The Ferrocenyldiphenylpropargyl Cation − A Spectroscopic Comparison Among Stabilizing Substituents and Nucleophilic Additions

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The stable ferrocenyldiphenylpropargyl cation (**3**) is readily and quantitatively generated from the propargylic alcohol **2** with a slight excess of tetrafluoroboric acid in dichloromethane at −78 °C. The cationic species **3** was characterized by ^{1}H- and ^{13}C-NMR spectroscopy; nucleophilic trapping reactions gave rise to the formation of ferrocenyldiphenylallenes **9**.

Introduction

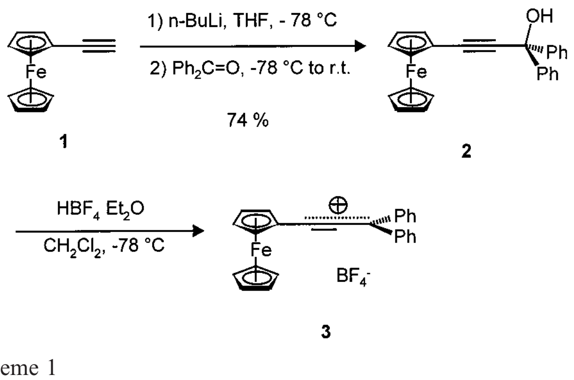
The discovery of transition metal stabilization of reactive intermediates[1] has not only initiated a remarkable theoretical interest but has also had a tremendous impact on the application of such species in synthetic chemistry, namely the synthesis of complex organic molecules.[2] Thus, carbenium ions can be stabilized by quite a number of organometallic substituents such as metallocene and half-sandwich complexes, particularly ferrocenyl, tricarbonylcyclobutadienyliron, cyclobutadienylcyclopentadienylcobalt, and benzenecarbonylchromium derivatives.[1,2] Electronically, this stabilization of cationic charges in the α-position of organometallic fragments can be rationalized by a strong d−p overlap from the transition metal centered occupied d orbitals to the vacant p_z orbital at the carbenium site, accompanied by a pronounced bending of the cationic side chain towards the metal center.[1a,1d,3] As a consequence, this strong electronic interaction manifests itself as a configurational and conformational fixation of the positively charged substituent and, ultimately, leads to highly stereoselective nucleophilic additions.

Although quite a number of substituted carbenium ions[4] have been known for some time, the investigation of the chemistry of transition metal stabilized cations with conjugated substituents, i.e. ambident electrophiles, is still in its infancy.[5] Recently, we showed that arenecarbonylchromium fragments efficiently stabilize α- and γ-propargyl cations and that α-propargyl cations can be trapped with nucleophiles to give arene complex substituted propargyl derivatives with excellent diastereoselectivity.[6] In particular, the peculiar ability to stabilize a cationic charge generated in the γ-position to the stabilizing substituent, as well as the ambident reactivity of propargyl cations giving rise either to allenes or alkynes,[7] prompted us to study the structure (UV/Vis and ^{13}C-NMR spectroscopy) and reactions of a related propargyl cation bearing the more powerful donor ferrocene as the stabilizing organometallic moiety in comparison to carbonylchromium-complexed arenes. Here, we wish to report our results on the spectroscopic characterization and nucleophilic trapping reactions of the stable ferrocenyldiphenylpropargyl cation[8] as well as on the spectroscopic comparison to the uncomplexed[9] and tricarbonylchromium-complexed[5b] phenyl analog.

Results and Discussion

Generation of the Ferrocenyldiphenylpropargyl Cation (3)

Generally, propargyl cations can be generated from the corresponding propargyl derivatives with suitable leaving groups upon treatment with Lewis or Brønsted acids, in particular, this can be achieved in a fairly facile way upon acid-mediated ionization of propargyl alcohols. According to the synthesis of highly stable perferrocenylated propargyl cations by Bildstein,[10] our strategy towards ferrocenyl-substituted γ-propargyl cations commences with the addition of ferrocenyl acetylide [by deprotonation of ethynylferrocene (**1**) with butyllithium] to benzophenone to give the propargyl alcohol **2** in good yield (Scheme 1). Treatment of the propargylic alcohol **2** with a 1.5-fold excess of tetrafluoroboric acid−diethyl ether in dichloromethane solution at −78 °C[5b] led to the formation of a deep-green solution of the persistent allenyl/propargyl cation **3** in quantitative yield (according to NMR and UV/Vis spectroscopy, vide infra) within 5 min.



Scheme 1

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Structure of the Propargyl Cation 3

As expected, and in agreement with cation generation studies of related propargyl cations,[5][9a] the ionization of the propargyl alcohol **2** to give the propargyl cation **3** results in a considerable downfield shift of almost all signals in the proton and carbon NMR spectra (Figure 1 and Figure 2, Table 1). Only the *ipso*-phenyl carbon resonance of **3** ($\delta = 141.52$, $\Delta_I = -3.35$) is shifted to high field, indicating an adjacent carbenium center. Thus, the positive charge is delocalized by resonance stabilization over the complete side chain including the substituted cyclopentadienyl ligand. Even the unsubstituted cyclopentadienyl ring of **3** (^{1}H: $\delta = 4.96$, $\Delta_I = +0.72$; ^{13}C: $\delta = 81.75$, $\Delta_I = +12.15$), and with it the ferrocenyl iron atom, experiences a significant downfield shift of the resonances, indicating their participation in the extensive charge stabilization. Most significantly, the downfield shifts of the carbon resonances of the quaternary signals of the propargyl/allenyl side chain reveal a dominant contribution of the allenylium canonical resonance structure **3B** to the stabilization of the cation generated at the γ-position as compared to the ferrocenyl moiety.

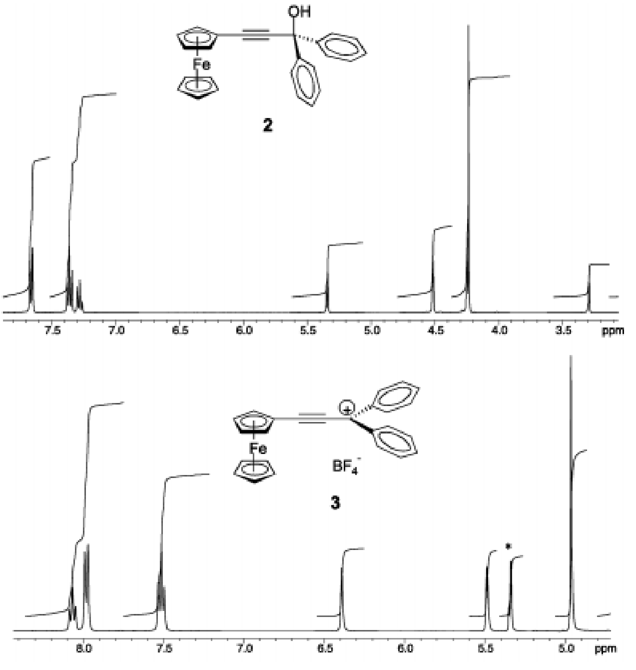
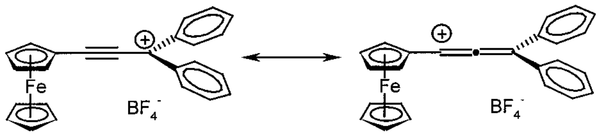


Figure 2. ^{1}H-NMR spectra (-70 °C, CD_2Cl_2, 400 MHz) of **2** (top) and **3** (bottom)



3A **3B**

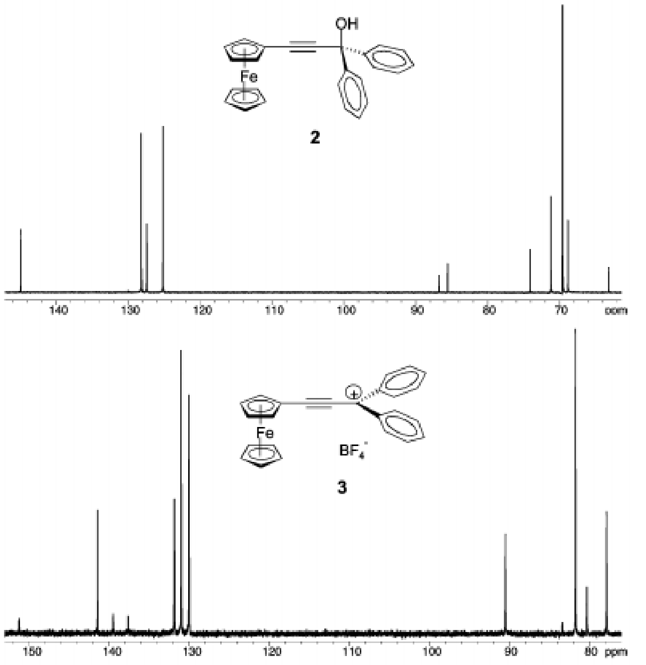
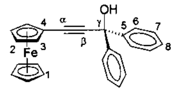
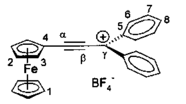


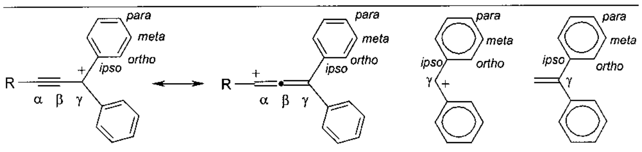
Figure 2. ^{13}C-NMR spectra of **2** (top) and **3** (bottom) (-70 °C, CD_2Cl_2, 100 MHz)

Table 1. Assignment and ionization shifts of ^{1}H- (400 MHz) and ^{13}C-NMR (100 MHz) signals (CD_2Cl_2, -70 °C) of **2** and **3**

	 2		 3		**ionization shift Δ_I**	
	^{1}H	^{13}C	^{1}H	^{13}C	$\Delta_I(^1H)$	$\Delta_I(^{13}C)$
C_1	4.24	69.90	4.96	81.75	+ 0.72	+12.15
C_2	4.25	68.85	5.49	77.85	+ 1.24	+9.00
C_3	4.52	71.24	6.39	90.50	+ 1.87	+19.26
C_4		74.09		80.30		+6.21
C_α		85.58		139.54		+53.96
C_β		86.81		137.68		+50.87
C_γ		63.21		151.30		+88.09
C_5		144.87		141.52		-3.35
C_6	7.68	128.10	7.98	131.01	+ 0.30	+2.91
C_7	7.36	125.13	7.51	130.02	+ 0.15	+4.89
C_8	7.28	127.37	8.07	131.89	+ 0.79	+4.52

A comparison of the carbon resonances of the propargyl cation bridge and the γ-terminal *p*-phenyl positions of the cations **4** (i.e., **5**,[9a] **6**,[5b] and **3**) reveals the increasing con-

Table 2. Selected carbon resonances of the propargylic cations **4** (i.e., **5**,[9a] **6**,[5b] and **3**) and the reference compounds **7**[11] and **8**[12]



4A **4B** **7** **8**

R	C_α	C_β	C_γ	C_{para}	C_{meta}	Δ_π
phenyl[a] (**5**)	159.1	105.9	186.8	144.0	131.4	12.6
phenylCr(CO)$_3$[b] (**6**)	150.3	120.8	161.4	136.5	130.2	6.3
ferrocenyl[b] (**3**)	139.5	137.7	151.3	131.9	131.0	1.9
benzhydryl cation **7**	-	-	191.1	151.2	134.1	17.1
1,1-diphenyl ethene (**8**)	-	-	141.1	126.4	127.6	-0.7

[a] $FSO_3H-SbF_5-SO_2$, −60 °C. – [b] CD_2Cl_2 + HBF_4OEt_2, −70 °C.

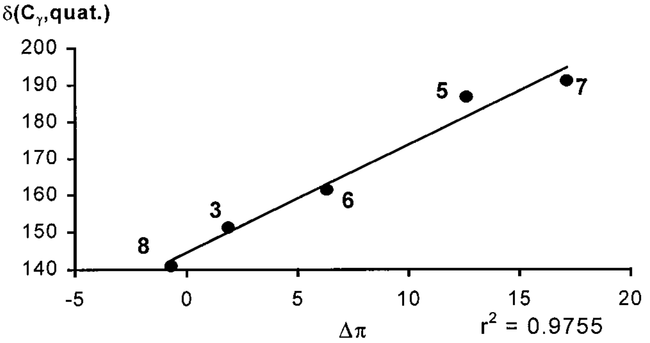


Figure 3. Correlation of the Δ_π values ($\Delta_\pi = \delta_{para} - \delta_{meta}$) and the C_γ resonance (carbenium or quaternary benzyl center) of the propargyl cations **3**, **5**, **6**, and the resonance compounds **7** and **8**

tribution of the allenylium resonance structure **4B** upon varying the α-substituent from phenyl (**5**) to the organometallic donors $(OC)_3(Ph)Cr$ (**6**) and ferrocenyl (**3**) (Table 2). More specifically, the α-, γ- and terminal *p*-phenyl resonances decrease in this order, indicating a charge delocalization shift towards the α-substituent fragment. Simultaneously, the β-resonances increase towards an "allenic" direction. As reference systems for localized cations, the benzylhydryl cation (**7**)[11] represents a model for a carbenium ion only delocalized at the C_γ position and its phenyl substituents, as depicted in structure **4A**, whereas 1,1-diphenylethene (**8**)[12] serves as a model for an allenylium structure (**4B**) assuming the γ-carbon atom does not bear a positive charge and the charge is completely stabilized at the C_α position.

A linear correlation between the C_γ resonance (carbenium or quaternary benzyl center) and the Δ_π values ($\Delta_\pi = \delta_{para} - \delta_{meta}$) of the propargyl cations **4** and the reference compounds **7** and **8** establishes the dominant influence of the α-substituent on the π-delocalization of the positive charge (Figure 3). According to a lever-rule model[5b,9a] the relative contributions of mesomeric forms to the stabilization of resonance-stabilized cations can be estimated by considering the C_γ-carbenium resonances or the *p*-phenyl carbon signal.[13] On applying the C_γ resonances the contribution of the α-substituent stabilization increases from 10 (**5**) to 59 (**6**) to 79% (**3**), whereas consideration of the *para* resonances gives rise to a 29 (**5**), 60 (**6**), and 78% (**3**) participation of the allenylium canonical structure **8B** in the electronic ground state.

Ionization with tetrafluoroboric acid–diethyl ether of a dichloromethane solution of **2** at −70 °C leads to a color change from yellow/orange to deep green. This change can be monitored by following the appearance of long-wavelength absorption bands with maxima at 310 (sh), 412, 483, and 856 nm (Figure 4) by UV/Vis spectroscopy. According to calculations on an MM2-optimized structure of **2** using the ZINDO/CI formalism with INDO/1 parameters[14] the absorptions at 856 nm (calcd. 688 nm; iron-centered $d_{x^2-y^2}$ orbital HOMO to the localized LUMO of the propargyl moiety), at 483 nm (calcd. 484 nm; d_{z^2} orbital HOMO-2 to the LUMO) and at 412 nm (calcd. 389 nm, d_{xz} orbital HOMO-3 to LUMO and calcd. 403 nm, d_{z^2} orbital HOMO-2 to LUMO) and at 310 nm (sh) [calcd. 326 nm, bound Cp ring (HOMO-8) to propargyl fragment (LUMO)

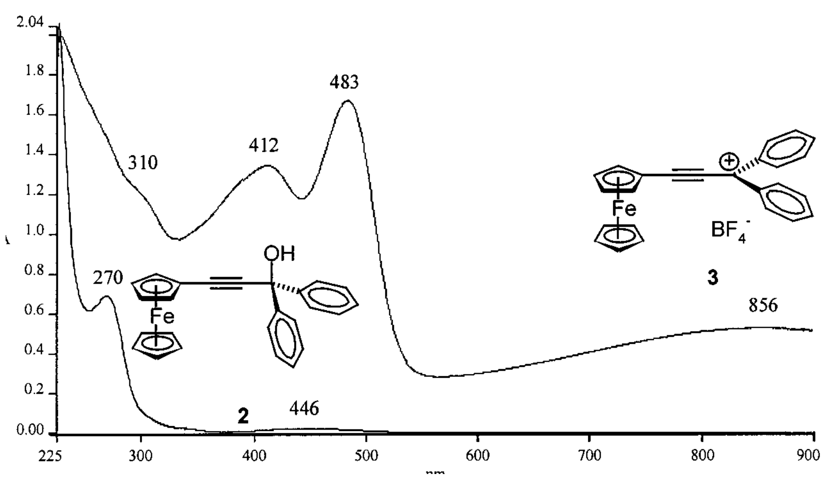
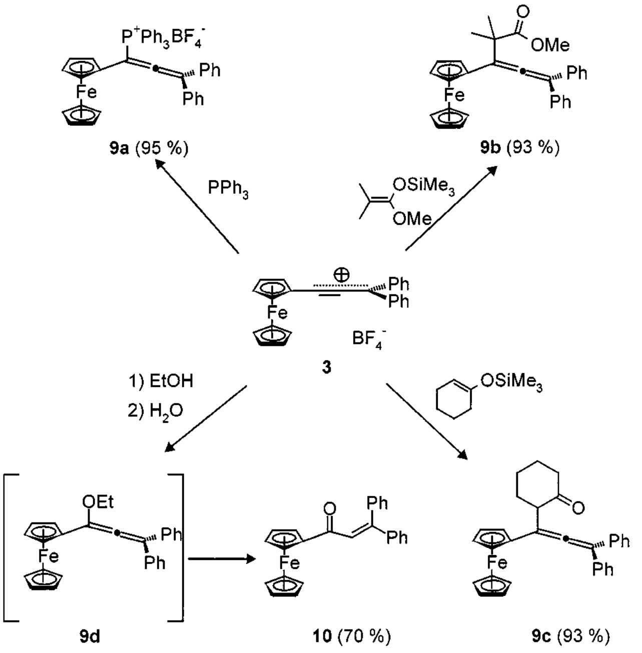


Figure 4. UV/Vis spectra of **2** (λ_{max} at 270 and 446 nm) and **3** (λ_{max} at 310sh, 412, 483, and 483 nm) at −70 °C (dichloromethane)

π-π* transition and calcd. 311 nm, from the phenyl rings to the propargyl fragment (HOMO-10 to LUMO)] are readily reproduced.

Nucleophilic Trapping Reactions of 3

The propargyl cation **3** can be trapped with different nucleophiles to furnish the allenes **9** in good to excellent yields (Scheme 2). Most interestingly, if ethanol is used as the nucleophile only the hydrolysis product, i.e. the enone **10**, can be isolated (70% yield). In significant contrast to the cations **5** and **6**, where the kinetically controlled ethanol attack gives rise to the formation of the corresponding propargyl ethers,[5b,15] the regioselectivity of the nucleophilic attack of ethanol on **3** is reversed to the α-position, which results in the generation of the allene intermediate **9d**. The increasing contribution of the allenylium canonical structure **4B** (vide supra) to the electronic ground state of **3** can be interpreted as an increase of the orbital coefficient at the α-position in the LUMO, the relevant orbital for kinetically controlled nucleophilic additions to the cations **4**.



Scheme 2

Due to the pronounced basicity the ferrocenyl-substituted allenes **9** tend to form ferrocenylallyl cations reversibly.[16] Only if the basicity is modulated by an electron-withdrawing group (**9a**), or if acid-sensitive nucleophiles, such as silyl enol ethers or silyl ketene acetals, successfully trap excess protons, by acting as proton sponges, can the formation of allyl cations be prevented.

The structural assignments of the allenes **9a**−**c** are fully supported by NMR, IR, elemental analysis and by an X-ray crystal structure analysis of **9b** (Figure 5, Table 3).[17] In the ^{1}H-NMR spectra the signals of the ferrocene protons appear between $\delta = 3.92$ and 4.34. Most characteristically,

Table 3. Crystal data and structure refinements for **9b**

	9b
Empirical formula	$C_{30}H_{28}FeO_2$
Molecular mass	476.37
Temperature	298(2) K
Radiation	0.71073 Å; Mo-K_α
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell dimensions [Å]	$a = 8.8576(17)$; $\alpha = 64.201(7)$, $b = 11.7194(7)$; $\beta = 75.284(12)$, $c = 13.3764(15)$; $\gamma = 84.435(9)$
Volume [Å^3]	1209.0(3)
Z	2
Density (calculated)	1.309 g/cm^3
Absorption correction	ω2θ-scans
Absorption coefficient	0.648 mm^{-1}
Max. and min. transmission	0.9994 and 0.9556
F(000)	500
Crystal size [mm]	0.20 × 0.27 × 0.53
2θ range (min./max.)	2.38/23.97°
Index ranges	$-10 \le h \le 10$; $0 \le k \le 13$ $-13 \le l \le 15$
Reflections collected	3989
Independent reflections	3781 [R(int) = 0.0087]
Observed reflections	3270 [$I > 2\sigma$(I)]
Refinement method	SHELXL-93 on F^2
Data/restraints/parameters	3781/0/301
Goodness of fit on F^2	1.092
Final R indices [$I > 2\sigma(I)$]	
R_1	0.0322
wR_2	0.0793
R indices (all data)	
R_1	0.0391
wR_2	0.0841
Largest diff. peak and hole [e/Å^3]	0.194 and −0.252

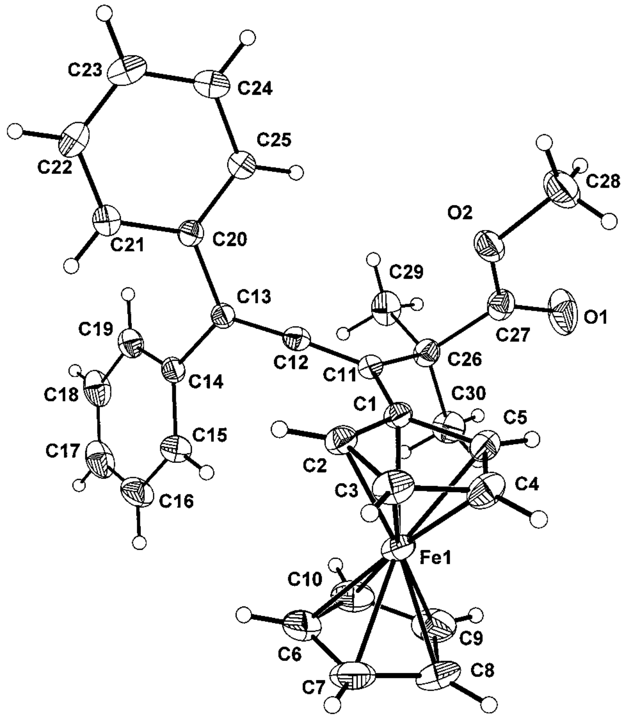


Figure 5. ORTEP plot of **9b**; selected bond lengths [Å], bond angles [°] and torsional angles [°]: C(1)−C(11) 1.482(3), C(11)−C(12) 1.312(3), C(12)−C(13) 1.316(3), C(1)−C(5) 1.431(3), C(4)−C(5) 1.412(3); C(12)−C(11)−C(1) 119.8(2), C(12)−C(11)−C(26) 119.9(2), C(11)−C(12)−C(13) 175.0(2); C(11)−C(1)−C(2)−C(3) 175.2(2), C(2)−C(1)−C(11)−C(12) 4.1(3), C(2)−C(1)−C(11)−C(26) 176.9(2)

the ^{13}C-NMR signals of the central allene carbon atoms are found between δ = 204.6 and 216.7 depending on the electronic nature of the substituent at the α-position. According to the X-ray crystal structure analysis (Figure 5) of the allene **9b**, the allene moiety is linear [C(11)−C(12)−C(13): 175°] and the allenic double bond lengths [C(11)−C(12): 1.31 Å and C(12)−C(13): 1.32 Å] lie within the expected range. Interestingly, the cyclopentadienyl ring and the allene fragment are arranged in an almost coplanar manner, although the ferrocenyl substituent is considered to be sterically bulky.

Conclusion

Ferrocene stabilizes propargyl cations generated at the γ-position to a large extent by delocalizing the positive charge evenly over the iron center and the unsubstituted cyclopentadienyl ring, as shown by NMR spectroscopy of the cation **3**. Therefore, the increasing contribution of the allenylium canonical structures in three different organic/organometallic propargyl cations **4** can be detected by carbon NMR spectroscopy and compared. For the ferrocenyl-substituted system a regioselectivity shift for the nucleophilic attack of ethanol from the propargyl to the allenyl position is the most significant difference between the phenyl and $(OC)_3(Ph)Cr$ analogs. Thus, organometallic substituents not only stabilize ambident electrophiles such as propargyl cations but also could allow a fine tuning of the regioselectivity of nucleophilic additions.

Experimental Section

All reactions involving ferrocene complexes were carried out in flame-dried Schlenk flasks under nitrogen by using septum and syringe techniques. Solvents were dried and distilled according to standard procedures.[18] − Column chromatography: Silica gel 60 (0.063−0.2 mm/70−230 mesh, Firma Merck Darmstadt). − TLC: Silica gel plates (60 F_{254} Merck, Darmstadt). − Melting points (uncorrected values): Reichert−Jung Thermovar. − Ethynylferrocene was synthesized according to a procedure of Rosenblum.[19] All other reagents were purchased from Merck, Aldrich, or Fluka, and used without further purification. − ^{1}H- and ^{13}C-NMR spectra: Bruker WM 300, Bruker AC 300, Bruker ARX 300 or Varian VXR 400S; [D$_6$]DMSO and [D$_2$]dichloromethane. − IR: Perkin−Elmer FT-IR spectrometer 1000 or Perkin−Elmer FT-IR Paragon 1000 PC. The samples were pressed into KBr pellets and the spectra recorded on NaCl plates. − UV/Vis: Beckman DK-2a, Beckman UV 5240, or Perkin−Elmer model Lambda 16; J& M TIDAS (transputer integrated diode array spectrometer) with a Hellma low-temperature quartz probe (UV/Vis cation characterization). − MS: Finnigan MAT 311-A/100MS, Finnigan MAT 90, and MAT 95Q. − Elemental analyses were carried out in the Microanalytical Laboratories of the Institut für Organische Chemie, Ludwig-Maximilians-Universität München.

3-Ferrocenyl-1,1-diphenylprop-2-yne-1-ol (2): To a cooled solution (−78 °C) of 1.00 g (4.90 mmol) of ethynylferrocene (**1**) in 40 mL of THF was added dropwise 3.20 mL (5.10 mmol) of a 1.6 M solution of butyllithium in hexanes over a period of 1 min. The reaction mixture was stirred for a further 60 min. To this reaction mixture was added dropwise a solution of 0.89 g (4.90 mmol) of benzophenone in 5 mL of THF and, after the addition, the mixture was allowed to warm up to room temperature over a period of 60 min. After the addition of 20 mL of water and extraction of the aqueous phase with diethyl ether (3 × 50 mL), the combined organic phases were dried with magnesium sulfate. After evaporation of the solvents, the residue was purified by chromatography on silica gel with a gradient of diethyl ether/pentane (1:10 → 1:1) to afford 1.42 g (74%) of the propargylic alcohol **2** as an orange crystalline product, m.p. 90−92 °C. − ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 4.25 (s, 5 H), 4.29 (d, J = 1.7 Hz, 2 H), 4.53 (dd, J = 1.7 Hz, 2 H), 6.74 (s, 1 H), 7.22 (m, 2 H), 7.33 (m, 4 H), 7.60 (m, 4 H); (CD_2Cl_2, 400 MHz): δ = 3.29 (s, 1 H), 4.24 (s, 5 H), 4.25 (m, 2 H), 4.52 (m, 2 H), 7.28 (t, J = 7.3 Hz, 2 H), 7.36 (dd, J = 7.3 Hz, 4 H), 7.68 (d, J = 7.8 Hz, 4 H). − ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 64.5 ($C_{quat.}$), 69.0 (CH), 69.8 (CH), 71.3 (CH), 73.4 ($C_{quat.}$), 84.6 ($C_{quat.}$), 89.5 ($C_{quat.}$), 125.9 (CH), 127.2 (CH), 128.2 (CH), 146.8 ($C_{quat.}$). − ^{13}C NMR (CD_2Cl_2, 100 MHz): δ = 63.2 ($C_{quat.}$), 68.9 (CH), 69.6 (CH), 71.2 (CH), 74.1 ($C_{quat.}$), 85.6 ($C_{quat.}$), 86.8 ($C_{quat.}$), 125.1 (CH), 127.4 (CH), 128.1 (CH), 144.9 ($C_{quat.}$). − MS (70 eV, EI); *m/z* (%): 392 [M$^+$] (61), 327 [M$^+$ − C_5H_5] (13), 254 [M$^+$ − CpFeOH] (31), 210 [M$^+$− Ph_2CO] (100), 182 [Ph_2CO^+] (52), 152 [Ph_2CO^+ − CH_2O] (18), 105 [$PhCO^+$] (70), 77 [Ph^+] (27), 56 [Fe^+] (8). − IR (KBr): $\tilde{\nu}$ = 2230 cm^{-1}, 1627, 1599, 1489, 1449, 1408, 1339, 1264, 1194, 1178, 1165, 1156, 1101, 1061, 1028, 998, 922, 903, 885, 843, 818, 772, 753, 715, 701, 641, 630, 594, 542, 519, 498, 488, 451, 415. − UV/Vis (DMSO): λ_{max} (ε) = 271 nm (8900), 445 (3200). − $C_{25}H_{20}FeO$ (392.28): calcd. C 76.54, H 5.13; found C 76.51, H 5.22.

Preparation of the Propargyl Cation 3 for the NMR-Spectroscopic Characterization: To a solution of 20 μL of tetrafluoroboric acid−diethyl ether in 0.3 mL of CD_2Cl_2, placed in a nitrogen-flushed NMR tube capped with a rubber septum, was added a solution of 25 mg of **2** in 0.4 mL of CD_2Cl_2 at −78 °C. The NMR tube with the dark green solution was then quickly transferred to the NMR spectrometer (precooled to −70 °C).

Generation of the Propargyl Cation 3 and Nucleophilic Trapping Reaction (General Procedure): To a cooled solution (−78 °C) of 52 μL (0.32 mmol) of tetrafluoroboric acid (54% in diethyl ether) in 10 mL of dichloromethane was added dropwise a solution of 100 mg (0.25 mmol) of **2** in 5 mL of dichloromethane. After stirring for 60 min, a solution of 1.0 mmol of the corresponding nucleophile in 5 mL of dichloromethane was added. The mixture was then allowed to warm up to room temperature. After the addition of 10 mL of water, the solution was extracted with diethyl ether (**9a**: dichloromethane) (3 × 50 mL) and the combined organic phases were dried with magnesium sulfate. Evaporation of the solvents under reduced pressure furnished the products **9** (or **10**), which were recrystallized from diethyl ether/pentane or dichloromethane/diethyl ether to give good to excellent yields.

1-Ferrocenyl-3,3-diphenyl-1-(triphenylphosphonium)propa-1,2-diene Tetrafluoroborate (9a): According to the GP with 131 mg (0.50 mmol) of triphenylphosphane to give 170 mg (95%) of **9a**. Red crystals, m.p. 216−218 °C (dichloromethane/diethyl ether). − ^{1}H NMR (CD_2Cl_2, 300 MHz): δ = 3.98 (s, 5 H), 4.15 (m, 2 H), 4.34 (m, 2 H), 7.04−7.88 (m, 25 H). − ^{13}C NMR (CD_2Cl_2, 75 MHz): δ = 70.2 (CH), 70.2 (CH), 70.4 (CH, $J_{P,C}$ = 3.3 Hz), 86.7 ($C_{quat.}$), 93.7 ($C_{quat.}$, $J_{P,C}$ = 86.2 Hz), 116.9 ($C_{quat.}$), 118.1 ($C_{quat.}$, $J_{P,C}$ = 88.2 Hz), 128.4 (CH), 129.7 (CH), 129.9 (CH), 130.6 (CH, $J_{P,C}$ = 12.6 Hz), 132.7 ($C_{quat.}$), 134.5 (CH, $J_{P,C}$ = 9.9 Hz), 136.0 (CH, $J_{P,C}$ = 2.6 Hz), 216.8 ($C_{quat.}$, $J_{P,C}$ = 5.9 Hz). − MS (FAB), *m/z*: 637 [M$^+$ − BF_4^-], 375 [M$^+$ − BF_4^- − PPh_3]. − IR

(KBr): ṽ = 3435 cm^{-1}, 3083, 3057, 1914, 1818, 1627, 1596, 1586, 1490, 1484, 1439, 1411, 1342, 1315, 1283, 1226, 1189, 1160, 1108, 1083, 1056, 998, 945, 923, 901, 825, 772, 754, 728, 717, 695, 626, 607, 574, 551, 533, 521, 497, 439. − UV/Vis (DMSO): λ_{max} (ε) = 275 nm (18490), 374 (1260), 470 (790). − $[C_{43}H_{34}FeP^{+}BF_4^{-}]$ (724.36): calcd. C 71.30, H 4.73; found C 71.37, H 4.47.

Methyl 3-Ferrocenyl-2,2-dimethyl-5,5-diphenylpenta-3,4-dienecarboxylate (9b): According to the GP with 0.20 mL (1.0 mmol) of 1-methoxy-2,2-dimethyl-1-trimethylsiloxyethene to give 108 mg (93%) of **9b**. Orange crystals, m.p. 132−133 °C. Crystals suitable for X-ray structure analysis were obtained by slow crystallization from a concentrated DMSO solution of **9b**. − ^{1}H NMR ($[D_6]$DMSO, 300 MHz): δ = 1.42 (s, 6 H), 3.63 (s, 3 H), 3.92 (s, 5 H), 4.22 (m, 4 H), 7.42−7.44 (m, 10 H). − ^{13}C NMR ($[D_6]$DMSO, 75 MHz): δ = 26.1 (CH_3), 45.5 ($C_{quat.}$), 52.4 (CH_3), 67.4 (CH), 68.2 (CH), 69.3 (CH), 80.5 ($C_{quat.}$), 112.4 ($C_{quat.}$), 112.5 ($C_{quat.}$), 127.7 (CH), 128.0 (CH), 128.9 (CH), 136.2 ($C_{quat.}$), 176.3 ($C_{quat.}$), 204.7 ($C_{quat.}$). − MS (70 eV, EI); *m/z* (%): 476 $[M^+]$ (100). − IR (KBr): ṽ = 3430 cm^{-1}, 3116, 3100, 3087, 3061, 2992, 2947, 1723, 1636, 1599, 1491, 1464, 1442, 1432, 1412, 1379, 1359, 1256, 1191, 1145, 1106, 1074, 1052, 1031, 1013, 1002, 973, 916, 867, 847, 823, 772, 762, 732, 695, 636, 624, 609, 601, 586, 505, 478. − UV/Vis (DMSO): λ_{max} (ε) = 283 nm (15100), 458 (2800). − $C_{30}H_{28}FeO_2$ (476.39): calcd. C 75.63, H 5.92; found C 75.84, H 6.07.

2-(1-Ferrocenyl-3,3-diphenylpropa-1,2-dienyl)cyclohexan-1-one (9c): According to the GP with 0.19 mL (1.0 mmol) of 1-trimethylsiloxycyclohexene to give 110 mg (93%) of **9c**. Orange crystals, m.p. 107−109 °C. − ^{1}H NMR ($[D_6]$DMSO, 300 MHz): δ = 1.64−2.33 (m, 9 H), 4.08 (m, 5 H), 4.20−4.34 (m, 4 H), 7.26−7.46 (m, 10 H). − ^{13}C NMR ($[D_6]$DMSO, 75 MHz): δ = 24.2 (CH_2), 27.6 (CH_2), 33.3 (CH_2), 41.6 (CH_2), 52.4 (CH), 66.1 (CH), 66.9 (CH), 68.6 (CH), 68.6 (CH), 69.1 (CH), 82.5 ($C_{quat.}$), 106.8 ($C_{quat.}$), 112.8 ($C_{quat.}$), 127.5 (CH), 127.6 (CH), 128.0 (CH), 128.0 (CH), 128.7 (CH), 128.8 (CH), 136.1 ($C_{quat.}$), 136.6 ($C_{quat.}$), 205.0 ($C_{quat.}$), 209.5 ($C_{quat.}$). − MS (70 eV, EI); *m/z* (%): 472 $[M^+]$ (100). − IR (KBr): ṽ = 3435 cm^{-1}, 3080, 3054, 3022, 2934, 2860, 1706, 1630, 1597, 1491, 1447, 1411, 1380, 1349, 1336, 1310, 1296, 1246, 1197, 1156, 1126, 1105, 1072, 1060, 1028, 1001, 962, 920, 900, 874, 818, 769, 740, 696, 625, 608, 551, 505, 478, 452. − UV/Vis (DMSO): λ_{max} (ε) = 281 nm (18320), 446 (4530). − $C_{31}H_{28}FeO$ (472.40): calcd. C 78.81, H 5.97; found C 78.80, H 5.85.

1-Ferrocenyl-3,3-diphenylprop-2-en-1-one (10): According to the GP with 100 mg (2.1) of ethanol to give 70 mg (70%) of **10**. Red crystals, m.p. 75−78 °C. − ^{1}H NMR ($[D_6]$DMSO, 300 MHz): δ = 4.24 (s, 5 H), 4.56 (m, 2 H), 4.81 (m, 2 H), 7.08 (s, 1 H), 7.12−7.46 (m, 10 H). − ^{13}C NMR ($[D_6]$DMSO, 75 MHz): δ = 69.6 (CH), 69.8 (CH), 72.5 (CH), 81.1 ($C_{quat.}$), 124.1 (CH), 127.7 (CH), 127.9 (CH), 128.3 (CH), 128.7 (CH), 129.2 (CH), 129.4 (CH), 139.5 ($C_{quat.}$), 141.3 ($C_{quat.}$), 151.0 ($C_{quat.}$), 193.4 ($C_{quat.}$). − MS (70 eV, EI), *m/z* (%): 392 $[M^+]$ (100). − IR (KBr): ṽ = 3435 cm^{-1}, 3082, 2927, 1647, 1570, 1490, 1443, 1411, 1376, 1278, 1232, 1156, 1106, 1076, 1029, 1000, 892, 823, 788, 769, 725, 698, 582, 527, 500, 485. − UV/Vis (DMSO): λ_{max} (ε) = 300 nm (12940), 377 (2400), 490 (14450). − $C_{25}H_{20}FeO$ (392.28): calcd. C 76.54, H 5.13; found C 76.67, H 5.21.

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[17] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-142337 (**9b**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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