evaporated to dryness. The residue was extracted with $CHCl_3$ (30 mL), and the insoluble potassium salts were filtered off. The filtrate was evaporated to dryness, and the residue stirred with acetone (10 mL) to give complex III as a yellow solid (87% yield).

$Pd_2(\mu\text{-}SCN)_2L_2$. A suspension of I(10) (0.13 g, 0.196 mmol) and KSCN (0.3 g) in $CHCl_3$:acetone (2:1, 40 mL) was stirred at room temperature for 24 h. The yellow suspension was filtered, washed with water to remove the potassium salts and then with acetone, and dried to give an 82% yield of IV as a yellow solid.

Techniques. NMR spectra were recorded on a Varian XL-200 (^1H, 200 MHz) spectrometer. IR spectra were obtained on a Perkin-Elmer 599 spectrometer. Microanalyses were performed with a Perkin-Elmer 240 B microanalyzer. Molecular weights were measured in $CHCl_3$ solution with a Knauer vapor pressure osmometer (isopiestic method).

The textures of the mesophases were studied with a Meiji polarizing microscope equipped with a Mettler FP82 hot stage and FP80 central processor. Transition temperatures were measured by differential scanning calorimetry with a Perkin-Elmer DSC-2 operated at a scanning rate of 5 K/min on heating. The apparatus was calibrated with indium (429.6 K, 28.4 J/g) and tin (505.06 K, 60.46 J/g) as standards.

The thermogravimetric analysis were obtained on a Perkin-Elmer TGS-2 equipped with a System 4 microprocessor controller at a heating rate of 10 °C/min under nitrogen.

Acknowledgment. This work was financed by the E.E.C. (Project ST2J-0387-C) and the CICYT (Project No. PB86-0028).

Registry No. *trans*-I(2), 124919-60-4; *trans*-I(6), 124942-34-3; *trans*-I(7), 124919-61-5; *trans*-I(8), 124919-62-6; *trans*-I(9), 124919-63-7; *trans*-I(10), 124919-64-8; *trans*-I(12), 124919-65-9; *trans*-I(14), 124919-66-0; *cis*-I(2), 124942-35-4; *cis*-I(6), 124942-36-5; *cis*-I(7), 124942-37-6; *cis*-I(8), 124942-38-7; *cis*-I(9), 124942-39-8; *cis*-I(10), 121756-13-6; *cis*-I(12), 124942-40-1; *cis*-I(14), 124942-41-2; II, 124919-67-1; III, 124919-68-2; *trans*-IV, 124919-69-3; *cis*-IV, 124942-42-3.

Iron-Promoted Nitrene-Extrusion Reactions in 7-Azanorbornadiene Derivatives

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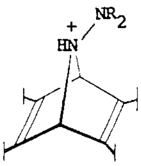
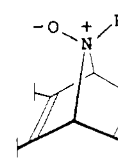
Nitrene-extrusion reactions are found to proceed in the thermolysis of a series of 7-azanorbornadiene derivatives (ANB) with diiron nonacarbonyl. Several intermediates of the structure $(ANB)Fe(CO)_3$ are isolated, and their geometries are identified by spectroscopic analyses. The nitrene-extrusion reactions proceed in excellent yields for the iron complexes, in which electron-withdrawing substituents appear at the C-2, C-3, and N-7 positions of ANB. However, when some of these substituents are removed, the efficiency of nitrene extrusion is reduced. The rates of reactions are measured and found to be related directly to the electronic nature of the substituents. The Fe–N bond distance also changes with respect to the N-7 substituents, as evidenced by the single-crystal X-ray diffraction analyses of (2,3-dicarbomethoxy-7-(methylsulfonyl)-ANB)$Fe(CO)_3$ and (2,3-dicarbomethoxy-7-phenyl-ANB)$Fe(CO)_3$. The benzo-fused ANB derivatives react in an analogous manner, whereas the 7-azanorbornene derivatives do not undergo the processes of deamination.

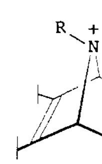
Nitrene-extrusion reactions in 7-azanorbornadiene (ANB) derivatives are of potential usefulness in organic synthesis for the preparation of aromatic products.[2,3] However, due to the lack of effective deamination reagents, these reactions have seldom been utilized in practical syntheses.[4] Recently it was found that certain ANB derivatives react with diiron nonacarbonyl to produce a series of complex adducts that, upon heating, undergo deamination reactions in high yields.[5] However, a prerequisite for these reactions is the existence of an electron-withdrawing substituent at the N-7 position. This condition accommodates perfectly the shortcomings of present deamination methods. Classical deamination methods generally require the presence of an electron-releasing group attached to the nitrogen,[6] yet such a requirement is unfavorable for pyrroles undergoing highly efficient Diels–Alder type cycloaddition reactions.[7,8] Moreover, classical deamination methods have to proceed through certain reactive intermediates such as the structures A–C.[2,6]



A



B



C

The yields, therefore, are limited due to the necessity of multistep treatments. In this report we provide, for the

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(1) (a) Soochow University. (b) Academia Sinica.

(2) (a) Wong, H. N. C.; Ng, T.-K.; Wong, T.-Y. *Heterocycles* **1983**, *20*, 1815. (b) Sha, C.-K.; Chuang, K.-S.; Wey, S.-J. *J. Chem. Soc., Perkin Trans. 1* **1987**, 977.

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(6) (a) Gribble, G. W.; Allen, R. W. *Tetrahedron Lett.* **1976**, 3673. (b) Gribble, G. W.; Allen, R. W.; LeHoullier, C. S.; Eaton, J. T.; Easton, N. R., Jr.; Slayton, R. I. *J. Org. Chem.* **1981**, *46*, 1025. (c) Carpino, L. A.; Padykula, R. E.; Barr, D. E.; Hall, F. H.; Krause, J. G.; Dufresne, R. F.; Thoman, C. J. *J. Org. Chem.* **1988**, *53*, 2565.

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0276-7333/90/2309-0560$02.50/0

Table I. Selected NMR Chemical Shifts (ppm) of ANB–Fe Complexes^a

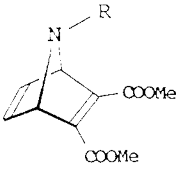
complex	nuclei	olefinic signals	complex	nuclei	olefinic signals
2a	^{1}H	6.70	**3a**	^{13}C	69.8, 146.4
2a	^{13}C	81.8, 140.6	**3c**	^{1}H	3.55
2b	^{1}H	6.69	**3d**	^{1}H	4.20
2b	^{13}C	79.1, 142.8	**3d**	^{13}C	45.9, 145.0
2c	^{1}H	6.60	**5c**	^{13}C	80.8
2c	^{13}C	80.3, 142.1	**5e**	^{13}C	57.5
2d	^{1}H	6.52	**7c**	^{1}H	3.55
2e	^{1}H	6.64	**7e**	^{1}H	4.01
2e	^{13}C	79.8, 143.9	**7e**	^{13}C	50.1
3a	^{1}H	3.50			

^{a} Spectra taken in $CDCl_3$. TMS was used as an internal standard for ^{1}H, and the center peak of $CDCl_3$ at δ 76.90 was used for ^{13}C.

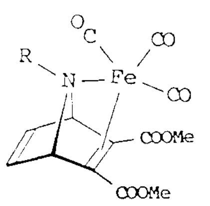
first time, a one-step method that can effectively extrude the nitrene possessing an electron-withdrawing substituent. The intermediates of these reactions are isolated, and their structures are identified by spectroscopic analyses. The kinetics of the deamination are rationalized on the basis of reaction rates and structure information collected from crystal diffraction analysis.

Results and Discussion

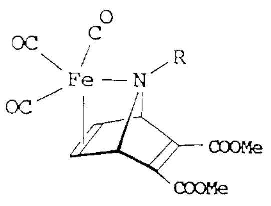
Nitrene-Extrusion Reactions. In a typical operation, the ANB derivative **1a**[9] and $Fe_2(CO)_9$ in ca. equal molar amounts were heated in THF at 60 °C for 24 h, and dimethyl phthalate was isolated from the resulting mixtures in 50% yield. During the reaction, two types of stable metal complexes were isolated and identified as structural isomers of $(\mathbf{1a})Fe(CO)_3$, i.e. **2a** and **3a**, where the metal is chelated on the exo sides of ANB ligands (Table I). Heating the purified sample of either **2a** or **3a** in acetonitrile at 60 °C produced dimethyl phthalate in 83 or 93% yield, respectively. Two other ANB derivatives (**1b** and **1c**) gave similar results, from which the iron complexes **2b**,**c** and **3c** were identified (Tables I and II). These results confirm that both **2a–c** and **3a**,**c** are intermediates of the deamination.[5]



1a, R = SO_2CH_3
b, R = $COCH_3$
c, R = $CO_2C_2H_5$
d, R = Ph



2a, R = SO_2CH_3
b, R = $COCH_3$
c, R = $CO_2C_2H_5$
d, R = Ph
e, R = H



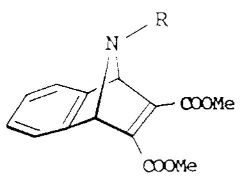
3a, R = SO_2CH_3
b, R = $COCH_3$
c, R = $CO_2C_2H_5$
d, R = Ph

Table II. Chemical Properties of ANB–Fe Complexes

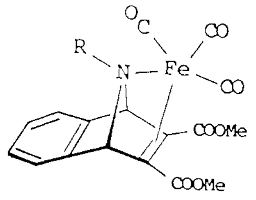
complex	yield of deamination, %	rate of deamination (CD_3CN, 60 °C), s^{-1} ^{a}	product of solvolysis^b
2a	83	2.8×10^{-5}	**2e**
2b	95	1.9×10^{-5}	**2e**
2c	100	6.0×10^{-6}	**2e**
2d	none^c		
2e	none^c		
3a	93	2.0×10^{-3}	dec
3d	24^d		
5c	96	2.6×10^{-5}	**5e**
5e	none^c		
7c	51^e	1.9×10^{-5}	dec
7e	none^f		

^{a} Substrates are sealed in an NMR tube, and the rates are measured according to ^{1}H signal integrations (see Experimental Section). ^{b} KOH in methanol at room temperature. ^{c} Starting materials recovered after heating at 60 °C for 18 h in CD_3CN. ^{d} 1-Phenylpyrrole was collected in 70% yield after heating at 60 °C in CD_3CN for 2 days. ^{e} Re-collection of **6c** in 38% yield at 60 °C with a rate constant $k = 1.3 \times 10^{-5}$ s^{-1}. ^{f} Re-collection of **6e** quantitatively with $k = 2.2 \times 10^{-6}$ s^{-1} at 60 °C.

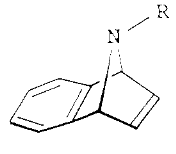
The reaction may be extended to other ANB derivatives, namely the benzo-fused derivatives **4c** and **6c**.[10] However, the deamination fails to work for the norbornene derivatives **8a** and **8c**. The iron carbonyl complex **9c** was isolated from the reaction of **8c**, but prolonged heating of **9c** destroyed the compound. It is apparent that the energy of aromatization provides the major driving force for the reaction.



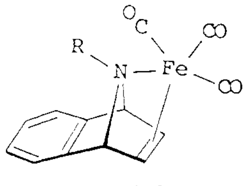
4c, R = $CO_2C_2H_5$
e, R = H



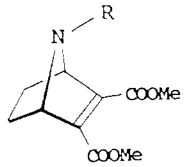
5c, R = $CO_2C_2H_5$
e, R = H



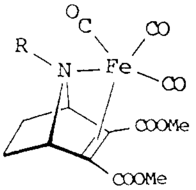
6c, R = $CO_2C_2H_5$
e, R = H



7c, R = $CO_2C_2H_5$
e, R = H



8a, R = SO_2CH_3
c, R = $CO_2C_2H_5$



9c, R = $CO_2C_2H_5$

Reactions of **4c** and **6c** with diiron nonacarbonyl produce **5c** and **7c**, respectively, with the iron coordinated to the olefin groups.[11] Thermolysis of **5c** yielded dimethyl 2,3-naphthalenedicarboxylate in 96% yield. This result

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(9) (a) Prinzbach, H.; Kaupp, G.; Fuchs, R.; Joyeux, M.; Kitzing, R.; Markert, J. *Chem. Ber.* **1973**, *106*, 3824. (b) Kitzing, R.; Fuchs, R.; Joyeux, M.; Prinzbach, H. *Helv. Chim. Acta* **1968**, *51*, 888. (c) Prinzbach, H.; Horst, B. *Heterocycles* **1978**, *11*, 113. (d) Frankel, M.; Gertner, D. *J. Chem. Soc.* **1961**, 459.

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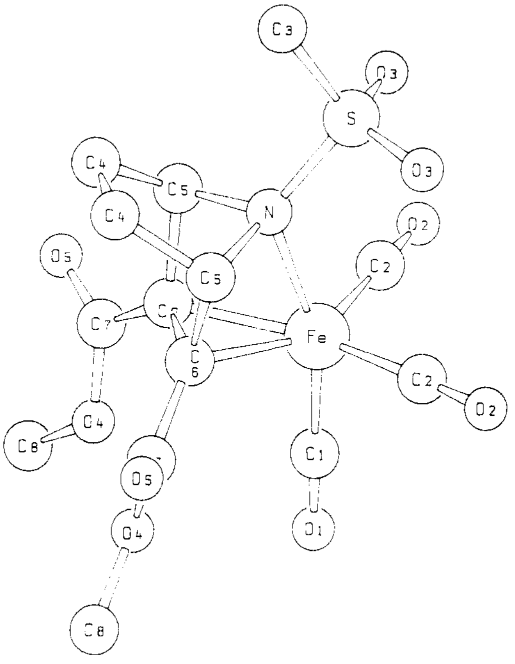

Figure 1. Molecular plot for **2a**. The H atoms are omitted for clarity.

is as good as that of **2c**, despite the structural difference between the two. The yield of naphthalene in the thermolysis of **7c** was 51%, somewhat lower than that of **5c**. This is due to the lower stability of **7c**, where dissociation competes with deamination (Table II); e.g., complex **6c** was recovered in 38% yield after the thermolysis.

The fate of the nitrene moieties that are extruded from ANB is worthy of special attention. It is believed that the nitrene moieties leaving their mother molecules are in a form of iron complexes, yet these complexes are not stable enough for isolation. For instance, a high yield of methanesulfonamide ($CH_3SO_2NH_2$, 90%) was obtained in the thermolysis of **3a**, which was produced from the iron–nitrene complex in the aqueous workup procedures. If the nitrene moiety is extruded from ANB molecules in a noncoordinated form, it ought to be intercepted by appropriate trapping agents such as olefins[12] as well as sulfoxides.[13] Several trapping experiments have been done in an attempt to collect such adducts but were all unsuccessful.

Structures of the Iron Carbonyl Complexes. In all the above-mentioned reactions only the exo-chelated iron complexes were observed.[14] The regiochemistry between each pair of isomers **2** and **3** can be resolved on the basis of their NMR spectroscopic characteristics. It is well-known for olefin–metal complexes that the NMR chemical shifts of olefinic ^1H as well as ^{13}C nuclei move significantly upfield upon coordination.[11,15] The chemical shift data for all the complexes are listed in Table I. Comparing the δ values of C(2,3) (or H(2,3)) with those of C(5,6) (or H-(5,6)), one can unambiguously assign the position of the metal. For example, the olefinic ^1H signal of **3a** (singlet at δ 3.50) appears at a higher field than that of **2a** (singlet at δ 6.70); likewise, the olefinic ^{13}C signal pattern of **2a** (a singlet at δ 81.8 and a doublet at δ 140.6) shows an analogous trend compared to those of **3a** (a doublet at δ 69.8 and a singlet at 146.4). These observations therefore settle the bonding positions between Fe and C=C. However, the bonding character between Fe and the nitrogen is still unclear by examining the NMR spectra. Therefore, single-crystal X-ray diffraction analyses of **2a** and **2b** were examined. It would be more worthwhile to examine the X-ray structures for two different isomers such as **2a**/**3a**

Table III. Crystal Data and Structure Refinement Details[a]

	2a	**2d**
solvent for crystallizn	methanol	ether/*n*-hexane
cryst size, mm	0.2 × 0.25 × 0.3	0.2 × 0.2 × 0.25
empirical formula	$C_{14}H_{13}FeNO_9S$	$C_{19}H_{15}FeNO_7$
fw	427.02	425.03
space group	*Pnma*	$P\bar{1}$
a, Å	8.547 (1)	9.339 (5)
b, Å	12.153 (2)	14.244 (3)
c, Å	17.709 (3)	22.483 (9)
α, deg	90	99.97 (3)
β, deg	90	94.18 (4)
γ, deg	90	98.84 (2)
cell const determn	24 rflns, 11.4 ≤ 2θ ≤ 13.8°	25 rflns, 8.25 ≤ 2θ ≤ 11.8°
Z	4	6
F(000)	871.87	1307.79
calcd density, g/cm^3	1.542	1.463
radiation	graphite-monochromated Mo Kα	
λ, Å	0.7093	0.7093
μ(Mo Kα), mm^{-1}	0.97	0.82
abs cor	yes	yes
max transmissn factor	1.00	1.00
min transmission factor	0.97	0.96
diffractometer	CAD-4	
scan method	θ/2θ	
scan rate	variable	
rfln profile range, deg	0.70 + 0.35 tan θ	0.75 + 0.35 tan θ
2θ(max), deg	50	50
hkl ranges	$0 \le h \le 10$; $0 \le k \le 14$; $0 \le l \le 21$	$0 \le h \le 11$; $-16 \le k \le 16$; $-26 \le l \le 26$
std rflns	3 ($23\bar{8}$, $\bar{3}4\bar{5}$, $2,3,\overline{10}$)	3 ($1\bar{7}3$, $2\bar{4}\bar{8}$, $3,2,\overline{10}$)
remeasd periodicity, s	7200	3600
no. of rflns measd	1697	10150
no. of rflns obsd (2.5σ)	1413	5690
no. of atoms	23	129
no. of params	128	757
structure soln	heavy-atom methods	
structure refinement	full-matrix least squares	
weighting	counting statistical weights	
quantity minimized	$\sum w\|\|F_o\| - \|F_c\|\|^2$	
ignorance factor	0.02	
H atoms	calcd	
R	0.045	0.040
R_w	0.060	0.047
goodness of fit	2.298	1.484
Δ/σ	0.01	0.06
resid peaks		
max peak, e/Å^3	0.59	0.27
min peak, e Å^3	−0.52	−0.43

[a] The intensity data were reduced after corrections of Lorentz and polarization effects, and of absorption factors by an empirical ψ rotation method. Hydrogen atoms were calculated and fixed at idealized positions. All calculations were carried out on a VAX 11/780 minicomputer employing the structure analysis package as developed and distributed by the National Research Council of Canada. The scattering factors and anomalous dispersion corrections were applied according to: *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

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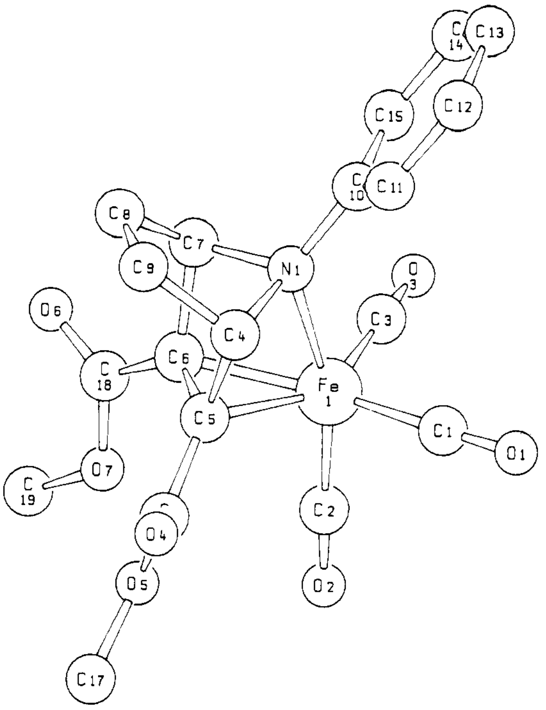
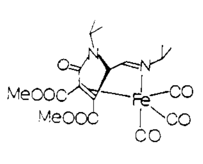


Figure 2. Molecular plot for one independent molecule of **2d**. The H atoms are omitted for clarity.

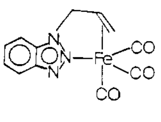
or **2d**/**3d**. However, due to difficulties in recrystallization of **3a** and **3d**, we have been unable to obtain suitable crystals for an X-ray diffraction study.

The X-ray structure analyses of **2a** and **2d** have resulted in the determination of structural parameters around Fe. Table III lists the X-ray diffraction experimental data and the refinement results for **2a** and **2d**. For **2d**, a Z value of 6 in $P\bar{1}$ is unusual. The cell reduction procedure has given no possible higher symmetry cells. $P\bar{1}$ has hence been accepted to result in a successful structure solution and refinement as reported here. Figures 1 and 2 are their molecular representations, respectively.

Both structures have been found to have ligands arranged in a distorted-tbp geometry around the central Fe atom with the olefin coordinated in the equatorial plane and the bridging N atom occupying an axial position. Both **2a** and **2d** have a molecular mirror symmetry. Only the solid-state structure of **2a** requires that the molecular mirror be superimposed on the crystallographic mirror. For **2a**, the atoms on the molecular plane, e.g., Fe, C1, O1, N, S, and C3, are on the crystallographic mirror perpendicular to the b axis. To elucidate the Fe–N bonding, the structures with both Fe–olefin and Fe–N fragments have been examined from the Cambridge Structure Database. Among those two are relevant structures for comparison, (1-allylbenzotriazole)tricarbonyliron(I), (ABC)Fe(CO)$_3$,[16] and (3,4-η^2-1-isopropyl-3,4-bis(methoxycarbonyl)-5-(σ^1-N-isopropylformimidoyl)-3-pyrrolin-2-one)tricarbonyliron(0), (FIP)Fe(CO)$_3$[17]—both bearing a connected N–olefin fragment. Other structures have only isolated olefin and N ligands. Table IV is a compilation of the relevant structural parameters. With a double four-membered-ring nature, **2a** and **2b** are found to have longer Fe—N bond lengths and longer olefinic C=C lengths (consequently, shorter Fe—C(olefin) bond lengths) than either (ABC)Fe(CO)$_3$ or (FIP)Fe(CO)$_3$.



(FIP)Fe(CO)$_3$



(ABC)Fe(CO)$_3$

Table IV. Selected Bond Lengths (Å) and Angles (deg) of 2a, 2d, (ABC)Fe(CO)$_3$, and (FIP)Fe(CO)$_3$

	2a	2d^a	(ABC)Fe(CO)$_3$^{b}	(FIP)Fe(CO)$_3$^{c}
Fe—N	2.059 (4)	2.041 (4)	1.977	2.035
Fe—C(olefin)	2.000 (3)	2.004 (4)	2.081^a	2.053^a
C=C	1.471 (6)	1.456 (6)	1.401	1.450
∠N—Fe—C(trans)	160.8 (2)	162.8 (2)	173.2	169.5

^{a} Values are averaged. ^{b} Reference 16. ^{c} Reference 17.

Due to the rigid geometry of the ligands, the N atoms in **2a** and **2d** deviate significantly from the apex position of tbp, i.e. ∠N–Fe–C(trans) values are 160.8 and 162.8°, respectively, as compared to 173.2° for (ABC)Fe(CO)$_3$ and 169.5° for (FIP)Fe(CO)$_3$. Usually N–C(paraffin) is known to have a bond length of 1.47–1.48 Å; however, the N–C distances in **2a** (1.511 Å) and **2d** (1.516 Å) are elongated, partly because of the bridging nature of the N atoms.

A comparison of the structural parameters of (ABC)Fe(CO)$_3$, (FIP)Fe(CO)$_3$, **2a** and **2d** is shown in Table IV. The correlation of a stronger Fe—N bond and a more labilized cis olefin can be observed; i.e., a shorter Fe—N bond length corresponds nicely with a longer cis Fe—C(olefin) length. The respective C=C lengths, when the back-bonding theory is taken into consideration, also follow the trends; i.e., a longer Fe—C(olefin) length corresponds nicely with a shorter C=C length. An electron-withdrawing methylsulfonyl group in **2a** is seemingly different from an electron-releasing phenyl group in **2d**: the former relatively destabilizes the Fe—N bond in **2a** as seen by the elongation of the Fe—N bond by 0.018 Å (2.059 Å in **2a** and 2.041 Å in **2d**).

Electronic Substituent Effects. It was found that the deamination of **3a** at 60 °C proceeds approximately 100 times faster than that of **2a** (Table II). The olefin group with carbomethoxy substituents binds the metal stronger than the one without the substituents;[14] therefore, the stabilities of **2a–c** are greater than those of **3a–c**. The variation in rate therefore can be referred to the difference in ground-state stabilities.

For an effective deamination, it is essential to have an electron-withdrawing substituent on the nitrogen. As previously mentioned, the reactions proceed well for N-mesyl, N-acyl, and N-carbethoxy derivatives but fail to work when these substituents are removed. Complexes **2c** and **5c** can be hydrolyzed under basic conditions to yield the corresponding complexes **2e** and **5e** in 71% and 52% yields, respectively (Table II), where the hydrolyses can be controlled without apparent interference from the maleic ester moieties. Hydrolyses of **3a** and **7c**, however, do not proceed well. This result is in agreement with the above observations that olefins without carbomethoxy substituents form a weaker bonding with the metal. Complex **7e** was prepared from **6e** independently in 48% yield.

Heating complexes **2d**, **2e**, **5e**, and **7e** at 60 °C for 18 h did not yield the corresponding phthalates; instead most of the starting materials were recovered. The thermal

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stabilities of **2e**, **5e**, and **7e** are significantly better than those of **2a–c**, **5c**, and **7c**, respectively, indicating that the nitrogen without an electron-withdrawing substituent forms a stronger coordination bond with the metal. The nitrogen with enhanced electron density releases, to a higher extent, its lone-pair electrons toward the metal. The consequence can be marginally seen in the Fe–N bond contraction in **2d** compared to that of **2a** (Table IV). This enhancement in bonding strength, however, does not seem to improve the nitrene extrusion efficiency.

For **2a–c**, the rates of deamination also change with respect to the chemical nature of the substituents. At 60 °C, the rate ratio of **2a**:**2b**:**2c** is approximately 4.7:3.2:1.0 (Table II), an order that parallels the electron-withdrawing ability of the N-substituents. It would appear that the electron deficiency induced in the nitrogen atom significantly influences the polarity of the C–N bonds and consequently promotes the elimination of the nitrene moieties.

Conclusion. The substituents of 7-azanorbornadiene derivatives have subtle yet significant influence on the iron-promoted nitrene-extrusion reactions. Their effect can be understood by analyzing the properties of the metal complex intermediates. The complex can be stabilized either by electron-withdrawing substituents on the olefin group or by an electron-releasing substituent on the amino group. However, when both groups are present, the deamination does not proceed at the operating temperature of 60 °C due to an insufficient energy of activation. Increasing the reaction temperature too much higher destroys the compounds. In the cases where electron-withdrawing substituents are absent from both positions, deamination proceeds in low yield along with competing side reactions (e.g. cycloreversion in **3d**). It appears that the ANB–Fe complexes best suited for iron-promoted deamination are the ones having electron-withdrawing substituents on both the olefin and the amino groups, where the yields range 83–100% (Table II).

Experimental Section

^{1}H and ^{13}C NMR spectra were obtained either on a Bruker MSL-200 FT spectrometer or on a Bruker AM 80 CW spectrometer. Chemical shifts of ^{1}H were measured downfield from TMS in δ units, while those of ^{13}C were recorded with the central peak of CDCl$_3$ at δ 76.90 as an internal reference. Infrared spectra were recorded on a Perkin-Elmer 297 infrared spectrophotometer. Melting points were determined by using a Yanaco Model MP micro melting point apparatus and were uncorrected. Elemental analyses were obtained on a Perkin-Elmer 240 EA instrument. High-resolution mass spectra were carried out on a JEOL JMS-HX110 mass spectrometer, while low-resolution ones (70 eV) were recorded on a Hewlett-Packard HP 5995B GC/MS system by direct injections.

The ANB derivatives used as the starting materials, i.e. **1a**,[9a] **1b–d**,[9b] **6c**[10a] and **6e**,[10b] were synthesized according to the published procedures.

General Procedures for the Preparation of Tricarbonyliron Complexes of the 7-Azanorbornadiene Derivatives. To a round-bottom flask fitted with a nitrogen gas inlet was added under a nitrogen atmosphere diiron nonacarbonyl (0.13 mmol) and degassed tetrahydrofuran (10 mL). To the resulting solution was injected through a syringe the 7-azanorbornadiene derivative (0.10 mmol), and the solution was stirred at room temperature for 20 h. The resulting mixture was filtered through silica gel, and the filtrate was concentrated in vacuo. The yellow residue was purified by passing it through a silica gel chromatographic column eluted with ether/*n*-hexane (1/1 v/v). Some of the tricarbonyliron complexes may be recrystallized.

(2,3-Dicarbomethoxy-7-(methylsulfonyl)-7-azanorbornadiene)tricarbonyliron (2a and 3a). Complex **3a** (yield 27%) was collected from the silica gel chromatographic column as a yellow band, followed by the complex **2a** (36%), which was recrystallized from methanol to form red-yellow prisms. Complex **2a**: mp 130–131 °C dec; ^{1}H NMR (CDCl$_3$) δ 2.60 (3 H, s), 3.75 (6 H, s), 5.40 (2 H, s), 6.70 (2 H, s); ^{13}C NMR (CDCl$_3$) δ 41.6 (q), 52.0 (q), 54.8 (d), 81.8 (s), 140.6 (d), 172.4 (s), 207.1 (s, 2 C), 207.5 (s); IR (KBr) $\nu_{C=O}$ 2060, 2000, 1980, 1680 cm^{-1}; mass spectrum (70 eV) *m/z* (relative intensity) 427 (M$^+$, 0.4), 396 (M$^+$ − OCH$_3$, 0.4), 371 (M$^+$ − 2CO, 1.9), 343 (M$^+$ − 3CO, 7.1), 285 (2.1), 264 (8.7), 194 (5.4), 163 (100). Anal. Calcd for $C_{14}H_{13}NO_9Fe$: C, 39.37; H, 3.28. Found: C, 39.39; H, 2.99. Complex **3a**: ^{1}H NMR (CDCl$_3$) δ 2.70 (3 H, s), 3.50 (s), 3.84 (6 H, s), 4.95 (2 H, s); ^{13}C NMR (CDCl$_3$) δ 40.4 (q), 52.6 (q), 57.6 (d), 69.8 (d), 146.4 (s), 163.2 (s), 207.8 (s); IR (KBr) $\nu_{C=O}$ 2095, 2015, 1985, 1730, 1630 cm^{-1}.

(2,3-Dicarbomethoxy-7-(methylcarbonyl)-7-azanorbornadiene)tricarbonyliron (2b). Complex **2b** (38%) was isolated as a yellow oil and recrystallized from *n*-hexane: mp 96–97 °C; ^{1}H NMR (CDCl$_3$) δ 1.90 (3 H, s), 3.80 (6 H, s), 5.44 (2 H, m), 6.69 (2 H, m); ^{13}C NMR (CDCl$_3$) δ 21.3 (q), 51.9 (q), 57.4 (d), 79.1 (s), 142.8 (d), 172.5 (s), 176.9 (s), 207.4 (s), 208.1 (s, 2 C); IR (KBr) $\nu_{C=O}$ 2060, 1990, 1747, 1723, 1691 cm^{-1}; mass spectrum (70 eV) *m/z* (relative intensity) 391 (M$^+$, 0.7), 363 (M$^+$ − CO, 0.9), 360 (M$^+$ − OCH$_3$, 0.6), 335 (M$^+$ − 2CO, 4.2), 307 (M$^+$ − 3CO, 0.7), 266 (23), 208 (44), 163 (100).

(2,3-Dicarbomethoxy-7-carbethoxy-7-azanorbornadiene)tricarbonyliron (2c and 3c). Complex **2c** was isolated as a yellow oil in 23% yield: ^{1}H NMR (CDCl$_3$) δ 1.10 (3 H, t, *J* = 7 Hz), 3.76 (6 H, s), 4.06 (2 H, q, *J* = 7 Hz), 5.35 (2 H, br), 6.60 (2 H, m); ^{13}C NMR (CDCl$_3$) δ 13.7 (q), 51.8 (s), 57.3 (d), 64.7 (t), 80.3 (s), 142.1 (d), 155.4 (s), 172.6 (s), 208.1 (s); IR (KBr) $\nu_{C=O}$ 2065, 2000, 1980, 1760, 1725, 1698 cm^{-1}; mass spectrum (70 eV) *m/z* (relatively intensity) 421 (M$^+$, 0.8), 393 (M$^+$ − CO, 1.1), 390 (M$^+$ − OCH$_3$, 1.5), 365 (M$^+$ − 2CO, 6.7), 337 (M$^+$ − 3CO, 11), 292 (46), 222 (21), 192 (14), 163 (100). Complex **3c** was obtained as a yellow oil in 18% yield: ^{1}H NMR (CDCl$_3$) δ 1.10 (3 H, t, *J* = 7 Hz), 3.80 (6 H, s), 3.55 (2 H, s), 4.08 (2 H, q, *J* = 7 Hz), 5.10 (2 H, s); IR (KBr) $\nu_{C=O}$ 2095, 2000, 1985, 1722, 1620 cm^{-1}.

(2,3-Dicarbomethoxy-7-phenyl-7-azanorbornadiene)tricarbonyliron (2d and 3d). Both complexes **2d** and **3d** were prepared from **1d** in 36% and 12% yields, respectively. Complex **2d** was recrystallized from ether/*n*-hexane to form yellow needles: mp 165.5–166 °C; ^{1}H NMR (CDCl$_3$) δ 3.80 (6 H, s), 5.58 (2 H, t, *J* = 1.3 Hz), 6.52 (t, *J* = 1.3 Hz), 6.83–6.87 (2 H, m), 7.22–7.26 (3 H, m); mass spectrum (70 eV) *m/z* (relative intensity) 425 (M$^+$, 4.3), 397 (M$^+$ − CO, 4.0), 369 (M$^+$ − 2CO, 15), 341 (M$^+$ − 3CO, 100), 309 (50), 281 (33), 253 (97), 223 (47), 200 (28), 192 (43), 163 (99); high-resolution mass spectrum, calcd for $C_{19}H_{15}NO_7Fe$ 425.0197, found 425.0199. Complex **3d** was recrystallized to form red crystals: mp 131–132 °C; ^{1}H NMR (CDCl$_3$) δ 3.80 (6 H, s), 4.20 (2 H, s), 5.60 (2 H, s), 6.90 and 7.10 (5 H, 2 m); ^{13}C NMR (CDCl$_3$) δ 45.9 (d), 52.3 (q), 84.0 (d), 120.2 (d), 126.1 (d), 129.4 (d), 142.0 (s), 145.0 (s), 162.2 (s), 211.9 (s); IR (KBr) $\nu_{C=O}$ 2054, 1950, 1735, 1700 cm^{-1}.

(7-Carbethoxy-7-azabenzonorbornadiene)tricarbonyliron Derivatives (5c, 7c, and 7e). Compound **4c** was prepared from dimethyl 1-carbethoxypyrrole-3,4-dicarboxylate and benzyne with a yield better than that previously reported.[10c] To a round-bottom flask fitted with a reflux condenser was added the above pyrrole (320 mg, 1.25 mmol), isoamyl nitrite (150 mg, 1.25 mmol), and THF (15 mL). The mixture was brought to reflux while into it was injected slowly through a syringe a solution of anthranilic acid (170 mg, 1.25 mmol) in THF (5 mL). After the injection was completed (ca. 30 min), the resulting mixture was heated to reflux for another 2 h. The reaction was quenched by adding distilled water, and the aqueous mixture was extracted several times with ether. The combined ether layers were washed with saturated sodium bicarbonate solution, dried over anhydrous calcium chloride, and filtered. The filtrate was concentrated in vacuo to give a dark brown oil, which was purified through a silica gel chromatography column eluted with ether/*n*-hexane (6/5 v/v). Compound **4c** was obtained (220 mg, 0.66 mmol, 53%) together with some starting pyrrole that was recollected (ca. 110 mg).

Complex **5c** (yield 42%) was prepared from **4c**, forming reddish yellow crystals: mp 115.5–117 °C dec; ^{1}H NMR (CDCl$_3$) δ 1.12 (3 H, t, *J* = 7 Hz), 3.70 (6 H, s), 3.97 (2 H, q, *J* = 7 Hz), 5.81 (2 H, s), 7.14 (2 H, m), 7.27 (2 H, m); ^{13}C NMR (CDCl$_3$) δ 13.6 (q), 51.7 (q), 56.8 (t), 64.7 (d), 80.8 (s), 120.3 (d), 127.8 (d), 145.8 (s), 155.7 (s), 172.0 (s), 207.6 (s), 208.1 (s, 2 C); IR (KBr) $\nu_{C=O}$ 2063, 1998, 1982, 1760, 1700, 1690 cm^{-1}; mass spectrum (70 eV) *m/z* (relative intensity) 471 (M$^+$, 0.8), 443 (M$^+$ - CO, 0.4), 415 (M$^+$ - 2CO, 2.0), 387 (M$^+$ - 3CO, 5.0), 342 (7.6), 272 (14), 244 (9), 213 (100). Complex **7c** was prepared from **6c** in 68% yield by following the procedures as previously described: ^{1}H NMR ($CDCl_3$) δ 1.05 (3 H, t, *J* = 6 Hz), 3.55 (2 H, s), 3.96 (2 H, q, *J* = 6 Hz), 7.00 (2 H, m), 7.20 (2 H, m).

Complex **7e** was obtained in 48% yield from **6e** as a reddish-yellow oil: ^{1}H NMR ($CDCl_3$) δ 2.20 (1 H, br), 4.01 (2 H, m), 5.30 (2 H, m), 7.10 (4 H, m); ^{13}C NMR ($CDCl_3$) δ 50.1 (d), 79.2 (d), 118.0 (d), 126.7 (d), 150.2 (s), 213.7 (s); IR (KBr) $\nu_{C=O}$ 2030, 1945 cm^{-1}; mass spectrum (70 eV) *m/z* (relative intensity) 283 (M$^+$, 5.3), 255 (M$^+$ - CO, 17), 227 (M$^+$ - 2CO, 36), 199 (M$^+$ - 3CO, 77), 184 (10), 172 (28), 143 (100); high-resolution mass spectrum, calcd for $C_{13}H_9NO_3Fe$ 282.9931, found 282.9944.

(2,3-Dicarbomethoxy-7-carbethoxy-7-azanorbornene)tricarbonyliron (9c). To a 50 mL round-bottom flask fitted with a gas inlet was added THF (12 mL), **1c** (28 mg, 0.10 mmol), and a catalytic amount of 10% Pd/C (5.6 mg). The resulting mixture was stirred for 35 min under a hydrogen atmosphere at 1-atm pressure. The crude product **8c** was obtained in 95% yield (27 mg) after filtration followed by evaporation of the solvent. It was then reacted with diiron nonacarbonyl in THF at 45 °C, similar to the procedure as previously described. Complex **9c** was collected as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 1.25 (3 H, t, *J* = 7 Hz), 1.4–1.5 (2 H, m), 1.8–2.1 (2 H, m), 3.70 (6 H, s), 4.10 (2 H, q, *J* = 7 Hz), 5.15 (2 H, m); IR (KBr) $\nu_{C=O}$ 1990, 1915, 1764, 1694 cm^{-1}; mass spectrum (70 eV) *m/z* (relative intensity) 423 (M$^+$, 0.1), 395 (M$^+$ - CO, 2.3), 367 (M$^+$ - 2CO, 7.8), 339 (M$^+$ - 3CO, 40), 294 (51), 224 (58), 194 (16), 165 (100).

General Procedure for the Hydrolysis of Iron Complexes. In a typical case, the iron complex **2a** (42 mg, 0.10 mmol) was dissolved in a solution of KOH (0.20 g, 3.6 mmol) in methanol (10 mL), and the resulting mixture was stirred at room temperature for 30 min. The reaction was quenched by the addition of distilled water (ca. 50 mL), and the product was extracted with ether (3 × 50 mL). The combined organic layers were washed with dilute hydrochloric acid and brine, dried over anhydrous calcium chloride, and concentrated in vacuo. The crude iron complex **2e** (25 mg, 71%) was obtained as a pale yellow solid. It was recrystallized from ether to form pale yellow needles, which are air-stable at ambient temperature: mp 198–200 °C dec; ^{1}H NMR ($CDCl_3$) δ 1.50 (1 H, br), 3.69 (6 H, s), 4.99 (2 H, m), 6.64 (2 H, s); ^{13}C NMR ($CDCl_3$) δ 51.7 (q), 58.0 (d), 79.8 (s), 143.9 (d), 173.3 (s), 208.4 (s), 209.5 (s, 2 C); IR (KBr) $\nu_{C=O}$ 2160, 1985, 1970, 1715 cm^{-1}; mass spectrum (70 eV) *m/z* (relative intensity) 349 (M$^+$, 5.1), 321 (M$^+$ - CO, 21), 292 (M$^+$ - 2CO, 50), 265 (M$^+$ - 3CO, 100), 233 (44), 210 (33), 207 (42), 179 (30), 163 (65), 149 (49); high-resolution mass spectrum, calcd for $C_{13}H_{11}NO_7Fe$ 348.9884, found 348.9885. In a similar procedure, complex **5c** (47 mg, 0.10 mmol) was hydrolyzed in 90 min to yield **5e** (21 mg, 52%), which was crystallized as pale yellow needles: mp 150 °C dec; ^{1}H NMR ($CDCl_3$) δ 3.72 (6 H, s), 5.52 (2 H, S), 7.18 and 7.26 (5 H, 2 m); ^{13}C NMR ($CDCl_3$) δ 51.7 (q), 57.5 (s), 80.2 (d), 119.6 (d), 127.4 (d), 148.2 (s), 172.7 (s), 208.2 (s), 209.5 (s, 2 C); IR (KBr) $\nu_{C=O}$ 2060, 1970, 1710 cm^{-1}; mass spectrum (70 eV) *m/z* (relative intensity) 399 (M$^+$, 2.4%), 371 (M$^+$ - CO), 343 (M$^+$ - 2CO), 315 (M$^+$ - 3CO), 283 (19), 257 (36), 230 (25), 213 (100), 199 (97), 197 (97).

Thermolysis of the Iron Carbonyl Complexes. To a 5 mm o.d. NMR tube containing CD_3CN (ca. 0.3 mL) was added the metal complex of interest (ca. 0.025 mmol) and TMS as internal standard. The tube was sealed and was immersed in a constant-temperature bath at 60 °C (±2 °C). The disappearance of metal complexes was monitored according to ^{1}H NMR signal integrations by periodically withdrawing the tube from the temperature bath and subjecting it to spectroscopic measurements. The signals used for quantitative measurements are those for the bridgehead hydrogens at ca. δ 5.5 ppm, where peaks are generally well separated. The measurements were completed at ca. 80% consumption of the starting materials. All reactions followed perfectly the first-order rate law, and the rate constants were calculated accordingly. After the kinetic measurements, the tubes were heated for an extended period of time until all the starting materials were consumed. The tubes were then opened, and the products were purified by silica gel column chromatography. The yields are listed in Table II.

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Registry No. **1a**, 51874-93-2; **1b**, 17620-34-7; **1c**, 59743-66-7; **1d**, 19375-84-9; **2a**, 119920-94-4; **2b**, 119920-95-5; **2c**, 119920-93-3; **2d**, 125050-46-6; **2e**, 125050-51-3; **3a**, 119886-15-6; **3c**, 119886-14-5; **3d**, 125050-47-7; **4c**, 86557-82-6; **4e**, 125050-45-5; **5c**, 125050-48-8; **5e**, 125050-52-4; **6c**, 39996-25-3; **6e**, 5176-20-5; **7c**, 125076-32-6; **7e**, 125050-49-9; **8c**, 125050-44-4; **9e**, 125050-50-2; diiron nonacarbonyl, 15321-51-4; dimethyl 1-carbethoxypyrrole-3,4-dicarboxylate, 54470-39-2; benzyne, 462-80-6; anthranilic acid, 118-92-3.

Supplementary Material Available: Tables of final fractional coordinates, thermal parameters, and bond distances and angles for **2a** and **2b** (13 pages); tables of structure factor amplitudes (77 pages). Ordering information is given on any current masthead page.