was observed after this time, as monitored by ^{11}B NMR spectroscopy, and only resonances from the unreacted B_5H_9 were observed.

(ii) With Triethylamine. In a typical reaction, 50 mL of a 0.1 M solution of B_5H_9 in THF was syringed onto 0.62 g (7.5 mmol) of 3-hexyne at −65 °C under an inert nitrogen atmosphere, and the reaction was allowed to warm slowly to room temperature. The synthesis continued with the addition of 0.43 g (4.3 mmol) of dry triethylamine to this solution at room temperature. The reaction was allowed to stir for 3 days and was monitored during this time by using ^{11}B NMR spectroscopy. The ^{11}B NMR spectra showed gradual decrease in the B_5H_9 resonances [at (δ ppm) −12.7 (d, B(2–4), J_{BH} = 162 Hz), −52.6 (d, B(5), J_{BH} = 172 Hz)][16,17] and the formation and growth of peaks assigned to *nido*-2,3-$(CH_3CH_2)_2C_2B_4H_6$ [at (δ ppm) −0.8 (d, B(5), J_{BH} = 146 Hz), −3.9 (d, B(4,6), J_{BH} = 146 Hz), −47.0 (d, B(1), J_{BH} = 176 Hz)][5,17,18] and to $BH_3{\cdot}N(CH_2CH_3)_3$ [at (δ ppm) −11.9 (q, J_{BH} = 92 Hz].[16,17] After 3 days, only the product carborane (47%), $BH_3{\cdot}N(CH_2CH_3)_3$, and unreacted pentaborane(9) (53%) were observed. The carborane yields reported by ^{11}B NMR spectroscopy were determined by using a calibrated BCl_3 capillary standardized against known concentration of carborane solutions to generate a standard curve. Then, by comparison with this standard curve, the concentration of the carborane in the unknown sample was accurately determined.[19] Continued standing at room temperature for several days yielded 80% of the carborane. The pure carborane was isolated in 74% total yield by repeated trap-to-trap distillation operations with the pure carborane remaining in the 0 °C trap.[9,19] Refluxing the solution did not result in appreciably greater yields.

B. 2-Phenyl-2,3-dicarba-*nido*-hexaborane(8). In a 500-mL flask, 0.77 g (7.5 mmol) of $C_6H_5C{\equiv}CH$, 0.43 g (4.25 mmol) of $N(CH_2CH_3)_3$, and 50 mL of THF were mixed and degassed by repeated freeze–thaw cycles. The solution was cooled to −196 °C, and 0.32 g (5.0 mmol) of B_5H_9 was condensed into the flask using standard vacuum-line techniques.[9] The reaction was warmed with an ice bath to 0 °C and allowed to stir. After several hours, the reaction was allowed to warm slowly to room temperature with continued stirring. The ^{11}B NMR spectra showed a gradual decrease in the B_5H_9 resonances[16,17] and the formation and growth of peaks assigned to *nido*-2,3-$(C_6H_5)HC_2B_4H_6$.[5a–e] After 2 days at room temperature, a 20% yield of the product carborane was found by ^{11}B NMR spectroscopy.

C. 2,3-Diphenyl-2,3-dicarba-*nido*-hexaborane(8). A 500-mL flask was charged with 1.1 g (6.0 mmol) of $C_6H_5C{\equiv}CC_6H_5$, evacuated, and cooled to 0 °C. To this flask were added by syringe 0.35 g (3.5 mmol) of $N(CH_2CH_3)_3$ and 50 mL of dry 0.1 M pentaborane(9)–THF solution (5.0 mmol) under inert conditions. The resulting solution was then degassed by a freeze–thaw cycle and allowed to slowly warm to room temperature with continued stirring. The ^{11}B NMR spectra showed a gradual decrease in the B_5H_9 resonances and the formation and growth of peaks assigned to *nido*-2,3-$(C_6H_5)_2C_2B_4H_6$.[10] After 1 day at room temperature, 21% yield of the product carborane was found. Refluxing the solution did not result in a significantly improved yield of the carborane product.

Acknowledgment. We wish to thank the National Science Foundation (Grant No. MSS-89-09793), the General Electric Co., the Wright-Patterson Laboratory (Award No. F33615-90-C-5291), and the Industrial Affiliates Program of the Center for Molecular Electronics for support of this work.

Registry No. THF, 109-99-9; B_5H_9, 19624-22-7; *nido*-$RR'C_2B_4H_6$ (R = R′ = CH_3CH_2), 138062-03-0; *nido*-$RR'C_2B_4H_6$ (R = H, R′ = C_6H_5), 138062-04-1; *nido*-$RR'C_2B_4H_6$ (R = R′ = C_6H_5), 138062-05-2; $C_6H_5C{\equiv}CH$, 536-74-3; $C_6H_5C{\equiv}CC_6H_5$, 501-65-5; 3-hexyne, 928-49-4.

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[17] The ^{11}B data shown here are our data which are comparable with those reported earlier.[5,10]

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Attack of N-Nucleophile on a Coordinated Carbonyl Ligand: Structures of (7-Azabenzonorbornadiene)tetracarbonyliron Derivatives

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Summary: Three crystal structures of (N-substituted 7-azabenzonorbornadiene)$Fe(CO)_4$ derivatives have been studied for substituents 7-$MeSO_2$ (**1**), 7-*p*-ClC_6H_4 (**2**), and 7-*p*-MeC_6H_4 (**3**), respectively. In the solid state, an intramolecular interaction between the N-nucleophile and the nearby coordinated CO ligand is clearly seen. As the $N{\cdots}C{=}O$ contact distance becomes shorter, the O atom of $Fe{-}C{-}O$ bends away from the N atom more, corresponding to a stronger interaction between the nucleophile and the coordinated CO.

The reactions of neutral iron carbonyls with nucleophiles have been extensively studied. The active site is generally the C atom of a coordinated CO. For a C-based nucleophile R^-, the immediate product is an anionic Fe–acyl species.[2] By analogy an O-based nucleophile RO^-, the first-stage product is an anionic iron carboxylate. Both are subsequently followed with various secondary reactions.[3]

When $Fe(CO)_5$ and R_2NH are mixed, a reaction ensures to yield initially the CO-inserted products.[4] A recent report on the nitrene-extrusion reactions mediated by $Fe_2(CO)_9$ indicates that an electron-withdrawing group or

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aryl group on the N atom in 7-azabenzonorbornadiene is able to lead to the isolation of intermediates.[5] 7-Azabenzonorbornadiene is hence employed as a model skeleton in this study to reveal the nucleophilic attack of N atom toward a coordinated CO, taking an advantage that the olefin functionality of 7-azabenzonorbornadiene anchors the skeleton (hence, the N-based nucleophile) in the proximity of Fe. An olefin is known to coordinate to an Fe atom in the equatorial plane of the trigonal-bipyramidal (tbp) sphere.[6,7] Therefore, (7-azabenzonorbornadiene)-$Fe(CO)_4$ would have an N-based nucleophile positioned close enough to the axial CO such that interactions between the N atom and the nearby CO can be extracted from X-ray structural data in a fine-tuning fashion by varying the substituent group on the N atom.

Experimental Section

General Procedures. ^1H and ^{13}C NMR spectra were recorded either on a Bruker MSL-200 FT spectrometer or on a Bruker AM 80 CW spectrometer. Chemical shifts of ^1H 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 using a Yanaco Model MP micro melting point apparatus and were uncorrected. Elemental analyses were obtained on an institute-operated Perkin-Elmer 240EA instrument. Reagents and chemicals were obtained from Merck and/or Aldrich. Solvents were dried with a common Na/benzophenone procedure.[8]

Synthesis of 7-azabenzonorbornadiene derivatives follows a procedure published elsewhere.[9] Three 7-azabenzonorbornadiene derivatives—7-(methylsulfonyl)-, 7-(*p*-chlorophenyl)-, and 7-*p*-tolyl-7-azabenzonorbornadiene—have been successfully coordinated to a $Fe(CO)_4$ moiety, resulting in complexes **1**–**3**, respectively.

General Procedure for the Synthesis of (N-Substituted 7-azabenzonorbornadiene)$Fe(CO)_4$ Complexes. A mixture of the required N-substituted 7-azabenzonorbornadiene (5.0×10^{-5} mol) and $Fe_2(CO)_9$ (1.0×10^{-4} mol) in THF was degassed and stirred at 25–30 °C under an atmosphere of nitrogen gas for 18–24 h. The corresponding (N-substituted 7-azabenzonorbornadiene)$Fe(CO)_4$ was prepared in 44–63% yields as the major product. After the solvent was removed in vacuo, the concentrated residue was purified by column chromatography (SiO_2, 20:1 *n*-hexane–THF) to give a yellow solid, followed by repeated recrystallizations from Et_2O–*n*-hexane to give fine, yellow crystals of X-ray crystallographic quality. Relevant spectroscopic data follow.

$C_{15}H_{11}FeNO_6S$ (**1**): ^1H NMR δ 2.05 (s, 3 H), 3.35 (s, 2 H), 5.01 (s, 2 H), 7.25 (m, 4 H); IR ν (CO) 2084 (m), 2002 (s), 1973 (s) cm^{-1}. Free ligand: ^1H NMR δ 2.37 (s, 3 H), 5.48 (s, 2 H), 7.0–7.55 (m, 6 H).

$C_{20}H_{12}ClFeNO_4$ (**2**): ^1H NMR δ 3.52 (s, 2 H), 4.77 (s, 2 H), 6.7–7.3 (m, 8 H); ^{13}C NMR δ 61.09, 67.45, 119.89, 122.39, 126.47, 126.96, 126.98, 141.57, 145.09, 209.77; IR ν(CO) 2064, 1999, 1965, 1943 cm^{-1}. Anal. Calcd for $C_{20}H_{12}ClFeNO_4$: C, 56.98; H, 2.87; N, 3.33. Found: C, 56.20; H, 2.42; N, 2.99. Free ligand: ^1H NMR δ 5.36 (s, 2 H), 6.75–7.30 (m, 10 H).

$C_{21}H_{15}FeNO_4$ (**3**): ^1H NMR δ 2.16 (s, 3 H), 3.51 (s, 2 H), 4.76 (s, 2 H), 6.7–7.3 (m, 8 H); ^{13}C NMR δ 20.51, 61.20, 67.19, 118.83, 122.35, 126.34, 129.55, 131.27, 139.73, 145.13, 210.05; IR ν(CO) 2060, 2000, 1965 cm^{-1}. Anal. Calcd for $C_{21}H_{15}FeNO_4$: C, 64.37; H, 4.05; H, 3.75. Found: C, 64.15; H, 3.73; N, 3.60. Free ligand: ^1H NMR δ 2.16 (s, 3 H), 5.38 (s, 2 H), 6.75–7.40 (m, 10 H).

Table I. Crystallographic Data and Refinement Details for 1–3

	1	2	3
empirical formula	$C_{15}H_{11}FeNO_6S$	$C_{20}H_{12}ClFeNO_4$	$C_{21}H_{15}FeNO_4$
crystal system	orthorhombic	orthorhombic	orthorhombic
space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
cell dimensions[a]			
a, Å	10.942 (2)	6.075 (1)	6.090 (1)
b, Å	11.910 (2)	12.671 (2)	12.605 (2)
c, Å	12.390 (3)	23.182 (3)	23.375 (2)
V, Å^3	1614.5 (6)	1784.3 (4)	1794.2 (3)
crystal size, mm	0.32 × 0.19 × 0.24	0.38 × 0.25 × 0.19	0.50 × 0.18 × 0.08
formula weight	389.16	421.62	401.06
Z	4	4	4
$F(000)$	791.87	855.87	823.86
D(calc), g/cm^3	1.601	1.570	1.485
μ, mm^{-1}	1.09	1.02	0.86
λ, Å	0.7093	0.7093	0.7093
2θ(max)	50	50	45
diffractometer		Nonius CAD-4	
scan mode	$\theta/2\theta$	$\theta/2\theta$	$\theta/2\theta$
hlk range	$0 < h < 12$ $0 < k < 14$ $0 < l < 14$	$0 < h < 7$ $0 < k < 15$ $0 < l < 27$	$0 < h < 7$ $0 < k < 15$ $0 < l < 27$
no. unique reflns	1634	1837	1395
no. obsns $I_o > 2\sigma(I_o)$	1293	1506	1234
absorption corr	yes	yes	yes
transmission factors	0.816–1.000	0.944–1.000	0.939–1.000
atoms refined	35	39	42
parameters	262	293	305
weights		counting statistics	
weight modifier	0.01	0.01	0.01
R	0.032	0.027	0.027
R_w	0.034	0.030	0.031
GOF	1.43	1.44	1.48
max Δ/σ	0.153	0.062	0.148
D-map high, e/Å^3	0.360	0.210	0.180
D-map low, e/Å^3	−0.200	−0.250	−0.210

[a] Cell dimensions were obtained from 22–25 reflections with 2θ angle in the range 14.6–29.5°.

X-ray Crystallography. The crystals of **1**–**3** obtained as described above proved to be of X-ray quality. Suitable data crystals were mounted within lithium glass capillary for data collection on an Enraf-Nonius CAD-4 automated diffractometer. The X-ray diffraction experiments are summarized in Table I, detailing the crystal data and refinement parameters. The cell parameters were obtained, for each compound, by the least-squares refinement of the setting angles of 22–25 high-angle reflections that had been accurately centered on the diffractometer. Only statistical fluctuations were observed in the intensity monitors over the course of the data collection. An empirical absorption correction based on ψ scans for three reflections near $\chi = 90°$ was applied. Coordinates for Fe atoms were obtained from Patterson maps and those of the remaining non-hydrogen atoms from successive Fourier maps. In the final stages, all non-hydrogen atoms were refined anisotropically and all hydrogen atoms were located in a difference map before being refined isotropically to convergence. Following convergence of the original models, the polarity of space group was checked to ensure a correct choice in the crystallographic chirality. The final difference map was essentially featureless. The atomic scattering factors were taken from ref 10. The calculation employed a Micro VAX3600 computer using the structure analysis package developed by NRCC.[11] Molecular drawings of **1**–**3** are shown in Figures 1–3, respectively. Additional fractional coordinates, thermal parameters, bond lengths and angles, and listings of structure factor amplitudes (F_o vs F_c) are included as supplementary material.

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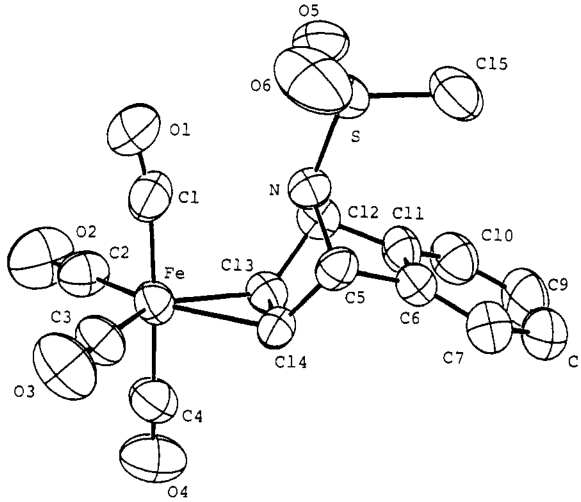

Figure 1. Molecular drawing of $C_{15}H_{11}FeNO_6S$ (1) showing the atom-labeling scheme. Hydrogen atoms have been omitted for clarity. Selected bond distances and angles: Fe–C(1) = 1.820 (7), Fe–C(2) = 1.804 (7), Fe–C(3) = 1.810 (6), Fe–C(4) = 1.808 (7), Fe–C(13) = 2.071 (5), Fe–C(14) = 2.078 (5), N···C(1) = 2.572 (8), N–C(5) = 1.483 (7), N–C(12) = 1.503 (7), O(1)–C(1) = 1.134 (8), O(2)–C(2) = 1.122 (8), O(3)–C(3) = 1.126 (8), O(4)–C(4) = 1.127 (8), C(13)–C(14) = 1.415 (8) Å; C(1)–Fe–C(2) = 86.8 (3), C(1)–Fe–C(3) = 90.3 (3), C(1)–Fe–C(4) = 174.9 (3), C(2)–Fe–C(3) = 109.0 (3), C(2)–Fe–C(4) = 88.2 (3), C(2)–Fe–C(13) = 110.1 (3), C(2)–Fe–C(14) = 149.7 (3), C(3)–Fe–C(4) = 92.1 (3), C(3)–Fe–C(13) = 140.8 (3), C(3)–Fe–C(14) = 100.9 (3), C(5)–N–C(12) = 96.0 (4), Fe–C(1)–O(1) = 168.2 (6), Fe–C(2)–O(2) = 178.7 (6), Fe–C(3)–O(3) = 178.6 (6), Fe–C(4)–O(4) = 178.7 (6)°.

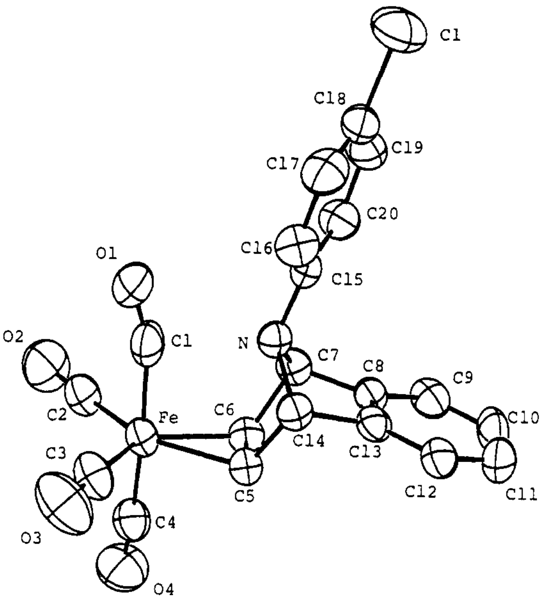

Figure 2. Molecular drawing of $C_{20}H_{12}ClFeNO_4$ (2) showing the atom-labeling scheme. Hydrogen atoms have been omitted for clarity. Selected bond distances and angles: Fe–C(1) = 1.828 (5), Fe–C(2) = 1.788 (4), Fe–C(3) = 1.813 (5), Fe–C(4) = 1.812 (5), Fe–C(5) = 2.083 (4), Fe–C(6) = 2.084 (4), N···C(1) = 2.315 (5), N–C(7) = 1.480 (5), N–C(14) = 1.488 (5), O(1)–C(1) = 1.148 (5), O(2)–C(2) = 1.136 (5), O(3)–C(3) = 1.132 (6), O(4)–C(4) = 1.129 (6), C(5)–C(6) = 1.421 (6) Å; C(1)–Fe–C(2) = 84.5 (2), C(1)–Fe–C(3) = 91.5 (2), C(1)–Fe–C(4) = 172.5 (2), C(2)–Fe–C(3) = 111.3 (2), C(2)–Fe–C(4) = 88.3 (2), C(2)–Fe–C(5) = 153.1 (2), C(2)–Fe–C(6) = 113.5 (2), C(3)–Fe–C(4) = 93.1 (2), C(3)–Fe–C(5) = 95.5 (2), C(3)–Fe–C(6) = 135.2 (2), C(7)–N–C(14) = 95.9 (3), Fe–C(1)–O(1) = 162.9 (4), Fe–C(2)–O(2) = 176.0 (4), Fe–C(3)–O(3) = 176.8 (4), Fe–C(4)–O(4) = 175.8 (4)°.

Results and Discussion

The molecular structures of 1–3 have revealed, first, that their olefin moiety is coordinated to a Fe center in the equatorial plane of tbp sphere, as in dozens of reported (olefin)Fe(CO)$_4$ structures.[6,7] Common features of a coordinated olefin also include the elongation of the C=C double bond, from 1.322 ± 0.014 Å as a free ligand[12] to 1.415 (8) Å in 1 and 1.423 (7) Å in 3 when coordinated. The degree of elongation is correlated with the back-bonding ability of Fe atom, which is in turn directly correlated to the π acidity of olefin functionality. To a first approximation, the Fe environments of 1–3 are equal so that their C=C lengths are equal within experimental standard deviations. Yet, taking account that there is an electron-withdrawing MeSO$_2$ substituent on N atom for 1 and there are more or less electron-releasing aryl substituents on N

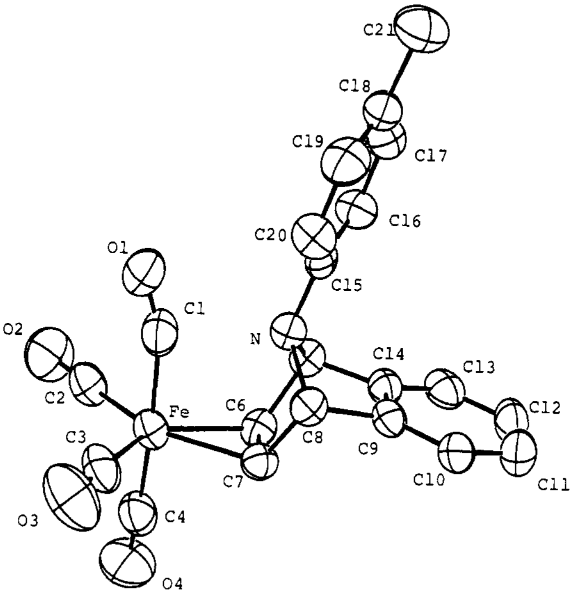

Figure 3. Molecular drawing of $C_{21}H_{15}FeNO_4$ (3) showing the atom-labeled scheme. Hydrogen atoms have been omitted for clarity. Selected bond distances and angle: Fe–C(1) = 1.842 (6), Fe–C(2) = 1.785 (5), Fe–C(3) = 1.810 (6), Fe–C(4) = 1.804 (5), Fe–C(6) = 2.082 (5), Fe–C(7) = 2.085 (5), N···C(1) = 2.261 (6), N–C(5) = 1.489 (5), N–C(8) = 1.499 (5), O(1)–C(1) = 1.142 (7), O(2)–C(2) = 1.142 (6), O(3)–C(3) = 1.131 (7), O(4)–C(4) = 1.136 (7), C(6)–C(7) = 1.423 (7) Å; C(1)–Fe–C(2) = 84.3 (2), C(1)–Fe–C(3) = 91.5 (2), C(1)–Fe–C(4) = 172.3 (2), C(2)–Fe–C(3) = 111.0 (2), C(2)–Fe–C(4) = 88.5 (2), C(2)–Fe–C(6) = 113.8 (2), C(2)–Fe–C(7) = 153.5 (2), C(3)–Fe–C(4) = 93.5 (2), C(3)–Fe–C(6) = 135.2 (2), C(3)–Fe–C(7) = 95.4 (2), C(5)–N–C(8) = 95.4 (3), Fe–C(1)–O(1) = 161.1 (4), Fe–C(2)–O(2) = 176.9 (4), Fe–C(3)–O(3) = 176.6 (5), Fe–C(4)–O(4) = 176.9 (4)°.

Table II. Compilation of Bonding Parameters for (Olefin)Fe(CO)$_4$

	1	2	3	7-O···C(1)
N···C(1), Å	2.572 (8)	2.315 (5)	2.261 (6)	2.47 (1)[a] 2.44 (1)[a]
Fe—C(1)—O(1), deg	168.2 (6)	162.9 (4)	161.1 (4)	170.5 (7) 168.8 (8)
Fe–C(1), Å	1.820 (7)	1.828 (5)	1.842 (6)	1.844 (8) 1.844 (8)
C=C, Å	1.415 (8)	1.421 (6)	1.423 (7)	1.39 (1) 1.40 (1)
Fe-C(olefin), Å	2.071 (5) 2.078 (5)	2.083 (4) 2.084 (4)	2.082 (5) 2.085 (5)	2.069 (8) 2.087 (9) 2.085 (8) 2.109 (9)

[a] The 7-O...C(1) contact distance.

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atom for **2** and **3**, the remote effect is fuzzily exhibiting: The C=C length of **1**, 1.415 Å, is shorter than those of **2** and **3**, 1.422 Å on average.

The N···C(1) distances in these three structures are all very short, much less than the van der Waals sums of an N atom and a C atom. The considerable angular distortion for the Fe–C(1)–O(1) unit from linearity is also obvious as compared with the rest of Fe–C–O units, averaging 177.9°. The distortion of the angle at C(1) is such that O(1) bends away from N. In Table II, a compilation of contacts N···C(1), angles Fe–C(1)–O(1), and lengths Fe–C(1) is given, from which it can be seen that the contact for N···C(1) in **1** is more distant that that in **2** or in **3**, whereas the angle of Fe–C(1)–O(1) in **1** tilting away from 180° is much less enhanced than those in **2** and **3**. With the N···C(1) contact distance serving as a measure of the extent of the attack of an N-based nucleophile toward a coordinated CO, a shorter N···C(1) contact distance means a stronger interaction between the nucleophile and the coordinated CO. It has been thus found that the angle Fe–C(1)–O(1) seriously evidences a distortion in response to the nucleophilic attack. The bond lengths of Fe–C(1) are seen to be longer, though not too significantly, than those of other Fe–C, averaging 1.804 Å. A trend is also vaguely seen on the Fe–C(1) length, which is less lengthened in **1** than in **2** or **3**.

There have been a number of examples employing crystallographic data statistically to provide information about the chemically dynamical aspects.[13] For example, nucleophiles approach the S atoms of organic sulfides and sulfonium ions preferentially in directions trans to existing bonds, where the Nu···S distances in the "incipient stages of a nuphilic substitution reaction" are less than the sum of the van der Waals radii and have strong angular correlations along the chemical reaction coordinate.[14]

The mechanism of addition of amino N to keto C and related reactions have been discussed with crystallographic statistics, too. The fragment of interest as extracted from a series of organic structures shows that the N···C=O distances range from ca. 3 to 1.5 Å when the keto groups deviate from the usual coplanar geometry, a decrease in N···C=O distance being accompanied by an increase in nonplanarity at carbonyl carbon.[15]

Extending to the addition of an N-based nucleophile to iron carbonyls in organometallic systems, the N···C=O distances listed in Table II are less than the sum of the van der Waals radii and are surely at a stage prior to being a transition complex. The reaction coordinate for amine adding to iron carbonyl can be reasonably presented by Figure 4, which shows the extracted X-ray structural parameters from nine structures with N···C=O distance less than 3.2 Å in iron carbonyl containing molecules with an N atom. When N···C distances are longer than 3.0 Å (a and b in Figure 4), the N-nucleophile is already positioned at ca. 105° from the linear Fe–C–O axis. For the intermediate N···C contacts in complexes **1**–**3**, the Fe–C–O bends back accordingly. When N–C becomes part of a carbamoyl group (f–i in Figure 4), the Fe–C–O angle is ca. 130° and the N—C=O angle is ca. 120°. Complexes **1**–**3** are apparently bridging the two chemically different moieties from the point of view of chemical dynamics.

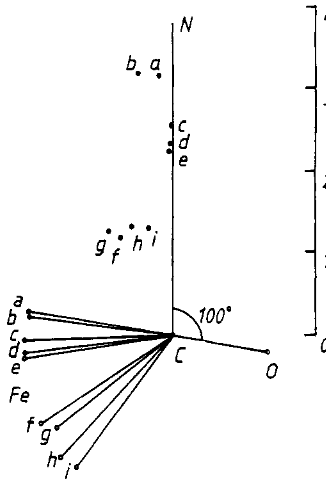

Figure 4. Relative positions of N, C, and O atoms and the deposition of Fe atom in response to the N···C=O interactions. Compounds and references are as follows: (a) (3-Acetyl-1*H*-azepine)tricarbonyliron(0): Waite, M. G.; Sim, G. A. *J. Chem. Soc. A* **1971**, 1009. (b) (Azepine)tricarbonyliron(0): Gieren, A.; Hoppe, W. *Acta Crystallogr.* **1972**, *28B*, 2766. (c) **1**: This text. (d) **2**: This text. (e) **3**: This text. (f) [1-(*N*-Benzylcarbamoyl)-1-methyl-3-phenylallyl]tricarbonyliron: Batsanov, A. S.; Struchkov, Yu. T. *J. Organomet. Chem.* **1983**, *248*, 101. (g) [1-(*N*-Cyclohexylcarbamoyl)-1,3-diphenylallyl]tricarbonyliron: Nesmeyanov, A. N.; Rybinskaya, M. I.; Rybin, L. V.; Gubenko, N. T.; Bokii, N. G.; Batsanov, A. S.; Struchkov, Yu. T. *J. Organomet. Chem.* **1978**, *149*, 177. (h) Hexamethylguanidinium [(dimethylamino)carbonyl-*C*]tetracarbonylferrate: Boese, R.; Blaser, D.; Petz, W. *Z. Naturforsch.* **1988**, *43B*, 945. (i) (μ-Dimethylarisido)(μ-*N*,*N*-dimethylcarbamoyl)bis(tricarbonyliron): Keller, E.; Trenkle, A.; Vahrenkamp, H. *Chem. Ber.* **1977**, *110*, 441.

With similar steric size for *p*-ClC_6H_4 and *p*-MeC_6H_4 moieties, the crystal structures of **2** and **3** have been found to be isomorphous. For **1**, the molecular symmetry C_s virtually retains in the crystalline state, but for **2** and **3**, the molecular symmetry is only C_1, with the aryl plane intersecting the three-point plane (Fe, C(1), N) at 67.0 (2)° and 67.4 (3)°, respectively.

For (olefin)$Fe(CO)_4$ complexes of *exo*-bicycloheptadiene derivative, the 7-oxobenzonorbornadiene complex has been known crystallographically.[16] Nonetheless, to the best of our knowledge, neither *exo*-norbornadiene nor *exo*-7-azanorbornadiene complexes have been studied by X-ray in the literature. Table II lists also, for (7-oxabenzonorbornadiene)$Fe(CO)_4$, the 7-O···C(1) contact distances and Fe–C(1)–O(1) angles: 2.46 Å and 169.7° on average, respectively. The extent of distortion in Fe–C(1)–O(1) angle would lay the stereochemical disposition of the 7-oxabenzonorbornadiene complex at about the same level as that of **1**, but less than those of **2** and **3**; the smaller size of the O atom relative to the N atom reasonably decreases the 7-O···C(1) contact distance relative to the N···C(1) contact distance. Apparently, the lone pair on the O or N atom contributes to the interaction between O/N and C(1), which in fact is an attractive force rather than a repulsive one.

Without any available lone pair, a bridging C atom in norbornadiene has also a much larger steric energy than a bridging O atom in 7-oxanorbornadiene or a bridging N atom in 7-azanorbornadiene such that in retrospect the (olefin)$Fe(CO)_4$ complexes of benzonorbornadiene derivatives are not isolable simply because of steric strain. For

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7-azabenzonorborandiene derivatives, it has been clearly demonstrated in this study that a fine-tuning of the electron-withdrawing substituent group on the bridging N atom gives fruitful information with regard to the nucleophilic attack on a coordinated CO. A strongly electron-releasing substituent or an H atom on the bridging N atom in 7-azabenzonorbornadiene, on the other hand, would cause the nucleophilic attack to proceed readily to a further stage such that the reaction of 7-azabenzonorbornadiene with $Fe_2(CO)_9$ failed to yield the analogous (olefin)$Fe(CO)_4$.[17]

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Registry No. 1, 138234-34-1; 2, 138234-35-2; 3, 138234-36-3; $Fe_2(CO)_9$, 15321-51-4; 7-(methylsulfonyl)-7-azabenzonorbornadiene, 138234-31-8; 7-(*p*-chlorophenyl)-7-azabenzonorbornadiene, 138234-32-9; 7-*p*-tolyl-7-azabenzonorbornadiene, 138234-33-0.

Supplementary Material Available: Tables listing details of the data collection and refinement, final atomic coordinates, temperature factors, bond lengths and angles, and torsional angles for the compounds (17 pages); listings of observed and calculated structure factors (17 pages). Ordering information is given on any current masthead page.

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[17] Sun, C. H.; Yang, C. Z. Unpublished results.

Intermolecular Hydrogen Bonding in Organometallic–Hormone Derivatives. Crystal and Molecular Structures of α-[Cp*Ru(estradiol)][CF_3SO_3] and α-[Cp*Ru(3-*O*-(hydroxypropyl)estradiol)][CF_3SO_3]

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Summary: The organometallic–hormone derivatives (α,-β)-[Cp*Ru(estradiol)] [CF_3SO_3] (**1a,b**) as well as (α,β)-[Cp*Ru(3-*O*-(hydroxypropyl)estradiol)] [CF_3SO_3] (**2a,b**) were obtained in good yield and identified by spectroscopic methods. In particular, the crystal and molecular structures of **1a** and **2a** were determined by X-ray diffraction (monoclinic space groups $P2_1$, $P2_1$, a = 8.596 (3), 8.533 (1) Å, b = 16.005 (3), 16.483 (8) Å, c = 10.674 (2), 11.798 (2) Å, β = 100.77 (2), 102.37 (1)°, Z = 2, 2, respectively), which reveal strong intermolecular hydrogen bonding in the solid state between the organometallic–hormone subunits, thus forming infinite chains, not a normal feature in steroid chemistry. Interestingly, the hydrogen donor and the hydrogen acceptor in **1a** and **2a** operate differently, and oppositely, depending on the nature of the hydroxyl group.

Hydrogen bonding plays a crucial role in the process of molecular recognition. This field has attracted considerable interest from both chemists and biochemists who are attempting to understand and explain the molecular basis of recognition.[1] Extensive research has been performed which shows that organic complexes and, more recently, organometallic complexes are capable of recognizing synthetic receptors[1,2] as well as natural and especially hormone receptors.[3] In the solid state, the "complex receptor" systems exhibit hydrogen bonding as a means of recognition.[4] Previously we have shown that the organometallic-labeled hormone α-[3-*O*-(hydroxypropyl)estradiol][$Cr(CO)_3$] is able to recognize the estradiol receptor with good binding affinities (relative binding affinity 28%);[3] however, the analogous α-[estradiol][$Cr(CO)_3$] was not studied, owing to its lack of stability. Consequently, we have become interested in preparing such stable complexes by direct introduction of the "Cp*Ru" (Cp* = C_5Me_5) adduct onto the A ring of estradiol but preserving the phenolic character. For comparison purposes, the [Cp*Ru(3-*O*-(hydroxypropyl)estradiol)][CF_3SO_3] derivative was also synthesized. It should be pointed out, however, that the presence of hydroxyl groups at C3 and C17 of β-estradiol is essential for effective binding, eventually by forming hydrogen bonds with the receptor sites.[5]

We have recently described the synthesis of some α-[Cp*Ru(estradiol)][PF_6] and (α,β)-[Cp*Ru(estradienonyl)] derivatives[6a] by following a one-pot reaction procedure.

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