DOI: 10.1002/anie.200704978

Redox-Active Ligands

Diaminocarbene[3]ferrocenophanes and Their Transition-Metal Complexes**

*Dimitri M. Khramov, Evelyn L. Rosen, Vincent M. Lynch, and Christopher W. Bielawski**

N-heterocyclic carbenes[1] (NHCs) form robust complexes with nearly every transition metal. In many instances, these complexes function as catalysts with superior activities and selectivities.[2] The broad utility and application of NHCs can be traced to synthetic advancements which enable access to derivatives with novel N substituents and architectures.[3] We envisioned that it would be possible to create a new class of carbene-based ligands with relatively wide N-C-N angles and redox-switchable functions[4] by linking diaminocarbenes to 1,1′-disubstituted metallocenes.[5] In view of the affinity of carbenes for transition metals, the use of such ligands may lead to new redox-active complexes with tunable electronic properties. Herein, we describe a novel carbene architecture that contains a 1,1′-disubstituted ferrocene moiety and demonstrate its ability to engage in unique electronic interactions with coordinated transition metals.[6]

The formamidinium salts **1a** and **1b** were synthesized in up to 95% yield by the formylative cyclization of the respective 1,1′-dianilino-[7] or 1,1′-dialkylaminoferrocene precursor upon treatment with trimethylorthoformate and HBF_4.[8] Diagnostic formamidinium signals were found at $\delta = 9.3$ and 8.8 ppm ([D$_6$]DMSO), respectively, in the ^{1}H NMR spectra of these compounds. The solid-state structure of **1a** reveals eclipsed cyclopentadienyl (Cp) ligands, which are tilted toward each other ($\phi = 15.7°$) as a result of the tethering effect of the diaminocarbene fragment (Figure 1, left). This strain is manifested in a relatively large N-C-N angle of 129.6(3)°, a value that is comparable to those commonly found for tetrasubstituted formamidinium ions (around 130°).[9]

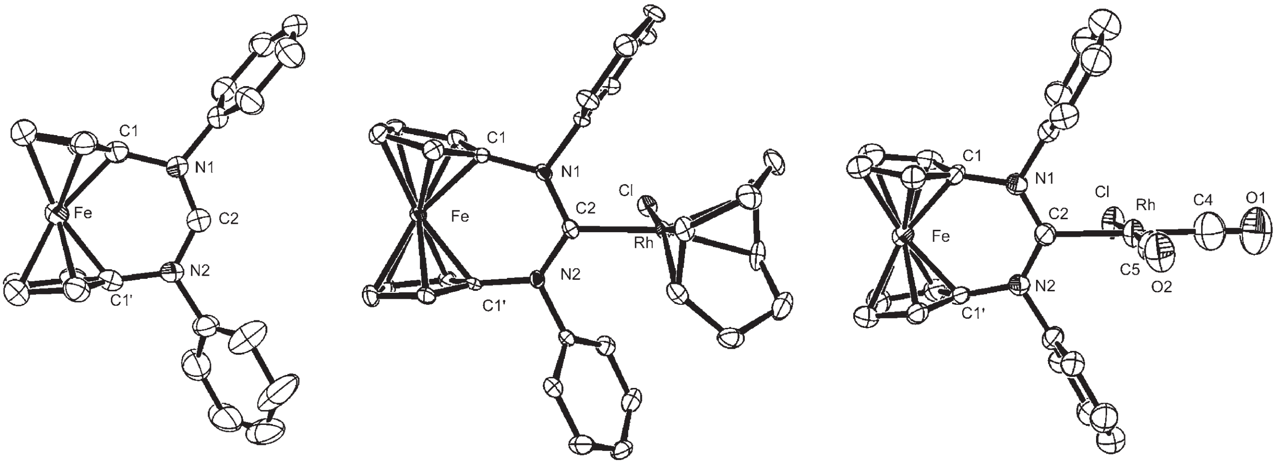


Figure 1. ORTEP views of **1a** (left), **3a** (middle), and **4a** (right). Ellipsoids are drawn at the 50% probability level. Hydrogen atoms and counterions have been omitted for clarity. Selected bond lengths [Å] and angles [°]: **1a**: C1–N1 1.437(4), C1′–N2 1.442(6), C2–N1 1.327(4), C2–N2 1.311(4); N1-C2-N2 129.6(3). The Fe–C2 distance is 3.284(3) Å. **3a**: C1–N1 1.443(5), C1′–N2 1.433(5), C2–N1 1.359(5), C2–N2 1.349(5), Rh–C2 2.044(4); N1-C2-N2 120.7(3). The Fe–C2 distance is 3.438(5) Å. **4a**: C1–N1 1.446(4), C1′–N2 1.441(4), C2–N1 1.348(4), C2–N2 1.345(4), Rh–C2 2.081(3), Rh–C4 1.900(4), Rh–C5 1.827(4); N1-C2-N2 120.4(3). The Fe–C2 distance is 3.406(4) Å.

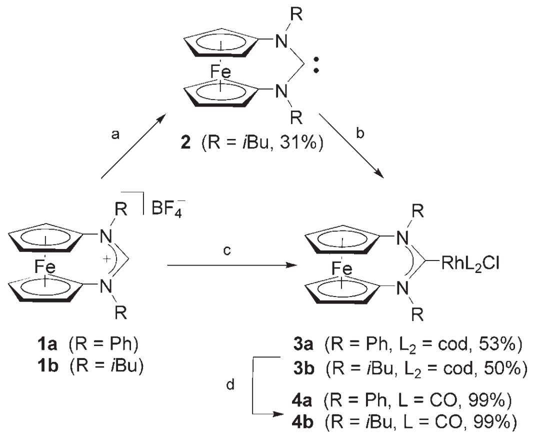
Attempts to generate a free carbene in situ through the deprotonation of **1a** with various bases in different solvents resulted in rapid decomposition. However, treatment of **1b**, which contains *N*-isobutyl groups,[10] with sodium hexamethyldisilazide (NaHMDS) in C_6D_6 resulted in a solution of the diaminocarbene[3]ferrocenophane **2** that was sufficiently stable to be analyzed by NMR spectroscopy (Scheme 1). The ^{13}C NMR spectrum of **2** revealed a signal at $\delta = 260$ ppm, which is slightly downfield of the correspond-

---

[*] D. M. Khramov, E. L. Rosen, V. M. Lynch, Prof. C. W. Bielawski
Department of Chemistry & Biochemistry
The University of Texas at Austin, Austin, TX 78712 (USA)
Fax: (+1) 512-471-8696
E-mail: bielawski@cm.utexas.edu

[**] We are grateful to the ARO (W911NF-05-1-0430 and W911NF-06-1-0147), the NSF (CHE-0645563), the donors of the Petroleum Research Fund as administered by the American Chemical Society (44077-G1), and the Welch Foundation (F-1621)for their generous financial support. C.W.B. is a Beckman Young Investigator and a Cottrell Scholar of Research Corporation.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.



Scheme 1. Synthesis of diaminocarbene[3]ferrocenophanes and related bimetallic complexes: a) NaHMDS, benzene; yield determined by ^{1}H NMR spectroscopy; b) [{RhCl(cod)}$_2$], benzene; c) from **1a**: KO*t*Bu, [{RhCl(cod)}$_2$], THF; from **1b**: NaHMDS, [{RhCl(cod)}$_2$], benzene; the yields reported for **3** are based on **1**; d) CO (1 atm), CH_2Cl_2. cod = 1,5-cyclooctadiene.

ing signal for known acyclic diaminocarbenes (δ = 237–256 ppm).[9] Unfortunately, **2** was found to decompose upon concentration, which precluded its isolation.[11]

Having demonstrated that free carbenes can be generated in situ, we focused subsequent efforts on the coordination of these Fe-containing ligands to various transition metals as well as the detection of electronic interactions between the two moieties. Previously, it was shown that Rh–olefin complexes ligated to NHCs are excellent systems for the latter.[12] In particular, the olefinic ligand can be replaced with carbon monoxide without disrupting other physical characteristics of the complex. For the systems reported herein, this exchange should result in detectable changes in the oxidation potential of the ferrocene moiety and support communication between the Rh and Fe centers.

The Rh complex **3a** was prepared in 53% yield by the in situ deprotonation of **1a** in the presence of [{RhCl(cod)}$_2$] (Scheme 1). Alternatively, addition of [{RhCl(cod)}$_2$] to a solution of **2** in benzene at ambient temperature resulted in the formation of the Rh complex **3b** as a yellow solid, which was subsequently isolated in 50% yield. When carbon monoxide was bubbled through solutions of **3a** or **3b** in CH_2Cl_2, the respective complexes **4a** and **4b** were obtained in excellent yield (> 99%). The carbonyl stretching frequencies for complexes **4a** and **4b** in CH_2Cl_2 were found to be $\tilde{\nu}_{CO}$ = 2074, 1994 cm^{-1} and $\tilde{\nu}_{CO}$ = 2075, 1995 cm^{-1}, respectively,[13] and therefore in accord with those observed for known complexes of the type [(NHC)RhCl(CO)$_2$].[12]

The solid-state structures of **3a** and **4a** were determined by X-ray crystallography (Figure 1, middle and right).[14] As expected, the N-C-N angles in these complexes are relatively wide (**3a**: 120.7(4)°; **4a**: 120.4(3)°) and comparable to the analogous angle found in [(bis(diisopropylamino)carbene)RhCl(CO)$_2$][15] (118°). Furthermore, these complexes exhibit relatively long C–N bond lengths (average value for **3a**: 1.36 Å; average value for **4a**: 1.35 Å) with respect to those observed in **1a** (1.32 Å). The existence of longer C–N bonds in **3a** and **4a** may be attributed to the relief of ring strain, Rh–carbene π backbonding,[12,16] or a combination thereof.

Following the synthesis and characterization of **3** and **4**, we studied the effect of ancillary-ligand exchange (i.e., replacing an olefin for a carbonyl ligand) on the electronic properties of these complexes using cyclic voltammetry.[17] Complex **3a** exhibited two reversible redox processes, at $E_{1/2}$ = +1.00 and +0.54 V, which were attributed to Rh^{I}/Rh^{II} and Fe^{II}/Fe^{III} couples, respectively.[18] As expected, the analogous redox couples detected for **4a**, which bears two carbonyl ligands, were found at relatively high potentials: $E_{1/2}$(Rh^{I}/Rh^{II}) = +1.07 V and $E_{1/2}$(Fe^{II}/Fe^{III}) = +0.91 V. Although σ inductive effects are possible,[19] the large difference in $E_{1/2}$ observed for the Fe^{II}/Fe^{III} couples in **3a** and **4a** may be rationalized in part by unique through-space interactions[20] between the Fe center and the diaminocarbene moiety. Close analysis of the crystal structures of these two complexes supports this view. The Fe–C$_{carbene}$ distances observed in **3a** (3.438(5) Å) and **4a** (3.406(4) Å) are within the van der Waals radii of the two atoms, and the respective Rh–C$_{carbene}$ bond lengths (**3a**: 2.044(4) Å; **4a**: 2.081(3) Å) coincide with established π-backbonding capabilities of (NHC)RhCl–olefin and (NHC)RhCl–carbonyl complexes.[12,21]

Additional support for the existence of through-space π-backbonding interactions in **3a** and **4a** was obtained from the cyclic voltammogram of **3b**, which revealed two redox processes, at $E_{1/2}$(Rh^{I}/Rh^{II}) = +0.98 V and $E_{1/2}$(Fe^{II}/Fe^{III}) = +0.69 V.[17] The Fe^{II}/Fe^{III} couple occurred at a significantly higher potential in **3b** than in its *N*-aryl analogue **3a**. We attribute the difference to diminished Rh→C$_{carbene}$ π donation, as evidenced by the relatively long Rh–C$_{carbene}$ bond observed in the solid-state structure of **3b** (2.059(4) Å; Figure 2),[14] as a result of the increased steric bulk of the *N*-isobutyl substituents.[22,23]

Finally, the ability of these redox-active diaminocarbenes to electronically modulate ligated transition metals was evaluated by examining the carbonyl stretching frequency

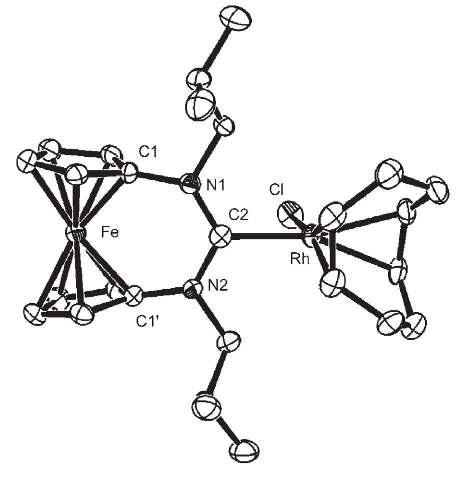


Figure 2. ORTEP view of **3b**. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: C1–N1 1.441(5), C1′–N2 1.434(5), C2–N1 1.358(4), C2–N2 1.356(4), Rh–C2 2.059(4); N1-C1-N2 121.2(3). The Fe–C2 distance is 3.434(4) Å.

of **4** as a function of the Fe oxidation state.[24] Since the addition of strong oxidants to **4** resulted in decomposition,[25] we devised a spectroelectrochemical experiment that combined bulk electrolysis with time-resolved FTIR spectroscopy.[26] A thin-layer cell was assembled, and a solution of complex **4a** was recorded as the background.[27] To selectively oxidize the Fe center, a potential of +0.9 V was applied while FTIR spectra were recorded over time. Signals attributable to **4a** disappeared as a new material (assigned as **4a**$^{+}$) with the carbonyl stretching frequencies $\tilde{\nu}_{CO}$ = 2088 and 2015 cm^{-1} formed (Figure 3).[28] These changes may be explained by the formation of stronger CO bonds and are consistent with diminished electron density at the Rh center induced by the development of a positive charge at the Fe center (i.e., Fe^{II}→Fe^{III}). To place this result into context, the $\tilde{\nu}_{CO}$ values exhibited by the **4a**/**4a**$^{+}$ couple correspond to those observed for a broad range of known Rh carbonyl complexes containing electron-rich and electron-deficient NHCs.[12]

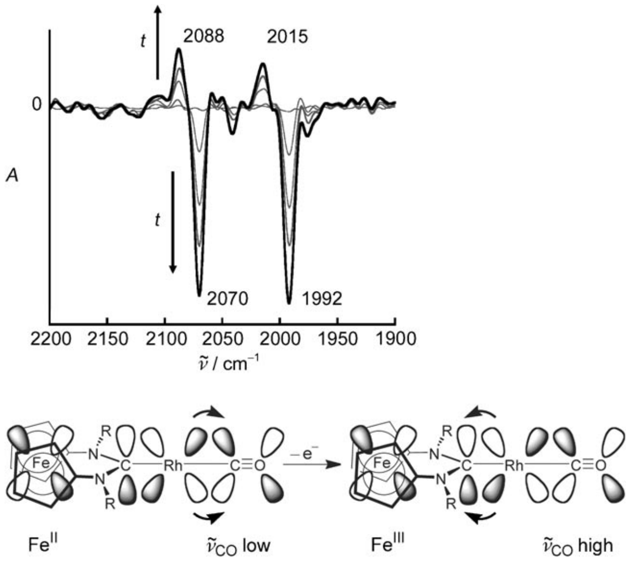


Figure 3. Top: Superimposed difference FTIR spectra showing the disappearance of **4a** ($\tilde{\nu}_{CO}$ = 2070, 1992 cm^{-1}) with concomitant formation of **4a**$^{+}$ ($\tilde{\nu}_{CO}$ = 2088, 2015 cm^{-1}) upon oxidation (E = +0.9 V) over a duration of 200 s.[27] Bottom: Graphical illustration explaining the effect of oxidizing **4a** to **4a**$^{+}$ on its carbonyl stretching frequency; see text for further details. The Rh moiety has been truncated for clarity; R = Ph.

In conclusion, we have synthesized transition-metal complexes of novel *N*-aryl and *N*-alkyl diaminocarbenes which each contain a 1,1′-disubstituted ferrocene moiety in its backbone. The well-known electrochemistry of ferrocene was utilized to confirm long-range, but significant, electronic communication between the Fe center in the redox-active carbenes and coordinated transition metals.

Received: October 27, 2007

Keywords: bimetallic complexes · carbenes · electrochemistry · ferrocene · redox-active ligands

---

[1] a) D. Bourissou, O. Guerret, F. P. Gabbaï, G. Bertrand, *Chem. Rev.* **2000**, *100*, 39; b) A. J. Arduengo III, *Acc. Chem. Res.* **1999**, *32*, 913; c) W. A. Herrmann, C. Köcher, *Angew. Chem.* **1997**, *109*, 2256; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2162.

[2] a) E. Peris, R. H. Crabtree, *Coord. Chem. Rev.* **2004**, *248*, 2239; b) A. C. Hillier, G. A. Gasa, M. S. Viciul, H. M. Lee, C. L. Yang, S. P. Nolan, *J. Organomet. Chem.* **2002**, *653*, 69; c) W. A. Herrmann, *Angew. Chem.* **2002**, *114*, 1342; *Angew. Chem. Int. Ed.* **2002**, *41*, 1290.

[3] For selected examples, see: a) S. Richeter, A. Hadj-Aïssa, C. Taffin, A. van der Lee, D. Leclercq, *Chem. Commun.* **2007**, 2148; b) R. S. Bon, F. J. J. de Kanter, M. Lutz, A. L. Spek, M. C. Jahnke, F. E. Hahn, M. B. Groen, R. V. A. Orru, *Organometallics* **2007**, *26*, 3639; c) A. Fürstner, M. Alcarazo, H. Krause, C. W. Lehmann, *J. Am. Chem. Soc.* **2007**, *129*, 12676; d) F. E. Hahn, *Angew. Chem.* **2006**, *118*, 1374; *Angew. Chem. Int. Ed.* **2006**, *45*, 1348; e) K. E. Krahulic, G. D. Enright, M. Parvez, R. Roesler, *J. Am. Chem. Soc.* **2005**, *127*, 4142; f) F. E. Hahn, M. Paas, D. L. Van, R. Fröhlich, *Chem. Eur. J.* **2005**, *11*, 5080; g) F. E. Hahn, M. Paas, D. L. Van, T. Lügger, *Angew. Chem.* **2003**, *115*, 5402; *Angew. Chem. Int. Ed.* **2003**, *42*, 5243.

[4] A. M. Allgeier, C. A. Mirkin, *Angew. Chem.* **1998**, *110*, 936; *Angew. Chem. Int. Ed.* **1998**, *37*, 894.

[5] U. Siemeling, T.-C. Auch, *Chem. Soc. Rev.* **2005**, *34*, 584.

[6] For a bimetallic complex containing an NHC annulated to the cyclopentadienyl ligand of a ruthenocene, see: a) A. J. Arduengo III, D. Tapu, W. J. Marshall, *J. Am. Chem. Soc.* **2005**, *127*, 16400; b) A. J. Arduengo III, D. Tapu, W. J. Marshall, *Angew. Chem.* **2005**, *117*, 7406; *Angew. Chem. Int. Ed.* **2005**, *44*, 7240; for NHCs that contain *N*-ferrocenyl substituents, see: c) A. Bertogg, F. Camponovo, A. Togni, *Eur. J. Inorg. Chem.* **2005**, 347; d) B. Bildstein, M. Malaun, H. Kopacka, K. Wurst, M. Mitterböck, K.-H. Ongania, G. Opromolla, P. Zanello, *Organometallics* **1999**, *18*, 4325; e) B. Bildstein, M. Malaun, H. Kopacka, K.-H. Ongania, K. Wurst, *J. Organomet. Chem.* **1999**, *572*, 177.

[7] U. Siemeling, T.-C. Auch, O. Kuhnert, M. Malaun, H. Kopacka, B. Bildstein, *Z. Anorg. Allg. Chem.* **2003**, *629*, 1334.

[8] See the Supporting Information for details.

[9] a) E. L. Rosen, M. D. Sanderson, S. Saravanakumar, C. W. Bielawski, *Organometallics* **2007**, *26*, 6042; b) R. W. Alder, M. E. Blake, L. Chaker, J. N. Harvey, F. Paolini, J. Schütz, *Angew. Chem.* **2004**, *116*, 6020; *Angew. Chem. Int. Ed.* **2004**, *43*, 5896; c) R. W. Alder, P. R. Allen, M. Murray, A. G. Orpen, *Angew. Chem.* **1996**, *108*, 1211; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1121.

[10] 1,1′-Disubstituted ferrocenes with bulky N substituents (i.e., mesityl, neopentyl, or diphenylmethyl) were reluctant to undergo formylative cyclization.

[11] The propensity of strained ferrocenophanes to undergo nucleophilic ring-opening reactions is well documented; see: a) F. Jäkle, R. Rulkens, G. Zech, D. A. Foucher, A. J. Lough, I. Manners, *Chem. Eur. J.* **1998**, *4*, 2117; b) R. Rulkens, D. P. Gates, D. Balaishis, J. K. Pudelski, D. F. McIntosh, A. J. Lough, I. Manners, *J. Am. Chem. Soc.* **1997**, *119*, 10976; furthermore, NHCs are known to ligate to metallocenes: C. D. Abernethy, J. A. C. Clyburne, A. H. Cowley, R. A. Jones, *J. Am. Chem. Soc.* **1999**, *121*, 2329.

[12] a) D. M. Khramov, V. M. Lynch, C. W. Bielawski, *Organometallics* **2007**, *26*, 6042; b) M. D. Sanderson, J. W. Kamplain, C. W. Bielawski, *J. Am. Chem. Soc.* **2006**, *128*, 16514; c) W. A. Herrmann, J. Schütz, G. D. Frey, E. Herdtweck, *Organometallics* **2006**, *25*, 2437.

[13] The margin of error in the reported values is ± 1 cm^{-1}.

[14] Complexes **3b** and **4a** were each found to exist as two crystallographically unique complexes within their asymmetric units cell.

[15] D. Denk, P. Sirsch, W. A. Herrmann, *J. Organomet. Chem.* **2002**, *649*, 219.

[16] a) E. S. Chernyshova, R. Goddard, K.-R. Pörschke, *Organometallics* **2007**, *26*, 3236; b) L. Mercs, G. Labat, A. Neels, A. Ehlers, M. Albrecht, *Organometallics* **2006**, *25*, 5648; c) S. Saravanakumar, K. M. Kindermann, J. Heinicke, M. C. Köckerling, *Chem. Commun.* **2006**, 640; d) H. Jacobsen, A. Correa, C. Costabile, L. Cavallo, *J. Organomet. Chem.* **2006**, *691*, 4350; e) X. Hu, I. Castro-Rodriguez, K. Olsen, K. Meyer, *Organometallics* **2004**, *23*, 755; f) D. Nemcsok, K. Wichmann, G. Frenking, *Organometallics* **2004**, *23*, 3640.

[17] Conditions for cyclic voltammetry: CH_2Cl_2 as the solvent, analyte (1 mM), Bu_4NPF_6 (0.1 M) as the electrolyte; reference: $[FeCp^*_2]^+/[FeCp^*_2]$ at -0.13 V versus SCE (the saturated calomel electrode); scan rate: 0.1 $V\,s^{-1}$ (Cp* = pentamethylcyclopentadienyl). Reported values have a margin of error of ± 0.01 V. Reversible or quasireversible cyclic voltammograms were observed for **1**, **3**, and **4**.[8]

[18] For additional electrochemical studies of Rh–NHC complexes, see: M. V. Baker, S. K. Brayshaw, B. W. Skelton, A. H. White, C. C. Williams, *J. Organomet. Chem.* **2005**, *690*, 2312.

[19] Since the diaminocarbene linkages are orthogonal to the Cp ligands in complexes **3** and **4**, π interactions between the Fe and Rh centers are likely to be minimal.

[20] Through-space interactions between Fe centers and various heteroatoms have been observed in ferrocenophanes by Mössbauer spectroscopy; see: a) J. Silver, D. A. Davies, R. M. G. Roberts, M. Herberhold, U. Dorfler, B. Wrackmeyer, *J. Organomet. Chem.* **1999**, *590*, 71; b) J. Silver, *J. Chem. Soc. Dalton Trans.* **1990**, 3513.

[21] Recently, we reported a napthoquinone-annulated NHC and demonstrated its utility in the study of π-backbonding interactions in NHC–metal complexes, see Ref. [12b]. The difference in the reduction potentials of {Rh(cod)Cl} and $\{Rh(CO)_2Cl\}$ complexes containing this redox-active NHC was 60 mV. For comparison, we observed differences of up to 370 mV for analogous complexes containing the diaminocarbenes described herein.

[22] The nearly identical oxidation potentials exhibited by **1a** ($E_{1/2} = +1.03$ V) and **1b** ($E_{1/2} = +1.07$ V) indicate that inductive effects due to the N substituents are relatively small.

[23] The Rh^I/Rh^{II} and Fe^{II}/Fe^{III} redox couples were not resolved in the cyclic voltammogram of **4b**.

[24] a) I. M. Lorkovic, M. S. Wrighton, W. M. Davis, *J. Am. Chem. Soc.* **1994**, *116*, 6220; b) T. M. Miller, K. J. Ahmed, M. S. Wrighton, *Inorg. Chem.* **1988**, *27*, 4326.

[25] The addition of strong oxidants, such as iodine, iodosobenzoic acid, various Ag^I salts, chloranil, or 1,2-dichloro-4,5-dicyanoquinone, to **4a** or **4b** resulted in decomposition. For examples of oxidizing ferrocene derivatives with chemical agents, see: a) J. S. Miller, D. T. Glatzhofer, C. Vazquez, R. S. McLean, J. C. Calabrese, W. J. Marshall, J. W. Raebiger, *Inorg. Chem.* **2001**, *40*, 2058; b) M. Sato, S. Akabori, M. Katada, I. Motoyama, H. Sano, *Chem. Lett.* **1987**, 1847; c) R. M. G. Roberts, J. Silver, J. Azizian, *J. Organomet. Chem.* **1986**, *303*, 387; d) M. T. Lee, B. M. Foxman, M. Rosenblum, *Organometallics* **1985**, *4*, 539.

[26] M. Krejcik, M. Danek, F. Hartl, *J. Electroanal. Chem.* **1991**, *317*, 179.

[27] Conditions: CH_2Cl_2 as the solvent, **4a** (10 mM), $Bu_4N)(PF_6)$ (0.1 M) as the electrolyte. Reported values have a margin of error of ± 2 cm^{-1}.

[28] For examples of the monitoring of $\tilde{\nu}_{CO}$ in carbonyl complexes as a function of oxidation state, see: a) N. Szesni, M. Drexler, J. Maurer, R. F. Winter, F. de Montigny, C. Lapinte, S. Steffens, J. Heck, B. Weibert, H. Fischer, *Organometallics* **2006**, *25*, 5774; b) T. Scheiring, J. Fiedler, W. Kaim, *Organometallics* **2001**, *20*, 1437; c) D. A. Weinberger, T. B. Higgins, C. A. Mirkin, L. M. Liable-Sands, A. L. Rheingold, *Angew. Chem.* **1999**, *111*, 2748; *Angew. Chem. Int. Ed.* **1999**, *38*, 2565.