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Remarkable Reactions of (η^4-1-azadiene)Fe(CO)$_3$ Complexes with Aryllithium Reagents. Syntheses and Structures of Novel Chelated Furanyl-Coordinated Alkoxy(amino)carbeneiron, η^4-Azadiene-Coordinated 17e Acyliron, and Iron Inner Salt Complexes

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The reactions of a (η^4-1-azadiene)Fe(CO)$_3$ complex, $[(\eta^4\text{-}C_4H_3OCH{=}CHCH{=}NC_6H_{11})Fe(CO)_3]$ (**1**), with aryllithium reagents, ArLi (Ar = C_6H_5, *p*-$CH_3C_6H_4$, *o*-$CH_3OC_6H_4$, *p*-$CH_3OC_6H_4$, *p*-$CF_3C_6H_4$), in ether at low temperature followed by alkylation with Et_3OBF_4 in aqueous solution at 0 °C or in CH_2Cl_2 at −60 °C gave novel chelated furanyl-coordinated alkoxy(amino)carbeneiron complexes $[\{\eta^4\text{-}C_4H_3OCH{=}CHCH(Ar)N(C_6H_5)C(OC_2H_5){=}\}Fe(CO)_2]$ (**4**, Ar = C_6H_5; **5**, Ar = *p*-$CH_3C_6H_4$; **6**, Ar = *o*-$CH_3OC_6H_4$; **7**, Ar = *p*-$CH_3OC_6H_4$; **8**, Ar = *p*-$CF_3C_6H_4$). The analogous reactions of compounds $[(\eta^4\text{-}C_4H_3OCH{=}CHCH{=}NC_6H_{11})Fe(CO)_3]$ (**2**) and $[(\eta^4\text{-}C_6H_5CH{=}CHCH{=}NC_6H_{11})Fe(CO)_3]$ (**3**) with ArLi (Ar = C_6H_5, *o*-, *m*-, *p*-$CH_3C_6H_4$) afforded novel η^4-azadiene-coordinated 17e acyliron complexes $[\{\eta^4\text{-}C_4H_3OCH{=}CHCH{=}NC_6H_{11}\}Fe(CO)_2(COAr)]$ (**9**, Ar = C_6H_5; **10**, Ar = *o*-$CH_3C_6H_4$; **11**, Ar = *m*-$CH_3C_6H_4$; **12**, Ar = *p*-$CH_3C_6H_4$) and $[(\eta^4\text{-}C_6H_5CH{=}CHCH{=}NC_6H_{11})Fe(CO)_2(COAr)]$ (**15**, Ar = C_6H_5; **16**, Ar = *m*-$CH_3C_6H_4$; **17**, Ar = *p*-$CH_3C_6H_4$), respectively. Unexpectedly, **2** reacts similarly with *p*-$CH_3OC_6H_4Li$ and *p*-$CF_3C_6H_4Li$ to yield novel η^2-azadiene-coordinated acyliron inner salt complexes $[\{\eta^2\text{-}C_4H_3O{-}CH{=}CHCH{=}N(C_2H_5)C_6H_{11}\}Fe(CO)_3(COAr)]$ (**13**, Ar = *p*-$CH_3OC_6H_4$; **14**, Ar = *p*-$CF_3C_6H_4$). Analogous acyliron inner salt complex $[\{\eta^2\text{-}C_6H_5CH{=}CHCH{=}N(C_2H_5)C_6H_{11}\}Fe(CO)_3(COC_6H_4CH_3\text{-}p)]$ (**18**) was also obtained from the reaction of **3** with *p*-$CH_3OC_6H_4Li$. However, similar reactions of **3** with ArLi (Ar = *o*-$CH_3C_6H_4$, *o*-$CH_3OC_6H_4$, *p*-$CF_3C_6H_4$) produced η^2-azadiene-coordinated aryliron inner salt complexes $[\{\eta^2\text{-}C_6H_5CH{=}CHCH{=}N(C_2H_5)C_6H_{11}\}Fe(CO)_3Ar]$ (**19**, Ar = *o*-$CH_3C_6H_4$; **20**, Ar = *o*-$CH_3OC_6H_4$; **21**, Ar = *p*-$CF_3C_6H_4$). The structures of **6**, **10**, **13**, and **18** have been established by X-ray diffraction studies.

Introduction

The synthesis, structure, and chemistry of alkene−metal carbene complexes are one area of current interest, stemming from the possible involvement of these species in some reactions catalyzed by organometallic compounds.[1,2] In recent years, olefin-coordinated transition-metal carbene and carbyne complexes and/or their isomerized products, as a part of a broader investigation of transition-metal carbene and carbyne complexes, have been examined extensively in our laboratory.[3−10] In previous studies, we have shown that a considerable number of the novel olefin-coordinated transition-metal carbene complexes and/or their isomerized products were isolated, and a number of novel isomerizations of olefin ligands have been observed in the reactions of olefin-ligated metal carbonyls with aryllithium reagents followed by alkylation with alkylating reagents. We have also shown that the isomerization of the olefin ligands and resulting products depend not only on the olefin ligands but also on the nucleophiles used and alkylation conditions.[3−5] For instance, the reaction of butadiene(tricarbonyl)iron with aryllithium reagents and subsequent alkylation with Et_3OBF_4 result in the formation of novel isomerized carbeneiron complexes with two types of structures, A and B, depending on the

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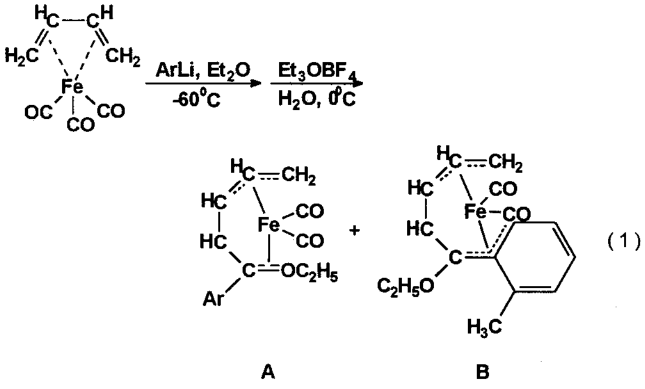
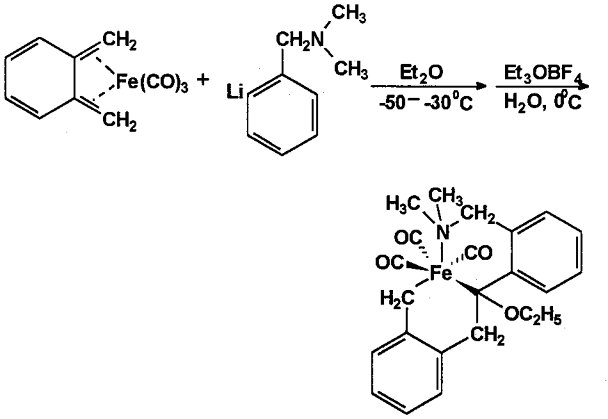
aryllithium reagents used (eq 1),[3] while *o*-chinodimethaneiron tricarbonyl, $[Fe\{o\text{-}(CH_2)_2C_6H_4\}(CO)_3]$, where the $Fe(CO)_3$ moiety is bonded to the butadiene-like residue of the *o*-chinomethane ligand, reacted with (*o*-lithiobenzyl)dimethylamine to give a novel coupling product of the *o*-chinomethane ligand with CO and benzyldimethylamino groups (eq 2).[10]



(1)

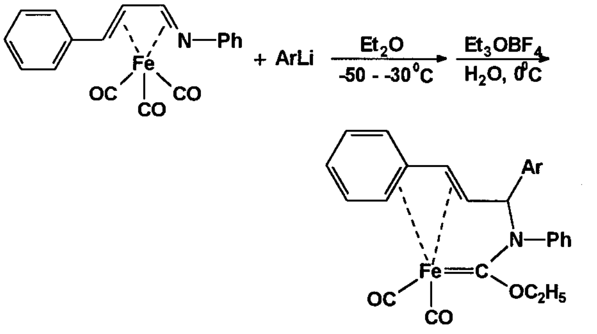
Ar = C_6H_5, m-, p-$CH_3C_6H_4$, p-$CH_3OC_6H_4$, m-, p-ClC_6H_4, p-$CF_3C_6H_4$, 2-C_4H_3S



(2)

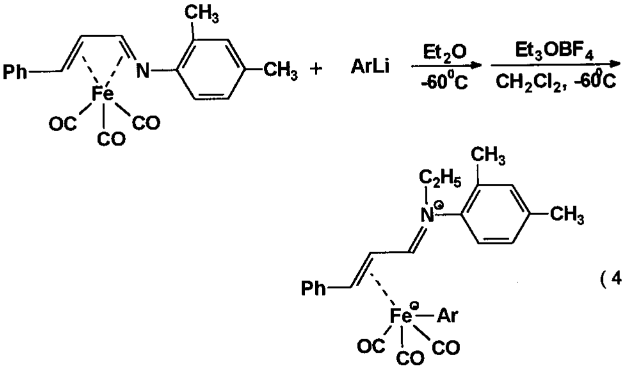
However, the isolobal (1-azadiene)$Fe(CO)_3$ complexes such as (cinnamaldehyde anil)iron tricarbonyl reacted with aryllithium reagents under similar conditions to give the chelated $(\eta^4$-styrene)dicarbonyl[ethoxy(amino)carbene]iron complexes (eq 3)[11] or aryliron inner salt complexes (eq 4)[12] depending on the substituent at the N atom of the azadiene ligand and aryllithium reagents used as well as alkylation conditions. In these reactions the initial step is the attack of the aryllithium reagent toward the iron-coordinated C=N double bond or an iron-bound CO ligand, which is, in the subsequent reaction steps, incorporated into the azadiene ligand together with the organic group attached to lithium.

Although (1,3-butadiene)$Fe(CO)_3$ complexes are widely used as starting materials in the synthesis of organic compounds and their reactions have been extensively examined[13] and there is also a number of reactions starting from the isolobal (1,4-diazadiene)$Fe(CO)_3$ complexes,[14] only very little is known about the reactivity of (1-azadiene)$Fe(CO)_3$ complexes so far. Up to now, only the reactions of (1-azadiene)$Fe(CO)_3$ with organo lithium compounds have been reported by us[11,12] and Thomas et al.[15] To explore the reactivity of (1-azadiene)$Fe(CO)_3$ compounds and to further investigate the effect of different azadiene ligands and different substituents at the N atom of the azadiene ligands on the isomerization of the olefin ligands and reaction products, we chose $(\eta^4$-1-azadiene)$Fe(CO)_3$ complexes $[(\eta^4\text{-}C_4H_3OCH{=}CHCH{=}NR)Fe(CO)_3]$ (**1**, R = C_6H_5; **2**, R = C_6H_{11}), where C_4H_3O is a 2-furanyl group, and $[(\eta^4\text{-}C_6H_5CH{=}CHCH{=}NC_6H_{11})Fe(CO)_3]$ (**3**), synthesized recently by Imhof et al.,[16] as the starting materials for the reaction with aryllithium reagents. These reactions lead to nucleophilic addition to an Fe-bound CO group or the azadiene ligand to afford the novel chelated furanyl-coordinated alkoxy(amino)carbeneiron complexes or η^4-azadiene-coordinated 17e acyliron complexes, or iron inner salt complexes. We report herein these novel reactions and the structures of the resulting products.



(3)

Ar = C_6H_5; p-, m-$CH_3C_6H_4$



(4)

Ar = C_6H_5; p-ClC_6H_4

Experimental Section

All procedures were performed under a dry, oxygen-free N_2 atmosphere using standard Schlenk techniques. All solvents employed were of reagent grade and dried by refluxing over appropriate drying reagents and stored over 4 Å molecular sieves under N_2 atmosphere. Diethyl ether (Et_2O) was 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

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deoxygenated at room temperature under high vacuum for 16 h, deactivated with 5% w/w N_2-saturated water and stored under N_2. The ligand $C_4H_3OCH{=}CHCH{=}NC_6H_5$[17] and compounds [($\eta^4$-$C_4H_3OCH{=}CHCH{=}NC_6H_{11}$)Fe(CO)$_3$] (**2**)[16] and [($\eta^4$-$C_6H_5CH{=}CH{-}CH{=}NC_6H_{11}$)Fe(CO)$_3$] (**3**),[16] Et_3OBF_4,[18] and aryllithium reagents[19−24] used were prepared by literature methods.

The IR spectra were measured on a Shimadzu-IR-440 spectrophotometer. All ^{1}H NMR spectra were recorded at ambient temperature in acetone-d_6 solution with TMS as the internal reference using a Bruker AM-300 spectrometer. Electron ionization mass spectra (EIMS) were run on a Hewlett-Packard 5989A spectrometer. Melting points obtained on samples in sealed capillaries are uncorrected.

Preparation of [(η^4-$C_4H_3OCH{=}CHCH{=}NC_6H_5$)Fe(CO)$_3$] (1). This compound was synthesized according to ref 16. $Fe_2(CO)_9$ (1.0 g, 2.75 mmol) was stirred together with an equimolar amount of ligand [$C_4H_3OCH{=}CHCH{=}NC_6H_5$][17] (0.547 g, 2.75 mmol) in 60 mL of *n*-heptane at 50 °C for 20 h, during which time the color of the solution darkened from orange to deep red and the undissolved $Fe_2(CO)_9$ slowly disappeared. After cooling to room temperature, the solvent was evaporated in vacuo and the residue was chromatographed on an alumina column with petroleum ether as the eluant. The orange band was eluted and collected. The solvent was removed under vacuum, and the crude product was recrystallized from petroleum ether at −60 °C to give 0.52 g (56%) of orange-red crystals of **1**: mp 107−110 °C dec; IR (CH_2Cl_2) ν(CO) 2058 (vs), 1996 (vs), 1985 (sh) cm^{-1}; ν (C=N) 1558 cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 7.49−6.42 (m, 9H, C_6H_5 + $C_4H_3OCH{=}CHCH{=}N{-}$), 5.92 (dd, 1H, $C_4H_3OCH{=}CHCH{=}N{-}$), 3.39 (d, 1H, $C_4H_3OCH{=}CHCH{=}N{-}$); MS *m/e* 337 (M^+), 309 (M^+ − CO), 281 (M^+ − 2CO), 253 (M^+ − 3CO), 197 (M^+ − Fe(CO)$_3$). Anal. Calcd for $C_{16}H_{11}O_4NFe$: C, 57.01; H, 3.29; N, 4.15. Found: C, 57.17; H, 3.18; N, 4.20.

Reaction of [(η^4-$C_4H_3OCH{=}CHCH{=}NC_6H_5$)Fe(CO)$_3$] (1) with C_6H_5Li to Give [{η^4-$C_4H_3OCH{=}CHCH(C_6H_5)N(C_6H_5)C(OC_2H_5){=}$}Fe(CO)$_2$] (4). To a solution of 0.40 g (1.19 mmol) of **1** dissolved in 60 mL of ether at −75 °C was added 1.54 mmol of C_6H_5Li[19] with stirring. The reaction mixture was stirred at −75 to −35 °C for 5 h, during which time the orange-red solution gradually turned deep red. The resulting solution was evaporated under high vacuum at −35 to −40 °C to dryness. To the red residue was added Et_3OBF_4[18] (ca. 2−3 g). This solid mixture was dissolved in 50 mL of N_2-saturated water at 0 °C with vigorous stirring and the mixture covered with petroleum ether (30−60 °C). Immediately afterward, Et_3OBF_4 was added to the aqueous solution portionwise, with strong stirring, until it became acidic. The aqueous solution was extracted with petroleum ether/CH_2Cl_2. The combined extract was evaporated to remove most of the solvent under vacuum and then chromatographed on an alumina column (1.6 × 15−25 cm) at −20 to −30 °C with petroleum ether followed by petroleum ether/CH_2Cl_2/Et_2O (10:3:3) as the eluant. The orange-yellow band was eluted and collected. The solvent was removed under vacuum, and the residue was recrystallized from petroleum ether/CH_2Cl_2 (5:1) solution at −80 °C to give 0.33 g (63%, based on **1**) of orange-yellow crystals of **4**: mp 120−122 °C dec; IR (CH_2Cl_2) ν(CO) 1970 (s), 1903 (s) cm^{-1}; ν(C=N) 1598 cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 7.57−7.29 (m, 11 H, C_6H_5 + C_4H_3O), 6.29 (d, 1H, C_4H_3O), 5.65 (d, 1H, $C_4H_3OCH{=}CHCHN{-}$), 5.28 (s, 1H, $C_4H_3OCH{=}CHCHN{-}$), 4.40−4.18 (m, 2H, OCH_2CH_3), 3.51 (d, 1H, C_4H_3O), 1.15 (t, 3H, OCH_2CH_3), 0.36 (d, 1H, $C_4H_3O{-}CH{=}CHCH{-}$); MS *m/e* 415 (M^+ − CO), 387 (M^+ − 2CO), 331 (M^+ − Fe(CO)$_2$), 302 (M^+ − Fe(CO)$_2$ − C_2H_5), 274 (M^+ − Fe(CO)$_2COC_2H_5$). Anal. Calcd for $C_{24}H_{21}O_4NFe$: C, 65.03; H, 4.77; N, 3.16. Found: C, 64.86; H, 4.62; N, 3.22.

Reaction of 1 with *p*-$CH_3C_6H_4Li$ to Give [{η^4-$C_4H_3OCH{=}CHCH(C_6H_4CH_3$-*p*$)N(C_6H_5)C(OC_2H_5){=}$}Fe(CO)$_2$] (5). Similar to the reaction of **1** with C_6H_5Li, the reaction of 0.50 g (1.48 mmol) of **1** with 1.71 mmol of *p*-$CH_3C_6H_4Li$[20] at −75 to −35 °C for 5 h, followed by alkylation and further treatment, afforded 0.44 g (65%, based on **1**) of orange-yellow crystalline **5**: mp 58−60 °C dec; IR (CH_2Cl_2) ν(CO) 2044 (vs), 1977 (vs, br) cm^{-1}; ν(C=N) 1599 cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 7.47−7.00 (m, 10H, C_6H_5 + $C_6H_4CH_3$ + C_4H_3O), 6.07 (d, 1H, C_4H_3O), 5.62 (d, 1H, $C_4H_3OCH{=}CHCHN{-}$), 5.23 (s, 1H, $C_4H_3OCH{=}CHCHN{-}$), 4.43−4.15 (m, 2H, OCH_2CH_3), 3.43 (d, 1H, C_4H_3O), 2.27 (s, 3H, $C_6H_4CH_3$), 1.15 (t, 3H, OCH_2CH_3), 0.35 (d, 1H, $C_4H_3OCH{=}CHCHN{-}$); MS *m/e* 457 (M^+), 429 (M^+ − CO), 401 (M^+ − 2CO), 345 (M^+ − Fe(CO)$_2$), 288 (M^+ − Fe(CO)$_2COC_2H_5$). Anal. Calcd for $C_{25}H_{23}O_4NFe$: C, 65.66; H, 5.07; N, 3.06. Found: C, 65.90; H, 4.99; N, 3.36.

Reaction of 1 with *o*-$CH_3OC_6H_4Li$ to Give [{η^4-$C_4H_3OCH{=}CHCH(C_6H_4OCH_3$-*o*$)N(C_6H_5)C(OC_2H_5){=}$}Fe(CO)$_2$] (6). *n*-$C_4H_9Li$[21] (1.19 mmol) was mixed with a solution of *o*-$CH_3OC_6H_4Br$ (0.21 g, 1.12 mmol) in 20 mL of ether at 0 °C. The mixture was stirred at room temperature for 1.5 h. The resulting ether solution of *o*-$CH_3OC_6H_4Li$[22] reacted, similar to that for the reaction of **1** with C_6H_5Li, with 0.25 g (0.74 mmol) of **1** in 50 mL of ether at −75 to −35 °C for 4.5 h, during which time the orange-red solution gradually turned deep red. After removal of the solvent under vacuum at −40 °C, the residue was dissolved in 30 mL of CH_2Cl_2 at −65 °C. To this solution was added dropwise 0.21 g (1.11 mmol) of Et_3OBF_4 dissolved in 10 mL of CH_2Cl_2 with stirring within 15 min. The reaction mixture turned from brown-red to orange-red. After being stirred at −65 to −30 °C for 2 h, the solvent was removed in vacuo at −30 °C. Further treatment of the resulting mixture as described for the preparation of **4** gave 0.25 g (71%, based on **1**) of orange-yellow crystals of **6**: mp 144−146 °C dec; IR (CH_2Cl_2) ν(CO) 1970 (s), 1902 (vs) cm^{-1}; ν(C=N) 1602 cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 7.56−6.85 (m, 10H, C_6H_5 + $C_6H_4CH_3$ + C_4H_3O), 6.06 (d, 1H, C_4H_3O), 5.78 (d, 1H, $C_4H_3OCH{=}CHCHN{-}$), 5.65 (s, 1H, $C_4H_3OCH{=}CHCHN{-}$), 4.44−4.17 (m, 2H, OCH_2CH_3), 3.66 (s, 3H, $C_6H_4OCH_3$), 3.39 (d, 1H, C_4H_3O), 1.16 (t, 3H, OCH_2CH_3), 0.31 (d, 1H, $C_4H_3OCH{=}CHCHN{-}$); MS *m/e* 473 (M^+), 445 (M^+ − CO), 417 (M^+ − 2CO), 361 (M^+ − Fe(CO)$_2$), 304 (M^+ − Fe(CO)$_2COC_2H_5$). Anal. Calcd for $C_{25}H_{23}O_5NFe$: C, 63.44; H, 4.90; N, 2.96. Found: C, 63.19; H, 4.89; N, 3.11.

Reaction of 1 with *p*-$CH_3OC_6H_4Li$ to Give [{η^4-$C_4H_3OCH{=}CHCH(C_6H_4OCH_3$-*p*$)N(C_6H_5)C(OC_2H_5){=}$}Fe(CO)$_2$] (7). A solution of 0.20 g (1.07 mmol) of *p*-$CH_3OC_6H_4Br$ in 20 mL of ether was mixed with 1.07 mmol of *n*-C_4H_9Li. After 40 min stirring at room temperature, the resulting ether solution of *p*-$CH_3O{-}C_6H_4Li$[23] was reacted, as in the reaction of **1** with C_6H_5Li, with 0.30 g (0.89 mmol) of **1** at −75 to −35 °C for 4 h. Further treatment of the resulting brown-red mixture as in the preparation of **6** yielded 0.28 g (67%, based on **1**) of **7** as orange crystals: mp 88−90 °C dec; IR (CH_2Cl_2) ν(CO) 1971 (vs), 1903 (s) cm^{-1}; ν(C=N) 1600 cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 7.57−6.82 (m, 10H, C_6H_5 + $C_6H_4CH_3$ + C_4H_3O), 6.08 (d, 1H, C_4H_3O), 5.62 (d, 1H, $C_4H_3OCH{=}CHCHN{-}$), 5.21 (s, 1H, $C_4H_3OCH{=}CHCHN{-}$), 4.42−4.15 (m, 2H, OCH_2CH_3), 3.75 (s, 3H, $C_6H_4OCH_3$), 3.44 (d, 1H, C_4H_3O), 1.14 (t, 3H, OCH_2CH_3), 0.37 (d, 1H, $C_4H_3OCH{=}CHCH{-}$); MS *m/e* 473 (M^+), 445 (M^+ − CO), 417 (M^+ − 2CO), 361 (M^+ − Fe(CO)$_2$), 304 (M^+ − Fe(CO)$_2$ − COC_2H_5). Anal. Calcd for $C_{25}H_{23}O_5NFe$: C, 63.44; H, 4.90; N, 2.96. Found: C, 64.05; H, 5.11; N, 2.76.

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Reaction of 1 with *p*-$CF_3C_6H_4Li$ to Give [{η^4-$C_4H_3OCH{=}CHCH(C_6H_4CF_3$-*p*)$N(C_6H_5)C(OC_2H_5){=}$}$Fe(CO)_2$] (8). A solution of 0.24 g (1.07 mmol) of *p*-$CF_3C_6H_4Br$ in 20 mL of ether was mixed with 1.07 mmol of *n*-C_4H_9Li. After 40 min stirring at room temperature, the resulting ether solution of *p*-$CF_3C_6H_4Li$ [24] was reacted, as in the reaction of **1** with C_6H_5Li, with 0.30 g (0.89 mmol) of **1** at −75 to −35 °C for 4 h, followed by alkylation; further treatment as described for the reaction of **1** with *o*-$CH_3OC_6H_4Li$ gave 0.28 g (62%, based on **1**) of orange-red crystals of **8**: mp 45−47 °C dec; IR (CH_2Cl_2) ν(CO) 2019 (s), 1933 (vs, br) cm^{-1}; ν(C=N) 1605 cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 7.81−7.07 (m, 10H, $C_6H_5 + C_6H_4CH_3 + C_4H_3O$), 5.90 (d, 1H, C_4H_3O), 5.67 (d, 1H, $C_4H_3OCH{=}CHCHN-$), 5.44 (s, 1H, $C_4H_3OCH{=}CH-CHN-$), 4.44−4.20 (m, 2H, OCH_2CH_3), 3.50 (d, 1H, C_4H_3O), 1.13 (t, 3H, OCH_2CH_3), 0.32 (d, 1H, $C_4H_3OCH{=}CHCHN-$); MS *m/e* 511 (M$^+$), 483 (M$^+$ − CO), 455 (M$^+$ − 2CO), 399 (M$^+$ − $Fe(CO)_2$), 342 (M$^+$ − $Fe(CO)_2COC_2H_5$). Anal. Calcd for $C_{25}H_{20}O_4F_3NFe$: C, 58.73; H, 3.94; N, 2.74. Found: C, 58.90; H, 4.06; N, 3.02.

Reaction of [(η^4-$C_4H_3OCH{=}CHCH{=}NC_6H_{11})Fe(CO)_3$] (2) with C_6H_5Li to Give [(η^4-$C_4H_3OCH{=}CHCH{=}NC_6H_{11})Fe(CO)_2(COC_6H_5)$] (9). To a solution of 0.30 g (0.87 mmol) of **2** dissolved in 60 mL of ether at −75 °C was added 1.05 mmol of C_6H_5Li with stirring. The reaction mixture was stirred at −75 to −35 °C for 4−5 h, during which time the orange solution gradually turned red. The resulting solution was evaporated under high vacuum at −40 °C to dryness. Subsequent alkylation and further treatment of the residue as in the reaction of **1** with *o*-$CH_3OC_6H_4Li$ gave 0.28 g (76%, based on **2**) of yellow crystals of **9**: mp 119−120 °C dec; IR (CH_2Cl_2) ν(CO) 1990 (vs), 1933 (vs), 1603 (m) cm^{-1}; ν(C=N) 1550 cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 7.29−7.07 (m, 6H, $C_6H_5 + C_4H_3O$), 6.79 (d, 1H, $C_4H_3OCH{=}CHCH{=}N-$), 6.26−5.99 (m, 2H, C_4H_3O), 5.63 (m, 0.5H, CH_2Cl_2), 5.03 (dd, 1H, $C_4H_3OCH{=}CHCH{=}N-$), 3.31 (d, 1H, $C_4H_3OCH{=}CHCH{=}N-$), 2.37−1.00 (m, 11H, C_6H_{11}); MS *m/e* 392 (M$^+$ − CO), 364 (M$^+$ − 2CO), 259 (M$^+$ − 2CO − COC_6H_5), 203 ($C_4H_3OCH{=}CHCH{=}NC_6H_{11}^+$), 105 ($COC_6H_5^+$), 84 ($CH_2Cl_2^+$). Anal. Calcd for $C_{22}H_{22}O_4NFe\cdot 0.25CH_2Cl_2$: C, 60.53; H, 5.24; N, 3.17. Found: C, 60.59; H, 5.58; N, 2.91.

Reaction of 2 with *o*-$CH_3C_6H_4Li$ to Give [(η^4-$C_4H_3OCH{=}CHCH{=}NC_6H_{11})Fe(CO)_2(COC_6H_4CH_3$-*o*)] (10). The procedure used in the reaction of **2** (0.30 g, 0.87 mmol) with *o*-$CH_3C_6H_4Li$ (1.10 mmol) was the same as that for the reaction of **2** with C_6H_5Li at −75 to −35 °C for 5 h, during which time the orange solution turned red. Further treatment as in the preparation of **9** yielded 0.28 g (73%, based on **2**) of orange-yellow crystalline **10**: mp 102−103 °C dec; IR (CH_2Cl_2) ν(CO) 1996 (vs), 1934 (vs), 1600 (m, br) cm^{-1}; ν(C=N) 1580 (m, br) cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 7.40−6.89 (m, 5H, $CH_3C_6H_4 + C_4H_3O$), 6.73 (d, 1H, $C_4H_3OCH{=}CHCH{=}N-$), 6.57−6.13 (m, 2H, C_4H_3O), 5.15 (dd, 1H, $C_4H_3OCH{=}CHCH{=}N-$), 3.37 (d, 1H, $C_4H_3O-CH{=}CHCH{=}N-$), 2.26−1.04 (m, 11H, C_6H_{11}), 1.87 (s, 3H, $CH_3C_6H_4$); MS *m/e* 406 (M$^+$ − CO), 378 (M$^+$ − 2CO), 287 (M$^+$ − 2CO − $C_6H_4CH_3$), 259 (M$^+$ − 2CO − $COC_6H_4CH_3$), 203 ($C_4H_3OCH{=}CHCH{=}NC_6H_{11}^+$), 119 ($COC_6H_4CH_3^+$). Anal. Calcd for $C_{23}H_{24}O_4-NFe\cdot 0.5C_4H_8O$: C, 63.84; H, 6.00; N, 2.98. Found: C, 63.83; H, 6.16; N, 2.90.

Reaction of 2 with *m*-$CH_3C_6H_4Li$ to Give [(η^4-$C_4H_3OCH{=}CHCH{=}NC_6H_{11})Fe(CO)_2(COC_6H_4CH_3$-*m*)] (11). As in the reaction of **2** with C_6H_5Li, compound **2** (0.30 g, 0.87 mmol) was treated with *m*-$CH_3C_6H_4Li$ (1.06 mmol) at −75 to −35 °C for 4 h. Further treatment similar to that used in the reaction of **2** with C_6H_5Li gave 0.31 g (80%, based on **2**) of **11** as yellow powder: mp 113−114 °C dec; IR (CH_2Cl_2) ν(CO) 1996 (vs), 1932 (vs), 1605 (m) cm^{-1}; ν(C=N) 1582 (m, br) cm^{-1}; ^{1}H NMR (CD_3CO-CD_3) δ 7.29−6.90 (m, 5H, $CH_3C_6H_4 + C_4H_3O$), 6.76 (d, 1H, $C_4H_3OCH{=}CHCH{=}N-$), 6.26−6.00 (m, 2H, C_4H_3O), 5.03 (dd, 1H, $C_4H_3OCH{=}CHCH{=}N-$), 3.30 (d, 1H, $C_4H_3OCH{=}CHCH{=}N-$), 2.27 (s, 3H, $CH_3C_6H_4$), 2.35−1.06 (m, 11H, C_6H_{11}); MS *m/e* 406 (M$^+$ − CO), 378 (M$^+$ − 2CO), 287 (M$^+$ − 2CO − $C_6H_4CH_3$), 259 (M$^+$ − 2CO − $COC_6H_4CH_3$), 203 ($C_4H_3OCH{=}CHCH{=}NC_6H_{11}^+$), 119 ($COC_6H_4CH_3^+$). Anal. Calcd for $C_{23}H_{24}O_4NFe$: C, 63.61; H, 5.57; N, 3.23. Found: C, 63.28; H, 6.05; N, 2.90.

Reaction of 2 with *p*-$CH_3C_6H_4Li$ to Give [(η^4-$C_4H_3OCH{=}CHCH{=}NC_6H_{11})Fe(CO)_2(COC_6H_4CH_3$-*p*)] (12). As used in the reaction of **2** with C_6H_5Li, 0.40 g (1.17 mmol) of **2** was treated with 1.32 mmol of *p*-$CH_3C_6H_4Li$ at −75 to −35 °C for 4 h. Further treatment of the resulting mixture as in the preparation of **9** afforded 0.31 g (82%, based on **2**) of yellow powder of **12**: mp 112−113 °C dec; IR (CH_2Cl_2) ν(CO) 1996 (vs), 1933 (vs), 1607 (m) cm^{-1}; ν(C=N) 1585 (m, br) cm^{-1}; ^{1}H NMR (CD_3CO-CD_3) δ 7.28−7.02 (m, 5H, $CH_3C_6H_4 + C_4H_3O$), 6.78 (d, 1H, $C_4H_3OCH{=}CHCH{=}N-$), 6.25−5.96 (m, 2H, C_4H_3O), 5.01 (dd, 1H, $C_4H_3OCH{=}CH$-$CH{=}N-$), 3.30 (d, 1H, $C_4H_3OCH{=}CHCH{=}N-$), 2.27 (s, 3H, $CH_3C_6H_4$), 2.33−1.12 (m, 11H, C_6H_{11}); MS *m/e* 406 (M$^+$ − CO), 378 (M$^+$ − 2CO), 287 (M$^+$ − 2CO − $C_6H_4CH_3$), 259 (M$^+$ − 2CO − $COC_6H_4CH_3$), 203 ($C_4H_3OCH{=}CHCH{=}NC_6H_{11}^+$), 119 ($COC_6H_4CH_3^+$). Anal. Calcd for $C_{23}H_{24}O_4NFe$: C, 63.61; H, 5.57; N, 3.23. Found: C, 63.48; H, 6.02; N, 3.14.

Reaction of 2 with *p*-$CH_3OC_6H_4Li$ to Give [{η^2-$C_4H_3OCH{=}CHCH{=}N(C_2H_5)C_6H_{11}$}$Fe(CO)_3(COC_6H_4OCH_3$-*p*)] (13). Compound **2** (0.40 g, 1.17 mmol) was treated, in a manner similar to that for the reaction of **2** with C_6H_5Li, with a fresh *p*-$CH_3OC_6H_4Li$ ether solution prepared by the reaction of *p*-$CH_3OC_6H_4Br$ (0.17 mL, 1.35 mmol) with *n*-C_4H_9Li (1.35 mmol) in ether at −75 to −35 °C for 4 h, during which time the orange solution turned dark red. Subsequent alkylation and further treatment of the resulting mixture as described in the reaction of **2** with C_6H_5Li produced 0.43 g (73%, based on **2**) of orange crystals of **13**: mp 92−94 °C dec; IR (CH_2Cl_2) ν(CO) 2019 (vs), 1957 (w), 1936 (vs), 1603 (m) cm^{-1}; ν(C=N) 1588 (m, br) cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 7.94−6.96 (m, 5H, $C_6H_4OCH_3 + C_4H_3O$), 6.63 (d, 1H, $C_4H_3OCH{=}CHCH{=}N-$), 6.35−6.25 (m, 2H, C_4H_3O), 4.39 (t, 1H, $C_4H_3O-CH{=}CHCH{=}N-$), 4.20 (d, 1H, $C_4H_3OCH{=}CHCH{=}N-$), 3.87 (s, 3H, $CH_3OC_6H_4$), 3.67−3.38 (m, 2H, CH_2CH_3), 3.21 (m, 1H, C_6H_{11}), 1.91−1.06 (m, 13H, $C_6H_{11} + CH_2CH_3$); MS *m/e* 451 (M$^+$ − 2CO), 423 (M$^+$ − 3CO), 288 (M$^+$ − 3CO − $COC_6H_4OCH_3$), 232 ($C_4H_3OCH{=}CHCH{=}N(C_2H_5)C_6H_{11}^+$), 135 ($COC_6H_4OCH_3^+$). Anal. Calcd for $C_{26}H_{29}O_6NFe$: C, 61.55; H, 5.76; N, 2.76. Found: C, 61.26; H, 5.74; N, 2.62.

Reaction of 2 with *p*-$CF_3C_6H_4Li$ to Give [{η^2-$C_4H_3OCH{=}CHCH{=}N(C_2H_5)C_6H_{11}$}$Fe(CO)_3(COC_6H_4CF_3$-*p*)] (14). A 0.40 g (1.17 mmol) sample of **2** was treated, as used in the reaction of **2** with C_6H_5Li, with a fresh *p*-$CF_3C_6H_4Li$ ether solution prepared by the reaction of *p*-$CF_3C_6H_4Br$ (0.30 g, 1.32 mmol) with *n*-C_4H_9Li (1.32 mmol) in ether at −75 to −35 °C for 4 h. Further treatment of the resulting mixture as described for the reaction of **2** with C_6H_5Li gave 0.45 g (71%,based on **2**) of crystals of **14**: 89−90 °C dec; IR (CH_2Cl_2) ν(CO) 2055 (w), 2028 (vs), 1960 (vs, br), 1586 (m, br) cm^{-1}; ν(C=N) 1570 (m, br) cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 7.95−6.30 (m, 5H, $CH_3OC_6H_4 + C_4H_3O$), 6.65 (d, 1H, $C_4H_3OCH{=}CHCH{=}N-$), 6.35−6.32 (m, 2H, C_4H_3O), 4.10 (m, 1H, $C_4H_3OCH{=}CHCH{=}N-$), 3.80 (d, 1H, $C_4H_3OCH{=}CHCH{=}N-$), 3.45 (m, 2H, CH_2CH_3), 3.41 (m, 1H, C_6H_{11}), 2.01−1.12 (m, 13H, $C_6H_{11} + CH_2CH_3$); MS *m/e* 545 (M$^+$), 517 (M$^+$ − CO), 489 (M$^+$ − 2CO), 461 (M$^+$ − 3CO), 288 (M$^+$ − 3CO − $COC_6H_4CF_3$), 232 ($C_4H_3OCH{=}CHCH{=}N(C_2H_5)$-$C_6H_{11}^+$), 173 ($COC_6H_4CF_3^+$). Anal. Calcd for $C_{26}H_{26}O_5F_3NFe$: C, 57.26; H, 4.81; N, 2.67. Found: C, 56.88; H, 4.86; N, 2.80.

Reaction of [(η^4-$C_6H_5CH{=}CHCH{=}NC_6H_{11})Fe(CO)_3$] (3) with C_6H_5Li to Give [(η^4-$C_6H_5CH{=}CHCH{=}NC_6H_{11})Fe(CO)_2(COC_6H_5)$] (15). To 0.60 g (1.70 mmol) of **3** dissolved in 60 mL of ether at −75 °C was added 1.87 mmol of C_6H_5Li. The mixture was stirred at −75 to −35 °C for 4.5 h, during which time the orange solution turned deep red. After vacuum removal of the solvent at −35 °C, subsequent alkylation and further treatment of the residue as that described in the reaction of **1** with C_6H_5Li (alkylation in H_2O) or in the reaction of **1** with o-$CH_3OC_6H_4Li$ (alkylation in CH_2Cl_2) yielded 0.59 g (80%, based on **3**) of yellow crystals of **15**: mp 118−120 °C dec; IR (CH_2Cl_2) ν(CO) 1994 (s),1932 (vs), 1597 (s) cm^{-1}; ν(C=N) 1549 (s) cm^{-1}; ^1H NMR (CD_3COCD_3) δ 7.19−6.80 (m, 11H, $2C_6H_5$ + $C_6H_5CH{=}CHCH{=}N{-}$), 5.26 (dd, 1H, $C_6H_5CH{=}CHCH{=}N{-}$), 3.29 (d, 1H, $C_6H_5CH{=}CHCH{=}N{-}$), 2.32−1.09 (m, 11H, C_6H_{11}); MS m/e 402 ($M^+ - CO$), 374 ($M^+ - 2CO$), 297 ($M^+ - 2CO - C_6H_5$], 269 ($M^+ - 2CO - COC_6H_5$), 213 ($C_6H_5CH{=}CHCH{=}NC_6H_{11}{}^+$), 105 ($COC_6H_5{}^+$). Anal. Calcd for $C_{24}H_{24}O_3NFe$: C, 66.99; H, 5.62; N, 3.26. Found: C, 66.67; H, 5.77; N, 3.27.

Reaction of 3 with m-$CH_3C_6H_4Li$ to Give [(η^4-$C_6H_5CH{=}CHCH{=}NC_6H_{11}$)$Fe(CO)_2$($COC_6H_4CH_3$-$m$)] (16). As used for the reaction of **3** with C_6H_5Li, 0.30 g (0.85 mmol) of **3** was treated with 1.08 mmol of m-$CH_3C_6H_4Li$ at −75 to −35 °C for 4.5 h. Further treatment of the resulting mixture as in the preparation of **15** gave 0.30 g (80%, based on **3**) of **16** as yellow crystals: mp 107−108 °C dec; IR (CH_2Cl_2) ν(CO) 1993 (s), 1930 (vs), 1603 (br, m) cm^{-1}; ν(C=N) 1584 (br, m) cm^{-1}; ^1H NMR (CD_3COCD_3) δ 7.16−6.47 (m, 9H, $C_6H_5 + C_6H_4CH_3$), 6.78 (dd, 1H, $C_6H_5CH{=}CH{-}CH{=}N{-}$), 5.63 (m, 0.5H, CH_2Cl_2), 5.25 (dd, 1H, $C_6H_5CH{=}CHCH{=}N{-}$), 3.30 (dd, 1H, $C_6H_5CH{=}CHCH{=}N{-}$), 2.19 (s, 3H, $CH_3C_6H_4$), 2.34−1.03 (m, 11H, C_6H_{11}); MS m/e 416 ($M^+ - CO$), 388 ($M^+ - 2CO$), 269 ($M^+ - 2CO - COC_6H_4CH_3$), 213 ($C_6H_5CH{=}CH{-}CH{=}NC_6H_{11}{}^+$), 119 ($COC_6H_4CH_3{}^+$), 84 ($CH_2Cl_2{}^+$). Anal. Calcd for $C_{25}H_{26}O_3NFe{\cdot}0.25CH_2Cl_2$: C, 65.14; H, 5.74; N, 3.01. Found: C, 65.17; H, 6.03; N, 3.09.

Reaction of 3 with p-$CH_3C_6H_4Li$ to Give [(η^4-$C_6H_5CH{=}CHCH{=}NC_6H_{11}$)$Fe(CO)_2$($COC_6H_4CH_3$-$p$)] (17). The procedure used in the reaction of **3** (0.30 g, 0.85 mmol) with p-$CH_3C_6H_4Li$ (1.11 mmol) was the same as that for the reaction of **3** with C_6H_5Li at −75 to −35 °C for 4 h. Further treatment of the resulting mixture in a manner similar to that described in the reaction of **1** with C_6H_5Li (alkylation in H_2O) or in the reaction of **1** with o-$CH_3OC_6H_4Li$ (alkylation in CH_2Cl_2) gave 0.32 g (79%, based on **3**) of yellow crystals of **17**: mp 103−104 °C dec; IR (CH_2Cl_2) ν(CO) 1993 (s), 1930 (vs), 1598 (m, br) cm^{-1}; ν(C=N) 1550 (m) cm^{-1}; ^1H NMR (CD_3COCD_3) δ 7.36−6.78 (m, 10H, $C_6H_5 + C_6H_4CH_3 + C_6H_5CH{=}CHCH{=}N{-}$), 5.23 (dd, 1H, $C_6H_5{-}CH{=}CHCH{=}N{-}$), 3.26 (d, 1H, $C_6H_5CH{=}CHCH{=}N{-}$), 2.31 (s, 3H, $C_6H_4CH_3$), 2.40−1.14 (m, 11H, C_6H_{11}); MS m/e 416 ($M^+ - CO$), 388 ($M^+ - 2CO$), 269 ($M^+ - 2CO - COC_6H_4CH_3$), 213 ($C_6H_5CH{=}CHCH{=}NC_6H_{11}{}^+$), 119 ($COC_6H_4CH_3{}^+$). Anal. Calcd for $C_{25}H_{26}O_3NFe$: C, 67.58; H, 5.98; N, 3.15. Found: C, 67.33; H, 6.01; N, 3.25.

Reaction of 3 with p-$CH_3OC_6H_4Li$ to Give [{η^2-$C_6H_5CH{=}CHCH{=}N(C_2H_5)C_6H_{11}$}$Fe(CO)_3$($COC_6H_4OCH_3$-$p$)] (18). As used in the reaction of **3** with C_6H_5Li, **3** (0.34 g, 0.963 mmol) was treated with a fresh p-$CH_3OC_6H_4Li$ solution prepared by the reaction of p-$CH_3OC_6H_4Br$ (0.18 mL, 1.43 mmol) with n-C_4H_9Li (1.43 mmol) in ether at −75 to −35 °C for 4 h, during which time the orange solution turned deep red. Subsequent alkylation and further treatment of the resulting mixture as described in the reaction of **3** with C_6H_5Li yielded 0.28 g (55%, based on **3**) of orange crystalline **18**: mp 104−105 °C dec; IR (CH_2Cl_2) ν(CO) 2052 (w), 2016 (vs), 1937 (vs, br), 1588 (m, br) cm^{-1}; ν(C=N) 1552 (m) cm^{-1}; ^1H NMR (CD_3COCD_3) δ 7.92−6.95 (m, 9H, $C_6H_5 + CH_3OC_6H_4$), 6.73 (d, 1H, $C_6H_5CH{=}CHCH{=}N{-}$), 4.67 (t, 1H, $C_6H_5CH{=}CH{-}CH{=}N{-}$), 4.33 (d, 1H, $C_6H_5CH{=}CHCH{=}N{-}$), 3.86 (s, 3H, $CH_3OC_6H_4$), 3.72−3.51 (m, 2H, CH_2CH_3), 3.24 (m, 1H, C_6H_{11}), 2.00−0.84 (m, 13H, $C_6H_{11} + CH_2CH_3$); MS m/e 517 (M^+), 489 ($M^+ - CO$), 461 ($M^+ - 2CO$), 326 ($M^+ - 2CO - COC_6H_4OCH_3$), 242 ($C_6H_5CH{=}CHCH{=}N(C_2H_5)C_6H_{11}{}^+$), 135 ($COC_6H_4OCH_3{}^+$). Anal. Calcd for $C_{28}H_{31}O_5NFe$: C, 65.00; H, 6.04; N, 2.71. Found: C, 64.80; H, 5.94; N, 2.85.

Reaction of 3 with o-$CH_3C_6H_4Li$ to Give [{η^2-$C_6H_5CH{=}CHCH{=}N(C_2H_5)C_6H_{11}$}$Fe(CO)_3C_6H_4CH_3$-$o$] (19). Similar to the procedures used in the reaction of **3** with C_6H_5Li, 0.30 g (0.85 mmol) of **3** was treated with 1.19 mmol of o-$CH_3C_6H_4Li$ at −75 to −35 °C for 4 h, during which time the orange solution turned deep red. Subsequent treatment of the resulting mixture as described for the preparation of **15** afforded 0.31 g (78%, based on **3**) of yellow powder of **19**: mp 102−103 °C dec; IR (CH_2Cl_2) ν(CO) 2052 (m), 1992 (s), 1931 (s) cm^{-1}; ν(C=N) 1595 (m, br) cm^{-1}; ^1H NMR (CD_3COCD_3) δ 7.36−6.40 (m, 10H, $C_6H_5 + C_6H_4CH_3 + C_6H_5CH{=}CHCH{=}N{-}$), 5.38 (dd,1H,$C_6H_5{-}CH{=}CHCH{=}N{-}$), 3.36 (d, 1H, $C_6H_5CH{=}CHCH{=}N{-}$), 1.74 (s, 3H, $C_6H_4CH_3$), 2.27−1.00 (m, 11H, C_6H_{11}); 3.40−3.28 (q, 2H, CH_2CH_3), 0.86 (t, 3H, CH_2CH_3); MS m/e 445 ($M^+ - CO$), 417 ($M^+ - 2CO$), 298 ($M^+ - 3CO - C_6H_4CH_3$), 242 ($C_6H_5CH{=}CHCH{=}N(C_2H_5)C_6H_{11}{}^+$), 91 ($C_6H_4CH_3{}^+$). Anal. Calcd for $C_{27}H_{31}O_3NFe$: C, 68.50; H, 6.60; N, 2.96. Found: C, 68.54; H, 7.01; N, 2.84.

Reaction of 3 with o-$CH_3OC_6H_4Li$ to Give [{η^2-$C_6H_5CH{=}CHCH{=}N(C_2H_5)C_6H_{11}$}$Fe(CO)_3C_6H_4OCH_3$-$o$] (20). Compound **3** (0.30 g, 0.85 mmol) was treated as in the reaction of **3** with C_6H_5Li with a fresh o-$CH_3OC_6H_4Li$ ether solution prepared by the reaction of o-$CH_3OC_6H_4Br$ (0.24 g, 1.28 mmol) with n-C_4H_9Li (1.28 mmol) in ether at −75 to −35 °C for 4 h. Further treatment of the resulting solution as in the reaction of **3** with C_6H_5Li yielded 0.30 g (60%, based on **3**) of orange-yellow crystalline **20**: mp 84−85 °C dec; IR (CH_2Cl_2) ν(CO) 2051 (s), 1986 (vs), 1925 (s) cm^{-1}; ν(C=N) 1601 (m) cm^{-1}; ^1H NMR (CD_3COCD_3) δ 7.36−7.08 (m, 9H, $C_6H_5 + C_6H_4OCH_3$), 6.72 (d, 1H, $C_6H_5CH{=}CHCH{=}N{-}$), 5.36 (t, 1H, $C_6H_5CH{=}CHCH{=}N{-}$), 3.82 (s, 3H, $CH_3OC_6H_4$), 3.45 (d, 1H, $C_6H_5CH{=}CHCH{=}N{-}$), 3.30−3.25 (m, 2H, CH_2CH_3), 3.21 (m, 1H, C_6H_{11}), 2.08−0.87 (m, 13H, $C_6H_{11} + CH_2CH_3$); MS m/e 461 ($M^+ -$ 2CO), 433 ($M^+ - 3CO$), 354 ($M^+ - 2CO - C_6H_4OCH_3$), 326 ($M^+ - 3CO - C_6H_4OCH_3$), 242 ($C_6H_5CH{=}CHCH{=}N(C_2H_5)C_6H_{11}{}^+$),107 ($C_6H_4OCH_3{}^+$). Anal. Calcd for $C_{28}H_{31}O_5NFe$: C, 65.00; H, 6.04; N, 2.71. Found: C, 64.98; H, 6.30; N, 2.97.

Reaction of 3 with p-$CF_3C_6H_4Li$ to Give [{η^2-$C_6H_5CH{=}CHCH{=}N(C_2H_5)C_6H_{11}$}$Fe(CO)_3C_6H_4CF_3$-$p$] (21). Compound **3** (0.40 g, 1.13 mmol) was treated, in a manner similar to that described in the reaction of **3** with C_6H_5Li, with a fresh p-$CF_3C_6H_4Li$ ether solution prepared by the reaction of p-$CF_3C_6H_4Br$ (0.31 g, 1.36 mmol) with n-C_4H_9Li (1.36 mmol) in ether at −75 to −35 °C for 4 h. Further treatment of the resulting mixture as described for the reaction of **3** with C_6H_5Li gave 0.48 g (80%, based on **3**) of yellow crystals of **21**: mp 118−120 °C dec; IR (CH_2Cl_2) ν(CO) 2025 (vs), 1951 (vs, br), 1930 (w) cm^{-1}; ν(C=N) 1586 (br, m) cm^{-1}; ^1H NMR (CD_3COCD_3) δ 8.04−7.07 (m, 9H, $C_6H_5 + C_6H_4CF_3$), 6.40 (d, 1H, $C_6H_5CH{=}CH{-}CH{=}N{-}$), 4.87 (m, 1H, $C_6H_5CH{=}CHCH{=}N{-}$), 4.11 (d, 1H, $C_6H_5CH{=}CHCH{=}N{-}$), 3.75 (m, 2H, CH_2CH_3), 3.12 (m, 1H, C_6H_{11}), 1.96−1.20 (m, 13H, $C_6H_{11} + CH_2CH_3$); MS m/e 499 ($M^+ - CO$), 471 ($M^+ - 2CO$), 443 ($M^+ - 3CO$), 298 ($M^+ - 3CO - C_6H_4CF_3$), 242 ($C_6H_5CH{=}CHCH{=}N(C_2H_5)C_6H_{11}{}^+$), 145 ($C_6H_4CF_3{}^+$). Anal. Calcd for $C_{27}H_{28}O_3F_3NFe$: C, 61.49; H, 5.35; N, 2.66. Found: C, 61.20; H, 5.39; N, 2.90.

X-ray Crystal Structure Determinations of Complexes 6, 10, 13, and 18. The single crystals of **6**, **10**, **13**, and **18** suitable for X-ray diffraction study were obtained by recrystallization from petroleum ether/CH_2Cl_2 solution or petroleum ether/THF at −80 °C. Single crystals were mounted on a glass fiber and sealed with epoxy glue. The X-ray diffraction intensity data for 3870, 7214, 3725, and 4719 independent reflections, of which 2159, 1840, and 2898 with $I > 2.50\sigma(I)$ for **6**, **10**, and **18** and 1307 with $I > 2.00\sigma(I)$ for **13** were observable, were collected with a Rigaku AFC7R diffractometer at 20 °C using Mo Kα radiation with an $\omega{-}2\theta$ scan mode within the ranges $5° \le 2\theta \le 50°$ for **6**, **10**, and **13** and $5° \le 2\theta \le 51°$ for **18**, respectively.

The structures of **6**, **10**, **13**, and **18** were solved by direct methods and expanded using Fourier techniques. For **6** and **18**, the non-hydrogen atoms were refined anisotropically. For **10** and **13**, some non-hydrogen atoms were refined anisotropically, while the rest were refined isotropically. For all four complexes, the hydrogen atoms were included but not refined.

Table 1. Crystal Data and Experimental Details for Complexes 6, 10, 13, and 18

	6	**10**·1/2C_4H_8O	**13**	**18**
formula	$C_{25}H_{23}O_5NFe$	$C_{25}H_{28}O_{4.5}NFe$	$C_{26}H_{28}O_6NFe$	$C_{28}H_{31}O_5NFe$
fw	473.31	470.35	506.36	517.40
space group	P-1 (No. 2)	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)
a (Å)	9.984(5)	10.524(7)	10.822(3)	12.799(2)
b (Å)	12.889(4)	12.313(10)	20.028(6)	10.276(2)
c (Å)	9.898(5)	37.64(1)	11.924(4)	20.649(4)
α (deg)	103.66(3)			
β (deg)	113.64(4)	96.31(7)	97.38(2)	105.64(1)
γ (deg)	82.28(4)			
V (Å^3)	1132.7(10)	4847(5)	2563(1)	2615.3(9)
Z	2	8	4	4
D_{calcd} (g/cm^3)	1.388	1.289	1.312	1.314
F(000)	492.00	1976.00	1060.00	1088.00
μ(Mo Kα) (cm^{-1})	7.01	6.53	6.27	6.13
radiation (monochromated in incident beam)	Mo Kα ($\lambda = 0.71069$ Å)	Mo Kα ($\lambda = 0.71069$ Å)	Mo Kα ($\lambda = 0.71069$ Å)	Mo Kα ($\lambda = 0.71069$ Å)
diffractometer	Rigaku AFC7R	Rigaku AFC7R	Rigaku AFC7R	Rigaku AFC7R
temperature (°C)	20	20	20	20
orientation reflns: no.; range (2θ) (deg)	24; 13.8−24.5	10; 9.6−15.6	18; 14.0−21.0	19; 14.3−20.8
scan method	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$
data coll. range, 2θ (deg)	5−50	5−50	5−50	5−51
no. of unique data, total	3870	7214	3725	4719
with $I > 2.50\sigma(I)$	2159	1840	1307 ($I > 2.00\sigma(I)$)	2898
no. of params refined	289	492	277	316
correct. factors, max. min.	0.9098−1.0000	0.6173−1.0000	0.7659−1.0816	0.9360−1.0000
R^a	0.048	0.077	0.073	0.039
$R_w{}^b$	0.050	0.070	0.067	0.046
quality of fit indicator^c	1.24	1.65	1.68	1.41
max. shift/esd. final cycle	0.00	0.00	0.00	0.00
largest peak, e$^-$/Å^3	0.32	0.42	0.38	0.24
min. peak, e$^-$/Å^3	−0.26	−0.48	−0.35	−0.22

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] Quality-of-fit $= [\sum w(|F_o| - |F_c|)^2/(N_{obs} - N_{params})]^{1/2}$.

Table 2. Selected Bond Lengths (Å)[a] and Angles (deg)[a] for Complexes 6 and 10

		Complex **6**			
Fe−C(3)	1.916(5)	C(13)−C(14)	1.393(7)	N−C(3)	1.358(6)
Fe−C(12)	2.021(5)	C(14)−C(15)	1.404(8)	O(3)−C(3)	1.331(5)
Fe−C(13)	2.018(5)	C(15)−C(16)	1.450(8)	N−C(4)	1.472(6)
Fe−C(14)	2.112(5)	C(16)−C(17)	1.286(9)	N−C(20)	1.448(6)
Fe−C(15)	2.261(5)	O(5)−C(14)	1.393(6)	C(4)−C(5)	1.509(7)
C(12)−C(13)	1.439(7)	O(5)−C(17)	1.398(8)	C(4)−C(12)	1.513(5)
Fe−C(3)−O(3)	134.2(4)	C(4)−C(12)−C(13)	119.9(4)	C(3)−N−C(20)	124.0(4)
Fe−C(3)−N	117.7(3)	C(12)−C(13)−C(14)	111.7(5)	C(4)−N−C(20)	118.0(4)
N−C(3)−O(3)	108.1(4)	C(13)−C(14)−C(15)	126.5(5)	N−C(4)−C(5)	112.5(4)
Fe−C(12)−C(4)	113.3(3)	C(14)−C(15)−C(16)	104.3(6)	C(5)−C(4)−C(12)	111.3(4)
Fe−C(15)−C(14)	65.6(3)	C(12)−C(4)−N	107.1(4)	C(3)−O(3)−C(18)	121.1(4)
Fe−C(15)−C(16)	124.0(4)	C(3)−N−C(4)	117.9(4)		
		Complex **10**			
Fe(1)−N(1)	2.11(2)	Fe(1)−C(12)	2.08(4)	C(13)−C(14)	1.45(3)
Fe(1)−C(13)	2.05(2)	O(4)−C(4)	1.22(2)	C(14)−C(15)	1.45(2)
Fe(1)−C(14)	2.16(2)	C(4)−C(5)	1.46(2)	N(1)−C(23)	1.45(3)
Fe(1)−C(4)	2.00(2)	N(1)−C(12)	1.41(3)	C(12)−C(13)	1.40(3)
Fe(1)−C(4)−O(4)	118(1)	Fe(1)−C(14)−C(15)	126(1)	C(12)−C(13)−C(14)	123(2)
Fe(1)−C(4)−C(5)	120(1)	C(23)−N(1)−C(12)	110(1)	C(13)−C(14)−C(15)	124(2)
Fe(1)−N(1)−C(23)	123(1)	N(1)−C(12)−C(13)	109(2)		

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

The final cycle of full-matrix least-squares refinement was respectively based on 2159, 1840, 1307, and 2898 observed reflections and 289, 492, 277, and 316 variable parameters and converged with unweighted and weighted agreement factors of $R = 0.048$ and $R_w = 0.050$ for **6**, $R = 0.077$ and $R_w = 0.070$ for **10**, $R = 0.073$ and $R_w = 0.067$ for **13**, and $R = 0.039$ and $R_w = 0.046$ for **18**, respectively. All the calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation.

The details of the crystallographic data and the procedures used for data collection and reduction information for **6**, **10**, **13**, and **18** are given in Table 1. The selected bond lengths and angles are listed in Tables 2 and 3. The atomic coordinates and B_{iso}/B_{eq}, anisotropic displacement parameters, complete bond lengths and angles, and least-squares planes for **6**, **10**, **13**, and **18** are given in the Supporting Information. The molecular structures of **6**, **10**, **13**, and **18** are given in Figures 1−4, respectively.

Results and Discussion

Compound [(η^4-$C_4H_3OCH{=}CHCH{=}NC_6H_5$)Fe(CO)$_3$] (**1**), which was synthesized by the reaction of $C_4H_3OCH{=}CHCH{=}NC_6H_5$ with an equimolar amount of $Fe_2(CO)_9$ according to the literature method,[16] reacted with about 20−30% molar excess of an aryllithium reagent, ArLi (Ar = C_6H_5, p-$CH_3C_6H_4$, o-,p-$CH_3OC_6H_4$, p-$CF_3C_6H_4$),

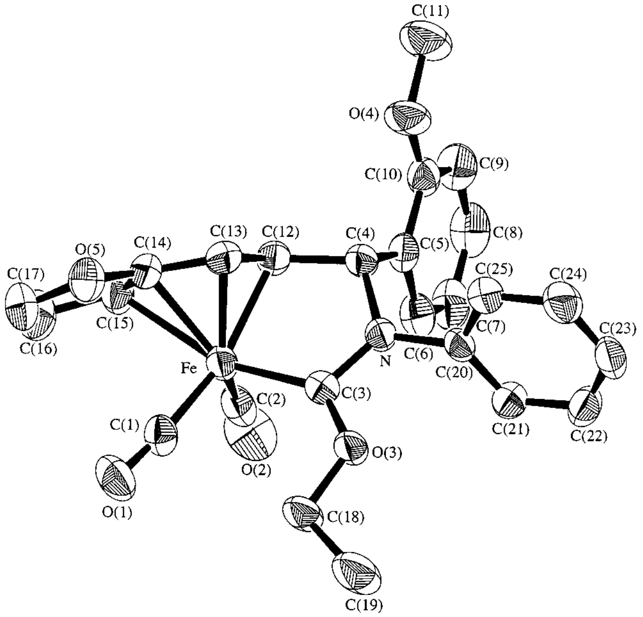

Figure 1. Molecular structure of **6**, showing the atom-numbering scheme. Thermal ellipsoids are shown at 45% probability.

in ether at low temperature (−75 to −35 °C), followed by alkylation with Et$_3$OBF$_4$ in aqueous solution at 0 °C or in CH$_2$Cl$_2$ at −60 °C. After separation of the resulting mixture by chromatography on an alumina column at −20 to −25 °C and recrystallization from petroleum ether/CH$_2$Cl$_2$ solution at −80 °C, the orange-yellow crystalline complexes **4**−**8** with general composition [{η^4-C$_4$H$_3$OCH=CHCH−(Ar)N(C$_6$H$_5$)C(OC$_2$H$_5$)=}Fe(CO)$_2$] were obtained in 62−71% yields. Scheme 1 shows a possible mechanism for the formation of complexes **4**−**8**. The initial attack of aryllithium reagent on the iron-coordinated C=N double bond with the addition of the phenyl group to the carbon atom and Li positive ion to the N atom of the imine moiety gave rise to the formation of the intermediate (a). Then the nucleophilic addition of the N negative ion to a CO ligand of the Fe(CO)$_3$ unit occurred, accompanied by dissociation of the coordination of the Fe atom to the C=N double bond and the formation of the coordination of the Fe atom to a double bond of the furanyl group, to generate the unstable adduct intermediate (b). Subsequent alkylation of adduct intermediate (b) with Et$_3$OBF$_4$ eventually converted into the stable chelated carbene complexes **4**−**8**, as that of the chelated (η^4-styrene)dicarbonyl[ethoxy(amino)carbene]iron complexes.[11]

The orange-yellow complexes **4**−**8** were soluble in polar solvents but only slightly soluble in nonpolar solvents. They are sensitive to air and temperature in solution but relatively stable in the solid. On the basis of elemental analyses and spectroscopic evidence, as well as X-ray crystallography, products **4**−**8** are formulated as novel chelated furanyl-coordinated alkoxy(amino)carbeneiron complexes with an η^2-bonding of the furanyl bonded to the Fe atom, similar to the chelated (η^4-styrene)dicarbonyl[ethoxy(amino)carbene]iron complexes obtained by the reaction of (cinnamaldehyde anil)iron tricarbonyl with aryllithium reagents (eq 3).[11] The ^{1}H NMR spectral data of complexes **4**−**8** are given in the Experimental Section, and the assignments of their resonances are based on the structural information elucidated by X-ray structure analysis and on the literature reports.[11,16,25] The upfield chemical shift (ca. 3.39−3.51 ppm) of the proton (3-position) of the furanyl coordinated to the Fe atom suggests that the aromaticity of the furan ring was considerably perturbed. This picture was further supported by X-ray structure determination of complex **6**.

IR spectra of complexes **4**−**8** showed two CO absorption bands at 2044−1902 cm^{-1} in the ν(CO) region, evidence for an Fe(CO)$_2$ moiety in these complexes. The molecular ion peaks and characteristic fragments produced by successive loss of CO ligands were shown in the mass spectra of complexes **5**−**8**; no parent ion but feature fragments are observed for **4**. To unambiguously confirm their structures, an X-ray diffraction study for complex **6** was carried out. The results of the X-ray diffraction work are summarized in Table 1, and the structure is given in Figure 1.

The molecular structure of complex **6** confirmed that the aryl group has been added to the carbon end of the imine unit so that C(4) atom forms three σ bonds to C(5), C(12), and N atoms with sp^3-hybridized orbitals, as confirmed by the values of the bond angles around C(4) (C(12)−C(4)−N 107.1(4)°, C(5)−C(4)−C(12) 111.3(4)°, C(5)−C(4)−N 112.5(4)°). The N atom forms a new bond with the carbene carbon atom (C(3)). The sum of the bond angles around C(3) is exactly 360°, indicating that the C(3) atom forms bonds to Fe, N, and O(3) atoms with sp^2-hybridized orbitals. The Fe, C(3), O(3), and N atoms lie in a plane. The bond lengths of Fe−C(3), C(3)−N, and C(3)−O(3) are 1.916(5), 1.358(6), and 1.331(5) Å, respectively, which indicates that there exists a certain extent of π bond character in the three bonds. The coordinated carbon atoms C(12), C(13), C(14), and C(15) are essentially coplanar to form an η^4-alkadiene ligand. The perpendicular distance from the Fe atom to this plane is 1.617 Å, and the dihedral angle between the C(12)C(13)C(14)C(15) plane and the furan ring plane is 6.71°. Thus, the C(12)C(13)C(14)C(15) plane is approximately parallel to the furan ring plane. These bond distances and angles suggest that the Fe, C(3), O(3), N, C(12), C(13) atoms and the furan ring could form a large conjugated system to stabilize the complex.

The dihedral angle between the plane defined by Fe, C(3), C(4), and C(12) and the plane comprised of C(12), C(13), C(14), and C(15) is 77.41°. The FeC(3)C(4)C(12) plane is, respectively, oriented at angles of 61.02° and 94.59° with respect to the benzene ring C(20)C(21)C(22)C(23)C(24)C(25) plane and *o*-methoxyphenyl ring C(5)C(6)C(7)C(8)C(9)C(10) plane, while the angle between the benzene ring plane and the *o*-methoxyphenyl ring plane is 93.76°, nearly perpendicular to each other, to avoid steric repulsion between them.

It is noteworthy that the bond lengths of the two double bonds of the furan ring in complex **6** are obviously different from each other; the bond distance of 1.404(8) Å for (C14)−C(15), which are both coordinated to the Fe atom, is much longer than that of 1.286(9) Å for C(16)−C(17). These bond lengths indicate that the aromaticity of the furan ring is considerably destroyed owing to the coordination of the Fe atom, as anticipated from the ^{1}H NMR spectrum. More interest-

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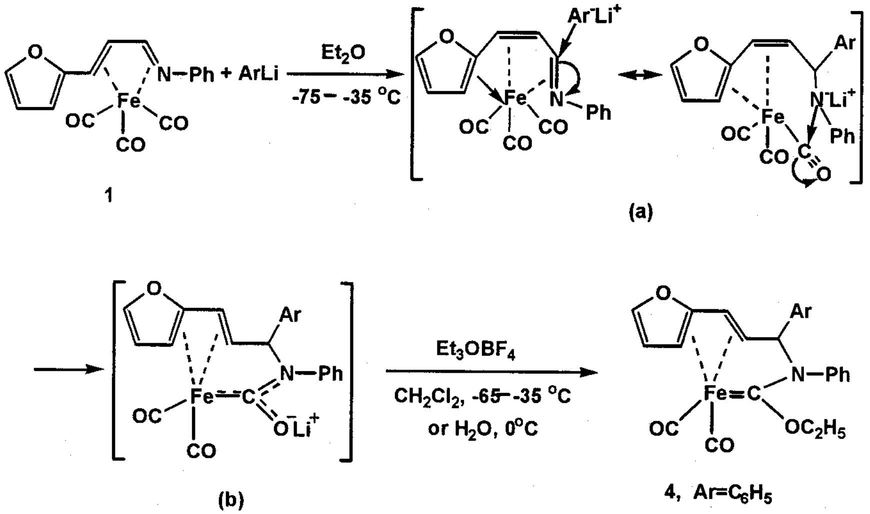
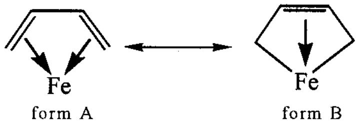
(25) Victor, R.; Ben-Shoshan, R.; Sarel, S. *J. Org. Chem.* **1972**, *37*, 1930.

Scheme 1



4, Ar=C_6H_5
5, Ar=p-$CH_3C_6H_4$
6, Ar=o-$CH_3OC_6H_4$
7, Ar=p-$CH_3OC_6H_4$
8, Ar=p-$CF_3C_6H_4$

ingly, the bond length of C(12)−C(13), 1.439(7) Å, is obviously longer than that (1.393(7) Å) of C(13)−(14). Kruger et al. have proposed that there exist two bonding arrangements, A and B, in *cis*-1,3-diene iron complexes.[26] Form A emphasizes a π-donation from the ligand to the metal. Form B emphasizes σ- and π-bonding contributions from the terminal and central carbon atoms, respectively, and supposedly indicates a stronger interaction than does form A. In the crystalline state, form B may be a superior configuration for **6**. However, based on the traditional presentation, complexes **4**−**8** show that form A rather than form B is the best description of the diene-iron bonding.



form A form B

To explore the effect of different azadiene ligands on the reactivities of (1-azadiene)Fe(CO)$_3$ complexes and reaction products, an attempt was made at the reaction of [(η^4-$C_4H_3OCH{=}CHCH{=}NC_6H_{11}$)Fe(CO)$_3$] (**2**) and [($\eta^4$-$C_6H_5CH{=}CH{-}CH{=}NC_6H_{11}$)Fe(CO)$_3$] (**3**), where the aryl substituents on the azadiene ligand are a furanyl and a phenyl, respectively, and the substituent at the N atom of the azadiene ligand is a cyclohexyl group, with aryllithium reagents under similar conditions. Thus, compound **2** reacted with about 15−30% molar excess of an aryllithium reagents, ArLi (Ar = C_6H_5, *o*-, *m*-, *p*-$CH_3C_6H_4$), in ether at low temperature (−75 to −35 °C), followed by alkylation with Et_3OBF_4 in CH_2Cl_2 at −65 to −30 °C. After workup as described in the Experimental Section, novel η^4-azadiene-coordinated 17e acyliron complexes [{η^4-$C_4H_3OCH{=}CHCH{=}NC_6H_{11}$}Fe(CO)$_2$(COAr)] (**9**−**12**) (Scheme 2) were obtained in 73−82% yields.

Unexpectedly, when *p*-$CH_3OC_6H_4Li$ and *p*-$CF_3C_6H_4Li$ were used as nucleophiles for the reaction with compound **2**, no analogous η^4-azadiene-coordinated acyliron complexes but novel η^2-azadiene-coordinated acyliron inner salt complexes [{η^2-$C_4H_3OCH{=}CHCH{=}N(C_2H_5)C_6H_{11}$}Fe(CO)$_3$($COC_6H_4OCH_3$-*p*)] (**13**) and [{($\eta^2$-$C_4H_3OCH{=}CHCH{=}N(C_2H_5)C_6H_{11}$}Fe(CO)$_3$($COC_6H_4CF_3$-*p*)] (**14**) (Scheme 3) were obtained in >70% yields, respectively.

The formulas of complexes **9**−**12** and **13**, **14** shown in Schemes 2 and 3, respectively, are supported by microanalytical and spectroscopic data as well as X-ray crystallography. A possible reaction pathway to complexes **9**−**12** (Scheme 2) could involve the acylmetalate intermediates (a) formed by initial attack of aryllithium nucleophiles on one of the three CO ligands. The fact that the acylmetalate intermediate (a) formed upon subsequent alkylation with Et_3OBF_4 in CH_2Cl_2 solution gave the acyliron complexes **9**−**12** having a 17-electron configuration for the acyliron moiety suggests that an oxidation of intermediate (a) to lose one electron occurred in the alkylation step. Apparently, the triethyloxonium tetrafluoroborate (Et_3OBF_4) acts as an oxidant of Fe(0) to Fe(I) in the reaction. Analogous transformation and oxidation of the central iron have been previously observed in the reactions of tricarbonyl(η^4-cyclopenta-1,3-diene)iron and (cyclooctatetraene)diiron hexacarbonyl with aryllithium reagents followed by alkylation with Et_3OBF_4, which gave the acyldicarbonyl(η^5-cyclopentadienyl)iron complexes [η^5-C_5H_5Fe(CO)$_2$(COAr)][27] and the 16e (8,8-dihydro-1−4-η:5−7-η-cyclooctatrienyl)tricarbonylirondicarbonyl(arylformacyl)iron complexes [(CO)$_3$Fe(1−4-η:5−7-η-C_8H_9)(CO)$_2$Fe(COAr)],[28] respectively. However, it is not yet clear how the oxidation of the central iron occurred during the reaction and what factors promote the formation of these stable 17e complexes. The formation of complexes **13** and **14**

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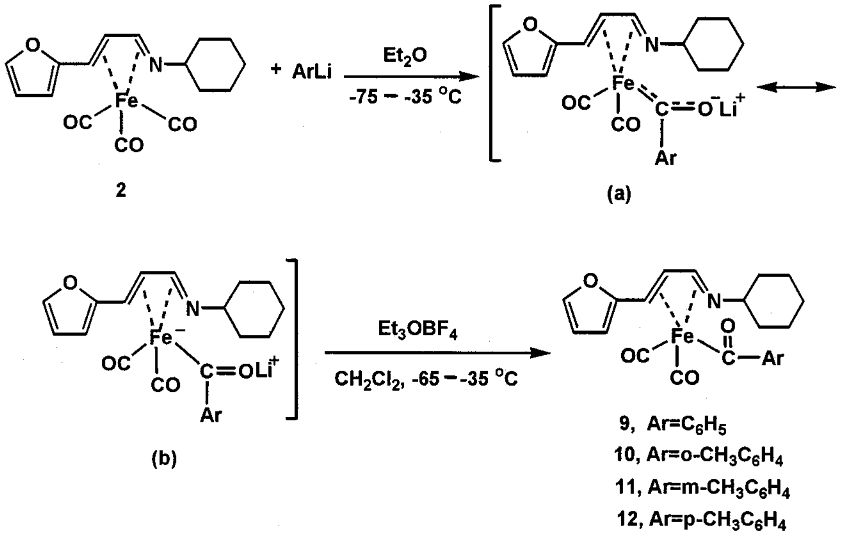
Scheme 2



Scheme 3

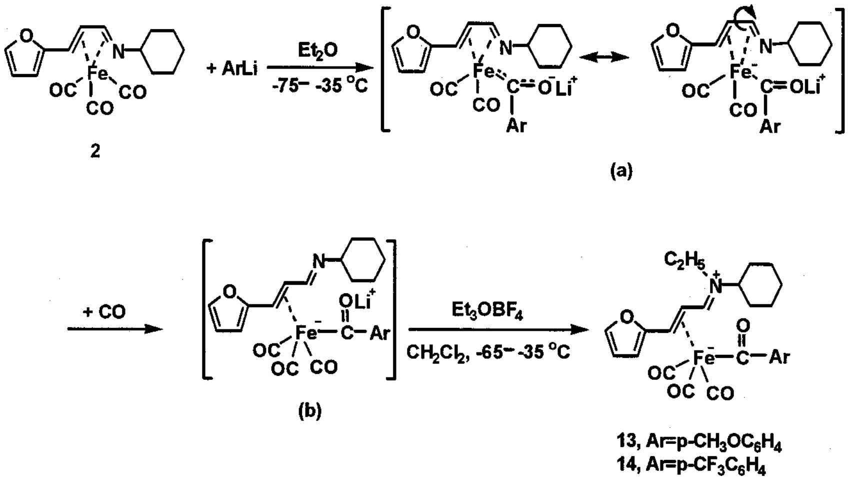


Table 3. Selected Bond Lengths (Å)[a] and Angles (deg)[a] for Complexes 13 and 18

	13	18		13	18
Fe−C(1)	1.78(1)	1.777(4)	N−C(21)	1.58(2)	1.472(4)
Fe−C(2)	1.76(2)	1.775(4)	N−C(23)	1.50(2)	1.485(4)
Fe−C(3)	1.80(1)	1.807(4)	C(12)−C(13)	1.39(2)	1.402(4)
Fe−C(4)	2.10(1)	2.073(3)	C(13)−C(14)	1.42(2)	1.421(4)
Fe−C(13)	2.10(1)	2.136(3)	C(14)−C(15)	1.46(2)	1.477(4)
Fe−C(14)	2.10(1)	2.116(3)	O(4)−C(4)	1.20(1)	1.225(4)
N−C(12)	1.34(1)	1.329(4)	C(4)−C(5)	1.49(2)	1.510(5)
Fe−C(1)−O(1)	178(1)	177.0(3)	Fe−C(14)−C(15)	121.5(10)	122.7(2)
Fe−C(2)−O(2)	178(1)	176.4(3)	C(12)−N−C(21)	121(1)	122.4(3)
Fe−C(3)−O(3)	175(1)	174.6(3)	C(12)−N−C(23)	122(1)	120.2(3)
Fe−C(4)−O(4)	120(1)	121.5(3)	N−C(12)−C(13)	125(1)	126.1(3)
Fe(1)−C(4)-C(5)	122(1)	121.9(3)	N−C(21)−C(22)	100(1)	114.2(3)
Fe−C(13)−C(12)	93.3(9)	94.0(2)	C(12)−C(13)−C(14)	122(1)	123.0(3)
Fe−C(13)−C(14)	70.2(8)	69.7(2)	C(13)−C(14)−C(15)	122(1)	123.2(3)
Fe−C(14)−C(13)	70.3(8)	71.2(2)	O(4)−C(4)−C(5)	117(3)	116.5(3)

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

(Scheme 3) could proceed via an analogous acylmetalate intermediate (a), which was then converted into another unstable intermediate (b) by abstracting one molecule of CO generated from decomposition of unstable intermediate (a) accompanied by dissociation of the coordination of the Fe to the C═N double bond. Subsequently, such an intermediate (b) can react with alkylating reagent Et$_3$OBF$_4$ to achieve electron charge equilibrium and be converted into the stable N-alkylation products **13** and **14**.

The yellow complexes **9**−**12** and **13**, **14** are only soluble in polar organic solvents and sensitive to air and temperature in solution but stable for a short period on exposure to air at room temperature in the crystalline state. The IR spectra, the solution ^{1}H NMR spectra, and mass spectra are consistent with the proposed structure

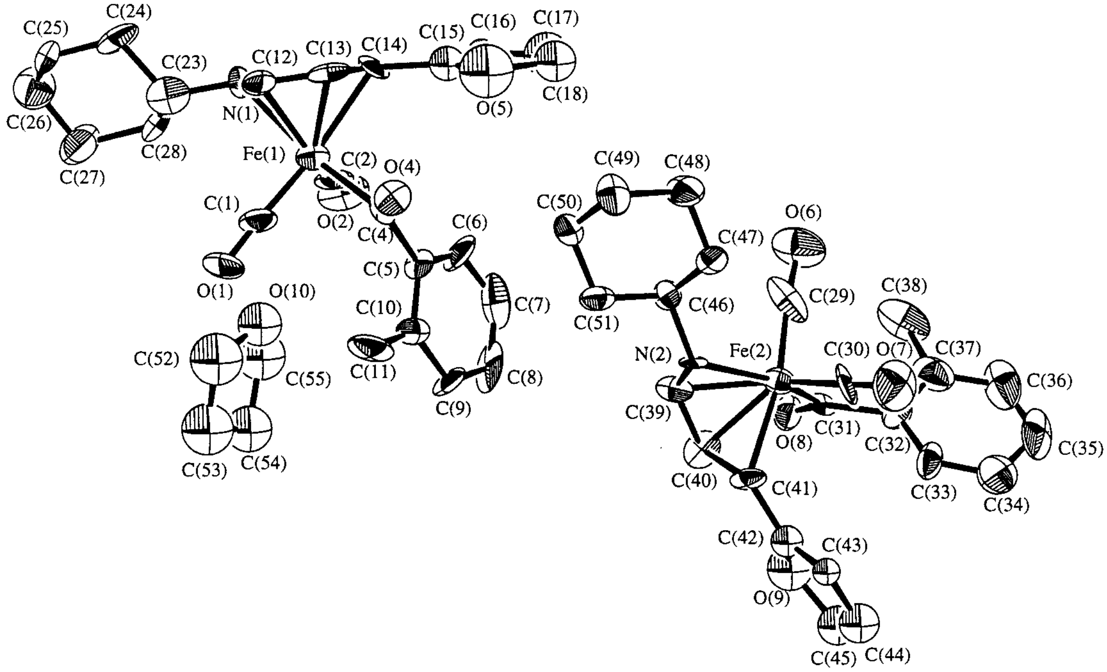


Figure 2. Molecular structure of **10**, showing the atom-numbering scheme. Thermal ellipsoids are shown at 45% probability.

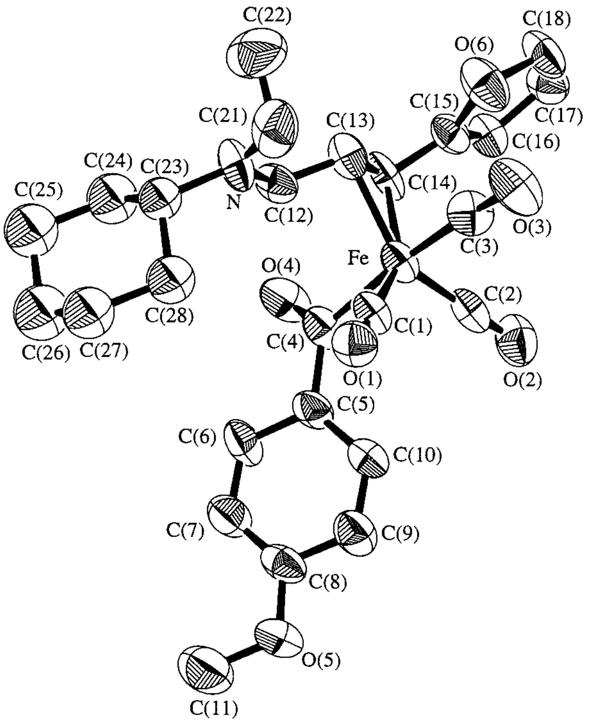


Figure 3. Molecular structure of **13**, showing the atom-numbering scheme with 40% thermal ellipsoids.

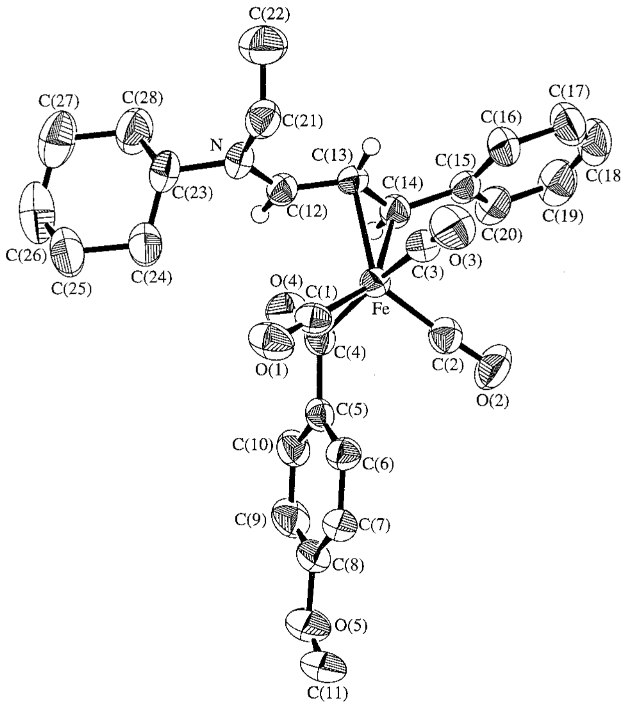
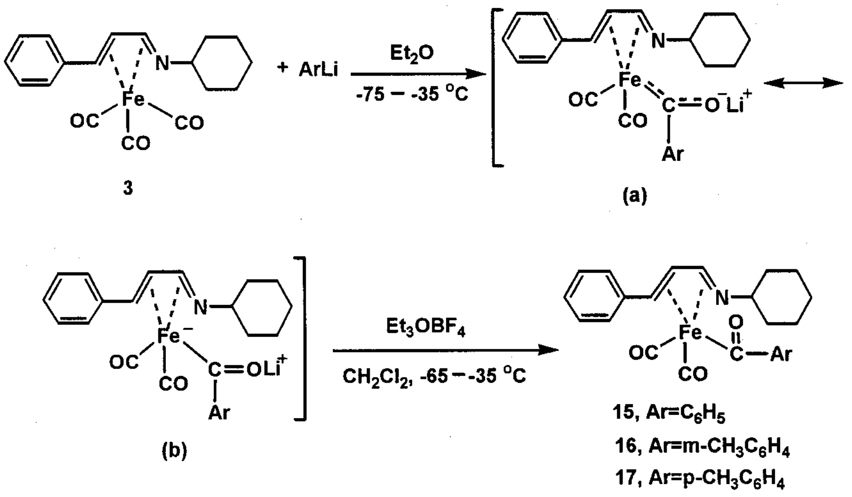


Figure 4. Molecular structure of **18**, showing the atom-numbering scheme with 45% thermal ellipsoids.

shown in Schemes 2 and 3, respectively. The IR spectra of **9**–**12** and **13**, **14** in CH_2Cl_2 solution showed an absorption band at 1586–1607 cm^{-1}, which is characteristic of the acyl ligand, besides the two or three terminal CO absorption bands in the ν(CO) region. In the ^1H NMR spectra of **9**–**12**, the chemical shifts of the protons of the η^4-azadiene ligand were similar to those of (η^4-1-azadiene)tricarbonyliron compound **2**,[16] indicating that the principal framework remained in these complexes, while the ^1H NMR spectra of complexes **13** and **14** showed complicated proton signals attributed to the azadiene ligand arising from the coordinating dissociation of the Fe to the C=N double bond and the bonding of C_2H_5 group to the N atom. As a result, the structure of the azadiene ligand consists of an η^2-coordinated C=C double bond and a free C=N double bond with an ethyl group bonded to the N atom. Thus, the proton signals of the original azadiene ligand shifted accordingly. In the ^1H NMR spectra of **13** and **14**, a triplet (ca. 2.01–1.06 ppm), a quartet (ca. 3.67–3.38 ppm), and a set of multiplet (ca. 7.95–6.96 ppm) bands were observed from both complexes, which showed characteristically the presence of the ethyl and aryl groups. The molecular ion peaks or characteristic fragments produced by successive loss of CO ligands were

Scheme 4



observed in the mass spectra of **9**−**12** and **13**, **14**. The acyl ions (COAr$^+$) are observed for all complexes of **9**−**12** and **13**, **14**.

The structures of complexes **9**−**12** and **13**, **14** have been further confirmed by X-ray crystallography of **10** and **13**, respectively. In complex **10**, one of the CO groups of the Fe(CO)$_3$ moiety has been converted into an acyl group (Figure 2). The structure of **10** resembled that of [(η^4-C$_4$H$_3$OCH=CHCH=NC$_6$H$_{11}$)Fe(CO)$_3$] (**2**),[16] except that the substituents on the Fe atom are two CO groups and one acyl group in **10** but three CO ligands in the latter. It is interesting that complex **10** crystallizes with two independent molecules and one THF solvent molecule in the asymmetric unit. The two molecules in the unit cell are nearly the same. The Fe atom shows an approximately square pyramidal coordination sphere with the azadiene ligand situated in the square plane. The complex consists of a 1-azadiene ligand adopting an s-cis conformation with respect to the central C(12)−C(13) bond in the azadiene chain. By comparison with **2**, the C−N bond (1.41(3) Å) of the azadiene is lengthened by 0.70 Å arising from the bonding of electron-withdrawing acyl to the Fe atom, leading to further weakness of the C=N bond of the azadiene ligand. The C(12)−C(13) bond length of 1.40(3) Å in **10** is slightly shorter than the corresponding distance in **2** (1.415(4) Å),[16] whereas the C(13)−C(14) distance (1.45(3) Å) is significantly longer than the corresponding distance in **2** (1.414(4) Å).[16] The Fe−C bond lengths of the C(12) and C(13) atoms, 2.08(4) and 2.05(2) Å, respectively, are similar to those of **2**.

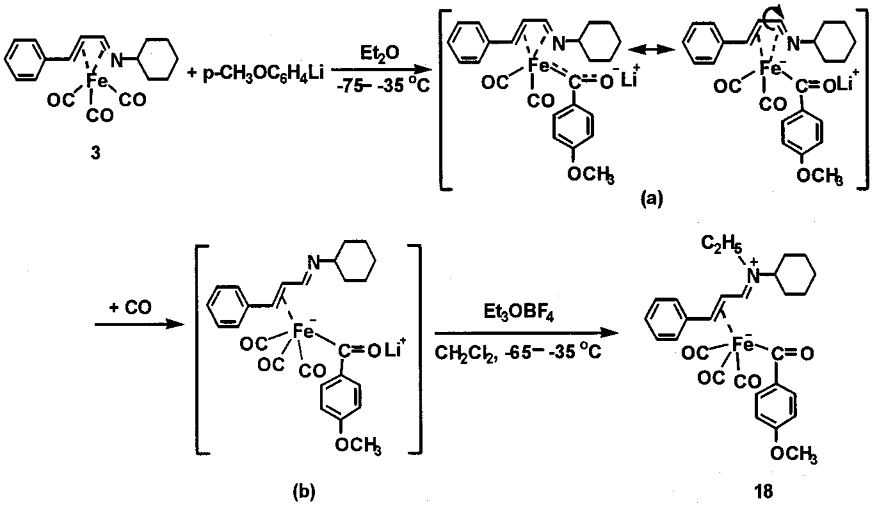
Complex **10** is a 17-electron species for the acyliron moiety, in which the 17 electrons participating in the central metal valence configuration consist of the eight electrons of the Fe atom, two pairs of electrons provided by the two CO ligands, and the other five electrons, one of which is a σ-electron, provided by the acyl group ligating the Fe atom in an end-on mode, and four of which are the π-electrons provided by an η^4-bonding orbital of the azadiene ligand bonded to the Fe atom.

The structure of **13** (Figure 3) resembled that of analogous aryliron inner salt complex [{η^2-C$_6$H$_5$CH=CHCH=N(C$_2$H$_5$)(2,4-Me$_2$C$_6$H$_3$)}Fe(CO)$_3$C$_6$H$_5$][12] obtained by the reaction of [(η^4-C$_6$H$_5$CH=CHCH=N(2,4-Me$_2$C$_6$H$_3$)-Fe(CO)$_3$] with C$_6$H$_5$Li (eq 4). The average Fe−C(CO) distance of1.78 Å is somewhat shorter than that found in [{(η^2-C$_6$H$_5$CH=CHCH=N(C$_2$H$_5$)(2,4-Me$_2$C$_6$H$_3$)}Fe(CO)$_3$C$_6$H$_5$] (1.803 Å).[12] The Fe−C bond lengths of the C(4), C(13), and C(14) in **13** are the same (2.10(1) Å). The C(12)−C(13) and C(13)−C(14) bond lengths are 1.39(2) and 1.42(2) Å, respectively, which are between the normal C−C and C=C distances; the C(12)−N bond length of 1.34(1) Å is also between the normal C−N and C=N distances. The N, C(12), C(13), and C(14) atoms are coplanar, with a N−C(12)−C(13) angle of 125(1)°, a C(12)−C(13)−C(14) angle of 122(1)°, and a C(13)−C(14)−C(15) angle of 122(1)°. Thus, the N, C(12), C(13), and C(14) atoms construct a conjugate system, and the C(12)−C(13) bond adopts steric stable s-trans configuration. The dihedral angle between the plane defined by N, C(12), C(13), and C(14) and the furan ring C(15)C(16)C(17)C(18)O(6) plane is only 13.52°, being approximately coplanar. Moreover, the C(14)−C(15) bond length is 1.46(2) Å, which is intermediate between C−C single-bond and C=C double-bond distances. The shorter C(14)−C(15) distance suggests some π-bond character between the C(14) atom and C(15) atom of the furan ring in **13**. Thus, the N, C(12), C(13), and C(14) atoms and the furan ring could form a large conjugate system, which could favorably disperse and neutralize the positive and negative charge on the Fe and N atoms to stabilize the complex.

The angles between the benzene ring plane comprised of C(5) through C(10) and the NC(12)C(13)C(14) plane and the C(5)C(6)C(7)C(8)C(9)C(10) and furan ring C(15)C(16)C(17)C(18)O(6) planes are 99.27° and 89.49°, respectively. Thus, the benzene ring plane of the methoxyphenyl group is perpendicularly warped toward both the NC(12)C(13)C(14) and C(15)C(16)C(17)C(18)O(6) planes due to intramolecular steric hindrance and intermolecular accumulation.

Analogous η^4-azadiene-coordinated 17e acyliron complexes [{η^4-C$_6$H$_5$CH=CH−CH=NC$_6$H$_{11}$}Fe(CO)$_2$(COAr)] (**15**, Ar = C$_6$H$_5$; **16**, Ar = *m*-CH$_3$C$_6$H$_4$; **17**, Ar = *p*-CH$_3$C$_6$H$_4$) (Scheme 4) and acyliron inner salt complexes [{η^2-C$_6$H$_5$CH=CHCH=N−(C$_2$H$_5$)C$_6$H$_{11}$}Fe(CO)$_3$-(COC$_6$H$_4$OCH$_3$-*p*)] (**18**) (Scheme 5) were also obtained in 79−80% and 55% yield, in the reaction of [(η^4-C$_6$H$_5$-CH=CHCH=NC$_6$H$_{11}$)Fe(CO)$_3$] (**3**) with aryllithium re-

Scheme 5



agents C_6H_5Li, *m*-$CH_3C_6H_4Li$, p-$CH_3C_6H_4Li$, and *p*-CH_3-OC_6H_4Li, respectively.

The formulas of complexes **15**−**17** and **18**, shown in Schemes 4 and 5, respectively, were supported by microanalytical and spectroscopic data, among which **18** has been further confirmed by its X-ray single-crystal structure determination. Complexes **15**−**17** are assigned to the analogous 17e structure since their spectral data are similar to those of complexes **9**−**12**. The IR spectra of **15**−**17** in CH_2Cl_2 solution showed an absorption band at 1597−1603 cm^{-1}, indicating characteristically the presence of the acyl ligand, besides the two terminal CO absorption bands in the ν(CO) region. In the ^1H NMR spectra of **15**−**17**, the chemical shifts of the protons at the coordinated C=C and C=N double bonds of the azadiene ligand are very similar to those of complexes **9**−**12**. Likely, complex **18** is assigned to a similar structure since its spectral data are similar to those of **13** and **14**. The possible reaction pathways to complexes **15**−**17** (Scheme 4) and **18** (Scheme 5) would be analogous to those of complexes **9**−**12** (Scheme 2) and complexes **13** and **14** (Scheme 3), respectively.

The structure of complex **18** shown in Figure 4 is very similar to that of **13**, except that the substituent on the azadiene ligand is a phenyl group in **18** but a furanyl group in **13**. Many structural features of **18** are essentially the same as those in **13**: the Fe−C bond lengths of C(4), C(13), and C(14), the bond distances of C(12)−C(13), C(13)−C(14), and N−C(12), the dihedral angle between the NC(12)C(13)C(14) plane and the benzene ring C(15)C(16)C(17)C(18)C(19)C(20) plane, and the angles between the benzene ring plane comprised of C(5) through C(10) and the NC(12)C(13)−C(14) plane and the C(5)C(6)C(7)C(8)C(9)C(10) and the benzene ring C(15)C(16)C(17)C(18)C(19)C(20) planes. Apparent differences in the structures of **13** and **18** are the shorter N−C(21) (1.472(4) Å) and N−C(23) (1.485(4) Å) bonds in **18** as compared to **13** (1.58(2) Å for N−C(21) and 1.50(2) Å for N−C(23)) arising from the different aryl substituent on the azadiene ligand. The NC(12)C(13)C(14) plane is oriented at an angle of 20.42° with respect to the benzene ring C(5) though C(10) plane, being approximately parallel to each other. The C(14)−C(15) bond length is 1.477(4) Å, which is shorter than the normal C−C single-bond distance. Thus, as in **13**, the conjugate system comprised of N, C(12), C(13), and C(14) atoms can also form a large conjugate system with the benzene ring to disperse and neutralize the positive and negative charge on the Fe and N atoms to stabilize the complex.

Of special interest are the reactions of **3** with aryllithium reagents *o*-$CH_3C_6H_4Li$, *o*-$CH_3OC_6H_4Li$, and *p*-$CF_3C_6H_4Li$. Their reactions under the same conditions gave no expected η^4-azadiene-coordinated acyliron complexes or acyliron inner salt complexes but η^2-azadiene-coordinated aryliron inner salt complexes [{η^2-C_6H_5−CH=CHCH=N(C_2H_5)C_6H_{11}}Fe(CO)$_3$Ar] (**19**−**21**) (Scheme 6) in 60−80% yields.

The formulas for complexes **19**−**21** shown in Scheme 6 are based on elemental analysis and spectroscopic evidence (Experimental Section), and their structures are established by an X-ray diffraction study of **19**,[29] which gave an *R* value of 0.20 due to serious decay. However, the IR, ^1H NMR, and mass spectra are consistent with this geometry. The IR spectra in the ν(CO) region of **19**−**21** showed three terminal CO absorption bands, similar to that of [{η^2-C_6H_5CH=CHCH=N(C_2H_5)(2,4-$Me_2C_6H_3$)}Fe(CO)$_3C_6H_5$].[12] In the ^1H NMR spectra of **19**−**21**, the chemical shifts of the two protons on the η^2-coordinating C=C double bond of the azadiene ligand (4.11−3.36 and 5.38−4.87 ppm) is similar to those (3.97−3.89 and 6.64−6.52 ppm)[12] of [{η^2-C_6H_5CH=CHCH=N(C_2H_5)(2,4-$Me_2C_6H_3$)}Fe(CO)$_3$-Ar] (Ar = C_6H_5, *p*-ClC_6H_4). In contrast to complex **18**, the IR spectra of complexes **19**−**21** showed no acyl absorption band in the ν(C=O) region, and the mass spectra of **19**−**21** showed no characteristic acyl ($COAr^+$) fragments but aryl (Ar^+) fragment peaks.

A possible reaction pathway to complexes **19**−**21** (Scheme 6) could involve initial formation of acylmetalate intermediates (a), analogous to that of complexes **13** and **14** (Scheme 3) and **18** (Scheme 5). The unstable intermediate (a) was then alkylated at the N atom accompanied by coordinating dissociation of Fe to the C=N double bond and aryl migration from acylcarbonyl carbon to the Fe atom, resulting in the formation of the stable N-alkylation products **19**−**21**. The formation of **19**−**21** is not surprising since analogous η^2-azadiene-

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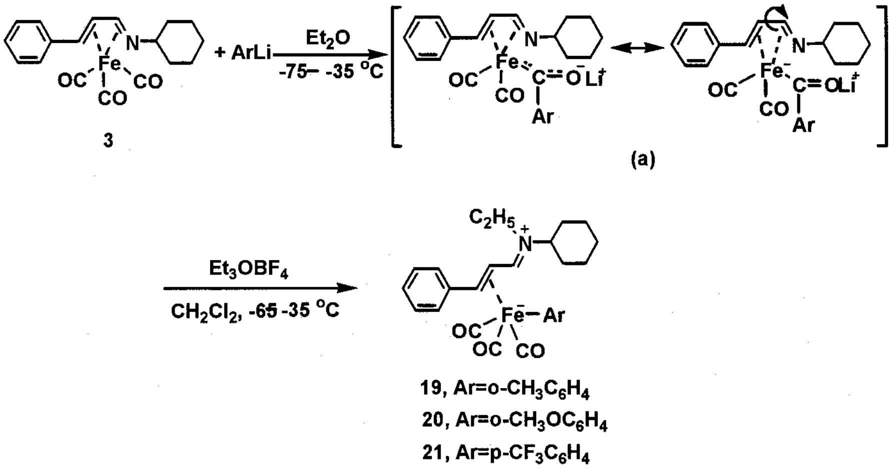
(29) Sun, J.; Chen, J.-B. Unpublished work.

Scheme 6



coordinated aryliron inner salt complexes have been observed in the reaction of [{η^4-C$_6$H$_5$CH=CHCH=N(2,4-Me$_2$C$_6$H$_3$)}Fe(CO)$_3$], where the substituent on the N atom is an electron-pushing 2,4-dimethylphenyl group as that of the cyclohexyl group, with aryllithium reagents (eq 4).[12]

The title reaction encompasses a variety of reactions of (η^4-1-azadiene)Fe(CO)$_3$ complex with aryllithium reagents. The formation of the various reaction products depends not only on the azadiene ligand and the substituents at the N atom of the azadiene ligand but also on the different aryllithium reagents used. The reaction results show that the azadiene ligand with different aryl substituents exerts no great influence upon the reation products. For example, compound **1** and (cinnamaldehyde anil)iron tricarbonyl, where the aryl substituents on the azadiene ligand are a furanyl and a phenyl, respectively, reacted with aryllithium reagents to give analogous chelated alkoxy(amino)carbeneiron complexes (eq 3 and Scheme 1); compound **2** and **3**, where the aryl substituents on the azadiene ligand also are a furanyl and a phenyl, reacted with aryllithium reagents to produce analogous η^4-azadiene-coordinated 17e acyliron complexes (Schemes 2 and 4) or η^2-azadiene-coordinated acyliron inner salt complexes (Schemes 3 and 5) based on the aryllithium reagents used. However, the substituents at the N atom of the azadiene ligand exert a great influence on the resulting products. For instance, compound **1**, where the substituent at the N atom is a phenyl group, reacted with aryllithium reagents to afford the chelated furanyl-coordinated alkoxy(amino)carbeneiron complexes (Scheme 1), while the analogous reactions of compound **2**, where the substituent at the N atom is a cyclohexyl group, gave novel η^4-azadiene-coordinated 17e acyliron complexes (Scheme 2). Likewise, compound **3**, where the substituent at the N atom is also a cyclohexyl group, reacted with aryllithium reagents yielding η^4-azadiene-coordinated 17e acyliron complexes, η^2-azadiene-coordinated acyliron inner salt complexes, or η^2-azadiene-coordinated aryliron inner salt complexes (Scheme 6) based on the aryllithium reagents used. The title reaction offers a new and useful method for the preparation of the chelated heteroatomic carbene complexes or their isomerized products and enriches the chemistry of (1-azadiene)Fe(CO)$_3$ complexes.

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

Supporting Information Available: Tables of the positional parameters and B_{iso}/B_{eq}, H atom coordinates, anisotropic displacement parameters, complete bond lengths and angles, and least-squares planes for **6**, **10**, **13**, and **18**. This material is available free of charge via the Internet at http://pubs.acs.org.

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