Amino Substituted Tricarbonyl(cyclobutadiene)iron Complexes: Pd-Catalyzed Coupling of Iodocyclobutadiene Complexes with Amines

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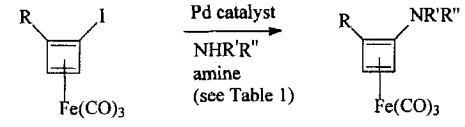
The coupling of the iodides **1** with amines under palladium catalysis affords the novel aminated cyclobutadiene derivatives **2** in preparative useful yields.

The Stille reaction[1] in its many variants[2], is the Pd-catalyzed coupling of unsaturated halides (bromides or iodides) with tin alkynes, as well as tin vinyls, in DMF or other polar solvents. It has developed as an effective tool for the introduction of ethynyl or vinyl groups into sensitive organic and organometallic[3] targets. These targets would not survive the harsher conditions of the Heck-Sonoshigara-Hagihara-Cassar coupling which uses the alkyne, CuI and Pd-catalyst in an amine solvent[4]. We are involved at the moment in a program to developd synthetic routes to ethynylated and highly ethynylated tricarbonyl(cyclobutadiene)iron complexes[5] using the Farina[2a] or the Beletskaya[2b] variant of the Stille method. Despite its mildness and the high yields of coupling products, the Stille reaction suffers from the toxicity and the high price of the involved tin compounds.

We therefore planned to utilize the less expensive and ecologically more sound variant of the Heck-Sonoshigara-Hagihara-Cassar coupling developed by Linstrumelle[4d] to achieve the ethynylation of iodocyclobutadiene complexes **1**. However, the result of our efforts was completely unexpected and steered our efforts in another direction. The literature revealed that not only was Boger able to use stoichiometric amounts of $Pd(PPh_3)_4$ to effect an intramolecular ring closure giving a dibenzylpyrrole derivative[6a], but also that Kameyama[6b,c] and Hartwig[6d] were able to perform the palladium-catalyzed reaction of aryl bromides with tin amides to afford the isolation of the respective anilines. Hartwig identified likely intermediates and shed some light on the mechanism of this reaction. Very recently[6e] the Yale group described the successful Pd-catalyzed reaction of two different amines (piperidine and diethylamine) with aryl bromides in the presence of an auxiliary base such as $LiN(SiMe_3)_2$ or sodium butoxides. This report prompted us to publish our own experiments in the field.

Reaction of **1a** in presence of piperidine, $(PPh_3)_2PdCl_2$ and trimethylsilylacetylene did not give the expected tricarbonyl[(trimethylsilylethynyl)cyclobutadiene]iron **1b**, but instead a yellow oil wich was identified by its NMR spectra as the piperidine adduct **2a** (yield 25%). The first assumption was that the piperidine had reacted with **1a** in a nucleophilic addition-elimination fashion[7a,b] without the participation of the Pd-catalyst. Control experiments showed that **1a** is stable as a solution in a piperidine/trichloromethane



1 **2**

1	R
a	H
b	C≡C–SiMe3

Table 1. Yields of amine product **2** for catalytic reactions with various catalysts, amines and iodides

entry	Pd catalyst	amine	iodide	conditions	2	yield of 2
1	$(PPh_3)_4$ Pd	piperidine R'=R"= $-(CH_2)_5-$	**1a**	24h, 21 °C	**a**	84 %
2	$(PPh_3)_4$ $PdCl_2$	piperidine R'=R"= $-(CH_2)_5-$	**1a**	24h, 21 °C	**a**	43 %
3	$(PPh_3)_4$ Pd	piperidine Schwesinger's base	**1a**	18h, 21 °C	**a**	traces
4	$(PPh_3)_4$ Pd	pyrrolidine R'=R"= $-(CH_2)_4-$	**1a**	18h, 21 °C	**b**	79 %
5	$(PPh_3)_4$ $PdCl_2$	pyrrolidine R'=R"= $-(CH_2)_4-$	**1a**	18h, 21 °C	**b**	48 %
6	$(PPh_3)_4$ Pd	piperidine R'=R"= $-(CH_2)_5-$	**1b**	22h, 21 °C	**c**	62 %
7	$(PPh_3)_4$ $PdCl_2$	piperidine R'=R"= $-(CH_2)_5-$	**1b**	22h, 21 °C	**c**	31 %
8	$(PPh_3)_4$ $PdCl_2$	triethylamine	**1a**	18h, 21 °C	decomposition	
9	$(PPh_3)_4$ Pd	dibutylamine R'=R"= $-CH_2CH_2$ CH_2CH_3	**1a**	52h, 40 °C	no reaction	
10	$(PPh_3)_4$ Pd	propylamine R'= –H R"= $-CH_2CH_2CH_3$	**1a**	36h, 40 °C	**d**	69 %
11	$(PPh_3)_4$ Pd	phenylethylamine R'= $-CH_2CH_3$ R"= –Ph	**1b**	4d, 40 °C	**e**	27 %
12	$(PPh_3)_4$ Pd	aniline R'= –H R"= –Ph	**1a**	2d, 40 °C	**f**	66 %

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mixture for days as was evident by ^{13}C NMR spectroscopy. In a second experiment we omitted the alkyne and as expected, **2a** was isolated but in better (43%) yield. Using the catalyst $(PPh_3)_4Pd$ under otherwise identical conditions led to an improved yield of product (Table 1, entry 1, 84%). We also tried to accelerate the reaction by adding a non-nucleophilic auxiliary, Schwesinger's base[7c] (entry 3) but without success. Under these conditions only traces of **2a** are isolated and an insoluble black residue formed instead.

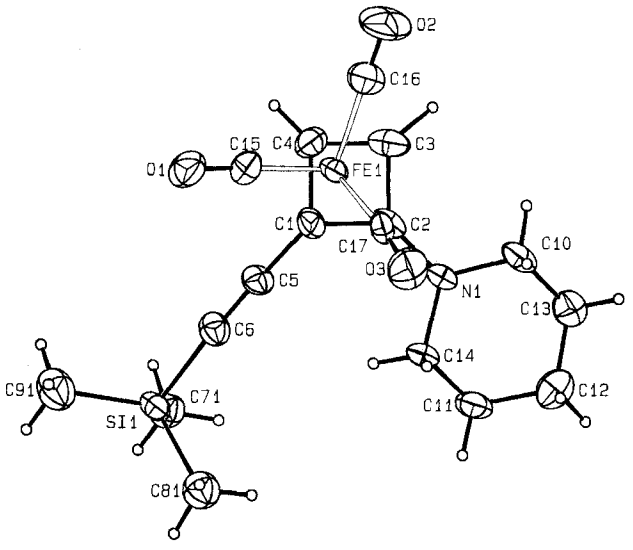
Pyrrolidine reacts with **1a** under the same conditions to give **2b**. Here again $(PPh_3)_4Pd$ gives better yields than $(PPh_3)_2PdCl_2$. To our suprise, dibutylamine did not couple to **1a**, but propylamine did (69%) as well as aniline (66%). In the latter two cases the temperature had to be increased to 40 °C and the reaction time prolonged to achieve complete consumption of the starting materials (see Table 1, entry 9, 10, 13).

A substituent in *ortho*-position to the iodide is tolerated as well, the coupling of piperidine to **1b** furnishes 62% of the adduct **2c**. In entry 11, the addition of S-(−)-phenylethylamine to **1b** gives a mixture of two diastereomeric complexes **A** and **B** in a (0.93:1 ratio) 27% yield, which could be separated by column chromatography. The observed ratio, close to 1:1 simply represents the fact, that the starting iodide **1b** was racemic in nature.

The conclusion we can draw from these experiments is that the palladium complex plays a crucial role in the substitution reaction of the iodide by the amines. Contrary to Hartwig's findings[6c], the addition of an auxiliary base to the reaction mixture was not necessary, and if added (Schwesinger's base[7c]) it suppressed the reaction. Dehalogenation processes were not observed in our hands either. The method we discovered here by accident, provides easy access to regiospecifically amino substituted cyclobutadiene complexes in good to excellent yields, which can otherwise be obtained only by lengthy multistep syntheses (if accessible at all)[7a,8]. An alkyne substituent in the *ortho* position does not seem to influence the Pd-catalyzed amination reaction.

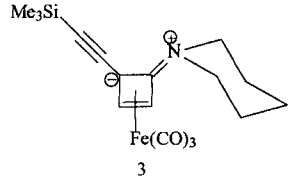
In order to corroborate the structure of our amine adducts with certainty, we conducted an X-ray crystal structure analysis of **2c** which was obtained by careful recrystallization from dichloromethane as fine needles. In Figure 1, an ORTEP plot of **2c** is shown. While the piperidine ring adopts the typical cyclohexane chair and the C−C bond lengths of the four and the six ring are inconspicuous, the position of the tricarbonyliron fragment in reference to the four-membered ring is unusual (see Figure 1). It is not located under the center of the ring but in the corner opposing the amine-nitrogen carrying ring carbon. An inspection of the bond distances of the iron atom to the ring C atoms shows a dramatic difference: Fe−C1 2.09 Å, Fe−C3 2.12 Å, Fe−C4 2.03 Å, however, Fe−C2 2.28 Å. The Fe−C2 bond is 0.2 Å elongated compared to the other three iron-carbon distances, which are very similar to the values found in typical tricarbonyl(cyclobutadiene)iron complexes. The reason for the distortion is not clear at the moment, it may be an electronic effect of the amine group. The unusual

Figure 1. Molecular structure of **2c**[a]



[a] Selected bond lengths [Å] and angles [°]: Fe−C15 1.71(1), Fe−C16 1.87(1), Fe−C17 1.75(1), Fe−C1 2.09(1), Fe−C2 2.28(2), Fe−C3 2.12(1), Fe−C4 2.03(1), C1−C2 1.42(2), C1−C5 1.40(2), C1−C4 1.45(2), C2−N 1.35(1), C2−N 1.35(1), C2−C3 1.43(2), C3−C4 1.44(2), C5−C6 1.20(2), C6−Si 1.86(1), N−C10 1.48(1), N−C14 1.45(1), C10−C13 1.51(2), C11−C12 1.53(2), C11−C14 1.50(2), C12−C13 1.48(2); C16−Fe−C15 97.7(6), C17−Fe−C15 104.0(6), C17−Fe−C16 97.2(5), C1−Fe−C15 98.2(5), C1−Fe−C16 141.7(6), C1−Fe−C17 112.4(5), C3−Fe−C15 138.7(6), C3−Fe−C16 88.4(6), C3−Fe−C17 115.8(5), C3−Fe−C1 57.4(5), C4−Fe−C15 98.7(6), C4−Fe−C16 102.0(5), C4−Fe−C17 147.9(5), C4−Fe−C1 41.1(5), C4−Fe−C3 40.4(5), O1−C15−Fe 177.2(12), O2−C16−Fe 179.4(13), O3−C17−Fe 173.9(11), C5−C1−C2 132.9(11), C4−C1−C2 90.3(10), C4−C1−C5 133.9(10), C3−C2−C1 90.1(10), C4−C3−C2 90.2(11), C3−C4−C1 89.0(9), C3−C2−N 133.9(12), C6−C5−C1 175.4(13), Si−C6−C5 172.7(12), N−C2−C1 135.7(11), C10−N−C2 119.8(9).

downfield shift of the cyclobutadiene ring C atom carrying the nitrogen to values between 125 and 134 ppm points in the same direction. But due to the almost identical bond distances in the four-membered ring and the almost unaltered C−N distance, we discard the possibility of an "allylic" binding of the tricarbonyl iron fragment (as depicted in **3**) to the π-ligand. Concomitant with the displaced tricarbonyl iron fragment is the deviation of C4 from the plane defined from C1−C3 by 0.12 Å. A strongly electron withdrawing group attached to the ring such as nitro, cyano or an ester may reinforce the distortion observed in **2c**. The synthesis of structures of this type as well as the examination of the full scope of the amination and the isolation of some or all of the presumed intermediates of the reaction is a future goal of our work.



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Experimental

All operations were carried out in flame-dried glassware under nitrogen. The Pd-catalysts and the amines were purchased from Aldrich and used as obtained. – Column chromatography was accomplished with Baker flash silica gel and pentane as eluent if not stated differently. – ^{1}H and ^{13}C NMR: Bruker AC 300. – IR Nicolet Magna 550. MS VG Trio 2000. – Elemental analyses: Mikroanalytisches Labor des Institutes für Organische Chemie der Johannes Gutenberg-Universität Mainz.

General Coupling Procedure: In a 25-ml Schlenk tube, the iodide **1** (250–600 mg) and 5 mol% catalyst ($(Ph_3P)_4Pd$ or $(Ph_3P)_2PdCl_2$) were introduced and 2–3 ml of the corresponding amine were added. After 18–96 h at 21 or 40 °C under the exclusion of light, the reaction mixture was poured into ca. 50 ml of brine and extracted several times with petroleum ether. The petroleum ether extracts were washed with water five times, dried over magnesium sulfate and brought to dryness in the rotary evaporator. Chromatography and removal of traces of volatile materials at 30 °C/0.01 Torr gave the desired aminated cyclobutadiene complexes **2**.

N-[Tricarbonyl(η⁴-cyclobutadien-1-yl)ferrio]piperidine[7d] (**2a**): According to the general procedure, 600 mg (1.89 mmol) **1a**, 109 mg (94.5 μmol) $(PPh_3)_4Pd$ and 3 ml freshly distilled piperidine were stirred for 18 h and worked up to yield 436 mg (84%) **2a** as light yellow oil. *With $PdCl_2(PPh_3)_2$ as catalyst:* According to the general procedure, 600 mg (1.89 mmol) **1a**, 72.0 mg (103 μmol) $PdCl_2(PPh_3)_2$ and 3 ml freshly distilled piperidine were stirred for 18 h and worked up to yield 223 mg (43%) **2a**. – IR (KBr): $\tilde{\nu}$ = 3062, 2988, 2951, 2859, 2311, 2028, 1948, 1554, 1264, 907 cm^{-1}. – ^{1}H NMR ($CDCl_3$): δ = 1.48–1.61 (m, 6H, CH_2-piperidinyl), 2.54–2.57 (m, 4H, CH_2-piperidinyl), 3.61 (s, 2H, 2-H, 4-H), 3.94 (s, 1H, 3-H). – ^{13}C NMR ($CDCl_3$): δ = 23.1 (1 C, piperidinyl-C), 24.3 (2 C, piperidinyl-C), 46.6 (2 C, cyclobutadiene-C), 46.9 (2 C, piperidinyl-C), 47.3 (1 C, cyclobutadiene-C), 133.9 (1 C, cyclobutadiene-C–N), 215.0 (3 C, CO). – MS (EI, 70 eV): *m/z* (%) = 275 (57, [M$^+$]), 247 (81, M – 1 CO), 219 (15, M – 2 CO), 191 (100, M – 3 CO). – $C_{12}H_{13}NO_3Fe$ (275.09): calcd. C 52.40, H 4.76, N 5.09; found C 52.41, H 4.82, N 4.86.

N-[Tricarbonyl(η⁴-cyclobutadien-1-yl)ferrio]pyrrolidine (**2b**): According to the general procedure, 500 mg (1.58 mmol) **1a**, 55.4 mg (79.0 μmol) $(PPh_3)_4Pd$ and 3 ml freshly distilled pyrrolidine are stirred for 18 h and worked up to yield 326 mg (79%) **2b** (m.p. 55 °C). – IR (KBr): $\tilde{\nu}$ = 3102, 3056, 2984, 2879, 2309, 2021, 1936, 1589, 1484, 1353, 1268, 743 cm^{-1}. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.82 (br. s, 4H, CH_2-pyrrolidinyl), 2.84 (br. s, 4H, CH_2-pyrrolidinyl), 3.55 (s, 2H, 2-H, 4-H), 3.60 (s, 1H, 3-H). – ^{13}C NMR ($CDCl_3$): δ = 25.0 (1 C, pyrrolidinyl-C), 47.0 (2 C, pyrrolidinyl-C), 47.4 (1 C, cyclobutadiene-C), 48.2 (2 C, cyclobutadiene-C), 126.8 (1 C, cyclobutadiene-C-N), 215.0 (3 C, CO). – MS (EI, 70 eV): *m/z* (%) = 261 (13, [M$^+$]), 233 (31, M – 1 CO), 205 (12, M – 2 CO), 177 (100, M – 3 CO). – $C_{11}H_{11}NO_3Fe$ (261.06): calcd. C 50.61, H 4.25, N 5.37; found C 50.54, H 4.29, N 5.25.

N-{Tricarbonyl[(2'-trimethylsilylethynyl)-η⁴-cyclobutadien-1-yl]-ferrio}piperidine (**2c**): According to the general procedure, 500 mg (1.21 mmol) of **1b** and 69.9 mg (60.5 μmol) $(Ph_3P)_4Pd$ were dissolved in 10 ml of piperidine and reacted for 22 h at 21 °C. After standard workup, the product was recrystallized from dichloromethane to give 278 mg (62%) **2c** (m.p. 96 °C). If the same reaction is conducted with $PdCl_2(PPh_3)_2$ as catalyst, the yield drops to 31%. – IR (KBr): $\tilde{\nu}$ = 3065, 2999, 2953, 2861, 2683, 2308, 2137, 2137, 2026, 1947, 1585, 1453, 1269, 1210, 861, 743 cm^{-1}. – ^{1}H NMR ($CDCl_3$): δ = 0.14 (s, 9H, $SiMe_3$), 1.51–1.60 (m, 6H, CH_2-piperidinyl), 2.66–2.70 (m, 2H, CH_2-piperidinyl), 3.00 (bs, 2H, CH_2-piperidinyl), 3.42 (s, 1H, 2-H), 3.97 (s, 1H, 4-H). – ^{13}C NMR ($CDCl_3$): δ = –0.23 (3 C, $SiMe_3$), 23.3 (1 C, piperidinyl-C), 24.3 (2 C, piperidinyl-C), 44.5, 45.5 (2 C, cyclobutadiene-C), 46.9 (2 C, piperidinyl-C), 51.4 (1 C, cyclobutadiene-C), 95.1, 99.6 (2 C, alkyne-C), 126.8 (1 C, cyclobutadiene-C-N), 213.7 (3 C, CO). – MS (EI, 70 eV): *m/z* (%) = 371 (15, [M$^+$]), 343 (81, M – 1 CO), 315 (84, M – 2 CO), 287 (100, M – 3 CO). – $C_{17}H_{21}FeNO_3Si$ (371.29): calcd. C 54.99, H 5.70, N 3.77; found C 54.87, H 5.62, N 3.79.

N-[Tricarbonyl(η⁴-cyclobutadien-1-yl)ferrio]-N-propylamine (**2d**): According to the general procedure 250 mg (787 μmol) **1a** and 45.5 mg (39.4 μmol) $(Ph_3P)_4Pd$ are dissolved in 3 ml of propylamine and stirred for 36 h at 40 °C. Standard workup yielded 136 mg (69%) of **2d** as yellow oil. – IR (KBr): $\tilde{\nu}$ = 3417, 3059, 2966, 2935, 2880, 2305, 2027, 1953, 1576, 1471, 1267, 1119, 896, 742 cm^{-1}. – ^{1}H NMR ($CDCl_3$): δ = 0.92 (t, *J* = 7.3 Hz, 3H, CH_3), 1.54 (sext, J_1 = 7.2 Hz, J_2 = 7.3 Hz, 2H, CH_2), 2.73 (q, *J* = 7.2 Hz, 2H, N–CH_2), 2.92 (br. s, 1H, NH), 3.60 (s, 2H, cyclobutadiene-H), 3.64 (s, 1H, cyclobutadiene-H). – ^{13}C NMR ($CDCl_3$): δ = 11.4 (1 C, CH_3), 22.4 (1 C, CH_2), 46.9 (1 C, CH_2–N), 47.1 (2 C, cyclobutadiene-C), 47.3 (1 C, cyclobutadiene-C), 125.7 (1 C, cyclobutadiene-C), 215.0 (3 C, CO). – MS (EI, 70 eV): *m/z* (%) = 249 (45, [M$^+$]), 221 (100, M – 1 CO), 193 (40, M – 2 CO), 165 (67, M – 3 CO).

N-{Tricarbonyl[(2'-trimethylsilylethinyl)-η⁴-cyclobutadien-1-yl]-ferrio}-[(S)-(–)-1-phenylethyl]amine (**2e**): According to the general procedure, 280 mg (676 μmol) **1b**, 39.1 mg (33.8 μmol) $(PPh_3)_4Pd$ and 1 ml of (S)-(–)-1-phenylethylamine were reacted for 48 h at 40 °C. Standard workup yielded diastereomer **A** as yellow oil (36 mg, 13%). Chromatography with pentane/dichloromethane (9:1) yielded 39 mg of diastereomer **B** as yellow oil (39 mg, 14%). The ratio of **A**:**B** is 0.93:1. – *Diastereomer A:* IR (KBr): $\tilde{\nu}$ = 3402, 3059, 2969, 2933, 2308, 2145, 2031, 1953, 1568, 1454, 1268, 865, 745 cm^{-1}. – ^{1}H NMR ($CDCl_3$): δ = 0.18 (s, 9H, $SiMe_3$), 1.44 (d, *J* = 7.4 Hz, 3H, CH_3), 2.90 (s, 1H, cyclobutadiene-H), 3.57 (br. s, 1H, NH), 3.84 (s, 1H, cyclobutadiene-H), 3.99 (m, 1H, CH–N), 7.28–7.35 (m, 5H, phenyl-H). – ^{13}C NMR ($CDCl_3$): δ = –0.07 (3 C, $SiMe_3$-C), 24.0 (1 C, CH_3), 46.7 (1 C, cyclobutadiene-C), 47.0 (1 C, *C*-HPh(CH_3)), 51.9 (1 C, cyclobutadiene-C), 56.3 (1 C, cyclobutadiene-C), 96.3, 97.8 (2 C, alkyne-C), 125.2 (1 C, cyclobutadiene-C–N), 126.3, 127.9, 129.0, 142.7 (6 C, phenyl-C), 213.9 (3 C, CO). – MS (EI, 70 eV): *m/z* (%) = 407 (6.6, [M$^+$]), 379 (9.0, M – 1 CO), 323 (100, M – 3 CO). – $C_{20}H_{21}NO_3SiFe$ (407.32): calcd. C 58.98, H 5.20, N 3.44; found C 59.03, H 5.38, N 3.68. – *Diastereomer B:* IR (KBr): $\tilde{\nu}$ = 3410, 3056, 2988, 2932, 2305, 2151, 2033, 1958, 1568, 1425, 1264, 749 cm^{-1}. – ^{1}H NMR ($CDCl_3$): δ = 0.18 (s, 9H, H-$SiMe_3$), 1.50 (d, *J* = 7.3 Hz, 3H, CH_3), 3.46 (s, 1H, cyclobutadiene-H), 3.58 (s, 1H, NH), 3.96 (s, 1H, cyclobutadiene-H), 4.29 (m, 1H, CH–NH), 7.30–7.48 (m, 5H, phenyl-H). – ^{13}C NMR ($CDCl_3$): δ = –0.16 (3 C, $SiMe_3$), 22.3 (1 C, CH_3), 45.5 (1 C, CH–N), 45.4, 51.6, 55.0 (3 C, cyclobutadiene-C), 96.3, 97.8 (2 C, alkyne-C), 127.4 (1 C, cyclobutadiene-C), 126.4, 127.9, 128.8, 142.1 (6 C, phenyl-C), 213.7 (3 C, CO). – MS (EI, 70 eV): *m/z* (%) = 407 (5.3, [M$^+$]), 379 (8.1, M – 1 CO), 323 (100, M – 3 CO).

N-[Tricarbonyl(η⁴-cyclobutadien-1-yl)ferrio]aniline (**2f**): According to the general procedure, 250 mg (787 μmol) **1a**, 45.5 mg

(39.4 μmol) $(PPh_3)_4Pd$ and 3 ml aniline were mixed and heated for 48 h at 40°C. Standard workup and chromatography (pentane/dichloromethane, 90:10) yielded 146 mg (66%) of **2f** as yellow oil. – IR (KBr): $\tilde{\nu}$ = 3422, 3058, 2029, 1944, 1598, 1549, 1500, 1483, 1263, 1075, 740 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 3.67 (s, 1H, cyclobutadiene-H), 3.99 (s, 2H, cyclobutadiene-H), 5.23 (br. s, 1H, NH), 6.72 (d, J = 7.9 Hz), 6.97 (t, J = 7.4 Hz), 7.28 (t, J = 7.8 Hz), (5H, phenyl-H). – ^{13}C NMR ($CDCl_3$): δ = 48.7 (1 C, cyclobutadiene-C), 50.1 (2 C, cyclobutadiene-C), 129.4 (1 C, cyclobutadiene-C), 112.5, 116.3, 121.9, 140.1 (6 C, phenyl-C), 214.2 (3 C, CO). – MS (EI, 70 eV): *m/z* (%) = 283 (33, $[M^+]$), 255 (63, M – 1 CO), 227 (33, M – 2 CO), 199 (89, M – 3 CO). – $C_{13}H_9NO_3Fe$ (283.07): calcd. C 55.16, H 3.20, N 4.95; found C 55.31, H 3.34, N 5.22.

Crystal Data and Structure Refinement of **2c**[9]: $C_{17}H_{21}FeNO_3Si$, M = 371.92, yellow needles, crystal size 0.80 × 0.30 × 0.30 mm, orthorhombic, space group *Fdd2*, a = 40.524(4), b = 31.409(2), c = 6.0127(2) Å, $\alpha = \beta = \gamma = 90°$, $C_{17}H_{21}NO_3Fe$ (371.29): V = 7653(2) $Å^3$, Z = 16, $d_{calcd.}$ = 1.287 g cm^{-3}, μ(Cu-K_α) = 70.51 cm^{-1}. Data collection on a Enraf-Nonius CAD-4 diffractometer at T = 298 K using graphite monochromated Cu-K_α radiation, $2\Theta_{max}$ = 65°. A total of 1865 reflections was collected, 1479 of these were observed ($I > 3\sigma(I)$). The structure was solved by heavy atom methods (Patterson), using an empirical absorption correction. The used programs were Molen and CRYSTALS. All non hydrogen atoms were refined anisotropically, while hydrogen atoms were refined isotropically in the riding mode; final R values: R = 5.78%, R_w = 6.85%.

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[9] Further details of the crystal structure investigation of **2c** are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-59110.

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