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Formation of (6-Alkylidene-η^5-cyclohexadienyl)iron Complexes by Rhodium-Catalyzed Carbenoid Reactions

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Summary: Reaction of ethyl lithiodiazoacetate with the cationic [Fe(arene)Cp] complexes 1 and 2 produces σ-adducts 6 and 7. Upon treatment with a catalytic amount of $Rh_2(OAc)_4$ in CH_2Cl_2, the adducts are transformed to metallocarbenes, which react further by 1,2-hydrogen migration. While reaction of 6 results in a mixture of equilibrating E and Z stereoisomers 8 and 9, a single product (10) is obtained from 7.

In connection with studies on the vicarious nucleophilic substitution of hydrogen [VNS reaction)[1] applied to metal–arene complexes, we have synthesized and characterized a number of σ-adducts (**3** and **4**) by reaction of the cationic Fe(Cp) complexes of benzonitrile (**1**) and nitrobenzene (**2**) with anionic nucleophiles carrying a leaving group at the anionic center,[2] with the objective of converting them to 6-alkylidene-η^5-cyclohexadienyl complexes **5**. However, it was impossible to find conditions under which the adducts would undergo the desired base-induced elimination. We attributed this failure to the low acidity of H–C(6) in **3** and **4**, which, in turn, should be due to the inability of the complex to accommodate negative charge at this position. In order to circumvent this problem, we have investigated the possibility of generating the required double bond under conditions where no negative charge develops at C(6). This paper reports the synthesis of complexes having structures analogous to **5** *via* 1,2-hydrogen migration of a carbene.

Ethyl lithiodiazoacetate[3] (3.0 mmol) reacted rapidly (THF, −90 °C, 15 min) with (η^5-cyclopentadienyl)(η^6-cyanobenzene)iron (II) hexafluorophosphate (**1a**; 1.0 mmol in 3 mL of dry HMPA) and (η^5-cyclopentadienyl)(η^6-nitrobenzene)iron(II) hexafluorophosphate (**2**; 1.0 mmol in 3 mL of dry HMPA) to give the adducts **6a** and **7**. The adducts were purified by column chromatography. Their structures were deduced by comparison of their NMR data (Table I) with those of **3** and **4**, the structures of which, in turn, have been determined by the X-ray structure of **4c**.[2] It is noteworthy that attack by lithio ethyldiazoacetate, like that by other nucleophiles on cationic [Fe(arene)Cp] complexes, occurs exclusively at the ortho position of the electron-withdrawing substituent.[2,4] In the absence of activating substituents, lithio ethyldiazoacetate was found to be unreactive towards cationic [Fe(arene)-Cp] complexes. When the reaction was carried out at −78 °C, the yields of **6a** and **7** dropped drastically to 12 and 9%, respectively.

The diazo compound **6a** reacted smoothly with a catalytic quantity of $Rh_2(OAc)_4$[5] (2 mol %) in CH_2Cl_2 at 25 °C to yield an inseparable 4.1:1 mixture of the exocyclic alkenes **8a** and **9a** in 86% yield as amorphous solids. The formation of alkenes in the reaction is indicated by the presence of doublets at 6.01 ppm for H–C(5) of the major component (**8a**) and at 4.55 ppm for H–C(5′) of the minor component (**9a**) and singlets at 5.39 and 5.47 ppm for H–C(7) and H–C(7′), respectively. The strong anisotropic effect of the carboxy group on the shift of the ring protons of the cyclohexadienylidene group suggests the tentative assignment of the *E* configuration to **8a** and the *Z* configuration to **9a**. This is consistent with thermodynamically controlled product composition, **8a** being more stable than **9a** for steric reasons.

Alkene formation upon reaction of **6a** with $Rh_2(OAc)_4$ is readily accounted for by Rh-catalyzed loss of nitrogen to an intermediate metallocarbene which undergoes 1,2-hydrogen migration. Such hydrogen migrations of Rh-complexed carbenes are usually kinetically controlled and result in preferential formation of the less stable (*Z*)-alkenes,[6] which is in contradiction with the stereochemical assignment of the products derived from **6a**. The preference for Rh-complexed carbenes to yield (*Z*)-alkenes may be ascribed to the steric requirements of the Rh moiety, which prefers to occupy the least hindered position in the conformation leading to products.[7] If we apply an analogous reasoning to **6**, the stereochemical assignments of **8a** and **9a** should be reversed. In order to confirm the assignment, the reaction mixture was subjected to 2D-NOE measurements,[8] which unveiled an exchange process between **8a** and **9a**. The NOESY experiment (Figure 1) shows a complete set of cross signals for exchange of the corresponding hydrogen atoms of the isomers. Typically, H_2–C(9), the methylene group of the ethoxycarbonyl substituent of **8a**, exhibits an exchange cross signal with the corresponding methylene group H_2–C(9′) of **9a** at 4.00/4.24 ppm, denoted in Figure 1 by EX 9/9′. Similarly, the cyclopentadienyl ligand (Cp) of **8a** undergoes exchange with Cp′ of **9a**, as shown by cross peaks at 4.43/4.57 ppm, denoted with EX Cp/Cp′. Analogous exchange cross peaks are found in the NOESY spectrum for all pairs of hydrogen atoms. In addition to these exchange signals, a limited number of real NOE's are observed. These latter NOE cross peaks are in antiphase to the exchange signals when

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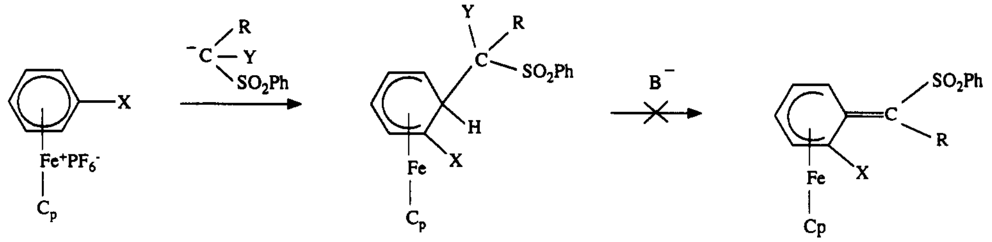
Scheme I



1 : X = CN

2 : X = NO$_2$

3a : X = CN ; Y = Cl ; R = H
3b : X = CN ; Y = Cl ; R = CH$_3$

4a : X = NO$_2$; Y = Cl ; R = H
4b : X = NO$_2$; Y = Cl ; R = CH$_3$
4c : X = NO$_2$; Y = Br ; R = H
4d : X = NO$_2$; Y = Br ; R = CH$_3$

5

Table I. ^{1}H and ^{13}C NMR[a] Data for σ Complexes 6 and 7 and Exocyclic Alkenes 8–10[b]

		C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C(10)	C$_p$	CH$_3$
6a	^{1}H	6.09 (d)	4.95 (t)	4.70 (t)	3.58 (t)	3.24 (d)			4.09 (q)	1.19 (t)	4.52 (s)	
	^{13}C	80.38	79.76	81.91	32.58	30.84		165.50	60.81	14.41	76.10	
6b	^{1}H	5.99 (d)	4.93 (d)		3.56 (d)	3.22 (d)			4.09 (q)	1.20 (t)	4.43 (s)	1.87 (s)
	^{13}C	81.96	78.56		34.04	31.62		164.50	61.59	14.37	76.69	22.41
7	^{1}H	6.19 (d)	5.92 (t)	4.86 (t)	3.77 (t)	4.50 (d)			4.08 (q)	1.17 (t)	4.43 (s)	
	^{13}C	80.60	76.68	81.27	38.76	29.81	65.62	165.00	60.65	14.30	76.47	
8a	^{1}H	3.85 (d)	5.21 (t)	6.87 (t)	6.01 (d)		5.39 (s)		4.24 (q)	1.36 (t)	4.43 (s)	
	^{13}C	59.61	87.37	94.92	92.71		148.1	175.15	60.57	14.70	77.73	
9a	^{1}H	5.61 (d)	6.76 (t)	5.20 (t)	4.55 (d)		5.47 (s)		4.00 (q)	1.16 (t)	4.57 (s)	
	^{13}C	90.72	95.01	88.31	60.46		140.1	164.00	60.55	14.10	78.49	
8b	^{1}H	3.80 (d)	5.14 (d)		5.91 (s)		5.40 (s)		4.24 (q)	1.37 (t)	4.33 (s)	2.70 (s)
	^{13}C	58.8	86.9		92.0		147.7	175.60	60.6	14.7	78.1	24.2
9b	^{1}H	5.61 (d)	6.55 (d)		4.21 (s)		5.50 (s)		4.00 (q)	1.18 (t)	4.49 (s)	1.98 (s)
	^{13}C	89.4	94.5		61.9		139.9	164.00	53.4	14.1	79.0	26.7
10	^{1}H	4.61 (d)	5.35 (t)	6.84 (t)	6.51 (d)		5.86 (s)		4.04 (q)	1.19 (t)	4.47 (s)	
	^{13}C	62.00	88.40	92.40	88.80	137.31	139.03	164.05	60.60	14.41	78.90	

[a] Signals corresponding to C(1) not identified. [b] All data in units of ppm.

the NOESY spectrum is recorded under conditions of phase-sensitive detection using the TPPI protocol.[9] These cross signals, denoted NOE 4/5, occur for instance between the protons of the six-membered ring of **8a** or within the ethyl group of the ester function. Unfortunately, they provide no additional structural information. In particular, no significant and reliable NOE signal is found for the olefinic proton H–C(7) of the major isomer **8a** and the minor isomer **9a**.

The exchange process unveiled by the NOESY experiment may be rationalized by assuming rotation around the exocyclic double bond, which allows interconversion of **8a** and **9a**. The experiment does not directly provide the rotational barrier. Since the isomers interconvert under the conditions of the NMR experiment, it follows that the product distribution is thermodynamically controlled. Accordingly, the more stable *E* isomer is the predominant product, as suggested by the tentative assignment based on chemical shifts. The population ratio of 4:1 for the stereoisomers corresponds to an energy difference of *ca.* 0.8 kcal/mol.

According to the NOESY experiment the sequence of the resonance lines changes dramatically on going from **8a** to **9a**. For example, H–C(2), which appears as a doublet at 3.85 ppm in **8a**, exchanges with the doublet at 5.61 ppm in **9a**, while the doublet for H–C(5) of **8a** at 6.01 ppm exchanges with that of **9a** at 4.55 ppm. A similar inversion occurs with the triplets of H–C(3) and H–C(4). Since the assignment of the resonance lines of H–C(2) and H–C(2) is not unambiguous, we have repeated the synthetic sequence starting with the methyl-substituted **1b**. Addition of ethyl lithiodiazoacetate afforded **6b**, which upon treatment with Rh$_2$(OAc)$_4$ was transformed to a 4.5:1 mixture of **8b** and **9b**. The regioselectivity of the addition leading to **6b** follows from the NMR pattern and from the analogy with other additions to methyl-substituted (nitroarene)FeCP$^+$ complexes.[10] In the major isomer of the decomposition product, **8b**, H–C(2) resonates as a doublet at 3.80 ppm, a chemical shift almost identical with that of the parent **8a** (3.85 ppm). H–C(5) in **8b**, however, appears as a singlet (5.91 ppm) at almost the same position (6.01 ppm) as H–C(5) in **8a**. The singlets of H–C(5) and H–C(7) may be assigned on the grounds of heteronuclear correlations (see Table I). With this experiment the assignments of the resonance lines of **8a** are experimentally confirmed. A similar reasoning applies to the minor isomers **9a** and **9b**: The doublet for H–C(2) of **9a** (5.61 ppm) is found in the same position in **9b**, while that for H–C(5) of **9a** appears as a singlet at 4.21 ppm in **9b**. It follows that the inversion of the order of the signals observed as one goes from **8a** to **9a** is not an artifact. In addition, a NOESY experiment with the **8b**/**9b** mixture gives the corresponding NOE's and exchange signals corresponding to those of **8a**/**9a**.

Exposure of **7** to Rh$_2$(OAc)$_4$ resulted in formation of the alkene **10** in 93% yield as a single stereoisomer. The alkene is characterized by a singlet at 5.86 ppm in the ^{1}H NMR

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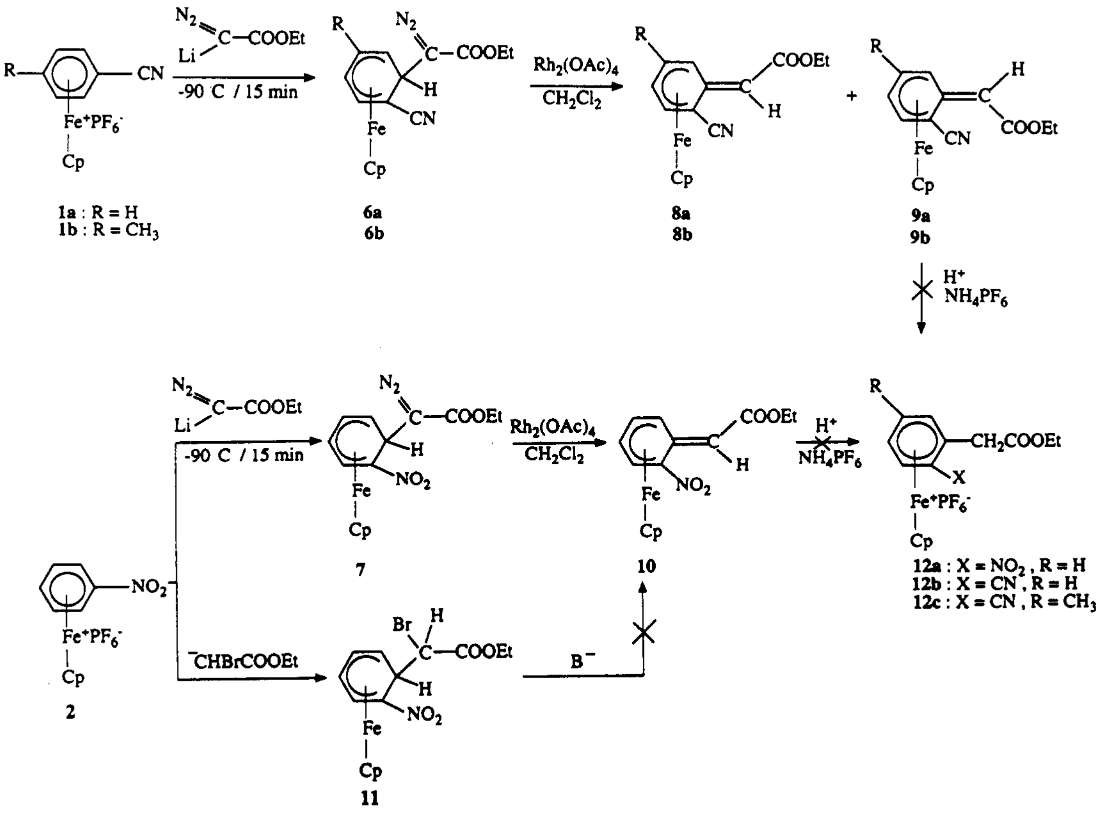
Scheme II



and a doublet at 139.03 ppm in the ^{13}C spectrum. If we assume the exchange observed for interconversion of the stereoisomers of 8 and 9 takes place also with 10, the configuration of 10 must be *E*. The increased bulk of the nitro substituent in 10 as compared to the cyano group displaces the equilibrium so strongly in favor of the less crowded *E* isomer that the *Z* isomer is not detectable.

With the structure of 10 established, the possibility of its access *via* the route outlined in Scheme I was reexamined. Reaction between the anion of ethyl bromoacetate and 2 afforded the σ adduct 11 in 32% yield as a 1:1 mixture of diastereoisomers, but base-induced elimination failed again. In principle, 11 could also suffer α-elimination of HBr to a carbene, which could undergo 1,2-hydrogen migration to 10 in analogy to 7, but under all conditions tried either unreacted 11 or decomposition products were all that were isolated.

6-Alkylidenecyclohexadienyl complexes 15 have been proposed as putative intermediates in S_NAr-type reactions of cationic Fe(Cp) complexes of *o*-dichlorobenzene 13 with diethyl malonate.[11] Their protonation is accompanied by decarboxylation and leads to 16 (Scheme III). By analogy, protonation of 8–10 would generate the cationic complexes 12a–c, which are the formal products of vicarious nucleophilic substitution of 1a,b and 2. This step could not be realized; the complexed alkylidenes decomposed upon treatment with acids such as HCl, H_2SO_4, HPF_6, and CF_3COOH. We attribute the failure of this protonation to the presence of the strongly electron-withdrawing cyano and nitro groups. While these groups are necessary to activate the complexed arenes toward nucleophilic attack by the diazoacetate anion, their presence reduces at the same time the electron density of the alkylidenes, so that the protonation of their double bond is inhibited.

Experimental Section

General Considerations.[2] Ethyl diazoacetate, ethyl bromoacetate, and rhodium(II) acetate dimer were purchased from Fluka.

Synthesis of (Arene)metal Complexes. (η^5-Cyclopentadienyl)(η^6-*p*-benzonitrile)iron(III) hexafluorophosphate (**1a**), (η^5-cyclopentadienyl)(η^6-*p*-cyanotoluene)iron(II) hexafluorophosphate (**1b**), (η^5-cyclopentadienyl)(η^6-nitrobenzene)iron hexafluorophosphate (**2**), and (η^5-cyclopentadienyl)(η^6-*o*-dichlorobenzene)iron(II) hexafluorophosphate (**13**) were prepared according to published procedures.[12–15]

Reaction of Ethyl Lithiodiazoacetate with (η^6-Arene)(η^5-cyclopentadienyl)iron(II) Hexafluorophosphate (1 and 2). General Procedure. Lithium diisopropylamide (3.0 mmol) was prepared from $(i\text{-Pr})_2NH$ (3.0 mmol) and BuLi (1.89 mL, 1.6 M in hexane) at 0 °C in 10.0 mL of THF. After the solution was stirred for 20 min, ethyl diazoacetate (342 mg, 3.0 mmol) in 5 mL of THF was added rapidly at −90 °C. The color changed immediately to orange. After 15 min at −90 °C, a solution of (η^6-arene)(η^5-cyclopentadienyl)iron(II) hexafluorophosphate (1.0 mmol in 5 mL of HMPA) was added, and the mixture was stirred for 30 min at −90 °C followed by quenching with H_2O (30 mL). The mixture was then extracted with CH_2Cl_2 (3 × 50 mL), and the combined extracts were washed with H_2O (2 × 50 mL). After drying ($MgSO_4$), the solvent was removed on a rotary evaporator and the product isolated by column chromatography.

6a: 71% yield (240 mg); orange-red oil; ^1H NMR, ^{13}C NMR, see Table I; IR (CH_2Cl_2) 2200 (w), 2090 (m), 1680 (m), 1260 (m), 1200 (w) cm^{-1}; MS *m/e* (relative intensity) 338 (2), 309 (10), 237 (11), 224 (50), 171 (34), 153 (10), 121 (100), 115 (22), 103 (14), 95

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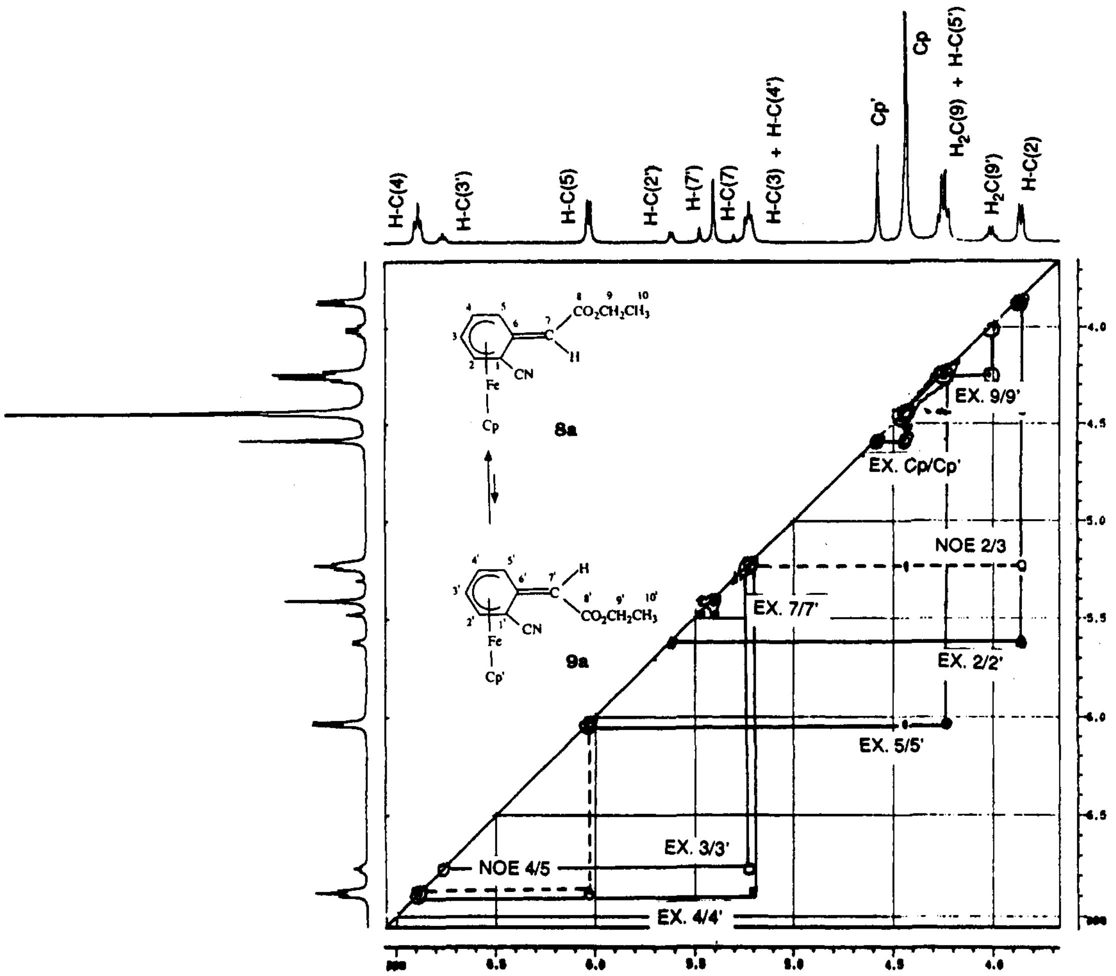
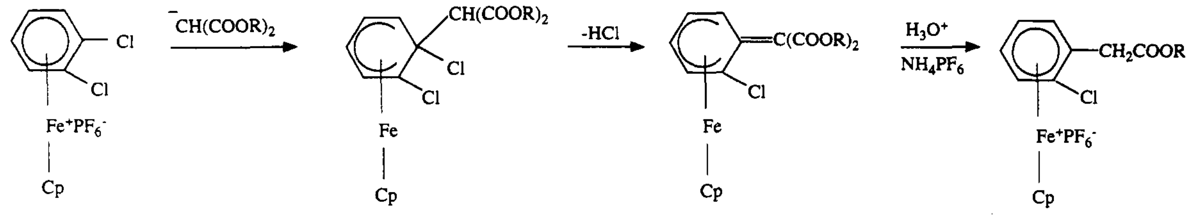


Figure 1. NOESYTP 2D homonuclear correlation via dipolar coupling for **8a** and **9a**. Abbreviations: EX, exchange signal; NOE, real NOE cross peak.

Scheme III



13 14 15 16

(12), 89 (54), 63 (19), 56 (94), 51 (8); HRMS calcd for $C_{16}H_{15}FeN_3O_2$ 337.0513, found 337.0562.

6b: 56% yield (197 mg); orange-red oil; ^1H NMR, ^{13}C NMR, see Table I; IR ($CHCl_3$) 2145 (m), 1720 (m), 1680 (m), 1335 (s), 1220 (s) cm^{-1}; MS *m/e* (relative intensity) 351 (7), 323 (100), 294 (15), 251 (15), 238 (50), 185 (27), 167 (14), 129 (26), 121 (83), 117 (68), 103 (43), 90 (15), 77 (24), 66 (34), 56 (59), 51 (12); HRMS calcd for $C_{17}H_{17}FeN_3O_2$ 351.067, found 351.073.

7: 59% yield (210 mg); dark red oil; ^1H NMR, ^{13}C NMR, see Table I; IR (CH_2Cl_2) 2075 (w), 1680 (w), 1510 (w) 1330 (m), 1280 (w), 1210 (w) cm^{-1} MS *m/e* (relative intensity) 357 (2), 244 (20), 133 (16), 121 (42), 105 (54), 89 (36), 81 (33), 77 (39), 65 (34), 56 (100), 51 (27); HRMS calcd for $C_{15}H_{15}FeN_3O_4$ 357.0411, found 357.0406.

Attachment of Ethyl Lithiobromoacetate to (η^5-Cyclopentadienyl)(η^6-nitrobenzene)iron Hexafluorophosphate (2). To a stirred solution of LDA (1.1 mmol in mL of THF) was added at −78 °C ethyl bromoacetate (167 mg, 1.0 mmol). After this mixture was stirred for 30 min, a solution of **2** (195 mg, 0.5 mmol in 3 mL of HMPA) was added, and the mixture was stirred for 30 min at −78 °C followed by quenching with water (30 mL). The mixture was then extracted with CH_2Cl_2 (3 × 50 mL), and the combined extracts were washed with H_2O (2 × 50 mL). After drying ($MgSO_4$), the solvent was removed on a rotary evaporator and the product isolated by column chromatography. **11** was obtained in 32% yield (66 mg) as a red-brown oil (mixture of two diastereoisomers, **11a** and **11b**, *ca.* 1:1) separable by column chromatography (silica gel/CH_2Cl_2). **11a**: red-brown oil; ^1H NMR 6.21 (t, 1H), 5.93 (d, 1H), 4.86 (t, 1H), 4.41 (s, 5H), 3.98 (m, 1H), 3.93 (q, 2H), 3.76 (t, 1H), 1.16 (t, 3H) ppm. **11b**: red-brown oil; ^1H NMR 6.17 (t, 1H), 5.97 (d, 1H), 4.82 (t, 1H), 4.40 (s, 5H), 4.24 (m, 1H), 4.12 (q, 2H), 3.52 (t, 1H), 1.24 (t, 3H) ppm; IR ($CHCl_3$, cm^{-1}) 1725 (s), 1500 (s), 1320 (s), 1160 (m), 1040 (w) cm^{-1}; MS *m/e* (relative intensity) 245 (14), 244 (100), 214 (12), 186 (6), 136 (2), 81 (10). Anal. Calcd for $C_{15}H_{16}BrFeNO_4$: C, 43.90; H, 3.90; N, 3.41. Found: C, 43.61; H, 3.69; N, 3.47.

Rhodium(II)-Catalyzed Decomposition of Diazo Compounds 6 and 7. General Procedure. To a stirred solution of $Rh_2(OAc)_4$ (12 mg, 5 mol % in 10 mL of dry CH_2Cl_2) was added a solution of diazo compound **6** or **7** (0.5 mmol in 5 mL of dry

CH_2Cl_2) by syringe pump over 3 h at 25 °C. After addition was complete, this mixture was stirred for 30 min and was then filtered through a 1-cm plug of silica gel to separate the catalyst. The plug was eluted with 50 mL of CH_2Cl_2. The combined organic solution was evaporated under reduced pressure, and the reaction products were separated by column chromatography on silica gel using hexane–ethyl acetate as the eluent.

8a and **9a** were obtained in 86% yield (133 mg) as an orange-red solid (mixture of two isomers **8a** and **9a** *ca.* 4:1): ^1H NMR, ^{13}C NMR, see Table I; IR (CH_2Cl_2) 2360 (s), 2340 (s), 1700 (s), 1250 (s), 1110 (w), 1060 (w) cm^{-1}; MS *m/e* (relative intensity): 309 (43), 280 (9), 237 (13), 209 (22), 171 (8), 158 (23), 153 (24), 136 (15), 121 (89), 115 (48), 89 (100), 81 (11), 77 (12), 63 (27), 56 (88); HRMS calcd for $C_{16}H_{15}FeNO_2$ 309.0452, found 309.0440.

8b and **9b** were obtained in 78% yield (126 mg) as an orange-red solid (mixture of two isomers **8b** and **9b** *ca.* 4.5:1): ^1H NMR, ^{13}C NMR, see Table I; IR ($CHCl_3$) 2931 (w), 1967 (s), 1892 (s), 1258 (s) cm^{-1}; MS *m/e* (relative intensity): 323 (100), 294 (13), 250 (7), 167 (6), 129 (16), 121 (36), 103 (25), 77 (12), 56 (30); HRMS calcd for $C_{17}H_{17}FeNO_2$ 323.060, found 323.057.

10: 93% yield (153 mg); brown solid; ^1H NMR, ^{13}C NMR, see Table I; IR ($CHCl_3$) 1710 (m), 1520 (m), 1320 (m), 1275 (s), 1100 (m), 1025 (m) cm^{-1}; MS *m/e* (relative intensity): 329 (6), 186 (29), 177 (9), 147 (10), 133 (10), 130 (34), 122 (30), 105 (100), 103 (13), 77 (34), 65 (33), 51 (16); HRMS calcd for $C_{15}H_{15}FeNO_4$ 329.0350, found 329.0294.

Acknowledgment. We are indebted to the Swiss National Science Foundation (Project Nos. 2-602-087 and 20-27-466.89) for financial support and to U. Burger and P. Kamalaprija for the NOESY experiments.

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