Iron Aminocarbene Complexes Containing a Double C=C Bond in the N-Substituent: Preparation and Reactivity

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Reaction of *N*,*N*-diallylbenzamide with $Na_2Fe(CO)_4$ and Me_3SiCl afforded chelated *cis*-tricarbonyl[(η^2-*N*-allyl-*N*-allylamino)(phenyl)carbene]iron(0) directly. The same reaction of *N*-(3-buten-1-yl)-*N*-methylbenzamide proceeded with migration of the double bond to the allylic position, giving a mixture of chelated *cis*-tricarbonyl[(η^2-*N*-(2-butenyl)-*N*-methylamino)-(phenyl)carbene]iron(0) and nonchelated tetracarbonyl[(*N*-(2-butenyl)-*N*-methylamino)(phenyl)carbene]iron(0). *N*-(3-Buten-2,2-dimethyl-1-yl)-*N*-methylbenzamide, in which migration of double bond is not possible, gave a mixture of *E* and *Z* isomers of nonchelated tetracarbonyl-[(*N*-(2,2-dimethyl-3-butenyl)-*N*-methylamino)(phenyl)carbene]iron(0). Thermolysis of the latter furnished 1-methyl-3,3-dimethyl-6-phenyl-1,2,3,4-tetrahydropyridine as the only product.

Introduction

Chelated metal−carbene−alkene complexes[1] of group 6 metals show unique reactivity. Tethering the η^2-alkene ligand to the carbene carbon changes the reactivity of these complexes substantially. Restricted geometry of these complexes results in stabilizing or activating the molecule for further reactions, usually favoring or suppressing some of the possible reaction pathways. The chelated complexes bearing two other atoms between the coordinated double C=C bond and the carbene atom are relatively stable.[2] With alkynes, however, facile insertion of the triple bond followed by other reactions resulting in formation of polycyclic compounds readily occur.[2e,3,4] The complexes with three or four atom spacers between the carbene atom and the double bond are more reactive. Thus, neither alkoxy- nor aminocarbene complexes cyclopropanate inactivated olefins in intermolecular reactions. However, when olefinic unsaturation is present in the alkoxy or amino side chain in two or three atoms from the heteroatom, the intramolecular cyclopropanation is facile and efficient.[5] In some cases the reactivity of the corresponding η^2-chelated complex was so high that it was not possible to isolate it, and the cyclopropanated product was obtained directly.[5d] Especially interesting is the case of intramolecular cyclopropanation of aminocarbenes,[5b,d] where intermolecular reaction does not occur at all. Examples of similar chelated complexes of other than group 6 transition metals are less common. Chelated carbene complexes of manganese,[6] cationic chelated Cp(CO)Fe bisalkoxycarbenes,[7a] and neutral chelated tricarbonyliron bisalkoxy- and aminoalkoxycarbenes prepared by reaction of the corresponding cationic (η^3-allyl)carbene complexes with nucleophiles[7b] were mentioned in the literature.

We have recently shown that the methodology for the preparation of the chromium aminocarbenes,[8] which is based on the reaction of tertiary amides with $Cr(CO)_5^{2-}$ followed by Me_3SiCl, can also be used for the preparation of neutral iron aminocarbenes.[9] In this paper we report on the preparation and reactivity of iron aminocarbene complexes bearing a double bond in the amine side chain prepared by the above methodology.

Results and Discussion

Reaction of *N*,*N*-diallylbenzamide (**1a**) with $Na_2[Fe(CO)_4]$ and Me_3SiCl in THF led directly to the chelated *cis*-tricarbonyl((η^2-*N*,*N*-diallylamino)phenylcarbene)iron-

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(1) For a recent review of a chelated metal−carbene−alkene complexes see: Schobert, R. *J. Organomet. Chem.* **2001**, *617*−*618*, 346.

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(3) (a) Parlier, A.; Rudler, H.; Platzer, N.; Fontanille, M.; Soum, A. *J. Chem. Soc., Dalton Trans.* **1987**, 1041. (b) Dötz, K. H.; Erben, H.-G.; Harms, K. *J. Chem. Soc., Chem. Commun.* **1989**, 692.

(4) For review of carbene−alkyne−alkene cyclization reactions see: Harvey, D. F.; Sigano, D. M. *Chem. Rev.* **1996**, *96*, 271.

(5) (a) Casey, C. P.; Schusterman, A. *J. Organometallics* **1985**, *4*, 736. (b) Casey, C. P.; Vollendorf, N. W.; Haller, K. *J. J. Am. Chem. Soc.* **1984**, *106*, 3754. (c) Casey, C. P.; Hornung, N. L.; Kosar, W. P. *J. Am. Chem Soc.* **1987**, *109*, 4908. (d) Söderberg, B. C.; Hegedus, L. S. *Organometallics* **1990**, *9*, 3113.

(6) (a) McGeary, M. J.; Tonker, T. L.; Templeton, J. L. *Organometallics* **1985**, *4*, 2102. (b) Hoye, T. R.; Rehberg, G. M. *Organometallics* **1990**, *9*, 3014.

(7) (a) Schobert, R.; Förtsch, W.; Hampel, F. *J. Organomet. Chem.* **1996**, *526*, 169. (b) Förtsch, W.; Hampel, F., Schobert, R. *Chem. Ber.* **1997**, *130*, 863. See also references cited in ref 1.

(8) (a) Imwinkelried, R.; Hegedus, L. S. *Organometallics* **1988**, *7*, 702. (b) Schwindt, M. A.; Lejon, T.; Hegedus, L. S. *Organometallics* **1990**, *9*, 2814.

(9) (a) Dvořák, D. *Organometallics* **1995**, *14*, 570. (b) Havránek, M.; Hušák, M.; Dvořák, D. *Organometallics* **1995**, *14*, 5024. (c) Dvořák, D.; Ludwig, M. *Organometallics* **1998**, *17*, 3627.

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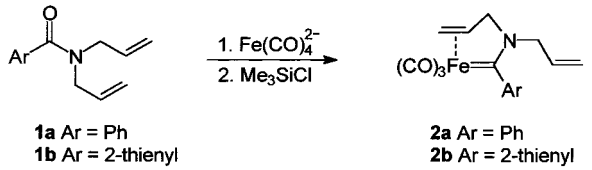
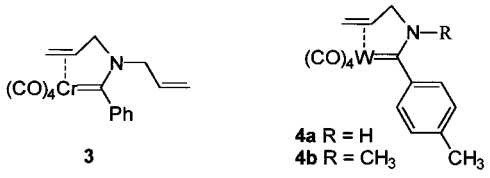
Scheme 1



(0) (**2a**) in 67% yield (Scheme 1). The fact that one double bond in **2a** is coordinated to the metal is apparent from the ^{1}H NMR spectrum, the three protons associated with the double bond being shifted to higher field at 1.52 and 2.04 ppm for $=CH_2$ and 3.20 ppm for $-CH=$. Similar effects can be seen from ^{13}C NMR with olefinic carbons shifted to 33.5 ppm for $=CH_2$ and 43.4 ppm for $-CH=$. Also *N*,*N*-diallyl-2-thiophene carboxamide (**1b**) furnished chelated aminocarbene complex (**2b**) in 30% yield (Scheme 1).

Chelated iron aminocarbene complex **2a**, as the only carbene product, was also obtained using Lappert methodology[10] by reaction of the chloroiminium salt derived from **1a** with $Na_2[Fe(CO)_4]$ (20% yield) and also by exchange reaction of $(CO)_4Fe{=}CPh(OEt)$ with allylamine and subsequent reaction with NaH and allyl bromide in 36% overall yield ($(CO)_4Fe{=}CPh(OEt)$ did not react with *N*,*N*-diallylamine directly). Interestingly, the reaction of $Na_2Cr(CO)_5$ with *N*,*N*-diallylamide **1a** and Me_3SiCl also gave chelated complex **3**, in this case accompanied with about 8% of nonchelated pentacarbonyl[(*N*,*N*-diallylamino)(phenyl)carbene]chromium-(0), under otherwise identical conditions. These results are somewhat surprising since most of the reported chelated *N*-allylaminocarbene complexes of Cr and W were prepared by thermolysis or photolysis of nonchelated complexes resulting from alkoxy to amine exchange reactions.[2,3,5a−c] The fact that iron chelate **2a** was formed in all cases as the only carbene product, no matter what method was used for its preparation, shows the higher tendency of iron to form chelated carbene complexes compared to the chromium. However, the finding that with chromium the chelated carbene complex is also the main product suggests that the method of preparation (reaction of $M(CO)_n^{2-}$ with carboxamide and Me_3SiCl) or (and) steric bulk of *N*,*N*-diallylamino group may play a role in the formation of the chelate.



Published X-ray analysis of similar tungsten *N*-allylaminocarbene complex **4a** revealed perpendicular orientation of the coordinated C=C and C=W bonds.[2d] Since chelated aminocarbene **2a** has low melting point, X-ray analysis was not possible. Therefore, the spatial orientation of the coordinated double bond was obtained from NOE experiments. The aromatic ring of aminocarbene complexes is known to be perpendicular to the plane defined by the metal, the carbene atom, and the

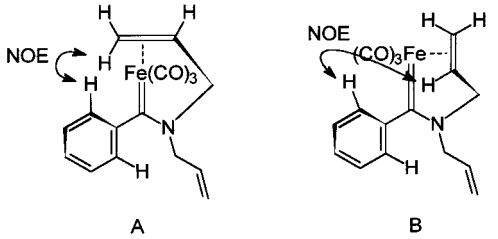
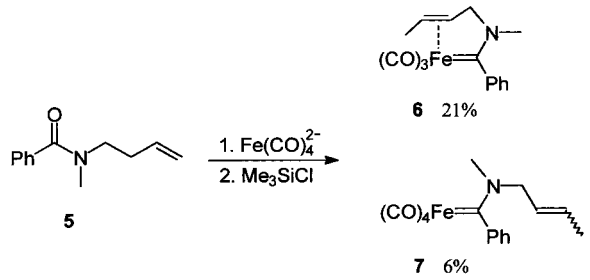


Figure 1. NOE interactions expected for perpendicular (A) and parallel (B) orientation of the chelated C=C and carbene bonds in **2a**.

Scheme 2



nitrogen atom.[11] For that reason there should be an NOE between *o*-hydrogens of the phenyl group either with one hydrogen atom of the chelated $=CH_2$ group in the case of perpendicular arrangement (Figure 1, A) or with the $-CH=$ hydrogen of the chelated double bond when both double bonds are parallel (Figure 1, B). Only an NOE between *o*-hydrogens of the aromatic ring and a hydrogen atom *cis* to the CH_2N group of the terminal $=CH_2$ of the chelated allyl group was observed, as required for perpendicular arrangement (Figure 1, A) of the chelated-alkene and carbene bonds.

The appearance of the signals of the *o*-hydrogens of the benzene ring (two very broad singlets) shows that these signals are near the coalescence at room temperature. Line shape analysis afforded $\Delta G^{\ddagger}_{298} = 60.7$ kJ/mol for the rotational barrier of the aromatic ring. This value is higher than that obtained previously for tungsten *N*-allyl-*N*-methyl complex **4b** ($\Delta G^{\ddagger}_{298} = 49.8$ kJ/mol)[2f] probably as a result of higher steric bulk of the *N*-allyl group of **2a** compared with the *N*-methyl group of **4b**. This is in agreement with previous findings that the rotational barrier is due to a *(E)*-*N*-substituent rather than the metal carbonyl moiety.[12] No other dynamic process was observed below 80 °C. At this temperature decomposition accompanied by formation of paramagnetic particles makes further NMR measurements impossible.

Reaction of *N*-(3-butenyl)-*N*-methylbenzamide (**5**) with $Na_2[Fe(CO)_4]$ and Me_3SiCl gave a mixture of two carbene complexes, chelated complex **6** and nonchelated aminocarbene **7** in about 3:1 ratio. In both compounds the double bond was isomerized to the allylic position (Scheme 2). The complexes **6** and **7** were separated by preparative HPLC. The nonchelated complex **7** is stable at room temperature, but slow conversion into complex **6** was observed at 80 °C in toluene. The ^{1}H NMR spectrum clearly shows the absence of a terminal double

(10) Hartshorn, A. *J*.; Lappert, M. F.; Turner, K. *J. Chem. Soc., Dalton Trans.* **1978**, 348.

(11) Amin, Sk. R.; Jayaprakash, K. N.; Nandi, M,; Sathe, K. M.; Sarkar, A. *Organometallics* **1996**, *15*, 3528.

(12) For discussion of another possible reason of hindered rotation of an aromatic ring see ref 2f.

bond in both cases, as apparent from the presence of doublets of the =CH−CH_3 groups (see Experimental Section).

The chelated complex **6** was obtained as a single geometrical isomer on the double C=C bond. The ^{1}H NMR spectrum of this compound exhibits a doublet of the methyl group at 1.61 ppm (J = 6.4 Hz), in agreement with an isomerized structure. The signals of the hydrogen atoms on the coordinated double bond are, as expected, shifted to higher field at 2.40 and 3.06 ppm. The coupling constant between these two protons is 10.4 Hz, identical with that found for the *trans* protons of the coordinated double bond of the diallylamino complex **2a**. Therefore *trans* geometry on the coordinated double bond was assigned for this compound.

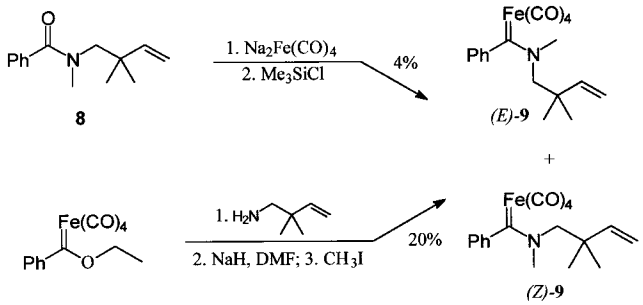
The nonchelated complex **7** was obtained as a mixture of two geometrical isomers on the double C=C bond in approximately 5:1 ratio. The ^{1}H NMR spectrum of the major isomer shows a doublet of the =CH−CH_3 methyl group at 1.61 ppm (J = 6.6 Hz) and two one-proton multiplets for the olefinic protons at 5.25 and 5.62 ppm, confirming the presence of an isomerized and uncoordinated double C=C bond. The signal of the N−CH_3 at 3.90 ppm is in agreement with the position of the methyl group pointing to the metal.[13] Because of the complex nature of the overlapping multiplets of the olefinic protons, we were not able to assign configuration to the C=C bond of the individual isomers of **7**.

Isomerization of the double bond to the position containing two atoms bridged between the carbene atom and the double C=C bond during its chelatation is relatively common[2a,b,d] and is ascribed to the high stability of such complexes. However, in contrast to the above-mentioned formation of **6** and **7** the isomerization associated with chelatation described in the literature occurs only at elevated temperature.

The mechanism of the isomerization of the double bond during the formation of **6** and **7** remains unclear. Both chelated and nonchelated carbene complexes have isomerized double bonds, and there is no equilibrium between chelated and nonchelated complexes at the temperature used for their preparation. This suggests that a fast isomerization proceeds before carbenes **6** and **7** are formed. Further experiments revealed that Na_2-$Fe(CO)_4$ itself does not isomerize the double bond of **5** even at room temperature and a prolonged reaction time. After addition of Me_3SiCl a rapid formation of the mixture of **6** and **7** occurs. Interestingly also exposure of the mixture of amide **5** and $Na_2Fe(CO)_4$ to air results in the migration of the double bond of **5** to the allylic position.[14]

To prevent the isomerization, we used the approach by Casey[5b] and the reaction was run with amide **8**, in which an isomerization of the double bond is not possible. Reaction of amide **8** with $Na_2[Fe(CO)_4]$ and Me_3SiCl furnished a nonchelated carbene complex **9** in a very low yield (4%) as a mixture of *E* and *Z* isomers

Scheme 3



with *E*:*Z* ratio >9:1. Most of the starting amide **8** was recovered. No aminocarbene **9** was obtained when amide **8** was first converted to the corresponding iminium salt by reaction with $(COCl)_2$ and then reacted with Na_2-$[Fe(CO)_4]$. An exchange reaction of $(CO)_4Fe$=C(OEt)Ph with 3,3-dimethyl-4-aminobut-1-ene followed by methylation (Scheme 3) gave the desired complex **9** in approximately 20% yield, however in this case accompanied with some difficult to separate impurities. The *E*:*Z* ratio was in this case 1:1. The structure of (*E*)- and (*Z*)-**9** was assigned on the basis of ^{1}H NMR. The shifts of alkene protons (5.09, 5.11, and 5.83 ppm for the main isomer and 5.11, 5.13, and 6.09 ppm for the minor isomer) point out that the double bond is not coordinated to the metal in both cases. The shift of the *N*-methyl group (3.94 ppm) shows the orientation of the methyl group toward the metal, providing an *E* configuration of the major isomer, while the chemical shift of the N−CH_3 group of the minor isomer (2.95 ppm) confirms the *Z* configuration of this compound.

Reactivity of Obtained Complexes. Despite the fact that chelatation of the double bond of *N*-allylaminocarbenes of chromium was reported to facilitate insertion of alkynes,[3b] the chelated iron (*N*,*N*-diallylamino)-carbene **2** failed to give any productive reaction with alkynes such as phenylacetylene, diphenylacetylene, and esters of propiolic or acetylenedicarboxylic acids. This is surprising, since nonchelated tetracarbonyl[*N*,*N*-dimethylamino(phenyl)methylene]iron(0) is known to form substituted 2-aminofurans[15] easily. The higher stability of the iron−alkene bond in the chelated aminocarbene **2** compared to its chromium analogue may be responsible for this behavior.

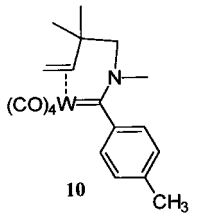
Thermolysis of tungsten carbene complex **10**, the chelated analogue of **9**, was reported to give the product of intramolecular cyclopropanation, **11a**, presumably via a metallacyclobutane intermediate.[5b] When iron carbene **9** was heated to 80 °C in toluene, reaction accompanied with formation of brown-black precipitate occurred. TLC analysis showed the presence of virtually one product, which did not contain iron. Formation of the chelated carbene complex was not observed. Attempts to isolate the product of thermolysis of **9** were unsuccessful. While relatively stable in solution, it quickly decomposed after evaporation of the solvent. Therefore the structure of this compound was determined in solution without its isolation. GC−MS showed a molecular peak m/z = 201 (EI), as expected for the product of cyclopropanation **11b**. The ^{1}H NMR spectrum of the reaction mixture in toluene-d_8, however, showed no cyclopropane derivative.

(13) (a) Moser, E.; Fischer, E. O. *J. Organomet. Chem*. **1969**, *16*, 275. (b) Fischer, E. O.; Leupold, M. *Chem. Ber*. **1972**, *105*, 599.

(14) The isomerization of the double bond of the amide **5** to the allylic position can also be achieved by treatment with 1 equiv of $Fe_2(CO)_9$ in THF solution at 40 °C. The conditions are similar to those reported for isomerization of *N*,*N*-diallylbenzamide (**1a**) to *N*-vinylbenzamide: Murai, T.; Kasai, Z.; Ishihara, H.; Kato, S. *J. Org. Chem*. **1992**, *57*, 5542. However, the isomerization leading to carbenes **6** and **7** is much faster even at −78 °C.

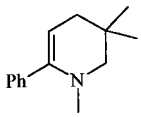
(15) Semmelhack, M. F.; Park, J. *Organometallics* **1986**, *5*, 2550.

Instead, besides the signals of aromatic protons one proton triplet in the alkene region (4.62 ppm, $J = 4.4$ Hz), two signals of the CH_2 groups (singlet 2.54 ppm and doublet 1.86 ppm, $J = 4.4$ Hz), the signal of the $N-CH_3$ group 2.41 ppm), and the singlet of six protons of two CH_3 groups (0.98 ppm) were observed. This spectrum is consistent with tetrahydropyridine derivative **12**, an isomer of **11b**. This structure was further confirmed with COSY and HMBC experiments.



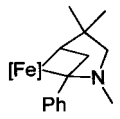
10

11a Ar = p-tolyl
11b Ar = Ph

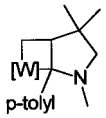


12

The mechanism of formation of **12** remains unclear. The most straightforward seems to be the formation of metallacyclobutane **13a**, which would form tetrahydropyridine **12** by a β-elimination−reductive elimination sequence. This, however, requires opposite regioselectivity in metallacyclobutane formation as previously suggested for the intramolecular formation of **11a**, which is supposed to be formed via metallacyclobutane **13b**.[5b]



13a



13b

In conclusion, iron tetracarbonylferrate reacts with aromatic *N*,*N*-diallylamides followed by Me_3SiCl with direct formation of chelated carbene complexes. In the case of *N*-homoallylic benzamide **5** shift of the double bond to the allylic position followed by the chelatation occurs. When isomerization for a structural reason is not possible, instead of intramolecular cyclopropanation, which is usual for structurally related group 6 carbene complexes, a new reaction—formation of tetrahydropyridine derivative **12**—was observed. Applicability of the reaction of metal carbonylates with *N*,*N*-diallylcarboxamides for the preparation of the corresponding chelated aminocarbene complexes of group 6 elements as well as the study of reactivity of chelated aminocarbene complexes is currently under study in our laboratory.

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 a Bruker DRX 500 Avance (^{1}H, 500.13 MHz; ^{13}C, 125.77 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. GC−MS was measured on a Saturn 2000 GC−MS system, column DB-5 (30m × 0.25 mm), He 0.8 mL/min, 80−230 °C. HPLC separation was done on reversed-phase LiChrospher 100 RP-18 with 90:10 methanol−water as a mobile phase. All experiments were carried out under argon. Tetrahydrofuran was distilled from benzophenone ketyl under Ar prior to use. Iron pentacarbonyl, chromium hexacarbonyl, Me_3SiCl, and methyl 3,3-dimethyl-4-pentenoate were purchased from Aldrich and were used without purification. Neutral aluminum oxide (Brockman III grade) and silica were obtained from Lachema.

***N*-(3-Buten-1-yl)benzamide.** To the stirred suspension of 1-amino-3-butene hydrochloride[16] (1.67 g, 15.5 mmol) in dry dichloromethane (40 mL) was added triethylamine (4.5 mL, 32 mmol). The mixture was cooled in an ice bath, benzoyl chloride (2 mL, 17 mmol) was added dropwise, and the mixture was stirred for 2 h without cooling. The reaction mixture was then diluted with diethyl ether and filtered, the solvent from the filtrate was evaporated, and the residue was dissolved in ether and again filtered and evaporated. The crude amide was purified by chromatography on silica (light petroleum−diethyl ether−acetone, 80:10:10), giving 2.44 g (90%) of the product with ^{1}H NMR identical with that reported.[17]

***N*-(3-Buten-1-yl)-*N*-methylbenzamide (5).** *N*-(3-Buten-1-yl)benzamide (2.0 g, 11.5 mmol) was dissolved in THF (30 mL), 80% dispersion of sodium hydride (0.45 g, 15 mmol) was added, and the mixture was stirred at room temperature. After 1 h iodomethane (2.5 g, 18 mmol) was added, and the mixture was stirred for another 2 h, quenched with methanol (1 mL), and filtered through 25 g of silica, which was subsequently washed with diethyl ether (50 mL). Evaporation of the solvents and purification by column chromatography on silica (light petroleum−diethyl ether−acetone, 8:1:1) afforded 2.5 g (90%) of the product. An analytical sample was obtained by short pass distillation, bp 105 °C/120 Pa (bath temperature). ^{1}H NMR (DMSO-d_6, 100 °C): δ 2.35 (q, $J = 7$ Hz, 2H, $-CH_2-CH{=}C$), 2.93 (s, 3H, $N-CH_3$), 3.43 (t, $J = 8$ Hz, 2H, $N-CH_2-$), 5.04 (d, $J = 10.4$ Hz, 1H, $=CH_2$), 5.08 (d, $J = 17.9$ Hz, 1H, $=CH_2$), 5.77 (m, 1H, $-CH{=}$), 7.35 (m, 2H, Ph), 7.42 (m, 3H, Ph). IR ($CHCl_3$): ν 3008, 1623, 1578, 1501, 1446, 1404 cm^{-1}. Anal. Calcd for $C_{12}H_{15}NO$: C, 76.16; H, 7.99; N, 7.40. Found: C, 76.27; H, 8.29; N, 7.12.

***N*-(3-Buten-2,2-dimethyl-1-yl)benzamide** was prepared analogously to *N*-(3-buten-1-yl)benzamide starting from the hydrochloride of 1-amino-2,2-dimethyl-3-butene[18] in 95% yield. Mp: 52−56 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.09 (s, 6H, $C(CH_3)_2$), 3.35 (s, 1H, CH_2), 3.37 (s, 1H, CH_2), 5.09 (d, $J = 17.6$ Hz, $=CH_2$), 5.12 (d, $J = 11.0$ Hz, $=CH_2$), 5.83 (dd, 11.0, 17.6 Hz, $-CH{=}$), 6.60 (bs, 1H, NH), 7.38−7.52 (m, 3H, Ph), 7.73 (m, 2H, Ph). IR ($CHCl_3$): ν 3449, 3011, 2970, 1657, 1580, 1525, 1488 cm^{-1}. Anal. Calcd for $C_{13}H_{17}NO$: C, 76.81; H, 8.43; N, 6.89. Found: C, 76.48; H, 8.02; N, 6.79.

***N*-(3-Buten-2,2-dimethyl-1-yl)-*N*-methylbenzamide (8).** The same method as was used for the preparation of *N*-(3-buten-1-yl)-*N*-methylbenzamide (**5**), starting from *N*-(3-buten-2,2-dimethyl-1-yl)benzamide (3.05 g, 15 mmol), 80% dispersion of sodium hydride (0.75 g, 25 mmol), and iodomethane (1.9 mL, 30.5 mmol) in THF (40 mL), afforded 2.63 g (80%) of the product after chromatography and distillation. Bp: 120−125 °C/27 Pa. Mp: 32−35 °C. ^{1}H NMR (DMSO-d_6, 100 °C): δ 1.05 (s, 6H, $C(CH_3)_2$), 2.94 (s, 3H, $N-CH_3$), 3.45 (s, 2H, $N-CH_2$), 4.98 (d, $J = 10.8$ Hz, 1H, $=CH_2$), 5.04 (d, $J = 17.8$ Hz, 1H, $=CH_2$), 5.94 (dd, $J = 10.8, 17.4$ Hz, $-CH{=}$), 7.36 (m, 2H, Ph), 7.42 (m, 3H, Ph). IR ($CHCl_3$): ν 3010, 2971, 1627, 1402, 1321

(16) Hydrochloride of 1-amino-3-butene was prepared in 81% yield by Curtius reaction of 4-pentenoyl chloride with inactivated sodium azide and subsequent hydrolysis by 36% hydrochloric acid analogously as described in: Smith, P. A. S. *Organic Reactions*, III; J. Wiley: New York, 1946; p 387, for the preparation of benzylamine hydrochloride. Mp: 167−173 °C. Grob, C. A.; Krasnobajew, V. *Helv. Chim. Acta* **1964**, *47*, 2145: 175−176 °C

(17) Katritzky, A. R.; Ignatchenko, A. V.; Lang, H. *J. Org. Chem.* **1995**, *60*, 4002.

(18) The hydrochloride of 1-amino-2,2-dimethyl-3-butene was prepared in 71% yield from 3,3-dimethyl-4-pentenoyl chloride (prepared from commercial methyl 3,3-dimethyl-4-pentenoate) by the same method as described in ref 15. Mp: 197−200 °C (EtOAc−EtOH). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.18 (s, 6H, $C(CH_3)_2$), 2.83 (s, 2H, CH_2), 5.18 (d, 1H, $J = 17.6$ Hz, $=CH_2$), 5.21 (d, 1H, $J = 10.5$ Hz, $=CH_2$), 5.78 (dd, 1H, $J = 17.6, 11.0$ Hz, $-CH{=}$), 8.26 (bs, 3H, NH_3).

cm^{-1}. Anal. Calcd for $C_{14}H_{19}NO$: C, 77.38; H, 8.81; N, 6.45. Found: C, 77.38; H, 8.41; N, 6.52.

***cis*-Tricarbonyl[(η^2-*N*-allyl-*N*-allylamino)(phenyl)carbene]iron(0) (2a).** To a solution of sodium naphthalenide prepared by dissolving sodium (0.6 g; 26 mmol) and naphthalene (3.4 g; 26.5 mmol) in THF (50 mL) in argon atmosphere was added iron pentacarbonyl (1.4 mL; 10 mmol) at −78 °C via a syringe. The reduction of iron pentacarbonyl proceeds almost instantaneously with evolution of CO gas. The reaction mixture was then allowed to warm to 0 °C, and the amide **1a** (1.0 g; 5 mmol) in THF (5 mL) was added through a double-ended needle. The solution was stirred at 0 °C for 10 min, then cooled to −78 °C, and Me_3SiCl (3.5 mL; 28 mmol) was added via a syringe. The solution was stirred at −78 °C for 0.5 h, then the cooling bath was removed, the mixture was allowed to warm to 0 °C, and neutral alumina (8 g) was added. The solvent was removed under reduced pressure on a rotatory evaporator, and the residue was dried for several hours under high vacuum to remove all the THF. Light petroleum (50 mL) was then added, and the mixture was stirred vigorously for several minutes under argon atmosphere. The suspension formed was then transferred on top of a column filled with neutral alumina (150 g). Naphthalene was eluted with pure light petroleum, and further elution with a light petroleum−CH_2Cl_2 mixture (5:1) gave **2a** as a yellow-orange oil (1.09 g, 67%), which solidified upon several days in a freezer. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.52 (d, J = 10.4 Hz, 1H, chelated =CH_2), 2.04 (d, J = 7.7 Hz, 1H, chelated =CH_2), 3.20 (m, 1H, chelated −CH=), 3.76 (dd, J = 14.9, 6.0 Hz, 1H, NCH_2), 3.87 (dd, J = 14.9, 5.6 Hz, 1H, NCH_2), 4.18 (dd, J = 14.3, 5.0 Hz, 1H, chelated NCH_2), 4.35 (d, J = 14.3 Hz, 1H, chelated NCH_2), 5.15 (d, J = 17 Hz, 1H, =CH_2), 5.26 (d, J = 10 Hz, 1H, =CH_2), 5.56 (m, 1H, −CH=), 6.76 (bs, 1H, *o*-H−Ph), 6.95 (bs, 1H, *o*-H−Ph), 7.20−7.40 (m, 3H, Ph). ^{13}C NMR ($CDCl_3$, 125.77 MHz): δ 268.6 (carbene), 217.0 (CO), 147.6 (C−Ph), 131.9 (nonchelated =CH−), 129.0 (CH−Ph, 128.1 (CH−Ph), 121.9 br (*o*-CH−Ph), 121.0 br (*o*-CH−Ph), 120.3 (nonchelated =CH_2), 63.7 (chelated N−CH_2), 56.0 (nonchelated N−CH_2), 43.4 (chelated =CH−), 33.5 (chelated =CH_2). IR ($CHCl_3$): ν 2021, 1953, 1923, 1537 cm^{-1}. Anal. Calcd for $C_{16}H_{15}NO_3Fe$: C, 59.10; H, 4.65; N, 4.31. Found: C, 58.98; H, 4.88; N, 4.42.

***cis*-Tricarbonyl[(η^2-*N*-allyl-*N*-allylamino)(2-thienyl)carbene]iron(0) (2b).** The same procedure as used for the preparation of **2a** starting from *N*,*N*-diallyl-2-thiophene carboxamide (**1b**) (0.6 g; 2.9 mmol) afforded carbene complex **2b** (0.17 g; 30%) as an orange oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.49 (d, J = 10.4 Hz, 1H, chelated =CH_{cis}H$_{trans}$), 2.06 (d, J = 7.7 Hz, 1H, chelated =CH$_{cis}H_{trans}$), 3.22 (m, 1H, chelated CH=CH_2), 3.88 (dd, J = 15.6, 5.7 Hz, 1H, chelated N−CH_2), 4.17 (m, 2H, N−CH_2), 4.42 (d, J = 14.3, 1H, chelated N−CH_2) 5.22 (d, J = 17 Hz, 1H, =CH_2), 5.32 (d, J = 9.9 Hz, 1H, =CH_2), 5.72 (m, 1H, CH=CH_2), 6.82 (m, 1H, thienyl), 7.00 (m, 1H, thienyl), 7.47 (m, 1H, thienyl). ^{13}C NMR ($CDCl_3$, 75.46 MHz): δ 258.7 (carbene), 216.8 (CO), 147.8, 119.5, 64.7, 56.3, 34.35; CH 132.5, 128.7, 127.5, 123.0, 43.8. IR ($CHCl_3$) ν 2020, 1954, 1923, 1532 cm^{-1}. Anal. Calcd for $C_{14}H_{13}NO_3FeS$: C, 50.78; H, 3.96; N, 4.23; S, 9.68. Found: C, 50.74; H, 4.32; N, 4.16; S, 9.38.

***cis*-Tetracarbonyl[(η^2-*N*-allyl-*N*-allylamino)(phenyl)carbene]chromium(0) (3).** The solution of sodium naphthalenide prepared from sodium (0.6 g; 26 mmol) and naphthalene (3.4 g; 26.5 mmol) in THF (50 mL) was slowly added under argon atmosphere to the stirred suspension of $Cr(CO)_6$ (2.20 g; 10 mmol) in THF (40 mL) at −78 °C. The mixture was allowed to warm to 0 °C and kept at this temperature until all $Cr(CO)_6$ dissolved (ca. 0.5 h). A solution of *N*,*N*-diallylbenzamide (**1a**) (1.0 g; 5 mmol) in THF (10 mL) was then added through a double-ended needle. Further procedure was the same as that used for the preparation of **2a**. The product **3** (1.0 g; 57%) was obtained as a yellow solid containing approximately 8% of nonchelated complex. Pure **3** was obtained by crystallization, mp 57.5−59 °C (heptane−CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.22 (d, J = 8.8 Hz, 1H, chelated CH=CH_2), 3.34 (d, J = 12.6 Hz, 1H, chelated CH=CH_2), 3.82 (m, 2H, N−CH_2), 4.10 (dd, J = 13.7, 3.8 Hz, 1H, chelated N−CH_2), 4.49 (dd, J = 14.0, 5.2 Hz, 1H, coor. N−CH_2), 4.55 (m, 1H, chelated CH=CH_2), 5.17 (dd, J = 17.0, 1.1 Hz, 1H, CH=CH_2), 5.27 (dd, J = 9.9, 1.1 Hz, 1H, CH=CH_2), 5.57 (m, 1H, CH=CH2), 6.70 (m, 2H, Ph), 7.18 (m, 1H, Ph), 7.34 (m, 2H, Ph). IR ($CHCl_3$): ν 2013, 1914 vbr, 1520 cm^{-1}. Anal. Calcd for $C_{17}H_{15}NO_4Cr$: C, 58.45; H, 4.33; N, 4.01. Found: C, 58.38; H, 4.40; N, 3.87.

Nonchelated complex: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.22 (d, J = 5.5 Hz, 2H, NCH_2), 4.95 (d, J = 5 Hz, 2H, NCH_2), 5.14 (d, J = 17 Hz, 1H, =CH_2), 5.30 (d, 1H, =CH_2), 5.40 (d, J = 17 Hz, 1H, =CH_2), 5.49 (d, J = 10.4 Hz, 1H, =CH_2), 5.55 (m, 1H, −CH=), 6.04 (m, 1H, −CH=), 6.74 (d, J = 8.2 Hz, 2H, *o*-PhH), 7.14−7.22 (m, 1H, *p*-PhH), 7.30−7.40 (m, 2H, *m*-PhH).

***cis*-Tricarbonyl[(η^2-*N*-(2-butenyl)-*N*-methylamino)(phenyl)carbene]iron(0) (6) and Tetracarbonyl[(*N*-(2-butenyl)-*N*-methylamino)(phenyl)carbene]iron(0) (7).** The same procedure as was used for the preparation of **2a** starting from the amide **5** (0.20 g, 1.06 mmol) gave a mixture of **6** and **7** (0.14 g). Preparative HPLC (methanol−water, 90:10) afforded pure **7** (less polar, yellow solid, 0.022 g, 6%) as a mixture of geometrical isomers and chelated complex **6** (more polar, yellow solid, 0.065 g, 27%).

6: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.61 (d, J = 6.6 Hz, 3H, =CH−CH_3), 2.40 (m, 1H, −CH=), 2.93 (s, 3H, N−CH_3), 3.06 (dd, J = 10.4, 5.0 Hz, −CH=), 4.14 (dd, J = 13.7, 4.6 Hz, 1H, N−CH_2), 4.29 (d, J = 13.7 Hz, 1H, N−CH_2), 6.87 (m, 2H, Ph), 7.25 (m, 1H, Ph), 7.37 (m, 2H, Ph); IR ($CHCl_3$) ν 2015, 1946, 1916, 1702, 1623, 1580, 1555 cm^{-1}. Anal. Calcd for $C_{15}H_{15}NO_3Fe$: C, 57.54; H, 4.83; N, 4.47. Found: C, 57.84; H, 4.96; N, 4.56.

7: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.49 (d, J = 7.1 Hz, =CH−CH_3 minor), 1.72 (d, J = 6.6 Hz, =CH−CH_3 major), 3.91 (s, N−CH_3 major), 3.88−3.95 (m, N−CH_3 minor., N−CH_2 major), 4.06 (d, J = 10 Hz, N−CH_2 minor), 5.18−5.32 (m, −CH= major + minor), 5.54−5.82 (m, −CH= major + minor), 6.84 (m, 2H, Ph), 7.20 (m, 1H, Ph), 7.36 (m, 2H, Ph); IR ($CHCl_3$) ν 2040, 1966, 1938, 1915, 1525 cm^{-1}. Anal. Calcd for $C_{16}H_{15}NO_4Fe$: C, 56.33; H, 4.43; N, 4.11. Found: C, 56.06; H, 4.56; N, 3.93.

Tetracarbonyl[(*N*-(2,2-dimethyl-3-butenyl)-*N*-methylamino)(phenyl)carbene]iron(0) (9). A. From Amide 8. The same procedure as was used for the preparation of **2a** starting from the amide **8** (1.06 g, 5.09 mmol) gave 0.077 g (4%) of carbene (*E*)-**9** containing a small amount of (*Z*)-**9** as a yellow solid after chromatography (light petroleum). Mp: 52−56 °C.

B. From $(CO)_4Fe$=C(OEt)Ph.[19] Ethoxycarbene complex $(CO)_4Fe$=C(OEt)Ph (0.344 g, 1,14 mmol) was dissolved in diethyl ether (5 mL), and an excess of an approximately 1 M solution of 4-amino-3,3-dimethyl-1-butene (2 mL, 2 mmol) in diethyl ether was added at room temperature. After 45 min TLC analysis showed that all alkoxycarbene was consumed. The volatiles were then evaporated under vacuum, and the residue was codistilled twice with 2 mL of dry benzene and dissolved in dry DMF (5 mL). The solution was cooled to 0 °C, and 80% sodium hydride (0.08 g, 2.7 mmol) was added. After 30 min of stirring an excess of iodomethane (0.5 mL, 8 mmol) was added, and the mixture was allowed to stay overnight. The reaction mixture was then poured into water, extracted with ether, and dried with $MgSO_4$. Chromatography of the residue after evaporation of the solvent (alumina, light petroleum) afforded 0.09 g (24%) of **9**.

E-isomer: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.93 (s, 6H, C(CH_3)$_2$), 3.49 (s, 2H, CH_2), 3.94 (s, 3H, N−CH_3), 5.09 (d, J = 17.5, 1H, =CH_2), 5.11 (d, J = 10.5, 1H, =CH_2), 5.83 (dd, J =

(19) Semmelhack, M. F.; Tamura, R. *J. Am. Chem. Soc.* **1983**, *105*, 4099.

17.0, 11.0 Hz, 1H, −C*H*═), 6.84 (m, 2H, Ph), 7.19 (m, 1H, Ph), 7.36 (m, 2H, Ph); IR ($CHCl_3$) ν 2041, 1966, 1938, 1915, 1517 cm^{-1}.

(Z)-isomer: ^1H NMR ($CDCl_3$, 300 MHz) δ 1.29 (s, 6H, C(CH_3)$_2$), 2.95 (s, 3H, N−CH_3), 4.52 (s, 2H, CH_2), 5.11 (d, J = 11.0, 1H, ═CH_2), 5.13 (d, J = 17.6, 1H, ═CH_2), 6.09 (dd, J = 17.6, 11.0 Hz, 1H, −C*H*═), 6.79 (m, 2H, Ph), 7.15−7.40 (m, 3H, Ph). Anal. Calcd for $C_{18}H_{19}NO_4Fe$: C, 58.56; H, 5.19; N, 3.79. Found: C, 58.23; H, 5.47; N, 3.74.

1-Methyl-3,3-dimethyl-6-phenyl-1,2,3,4-tetrahydropyridine (12). A solution of **9** (0.045 g, 0.12 mmol) in toluene-d_8 was heated under argon atmosphere at 80 °C for 20 h. TLC analysis (silica−light petroleum−diethyl ether−acetone, 8:1:1) showed the presence of virtually one product. The solution was after filtration analyzed by GC−MS and ^1H and ^{13}C NMR spectroscopy. GC−MS (EI) afforded a molecular peak m/z = 201, which is in agreement with molecular formula $C_{14}H_{19}N$. ^1H NMR (toluene-d_8, 500 MHz): δ 0.98 (s, 6H, 2CH_3), 1.86 (d, J = 4.4 Hz, 2H, ═CH−CH_2), 2.41 (s, 3H, NCH_3), 2.54 (s, 2H, N−CH_2), 4.62 (t, J = 4.4 Hz, 1H, ═C*H*−), 7.05−7.20 (m, 3H, Ph*H*), 7.30−7.40 (m, 2H, Ph*H*). ^{13}C NMR−APT (100.6 MHz, toluene-d_8) CH, CH_3: δ 27.1 (C(*C*H$_3$)$_3$), 41.1 (N*C*H$_3$), 100.7 (═*C*H−), 127.2 (Ph), 128.0 (Ph), 128.2 (Ph); C, CH_2: 29.5 (*C*(CH$_3$)$_2$), 37.80 (═CH−*C*H$_2$), 63.5 (N*C*H$_2$), 69.28 (Ph−*C*═).

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