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Reactions of coordinated cyclic polyolefins*. Substituent effects on the 1,3-haptotropic rearrangement of tricarbonyl(η^4-heptafulvene)iron complexes

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Abstract

The kinetics of the fluxional 1,3-haptotropic rearrangement of two 8-substituted tricarbonyl(η^4-heptafulvene)iron complexes have been studied by dynamic NMR methods. The first order rate constants for the *anti-syn* interconversion of (8-diphenylmethylheptafulvene)$Fe(CO)_3$ (acetone-d_6, $-1°C$) are $k_{as} = 6.77 \times 10^{-5}$ s^{-1} and $k_{sa} = 8.47 \times 10^{-5}$ s^{-1}, with free activation energies $\Delta G^{\#}$ of 21.06 and 20.94 kcal mol^{-1}, respectively. The rate constants for (8-methoxyheptafulvene)$Fe(CO)_3$ (acetone-d_6, 25°C) are $k_{as} = 0.26$ s^{-1} and $k_{sa} = 0.13$ s^{-1}, with activation barriers $\Delta G^{\#}$ of 18.24 and 18.65 kcal mol^{-1}, respectively. Analysis of the substituent effects on the metal shift by Hammett and Taft linear free-energy correlations reveal the dominance of steric over electronic effects, indicating the preference for an η^2 way-point mechanism.

Introduction

1,3-Haptotropic rearrangements are fluxional processes commonly observed in both cyclic [2,3] (eq. 1) and acyclic [4] (eq. 2) η^4-hexatrienes. Previous investigations indicate that these metal migrations occur in a thermodynamically controlled pathway involving an η^2-intermediate, which collapses to the corresponding more stable η^4-isomer [4]. Activation energies range between 15–35 kcal/mole, usually being higher for the acyclic complexes.

* For previous paper in this series see ref. 1.

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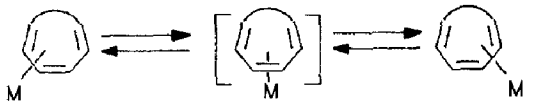

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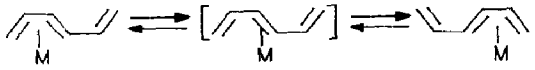

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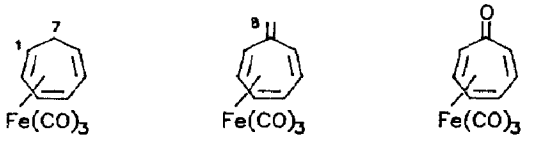
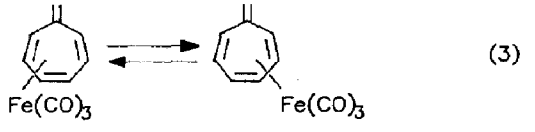
Recent kinetic and theoretical studies [3] of (cycloheptatriene)$Fe(CO)_3$ (I) derivatives show that the energy barriers to rearrangement are sensitive to electronic rather than steric effects of substituents at the 7-position. Qualitatively it was found that higher activation energies are required for metal migration with electron-withdrawing groups, whereas electron donors lower the energy barriers relative to that for the parent complex. This suggested a direct rearrangement pathway involving an η^2-like way-point transient [3,5].



I II III

While rearrangement barriers of a large number of substituted cycloheptatriene (cht) complexes have been studied, only a few examples of the closely related 8-substituted heptafulvenes (II) [3,6,7] and tropone (III) [8] analogs have been reported. In order to gain more insight into the mechanism of metal migrations in coordinated cyclic polyolefins, we decided to investigate further both the steric and electronic effects on the 1,3-haptotropic rearrangement of (heptafulvene)$Fe(CO)_3$ derivatives (eq. 3). We report here on the rearrangement kinetics of two 8-substituted heptafulvenes, one with the bulky benzhydryl group (IV), and the other with the electron-donating methoxy group (V).



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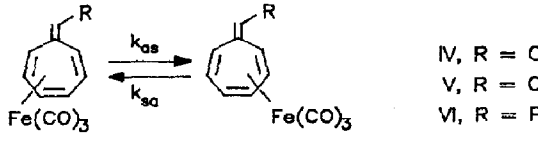
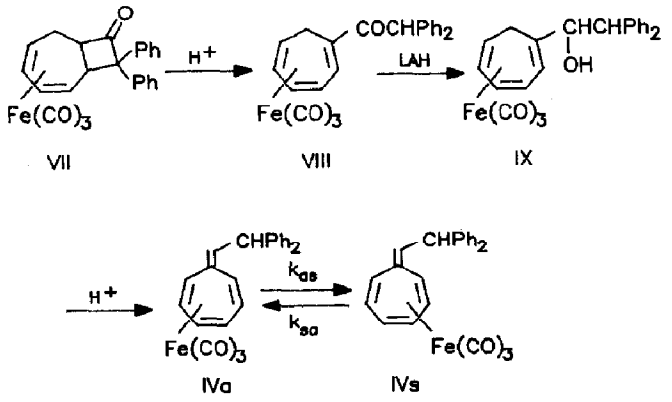


IV, R = $CHPh_2$
V, R = OCH_3
VI, R = Ph

Results

The synthesis of IV is described in Scheme 1. The 2 + 2 adduct VII of (cht)$Fe(CO)_3$ and diphenyl ketene [9] readily rearranged upon acid catalysis to the ketone VIII [10]. Reduction of VIII with $LiAlH_4$, followed by acid catalysed dehydration of the alcohol IX, afforded IV. The ^1H NMR spectrum of IV revealed



Scheme 1. Synthesis of (8-diphenylmethylheptafulvene)$Fe(CO)_3$.

it to be an equilibrium mixture of the *anti* (IVa) and *syn* (IVs) stereoisomers in a ratio of 5/4 (Fig. 1d). The structural assignment of the major heptafulvene as the *anti* isomer (IVa) is based on the larger coupling constant (J_{58} 1.6 Hz) between H5 and H8, compared with the corresponding coupling constant (J_{58} 0.7 Hz) of the minor *syn* isomer (IVs) (Table 1). This was confirmed by NOE experiments.

When the equilibrium mixture of the two isomers in pentane is allowed to crystallize slowly it is all transformed into the crystalline *anti* isomer (IVa). This was clearly demonstrated by taking an ^1H NMR spectrum shortly after redissolving the

Table 1

^1H NMR data for (heptafulvene)$Fe(CO)_3$ complexes [a]

Complex	Solvent	H(1)	H(2)	H(3)	H(4)	H(5)	H(6)	H(8)	H(X) [b]
IVa	$CDCl_3$	3.77	5.42	5.54	3.02	5.81	5.84	6.05	4.96
		aromatic: 7.1–7.3							
	$(CD_3)_2CO$	4.02	5.65	5.75	3.17	5.88	6.00	6.28	5.23
		aromatic: 7.2–7.3							
		J_{12} 7.8, J_{13} 1.3, J_{16} 1.8, J_{23} 4.7, J_{24} 1.5, J_{34} 7.4,							
		J_{45} 7.8, J_{46} 1.1, J_{56} 10.8, J_{58} 1.6, J_{68} 0.8, J_{69} 0.5,							
		J_{89} 9.2, J_{9Ph} 1.0							
IVs	$CDCl_3$	3.83	5.43	5.53	3.05	5.64	5.44	5.89	5.00
		aromatic: 7.1–7.3							
	$(CD_3)_2CO$	4.18	5.67	5.77	3.19	5.69	5.53	6.02	5.10
		aromatic: 7.2–7.3							
		J_{12} 7.8, J_{13} 1.3, J_{16} 1.9, J_{18} 0.5, J_{19} 0.5, J_{23} 4.7, J_{24} 1.5,							
		J_{28} 0.4, J_{34} 7.4, J_{45} 7.8, J_{46} 1.0, J_{56} 10.6, J_{58} 0.7, J_{59} 0.2,							
		J_{68} 0.8, J_{89} 9.9, J_{9Ph} 0.9							
Va	$CDCl_3$	3.68	5.19	5.33	3.17	5.67	5.90	6.26	3.67
	$(CD_3)_2CO$	3.92	5.32–5.52		3.31	5.65	5.88	6.51	3.68
		J_{12} 7.8, J_{13} 1.4, J_{16} 1.7, J_{18} 0.5, J_{23} 4.6, J_{24} 1.5, J_{34} 7.5,							
		J_{35} 0.2, J_{45} 7.9, J_{46} 1.0, J_{56} 10.7, J_{58} 1.7, J_{68} 0.8							
Vs	$CDCl_3$	4.20	5.25	5.30	3.23	5.50	5.30	6.20	3.74
	$(CD_3)_2CO$	4.28	5.32–5.52		3.37	5.32–5.52		6.42	3.76
		J_{12} 7.6, $J_{13} = J_{16}$ 1.7, J_{18} 0.5, J_{23} 4.7, J_{24} 1.7, J_{28} 0.4,							
		J_{34} 7.5, J_{45} 7.9, J_{46} 1.0, J_{56} 10.5, J_{58} 0.6, J_{68} 0.5							

[a] δ (ppm) from TMS; J (Hz). [b] H(9) signal in IV, methyl signal in V.

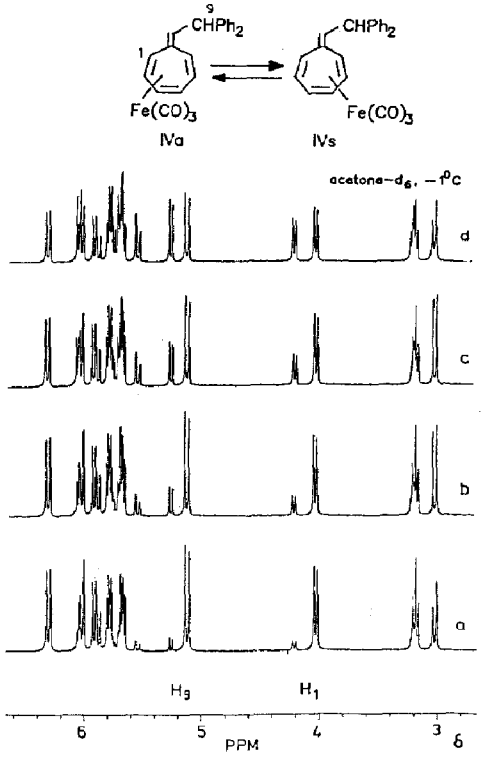
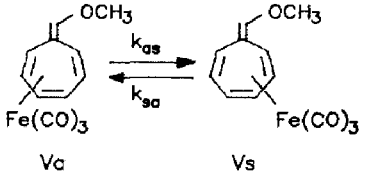


Fig. 1. Progress of the 1,3-haptotropic rearrangement for complex IV.

crystals of IVa in acetone-d_6 at $-1°C$ and monitoring the equilibration process (Fig. 1). This allowed the determination of the rate constants and energy barriers of the interconversion (vide infra).



(4)

We made the 8-methoxyheptafulvene complex (V) previously [11]. The ^1H NMR spectrum in acetone-d_6 at room temperature, shows there to be an equilibrium mixture of the *syn* (Vs) and *anti* (Va) isomers (eq. 4), in a ratio of 2/1 respectively (Table 1). $^1H\{^1H\}$ double irradiation experiments indicated spin saturation transfer (SST). This enabled evaluation of the kinetic rate constants for the haptotropic rearrangement by use of the Hoffman–Forsen SST technique [12], as described below.

Kinetics

Crystals of (*anti*-8-benzhydrylheptafulvene)$Fe(CO)_3$ (IVa) were dissolved in acetone-d_6 at $-1°C$ and the progress of the rearrangement immediately monitored by ^1H NMR spectroscopy (Fig. 1). The relative concentrations of the stereoisomers were determined from the integrals of the relevant proton signals. The value of first

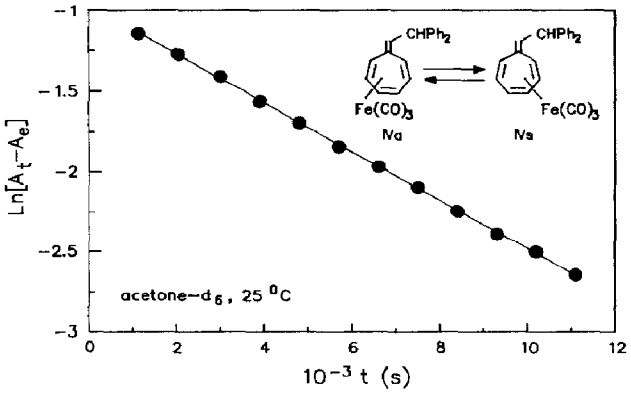


Fig. 2. Plot of ln $[A_t - A_e]$ vs. time.

Table 2

Kinetic data for 1,3-haptotropic rearrangements

Compound	Solvent	T (°C)	k (s^{-1})	$\Delta G^{\#}$ (kcal mol^{-1})
IVa → IVs	$(CD_3)_2CO$	−1	6.77×10^{-5}	21.06
IVs → IVa		−1	8.42×10^{-5}	20.94
Va → Vs	$(CD_3)_2CO$	25	0.26	18.24
Vs → Va		25	0.13	18.65
VI	C_7D_8[a]	60	0.41	20.0
	CH_2Cl_2[b]	25	3.0×10^{-2}	19.5
	$\Delta H^{\#}$ 15.7 kcal mol^{-1}, $\Delta S^{\#}$ −13 e.u.[c]			

[a] Ref. 3. [b] Ref. 6. [c] Calculated from data in ref. 3.

order rate constant, $k_{obs} = (k_{as} + k_{sa}) = (1.52 \pm 0.02) \times 10^{-4}$ s^{-1}, was derived from the slope of the plot of ln $[A_t - A_e]$ against time, where A_t and A_e are the mole fractions of Ia at time t and at equilibrium, respectively [13] (Fig. 2). The rate constants and activation data for this and related interconversions are summarized in Table 2.

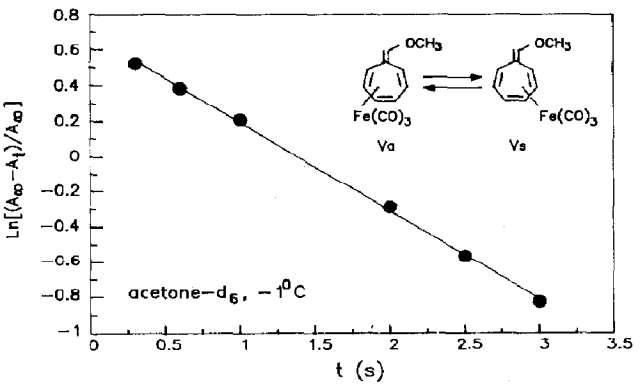


Fig. 3. Plot of ln $[(A_\infty - A_t)/A_\infty]$ vs. time.

The rate constants for the interconversion of the 8-methoxy heptafulvene complexes V (eq. 4) were evaluated by measuring the rates of exchange of the interchanging protons by the Fourier transform version of the Hoffman–Forsen SST method [1,12]. The kinetic data listed in Table 2 are based on the exchange process between the two H(8) nuclei. Thus, the *anti* → *syn* rate of metal migration, k_{as} 0.26 s^{-1}, was calculated from eq. 5, which is derived from eqs. 6 and 7. In these equations τ and T_1 are the spin lifetime and spin-lattice relaxation time of the *anti*-H(8), and r is the ratio between the intensities of the *anti*-H(8) signal, with and without irradiation of *syn*-H(8), respectively. τ is obtained by the usual inversion-recovery experiment ($180° \geqslant t \geqslant 90°_{acq.}$) [14], from the slope of the plot of ln $[(A_\infty - A_t)/A_\infty]$ against time (t), were A_∞ and A_t are the integrals of the *anti*-H(8) signal at t_∞ ($= 10$ s) and t, respectively (Fig. 3). In these experiments the signal of *anti*-H(8) was integrated while *syn*-H(8) was continuously irradiated.

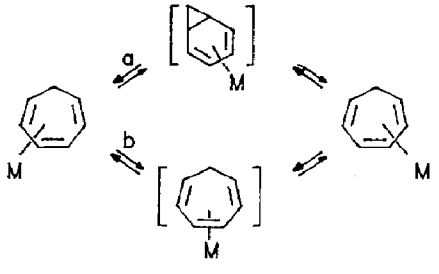
$$k_{as} = (1 - r)/\tau \tag{5}$$

$$1/\tau = k_{as} + (1/T_1) \tag{6}$$

$$r = (1/T_1)/[k_{as} + (1/T_1)] \tag{7}$$

Discussion

It has been previously noted that in contrast to the very large electronic substituent effects observed for the free cycloheptatriene-norcaradiene equilibrium, the η^4-coordinated 7-substituted cycloheptatrienes show a reversed and only moderate substituent effect on the 1,3-haptotropic rearrangement [3]. This eliminated a mechanism involving an η^4-norcaradiene intermediate (eq. 8a) [15] in favor of a way-point [3] metal migration, via a transition state resembling an η^2-complex (eq. 8b).



(8)

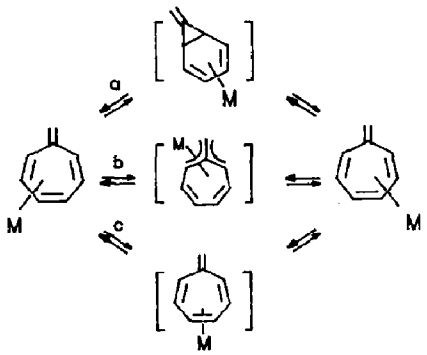
Free heptafulvenes do not equilibrate with their high energy methylene-norcaradiene valence isomers. It is thus unlikely that the analogous norcaradiene complexes will be intermediates in the 1,3-metal shift (eq. 9a). On the other hand, a trimethylenemethane intermediate complex [7,16] (eq. 9b) cannot be excluded a priori, especially in the presence of electron-donating groups at position 8 [7]. However, it would be expected that 8-substituted heptafulvene complexes would then be highly susceptible to substituent electronic effects, and this is inconsistent with the present experimental results, since, if we plot the logarithm of the rate constants (corrected to 25 °C) against Hammett's σ_p values [17] (Table 3) a very poor correlation is obtained (Fig. 4). Thus, it appears that electronic effects do not play an important role in the migration process.

Table 3

Kinetic data for Hammett and Taft correlations

Compound	σ_p	E_s	$k(s^{-1})$ [a]	log k
IVs → IVa [b]	−0.04 [c]	−2.7	1.55×10^{-3}	−2.81
Vs → Va	−0.27	−0.55	0.13	−0.89
VI [d]	−0.01	−1.01	3.0×10^{-2}	−1.52

[a] 25 °C. [b] k was calculated assuming $\Delta S^{\#}$ −13 e.u., as in VI (cf. Table 2). [c] Ref. 17b. [d] Ref. 6.



(9)

Because of the low sensitivity of the haptotropic rearrangements to electronic effects, we considered the alternative possibility of a linear correlation between the steric effects. A plot of log k against Taft's steric constants E_s [17] did indeed, give an excellent straight line (Fig. 5), indicating the dominance of steric effects on the 1,3-metal shift.

Large contributions of steric effects are characteristic of conformational processes in systems where no bonds are broken or formed and the substituents are far from the pivot bonds [18]. The experimental results clearly imply that the 1,3-haptotropic rearrangements in heptafulvene complexes in fact involve essentially conformational transitions. Accordingly, this suggests the exclusion of migration pathways via trimethylenemethane (eq. 9b) or norcaradiene (eq. 9a) intermediates, and is highly

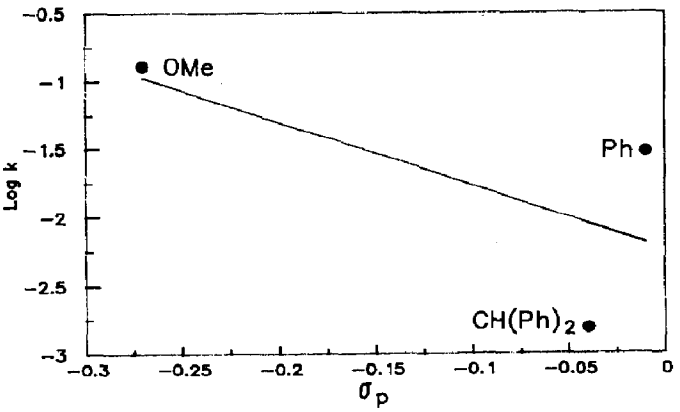


Fig. 4. Hammett plot, electronic effects (25 °C).

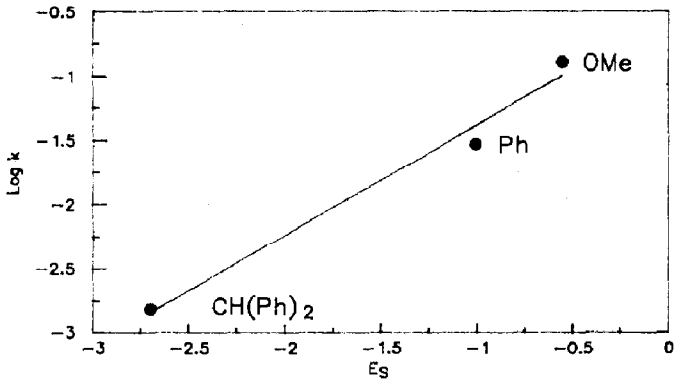


Fig. 5. Taft plot, steric effects (25 °C).

consistent with the way-point mechanism [3] previously proposed for η^4-cycloheptatriene complexes (Fig. 9c).

Experimental

General. IR spectra were measured with a Perkin–Elmer Model 257 spectrometer. Mass spectra were determined with a gc/ms Finnigan Model 4021 spectrometer. ^{1}H NMR spectra were recorded on Varian HA-100 and Bruker AM300 spectrometers. Elemental analyses were determined in the analytical laboratories of the Hebrew University, Jerusalem. Reactions were conducted under nitrogen.

All the kinetic experiments were performed with reaction solutions in NMR tubes on the Bruker AM300 spectrometer. Dilute solutions (approx. 60 mM) of the heptafulvenes in $(CD_3)_2CO$ were purged with nitrogen and were sufficiently stable for the experimental period. The sample temperatures were measured with a Eurotherm 840/T digital thermometer, and are estimated to be correct within ± 0.5 °C.

[1-(η-1–4)-Cycloheptatrien-6-yl-diphenylethanone]Fe(CO)$_3$ (VIII) [10]

A benzene solution of VII [9] and *p*-TsOH (2 mol%) was refluxed for 12 h under nitrogen. The solvent was removed under reduced pressure and the residue was recrystallized from CH_2Cl_2/hexane, m.p. 159–161 °C. IR ($CDCl_3$): 2020, 1975 (ligand CO), 1640 (organic carbonyl) cm^{-1}; *m/e* 398 (M − CO). Anal. Found: C, 67.39; H, 4.51. $C_{24}H_{18}FeO_4$ calcd.: C, 67.65; H, 4.22%. For ^{1}H NMR see ref. 10.

[1-(η-1–4)-Cycloheptatrien-6-yl-2,2-diphenylethanol]Fe(CO)$_3$ (IX)

A solution of ketone VIII (230 mg, 0.54 mmol) in ether (30 ml) was added dropwise to a cold (−78 °C) slurry of $LiAlH_4$ (100 mg, 2.63 mmol) in ether (30 ml). The mixture was stirred for 1 h at −78° then for 1 h at room temperature, and then treated with cold aqueous NH_4Cl. The organic layer was washed with 5% aqueous $NaHCO_3$ and with saturated aqueous NaCl then dried over anhydrous Na_2SO_4. Removal of the ether and trituration with hot hexane gave yellow crystals of IX, m.p. 132 °C (90 mg, 40% yield). IR ($CDCl_3$): 3580 (OH), 2025, 1975 (ligand CO) cm^{-1}; mass spectrum (CI, CH_4): 411 (M − 17), 373, 355, 345, 327, 271. Anal. Found: C, 67.12; H, 4.71. $C_{24}H_{20}FeO_4$ calcd.: C, 67.33; H, 4.67%. ^{1}H NMR (100

MHz, $CDCl_3$) 2.12 (H7, d, J 23 Hz), 2.68 (H7', dd, J 6, 23 Hz), 2.92 (H4, t, J 8 Hz), 3.30 (H1, m), 3.95 ($CHPh_2$, d, J 10 Hz), 4.56 (CHOH, d, J 10 Hz), 5.13 (H2, H3, m), 5.78 (H5, d, J 8 Hz), 7.2 (10H, m, aromatic).

[8-Diphenylmethyl-(η-1–4)-heptafulvene]Fe(CO)$_3$ (IV)

A benzene solution of alcohol IX (240 mg, 0.56 mmol) and *p*-TsOH (5 mg) was heated under reflux for 1/2 h. Removal of the solvent and flash chromatography on silica gel (hexane) afforded orange red crystals of IV (pentane), m.p. 101–102°C, (125 mg, 54% yield). IR (KBr): 2025, 1950 (CO); m/e 382 (M − CO); Anal. Found: C, 70.43; H, 4.56. $C_{24}H_{18}FeO_3$ calcd.: C, 70.29; H, 4.39%. ^{1}H NMR see Table 1.

[8-Methoxy-(η-1–4)-heptafulvene]Fe(CO)$_3$ (V) was prepared as described before [11]. ^{1}H NMR see Table 1.

Acknowledgment

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