The Regiochemistry of the Addition of PhSeCl to Arylferrocenylethynes: A Cooperative Effect?

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PhSeCl adds to arylferrocenylethynes giving two regioisomers, ArC(Cl)=C(SePh)Fc and ArC(SePh)=C(Cl)Fc in different amounts, due to a favourable Se–Fe interaction. ^{77}Se NMR spectroscopy was useful for identifying the addition products. Kinetic experiments were also performed and a correlation was found using Hammett σ values.

Introduction

Organoselenium chemistry has recently become more widely used in strategies for organic synthesis, because of the availability of both electrophilic and nucleophilic selenium species.[1] New compounds have been prepared and used in organometallic[2] and organic[3] transformations, as well in stereoselective and asymmetric synthesis.[4] A number of selenium-containing ferrocene derivatives have been prepared[5] and their properties investigated.

Investigations have been carried out into the mechanism of electrophilic addition of PhSeCl to alkenes,[6] and there is still interest in this area.[7] However, much less work has been done on the addition of PhSeCl (or other selenyl reagents) to alkynes.[8]

With this in mind, we wanted to prepare compounds containing two active sites (Fe and Se), in order to see if there was any evidence of the so-called "co-operative effect". A strong electronic "communication" between linked active sites may enhance phenomena such as conductivity, hyperpolarizability, and susceptivity.[9]

Results and Discussion

Arylferrocenylethynes were treated with an excess of PhSeCl in dichloromethane at room temperature. In general, two addition products were obtained, with overall yields in the range 40−83 % (Scheme 1).

The reactions could be followed by TLC only, because the conditions required for GC analysis caused the product mixture to revert, at least partially, to the starting materials, thus indicating that we were dealing with a reversible reaction. The two regioisomers could not be separated by column chromatography, and coeluted even in hexane. Mass spectra gave M^+ values in agreement with the molecular formula expected for the addition products. Unfortunately, these compounds do not burn well, making elemental analyses unreliable. ^{1}H and ^{13}C NMR spectra were of no use in identifying the compounds, the former because of the lack of protons on the double bond, the latter because the signals due to the different aromatic rings were superimposed. However, ^{77}Se NMR spectroscopy proved to be very useful and allowed to us to identify the two products in the reaction mixture — ^{77}Se NMR is known to be very sensitive to the molecular environment.[10] The peaks were sharp and distinct, as can be seen in the example in Figure 1.

The areas under the signals indicated the relative amounts of the two regioisomers, the values for which were confirmed by HPLC analysis. The agreement between the two techniques was very good, the only exceptions being the products from the reactions of ferrocenyl(4-methoxyphenyl)ethyne and ferrocenyl(4-methylphenyl)ethyne. In these cases, a single product was detected by NMR, whereas HPLC suggested the presence of both adducts. The NMR spectra of the corresponding starting alkynes were also very broad, probably due to paramagnetic impurities, which could not be removed.

The chemical shifts in the ^{77}Se NMR spectra and relative amounts of the two isomers **A** and **B** are reported in Table 1. The assignment of the chemical shift of the regioisomers **B** was made on the basis of the ^{77}Se NMR spectrum of PhC(Cl)=C(SePh)Ph (obtained from diphenylethyne), which does not contain the ferrocenyl moiety and shows a resonance at $\delta = 499.3$ ppm, i.e. very close to the downfield resonance of the adducts. The chemical shifts in the ^{77}Se NMR spectrum are only slightly affected by the substituents on the aryl group, probably due to the levelling effect of the ferrocenyl moiety. Nevertheless, a significant

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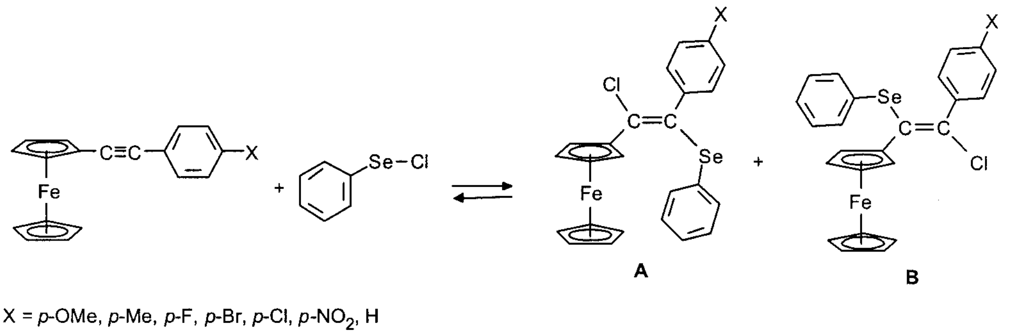


Scheme 1. Phenylselenylation of arylferrocenylethynes in dichloromethane

downfield shift can be observed with the strongly electron-withdrawing nitro group.

Although ^{77}Se NMR spectroscopy has become increasingly used of late, to the best of our knowledge this is the first systematic use of the technique in product identification.

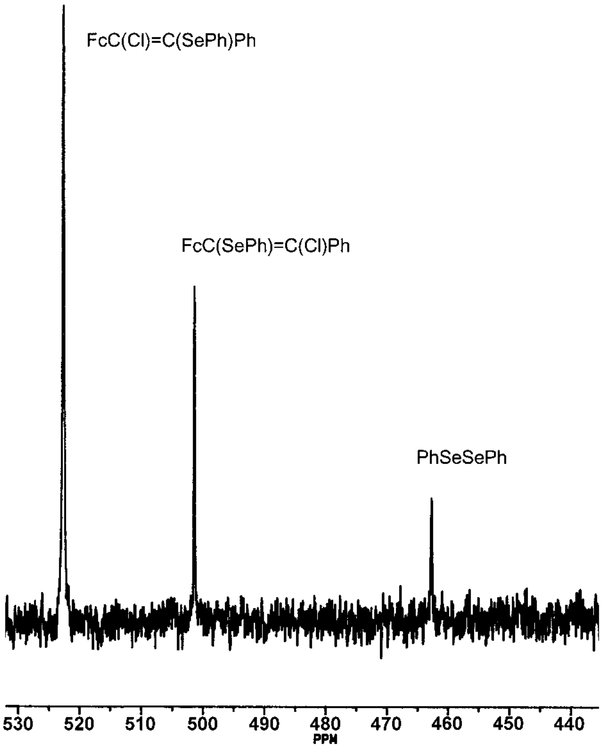


Figure 1. ^{77}Se NMR spectrum of products from the phenylselenylation of ferrocenylphenylethyne

It is known that phenylselenylation occurs via an intermediate bridged cation, as does phenylsulfenylation.[7] The reaction between PhSCl and PhC≡CFc gave comparable amounts of the two regioisomeric adducts.[11] Instead, different amounts of the regioisomers were obtained from PhSeCl addition, and PhSeSePh was always present as a byproduct. The question then arose as to why phenylsulfenylation and phenylselenylation, two apparently very similar reactions, should exhibit such a different product distribution. The possibility of the formation of a carbocation or an unsymmetrically bridged selenium cation is ruled out by the product distribution, although it should noted that acetoxymercuration of arylferrocenylethynes has been shown to occur via an unsymmetrical mercurinium ion, to yield a single regioisomer.[12]

In reversible reactions, the product composition is determined either by kinetics (transition states of different energy) or thermodynamics (products of different energy). The transition state of the product-determining step formed should resemble the intermediate, i.e. the selenirenium cation. To investigate this, we performed semiempirical calculations on the intermediate and on the addition products. The two carbon atoms in the three-membered ring of the

Table 1. ^{77}Se NMR chemical shifts and relative ratios of regioisomers from phenylselenylation of arylferrocenylethynes

X	FcC(Cl)=C(SePh)Ar (**A**) δ (ppm)	FcC(SePh)=C(Cl)Ar (**B**) δ (ppm)	Ratio **A**/**B**
H	522.6	501.4	66:34
4-OMe	524.2	–	100:0[a]
4-Me	520.2	–	100:0[a]
4-F	523.8	503.9	91:9
4-Cl	524.4	502.9	72:28
4-Br	525.1	503.1	63:37
4-NO_2	532.1	508.5	66:34

[a] 80:20, according to HPLC.

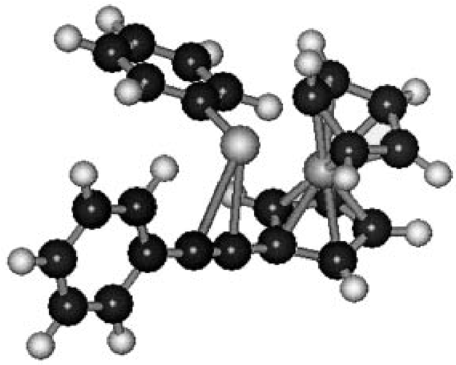


Figure 2. Calculated structure of the cationic selenirenium intermediate (X = H)

intermediate appeared to have practically the same charge density and a very similar degree of steric hindrance (Figure 2).

For the two regioisomeric products, a 7.9 kJ/mol difference in the enthalpy of formation was obtained (Figure 3). The more stable compound was identifiable with **A** (Figure 3), where the Se and Fe atoms are quite close in the minimum energy conformation.

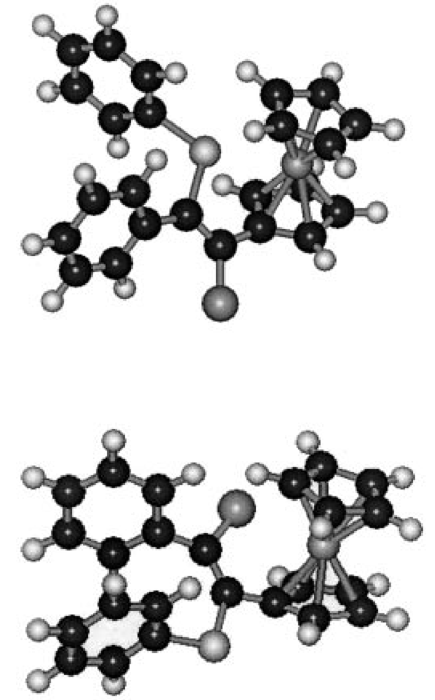


Figure 3. Minimum energy structures of the addition products **A** (top) and **B** (bottom) (X = H)

It seems reasonable that, in the ^{77}Se NMR spectra, the more stable adduct **A** should have a signal downfield of the signal from the **B** isomer, since, according to calculations, the Se nucleus lies in the cone of the magnetic field generated by the ring current of ferrocene π electrons. We think that the favourable interaction between Se and Fe is already present in the cationic intermediate, thus forcing the nucleophilic chloride anion towards the position nearest the ferrocenyl moiety, where the perturbation of this interaction will be smallest. In support of this hypothesis, when Fe is not present [as in PhC(SePh)=C(Cl)Ph], the ^{77}Se chemical shift (δ = 499 ppm) is very similar to the values observed for the addition products **B** (δ = 501−508 ppm).

Kinetic experiments were performed under pseudo-first order conditions, using spectrophotometry to follow the reaction up to 90−95 % conversion. The reaction followed a second-order rate law, and was first-order in both substrate and alkyne. The results are summarised in Table 2.

Table 2. Second-order rate constants for the phenylselenylation of arylferrocenylethynes at 25 °C

Alkyne	k_2 ($\mathrm{M}^{-1}\mathrm{s}^{-1}$)	Wavelength (nm)
PhC≡CFc	0.77 ± 0.04	350, 374
(4-MeO-C_6H_4)C≡CFc	2.21 ± 0.02	344, 366
(3-MeO-C_6H_4)C≡CFc	0.58 ± 0.05	330, 362
(4-Me-C_6H_4)C≡CFc	1.4 ± 0.2	360, 390
(4-F-C_6H_4)C≡CFc	0.48 ± 0.06	360, 390
(4-Cl-C_6H_4)C≡CFc	0.46 ± 0.02	350, 390
(3-Cl-C_6H_4)C≡CFc	0.31 ± 0.02	362, 400
(4-Br-C_6H_4)C≡CFc	0.5 ± 0.1	362
(4-NO_2−C_6H_4)C≡CFc	(7.8 ± 0.4) × 10^{-2}	450
PhC≡CPh	(7.2 ± 0.2) × 10^{-3}	324

Phenylselenylation is favoured by electron-donating substituents, as expected if electrophilic attack is the rate-determining step. In order to evaluate substituent effects quantitatively, free energy relationships were considered. The best correlation was obtained with Hammett σ values[13] (Figure 4), in agreement with the intermediacy of the selenirenium cation. Moreover, the reaction shows a low sensitivity to substituent effects (ρ = −1.3). As a comparison, acetoxymercuration of the same substrates, which occurs via an unsymmetrically bridged mercurinium ion, shows a good correlation with σ^+ values and a higher sensitivity (ρ = −2.5).[12]

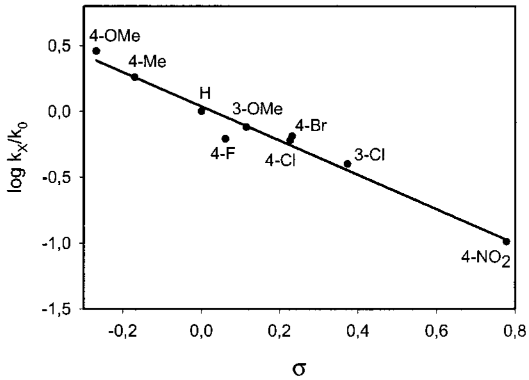
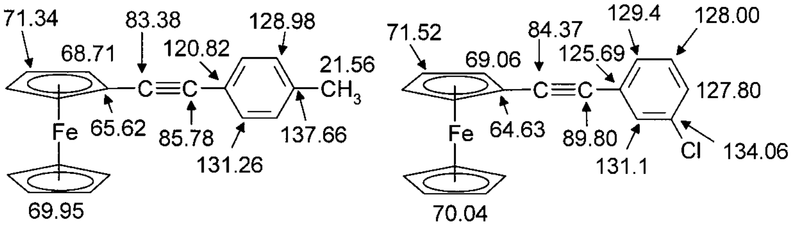


Figure 4. Linear free energy relationship for the phenylselenation of ferrocenylarylethynes

In order to compare the importance of the ferrocenyl group with respect the phenyl group, the phenylselenylation



Scheme 2. ^{13}C NMR spectra in $CDCl_3$ for the two new arylferrocenylethynes

of diphenylethyne was investigated kinetically; ferrocenylphenylethyne was found to react two orders of magnitude faster than diphenylethyne. In the case of acetoxymercuration,[12,14] the corresponding ratio is even higher, in agreement with the partially carbocationic character of of the intermediate in the latter reaction:
with PhSeCl: $k_{FcC\equiv CPh}/k_{PhC\equiv CPh} = 100$
with $Hg(OAc)_2$: $k_{FcC\equiv CPh}/k_{PhC\equiv CPh} = 2500$

A comparision of the reactions of ferrocenylphenylethyne with PhSeCl and PhSCl[11] gives:
with FeC≡CPh: $k_{PhSeCl}/k_{PhSCl} = 4$,
which is in agreement with the more strongly electrophilic nature of PhSeCl.

Conclusions

The first example of organoselenium ferrocenyl alkenes, obtained by electrophilic addition of phenylselenyl chloride to arylferrocenylalkynes, has been described. Regioselective electrophilic addition yielded preferentially the adduct **A** (as shown in Scheme 1), probably because of a favourable iron-selenium interaction, as suggested by a semiempirical calculation. Standard spectroscopic methods (^{1}H and ^{13} NMR spectroscopy) proved ineffective in providing information on the phenylselenylation adducts, but the regiochemistry could be determined by ^{77}Se NMR spectroscopy, and confirmed by HPLC. Kinetic experiments allowed us to assess the electronic effects of substituents in the aryl ring and were in agreement with the formation of a selenirenium cation in the rate-determining step. Further work will be aimed at exploring the reaction in terms of its mechanism, verifying whether radical pathways occur and how PhSeSePh is formed.

Experimental Section

General Methods: All the reactions were performed under argon with anhydrous solvents. GC analyses were carried out with a Carlo Erba HGRC 5300 Mega Series Instrument, equipped with a 2 m 3 % OV-17 or a 30 m × 0.25 mm capillary column. Bruker WP80 (^{1}H and ^{13}C) and AM400 (^{77}Se) spectrometers were used to obtain the NMR spectra. The solvent used was $CDCl_3$, with tetramethylsilane as the internal standard. ^{77}Se NMR spectra were recorded at 76.286 MHz at 298 K, with an acquisition number in the range 500−1028. A 1 M solution of PhSeSePh was used as the external reference ($\delta = 463$ ppm) and chemical shifts were referred to dimethyldiselenide, MeSeSeMe ($\delta = 0$ ppm). Direct inlet spectra (E.I., 70 eV) were obtained with a VG QUATTRO instrument. HPLC analyses were performed with a Shimadzu LC-10 AD instrument, equipped with an analytical Supelco LcC18 column and an UV/Vis diode array SPD-M10A detector, with MeCN with 10% water as the solvent. IR spectra were recorded with a Perkin−Elmer 983 spectrophotometer, using a NaCl cell and CCl_4 as the solvent. Kinetic experiments were carried out on a thermostatted Hewlett−Packard 8452 diode array spectrophotometer, using silica cells with sealed with septa. Semiempirical calculations were carried out with the PM3 method,[13] using the Hyperchem program.[14] The values of atomic charges were calculated using the Mulliken population analysis (MPA), by means of a RHF/Lan L2Dz basis set[15] single point calculation, starting from a PM3 geometry. The intrinsic limitations in such calculations have been discussed previously.[16] Iodoferrocene (FcI) was prepared by iododemercuration of acetoxymercurioferrocene, which in turn was obtained from ferrocene and mercuric acetate.[17] Phenylselenyl chloride (PhSeCl) was obtained from a commercial source (Aldrich).

General Procedure for the Synthesis of Alkynes: A modification of the literature method[18] was used to synthesize substituted arylferrocenylethynes. Data for known ferrocenylethynes has been reported previously.[12] ArC≡CCu and FcI were heated at reflux in DMF with a catalytic amount of triphenylphosphane for 2 d, and the product purified by column chromatography [silica gel, eluent: petroleum ether (b.p. 40−70°)]. The requisite ArC≡CCu was prepared (in yields of 65−86 %) by treating ArC≡CH with CuI in aqueous NH_4OH solution.[19] Arylethynes (ArC≡CH) were obtained from commercially available acetophenones by halogenation with PCl_5 and subsequent dehydrohalogenation with KOH in refluxing ethanol, with yields in the range 21−35 %.[20]

Ferrocenyl(4-methylphenyl)ethyne was obtained as a solid (m.p. 66−68 °C) in 21 % yield from FcI (11 mmol) and (4-MeC_6H_4)C≡CCu (11 mmol), which in turn was obtained from (4-MeC_6H_4)C≡CH in 65 % yield. MS (E.I., 70 eV): m/z = cluster of signals near 300 (M^+, MW 299.85, Fe isotopes), cluster of signals near 186 (Fc^+, Fe isotopes), cluster of signals near 121 ($CpFe^+$, Fe isotopes), 179 ($M^+ - CpFe$) and 163 ($M^+ - CpFe - Me$). IR (CCl_4): $\tilde{\nu}$ (cm^{-1}) = 2210 (C≡C), 1004, 1107 (Cp).[21] ^{1}H NMR ($CDCl_3$): $\delta = 1.6$ (s, 3 H, Me), 4.3−4.5 (complex, 9 H, superposition of signals from both Cp rings), 7.18 (d, 2 H, 8.0 Hz, Ar-H), 7.41 (d, 2 H, $J = 8.0$ Hz, Ar-H) ppm. The data from the ^{13}C NMR spectrum is given in Scheme 2.

Ferrocenyl(3-methoxylphenyl)ethyne was obtained as an oil in 26 % yield from FcI (3.5 mmol) and (3-$MeOC_6H_4$)C≡CCu (3.5 mmol), which in turn was obtained from (3-$MeOC_6H_4$)C≡CH in 67 % yield. MS (E.I., 70 eV): m/z = cluster of signals near 316 (M^+, MW 316.04, Fe isotopes), cluster of signals near 121 ($CpFe^+$, Fe isotopes), 182 ($M^+ - CpFe - Me$). IR (CCl_4): $\tilde{\nu}$ (cm^{-1}) = 2215 ($C{\equiv}C$), 1004, 1107 (Cp).[21] The ^1H and ^{13}C NMR spectra in $CDCl_3$ were very broad and not resolvable, probably due to traces of paramagnetic Fe^{III} that could not be eliminated.

Ferrocenyl(3-chlorophenyl)ethyne was obtained as a solid (m.p. 95−97 °C) in 23 % yield from FcI (7.1 mmol) and ($3-ClC_6H_4)C{\equiv}CCu$ (7.0 mmol), which in turn was obtained from ($3-ClC_6H_4)C{\equiv}CH$ in 86 % yield. MS (E.I., 70 eV): *m*/*z*: cluster of signals near 320 and 322 (M^+, MW 320.49, Cl and Fe isotopes), 121 ($CpFe^+$, Fe isotopes), 163 ($M^+ - CpFe - Cl$). IR (CCl_4): $\tilde{\nu}$ (cm^{-1}) = 2210 ($C{\equiv}C$), 1003, 1108 (Cp).[21] ^1H NMR ($CDCl_3$): δ = 4.3−4.5 (m, 9 H, superposition of signals from both Cp rings), 7.25 (m, 2 H, Ar-H), 7.60 (m, 2 H, Ar-H) ppm. The data from the ^{13}C NMR spectrum ($CDCl_3$) is given in Scheme 2.

Product Analysis: Typically, $FcC{\equiv}CAr$ (0.2 mmol) was treated with PhSeCl (0.6 mmol) in CH_2Cl_2 (15 mL). The reaction was followed by TLC. GC analysis could not be used, because the addition products revert to alkynes. The reaction mixture was purified by column chromatography (silica gel, eluent: hexane and hexane/diethyl ether mixtures as eluents). The regioisomeric addition products were eluted together and were characterised by MS and ^{77}Se NMR spectroscopy. The relative ratios of the regioisomers were confirmed by HPLC.

Reaction of Ferrocenylphenylethyne: The addition products (61 mg, 62 %) were isolated as an oil. MS (E.I., 70 eV): *m*/*z* = clusters of signals near 478 (M^+, MW 477.67, Cl, Se and Fe isotopes), 322 ($M^+ - PhSe$, Cl and Fe isotopes), 256 ($M^+ - PhSe - Cp$, Cl and Fe isotopes), and 155 ($PhSe^+$, Se isotopes), 165 ($M^+ - PhSeCl - CpFe$), 77 (Ph^+). ^{13}C NMR ($CDCl_3$): δ = 136−127 ppm (several signals, Ph and C=C), 69−78 ppm (several signals, Fc).

Reaction of Ferrocenyl(4-methoxyphenyl)ethyne: The addition products (63 mg, 58 %) were isolated as an oil. MS (E.I., 70 eV): *m*/*z* = clusters of signals near 508 (M^+, MW 507.64, Cl, Se and Fe isotopes), 386 ($M^+ - CpFe$, Cl and Se isotopes), and 155 ($PhSe^+$, Se isotopes), 195 ($M^+ - PhSeCl - CpFe$), 77 (Ph^+).

Reaction of Ferrocenyl(3-methoxyphenyl)ethyne: The addition products (64.5 mg, 62 %) were isolated as an oil. MS (E.I., 70 eV): *m*/*z* = clusters of signals near 509 (M^+, MW 507.64, Cl, Se and Fe isotopes), 496 ($M^+ - Me$, Cl, Se and Fe isotopes), 478 ($M^+ - Cl$, Se and Fe isotopes), 314 ($M^+ - Ph - CpFe$, Cl and Se isotopes), and 155 ($PhSe^+$, Se isotopes), 195 ($M^+ - PhSeCl - CpFe$), 77 (Ph^+).

Reaction of Ferrocenyl(4-methylphenyl)ethyne: The addition products (72 mg, 67 %) were isolated as an oil. MS (E.I., 70 eV): *m*/*z* = clusters of signals near 491 (M^+, MW 491.69, Cl, Se and Fe isotopes), 479 ($M^+ - Me$, Cl, Se and Fe isotopes), 336 ($M^+ - PhSe$, Cl and Fe isotopes), 179 ($M^+ - PhSe - Cp - Ar$, Cl and Fe isotopes), and 120 ($CpFe^+$, Fe isotopes), 77 (Ph^+).

Reaction of Ferrocenyl(4-fluorophenyl)ethyne: The addition products (54 mg, 54 %) were isolated as an oil. MS (E.I., 70 eV): *m*/*z* = clusters of signals near 496 (M^+, MW 495.65, Cl, Se and Fe isotopes), 340 ($M^+ - PhSe$, Cl and Fe isotopes), 314 ($M^+ - Fc$, Cl and Se isotopes), and 155 ($PhSe^+$, Se isotopes), 77 (Ph^+).

Reaction of (4-Chlorophenyl)ferrocenylethyne: The addition products (83 mg, 83 %) were isolated as an oil. MS (E.I., 70 eV): *m*/*z* = clusters of signals near 514 (M^+, MW 512.11, Cl, Se and Fe isotopes), 358 ($M^+ - PhSe$, Cl and Fe isotopes), 320 ($M^+ - PhSeCl$, Fe isotopes), and 234 ($M^+ - PhSe - CpFe$, Cl isotopes), 199 and 201 ($M^+ - PhSeCl - CpFe$, Cl isotopes), cluster of signals near 155 ($PhSe^+$, Se isotopes), 77 (Ph^+).

Reaction of (3-Chlorophenyl)ferrocenylethyne: The addition products (41 mg, 40 %) were isolated as an oil. MS (E.I., 70 eV): *m*/*z* = clusters of signals near 514 (M^+, MW 512.11, Cl, Se and Fe isotopes), 358 ($M^+ - PhSe$, Cl and Fe isotopes), 320 ($M^+ - PhSeCl$, Fe isotopes), and 234 ($M^+ - PhSe - CpFe$, Cl isotopes), 199 and 201 ($M^+ - PhSeCl - CpFe$, Cl isotopes), cluster of signals near 155 ($PhSe^+$, Se isotopes), 77 (Ph^+).

Reaction of (4-Bromophenyl)ferrocenylethyne: The addition products (54 mg, 50 %) were isolated as an oil. MS (E.I., 70 eV): *m*/*z* = clusters of signals near 556 (M^+, MW 556.56, Br, Cl, Se and Fe isotopes), 402 ($M^+ - PhSe$, Br, Cl and Fe isotopes), 364 ($M^+ - PhSeCl$, Br, Cl and Fe isotopes), and 155 ($PhSe^+$, Se isotopes), 77 (Ph^+).

Reaction of Ferrocenyl(4-nitrophenyl)ethyne: The addition products (32 mg, 31 %) were isolated as an oil. MS (E.I., 70 eV): *m*/*z* = clusters of signals near 523 (M^+, MW 522.66, Cl, Se and Fe isotopes), 367 ($M^+ - PhSe$, Cl and Fe isotopes), and 155 ($PhSe^+$, Se isotopes), 165 ($M^+ - PhSeCl - CpFe - NO_2$), 77 ($Ph^+$).

Kinetic Experiments: Preliminary experiments indicated that the most suitable region for spectrophotometric kinetics was the range 280−400 nm, where a significant absorbance increase occurred. Solutions of known amounts of the alkyne and PhSeCl in CH_2Cl_2 (1 mL) were put in the two compartments, allowed to reach the thermostat temperature, and then quickly mixed. Kinetic experiments were carried out under pseudo first-order conditions (excess PhSeCl). Pseudo-first-order rate constants were calculated using SigmaPlot.[22] The overall second-order rate constants, as mean values of several runs, are reported in Table 2. The concentrations used were 2.58×10^{-5} M -2.79×10^{-4} M for the alkynes and 2.34×10^{-3} M -0.219 M for PhSeCl. In the case of ferrocenyl(4-nitrophenyl)ethyne, kinetic studies were also performed with an excess of alkyne (concentration 1.03×10^{-2} M) over PhSeCl (concentration 1.46×10^{-5} M). The same second-order rate constant was obtained, within experimental error.

Acknowledgments

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[1] [1a] T. Wirth (Ed.), *Organoselenium Chemistry. Modern Developments in Organic Synthesis*, Springer-Verlag, Berlin, **2000**. [1b] T. G. Back (Ed.), *Organoselenium Chemistry. A Practical Approach*, Oxford University Press, Oxford, **1999**. [1c] C. Paulmier, *Selenium Reagents and Intermediates in Organic Synthesis*, Pergamon, Oxford, **1986**.

[2] [2a] A. V. Martynov, V. A. Potapov, S. V. Amosova, N. A. Makhaeva, I. P. Beletskaya, L. Hevesi, *J. Organomet. Chem.* **2003**, *674*, 101. [2b] S. Evans, J. W. Faller, J. Parr, *J. Organomet. Chem.* **2003**, *674*, 56. [2c] R. K. Gujadur, D. Venkataraman, *Tetrahedron Lett.* **2003**, *44*, 81. [2d] T. Murai, Y. Mutoh, S. Kato, *Org. Lett.* **2001**, *3*, 1993. [2e] G. Zahn, G. Großmann, D. Scheller, *Z. Anorg. Allg. Chem.* **2000**, *626*, 524. [2f] T. Murai, Y. Mutoh, S. Kato, *J. Am. Chem. Soc.* **2000**, *122*, 9850. [2g] T. Maaninen, T. Chivers, R. Laitinen, G. Schatte, M. Nissinen, *Inorg. Chem.* **2000**, *39*, 5341. [2h] M. Iwaoka, H. Komatsu, S. Tomoda, *J. Organomet. Chem.* **2000**, *611*, 164. [2i] H. Taka, T. Shimizu, M. Yasui, N. Kamigata, *J. Org. Chem.* **1999**, *64*, 7433. [2j] T. Murai, H. Endo, M. Ozaki, S. Kato, *J. Org. Chem.* **1999**, *64*, 2130. [2k] A. Krief, C. Delmotte, W. Dumont, *Tetrahedron Lett.* **1997**, *38*,

3079. [2l] A. Toshimitsu, K. Nakano, T. Mukai, K. Tamao, *J. Am. Chem. Soc.* **1996**, *118*, 2756.

[3] [3a] K. Fujita, S. Hashimoto, A. Oishi, Y. Taguchi, *Tetrahedron Lett.* **2003**, *44*, 3793. [3b] M. Tiecco, L. Testaferri, A. Temperini, L. Bagnoli, F. Marini, C. Santi, *Synlett* **2003**, 655. [3c] M. Hibino, T. Koike, M. Yoshimatsu, *J. Org. Chem.* **2002**, *67*, 1078. [3d] M. Osajda, J. Młochowski, *Tetrahedron* **2002**, *58*, 7531. [3e] H. S. Kim, Y. J. Kim, H. Lee, K. Y. Park, C. Lee, C. S. Chin, *Angew. Chem. Int. Ed.* **2002**, *114*, 4476. [3f] G.-J. ten Brink, J.-M. Vis, I. W. C. E. Arends, R. A. Sheldon, *J. Org. Chem.* **2001**, *66*, 2429.

[4] [4a] M. Tiecco, L. Testaferri, C. Santi, C. Tomassini, F. Marini, L. Bagnoli, A. Temperini, *Angew. Chem. Int. Ed.* **2003**, *42*, 313. [4b] M. Tiecco, L. Testaferri, F. Marini, S. Sternativo, C. Santi, L. Bagnoli, A. Temperini, *Tetrahedron: Asymmetry* **2003**, *14*, 2651. [4c] M. Tiecco, L. Testaferri, C. Santi, C. Tomassini, F. Marini, L. Bagnoli, A. Temperini, *Chem. Eur. J.* **2002**, *8*, 1118. [4d] M. Tiecco, L. Testaferri, C. Santi, C. Tomassini, F. Marini, L. Bagnoli, A. Temperini, *Tetrahedron: Asymmetry* **2002**, *13*, 429. [4e] L. Uehlin, G. Fragale, T. Wirth, *Chem. Eur. J.* **2002**, *8*, 1125. [4f] M. Tiecco, L. Testaferri, F. Marini, S. Sternativo, C. Santi, L. Bagnoli, A. Temperini, *Tetrahedron: Asymmetry* **2001**, *12*, 3053. [4g] M. Tiecco, L. Testaferri, F. Marini, S. Sternativo, L. Bagnoli, C. Santi, A. Temperini, *Tetrahedron: Asymmetry* **2001**, *12*, 1493. [4h] A. G. Martínez, E. T. Vilar, A. G. Fraile, S. Cerero, B. L. Maroto, *Tetrahedron Lett.* **2001**, *42*, 5017. [4i] X. Huang, A. Sun, *J. Org. Chem.* **2000**, *65*, 6561. [4j] M. Tiecco, L. Testaferri, C. Santi, C. Tomassini, F. Marini, L. Bagnoli, A. Temperini, *Eur. J. Org. Chem.* **2000**, 3451. [4k] T. Wirth, *Tetrahedron* **1999**, *55*, 1. [4l] T. G. Back, R. J. Bethell, M. Parvez, J. A. Taylor, D. Wehrli, *J. Org. Chem.* **1999**, *64*, 7426. [4m] L. Engman, M. J. Laws, J. Malmström, C. H. Schiesser, L. M. Zugaro, *J. Org. Chem.* **1999**, *64*, 6764. [4n] T. Wirth, *Angew. Chem. Int. Ed.* **2000**, *39*, 3740.

[5] [5a] M. Heberhold, H.-D. Brendel, A. Hofman, B. Hofman, W. Milius, *J. Organomet. Chem.* **1998**, *556*, 173. [5b] M. Heberhold, U. Steffl, W. Milius, B. Wrackmeyer, *J. Organomet. Chem.* **1997**, *553*, 109. [5c] S.-I. Fukuzawa, K. Takahashi, H. Kato, H. Yamazaki, *J. Org. Chem.* **1997**, *62*, 7711.

[6] [6a] G. H. Schmid, in: *The Chemistry of Double-bonded Functional Groups*, S. Patai (Ed.), John Wiley & Sons, **1989**, Ch. 11. [6b] P. Kočovský, in: *Organic Reaction Mechanisms 1994*, A. C. Knipe, W. B. Watts (Eds.), John Wiley & Sons, **1996**, Ch. 13.

[7] [7a] J. M. White, J. B. Lambert, M. Spiniello, S. A. Jones, R. W. Gable, *Chem. Eur. J.* **2002**, *8*, 2799. [7b] K. Noda, Y. Sugihara, J. Nakayama, *Heteroatom Chem.* **2001**, *12*, 625. [7c] M. Spitchy, G. Fragale, T. Wirth, *J. Am. Chem. Soc.* **2000**, *122*, 10914. [7d] T. Wirth, G. Fragale, M. Spitchy, *J. Am. Chem. Soc.* **1998**, *120*, 3376.

[8] [8a] W. Drenth, in: *The Chemistry of Triple-bonded Functional Groups. Supplement C2*, S. Patai (Ed.), John Wiley & Sons, **1994**, Ch. 15.[8b] G. H. Schmid, in: *The Chemistry of Triple-bonded Functional Groups*, S. Patai (Ed.), John Wiley & Sons, **1978**, Ch. 8. [8c]P. Bhattacharyya, A. M. Z. Slawin, J. D. Woollins, *Chem. Eur. J.* **2002**, *8*, 2705. [8d] A. Ogawa, R. Obayashi, H. Ine, Y. Tsuboi, N. Sonoda, T. Hirao, *J. Org. Chem.* **1999**, *63*, 881. [8e] T. Kanda, T. Koike, S. Kagohashi, K. Mizoguchi, T. Murai, S. Kato, *Organometallics* **1995**, *14*, 4975. [8f] A. Ogawa, H. Yokoyama, K. Yokoyama, T. Masawaki, N. Kambe, N. Sonoda, *J. Org. Chem.* **1991**, *56*, 5721.

[9] [9a] V. Balzani, S. Campagna, G. Denti, A. Juris, S. Serroni, M. Venturi, *Acc. Chem. Res.* **1998**, *31*, 26. [9b] D. Astruc, *Acc. Chem. Res.* **1997**, *30*, 383.

[10] [10a] N. P. Lutra, J. D. Odom in: *The Chemistry of Organic Selenium and Tellurium Compounds*, S. Patai, Z. Rappoport (Eds.), Vol. I, John Wiley & Sons, **1986**, Ch. 6, p. 189. [10b] H. Duddeck, *Progress in NMR Spectroscopy*, **1995**, *27*, 1. [10c] H. C. E. McFarlane, W. McFarlane, in: *Multinuclear NMR*, J. Mason (Ed.), Plenum Press, New York, **1987**, Ch.15. [10d]J. Oddershede, L. Henriksen, S. Larsen, *Org. Biomol. Chem.* **2003**, *1*, 1053. [10e] X. Pannecoucke, F. Outurquin, C. Paulmier, *Eur. J. Org. Chem.* **2002**, 995. [10f] H. Duddeck, R. Bradenhal, L. Stefaniak, J. Jazwinski, B. Kamienski, *Magn. Reson. Chem.* **2001**, *39*, 709. [10g] U. Herzog, *J. Prakt. Chem.* **2000**, *342*, 379. [10h] S. Hayashi, W. Nakanishi, *J. Org. Chem.* **1999**, *64*, 6688. [10i] M. Iwaoka, S. Tomoda, *J. Am. Chem. Soc.* **1996**, *118*, 8077. [10j] D. Crich, X.-Y. Jiao, Q. Yao, J. S. Harwood, *J. Org. Chem.* **1996**, *61*, 2368. [10k] M. J. Potrzebowski, M. Michalska, J. Błaszczyk, M. W. Wieczorek, W. Ciesieslki, S. Kaźmierski, J. Pluskowski, *J. Org. Chem.* **1995**, *60*, 3139. [10l] C. J. White, T. Wang, R. A. Jacobson, R. J. Angelici, *Organometallics* **1995**, *14*, 332. [10m] J. Campbell, D. P. DiCiommo, H. P. A. Mercier, A. M. Pirani, G. J. Schrobilgen, M. Willhun, *Inorg. Chem.* **1995**, *34*, 6265. [10n] P. J. Barrie, R. J. H. Clark, D. Y. Chung, D. Chakrabarty, M. G. Kanatzidis, *Inorg. Chem.* **1995**, *34*, 4299. [10o] M. Bühl, W. Thiel, U. Fleischer, W. Kutzelnigg, *J. Phys. Chem.* **1995**, *99*, 4000. [10p] C. J. White, T. Wang, R. A. Jacobson, R. J. Angelici, *Organometallics* **1994**, *13*, 4474. [10q] P. J. Barrie, R. J. H. Clark, D. Y. Chung, K.-W. Kim, M. G. Kanatzidis, *Inorg. Chem.* **1994**, *33*, 1212.

[11] B. Floris, *Gazz. Chim. Ital.* **1986**, *116*, 665.

[12] L. Carollo, B. Floris, *J. Organomet. Chem.* **1999**, *583*, 80.

[13] J. J. Stewart, *J. Comput. Chem.* **1989**, *10*, 1.

[14] Hyperchem, release 6.02 for Windows, Hypercube Inc., 2000.

[15] W. R. Wadt, P. J. Hay, *Tetrahedron Lett.* **1988**, *29*, 4631.

[16] M. L. Di Vona, B. Floris, S. Licoccia, *Magn. Reson. Chem.* **1998**, *36*, 707.

[17] K. Okuto, M. Furuune, M. Enna, M. Miura, M. Nomura, *J. Org. Chem.* **1994**, *58*, 4716.

[18] [18a] C. E. Castro, R. D. Stephens, *J. Org. Chem.* **1963**, *28*, 2163. [18b] R. D. Stephens, C. E. Castro, *J. Org. Chem.* **1963**, *28*, 3313.

[19] A. D. Allen, C. D. Cook, *Can. J. Chem.* **1963**, *41*, 1084.

[20] R. W. Fish, M. Rosenblum, *J. Org. Chem.* **1965**, *30*, 1253.

[21] M. Rosenblum, *Chemistry of the Iron Group Metallocenes*, John Wiley & Sons, New York, **1965**.

[22] Jandel Scientific, SigmaPlot, Version 5.0 for Windows, Jandel Scientific GmbH, Erkrathm Germany, **1999**.

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