Published in final edited form as:

New J Chem. 2011 January 1; 35(10): 2037–2042. doi:10.1039/C1NJ20170K.

A persistent (amino)(ferrocenyl)carbene^{†,‡}

Alan DeHope, Daniel Mendoza-Espinosa, Bruno Donnadieu, and Guy Bertrand

UCR-CNRS Joint Research Chemistry Laboratory (UMI 2957), Department of Chemistry, University of California Riverside, Riverside, CA 92521-0403, USA

Guy Bertrand: guy.bertrand@ucr.edu

Abstract

Deprotonation of *N,N*-diisopropyl-*C*-ferrocenylaldiminium triflate **2** cleanly leads to the corresponding 1,2-diamino-1,2-diferrocenylethene **3**, the dimer of the desired (amino)(ferrocenyl)carbene. Fulvene **6**, obtained by addition of the lithium salt of tetramethylcyclopentadiene to methoxyformamidinium methylsulfate **5**, reacts with dicarbonylcyclopentadienylbromoiron(II), and with a mixture of FeCl₂ and Cp* lithium salt, affording the corresponding tetramethylferrocenylaldiminium salt **7**, and nonamethylferrocenylaldiminium salt **8**, respectively. Although the deprotonation of **7** gives a complex mixture of products, the treatment of **8** at –78 °C with sodium hexamethyldisilazide allowed for the isolation of the corresponding (amino)(ferrocenyl)carbene **9** as a yellow powder. However, even in the solid state, it is stable for less than 48 h at –20 °C. In addition to NMR spectroscopy, evidence for the carbene nature of **9** was found by a trapping experiment with sulfur that leads to the corresponding adduct **10**, which was characterized by a single crystal X-ray diffraction study.

Introduction

Over the years, metallocene derivatives have attracted considerable attention, as exemplified by recent works by Astruc, to whom this paper is dedicated.¹ Among their numerous applications, metallocene and especially ferrocene units have been incorporated in ligands for transition metal complexes. There are countless examples of commercially available ferrocenylphosphines such as **A**² and **B**³ (Fig. 1), which have led to very efficient metal catalysts for a variety of coupling reactions, hydroaminations, hydrogenations, *etc.*⁴ Among the interesting properties, ferrocenyl substituents confer to these ligands their strong electron donating ability, cylindrical shape, planar chirality, and their reversible redox-properties.

Over the last two decades, the replacement of phosphine ligands by carbenes on transition metal centers has led to considerable improvements in catalyst development.⁵ Carbenes bind more strongly to metal centers, thus avoiding the necessity for the use of excess ligand. The NHC–transition metal complexes are commonly less sensitive to air and moisture than their phosphine counterparts, and have proven remarkably resistant to oxidation.⁶ Moreover, they are strong σ -donor ligands, and their steric environment, best defined as fence- or fan-like,⁷ differentiates them substantially from that of tertiary phosphines, usually regarded as a cone. Beginning with the work of Bildstein *et al.*,⁸ a number of *N*-heterocyclic carbenes (NHCs)

[†]Dedicated to Professor Didier Astruc on the occasion of his 65th birthday.

[‡]Electronic supplementary information (ESI) available: X-Ray crystal structure analysis of compounds **3** and **10**. CCDC reference numbers 815176 (**3**) and 815177 (**10**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1nj20170k

Correspondence to: Guy Bertrand, guy.bertrand@ucr.edu.

containing ferrocene moieties have been prepared.⁹ They can be divided into four classes **C–F**, depending on the position of the ferrocene unit with respect to the carbene center.

Obviously, the influence of a ferrocene unit is maximized when directly bonded to the active coordination center, as in phosphines **A** and **B**. Because of the topology of NHC scaffolds, such an arrangement is impossible. Attempts to prepare (ferrocenyl)(phenyl)carbene **G** and diferrocenyl-carbene **H**, featuring the ferrocenyl group(s) in the desired position, have been reported (Fig. 2).¹⁰ The authors concluded that neither one nor two ferrocenyl substituents are capable of stabilizing a carbene center, and that “most likely such carbenes are triplet species, similarly to purely organic aryl-substituted methylenes.”¹¹

These disappointing results are readily understandable since it is well recognized that σ -electron-donating substituents induce a small σ – π gap, which favors the triplet state.¹² On the other hand, it is well established that π -electron-donating substituents such as phosphino and amino groups favor the singlet states. Moreover, we have already shown that a single π -electron-donating group is sufficient to stabilize a singlet carbene, as shown by the isolation of (alkyl and aryl)-(phosphino)- and (amino)-carbenes of types **I**¹³ and **J**,¹⁴ respectively.¹⁵ Based on this analysis, it seemed likely that stable (amino)(ferrocenyl)carbenes in which the ferrocenyl group is directly bonded to the carbene center could be prepared, and here we report our preliminary results.

Results and discussion

Analogous to the synthetic route used to prepare other aminocarbenes, we targeted aldiminium precursors. Addition of lithium diisopropylamide to ferrocenecarboxaldehyde **1**, followed by treatment with trifluoromethanesulfonic anhydride afforded the *N,N*-diisopropyl-*C*-ferrocenylaldiminium triflate **2** in 46% yield (Scheme 1). Deprotonation of salt **2** with sodium hexamethyldisilazide gave, after workup, a red crystalline material. However, the ¹³C NMR spectrum did not show a low field signal, as expected for aminocarbenes,^{14,16} but instead a singlet at δ 145 ppm corresponding to a quaternary carbon. A single crystal X-ray diffraction study unambiguously established that the product was alkene **3** (Fig. 3), which results from the dimerization of the desired carbene, as already observed for a variety of aminocarbenes bearing non-bulky substituents.¹⁷

We then investigated the possibility of increasing the kinetic protection around the carbene center through incorporation of methyl groups on the cyclopentadiene ring. A new synthetic route was necessary. Over 40 years ago, it had been shown that 6-aminofulvenes can form π -complexes with transition metals,¹⁸ and thus we envisaged that they could allow for the preparation of diversely substituted ferrocenylaldiminium salts. Fulvene **6** was synthesized in 74% yield from the lithium salt of tetramethylcyclopentadiene **4** and methoxyformamidinium methylsulfate **5**¹⁹ (Scheme 2). Then, addition of dicarbonylcyclopentadienylbromoirron(II)²⁰ to **6** led to the corresponding ferrocenylaldiminium salt **7**. The latter is only sparingly soluble in aprotic polar solvents, such as THF, and when treated with various bases, a complex mixture of products was obtained. Since 1,2,3,4,5-pentamethylcyclopentadiene is a better electron donor than cyclopentadiene, and oftentimes gives organometallic complexes with improved stability and solubility,²¹ we turned our attention to the preparation of the nonamethylferrocenylaldiminium chloride **8a**. The latter was obtained in 29% yield by adding FeCl₂ to the Cp* lithium salt and fulvene **6**. Anion exchange with trimethylsilyl trifluoromethanesulfonate afforded *N,N*-diisopropylnonamethylferrocenylaldiminium trifluoromethanesulfonate **8b** in 94% yield.

The deprotonation of **8b** led, after workup at room temperature, to a complex mixture of products. However, monitoring by ^{13}C NMR spectroscopy the reaction of **8b** with sodium hexamethyldisilazide at $-78\text{ }^{\circ}\text{C}$, allowed for the observation of a very deshielded signal at $\delta = 315\text{ ppm}$, which is in the range observed for acyclic (alkyl and aryl)aminocarbenes.^{14,16} Carbene **9** is stable enough to allow the evaporation of the solvent under vacuum at low temperatures, and extraction of the residue with hexane at $-78\text{ }^{\circ}\text{C}$. The resulting yellow solution can even be concentrated at $-78\text{ }^{\circ}\text{C}$, and after a night at $-20\text{ }^{\circ}\text{C}$, carbene **9** was isolated as a yellow solid. Unfortunately, even in the solid state, **9** appeared to be stable for less than 48 hours at $-20\text{ }^{\circ}\text{C}$, precluding its characterization by X-ray diffraction. In addition to NMR spectroscopy, evidence for the carbene nature of **9** was found in a trapping experiment with sulfur. Adduct **10** was isolated in 72% yield, and its structure unambiguously determined by a single crystal X-ray diffraction study (Scheme 3 and Fig. 4).

Conclusion

Compound **9** is the first spectroscopically characterized carbene featuring a ferrocenyl unit directly bonded to the electron-deficient center. Although it is not stable enough to allow for applications, it demonstrates that such carbenes are not inherently unstable. Since it has been shown that cyclic carbenes are generally more stable than their acyclic versions, the preparation of cyclic ferrocenylaldiminium systems, in which the putative carbene center is fused to the ferrocene in a ring, are under active investigations.

Experimental section

All reactions were performed under an atmosphere of argon, and solvents were dried over Na metal or CaH_2 . Reagents were of analytical grade, obtained from commercial suppliers and used without further purification. ^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were obtained with a Bruker Avance 300 spectrometer at 298 K. ^1H and ^{13}C chemical shifts (δ) are reported in parts per million (ppm) relative to TMS, and were referenced to the residual solvent peak. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, sept. = septet, m = multiplet, br = broad signal. Coupling constants (J) are reported in hertz (Hz). High-resolution mass spectra (HR-MS) were acquired on a GC-TOF instrument using an electron impact ionization mode (EI). Melting points were measured with a Mel-Temp melting point apparatus system.

Ferrocenylaldiminium triflate (**2**)

An ethereal solution of lithium diisopropylamide (1.00 g, 9.34 mmol) was added dropwise to a stirred ethereal solution of ferrocenecarboxaldehyde (2.00 g, 9.34 mmol) cooled to $-78\text{ }^{\circ}\text{C}$ under an atmosphere of argon. After the addition, the reaction mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 30 min, warmed to room temperature, and stirred for an additional 30 min. The mixture was cooled to $-78\text{ }^{\circ}\text{C}$, and an ethereal solution of trifluoromethanesulfonic anhydride (1.57 mL, 9.34 mmol) was slowly added *via* a syringe. The reaction mixture was stirred for 10 min at $-78\text{ }^{\circ}\text{C}$ during which time a red precipitate was formed. After filtration, the solid was washed repeatedly with ether and dried under reduced pressure. Extraction with dichloromethane, concentration, precipitation with ether, and filtration afforded **2** as a moisture-sensitive red solid (1.94 g, 46% yield); mp: $140\text{ }^{\circ}\text{C}$; ^1H NMR (300 MHz, acetone- D_6) δ 9.06 (s, 1 H), 5.23 (dt, $J = 4$ and 2 Hz, 4 H), 4.80 (sept., $J = 7$ Hz, 1 H), 4.55 (s, 5 H), 4.46 (sept., $J = 7$ Hz, 1 H), 1.63 (d, $J = 7$ Hz, 6 H), 1.56 (d, $J = 7$ Hz, 6 H); ^{13}C NMR (75 MHz, acetone- D_6) δ 168.51, 79.00, 75.36, 72.47, 70.27, 56.98, 53.78, 23.68, 19.41.

(Amino)(ferrocenyl)carbene dimer (3)

A Schlenk flask charged with sodium hexamethyldisilazide (123 mg, 0.67 mmol) and **2** (300 mg, 0.67 mmol) was placed in a dry ice/acetone bath under argon, and 5 mL THF was added. The reaction mixture was stirred for 30 min at -78°C , warmed to room temperature and stirred for an additional 30 min. The volatiles were removed under vacuum and the residue extracted with toluene. Removal of toluene under reduced pressure affords a red solid. Red crystals of **3** were grown from a concentrated toluene solution at -20°C (306 mg, 77% yield); ^1H NMR (300 MHz, CDCl_3) δ 4.80 (s, 4 H), 4.13 (s, 4 H), 4.00 (s, 10 H), 3.80 (sept., $J=6$ Hz, 4 H), 1.27 (d, $J=6$ Hz, 12 H), 1.11 (d, $J=6$ Hz, 12 H); ^{13}C NMR (75 MHz, CDCl_3) δ 145.33, 89.21, 70.13, 68.97, 66.69, 49.62, 23.02, 22.75; HR-MS (ESI): calcd. 594.2355, found 594.2361%.

1,2,3,4-Tetramethyl-6-(diisopropylamino)fulvene (6)

Tetramethylcyclopentadienyllithium (0.96 g, 7.5 mmol) was loaded into a flask equipped with a gas inlet. Anhydrous THF (25 mL) was added and the mixture stirred at -78°C in a dry ice–acetone bath. Methoxyformamidinium methyl sulfate **5** (1.91 g, 7.5 mmol) was added dropwise to the slurry, and the reaction warmed to room temperature and stirred for 12 h. The volatiles were removed under reduced pressure affording an orange residue. The product was extracted from the solids with hot heptane, affording fulvene **8** as a crystalline orange solid (1.30 g, 74% yield); mp: 77°C ; ^1H NMR (300 MHz, C_6D_6) δ 6.97 (s, 1 H), 3.65 (sept., $J=7$ Hz, 2 H), 2.26 (s, 3 H), 2.23 (s, 3 H), 2.12 (s, 3 H), 2.11 (s, 3 H), 0.90 (d, $J=7$ Hz, 12 H); ^{13}C NMR (75 MHz, C_6D_6) δ 136.80, 135.02, 126.00, 121.81, 116.79, 50.35, 22.60, 15.48, 12.34, 12.04, 11.53.

Ferrocenylaldiminium bromide (7)

Dicarbonylcyclopentadienylbromoiron(II) (1.00 g, 3.9 mmol) and **6** (915 mg, 3.92 mmol) were loaded into a Schlenk flask, and THF (15 mL) was added. The reaction mixture was refluxed overnight under argon. THF was removed under reduced pressure, and the residue washed repeatedly with ether affording **7** as a dark purple solid (640 mg, 38% yield); mp: 198°C ; ^1H NMR (300 MHz, acetone- d_6) δ 8.43 (s, 1 H), 4.58 (br s, 1 H), 4.10 (br s, 1 H), 4.06 (s, 5 H), 2.84 (s, 6 H), 2.00 (s, 6 H), 1.40 (s, 6 H), 1.29 (s, 6 H); ^{13}C NMR (75 MHz, acetone- d_6) δ 173.02, 89.50, 83.52, 75.49, 69.32, 57.97, 55.12, 28.62, 23.87, 17.26, 12.10.

Ferrocenylaldiminium salts (8)

A Schlenk flask was loaded with iron(II) chloride (4.72 g, 37.3 mmol) and pentamethylcyclopentadienyllithium (prepared by deprotonation of pentamethylcyclopentadiene with *n*BuLi) (5.40 g, 38 mmol) under an atmosphere of argon. The solids were cooled to -78°C , THF (90 mL) was added, and the reaction mixture stirred for 10 min. Warming up to room temperature resulted in a green slurry to which a solution of 1,2,3,4-tetramethyl-6-(diisopropylamino)fulvene **6** (8.70 g, 37.3 mmol) in THF (10 mL) was added *via* a syringe. The resulting solution was refluxed overnight. Evaporation of the solvent afforded a dark blue solid which was washed repeatedly with ether. The residue was dissolved in dichloromethane and filtered through a pad of celite under an atmosphere of argon. The solvent was removed under vacuum to afford **8a** as a blue solid (5.0 g, 29% yield); ^1H NMR (300 MHz, CDCl_3) δ 8.13 (s, 1 H), 4.80 (sept., $J=7$ Hz, 1 H), 4.38 (sept., $J=7$ Hz, 1 H), 1.94 (s, 6 H), 1.88 (s, 6 H), 1.70 (s, 15 H), 1.69 (d, $J=7$ Hz, 6 H), 1.55 (d, $J=7$ Hz, 6 H); ^{13}C NMR (75 MHz, CDCl_3) δ 168.59, 90.66, 83.20, 83.14, 81.81, 58.51, 53.85, 25.08, 20.64, 11.75, 9.95, 9.48. Dry chloroform (15 mL) and trimethylsilyl trifluoromethanesulfonate (1.2 mL, 6.5 mmol) were added *via* a syringe to chloride salt **8a** (1.00 g, 2.2 mmol) and the mixture stirred overnight at 50°C . After filtration, the residue was extracted with an additional portion of chloroform. The volatiles were removed under

vacuum, the residue washed with ether and dried under vacuum, affording **8b** as a purple solid (1.19 g, 94% yield).

(Amino)(ferrocenyl)carbene (**9**)

Ferrocenylaldiminium trifluoromethanesulfonate **8b** (100 mg, 0.174 mmol) and sodium hexamethyldisilazide (32.0 mg, 0.174 mmol) were loaded into a Schlenk flask under an atmosphere of argon. The solids were cooled to $-78\text{ }^{\circ}\text{C}$ in a dry ice/acetone bath and THF (3 mL) was added. The reaction was stirred at this temperature for 1 h, at which point a yellow solution was obtained. The Schlenk flask was removed from the cold bath and the solution was evaporated under vacuum, with periodic re-immersion in the cold bath. The residue was extracted at $-78\text{ }^{\circ}\text{C}$ with hexanes and the yellow solution was concentrated at this temperature and placed in a $-20\text{ }^{\circ}\text{C}$ freezer, affording a yellow solid which decomposes within 48 h at $-20\text{ }^{\circ}\text{C}$. The ^1H NMR spectrum was obtained by *in situ* deprotonation in deuterated benzene, and the ^{13}C NMR spectrum was recorded from a concentrated THF solution at $-50\text{ }^{\circ}\text{C}$. ^1H NMR (300 MHz, C_6D_6) δ 4.06 (sept., $J=7\text{ Hz}$, 1 H), 3.75 (sept., $J=7\text{ Hz}$, 1 H), 1.94 (s, 15 H), 1.84 (s, 6 H), 1.73 (s, 6 H), 1.41 (d, $J=7\text{ Hz}$, 6 H), 0.70 (d, $J=7\text{ Hz}$, 6 H); ^{13}C NMR (75 MHz, THF) δ 315.48, 88.79, 78.78, 78.12, 72.11, 54.89, 50.70, 20.60, 20.57, 10.19, 9.05, 9.01.

Sulfur adduct (**10**)

Ferrocenylaldiminium trifluoromethanesulfonate **8b** (200 mg, 0.35 mmol) and sodium bis(trimethylsilyl)amide (64.0 mg, 0.35 mmol) were loaded into a Schlenk flask under an atmosphere of argon, the solids were cooled to $-78\text{ }^{\circ}\text{C}$, and THF (10 mL) was added. The reaction mixture was stirred at low temperature for 1 h, and elemental sulfur (90 mg, 2.8 mmol) was added, giving an immediate color change. The dark orange solution was stirred for 30 min, and allowed to warm to room temperature. The solvent was evaporated under vacuum and the residue was extracted with ether. Slow evaporation of the solvent afforded **10** as single orange crystals (130 mg, 72% yield); mp: $197\text{ }^{\circ}\text{C}$; ^1H NMR (300 MHz, CDCl_3) δ 3.64 (br, 2 H), 2.02 (s, 15 H), 2.00 (s, 6 H), 1.86 (s, 6 H), 0.72 (br, 12 H); ^{13}C NMR (75 MHz, CDCl_3) δ 197.24, 99.86, 80.59, 77.97, 75.73, 54.96, 50.19, 20.47, 19.86, 9.83, 9.59, 9.24.

Crystal structure determination of complexes **3** and **10**

A Bruker X8-APEX X-ray diffraction instrument with Mo-radiation was used for data collection. All data frames were collected at low temperatures ($T = 100\text{ K}$) using an ω , ϕ -scan mode (0.5° ω -scan width, hemisphere of reflections) and integrated using a Bruker SAINTPLUS software package. The intensity data were corrected for Lorentzian polarization. Absorption corrections were performed using the SADABS program. The SIR97 was used for direct methods of phase determination, and Bruker SHELXTL software package for structure refinement and difference Fourier maps. Atomic coordinates, isotropic and anisotropic displacement parameters of all the non-hydrogen atoms of compounds were refined by means of a full matrix least-squares procedure on I^2 . All H-atoms were included in the refinement in calculated positions riding on the C atoms. Drawings of molecules were performed using Ortep 3. Crystal and structure parameters of **3**: size $0.32 \times 0.13 \times 0.01\text{ mm}^3$, monoclinic, space group $P2_1/c$, $a = 20.159(3)\text{ \AA}$, $b = 9.9740(13)\text{ \AA}$, $c = 15.1210(19)\text{ \AA}$, $\alpha = 90^{\circ}$, $\beta = 111.024(2)^{\circ}$, $\gamma = 90^{\circ}$, $V = 2837.9(6)\text{ \AA}^3$, $\rho_{\text{calcd}} = 1.391\text{ g cm}^{-3}$, Mo-radiation ($\lambda = 0.71073\text{ \AA}$), $T = 100(2)\text{ K}$, reflections collected = 20 218, independent reflections = 5722 ($R_{\text{int}} = 0.0989$); absorption coefficient $\mu = 1.048\text{ mm}^{-1}$; max/min transmission = 0.9896 and 0.7302, 381 parameters were refined and converged at $R_1 = 0.0495$, $wR_2 = 0.0973$, with intensity $I > 2\sigma(I)$. Crystal and structure parameters of **10**: size $0.21 \times 0.19 \times 0.16\text{ mm}^3$, monoclinic, space group $P2_1/c$, $a = 8.526(7)\text{ \AA}$, $b = 34.96(3)\text{ \AA}$, $c = 10.440(6)\text{ \AA}$,

$\alpha = 90^\circ$, $\beta = 126.26(4)^\circ$, $\gamma = 90^\circ$, $V = 2509(3) \text{ \AA}^3$, $\rho_{\text{calcd}} = 1.206 \text{ g cm}^{-3}$, Mo-radiation ($\lambda = 0.71073 \text{ \AA}$), $T = 100(2) \text{ K}$, reflections collected = 16 524, independent reflections = 4424 ($R_{\text{int}} = 0.0385$), absorption coefficient $\mu = 0.696 \text{ mm}^{-1}$; max/min transmission = 0.8968 and 0.8676, 276 parameters were refined and converged at $R_1 = 0.0321$, $wR_2 = 0.1099$, with intensity $I > 2\sigma(I)$. CCDC 815176 (**3**) and 815177 (**10**).[‡]

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

Thanks are due to the NSF (CHE-0808825) and NIH (R01 GM 68825) for financial support of this work.

References

- (a) Djeda R, Rapakousiou A, Liang LY, Guidolin N, Ruiz J, Astruc D. *Angew Chem, Int Ed.* 2010; 49:8152–8156. (b) Astruc D, Boisselier E, Omelas C. *Chem Rev.* 2010; 110:1857–1959. [PubMed: 20356105] (c) Astruc D, Ornelas C, Ruiz J. *Acc Chem Res.* 2008; 41:841–856. [PubMed: 18624394]
- (a) Shelby Q, Kataoka N, Mann G, Hartwig J. *J Am Chem Soc.* 2000; 122:10718–10719. (b) Kataoka N, Shelby Q, Stambuli JP, Hartwig JF. *J Org Chem.* 2002; 67:5553–5566. [PubMed: 12153253]
- (a) Bishop JJ, Davison A, Katcher ML, Lichtenberg DW, Merrill RE, Smart JC. *J Organomet Chem.* 1971; 27:241–249. (b) Bandoli G, Dolmella A. *Coord Chem Rev.* 2000; 209:161–196.
- (a) Togni, A.; Hayashi, T. *Ferrocenes: Homogeneous Catalysis, Organic Synthesis, Materials Science.* Wiley-VCH; Weinheim, Germany: 1995. (b) Arrayas RG, Adrio J, Carretero JC. *Angew Chem, Int Ed.* 2006; 45:7674–7715. (c) Dai, LF.; Hou, XL. *Chiral Ferrocenes in Asymmetric Catalysis.* Wiley-VCH; Weinheim, Germany: 2010.
- For recent reviews, see: Lin JCY, Huang RTW, Lee CS, Bhattacharyya A, Hwang WS, Lin IJB. *Chem Rev.* 2009; 109:3561–3598. [PubMed: 19361198] Arnold PL, Casely IJ. *Chem Rev.* 2009; 109:3599–3611. [PubMed: 19358527] Díez-González S, Marion N, Nolan SP. *Chem Rev.* 2009; 109:3612–3676. [PubMed: 19588961] Poyatos M, Mata JA, Peris E. *Chem Rev.* 2009; 109:3677–3707. [PubMed: 19236010] Samojłowicz C, Bieniek M, Grela K. *Chem Rev.* 2009; 109:3708–3742. [PubMed: 19534492] van Otterlo WAL, de Koning CB. *Chem Rev.* 2009; 109:3743–3782. [PubMed: 19618929] Monfette S, Fogg DE. *Chem Rev.* 2009; 109:3783–3816. [PubMed: 19537778] Alcaide B, Almendros P, Luna A. *Chem Rev.* 2009; 109:3817–3858. [PubMed: 19572654] Vougioukalakis GC, Grubbs RH. *Chem Rev.* 2010; 110:1746–1787. [PubMed: 20000700] Díez-González S. *N-Heterocyclic Carbenes, from Laboratory Curiosities to Efficient Synthetic Tools.* RSC PublishingCambridge, UK2011
- Peris E, Crabtree RH. *C R Chim.* 2003; 6:33–37.
- (a) Hillier AC, Sommer WJ, Yong BS, Petersen JL, Cavallo L, Nolan SP. *Organometallics.* 2003; 22:4322–4326. (b) Viciu MS, Navarro O, Germaneau RF, Kelly RA, Sommer WJ, Marion N, Stevens ED, Cavallo L, Nolan SP. *Organometallics.* 2004; 23:1629–1635.
- Bildstein B, Malaun M, Kopacka H, Ongania KH, Wurst K. *J Organomet Chem.* 1998; 552:45–61.
- See for examples: Bolm C, Kesselgruber M, Raabe G. *Organometallics.* 2002; 21:707–710. Bertogg A, Camponovo F, Togni A. *Eur J Inorg Chem.* 2005:347–356. Coleman KS, Turberville S, Pascu SI, Green MLH. *J Organomet Chem.* 2005; 690:653–658. Arduengo AJ, Tapu D, Marshall WJ. *Angew Chem, Int Ed.* 2005; 44:7240–7244. Labande A, Daran JC, Manoury E, Poli R. *Eur J Inorg Chem.* 2007:1205–1209. Rosen EL, Varnado CD, Tennyson AG, Khramov DM, Kamplain JW, Sung DH, Cresswell PT, Lynch VM, Bielawski CW. *Organometallics.* 2009; 28:6695–6706. Siemeling U, Farber C, Bruhn C, Leibold M, Selent D, Baumann W, Fopffgarten Mv, Goedecke C, Frenking G. *Chem Sci.* 2010; 1:697–704. Khramov DM, Rosen EL, Lynch VM, Bielawski CW. *Angew Chem, Int Ed.* 2008; 47:2267–2270.
- Bildstein B. *J Organomet Chem.* 2001; 617–618:28–38.

11. Moss, RA.; Platz, MS.; Jones, M. *Reactive Intermediate Chemistry*. Wiley-Interscience; Hoboken, New Jersey: 2004.
12. Bourissou D, Guerret O, Gabbai FP, Bertrand G. *Chem Rev*. 2000; 100:39–91. [PubMed: 11749234]
13. (a) Igau A, Grutzmacher H, Baceiredo A, Bertrand G. *J Am Chem Soc*. 1988; 110:6463–6466.(b) Kato T, Gornitzka H, Baceiredo A, Savin A, Bertrand G. *J Am Chem Soc*. 2000; 122:998–999.(c) Buron C, Gornitzka H, Romanenko V, Bertrand G. *Science*. 2000; 288:834–836. [PubMed: 10796999] (d) Despagne E, Gornitzka H, Rozhenko A, Schoeller WW, Bourissou D, Bertrand G. *Angew Chem, Int Ed*. 2002; 41:2835–2837.(e) Despagne-Ayoub E, Sole S, Gornitzka H, Rozhenko AB, Schoeller WW, Bourissou D, Bertrand G. *J Am Chem Soc*. 2003; 125:124–130. [PubMed: 12515513]
14. (a) Sole S, Gornitzka H, Schoeller WW, Bourissou D, Bertrand G. *Science*. 2001; 292:1901–1903. [PubMed: 11397943] (b) Cattoën X, Gornitzka H, Bourissou D, Bertrand G. *J Am Chem Soc*. 2004; 126:1342–1343. [PubMed: 14759183] (c) Otto M, Conejero S, Canac Y, Romanenko VD, Rudzevitch V, Bertrand G. *J Am Chem Soc*. 2004; 126:1016–1017. [PubMed: 14746458] (d) Lavallo V, Mafhouz J, Canac Y, Donnadiou B, Schoeller WW, Bertrand G. *J Am Chem Soc*. 2004; 126:8670–8671. [PubMed: 15250717] (e) Lavallo V, Canac Y, Prasang C, Donnadiou B, Bertrand G. *Angew Chem, Int Ed*. 2005; 44:5705–5709.(f) Zeng X, Frey GD, Kinjo R, Donnadiou B, Bertrand G. *J Am Chem Soc*. 2009; 131:8690–8696. [PubMed: 19456108]
15. For reviews on carbenes, other than NHCs, see: Schuster O, Yang L, Raubenheimer HG, Albrecht M. *Chem Rev*. 2009; 109:3445–3478. [PubMed: 19331408] Vignolle J, Cattoën X, Bourissou D. *Chem Rev*. 2009; 109:3333–3384. [PubMed: 19368393] Melaimi M, Soleilhavoup M, Bertrand G. *Angew Chem, Int Ed*. 2010; 49:8810–8849.Canac Y, Soleilhavoup M, Conejero S, Bertrand G. *J Organomet Chem*. 2004; 689:3857–3865.
16. Tapu D, Dixon DA, Roe C. *Chem Rev*. 2009; 109:3385–3407. [PubMed: 19281270]
17. Alder RW, Blake ME, Chaker L, Harvey JN, Paolini F, Schütz J. *Angew Chem, Int Ed*. 2004; 43:5896–5911.
18. King RB, Bisnette MB. *Inorg Chem*. 1964; 3:801–807.
19. Meerwein H, Stopp G, Florian W, Schon N. *Ann Chem (Warsaw)*. 1961; 641:1.
20. Barras JP, Davies SG, Metzler MR, Edwards AJ, Humphreys VM, Prout K. *J Organomet Chem*. 1993; 461:157–165.
21. (a) Bercaw JE, Marvich RH, Bell LG, Brintzinger HH. *J Am Chem Soc*. 1972; 94:1219–1238.(b) Bercaw JE. *J Am Chem Soc*. 1974; 96:5087–5095.

Fig. 1.

Two prototypical examples of ferrocenylphosphines (**A** and **B**), and the four classes of known ferrocene-derived carbenes (**C–F**).

Fig. 2. Transient triplet ferrocenylcarbenes (**G** and **H**), and stable amino- and phosphino-carbenes (**I** and **J**).

Fig. 3.
X-Ray crystal structure of (amino)(ferrocenyl)carbene dimer **3**. Ellipsoids are given at 50% probability. Hydrogen atoms are omitted for clarity. Bond lengths and angles are given in the ESI.[‡]

Fig. 4. X-Ray crystal structure of (amino)(ferrocenyl)carbene sulfur-adduct **10**. Ellipsoids are given at 50% probability. Hydrogen atoms are omitted for clarity. Bond lengths and angles are given in the ESI.[†]

Scheme 1.
Synthesis of (amino)(ferrocenyl)carbene dimer **3**.

Scheme 2.
Synthesis of ferrocenylaldiminium salts **7** and **8**.

Synthesis of persistent (amino)(ferrocenyl)carbene **9** and its sulfur adduct **10**.