isotopes. The measurements of $^{1}J_{SiN}$ in the case of compounds **1**-**9** and for the exocyclic Si-N bonds of compounds **10** and **12** posed no problems. With use of polarization transfer from protons, ^{15}N satellites were observed in the ^{29}Si spectra under "near ultrahigh resolution" conditions (instrumental broadening of 0.02-0.1 Hz) after 50-100 scans, which corresponds to 2-5 min of accumulation. Their detection was significantly facilitated by the broadening of the central line due to the partially relaxed scalar ^{29}Si-^{14}N coupling,[19] the ^{15}N satellites remaining narrow. As has been found earlier,[10] the DEPT sequence is favored in such conditions because of a substantial decrease in the intensity of the central line but not of the ^{15}N satellites.

At low $^{1}J_{SiN}$ values the broadening of the central line in the ^{29}Si spectra was negligible (compounds **6** and **7** and the intracyclic Si atom in compounds **10**-**12**), hence complicating $^{1}J_{SiN}$ measurements.[9] In these cases, ^{29}Si-^{15}N coupling constants were measured by ultrahigh resolution methodology,[21] as described earlier.[22] This enabled, for the first time, the measurement of geminal ^{29}Si-^{29}Si coupling constants via the nitrogen atom in compounds **10**-**12** (see Table I) as well as the observation of ^{15}N satellites in the ^{29}Si spectra of compounds even with two nitrogen atoms at Si (compound **16** and the intracyclic Si atom in compounds **10**-**12**). In the latter case the ^{15}N satellites are also broadened due to partially relaxed scalar ^{29}Si-^{14}N coupling in the ^{15}N-^{29}Si-^{14}N fragment. At higher $^{1}J_{SiN}$ values this broadening was too large to observe the ^{15}N satellites (compounds **13**-**15** and the exocyclic Si atom in compound **12**). In these cases $^{1}J_{SiN}$ were measured in ^{15}N spectra.

With the proton attached to the N atom (compounds **13**-**16**) the INEPT method allows one to observed ^{29}Si satellites in ^{15}N spectra after 2000-4000 scans (1-2 h of accumulation). If several peaks are present in the ^{15}N spectra of silazanes, the ^{29}Si satellites can facilitate their assignment (see Figure 1). In the absence of NH protons, long-range ^{15}N-^{1}H coupling to the SiMe protons of 1-1.5 Hz was assumed for the INEPT sequence[9] permitting observation of ^{29}Si satellites after 6-12 h of accumulation (Figure 2). For the first time, long-range couplings ^{29}Si-^{15}N were observed in ^{15}N spectra (Figures 1 and 2).

Registry No. **1**, 999-97-3; **2**, 3449-26-1; **3**, 7453-26-1; **4**, 3449-24-9; **5**, 114691-61-1; **6**, 1070-89-9; **7**, 22737-37-7; **8**, 7482-02-2; **9**, 91308-43-9; **10**, 2329-10-4; **11**, 13270-82-1; **12**, 13270-86-5; **13**, 1009-93-4; **14**, 50781-21-0; **15**, 1020-84-4; **16**, 63374-38-9.

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Studies on Olefin-Coordinating Transition-Metal Carbene Complexes. 15.[†] Novel Reaction of (Limonene)tricarbonyliron with Nucleophiles: Synthesis, Spectra, and Crystal and Molecular Structure of Several Carbene and Isomerized Carbene Complexes Therefrom

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Reaction of (limonene)tricarbonyliron (**1**) with aryllithium reagents, ArLi (Ar = C_6H_5, *p*-, *o*-$CH_3C_6H_4$, *p*-$CH_3OC_6H_4$, *p*-$CF_3C_6H_4$), in ether at low temperature afforded acylmetalate intermediates. Subsequent alkylation with Et_3OBF_4 in aqueous solution at 0 °C gave five new complexes, $(\eta^4\text{-}C_{10}H_{16})(CO)_2FeC(OC_2H_5)Ar$ (**4**, Ar = *o*-$CH_3C_6H_4$) and $(\eta^3\text{-}C_{10}H_{16})(CO)_2FeC(OC_2H_5)Ar$ (**2**, Ar = C_6H_5; **3**, Ar = *p*-$CH_3C_6H_4$; **5**, Ar = *p*-$CH_3OC_6H_4$; **6**, Ar = *p*-$CF_3C_6H_4$). The structures of two of the new compounds have been determined by X-ray diffraction analyses. Complexes **3** and **4** crystallize in the monoclinic system: space group $P2_1/c$ with a = 14.188 (3) Å, b = 9.157 (2) Å, c = 16.269 (3) Å, β = 106.22 (2)°, V = 2029.5 (8) Å^3, Z = 4, D_{calcd} = 1.30 g/cm^3, R = 0.0318, and R_w = 0.0306 for 1728 reflections with $F_o \geqslant 3\sigma(F_o)$ for **3**; space group $P2_1/a$ with a = 7.795 (5) Å, b = 26.677 (13) Å, c = 9.989 (5) Å, β = 93.19 (4)°, V = 2047.0 (17) Å^3, Z = 4, D_{calcd} = 1.27 g/cm^3, R = 0.0847, and R_w = 0.0616 for 1755 reflections with $F_o \geqslant 3\sigma(F_o)$ for **4**.

Introduction

In recent years, the syntheses and characterizations of olefin-coordinating transition-metal carbene complexes have been of interest in this laboratory.[2-7] In extension of our research, we found that polyolefin ligated carbonyliron compounds reacted with aryllithium reagents to give acylmetalate intermediates that could be alkylated with Et_3OBF_4 to give variety of products. For example, the reaction of (butadiene)- and (isoprene)tricarbonyliron, where the olefin ligands are a straight-chain and a branched-chain conjugated diene, gave a series of novel isomerized olefin-coordinated carbene complexes,[2,3] while in the case of (cyclooctatetraene)-, (cycloheptatriene)-, and (1,3-cyclohexadiene)-, and (norbornadiene)tricarbonyliron a series of novel diallyliron complexes were obtained.[4-7] In the present work, we attempt a similar reaction with (limonene)tricarbonyliron (**1**),[8] where the limonene is

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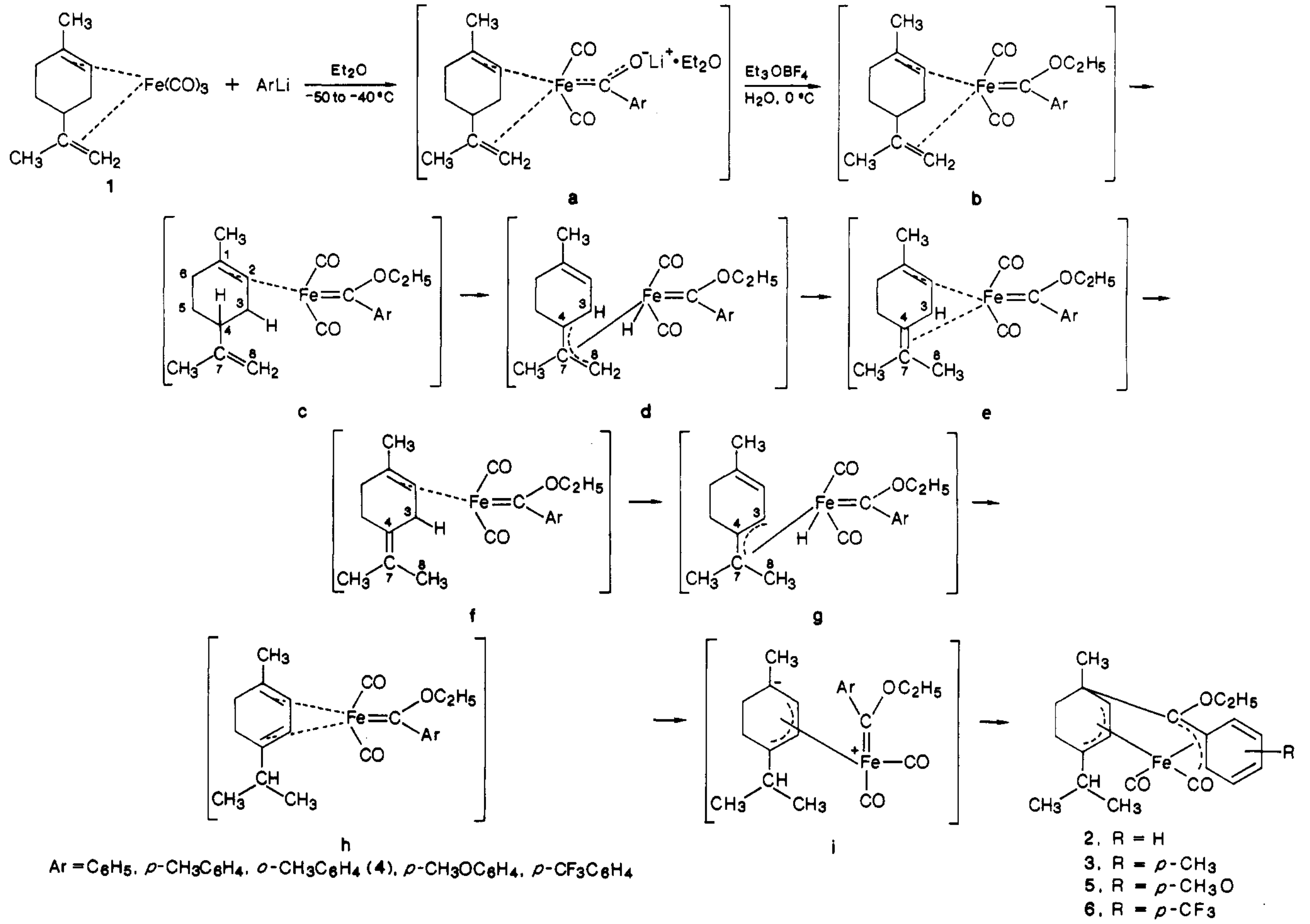
Scheme I



bonded to $Fe(CO)_3$ moiety through two of its nonconjugated double bonds, one of which is a cyclic and the other is an acyclic double bond. Herein we report the syntheses, spectroscopic characterizations, and X-ray diffraction analyses on several carbene and isomerized carbene complexes. We have also discussed the possible reaction mechanism in this paper.

Results and Discussion

Preparation of Complexes 2–6. By analogy with previously described methods,[2] equimolar quantities of 1 and aryllithium, ArLi (Ar = C_6H_5, p-, o-$CH_3C_6H_4$, p-$CH_3OC_6H_4$, p-$CF_3C_6H_4$), were used for the reaction in ether at −50 to −40 °C, and the acylmetalate intermediates obtained were subsequently alkylated with Et_3OBF_4 in aqueous solution at 0 °C. After removal of solvent in a high vacuum, the solid residue was chromatographed on an alumina column at −20 °C, and the crude product was recrystallized from petroleum ether at −80 °C to give the five orange-red crystalline compounds 2–6 of the general composition $C_{10}H_{16}(CO)_2FeC(OC_2H_5)Ar$.

Compounds 2–6 are diamagnetic and readily soluble in both polar and nonpolar solvents. Except 3 and 6, the other are crystals of low melting point, among which 5 is a red oil at room temperature, and the melting point of 4 is only 38 °C dec. They are air-sensitive in solution but relatively stable in the solid state. Compounds 2, 3, and 6 are rather sensitive to temperature; oxidative decomposition occurred on exposure to air at room temperature for a few hours. On the basis of elemental analyses, spectral studies, and single-crystal X-ray structure determinations, compound 4 is formulated as (1-methyl-4-isopropyl-1,3-cyclohexadiene)dicarbonyl[ethoxy(o-tolyl)carbene]iron complex, which is the first example of cyclodiene-coordinated iron carbene complex isolated, and 2, 3, 5, and 6 are formulated as isomerized (limonene)dicarbonyl[ethoxy(aryl)carbene]iron complexes.

The mechanism for formation of 4 and 2, 3, 5, and 6, as shown in Scheme I, may involve a series of 1,3-σ-shifts from 1,5-diene to 1,3-diene to afford 4, followed by 1,4-addition of carbene ligand to the six-membered ring to give 2, 3, 5, and 6. Alkylation of the acylmetalate intermediates **a** formed by the reaction of 1 with aryllithium with Et_3OBF_4 in aqueous solution at 0 °C is proposed to give the unstable ethoxycarbene complexes **b**, which isomerizes to a 16e species (**c**) prior to the formation of the hydride intermediates **d**. The latter than isomerizes to 1,4-diene coordinated compounds **e**. From **b** to **e**, the hydrogen atom at the C-4 ring position migrates to the C-8 position. **e** isomerizes to the other 16e intermediate **f** prior to the formation of **g**. Further isomerization of **g** would give the (1,3-diene)iron–carbene intermediates **h**. Compounds **h** can be isolated as complex 4 (Ar = o-$CH_3C_6H_4$) or subsequently transformed into complexes 2, 3, 5, and 6 via a analogous reaction route involving the transition states **i** (cf. the reaction of (cyclooctatetraene)tricarbonyliron compound[4]), which is rather similar to that of nucleophilic addition on cyclic diene complexes reported by Semmelhack et al.[9]

Interestingly, only when o-tolyllithium was used as the nucleophile, complex 4 was obtained, while when C_6H_5Li,

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Table I. ^{1}H NMR Spectra of Complexes 2–6 in Acetone-d^6 at 20 °C[a]

complex	δ(cycloolefin proton)	δ(OCH_2CH_3)	δ-(OCH_2CH_3)	δ(aryl proton)
2	6.17 (d, 1 H), 5.25 (d, 1 H), 2.60–2.42 (7, 1 H), 1.95–1.84 (m, 2 H), 1.72–1.63 (m, 2 H), 1.20–1.13 (dd, 6 H), 0.83 (s, 3 H)	3.97 (q, 1 H), trans, 3.84 (q, 1 H) cis	1.40 (t, 3 H)	7.82 (m, 1 H), 7.43 (m, 1 H), 7.21 (m, 2 H)
3	6.26 (d, 1 H), 5.20 (d, 1 H), 2.59–2.37 (m, 1 H), 1.94–1.83 (m, 2 H), 1.69–1.59 (m, 1 H), 1.17–1.13 (d, 6 H), 0.82 (s, 3 H)	3.96 (q, 1 H) trans, 3.80 (q, 1 H) cis	1.37 (t, 3 H)	7.78 (m, 2 H), 7.14 (m, 2 H), 2.22 (s, 3 H)
4	5.12 (d, 1 H), 5.00 (d, 1 H), 2.68 (m, 1 H), 2.08 (m, 2 H), 1.88–1.68 (m, 2 H), 1.40 (s, 3 H), 1.10–1.01 (dd, 6 H)	4.71 (q, 2 H)	1.55 (t, 3 H)	7.24 (m, 2 H), 7.16 (m, 2 H), 2.14 (s, 3 H)
5	6.62 (d, 1 H), 5.15 (d, 1 H), 2.62–2.42 (m, 1 H), 2.10 (m, 2 H), 1.80–1.54 (m, 2 H), 1.24–1.08 (dd, 6 H), 0.84 (s, 3 H)	3.96 (q, 1 H) trans, 3.74 (q, 1 H) cis	1.36 (t, 3 H)	7.87 (m, 1 H), 7.44 (m, 1 H), 6.94 (m, 2 H), 3.80 (s, 3 H)
6	5.96 (d, 1 H), 5.38 (d, 1 H), 2.60–2.36 (m, 1 H), 2.00–1.88 (m, 2 H), 1.76–1.60 (m, 2 H), 1.26–1.07 (dd, 6 H), 0.85 (s, 3 H)	4.00 (q, 1 H) trans, 3.85 (q, 1 H) cis	1.39 (t, 3 H)	8.06–7.86 (m, 3 H), 7.35 (m, 1 H)

[a] TMS as internal reference.

p-$CH_3C_6H_4Li$, p-$CH_3OC_6H_4Li$, and p-$CF_3C_6H_4Li$ were used as nucleophiles, diallyl complexes **2**, **3**, **5**, and **6**, respectively, were formed.

Spectral Studies. The IR and characteristic mass spectra peaks (m/e) for complexes 2–6 are given in the Experimental Section. The ^{1}H NMR spectral data of complexes 2–6 in acetone-d_6 at 20 °C are listed in Table I. The assignment of the resonances for **2–6** are based on the structural information elucidated by X-ray structure analyses and on the literature reports.[8,10] All of these complexes showed the complex proton signals attributed to the cycloolefin ligand arising from σ–π rearrangement of the limonene ligand. As a result of rearrangement, the structure of the cycloolefin ligand consists of a η^3-allyl and one carbon atom of limonene ring bonding to the "carbene" carbon atom in complexes **2**, **3**, **5**, and **6** or a η^4-bond coordinating to the iron atom in complex **4**, which led to shifting of the proton signals of the original limonene ligand accordingly.

In addition, as in isomerized (butadiene)- and (cyclooctatetraene)dicarbonyl[ethoxy(aryl)carbene]iron complexes,[2,4] the ^{1}H NMR spectra of **2**, **3**, **5**, and **6** showed two different proton signals assigned to the $-OCH_2-$ group of the $-OCH_2Ch_3$ substituent, which suggests that in solution two possible cis–trans geometrical isomers (with regard to the C(1)–O(1) bond) result from the difference in steric arrangement of the ethyl and aryl groups, since C(1)–O(1) of 1.406 (4) Å is a partial double bond on the basis of the X-ray structure determination of **3**. A possible alternative explanation is two different modes of coordination giving rise to two complexes in equilibrium with one another. However, in the case of **4**, where C(1)–O(1) of 1.324 (17) Å is a shorter double bond, no analogous cis–trans isomers have been observed in the solution. This may be due to the steric hindrance of the methyl group at the o-tolyl substituent.

Structure and Bonding Descriptions of Complexes 3 and 4. The results of the X-ray diffraction analyses of **3** and **4** are illustrated in Figures 1 and 2, respectively. The X-ray structure of complex **3** demonstrates that in the reaction that π bond of the limonene ring has been opened with the aid of the iron medium, causing the C(26) atom to form a new σ bond with the "carbene" carbon atom C(1) and leaving the other three carbon atoms C(21), C(22), and C(23) of the limonene ligand to form an allyl-type $\pi_3{}^3$-bonding orbital[4] which bonds to the iron atom in a side-on mode, resulting in the formation of novel isomerized (limonene)dicarbonyl[ethoxy(aryl)carbene]iron complexes. In molecule **3**, the bonding modes of the central metal with the ligand obeys the "18-electron rule". The iron atom is coordinated by eight carbon atoms. Each of the two CO ligands forms a σ–π bond with the iron atom and provides an iron atom with a pair of electrons. The "carbene" carbon atom C(1) is now bonded to the ethoxy and aryl groups in addition to bonding to C(26) of the limonene ligand, which is similar to that of the isomerized (butadiene)- and (1,3-cyclohexadiene)carbeneiron complexes.[2,6] The three bond angles around C(1) are C(13)–C(1)–O(1) = 144°, C(26)–C(1)–O(1) = 118°, and C(26)–C(1)–C(13) = 125°. The sum is 357; very close to 360°, indicating that C(1) forms three σ bonds with C(13), C(26), and O(1) by using its sp^2-hybridized orbitals and a coordinated π bond with the iron atom by using its approximate pure p$_z$ orbitals. The dihedral angle between the plane of the

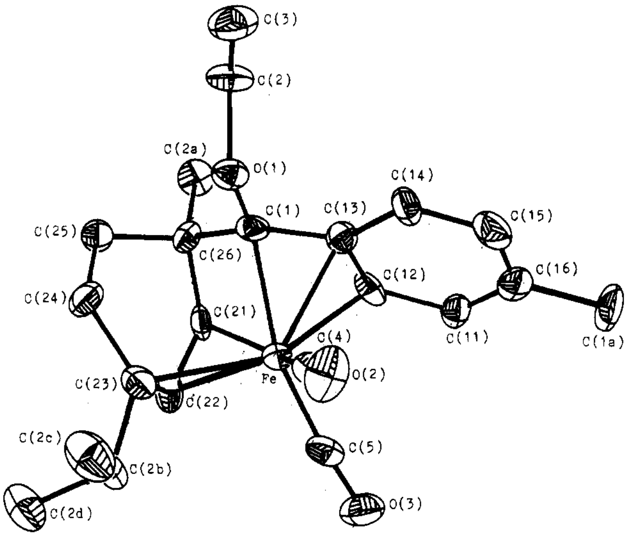

Figure 1. The molecular structure of **3** showing atom-numbering scheme.

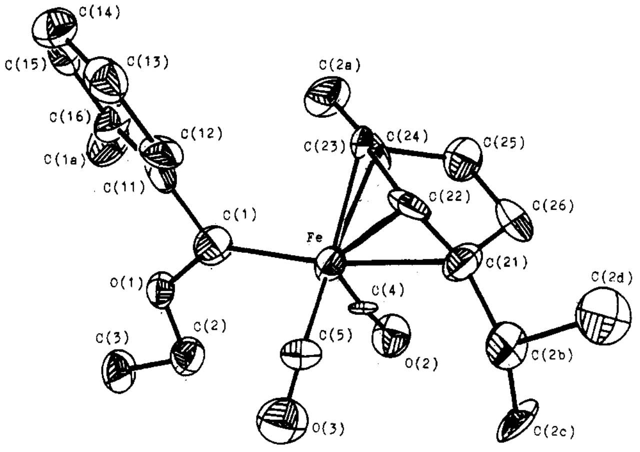

Figure 2. The molecular structure of **4** showing atom-numbering scheme.

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Table II. Crystallographic Data for Complexes 3 and 4

complex	3	4
chemical formula	$C_{22}H_{28}O_3Fe$	$C_{22}H_{28}O_3Fe$
mol wt	396.31	396.31
cryst system	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/a$
a (Å)	14.188 (3)	7.795 (5)
b (Å)	9.157 (2)	26.677 (13)
c (Å)	16.269 (3)	9.989 (5)
β (deg)	106.22 (2)	93.19 (4)
V (Å^3)	2029.5 (8)	2074.0 (17)
Z	4	4
D_{calcd} (g/cm^3)	1.30	1.27
μ(Mo Kα) (cm^{-1})	7.8	7.7
F(000)	840	840

benzene ring and the plane composed of Fe, C(12), and C(13) is 115.6°; hence, the π molecular oribtals composed of the C(12) and C(13) atoms of the coordinated benzene ring interact with the iron atom and provide a pair of π-electrons. In addition, since the C(1)C(13)C(2)O(1) plane is approximately parallel to the plane of the benzene ring (the dihedral angle is only 8.7°), the p_z orbital of the C(1) atom is parallel to that of the C(12) and C(13) atoms and a three-electronic group molecular orbital composed of the three p_z orbitals of the C(1), C(13), and C(12) atoms can be formed and further coordinated with the iron atom. The Fe–C(1), Fe–C(13), and Fe–C(12) bond lengths are 2.075 (4), 2.13 (4), and 2.277 (4) Å, respectively. The C(24), C(25), and C(26) atoms of the limonene ligand form bonds by using their sp^3-hybridized orbitals. From the bond angles given in Table IV, it can be seen that the C(21), C(22), and C(23) atoms form bonds with the adjacent carbon and hydrogen atoms by using their sp^2-hybridized orbitals, construct the second group molecular orbital by using their three pure p_z orbitals to coordinate with the iron atom, and provide three electrons to satisfy the 18-electron rule.

In complex 4, the bonding mode of the central metal atom with the ligands is still governed by the 18-electron rule. The carbene carbon C(1) is directly bonded to the iron atom. The Fe–C(1) bond length of 1.915 (15) Å indicates that there exists a high degree of π-bond character in this bond. The sum of the bond angles of Fe–C(1)–O(1) of 130.5 (11)°, Fe–C(1)–C(11) of 123.9 (10)°, and O(1)–C(1)–C(11) of 105.3 (11)° is 359.7°, which only slightly deviates from 360°. Thus, it can be concluded that the carbene carbon C(1) forms three bonds with Fe, O(1), and C(11) by using its sp^2-hybridized orbitals and should independently provide a pair of electrons to form a coordinate π bond with the iron atom. Each of the two CO ligands forms a σ–π bond with the iron atom and provides the Fe atom with a pair of electrons. The average Fe–C bond length is 1.750 Å. In the limonene ligand, the C(25) and C(26) atoms form the bonds by using their sp^3-hybridized orbitals, while the carbon atoms C(21), C(22), C(23), and C(24) form the bonds with the adjacent carbon and hydrogen atoms by using their sp^2-hybridized orbitals, compose a group molecular orbital by using their four pure p_z orbitals to combine with the iron atom, with the average Fe–C bond length of 2.098 Å, and provide four electrons to satisfy the 18-electron rule.

Complexes 3 and 4 are isomers. The difference between the two structures arises only from the different aryl substituent bonded to the carbene carbon atom. Considering the steric hindrance, the paramethyl group of tolyl substituent does not influence the dense packing of the molecule. The two carbon atoms C(12) and C(13) of the benzene ring are coordinated to the iron atom, and the carbene carbon C(1) is bonded to C(26) atom of the limonene ring. The iron atom is combined with eight carbon atoms. Thus, the molecular structure appears to be more compact.

Experimental Section

IR, ^{1}H NMR, and mass spectra were measured on a Zeiss Specord-75 spectrophotometer, a Varian XL-200 spectrometer, and a Finnigan 4021 GC/MS/DS spectrometer, respectively.

All manipulations were carried out under prepurified N_2 atmosphere with standard Schlenk techniques. All solvents used were distilled from CaH_2, sodium benzophenone ketyl, and P_2O_5, respectively, and purged with N_2. The 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. Compound 1,[8] Et_3OBF_4,[11] and aryllithium reagents[12–16] em-

Table III. Atom Coordinates (×10^4) and Temperature Factors (×10^3) for 3 and 4

	3				4			
atom	x	y	z	U_{eq}, Å^2	x	y	z	U_{eq}, Å^2
Fe	2027 (1)	6921 (1)	5061 (1)	25 (1)	3125 (3)	1262 (1)	225 (2)	29 (1)
O(1)	3886 (2)	7744 (3)	4538 (2)	28 (1)	2626 (12)	921 (4)	−2581 (8)	32 (4)
O(2)	2882 (2)	9330 (3)	6205 (2)	47 (1)	1569 (13)	347 (4)	1229 (10)	42 (4)
O(3)	614 (2)	6092 (3)	5994 (2)	49 ((1)	83 (14)	1817 (4)	−654 (10)	51 (4)
C(1)	3193 (3)	6648 (4)	4539 (2)	25 (2)	3531 (19)	1167 (6)	−1631 (14)	38 (6)
C(2)	4733 (3)	7250 (4)	4290 (3)	34 (2)	1261 (19)	583 (6)	−2313 (14)	43 (6)
C(3)	5517 (3)	8359 (5)	4573 (3)	41 (2)	847 (22)	264 (7)	−3506 (15)	55 (7)
C(4)	2548 (3)	8370 (4)	5764 (2)	29 (2)	2192 (15)	696 (5)	761 (12)	22 (5)
C(5)	1142 (3)	6464 (4)	5608 (2)	31 (2)	1320 (18)	1596 (6)	−327 (14)	44 (6)
C(11)	2898 (3)	4120 (5)	6287 (3)	37 (2)	4960 (20)	1423 (5)	−2340 (12)	34 (5)
C(12)	2757 (3)	4715 (4)	5450 (2)	30 (2)	5235 (18)	1949 (5)	−2217 (14)	37 (6)
C(13)	3402 (3)	5804 (4)	5315 (2)	22 (1)	6454 (19)	2189 (6)	−2868 (14)	43 (6)
C(14)	4187 (3)	6219 (4)	6046 (2)	29 (2)	7589 (19)	1913 (6)	−3658 (14)	44 (6)
C(15)	4295 (3)	5620 (5)	6821 (2)	40 (2)	7377 (20)	1402 (6)	−3769 (14)	43 (6)
C(16)	3640 (3)	4552 (5)	6963 (3)	37 (2)	6111 (19)	1139 (5)	−3175 (13)	35 (6)
C(21)	1557 (3)	5831 (4)	3853 (2)	30 (2)	3130 (18)	1553 (6)	2234 (13)	31 (5)
C(22)	942 (3)	6985 (5)	3897 (2)	30 (2)	4203 (17)	1814 (6)	1389 (14)	36 (6)
C(23)	1318 (3)	8409 (4)	4004 (2)	29 (2)	5512 (19)	1534 (7)	835 (12)	39 (6)
C(24)	2009 (3)	8794 (5)	3472 (3)	32 (2)	5567 (19)	1032 (6)	1132 (13)	36 (6)
C(25)	2360 (3)	7479 (4)	3071 (2)	30 (2)	5349 (20)	840 (7)	2582 (15)	52 (7)
C(26)	2535 (3)	6149 (4)	3676 (2)	28 (2)	4017 (19)	1175 (6)	3196 (14)	50 (7)
C(1a)	3813 (4)	3905 (6)	7842 (3)	62 (2)	5905 (22)	578 (6)	−3398 (17)	54 (7)
C(2a)	2910 (3)	4828 (5)	3289 (3)	39 (2)	6803 (22)	670 (7)	407 (17)	58 (8)
C(2b)	696 (3)	9638 (5)	4179 (3)	38 (2)	1490 (21)	1835 (6)	2743 (15)	50 (7)
C(2c)	1250 (3)	11057 (5)	4456 (3)	49 (2)	−50 (20)	1480 (7)	2960 (14)	57 (7)
C(2d)	−198 (4)	9914 (7)	3401 (3)	63 (2)	2053 (25)	2128 (8)	4086 (20)	81 (9)

Table IV. Selected Bond Lengths (Å) and Angles ((deg) for 3 and 4

	3	4		3	4		3	4
Fe–C(1)	2.075 (4)	1.915 (15)	O(2)–C(4)	1.149 (5)	1.161 (17)	C(15)–C(16)	1.413 (6)	1.372 (21)
Fe–C(4)	1.773 (4)	1.771 (14)	O(3)–C(5)	1.155 (5)	1.162 (18)	C(21)–C(22)	1.385 (6)	1.406 (20)
Fe–C(5)	1.781 (4)	1.729 (15)	C(2)–C(3)	1.482 (6)	1.486 (22)	C(21)–C(26)	1.522 (6)	1.531 (21)
Fe–C(12)	2.277 (4)		C(1)–C(11)		1.515 (21)	C(22)–C(23)	1.402 (6)	1.403 (21)
Fe–C(13)	2.138 (4)		C(1)–C(26)	1.523 (5)		C(23)–C(24)	1.519 (7)	1.374 (23)
Fe–C(21)	2.139 (4)	2.152 (13)	C(1)–C(13)	1.439 (5)		C(24)–C(25)	1.518 (6)	1.554 (20)
Fe–C(22)	2.081 (3)	2.029 (15)	C(11)–C(12)	1.427 (6)	1.424 (21)	C(25)–C(26)	1.541 (6)	1.526 (23)
Fe–C(23)	2.205 (4)	2.058 (15)	C(11)–C(16)	1.352 (5)	1.468 (20)	C(21)–C(2b)		1.590 (22)
Fe–C(24)		2.152 (14)	C(12)–C(13)	1.412 (6)	1.344 (21)	C(23)–C(2b)	1.506 (6)	
O(1)–C(1)	1.406 (4)	1.324 (17)	C(13)–C(14)	1.436 (5)	1.424 (22)	C(2b)–C(2c)	1.520 (6)	1.552 (24)
O(1)–C(2)	1.443 (5)	1.431 (18)	C(14)–C(15)	1.343 (6)	1.377 (22)	C(2b)–C(2d)	1.543 (6)	1.594 (25)
C(1)–Fe–C(4)	96.8 (2)	105.8 (6)	C(13)–Fe–C(21)	89.3 (2)		Fe–C(1)–C(13)	72.4 (2)	
C(1)–Fe–C(5)	158.5 (2)	86.3 (7)	C(13)–Fe–C(22)	126.3 (3)		Fe–C(1)–C(26)	93.5 (2)	
C(1)–Fe–C(21)	69.3 (1)	163.6 (6)	C(13)–Fe–C(23)	129.7 (2)		Fe–C(12)–C(11)	122.4 (3)	
C(1)–Fe–C(22)	95.9 (1)	124.5 (6)	C(21)–Fe–C(22)	38.3 (2)	39.1 (6)	Fe–C(12)–C(13)	66.1 (2)	
C(1)–Fe–C(23)	89.9 (1)	97.9 (6)	C(21)–Fe–C(23)	67.3 (1)	69.0 (5)	Fe–C(13)–C(1)	67.7 (2)	
C(1)–Fe–C(24)		100.4 (6)	C(21)–Fe–C(24)		75.8 (5)	Fe–C(13)–C(12)	76.8 (2)	
C(1)–Fe–C(12)	69.8 (2)		C(22)–Fe–C(23)	38.0 (2)	40.2 (6)	Fe–C(13)–C(14)	119.2 (3)	
C(1)–Fe–C(13)	39.9 (1)		C(22)–Fe–C(24)		68.8 (6)	Fe–C(21)–C(22)	68.6 (2)	65.7 (8)
C(4)–Fe–C(5)	94.5 (2)	101.2 (7)	C(23)–Fe–C(24)		38.0 (6)	Fe–C(21)–C(26)	91.0 (2)	109.0 (10)
C(4)–Fe–C(12)	114.1 (1)		C(21)–C(2b)–C(2c)		133.5 (13)	Fe–C(22)–C(21)	73.1 (2)	75.2 (8)
C(4)–Fe–C(13)	92.3 (2)		C(21)–C(2b)–C(2d)		108.2 (12)	Fe–C(22)–C(23)	75.7 (2)	71.0 (9)
C(4)–Fe–C(21)	155.4 (2)	90.3 (6)	C(23)–C(2b)–C(2c)	114.4 (4)		Fe–C(23)–C(22)	66.2 (2)	68.8 (8)
C(4)–Fe–C(22)	129.4 (2)	127.5 (6)	C(23)–C(2b)–C(2d)	110.9 (4)		Fe–C(23)–C(24)	111.2 (3)	74.7 (9)
C(4)–Fe–C(23)	93.3 (2)	126.6 (6)	C(2c)–C(2b)–C(2d)	110.0 (4)	110.7 (10)	Fe–C(24)–C(23)		67.3 (8)
C(4)–Fe–C(24)		89.8 (6)	C(1)–O(1)–C(2)	114.4 (3)	123.4 (11)	Fe–C(24)–C(25)		110.3 (10)
C(5)–Fe–C(12)	88.9 (2)		O(1)–C(2)–C(3)	108.0 (3)	110.0 (12)	C(1)–C(26)–C(21)	103.8 (3)	
C(5)–Fe–C(13)	121.6 (2)		O(1)–C(1)–C(11)		105.3 (11)	C(1)–C(26)–C(25)	107.4 (3)	
C(5)–Fe–C(21)	105.5 (2)	94.1 (6)	O(1)–C(1)–C(13)	114.3 (3)		C(21)–C(22)–C(23)	119.5 (3)	116.3 (14)
C(5)–Fe–C(22)	90.9 (2)	96.5 (7)	O(1)–C(1)–C(26)	117.6 (3)		C(22)–C(23)–C(24)	115.4 (4)	116.7 (13)
C(5)–Fe–C(23)	107.7 (2)	128.3 (7)	C(13)–C(1)–C(26)	124.8 (3)		C(22)–C(21)–C(26)	119.0 (4)	116.1 (12)
C(5)–Fe–C(24)		165.1 (7)	Fe–C(1)–O(1)	123.5 (3)	130.5 (11)	C(23)–C(24)–C(25)		121.3 (13)
C(12)–Fe–C(21)	80.9 (1)		Fe–C(4)–O(2)	178.5 (3)	173.5 (11)	C(12)–C(13)–C(1)	122.2 (3)	
C(12)–Fe–C(22)	116.2 (2)		Fe–C(5)–O(3)	175.1 (3)	177.6 (13)	C(12)–C(13)–C(14)	116.4 (3)	
C(12)–Fe–C(23)	147.0 (1)		Fe–C(1)–C(11)		123.9 (10)	C(14)–C(13)–C(1)	120.4 (3)	

Table V. Least-Squares Planes for Complexes 3 and 4

complex	plane	eq, atoms and composing plane, and dev of atoms (Å)	sum of inner angles (deg)	dihedral angles (deg)
3	1	$9.476x - 6.535y - 6.334z = -3.93$ C(11), C(12), C(13), C(14), C(15), C(16) 0.00, 0.01, –0.01, 0.00, 0.01, –0.01	720.0 (4)	89.2
	2	$5.984x + 0.988y + 12.147z = 6.24$ C(21), C(22), C(23), C(24), C(25), C(26) –0.05, –0.25, 0.24, 0.06, –0.36, 0.35	685.3 (4)	
4	1	$4.507x - 3.789y + 7.692z = -0.11$ C(11), C(12), C(13), C(14), C(15), C(16) –0.01, 0.02, –0.01, –0.01, 0.02, –0.01	719.9 (10)	39.6
	2	$5.187x + 12.960y + 5.282z = 5.12$ C(21), C(22), C(23), C(24), C(25), C(26) –0.32, 0.16, 0.17, –0.29, 0.09, 0.18	691.4 (9)	

ployed were prepared by literature methods.

1. **Preparation of $C_{10}H_{16}(CO)_2FeC(OC_2H_5)C_6H_5$ (2).** To a solution of 1.0 g (3.6 mmol) of 1 in 50 mL of ether was added dropwise 3.6 mmol of C_6H_5Li[12] in 15 mL of ether at –70 °C. The reaction mixture was allowed to warm to –50 °C and stirred at –50 to –40 °C for 3 h. The color of mixture changed gradually from orange-red to dark red. After evaporation of solvent under vacuum, to the dark red solid residue obtained was added Et_3OBF_4 (ca. 1 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 portionwise, with strong stirring, to the aqueous solution until it became acidic. The aqueous solution was extracted with petroleum ether. The combined extract was dried over anhydrous Na_2SO_4. After removal of solvent under vacuum, the residue was chromatographed on an alumina column at –25 °C with petroleum ether followed by petroleum ether/ether (10/1) as eluant. Removal of solvent under vacuum and recrystallization of crude product from petroleum ether at –80 °C gave 0.50 g (36%, based on 1) of red crystals, mp 79–80 °C dec. Anal. Calcd for $C_{21}H_{26}O_3Fe$ (mol wt 382.29): C, 65.98; H, 6.86; Fe, 14.61. Found: C, 65.76; H, 7.00; Fe, 14.29. IR [ν(CO)]: 1968 vs, 1903 vs cm^{-1} (CH_2Cl_2); 1986 vs, 1933 vs cm^{-1} (cyclohexane). MS: *m/z* (relative intensity) 382 $[M]^+$ (8.9), 354 $[M - CO]^+$ (26.6), 326 $[M - 2CO]^+$ (100).

2. **Preparation of $C_{10}H_{16}(CO)_2FeC(OC_2H_5)C_6H_4CH_3$-*p* (3).** The reaction of 2.0 g (7.2 mmol) of 1 with 7.2 mmol of *p*-$CH_3C_6H_4Li$[13] at –50 °C in a similar manner as described in preparation 1 gave 1.3 g (45%, based on 1) of orange-red crystals, mp 79–81 °C dec. Anal. Calcd for $C_{22}H_{28}O_3Fe$ (mol wt 396.31): C, 66.68; H, 7.12; Fe, 14.09. Found: C, 66.97; H, 7.11; Fe, 13.80. IR [ν(CO)]: 1967 vs, 1902 vs cm^{-1} (CH_2Cl_2); 1983 vs, 1923 vs cm^{-1} (cyclohexane). MS: *m/z* (relative intensity) 396 $[M]^+$ (0.8), 368 $[M - CO]^+$ (7.8), 340 $[M - 2CO]^+$ (100).

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3. Preparation of $C_{10}H_{16}(CO)_2FeC(OC_2H_5)C_6H_4CH_3$-*o* (4). 1 (2.0 g, 7.2 mmol) reacted with 7.2 mmol of *o*-$CH_3C_6H_4Li$[13] at −40 °C for 3 h followed by the alkylation and further treatment similar to the procedures described above for 2 gave 1.1 g (38%, based on 1) of orange-red crystals, mp 38 °C dec. Anal. Calcd for $C_{22}H_{28}O_3Fe$ (mol wt 396.31): C, 66.68; H, 7.12; Fe, 14.09. Found: C, 66.38; H, 7.30; Fe, 13.86. IR [ν(CO)]: 1955 vs, 1901 vs cm^{-1} (CH_2Cl_2); 1974 sh, 1960 vs, 1930 sh, 1915 vs cm^{-1} (cyclohexane). MS: *m/z* (relative intensity) 396 $[M]^+$ (4.5), 368 $[M - CO]^+$ (7.0), 340 $[M - 2CO]^+$ (100).

4. Preparation of $C_{10}H_{16}(CO)_2FeC(OC_2H_5)C_6H_4OCH_3$-*p* (5). *n*-$C_4H_9Li$[14] (7.4 mmol) was mixed with a solution of 1.40 g (7.4 mmol) of *p*-$CH_3OC_6H_4Br$ in 15 mL of ether. The mixture was stirred at room temperature for 1 h. The resulting ether solution of *p*-$CH_3OC_6H_4Li$[15] reacted with 2.0 g (7.2 mmol) of 1 in 50 mL of ether at −50 °C for 3 h. Subsequent alkylation and treatment in a similar manner as described in preparation 1 afforded 1.2 g (40%, based on 1) of red oil. Anal. Calcd for $C_{22}H_{28}O_4Fe$ (mol wt 412.31): C, 64.09; H, 6.85; Fe, 13.54. Found: C, 64.02; H, 6.84; Fe, 13.25. IR [ν(CO)]: 1962 vs, 1895 vs cm^{-1} (CH_2Cl_2); 1977 vs, 1960 sh, 1915 vs cm^{-1} (cyclohexane). MS: *m/z* (relative intensity) 412 $[M]^+$ (5.3), 384 $[M - CO]^+$ (14.3), 356 $[M - 2CO]^+$ (90.0).

5. Preparation of $C_{10}H_{16}(CO)_2FeC(OC_2H_5)C_6H_4CF_3$-*p* (6). 1 (2.0 g, 7.2 mmol) reacted, in a manner similar to that described in preparation 1, with fresh *p*-$CF_3oC_6H_4Li$[16] prepared by reaction of 1.63 g (7.2 mmol) of *p*-$CF_3C_6H_4Br$ with 7.2 mmol of *n*-C_4H_9Li, in ether solution at −45 °C for 3 h to give 1.40 g (43%, based on 1) of red crystals, mp 82 °C dec. Anal. Calcd for $C_{22}H_{25}O_3F_3Fe$ (mol wt 450.28): C, 58.68; H, 5.60; Fe, 12.66. Found: C, 59.16; H, 5.63; Fe, 12.70. IR [ν(CO)]: 1980 vs, 1917 vs cm^{-1} (CH_2Cl_2); 1997 vs, 1940 vs cm^{-1} (cyclohexane). MS: *m/z* (relative intensity) 450 $[M]^+$ (6.4), 422 $[M- CO]^+$ (41.5), 394 $[M- 2CO]^+$ (100).

Crystal Structure Determination. The single crystals of 3 and 4 suitable for X-ray diffraction study were obtained by recrystallization from petroleum ether at −80 °C. A single crystal of approximate dimension of 0.20 × 0.30 × 0.30 mm for 3 and 0.20 × 0.30 × 0.40 mm for 4 were sealed in capillaries under N_2 atmosphere. The X-ray diffraction intensity data of 2476 and 2986 independent reflections, of which 1728 and 1755 with $F_o \geqslant 3\sigma(F_o)$ were observable, were collected with a R_3M/E four-circle diffractometer at −90 °C using Mo Kα radiation with a $\theta/2\theta$ scan mode within the ranges $3° \leq 2\theta \leq 42°$ and $3° \leq 2\theta \leq 45°$ for 3 and 4, respectively. The intensity data were corrected for Lorentz and Polarization factors, but no absorption correction was made.

3 and 4 crystallize in the monoclinic system. The space groups for 3 and 4 were determined to be $P2_1/c$ and $P2_1/a$, respectively, according to the following systematic absences: $h0l$ reflections, $l = 2n + 1$ for 3 and $h = 2n + 1$ for 4; $0k0$ reflections, $k = 2n + 1$ for 3 and 4.

The crystal structures of 3 and 4 were solved by using the Patterson function method. After the position of the Fe atom was determined, the coordinates of the other non-hydrogen atoms were located by the Fourier synthesis. The coordinates of all hydrogen atoms of 3 were located at difference Fourier map and those of 4 were obtained by theoretical calculation. The coordinates and thermal parameters of all the atoms of 3 and 4 were refined by a block-diagonal-matrix least-squares method to give the final discrepancy indices $R = 0.0318$ and $R_w = 0.306$ and $R = 0.0847$ and $R_w = 0.0616$ for 3 and 4, respectively. The crystallographic data for 3 and 4 are listed in Table II. The atomic coordinates and temperature factors of non-hydrogen atoms for 3 and 4 are presented in Table III. The bond lengths and angles and the equations of the least-squares planes for 3 and 4 are given in Tables IV and V, respectively.

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Registry No. 1, 98212-66-9; 2, 114719-40-3; 3, 114719-41-4; 4, 114719-42-5; 5, 114719-43-6; 6, 114719-44-7; a (Ar = Ph), 114719-45-8; a (Ar = *p*-MeC_6H_4), 114719-46-9; a (Ar = *o*-MeC_6H_4), 114719-47-0; a (Ar = *p*-$MeOC_6H_4$), 114719-48-1; a (Ar = *p*-$CF_3C_6H_4$), 114719-49-2.

Supplementary Material Available: Table of H-atom coordinates and isotropic thermal parameters and anisotropic thermal parameters for complexes 3 and 4, the selected mass spectra of complexes 2–6, and the unit cell drawings of complexes 3 and 4 (7 pages); a listing of observed and calculated structure factor amplitudes (18 pages). Ordering information is given on current masthead page.

Communications

Reaction of Sulfur Dioxide with $(\eta^5\text{-}C_5Me_5)Ru(CO)_2H$: Insertion of SO_2 into the Ru–H Bond and Oxygen Transfer To Form $(\eta^5\text{-}C_5Me_5)Ru(CO)_2SO_3H$

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Summary: The addition of SO_2 to $(\eta^5\text{-}C_5Me_5)Ru(CO)_2H$ yields $(\eta^5\text{-}C_5Me_5)Ru(CO)_2SO_3H$. Reaction of the starting hydride with $S^{18}O_2$ results in the formation of the product with a completely labeled SO_3H ligand, demonstrating that SO_2 provides the additional oxygen atom for the formation of this ligand.

Any process that will convert SO_2 in stack gases to inoffensive products such as sulfur and water will be based on the reduction/oxygen transfer chemistry of SO_2. To better understand this chemistry, we have been investigating reactions of SO_2 with transition-metal hydride complexes.[1,2] This work has now been extended to include the addition of SO_2 to $Cp^*Ru(CO)_2H$ ($Cp^* = \eta^5\text{-}C_5Me_5$).

Reactions of SO_2 with metal hydride species typically give products containing ligands formed from reduction of SO_2.[1-3] In particular, we have achieved partial reductions of SO_2 on Mo and W centers:[1,2]

$$CpM(CO)_3H + SO_2 \rightarrow CpM(CO)_3(SO_2H) \qquad (1)$$

$$Cp_2MH_2 + 2SO_2 \rightarrow Cp_2M(S_2O_3) + H_2O \qquad (2)$$

The SO_2H complexes are thermally unstable and undergo autoredox reactions to form oxo–sulfide clusters. In the $Cp^*Ru(CO)_2H$ case, however, a structural study revealed

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