# Remarkable Reactions of Cyclooctatetraene Diiron-Bridging Carbyne Complexes with Amino and Amido Compounds: Nucleophilic Addition to and Breaking of the Cyclooctatetraene Ring

**Shu Zhang,[a] Qiang Xu,*[b] Jie Sun,[a] and Jiabi Chen*[a]**

**Abstract:** The reactions of the cationic, diiron-bridging carbyne complexes $[Fe_2(\mu\text{-}CAr)(CO)_4(\eta^8\text{-}C_8H_8)]BF_4$ (**1**, $Ar = C_6H_5$; **2**, $Ar = p\text{-}CH_3C_6H_4$; **3**, $Ar = p\text{-}CF_3C_6H_4$) with $LiN(C_6H_5)_2$ in THF at low temperature gave novel N-nucleophilic-addition products, namely, the neutral, diiron-bridging carbyne complexes $[Fe_2(\mu\text{-}CAr)(CO)_4(\eta^7\text{-}C_8H_8N(C_6H_5)_2)]$ (**4**, $Ar = C_6H_5$; **5**, $Ar = p\text{-}CH_3C_6H_4$; **6**, $Ar = p\text{-}CF_3C_6H_4$)). Cationic bridging carbyne complexes **1**–**3** react with $(C_2H_5)_2NH$, $(iC_3H_7)_2NH$, and $(C_6H_{11})_2NH$ under the same conditions with ring cleavage of the COT ligand to produce the novel diiron-bridging carbene inner salts $[Fe_2\{\mu\text{-}C(Ar)C_8H_8NR_2\}(CO)_4]$ (**7**, $Ar = C_6H_5$, $R = C_2H_5$; **8**, $Ar = p\text{-}CH_3C_6H_4$, $R = C_2H_5$; **9**, $Ar = p\text{-}CF_3C_6H_4$, $R = C_2H_5$; **10**, $Ar = C_6H_5$, $R = iC_3H_7$; **11**, $Ar = p\text{-}CH_3C_6H_4$, $R = iC_3H_7$; **12**, $Ar = p\text{-}CF_3C_6H_4$, $R = iC_3H_7$; **13**, $Ar = C_6H_5$, $R = C_6H_{11}$; **14**, $Ar = p\text{-}CH_3C_6H_4$, $R = C_6H_{11}$, **15**, $Ar = p\text{-}CF_3C_6H_4$, $R = C_6H_{11}$). Piperidine reacts similarly with cationic carbyne complex **3** to afford the corresponding bridging carbene inner salt $[Fe_2\{\mu\text{-}C(Ar)C_8H_8N(CH_2)_5\}(CO)_4]$ (**16**). Compound **9** was transformed into a new diiron-bridging carbene inner salt **17**, the *trans* isomer of **9**, by heating in benzene. Unexpectedly, the reaction of $C_6H_5NH_2$ with **2** gave a novel COT iron–carbene complex $[Fe_2\{{=}C(C_6H_4CH_3\text{-}p)NHC_6H_5\}(\mu\text{-}CO)(CO)_3(\eta^8\text{-}C_8H_8)]$ (**18**). However, the analogous reactions of 2-naphthylamine with **2** and of $p\text{-}CF_3C_6H_4NH_2$ with **3** produce novel chelated iron–carbene complexes $[Fe_2\{{=}C(C_6H_4CH_3\text{-}p)NC_{10}H_7\}(CO)_4(\eta^2{:}\eta^3{:}\eta^2\text{-}C_8H_9)]$ (**19**) and $[Fe_2\{{=}C(C_6H_4CF_3\text{-}p)NC_6H_4CF_3\text{-}p\}(CO)_4(\eta^2{:}\eta^3{:}\eta^2\text{-}C_8H_9)]$ (**20**), respectively. Compound **18** can also be transformed into the analogous chelated iron–carbene complex $[Fe_2\{{=}C(C_6H_4CH_3\text{-}p)NC_6H_5\}(CO)_4(\eta^2{:}\eta^3{:}\eta^2\text{-}C_8H_9)]$ (**21**). The structures of complexes **6**, **9**, **15**, **17**, **18**, and **21** have been established by X-ray diffraction studies.

**Keywords:** alkene ligands · carbyne ligands · iron · nucleophilic addition · ring-opening

## Introduction

The addition of organic nucleophiles to unsaturated hydrocarbon ligands promoted by transition metals is one of the most investigated and important reactions in organometallic chemistry.[1] It has found broad application in organic synthesis[2] and is also a crucial step in industrial processes such as the Wacker process.[3] In this field cyclic polyolefin ligands are of great importance because attack on them has led to the synthesis of many otherwise inaccessible substituted polyolefin complexes.[4] 1,3,5,7-Cyclooctatetraene (COT), a medium-ring polyene and the next higher vinylogue of benzene, forms an exceptional variety of complexes with transition metals and plays a notable role in many aspects of organic and organometallic chemistry.[5]

On the other hand, dimetal bridging carbene complexes have been the subject of intensive research[6] due to their unique structure and chemical properties, as well as their potential use as models for intermediates in Fischer–Tropsch reactions.[6a, 7] As an extension of our studies on olefin-coordinated metal carbene and carbyne complexes,[8] we investigated the COT- and alkoxycarbene-bridged diiron complexes $[Fe_2\{\mu\text{-}C(OC_2H_5)Ar\}(CO)_4(\eta^8\text{-}C_8H_8)]$, which were prepared by the reaction of $[Fe_2(CO)_5(\eta^8\text{-}C_8H_8)]$ with aryllithium reagents, followed by alkylation with $Et_3OBF_4$.[9] The bridging COT ligand in these bridging alkoxycarbene complexes participates in a novel two-electron, three-center Fe-C-Fe interaction, similar to that in the starting material $[Fe_2(CO)_5(\eta^8\text{-}C_8H_8)]$.[9, 10]

---

[a] Prof. J.-B. Chen, S. Zhang, J. Sun
State Key Laboratory of Organometallic Chemistry
Shanghai Institute of Organic Chemistry
Chinese Academy of Sciences
354 Fenglin Lu, Shanghai 200032 (China)
Fax: (+86) 21-6416-6128
E-mail: chenjb@mail.sioc.ac.cn

[b] Dr. Q. Xu
National Institute of Advanced Industrial Science and Technology (AIST)
1-8-31 Midorigaoka, Ikeda, Osaka 563-8577 (Japan)
Fax: (+81) 727-51-9629
E-mail: q.xu@aist.go.jp

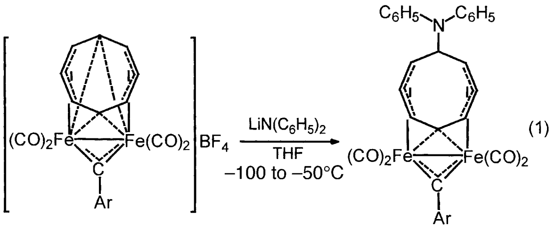
DOI: 10.1002/chem.200305130

It is well known that nucleophiles such as amines attack a carbon atom of coordinated alkenes in transition-metal complexes if the metal is sufficiently electropositive to promote such an attack.[11] While the COT ligand in [$Fe_2${μ-$C(OC_2H_5)Ar$}$(CO)_4$($η^8$-$C_8H_8$)] is not sufficiently electropositive to undergo attack by nucleophiles, we thought that protonation[12] of the iron centers would make such an attack possible. Thus, we studied the reaction of diiron-bridging alkoxycarbene complexes with acids such as $HBF_4$, but instead of the proton-addition product they gave highly electrophilic, cationic, bridging carbyne complexes [$Fe_2$(μ-CAr)($η^8$-$C_8H_8$)$(CO)_4$]$BF_4$, the COT ligand of which are activated towards attack by nucleophiles. Recently,[13] we showed that reaction of cationic, diiron-bridging carbyne complexes [$Fe_2$(μ-CAr)($η^8$-$C_8H_8$)$(CO)_4$]$BF_4$ (**1**, Ar = $C_6H_5$; **2**, Ar = *p*-$CH_3C_6H_4$; **3**, Ar = *p*-$CF_3C_6H_4$) with nucleophiles such as $NaN(SiMe_3)_2$, $LiN(SiMe_3)_2$, and $LiNEt_2$ leads to nucleophilic addition to and breaking of the coordinated cyclooctatetraene ring. To the best of our knowledge, this is the first example of such an activation of an olefin by a cationic, diiron-bridging carbyne moiety. The study on these complexes has revealed a variety of new and interesting transformations. Here we report the remarkable reactions of cationic, diiron-bridging carbyne complexes **1**–**3** with a variety of amino and amido compounds. These reactions lead to a range of products, including those of nucleophilic addition and ring opening.

## Results and Discussion

The freshly prepared cationic, diiron–carbyne complexes **1**–**3** were treated in situ with $LiN(C_6H_5)_2$ in THF at −100 to −50 °C for 4–5 h. After workup (see Experimental Section) the novel nucleophilic cycloaddition products, namely, the diiron-bridging carbyne complexes [$Fe_2$(μ-CAr)$(CO)_4$($η^7$-$C_8H_8N(C_6H_5)_2$)] (**6**, Ar = $C_6H_5$; **7**, Ar = *p*-$CH_3C_6H_4$; **8**, Ar = *p*-$CF_3C_6H_4$), were obtained in 37–45 % yield (isolated product) [Eq. (1)].

Different reaction rates were observed for the three cationic complexes, which were in the order of **3** > **1** > **2**. This might be caused by the strongly electron-withdrawing *p*-$CF_3C_6H_4$ group on the bridging carbyne carbon atom in **3**, which increases the electrophilicity of the μ-carbyne carbon atom, and by the electron-donating *p*-$CH_3C_6H_4$ group in **2**, which decreases the electrophilicity of the μ-carbyne carbon atom.



**1** Ar = $C_6H_5$
**2** Ar = *p*-$CH_3C_6H_4$
**3** Ar = *p*-$CF_3C_6H_4$

**4** Ar = $C_6H_5$
**5** Ar = *p*-$CH_3C_6H_4$
**6** Ar = *p*-$CF_3C_6H_4$

Complexes **4**–**6** are similar to the products obtained from the reactions of cationic carbyne complexes **1**–**3** with $NaN(SiMe_3)_2$.[13] They are air- and temperature-sensitive, purple-red crystals. Their infrared spectra exhibit three strong bands at about 2053–2048, 2019–2016, and 1987–1978 $cm^{-1}$ with patterns similar to that of [$Fe_2(CO)_5$($η^8$-COT)], except for the absent bridging CO band; this indicates the symmetry of these complexes. This was confirmed by an X-ray diffraction study on **6** (Figure 1). The X-ray structure shows that products **4**–**6** are neutral, diiron-bridging carbyne complexes in which an $(C_6H_5)_2N$ group has added to a central carbon atom of the COT ring on the face *anti* to the diiron moiety, that is, the same stereoselectivity of many nucleophilic attacks on hydrocarbon ligands in transition-metal complexes.[1e, 14] This site of nucleophilic attack contrasts with the

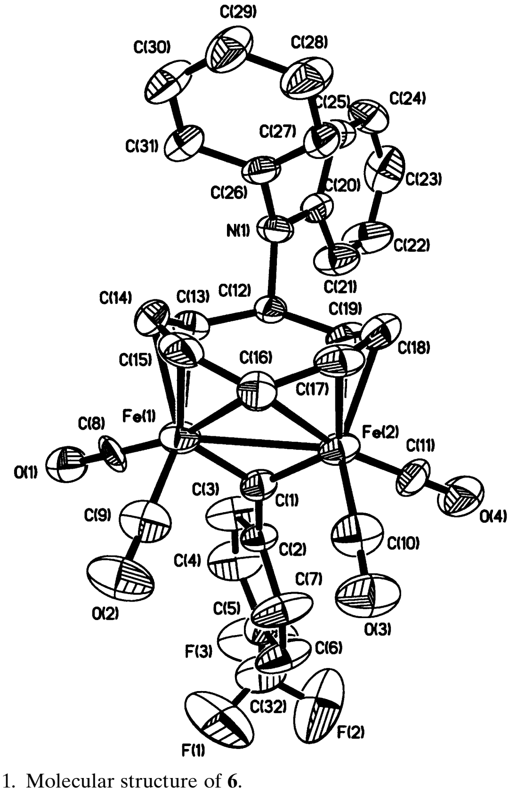


Figure 1. Molecular structure of **6**.

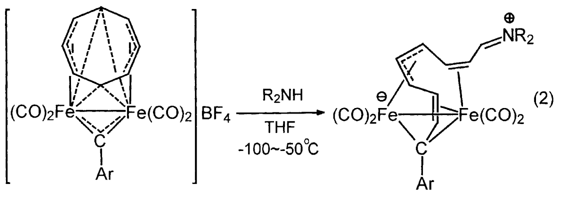
**Abstract in Chinese:**

环辛四烯配位的双铁阳离子桥卡拜络合物 **1-3** 同二苯基胺锂在四氢呋喃中低温下反应得到环加成产物，中性双铁桥卡拜络合物 **4-6**；而阳离子桥卡拜络合物 **1-3** 与二乙胺，二异丙胺及二环己胺在同样条件下反应，得到的是新奇的环辛四烯开环的内盐络合物 **7-15**。 络合物 **3** 与哌啶反应也生成类似的开环内盐化合物 **16**。产物 **9** 在热解条件下生成其反式双键异构体，络合物 **17**。出乎意料的是，苯胺与阳离子桥卡拜络合物 **2** 反应后得到的是卡宾络合物 **18**。2-萘胺同 **2** 以及对三氟甲基苯胺同 **3** 也发生类似的反应，但是所生成的产物分别是新奇的氮螯合的卡宾络合物 **19** 和 **20**。产物 **18** 也可在室温下转化为类似的氮螯合的卡宾络合物 **21**。络合物 **6**，**9**，**15**，**17**，**18** 和 **21** 的结构都通过了 X-射线衍射研究。

reactions[15, 16] of the diiron-bridging carbyne complexes $[Fe_2(\mu\text{-}CO)(\mu\text{-}CAr)(CO)_2(\eta^5\text{-}C_5H_5)]BBr_4$ and $[Fe_2(\mu\text{-}CO)(\mu\text{-}CAr)(CO)_2\{(\eta^5\text{-}C_5H_4)_2Si(CH_3)_2\}]BBr_4$ with nucleophiles, which result in nucleophilic addition to the μ-carbyne carbon atom to give diiron-bridging carbene complexes.

In **6** the two Fe atoms are symmetrically bridged by the $C_8$ ring; three of the eight ring atoms [C(13)–C(15)] are $\eta^3$-bonded to Fe(1), and three others [C(17)–C(19)] are $\eta^3$-bonded to Fe(2). The Fe–Fe distance of 2.684(2) Å in **6** is essentially the same as that in the bridging carbene complex $[Fe_2\{\mu\text{-}C(OC_2H_5)C_6H_4CF_3\text{-}p\}(CO)_4(\eta^8\text{-}C_8H_8)]$ (2.686(1) Å).[9] In **6**, the distances from the Fe atoms to the $\eta^3$- and μ-C atoms of the $C_8$ ring are very close to those in $[Fe_2\{\mu\text{-}C(OC_2H_5)C_6H_4CF_3\text{-}p\}(CO)_4(\eta^8\text{-}C_8H_8)]$. The change from the bridging carbene carbon atom in $[Fe_2\{\mu\text{-}C(OC_2H_5)C_6H_4CF_3\text{-}p\}(CO)_4(\eta^8\text{-}C_8H_8)]$ to the bridging carbyne carbon atom in **6** is responsible for the short μ-C–Fe bond lengths in **6** (av 2.037 Å in $[Fe_2\{\mu\text{-}C(OC_2H_5)C_6H_4CF_3\text{-}p\}(CO)_4(\eta^8\text{-}C_8H_8)]$,[9] 1.809 Å in **6**).

Surprisingly, when more than two equivalents of $(C_2H_5)_2NH$ was used instead of $LiN(C_6H_5)_2$ for the reaction with the cationic carbyne complexes **1**–**3** under the same conditions, violet-red crystals of $[Fe_2\{\mu\text{-}C(Ar)C_8H_8N(C_2H_5)_2\}(CO)_4]$ (**7**, Ar = $C_6H_5$; **8**, Ar = $p\text{-}CH_3C_6H_4$; **9**, Ar = $p\text{-}CF_3C_6H_4$), formulated as diiron-bridging carbene inner salts, were obtained in 53–69% yields of isolated products [Eq. (2)]. Complexes **7**–**9** can also be obtained from the reactions of cationic complexes **1**–**3** with one equivalent of $LiNEt_2$. Other dialkylamines such as diisopropylamine and dicyclohexylamine, which are more sterically hindered and are usally regarded as very weak nucleophiles, also react similarly with cationic carbyne complexes **1**–**3** [Eq. (2)] to afford the corresponding bridging carbene inner salts $[Fe_2\{\mu\text{-}C(Ar)C_8H_8N(iC_3H_7)_2\}(CO)_4]$ (**10**–**12**) in lower yields (28–31%) and $[Fe_2\{\mu\text{-}C(Ar)C_8H_8N(C_6H_{11})_2\}(CO)_4]$ (**13**–**15**) in moderate yields (50–56%).



**1** Ar = $C_6H_5$
**2** Ar = $p\text{-}CH_3C_6H_4$
**3** Ar = $p\text{-}CF_3C_6H_4$

| Ar | R: $C_2H_5$ | R: $iC_3H_7$ | R: $C_6H_{11}$ | $R_2$ = $(CH_2)_5$ |
|---|---|---|---|---|
| $C_6H_5$ | **7** | **10** | **13** | |
| $p\text{-}CH_3C_6H_4$ | **8** | **11** | **14** | |
| $p\text{-}CF_3C_6H_4$ | **9** | **12** | **15** | **16** |

Piperidine reacted with the cationic diiron–carbyne complex **3** under the same conditions to give the analogous bridging carbene inner salt $[Fe_2\{\mu\text{-}C(C_6H_4CF_3\text{-}p)C_8H_8N(CH_2)_5\}(CO)_4]$ (**16**) in 38% yield of isolated product.

The $^1H$ NMR spectra of **7**–**16** with eight 1H signals for the COT ring (at $\delta \approx 6.69–6.51$, 6.42–6.25, 5.25–5.06, 4.60–4.35, 3.94, 3.38–3.21, 2.76–2.59, 2.10–1.74 ppm) suggest that ring cleavage of the $C_8H_8NEt_2$, $C_8H_8N(iC_3H_7)_2$, $C_8H_8N(C_6H_{11})_2$, and $C_8H_8N(CH_2)_5$ ligands has occurred. X-ray diffraction studies on **9** and **15** were therefore undertaken, which unequivocally established the opening of the COT ring.

The X-ray crystal structures of **9** (Figure 2) and **15** (Figure 3) are highly unusual. The $Fe(CO)_2\text{-}\mu\text{-}C(Ar)\text{-}Fe(CO)_2$

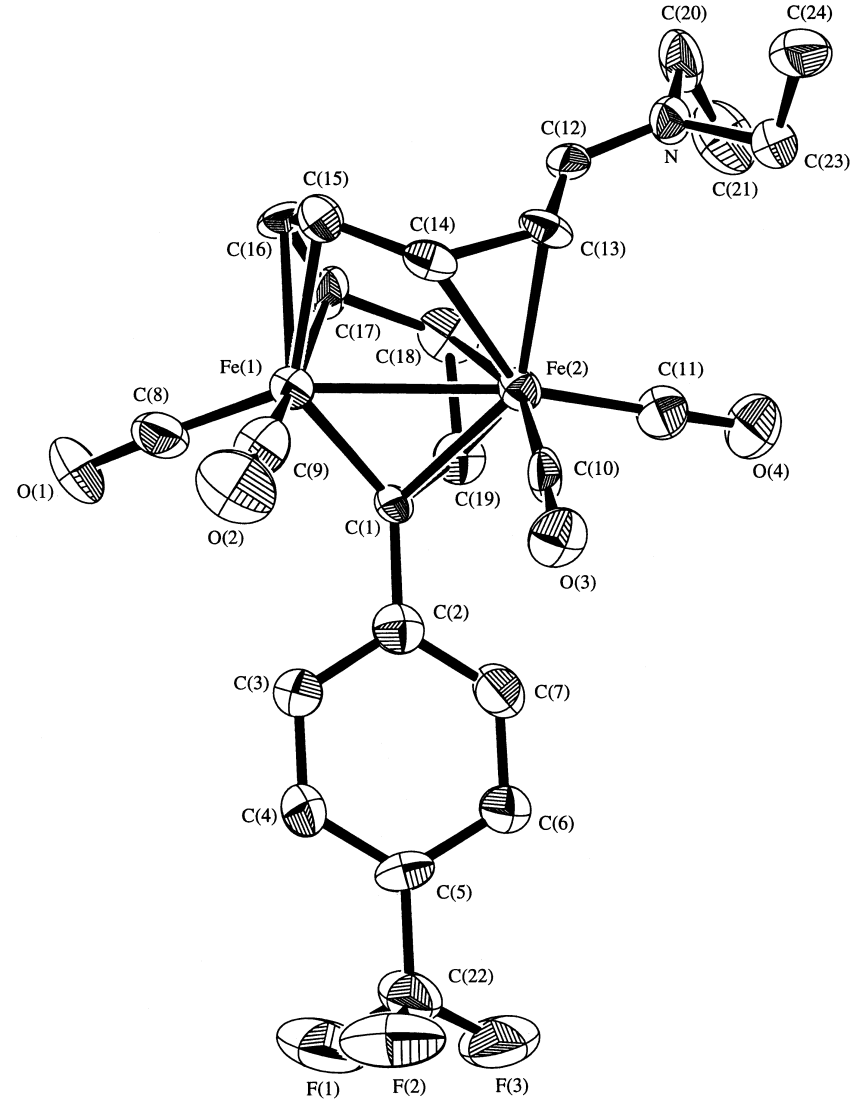


Figure 2. Molecular structure of **9**.

core is retained, but the COT ring has opened to form a chain, C(12) – C(19), carrying an $(C_2H_5)_2N$ or $(C_6H_{11})_2N$ group on C(12) with C(19) directly bonded to bridging carbene carbon atom C(1). Atoms C(15) – C(17) form an allyl-type unit $\eta^3$-bonded to Fe(1), while C(13), C(14) and C(18), C(19) are $\eta^2$-bonded to Fe(2). The terminal carbon atom C(12) of the $C_8$ chain is linked to the $(C_2H_5)_2N$ (in **9**) or $(C_6H_{11})_2N$ (in **15**) unit to form a C=N double bond with a positive charge on the N atom, whereas the Fe(1) atom bears a negative charge, thereby satisfying the 18-electron rule. The Fe–Fe distances in **9** and **15** of 2.649(3) and 2.6329(10) Å, respectively, are somewhat shorter than that in **6** (2.684(2) Å). The average μ-C(1)–Fe bond lengths in **9** and **15** are 2.025 and 2.030 Å, respectively, which are very close to that in $[Fe_2\{\mu\text{-}C(OC_2H_5)C_6H_4CF_3\text{-}p\}(CO)_4(\eta^8\text{-}C_8H_8)]$ (2.037 Å ).[9]

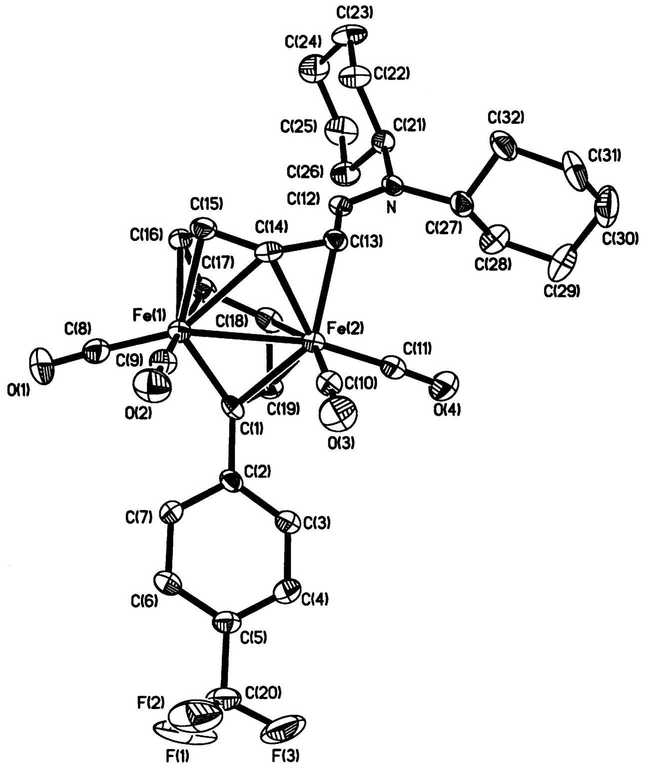
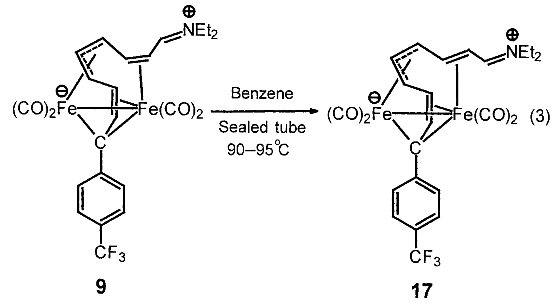


Figure 3. Molecular structure of **15**.

Although a mechanism for the COT ring opening in [Eq. (2)] has not yet been established, it seems possible that $R_2NH$ first attacks the COT ring of the cationic carbyne complexes, as in the reactions of $LiN(C_6H_5)_2$ with complexes **1** – **3**, in which the $(C_6H_5)_2N^-$ ion added to the COT ligand of complexes **1** – **3**. Subsequently, deprotonation by the excess of amine gives an intermediate similar to **4** – **6**. Then C=N bond formation and cleavage of a C–C bond bearing the N substituent (C(12)–C(19)) could occur at the same time. The resulting electron-rich carbon atom C(19) could then attack the electrophilic bridging carbyne carbon atom, which would lead to coupling of the resulting chain with the carbyne ligand to produce **7** – **16**. To the best of our knowledge, there is no precedent for such an activation that leads to ring opening of the COT ligand in a metal complex at very low temperature. There is only one example of a COT ring-opening reaction, which is observed for the Si-substituted $C_8$ ring in the diruthenium complex $[Ru_2(CO)_4(SiMe_3)(\eta^7\text{-}C_8H_8SiMe_3)]$ in boiling octane.[17]

It is well known that thermal decomposition of bridging carbene complexes usually results in dimerization of the carbene ligand to produce alkene derivatives.[18] In addition, the thermolysis of some bridging carbene complexes leads to novel rearrangements.[19] To explore the reactivity of the bridging carbene inner salts, we investigated the thermolysis of **9**. Heating a benzene solution of **9** in a sealed tube at 90 – 95 °C for 72 h gave the new diiron-bridging carbene inner salt $[Fe_2\{\mu\text{-}C(C_6H_4CF_3\text{-}p)C_8H_8NEt_2\}(CO)_4]$ (**17**), the thermodynamically more stable *trans* double-bond isomer of **9**, in 60 % yield [Eq. (3)].



The structure of **17** (Figure 4) was established by single-crystal X-ray structure analysis. The C(12)-C(13)=C(14)-C(15) torsion angle in **17** is 160°, while in **9** it is – 11°, which indicates that the C(13)–C(14) double bond has isomerized from a *cis* configuration in **9** to a *trans* configuration in **17**, as inferred from its $^1H$ NMR spectrum (Experimental Section). The signal of the proton on the C=N group (H(12)) in **17** is shifted downfield by about $\Delta\delta = 0.8$ ppm relative to the corresponding signal in **9**, and the coupling constant of the

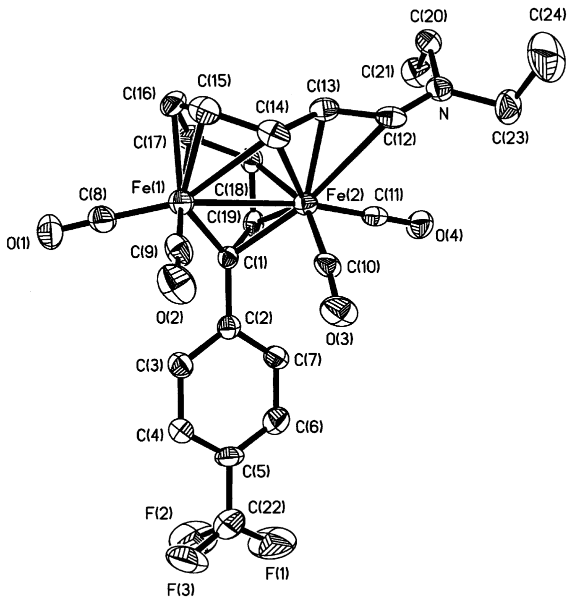


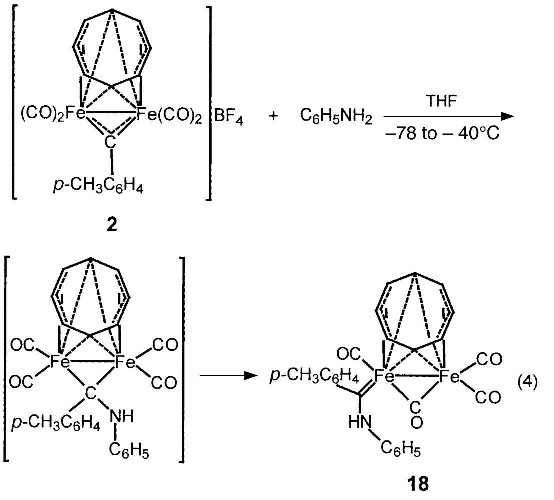
Figure 4. Molecular structure of **17**.

former (10.1 Hz) is smaller than that of the latter (11.1 Hz). In addition, the signals of the two $C_2H_5$ groups on the N atom in **17** are very close, while in **9** the signals of the two methyl and two methylene groups are easily distinguishable because their chemical shifts differ by about $\Delta\delta = 0.3$ and 0.5 ppm, respectively. Apart from this, the basic framework and the structural parameters of **17** are nearly the same as those of **9**, including the Fe–Fe distance, C=C bond length, and most bond angles.

Of special interest is the reaction of cationic, diiron-bridging carbyne complexes with the less basic aniline. Unlike the reactions of $LiNPh_2$ and $Et_2NH$, the reaction of aniline with cationic carbyne complex **2** under analogous conditions gave neither nucleophilic addition products nor COT-opened, diiron-bridging carbene inner salts; instead, the unexpected COT iron–carbene complex $[Fe_2\{=C(C_6H_4CH_3\text{-}p)NHC_6H_5\}(\mu\text{-}CO)(CO)_3(\eta^8\text{-}C_8H_8)]$ (**18**) was obtained in 61% yield [Eq. (4)].

However, the analogous reactions of cationic **2** with 2-naphthylamine and cationic **3** with $p\text{-}CF_3C_6H_4NH_2$ did not produce analogous iron–carbene complexes; instead, novel chelated iron–carbene complexes $[Fe_2\{=C(C_6H_4CH_3\text{-}p)NC_{10}H_7\}(CO)_4(\eta^2{:}\eta^3{:}\eta^2\text{-}C_8H_9)]$ (**19**) and $[Fe_2\{=C(C_6H_4CF_3\text{-}p)NC_6H_4CF_3\text{-}p\}(CO)_4(\eta^2{:}\eta^3{:}\eta^2\text{-}C_8H_9)]$ (**20**) were obtained in 80 and 83% yield, respectively [Eq. (5)].

The IR spectrum of **18** showed a CO absorption band at 1697 cm$^{-1}$ in the $\nu$(CO) region, characteristic for a bridging CO ligand, in addition to the two strong CO absorption bands at 1987 and 1930 cm$^{-1}$, while the IR spectra of **19** and **20** showed four terminal CO bands at 2001–1919 cm$^{-1}$. The $^1$H NMR spectrum of **18** showed a singlet for the COT ligand, like the starting materials $[Fe_2\{\mu\text{-}C(OC_2H_5)Ar\}(CO)_4(\eta^8\text{-}C_8H_8)]$, which are fluxional,[9, 20] and this suggests that the COT ring is retained in **18**. The $^1$H NMR spectra of **19** and **20** showed nine signals attributable to the $C_8H_9$ ring protons, in addition to the four proton signals attributed to the aryl groups; hence, the COT rings in **19** and **20** are no longer planar, and the structures of **19** and **20** are quite different from that of **18**.



The product **18** was shown by X-ray crystallography to be an iron–carbene complex with a carbene ligand $C(C_6H_4CH_3\text{-}p)NHC_6H_5$ bonded to an Fe atom of the $(CO)_3Fe_2(\mu\text{-}CO)$ core. The molecular structure of **18** (Figure 5) shows that the two Fe atoms are bridged by a CO group, as inferred from its IR spectrum. One of the two Fe atoms bears two terminal CO groups, and the other one terminal CO group and a $C(C_6H_4CH_3\text{-}p)NHC_6H_5$ ligand, in addition to coordination to the COT ring and a bridging CO ligand; thus, each Fe atom has 18 valence electrons. The Fe–Fe distance of 2.7589(19) Å

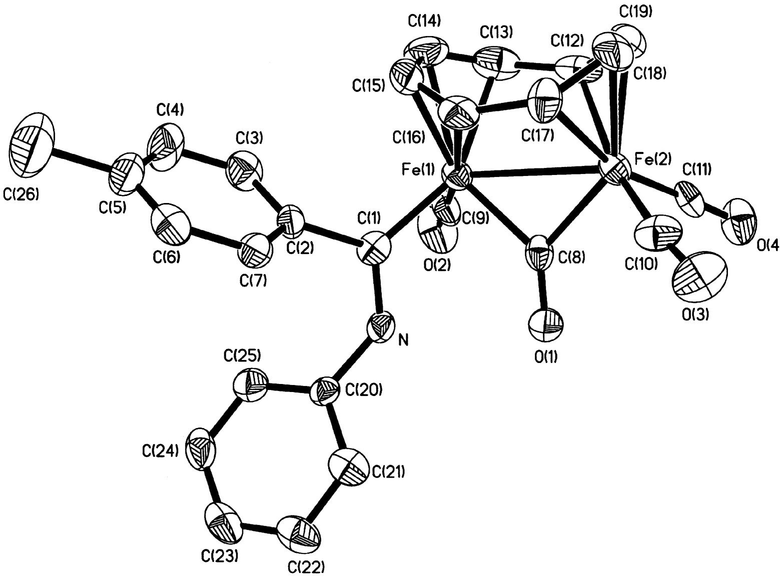
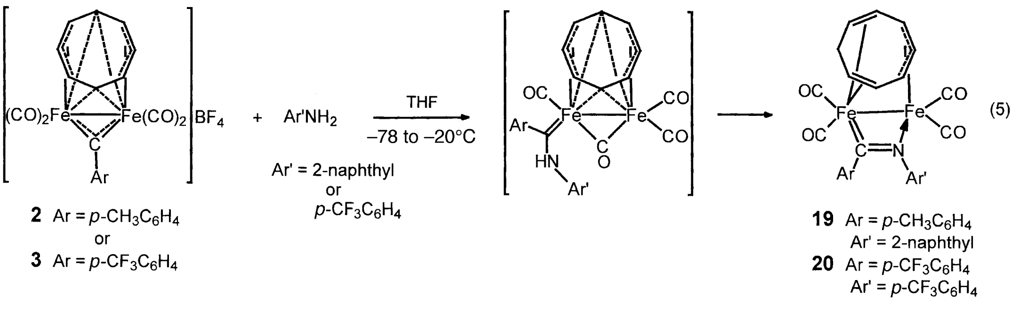


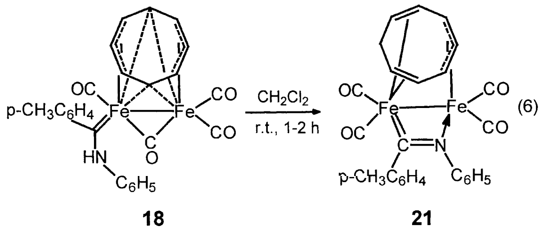
Figure 5. Molecular structure of **18**.



is slightly longer than that in the diiron-bridging carbene complex [$Fe_2\{\mu$-$C(OC_2H_5)C_6H_4CF_3$-$p\}(CO)_4(\eta^8$-$C_8H_8)$] (2.686(1) Å),[9] but is significantly longer than those in **6**, **9**, and **15**. The Fe–C(1) bond length of 1.895(8) Å, which is comparable to the corresponding Fe–$C_{carbene}$ bond length in analogous iron–carbene complexes [($\eta^4$-$C_{10}H_{16})(CO)_2Fe$-$C(OC_2H_5)C_6H_4CH_3$-*o*] (1.915(15) Å)[21] and [$(CO)_3Fe(1,2,3,4$-$\eta$:$5,6,7,8$-$\eta$-$C_8H_8)(CO)_2FeC(OC_2H_5)C_6H_5$] (1.87(2) Å).[22] The C(1)–N bond length of 1.333(10) Å lies between normal C–N and C=N distances.

A possible reaction pathway to complex **18** could be via an intermediate [$Fe_2\{\mu$-$C(C_6H_4CH_3$-$p)NHC_6H_5\}(CO)_4(\eta^8$-$C_8H_8)$], formed by the attack of neutral $C_6H_5NH_2$ on the bridging carbyne carbon atom of **2** followed by deprotonation by the excess of amine. This intermediate is analogous to the diiron-bridging carbene complexes which were obtained from the reactions[15, 16] of the diiron-bridging carbyne complexes [$Fe_2(\mu$-$CO)(\mu$-$CAr)(CO)_2(\eta^5$-$C_5H_5)$]$BBr_4$ and [$Fe_2(\mu$-$CO)(\mu$-$CAr)(CO)_2\{(\eta^5$-$C_5H_4)_2Si(CH_3)_2\}$]$BBr_4$ with nucleophiles. Then cleavage of the μ-C(1)–Fe(2) bond and formation of the Fe(1)–$C_{carbene}$ bond with bridging of a terminal CO ligand on Fe(1) to the Fe(2) atom could occur to produce complex **18**. Formation of **19** and **20** might occur via an iron–carbene complex intermediate [$Fe_2\{{=}C(C_6H_4CH_3$-$p)NHC_{10}H_7\}(\mu$-$CO)(CO)_3(\eta^8$-$C_8H_8)$] and [$Fe_2\{{=}C(C_6H_4CF_3$-$p)NHC_6H_4CF_3$-$p\}(\mu$-$CO)(CO)_3(\eta^8$-$C_8H_8)$], analogous to complex **18**. These are then transformed into the chelated iron–carbene complexes **19** and **20** due to their lability in solution due to the relatively high reaction temperature. This was confirmed by the transformation of **18** into **21**.

A solution of **18** in $CH_2Cl_2$ or acetone or THF was kept at room temperature for 1–2 h, during which time the deep red solution gradually turned red. After workup, as described in the Experimental Section, the red, chelated iron–carbene complex [$Fe_2\{{=}C(C_6H_4CH_3$-p$)NC_6H_5\}(CO)_4(\eta^2{:}\eta^3{:}\eta^2$-$C_8H_9)$] (**21**) was obtained in 84% yield [Eq. (6)], whose structure was established by X-ray crystallography.



The transformation of **18** into **21** was initially revealed by $^1H$ NMR spectroscopy. Keeping the solution of **18** in [$D_6$]acetone at room temperature for about 1–2 h led to the disappearance of the original $^1H$ NMR signals assigned to **18** from the spectrum, and consequently only the signals attributable to the $C_8H_9$ ring and aryl protons of **21** were observed. Further evidence for this transformation came from the isolation of crystalline **21** from a solution in $CH_2Cl_2$.

Complex **21** is an isomer of complex **18**. The difference between the two structures arises from the migration of the H atom of the $HNC_6H_5$ group in **18** to a carbon atom of the COT ring and coordination of the N atom to Fe(2). Complexes **19** and **20** are assigned similar structures, since their spectral data are similar to those of **21** (Experimental Section)

The molecular structure of **21** (Figure 6) shows that the eight-membered ring of the COT ligand is retained, but the formerly planar COT ring has adopted a boatlike configuration. Atoms C(12), C(19), and C(18) form an allyl-type unit $\eta^3$-bonded to Fe(2), while C(13), C(14) and C(16), C(17) are $\eta^2$-bonded to Fe(1). The N atom is now coordinated to Fe(2), to which it provides two electrons to satisfy the 18-electron rule. The Fe(2)–N(1) bond length is 1.966(11) Å, which is somewhat shorter than the Fe–N bond lengths in diiron complexes with a bridging RC=NR(E) unit: [($\mu$-*p*-$MeC_6H_4Te)(\mu$-$PhC{=}NPh)Fe_2(CO)_6$] (1.993(4) Å),[23] [$Fe_2(CO)_4(\mu_2$-$RN{=}CH)(\mu$-$PCy_2)(\mu$-dppm)] (R = allyl) (2.015(13) Å),[24] and [($\mu$-$PhSe)(\sigma,\mu$-$PhC{=}NPh)Fe_2(CO)_6$](2.000(3) Å),[25] but it is nearly the same as that in the diiron-bridging carbyne complex [$Fe_2(\mu$-$CO)(\mu$-$CC_6H_5)(CO)_2(\eta^5$-$C_5H_5)_2NCW(CO)_5$] (1.95(1) Å)[15b] and the diiron complex [$Fe_2(CO)_6(N{=}CHCH_3)_2$] (1.942(7) Å),[26] in which closing of the $Fe_2N_2$ core with shorter Fe–N bond lengths results in partial double-bond character in the Fe–N bonds. The shorter Fe(2)–N distance suggests that there is some double-bond character in the Fe(2)–N bond in **21**. The Fe–Fe distance of 2.691(3) Å in **21** is somewhat shorter than that in **18**. The Fe(1)–C(1) bond length of 1.972(13) Å is slightly longer than that in **18**, while the C(1)–N distance of 1.266(16) Å is significantly shorter than that in **18** (1.333(10) Å), which indicates high double-bond character.

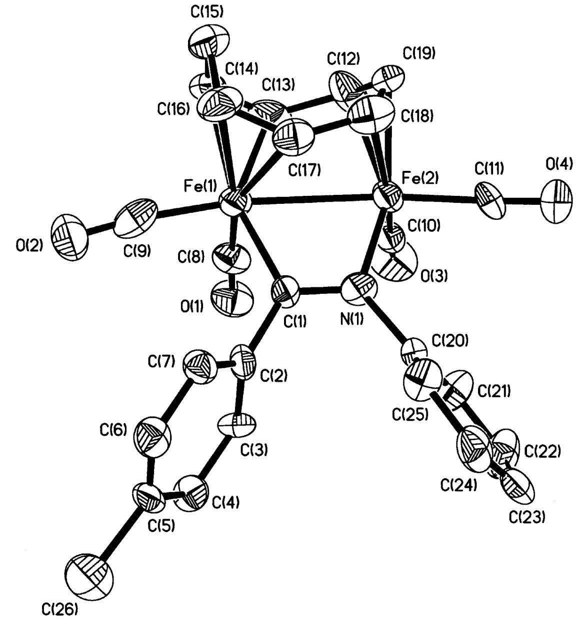
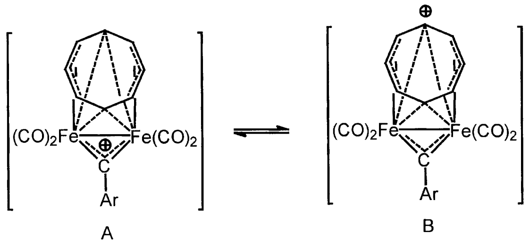


Figure 6. Molecular structure of **21**.

The most interesting structural feature of **21** is the $C_8H_9$ ligand. In contrast with the nearly planar eight-membered ring in **18**, in **21** C(13), C(14), C(16), and C(17) are in a plane (±0.0172 Å), and C(12), C(13), C(17) and C(18) are in another (±0.0289 Å); C(15) lies out of the C(13)-C(14)-C(16)-C(17) plane by 0.7875 Å, and C(19) out of the C(12)-C(13)-C(17)-C(18) plane by 0.2750 Å. Another measure of the nonplanarity of the ring is the dihedral angle of 40.22° between the C(13)-C(14)-C(16)-C(17) and C(12)-C(13)-C(17)-C(18) planes, and that of 25.28° between the C(12)-C(13)-C(17)-C(18) and C(12)-C(18)-C(19) planes. The nonplanarity of the COT ring in **21** suggests that the $\pi$ system is not delocalized, in contrast to that in **18**.

The above three types of reactions suggest that the COT-coordinated, cationic, bridging carbyne complexes are best represented by a combination of resonance forms (Scheme 1).



Scheme 1. Two possible resonance forms of cationic bridging carbyne complexes **1**–**3**.

In form A, the positive charge is located on the bridging carbyne carbon atom, whereas in form B one carbon atom of the COT ring bears a positive charge. In the reactions of cationic bridging carbyne complexes **1**–**3** with various N nucleophiles, the regioselectivity of nucleophilic attack depends on the type of N nucleophile: 1) Disubstituted N nucleophiles selectively attack the COT ring of form B. Thus, reactions of $(SiMe_3)_2N^-$ and $Ph_2N^-$ with cationic complexes **1**–**3** gave the ring-addition products. In the reactions of dialkyl-substituted N nucleophiles, such as $Et_2N^-$ and dialkylamines, with cationic **1**–**3**, the COT ring can be further opened to give the ring-opened products, which could be due to the lack of delocalization of the lone pair electrons on the N atom due to the phenyl or trimethylsilyl groups. 2) Primary arylamines selectively attack the cationic carbyne carbon atom of form A to give carbene complexes.

In conclusion, we have discovered novel reactions of COT-coordinated, cationic, diiron-bridging carbyne complexes with a variety of amino and amido compounds to give a series of COT ring-addition bridging carbyne complexes, ring-opened COT bridging carbene complexes, and iron–carbene complexes, depending on the nature of the N compound. It appears that the cationic, bridging carbyne, dimetal moiety promotes nucleophilic attack on the unsaturated ligand and thus facilitates novel chemistry. The title reaction represents a new and useful approach to the preparation and structural modification of dimetal bridging carbene and bridging carbyne complexes. Further studies on reactions with other nucleophiles and their applications in organic and organometallic synthesis are in progress.

## Experimental Section

**General procedures**: All procedures were performed under a dry, oxygen-free $N_2$ atmosphere by using standard Schlenk techniques. All solvents employed were of reagent grade and dried by refluxing over appropriate drying agents and stored over 4 Å molecular sieves under $N_2$ atmosphere. Tetrahydrofuran and diethyl ether were distilled from sodium benzophenone ketyl, while petroleum ether (30–60 °C) and $CH_2Cl_2$ were distilled from $CaH_2$. The neutral alumina ($Al_2O_3$, 100–200 mesh) used for chromatography was deoxygenated at room temperature under high vacuum for 16 h, deactivated with 5 wt% $N_2$-saturated water, and stored under an $N_2$ atmosphere. $HBF_4 \cdot Et_2O$, $Et_2NH$, $PhNH_2$, $p$-$CF_3C_6H_4NH_2$, $(iC_3H_7)_2NH$, $(C_6H_{11})_2NH$, piperidine, and $nC_4H_9Li$ were purchased from Aldrich Chemical Co. $[Fe_2(\mu\text{-}CAr)(\eta^8\text{-}C_8H_8)(CO)_4]BF_4$ (**1**, Ar = $C_6H_5$; **2**, Ar = $p$-$CH_3C_6H_4$; **3**, Ar = $p$-$CF_3C_6H_4$) were prepared as previously described.[9]

IR spectra were measured on a Nicolet AV-360 spectrophotometer in NaCl cells with 0.1 mm spacers. All $^1H$ NMR spectra were recorded at ambient temperature in $[D_6]$acetone with TMS or deuterated solvents as the internal reference on a Varian Mercury 300 spectrometer running at 300 MHz. Electron ionization mass spectra (EIMS) were recorded on a Hewlett Packard 5989A spectrometer. Melting points, obtained on samples in sealed nitrogen-filled capillaries, are uncorrected.

**Reaction of 1 with $LiN(C_6H_5)_2$ to give $[Fe_2(\mu\text{-}CC_6H_5)(CO)_4(\eta^7\text{-}C_8H_8N(C_6H_5)_2)]$ (4)**: A solution of $(C_6H_5)_2NH$ (0.067 g, 0.40 mmol) in THF (10 mL) was mixed with $nC_4H_9Li$ (0.40 mmol) at −50 °C. After 30 min stirring at −50 °C, the solution was added to **1** (0.150 g, 0.30 mmol), freshly prepared in situ, in THF (50 mL) at −100 °C with stirring. The reaction mixture gradually turned from brick red to brown-red. After stirring at −100 to −50 °C for 4–5 h, the resulting solution was evaporated to dryness under high vacuum at −50 °C, and the dark red residue was extracted with petroleum ether/$CH_2Cl_2$ (10:1). The red extract was evaporated to dryness in vacuo at −30 °C, and the residue was recrystallized from petroleum ether/$CH_2Cl_2$ (15:1) at −80 °C to give purple-red crystals of **4** (0.072 g, 41% based on **1**). M.p. 64–66 °C decomp; IR ($CH_2Cl_2$): $\tilde{\nu}(CO) = 2053$ (m), 2016 (m), 1985 $cm^{-1}$ (s); $^1H$ NMR ($CD_3COCD_3$): $\delta = 6.62-8.04$ (m, 15H; $C_6H_5$), 5.85 (br, 2H; $C_8H_8$), 5.16 (br, 2H; $C_8H_8$), 4.81 (br, 0.5H; $CH_2Cl_2$), 3.38 (br, 2H; $C_8H_8$), 0.88 ppm (br, 2H; $C_8H_8$); MS: $m/z$: 473 $[M^+ - Fe(CO)_2]$, 417 $[M^+ - Fe(CO)_2 - 2CO]$ or $[M^+ - N(C_6H_5)_2)]$, 389 $[M^+ - N(C_6H_5)_2 - CO]$, 361 $[M^+ - 2Fe(CO)_2]$, 333 $[M^+ - N(C_6H_5)_2 - 3CO]$; elemental analysis (%) calcd for $C_{31}H_{23}Fe_2NO_4 \cdot 0.25CH_2Cl_2$: C 61.89, H 3.97, N 2.31; found: C 61.91, H 4.41, N 2.70.

**Reaction of 2 with $LiN(C_6H_5)_2$ to give $[Fe_2(\mu\text{-}CC_6H_4CH_3\text{-}p)(CO)_4(\eta^7\text{-}C_8H_8N(C_6H_5)_2)]$ (5)**: Compound **2** (0.161 g, 0.31 mmol) was treated with a fresh solution of $LiN(C_6H_5)_2$, prepared by the reaction of $(C_6H_5)_2NH$ (0.085 g, 0.50 mmol) with $nC_4H_9Li$ (0.50 mmol), in THF at −100 to −50 °C for 5 h. Further treatment of the resulting solution as in the preparation of **7** yielded purple-red crystalline **5** (0.083 g, 45% based on **2**). M.p. 70–72 °C decomp; IR ($CH_2Cl_2$): $\tilde{\nu}(CO) = 2048$ (m), 2017 (m), 1978 $cm^{-1}$ (s); $^1H$ NMR ($CD_3COCD_3$): $\delta = 6.73-7.24$ (m, 14H; $C_6H_5$, $C_6H_4CH_3$), 6.06 (br, 2H; $C_8H_8$), 5.36 (br, 2H; $C_8H_8$), 5.07 (br, 1H; $CH_2Cl_2$), 3.30 (br, 2H; $C_8H_8$), 1.93 (s, 3H; $CH_3$), 0.92 ppm (br, 2H; $C_8H_8$); MS: $m/z$: 375 $[M^+ - 2Fe(CO)_2]$, 207 $[M^+ - 2Fe(CO)_2 - N(C_6H_5)_2]$, 84 $[CH_2Cl_2^+]$; elemental analysis (%) calcd for $C_{32}H_{25}Fe_2NO_4 \cdot 0.5CH_2Cl_2$: C 60.83, H 4.08, N 2.18; found: C 60.55, H 4.50, N 2.51.

**Reaction of 3 with $LiN(C_6H_5)_2$ to give $[Fe_2(\mu\text{-}CC_6H_4CF_3\text{-}p)(CO)_4(\eta^7\text{-}C_8H_8N(C_6H_5)_2)]$ (6)**: Similar to the procedure used in the reaction of **1** with $LiN(C_6H_5)_2$, compound **3** (0.139 g, 0.24 mmol) was treated with $LiN(C_6H_5)_2$ prepared by the reaction of $(C_6H_5)_2NH$ (0.071 g, 0.41 mmol) with $nC_4H_9Li$ (0.41 mmol) at −100 to −50 °C for 4 h. Further treatment of the resulting solution as described for the preparation of **7** produced purple-red crystalline **6** (0.060 g, 37% based on **3**). M.p. 96–98 °C decomp; IR ($CH_2Cl_2$): $\tilde{\nu}(CO) = 2053$ (m), 2019 (m), 1987 $cm^{-1}$ (s); $^1H$ NMR ($CD_3COCD_3$): $\delta = 6.85-7.59$(m, 14H; $C_6H_5$ and $C_6H_4CF_3$), 6.15 (br, 2H; $C_8H_8$), 5.15 (br, 2H; $C_8H_8$), 3.26 (br, 2H; $C_8H_8$), 1.10 ppm (br, 2H; $C_8H_8$); MS: $m/z$: 429 $[M^+ - 2Fe(CO)_2]$, 352 $[M^+ - 2Fe(CO)_2 - C_6H_5]$, 261 $[M^+ - 2Fe(CO)_2 - N(C_6H_5)_2]$; elemental analysis (%) calcd for $C_{32}H_{22}F_3Fe_2NO_4$: C 58.84, H 3.39, N 2.14; found: C 58.60, H 3.65, N 2.31.

**Reaction of 1 with $(C_2H_5)_2NH$ to give $[Fe_2\{\mu\text{-}C(C_6H_5)C_8H_8N(C_2H_5)_2\}(CO)_4]$ (7)**: $(C_2H_5)_2NH$ (0.063 mL, 0.60 mmol) was added to **1** (0.100 g, 0.20 mmol), freshly prepared in situ, in THF (50 mL) at −100 °C. The reaction solution immediately turned from brick red to bright red. After stirring at −100 to −50 °C for 3 h, the resulting solution was evaporated to dryness under high vacuum at −50 °C, and the dark red residue was extracted with petroleum ether/$CH_2Cl_2$ (10:1). The red extract was evaporated to dryness in vacuo at −30 °C, and the residue was recrystallized from petroleum ether/$CH_2Cl_2$ (15:1) at −80 °C to give violet-red crystals of **7** (0.051 g, 53% based on **1**). M.p. 131–133 °C decomp; IR ($CH_2Cl_2$): $\tilde{\nu}$(CO) = 1988 (s), 1953 (vs), 1915 (m), 1898 cm$^{-1}$ (m); $^1$H NMR ($CD_3COCD_3$): $\delta$ = 7.81 (m, 2H; $C_6H_5$), 7.07 (m, 3H; $C_6H_5$), 6.51 (d, J = 11.2 Hz, 1H; CH), 6.25 (d, J = 3.5 Hz, 1H; CH), 5.06 (t, J = 6.3 Hz, 1H; CH), 4.35 (t, J = 7.5 Hz, 1H; CH), 4.00–3.94 (m, 2H; $CH_2CH_3$ + CH), 3.47–3.36 (m, 3H; $CH_2CH_3$), 3.21 (t, J = 6.8 Hz, 1H; CH), 2.59 (dd, J = 2.6, 7.9 Hz, 1H; CH), 2.00 (t, J = 2.7 Hz, 1H; CH), 1.38 (t, J = 7.1 Hz, 3H; $CH_2CH_3$), 1.08 ppm (t, J = 7.1 Hz, 3H; $CH_2CH_3$); $^{13}$C NMR ($CD_3COCD_3$): $\delta$ = 218.3, 214.6, 210.3, 209.2 (CO), 177.0 (μ-C), 160.8 (C=N), 154.5, 128.8, 127.8, 125.7 ($C_6H_5$), 101.8, 101.1, 72.7, 54.8 (CH), 51.2, 43.5 ($CH_2$), 40.9, 37.4, 22.3 (CH), 13.2, 12.4 ppm ($CH_3$); MS: m/z: 489 [$M^+$], 461 [$M^+$ − CO], 433 [$M^+$ − 2CO), 405 [$M^+$ − 3CO], 377 [$M^+$ − Fe(CO)$_2$], 349 [$M^+$ − Fe(CO)$_2$ − CO], 265 [$M^+$ − 2Fe(CO)$_2$]; elemental analysis (%) calcd for $C_{23}H_{23}Fe_2NO_4$: C 56.48, H 4.74, N 2.86; found: C 55.85, H 4.42, N 3.19.

**Reaction of 2 with $(C_2H_5)_2NH$ to give [$Fe_2${μ-C($C_6H_4CH_3$-p)$C_8H_8N(C_2H_5)_2$}(CO)$_4$] (8)**: Using the same procedure as for the reaction of **1** with $(C_2H_5)_2NH$, **2** (0.104 g, 0.20 mmol) was treated with $(C_2H_5)_2NH$ (0.060 mL, 0.58 mmol) at −100 to −50 °C for 4–5 h. Further treatment of the resulting solution as described for the reaction of **1** with $(C_2H_5)_2NH$ yielded **8** (0.057 g, 57% based on **2**) as violet-red crystals. M.p. 100–101 °C decomp; IR ($CH_2Cl_2$): $\tilde{\nu}$(CO) = 1986 (s), 1952 (vs), 1915 (m), 1897 cm$^{-1}$ (m); $^1$H NMR ($CD_3COCD_3$): $\delta$ = 7.75 (d, J = 8.0 Hz, 2H; $CH_3C_6H_4$), 7.08 (d, J = 8.0 Hz, 2H; $CH_3C_6H_4$), 6.55 (d, J = 11.1 Hz, 1H; CH), 6.29 (d, J = 2.9 Hz, 1H; CH), 5.10 (t, J = 6.3 Hz, 1H; CH), 4.39 (t, J = 6.9 Hz, 1H; CH), 4.05–3.96 (m, 2H; $CH_2CH_3$ + CH), 3.51–3.37 (m, 3H; $CH_2CH_3$), 3.23 (t, J = 6.9 Hz, 1H; CH), 2.64 (dd, J = 1.5, 7.5 Hz, 1H; CH), 2.26 (s, 3H; $CH_3C_6H_4$), 2.05 (m, 2H; CH), 1.42 (t, J = 7.2 Hz, 3H; $CH_2CH_3$), 1.12 ppm (t, J = 7.2 Hz, 3H; $CH_2CH_3$); $^{13}$C NMR ($CD_3COCD_3$): $\delta$ = 218.3, 214.7, 210.4, 209.2 (CO), 177.5 (μ-C), 160.4 (C=N), 151.6, 135.0, 128.6, 128.4 ($CH_3C_6H_4$), 101.2, 101.1, 72.7, 54.9 (CH), 51.2, 43.5 ($CH_2$), 40.8, 37.3, 22.3 (CH), 20.5 ($CH_3C_6H_4$), 13.3, 12.4 ppm ($CH_3$); MS: m/z: 503 [$M^+$], 475 [$M^+$ − CO], 447 [$M^+$ − 2CO), 419 [$M^+$ − 3CO], 391 [$M^+$ − Fe(CO)$_2$], 279 [$M^+$ − 2Fe(CO)$_2$]; elemental analysis (%) calcd for $C_{24}H_{25}Fe_2NO_4$: C 57.29, H 5.01, N 2.78; found: C 56.98, H 5.10, N 2.75.

**Reaction of 3 with $(C_2H_5)_2NH$ to give [$Fe_2${μ-C($C_6H_4CF_3$-p)$C_8H_8N(C_2H_5)_2$}(CO)$_4$] (9)**: As in the reaction of **1** with $(C_2H_5)_2NH$, **3** (0.122 g, 0.21 mmol) was treated with $(C_2H_5)_2NH$ (0.068 mL, 0.65 mmol) in THF (50 mL) at −100 to −50 °C for 3–4 h. Further treatment of the resulting solution as in the reaction of **1** with $(C_2H_5)_2NH$ produced violet-red crystalline **9** (0.080 g, 69% based on **3**). M.p. 143–144 °C decomp; IR ($CH_2Cl_2$): $\tilde{\nu}$(CO) = 1989 (m), 1955 (s), 1918 (m), 1900 cm$^{-1}$ (w); $^1$H NMR ($CD_3COCD_3$): $\delta$ = 8.07 (d, J = 8.2 Hz, 2H; $CF_3C_6H_4$), 7.68 (d, J = 8.2 Hz, 2H; $CF_3C_6H_4$), 6.66 (d, J = 11.1 Hz, 1H; N-CH), 6.42 (d, J = 3.4 Hz, 1H; CH), 5.23 (t, J = 6.4 Hz, 1H; CH), 4.50 (t, J = 6.9 Hz, 1H; CH), 4.19–4.09 (m, 2H; $CH_2CH_3$ + CH), 3.62–3.49 (m, 3H; $CH_2CH_3$), 3.35 (t, J = 6.9 Hz, 1H; CH), 2.75 (ddd, J = 1.0, 2.6, 8.1 Hz, 1H; CH), 2.12 (t, J = 2.8 Hz, 1H; CH), 1.51 (t, J = 7.1 Hz, 3H; $CH_2CH_3$), 1.21 ppm (t, J = 7.1 Hz, 3H; $CH_2CH_3$); $^{13}$C NMR ($CD_3COCD_3$): $\delta$ = 218.5, 214.8, 210.6, 209.7 (CO), 172.9 (μ-C), 162.6 (C=N), 151.6, 135.0, 128.6, 128.4 ($CF_3C_6H_4$), 103.3, 101.6, 73.6, 55.4 (CH), 51.8, 44.2 ($CH_2$), 41.2, 38.3, 22.7 (CH), 13.8, 12.9 ppm ($CH_3$); MS: m/z: 557 [$M^+$], 529 [$M^+$ − CO], 501 [$M^+$ − 2CO), 473 [$M^+$ − 3CO], 445 [$M^+$ − Fe(CO)$_2$], 417 [$M^+$ − Fe(CO)$_2$ − CO], 333 [$M^+$ − 2Fe(CO)$_2$]; elemental analysis (%) calcd for $C_{24}H_{22}F_3Fe_2NO_4$: C 51.74, H 3.98, N 2.51; found: C 51.61, H 4.20, N 2.68.

**Reaction of 1 with $(iC_3H_7)_2NH$ to give [$Fe_2${μ-C($C_6H_5$)$C_8H_8N(iC_3H_7)_2$}(CO)$_4$] (10)**: $(iC_3H_7)_2NH$ (0.095 mL, 0.68 mmol) was added to **1** (0.160 g, 0.32 mmol), freshly prepared in situ, in THF (50 mL) at −100 °C. After stirring at −78 to −50 °C for 3 h, the resulting solution was evaporated to dryness under high vacuum at −40 °C, and the dark red residue was extracted with petroleum ether/$CH_2Cl_2$ (10:1). The red extract was evaporated to dryness in vacuo at −20 °C, and the residue was recrystallized from petroleum ether/$CH_2Cl_2$ (15:1) at −80 °C to give violet-red crystals of **10** (0.051 g, 31% based on **1**). M.p. 147–149 °C decomp; IR ($CH_2Cl_2$): $\tilde{\nu}$(CO) = 1985 (s), 1952 (vs), 1913 (s), 1896 cm$^{-1}$ (s); $^1$H NMR ($CD_3COCD_3$): $\delta$ = 7.95–7.18 (m, 5H; $C_6H_5$), 6.67 (d, J = 11.0 Hz, 1H; CH), 6.37 (br, 1H; CH), 5.19 (t, J = 6.0 Hz, 1H; CH), 4.85 (m, 1H; NCHMe$_2$), 4.56 (t, J = 7.0 Hz, 1H; CH), 4.15 (dd, J = 11.0, 7.6 Hz, 1H; CH), 3.98 (m, 1H; NCHMe$_2$), 3.39 (t, J = 6.6 Hz, 1H; CH), 2.79 (m, 1H; CH), 1.94 (br, 1H; CH), 1.55 (t, J = 6.6 Hz, 3H; NCHC$H_3$), 1.32 (t, J = 6.6 Hz, 6H; NCHC$H_3$), 1.18 ppm (t, J = 6.6 Hz, 3H; NCHC$H_3$); $^{13}$C NMR ($CD_3COCD_3$): $\delta$ = 218.9, 215.2, 211.1, 209.9, 178.3, 162.6, 155.2, 129.4, 128.4, 126.4, 102.7, 101.8, 73.4, 55.2, 52.4, 49.8, 41.6, 38.9, 24.8, 23.5, 21.4, 20.5, 19.5 ppm; MS: m/z: 517 [$M^+$], 489 [$M^+$ − CO], 461 [$M^+$ − 2CO), 405 [$M^+$ − Fe(CO)$_2$], 293 [$M^+$ − 2Fe(CO)$_2$]; elemental analysis (%) calcd for $C_{25}H_{27}Fe_2NO_4$: C 58.06, H 5.26, N 2.71; found: C 57.46, H 5.42, N 2.89.

**Reaction of 2 with $(iC_3H_7)_2NH$ to give [$Fe_2${μ-C($C_6H_4CH_3$-p)$C_8H_8N(iC_3H_7)_2$}(CO)$_4$] (11)**: Freshly prepared **2** (0.188 g, 0.36 mmol) was treated, in a manner similar to that for the reaction of **1** with $(iC_3H_7)_2NH$, with $(iC_3H_7)_2NH$ (0.110 mL, 0.78 mmol) in THF at −78 to −50 °C for 3 h. Further treatment of the resulting mixture as described for the preparation of **10** yielded **11** (0.058 g, 30% based on **2**) as violet-red crystals. M.p. 146–148 °C decomp; IR ($CH_2Cl_2$): $\tilde{\nu}$(CO) = 1985 (s), 1951 (vs), 1912 (s), 1896 cm$^{-1}$ (m); $^1$H NMR ($CD_3COCD_3$): $\delta$ = 7.82 (d, J = 7.3 Hz, 2H; p-$CH_3C_6H_4$), 7.14 (d, J = 7.3 Hz, 2H; p-$CH_3C_6H_4$), 6.66 (d, J = 10.5 Hz, 1H, CH), 6.35 (br, 1H; CH), 5.62 (s, 1H; $CH_2Cl_2$), 5.17 (t, J = 5.9 Hz, 1H; CH), 4.83 (m, 1H; NCHMe$_2$), 4.55 (t, J = 6.5 Hz, 1H; CH), 4.12 (t, J = 8.8 Hz, 1H; CH), 3.96 (m, 1H; NCHMe$_2$), 3.38 (t, J = 6.5 Hz, 1H; CH), 2.77 (m, 1H; CH), 2.33 (s, 3H; p-$CH_3C_6H_4$), 1.93 (br, 1H CH), 1.52 (t, J = 6.7 Hz, 3H; NCHC$H_3$), 1.33 (t, J = 6.7 Hz, 6H; NCHC$H_3$), 1.17 ppm (t, J = 6.7 H, 3H; NCHC$H_3$); $^{13}$C NMR ($CD_3COCD_3$): $\delta$ = 219.0, 215.2, 211.2, 209.9, 178.9, 162.3, 152.3, 135.7, 129.3, 129.1, 102.0, 101.8, 73.4, 55.2, 52.4, 49.7, 41.5, 38.7, 24.9, 23.5, 21.4, 21.1, 20.5, 19.6 ppm; MS: m/z: 531 [$M^+$], 503 [$M^+$ − CO], 475 [$M^+$ − 2CO], 419 [$M^+$ − Fe(CO)$_2$], 363 [$M^+$ − 2Fe(CO)$_2$ − 2CO], 84 [$CH_2Cl_2^+$]; elemental analysis (%) calcd for $C_{26}H_{29}Fe_2NO_4$ · 0.5 $CH_2Cl_2$: C 55.48, H 5.27, N 2.44; found: C 55.28, H 5.22, N 2.57.

**Reaction of 3 with $(iC_3H_7)_2NH$ to give [$Fe_2${μ-C($C_6H_4CF_3$-p)$C_8H_8N(iC_3H_7)_2$}(CO)$_4$] (12)**: Freshly prepared **3** (0.150 g, 0.26 mmol) was treated, in a manner similar to that for the reaction of **1** with $(iC_3H_7)_2NH$, with $(iC_3H_7)_2NH$ (0.10 mL, 0.71 mmol) in THF at −78 to −50 °C for 3 h. Further treatment of the resulting mixture as described in the reaction of **1** with $(iC_3H_7)_2NH$ afforded **12** (0.050 g, 28% based on **2**) as violet-red crystals. M.p. 86–88 °C decomp; IR ($CH_2Cl_2$): $\tilde{\nu}$(CO) = 1987 (m), 1954 (vs), 1916 (m), 1899 cm$^{-1}$ (m); $^1$H NMR ($CD_3COCD_3$): $\delta$ = 8.09 (d, J = 8.0 Hz, 2H; p-$CF_3C_6H_4$), 7.68 (d, J = 8.0 Hz, 2H; p-$CF_3C_6H_4$), 6.69 (d, J = 10.5 Hz, 1H; CH), 6.42 (d, J = 3.1 Hz, 1H; CH), 5.63 (s, 2H; $CH_2Cl_2$), 5.25 (t, J = 6.3 Hz, 1H; CH), 4.90 (m, 1H; NCHMe$_2$), 4.60 (t, J = 6.9 Hz, 1H; CH), 4.21 (dd, J = 10.5, 7.5 Hz, 1H; CH), 4.00 (m, 1H; NCHMe$_2$), 3.43 (t, J = 6.8 Hz, 1H; CH), 2.80 (m, 1H; CH), 1.94 (t, J = 3.0 Hz, 1H; CH), 1.55 (t, J = 6.8 Hz, 3H; NCHC$H_3$), 1.36 (t, J = 6.8 Hz, 6H; NCHC$H_3$), 1.19 ppm (t, J = 6.8 Hz, 3H; NCHC$H_3$); $^{13}$C NMR ($CD_3COCD_3$): $\delta$ = 218.4, 214.5, 210.5, 209.5, 173.5, 163.4, 159.5, 129.5, 125.0, 103.5, 101.5, 73.4, 55.0, 52.3, 49.7, 41.7, 39.0, 24.6, 23.2, 21.1, 20.2, 19.3 ppm; MS: m/z: 557 [$M^+$ − CO], 529 [$M^+$ − 2CO], 473 [$M^+$ − Fe(CO)$_2$], 361 [$M^+$ − 2Fe(CO)$_2$], 84 [$CH_2Cl_2^+$]; elemental analysis (%) calcd for $C_{26}H_{26}F_3Fe_2NO_4 \cdot CH_2Cl_2$: C 48.39, H 4.21, N 2.09; found: C 48.70, H 4.24, N 2.46.

**Reaction of 1 with $(C_6H_{11})_2NH$ to give [$Fe_2${μ-C($C_6H_5$)$C_8H_8N(C_6H_{11})_2$}(CO)$_4$] (13)**: $(C_6H_{11})_2NH$ (0.15 mL, 0.73 mmol) was added to **1** (0.130 g, 0.26 mmol), freshly prepared in situ, in THF (50 mL) at −100 °C. After stirring at −78 to −40 °C for 3 h, the resulting solution was evaporated to dryness under high vacuum at −20 °C, and the dark red residue was extracted with petroleum ether/$CH_2Cl_2$ (10:1). The red extract was evaporated to dryness in vacuo at −20 °C and the residue was recrystallized from petroleum ether/$CH_2Cl_2$ (15:1) at −80 °C to give violet-red crystals of **13** (0.078 g, 50% based on **1**). M.p. 110–112 °C decomp; IR ($CH_2Cl_2$): $\tilde{\nu}$(CO) = 1984 (s), 1950 (vs), 1912 (s), 1895 cm$^{-1}$ (m); $^1$H NMR ($CD_3COCD_3$): $\delta$ = 7.95–7.18 (m, 5H; Ph), 6.68 (d, J = 10.7 Hz, 1H; NCH), 6.36 (br, 1H; CH), 5.63 (s, 1H; $CH_2Cl_2$), 5.16 (t, J = 6.0 Hz, 1H; CH), 4.56 (t, J = 7.0 Hz, 1H; CH), 4.42 (br, 1H; NCHCH$_2$), 4.22 (dd, J = 10.7, 8.0 Hz, 1H; CH), 3.59 (br, 1H; NCHCH$_2$), 3.41 (m, 1H; CH), 2.77 (d, J = 7.3 Hz, 1H; CH), 2.09–0.85 ppm (m, 21H; $CH_2$ in $C_6H_{11}$ + CH); MS: m/z: 569 [$M^+$ − CO], 485 [$M^+$ − Fe(CO)$_2$], 429 [$M^+$ − Fe(CO)$_2$ − 2CO], 373 [$M^+$ − 2Fe(CO)$_2$], 193 [$M^+$ − Fe(CO)$_2$ − N($C_6H_{11}$)$_2$]; elemental analysis (%) calcd for $C_{31}H_{35}Fe_2NO_4$: C 62.34, H 5.86, N 2.34; found: C 61.78, H 6.03, N 2.30.

**Reaction of 2 with $(C_6H_{11})_2NH$ to give [$Fe_2${μ-C($C_6H_4CH_3$-p)$C_8H_8N(C_6H_{11})_2$}(CO)$_4$] (14)**: Freshly prepared **2** (0.147 g, 0.28 mmol) was treated, in a manner similar to that for the reaction of **1** with $(C_6H_{11})_2NH$, with $(C_6H_{11})_2NH$ (0.18 mL, 0.90 mmol) in THF at −78 to −40 °C for 3 h. Further treatment of the resulting mixture as described for the preparation of **13** afforded **14** (0.089 g, 52% based on **2**) as violet-red crystals. M.p. 112–114 °C decomp; IR ($CH_2Cl_2$): $\tilde{\nu}$(CO) = 1983 (m), 1949

Table 1. Crystal data and experimental details for **6**, **9**, **15**, **17**, **18**, and **21**.

|  | **6** · THF | **9** | **15** · $CH_2Cl_2$ | **17** | **18** · 0.5 $CH_2Cl_2$ | **21** |
|---|---|---|---|---|---|---|
| formula | $C_{36}H_{30}F_3Fe_2NO_5$ | $C_{24}H_{22}F_3Fe_2NO_4$ | $C_{33}H_{36}Cl_2F_3Fe_2NO_4$ | $C_{24}H_{22}F_3Fe_2NO_4$ | $C_{26.5}H_{22}ClFe_2NO_4$ | $C_{26}H_{21}O_4NFe_2$ |
| $M$ | 725.31 | 557.13 | 750.23 | 557.13 | 565.59 | 523.14 |
| space group | $P\bar{1}$ (No. 2) | $P2_1/c$ (No. 14) | $P\bar{1}$ (No. 2) | $P2_1/n$ (No. 14) | $P\bar{1}$ (No. 2) | $P2_1$ (No. 4) |
| $a$ [Å] | 11.866(7) | 11.209(9) | 11.4227(9) | 10.7508(7) | 8.0326(9) | 9.7867(14) |
| $b$ [Å] | 12.708(8) | 18.410(5) | 11.8084(10) | 20.2454(15) | 9.9497(11) | 12.2996(18) |
| $c$ [Å] | 12.850(8) | 11.871(8) | 13.7302(11) | 11.1025(8) | 16.444(2) | 19.417(3) |
| $\alpha$ [°] | 60.547(8) |  | 108.834(2) |  | 94.911(2) |  |
| $\beta$ [°] | 83.224(14) | 102.79(5) | 107.157(2) | 97.570(2) | 95.612(2) | 97.262(2) |
| $\gamma$ [°] | 70.250(9) |  | 90.486(2) |  | 108.620(3) |  |
| $V$ [Å$^3$] | 1585.3(17) | 2388(2) | 1663.8(2) | 2395.4(3) | 1229.9(2) | 2318.6(6) |
| $Z$ | 2 | 4 | 2 | 4 | 2 | 4 |
| $\rho_{calcd}$ [g cm$^{-3}$] | 1.520 | 1.549 | 1.498 | 1.545 | 1.541 | 1.499 |
| $F(000)$ | 744 | 1136.00 | 772 | 1136 | 582 | 1072 |
| $\mu(Mo_{K\alpha})$ [cm$^{-1}$] | 9.78 | 12.67 | 10.87 | 12.65 | 13.22 | 12.84 |
| $T$ [K] | 293 | 293 | 293 | 293 | 293 | 293 |
| $2\theta$ range [°] | 3.84 – 56.34 | 5 – 51.0 | 3.30 – 50.00 | 4.02 – 56.58 | 4.36 – 50.00 | 2.12 – 56.50 |
| unique reflections | 5878 | 4613 | 5808 | 5486 | 4268 | 7954 |
| obseverd reflections [$I > 2.00\sigma(I)$] | 1647 | 1624 (3.00$\sigma$(I)) | 3527 | 2010 | 1727 | 2831 |
| parameters | 427 | 308 | 474 | 393 | 329 | 598 |
| correction factors max/min | 0.2900/1.0000 | 0.7782/1.0000 | 0.7701/1.0000 | 0.86393/1.00000 | 0.69949/1.00000 | 0.39162/100000 |
| $R$[a] | 0.0750 | 0.060 | 0.0620 | 0.0516 | 0.0730 | 0.0643 |
| $R_w$[b] | 0.1889 | 0.066 | 0.0987 | 0.0628 | 0.1198 | 0.1573 |
| GOF[c] | 0.711 | 1.54 | 0.948 | 0.681 | 0.814 | 0.775 |
| max. shift/esd, final cycle | 0.125 | 0.05 | 0.001 | 0.003 | 0.000 | 0.000 |
| largest peak [e Å$^3$] | 0.864 | 0.61 | 0.577 | 0.296 | 0.538 | 0.505 |
| largest hole [e Å$^3$] | − 0.464 | − 0.45 | − 0.353 | − 0.365 | − 0.579 | − 0.528 |

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o^2)^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] $GOF = [\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{parameters})]^{1/2}$.

(s), 1911 (m), 1894 cm$^{-1}$ (m); $^1$H NMR ($CD_3COCD_3$): $\delta = 7.83$ (d, $J$ = 7.7 Hz, 2H; $CH_3C_6H_4$), 7.15 (d, $J$ = 7.7 Hz, 2H; $CH_3C_6H_4$), 6.66 (d, $J$ = 10.6 Hz, 1H; NCH), 6.34 (br, 1H; CH), 5.63 (s, 1H; $CH_2Cl_2$), 5.16 (t, $J$ = 6.1 Hz, 1H; CH), 4.55 (t, $J$ = 6.9 Hz, 1H; CH), 4.43 (br, 1H; NC*H*CH$_2$), 4.19 (dd, $J$ = 10.6, 7.6 Hz, 1H; CH), 3.54 (br, 1H; NC*H*CH$_2$), 3.38 (t, $J$ = 6.6 Hz, 1H; CH), 2.76 (d, $J$ = 6.9 Hz, 1H; CH), 2.33 (s, 3H; C*H*$_3$C$_6$H$_4$), 2.10 – 0.85 ppm (m, 21H; CH$_2$ in C$_6$H$_{11}$ + CH); $^{13}$C NMR ($CD_3COCD_3$): $\delta = 218.4$, 214.5, 210.6, 209.4, 178.2, 162.7, 151.7, 135.0, 128.6, 128.4, 101.5, 100.9, 72.8, 60.1, 58.1, 54.5, 41.5, 38.6, 35.6, 34.2, 30.4, 29.3, 25.7, 25.3, 25.2, 24.9, 24.8, 24.7, 20.5, 20.4 ppm; MS: $m/z$: 611 [$M^+$], 583 [$M^+ - CO$], 555 [$M^+ - 2CO$], 527 [$M^+ - 3CO$], 499 [$M^+ - Fe(CO)_2$], 471 [$M^+ - Fe(CO)_2 - CO$], 443 [$M^+ - Fe(CO)_2 - 2CO$], 387 [$M^+ - 2Fe(CO)_2$], 84 [$CH_2Cl_2^+$]; elemental analysis (%) calcd for $C_{32}H_{37}Fe_2NO_4 \cdot 0.5CH_2Cl_2$: C 59.71, H 5.86, N 2.14; found: C 60.26, H 5.96, N 2.56.

**Reaction of 3 with ($C_6H_{11})_2$NH to give [$Fe_2${µ-C($C_6H_4CF_3$-*p*)$C_8H_8N(C_6H_{11})_2$}(CO)$_4$] (15)**: The procedure used in the reaction of **3** (0.150 g, 0.26 mmol) with ($C_6H_{11})_2$NH (0.17 mL, 0.85 mmol) was the same as that in the reaction of **1** with ($C_6H_{11})_2$NH in THF at − 78 to − 40 °C for 3 h, and gave violet-red crystalline **15** (0.096 g, 56 % based on **3**). M.p. 149 – 150 °C decomp; IR ($CH_2Cl_2$): $\tilde{\nu}$(CO) = 1986 (m), 1952 (s), 1914 (m), 1897 cm$^{-1}$ (w); $^1$H NMR ($CD_3COCD_3$): $\delta = 7.96$ (d, $J$ = 8.1 Hz, 2H; $CF_3C_6H_4$), 7.37 (d, $J$ = 8.1 Hz, 2H; $CF_3C_6H_4$), 6.56 (d, $J$ = 10.5 Hz, 1H; NCH), 6.28 (br, 1H; CH), 5.49 (s, 2H; $CH_2Cl_2$), 5.09 (t, $J$ = 6.0 Hz, 1H; CH), 4.46 (t, $J$ = 6.6 Hz, 1H; CH), 4.36 (br, 1H; NC*H*CH$_2$), 4.14 (t, $J$ = 8.9 Hz, 1H; CH), 3.45 (br, 1H; N-C*H*CH$_2$), 3.30 (t, $J$ = 6.3 Hz, 1H; CH), 2.66 (d, $J$ = 7.2 Hz, 1H; CH), 1.74 – 1.04 ppm (m, 21H; CH$_2$ in C$_6$H$_{11}$ + CH); $^{13}$C NMR ($CD_3COCD_3$): $\delta = 218.7$, 214.7, 210.8, 210.0, 173.7, 164.6, 159.8, 129.7, 125.3, 103.8, 101.5, 73.8, 61.0, 58.9, 55.2, 42.7, 39.7, 36.2, 34.8, 31.0, 26.3, 25.9, 25.8, 25.5, 25.4, 25.3, 21.1 ppm; MS: $m/z$: 665 [$M^+$], 637 [$M^+ - CO$], 609 [$M^+ - 2CO$), 553 [$M^+ - Fe(CO)_2$], 443 [$M^+ - 2Fe(CO)_2$], 84 [$CH_2Cl_2^+$]; elemental analysis (%) calcd for $C_{32}H_{34}F_3Fe_2NO_4 \cdot CH_2Cl_2$: C 52.83, H 4.84, N 1.87; found: C 52.41, H 4.86, N 2.10.

**Reaction of 3 with piperidine to give [$Fe_2${µ-C($C_6H_4CF_3$-*p*)$C_8H_8N(CH_2)_5$}(CO)$_4$] (16)**: Piperidine (0.060 mL, 0.60 mmol) was added to **3** (0.150 g, 0.26 mmol), freshly prepared in situ, in THF (50 mL) at − 100 °C. After stirring at − 78 to − 50 °C for 3 h, the resulting solution was evaporated to dryness under high vacuum at − 40 °C, and the dark red residue was extracted with petroleum ether/$CH_2Cl_2$ (10:1). The red extract was evaporated to dryness in vacuo at − 20 °C, and the residue was recrystallized from petroleum ether/$CH_2Cl_2$ (15:1) at − 80 °C to give **16** (0.056 g, 38 % based on **2**) as orange crystals. M.p. 106 – 108 °C decomp; IR ($CH_2Cl_2$): $\tilde{\nu}$(CO) = 1988 (s), 1954 (vs), 1917 (m), 1899 cm$^{-1}$ (m); $^1$H NMR ($CD_3COCD_3$): $\delta = 7.96$ (d, $J$ = 8.3 Hz, 2H; *p*-$CF_3C_6H_4$), 7.55 (d, $J$ = 8.3 Hz, 2H; $CF_3C_6H_4$), 6.52 (d, $J$ = 10.8 Hz, 1H; CH), 6.29 (d, $J$ = 2.7 Hz, 1H; CH), 5.08 (t, $J$ = 6.3 Hz, 1H; CH), 4.38 (t, $J$ = 7.2 Hz, 1H; CH), 4.14 (dd, $J$ = 10.8, 7.5 Hz, 1H; CH), 4.00 – 3.40 (m, 4H; NC*H*$_2$), 3.25 (t, $J$ = 6.9 Hz, 1H; CH), 2.61 (dd, $J$ = 8.0, 2.5 Hz, 1H; CH), 1.92 (m, 1H; CH), 1.73 – 1.58 ppm (m, 6H; CH$_2$); $^{13}$C NMR ($CD_3COCD_3$): $\delta = 218.9$, 214.8, 210.9, 210.0, 173.2, 163.4, 163.3, 160.0, 129.9, 125.4, 103.7, 101.4, 74.1, 57.6, 55.4, 48.2, 41.9, 39.1, 27.1, 26.1, 24.0, 21.6 ppm; MS: $m/z$: 569 [$M^+$], 541 [$M^+ - CO$], 513 [$M^+ - 2CO$], 457 [$M^+ - Fe(CO)_2$], 345 [$M^+ - 2Fe(CO)_2$]; elemental analysis (%) calcd for $C_{25}H_{22}F_3Fe_2NO_4$: C 52.76, H 3.90, N 2.46; found: C 52.80, H 4.02, N 2.41.

**Thermolysis of 9 to give [$Fe_2${µ-C($C_6H_4CF_3$-*p*)$C_8H_8N(C_2H_5)_2$}(CO)$_4$] (17)**: **9** (0.090 g, 0.16 mmol) was dissolved in benzene (30 mL) in a quartz tube. The tube was cooled at − 80 °C to freeze the benzene solution and sealed under high vacuum. The sealed tube was heated at 90 – 95 °C for 72 h. After cooling, the dark red solution was evaporated to dryness in vacuo. The dark residue was subjected to chromatography on $Al_2O_3$ with petroleum ether/$CH_2Cl_2$ (5:1) as eluant. The orange-red band was collected. After removal of the solvent under vacuum, the crude product was recrystallized from petroleum ether/$CH_2Cl_2$ at − 80 °C to give red crystals of **17** (0.054 g, 60 %). M.p. 154 – 156 °C, decomp; IR ($CH_2Cl_2$): $\tilde{\nu}$(CO) = 1988 (m), 1956 (s), 1921 (m), 1901 cm$^{-1}$ (m); $^1$H NMR ($CD_3COCD_3$): $\delta = 8.17$ (d, $J$ = 8.0 Hz, 2H; $CF_3C_6H_4$), 7.71 (d, $J$ = 8.2 Hz, 2H; $CF_3C_6H_4$), 7.43 (d, $J$ = 10.1 Hz, 1H; NCH), 6.40 (d, $J$ = 2.8 Hz, 1H; CH), 5.57 (t, $J$ = 5.7 Hz, 1H; CH), 4.50 (t, $J$ = 7.0 Hz, 1H; CH), 3.73 – 3.45 (m, 4H; C*H*$_2$CH$_3$), 2.60 (m, 1H; CH), 2.53 (d, $J$ = 9.9 Hz, 1H; CH), 2.48 (m, 1H; CH), 2.21 (t, $J$ = 3.0 Hz, 1H; CH$_2$C*H*$_3$), 1.40 – 1.32 ppm (m, 6H; CH$_2$C*H*$_3$); $^{13}$C NMR ($CD_3COCD_3$): $\delta = 219.0$, 214.5, 211.1, 210.1, 169.6, 159.4, 129.9, 125.4, 104.0, 97.8, 74.6, 59.1, 51.5, 50.1, 44.9, 40.7, 31.6, 13.8, 12.7 ppm; MS: $m/z$: 557 [$M^+$], 529 [$M^+ - CO$], 501 [$M^+ - 2CO$], 473 [$M^+ - 3CO$], 445 [$M^+ - Fe(CO)_2$], 333 [$M^+ - 2Fe(CO)_2$]; elemental analysis (%) calcd for $C_{24}H_{22}F_3Fe_2NO_4$: C 51.74, H 3.98, N 2.51; found: C 51.46, H 4.12, N 2.32.

**Reaction of 2 with $C_6H_5NH_2$ to give [$Fe_2${=C($C_6H_4CH_3$-*p*)NHC$_6$H$_5$}(µ-CO)(CO)$_3$($\eta^8$-$C_8H_8$)] (18)**: $C_6H_5NH_2$ (0.066 mL, 0.73 mmol) was added to freshly prepared **2** (0.125 g, 0.24 mmol) in THF (50 mL) at − 78 °C. After stirring at − 78 to − 40 °C for 3 h, the resulting solution was evaporated to

Table 2. Selected bond lengths [Å][a] and angles [°][a] for **6**, **9**, **15**, and **17**.

| | **6** | **9** | **15** | **17** |
|---|---|---|---|---|
| Fe(1)–Fe(2) | 2.684(2) | 2.649(3) | 2.6329(10) | 2.6416(10) |
| Fe(1)–C(1) | 1.806(8) | 1.97(1) | 1.957(5) | 1.956(4) |
| Fe(2)–C(1) | 1.811(9) | 2.08(1) | 2.103(4) | 2.069(4) |
| Fe(1)–C(13) | 2.130(8) | | | |
| Fe(1)–C(14) | 2.098(9) | 2.43(1) | 2.456(5) | 2.468(6) |
| Fe(1)–C(15) | 2.119(9) | 2.08(1) | 2.076(6) | 2.070(5) |
| Fe(1)–C(16) | 2.305(11) | 2.08(1) | 2.067(5) | 2.057(6) |
| Fe(1)–C(17) | | 2.08(1) | 2.095(5) | 2.078(5) |
| Fe(2)–C(13) | | 2.07(1) | 2.084(5) | 2.099(5) |
| Fe(2)–C(14) | | 2.20(1) | 2.204(5) | 2.201(5) |
| Fe(2)–C(16) | 2.325(11) | | | |
| Fe(2)–C(17) | 2.079(9) | | | |
| Fe(2)–C(18) | 2.118(12) | 2.11(1) | 2.094(5) | 2.073(5) |
| Fe(2)–C(19) | 2.154(8) | 2.03(1) | 2.018(5) | 2.027(5) |
| Fe(1)–C(8) | 1.642(12) | 1.75(2) | 1.726(6) | 1.717(6) |
| Fe(1)–C(9) | 1.829(12) | 1.77(2) | 1.736(6) | 1.748(6) |
| Fe(2)–C(10) | 1.799(11) | 1.76(1) | 1.778(6) | 1.758(5) |
| Fe(2)–C(11) | 1.732(11) | 1.77(1) | 1.742(6) | 1.759(5) |
| C(1)–C(2) | 1.475(10) | 1.48(2) | 1.492(7) | 1.492(6) |
| C(12)–C(13) | 1.417(11) | 1.41(2) | 1.403(7) | 1.391(7) |
| C(13)–C(14) | 1.443(12) | 1.45(2) | 1.431(7) | 1.429(7) |
| C(14)–C(15) | 1.392(14) | 1.44(2) | 1.429(7) | 1.440(7) |
| C(15)–C(16) | 1.408(15) | 1.37(2) | 1.379(8) | 1.368(7) |
| C(16)–C(17) | 1.424(14) | 1.42(2) | 1.416(8) | 1.406(7) |
| C(17)–C(18) | 1.383(15) | 1.49(2) | 1.477(8) | 1.490(7) |
| C(18)–C(19) | 1.462(13) | 1.44(2) | 1.405(7) | 1.397(6) |
| C(12)–C(19) | 1.523(12) | | | |
| C(1)–C(19) | | 1.41(2) | 1.399(7) | 1.404(6) |
| C(12)–N | 1.458(9) | 1.33(1) | 1.303(6) | 1.316(6) |
| N–C(20) | 1.421(10) | 1.47(2) | | 1.469(6) |
| N–C(21) | | | 1.494(6) | |
| N–C(23) | | 1.44(2) | | 1.466(7) |
| Fe(1)-C(1)-Fe(2) | 95.8(4) | 81.7(4) | 80.76(18) | 81.96(16) |
| Fe(1)-Fe(2)-C(1) | 42.0(3) | 47.4(3) | 47.20(14) | 47.17(12) |
| Fe(2)-Fe(1)-C(1) | 42.2(3) | 51.0(3) | 52.04(13) | 50.87(13) |
| Fe(1)-C(14)-Fe(2) | | 69.5(3) | 68.55(14) | 68.63(14) |
| Fe(1)-Fe(2)-C(14) | | 59.4(3) | 60.26(14) | 60.48(16) |
| Fe(2)-Fe(1)-C(14) | | 51.1(3) | 51.19(12) | 50.88(13) |
| Fe(1)-C(16)-Fe(2) | 70.9(3) | | | |
| Fe(1)-Fe(2)-C(16) | 54.2(3) | | | |
| Fe(2)-Fe(1)-C(16) | 54.9(3) | | | |
| C(1)-Fe(1)-C(16) | 96.5(4) | | | |
| C(1)-Fe(2)-C(16) | 95.7(4) | | | |
| Fe(1)-C(17)-C(18) | | 99.3(7) | 99.2(4) | 98.7(3) |
| C(17)-C(18)-Fe(2) | 69.2(7) | 107.9(8) | 108.3(4) | 109.1(4) |
| C(17)-C(18)-C(19) | 121.7(13) | 114(1) | 112.6(5) | 113.0(5) |
| Fe(2)-C(18)-C(19) | 71.3(6) | 66.8(7) | 67.1(3) | 68.3(3) |
| Fe(2)-C(19)-C(1) | | 71.6(7) | 73.5(3) | 71.6(3) |
| Fe(2)-C(19)-C(18) | 68.7(6) | 72.6(7) | 73.0(3) | 71.9(3) |
| Fe(2)-C(13)-C(12) | | 101.6(8) | 109.1(3) | 98.1(3) |
| Fe(1)-C(1)-C(2) | 132.7(7) | 129.5(9) | 128.8(4) | 128.9(3) |
| Fe(2)-C(1)-C(2) | 131.4(6) | 123.8(8) | 123.0(4) | 123.8(3) |
| Fe(1)-C-O (av) | 177 | 176.5 | 178.2 | 178.0 |
| Fe(2)-C-O (av) | 176.9 | 176.5 | 177.2 | 175.3 |
| C(12)-C(13)-C(14) | 134.7(9) | 122(1) | 121.1(5) | 121.4(5) |
| C(13)-C(14)-C(15) | 124.4(11) | 130(1) | 127.4(5) | 123.8(5) |
| C(14)-C(15)-C(16) | 129.2(11) | 125(1) | 126.0(6) | 122.5(5) |
| C(15)-C(16)-C(17) | 129.7(11) | 124(1) | 124.6(6) | 124.3(6) |
| C(16)-C(17)-C(18) | 132.8(12) | 132(1) | 132.1(5) | 132.9(5) |
| C(17)-C(18)-C(19) | 121.7(13) | 114(1) | 112.6(5) | 113.0(5) |
| C(18)-C(19)-C(12) | 133.9(9) | | | |
| C(19)-C(12)-C(13) | 123.2(8) | | | |
| C(13)-C(12)-N | 108.7(7) | 126(1) | 129.6(5) | 127.6(5) |
| C(19)-C(12)-N | 110.0(7) | | | |

[a] Estimated standard deviations in the least significant figure are given in parentheses.

dryness under high vacuum at –40°C, and the dark red residue was extracted with petroleum ether/$CH_2Cl_2$ (10:3). The red extract was evaporated to dryness in vacuo at –40°C and the residue recrystallized from petroleum ether/$CH_2Cl_2$ (5:1) at –80°C to give deep red crystals of **18** (0.080 g, 61% based on **2**). M.p. 100–102°C decomp; IR ($CH_2Cl_2$): $\tilde{\nu}(CO) = 1987$ (s), 1930 (s), 1697 cm$^{-1}$ (br, w); $^1H$ NMR ($CD_3COCD_3$): $\delta =$ 11.4 (br, 1H; $C_6H_5N\mathit{H}$), 7.22–6.80 (m, 9H; $CH_3C_6\mathit{H}_4 + C_6\mathit{H}_5NH$), 5.63 (s, 1H; $CH_2Cl_2$), 4.38 (s, 8H; $C_8H_8$), 2.28 ppm (s, 3H; $C\mathit{H}_3C_6H_4$); MS: *m/z*: 467 $[M^+ - 2CO]$, 439 $[M^+ - 3CO]$, 411 $[M^+ - Fe(CO)_2]$, 355 $[M^+ - Fe(CO)_2 - 2CO]$, 299 $[M^+ - 2Fe(CO)_2]$, 84 $[CH_2Cl_2^+]$; elemental analysis (%) calcd for $C_{26}H_{21}Fe_2NO_4 \cdot 0.5CH_2Cl_2$: C 56.27, H 3.92, N 2.48, found: C 55.99, H 4.08, N 2.62.

**Reaction of 2 with 2-naphthylamine to give $[Fe_2\{{=}C(C_6H_4CH_3\text{-}p)NC_{10}H_7\}(CO)_4(\eta^2{:}\eta^3{:}\eta^2\text{-}C_8H_9)]$ (19)**: 2-$C_{10}H_7NH_2$ (0.083 g, 0.58 mmol) was added to freshly prepared **2** (0.138 g, 0.29 mmol) in THF (50 mL) at –78°C. After stirring at –78 to –20°C for 3 h, the resulting solution was evaporated to dryness under high vacuum at –40°C, and the dark red residue was subjected to chromatography on $Al_2O_3$ with petroleum/$CH_2Cl_2$ (10:1) as eluant. The orange-red band was eluted and collected. After removal of the solvent, the residue was recrystallized from petroleum/$CH_2Cl_2$ (15:1) at –50°C to give red crystalline **19** (0.133 g, 80% based on **2**). M.p. 154–156°C decomp; IR ($CH_2Cl_2$): $\tilde{\nu}(CO) = 1996$ (m), 1962 (s), 1933 (m), 1911 cm$^{-1}$ (w); $^1H$ NMR ($CD_3COCD_3$): $\delta = 6.53$–7.88 (m, 11H; $CH_3C_6\mathit{H}_4 + C_{10}\mathit{H}_7N$), 4.49 (t, $J = 6.8$ Hz, 1H; CH), 4.08 (t, $J = 6.6$ Hz, 1H; CH), 3.65 (dd, $J = 13.6$, 8.3 Hz, 1H; CH), 3.46–3.30 (m, 2H; CH), 3.08 (dd, $J = 8.8$, 5.8 Hz, 1H; CH), 2.78 (m, 1H; $CH_2$), 2.64 (dd, $J = 13.6$, 7.8 Hz, 1H; CH), 1.64 ppm (m, 1H; $CH_2$); $^{13}C$ NMR ($CD_3COCD_3$) = $\delta = 237.3$ ($C_{carbene}$), 218.5, 217.9, 217.2, 216.2 (CO), 156.8, 149.0, 136.8, 134.5, 131.9, 129.1, 128.5, 127.2, 126.1, 124.6, 124.0, 120.5 (Ar-C), 88.5, 80.8, 69.4, 54.6, 53.5, 43.0, 21.4, 21.0, 20.1 ppm; MS: *m/z*: 545 $[M - CO]$, 489 $[M - Fe(CO)]$, 462 $[M{+}1 - Fe(CO)_2]$, 434 $[M{+}1 - Fe(CO)_2 - CO]$, 349 $[M^+ - 2Fe(CO)_2]$; elemental analysis (%) calcd for $C_{30}H_{23}Fe_2NO_4$: C 62.86, H 4.04, N 2.44; found: C 62.55, H 4.09, N 2.64.

**Reaction of 3 with *p*-$CF_3C_6H_4NH_2$ to give $[Fe_2\{{=}C(C_6H_4CF_3\text{-}p)N(C_6H_4CF_3\text{-}p)\}(CO)_4(\eta^2{:}\eta^3{:}\eta^2\text{-}C_8H_9)]$ (20)**: *p*-$CF_3C_6H_4NH_2$ (0.062 mL, 0.50 mmol) was added to freshly prepared **3** (0.125 g, 0.24 mmol) in THF (50 mL) at –78°C. After stirring at –78 to –40°C for 3 h, the resulting solution was evaporated to dryness under high vacuum at –40°C and the dark red residue was subjected to chromatography on $Al_2O_3$ with petroleum/$CH_2Cl_2$ (10:1) as eluant. The orange-red band was eluted and collected. After removal of the solvent, the residue was recrystallized from petroleum/$CH_2Cl_2$ (15:1) at –50°C to give red crystalline **20** (0.117 g, 83% based on **3**). M.p. 136–138°C decomp; IR ($CH_2Cl_2$): $\tilde{\nu}(CO) = 2001$ (m), 1968 (s), 1940 (m), 1919 cm$^{-1}$ (w); $^1H$ NMR ($CD_3COCD_3$): $\delta = 7.59$ (d, $J = 8.1$ Hz, 2H; $CF_3C_6H_4$), 7.48 (d, $J = 8.1$ Hz, 2H; $CF_3C_6H_4$), 7.22 (d, $J = 8.1$ Hz, 2H; $CF_3C_6H_4$), 6.83 (d, $J = 8.1$ Hz, 2H; $CF_3C_6H_4$), 5.63 (s, 1H; $CH_2Cl_2$), 4.51 (t, $J = 6.3$ Hz, 1H; CH), 4.15 (t, $J = 6.8$ Hz, 1H; CH), 3.70 (dd, $J = 8.4$, 15.6 Hz, 1H; CH), 3.50 (t, $J = 6.2$ Hz, 1H; CH), 3.43 (t, $J = 6.5$ Hz, 1H; CH), 3.11 (dd, $J = 8.9$, 5.9 Hz, 1H; CH), 2.82 (m, 1H; $CH_2$), 2.75 (m, 1H; CH), 1.60 ppm (m, 1H; $CH_2$); $^{13}C$ NMR ($CD_3COCD_3$): $\delta = 238.1$ ($C_{carbene}$), 217.3, 216.5, 215.8, 215.2 (CO), 160.4, 153.4, 126.13, 126.08, 125.24, 125.19, 124.2, 123.93, 123.86 (Ar-C), 87.3, 80.4, 68.9, 54.3, 52.9, 42.8, 20.6, 19.2 ppm; MS: *m/z*: 421 $[M^+ - 2Fe(CO)_2]$, 276 $[M^+ - 2Fe(CO)_2 - CF_3C_6H_4]$, 262 $[M^+ - 2Fe(CO)_2 - NC_6H_4CF_3]$; elemental analysis (%) calcd for $C_{27}H_{17}F_6Fe_2NO_4 \cdot 0.5CH_2Cl_2$: C 48.03, H 2.64, N 2.04, found: C 48.12, H 2.66, N 2.31.

**Transformation of 18 into $[Fe_2\{{=}C(C_6H_4CH_3\text{-}p)NC_6H_5\}(CO)_4(\eta^2{:}\eta^3{:}\eta^2\text{-}C_8H_9)]$ (21)**: A solution of **18** (0.050 g, 0.10 mmol) in $CH_2Cl_2$ (10 mL) was kept at room temperature for 1–2 h, during which time the deep red solution gradually turned red. The solvent was removed in vacuo, and the residue was subjected to chromatography on $Al_2O_3$ with petroleum/$CH_2Cl_2$ (10:1) as eluant. The orange-red band was eluted and collected. After removal of the solvent, the residue was recrystallized from petroleum/$CH_2Cl_2$ (15:1) at –50°C to give **19** (0.042 g, 84%) as orange-red crystals. M.p. 170–172°C decomp; IR ($CH_2Cl_2$): $\tilde{\nu}(CO)$ 1997 (m), 1960 (s), 1932 cm$^{-1}$ (m); $^1H$ NMR ($CD_3COCD_3$): $\delta = 7.21$–6.47 (m, 9H; $CH_3C_6\mathit{H}_4 + C_6H_5$), 4.42 (t, $J = 6.3$ Hz, 1H; CH), 4.05 (t, $J = 6.5$ Hz, 1H; CH), 3.60 (dd, $J = 14.9$, 8.2 Hz, 1H; CH), 3.41 (t, $J = 5.8$ Hz, 1H; CH), 3.36 (t, $J = 5.5$ Hz, 1H; CH), 2.98 (dd, $J = 8.2$, 6.1 Hz, 1H; CH), 2.72 (m, 1H; $CH_2$), 2.58 (dd, $J = 13.5$, 7.9 Hz, 1H; CH), 2.19 (s, 3H; $C\mathit{H}_3C_6H_4$), 1.60 ppm (m, 1H; $CH_2$); $^{13}C$ NMR ($CD_3COCD_3$): $\delta = 236.2$ ($C_{carbene}$), 218.4, 217.8, 217.1, 216.1 (CO), 159.1, 148.8, 136.63, 136.61, 129.1, 129.0, 126.8, 125.2, 124.5, 123.7 (Ar-C), 88.2, 80.7, 69.2, 54.4, 53.3, 42.7, 21.2, 19.9 ppm; MS: $m/z$: 467 [$M^+ - 2$CO], 439 [$M^+ - 3$CO], 411 [$M^+ -$ Fe(CO)$_2$], 355 [$M^+ -$ Fe(CO)$_2 - 2$CO], 299 [$M^+ - 2$Fe(CO)$_2$]; elemental analysis (%) calcd for $C_{26}H_{21}Fe_2NO_4$: C 59.69, H 4.05, N 2.68; found: C 59.54, H 4.31, N 2.65.

**X-ray crystal structure determinations of complexes 6, 9, 15, 17, 18, and 21**: Single crystals of **6**, **9**, **15**, **17**, **18**, and **21** suitable for X-ray diffraction studies were obtained by recrystallization from petroleum ether/$CH_2Cl_2$ or petroleum ether/THF at $-80\,^{\circ}$C. Single crystals were mounted on a glass fibers and sealed with epoxy adhesive. The X-ray diffraction intensity data for **6**, **15**, **17**, **18**, and **21** were collected with a Brock Smart diffractometer [radiation (monochromated in incident beam): $Mo_{K\alpha}$ ($\lambda = 0.71073$ Å)] and those for **9** on Rigaku AFC7R [radiation (monochromated in incident beam): $Mo_{K\alpha}$ ($\lambda = 0.71069$ Å)] diffractometer at 293 K. The scan method for all measurements was $\omega - 2\theta$.

The structures of **6**, **9**, **15**, **17**, **18** and **21** were solved by direct methods and expanded by using Fourier techniques. For complexes **6**, **15**, **17**, **18**, and **21**, the non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were included, of which some were refined isotropically. For complex **9**, the non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included but not refined. The absorption corrections were applied with SADABS.

The details of the crystallographic data and the procedures used for data collection and refinement for complexes **6**, **9**, **15**, **17**, **18**, and **21** are given in Table 1. Selected bond lengths and angles are listed in Tables 2 and 3, respectively.

CCDC 212534 (**6**·THF), 212535 (**9**), 212536 (**15**·$CH_2Cl_2$), 212537 (**17**), 212538 (**18**·0.5$CH_2Cl_2$) and 212539 (**21**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.uk).

Table 3. Selected bond lengths [Å][a] and angles [°][a] for **18** and **21**.

| | **18** | **21** | | **18** | **21** |
|---|---|---|---|---|---|
| Fe(1)–Fe(2) | 2.7589(19) | 2.691(3) | Fe(2)–C(11) | 1.762(10) | 1.791(15) |
| Fe(1)–C(1) | 1.895(8) | 1.972(13) | C(1)–N | 1.333(10) | 1.266(16) |
| Fe(2)–N(1) | | 1.966(11) | N–C(20) | 1.421(10) | 1.476(16) |
| Fe(1)–C(13) | 2.173(10) | 2.215(15) | C(1)–C(2) | 1.487(11) | 1.440(18) |
| Fe(1)–C(14) | 2.115(11) | 2.182(15) | C(12)–C(13) | 1.439(15) | 1.52(2) |
| Fe(1)–C(15) | 2.116(10) | | C(13)–C(14) | 1.399(16) | 1.43(2) |
| Fe(1)–C(16) | 2.296(9) | 2.274(14) | C(14)–C(15) | 1.370(15) | 1.43(2) |
| Fe(1)–C(17) | | 2.356(14) | C(15)–C(16) | 1.382(14) | 1.49(2) |
| Fe(2)–C(12) | 2.274(11) | 2.150(17) | C(16)–C(17) | 1.407(13) | 1.351(19) |
| Fe(2)–C(17) | 2.157(8) | | C(17)–C(18) | 1.388(11) | 1.44(2) |
| Fe(2)–C(18) | 2.073(9) | 2.156(15) | C(18)–C(19) | 1.400(12) | 1.42(2) |
| Fe(2)–C(19) | 2.092(9) | 2.065(15) | C(12)–C(19) | 1.417(14) | 1.46(2) |
| Fe(1)–C(8) | 1.916(9) | 1.721(17) | C(8)–O(1) | 1.209(9) | 1.189(16) |
| Fe(1)–C(9) | 1.770(11) | 1.79(2) | C(9)–O(2) | 1.137(10) | 1.16(2) |
| Fe(2)–C(8) | 1.944(8) | | C(10)–O(3) | 1.200(12) | 1.054(15) |
| Fe(2)–C(10) | 1.701(12) | 1.882(16) | C(11)–O(4) | 1.152(9) | 1.150(15) |
| Fe(1)-C(8)-Fe(2) | 91.2(4) | | C(1)-N-C(20) | 133.1(8) | 123.4(12) |
| Fe(1)-Fe(2)-C(8) | 44.0(3) | | C(12)-C(13)-C(14) | 133.4(11) | 121.3(17) |
| Fe(2)-Fe(1)-C(8) | 44.8(3) | 90.4(5) | C(13)-C(14)-C(15) | 127.8(13) | 127.6(17) |
| Fe(1)-Fe(2)-N(1) | | 68.8(4) | C(14)-C(15)-C(16) | 129.1(11) | 103.4(14) |
| Fe(2)-Fe(1)-C(1) | 127.1(3) | 68.8(4) | C(15)-C(16)-C(17) | 136.5(10) | 123.9(17) |
| Fe(1)-C(1)-N | 122.9(6) | 110.9(10) | C(16)-C(17)-C(18) | 133.7(10) | 129.2(16) |
| Fe(2)-N(1)-C(1) | | 111.5(9) | C(17)-C(18)-C(19) | 126.8(10) | 129.5(14) |
| Fe(1)-C(1)-C(2) | 122.7(6) | 123.7(10) | C(18)-C(19)-C(12) | 127.0(9) | 126.5(15) |
| Fe(2)-N(1)-C(20) | | 125.0(9) | C(19)-C(12)-C(13) | 132.9(11) | 128.6(16) |
| Fe(1)-C(8)-O(1) | 135.9(7) | 174.9(13) | Fe(1)-C-O (av) | 177.4 | 173.8 |
| Fe(2)-C(8)-O(1) | 132.9(7) | | Fe(2)-C-O (av) | 173.7 | 178.4 |
| N-C(1)-C(2) | 114.3(7) | 123.8(12) | | | |

[a] Estimated standard deviations in the least significant figure are given in parentheses.

## Acknowledgement

Financial support from the National Natural Science Foundation of China, the Science Foundation of the Chinese Academy of Sciences, and NEDO of Japan is gratefully acknowledged.

---

[1] a) K. F. McDaniel in *Comprehensive Organometallic Chemistry, Vol. 12* (Eds.: G. Wilkinson, F. G. A. Stone, E. W. Abel), Pergamon, Oxford, New York, **1995**, pp. 601 – 622; b) J. P. Collman, L. S. Hegedus, J. R. Norton, R. G. Finke, *Principles and Applications of Organotransition Metal Chemistry*, University Science Books: Mills Valley, CA, **1987**, Chapter 7; c) A. Yamamoto, *J. Organomet. Chem.* **2000**, *600*, 159 – 167; d) M. V. Ovchinnikov, E. LeBlanc, I. A. Guzei, R. J. Angelici, *J. Am. Chem. Soc.* **2001**, *123*, 11494 – 11495; e) C. Shu, L. S. Liebeskind, *J. Am. Chem. Soc.* **2003**, *125*, 2878 – 2879.

[2] S. G. Davies, *Organotransition Metal Chemistry: Application to Organic Chemistry*, Pergamon, Oxford, **1982**.

[3] a) J. Smidt, W, Hafner, R, Jira, R, Sieber, J. Sedlmeier, A, Sabel, *Angew. Chem.* **1962**, *74*, 93 – 102; *Angew. Chem. Int. Ed. Engl.* **1962**, *1*, 80 – 85; b) G. W. Parshall, *Homogeneous Catalysis*, Wiley, New York, **1980**.

[4] a) G. Deganello, *Transition Metal Complexes of Cyclic Polyolefins*, Academic Press, New York, **1979**; b) A. J. Pearson, *Synlett* **1990**, 10 – 19; c) G. R. Stephenson, H. Finch, D. A. Owen, S. Swanson, *Tetrahedron* **1993**, *49*, 5649 – 5662; d) J. Heck, G. Lange, O. Reimelt, *Angew. Chem.* **1998**, *110*, 533 – 535; *Angew. Chem. Int. Ed.* **1998**, *37*, 520 – 522.

[5] a) G. I. Fray, R. G. Saxton, *The Chemistry of Cyclooctatetraene and Its Derivatives*, Cambridge University Press, Cambridge, **1978**; b) G. Lange, O. Reimelt, L. Jessen, J. Heck, *Eur. J. Inorg. Chem.* **2000**, 1941 – 1952.

[6] a) W. A. Herrmann, *Angew. Chem.* **1982**, *94*, 118 – 131; *Angew. Chem. Int. Ed.* **1982**, *21*, 117 – 130; b) W. A. Herrmann, *Adv. Organomet. Chem.* **1982**, *20*, 159 – 263; c) J. Holton, M. F. Lappert, R. Pearce, P. I. W. Yarrow, *Chem. Rev.* **1983**, *83*, 135 – 201.

[7] a) R. C. Brady, III, R. Pettit, *J. Am. Chem. Soc.* **1980**, *102*, 6181 – 6182; b) W. T. Osterloh, M. E. Cornell, R. Pettit, *J. Am. Chem. Soc.* **1982**, *104*, 3759 – 3761; c) C. Masters, *Adv. Organomet. Chem.* **1979**, *17*, 61 – 103.

[8] a) Y. Yu, J.-B. Chen, X. Wang, Q. Wu, Q. Liu, *J. Organomet. Chem.* **1996**, *516*, 81 – 89; b) J.-B. Chen, Y. Yu, J. Sun, *Organometallics* **1997**, *16*, 3608 – 3614; c) S. Zhang, Q. Xu, J. Sun, J.-B. Chen, *Organometallics*, **2001**, *20*, 2387 – 2399; d) N. Xiao, S. Zhang, Z. Qiu, R. Li, B. Wang, Q. Xu, J. Sun, J.-B. Chen, *Organometallics* **2002**, *21*, 3709 – 3715.

[9] J.-B. Chen, D.-S. Li, Y. Yu, Z.-S. Jin, Q.-L. Zhou, G.-C. Wei, *Organometallics* **1993**, *12*, 3885 – 3889.

[10] E. B. Fleischer, A. L. Stone, R. B. K. Dewar, J. D. Wright, C. E. Keller, R. Pettit, *J. Am. Chem. Soc.* **1966**, *88*, 3158 – 3159.

[11] R. C. Bush, R. J. Angelici, *J. Am. Chem. Soc.* **1986**, *108*, 2735 – 2742.

[12] a) R. J. Angelici, *Acc. Chem. Res.* **1995**, *28*, 51 – 56; b) R. M. Bullock, *Comments Inorg. Chem.* **1991**, *12*, 1 – 33.

[13] S. Zhang, Q. Xu, J. Sun, J.-B. Chen, *Organometallics* **2002**, 21, 4572 – 4574.

[14] Y. Takemoto, N. Yoshikawa, Y. Baba, C. Iwata, T. Tanaka, T.

Ibuka, H. Ohishi, *J. Am. Chem. Soc.* **1999**, *121*, 9143–9145.

[15] a) Y.-J. Liu, R.-T. Wang, J. Sun, J.-B. Chen, *Organometallics* **2000**, *19*, 3498–3506; b) Y.-J. Liu, R.-T. Wang, J. Sun, J.-B. Chen, *Organometallics* **2000**, *19*, 3784–3790.

[16] R.-T. Wang, Q. Xu, J. Sun, L.-C. Song, J.-B. Chen, *Organometallics* **2001**, *20*, 4092–4099.

[17] J. D. Edwards, R. Goddard, S. A. R. Knox, R. J. McKinney, F. G. A. Stone, P. Woodward, *J. Chem. Soc. Chem. Commun.* **1975**, 828–829.

[18] D. J. S. Guthrie, I. U. Khand, G. R. Knox, J. Kollmeier, P. L. Pauson, W. E. Watts, *J. Organomet. Chem.* **1975**, *90*, 93–100.

[19] a) K. H. Theopold, R. G. Bergman, *J. Am. Chem. Soc.* **1983**, *105*, 464–475; b) K. H.Theopold, R. G. Bergman, *Organometallics* **1982**, *1*, 219–222.

[20] For more detailed review on fluxional organometallics, see F. A. Cotton, *Inorg. Chem.* **2002**, *41*, 643–658.

[21] J.-B. Chen, G.-X. Lei, Z.-S. Jin, L.-H. Hu, G.-C. Wei, *Organometallics* **1988**, *7*, 1652–1657.

[22] Y. Yu, J. Sun, J.-B. Chen, *J. Organomet. Chem.* **1997**, *533*, 13–23.

[23] L. Song, G. Lu, Q. Hu, X. Qin, C. Sun, J. Yang, J. Sun, *J. Organomet.* Chem. **1998**, *571*, 55–63.

[24] G. Hogarth, M. H. Lavender, K. Shukri, *Organometallics* **1995**, *14*, 2325–2341.

[25] C. Yan, J. Sun, J. Sun, *J. Organomet.* Chem. **1999**, *585*, 63–67.

[26] G. Gervasio, P. L. Stanghellini, R. Rossetti, *Acta Crystallogr.* **1981**, *B37*, 1198–1202.

Received: May 13, 2003 [F5130]