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FULL PAPER

Mechanistic studies on the iron-promoted deamination reactions of 7-azanorbornadiene derivatives

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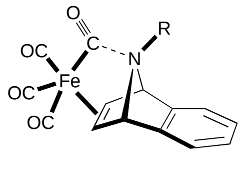
The reaction mechanism for the fragmentation of 7-azanorbornadiene derivatives (ANB; 7-azabicyclo[2.2.1]hepta-2,5-diene) mediated by iron carbonyl compounds was analyzed by substituent effects. The reactions proceed through two stages: a tetracarbonyliron complex (ANB)Fe(CO)$_4$ forms first followed by a tricarbonyliron complex (ANB)Fe(CO)$_3$. A linear free energy correlation was found for the decomposition of the latter group of complexes, which implied the existence of a polar transition state. The proposed mechanism was then confirmed by the isolation of new products from certain 2-tosyl ANB complexes in a related reaction.

In our previous studies of iron-promoted deamination reactions of 7-azanorbornadiene (ANB; 7-azabicyclo[2.2.1]hepta-2,5-diene) derivatives, two major types of metallic intermediates (ANB)Fe(CO)$_4$ (**1** or **3**) and (ANB)Fe(CO)$_3$ (**2** or **4**) have been identified.[1,2] The chemical reactivity of these complexes was found to depend heavily on the electronic properties of substituents at the N(7) position, *i.e.* elimination of nitrene moieties was most efficient with electron-withdrawing substituents appearing either at N(7) or at the C(2)=C(3) positions of ANB derivatives. Extended Hückel molecular orbital (EHMO) calculations showed that this substituent effect may be correlated with charge redistributions through the transition state.[3] In this report the kinetic data for a series of benzo-fused ANB derivatives are measured. Fitting these data into the Hammett equation can give information regarding the build-up of charge separation during the transition state,[4] so that answers for the following two questions may be realized: (1) does the nucleophilicity of nitrogen assist CO extrusion in the conversion of (ANB)Fe(CO)$_4$ to (ANB)Fe(CO)$_3$ (rate constant k_1) and (2) is C–N bond breakage in the nitrene extrusion process of (ANB)Fe(CO)$_3$ synchronous or stepwise (rate constant k_2)?



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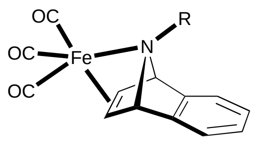
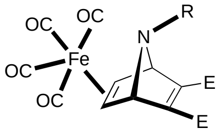


2

	R
a	H
b	$CO_2C_2H_5$
c	SO_2CH_3
d	Ph
e	*p*-$CH_3C_6H_4$
f	*p*-$CF_3C_6H_4$
g	*p*-$CH_3OC_6H_4$
h	*p*-FC_6H_4
i	*p*-ClC_6H_4
j	*p*-BrC_6H_4
k	*p*-IC_6H_4



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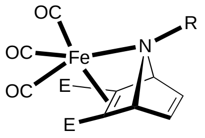


4

	R	E
a	SO_2CH_3	CO_2CH_3
b	*p*-$SO_2C_6H_4CH_3$	CO_2CH_3
c	$COCH_3$	CO_2CH_3
d	$CO_2C_2H_5$	CO_2CH_3

Results and Discussion

For some ANB derivatives only one of the two types of metal complexes, *e.g.* either **1** or **2**, is isolable during the course of reaction depending on the relative magnitudes of k_1 or k_2. However, complexes **2** may be prepared from **1** by reacting with amine *N*-oxides.[5] Kinetic analyses of complexes **1** and **2** were performed by measuring the integrals of specific ^1H signals from their NMR spectra. The rates of reaction were found to follow strictly the first-order rate law, and the rate constants k_1 and k_2 are listed in Tables 1 and 2 respectively.

Carbonyl extrusion reactions

According to the crystal geometries of **1c** (R = SO_2CH_3), **1e** (R = *p*-$CH_3C_6H_4$) and **1i** (R = *p*-ClC_6H_4), the axial Fe–C≡O angles bend away from atom N(7) forming angles of 161.1°, 162.9° and 168.2° respectively.[5] The amounts of deviation from linearity are roughly proportional to their calculated (EHMO) charges on N(7), *i.e.* −0.48, −0.46 and −0.37.[3] The distance between the carbon of the axial Fe–C≡O moiety N(7) is in the range 2.26–2.57 Å,[6] significantly shorter than the sums of their van der Waals radii. This implies the existence of an interaction between the two atoms; but the question is whether this interaction accelerates the extrusion of CO.[7]

The rates of decarbonylation (k_1) of six *para*-substituted phenyl derivatives of **1** were measured in C_6D_6 at 70 °C (Table 1). The correlation between log(k_1) and σ_p values is plotted in Fig. 1.[8] The random scattering of points along a horizontal level indicates that the CO extrusion rates were insensitive to the substituents on N(7). The observed interaction between N(7) and CO occurring in the crystalline state did not seem to persist in solution. In solution the CO ligands exchange rapidly so that the four CO absorptions in the ^{13}C NMR spectra coalesce to one peak at room temperature.

Table 1 Rates of decarbonylation of (ANB)Fe(CO)$_4$ **1** in C_6D_6 at 70 °C

	R	$10^4\,k_1$/s^{-1}	r*	log(k)	σ_p
1k	C_6H_4I	1.19	0.998	−3.92	0.28
1j	C_6H_4Br	0.781	0.982	−4.11	0.26
1i	C_6H_4Cl	2.03	0.9998	−3.69	0.24
1d	C_6H_4H	2.05	0.991	−3.69	0.0
1e	$C_6H_4CH_3$	1.45	0.998	−3.84	−0.14
1g	$C_6H_4OCH_3$	1.78	0.996	−3.75	−0.12

* Linear correlation coefficient.

Table 2 Rates of deamination of (ANB)Fe(CO)$_3$ **2** in C_6D_6 at 70 °C

	R	$10^5\,k_2$/s^{-1}	r*	log(k/k_H)	σ_p
2f	$C_6H_4CF_3$	30.9	0.998	0.90	0.53
2k	C_6H_4I	12.3	0.998	0.50	0.28
2j	C_6H_4Br	10.2	0.994	0.42	0.26
2i	C_6H_4Cl	7.69	0.996	0.30	0.24
2h	C_6H_4F	2.95	0.99	−0.12	0.15
2d	C_6H_5	3.89	0.987	0.0	0.0
2e	$C_6H_4CH_3$	2.33	0.992	−0.22	−0.14
2g	$C_6H_4OCH_3$	1.97	0.995	−0.30	−0.12
2a	H	2.2 (decomp.)			
2b	$CO_2C_2H_5$	1.9 1.3 (decomp.)			

* Linear correlation coefficient.

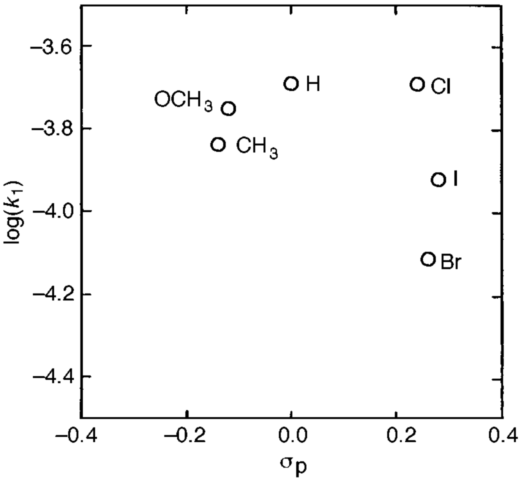


Fig. 1 Plot of log(k_1) *vs.* σ_p for several *para*-substituted phenyl derivatives of complexes **1** (relating to their conversion into complexes **2**). A linear correlation between the two parameters is not observed

The interaction with solvents may have played a more significant role than the N-substituent in the CO extrusion process. It was found in Table 3 that the decomposition of **3a** proceeded 10 times faster in CD_3CN than in C_6D_6, however changing the N-substituent from SO_2CH_3 (**3a**) to *p*-$SO_2C_6H_4CH_3$ (**3b**) has nearly no effect on the rate. Solvent molecules capable of acting as stronger ligands (*e.g.* CH_3CN *vs.* C_6D_6) showed a promoting effect for the depletion of CO.

Nitrene extrusion reactions[9]

Our previous works indicated that the rates of nitrene extrusion are proportional to the electron-withdrawing ability of N(7)-substituents as shown in Table 3 for **4a** (R = SO_2CH_3), **4b** (R = *p*-$SO_2C_6H_4CH_3$) and **4c** (R = $COCH_3$).[1] The EHMO calculations indicated that strong electron-withdrawing groups reduce the electron density on N and weaken the N(7)–C(1,4) bonds.[3] For derivatives of ANB without strong electron-withdrawing groups on N, *i.e.* R = H or Ph, the reactions do not proceed at all at 60 °C.[1a]

Table 3 Rates of reaction of complexes **3** and **4** at 60 °C

	R	k/s^{-1}	Solvent
3a	SO_2CH_3	2.0×10^{-3}	CD_3CN
3a	SO_2CH_3	1.8×10^{-4}	C_6D_6
3b	*p*-$SO_2C_6H_4CH_3$	2.0×10^{-4}	C_6D_6
4a*	SO_2CH_3	2.8×10^{-5}	CD_3CN
4b*	*p*-$SO_2C_6H_4CH_3$	1.9×10^{-5}	CD_3CN
4c*	$COCH_3$	6.0×10^{-6}	CD_3CN

* Data collected from ref. 1(*b*).

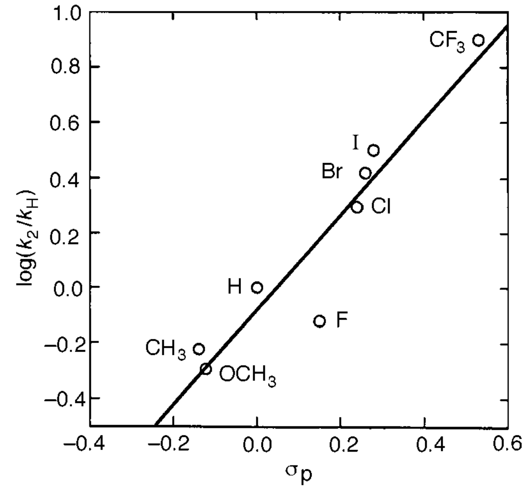


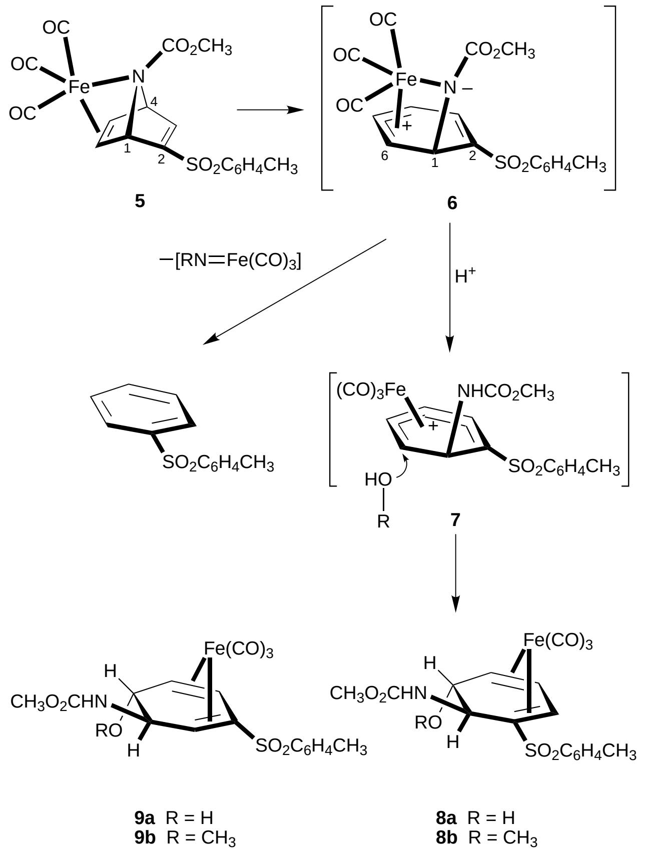
Fig. 2 Plot of log(k_2/k_H) *vs.* σ_p for several *para*-substituted phenyl derivatives of complexes **2** (relating to their fragmentation reactions). A liner correlation is observed with ρ approximately 1.5

However this information is not sufficient to allow us to draw conclusions on the mechanism of the reactions. The bond breakage may proceed *via* two types of mechanisms: in a concerted pathway, the two N(7)–C(1,4) bonds break synchronously to expel a metallic nitrene complex. Previous attempts at trapping such a complex were unsuccessful, although in most cases high yields of the amine were collected after aqueous work-up procedures.[1a] In an alternative mechanism one N–C bond breaks before the other in a stepwise manner to produce either a biradical or a zwitterionic intermediate. Placing appropriate substituents on the nitrogen atom would have a limited stabilizing effect on the intermediate.

A plot of log(k_2/k_H) *versus* σ_p values (Table 2) for seven *para*-substituted phenyl derivatives of **2** is shown in Fig. 2. A fairly good linear correlation was obtained with ρ *ca.* 1.5. As expected the slope of the line indicates that the reactions proceed faster for derivatives containing electron-withdrawing groups. The results complied well with earlier observations for **4a**–**4c** (Table 3), and implied the existence of a polar intermediate. The negative electron density developed on nitrogen upon heterolytic bond fission can delocalize over the N-substituents.

Ring-opening rearrangement

In an attempt to trap the polar intermediate mentioned above, we prepared 7-methoxycarbonyl-2-tosyl-7-azanorbornadiene in which the electron-withdrawing substituent at C(2) may be helpful in stabilizing the transition state. In the reaction with nonacarbonyl diiron in tetrahydrofuran (THF), a series of products were isolated including the two isomeric η^2 iron carbonyl complexes (**5** and another *exo*-co-ordinated isomer), phenyl tolyl sulfone, and two η^4 iron carbonyl complexes **8a** and **9a** (Scheme 1). Phenyl tolyl sulfone was formed from **5** *via* nitrene elimination as previously observed, whereas complexes **8a** and **8b** were derived from **5** *via* rearrangement with the addition of a solvent molecule. For both processes a transient



Scheme 1

intermediate **6** is proposed, which exists as a common intermediate. In the presence of water, protonation at N(7) of **6** occurred first followed by Fe–N bond fission to form complex **7**. Iron carbonyl salts similar to **7** have been identified previously[10] and are usually susceptible to nucleophilic attack. A water molecule approaches atom C(6) of **7** from the opposite direction to the metal, as a result a transoid geometry for $NHCO_2CH_3$ and OR is found in the product. The yields of phenyl tolyl sulfone and **8a** are comparable in this reaction. The geometry of **8a** was confirmed by an X-ray crystal diffraction analysis. Am ORTEP[11] drawing of **8a** is shown in Fig. 3, and some selected bond lengths and angles are given in Table 4.

The ring-opening reaction of complex **5** was also examined in methanol, in which the corresponding methanol adduct **8b** was found (derived from the same mechanism described for **8a** above). The ^1H NMR spectrum of **8b** shows five well separated multiplets at δ 3.0, 3.2, 3.5, 5.5 and 6.2, where the latter two low-field signals correspond to the olefinic C(2) ad C(3) atoms. The NMR signals for the terminal C and H atoms of a diene [C(1,4)] co-ordinated to $Fe(CO)_3$ are generally shifted to higher field with respect to the inner C and H nuclei [C(2,3)].[10] The NMR spectral pattern of **8b** is quite similar to that of **8a**, with the exception of the OCH_3 group of the former complex giving a broadened peak at δ 3.6. The peak broadening may be ascribed to slow conformational changes with respect to the NMR time-scale.[12]

The appearance of complexes **9a** and **9b** in these reactions reveals further details on the mechanism. They are structural isomers of **8a** and **8b** with the tosyl group shifted from C(1) to C(2). The ^1H NMR spectrum of complex **9b** shows five signals for the protons on the ring, one at δ 6.0 [H(2)] and four at δ 3.1–3.4. A two-dimensional ^1H correlation (COSY) NMR spectroscopic analysis established their relative positions on the ring, while the corresponding positions of the five carbons are obtained by a two-dimensional ^1H–^{13}C COSY spectrum. The chemical shift of C(2) (δ 88.54) is found to be larger than those of C(3) (δ 58.45) and C(6) (δ 55.69) as a result of metal co-ordination. Complexes **9a** or **9b** are derived from **5** by the same mechanism as that of **8a** or **8b**, *i.e.* the former complexes are formed from **5** by breaking of the C(4)–N bond whereas the latter complexes formed by breaking of the C(1)–N bond instead. The isolation of complexes **8a**, **8b** and **9a**, **9b** provides direct evidence for heterolytic C–N bond fission in the nitrene elimination mechanism.

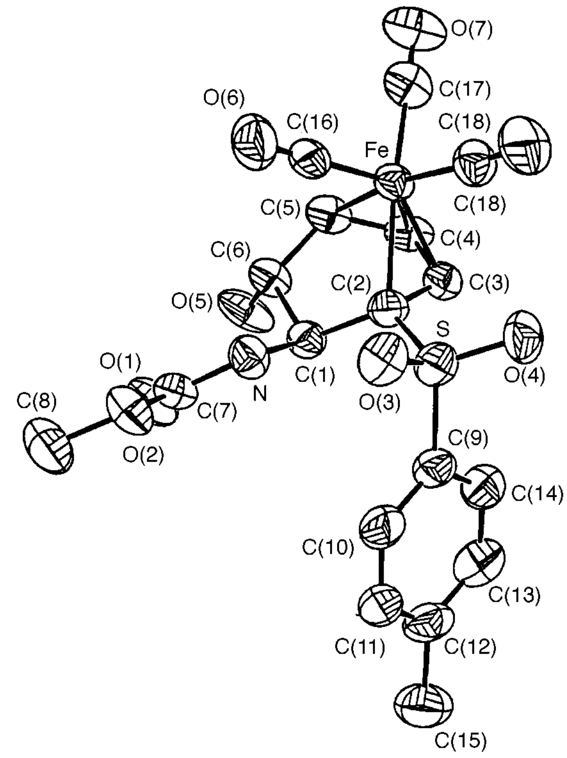


Fig. 3 An ORTEP drawing of complex **8a** with the numbering scheme. Hydrogens are omitted for clarity. The $NHCO_2CH_3$ moiety on C(1) is transoid to the OH on C(6)

Table 4 Selected bond lengths (Å) and angles (°) of complex **8a**. Standard deviations in parentheses

Fe–C(2)	2.091(7)	Fe–C(3)	2.037(7)
Fe–C(4)	2.047(7)	Fe–C(5)	2.083(7)
C(1)–C(2)	1.53(1)	C(1)–C(6)	1.56(1)
C(2)–C(3)	1.45(1)	C(3)–C(4)	1.37(1)
C(4)–C(5)	1.43(1)	C(5)–C(6)	1.50(1)
C(1)–N	1.45(1)	C(7)–N	1.34(1)
C(7)–O(1)	1.22(1)	C(7)–O(2)	1.33(1)
C(2)–S	1.769(7)	C(9)–S	1.776(7)
S–O(3)	1.448(5)	S–O(4)	1.441(5)
C(1)–C(2)–C(3)	117.5(6)	C(1)–C(6)–C(5)	112.6(5)
C(2)–C(1)–C(6)	108.9(5)	C(2)–C(3)–C(4)	114.5(6)
C(3)–C(4)–C(5)	116.1(6)	C(4)–C(5)–C(6)	120.1(6)
C(5)–C(6)–O(5)	108.1(5)	C(1)–N–C(7)	119.5(6)
C(2)–C(3)–C(4)–C(5)	2.2(4)	C(4)–C(5)–C(6)–C(1)	36.4(4)
C(1)–C(2)–S–O(4)	166.9(6)	C(3)–C(2)–S–O(4)	25.2(3)
C(1)–N–C(7)–O(1)	−6.4(3)	C(1)–N–C(7)–O(2)	174.9(8)

Conclusion

The result of linear free energy correlation indicates that the extrusion of CO from tetracarbonyliron complexes **1** and **3** is independent of the influence of N(7). The nitrene extrusions of **2** and **4**, however, depend on the electronic property of N(7). An electron-withdrawing substituent on N(7) stabilizes the zwitterionic intermediate **6**, thus accelerating the rate of reaction. The C–N bond breakage proceeds *via* a stepwise mechanism.

Experimental

General

Proton and ^{13}C NMR spectra were obtained on either Bruker AC-200 or AC-300 FT spectrometers. Chemical shifts for ^{1}H and ^{13}C NMR spectra are recorded downfield from SiMe$_4$, IR spectra on a Perkin-Elmer 882 infrared spectrophotometer, elemental analyses on a Perkin-Elmer 2400 EA instrument and mass spectra were carried out on a JEOL SX-102A spectrometer. Melting points were measured by a Yanato MICRO m.p. apparatus model MP-S3 and are uncorrected.

The spectroscopic data for compounds **1a**, **1d**, **1e**, **1h**–**1k**,[12] **1b**,[1,5] **1c**, **1e**, **1i**,[6] **2a**, **2b**,[1,5] **2a**, **2d**, **2e**, **2h**–**2k**,[13] **3a**, **3c**, **3d**,[1,5] **3b**,[5] **4a**, **4c**, **4d**[1,5] and **4b**[5] have been published elsewhere.

Syntheses

Tetracarbonyl- and tricarbonyl-[1,4-dihydro-1,4-(*p*-trifluoromethylphenylimino)naphthalene]iron 1f and 2f. To a three-necked round-bottomed flask fitted with a condenser and two dropping funnels was added *N*-(*p*-trifluoromethylphenyl)pyrrole (5.00 g, 23.7 mmol) in THF (30 cm^3). The solution was heated to reflux, and from the dropping funnels were added simultaneously two kinds of THF solutions (20 cm^3 each): one containing isopentylnitrile (2.90 g, 24.7 mmol) and the other *o*-aminobenzoic acid (3.3 g, 24 mmol). After the addition the resulting mixture was heated to reflux for 3 h. The solvent was evaporated *in vacuo*, and the product dissolved again in CH$_2$Cl$_2$. It was washed with 10% NaOH followed by distilled water (50 cm^3 × 2), dried over anhydrous MgSO$_4$, then concentrated. 1,4-Dihydro-1,4-(*p*-trifluoromethylphenylimino)naphthalene was purified by passing through a silica gel column chromatograph eluted with hexane–ethyl acetate (5:1) and was recrystallized from CH$_2$Cl$_2$–hexane (yield 3.34 g, 53.3%), m.p. 102–102.5 °C (Found: C, 70.80; H, 4.36; N, 4.92. Calc. for C$_{17}$H$_{12}$F$_3$N: C, 71.08; H, 4.21; N, 4.88%); ν/cm^{-1} 3077, 3026, 1599, 1506, 1445, 1417 (KBr); δ_H(200 MHz, CDCl$_3$) 5.45 (d, 2 H, *J* 1), 6.84 (d, 2 H, *J* 8), 6.90–6.94 (m, 2 H), 6.96 (m, 2 H), 7.23–7.27 (m, 2 H), 7.40 (d, 2 H, *J* 8 Hz); δ_C(50 MHz, CDCl$_3$, ^{1}H decoupled) 68.81, 117.17, 121.51, 122.66 (q, weak, CF$_3$), 125.09, 126.10, 141.97, 147.98, 149.67; electron impact (EI) mass spectrum: *m*/*z* 287 (*M*$^+$, 100), 268 (8), 261 (12), 246 (2), 233 (2), 217 (16%). The above compound (320 mg, 1.11 mmol) and nonacarbonyl diiron (575 mg, 1.58 mmol) were dissolved in degassed THF (110 cm^3) in a two-necked round-bottomed flask under nitrogen. The solution was stirred magnetically for 18 h at room temperature. It was filtered through Celite and concentrated *in vacuo*. The iron carbonyl complexes **1f** (252 mg, 0.55 mmol, 49.7%) and **2f** (88 mg, 0.206 mmol., 18.5%) were separated by a silica gel chromatograph eluted with hexane–ethyl acetate. Physical data for **1f**: ν/cm^{-1} 2075, 2008, 1975 (neat); δ_H(300 MHz, CDCl$_3$) 3.53 (s, 2 H), 4.91 (s, 2 H), 6.77 (d, 2 H, *J* 8), 6.98–7.01 (m, 2 H), 7.22–7.26 (m, 2 H), 7.37 (d, 2 H, *J* 8 Hz); δ_C(75 MHz, CDCl$_3$, ^{1}H decoupled) 60.89, 67.29, 118.10, 122.29, 123.26 (q, weak, CF$_3$), 126.20, 126.24, 126.48, 145.27, 146.32, 209.60; FAB mass spectrum (Fe = 56): *m*/*z* 456 (2, *M*$^+$ + 1), 427 (26, *M*$^+$ − CO), 399 (64, *M*$^+$ − 2CO), 371 (64, *M*$^+$ − 3CO), 343 (100, *M*$^+$ − 4CO), 307 (15), 288 (24%). Physical data for **2f** [Found: C, 56.51; H, 2.87; N, 3.25%; high resolution mass spectrum (HRMS): *M* 427.0114. C$_{20}$H$_{12}$F$_3$FeNO$_3$ requires C, 56.24; H, 2.83; N, 3.28%; *M* 427.0119]; ν/cm^{-1} (CO) 2030, 1934 (KBr); δ_H(300 MHz, CDCl$_3$) 4.20 (m, 2 H), 5.77 (m, 2 H), 6.94 (d, 2 H, *J* 8), 7.10–7.17 (m, 4 H), 7.38 (d, 2 H, *J* 8 Hz); δ_C(75 MHz, CDCl$_3$, ^{1}H decoupled) 48.86, 84.25, 119.17, 120.90, 126.43, 127.40, 146.69, 147.10, 213.13; FAB mass spectrum (Fe = 56): *m*/*z* 427 (22, *M*$^+$), 399 (63, *M*$^+$ − CO), 371 (64, *M*$^+$ − 2CO), 343 (100, *M*$^+$ − 3CO), 288 (22%).

Tetracarbonyl- and tricarbonyl-[1,4-dihydro-1,4-(*p*-methoxyphenylimino)naphthalene]iron (1g and 2g). 1,4-Dihydro-1,4-(*p*-methoxyphenylimino)naphthalene was synthesized similarly from *N*-(*p*-methoxyphenyl)pyrrole in 23.2% yield, which was recrystallized from ethyl acetate–hexane; m.p. 86–87 °C (Found: C, 81.73; H, 6.09; N, 5.23. C$_{17}$H$_{15}$NO requires C, 81.90; H, 6.06; N, 5.62%); ν/cm^{-1} 3071, 3049, 3013, 2982, 2951, 2901, 2845, 1583, 1500, 1465, 1449, 1437 (KBr); δ_H(200 MHz, CDCl$_3$) 3.70 (s, 3 H), 5.33 (t, 3 H, *J* 1 Hz), 6.74 (s, 2 H), 6.75 (s, 2 H), 6.90–6.94 (m, 4 H), 7.23–7.27 (m, 2 H); δ_C(75 MHz, CDCl$_3$, ^{1}H decoupled) 55.30, 69.86, 114.08, 119.25, 121.45, 124.83, 140.62, 141.66, 148.56, 154.04; EI mass spectrum: *m*/*z* 249 (100, *M*$^+$), 234 (82), 217 (5), 206 (14%).

The iron complexes **1g** and **2g** were prepared by the reaction of this compound (53 mg, 0.213 mmol) with Fe$_2$(CO)$_9$ (100 mg, 0.275 mmol) according to previously mentioned procedure to yield 54 mg (0.22 mmol, 61%) and 17 mg (0.044 mmol, 20%) respectively. Physical data for **1g**: ν/cm^{-1} 2067, 1976 (CH$_2$Cl$_2$); δ_H(300 MHz, CDCl$_3$) 3.51 (s, 2 H), 3.67 (s, 3 H), 4.70 (s, 2 H), 6.64 (dm, 2 H, *J* 12), 6.70 (dm, 2 H, *J* 12 Hz), 6.98 (m, 2 H), 7.19 (m, 2 H); δ_C(75 MHz, CDCl$_3$, ^{1}H decoupled) 55.22, 61.13, 67.52, 114.34, 120.14, 122.43, 126.42, 135.40, 144.96, 154.95, 210.16; FAB mass spectrum (Fe = 56): *m*/*z* 418 (2, *M*$^+$ + 1), 389 (7, *M*$^+$ − CO), 361 (16, *M*$^+$ − 2CO), 333 (24, *M*$^+$ − 3CO), 305 (100, *M*$^+$ − 4CO), 249 (17%). Physical data for **2g** (HRMS: *M* 389.0355. C$_{20}$H$_{15}$FeNO$_4$ requires 389.0351); ν/cm^{-1} 2016, 1923 (KBr); δ_H(200 MHz, CDCl$_3$) 3.65 (s, 3 H), 4.13 (t, 2 H, *J* 1), 5.64 (t, 2 H, *J* 1), 6.60 (dm, 2 H, *J* 9), 6.75 (dm, 2 H, *J* 9 Hz), 7.08–7.13 (m, 4 H); δ_C(50 MHz, CDCl$_3$, ^{1}H decoupled) 48.93, 55.29, 84.86, 114.21, 119.10, 122.01, 127.18, 136.75, 147.27, 157.12, 213.69; FAB mass spectrum (Fe = 56): *m*/*z* 389 (18, *M*$^+$), 361 (25, *M*$^+$ − CO), 333 (32, *M*$^+$ − 2CO), 305 (100, *M*$^+$ − 3CO), 249 (12%).

Tricarbonyl{methyl *N*-[(6-hydroxy-2-tosyl)cyclohexa-2,4-dienyl]carbamate}iron 8a and tricarbonyl{methyl *N*-[(6-hydroxy-3-tosyl)cyclohexa-2,4-dienyl]carbamate}iron 9a. To a round-bottomed flask fitted with a condenser was added *N*-(methoxycarbonyl)pyrrole (3.24 g, 26 mmol) and ethynyl tolyl sulfone (1.17 g, 6.5 mmol). The mixture was heated to 80–85 °C under argon atmosphere for 10 h. The resulting mixture was purified by a silica gel column chromatograph eluted with ethyl acetate–hexane (1:4). 7-Methoxycarbonyl-2-tosyl-7-azanorbornadiene (1.21 g, 61%) was recrystallized from ethyl acetate–hexane, m.p. 91.5–92.3 °C (Found: C, 59.01; H, 4.94; N, 4.52. C$_{15}$H$_{15}$NO$_4$S requires C, 59.00; H, 4.95; N, 4.59%); ν/cm^{-1} 3275, 3064, 2958, 2852, 1943, 1727, 1594, 1588, 1557, 1442, 1329, 1315, 1288, 1261.9 (KBr); δ_H(300 MHz, CDCl$_3$) 2.45 (s, 3 H), 3.5 (m, 3 H), 5.22 (s, 1 H), 5.44 (s, 1 H), 6.92 (m, 1 H), 6.96 (m, 1 H), 7.33 (d, 2 H, *J* 8), 7.62 (m, 1 H), 7.75 (d, 2 H, *J* 8 Hz); δ_C(75 MHz, CDCl$_3$, ^{1}H decoupled) 21.49, 52.72, 66.36, 67.62, 127.85, 129.87, 135.28, 141.69, 143.25, 144.84, 151.66, 154.78, 158.82. This compound (305 mg, 1 mmol) was allowed to react with nonacarbonyldiiron (472 mg, 1.29 mmol) in wet THF (80 cm^3 containing *ca.* 1% H$_2$O) at room temperature for 10 h, then under reflux for another 24 h. The resulting mixture was filtered, and the filtrate was concentrated *in vacuo*. The yellow residue was purified by passing through a silica gel column chromatograph eluted with ethyl acetate–hexane (1:2). Complex **8a** (71 mg, 21%) and **9a** (35 mg, 10%) were recrystallized from CH$_2$Cl$_2$–hexane. An amount of phenyl tolyl sulfone (44 mg, 26%) was also obtained. Physical data for **8a**: m.p. 175–177 °C (decomp.) (Found: C, 46.56; H, 3.71; N, 2.90. C$_{18}$H$_{17}$FeNO$_8$S requires C, 46.67; H, 3.70; N, 3.02%); ν/cm^{-1} 3500, 3395, 2958, 2076, 2018, 1696 (CDCl$_3$); δ_H(CDCl$_3$, 300 MHz) 2.42 (s, 3 H), 2.62 (s, 1 H, =CHN), 3.18 (m, 1 H), 3.68 (s, 3 H), 4.01 (s, 1 H, =OCH), 5.54 (t, 1 H, *J* 5), 6.14 (d, 1 H, *J* 4), 6.64 (s, 1 H, NH), 7.31 (d, 2, H, *J* 8), 7.68 (d, 2 H, *J* 8 Hz); δ_C(CDCl$_3$, 75 MHz, ^{1}H decoupled) 21.62 (CH$_3$), 52.58 (OCH$_3$), 56.07 (=CHN), 60.36, 75.72 (=CHS), 80.36 (=CHO), 85.96, 86.49, 127.80, 130.10, 134.40, 145.07, 157.40. Physical data for **9a**: m.p. 163–165 °C (decomp.) (Found: C, 46.50; H, 3.54; N, 2.82. C$_{18}$H$_{17}$FeNO$_8$S requires C, 46.67; H, 3.70; N, 3.02%);

ν/cm^{-1} 2072, 2005, 1702 (CDCl$_3$); δ_H(CDCl$_3$, 300 MHz) 2.46 (s, 3 H), 2.98 (m, 1 H, =CHN), 3.03 (s, 1 H), 3.16 (m, 1 H), 3.56 (br, 1 H, OH), 3.66 (s, 3 H), 3.90 (s, 1 H, =CHO), 5.01 (m, 1 H), 6.02 (d, 1 H, *J* 6), 7.39 (d, 1 H, *J* 8), 7.89 (d, 2 H, *J* 8 Hz); δ_C(CDCl$_3$, 75 MHz, ^{1}H decoupled) 21.66, 51.04, 52.58 (OCH$_3$), 55.34 (=CHN), 61.63, 79.09 (=CHO), 89.28, 105.35 (=CHS), 127.72, 130.41, 136.97, 145.25, 157.56, 207.61.

Tricarbonyl{methyl *N*-[(6-methoxy-2-tosyl)cyclohexa-2,4-dienyl]carbamate}iron 8b and tricarbonyl{methyl *N*-[(6-methoxy-3-tosyl)cyclohexa-2,4-dienyl]carbamate}iron 9b. The procedure was similar to that for **8a** and **9a**, but using methanol as a solvent. The compounds ANB (366 mg, 1.2 mmol), nonacarbonyl diiron (612 mg, 1.68 mmol) and MeOH (80 cm^3) were heated at 70 °C for 24 h to yield **8b** (54.4 mg, 9.5%), **9b** (78 mg, 13.6%) and phenyl tolyl sulfone (44 mg, 16%). The iron complexes were recrystallized from CH$_2$Cl$_2$–hexane. Physical data for **8b** m.p. 183–185 °C (decomp.) (Found: C, 47.69; H, 4.00; N, 2.82. C$_{19}$H$_{19}$FeNO$_8$S requires C, 47.82; H, 4.01; N, 2.93%); ν/cm^{-1} 3422, 2931, 2074, 2017, 1727 (CDCl$_3$); δ_H(CDCl$_3$, 300 MHz) 2.42 (s, 3 H), 2.95 (d, 1 H, *J* 6), 3.21 (m, 1 H), 3.25 (s, 3 H), 3.51 (m, 1 H), 3.64 (br, 3 H), 5.52 (t, 1 H, *J* 5), 5.89 (br, 1 H, NH), 6.21 (d, 1 H, *J* 5), 7.30 (d, 2 H, *J* 8), 7.66 (d, 2 H, *J* 8 Hz); δ_C(CDCl$_3$, 75 MHz, ^{1}H decoupled) 21.66 (CH$_3$), 52.17 (OCH$_3$), 54.08 (=CHN), 57.79 (OCH$_3$), 57.96, 79.24 (=CHS), 84.31, 87.95, 88.65 (=CHO), 127.85, 130.04, 134.24, 144.88, 155.21. Physical data for **9b** m.p. 177–179 °C (decomp.) (Found: C, 47.56; H, 4.09; N, 2.73. C$_{19}$H$_{19}$FeNO$_8$S requires C, 47.82; H, 4.01; N, 2.93%); ν/cm^{-1} 3441, 2931, 2071, 2016, 1728 (CDCl$_3$); δ_H(CDCl$_3$, 300 MHz) 2.47 (s, 3 H), 3.13 (m, 1 H), 3.19 (s, 3 H), 3.29 (s, 1 H), 3.31 (m, 1 H), 3.38 (s, 1 H), 3.70 (s, 3 H), 4.76 (dm, 1 H, *J* 8), 6.02 (d, 1 H, *J* 6), 7.41 (d, 2 H, *J* 8), 7.92 (d, 2 H, *J* 8 Hz); δ_C(CDCl$_3$, 75 MHz, ^{1}H decoupled) 21.67, 52.15 (=CHN), 52.35 (OCH$_3$), 55.69, 57.59 (OCH$_3$), 58.45, 86.81, 88.54, 105.71, 127.73, 130.40, 137.06, 145.14, 155.68, 207.88.

NMR kinetic measurements for the thermolyses of iron carbonyl complexes.

An NMR tube (outside diameter 5 mm) containing C$_6$D$_6$ was filled with the tetracarbonyliron complex **1** or tricarbonyliron complex **2** and cyclooctaquinane (heptacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{4,11}.0^{5,9}.0^{10,14}]tetradecane)[14] as an internal standard (singlet at δ 1.83). The tube was sealed and immersed in a thermostatted oil bath maintained at 70 ± 0.5 °C. The disappearance of the metal complex was monitored by its ^{1}H NMR signal integrations. The tube was periodically withdrawn from the oil bath and subjected to spectroscopic measurement after cooling and filtration. The signals used for kinetic measurements are those of the olefin hydrogens (δ 3.0 for **1**, 3.8 for **2**) and the bridgehead hydrogens (δ 4.02 for **1**, 5.10 for **2**) of the metal complexes and the signal at δ 7.60 for naphthalene. In these regions the absorption peaks are generally well separated. The measurements were completed at *ca.* 80% consumption of the starting materials.

Crystallography

Crystal structure of complex 8a. C$_{18}$H$_{17}$FeNO$_8$S, $M = 463.24$, crystal dimensions: 0.39 × 0.20 × 0.27 mm, monoclinic *C*2/*c*, $a = 32.242(5)$, $b = 9.1126(19)$, $c = 13.399(3)$ Å, $\beta = 99.005(14)°$, $U = 3888.3(12)$ Å^3, $Z = 8$, $F(000) = 1904$, $D_c = 1.583$ g cm^{-3}.

Data collection and refinement. Cell dimensions were obtained from 20 reflections with 2θ angles in the range 20.24–35.54°. $\mu = 7.65$ mm^{-1}, $\lambda = 1.540\,56$ Å, $2\theta_{(max)} = 120.0°$. The intensity data were collected on a Nonius diffractometer using the θ–2θ scan method. The *hkl* ranges were: $-36 < h < 35$, $0 < k < 10$, $0 < l < 15$. There are 2952 reflections measured, among which 2854 were unique and 1773 with $I_o > 2.0\ \sigma(I_o)$. Absorption corrections were made, and the minimum and maximum transmission factors were 0.765 400 and 0.998 900 respectively. The last least-squares cycle was calculated with 46 atoms, 262 parameters and 1773 of 2894 reflections. Weights based on counting statistics were used; the weight modifier *K* in KF_o^2 is 0.000 100. The residuals for significant reflections were $R_f = 0.055$, $R' = 0.059$, goodness of fit, $S = 1.58$, and for all reflections $R_f = 0.111$, $R' = 0.088$, in which $R_f = \Sigma(F_o - F_c)/\Sigma(F_o)$, $R' = \Sigma w(F_o - F_c)^2/\Sigma(wF_o^2)$, and $S = \Sigma w(F_o - F_c)^2/$(no. of reflections − no. of parameters). The maximum Δ/σ ratio was 0.014. In the last density map, the deepest hole was −0.340 and the highest peak 0.530 e Å^{-3}.

CCDC reference number 186/776.

Acknowledgements

This work is supported by the National Science Council of the Republic of China.

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Received 4*th September* 1997; *Paper* 7/06467E