Thermolysis of Iron *N*-Allylaminocarbene Complexes: Formation of η^3-1-Azaallylirontricarbonyl Complexes. Synthetic and Theoretical Study

Luděk Meca,[†] Ivana Císařová,[‡] and Dalimil Dvořák*,[†]

Department of Organic Chemistry, Prague Institute of Chemical Technology, Technická 5, 166 28 Prague 6, Czech Republic, and Department of Inorganic Chemistry, Charles University, Hlavova 2030, 128 40 Prague 2, Czech Republic

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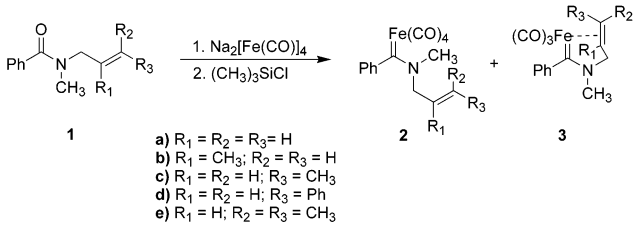
Both chelated and nonchelated *N*-allyl-*N*-methylaminocarbene complexes of iron unsubstituted at the 1- and 3-positions of an allyl substituent afforded by thermolysis new η^3-iron tricarbonyl complexes of 2,3-dihydropyrrole. The proposed mechanism of these reactions involves bicyclo[2.1.1]-2-aza-5-ferrahexane as an intermediate formed by [2+2] cycloaddition. Formation of this intermediate requires antiparallel arrangement of Fe=C and C=C double bonds in the cycloaddition step. This mechanism was supported by reaction of deuterium-labeled complexes and by the density functional calculations of B3LYP quality. The structure of tricarbonyl[(η^3-*N*-methyl-2-(biphenyl-4-yl)-4,5-dihydropyrrole]iron(0) (**4f**) has been determined by X-ray diffraction.

Introduction

N-Allylaminocarbene complexes of group 6 transition metals and their carba analogues are known to form stable chelates.[1] These compounds were used as models for the study of coordination of alkene to metal carbene, the first step in the reaction of Fischer carbene complexes with alkenes. Thermal reaction of group 6 metal *N*-allylaminocarbenes with alkynes was reported to form 3-azabicyclo[4.1.0]heptane derivatives as a result of metathesis followed by intramolecular cyclopropanation.[2] In some cases also a ring expansion with formation of dihydroazepine derivatives[2b] or CO insertion with formation of 2-pyrrolinones[3] was observed. To the best of our knowledge productive thermolysis of *N*-allylaminocarbene complexes of transition metals has never been reported. Recently we have observed unexpected formation of a tetrahydropyridine derivative in the course of thermolysis of an *N*-homoallylaminocarbene complex of iron.[4] Because of the different behavior of iron compared to chromium in the above reaction, the study of thermolysis of iron *N*-allyl-*N*-methylaminocarbene complexes was undertaken.

Scheme 1



Results and Discussion

Starting *N*-allyl-*N*-methylaminocarbene complexes were prepared using the Hegedus method[5] by reaction of the corresponding carboxamide with $Na_2Fe(CO)_4$ in the presence of Me_3SiCl.[6] The reaction produced a mixture of chelated *Z*-complexes **2** and nonchelated *E*-carbenes **3** (Scheme 1).[7]

Thermolysis of the mixture of iron *N*-methyl-*N*-allylaminocarbene complexes **2a** and **3a** in toluene solution at 100 °C resulted in formation of a new iron complex. IR revealed the presence of carbonyl ligands. The ^{1}H NMR spectrum showed, besides aromatic protons and the signal of the *N*-methyl group at 2.69 ppm, five separated one-proton signals, four multiplets at 2.09, 2.49, 2.64−2.71, and 2.92 ppm. These signals can be attributed to four protons of two CH_2 groups, and a doublet at 3.06 ppm (J = 4.0 Hz) was assigned to the proton on the coordinated double bond. ^{13}C NMR

* Corresponding author. E-mail: dvorakd@vscht.cz. Fax: ++ 420-2-24354288.
[†] Prague Institute of Chemical Technology.
[‡] Charles University.

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(7) Iron complexes **2** and **3** were obtained as inseparable mixtures. Since **2** and **3** are not isomers, elemental analysis cannot be used for their characterization. Also characterization using MS is problematic. The molecular ion of iron aminocarbene complexes splits[6] CO, which in the case of **2** gives the fragment identical with [M$^+$] of **3**. Therefore carbene complexes **2a**−**e** and **3a**,**b**,**f** were characterized only by ^{1}H and ^{13}C NMR and IR spectroscopy.

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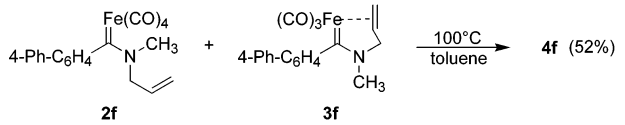
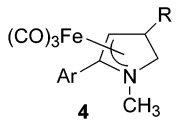
Scheme 2



excluded the presence of a carbene ligand with a characteristic signal around 270 ppm. Instead, a signal of the carbonyl ligand at 213.7 ppm and the signals of the carbons of the coordinated double bond, the quaternary carbon at 93.4 ppm and a signal of the CH group at 46.9 ppm, were observed together with two signals of CH_2 groups (59.3 and 32.6 ppm) and the signal of the NCH_3 group at 43.8 ppm. The connectivities obtained from COSY, HETCOR, and HMBC experiments were in agreement with structure **4a**. However, all attempts to liberate free 1-methyl-2-phenyl-4,5-dihydropyrrole ligand (by oxidation with trimethylamine *N*-oxide, Fe(III) or Ce(IV) salts) have failed. Also attempts to prepare **4a** by direct complexation of independently prepared 1-methyl-2-phenyl-4,5-dihydropyrrole[8] with $Fe(CO)_5$ or $Fe_2(CO)_9$ have not been successful.



4

a) Ar = Ph, R = H
b) Ar = Ph, R = CH_3
f) Ar = 4-Ph-C_6H_4, R = H

The substitution pattern of the allyl group of the starting carbene complex has substantial influence on the outcome of the reaction. The mixture of carbene complexes bearing a methyl group at position 2 of the allyl substituent, **2b** and **3b**, afforded the corresponding dihydropyrrole complex **4b** in 62% yield. On the contrary, 3-substituted or 3,3-disubstituted derivatives did not give a dihydropyrrole complex, instead quantitative formation of chelates **3c**−**e** occurred.

Due to low melting point, the complex **4a** was not suitable for X-ray structure analysis. Therefore the mixture of chelated and nonchelated iron (*N*-allyl-*N*-methylamino)-4-fenylfenylcarbene complexes **2f** and **3f** was prepared from the corresponding amide **1f** and thermolyzed, giving crystalline 1-methyl-2-(4-phenylphenyl)-4,5-dihydropyrrole iron tricarbonyl complex **4f** (Scheme 2). Crystallization from a mixture of diethyl ether and *n*-pentane afforded single crystals of **4f** suitable for X-ray analysis.

The structure of compound **4f** was confirmed by the single-crystal X-ray diffraction analysis (see Figure 1). The selected bond distances and angles (Table 1) are consistent with parameters of the Fe -η^3-N−C═C moiety found in the literature,[9,10] witnessing η^3-coordination of metal to the dihydrogen pyrrole as well as delocalization of the double bond (C2−C3) along the N1−C2−C3 moiety.

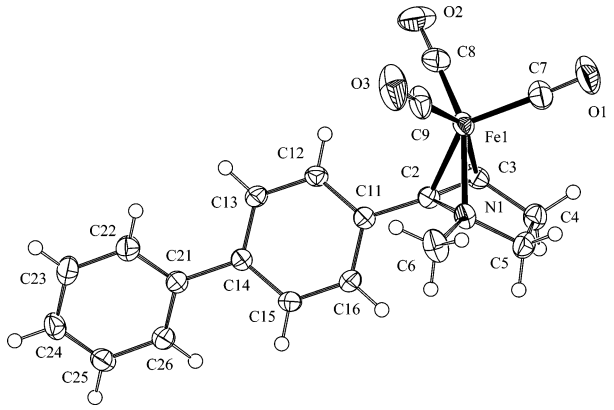
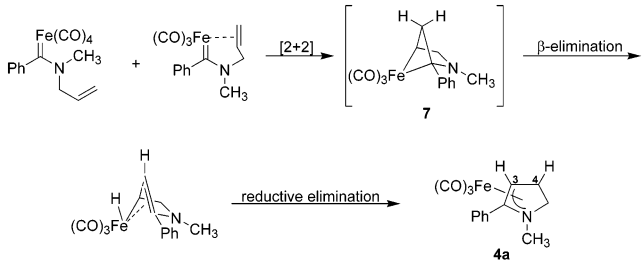


Figure 1. Overall view of **4f**. The displacement ellipsoids are drawn at the 50% probability level.

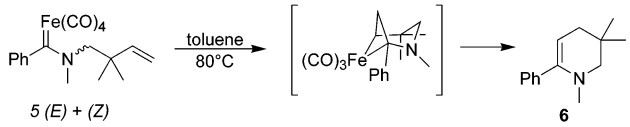
Table 1. Selected Bond Lengths (Å) and Angles (deg) for 4f

Fe(1)−C(8)	1.759(2)
Fe(1)−C(9)	1.788(2)
Fe(1)−C(7)	1.817(2)
Fe(1)−C(2)	1.9263(16)
Fe(1)−N(1)	2.0192(15)
Fe(1)−C(3)	2.0677(18)
N(1)−C(2)	1.443(2)
N(1)−C(5)	1.493(2)
C(2)−C(3)	1.439(2)
C(3)−C(4)	1.518(2)
C(4)−C(5)	1.524(3)
C(2)−N(1)−C(6)	121.20(14)
C(2)−N(1)−C(5)	109.87(13)
C(6)−N(1)−C(5)	115.01(15)
C(3)−C(2)−N(1)	100.32(13)
C(2)−C(3)−C(4)	110.36(14)
C(3)−C(4)−C(5)	102.68(14)
N(1)−C(5)−C(4)	103.66(14)

Scheme 3



Scheme 4



5 (E) + (Z)

The formation of complexes **4** can be explained by intramolecular generation of bicyclo[2.1.1]-2-aza-5-ferrahexane intermediate **7**, followed by β-hydrogen elimination and reductive elimination (Scheme 3). Creation of intermediate **7** requires antiparallel orientation of double Fe═C and C═C bonds. We have already proposed this reaction mode to explain formation of 1-methyl-3,3-dimethyl-6-phenyl-1,2,3,4-tetrahydropyridine (**6**) from the pyrolysis of tetracarbonyl[(*N*-(2,2-dimethyl-3-butenyl)-*N*-methylamino)(phenyl)carbene]iron(0) (**5**) (Scheme 4).[4] Hegedus suggested a similar intermediate to explain formation of dihydropyranes in the course of thermolysis of (3-methylbut-3-en-1-yloxy)carbene com-

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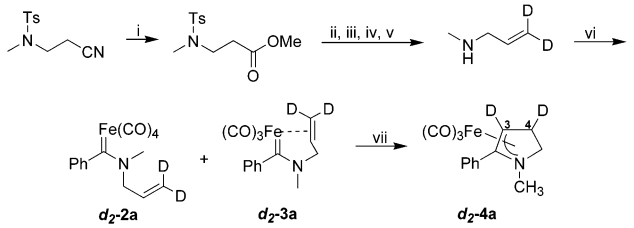
(10) de Lange, P. P. M.; van Wijnkoop, M.; Fruhauf, H.-M.; Vrieze, K.; Goubitz, K. *Organometallics* **1993**, *2*, 428.

Scheme 5[a]



[a] (i) CH_3OH, HCl, 96%; (ii) 1. $LiAlD_4$, 2. H_2O, 66%; (iii) MsCl, $(C_2H_5)_3N$; (iv) 1. PhSeNa, 2. $NaIO_4$; (v) sodium naphthalenide; (vi) $(CO)_4Fe{=}C(OMe)Ph$; (vii) toluene, 100 °C.

plexes of chromium.[11] In this case the formation of an "antiparallel intermediate" was explained by steric interactions between the carbene substituent and the methyl group of the olefin. Results presented here together with the above-mentioned formation of tetrahydropyridine **6** suggest that iron aminocarbenes form the "antiparallel intermediate" more often than the corresponding chromium complexes.

The above mechanism was supported by thermolysis of a mixture of the carbene complexes ***d*$_2$-2a** and ***d*$_2$-3a** dideuterated in position 3 of the *N*-allyl group, prepared from methyl 3-(*N*-methyl-*N*-tosylamino)propanoate as outlined in Scheme 5. The deuterium label appeared in positions 3 and 4 of the product ***d*$_2$-4a**, as required by the mechanism described in Scheme 3.

Another support of this mechanism comes from the unreactivity of the complexes **2c** + **3c** and **2d** + **3d**. This can be explained by the structure of intermediate **7**, in which, due to the *E*-configuration on the double C=C bond, the substituent (Me or Ph) points in the direction of the metal (Scheme 3), and therefore β-elimination of hydrogen is not possible. On the contrary, *Z*-analogues of the complexes **2c** + **3c** and **2d** + **3d** should react. However, we were not able to prepare *Z*-isomers of **2c** + **3c** since complete isomerization of the double C=C bond proceeded in the course of the reaction of (*Z*)-*N*-(but-2-en-1-yl)-*N*-methylbenzamide with $Na_2Fe(CO)_4$ and Me_3SiCl.

To further support the mechanism outlined in Scheme 3, density functional calculations of B3LYP quality and with basis sets 6-31G(d,p) were carried out. The computed reaction path is depicted in Figure 2. It shows that an energy minimum for the possible intermediate, bicyclo[2.1.1]-2-aza-5-ferrahexane (**7**), is of relatively high energy. In contrast to the proposed mechanism, the following β-elimination leads to the formation of a double bond between C(3) and C(4) instead of the proposed C(2) and C(3). A product of this process, **8**, has a partial zwitterionic character, and the transition state forms a distorted π-allyl complex. Reinsertion of the double C(3)=C(4) bond requires relatively high activation energy (88 kJ/mol) connected with a change of geometry and leads to the partially zwitterionic σ-alkyliron intermediate **9**. Conversion to the final product **4a** goes through transition state **13**. The geometry of **13** differs from the local minimum **9** mainly in the Fe−C(3)−C(4) angle. The highest activation energy in this process (123 kJ/mol) is in agreement with the temperature required for the reaction to proceed (100 °C).

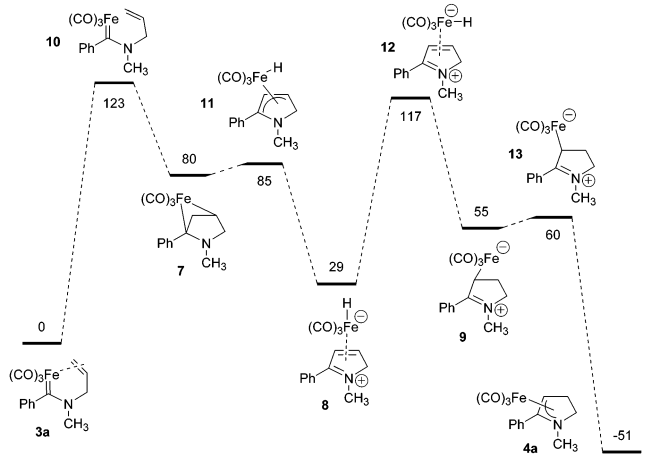


Figure 2. Energy profile for the thermolysis of **3a** leading to **4a** (relative energies of stationary points are in kJ/mol).

In conclusion, the obtained results show that unlike group 6 transition metal Fischer carbenes, η^3-allylaminocarbene complexes of iron undergo thermolysis with formation of η^3-1-azaallyliron tricarbonyl complexes. This transformation proceeds very probably via a bicyclo[2.1.1]-2-aza-5-ferrahexane intermediate.

Experimental Section

Melting points were determined on a Kofler block and are uncorrected. NMR spectra were measured on either a Varian Gemini 300 (^{1}H, 300.07 MHz; ^{13}C, 75.46 MHz) or Bruker DRX 500 Avance (^{1}H, 500.13 MHz; ^{13}C, 125.77 MHz; ^{2}H, 76.75 MHz) spectrometer at 298 K. Unambiguous assignment of the NMR signals is based on $^{13}C\{^1H\}$, ^{13}C APT, COSY, and ^{13}C HMBC spectra. All experiments were carried out under argon. Tetrahydrofuran was distilled from benzophenone ketyl under Ar prior to use. Iron pentacarbonyl, trimethylchlorosilane, 3-chloropropene, 3-chloro-2-methylpropene, 1-chlorobut-2-ene, cinnamyl chloride, 1-chloro-3-methylbut-2-ene, and 4-biphenylcarbonyl chloride were purchased from Aldrich and were used without purification. Neutral aluminum oxide (Brockmann grade) and silica were obtained from Merck.

The density functional calculations of B3LYP quality and with basis sets 6-31G(d,p) were carried out using the GAUSSIAN 98[12] package of programs. Transition structure optimizations have been done using the STQN routine without any geometry constraints. Second derivative (frequency) calculations established the nature of stationary points (exactly one negative eigenvalue). The reaction path was determined by IRC calculations (6-31G basis sets).

Crystal data for **4f**: $C_{20}H_{17}FeNO_3$, $M = 375.2$, monoclinic, $P2_1/c$ (No. 14), $a = 7.2350(2)$ Å, $b = 9.1180(2)$ Å, $c = 26.9660(5)$ Å, $\beta = 93.075(1)°$, $V = 1776.35(7)$ Å^3, $Z = 4$, $D_x = 1.403$ Mg m^{-3}. An orange crystal of dimensions 0.4 × 0.3 × 0.25 mm was mounted on a glass capillary with epoxy glue and measured on a Nonius Kappa CCD diffractometer by monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) at 150(2) K. An

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absorption was neglected ($\mu = 0.866$ mm^{-1}); a total of 16 862 reflections were measured in the range $h = -9$ to 9, $k = -11$ to 11, $l = -34$ to 34 ($\theta_{max} = 27.5°$), of which 4035 were unique ($R_{int} = 0.057$), 3651 observed according to the $I > 2\sigma(I)$ criterion. Cell parameters were from 23 760 reflections ($\theta = 1-27.5°$). The structure was solved by direct methods (SIR92)[13] and refined by full-matrix least-squares based on F^2 (SHELXL97).[14] The hydrogen atoms of the dihydropyrrole ring were refined isotropically; the others were fixed into idealized positions (riding model) and assigned temperature factors either $H_{iso}(H) = 1.2U_{eq}$(pivot atom) or $H_{iso}(H) = 1.5U_{eq}$(pivot atom) for the methyl moiety. The refinement converged ($\Delta/\sigma_{max} = 0.000$) to $R = 0.0374$ for observed reflections and $R_w = 0.104$, GOF = 1.095 for 247 parameters and all 4035 reflections. The final difference map displayed no peaks of chemical significance ($\Delta\rho_{max} = 0.436$, $\Delta\rho_{min}$ -0.548 e Å^{-3}).

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 201179. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EY, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

***N*-Allyl-*N*-methylbenzamide (1a).** *N*-Methylbenzamide (1.08 g; 8 mmol) and 60% dispersion of sodium hydride (0.38 g; 9.5 mmol) in DMF (15 mL) were stirred at 50 °C for 1 h. Then 3-chloropropene (0.82 mL; 10 mmol) was added, the mixture was stirred overnight at room temperature, and the solvents were removed under reduced pressure. Water (5 mL) was added, and the product was extracted with dichloromethane (2 × 5 mL). Extracts were dried with Na_2SO_4, solvents were evaporated, and the residue was subjected to column chromatography on silica. Elution with a dichloromethane−methanol mixture (25:1) afforded **1a** (0.95 g; 68%). ^{1}H NMR ($CDCl_3$, 300 MHz),[15] two rotamers in 3:2 ratio: δ 2.89 (bs, 3H, N−C*H*$_3$, minor), 3.04 (bs, 3H, N−C*H*$_3$, major), 3.83 (bs, 2H, −C*H*$_2$−, major), 4.14 (bs, 2H, −C*H*$_2$−, minor), 5.15−5.28 (m, 2H, =C*H*$_2$), 5.65−5.92 (m, 1H, −C*H*=), 7.34−7.44 (m, 5H, Ph−*H*). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 171.9 (C=O), 136.0 (C), 132.8 (=CH, major), 132.5 (=CH, minor), 129.4 (CH−Ph), 128.2 (CH−Ph), 126.8 (*o*-CH−Ph, minor), 126.4 (*o*-CH−Ph, major), 117.5 (=CH_2, minor), 117.3 (=CH_2, major), 53.7 (−CH_2−, major), 49.7 (−CH_2−, minor), 36.8 (N−CH_3, minor), 32.8 (N−CH_3, major). IR[15] ($CHCl_3$): ν 2922, 1625, 1604, 1446, 1402, 1265, 1070 cm^{-1}. Anal. Calcd for $C_{11}H_{13}NO$: C, 75.40; H, 7.48; N, 7.99. Found: C, 75.22; H, 7.57; N, 7.95.

***N*-(2-Methyl-2-propenyl)-*N*-methylbenzamide (1b).** The same procedure as used for the preparation of **1a** starting from *N*-methylbenzamide (1.08 g; 8 mmol) and 3-chloro-2-methylpropene (0.98 mL; 10 mmol) gave **1b** (1.09 g; 72%). ^{1}H NMR ($CDCl_3$, 300 MHz), two rotamers in 3:2 ratio: δ 1.58 (bs, 3H, −C*H*$_3$, major), 1.76 (bs, 3H, −C*H*$_3$, minor), 2.85 (bs, 3H, N−C*H*$_3$, minor), 3.02 (bs, 3H, N−C*H*$_3$, major), 3.75 (bs, 2H, −C*H*$_2$−, major), 4.11 (bs, 2H, −C*H*$_2$−, minor), 4.89 (bs, 2H, =C*H*$_2$, minor), 4.95 (bs, 2H, =C*H*$_2$, major), 7.32−7.46 (m, 5H, Ph−*H*). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 172.2 (C=O), 140.4 (C), 136.2 (C), 129.4 (CH−Ph), 128.3 (CH−Ph), 126.7 (CH−Ph), 126.5 (CH−Ph), 112.4 (=CH_2, minor), 112.1 (=CH_2, major), 57.2 (−CH_2−, major), 52.7 (−CH_2−, minor), 36.8 (N−CH_3, minor), 33.1 (N−CH_3, major), 19.8 (−CH_3). Anal. Calcd for $C_{12}H_{15}NO$: C, 76.16; H, 7.99; N, 7.40. Found: C, 75.92; H, 7.76; N, 7.38.

***N*-((*E*)-2-Butenyl)-*N*-methylbenzamide (1c).** The same procedure as used for the preparation of **1a** starting from *N*-methylbenzamide (1.08 g; 8 mmol) and 1-chlorobut-2-ene (0.97 mL; 10 mmol) provided **1c** (1.12 g; 74%). ^{1}H NMR ($CDCl_3$, 300 MHz), two rotamers in 3:2 ratio, 30% content of *Z*-isomer (rotamers in 1:1 ratio): δ 1.50 (d, $J = 6.1$ Hz, 3H, −C*H*$_3$ (*Z*)), 1.72 (d, $J = 6.1$ Hz, 3H, −C*H*$_3$ (*E*)), 1.74 (bs, 3H, −C*H*$_3$ (*Z*)), 2.86 (bs, 3H, N−C*H*$_3$ (*E*, minor + *Z*)), 3.01 (bs, 3H, N−C*H*$_3$ (*E*, major + *Z*)), 3.75 (bs, 2H, −C*H*$_2$− (*E*, major), 3.87 (bs, 2H, −C*H*$_2$− (*Z*)), 4.06 (bs, 2H, −C*H*$_2$− (*E*, minor)), 4.21 (bs, 2H, −C*H*$_2$− (*Z*)), 5.30−5.80 (m, 2H, −C*H*= (*E* + *Z*), 7.32−7.50 (m, 5H, Ph−*H*). ^{1}H NMR (DMSO-d_6, 300 MHz, 130 °C), 30% content of *Z*-isomer: δ 1.59 (d, $J = 6.1$ Hz, 3H, −C*H*$_3$ (*Z*)), 1.70 (d, $J = 6.0$ Hz, 3H, −C*H*$_3$ (*E*)), 2.89 (s, 3H, N−C*H*$_3$ (*E*)), 2.91 (s, 3H, N−C*H*$_3$ (*Z*)), 3.88 (d, $J = 6.0$ Hz, 2H, −C*H*$_2$− (*E*)), 4.00 (d, $J = 7.1$ Hz, 2H, −C*H*$_2$− (*Z*)), 5.42−5.55 (m, 1H, −C*H*= (*E* + *Z*)), 5.55−5.75 (m, 1H, −C*H*= (*E* + *Z*)), 7.35−7.50 (m, 5H, Ph−*H*). Anal. Calcd for $C_{12}H_{15}NO$: C, 76.16; H, 7.99; N, 7.40. Found: C, 76.12; H, 7.83; N, 7.51.

***N*-((*E*)-3-Phenyl-2-propenyl)-*N*-methylbenzamide (1d).** The same procedure as used for the preparation of **1a** starting from *N*-methylbenzamide (1.08 g; 8 mmol) and cinnamyl chloride (1.39 mL; 10 mmol) afforded **1d** (1.53 g; 76%). Mp: 84−86 °C. ^{1}H NMR ($CDCl_3$, 300 MHz), two rotamers in 4:3 ratio: δ 2.96 (bs, 3H, N−C*H*$_3$, minor), 3.12 (bs, 3H, N−C*H*$_3$, major), 4.03 (bs, 2H, −C*H*$_2$−, major), 4.32 (bs, 2H, −C*H*$_2$−, minor), 6.04-6.35 (m, 1H, −C*H*=), 6.43−6.66 (m, 1H, −C*H*=), 7.25−7.50 (m, 10H, Ph−*H*). ^{1}H NMR (DMSO-d_6, 300 MHz, 130 °C): δ 2.98 (s, 3H, N−C*H*$_3$), 4.13 (d, $J = 5.5$ Hz, 2H, −C*H*$_2$−), 6.25 (dt, $J = 15.9$, 5.5 Hz, 1H, −CH$_2$−C*H*=), 6.56 (d, $J = 15.9$ Hz, 1H, Ph−C*H*=), 7.20−7.50 (m, 10H, Ph−*H*). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 172.0 (C=O), 136.3 (CH−Ph), 133.4 (C−Ph), 132.6 (C−Ph), 129.6 (CH−Ph), 128.6 (CH−Ph), 128.4 (CH−Ph), 127.9, 127.0, 126.7, 126.4 (CH−Ph), 124.2 (CH−Ph), 53.5 (−CH_2−), 49.5 (−CH_2−), 36.9 (N−CH_3), 33.0 (N−CH_3). IR ($CHCl_3$): ν 3011, 1825, 1578, 1498, 1448, 1402, 1264, 1085, 1071, 967 cm^{-1}. Anal. Calcd for $C_{17}H_{17}NO$: C, 81.24; H, 6.82; N, 5.57. Found: C, 81.10; H, 6.96; N, 5.63.

***N*-(3-Methyl-2-butenyl)-*N*-methylbenzamide (1e).** The same procedure as used for the preparation of **1a** starting from *N*-methylbenzamide (1.08 g; 8 mmol) and 1-chloro-3-methylbut-2-ene (1.13 mL; 10 mmol) gave **1e** (1.12 g; 69%). ^{1}H NMR ($CDCl_3$, 300 MHz), two rotamers in 3:2 ratio: δ 1.48 (bs, 3H, −C*H*$_3$, major), 1.73 (bs, 3H, −C*H*$_3$), 1.76 (bs, 3H, −C*H*$_3$, minor), 2.86 (bs, 3H, N−C*H*$_3$, minor), 3.01 (bs, 3H, N−C*H*$_3$, major), 3.80 (bd, $J = 5.5$ Hz, 2H, −C*H*$_2$−, major), 4.14 (bd, $J = 6.0$ Hz, 2H, −C*H*$_2$−, minor), 5.10−5.28 (m, 1H, −C*H*=), 7.34−7.44 (m, 5H, Ph−*H*). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 171.5 (C=O, major), 170.9 (C=O, minor), 136.3 (C−Ph), 129.1 (CH−Ph), 128.1 (CH−Ph), 126.7 (CH, minor), 126.6 (CH, major), 119.3 (CH, major), 119.1 (CH, minor), 49.1 (−CH_2−, major), 44.6 (−CH_2−, minor), 36.5 (N−CH_3, minor), 32.2 (N−CH_3, major), 25.5 (−CH_3), 17.6 (−CH_3, minor), 17.5 (−CH_3, major). IR ($CHCl_3$): ν 3007, 2935, 1620, 1578, 1501, 1449, 1403, 1267, 1069 cm^{-1}. Anal. Calcd for $C_{13}H_{17}NO$: C, 76.81; H, 8.43; N, 6.89. Found: C, 76.63; H, 8.34; N, 6.56.

***N*-Allyl-*N*-methylbiphenyl-4-carboxamide (1f).** To a solution of *N*-methylallylamine (0.88 mL; 9.2 mmol) and triethylamine (1.4 mL; 10 mmol) in dichloromethane (30 mL) was added a solution of 4-biphenylcarbonyl chloride (1.66 g; 7.7 mmol) in dichloromethane (20 mL) via syringe. Stirring was continued for 3 h, and the mixture was then washed with diluted HCl (2 × 5 mL) and 5% $NaHCO_3$ (5 mL), dried with $MgSO_4$, and evaporated. The residue was subjected to column chromatography on silica (100 g). Elution with a dichloromethane−methanol mixture (100:1) provided **1f** (1.45 g; 73%) as a pale yellow oil. ^{1}H NMR ($CDCl_3$, 500 MHz), two rotamers in 3:2 ratio: δ 2.98 (bs, 3H, N−C*H*$_3$, minor), 3.08 (bs, 3H, N−C*H*$_3$, major), 3.92 (bs, 2H, −C*H*$_2$−, major), 4.18 (bs, 2H, −C*H*$_2$−, minor), 5.22−5.35 (m, 2H, =C*H*$_2$), 5.73−5.96 (m, 1H, −C*H*=), 7.34−7.41 (m, 1H, Ph), 7.43−7.48 (m, 2H, Ph), 7.50−7.55 (m, 2H, Ph−*H*), 7.57−7.66 (m, 4H, Ph−*H*). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 142.4 (C−Ph), 140.2 (C−Ph), 135.0 (C−Ph), 133.0 (−CH=, major), 132.7 (−CH=, minor), 128.8 (CH−

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Ph), 127.6 (CH−Ph), 127.0 (CH−Ph), 126.9 (CH−Ph), 117.4 (=CH_2), 53.9 (−CH_2−, major), 49.9 (−CH_2−, minor), 36.9 (N−CH_3, minor), 33.0 (N−CH_3, major). IR ($CHCl_3$): ν 3011, 1623, 1482, 1450, 1403, 1265, 1071, 1009, 930, 848 cm^{-1}. Anal. Calcd for $C_{17}H_{17}NO$: C, 81.24; H, 6.82; N, 5.57. Found: C, 81.06; H, 6.97; N, 5.54.

Tetracarbonyl[(*N*-allyl-*N*-methylamino)(phenyl)carbene]iron(0) (2a) and *cis*-Tricarbonyl[(η^2-*N*-allyl-*N*-methylamino)(phenyl)carbene]iron(0) (3a). To a solution of iron pentacarbonyl (1.3 mL, 10 mmol) in THF (50 mL) was added a solution of sodium naphthalenide prepared from sodium (0.6 g; 26 mmol) and naphthalene (3.4 g; 26.5 mmol) in THF (50 mL) at −78 °C via syringe. The reaction mixture was then allowed to warm to 0 °C, stirred at this temperature for 30 min, and cooled to −78 °C, and *N*-allyl-*N*-methylbenzamide (**1a**) (0.88 g; 5 mmol) in THF (5 mL) was added via syringe. The solution was allowed to warm to 0 °C, stirred for 30 min at 0 °C, and then cooled to −78 °C, and trimethylchlorosilane (2.5 mL; 20 mmol) was added via syringe. The solution was stirred at −78 °C for 30 min, then the cooling bath was removed, the mixture was stirred for 1 h without cooling, and neutral alumina (8 g) was added. THF was removed under reduced pressure, and the residue was dried under high vacuum to remove all solvents. Light petroleum (20 mL) was then added, and the suspension formed was transferred on top of a column filled with neutral alumina (150 g). Naphthalene was eluted with light petroleum, and further elution with a light petroleum−dichloromethane mixture (5:1) gave a mixture of **2a** and **3a** in a ratio 1:1 as an orange oil (0.95 g; 60%). ^{1}H NMR ($CDCl_3$, 300 MHz): **2a**: δ 3.95 (s, 3H, N−CH_3), 4.02 (d, J = 5.2 Hz, 2H, N−CH_2), 5.21 (d, J = 17 Hz, 1H, =CH_2), 5.33 (d, J = 10.4 Hz, 1H, =CH_2), 5.62 (m, 1H, −CH=), 6.85 (d, J = 7.7 Hz, 2H, Ph−H), 7.18−7.28 (m, 1H, Ph−H), 7.30−7.40 (m, 2H, Ph−H); **3a**: δ 1.53 (d, J = 10.4 Hz, 1H, =CH_2), 2.04 (d, J = 8.0 Hz, 1H, =CH_2), 2.94 (s, 3H, N−CH_3), 3.21 (m, 1H, −CH=), 4.18−4.34 (m, 2H, N−CH_2−), 6.85 (d, J = 7.7 Hz, 2H, Ph−H), 7.18−7.28 (m, 1H, Ph−H), 7.30−7.40 (m, 2H, Ph−H). ^{13}C NMR ($CDCl_3$, 75 MHz): **2a**: δ 261.3 (carbene), 214.3 (CO), 152.4 (C−Ph), 130.5 (CH−Ph), 126.6 (CH−Ph), 119.8 (=CH_2), 119.6 (−CH=), 60.2 (N−CH_2), 47.6 (N−CH_3); **3a**: δ 265.4 (carbene), 215.8 br (CO), 146.8 (C−Ph), 128.2 (CH−Ph), 127.3 (CH−Ph), 120.8 br (*o*-CH−Ph), 66.1 (N−CH_2−), 42.8 (−CH=), 40.6 (N−CH_3), 32.8 (=CH_2). IR ($CHCl_3$): ν 3020, 2042, 2021, 1939, 1919 cm^{-1}.

Tetracarbonyl[(*N*-(2-methyl-2-propenyl)-*N*-methylamino)(phenyl)carbene]iron(0) (2b) and *cis*-Tricarbonyl[(η^2-*N*-(2-methyl-2-propenyl)-*N*-methylamino)(phenyl)carbene]iron(0) (3b). The same method as was used for the preparation of **2a** and **3a**, starting from *N*-(2-methyl-2-propenyl)-*N*-methylbenzamide (**1b**) (0.56 g; 3.75 mmol), iron pentacarbonyl (0.98 mL, 7.5 mmol), sodium (0.45 g; 19.5 mmol), naphthalene (2.55 g; 19.9 mmol), and Me_3SiCl (1.88 mL; 15 mmol) gave a mixture of **2b** and **3b** in a ratio 5:2 as a yellow-orange oil (0.7 g; 56%), which solidified upon several days in a freezer. ^{1}H NMR ($CDCl_3$, 300 MHz): **2b**: δ 1.57 (s, 3H, −CH_3), 3.93−3.95 (s, 3H, N−CH_3 + s, 2H, N−CH_2), 4.90 (s, 1H, =CH_2), 5.05 (s, 1H, =CH_2), 6.85 (d, J = 7.7 Hz, 2H, Ph−H), 7.17−7.29 (m, 1H, Ph−H), 7.29−7.41 (m, 2H, Ph−H); **3b**: δ 1.68 (s, 1H, =CH_2), 1.86 (s, 3H, −CH_3), 2.11 (s, 1H, =CH_2), 2.97 (s, 3H, N−CH_3), 4.13 (s, 2H, N−CH_2−), 6.85 (d, J = 7.7 Hz, 2H, Ph−H), 7.17−7.29 (m, 1H, Ph−H), 7.29−7.41 (m, 2H, Ph−H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 263.1 (carbene), 262.0 (carbene), 215.9 br (CO, **3b**), 214.5 (CO, **2b**), 152.6 (C−Ph, **2b**), 147.0 (C−Ph, **3b**), 138.4 (=C(CH_3)−, **2b**), 128.2 (CH−Ph, **2b**), 127.4 (CH−Ph, **3b**), 126.6 (CH−Ph, **2b**), 121.0 br (*o*-CH−Ph, **3b**), 120.1 (=CH_2, **2b**), 114.4 (CH−Ph, **2b**), 69.7 (N−CH_2−, **3b**), 63.3 (N−CH_2, **2b**), 47.5 (N−CH_3, **2b**), 40.7 (N−CH_3, **3b**), 38.3 (=CH_2, **3b**), 26.2 (−CH_3, **3b**), 20.0 (−CH_3, **2b**). IR ($CHCl_3$): ν 2042, 2017, 1967, 1939, 1917, 1522 cm^{-1}.

Tetracarbonyl[(*N*-((*E*)-2-butenyl)-*N*-methylamino)(phenyl)carbene]iron(0) (2c) and *cis*-Tricarbonyl[(η^2-*N*-((*E*)-2-butenyl)-*N*-methylamino)(phenyl)carbene]iron(0) (3c). The same method as was used for the preparation of **2a** and **3a** starting from *N*-((*E*)-2-butenyl)-*N*-methylbenzamide (**1c**) (0.946 g; 5 mmol) provided a mixture of **2c** and **3c** in the ratio 3:1 (1.30 g; 78%). ^{1}H NMR (C_6D_6, 300 MHz): **2c**: δ 1.27 (d, J = 6.0 Hz, 3H, −CH_3), 3.13 (d, J = 5.5 Hz, 2H, N−CH_2−), 3.40 (s, 3H, N−CH_3), 4.63−4.78 (m, 1H, −CH=), 4.96−5.07 (m, 1H, −CH=), 6.63 (d, J = 7.1 Hz, 2H, Ph−H), 6.83−7.07 (m, 3H, Ph-H); **3c**: δ 1.78 (d, J = 6.1 Hz, 3H, −CH_3), 1.89 (s, 3H, N−CH_3), 2.28 (m, 1H, CH_3−CH=), 2.90 (d, J = 9.6 Hz, 1H, N−CH=), 3.44 (s, 2H, N−CH_2−), 6.69 (bs, 2H, Ph−H), 6.91−6.97 (m, 1H, Ph−H), 7.01−7.08 (m, 2H, Ph-H). ^{13}C NMR (C_6D_6, 75 MHz): **2c**: δ 260.5 (carbene), 216.0 (CO), 153.7 (C−Ph), 132.3 (CH−Ph), 127.4 (CH−Ph), 124.3 (CH−Ph), 121.2 (−CH=), 121.1 (−CH=), 60.2 (N−CH_2−), 47.6 (N−CH_3), 18.3 (−CH_3); **3c**: δ 264.8 (carbene), 217.5 (CO), 147.8 (C−Ph), 129.2 (CH−Ph), 128.2 (CH−Ph), 122.0 br (*o*-CH−Ph), 66.5 (N−CH_2−), 51.0 (−CH=), 50.8 (−CH=), 40.5 (N−CH_3), 25.0 (−CH_3). IR ($CHCl_3$): ν 3024, 2041, 2015, 1966, 1938, 1916, 1525, 1440 cm^{-1}.

Tetracarbonyl[(*N*-((*E*)-3-phenyl-2-propenyl)-*N*-methylamino)(phenyl)carbene]iron(0) (2d) and *cis*-Tricarbonyl[(η^2-*N*-((*E*)-3-phenyl-2-propenyl)-*N*-methylamino)(phenyl)carbene]iron(0) (3d). The same method as was used for the preparation of **2a** and **3a** starting from *N*-((*E*)-3-phenyl-2-propenyl)-*N*-methylbenzamide (**1d**) (0.754 g; 3 mmol) gave a mixture of **2d** and **3d** in 3:1 ratio (0.85 g; 72%), which solidified upon several days in a freezer. ^{1}H NMR (C_6D_6, 300 MHz): **2d**: δ 3.32 (dm, J = 5.7 Hz, 2H, −CH_2−), 3.45 (s, 3H, N−CH_3), 5.33 (dt, J = 15.7, 5.8 Hz, 1H, −CH=), 6.03 (d, J = 15.7 Hz, 1H, Ph−CH=), 6.67 (m, 2H, Ph-H), 6.83−7.33 (m, 3H, Ph−H); **3d**: δ 1.92 (s, 3H, N−CH_3), 3.45−3.62 (m, 4H, 2 −CH= + −CH_2−), 6.74 (bs, 2H, Ph−H), 6.92−7.01 (m, 2H, Ph−H), 7.03−7.10 (m, 2H, Ph−H), 7.16−7.23 (m, 2H, Ph−H), 7.28−7.33 (m, 2H, Ph−H). ^{13}C NMR (C_6D_6, 75 MHz): **2d**: δ 262.0 (carbene), 215.8 br (CO), 153.6 (C−Ph), 136.5 (C−Ph), 135.0 (CH−Ph), 129.7 (CH−Ph), 129.2 (CH−Ph), 127.5 (CH−Ph), 122.0 (−CH=), 121.0 (−CH=), 60.1 (N−CH_2−), 48.1 (N−CH_3); **3d**: δ 263.9 (carbene), 217.7 br (CO), 147.7 (C−Ph), 147.6 (C−Ph), 129.3 (CH−Ph), 128.4 (CH−Ph), 126.6 (CH−Ph), 125.3 (CH−Ph), 122.1 br (*o*-CH−Ph), 66.7 (N−CH_2−), 55.2 (−CH=), 42.7 (−CH=), 40.6 (N−CH_3). IR ($CHCl_3$): ν 3027, 2042, 2022, 1966, 1939, 1917, 1522 cm^{-1}.

Tetracarbonyl[(*N*-(3-methyl-2-butenyl)-*N*-methylamino)(phenyl)carbene]iron(0) (2e) and *cis*-Tricarbonyl[(η^2-*N*-(3-methyl-2-butenyl)-*N*-methylamino)(phenyl)carbene]iron(0) (3e). The same method as was used for the preparation of **2a** and **3a** starting from *N*-(3-methyl-2-butenyl)-*N*-methylbenzamide (**1e**) (0.816 g; 4 mmol) afforded a mixture of **2e** and **3e** in 9:1 ratio (1.22 g; 87%), which solidified upon several days in a freezer. ^{1}H NMR (C_6D_6, 300 MHz): **2e**: δ 0.93 (s, 3H, −CH_3), 1.31 (s, 3H, −CH_3), 3.23 (d, J = 7.1 Hz, 2H, N−CH_2−), 3.41 (s, 3H, N−CH_3), 4.62 (t, J = 7.1 Hz, 1H, −CH=), 6.65 (d, J = 7.7 Hz, 2H, Ph−H), 6.83−6.89 (m, 1H, Ph−H), 7.02 (t, J = 7.7 Hz, 2H, Ph−H); **3e**: δ 1.49 (s, 3H, −CH_3), 1.78 (s, 3H, −CH_3), 1.88 (s, 3H, −CH_3), 3.16−3.23 (m, 1H, −CH=), 3.35−3.57 (m, 2H, N−CH_2−), 6.79 (bs, 2H, Ph−H), 6.91 (m, 1H, Ph−H), 7.04 (m, 2H, Ph−H). ^{13}C NMR (C_6D_6, 75 MHz): **2e**: δ 259.6 (carbene), 216.0 (CO), 153.8 (C−Ph), 139.5 (=C(CH_3)$_2$), 129.3 (CH−Ph), 127.2 (CH−Ph), 121.2 (−CH=), 118.2 (CH−Ph), 56.6 (N−CH_2−), 47.5 (N−CH_3), 26.1 (−CH_3), 18.2 (−CH_3); **3e**: δ 263.4 (carbene), 217.9 (CO), 147.9 (C−Ph), 129.2 (CH−Ph), 128.2 (CH−Ph), 121.9 br (*o*-CH−Ph), 65.3 (=C(CH_3)$_2$), 64.8 (N−CH_2−), 55.2 (−CH=), 39.5 (N−CH_3), 35.5 (−CH_3), 25.6 (−CH_3). IR ($CHCl_3$): ν 2041, 1966, 1938, 1915, 1525 cm^{-1}.

***cis*-Tricarbonyl[(η^2-*N*-((*E*)-2-butenyl)-*N*-methylamino)(phenyl)carbene]iron(0) (3c).** The same method as was used for the preparation of **4a** starting from the above mixture of **2c** and **3c** (0.80 g; 2.39 mmol) provided pure **3c** (0.68 g; 91%) as a red-orange oil. IR ($CHCl_3$): ν 2015, 1946, 1916, 1556 cm^{-1}.

Anal. Calcd for $C_{15}H_{15}NO_3Fe$: C, 57.54; H, 4.83; N, 4.47. Found: C, 57.36; H, 4.96; N, 4.46.

***cis*-Tricarbonyl[(η^2-*N*-((*E*)-3-phenyl-2-propenyl)-*N*-methylamino)(phenyl)carbene]iron(0) (3d).** The same method as was used for the preparation of **4a** starting from the above mixture of **2d** and **3d** (0.55 g; 1.39 mmol) gave pure **3d** (0.50 g; 96%) as an orange foam. IR ($CHCl_3$): ν 3029, 2022, 1959, 1925, 1556 cm^{-1}. Anal. Calcd for $C_{20}H_{17}NO_3Fe$: C, 64.02; H, 4.57; N, 3.73. Found: C, 63.71; H, 4.62; N, 3.67.

***cis*-Tricarbonyl[(η^2-*N*-(3-methyl-2-butenyl)-*N*-methylamino)(phenyl)carbene]iron(0) (3e).** The same method as was used for the preparation of **4a** starting from the above mixture of **2e** and **3e** (0.25 g; 0.71 mmol) provided orange crystals of pure **3e** (0.22 g; 95%). IR ($CHCl_3$): ν 3020, 2030, 1940, 1912, 1617, 1556 cm^{-1}. Anal. Calcd for $C_{16}H_{17}NO_3Fe$: C, 58.74; H, 5.24; N, 4.28. Found: C, 58.55; H, 5.20; N, 4.19.

Tricarbonyl[(η^3-*N*-methyl-2-phenyl-4,5-dihydropyrrole]iron(0) (4a). A solution of the above mixture of **2a** and **3a** (0.95 g; 3 mmol) in toluene (10 mL) was heated to 100 °C for 8 h under argon. Toluene was removed under reduced pressure, and the residue was subjected to column chromatography (neutral alumina, 20 g). Elution with a light petroleum−dichloromethane mixture (10:1) afforded an orange oil of **4a** (0.61 g; 68%), which solidified upon several days in a freezer. Mp: 18−20 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.08 (m, 1H, =CH−CH_2−), 2.48 (m, 1H, =CH−CH_2−), 2.64-2.71 (m, 1H, N−CH_2−), 2.69 (s, 3H, N−CH_3), 2.91 (m, 1H, N−CH_2−), 3.05 (d, J = 4.0 Hz, 1H, −C*H*=), 7.37−7.43 (m, 3H, Ph−*H*), 7.47−7.51 (m, 2H, Ph−*H*). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 213.7 (CO), 135.5 (C−Ph), 131.5 (CH−Ph), 128.3 (CH−Ph), 128.2 (CH−Ph), 93.4 (Ph-C(−N)=), 59.3 (N−CH_2−), 46.9 (−CH=), 43.8 (N−CH_3), 32.6 (−CH_2−). IR ($CHCl_3$): ν 2928, 2873, 2024, 1944, 1478, 1453 cm^{-1}. HRMS: calcd 299.02448, found 299.02209.

Tricarbonyl[(η^3-*N*,4-dimethyl-2-phenyl-4,5-dihydropyrrole]iron(0) (4b). The same method as was used for the preparation of **4a** starting from the above mixture of **2b** and **3b** (0.5 g; 1.5 mmol) afforded **4b** (0.29 g; 62%) as a mixture of two diastereoisomers in 4:1 ratio. The complex was obtained as an orange oil, which solidified upon several days in a freezer. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.14 (d, J = 6.5 Hz, 3H, −CH_3, minor), 1.24 (d, J = 6.7 Hz, 3H, −CH_3, major), 2.04 (dd, J = 9.5, 4.0 Hz, 1H, minor), 2.35 (dd, J = 9.5, 3.8 Hz, 1H, major), 2.53 (m, 1H, major), 2.59 (s, 3H, N−CH_3, minor), 2.61 (s, 3H, N−CH_3, major), 2.88 (s, 1H, major), 2.92 (dd, J = 9.5, 7.4 Hz, 1H, major), 3.00−3.05 (m, 2H, minor), 7.36−7.43 (m, 3H, Ph−*H*), 7.46−7.49 (m, 2H, Ph−*H*, minor), 7.52−7.56 (m, 2H, Ph−*H*, major). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 214.0 (CO, minor), 213.7 (CO, major), 136.1 (C−Ph, minor), 135.6 (C−Ph, major), 131.6 (CH−Ph, major), 131.0 (CH−Ph, minor), 128.3 (CH−Ph, major), 128.2 (CH−Ph, major), 128.1 (CH−Ph, minor), 93.8 (Ph−C(−N)=, major), 92.9 (Ph−C(−N)=, minor), 68.0 (N−CH_2−, major), 67.4 (N−CH_2−, minor), 56.2 (−CH=, minor), 54.5 (−CH=, major), 44.0 (N−CH_3, minor), 43.8 (N−CH_3, major), 41.1 (−CH_2−, major), 36.6 (−CH_2−, minor), 23.8 (−CH_3, major), 19.3 (−CH_3, minor). IR ($CHCl_3$): ν 2024, 1945 cm^{-1}. Anal. Calcd for $C_{15}H_{15}NO_3Fe$: C, 57.54; H, 4.83; N, 4.47. Found: C, 57.91; H, 5.09; N, 4.34.

Tetracarbonyl[(*N*-allyl-*N*-methylamino)(biphenyl-4-yl)carbene]iron(0) (2f) and *cis*-Tricarbonyl[(η^2-*N*-allyl-*N*-methylamino)(biphenyl-4-yl)carbene]iron(0) (3f). The same method as was used for the preparation of **2a** and **3a** starting from *N*-allyl-*N*-methylbiphenyl-4-carboxamide (**1f**) (0.754 g; 3 mmol) afforded a mixture of **2f** and **3f** in 3:1 ratio (0.64 g; 54%) as an oil, which solidified upon several days in a freezer. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.52 (bs, 1H, =CH_2, minor), 2.06 (bs, 1H, =CH_2, minor), 2.99 (s, 3H, N−CH_3, minor), 3.22 (m, 1H, −C*H*=, minor), 3.97 (s, 3H, N−CH_3, major), 4.08 (m, 2H, N−CH_2, major), 4.17−4.37 (m, 2H, N−CH_2−, minor), 5.18−5.40 (m, 2H, =CH_2, major), 5.60−5.70 (m, 1H, −C*H*=, major), 6.94 (m, 2H, Ph−*H*), 7.30−7.70 (m, 3H, Ph−*H*). ^{1}H NMR (C_6D_6, 300 MHz): δ 1.48 (d, J = 10.7 Hz, 1H, =CH_2, minor), 1.86 (s, 3H, N−CH_3, minor), 2.19 (d, J = 7.2 Hz, 1H, =CH_2, minor), 3.00−3.09 (m, 1H, −C*H*=, minor), 3.15 (d, J = 5.2 Hz, 2H, N−CH_2, major), 3.38 (s, 3H, N−CH_3, major), 3.47 (bs, 2H, N−CH_2−, minor), 4.63−4.78 (m, 2H, =CH_2, major), 4.82−4.97 (m, 1H, −C*H*=, major), 6.69 (d, J = 8.3 Hz, 2H, Ph−*H*, major), 6.74 (bs, 2H, Ph−*H*, minor), 7.12−7.24 (m, 2H, Ph−*H*), 7.30−7.44 (m, 5H, Ph−*H*). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 265.7 (carbene, minor), 261.9 (carbene, major), 216.1 br (CO, minor), 214.6 (CO, major), 151.5 (C−Ph, major), 145.8 (C−Ph, minor), 140.0 (C−Ph, major), 139.4 (C−Ph, major), 130.7 (CH−Ph), 128.8 (CH−Ph, major), 127.6 (CH−Ph, major), 126.9 (CH−Ph, major), 121.7 br (*o*-CH−Ph, minor), 120.5 (=CH_2, major), 119.7 (−CH=, major), 66.1 (N−CH_2−, minor), 60.3 (N−CH_2, major), 47.6 (N−CH_3, major), 42.8 (−CH=, minor), 40.6 (N−CH_3, minor), 32.8 (=CH_2, minor). IR ($CHCl_3$): ν 2042, 2021, 1967, 1939, 1917, 1623, 1525, 1484, 1403 cm^{-1}.

Tricarbonyl[(η^3-*N*-methyl-2-(biphenyl-4-yl)-4,5-dihydropyrrole]iron(0) (4f). The same method as used for the preparation of **4a** starting from the above mixture of **2f** and **3f** (0.4 g; 1 mmol) afforded after crystallization from a pentane−ether mixture pure **4f** (0.195 g; 52%) as a yellow-orange plates. Mp: 77−79 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.10 (m, 1H, =CH−CH_2−), 2.50 (m, 1H, =CH−CH_2−), 2.69 (m, 1H, N−CH_2−), 2.75 (s, 3H, N−CH_3), 2.93 (dt, J = 4.1, 9.0 Hz, 1H, N−CH_2−), 3.09 (d, J = 3.8 Hz, 1H, −C*H*=), 7.37−7.42 (m, 1H, Ph−*H*), 7.46−7.51 (m, 2H, Ph−*H*), 7.54−7.58 (m, 2H, Ph−*H*), 7.61−7.66 (m, 4H, Ph−*H*). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 213.7 (CO), 141.1 (C−Ph), 140.4 (C−Ph), 134.7 (C−Ph), 131.7 (CH−Ph), 128.9 (CH−Ph), 127.6 (CH−Ph), 127.1 (CH−Ph), 127.0 (CH−Ph), 92.9 (Ph−C(−N)=), 59.4 (N−CH_2−), 46.8 (−CH=), 43.8 (N−CH_3), 32.6 (−CH_2−). IR ($CHCl_3$): ν 2874, 2025, 1945, 1489 cm^{-1}. Anal. Calcd for $C_{20}H_{17}NO_3Fe$: C, 64.02; H, 4.57; N, 3.73. Found: C, 63.76; H, 4.79; N, 3.68.

Methyl 3-(*N*-Methyl-*N*-tosylamino)propanoate.[16] 3-(*N*-Methyl-*N*-tosylamino)propannitrile[17] (17.16 g; 72 mmol) in dry HCl−CH_3OH (20%; 90 g) was stirred and heated at reflux for 3 h. The reaction mixture containing precipitated NH_4Cl was evaporated to dryness and the residue neutralized with ice and K_2CO_3 solution. The product was extracted with dichloromethane (3 × 30 mL). Combined extracts were dried with Na_2SO_4, and evaporation of the solvent gave the title compound (18.69 g; 96%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.41 (s, 3H, C−CH_3), 2.60 (t, J = 7.1 Hz, 2H, −CH_2−), 2.74 (s, 3H, N−CH_3), 3.29 (t, J = 7.1 Hz, 2H, −CH_2−), 3.66 (s, 3H, O−CH_3), 7.30 (d, J = 8.2 Hz, 2H, Ph−*H*), 7.65 (d, J = 8.2 Hz, 2H, Ph−*H*). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 171.7 (C=O), 143.5 (C−Ph), 134.2 (C−Ph), 129.7 (CH−Ph), 127.3 (CH−Ph), 51.8 (O−CH_3), 46.0 (−CH_2−), 35.6 (N−CH_3), 33.5 (−CH_2−), 21.4 (C−CH_3).

3-(*N*-Methyl-*N*-tosylamino)propanol-*1,1-d*$_2$. To the stirred suspension of lithium aluminum deuteride (1.75 g; 41.7 mmol) in THF (40 mL) was added dropwise methyl 3-(*N*-methyl-*N*-tosylamino)propanoate (13.6 g; 50 mmol) in THF (60 mL) via a syringe at 0 °C. The mixture was then refluxed for 6 h, and after cooling excess deuteride was carefully decomposed with $Na_2SO_4 \cdot 10H_2O$ (10 g). The resulting suspension was stirred for 3 h and then filtered with suction, and the precipitate was washed with THF (20 mL). The solvent was then removed under reduced pressure, the residue was treated with water (20 mL), and the product was extracted with dichloromethane (3 × 20 mL). Combined extracts were dried with Na_2SO_4, and evaporation of the solvent gave the desired product (9.32 g; 76%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.71 (t, J = 6.3 Hz, 2H, −CH_2−), 2.42 (s, 3H, C−CH_3), 2.42 (bs, 1H,

(16) The methodology described for the preparation of *N*-Ts-*β,β′*-dicarbomethoxydiethylamine was used: Speckamp, W. N.; Dijkink, J.; Dekkers, A. W. J. D.; Huisman, H. O. *Tetrahedron* **1971**, *27*, 3143.

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−O*H*), 2.73 (s, 3H, N−CH_3), 3.10 (t, J = 6.3 Hz, 2H, −CH_2−), 7.31 (d, J = 8.2 Hz, 2H, Ph−*H*), 7.66 (d, J = 9.1 Hz, 2H, Ph−*H*). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 143.4 (C−Ph), 134.2 (C−Ph), 129.7 (CH−Ph), 127.2 (CH−Ph), 46.5 (−CH_2−), 34.9 (N−CH_3), 29.6 (−CH_2−), 21.4 (C−CH_3).

1-Mesyloxy-3-(*N*-methyl-*N*-tosylamino)propane-*1,1-d*$_2$. To a stirred solution of 3-(*N*-methyl-*N*-tosylamino)propanol-*1,1-d*$_2$ (7.36 g; 30 mmol) and triethylamine (4.9 mL; 35 mmol) in dichloromethane (60 mL) was added methanesulfonyl chloride (2.55 mL; 33 mmol) via a syringe. After stirring for 2 h at room temperature water (10 mL) was added, and the water layer was made acidic with dilute hydrochloric acid. The solution was then washed with 5% $NaHCO_3$ (5 mL) and dried with Na_2SO_4. Evaporation of solvents gave the title compound (9.6 g; 99%) as a yellowish oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.98 (t, J = 6.6 Hz, 2H, −CH_2−), 2.43 (s, 3H, C−CH_3), 2.72 (s, 3H, N−CH_3), 3.07 (s, 3H, S−CH_3), 3.10 (t, J = 6.6 Hz, 2H, −CH_2−), 7.33 (d, J = 8.2 Hz, 2H, Ph−*H*), 7.66 (d, J = 8.2 Hz, 2H, Ph−*H*). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 143.6 (C−Ph), 133.8 (C−Ph), 129.8 (CH−Ph), 127.4 (CH−Ph), 46.4 (−CH_2−), 37.2 (S−CH_3), 35.2 (N−CH_3), 27.2 (−CH_2−), 21.5 (C−CH_3).

***N*-Allyl-*3,3-d*$_2$-*N*-methyltoluenesulfonamide.** Sodium borohydride (1.42 g; 37.5 mmol) was slowly added to a stirred solution of $(PhSe)_2$ (4.7 g; 15 mmol) in ethanol (60 mL), and the mixture was cooled to 0 °C. After 20 min a solution of 1-mesyloxy-3-(*N*-methyl-*N*-tosylamino)propane-*1,1-d*$_2$ (9.06 g; 28 mmol) in THF (50 mL) was added via a syringe. The mixture was stirred overnight at room temperature, ethanol was evaporated in a vacuum, and the residue was partitioned between water and dichloromethane. The organic phase was dried with Na_2SO_4, solvent was evaporated, and the residue was dissolved in THF (50 mL). The resulting solution was added to a stirred solution of $NaIO_4$ (16 g; 75 mmol) in a mixture of water (125 mL) and THF (100 mL) at 0 °C followed by $NaHCO_3$ (2.35 g; 28 mmol). The resulting solution was stirred at 0 °C for 80 min, at room temperature for 1 h, and at 70 °C for 4 h and then allowed to cool to room temperature. THF was removed under reduced pressure, and the product was extracted with dichloromethane (3 × 30 mL). Combined extracts were dried with Na_2SO_4, solvents were evaporated, and the product was purified by column chromatography on silica. Elution with dichloromethane afforded *N*-allyl-*3,3-d*$_2$-*N*-methyltoluenesulfonamide (5.79 g; 91%) as a yellowish oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.43 (s, 3H, C−CH_3), 2.66 (s, 3H, N−CH_3), 3.62 (d, J = 6.6 Hz, 2H, −CH_2−), 5.70 (bs, 1H, −C*H*═), 7.32 (d, J = 7.7 Hz, 2H, Ph−*H*), 7.67 (d, J = 8.2 Hz, 2H, Ph−*H*).

Tetracarbonyl[(*N*-allyl-*3,3-d*$_2$-*N*-methylamino)(phenyl)carbene]iron(0) (*d*$_2$-2a) and *cis*-Tricarbonyl[(η^2-*N*-allyl-*3,3-d*$_2$-*N*-methylamino)(phenyl)carbene]iron(0) (*d*$_2$-3a). To a stirred solution of *N*-allyl-*3,3-d*$_2$-*N*-methyltoluenesulfonamide (3.41 g; 15 mmol) in THF (40 mL) was added at −78 °C via a syringe a solution of sodium naphthalenide prepared by dissolving sodium (0.6 g; 26 mmol) and naphthalene (3.4 g; 26.5 mmol) in THF (40 mL), until the dark green color remained. The reaction mixture was then stirred for 15 min at −78 °C, and water (1 mL) was added. After warming to room temperature 3 M HCl (10 mL) was added, THF was evaporated under reduced pressure, and the remaining acidic water solution was extracted with ether (3 × 10 mL). Then the water layer was made strongly alkaline with solid NaOH, and released *N*-methylallylamine-*3,3-d*$_2$ was extracted with ether (4 × 10 mL). Extracts were dried with NaOH and used without further purification.

To a solution of tetracarbonyl[ethoxy(phenyl)carbene]iron-(0)[18] (1.0 g; 3.3 mmol) and CH_3ONa (0.02 g) in THF (2 mL) was added an ethereal solution of the above amine at room temperature. The reaction mixture was stirred for 30 min, the solvent was evaporated, and the residue was chromatographed on neutral alumina (150 g). Elution with a light petroleum−dichloromethane mixture (10:1) gave a mixture of ***d*$_2$-2a** and ***d*$_2$-3a** in 3:2 ratio as an orange oil (0.52 g; 50%). ^{1}H NMR ($CDCl_3$, 300 MHz): ***d*$_2$-2a**: δ 3.95 (s, 3H, N−CH_3), 4.01 (d, J = 5.5 Hz, 2H, N−CH_2−), 5.61 (bs, 1H, −C*H*═), 6.85 (d, J = 7.1 Hz, 2H, Ph−*H*), 7.17−7.30 (m, 1H, Ph−*H*), 7.30−7.42 (m, 2H, Ph−*H*); ***d*$_2$-3a**: 2.94 (s, 3H, N−CH_3), 3.18 (d, J = 3.9 Hz, 1H, −C*H*═), 4.18−4.35 (m, 2H, N−CH_2−), 6.85 (d, J = 7.1 Hz, 2H, Ph−*H*), 7.17−7.30 (m, 1H, Ph−*H*), 7.30−7.42 (m, 2H, Ph−*H*).

Tricarbonyl[(η^3-*N*-methyl-2-phenyl-4,5-dihydropyrrole-*3,4-d*$_2$]iron(0) (*d*$_2$-4a). The same method as was used for the preparation of **4a** starting from (0.32 g; 1 mmol) afforded ***d*$_2$-4a** (0.2 g; 66%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.05 (m, 1/2H, ═CD−C*H*D−), 2.44 (m, 1/2H, ═CD−C*H*D−), 2.62−2.69 (m, 1H, N−CH_2−), 2.67 (s, 3H, N−CH_3), 2.85−2.92 (m, 1H, N−CH_2−), 7.34-7.42 (m, 3H, Ph−*H*), 7.44−7.50 (m, 2H, Ph−*H*). ^{2}H NMR ($CDCl_3$, 76.75 MHz): δ 2.07 (s, $^1/_2$D, ═CD−CH*D*−), 2.47 (s, $^1/_2$D, ═CD−CH*D*−), 3.05 (s, 1D, ═*CD*−). IR ($CHCl_3$): ν 3020, 2024, 1944, 1445 cm^{-1}. HRMS calcd 301.0371, found 301.0367.

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Supporting Information Available: Complete listings of structural parameters for **4f**. Absolute energies and Cartesian coordinates of all stationary points, using 6-31G(d,p) basis sets. This material is available free of charge via the Internet at http://pubs.acs.org.

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