Comparison of the Electrophilicities of the Free and the (Tricarbonyl)iron-Coordinated Tropylium Ion

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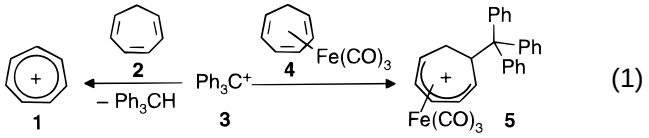
Abstract: The kinetics of the reactions of the tropylium ion (**1**) and the (tricarbonyl)iron-coordinated tropylium ion (**6**) with allylsilanes, allylstannanes, and other uncharged nucleophiles were studied photometrically and conductometrically. The second-order rate constants were independent of the counterions, indicating rate-determining carbon−carbon bond formation. The electrophilicity parameters of the (tricarbonyl)iron complexes of the tropylium ion $E(\mathbf{6}) = -3.81 \pm 0.24$ and of the dihydrotropylium ion $E(\mathbf{22}) = -9.88$ indicate that the former is 10^5-10^6 times more reactive toward nucleophiles. Comparison with the electrophilicity parameter of the free tropylium ion $E(\mathbf{1}) = -4.62 \pm 0.57$ shows that coordination by $Fe(CO)_3$ affects its electrophilic reactivity only slightly. Density-functional calculations are used to rationalize the relative reactivities in terms of thermodynamic effects and frontier orbital interactions. On the basis of the linear free enthalpy relationship $\log k = s(E + N)$ one can predict that the free and the $Fe(CO)_3$-coordinated tropylium ion react with nucleophiles ($N > -1$) at room temperature.

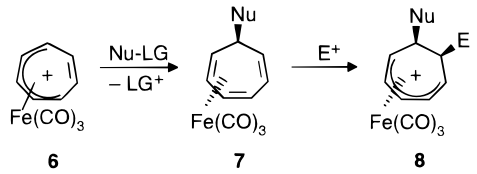
Introduction

The high stability and low electrophilic reactivity of the tropylium ion **1** has been rationalized by its planar delocalized aromatic 6π electron system.[1,2] It is readily produced by reactions of cycloheptatriene (**2**) with hydride abstractors, e.g. the tritylium ion (**3**)[3,4] (eq 1). In contrast, the (tricarbonyl)iron complex of cycloheptatriene (**4**) reacts with tritylium ions (**3**) with formation of a new CC bond[5,6] (eq 1).



(1)

Since analogous alkylations can be expected for substituted cycloheptatriene complexes, e.g. **7**, the reaction sequence **6** → **7** → **8** may provide a new and general access to vicinally substituted cycloheptatrienes (eq 2). It is the topic of this work to elucidate the scope and limitations of the first step of this sequence.



(2)

As we have previously shown, the rates of the reactions of cationic electrophiles with uncharged nucleophiles (alkenes, arenes, allylsilanes, etc.) are given by eq 3, where E is a reactivity parameter for the cationic electrophiles, while N and s are reactivity parameters of the nucleophiles.[7] Because the s

$$\log k_{20\,^\circ C} = s(N + E) \tag{3}$$

and N parameters are known for most classes of π-nucleophiles,[7] knowledge of the electrophilicity parameter E of cation **6** would allow one to select potential nucleophilic reaction partners for it. We, therefore, set out to measure the rates of the reactions of **6** with some reference nucleophiles (i.e., compounds with known N and s values), to determine the electrophilicity

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(1) Doering, W. v. E.; Knox, L. H. *J. Am. Chem. Soc.* **1954**, *76*, 3203−3206.

(2) For reviews, see: (a) Doering, W. v. E.; Krauch, H. *Angew. Chem.* **1956**, *68*, 661−667. (b) Kolomnikova, G. D.; Parnes, Z. N. *Russ. Chem. Rev. (Engl. Transl.)* **1967**, *36*, 735−753; *Usp. Khim.* **1967**, *36*, 1721−1759. (c) Harmon, K. M. In *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley: NY, 1973; Vol. IV, pp 1579−1641. (d) Pietra, F. *Chem. Rev.* **1973**, *73*, 293−364. (e) Bertelli, D. J. *Top. Nonbenzenoid Aromat. Chem.* **1973**, *1*, 29−46.

(3) Dauben, H. J., Jr.; Gadecki, F. A.; Harmon, K. M.; Pearson, D. L. *J. Am. Chem. Soc.* **1957**, *79*, 4557−4558.

(4) Dauben, H. J., Jr.; Honnen, L. R.; Harmon, K. M. *J. Org. Chem.* **1960**, *25*, 1442−1444.

(5) Dauben, H. J., Jr.; Bertelli, D. J. *J. Am. Chem. Soc.* **1961**, *83*, 497−498.

(6) For analogous CC bond-forming reactions, see: (a) McArdle, P.; Sherlock, H. *J. Organomet. Chem.* **1976**, *116*, C23−C24. (b) McArdle, P. *J. Chem. Soc., Chem. Commun.* **1973**, 482−483. (c) Johnson, B. F. G.; Lewis, J.; McArdle, P.; Randall, G. L. P. *J. Chem. Soc., Dalton Trans.* **1972**, 456−462.

(7) (a) Mayr, H.; Patz, M. *Angew. Chem.* **1994**, *106*, 990−1010; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 938−957. (b) Mayr, H.; Kuhn, O.; Gotta, M. F.; Patz, M. *J. Phys. Org. Chem.* **1998**, *11*, 642−654. (c) Mayr, H.; Patz, M.; Gotta, M. F.; Ofial, A. R. *Pure Appl. Chem.* **1998**, *70*, 1993−2000.

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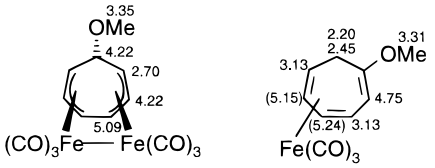
Chart 1. ^{1}H NMR Chemical Shifts of the Complexes **10** and **11** in $CDCl_3$

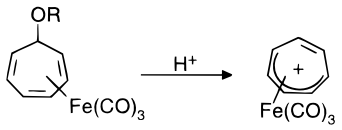


10 **11**

parameter E(**6**). For comparison, the electrophilicity parameter of the free tropylium ion (**1**) was also determined.

Results

Preparation and Characterization of $(C_7H_7)Fe(CO)_3^+$ (6). As mentioned above, the tricarbonyliron cycloheptatriene complex **4** does not undergo the typical hydride transfer reaction with Ph_3C^+. Dauben has shown that the reaction of **4** with Ph_3C^+ leads to tritylation (→**5**) and not to the formation of **6**.[5] Access to the tropylium complex **6** has been reported, however, to be possible by acid treatment of **9a**,[8] **9b**,[8] or the corresponding thioethers[9] (eq 4).



9a (R = Me)
9b (R = H) **6** (4)

Our attempts to obtain the complex **9a** by reaction of 7-methoxycycloheptatriene (**16**) with $Fe_2(CO)_9$ in refluxing diethyl ether as described in the literature[8,10] gave a complex mixture of products from which only 6% of the diiron complex **10**[11,12] could be isolated by chromatography (silica gel, toluene/hexane). Ultrasonification of a solution of 7-methoxycycloheptatriene (**16**) and $Fe_2(CO)_9$ in toluene[13] did not yield **9a**[14] but a mixture of compounds, from which 8% of **11** was isolated by chromatography on alumina (Chart 1). The absence of the methylene resonance in the ^{13}C NMR spectrum of the crude product indicates that **11** was formed during the chromatographic purification.

Preparation of the tropylium complexes **6-X** was finally achieved by ionization of the cycloheptatrienol complex **9b**,[8] which was synthesized via **13**[15−18] as described in Scheme 1 (for details see Supporting Information).

Scheme 1

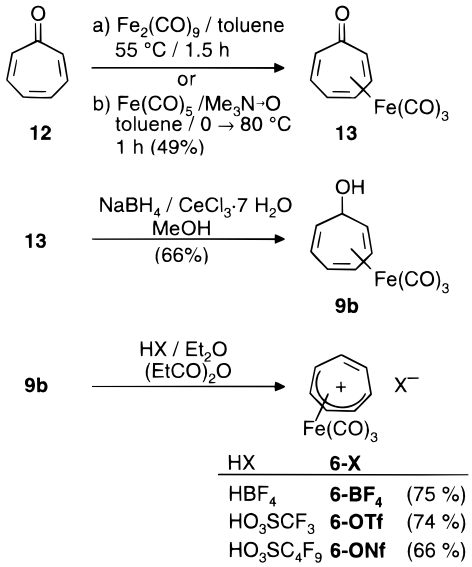
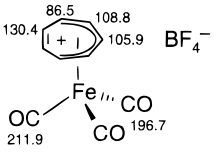
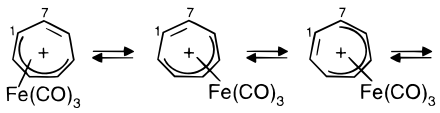


Chart 2. ^{13}C NMR Chemical Shifts of the Complex **6-BF$_4$** in Acetone-d_6 at −70 °C



6-BF$_4$

Cation **6** is known to exist as a set of equilibrating η^5-coordinated complexes **6a**/**6b**/**6c** etc.[8,19] (eq 5), giving rise to *four* resonances in the ^{1}H NMR spectrum at −80 °C and *one* proton resonance at +10 °C.[20]



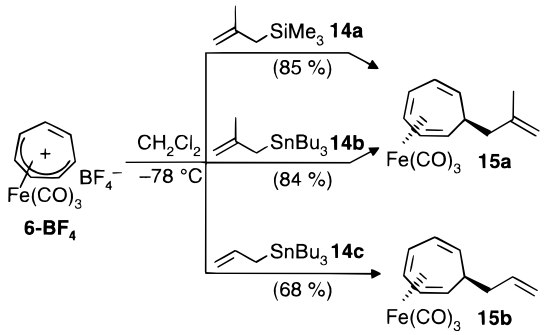
6a **6b** **6c** (5)

In accord with this interpretation and the reported spectra of monoalkyl substituted tropylium (tricarbonyl)iron complexes,[19] we observed a ^{13}C NMR spectrum of **6-BF$_4$** at −70 °C in which the two noncoordinated carbons are more deshielded than those of the pentadienyl fragment (Chart 2). The C_s symmetry of the complex is also indicated by quantum-chemical calculations (see below) and the nonequivalence of the carbonyl resonances. While attempts to observe coalescence of the signals in acetone-d_6 at elevated temperature led to decomposition of **6-BF$_4$** (above −40 °C), it was possible to obtain a ^{13}C NMR spectrum of **6-X** at room temperature when trifluoroacetic acid was employed as the solvent. The observed chemical shift of the cycloheptatrienyl ring (δ_C 109.1) is close to the average of the corresponding resonances observed at low temperature (Chart 2). We were not able, however, to detect the ^{13}C NMR signals of the carbonyl groups at room temperature.

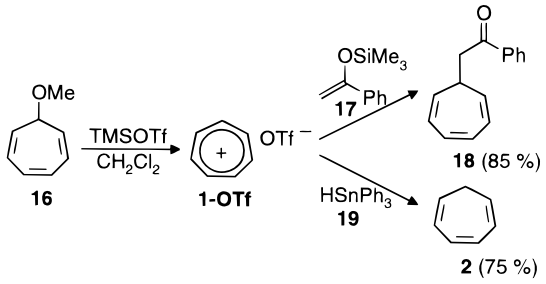
Reactions of $(C_7H_7)Fe(CO)_3^+$ (6) and $C_7H_7^+$ (1) with Nucleophiles. The tricarbonyliron complex **6-BF$_4$** reacted with (2-methylallyl)trimethylsilane (**14a**) and with (2-methylallyl)-

(8) Mahler, J. E.; Jones, D. A. K.; Pettit, R. *J. Am. Chem. Soc.* **1964**, *86*, 3589−3590.
(9) Cavazza, M.; Morganti, G.; Pietra, F. *J. Org. Chem.* **1980**, *45*, 2001−2004.
(10) Nitta, M.; Nishimura, M.; Miyano, H. *J. Chem. Soc., Perkin Trans. 1* **1989**, 1019−1024.
(11) Complex **10** was characterized by ^{1}H and ^{13}C NMR and mass spectroscopy.
(12) Emerson, G. F.; Mahler, J. E.; Pettit, R.; Collins, R. *J. Am. Chem. Soc.* **1964**, *86*, 3590−3591.
(13) For analogous preparations of tricarbonyliron diene complexes, see: Ley, S. V.; Low, C. M. R.; White, A. D. *J. Organomet. Chem.* **1986**, *302*, C13−C16.
(14) We also failed to synthesize **9a** via 1-(4-methoxyphenyl)-4-phenyl-1-aza-1,3-butadiene-catalyzed reactions of 7-methoxycycloheptatriene (**16**) with $Fe(CO)_5$ or $Fe_2(CO)_9$: (a) Knölker, H.-J.; Gonser, P. *Synlett* **1992**, 517−520. (b) Knölker, H.-J.; Gonser, P.; Jones, P. G. *Synlett* **1994**, 405−408.
(15) Hunt, D. F.; Farrant, G. C.; Rodeheaver, G. T. *J. Organomet. Chem.* **1972**, *38*, 349−365.
(16) Shvo, Y.; Hazum, E. *J. Chem. Soc., Chem. Commun.* **1975**, 829−830.
(17) Rigby, J. H.; Ogbu, C. O. *Tetrahedron Lett.* **1990**, *31*, 3385−3388.
(18) Pearson, A. J.; Srinivasan, K. *J. Org. Chem.* **1992**, *57*, 3965−3973.
(19) Lewis, C. P.; Kitching, W.; Eisenstadt, A.; Brookhart, M. *J. Am. Chem. Soc.* **1979**, *101*, 4896−4906.
(20) Whitesides, T. H.; Budnik, R. A. *J. Chem. Soc., Chem., Commun.* **1971**, 1514.

Scheme 2

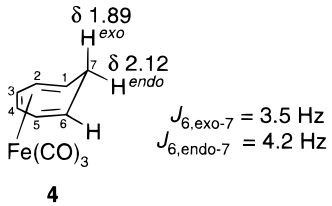


Scheme 3



tributylstannane (**14b**) in dichloromethane at ambient temperature to give the (2-methylallyl)cycloheptatriene complex **15a** in high yield (Scheme 2). The analogous reaction with allyltributylstannane (**14c**) afforded the complex **15b** (Scheme 2). The corresponding reaction of the noncoordinated tropylium ion **1** with (2-methylallyl)trimethylsilane (**14a**) has already been reported.[21] As shown in Scheme 3, tropylium triflate (**1-OTf**) reacts with α-(trimethylsiloxy)styrene (**17**) to give the ketone **18**, which had previously been obtained by treatment of tropylium tetrafluoroborate (**1-BF$_4$**) with acetophenone.[22] Hydride transfer from triphenylstannane (**19**) to the tropylium ion (**1**) gave cycloheptatriene (**2**) (Scheme 3), in analogy to the reported reaction of **1** with dimethylphenylsilane (**20**).[23]

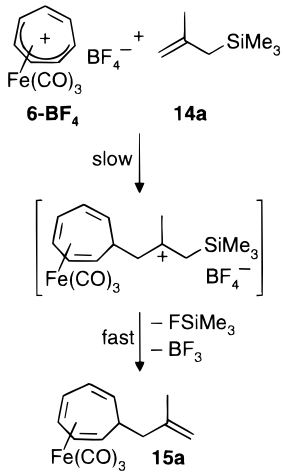
Stereochemistry of 15a and 15b. While the constitution of the complexes **15a** and **15b** could completely be elucidated from their ^{1}H and ^{13}C NMR spectra, there is some ambiguity with respect to their configuration. The observed $J_{6,7} = 4.3$ Hz in compound **15a** may be considered as weak evidence for the trans arrangement of the metal and the allyl group, since in the ^{1}H NMR spectrum of the parent cycloheptatriene complex **4**, the coupling constants of 6-H with the two protons attached to C-7 were assigned to be $J_{6,\text{exo}-7} = 3.5$ Hz and $J_{6,\text{endo}-7} = 4.2$ Hz.[24] Accordingly, mechanistic considerations suggest the approach of the nucleophiles **14** to the cycloheptatrienyl ring of **6** from the face opposite to the Fe(CO)$_3$ fragment.[17,25]



4

Kinetics. All reactions described in this article followed second-order kinetics, first order with respect to carbocations and first order with respect to nucleophiles. The rate constants were independent of the method of determination[26] (conductometry or photometry), in agreement with rate-determining electrophile−nucleophile combinations followed by rapid consecutive reactions to yield neutral products (example in Scheme 4).

Scheme 4



The suggested mechanism is supported by the fact that the rates of the reactions of (2-methylallyl)trimethylsilane (**14a**) with **1-OTf**, **1-ZnCl$_3$**, or **1-BCl$_4$** and with **6-BF$_4$** or **6-ONf**, respectively, were independent of the nature of the counterion (see Supporting Information). If desilylation were rate-determining, the different rates of formation of Me$_3$SiOTf, Me$_3$SiCl, and Me$_3$SiF would influence the overall rates.

Like other reactions of carbocations with uncharged nucleophiles,[7a] the reactions of the electrophiles **1** and **6** reported in this work are characterized by negative activation entropies, ranging from −75 to −126 J mol^{-1} K^{-1} (Table 1).

Comparison of the rate constants determined for the reactions of **14a** with the tropylium ion (**1**) ($k_{20\ °C} = 5.0$ L mol^{-1} s^{-1}) and with the tricarbonyliron-coordinated tropylium ion (**6**) ($k_{20\ °C} = 9.1$ L mol^{-1} s^{-1}) indicates that the Fe(CO)$_3$ ligand in **6** has little effect on the electrophilicity of the carbocation. This conclusion is corroborated by the results of further kinetic experiments.

The rate constants of the reactions of **6** and **1** with further nucleophiles combined with the *N* and *s* parameters[7a] of these nucleophiles (Tables 2 and 3) allow the calculation of the electrophilicity parameters *E* for the cations **1** and **6** by using eq 3. As shown in Table 2, closely similar *E* values were derived for **6** from its reactivities toward the π-nucleophiles **14a**−**c**, indicating that the reactions of **6** with these nucleophiles follow the linear free enthalpy relationship (eq 3).

Analogously, closely similar values of *E*(**1**) have been derived from the reactions of the tropylium ion (**1**) with the π-nucleophiles **14a** and **17** and the hydride donor **19**. The *E* value calculated from the reaction of **1** with **20** deviates conspicuously. The reason for this anomaly is unknown, but one can exclude an experimental error in the rate constant of this reaction, since similar values of this rate constant have been determined by us and by Chojnowski.[23] As a consequence of the larger set of kinetic data now available, it is possible to base the determination of *E*(**1**) exclusively on reactions of **1** with reference

(21) Picotin, G.; Miginiac, P. *Tetrahedron Lett.* **1988**, *29*, 5897−5898.
(22) Reingold, I. D.; Trujillo, H. A.; Kahr, B. E. *J. Org. Chem.* **1986**, *51*, 1627−1629.
(23) Chojnowski, J.; Fortuniak, W.; Stanczyk, W. *J. Am. Chem. Soc.* **1987**, *109*, 7776−7781.
(24) Karel, K. J.; Albright, T. A.; Brookhart, M. *Organometallics* **1982**, *1*, 419−430.
(25) Pearson, A. J.; Srinivasan, K. *Synlett* **1992**, 983−984.
(26) Mayr, H.; Schneider, R.; Schade, C.; Bartl, J.; Bederke, R. *J. Am. Chem. Soc.* **1990**, *112*, 4446−4454.

Table 1. Second-Order Rate Constants $k(CH_2Cl_2, 20\ °C)$ and Activation Parameters for the Reactions of the Free (**1**) and the Tricarbonyliron-Coordinated Tropylium Ion (**6**) with π-Nucleophiles and Hydride Donors

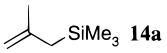
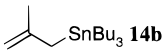
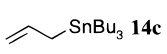
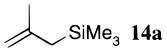
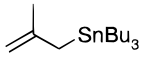
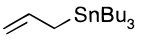
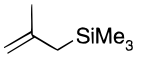
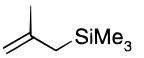
nucleophile		k / L mol^{-1} s^{-1}	$\Delta H^{\ddagger}$ / kJ mol^{-1}	$\Delta S^{\ddagger}$ / J mol^{-1} K^{-1}	T-range / °C
	**6**				
	**14a**	9.14	35.76 ± 0.83	−104.4 ± 3.6	−64 to −10
	**14b**	2.16×10^3	25.93 ± 0.47	−92.5 ± 2.1	−65 to −10
	**14c**	75.4	39.09 ± 1.66	−75.5 ± 7.0	−70 to −10
	**1**				
	**14a**	5.01	31.10 ± 0.84	−125.3 ± 3.6	−70 to 0
	**17**	227	34.18 ± 1.42	−83.1 ± 6.3	−70 to −20
$HSnPh_3$	**19**	12.0	–	–	20
$HSiMe_2Ph$	**20**	3.04×10^{-2}	–	–	20

Table 2. Calculation of the Electrophilicity Parameter E of the Tricarbonyliron Tropylium Ion (**6**) from the Nucleophilicity Parameters N and s of Its Reaction Partners and the Measured Second-Order Rate Constants k(20 °C, CH_2Cl_2) by Eq 3

nucleophile		N[a]	s[a]	log k	E(**6**)
	**14b**	7.92	0.87	3.33	−4.09
	**14c**	5.72	0.85	1.88	−3.51
	**14a**	4.90	0.89	0.96	−3.82
					∅ = −3.81 ± 0.24[b]

[a] From ref 7a. [b] One reviewer has suggested that we derive the averaged value of E from a plot of (log k)/s vs N. Though there are arguments for this procedure, we prefer to average individual values of E, since in this way, each rate constant contributes with equal weight.

Table 3. Calculation of the Electrophilicity Parameter E of the Tropylium Ion (**1**) from the Nucleophilicity Parameters N and s of Its Reaction Partners and the Measured Second-Order Rate Constants k(20 °C, CH_2Cl_2) by Eq 3

nucleophile		N^a	s^a	log k	E(**1**)
	**14a**	4.90	0.89	0.70	−4.11
	**17**	6.66	0.89	2.36	−4.01
$HSnPh_3$	**19**	5.94	0.56	1.08	−4.01
$HSiMe_2Ph$	**20**	3.39	0.72	−1.52[b]	−5.50
H_2O		5.80[c]	0.80	0.42[d]	−5.28
$CF_3CH_2NH_2$		9.55	0.77	3.86[e]	−4.54
BNAH[f]		9.45	0.97	4.40[g]	−4.91
					∅ = −4.62 ± 0.57

[a] From ref 7a. [b] Reference 23 reports log $k = -1.46$ at 25 °C. [c] Referring to pseudo-first-order rate constants in H_2O. [d] First-order rate constant from ref 27. [e] From ref 28. [f] BNAH = *N*-benzyl-1,4-dihydronicotinamide. [g] From ref 29.

nucleophiles with well-established N and s parameters (Table 3). The E parameter of the tropylium ion thus calculated is 0.5 unit larger than the originally derived value, which was predominantly based on reactions of **1** with hydrides and amines.[7a]

Comparison of the averaged E values derived from Tables 2 and 3 again leads to the conclusion that the tropylium ion (**1**) and its tricarbonyliron-coordinated analogue (**6**) differ little in electrophilicity.

Since our model aims to compare reactivities of different molecules and not of different positions, we generally omit statistical corrections. If the reactivity of one position in **1** were compared with the reactivity of one position in **6**, a slightly higher reactivity of **6** over **1** would be derived, which would not affect our conclusion.

In their comprehensive kinetic investigations on the reactions of metal−π-complexes with nucleophiles, Kane-Maguire and Sweigart have also included the tropylium complexes of the 12e fragments $Cr(CO)_3$, $Mo(CO)_3$, and $W(CO)_3$.[30,31] These data allow us to calculate the electrophilicity parameters $E = -9.3$ to -10.2 for these η^7 complexes,[32] indicating a strongly reduced electrophilicity compared to the free tropylium ion **1**.

Previous work of this group[33] has shown that the dihydrotropylium complex **22** is also less electrophilic than **6** by 6 orders of magnitude.

DFT Calculations. To rationalize these widely differing reactivities, we have performed computations at a gradient-corrected level of density-functional theory (DFT), denoted BP86/AE1. This or comparable levels have been shown to afford reliable geometries and energies of transition-metal compounds.[34,35] In accord with experimental findings (see above), the η^5 structure **6** is a minimum on the potential energy surface in C_s symmetry (Figure 1, top), while the $Cr(CO)_3$ complex **21** (Figure 1, middle) adopts a η^7 coordination with an essentially planar C_7H_7 moiety. Saturation of the noncoordinated double bond of **6**, affording **22**, has little effect on the coordination geometry about Fe (Figure 1, bottom). The calculated minimum structure of **22** shows a normal $C(sp^3)-C(sp^3)$ bond length (1.534 Å) and a staggered conformation of the ethano bridge (Figure 1, bottom). In contrast, a nearly eclipsed conformation of the ethano bridge and very short $C(sp^3)-C(sp^3)$ distances (down to 1.400 Å) were reported for the solid state of **22-BF$_4$**.[36] A possible explanation for this apparent discrepancy is torsional vibrational averaging in the solid state.[37]

(27) Ritchie, C. D.; Fleischhauer, H. *J. Am. Chem. Soc.* **1972**, *94*, 3481−3483.
(28) Ritchie, C. D.; Virtanen, P. O. I. *J. Am. Chem. Soc.* **1973**, *95*, 1882−1889.
(29) Bunting, J. W. *Bioorg. Chem.* **1991**, *19*, 456−491.
(30) Kane-Maguire, L. A. P.; Honig, E. D.; Sweigart, D. A. *Chem. Rev.* **1984**, *84*, 525−543.
(31) John, G. R.; Kane-Maguire, L. A. P.; Sweigart, D. A. *J. Organomet. Chem.* **1976**, *120*, C47−C48.
(32) The electrophilicity parameter E was calculated by eq h and Table 12 in ref 7a.
(33) Mayr, H.; Müller, K.-H.; Rau, D. *Angew. Chem.* **1993**, *105*, 1732−1734; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1630−1632.
(34) See e.g.: Ziegler, T. *Can. J. Chem.* **1995**, *73*, 743−761.
(35) Rotational barriers and vibrational frequencies of related $Fe(CO)_3$-(diene) complexes are well-reproduced at the BP86/AE1 level: (a) Bühl, M.; Thiel, W. *Inorg. Chem.* **1997**, *36*, 2922−2924. For DFT calculations of transition-metal carbonyls and hydrides at this level see also: (b) Jonas, V.; Thiel, W. *J. Chem. Phys.* **1995**, *102*, 8474−8484. (c) Jonas, V.; Thiel, W. *J. Chem. Phys.* **1996**, *105*, 3636−3648.
(36) Brougham, D. F.; Barrie, P. J.; Hawkes, G. E.; Abrahams, I.; Motevalli, M.; Brown, D. A.; Long, G. J. *Inorg. Chem.* **1996**, *35*, 5595−5602.
(37) However, no unusual U(eq) values or thermal ellipsoids are apparent in the solid state for **22-BF$_4$**. Nevertheless, see the related case of 1,2-diarylethanes, e.g.: Harada, J.; Ogawa, K.; Tomoda, S. *J. Am. Chem. Soc.* **1995**, *117*, 4476−4478.

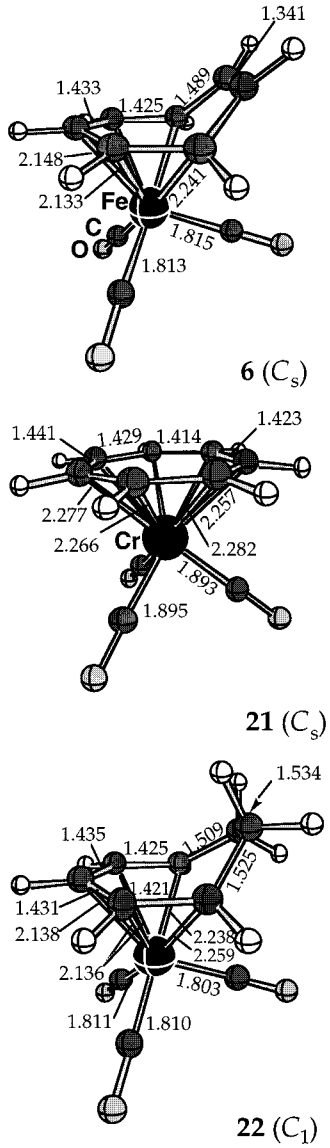
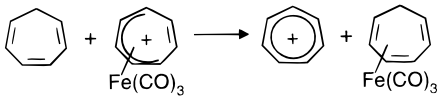


Figure 1. BP86/AE1 optimized geometries of cationic complexes **6**, **21**, and **22**, including key parameters (in Å).

The isodesmic reaction eq 6 indicates that the hydride affinity



(6)

2 **6** **1** **4**

$\Delta H_{calc} = -13.1$ kcal/mol

of **6** is greater than that of the free tropylium ion **1** by 13.1 kcal mol^{-1}, reflecting the aromatic stabilization of the latter. For that reason, the thermodynamic driving force for the reaction with nucleophiles can be expected to be much greater for **6** than for **1**.

PMO theory, on the other hand, suggests that the activation energies are predominantly controlled by HOMO(nucleophile)−LUMO(electrophile) interactions. The LUMO of **6** sketched in Figure 2 (top) shows much smaller coefficients at the cycloheptatrienyl fragment than the LUMO of **1** (π^*, not depicted). In addition, the former is computed higher in energy than the latter by almost 1 eV (Table 4). For both reasons, the frontier orbital interactions are less favorable in reactions of nucleophiles with **6** than with **1**. A reduced reactivity of **6** compared to that

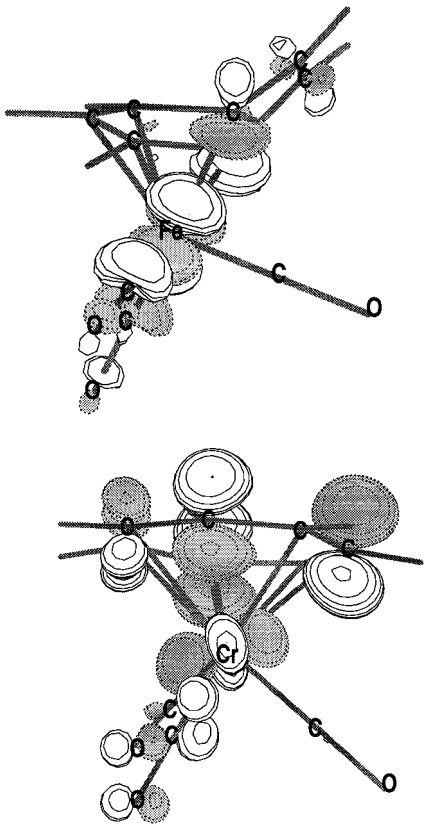
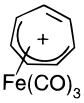
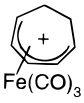


Figure 2. LUMOs of the cations **6** (top) and **21** (bottom, BP86/AE1 level).

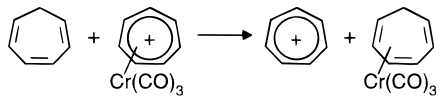
Table 4. Comparison of the Electrophilicity *E* and the LUMO Energies (from DFT Calculations[a]) for the Free Tropylium Ion **1** and the Tropylium Complexes **6**, **21**, and **22**.

electrophile		*E*	ϵ(LUMO)/eV
	**1**	−4.62	−8.45
	**6**	−3.81	−7.53
	**21**	−9.3	−7.58
	**22**	−9.88[b]	−7.28

[a] Note that in contrast to Hartree−Fock theory, DFT-based virtual MOs are in the same average field of $N - 1$ electrons as the occupied MOs, hence the very low LUMO energies for these cations. [b] From ref 33.

of **1** can be expected for steric reasons, since the noncoordinated double bond of **6** is bent away from the $Fe(CO)_3$ moiety, in the direction of the incoming nucleophile (see above). Though it is difficult to quantify the effects, the observed similarity of the electrophilicities of **1** and **6** indicates that the higher thermodynamic driving force for the reactions involving **6** is almost compensated by weaker HOMO−LUMO interactions and steric effects.

The isodesmic reaction (eq 7) indicates that the hydride affinity of the $Cr(CO)_3$ complex **21** is only slightly greater than that of the tropylium ion. For that reason, the thermodynamic

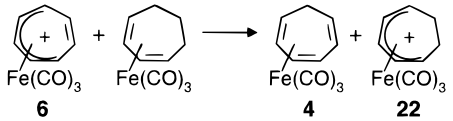


2 **21** **1** (7)

$\Delta H_{calc} = -2.0$ kcal/mol

driving force of the reactions of **1** and **21** can be assumed to be similar. Likewise, the LUMOs of both **1** and **21** (Figure 2, bottom) show large coefficients at the C_7H_7 moieties. Thus, the strongly reduced electrophilicity of **21** with respect to that of **1** must be due to the considerably higher LUMO energy of the former (Table 4).

How can one rationalize the reduced electrophilicity of the dihydro compound **22** with respect to the tropylium complex **6**? Using the same analysis as before, one can derive from eq 8 that the thermodynamic driving force for reactions with



6 **4** **22** (8)

$\Delta H_{calc} = -4.6$ kcal/mol

nucleophiles is greater for **6** than for **22** by 4.6 kcal mol^{-1}. This effect is enhanced by the slightly more favorable frontier orbital interactions in the reactions of **6** due to the lower lying LUMO of **6** compared to that of **22** (Table 4), consistent with the observed relative electrophilicities of both complexes.

In summary, the relative reactivities of the cationic complexes **6**, **21**, and **22** cannot be rationalized by a single effect but are due to variations in the thermodynamic driving force as well as variable HOMO−LUMO interactions and steric effects.

Conclusions

Coordination of the tropylium ion (**1**) with the $Fe(CO)_3$ fragment only slightly affects the electrophilicity of the cation, because the increase of the thermodynamic driving force (hydride affinity) is compensated by a concomitant increase of the LUMO energy. Since the reactions of **6** with π-nucleophiles were found to obey the linear free enthalpy relationship (eq 3), one can use this equation to predict that nucleophiles with $N > -1$, i.e., nucleophiles stronger than anisole, 1,3-butadiene, or isobutylene,[7,38] should be capable of attacking **6** at room temperature.

Experimental Section

General Considerations. All reactions were carried out under dry, oxygen-free nitrogen or argon. Solvents were purified and dried as reported.[39] (2-Methylallyl)trimethylsilane (**14a**),[40] (2-methylallyl)tributylstannane (**14b**),[40] and 1-phenyl-1-(trimethylsiloxy)ethene (**17**)[41] were prepared as described in the literature. Allyltributylstannane (**14c**), triphenylstannane (**19**), and dimethylphenylsilane (**20**) are commercially available. ^{1}H (300 MHz) and ^{13}C NMR (75 MHz) spectra of solutions in $CDCl_3$ were calibrated to the solvent signals (δ_H 7.24, δ_C 77.0).

Tricarbonyl[(1−4-η)-7-(2-methylallyl)-cycloheptatrienyl]iron (**15a**). The salt **6-BF_4** (670 mg, 2.11 mmol) was suspended in CH_2Cl_2 (5 mL) at −78 °C in the dark. After the addition of **14a**[40] (920 mg, 7.17 mmol)the dry ice bath was removed and the reaction mixture was stirred at ambient temperature until the solid component was completely dissolved (6 h). The residue remaining after the solvent was evaporated in vacuo was filtered through a short column of silica gel/Celite (1:1) with pentane as eluent. The solvent was removed in vacuo to give the crude product, which was distilled (60−70 °C/3 × 10^{-4} mbar) to yield 510 mg of **15a** (85%): yellow oil; IR (film) 2060, 2020−1960 (C≡O), 1650 (C═C) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.71 (s, 3 H, CH_3), 2.10 (d, J = 7.3 Hz, 2 H, 7-CH_2), 2.69 (m_c, 1 H, 7-H), 2.95 (m_c, 1 H, 4-H), 3.14 (m_c, 1 H, 1-H), 4.71, 4.79 (2 m_c, 2 H, ═CH_2), 5.10 (dddd, $J_{6,5}$ = 10.7 Hz, $J_{6,7}$ = 4.3 Hz, J = 1.8 Hz, 0.7 Hz, 1 H, 6-H), 5.32 (m_c, 2 H, 2-H, 3-H), 5.74 (ddd, $J_{5,6}$ = 10.7 Hz, $J_{5,4}$ = 7.8 Hz, J = 1.7 Hz, 1 H, 5-H); ^{13}C NMR ($CDCl_3$) δ 22.1 (q, CH_3), 40.3 (d, C-7), 47.7 (t, 7-CH_2), 55.4 (d, C-4), 65.6 (d, C-1), 87.5, 94.6 (2 d, C-2, C-3), 112.9 (t, ═CH_2), 128.0 (d, C-5), 129.5 (d, C-6), 143.5 (s, *C*═CH_2), 211.1 (s, CO) (signal assignments are based on ^{1}H,^{13}C- and ^{1}H,^{1}H-COSY experiments); MS (70 eV, EI) *m*/*z* 258 (23) [M^+ − CO], 230 (23) [M^+ − 2 CO], 202 (42) [M^+ − 3 CO], 148 (44), 147 (100) [$C_7H_7Fe^+$], 91 (97) [$C_7H_7^+$], 56 (32) [Fe^+]. Anal. Calcd for $C_{14}H_{14}FeO_3$ (286.1): C, 58.77; H, 4.93. Found: C, 58.73; H, 5.11.

As described above for **14a**, the iron complex salt **6-BF_4** (160 mg, 0.503 mmol) and (2-methylallyl)tributylstannane[40] (**14b**; 220 mg, 0.637 mmol) were allowed to react for 2 h. After filtration and distillation (60−70 °C/3 × 10^{-4} mbar) 121 mg of **15a** (84%) was obtained as a yellow oil (for characterization see above).

Tricarbonyl[(1−4-η)-7-allylcycloheptatrienyl]iron (**15b**). Following the procedure described for the formation of **15a**, a suspension of **6-BF_4** (586 mg, 1.85 mmol) and allyltributylstannane (**14c**; 630 mg, 1.90 mmol) in CH_2Cl_2 was stirred for 2 h. After filtration and distillation (55−65 °C/3 × 10^{-4} mbar) 342 mg of **15b** (68%) was obtained: yellow oil; IR (film) 2055, 2020−1960 (C≡O), 1650 (C═C) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.06−2.30 (m, 2 H, 7-CH_2), 2.63 (m_c, 1 H, 7-H), 2.93 (m_c, 1 H, 4-H), 3.13 (m_c, 1 H, 1-H), 5.02−5.12 (m, 3 H, 6-H, ═CH_2), 5.32 (m_c, 2 H, 2-H, 3-H), 5.66−5.84 (m, 2 H, 5-H, C*H*═CH_2); ^{13}C NMR ($CDCl_3$) δ 42.5 (d, C-7), 42.8 (t, 7-CH_2), 55.3 (d, C-4), 65.2 (d, C-1), 88.1 (d, C-2), 94.2 (d, C-3), 116.9 (t, ═CH_2), 128.5 (d, C-5), 129.1 (d, C-6), 136.4 (d, *C*H═CH_2), 211.2 (s, CO) (signal assignments are based on ^{1}H,^{13}C- and ^{1}H,^{1}H-COSY experiments).

DFT Calculations. Calculations were carried out at the BP86/AE1 level of DFT, i.e., employing the gradient-corrected functionals for exchange and correlation from Becke[42] and Perdew,[43] respectively, Wachters' (14s11p6d)/[8s7p4d] all-electron basis for Fe and Cr,[44] augmented with two additional 4p functions[44] and a diffuse d function,[45] and standard 6-31G* basis[46] on the ligands. Spherical d functions were used throughout. C_s symmetry was imposed in most cases (**1**, D_{7h}; **22**, C_1), and the nature of each minimum was verified by analytic calculation of the harmonic vibrational frequencies.

The reported reaction enthalpies include zero-point and thermic corrections (25 °C) from the BP86/AE1 harmonic frequencies. All computations were performed with the Gaussian 94 package.[47]

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(38) Burfeindt, J.; Patz, M.; Müller, M.; Mayr, H. *J. Am. Chem. Soc.* **1998**, *120*, 3629−3634.
(39) Perrin, D. D.; Armarego, W. L.; Perrin, D. R. *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon Press: Frankfurt, Germany, 1980.
(40) Hagen, G.; Mayr, H. *J. Am. Chem. Soc.* **1991**, *113*, 4954−4961.
(41) Emde, H.; Götz, A.; Hofmann, K.; Simchen, G. *Justus Liebigs Ann. Chem.* **1981**, 1643−1657.
(42) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098−3100.
(43) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822−8824; **1986**, *34*, 7406.
(44) Wachters, A. J. H. *J. Chem. Phys.* **1970**, *52*, 1033−1036.
(45) Hay, P. J. *J. Chem. Phys.* **1977**, *66*, 4377−4384.
(46) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab initio Molecular Orbital Theory*; Wiley: New York, 1986.
(47) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A.; *Gaussian 94*, Revision D4; Gaussian Inc., Pittsburgh, PA, 1995.

performed on Silicon Graphics PowerChallenge (Organisch-chemisches Institut, Universität Zürich) and on IBM RS6000 workstations (C4 cluster, ETH Zürich). This paper is dedicated to Professor Heinrich Nöth on the occasion of his 70th birthday.

Supporting Information Available: Text and tables giving synthetic procedures and spectroscopic data for compounds **6-X**, **9b**, **11**, and **13**, details of the kinetic experiments and tables with concentrations and rate constants at variable temperature, and Gaussian archive entries of the optimized geometries, together with ZPEs and thermic corrections. This material is available free of charge via the Internet at http://pubs.acs.org.

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