

# Synthesis, Structural Characterization, and Bonding Analysis of ( $\eta^4$ -1-azadiene)Fe(CO)<sub>3</sub> Complexes: Consequences of the Electronic Structure on Molecular and Crystal Properties

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A series of 1-azadiene ligands as well as the corresponding ( $\eta^4$ -azadiene)Fe(CO)<sub>3</sub> complexes have been synthesized and structurally characterized by means of single-crystal X-ray diffraction. At the molecular level, the 1-azadiene assumes a trans conformation as free ligand, while a cis coordination is found in the organometallic complexes. In the coordinated ligand the H(C3) hydrogen is found nonplanar with respect to the C–C–C–N plane. A molecular orbital analysis has been carried out by means of extended Hückel calculations. The electronic origin of the out-of-plane position of the 1-azadiene hydrogen atom H(C3) has been justified in terms of a better  $\pi^*$ -back-bonding between the 1-azadiene and Fe(CO)<sub>3</sub> molecular fragments. A comparison of cis and trans conformations of the ligand has also been performed. The organometallic crystals show the presence of a large number of hydrogen bond interactions of the C–H...O type involving CO-ligand acceptors. Hydrogen bonding of the azadiene moiety is always realized by the hydrogen atom at the C–N double bond and the hydrogen atom in  $\alpha$ -position with respect to the imine group.

## Introduction

(1,3-butadiene)Fe(CO)<sub>3</sub> complexes are widely used as starting materials in the synthesis of organic compounds due to the properties of the Fe(CO)<sub>3</sub> moiety to act not only as an activating group but also as a protecting and stereo directing group.<sup>1</sup> There is also a number of reactions starting from the isolobal (1,4-diazadiene)Fe(CO)<sub>3</sub> complexes,<sup>2</sup> but only very little is known about the reactivity of (1-azadiene)Fe(CO)<sub>3</sub> compounds so far. Up to now there have been reports about the reaction of (1-azadiene)Fe(CO)<sub>3</sub> complexes with organo lithium compounds.<sup>3</sup> In these reactions the initial step is always the attack of the organo lithium reagent toward an iron-bound CO ligand which is, in subsequent reaction steps, incorporated into the azadiene ligand together with the organic group attached to lithium. (1-azadiene)Fe(CO)<sub>3</sub> complexes have also been used as catalysts in the synthesis of (1,3-butadiene)Fe(CO)<sub>3</sub> compounds.<sup>4</sup> The synthesis and properties of some other (1-azadiene)Fe(CO)<sub>3</sub> complexes have also been reported in the literature.<sup>5</sup> Nevertheless there has been little information on

the structural features of these compounds.<sup>4c–e,5c</sup> All structures of Fe(CO)<sub>3</sub> complexes that have been reported so far show the 1,3-butadiene, 1,4-diazadiene, or 1-azadiene ligands to adopt an s-cis configuration.<sup>6</sup> This is in agreement with the results of extended Hückel calculations for (1,3-butadiene)Fe(CO)<sub>3</sub> complexes.<sup>7</sup> Butadienes that are stabilized by organometallic fragments in s-trans conformation are less common and mainly known for Cp<sub>2</sub>M (M = Zr, Hf)<sup>8</sup> and CpMo(NO) moieties.<sup>9</sup>

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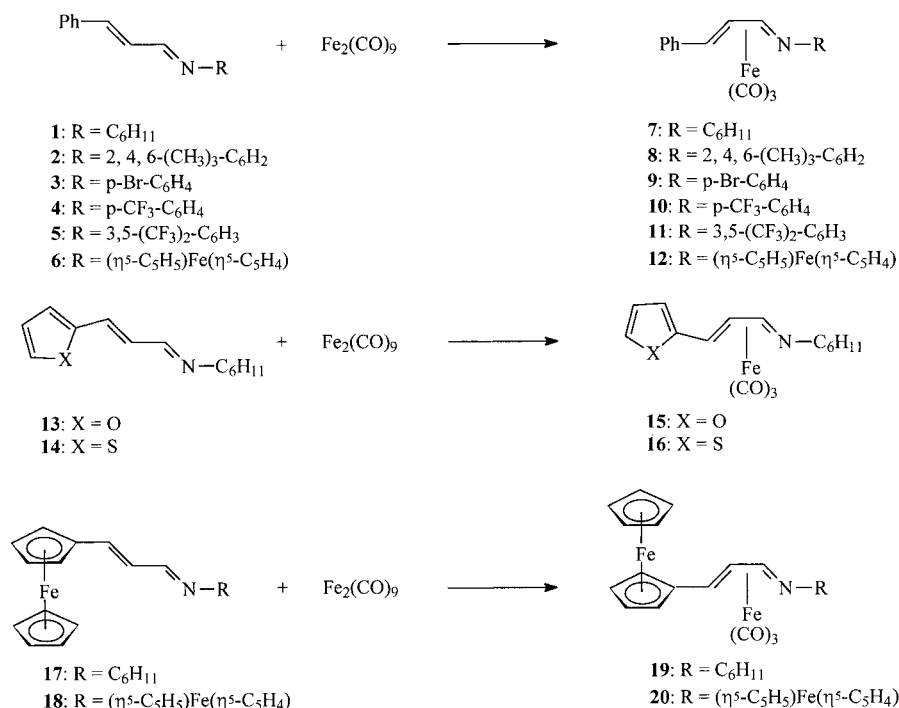
(6) Marr, G.; Rockett B. W. In *The Chemistry of the Metal-Carbon Bond*; Hartley, F. R., Patai, S., Eds.; Wiley: New York, 1982; Vol. I, Chapter 9, p 237.

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Scheme 1



Calculations have also been carried out for tantalum compounds with butadiene ligands<sup>10</sup> in order to decide whether these group 5 compounds have to be formulated as  $\eta^4$ -coordinated complexes, which is believed to be the case for the group 8 compounds, or as a metallacyclopent-3-ene, as for the group 4 complexes.

In this paper we describe the synthesis of a number of new 1-azadienes together with their Fe(CO)<sub>3</sub> complexes. Some of the ligands and all of the Fe(CO)<sub>3</sub> complexes have also been characterized by X-ray crystallography. Their molecular and crystal structures are presented. The results of extended Hückel calculations on the ligand system and on the organometallic compounds are discussed in order to explain some of the common features in the molecular structures and crystal packings of the (1-azadiene)Fe(CO)<sub>3</sub> complexes.

### Synthesis and Spectroscopical Properties of 1-Azadienes and (1-azadiene)Fe(CO)<sub>3</sub> Complexes

Scheme 1 shows the synthesis of (1-azadiene)Fe(CO)<sub>3</sub> complexes from the corresponding ligands and Fe<sub>2</sub>(CO)<sub>9</sub>. Three groups of organometallic compounds are described in this paper. The first group (7–12) is derived from ligands (1–6), which are synthesized by condensation of cinnamaldehyde with the corresponding amine. **15** and **16** are prepared by the reaction of Fe<sub>2</sub>(CO)<sub>9</sub> and  $\alpha,\beta$ -unsaturated imines with a heteroaromatic group at the C terminus, whereas for **19** and **20** a ferrocenyl moiety has been introduced in the same position. The synthesis, spectroscopical properties, and molecular structures of the ligands and Fe(CO)<sub>3</sub> complexes bearing ferrocenyl groups (**6**, **12**, **17–20**) have already been published by some of us elsewhere.<sup>11</sup>

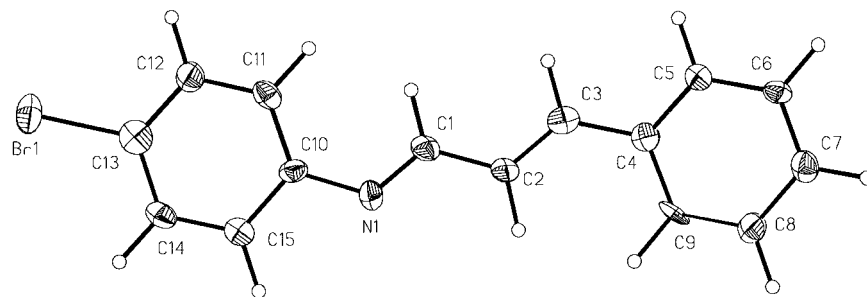
The Fe(CO)<sub>3</sub> complexes are easily prepared by reacting the ligands with Fe<sub>2</sub>(CO)<sub>9</sub> in *n*-heptane at 50 °C. Chromatographic workup gives the organometallic compounds in reasonable to good yields. By recrystallization from mixtures of light petroleum (bp 40–60 °C) and CH<sub>2</sub>Cl<sub>2</sub>, the complexes are obtained as crystalline orange solids.

The IR spectra of the ligands show as the most typical resonance a band in the region around 1630 cm<sup>-1</sup> representing the C=N stretching vibration. The iron complexes are easily identified by the IR bands of the three terminal CO ligands, which show the pattern typical for Fe(CO)<sub>3</sub> groups.

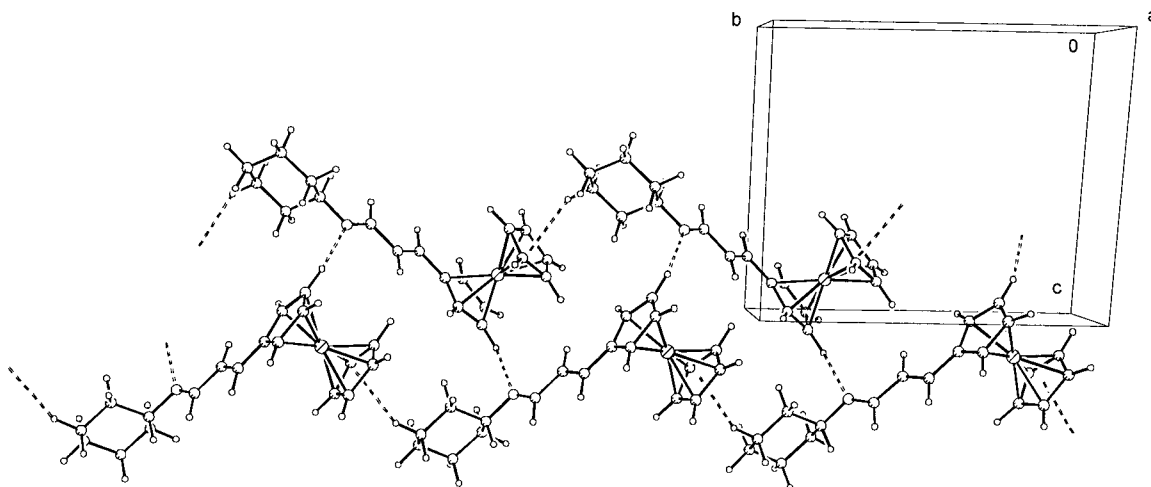
The NMR spectra of the mononuclear iron complexes show significant differences compared to those of the free ligands. In the <sup>1</sup>H NMR spectra of the ligands the resonance for the imine hydrogen atom is observed at about 8 ppm; the olefinic protons show signals in the region between 6.5 and 7.5 ppm. The corresponding <sup>13</sup>C resonances are observed at about 160 ppm (C=N) and between 130 and 150 ppm (=CH). These signals are shifted to higher field by complexation of the ligand with a Fe(CO)<sub>3</sub> moiety. The <sup>1</sup>H NMR spectra of the iron compounds thus show the resonance for the imine hydrogen atom at about 6.2–6.9 ppm, whereas the signals representing the olefinic hydrogen atoms are observed at about 2.9–3.4 and 5.4–6.1 ppm, respectively. The same effect can be seen in the <sup>13</sup>C NMR spectra. Resonances of the carbon atoms of the azadiene are shifted to higher field for 50–70 ppm and are observed at about 110 ppm (C=N) and 75 and 60 ppm (=CHR), respectively. The organic groups at the imino nitrogen atom and at the C-terminal end of the 1-azadiene chain give the expected signals in the <sup>1</sup>H and <sup>13</sup>C NMR spectra. The terminal CO ligands at the iron atom show very broad signals in the <sup>13</sup>C NMR spectra of **7–10**, **15**, and **16**; no resonance is observed for **11**. The corresponding signals in the <sup>13</sup>C NMR spectra of **12** and

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**Figure 1.** Molecular structure of **3**.



**Figure 2.** Crystal packing of **17**. A combination of C–H...N and weak C–H... $\pi_{Cp}$  interactions builds up a double-chain arrangement.

**Table 1. Bond Lengths [pm] and Angles [deg] of **3**, **4**, **5**, and **17****

	<b>3</b>	<b>4</b>	<b>5</b>	<b>17</b>
N1–C1	128(2)	127.1(8)	125.6(5)	124.0(9)
C1–C2	143(2)	144.9(8)	144.4(5)	146.1(9)
C2–C3	134(2)	131.4(9)	131.8(5)	135.3(9)
C3–C4	145(2)	145.9(8)	146.0(5)	146.3(9)
C <sub>ipso</sub> –N1	141(2)	141.9(7)	142.0(5)	145.5(8)
C <sub>ipso</sub> –N1–C1	121(1)	119.1(5)	120.7(3)	116.9(6)
N1–C1–C2	122(1)	122.6(6)	122.5(4)	123.3(7)
C1–C2–C3	123(1)	123.4(6)	123.1(4)	122.2(6)
C2–C3–C4	128(1)	126.8(6)	128.7(4)	126.9(6)

**Table 2. Shortest Intermolecular Distances and Angles in the Crystal Packings of **3**, **5**, and **17****

compound	C–H...Y hydrogen bond	H...Y [pm]	C–H...Y [deg]
<b>3</b>	C–H... $\pi_{Ph}$	268.2	130.8
<b>5</b>	C–H...F	253.4	173.0
<b>17</b>	C–H...F	265.9	147.3
	C–H...N	247.8	166.0
	C–H... $\pi_{Cp}$	264.0	148.4
	C–H... $\pi_{Cp}$	264.7	177.3

**19** are also broad, whereas the spectrum of **20** shows three different signals for the CO groups.<sup>11</sup> This behavior indicates that the fluxionality of the (1-azadiene)-Fe(CO)<sub>3</sub> complexes shows coalescence temperatures near room temperature.<sup>4d,12</sup>

### Structural Analysis

**1-Azadiene Ligands.** Table 1 summarizes the most important bond lengths and angles of **3**, **4**, **5**, and **17**. The molecular structure of **3**, of which the numbering scheme for the azadiene chain has been retained for all other compounds, is shown in Figure 1.

All the structures show some common features: the  $\alpha,\beta$ -unsaturated 1-azadiene chain N1–C1–C2–C3 presents an s-trans conformation with respect to the central single bond C1–C2. In addition the N1–C1 and C2–C3 bond lengths clearly indicate a double bond, whereas

the central bond between C1 and C2 shows a value typical for a single bond.

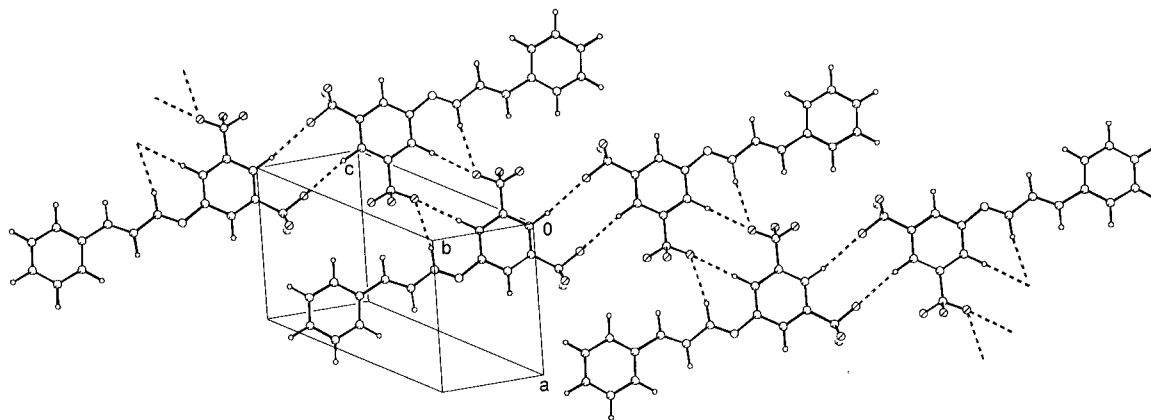
The shortest intermolecular C–H...X (X = F, N,  $\pi$ ) contacts in crystalline **3**, **5**, and **17** are reported in Table 2. In the crystal structures of **3** and **17** the shortest intermolecular distances are those of hydrogen atoms being orientated toward the center of a phenyl group ( $\pi_{Ph}$  as in **3**) or of a cyclopentadienyl ligand ( $\pi_{Cp}$  as in **17**), respectively. These distances are about 15–20 pm below the sum of the contact radii defined by Bondi et al.,<sup>13</sup> indicating a rather weak interaction.

The crystal packing of **3** shows the existence of weak hydrogen bonding between a proton of the bromine-substituted phenyl group and the electron density centroid of the corresponding phenyl group in the next molecule (C–H... $\pi_{Ph}$  = 268.2 pm). As a result, a chain of molecules is formed. The angle between the two phenyl groups is 61.7°; the bond angle between the CH group and the center of the next phenyl ring is 130.8°.

The arrangement of **17** in the solid state (see Figure 2) shows chains built up by C–H...N hydrogen bonds

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**Figure 3.** Crystal packing of **5**. Interactions of the C–H...F type build up a chain of dimers.

**Table 3. Bond Lengths [pm] and Angles [deg] of 7–12, 15, 16, 19, and 20**

	7	8	9	10	11	12	15	16	19	20
Fe1–N1	208.0(1)	212.5(6)	207.2(3)	206.5(3)	204.2(3)	209.8(4)	207.7(2)	208.2(2)	208.2(3)	213.2(4)
Fe1–C1	208.1(2)	205.4(7)	206.4(4)	205.7(5)	207.2(4)	206.4(5)	208.0(3)	208.3(2)	207.7(3)	207.5(5)
Fe1–C2	205.0(2)	206.0(8)	207.2(4)	207.1(5)	206.0(4)	205.3(5)	204.9(3)	204.5(2)	206.9(3)	205.6(4)
Fe1–C3	216.0(2)	214.4(8)	215.7(4)	215.4(4)	214.5(4)	214.7(5)	214.3(3)	215.7(2)	215.3(2)	213.7(4)
N1–C1	134.0(2)	136(1)	135.3(5)	135.7(5)	135.8(5)	134.8(7)	134.1(4)	134.5(3)	134.0(4)	137.8(5)
C1–C2	141.8(2)	141(1)	141.4(5)	141.9(6)	140.6(6)	140.4(7)	141.5(4)	141.4(3)	141.1(5)	140.0(6)
C2–C3	142.1(2)	142(1)	141.5(5)	141.2(6)	140.1(5)	140.4(7)	141.4(4)	141.7(3)	141.9(5)	136.3(6)
C3–C4	147.1(2)	148(1)	148.2(5)	148.4(6)	147.4(5)	147.8(7)	145.3(4)	146.1(3)	147.1(5)	142.1(6)
C <sub>ipso</sub> –N1	146.8(2)	143(1)	141.9(5)	141.6(5)	138.8(5)	141.3(6)	147.3(3)	147.3(3)	146.6(4)	144.5(5)
C <sub>ipso</sub> –N1–C1	116.2(1)	117.8(6)	118.3(3)	118.8(3)	119.3(3)	118.7(4)	116.1(2)	116.0(2)	114.5(3)	118.9(4)
N1–C1–C2	115.0(2)	116.7(7)	115.3(2)	114.3(4)	114.2(3)	115.7(5)	114.6(3)	115.0(2)	116.8(3)	115.7(4)
C1–C2–C3	116.0(2)	117.9(8)	118.2(3)	118.3(4)	118.6(4)	117.8(5)	116.6(3)	116.3(2)	117.4(3)	119.0(4)
C2–C3–C4	124.9(2)	123.7(8)	121.9(3)	122.5(4)	124.6(3)	125.5(5)	122.4(3)	123.4(2)	120.7(3)	120.7(4)

from the substituted cyclopentadienyl ligand of one molecule to the imino nitrogen atom of the next molecule, with a resulting bond length of 264.0 pm. There are additional weak interactions of the C–H... $\pi_{\text{Cp}}$  type that form chains in the solid-state structure of **17**.

In the X-ray structure of **5** interactions between the  $\text{CF}_3$  groups and aromatic C–H bonds of neighboring molecules are observed. The distances reported in Table 2 (C–H...F of 247.8–265.9 pm) demonstrate that covalently bonded fluorines are poor hydrogen bond acceptors, as it has been shown previously.<sup>14a,b</sup> On the other hand the interactions are well in the range that has been reported for C–H...F interactions in the solid-state structures of several fluorobenzene derivatives.<sup>14c</sup> We shall get back to this point later when considering the corresponding organometallic complexes. The  $\text{CF}_3$  groups in ortho position with respect to the azadiene chain in the solid-state structure of **5** form two different kinds of dimers linked by C–H...F hydrogen bonds (Figure 3). One dimer is constructed by the interaction of one  $\text{CF}_3$  group with the aromatic C–H bond in para position to the imine nitrogen atom. The C–H...F bond length is 253.4 pm; the bond angle is 173.0°. The other  $\text{CF}_3$  moiety builds up a second type of dimer via a bifurcated hydrogen bond to an aromatic hydrogen atom of the 3,5-( $\text{CF}_3$ )<sub>2</sub>-C<sub>6</sub>H<sub>3</sub> group (C–H...F 247.8 pm) as well as toward the hydrogen atom of the imine carbon of the next molecule (C–H...F 265.9 pm). As a result, a chain of dimers is formed. So the C–H...F interac-

**Table 4. Deviations [pm] from the Plane [N1–C1–H1–C2–H2–C3] of 7–12, 15, 16, 19, and 20**

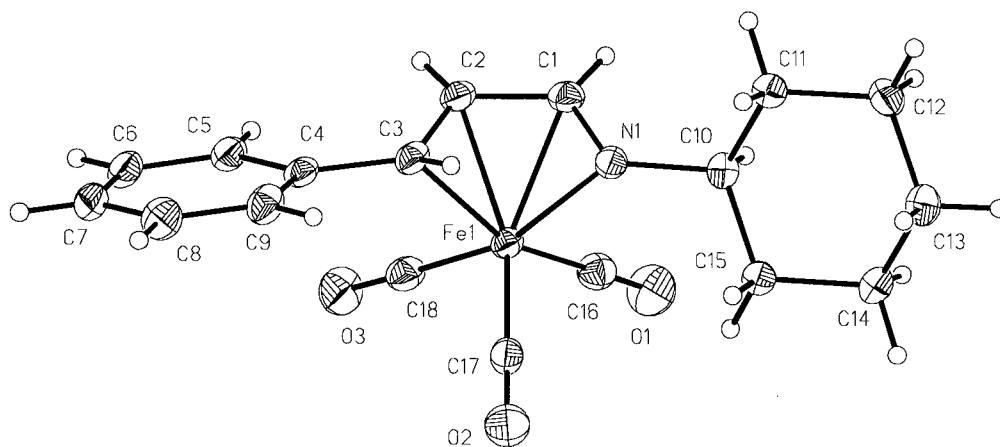
	7	8	9	10	11	12	15	16	19	20
N1	-5.5	-1.4	-0.8	-2.1	-4.9	-1.5	-3.2	-5.5	-5.3	-2.0
C1	2.5	2.2	2.4	-0.3	2.1	1.2	3.4	2.1	0.8	3.0
H1	3.7	-1.1	-1.5	2.2	3.1	0.4	0.5	4.2	4.8	-0.9
C2	1.2	4.3	1.6	2.1	2.7	0.8	1.1	0.6	2.3	-2.9
H2	-5.9	-2.9	-0.9	-3.3	-6.1	-1.6	-3.3	-5.8	-6.3	-2.9
C3	4.0	-1.2	-0.8	1.4	3.1	0.6	1.5	4.4	3.7	-0.4
H3	48.4	38.5	44.0	45.1	51.2	48.6	46.9	56.8	46.6	36.3

tions in **5** are also close to the sum of the van der Waals radii of fluorine and hydrogen.

**(1-Azadiene)Fe(CO)<sub>3</sub> Complexes.** The most important bond lengths and angles of **7–12**, **15**, **16**, **19**, and **20** are reported in Table 3, while Table 4 collects the deviation from the molecular 1-azadiene plane of the constituent atoms found in these structures. The hydrogen bond distances and angles are summarized in Table 5. The molecular structure of **7**, used as a model for the other compounds, is shown in Figure 4.

In all complexes the iron atom shows a square pyramidal coordination sphere with the azadiene ligand always situated in the square plane of the complex. In contrast to the solid-state structures of the free ligands, the complexes consist of a 1-azadiene ligand adopting an s-cis conformation with respect to the central C1–C2 bond in the azadiene chain. The C–N bond of the azadiene is lengthened by about 10 pm upon coordination to the  $\text{Fe}(\text{CO})_3$  moiety, as is the C1–C2 bond length, while a shortening of the central C2–C3 distance is observed. The Fe–C bond lengths of the C1 and C2 atoms are also similar for all compounds, whereas the Fe–C3 bond is about 10 pm longer than the other bonds. The hydrogen atoms of the azadiene chains were local-

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**Figure 4.** Molecular structure of **7**.

**Table 5. Hydrogen Bond Distances and Angles in the Crystal Structures of 8–12, 15, 16, 19, and 20**

compound	C–H...Y hydrogen bond	H...Y [pm]	C–H...Y [deg]
<b>8</b>	C–H...O	258.0	134.4
	C–H...O	226.8	152.3
<b>9</b>	C–H...N	246.2	150.0
	C–H...O	253.6	130.4
<b>10</b>	C–H...F	242.5	155.6
	C–H...N	245.8	156.8
<b>11</b>	C–H...O	238.5	135.3
	C–H...O	250.8	161.3
<b>12</b>	C–H...O	249.8	136.3
	C–H...O	261.4	137.5
<b>15</b>	C–H...O	252.7	160.6
	C–H...O	267.2	168.1
<b>16</b>	C–H...O	245.0	171.4
	C–H...O	256.2	149.1
<b>19</b>	C–H...O	243.4	172.4
	C–H...O	252.0	137.7
<b>20</b>	C–H...O	257.2	164.0
	C–H...O	258.4	159.2

ized from the difference electron density map and were refined without constraints for all complexes. The nitrogen and carbon atoms of the azadiene as well as the hydrogen atoms at C1 and C2 are situated in one plane for all complexes, whereas the hydrogen atom at C3 always shows a deviation from this plane of about 40–50 pm (see Table 4). All these structural features will be taken into account in the molecular orbital analysis (see below).

The hydrogen bond pattern of these complexes is deeply modified from that of the free ligands by the introduction of the  $\text{Fe}(\text{CO})_3$  moiety, because the CO ligands are good hydrogen bond acceptors,<sup>15</sup> and by the *s-cis* conformation of the 1-azadiene ligand. In eight out of ten complexes (**8**, **9**, **11**, **12**, **15**, **16**, **19**, **20**) the oxygen atom of the CO ligands acts as the acceptor of intermolecular interactions. With the exception of **8**, **15**, and **16** in all structures the H1 or H2 hydrogens are involved in some hydrogen bonding. There is no short intermolecular contact in which H3 takes part. These results are consistent with the extended Hückel calculations, which show C1 and C2 to be mostly  $\text{sp}^2$  hybridized, whereas C3 should be considered more an  $\text{sp}^3$  carbon

atom with a partial negative charge. Therefore the hydrogen atoms bound to C1 and C2 are more acidic and they are more effective C–H donor groups compared to H(C3).

While in crystalline **7** there are no short intermolecular interactions worth noticing, in the crystal structure of **10** a C–H...F interaction of 242.5 pm between an aromatic C–H group and the  $\text{CF}_3$  substituent of a neighboring molecule is observed. There is also a second type of hydrogen bond, namely of the C2–H2...N1 type (245.8 pm) responsible for building up chains of molecules (Figure 5).

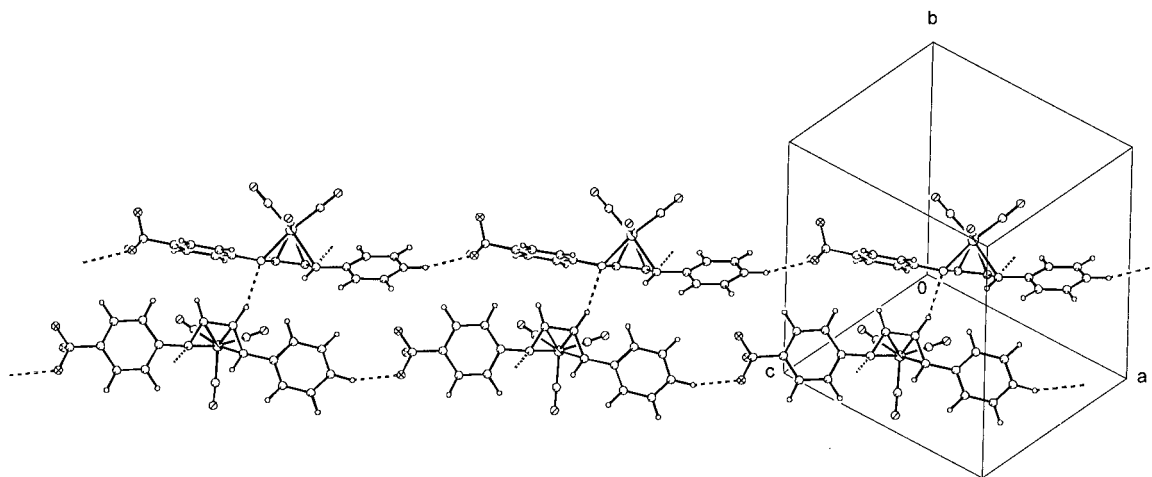
The packing of **9** is similar to that described for **10**. It consists of chains linked by hydrogen bonds between a hydrogen atom of the phenyl group and a CO ligand of a neighboring molecule (253.6 pm). Interchain links are provided by further hydrogen bonding (246.2 pm) involving atom H2 and the imine nitrogen of neighboring chains.

The crystal structure of **11** shows the formation of dimers, which are constructed by an interaction of H2 with a CO ligand of the next molecule (238.5 pm). The dimers are connected to give infinite chains by hydrogen bonds between the proton next to both  $\text{CF}_3$  groups toward another CO ligand of the neighboring dimer (250.8 pm, Figure 6). In contrast to the free ligand (**5**), the  $\text{CF}_3$  groups are not involved in any significantly short intermolecular contacts. This is a clear evidence that CO ligands are better hydrogen bond acceptor groups than organic fluorine.<sup>14</sup>

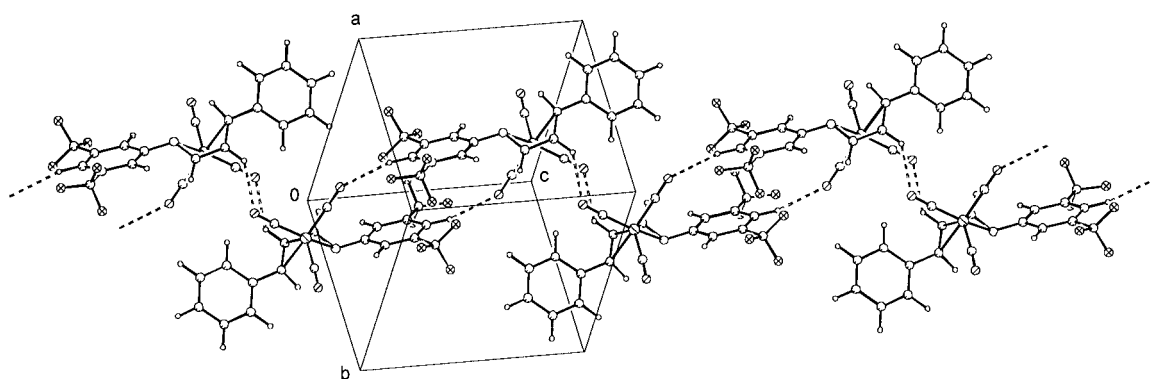
The crystal packing of **8**, closely related to that of **11**, contains dimeric subunits that are linked by C–H...O bond between a proton of the phenyl group and a CO ligand of the next molecule (258.0 pm). In addition these dimers are linked in infinite chains by interaction of a methyl group of the mesityl moiety with another CO ligand (226.8 pm).

The structure of **12** contains a bifurcated interaction (see Figure 7) in which the same CO-ligand interacts simultaneously with an aromatic proton and the H2 atom (252.7 and 238.5 pm, respectively). The chains formed by the bifurcated hydrogen bonds build up an infinite network by combination with a second chain via a C–H...O interaction between a proton of the unsubstituted cyclopentadienyl ligand and another CO ligand (249.8 pm).

(15) (a) Braga, D.; Grepioni, F.; K. Biradha, F.; Pedireddi, V. R.; Desiraju, G. R. *J. Am. Chem. Soc.* **1995**, *117*, 3156. (b) Braga, D.; Grepioni, F. *Acc. Chem. Res.* **1997**, *30*, 81. (c) Braga, D.; Grepioni, F.; Desiraju, G. R. *J. Organomet. Chem.* **1997**, *548*, 33.



**Figure 5.** Crystal packing of **10**. A combination of C–H...N and weak C–H...F interactions builds up an infinite network.



**Figure 6.** Crystal packing of **11**. Interactions of the C–H...O type build up a chain of dimers.

The similarity of crystalline **15** and **16** shows that there is no effect on the crystal packing by substitution of sulfur for oxygen. Both compounds form infinite chains via C–H...O interactions between the proton in 4-position of the heterocycle toward a CO group of the next molecule.

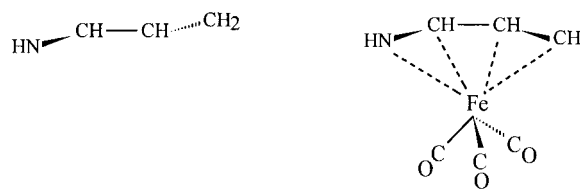
Crystalline **19** again shows a network similar to that of **9** and **10** (Figure 5). In **19** one of the chains is formed by interaction of a proton belonging to the cyclopentadienyl ligand which bears the azadiene moiety with a CO ligand of the next molecule with a bond length of 243.4 pm. These chains are connected by interactions between H2 and another CO ligand of a molecule of the neighboring chain (252.0 pm). In addition, each molecule of the infinite network forms a dimeric substructure via hydrogen bonding between H2 and another CO ligand of a neighboring molecule (256.2 pm).

In contrast, the crystal packing of **20** only shows the formation of dimeric units via hydrogen bonds between H1 and H2 with two different CO ligands of the neighboring molecule. Both C–H...O bond lengths are of nearly the same value (257.2 and 258.4 pm).

### Molecular Orbital Calculations

In this section we investigate the bonding interaction in the (1-azadiene)Fe(CO)<sub>3</sub> system starting from the observation of the structural data described above. In particular we will address two issues: (i) the relationship between the cis conformation of the 1-azadiene ligand when coordinated to the Fe(CO)<sub>3</sub> and the trans

### Scheme 2

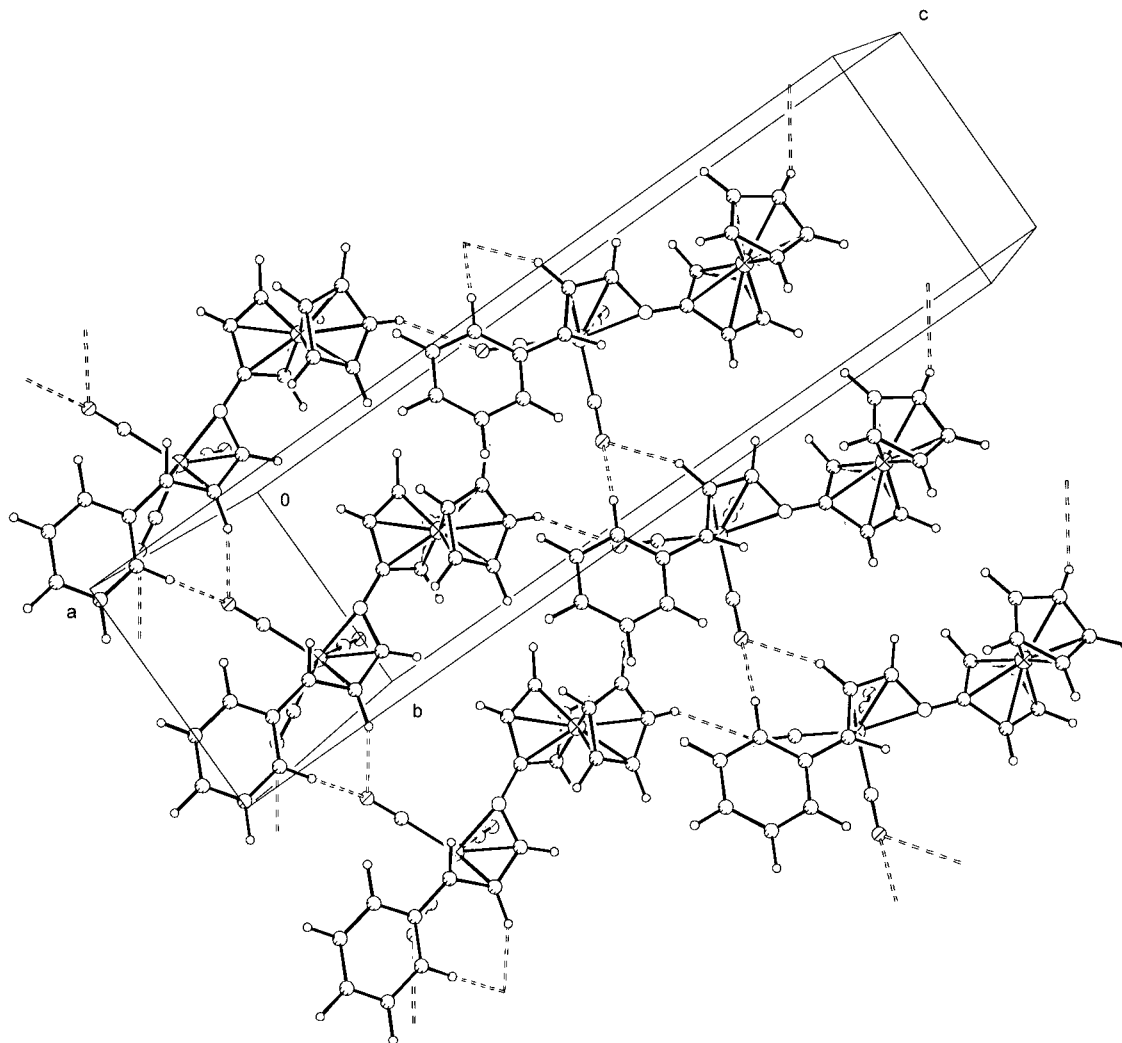


arrangement of the free ligand; (ii) the out-of-plane displacement of the hydrogen atom bonded to C3 with respect to the N–C1–C2–C3 plane of the azadiene ligand.

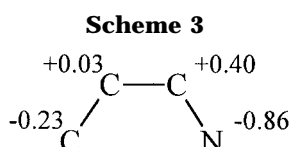
The model structures used in our extended Hückel analysis are sketched in Scheme 2 (see Experimental Section for geometric details and parameters).

On the free azadiene ligand we performed a cis–trans torsional analysis, obtaining the same qualitative trend as observed for the butadiene torsional energy profile, the *trans*-azadiene being approximately 5.8 kcal mol<sup>−1</sup> more stable than the *cis* conformer. Hückel theory predicts an energy stabilization of 7 kcal mol<sup>−1</sup> for butadiene, in good agreement with the experimental value of 3–4 kcal mol<sup>−1</sup>.<sup>16</sup> We also compared the coordination of the ligand bound to the Fe(CO)<sub>3</sub> moiety in both *cis* and *trans* conformations. The (*cis*-azadiene)-Fe(CO)<sub>3</sub> compound is more stable than the (*trans*-azadiene)-Fe(CO)<sub>3</sub> by approximately 4.2 kcal mol<sup>−1</sup>

(16) Streitwieser, A., Jr. *Molecular Orbital Theory for Organic Chemists*; Wiley: New York, 1961.



**Figure 7.** Crystal packing of **12**. A combination of different C–H...O interactions builds up an infinite network.



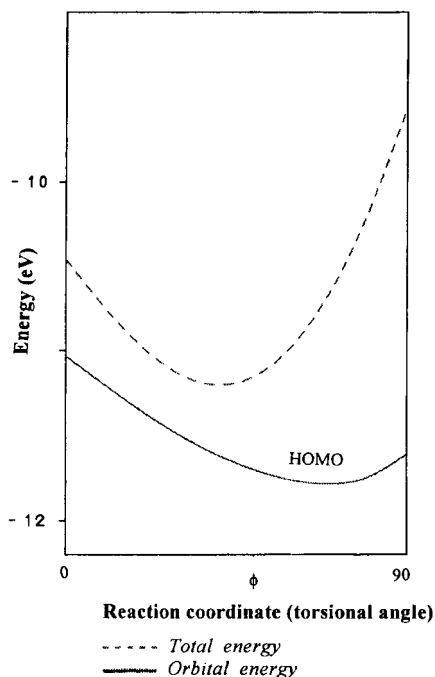
because of better overlap between the  $\text{Fe}(\text{CO})_3$  fragment molecular orbitals (MOs). Therefore in the *cis* isomer the peripheral azadiene atoms (in particular the N atom) attain a better overlap than in the *trans* isomer, though accompanied by a slight loss of overlap in the Fe–C1 and Fe–C2 bonding. The reduced overlap populations (OPs) between the azadiene atoms and the iron in the *cis* and *trans* cases are respectively Fe–N = 0.216 and 0.025; Fe–C1 = 0.065 and 0.197; Fe–C2 = 0.092 and 0.141; Fe–C3 = 0.080 and 0.045. Charges on the bonded *trans*-azadiene atoms are N = –0.96; C1 = 0.40; C2 = 0.08; C3 = 0.016. The most significant change in the atomic charge distribution on passing from *trans* to *cis* coordination is the charge at C3, which becomes negative (–0.230, see also Scheme 3).

To explain why the H(C3) atom is found nonplanar in the iron complexes (Table 4), we followed the reaction coordinate when the hydrogen atom is moved out of the ligand plane, i.e., varying the H–C–C–C dihedral angle ( $\phi$ ) by 90°. The Walsh diagram (see Figure 8) corresponding to the above-mentioned process shows that the

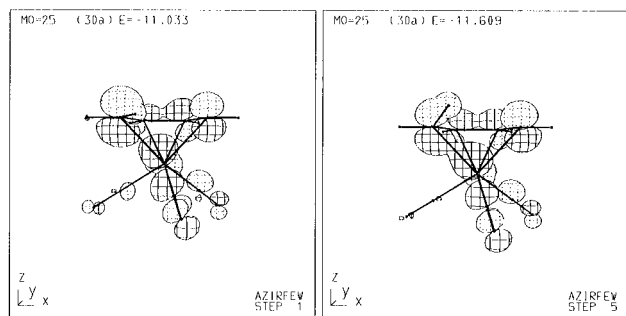
stability of the system increases by about 16.2 kcal mol<sup>–1</sup> when the hydrogen atom is above the azadiene molecular plane ( $\phi = 40^\circ$ ). The HOMO of the organometallic complex is found responsible for this stabilization, having a similar energy profile. Drawings of this orbital relative to  $\phi = 0^\circ$  and  $\phi = 40^\circ$  values are reported in Figure 9. The out-of-plane position of H(C3) strengthens the Fe–C3 bonding, as proved by the calculated overlap populations (Fe–C3 and C3–H OP values increase from 0.078 to 0.229 and from 0.786 to 0.806 when H(C3) is moved by 40°; the Fe–N OP keeps a constant value of 0.216 during the process). This is in agreement with the hypothesis that the C3 atom bears a partial  $\text{sp}^3$  hybridization rather than a pure  $\text{sp}^2$  when interacting with the  $\text{Fe}(\text{CO})_3$  fragment. In fact the H(C3) atom does not participate in any hydrogen bond interaction (see above), in agreement with the  $\text{sp}^3$  character of C3 with respect to C1 and C2.

In this respect we developed a molecular orbital analysis of (*cis*-azadiene) $\text{Fe}(\text{CO})_3$  allowing the valence orbitals of the  $\text{Fe}(\text{CO})_3$  fragment to interact with those of the ligand.<sup>17</sup> The orbital interaction diagram is shown in Figure 10. The complex has been divided into a 1-azadiene ligand and an  $\text{Fe}(\text{CO})_3$  fragment, the latter

(17) Albright, T.; Burdett, J. K.; Whangbo, M.-H. *Orbital Interactions in Chemistry*; Wiley: New York, 1985.



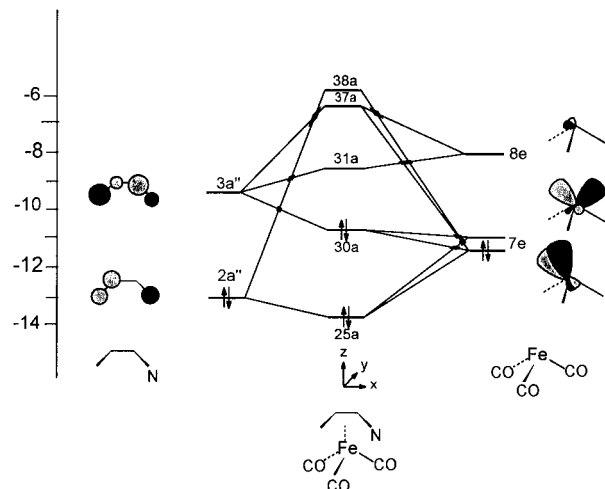
**Figure 8.** Walsh diagram showing the total energy curve (dashed line, in scale) together with the selected HOMO (solid line) associated with the out-of-plane moving of the H(C3) atom of  $90^\circ$  ( $\phi = 0^\circ$  planar C3 hydrogen).



**Figure 9.** Molecular orbital (HOMO) responsible for the major energy stabilization of the iron complex when H(C3) is nonplanar: (a)  $\phi = 0^\circ$  and (b)  $\phi = 40^\circ$ . Notice the increased overlap between Fe and C3.

being treated as a  $C_{3v}$   $\text{ML}_3$  unit with a  $d^8$  electronic configuration.

Lowering the symmetry of the azadiene ligand with respect to 1,3-butadiene results in a more complicated mixing of MOs of the two fragments. The HOMO and LUMO (7e in Figure 10) of the  $\text{Fe}(\text{CO})_3$  fragment interact with the HOMO ( $2a''$ ) and LUMO ( $3a''$ ) of the azadiene ligand, respectively. The bonding orbitals of the organometallic complex are described as a  $\pi$ -donation from the 1-azadiene ligand (MO  $2a''$ ) to the empty  $d_{xz}$  orbital of the metal with a strongly localized Fe–C3 and Fe–N character and a  $\pi^*$ -back-bonding from the occupied  $d_{xy}$  MO of the  $\text{Fe}(\text{CO})_3$  moiety and the LUMO ( $3a''$ ) of the organic fragment. The latter interaction, corresponding to the  $(1\text{-azadiene})\text{Fe}(\text{CO})_3$  HOMO (30a in Figures 9 and 10), is stabilized by the H(C3) nonplanarity as shown above. The increasing  $\pi^*$ -back-bonding from the  $\text{Fe}(\text{CO})_3$  fragment to the azadiene ligand weakens the C2–C3 and C1–N bonds and strengthens the central C–C bond, as noted in the molecular structures.



**Figure 10.** Orbital interaction diagram of the  $(1\text{-azadiene})\text{Fe}(\text{CO})_3$  model structure. The complex has been divided into an  $\text{Fe}(\text{CO})_3$  unit ( $C_{3v}$ , right) and the azadiene fragment (left); the C and O components are omitted for clarity.

## Conclusions

In this paper we have discussed the synthesis and characterization of a series of 1-azadiene ligands as well as the corresponding  $(\eta^4\text{-azadiene})\text{Fe}(\text{CO})_3$  complexes at the molecular and crystal level. While the 1-azadiene moiety adopts a trans conformation as free molecule, all complexes carry the ligand in cis conformation in order to bind to the  $\text{Fe}(\text{CO})_3$  unit. Besides this conformational difference, a more subtle effect has been observed. Upon coordination, the  $\beta$ -hydrogen atom of the azadiene is pushed out-of-plane with respect to the C–C–N plane. These two aspects have been addressed by means of extended Hückel molecular orbital calculations. The electronic origin of the out-of-plane position of the hydrogen atom HC(3) has been justified in terms of a better  $\pi^*$ -back-bonding between the 1-azadiene and  $\text{Fe}(\text{CO})_3$  molecular fragments.

In terms of crystal structure, we have been able to show that if the azadiene moiety is involved in hydrogen bonding, the interactions are realized by the hydrogen atom at the C–N double bond and the hydrogen atom in  $\alpha$ -position with respect to the imine group. In agreement with the observations made in other organometallic crystals of carbonyl species, all crystalline materials discussed herein show the presence of a large number of weak hydrogen bond interactions of the C–H...O type involving the CO-ligand acceptors.

## Experimental Section

**Reagents and Solvents.** All procedures were carried out under an argon atmosphere in anhydrous, freshly distilled solvents. Chromatography was done using silica gel 60 and silanized silica gel 60, 70–230 mesh ASTM (Merck), which were dried at  $10^{-2}$  bar ( $10^3$  Pa) for 2 days before use. 3-(2-furanyl)prop-2-enal<sup>18</sup> and 3-(2-thiophenyl)prop-2-enal<sup>19</sup> were synthesized by methods described in the literature.  $\text{Fe}_2(\text{CO})_9$  was prepared from  $\text{Fe}(\text{CO})_5$  (Lancaster) by irradiation in acetic acid.<sup>20</sup> The preparation of the ligands **6**, **17**, and **18** as well as

(18) König, W. *Chem. Ber.* **1925**, *58*, 2559.

(19) Aumann, R.; Hinterding, P.; Krüger, C.; Goddard, R. *J. Organomet. Chem.* **1993**, *459*, 145.



of the corresponding iron carbonyl complexes **12**, **19**, and **20** has been published by some of us.<sup>11</sup>

**Preparation of the Ligands.** Equimolar amounts (20 mmol) of the  $\alpha,\beta$ -unsaturated aldehyde and the corresponding amine are stirred together at 40 °C in just enough ethanol to dissolve all of the starting material. If both reactants are liquids, they are reacted without any solvent. The reaction is monitored by thin-layer chromatography. When the reaction is finished, **1** and **14** are purified by distillation, whereas **2**, **3**, **4**, **5**, and **13** had precipitated and were purified by recrystallization from ethanol. **6**, **17**, and **18** had to be chromatographed after the solvent was removed, as described in ref 11. **1**, **2**, **3**, and **4** have been described in the literature;<sup>21</sup> their identity and purity were determined by comparing their physical and spectroscopic properties with those reported. The physical and spectroscopic properties of **6**, **17**, and **18** have been described by us.<sup>11</sup>

**5:** yield 5.96 g (86.9%). Anal. Calcd for C<sub>17</sub>H<sub>11</sub>NF<sub>6</sub>: C, 59.48; H, 3.23; N, 4.08. Found: C, 59.18; H, 3.41; N, 4.06.

**13:** yield 1.89 g (46.6%). Anal. Calcd for C<sub>13</sub>H<sub>17</sub>NO: C, 76.81; H, 8.43; N, 6.89. Found: C, 76.47; H, 8.64; N, 6.93.

**14:** yield 3.02 g (68.9%). Anal. Calcd for C<sub>13</sub>H<sub>17</sub>N<sub>3</sub>: C, 71.19; H, 7.81; N, 6.39. Found: C, 71.03; H, 8.01; N, 6.42.

**Preparation of the Iron Carbonyl Complexes.** The synthesis of **12**, **19**, and **20** has been described previously.<sup>11</sup> In a typical experiment 500 mg (1.4 mmol) of Fe<sub>2</sub>(CO)<sub>9</sub> is stirred together with an equimolar amount of the corresponding ligand in 30 mL of *n*-heptane at 50 °C. During the reaction the color of the solution darkens from orange to deep red and the undissolved Fe<sub>2</sub>(CO)<sub>9</sub> slowly disappears. After all of the starting material is dissolved, the solvent is evaporated in vacuo. The resulting oily residue is dissolved in 10 mL of CH<sub>2</sub>-Cl<sub>2</sub>, and 1 g of silanized silica gel is added. Chromatography yields an orange fraction of ( $\eta^4$ -azadiene)Fe(CO)<sub>3</sub> using a mixture of light petroleum (bp 40–60 °C)/CH<sub>2</sub>Cl<sub>2</sub> (10:1) as the eluent. The complexes are recrystallized from light petroleum/CH<sub>2</sub>Cl<sub>2</sub> (20:1) at –20 °C.

**7:** yield 277 mg (56.2%). Anal. Calcd for C<sub>18</sub>H<sub>19</sub>NO<sub>3</sub>Fe: C, 61.21; H, 5.42; N, 3.87. Found: C, 60.96; H, 5.55; N, 3.98.

**8:** yield 232 mg (42.7%). Anal. Calcd for C<sub>21</sub>H<sub>19</sub>NO<sub>3</sub>Fe: C, 64.80; H, 4.92; N, 3.60. Found: C, 64.45; H, 5.03; N, 3.58.

**9:** yield 406 mg (68.3%). Anal. Calcd for C<sub>18</sub>H<sub>12</sub>NO<sub>3</sub>FeBr: C, 50.74; H, 2.84; N, 3.29; Br, 18.75. Found: C, 50.53; H, 2.83; N, 3.29; Br, 18.48.

**10:** yield 361 mg (62.2%). Anal. Calcd for C<sub>19</sub>H<sub>12</sub>NO<sub>3</sub>F<sub>3</sub>Fe: C, 54.97; H, 2.91; N, 3.37. Found: C, 54.72; H, 2.90; N, 3.37.

**11:** yield 261 mg (38.6%). Anal. Calcd for C<sub>20</sub>H<sub>11</sub>NO<sub>3</sub>F<sub>6</sub>Fe: C, 49.72; H, 2.29; N, 2.90. Found: C, 49.61; H, 2.41; N, 2.94.

**15:** yield 210 mg (43.6%). Anal. Calcd for C<sub>16</sub>H<sub>17</sub>NO<sub>4</sub>Fe: C, 56.00; H, 4.99; N, 4.08. Found: C, 56.23; H, 5.03; N, 4.09.

**16:** yield 350 mg (69.6%). Anal. Calcd for C<sub>16</sub>H<sub>17</sub>NO<sub>3</sub>SFe: C, 53.50; H, 4.77; N, 3.90. Found: C, 53.71; H, 4.86; N, 3.87.

**Spectroscopic Measurements.** Infrared spectra were recorded on a Perkin-Elmer FT-IR System 2000 using 0.2 mm KBr cuvettes; NMR spectra on a Bruker AC 200 spectrometer (<sup>1</sup>H, 200 MHz with SiMe<sub>4</sub> as internal standard; <sup>13</sup>C, 50.32 MHz with CDCl<sub>3</sub> as internal standard); mass spectra on a Finnigan MAT SSQ 710 instrument. Elemental analyses were carried out at the laboratory of the Institute of Organic Chemistry and Macromolecular Chemistry of the Friedrich-Schiller-University Jena.

**MS and Spectroscopic Data for 5.** MS (EI): *m/z* (%) 342 (M<sup>+</sup> – H, 100), 324 (C<sub>17</sub>H<sub>11</sub>NF<sub>5</sub><sup>+</sup>, 4), 272 (C<sub>16</sub>H<sub>10</sub>NF<sub>3</sub><sup>+</sup>, 2), 213 (C<sub>14</sub>H<sub>12</sub>NF<sup>+</sup>, 8), 128 (C<sub>9</sub>H<sub>6</sub>N<sup>+</sup>, 11), 115 (C<sub>8</sub>H<sub>5</sub>N<sup>+</sup>, 13), 103

(C<sub>7</sub>H<sub>5</sub>N<sup>+</sup>, 8), 77 (C<sub>6</sub>H<sub>5</sub><sup>+</sup>, 9), 51 (C<sub>4</sub>H<sub>3</sub><sup>+</sup>, 3). IR (in CH<sub>2</sub>Cl<sub>2</sub>, 298 K) [cm<sup>-1</sup>]: 1632 (C=N). <sup>1</sup>H NMR (in CDCl<sub>3</sub>, 298 K) [ppm]: 7.07 (dd, 1H, <sup>3</sup>J<sub>HH</sub> = 8.5 Hz, <sup>3</sup>J<sub>HH</sub> = 15.9 Hz, =CH), 7.24 (d, 1H, <sup>3</sup>J<sub>HH</sub> = 15.9 Hz, =CH), 7.34–7.42 (m, 3H, H<sub>ar</sub>), 7.51–7.56 (m, 4H, H<sub>ar</sub>), 7.69 (s, 1H, H<sub>ar</sub>), 8.22 (d, 1H, <sup>3</sup>J<sub>HH</sub> = 8.5 Hz, N=CH). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 298 K) [ppm]: 119.1 (<sup>3</sup>J<sub>CF</sub> = 3.8 Hz, C<sub>ar</sub>), 121.1 (<sup>3</sup>J<sub>CF</sub> = 3.4 Hz, C<sub>ar</sub>), 123.2 (<sup>1</sup>J<sub>CF</sub> = 272.7 Hz, CF<sub>3</sub>), 127.7 (C<sub>ar</sub>), 127.8 (C<sub>ar</sub>), 129.0 (C<sub>ar</sub>), 130.2 (=C), 132.6 (<sup>2</sup>J<sub>CF</sub> = 33.3 Hz, C<sub>ar</sub>), 135.1 (C<sub>ar</sub>), 146.6 (=C), 153.2 (C<sub>ar</sub>), 164.3 (N=C).

**MS and Spectroscopic Data for 13.** MS (EI): *m/z* (%) 203 (M<sup>+</sup>, 100), 186 (C<sub>12</sub>H<sub>14</sub>NO<sup>+</sup>, 5), 174 (C<sub>11</sub>H<sub>12</sub>NO<sup>+</sup>, 59), 160 (C<sub>10</sub>H<sub>10</sub>NO<sup>+</sup>, 60), 146 (C<sub>9</sub>H<sub>8</sub>NO<sup>+</sup>, 42), 132 (C<sub>8</sub>H<sub>6</sub>NO<sup>+</sup>, 19), 120 (C<sub>7</sub>H<sub>6</sub>NO<sup>+</sup>, 47), 107 (C<sub>7</sub>H<sub>7</sub>O<sup>+</sup>, 14), 93 (C<sub>6</sub>H<sub>5</sub>O<sup>+</sup>, 35), 80 (C<sub>5</sub>H<sub>4</sub>O<sup>+</sup>, 18), 78 (C<sub>5</sub>H<sub>4</sub>N<sup>+</sup>, 26), 67 (C<sub>4</sub>H<sub>5</sub>N<sup>+</sup>, 28), 55 (C<sub>3</sub>H<sub>5</sub>N<sup>+</sup>, 30), 41 (C<sub>2</sub>H<sub>3</sub>N<sup>+</sup>, 25). IR (in CH<sub>2</sub>Cl<sub>2</sub>, 298 K) [cm<sup>-1</sup>]: 1624 (C=N). <sup>1</sup>H NMR (in CDCl<sub>3</sub>, 298 K) [ppm]: 1.16–1.81 (m, 10H, CH<sub>2</sub>), 2.94–3.07 (m, 1H, CH), 6.38–6.43 (m, 2H, =CH, H<sub>ar</sub>), 6.69–6.76 (m, 2H, =CH, H<sub>ar</sub>), 7.40 (d, 1H, <sup>3</sup>J<sub>HH</sub> = 1.4 Hz, H<sub>ar</sub>), 7.95 (d, 1H, <sup>3</sup>J<sub>HH</sub> = 7.9 Hz, N=CH). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 298 K) [ppm]: 24.8 (CH<sub>2</sub>), 25.6 (CH<sub>2</sub>), 34.5 (CH<sub>2</sub>), 69.7 (CH), 111.0, 111.8 (C<sub>ar</sub>), 127.0, 127.8 (=CH), 143.5 (C<sub>ar</sub>), 152.2 (C<sub>ar</sub>), 159.7 (N=CH).

**MS and Spectroscopic Data for 14.** MS (EI): *m/z* (%) 219 (M<sup>+</sup>, 89), 218 (M<sup>+</sup> – H, 95), 204 (C<sub>12</sub>H<sub>14</sub>NS<sup>+</sup>, 3), 190 (C<sub>11</sub>H<sub>12</sub>NS<sup>+</sup>, 12), 176 (C<sub>10</sub>H<sub>10</sub>NS<sup>+</sup>, 23), 162 (C<sub>9</sub>H<sub>8</sub>NS<sup>+</sup>, 35), 148 (C<sub>8</sub>H<sub>6</sub>NS<sup>+</sup>, 11), 136 (C<sub>7</sub>H<sub>6</sub>NS<sup>+</sup>, 100), 121 (C<sub>7</sub>H<sub>5</sub>S<sup>+</sup>, 27), 109 (C<sub>6</sub>H<sub>5</sub>S<sup>+</sup>, 27), 97 (C<sub>5</sub>H<sub>5</sub>S<sup>+</sup>, 19), 80 (C<sub>5</sub>H<sub>6</sub>N<sup>+</sup>, 8), 77 (C<sub>5</sub>H<sub>3</sub>N<sup>+</sup>, 10), 67 (C<sub>4</sub>H<sub>7</sub>N<sup>+</sup>, 6), 55 (C<sub>3</sub>H<sub>5</sub>N<sup>+</sup>, 24), 41 (C<sub>2</sub>H<sub>3</sub>N<sup>+</sup>, 22). IR (in CH<sub>2</sub>-Cl<sub>2</sub>, 298 K) [cm<sup>-1</sup>]: 1628 (C=N); <sup>1</sup>H NMR (in CDCl<sub>3</sub>, 298 K) [ppm]: 1.07–1.78 (m, 10H, CH<sub>2</sub>), 2.92–3.06 (m, 1H, CH), 6.67 (dd, 1H, <sup>3</sup>J<sub>HH</sub> = 8.7 Hz, <sup>3</sup>J<sub>HH</sub> = 15.7 Hz, =CH), 6.86–7.06 (m, 3H, =CH, H<sub>ar</sub>), 7.20 (d, 1H, <sup>3</sup>J<sub>HH</sub> = 5.0 Hz, H<sub>ar</sub>), 7.92 (d, 1H, <sup>3</sup>J<sub>HH</sub> = 8.7 Hz, N=CH). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 298 K) [ppm]: 24.6 (CH<sub>2</sub>), 25.5 (CH<sub>2</sub>), 34.3 (CH<sub>2</sub>), 69.4 (CH), 126.5, 127.6, 127.8, 128.0 (=CH, C<sub>ar</sub>), 133.1 (C<sub>ar</sub>), 141.1 (C<sub>ar</sub>), 159.4 (N=CH).

**MS and Spectroscopic Data for 7.** MS (EI): *m/z* (%) 353 (M<sup>+</sup>, 1), 325 (M<sup>+</sup> – CO, 8); 297 (M<sup>+</sup> – 2 CO, 18), 269 (M<sup>+</sup> – 3 CO, 100), 187 (M<sup>+</sup> – 3 CO – C<sub>6</sub>H<sub>10</sub>, 23), 133 (C<sub>9</sub>H<sub>11</sub>N<sup>+</sup>, 29), 115 (C<sub>8</sub>H<sub>5</sub>N<sup>+</sup>, 54), 91 (C<sub>6</sub>H<sub>5</sub>N<sup>+</sup>, 12), 56 (C<sub>3</sub>H<sub>6</sub>N<sup>+</sup>, Fe<sup>+</sup>, 26). IR (in CH<sub>2</sub>Cl<sub>2</sub>, 298 K) [cm<sup>-1</sup>]: 2051 (vs), 1987 (vs), 1969 (s). <sup>1</sup>H NMR (in CDCl<sub>3</sub>, 298 K) [ppm]: 1.17–1.68 (m, 11H, C<sub>6</sub>H<sub>11</sub>), 2.94 (d, 1H, <sup>3</sup>J<sub>HH</sub> = 9.2 Hz, =CH), 5.48 (dd, 1H, <sup>3</sup>J<sub>HH</sub> = 2.7 Hz, <sup>3</sup>J<sub>HH</sub> = 9.2 Hz, =CH), 6.56 (d, 1H, <sup>3</sup>J<sub>HH</sub> = 2.7 Hz, =CH), 7.13–7.24 (m, 5H, H<sub>ar</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 298 K) [ppm]: 24.8 (CH<sub>2</sub>), 24.9 (CH<sub>2</sub>), 25.8 (CH<sub>2</sub>), 36.3 (CH<sub>2</sub>), 37.8 (CH<sub>2</sub>), 60.9 (=CH), 67.2 (CH), 71.9 (=CH), 111.0 (N=CH), 126.5 (C<sub>ar</sub>), 126.6 (C<sub>ar</sub>), 128.6 (C<sub>ar</sub>), 139.5 (C<sub>ar</sub>), 210.6 (CO, br).

**MS and Spectroscopic Data for 8.** MS (EI): *m/z* (%) 389 (M<sup>+</sup>, 2), 361 (M<sup>+</sup> – CO, 14); 333 (M<sup>+</sup> – 2 CO, 8), 305 (M<sup>+</sup> – 3 CO, 100), 249 (M<sup>+</sup> – 3 CO – Fe, 52), 152 (C<sub>12</sub>H<sub>8</sub><sup>+</sup>, 36), 130 (C<sub>9</sub>H<sub>8</sub>N<sup>+</sup>, 25), 115 (C<sub>8</sub>H<sub>5</sub>N<sup>+</sup>, 34), 91 (C<sub>6</sub>H<sub>5</sub>N<sup>+</sup>, 34), 78 (C<sub>6</sub>H<sub>6</sub><sup>+</sup>, 33), 56 (C<sub>3</sub>H<sub>6</sub>N<sup>+</sup>, Fe<sup>+</sup>, 56). IR (in CH<sub>2</sub>Cl<sub>2</sub>, 298 K) [cm<sup>-1</sup>]: 2053 (vs), 1990 (vs), 1978 (sh). <sup>1</sup>H NMR (in CDCl<sub>3</sub>, 298 K) [ppm]: 2.05 (s, 3H, CH<sub>3</sub>), 2.43 (s, 6H, CH<sub>3</sub>), 3.27 (d, 1H, <sup>3</sup>J<sub>HH</sub> = 9.5 Hz, =CH), 6.08 (d, 1H, <sup>3</sup>J<sub>HH</sub> = 9.2 Hz, =CH), 6.72 (s, 1H, =CH), 7.26–7.53 (m, 7H, H<sub>ar</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 298 K) [ppm]: 20.5 (CH<sub>3</sub>), 21.9 (CH<sub>3</sub>), 64.1 (=CH), 74.2 (=CH), 107.4 (N=CH), 127.5 (C<sub>ar</sub>), 127.6 (C<sub>ar</sub>), 129.4 (C<sub>ar</sub>), 130.9 (C<sub>ar</sub>), 131.1 (C<sub>ar</sub>), 132.6 (C<sub>ar</sub>), 139.6 (C<sub>ar</sub>), 147.3 (C<sub>ar</sub>), 211.0 (CO, br).

**MS and Spectroscopic Data for 9.** MS (EI): *m/z* (<sup>79</sup>Br) (%) 425 (M<sup>+</sup>, 5), 397 (M<sup>+</sup> – CO, 11); 369 (M<sup>+</sup> – 2 CO, 11), 341 (M<sup>+</sup> – 3 CO, 100), 284 (M<sup>+</sup> – 3 CO – FeH, 10), 264 (M<sup>+</sup> – 3 CO – C<sub>6</sub>H<sub>5</sub>, 14), 204 (C<sub>15</sub>H<sub>10</sub>N<sup>+</sup>, 67), 170 (C<sub>6</sub>H<sub>5</sub>NBr<sup>+</sup>, 46), 155 (C<sub>6</sub>H<sub>4</sub>Br<sup>+</sup>, 16), 135 (C<sub>4</sub>H<sub>8</sub>Br<sup>+</sup>, 35), 115 (C<sub>6</sub>H<sub>5</sub>N<sup>+</sup>, 79), 103 (C<sub>7</sub>H<sub>5</sub>N<sup>+</sup>, 35), 76 (C<sub>6</sub>H<sub>4</sub><sup>+</sup>, 48), 56 (C<sub>3</sub>H<sub>6</sub>N<sup>+</sup>, Fe<sup>+</sup>, 26). IR (in CH<sub>2</sub>-Cl<sub>2</sub>, 298 K) [cm<sup>-1</sup>]: 2060 (vs), 1998 (vs), 1988 (sh). <sup>1</sup>H NMR (in CDCl<sub>3</sub>, 298 K) [ppm]: 3.41 (d, 1H, <sup>3</sup>J<sub>HH</sub> = 9.5 Hz, =CH), 5.79 (dd, 1H, <sup>3</sup>J<sub>HH</sub> = 2.8 Hz, <sup>3</sup>J<sub>HH</sub> = 9.5 Hz, =CH), 6.80–6.84 (m, 2H, H<sub>ar</sub>), 6.92 (d, 1H, <sup>3</sup>J<sub>HH</sub> = 2.8 Hz, =CH), 7.21–7.38 (m, 7H, H<sub>ar</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 298 K) [ppm]: 63.1 (=CH), 75.5

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(=CH), 103.5 (N=CH), 115.1 (C<sub>ar</sub>), 123.8 (C<sub>ar</sub>), 127.1 (C<sub>ar</sub>), 127.5 (C<sub>ar</sub>), 129.2 (C<sub>ar</sub>), 132.2 (C<sub>ar</sub>), 139.1 (C<sub>ar</sub>), 153.3 (C<sub>ar</sub>), 210.1 (CO, br).

**MS and Spectroscopical Data for 10.** MS (EI):  $m/z$  (%) 415 (M<sup>+</sup>, 1), 387 (M<sup>+</sup> - CO, 5); 359 (M<sup>+</sup> - 2 CO, 4), 331 (M<sup>+</sup> - 3 CO, 25), 274 (M<sup>+</sup> - 3 CO - FeH, 15), 256 (C<sub>16</sub>H<sub>12</sub>F<sub>2</sub>N<sup>+</sup>, 15), 237 (C<sub>16</sub>H<sub>12</sub>FN<sup>+</sup>, 15), 166 (C<sub>12</sub>H<sub>8</sub>N<sup>+</sup>, 15), 126 (C<sub>6</sub>H<sub>4</sub>N<sup>+</sup>, 16), 115 (C<sub>8</sub>H<sub>5</sub>N<sup>+</sup>, 100), 107 (C<sub>7</sub>H<sub>9</sub>N<sup>+</sup>, 13), 91 (C<sub>6</sub>H<sub>5</sub>N<sup>+</sup>, 9), 75 (C<sub>6</sub>H<sub>3</sub><sup>+</sup>, 13), 56 (C<sub>3</sub>H<sub>6</sub>N<sup>+</sup>, Fe<sup>+</sup>, 26). IR (in CH<sub>2</sub>Cl<sub>2</sub>, 298 K) [cm<sup>-1</sup>]: 2062 (vs), 2000 (vs), 1990 (sh). <sup>1</sup>H NMR (in CDCl<sub>3</sub>, 298 K) [ppm]: 3.37 (d, 1H, <sup>3</sup>J<sub>HH</sub> = 8.0 Hz, =CH), 5.75 (d, 1H, <sup>3</sup>J<sub>HH</sub> = 8.0 Hz, =CH), 6.82–7.48 (m, 10H, =CH, H<sub>ar</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 298 K) [ppm]: 63.1 (=CH), 75.7 (=CH), 102.1 (N=CH), 121.8 (C<sub>ar</sub>), 124.1 (<sup>2</sup>J<sub>CF</sub> = 33 Hz, C<sub>ar</sub>), 125.0 (<sup>1</sup>J<sub>CF</sub> = 272 Hz, CF<sub>3</sub>), 126.2 (C<sub>ar</sub>), 126.7 (C<sub>ar</sub>), 127.3 (C<sub>ar</sub>), 128.9 (C<sub>ar</sub>), 138.4 (C<sub>ar</sub>), 156.7 (C<sub>ar</sub>), 205.1 (CO, br), 208.6 (CO, br), 211.3 (CO, br).

**MS and Spectroscopical Data for 11.** MS (EI):  $m/z$  (%) 483 (M<sup>+</sup>, 1), 455 (M<sup>+</sup> - CO, 5); 427 (M<sup>+</sup> - 2 CO, 6), 399 (M<sup>+</sup> - 3 CO, 61), 342 (M<sup>+</sup> - 3 CO - FeH, 7), 323 (C<sub>17</sub>H<sub>10</sub>NF<sub>5</sub><sup>+</sup>, 1), 304 (C<sub>17</sub>H<sub>10</sub>NF<sub>4</sub><sup>+</sup>, 15), 285 (C<sub>17</sub>H<sub>10</sub>NF<sub>3</sub><sup>+</sup>, 13), 254 (C<sub>16</sub>H<sub>10</sub>NF<sub>2</sub><sup>+</sup>, 9), 235 (C<sub>16</sub>H<sub>10</sub>NF<sup>+</sup>, 7), 213 (C<sub>14</sub>H<sub>12</sub>NF<sup>+</sup>, 13), 200 (C<sub>13</sub>H<sub>11</sub>NF<sup>+</sup>, 15), 163 (C<sub>10</sub>H<sub>10</sub>NF<sup>+</sup>, 16), 115 (C<sub>8</sub>H<sub>5</sub>N<sup>+</sup>, 46), 91 (C<sub>6</sub>H<sub>5</sub>N<sup>+</sup>, 100), 77 (C<sub>6</sub>H<sub>5</sub><sup>+</sup>, 22), 56 (C<sub>3</sub>H<sub>6</sub>N<sup>+</sup>, Fe<sup>+</sup>, 26); IR (in CH<sub>2</sub>Cl<sub>2</sub>, 298 K) [cm<sup>-1</sup>]: 2064 (vs), 2003 (vs), 1991 (sh). <sup>1</sup>H NMR (in CDCl<sub>3</sub>, 298 K) [ppm]: 3.42 (d, 1H, <sup>3</sup>J<sub>HH</sub> = 9.4 Hz, =CH), 5.84 (d, <sup>3</sup>J<sub>HH</sub> = 9.2 Hz, =CH), 6.87 (s, 1H, =CH), 7.23–7.38 (m, 8H, H<sub>ar</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 298 K) [ppm]: 63.8 (=CH), 77.2 (=CH), 101.1 (N=CH), 115.3 (<sup>3</sup>J<sub>FC</sub> = 3.8 Hz, C<sub>ar</sub>), 121.5 (<sup>3</sup>J<sub>CF</sub> = 3.9 Hz, C<sub>ar</sub>), 123.2 (<sup>1</sup>J<sub>CF</sub> = 272 Hz, CF<sub>3</sub>), 126.7 (C<sub>ar</sub>), 127.5 (C<sub>ar</sub>), 129.0 (C<sub>ar</sub>), 132.4 (<sup>2</sup>J<sub>CF</sub> = 33 Hz, C<sub>ar</sub>), 137.9 (C<sub>ar</sub>), 155.0 (C<sub>ar</sub>), no resonances for CO ligands have been observed.

**MS and Spectroscopical Data for 15.** MS (EI):  $m/z$  (%) 343 (M<sup>+</sup>, 3), 315 (M<sup>+</sup> - CO, 16); 287 (M<sup>+</sup> - 2 CO, 37), 259 (M<sup>+</sup> - 3 CO, 100), 203 (M<sup>+</sup> - 3 CO - Fe, 6), 176 (C<sub>11</sub>H<sub>14</sub>NO<sup>+</sup>, 14), 149 (C<sub>9</sub>H<sub>11</sub>NO<sup>+</sup>, 41), 122 (C<sub>7</sub>H<sub>8</sub>NO<sup>+</sup>, 12), 104 (C<sub>7</sub>H<sub>10</sub>NO<sup>+</sup>, 17), 93 (C<sub>6</sub>H<sub>5</sub>O<sup>+</sup>, 12), 83 (C<sub>6</sub>H<sub>11</sub><sup>+</sup>, 9), 77 (C<sub>6</sub>H<sub>5</sub><sup>+</sup>, 6), 56 (C<sub>3</sub>H<sub>6</sub>N<sup>+</sup>, Fe<sup>+</sup>, 26), 41 (C<sub>2</sub>H<sub>3</sub>N<sup>+</sup>). IR (in CH<sub>2</sub>Cl<sub>2</sub>, 298 K) [cm<sup>-1</sup>]: 2052 (vs), 1989 (vs), 1972 (s). <sup>1</sup>H NMR (in CDCl<sub>3</sub>, 298 K) [ppm]: 1.14–1.71 (m, 11H, C<sub>6</sub>H<sub>11</sub>), 2.88 (d, 1H, <sup>3</sup>J<sub>HH</sub> = 8.9 Hz, =CH), 5.44 (dd, 1H, <sup>3</sup>J<sub>HH</sub> = 2.7 Hz, <sup>3</sup>J<sub>HH</sub> = 8.9 Hz, =CH), 6.16 (d, 1H, <sup>3</sup>J<sub>HH</sub> = 2.7 Hz, =CH), 6.26 (dd, 1H, <sup>3</sup>J<sub>HH</sub> = 1.8 Hz, <sup>3</sup>J<sub>HH</sub> = 3.0 Hz, H<sub>ar</sub>), 6.50 (dd, 1H, <sup>3</sup>J<sub>HH</sub> = 0.8 Hz, <sup>3</sup>J<sub>HH</sub> = 3.0 Hz, H<sub>ar</sub>), 7.24 (d, 1H, <sup>3</sup>J<sub>HH</sub> = 1.8 Hz, H<sub>ar</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 298 K) [ppm]: 23.8 (CH<sub>2</sub>), 23.7 (CH<sub>2</sub>), 24.8 (CH<sub>2</sub>), 35.3 (CH<sub>2</sub>), 36.8 (CH<sub>2</sub>), 50.6 (=CH), 65.8 (CH), 69.0 (=CH), 105.4 (N=CH), 109.6 (C<sub>ar</sub>), 110.5 (C<sub>ar</sub>), 140.2 (C<sub>ar</sub>), 153.9 (C<sub>ar</sub>), 207.5 (CO, br).

**MS and Spectroscopical Data for 16.** MS (EI):  $m/z$  (%) 359 (M<sup>+</sup>, 1), 331 (M<sup>+</sup> - CO, 8); 303 (M<sup>+</sup> - 2 CO, 24), 275 (M<sup>+</sup> - 3 CO, 100), 193 (C<sub>11</sub>H<sub>15</sub>NS<sup>+</sup>, 12), 159 (C<sub>9</sub>H<sub>5</sub>NS<sup>+</sup>, 26), 137 (C<sub>7</sub>H<sub>7</sub>NS<sup>+</sup>, 54), 104 (C<sub>7</sub>H<sub>6</sub>N<sup>+</sup>, 11), 97 (C<sub>5</sub>H<sub>5</sub>S<sup>+</sup>, 5), 56 (C<sub>3</sub>H<sub>6</sub>N<sup>+</sup>, Fe<sup>+</sup>, 11), 41 (C<sub>3</sub>H<sub>5</sub><sup>+</sup>, 5). IR (in CH<sub>2</sub>Cl<sub>2</sub>, 298 K) [cm<sup>-1</sup>]: 2052 (vs), 1988 (vs), 1971 (s). <sup>1</sup>H NMR (in CDCl<sub>3</sub>, 298 K) [ppm]: 1.18–1.85 (m, 11H, C<sub>6</sub>H<sub>11</sub>), 3.20 (d, 1H, <sup>3</sup>J<sub>HH</sub> = 9.0 Hz, =CH), 5.36 (dd, 1H, <sup>3</sup>J<sub>HH</sub> = 2.8 Hz, <sup>3</sup>J<sub>HH</sub> = 9.0 Hz, =CH), 6.50 (d, 1H, <sup>3</sup>J<sub>HH</sub> = 2.8 Hz, =CH), 6.85–6.95 (m, 2H, H<sub>ar</sub>), 7.09 (dd, 1H, <sup>3</sup>J<sub>HH</sub> = 1.1 Hz, <sup>3</sup>J<sub>HH</sub> = 5.0 Hz, H<sub>ar</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 298 K) [ppm]: 24.7 (CH<sub>2</sub>), 24.8 (CH<sub>2</sub>), 25.7 (CH<sub>2</sub>), 36.3 (CH<sub>2</sub>), 37.8 (CH<sub>2</sub>), 56.0 (=CH), 66.9 (CH), 72.3 (=CH), 110.3 (N=CH), 123.4 (C<sub>ar</sub>), 123.9 (C<sub>ar</sub>), 127.5 (C<sub>ar</sub>), 144.9 (C<sub>ar</sub>), 209.0 (CO, br).

**Crystal Structure Determinations.** Crystals suitable for X-ray structure analysis have been grown from mixtures of light petroleum/CH<sub>2</sub>Cl<sub>2</sub>. The crystal structure determinations of **3**, **5**, **7**, **9**, **10**, and **11** were carried out on an Enraf Nonius CAD4 diffractometer, those of **8**, **15**, and **16** on a Siemens P4 diffractometer, the one of **4** on an Enraf Nonius Kappa CCD diffractometer. In all cases graphite-monochromated Mo K $\alpha$  radiation was used. The crystals were mounted in a stream of cold nitrogen. Data were corrected for Lorentz and polarization effects but not for absorption. The structures were solved by direct methods and refined by full-matrix least-squares techniques against  $F^2$  using the programs SHELXS86 and

**Table 6. Crystal and Intensity Data for the Compounds 3, 4, and 5**

	3	4	5
formula	C <sub>15</sub> H <sub>12</sub> NBr	C <sub>16</sub> H <sub>12</sub> NF <sub>3</sub>	C <sub>17</sub> H <sub>11</sub> NF <sub>6</sub>
mol weight [g mol <sup>-1</sup> ]	286.17	275.27	343.27
radiation	Mo K $\alpha$	Mo K $\alpha$	Mo K $\alpha$
monochromator	graphite	graphite	graphite
temp [K]	183	293	183
cryst color	pale yellow	pale yellow	yellow
cryst size [mm]	0.8 × 0.2 × 0.2	1.2 × 0.03 × 0.5	0.1 × 0.1 × 0.1
<i>a</i> [Å]	7.617(2)	6.2193(9)	8.0648(9)
<i>b</i> [Å]	5.567(1)	15.366(3)	8.627(2)
<i>c</i> [Å]	29.917(6)	7.313(2)	11.569(2)
$\alpha$ [deg]	90	94.979(6)	97.07(1)
$\beta$ [deg]	90	90.18(1)	93.20(1)
$\gamma$ [deg]	90	91.66(1)	107.41(1)
<i>V</i> [Å <sup>3</sup> ]	1268.6(4)	696.0(2)	758.5(2)
<i>Z</i>	4	2	2
<i>F</i> (000)	576	284	348
$\rho_{\text{calc}}$ [g cm <sup>-3</sup> ]	1.498	1.314	1.503
cryst syst	orthorhombic	triclinic	triclinic
space group	<i>Pna</i> 2 <sub>1</sub>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
abs coeff [mm <sup>-1</sup> ]	3.216	0.105	0.140
$\theta$ -limit [deg]	2.72–22.07	3.50–23.28	2.50–23.99
scan mode	$\omega$ -2 $\theta$	$\varphi$	$\omega$ -2 $\theta$
scan speed [deg min <sup>-1</sup> ]	1–10		1–10
no. of reflns measd	719	1864	2560
no. of ind reflns	719	1864	2381
<i>R</i> (int)	0.0000	0.000	0.0135
no. of obs reflns	663	1407	1705
$F_0^2 > 2\sigma(F_0^2)$			
no. of params	157	250	250
GOOF	1.085	1.165	1.052
<i>R</i> 1	0.0453	0.1284	0.0716
<i>wR</i> 2	0.1281	0.3367	0.1719
final diff map electron density [e Å <sup>-3</sup> ]	0.649	0.443	0.456

SHELXL93.<sup>22</sup> Computations of the structures were done with the program XPLOR, and the molecular illustrations were drawn using the program ZORTEP.<sup>23</sup> The crystal and intensity data are given in Tables 6 (**3**, **4**, and **5**) and 7 (**6**–**10**, **15**, and **16**). Details concerning the crystal structure analyses of **12**, **17**, **19**, and **20** have been reported by us in ref 11. Analyses of the packings were done using the program PLATON.<sup>24</sup> For this purpose the C–H distances have been normalized to 108.0 pm. Additional material on the structure analyses is available from the Fachinformationszentrum Chemie, Physik, Mathematik GmbH, 76344 Eggenstein-Leopoldshafen 2, Germany, by mentioning the deposition numbers CSD-408468 (**3**), -408469 (**4**), -408470 (**5**), -408471 (**7**), -408472 (**8**), -408473 (**9**), -408474 (**10**), -408475 (**11**), -407879 (**12**), -408476 (**15**), -408477 (**16**), -407880 (**17**), -407881 (**19**), -407882 (**20**), the authors, and the journal citation.

**Extended Hückel Analysis.** All the calculations were of the extended Hückel type,<sup>25</sup> with modified  $H_{ij}$ 's.<sup>26</sup> The basis set used for the Fe atom consisted of 3d, 4s, and 4p orbitals. For N, C, H, and O atoms standard parameters were used. The following valence-state ionization potentials were used for the Fe atom: ( $H_{ij}/\text{eV}$ ,  $\zeta$ ), 4s, -9.10, 1.9; 4p, -5.32, 1.9; 3d, -12.6, 5.35, 2.0 ( $\zeta_2$ ), 0.5505 (C<sub>1</sub>), 0.6260 (C<sub>2</sub>). Three-dimensional representations of orbitals as well as the Walsh diagram were drawn using the program CACAO.<sup>27</sup>

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**Table 7. Crystal and Intensity Data for the Compounds 7–11, 15, and 16**

	7	8	9	10	11
formula	C <sub>18</sub> H <sub>19</sub> NO <sub>3</sub> Fe	C <sub>21</sub> H <sub>19</sub> NO <sub>3</sub> Fe	C <sub>18</sub> H <sub>12</sub> NO <sub>3</sub> BrFe	C <sub>19</sub> H <sub>12</sub> NF <sub>3</sub> O <sub>3</sub> Fe	C <sub>20</sub> H <sub>11</sub> NF <sub>6</sub> O <sub>3</sub> Fe
mol weight [g mol <sup>-1</sup> ]	353.19	389.22	426.05	415.15	483.15
radiation	Mo K $\alpha$	Mo K $\alpha$	Mo K $\alpha$	Mo K $\alpha$	Mo K $\alpha$
monochromator	graphite	graphite	graphite	graphite	graphite
temp [K]	183	183	183	183	183
cryst color	orange	orange	orange	orange	orange
cryst size [mm]	0.6 × 0.4 × 0.3	0.8 × 0.5 × 0.2	0.6 × 0.3 × 0.1	0.6 × 0.2 × 0.1	0.3 × 0.2 × 0.05
<i>a</i> [Å]	11.979(3)	10.375(4)	11.463(2)	11.631(3)	8.556(3)
<i>b</i> [Å]	7.808(1)	9.036(4)	15.677(9)	16.015(7)	9.505(6)
<i>c</i> [Å]	18.376(3)	20.328(9)	9.463(3)	9.558(6)	13.353(5)
$\alpha$ [deg]	90	90	90	90	102.35(3)
$\beta$ [deg]	104.81(2)	95.25(3)	100.75(2)	100.12(4)	93.02(3)
$\gamma$ [deg]	90	90	90	90	110.88(4)
<i>V</i> [Å <sup>3</sup> ]	1661.6(5)	1898(1)	1671(1)	1753(1)	981.2(8)
<i>Z</i>	4	4	4	4	2
<i>F</i> (000)	736	808	848	840	484
$\rho_{\text{calc}}$ [g cm <sup>-3</sup> ]	1.412	1.362	1.694	1.573	1.635
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> $\bar{1}$
abs coeff [mm <sup>-1</sup> ]	0.923	0.816	3.312	0.912	0.849
$\theta$ -limit [deg]	2.29–24.68	2.13–23.50	2.55–28.48	2.51–28.62	2.50–28.49
scan mode	$\omega$ -2 $\theta$	$\omega$ -2 $\theta$	$\omega$ -2 $\theta$	$\omega$ -2 $\theta$	$\omega$ -2 $\theta$
scan speed [deg min <sup>-1</sup> ]	1–10	1–10	1–10	1–10	1–10
no. of reflns measd	2963	2721	4437	4666	4751
no. of ind reflns	2817	2721	4195	4412	4580
<i>R</i> (int)	0.0152	0.0000	0.0407	0.0442	0.0218
obs reflns $F_o^2 > 2\sigma(F_o^2)$	2599	2038	2962	3157	3639
no. of params	223	250	231	282	294
GOOF	1.047	1.073	1.031	1.228	1.032
<i>R</i> 1	0.0248	0.0694	0.0383	0.0703	0.0436
w <i>R</i> 2	0.0657	0.1859	0.0957	0.1804	0.0888
final diff map electron density [e Å <sup>-3</sup> ]	0.261	1.118	0.630	0.890	0.630

	15	16
formula	C <sub>16</sub> H <sub>17</sub> NO <sub>4</sub> Fe	C <sub>16</sub> H <sub>17</sub> NO <sub>4</sub> Fe
mol weight [g mol <sup>-1</sup> ]	343.16	359.22
radiation	Mo K $\alpha$	Mo K $\alpha$
monochromator	graphite	graphite
temp [K]	213	213
cryst color	orange	orange
cryst size [mm]	0.4 × 0.4 × 0.05	0.2 × 0.2 × 0.2
<i>a</i> [Å]	11.034(3)	11.868(2)
<i>b</i> [Å]	7.647(2)	7.853(1)
<i>c</i> [Å]	19.006(4)	18.147(2)
$\alpha$ [deg]	90	90
$\beta$ [deg]	102.17(1)	103.44(1)
$\gamma$ [deg]	90	90
<i>V</i> [Å <sup>3</sup> ]	1567.6(7)	1645.0(4)
<i>Z</i>	4	4
<i>F</i> (000)	712	744
$\rho_{\text{calc}}$ [g cm <sup>-3</sup> ]	1.454	1.450
cryst syst	monoclinic	monoclinic
space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
abs coeff [mm <sup>-1</sup> ]	0.981	1.056
$\theta$ -limit [deg]	1.89–24.36	1.87–27.50
scan mode	$\theta$ -2 $\theta$	$\theta$ -2 $\theta$
scan speed [deg min <sup>-1</sup> ]	3–60	3–60
no. of reflns measd	3385	4948
no. of ind reflns	2473	3785
<i>R</i> (int)	0.0566	0.0330
no. of obs reflns $F_o^2 > 2\sigma(F_o^2)$	2016	2889
no. of params	214	234
GOOF	1.060	1.021
<i>R</i> 1	0.0332	0.0390
w <i>R</i> 2	0.0829	0.0916
final diff map electron density [e Å <sup>-3</sup> ]	0.321	0.306

**The Model.** For the azadiene ligand we used the simplified CH<sub>2</sub>=CH–CH=NH system (the hydrogen atoms bonded to the nitrogen and terminal carbon atoms instead of the organic substituents). The N–H and C–H bond lengths used are 1.0 and 1.08 Å, respectively; the bond length of C<sub>1</sub>–C<sub>2</sub> is 1.34 Å, C<sub>2</sub>–C<sub>3</sub> 1.43 Å, and N–C 1.27 Å. All the ligand atoms were considered to be in a planar arrangement (unless otherwise stated) with all bond angles being 120°. For the organometallic

complex the azadiene geometry was taken as previously, while an optimization of the Fe–(azadiene) centroid along the perpendicular from the azadiene plane to the Fe nucleus has been carried out for both cis and trans conformers. The bond distances of the Fe(CO)<sub>3</sub> fragment used in the model are Fe–centroid = 1.5 Å (cis), 2.0 Å (trans), Fe–C1 = 2.04 Å, Fe–C2 = 2.07 Å, Fe–C3 = 2.07 Å, Fe–N = 2.02 Å, Fe–C = 1.8 Å, C–O = 1.3 Å.

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**Supporting Information Available:** Details about the X-ray crystal structures including ORTEP diagrams of the

crystal packings, tables of crystal data and structure refinement, atomic coordinates, bond lengths and angles, and anisotropic displacement parameters for **3**, **4**, **5**, **7**, **8**, **9**, **10**, **11**, **12**, **15**, **16**, **17**, **19**, and **20** (103 pages). See any current masthead page for ordering information and Internet access instructions.

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