical process. Thus, we consider this reaction strong evidence for the formation of radical **2**.

We also hoped to demonstrate the intermediacy of radicals similar to **2** through successful atom-transfer addition reactions to vinyl[19] (**6**) and ethynyl-CBIT[20] (**7**). Dimethyl methylphenylselenomalonate[21] did not react with either of these olefins upon reaction in refluxing benzene in the presence of AIBN. This was not surprising, in light of the fact that this reagent will not react with styrene due to slow rates of phenylseleno transfer to well-stabilized benzylic radicals.[22] The more reactive reagent, methylphenylselenomalononitrile,[23] which is known to add to styrene, could be added to these CBIT-substituted olefins **6** and **7** upon radical initiation, in 64% and 25% yields, respectively (Scheme 2). These proved to be very sluggish reactions, however, probably due to the intermediacy of CBIT-stabilized radicals, which would be expected to undergo the phenylselenide-transfer step slowly due to their low reactivity. NMR analysis of the crude reaction mixture yielding **9** showed only one singlet in the normal olefinic region (5.9 ppm), leading us to conclude that only one olefin stereoisomer was generated. Phase-sensitive NOESY NMR spectroscopy of purified **9** gave a significant negative off-diagonal peak showing correlation between this vinylic resonance and the *ortho*-proton on the CBIT ring, supporting the *Z*-stereochemical assignment shown.

Scheme 2



Scheme 3



With the above evidence in hand, we turned our attention to radical reactions arising from the SmI_2 ketyl derived from formyl CBIT (**10**). The $Sm^{(III)}$ ketyl generated from benzaldehyde-$Cr(CO)_3$ has been successfully trapped with acrylate esters, leading to butyrolactones.[24] Treatment of **10** with SmI_2 in the presence of methyl acrylate or ethyl 2-cyanoacrylate yielded only diol **11**. Apparently, the ketyl intermediate is too unreactive to add to even highly reactive olefins. Optimizing this reaction by omitting the electron-deficient olefin, we obtained diol **11** as one diastereomer in 94% yield (Scheme 3). While we were unable to generate crystals suitable for X-ray crystallographic analysis from diol **11**, its di-*p*-nitrobenzoate ester (**12**) did prove suitable for this purpose and indicated that the stereochemistry was indeed the *syn* stereochemistry shown. High *syn* diastereoselectivity has also been observed in the SmI_2-promoted dimerizations of other similar organometallic aldehydes, such as ferrocenecarboxaldehyde,[25,26] (benzaldehyde)$Cr(CO)_3$,[25] (di-

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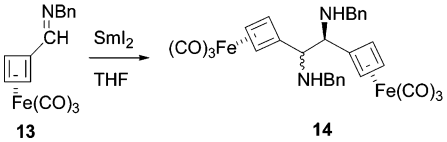
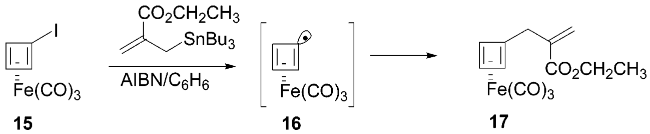
Scheme 4



Scheme 5



enal)Fe(CO)$_3$ complexes,[25] and (propargyl aldehyde)Co(CO)$_6$ complexes.[27]

Stereoselectivity in SmI$_2$-promoted pinacolization has been described as arising from binding of the Sm^{III} ketyl to the unreduced second aldehyde prior to C−C bond formation and the subsequent second reduction.[25]

Aldehyde **10** could be converted to its benzyl imine (**13**), which underwent reductive dimerization with SmI$_2$ to form diamine **14** (Scheme 4), albeit in diminished yield (44%) and with poor (1.1:1) diastereoselectivity, again, as expected from the literature.[28] Given the poor stereoselectivity, no attempt was made to assign stereochemistry to either of the otherwise fully characterized isolated dimers. The N-stabilized radical generated in this reaction should be less reactive than the previously studied O-stabilized radicals.[29] This diminished reactivity could preclude reaction with a formally nonradical species, somewhat akin to the behavior observed in other well-stabilized radicals, such a capto-dative radicals.[17] Thus, the dimerization may occur between two fully reduced, discrete Sm-bound species, leading to an intermolecular coupling through an open, and less stereoselective, transition state.

Finally, we were interested in studying the formation of radical **16**, in which the radical is formed directly on one of the ring carbons. The isodesmic reaction of **16** with benzene to form CBIT and a phenyl radical gave a ΔE of -3.7 kcal/mol at the B3LYP/LANL2DZ level. The spin density of radical **16** also showed that the radical was mostly localized on the ring carbon, orthogonal to the π system, similar to a phenyl radical. Reaction of iodide **15** with 2-carboethoxyallyltributylstannane (Scheme 5) led to ester **17** in 39% yield, indicative of a reaction proceeding through radical **16**.

Conclusion

In conclusion, we have provided the first strong evidence for the formation and trapping of a variety of radicals derived from CBIT. Radicals generated α to the cyclobutadiene ring appear to be quite stable, as evidenced by their sluggish reactivity, and highly nucleophilic, given that they only appear to react with electron-deficient olefins. The radical intermediate generated directly on the ring carbon of CBIT behaves rather similarly to the phenyl radical.

Experimental Section

General Methods. Reagent grade hexane and ethyl acetate were distilled prior to use. Tetrahydrofuran (THF) was distilled from potassium/benzophenone prior to use. Dry benzene was distilled from CaH$_2$ prior to use. Nuclear magnetic resonance (NMR) analysis was conducted on a 400-MHz Brüker Avance nuclear magnetic resonance spectrometer. Gas chromatography and mass spectrometry (GC/MS) were performed with a 15 m × 0.25 μm Agilent cross-linked methyl silicone HP-5 capillary column on an Agilent 6890/5973 GC/MS. Zero-point energies were calculated at the B3LYP/LANL2DZ level using Gaussian 2003 on a Compaq ES40 cluster. Spin density was determined at the B3LYP/6-31G* level using Spartan 2002 on a Dell Latitude D610 personal computer. Vibrational analyses were carried out to ensure energy minima.

[1,2-Di-η^4-cyclobutadienylethane]bis(tricarbonyliron) (3). Phenylselenide **4** (120 mg, 0.33 mmol), allyltributylstannane (331 mg, 1.0 mmol), and AIBN (55 mg, 0.33 mmol) were dissolved in 2 mL of benzene. The reaction mixture was deoxygenated with bubbling N$_2$ for 10 min and heated to reflux for 18 h. Analysis of the crude reaction mixture by TLC showed unreacted limiting reagent **4**, so an additional 25 mg (0.15 mmol) of AIBN was added. The mixture was deoxygenated and heated to reflux for an additional 4 h. Analysis by TLC and GC/MS showed complete consumption of **4**. Trace quantities of 3-butenyl CBIT could be detected in the GC/MS: (m/z) 245 (M$^+ - 1$), 217, (M$^+ - 1 - 28$), 189 (M$^+ - 1 - 56$), 163 (M$^+ - 1 - 84$). MPLC with 97% hexane/3% EtOAC (v/v) gave 34 mg of **3** (50%), homogeneous by TLC. ^{1}H NMR matched that reported in the literature.[7] MS (m/z): 410 (M$^+$).

Tricarbonyl(η^4-phenylselenomethylcyclobutadiene)iron (4). Hydroxymethyl CBIT (270 mg, 1.21 mmol) was dissolved in 10 mL of benzene, and 288 mg (1.8 mmol) of PhSeH was added. The mixture was cooled to 5 °C, and 3 drops (~50 mg) of concentrated H$_2$SO$_4$ was added. The mixture was stirred for 2 h, gradually warming to room temperature. The crude reaction mixture was washed with two 10 mL portions of 10% NaOH and 20 mL of water, dried over MgSO$_4$, and filtered, and solvents were removed by rotary evaporation. MPLC with hexane gave 380 mg (87%) of **4**, homogeneous by TLC, as a yellow oil. ^{1}H NMR (CDCl$_3$): δ 3.40 (s, 2H); 3.92 (s, 2H); 3.97 (s, 1H); 7.35 (m, 3H), 7.61 (m, 2H). ^{13}C NMR (CDCl$_3$): δ 25.9, 61.8, 64.6, 84.3, 128.3, 129.6, 129.9, 134.8, 214.8. IR (neat): 2042, 1958 cm^{-1} (CO). MS (m/z): 334 (M$^+ -28$). Anal. Calcd for C$_{14}$H$_{10}$O$_3$SeFe: C, 46.56, H, 2.79. Found: C, 46.76, H, 2.88

Tricarbonyl(η^4-(3-carboethoxy-3-butenyl)cyclobutadiene)iron (5). Phenylselenide **4** (200 mg, 0.55 mmol), 2-carboethoxyallyltributylstannane (0.688 mg, 1.7 mmol), and AIBN (18 mg, 0.11 mmol) were dissolved in 2 mL of benzene. The solution was deoxygenated with bubbling N$_2$, and the mixture was heated to reflux under N$_2$ for 18 h. The reaction mixture was cooled to room temperature, and TLC analysis showed complete consumption of limiting reagent **4**. The reaction mixture was purified by MPLC with hexane (to elute PhSeSePh), followed by 99% hexane/1% EtOAc (v/v) to remove 2-carboethoxyallyltributylstannane, and 95% hexane/5% EtOAc (v/v) to elute 146 mg of an oil, which while homogeneous by TLC, appeared to be a mixture of **5** and a second, unidentified component by ^{1}H NMR. Kugelrohr distillation (3 mmHg, 175 °C) yielded 96 mg (55%) of **5**, pure by TLC and NMR, as an oil. ^{1}H NMR (CDCl$_3$): δ 1.07 (t, 3H, $J = 7.0$ Hz), 2.00 (t, 2H, $J = 7.5$ Hz), 2.33 (t, 2H, $J = 7.5$ Hz), 3.37 (s, 1H), 3.49 (s, 2H), 4.08 (q, 2H, $J = 7.0$ Hz), 5.27 (d, 1H, $J = 2$ Hz), 6.23 (d, 1H, $J = 2$ Hz). ^{13}C NMR (CDCl$_3$): δ 14.3, 27.0, 32.6, 59.9, 60.8, 64.2, 88.6, 125.3, 140.2, 166.5, 215.6. IR (neat): 2042, 1961, 1716 cm^{-1} (CO). MS: m/z 290 (M$^+ - 28$). Anal. Calcd for C$_{14}$H$_{14}$O$_5$Fe: C, 52.86, H, 4.44. Found: C, 52.55, H, 4.34.

Tricarbonyl(η^4-2, 2-dicyano-4-phenylselenobutylcyclobutadiene)iron (8). A 10 mm NMR tube fitted with a resealable valve was charged with 0.225 g (1.03 mmol) of vinyl CBIT (**6**) and 0.470 g (2.00 mmol) of methylphenylselenomalononitrile in 2 mL of CDCl$_3$. A catalytic amount of AIBN (5 mg, 0.03 mmol) was also

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added to the tube and was dissolved in the $CDCl_3$. The tube was then sealed, and the solution was deoxygenated by three freeze−pump−thaw cycles on a 3 Torr vacuum manifold. The tube was heated to 68 °C in an oil bath for 68 h. Progress of the reaction was monitored by NMR and GC/MS after the first 68 h and every 24 h after that until the reaction was complete. Every 24 h time the tube was opened, an additional 5 mg portion of AIBN was added, and the reaction mixture was redeoxygenated. After 240 h, the reaction was complete. The crude product was purified by flash chromatography on silica gel with 10% EtOAc/90% hexane (v/v) to obtain 0.302 g (65%) of an amber oil, homogeneous by TLC. ^{1}H NMR ($CDCl_3$): δ 1.89 (s, 3H); 2.18 (m, 2H); 3.89 (s, 1H); 4.0 (m, 1H); 4.18 (s, 2H); 7.3−7.85 (m, 5H). ^{13}C NMR ($CDCl_3$): δ 26.3, 30.8, 36.8, 42.8, 62.8, 64.1, 86.0, 117.4, 117.8, 127.4 129.5, 213.9. MS: *m*/*z* 218 (M^+), 190 ($M^+ - CO$), 162 ($M^+ - 2CO$), 134 ($M^+ - 3CO$). Anal. Calcd for $C_{19}H_{14}FeN_2O_3Se$: C, 50.36, H, 3.11, N, 6.18. Found: C, 50.69, H, 2.73, N, 6.28.

Tricarbonyl(η^4-2,2-dicyano-4-phenylseleno-3-butenylcyclobutadiene)iron (9). A 10 mm NMR tube fitted with a resealable valve was charged with 0.234 g (1.08 mmol) of ethynyl CBIT (**7**) and 0.51 g (2.16 mmol) of methylphenylselenomalononitrile in 2 mL of C_6D_6. A catalytic portion of AIBN (5 mg, 0.03 mmol) was also added to the tube. The tube was then sealed, and the solution was deoxygenated by three freeze−pump−thaw cycles. The tube was heated to 85 °C in an oil bath and left for 24 h. Progress of the reaction was monitored by NMR in 24 h increments. An additional 5 mg portion of AIBN was added after each 24 h increment. After 72 h, the reaction was complete, as evidenced by the disappearance of limiting reagent **7**. The crude product was purified by MPLC with 20% EtOAc/80% hexane (v/v), to give 122 mg (25%) of addition product **9**, homogeneous by TLC. ^{1}H NMR ($CDCl_3$): δ 2.08 (s, 3H); 4.06 (s, 2,H); 4.12 (s, 1H); 5.87 (s, 1H); 7.20−7.70 (m, 5H). ^{13}C NMR ($CDCl_3$): δ 27.0, 31.8, 64.1, 64.6, 80.2, 114.9, 122.9, 128.2, 128.9, 129.8, 132.4, 171.0, 213.0. IR (neat): 2048, 1977 cm^{-1} (CO). Anal. Calcd for $C_{19}H_{12}O_3N_2SeFe$: C, 50.59, H, 2.68, N, 6.21. Found: C, 50.61, H, 2.62, N, 6.17.

[*syn*-1,2-Di-η^4-cyclobutadien-yl-1,2-dihydroxyethane]bis(tricarbonyliron) (11). Formyl CBIT (**10**) (176 mg, 0.8 mmol) was dissolved in 10 mL of dry THF. After cooling the contents of the flask to −78 °C, 17.6 mL (1.76 mmol) of SmI_2 solution (0.1 M in THF) was slowly added to the stirred solution via syringe. The blue solution was stirred for an additional 40 min under N_2 and then quenched with 2 mL of methanol. Saturated $NaHCO_3$ was added, and the resulting solution was extracted twice with 50 mL portions of EtOAc. The combined organic layers were dried over $MgSO_4$ and concentrated on a rotary evaporator. The residue was purified by column chromatography on silica gel with 50% EtOAc/50% hexane (v/v) to give 166 mg of diol **11** as pale orange crystals (94%), homogeneous by TLC. Mp: 115−119 °C (dec). ^{1}H NMR (CD_3COCD_3): δ 4.45 (s, 2H), 4.40 (s, 6H), 3.95 (s, 2H). ^{13}C NMR (CD_3COCD_3): δ 215.2, 86.8, 71.6, 64.6, 64.2, 62.7. IR (KBr): 3430 (OH), 2047, 1971, 1957 cm^{-1} (CO). Anal. Calcd for $C_{16}H_{10}O_8Fe_2$: C, 43.48, H, 2.28. Found: C, 43.83, H, 2.31.

[*syn*-1,2-Di-η^4-cyclobutadien-yl-1,2-di-*p*-nitrobenzoylethane]bis(tricarbonyliron) (12). A 104 mg (0.24-mmol) portion of diol **11** was dissolved in 10 mL of THF under N_2. The resulting solution was cooled to 0 °C, and 47 mg (1.18 mmol, 60% by wt in mineral oil) of NaH was added. After evolution of H_2 was complete, 139 mg (0.875 mmol) of *p*-nitrobenzoyl chloride was added. The reaction was stirred for 72 h, warming to room temperature. TLC analysis showed the presence of unreacted diol, so an additional 24 mg (0.59 mmol) of NaH was added, followed by 50 mg (0.27 mmol) of *p*-nitrobenzoyl chloride. The reaction mixture was allowed to stir overnight. The crude reaction mixture was then added to 50 mL of EtOAc, washed with 50 mL of water, dried over $MgSO_4$, and filtered, and solvents were removed by rotary evaporation. Flash chromatography with 80% hexane/20% EtOAc (v/v) gave 51 mg (34%) of **12** as a pale yellow crystalline solid, homogeneous by TLC. ^{1}H NMR ($CDCl_3$): δ 8.30 (m, 4H), 8.18 (m, 4H), 5.71 (s, 2H), 4.31 (s, 2H), 4.24 (s, 4H). IR (KBr): 2048, 1974, 1736 (CO) cm^{-1}. Crystals suitable for X-ray analysis were grown by slow diffusion of hexane into a THF solution of **12**.

(1,2-Di-η^4-cyclobutadien-yl-1,2-dibenzylamino)bis(tricarbonyliron) (14). Formyl CBIT (**10**) (579 mg, 2.6 mmol) was dissolved in 5 mL of toluene. Benzylamine (0.31 g, 2.9 mmol) was added, and the toluene was removed by rotary evaporation, yielding imine **13**, which was used without further purification. ^{1}H NMR ($CDCl_3$): δ 7.62 (s, 1H), 7.20−7.45 (m, 5H), 4.59 (s, 1H), 4.52 (s, 2H), 4.24 (s, 2H). Imine **13** was dissolved in 10 mL of THF, and the resulting solution was cooled to −78 °C. A 50 mL portion of SmI_2 (0.1 M in THF) was added via syringe, and the resulting solution was stirred for 1 h, gradually warming to room temperature. Methanol (2 mL) was added in order to quench the reaction, and 50 mL of ether was added. The resulting solution was washed with two 50 mL portions of water, the remaining organic phase was dried over $MgSO_4$ and filtered, and solvents were removed by rotary evaporation. MPLC with 10% EtOAc/90% hexane (v/v) gave 181 mg (23%) of a higher rf diamine and 167 mg (21%) of a lower rf diamine, each homogeneous by TLC. High rf diamine: ^{1}H NMR ($CDCl_3$) δ 7.2−7.4 (m, 10H), 4.19 (d, J = 9.1 Hz, 2H), 4.15 (s, 2H), 3.90, (d, J = 9.1 Hz, 2H), 3.90 (d, J = 12.7 Hz, 2H), 3.71 (d, J = 12.7 Hz, 2H), 3.13 (s, 2H), 1.4 (bs, 2H); ^{13}CNMR ($CDCl_3$) δ 214.7, 139.9, 128.6, 128.3, 127.3, 87.1, 64.1, 63.7, 62.1, 59.0, 52.4. Anal. Calcd for $C_{30}H_{24}Fe_2N_2O_6$: C, 58.08, H, 3.90, N, 4.54. Found: C, 58.08, H, 3.98, N, 4.49. Low rf diamine: ^{1}H NMR ($CDCl_3$) δ 7.2−7.4 (m, 10H), 4.40 (d, J = 9.1 Hz, 2H), 4.16 (s, 2H), 3.92 (d, J = 9.1 Hz, 2H), 3.80 (d, J = 13.1 Hz, 2H), 3.64 (d, J = 13.1 Hz, 2H), 3.15 (s, 2H), 2.22 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 214.4, 140.0, 128.5, 128.2, 127.2, 86.9, 66.1, 61.3 (2 peaks), 58.0, 52.1. IR (neat): 2040, 1965 Anal. Calcd for $C_{30}H_{24}Fe_2N_2O_6$: C, 58.08, H, 3.90, N, 4.54. Found: C, 58.08, H, 3.93, N, 4.52.

Tricarbonyl(η^4-(2-carboethoxy-2-propenyl)cyclobutadiene)iron (17). Iodo CBIT[30] (0.268 g, 0.840 mmol) and 2-carboethoxylallyltributylstannane (0.682 g, 1.68 mmol) were dissolved in 1 mL of C_6D_6 and added to a 10 mm NMR tube fitted with a resealable valve. A catalytic amount of AIBN (5 mg, 0.03 mmol) was then added to the tube, and the solution was deoxygenated by three freeze−pump−thaw cycles, sealed, and then heated to 80 °C for 50 h. The crude product was purified by MPLC on silica gel with 3% EtOAc/97% hexane (v/v) to yield 100 mg (39%) of **17**, homogeneous by TLC. ^{1}H NMR ($CDCl_3$): δ 0.89 (t, J = 7.1 Hz, 3H); 1.30 (q, J = 7.1 Hz, 2H); 3.00 (s, 2H); 4.12 (s, 2H); 4.26 (s, 1H); 5.20 (s, 1H); 6.24 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 14.2, 30.6, 60.6, 61.0, 64.5, 84.8, 126.3, 138.4, 167.3, 214.7. MS: *m*/*z* 304 (M^+), 276 ($M^+ - CO$), 248 ($M^+ - 2CO$), 220 ($M^+ - 3CO$). Anal. Calcd for $C_{13}H_{12}O_2Fe$: C, 51.34, H, 3.98. Found: C, 51.71, H, 4.25.

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Supporting Information Available: Crystallographic infomation files (CIF) and experimental parameters for **12**, results of calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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[30] Bunz, U. *Organometallics* **1993**, *12*, 3594.