Organometallics 1988, *7,* 21-25

The same experiment starting with 500 mg of **3** gave 70 mg of **4** (12% yield) as brown crystals. Anal. Calcd for $C_{19}H_{10}Fe_3O_9$: C, 41.51; H, 1.83. Found: C, 41.58; H, 1.69.

Synthesis of 5 and 6. To **1** (500 mg) dissolved in hexane was added 3-3-dimethyl-1-butyne (130 μL) and the solution was refluxed for $^1/_2$ h. The solution was evaporated to dryness and the residue chromatographed on a Florisil column. Elution with hexane/toluene with increasing toluene content gave successively an orange fraction of **6** and a brown fraction of **5**.

6 was an orange oil, which was purified by elimination of the solvents under vacuum (140 mg, 25% yield). Anal. Calcd for $C_{17}H_{14}Fe_3O_9$: C, 38.54; H, 2.66. Found: C, 38.95; H, 2.95.

5 was crystallized in hexane at −20 °C as brown crystals (50 mg, 8% yield). Anal. Calcd for $C_{17}H_{14}Fe_3O_9$: C, 38.54; H, 2.66. Found: C, 38.32; H, 2.53.

Reaction of 5 with Carbon Monoxide under Pressure. A 20-mg sample of **5** was dissolved in 20 mL of hexane; the solution was the transferred to a stainless steel autoclave and pressurized to 40 atm with carbon monoxide. The solution was stirred for 24 h. After depressurization infrared spectra of the solution gave evidence of the formation of **7**, which reverted back to **5** after 1 h at atmospheric pressure under nitrogen atmosphere.

Reaction of 6 with Carbon Monoxide under Pressure. A 50-mg sample of **6** was dissolved in 20 mL of hexane and the solution was pressurized to 40 atm in the same way as for **5**. After the solution was stirred for 48 h, infrared spectroscopy gave only evidence of **6**, which was recovered in nearly quantitative yield.

Synthesis of 8. It was synthesized under the same experimental conditions as **5** and **6** but it was not purified (see text).

Synthesis of 9. To **1** (350 mg) dissolved in methylcyclohexane was added phenylacetylene (81 μL) and the solution was refluxed for 2 h. The solution was then evaporated to dryness and chromatographed on a Florisil column. Elution with hexane/toluene with increasing toluene content gave successively $Fe_3(CO)_{10}(\mu\text{-}CCH_2)$, an unidentified yellow band, and a green band of **9**.

Crystallization in hexane at −20 °C gave 93 mg of **9** as green crystals (31% yield). Anal. Calcd for $C_{17}H_{10}Fe_3O_8$: C, 40.0; H, 1.96. Found: C, 39.82; H, 1.76.

Synthesis of 10. The synthesis was carried out according to the same procedure as for **9** but in refluxing benzene. Chromatography on a Florisil column and crystallization in hexane gave 11 mg of **10** as orange crystals (28% yield). Anal. Calcd for $C_{18}H_{10}Fe_3O_9$: C, 40.14; H, 1.85. Found: C, 39.90; H, 1.73.

Synthesis of 11 and 12. **1** (500 mg) and diphenylacetylene (200 mg) were dissolved in methylcyclohexane and the solution was refluxed for $^1/_2$ h. The solution was then evaporated to dryness and the residue was chromatographed on a Florisil column. Elution with hexane/toluene with an increasing content of toluene gave successively $Fe_3(CO)_{10}(\mu\text{-}CCH_2)$, a red band of **12**, and an orange band of **11**.

11 was crystallized in hexane and gave 195 mg of orange crystals (28% yield). Anal. Calcd for $C_{36}H_{24}Fe_2O_6$: C, 65.09; H, 3.64. Found: C, 65.40; H, 3.74.

12 was a red oil, which was dried in vacuo to give 0.100 mg of product (19% yield). Anal. Calcd for $C_{22}H_{14}Fe_2O_6$: C, 54.32; H, 2.88. Found: C, 54.02; H, 2.92.

Synthesis of 13. To **1** (400 mg) dissolved in methylcyclohexane was added 2-butyne (70 μL) and the solution was refluxed for $^1/_2$ h. The solution was evaporated to dryness and the residue was chromatographed on a Florisil column. Elution with hexane gave successively $Fe_3(CO)_{10}(\mu\text{-}CCH_2)$, the complex **2**, and an orange fraction containing **13**.

Crystallization in hexane gave 75 mg of **13** as orange crystals (25% yield). Anal. Calcd for $C_{16}H_{16}Fe_2O_6$: C, 46.15; H, 3.84. Found: C, 45.78; H, 3.79.

Registry No. 1, 88610-52-0; 2, 101315-98-4; 3, 102774-28-7; 4A, 110935-08-5; 4B, 110935-09-6; 5, 110935-10-9; 6, 110935-11-0; 7, 110935-12-1; 8, 110935-13-2; 9, 110935-14-3; 10, 110970-98-4; 11, 110935-15-4; 12, 110935-17-6; 13, 110935-16-5; $Fe_3(CO)_{10}(\mu\text{-}CCH_2)$, 103751-58-2; acetylene, 74-86-2; 3,3-dimethyl-1-butyne, 917-92-0; phenylacetylene, 536-74-3; diphenylacetylene, 501-65-5; 2-butyne, 503-17-3.

Studies on Olefin-Coordinating Transition-Metal Carbene Complexes. 9. Synthesis, Structure, and Reactivities of Novel Chelated (η^4-Styrene)dicarbonyl[ethoxy(amino)carbene]iron Complexes[†]

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The three title compounds $[(\eta^4\text{-}C_6H_5CH{=}CH)CH(Ar)N(C_6H_5)C(OC_2H_5){=}]Fe(CO)_2$ (**2**, Ar = C_6H_5; **3**, Ar = $m\text{-}CH_3C_6H_4$; **4**, Ar = $p\text{-}CF_3C_6H_4$) have been prepared by the reaction of (cinnamaldehyde anil)iron tricarbonyl, $(\eta^4\text{-}C_6H_5CH{=}CHCH{=}NC_6H_5)Fe(CO)_3$ (**1**), with an aryllithium reagent in ether at low temperature, followed by the alkylation of the adducts formed with Et_3OBF_4 in aqueous solution at 0 °C. Compound **2** reacted with the Lewis bases PPh_3, $P(OPh)_3$, $AsPh_3$, CH_3CN, $PhCH_2NH_2$, and 4-vinylpyridine to give six chelated η^2-olefin carbene complexes (**5**–**10**). These new compounds are characterized by elemental analyses and IR, ^{1}H NMR, and mass spectra; one has been characterized by X-ray diffraction: $[(\eta^4\text{-}C_6H_5CH{=}CH)CH(m\text{-}CH_3C_6H_4)N(C_6H_5)C(OC_2H_5){=}]Fe(CO)_2\cdot{}^1/_2C_6H_5CH_3$, monoclinic, space group C_{2h}^5–$P2_1/c$ with unit cell constants a = 12.457 (3) Å, b = 10.560 (2) Å, c = 20.072(4) Å, β = 96.63 (2)°, V = 2622.71 Å^3, and Z = 4; R = 0.047 for 3239 reflections with $F_o^2 \geqslant 3\sigma(F_o)^2$. The ^{1}H NMR spectral data of **2**–**4** and the results of an X-ray structure analysis for **3** show that the benzene ring of the styrene is coordinated to the iron atom with a double bond in the complexes **2**–**4** and shows alternating long and short bond lengths.

Introduction

Transition-metal carbene alkene complexes have been postulated to exist as important intermediates in the reaction of olefin metathesis,[2] cyclopropanation of alkenes,[3] and Ziegler–Natta polymerization of alkenes.[4] As model compounds, some η^2-olefin metal carbene complexes have

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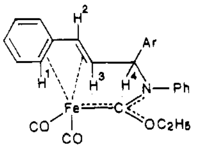
Table I. ^{1}H NMR Spectra of the Complexes 2–10 at 20 °C (δ, TMS as Internal Reference)

compd	solv	H^1	H^2	H^3	H^4	other protons
2	C_3D_6O	2.82 (m, 1)	5.51 (d, 1)	0.94 (m, 1)	5.32 (s, 1)	1.10 (t, 3), 4.00–4.30 (m, 2),[b] 6.80–7.5 (m, 15)
3	C_3D_6O	2.83 (m, 1)	5.52 (t, 1)	0.96 (m, 1)	5.25 (s, 1)	1.10 (t, 3), 2.34 (s, 3), 4.00–4.30 (m, 2),[b] 6.80–7.4 (m, 14)
4	C_3D_6O	2.90 (d, 1)	5.54 (t, 1)	0.96 (d, 1)	5.48 (s, 1)	1.10 (t, 3), 4.00–4.35 (m, 2),[b] 6.8–7.3 (m, 10), 7.70 (s, 4)
5	$CDCl_3$		4.6–4.8 (br, 2)		5.28 (s, 1)	1.22 (t, 3), 3.50 (m, 2), 6.9–7.8 (m, 30)
6	$CDCl_3$		4.50 (m, 1) 4.70 (m, 1)		5.58 (s, 1)	1.22 (t, 3), 3.50 (m, 2), 6.9–7.8 (m, 30)
7	$CDCl_3$		4.7–4.9 (m, 2)		5.34 (m, 1)	1.27 (m, 3), 3.62 (m, 2), 6.7–7.6 (m, 30)
8	$CDCl_3$		4.50–4.70 (m, 2)		5.36 (s, 1)	1.27 (m, 3), 2.24 (s, 3), 3.80–3.90 (m, 2), 6.9–7.4 (m, 15)
9	$CDCl_3$		4.6–4.7 (m, 2)		5.26 (s, 1)	1.20 (br, 3), 3.34 (br, 2), 4.14 (br, 2), 6.7–7.6 (m, 20)[c]
10	$CDCl_3$		4.4–4.6 (br, 2)		5.39 (s, 1)	1.27 (br, 3), 3.8 (br, 2), 4.2 (br, 2), 5.0 (br, 1), 6.8–7.4 (m, 20)[c]

[a] The numbering of ^{1}H-protons in η^4-olefin for 2–4.



[b] Two groups of peaks with about equivalent intensity were shown due to the "trans" and "cis" isomers produced by arrangement of ethoxy related to the amino group.[11] [c] The resolution is relatively poor owing to slight decomposition during the measurement.

been synthesized by Casey and others.[5,6] We have recently reported the synthesis and structure of a series of isomerized (butadiene)- and (isoprene)dicarbonyl[ethoxy(aryl)carbene]iron complexes. These were prepared by the reaction of (butadiene)- and (isoprene)tricarbonyliron with an aryllithium reagent and subsequent alkylation with Et_3OBF_4 in aqueous solution at 0 °C.[7,8] Now we chose, as starting material, (cinnamaldehyde anil)iron tricarbonyl (1),[9] in which the olefin ligand is a heterodiene, for reaction with aryllithium reagents to study the effect of the heteroatomic olefin ligand on the carbene complexes. Herein, we report the synthesis, structure, and reactivities of the title complexes which are the first examples of η^4-1,3-diene carbene complexes.

Results and Discussion

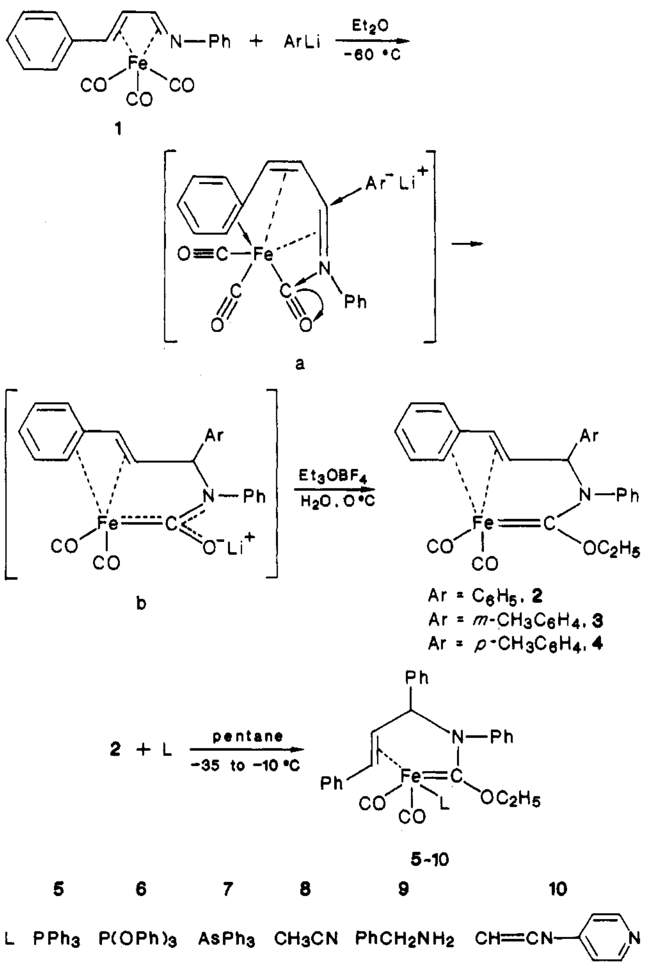
Synthesis and Reactivities of the Complexes 2–4. Compound 1 reacted with about 10% molar excess of an aryllithium, ArLi (Ar = C_6H_5, m-$CH_3C_6H_4$, p-$CF_3C_6H_4$), in ether at low temperature, and the adducts formed were alkylated with Et_3OBF_4 in aqueous solution at 0 °C. After separation of the resulting mixture by chromatography on an alumina column at −20 °C and recrystallization from pentane or CH_2Cl_2/pentane solution at −80 °C, orange–red crystalline complexes 2–4 were obtained. A possible mechanism for the formation of 2–4, as shown in Scheme I, is suggested to involve unstable adduct **b** that might be formed through a cooperative electron-transport path of the former intermediate **a**. Subsequent alkylation of adduct **b** with Et_3OBF_4 gave the title complexes 2–4.

The diamagnetic complexes 2–4 were readily soluble in polar solvents and moderately soluble in nonpolar solvents. In the solid state they began to decompose on exposure to air at room temperature for several hours and in solution they rapidly air oxidized.

A preliminary study was made of the addition reactions of complex 2 with Lewis bases such as PPh_3, $P(OPh)_3$, $AsPh_3$, CH_3CN, $PhCH_2NH_2$, and 4-vinylpyridine at −35 to −10 °C. Chelated η^2-olefin carbene complexes **5–10** were produced in high yield (Scheme I). However, no reaction occurred between complex 2 and alkenes such as maleic anhydride, cycloheptatriene, and α-methylstyrene. A rapid decomposition of complex 2 was observed when it was mixed with phenylacetylene in petroleum ether solution even at −78 °C.

Spectral Studies. ^{1}H NMR spectral data of the complexes 2–10 are listed in Table I. The assignments of resonance peaks for 2–4 are based on the structural in-

Scheme I



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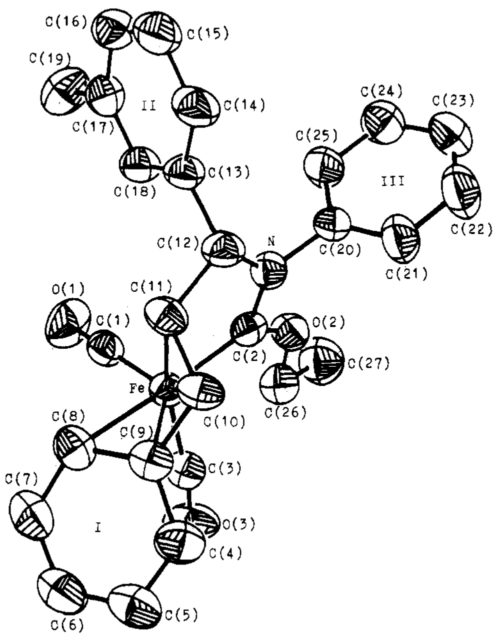

Figure 1. Molecular structure for **3**.

formation elucidated by X-ray structure analysis and on a literature report.[10] The upfield chemical shift of the H^1, H^2, and H^3 (2.8, 5.5, and 0.9 ppm in C_3D_6O) were similar to those of corresponding protons of the (η^4-styrene)tricarbonyliron complex (3.0, 5.6, and 0.2 ppm).[10] The chemical shift of H^1 suggests that the aromaticity of the benzene ring coordinated was considerably perturbed. This picture was further supported by X-ray structure analysis of **3**.

The IR and mass spectra of the complexes **2**–**10** are given in the Experimental Section. The IR spectra of **2**–**10** show the two expected stretching vibration bands in the ν(CO) region in accordance with that of metal carbonyl compounds with the general formula $M(CO)_2LL'$. The molecular ion peaks and characteristic fragments produced by successive loss of CO ligand were shown in the mass spectra of **2**, **3**, **4**, **6**, and **9**. Loss of the Lewis base ligand is favorable, no parent ions are observed for **5**, **7**, **8**, and **10**.

Discussion of the Structure Details for 3. The configuration of **3** is shown in Figure 1. The aryllithium has added to the carbon end of the imine unit in **1** so that C12 forms three σ bonds to C11, C13, and N atoms with sp^3 hybridized orbitals as confirmed by the values of the bond angles around C12 (C11–C12–N 107.0 (3)°, C13–C12–N 110.7 (3)°, C11–C12–C13 114.1(3)°). The N atom forms a new bond with the carbene carbon atom C2. The sum of bond angles around C2 is exactly 360°, which indicates that C2 forms bonds to Fe, N, and O2 atoms with sp^2-hybridized orbitals. The Fe, C2, O2, and N atoms are in a plane. The bond lengths of Fe–C2, C2–N, and C2–O2 are 1.918 (3), 1.329 (4), and 1.333 (4) Å, respectively, which indicates that there exists a certain degree of π bond character in the three bonds. These values of the bond lengths and angles show that the Fe, C2, O2, and N atoms form a large conjugated system.

It is interesting to see the alternating long and short bond lengths of the benzene ring I in complex **3**, the shorter bond lengths of 1.395 (5), 1.353 (6), and 1.309 (7) Å for C8–C9, C4–C5, and C6–C7, and the longer bond lengths of 1.467 (5), 1.420 (7), and 1.432 (6) Å for C4–C9, C5–C6, and C7–C8, respectively. These bond lengths indicate that the aromaticity of the benzene ring is considerably perturbed.

The sums of the bond angles around C10 and C11 are 359.4° and 351.9°, respectively, which only slightly deviate from 360°; thus it can be considered that C10 and C11 form, respectively, three σ bonds with the adjacent three atoms with sp^2-hybridized orbitals, and each carbon atom provides an approximate pure p_z atomic orbital to interact with theFe atom. It is notable that the coordinated carbon atoms C8, C9, C10, and C11 are essentially coplanar to form an η^4-alkadiene ligand. The perpendicular distance from the iron atom to this plane is 1.639 Å, and the dihedral angle between the C8C9C10C11 plane and the plane of the benzene ring I is 8.4°. Thus, the C8C9C10C11 plane is approximately parallel to the plane of benzene ring I, and it may be considered that the p_z π orbitals of the C8 and C9 atoms and the two p_z orbitals provided by the C10 and C11 atoms are parallel to each other and result in the formation of a π-group orbital of the η^4-olefin ligand to further interact with the Fe atom. In addition, the π-group orbital of the η^4-olefin ligand and π orbital of the carbene carbon C2 are almost perpendicular to each other since the dihedral angles between the FeC2O2N plane and the C8C9C10C11 plane and the FeC2O2N plane and the plane of the benzene ring I are 77.7° and 76.1°, respectively.

Experimental Section

IR, ^1H NMR, and mass spectra were recorded on a Perkin-Elmer 683 spectrophotometer, Varian XL-200 spectrometer, and Finnigan 4021 GC/MS/DS spectrometer, respectively. The melting points were determined in sealed, nitrogen-filled capillaries and not corrected.

All manipulations were carried out under purified N_2 atmosphere with standard Schlenk techniques. All solvents employed were saturated with N_2 and distilled over Na, CaH_2, and P_2O_5 prior to use. Alumina (neutral) used for chromatography was deoxygenated in a high vacuum for 16 h, deactivated with 5% (w/w) N_2-saturated water, and stored under N_2. The (cinnamaldehyde anil)iron tricarbonyl (**1**),[9,12] Et_3OBF_4,[13] and aryllithium reagents[14-17] used were prepared by literature methods.

Preparation of $[(\eta^4\text{-}C_6H_5CH{=}CH)CH(C_6H_5)N(C_6H_5)C(OC_2H_5){=}]Fe(CO)_2$ (2). To a solution of 1.0 g (2.9 mmol) of **1** in 80 mL of ether was added dropwise 3.1 mmol of C_6H_5Li[14] in 20 mL of ether at −65 °C. After being stirred at −50 to −40 °C for 3–4 h, the resulting dark red solution was concentrated to dryness under high vacuum at −40 °C. The residue was dissolved in 30 mL of N_2-saturated water at 0 °C and covered with pentane, then Et_3OBF_4 was added portionwise with strong stirring to the solution until it became acidic. The water solution was extracted with pentane and the combined extracts were concentrated under high vacuum at −20 °C. The residue was submitted to column chromatography on alumina at −20 °C with pentane followed by pentane/ether (10/1) as eluant. Evaporation of solvent under high vacuum give a product, which was recrystallized from CH_2Cl_2/pentane at −80 °C to give orange-red crystals, mp 75–76 °C (dec), yield 0.30 g (22%, based on **1**). IR (ν(CO), KCl): 1960 vs, 1895 vs cm^{-1}. MS, *m/e* 453 (M^+, 1.4%), 425($(M - CO)^+$, 54%), 397($(M - 2CO)^+$, 35%), 353($(M - 2CO - CH_3CHO)^+$, 14%). Anal. Calcd for $C_{26}H_{23}O_3NFe$: C, 68.93; H, 5.11; N, 3.09. Found: C, 68.89; H, 5.11; N, 3.02.

Preparation of $[(\eta^4\text{-}C_6H_5CH{=}CH)CH(m\text{-}CH_3C_6H_4)N(C_6H_5)C(OC_2H_5){=}]Fe(CO)_2$ (3). Similar to the preparation for

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2, 1.1 g (3.2 mmol) of **1** and 3.5 mmol of *m*-$CH_3C_6H_4Li$[15] were allowed to react at −60 °C, the reaction mixture was stirred at −60 to −20 °C for 10 h. Further treatment as described in the preparation of **2** and repeated recrystallization from pentane gave 0.28 g (19%, based on **1**) of red crystals, mp 78–79 °C (dec). IR(ν(CO), KCl) 1965 vs, 1895 vs cm^{-1}. MS, *m/e* 467(M^+, 1.9%), 439($(M - CO)^+$, 24%), 411($(M - 2CO)^+$, 13%). Anal. Calcd for $C_{27}H_{25}O_3NFe$: C, 69.39; H, 5.39; N, 3.00. Found: C, 69.30; H, 5.59; N, 2.65.

Preparation of [(η^4-$C_6H_5CH{=}CH$)CH(*p*-$CF_3C_6H_4$)N(C_6H_5)C(OC_2H_5)=]Fe(CO)$_2$ (4). To a solution of 0.65 g (2.9 mmol) of *p*-$CF_3C_6H_4Br$ in 20 mL of ether was added dropwise 3.0 mmol of C_4H_9Li[16] in 10 mL of ether at 0 °C. After being stirred for 20 min at room temperature, the resulting solution of *p*-$CF_3C_6H_4Li$[17] was allowed to react with 1.0 g (2.9 mmol) of **1** at −55 °C as described above for **2** to give 0.16 g (11%, based on **1**) of orange crystals, mp 73 °C(dec). IR(ν(CO), KCl) 1960 vs, 1895 vs cm^{-1}; MS, *m/e* 521 (M^+, 3.4%), 493 ($(M - CO)^+$, 61%), 465 ($(M - 2CO)^+$, 27%). Anal. Calcd for $C_{27}H_{22}O_3F_3NFe$: C, 62.20; H, 4.25; N, 2.69. Found: C, 62.46; H, 4.46; N, 2.46.

Reaction of 2 with PPh$_3$ → [(η^2-$C_6H_5CH{=}CH$)CH(C_6H_5)N(C_6H_5)C(OC_2H_5)=]Fe(CO)$_2$PPh$_3$ (5). A solution of PPh_3 (0.12 g, 0.44 mmol) in 30 mL of pentane was added dropwise to a solution of **2** (0.20 g, 0.44 mmol) in 40 mL of pentane at −30 °C. After the reaction mixture was stirred for 3 h at −30 to −20 °C, a large amount of precipitate was formed and the orange-red solution became yellowish. The solvent was removed by filtration. The precipitate was washed with pentane three times and dried under high vacuum for 4 h at −20 °C to give 0.28 g (90%, based on **2**) of a pale yellow powder, mp 138 °C (dec). IR(ν(CO), KCl) 1945 vs, 1880 vs cm^{-1}. MS, *m/e* 453 ($(M - PPh_3)^+$, 1.1%), 425 ($(M - PPh_3 - CO)^+$, 56%), 397 ($(M - PPh_3 - 2CO)^+$, 14%). Anal. Calcd for $C_{44}H_{38}O_3NPFe$: C, 73.85; H, 5.35; N, 1.95. Found: C, 73.65; H, 5.45; N, 1.83.

Reaction of 2 with P(OPh)$_3$ → [(η^2-$C_6H_5CH{=}CH$)CH(C_6H_5)N(C_6H_5)C(OC_2H_5)=]Fe(CO)$_2$P(OPh)$_3$ (6). To a solution of **2** (0.20 g, 0.44 mmol) in 40 mL of pentane was added 0.20 g (0.64 mmol) of $P(OPh)_3$ at −30 °C. Further treatment of reaction mixture as described in the reaction with PPh_3 gave 0.28 g (84%, based on **2**) of pale powder, mp 126 °C(dec). IR (ν(CO), KCl), 1985 vs, 1925 vs cm^{-1}; MS, *m/e* 763 (M^+, 1.5%), 707 ($(M - 2CO)^+$, 2.0%), 425 ($(M - P(OPh)_3 - CO)^+$, 27%), 310 ($P(OPh)_3^+$, 27%). Anal. Calcd for $C_{44}H_{38}O_6NPFe$: C, 69.20; H, 5.02; N, 1.83. Found: C, 69.34; H, 5.11; N, 1.80.

Reaction of 2 with AsPh$_3$ → [(η^2-$C_6H_5CH{=}CH$)CH(C_6H_5)N(C_6H_5)C(OC_2H_5)=]Fe(CO)$_2$AsPh$_3$ (7). A 0.10-g (0.22 mmol) portion of **2** and 0.10-g (0.32 mmol) portion of $AsPh_3$ were allowed to react in a similar manner as described in the reaction of **2** with PPh_3. The color of the reaction mixture changed from orange-red to pale yellow. The solution was decanted and the precipitate was recrystallized from pentane at −20 °C to give 0.14 g (83%, based on **2**) of orange crystals, mp 140 °C (dec). IR(ν(CO), KCl) 1938 vs, 1873 vs cm^{-1}. MS, *m/e* 425 ($(M - AsPh_3 - CO)^+$, 27%), 397 ($(M - AsPh_3 - 2CO)^+$, 22%), 306 ($AsPh_3^+$, 37%), 152 ($AsPh_3^+$, 100%). Anal. Calcd for $C_{44}H_{38}O_3NAsFe$: C, 69.58; H, 5.04; N, 1.84. Found: C, 69.34; H, 5.10; N, 1.72.

Reaction of 2 with CH$_3$CN → [(η^2-$C_6H_5CH{=}CH$)CH(C_6H_5)N(C_6H_5)C(OC_2H_5)=]Fe(CO)$_2$CH$_3$CN (8). To a stirred solution of **2** (0.10 g, 0.22 mmol) in 30 mL of pentane was added CH_3CN (0.20 g, 4.8 mmol) at −30 °C. After the reaction mixture was stirred for 3 h at −20 to −10 °C, the precipitate formed was treated as described above for **5** to give 0.09 g (85%, based on **2**) of yellow powder, mp 71 °C(dec). IR (ν(CO) KCl) 1935 vs, 1880 sh, 1869 vs cm^{-1}. MS, *m/e* 453 ($(M - CH_3CN)^+$, 0.2%), 425 ($(M-CH_3CN-CO)^+$, 35%). Anal. Calcd for $C_{28}H_{26}O_3N_2Fe$: C, 68.03; H, 5.30; N, 5.66. Found: C, 67.99, H, 5.14; N, 5.34.

Reaction of 2 with PhCH$_2$NH$_2$ → [(η^2-$C_6H_5CH{=}CH$)CH(C_6H_5)N(C_6H_5)C(OC_2H_5)=]Fe(CO)$_2$PhCH$_2$NH$_2$ (9). To a solution of **2** (0.10 g, 0.22 mmol) in 30 mL of pentane was added benzylamine (0.22 g, 1.96 mmol) at −30 °C. After the reaction mixture was stirred for 3 h at −20 °C, the solvent was evaporated to dryness and the residue was chromatographed on alumina with pentane/ether (10/1) as eluant at −20 °C. The yellow zone was collected and solvent was evaporated. The crude product was recrystallized from pentane at −78 °C to give 0.11 g (80%, based on **2**) of yellowish powder, mp 54 °C(dec). IR(ν(CO), KCl) 1930 vs, 1850 vs cm^{-1}. MS, *m/e* 560(M^+, 2%), 453 ($(M - PhCH_2NH_2)^+$, 2.5%), 107 ($PhCH_2NH_2^+$, 34%). Anal. Calcd for $C_{31}H_{32}O_3N_2Fe$: C, 70.72; H, 5.75; N, 4.99. Found: C, 70.72; H, 5.52; N, 4.73.

Table II. Atom Coordinates and Thermal Parameters for 3

atom	$x \times 10^4$	$y \times 10^4$	$z \times 10^4$	$U_{eq} \times 10^3$
Fe	3013.9 (4)	3778.6 (4)	6983.7 (2)	42.2 (2)
O1	5165 (3)	3603 (3)	6547 (2)	81 (1)
O2	2442 (2)	5306 (2)	5741 (1)	53.2 (8)
O3	2115 (3)	1495 (3)	6342 (2)	83 (1)
N	1416 (2)	5555 (3)	6526 (1)	45.4 (8)
C1	4313 (3)	3727 (3)	6695 (2)	55 (1)
C2	2284 (3)	4956 (3)	6359 (2)	42.7 (9)
C3	2461 (3)	2376 (3)	6599 (2)	51 (1)
C4	4844 (3)	4652 (4)	8176 (2)	64 (1)
C5	3681 (4)	3831 (5)	8281 (3)	67 (2)
C6	5495 (3)	2506 (5)	8236 (2)	76 (2)
C7	4519 (5)	2046 (5)	8100 (2)	69 (2)
C8	3593 (3)	2855 (3)	7984 (2)	56 (1)
C9	3748 (3)	4164 (4)	7990 (2)	53 (1)
C10	2864 (3)	4976 (4)	7751 (2)	50 (1)
C11	1862 (3)	4406 (3)	7552 (2)	47 (1)
C12	1012 (3)	5226 (6)	7166 (2)	49 (1)
C13	−104 (3)	4608 (3)	7042 (2)	53 (1)
C14	−951 (3)	5143 (4)	7319 (2)	65 (2)
C15	8039 (4)	4575 (5)	7205 (3)	74 (2)
C16	7898 (3)	3507 (5)	6824 (3)	69 (2)
C17	−1246 (3)	2962 (4)	6529 (3)	60 (1)
C18	−251 (3)	3522 (4)	6657 (2)	55 (1)
C19	8604 (4)	1828 (6)	6091 (3)	85 (2)
C20	831 (3)	6536 (3)	6128 (2)	48 (1)
C21	1076 (4)	7761 (4)	6256 (2)	74 (2)
C22	498 (5)	8700 (4)	5908 (3)	89 (2)
C23	−335 (4)	8388 (5)	5414 (3)	79 (2)
C24	−561 (4)	7172 (5)	5291 (3)	80 (2)
C25	22 (4)	6223 (3)	5640 (2)	67 (2)
C26	3327 (3)	4798 (4)	5419 (2)	65 (1)
C27	3164 (5)	5145 (6)	4696 (2)	94 (2)
C28	4412 (14)	5874 (13)	−46 (5)	184 (7)
C29	3706 (15)	3783 (14)	−132 (7)	240 (9)
C30	4467 (23)	4663 (18)	−53 (7)	122 (7)[a]
C31	4808 (17)	3211 (23)	−26 (8)	152 (8)[a]
C32	3554 (15)	4936 (23)	−100 (11)	158 (9)[a]

[a] Atomic occupanices are 0.5.

Reaction of 2 with 4-Vinylpyridine → [(η^2-$C_6H_5CH{=}CH$)CH(C_6H_5)N(C_6H_5)C(OC_2H_5)=]Fe(CO)$_2$(4-vinylpyridine) (10). To a stirred solution of **2** (0.10 g, 0.22 mmol) in 30 mL of pentane was added 0.10 g (0.9 mmol) of 4-vinylpyridine at −30 °C. The color of the reaction solution changed from orange to red immediately. After the reaction mixture was stirred for 2 h at −25 to −10 °C, the solvent was evaporated and the residue was chromatographed on alumina at −10 °C with pentane/ether (20/1) as eluant. Repeated recrystallization of the crude product from pentane at −80 °C gave 0.05 g (41%, based on **2**) of orange powder, mp 71 °C (dec). IR (ν(CO), KCl) 1935 vs, 1858 vs cm^{-1}; MS, *m/e* 425 ($(M - CH_2{=}CHC_5H_5N - CO)^+$, 16%), 397 ($(M-CH_2{=}CHC_5H_5N - 2CO)^+$, 13%), 105 ($CH_2{=}CHC_5H_5N^+$, 4%). Anal. Calcd for $C_{33}H_{30}O_3N_2Fe$: C, 70.97; H, 5.41; N, 5.01. Found: C, 70.91; H, 5.25; N, 4.80.

X-ray Data Collection and Structure Solution for 3. Single crystals of complex **3** with solvent, [(η^4-$C_6H_5CH{=}CH$)CH(*m*-$CH_3C_6H_4$)N(C_6H_5)C(OC_2H_5)=]Fe(CO)$_2$·$^1/_2C_6H_5CH_3$, were obtained by recrystallization from toluene solution at −35 °C. A single crystal of approximate dimension of 0.27 × 0.35 ×0.50 mm was sealed in a capillary under N_2 for X-ray study. A total of 4593 independent reflections, of which 3293 were observed ($F_o^2 \geq 3\sigma(F_o)^2$), were collected with a Syntex R_3 four-circle diffractometer using Mo Kα radiation by $\theta/2\theta$ scan mode within the range $3° \leq 2\theta \leq 50°$. The LP factors and empirical absorption correction were used to treat the intensity data. The single crystals crystallize in monoclinic system, space group C_{2h}^5—$P2_1/c$ with cell dimensions a = 12.457 (3) Å, b = 10.560 (2) Å, c = 20.072 (4) Å, β = 96.63 (2)°, V = 2622.71 Å^3, Z = 4, D_c = 1.30 g/cm^3, and μ(Mo Kα) = 5.97 cm^{-1}.

The position of the Fe atom was located by the direct method, using the SHELXTL program. The other non-hydrogen atoms,

Table III. Bond Lengths (Å) and Angles (deg) for 3[a]

Bond Lengths

Fe–C1	1.781 (4)	Fe–C2	1.918 (3)	Fe–C3	1.772 (3)	Fe–C8	2.274 (3)
Fe–C9	2.157 (3)	Fe–C10	2.017 (4)	Fe–C11	2.044 (4)	O1–C1	1.142 (5)
O2–C2	1.333 (4)	O3–C3	1.125 (5)	O2–C26	1.439 (5)	N–C2	1.329 (4)
N–C12	1.474 (4)	N–C20	1.452 (4)	C4–C5	1.353 (6)	C5–C6	1.420 (7)
C6–C7	1.309 (7)	C7–C8	1.432 (6)	C8–C9	1.395 (5)	C9–C4	1.467 (5)
C9–C10	1.434 (5)	C10–C11	1.402 (5)	C11–C12	1.510 (5)	C12–C13	1.530 (5)
C13–C14	1.370 (6)	C14–C15	1.393 (6)	C15–C16	1.364 (7)	C16–C17	1.401 (6)
C17–C18	1.370 (5)	C18–C13	1.383 (5)	C19–C17	1.483 (7)	C20–C21	1.347 (5)
C21–C22	1.368 (6)	C22–C23	1.389 (8)	C23–C24	1.332 (7)	C24–C25	1.380 (6)
C25–C20	1.363 (5)	C26–C27	1.488 (6)	C28–C31	1.37 (3)	C31–C29	1.49 (3)
C29–C32	1.24 (3)	C32–C′28	1.45 (3)	C′28–C′30	1.50 (3)	C′30–C28	1.28 (2)
C29–C′30	1.33 (3)						

Bond Angles

C1–Fe–C2	100.8 (2)	C1–Fe–C3	98.9 (2)	C1–Fe–C8	93.8 (1)
C1–Fe–C9	90.4 (2)	C1–Fe–C10	115.8 (2)	C1–Fe–C11	156.1 (1)
C2–Fe–C3	97.2 (1)	C2–Fe–C8	158.9 (1)	C2–Fe–C9	127.4 (1)
C2–Fe–C10	90.9 (1)	C2–Fe–C11	81.0 (1)	C3–Fe–C8	95.4 (1)
C3–Fe–C9	131.9 (2)	C3–Fe–C10	147.3 (2)	C3–Fe–C11	104.6 (1)
C8–C9–C4	118.3 (3)	C8–Fe–C9	36.6 (1)	C8–Fe–C10	67.1 (1)
C8–Fe–C11	79.5 (1)	C9–Fe–C10	40.0 (1)	C9–Fe–C11	70.5 (1)
C10–Fe–C11	40.4 (1)	O1–C1–Fe	173.9 (3)	O3–C3–Fe	172.6 (3)
O2–C2–Fe	132.5 (2)	O2–C2–N	108.6 (3)	Fe–C2–N	118.9 (2)
C12–N–C2	118.5 (3)	C12–N–C20	116.6 (3)	C20–N–C2	124.9 (3)
C5–C4–C9	119.5 (4)	C6–C5–C4	120.3 (4)	C5–C6–C7	121.3 (4)
C6–C7–C8	121.6 (4)	C7–C8–C9	118.4 (4)	C8–C9–C10	119.3 (3)
C4–C9–C10	122.1 (4)	C9–C10–C11	117.5 (3)	C10–C11–C12	116.6 (3)
C11–C12–N	107.0 (3)	C11–C12–C13	114.1 (3)	C13–C12–N	110.7 (3)
C12–C13–C14	119.1 (3)	C12–C13–C18	120.2 (3)	C18–C13–C14	120.7 (4)
C13–C14–C15	119.8 (4)	C14–C15–C16	120.3 (4)	C15–C16–C17	121.5 (4)
C16–C17–C18	117.4 (4)	C16–C17–C19	122.1 (4)	C19–C17–C18	120.6 (4)
C17–C18–C13	121.4 (4)	C21–C20–N	119.5 (3)	C25–C20–N	120.3 (3)
C21–C20–C25	120.2 (3)	C20–C21–C22	120.2 (4)	C21–C22–C23	119.9 (4)
C22–C23–C24	119.0 (4)	C23–C24–C25	121.3 (4)	C20–C25–C24	119.4 (4)
O2–C26–C27	108.7 (3)	C28–C′30–C′28	115 (2)	C28–C31–C29	111 (2)
C31–C28–C′30	132 (2)	C31–C29–C32	122 (2)	C29–C32–C′28	124 (2)
C32–C′28–C′30	115 (2)				

[a] C28 to C32 are the carbon atoms of the solvent molecules; the bond lengths and angles deviated from normal values because of disorder.

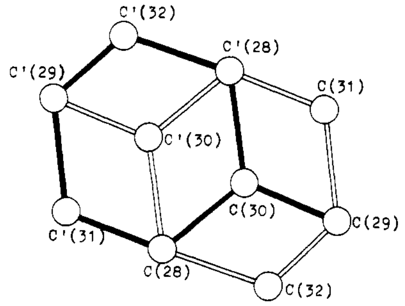

Figure 2. Arrangement of disordered solvent (toluene) molecules.

except those of solvent molecules, were also found from successive Fourier syntheses. The positional parameters, isotropic temperature factors, and scale factor were refined by block-diagonal matrix least squares to give R value of 0.124 ($R = \sum|F_o| - |F_c|/\sum|F_o|$). There were five higher peaks (C28 to C32) on the difference Fourier map. By careful analysis of their positional parameters, it was discovered that the Z coordinates of these peaks are close to zero, while X and Y coordinates are approximately ±0.5. The projection maps on the Z direction appeared to show a disordered arrangement of the solvent molecules (see Figure 2). To further corroborate this assumption, the occupancies of the five atoms were allowed to refine with block-diagonal matrix least squares. The result is that of the occupancies of C28 and C29 still were 1, while those of C30, C31, and C32 were decreased to 0.5. After the disordered solvent molecules were introduced, the refinement of four cycles with anisotropic thermal parameters gave an R value of 0.070. The coordinates of all hydrogen atoms were obtained from difference Fourier synthesis. Final refinement including hydrogen atoms gave an R value of 0.047. The final positional parameters and anisotropic thermal parameters of non-hydrogen atoms including those of solvent molecules are listed in Table II. The bond lengths and angles are given in Table III.

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Registry No. **1**, 12112-97-9; **2**, 110796-11-7; **3**, 110796-12-8; **3**·$^1/_2$$C_7H_8$, 110796-13-9; **4**, 110796-14-0; **5**, 110796-15-1; **6**, 110796-16-2; **7**, 110796-17-3; **8**, 110796-18-4; **9**, 110796-19-5; **10**, 110825-35-9; C_6H_5Li, 591-51-5; *m*-$CH_3C_6H_4Li$, 10325-82-3; *p*-$CF_3C_6H_4Br$, 402-43-7; *p*-$CF_3C_6H_4Li$, 2786-01-8.

Supplementary Material Available: Tables of positional parameters for hydrogen atoms and anisotropic thermal parameters (2 pages); a listing of observed and calculated structure factor amplitudes (20 pages). Ordering information is given on any current masthead page.