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Synthesis and Characterization of 14-Electron Cyclopentadienyl Chromium(II) Complexes Containing a Heterocyclic Carbene Ligand

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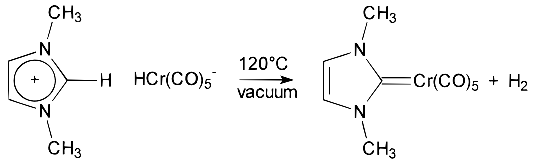
Chromocene reacts with 1,3-dimesitylimidazolium chloride in THF to yield cyclopentadiene and CpCrCl(1,3-dimesitylimidazolin-2-ylidene) (**1**), which contains an *N*,*N*-heterocyclic carbene ligand. This new complex is a relatively rare example of a CpCr(II) complex containing four unpaired electrons. The reaction of **1** with phenylmagnesium bromide yields CpCrPh(1,3-dimesitylimidazolin-2-ylidene) (**2**). An X-ray crystallographic investigation of **2** reveals a two-legged piano stool structure with a planar central Cr atom.

Introduction

The chemistry of organochromium compounds containing the Cp and Cp* ligands[2] has received considerable attention, especially during the past decade. Much of the recent work has focused on the Cr(III) oxidation state.[3] A number of complexes containing the CpCr(II) fragment have also been reported, but most of these rely on carbonyl or other strongly π-accepting coligands to impart stability to the low oxidation state.[4] In contrast, far less is known about the chemistry of CpCr(II) complexes in the absence of such coligands.[5] We have started our exploration of CpCr(II) complexes with the recently popularized class of ligands: *N*,*N*-heterocyclic carbenes (1,3-disubstituted imidazol-2-ylidenes). These were first reported as stable entities by Arduengo and co-workers in 1991[6] and have since then found significant uses as ligands in organometallic complexes.[7] They are best considered neutral two-electron-donor ligands with insignificant π-back-bonding tendency. As such, they can be viewed as appealing alternatives to phosphines.[7,8] Some of the advantages of such diaminocarbene ligands include their ease of synthesis[6,9,10] and the robustness of the complexes they form: excellent thermal stabilities at temperatures as high as 290 °C have been noted.[11] Both characteristics are deemed essential for the potential large-scale, industrial catalytic applications of these compounds. For example, organochromium complexes are interesting alternatives[12] to the ubiquitous group 4 metallocenes[13] in the area of homogeneous olefin polymerization.

In 1968, Öfele and co-workers made use of the acidic nature of imidazolium salts to synthesize the first Cr−diaminocarbene complex (eq 1).[14] We have employed a similar strategy in our approach and will report here the details about novel 14-electron CpCr(II) complexes containing the 1,3-dimesitylimidazol-2-ylidene ligand.



(1)

Results and Discussion

The reaction of chromocene with 1,3-dimesitylimidazolium chloride in THF at ambient temperature yields CpCrCl(1,3-dimesitylimidazoline-2-ylidene) (**1**) as a dark purple powder in 67% isolated yield (eq 2). The novel complex **1** is highly air sensitive; solid samples of **1** immediately turn black upon exposure to air. On the other hand, it possesses a surprising thermal stability

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(2) Abbreviations: Cp = η^5-C_5H_5; Cp* = η^5-C_5Me_5.

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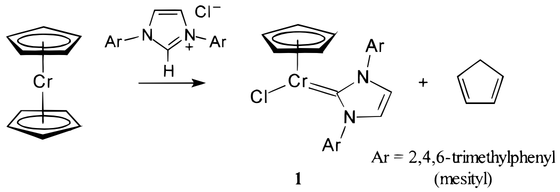
and melts without decomposition at 250 °C. The carbene complex **1** is soluble in aromatic solvents, chlorinated solvents, and THF. It is slightly soluble in diethyl ether, but virtually insoluble in aliphatic solvents. Exposure of a toluene solution to air results in an immediate color change to green, followed by a slower change to black. The products of the air oxidation have not been characterized.



1

(2)

The ^1H NMR spectrum (C_6D_6) of **1** shows broad peaks characteristic of a paramagnetic material. The following peak assignments are made primarily on the basis of the integrated intensities of the ^1H NMR signals. Upon complexation, the imidazolin-2-ylidene ring protons are shifted upfield (δ −4.4), while the Cp protons resonate as a very broad signal far downfield (δ 205). The *m*-protons of the mesityl rings also experience a downfield shift (δ 11.4), but much less so as they are further removed from the metal center. The *o*- and *p*-methyl resonances are shifted to δ 3.7 and δ 7.2, respectively. When the reaction (eq 2) is performed in THF-d_8 in an NMR tube, the initial spectrum shows that product formation is immediate and also confirms that cyclopentadiene is formed in addition to **1**.

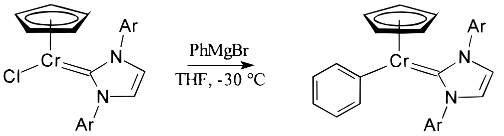
A mass spectrometry analysis of the solid indicates the M^+ ion at *m*/*e* 456 with the correct isotopic distribution. There are no indications of dimers or higher oligomers in the mass spectrum. The magnetic susceptibility of **1** was measured between 5 and 300 K. It displays the Curie−Weiss behavior of a simple paramagnet. The solution magnetic susceptibility (Evan's method, 298 K, $\mu_{eff} = 4.62\ \mu_B$)[15] was found to be consistent with the solid-phase measurements, indicating a high-spin d^4 ion with four unpaired electrons. The presence of four unpaired electrons is unusual for a CpCr(II) derivative. Most known examples are low-spin with two unpaired electrons.[5] However, in all these examples, the Cr ion is six-coordinate, and the valence electron count is either 15 or 16. In this regard, the 14-electron complex **1** has more in common with non-Cp-containing Cr(II) complexes, especially the recently reported substituted hydridotris(pyrazolyl)borate (Tp) complexes.[16,17]

Structural characterization of **1** by X-ray crystallography proved impossible. The one-dimensional crystals that were obtained from a variety of solvent systems were invariably disordered. Currently, the best evidence that **1** is a monomer is the combined mass spectrometry and magnetic susceptibility data, along with the fact that the phenyl derivative (**2**, see below) is monomeric.

Table 1. Summary of Crystallographic Data for Complex 2

empirical formula	$C_{32}H_{34}CrN_2$
fw	498.61
cryst color, habit	brown, cubic
cryst dimens	0.60 × 0.55 × 0.40 mm
cryst syst	triclinic
θ range for data collection	2.00−33.05°
unit cell dimens	a = 8.37150(10) Å
	b = 8.49780(10) Å
	c = 20.4745(3) Å
	α = 94.1140(10)°
	β = 93.8870(10)°
	γ = 107.0170(10)°
	V = 13833.15(3) Å^3
space group	$P\bar{1}$
Z	2
D_{calcd}	1.197 g cm^{-3}
wavelength	0.710 73 Å
temp	150(2) K
no. of reflns collected	19 689
no. of ind reflns	9879 [$R_{(int)} = 0.0356$]
abs coeff	0.435 mm^{-1}
F(000)	528
limiting indices	$-12 \le h \le 12, -12 \le k \le 13, -31 \le l \le 27$
refinement method	full-matrix least-squares on F^2
no. of data/restraints/params	9879/0/453
goodness-of-fit on F^2	1.074
final R indices [$I > 2\sigma(I)$]	R1 = 0.052, wR2 = 0.123
R indices (all data)	R1 = 0.063, wR2 = 0.131
extinction coeff	0.009(2)
largest diff peak and hole	0.872 and −0.534 e Å^{-3}

Complex **1** reacts with PhMgCl in THF at −30 °C to give a brown solution. Workup of the reaction mixture yields CpCrPh(1,3-dimesitylimidazolin-2-ylidene) (**2**) as brown crystals in 55% yield (eq 3).



1 **2**

(3)

The Cp and carbene ligands in **2** displayed ^1H NMR characteristics similar to those of **1**. The broad Cp signal was located at δ 209, whereas the carbene ring protons came to resonate at δ −6.5. The phenyl ring protons appeared at δ −14.8 (*m*), −111 (*p*), and −164 (*o*). Full details are given in the Experimental Section. The mass spectrum of **2** showed a parent ion at *m*/*e* 498 with the correct isotopic distribution.

The molecular structure of complex **2** was confirmed by X-ray crystallography. Crystallographic data are summarized in Table 1, and selected bond distances and angles are summarized in Table 2. Figure 1 shows an ORTEP plot of the crystal structure. Complex **2** is the first structurally characterized Cr compound to employ an *N*,*N*-heterocyclic carbene ligand. The only other Cr(*N*,*N*-heterocyclic carbene) complexes described in the literature are Cr(0) examples. These are $Cr(CO)_5$(carbene) and $Cr(CO)_4$(biscarbene) species; the latter employs a bidentate chelating carbene.[8,14]

The phenyl complex **2** adopts a two-legged piano stool structure in which the phenyl and carbene ligands constitute the legs. The Cr, Cp centroid, phenyl-C6, and carbene-C12 atoms are located in a plane. The sum of the Cp(centroid)−Cr−C12, C6−Cr−C12, and Cp(cen-

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Table 2. Selected Interatomic Distances and Angles for CpCrPh(carbene) (2)[a]

Distances (Å)

Cr1−C6	2.089 (2)	C1−C5	1.380 (4)
Cr1−C12	2.1232 (13)	C1−C2	1.401 (4)
Cr1−C1	2.316 (2)	C2−C3	1.444 (4)
Cr1−C3	2.343 (2)	C3−C4	1.400 (4)
Cr1−C5	2.347 (2)	C4−C5	1.368 (4)
Cr1−C4	2.351 (2)	C6−C7	1.416 (2)
Cr1−C2	2.352 (2)	C6−C11	1.416 (2)
N1−C12	1.371 (2)	C7−C8	1.403 (2)
N1−C13	1.393 (2)	C8−C9	1.392 (3)
N1−C15	1.446 (2)	C9−C10	1.398 (3)
N2−C12	1.373 (2)	C10−C11	1.403 (2)
N2−C14	1.395 (2)	C13−C14	1.357 (2)
N2−C24	1.447 (2)	Cr1−Ctr	2.017

Angles (deg)

C6−Cr1−C12	97.98 (5)	C8−C7−C6	122.9 (2)
C12−N1−C13	111.85 (12)	C10−C11−C6	122.8 (2)
C12−N1−C15	125.99 (11)	N1−C12−N2	103.26 (11)
C13−N1−C15	122.16 (12)	N1−C12−Cr1	128.66 (10)
C12−N2−C14	111.76 (12)	N2−C12−Cr1	128.06 (10)
C12−N2−C24	124.36 (12)	C14−C13−N1	106.64 (13)
C14−N2−C24	123.77 (12)	C13−C14−N2	106.50 (13)
C7−C6−C11	115.05 (14)	C6−Cr1−Ctr	126.3
C7−C6−Cr1	120.61 (11)	C12−Cr1−Ctr	135.5
C11−C6−Cr1	124.33 (11)		

[a] Ctr = centroid of Cp ligand.

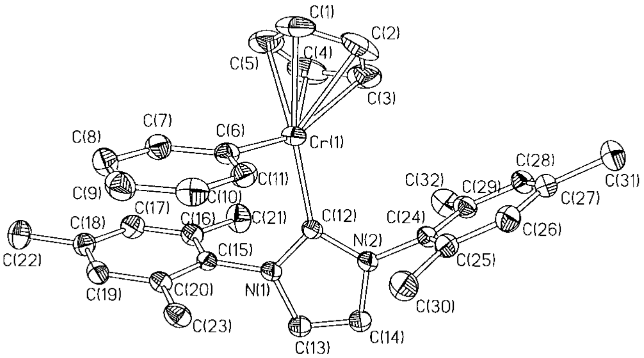


Figure 1. ORTEP view of the molecular structure of CpCrPh(carbene) (**2**).

troid)−Cr−C6 bond angles is 359.8°, and the maximum deviation, for Cr, from the least-squares plane is 0.032 Å. The central Cr atom is bonded only to carbon atoms with Cr−C bond lengths of Cr−C(Cp) average 2.342 Å, Cr−C(Ph) 2.089 Å, and Cr−C(carbene) 2.123 Å. The Cr−C(carbene) bond distance is within the range commonly observed for Fischer carbenes bonded to the Cr-$(CO)_5$ fragment.

The phenyl derivative **2** also bears structural similarity to the above-mentioned TpCr species. This coordinatively unsaturated complex is most likely stabilized by the sterically demanding mesityl groups. These would also serve to keep the complexes monomeric by preventing ligands from bridging and metal−metal bonding interactions from forming.[5c,e] It remains to be seen whether higher-nuclearity species are formed when sterically less demanding *N*-substituents at the carbene ligand are employed.

In chloroform, **1** reacts immediately with the solvent at ambient temperature to give a blue homogeneous solution. The color is highly characteristic of $CpCrCl_2L$ compounds, where L is a neutral or anionic two-electron-donor ligand.[18] A likely candidate (eq 4) is $CpCrCl_2$(1,3-

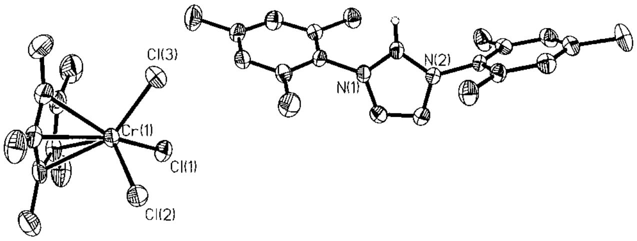
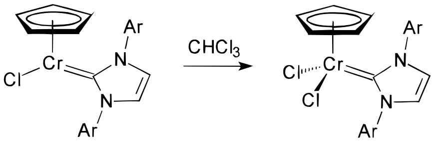


Figure 2. ORTEP view of the molecular structure of [1,3-bis(2,4,6-trimethylphenyl)imidazolium][Cp^*CrCl_3].

dimesitylimidazolin-2-ylidene) (**3**), which is in agreement with spectroscopic evidence that has been obtained. Monitoring the progress of this reaction by ^{1}H NMR ($CDCl_3$) clearly shows the decrease in resonances attributed to **1** and the growth of new resonances attributable to **3**. These are also broad and paramagnetically shifted (δ 219 for the Cp ligand). Subsequent removal of the solvent gives a blue residue. Dissolution of the blue product in C_6D_6 and analysis by ^{1}H NMR confirm that a new species, clearly distinct from **1**, has formed. The solution magnetic susceptibility of **3** (Evan's method, 298 K, $\mu_{eff} = 3.39\ \mu_B$) is in good agreement with that expected for a Cr(III) species with three unpaired electrons. Further characterization is provided by its UV−vis spectrum and mass spectrometry. The oxidation of the chloride complex **1** to the dichloride **3** is not unexpected. Early work by E. O. Fischer and co-workers offers precedent for the oxidation of low-valent CpCr compounds by halocarbons to various CpCr(III) halides.[19]



1 **3** (4)

Complexes **1** and **2** are EPR silent, both in solution and in frozen toluene glasses.[20] These observations are consistent with those reported for other paramagnetic Cr(II) complexes.[21]

Unlike Cp_2Cr, Cp^*_2Cr does not readily react with 1,3-dimesitylimidazolium chloride. A deep blue solution is formed only after 48 h of reflux in THF. Addition of pentane yields a blue solid, [1,3-bis(2,4,6-trimethylphenyl)imidazolium$^+$][$Cp^*CrCl_3^-$]. Its structure was determined by X-ray crystallography; however, the quality of the structure was poor and did not allow for satisfactory refinement. The structure is shown here (Figure 2) only as a proof of chemical connectivity.[22] We note that the constituent ions of this salt have been previously characterized by X-ray crystallography as the

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(20) A small, sharp, low-intensity signal was detected around $g = 2$ in many, but not all samples of **1** and **2**. This feature is believed to arise from an impurity or decomposition product.

(21) For a leading reference, see: Fryzuk, M. D.; Leznoff, D. B.; Rettig, S. J. *Organometallics* **1995**, *14*, 5193−5202.

(22) Crystal data for [1,3-bis(2,4,6-trimethylphenyl)imidazolium]-[Cp^*CrCl_3]·toluene (M_r = 704.15): monoclinic, space group $P_{2/c}$, a = 16.5453(4) Å, b = 14.1803(4) Å, c = 15.9328(4) Å, β = 96.148(1)°, V = 3716.6(2) Å^3, Z = 4, d_{calc} = 1.258 Mg m^{-3}, μ(Mo Kα) = 0.552 mm^{-1}.

salts [$Cp^*CrCl_3^-$][$Cp^*_2Cr^+$][23a] and [1,3-bis(2,4,6-trimethylphenyl)imidazolium$^+$]Cl^-.[23b]

The lack of reactivity of Cp^*_2Cr when exposed to 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride was surprising. It was anticipated that the higher basicity of Cp^*_2Cr would make it more reactive. Since this was not the case, we tentatively suggest that the coordination of 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene is prevented for steric reasons. The use of less sterically demanding substituents on the imidazolium ring may allow a reaction analogous to eq 2 to proceed with Cp^*_2Cr. This possibility and further studies of these and related chromium complexes are in progress and will be reported in due time.

Experimental Section

General Procedures. All manipulations involving organometallic compounds were carried out with use of vacuum line, Schlenk, syringe, and/or drybox techniques. Dichloromethane, dichloromethane-d_2, and chloroform-d were distilled from CaH_2. THF was distilled from sodium benzophenone ketyl. ^1H NMR spectra were recorded on Bruker DPX 200 and 300 instruments. Chemical shifts are reported in ppm relative to tetramethylsilane, with the residual solvent proton resonance as an internal standard. Melting points were measured in capillary tubes sealed under vacuum. Elemental analyses were performed by Ilse Beetz Mikroanalytisches Laboratorium, Kronach, Germany, and by Canadian Microanalytical Service, Delta, B.C., Canada. The solid-state magnetic susceptibility study of **1** was conducted on a Quantum Design MPMS with a 5.5 T superconducting magnet and a SQUID detection system. Solution magnetic moments were measured by a modification of the Evan's method (C_6D_5H as a reference).[15] EPR spectra were taken on a Bruker 200D-SRC instrument.

The elemental analyses for neither **1** nor **2** were satisfactory despite several attempts, including adding oxidants to the samples, using separately synthesized material, and using two different microanalytical laboratories. For **2**, X-ray quality crystals as well as microcrystalline powder were subjected to analysis. Despite the effort, both **1** and **2** gave carbon analysis results that were too low by 2−3%; at the same time, the nitrogen and hydrogen contents were within an acceptable range. Metal−carbide formation is known to be a common problem for early transition metals. In our case, the carbene ligand may make these compounds especially prone toward carbide formation under combustion conditions.

1,3-Bis(2,4,6-trimethylphenyl)imidazolium Chloride. Synthesis of 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride followed a modification of the procedure given for 1,3-bis(4-methylphenyl)imidazolium chloride.[24] 2,4,6-Trimethylaniline (13.5 g, 100 mmol), paraformaldehyde (1.50 g, 50 mmol), and toluene (40 mL) were combined in a round-bottom flask, resulting in an orange slurry (the color of the trimethylaniline that was used). Heating to 100 °C for 1 h under inert atmosphere caused the mixture to become homogeneous. After cooling the reaction mixture to 40 °C, concentrated HCl (37% in H_2O, 4.93 g, 50 mmol) was added, resulting in the immediate precipitation of copious amounts of white solid. To this suspension, glyoxal (40% in H_2O, 7.26 g, 50 mmol) was added and caused a color change to yellow. The mixture was heated to reflux for 1.5 h, during which it turned black. Cooling the mixture and removing the volatiles in vacuo left a sticky black tar. The substance was triturated and washed with acetone (15 mL). Upon filtration, 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride was isolated as a pure (by ^1H NMR) white solid in 40% yield.

Preparation of CpCrCl(1,3-dimesitylimidazoline-2-ylidene) (1). Solid 1,3-dimesitylimidazolium chloride (1.16 g, 3.40 mmol) was added to a dark solution of Cp_2Cr (617 mg, 3.39 mmol) in THF (30 mL). After stirring for 1.5 h, the resulting violet solution was filtered through a fine glass frit to remove dark insoluble impurities. Diethyl ether (30 mL) was added to the filtrate, and the solution was stored overnight at −35 °C. The product was obtained as a violet powder upon filtration (1.04 g, 67%). ^1H NMR (C_6D_6, 200 MHz): δ 205 (br, $\omega_{1/2}$ = 2,800 Hz, 5H, Cp), 11.4 (br, $\omega_{1/2}$ = 250 Hz, 4H, *m*-H), 7.2 (br, $\omega_{1/2}$ = 50 Hz, 6 H, *p*-CH_3) 3.7 (br, $\omega_{1/2}$ = 790 Hz, 12 H, *o*-CH_3), −4.4 (br, $\omega_{1/2}$ = 300 Hz, 2H, NCH). UV/vis (THF, nm (ϵ, M^{-1} cm^{-1})): λ_{max} = 535 (120), 360 (680). μ_{eff} = 4.62 μ_B (Evan's method). Mp: 248−254 °C (no dec). Anal. Calcd for $C_{26}H_{29}ClCrN_2$: C, 68.34; H, 6.40; N, 6.13; Cr, 11.38. Found: C, 66.27; H, 6.33; N, 6.01; Cr, 11.50 and 11.53. MS (EI): *m/e* 456 (M^+), 391 (M^+ − Cp), 356 (M^+ − Cp − Cl).

Preparation of CpCrPh(1,3-dimesitylimidazoline-2-ylidene) (2). Solid **1** (419.1 mg, 0.917 mmol) was dissolved in THF (20 mL). After the solution was cooled at −35 °C, 1 equiv of PhMgCl (0.510 mL, 1.8 M) was added via syringe. The solution was observed to darken quickly and become brown. THF was removed under vacuum, and the brown solid residue was extracted with toluene (2 × 10 mL). A grayish, fine solid was removed when the toluene mixture was filtered through Celite. Pentane (50 mL) was added to the solution, causing the appearance of more fine powder. This too was removed by filtration through Celite. Large, brown, X-ray quality product crystals, in addition to smaller microcrystals, were formed upon cooling the solution at −35 °C overnight. Additional cooling resulted in the formation of more product. The product (240 mg, 49%) was isolated by decanting the mother liquor. ^1H NMR (C_6D_6, 200 MHz): δ 209 (br, $\omega_{1/2}$ = 3,660 Hz, 5 H, Cp), 14.8 (br, $\omega_{1/2}$ = 210 Hz, 2H, Cr−Ph *m*-H), 11.2 (br, $\omega_{1/2}$ = 255 Hz, 4H, mesityl *m*-H), 7.96 (br, $\omega_{1/2}$ = 70 Hz, 6H, *p*-CH_3), 3.8 (br, $\omega_{1/2}$ = 1,100 Hz, 12H, *o*-CH_3), −6.5 (br, $\omega_{1/2}$ = 350 Hz, 2H, NCH), −111 (br, $\omega_{1/2}$ = 1100 Hz, 1H, Cr−Ph *p*-H), −164 (br, $\omega_{1/2}$ = 5,600 Hz, 2H, Cr−Ph *o*-H). UV/vis (THF, nm (ϵ, M^{-1} cm^{-1})): λ_{max} = 505 (100), 385 (380). Anal. Calcd for $C_{32}H_{34}CrN_2$: C, 77.08; H, 6.87; N, 5.62. Found: C, 74.59; H, 6.79; N, 5.53. MS (EI): *m/e* 498 (M^+), 496 (M^+ − 2H), 421 (M^+ − Ph), 420 (M^+ − Ph-H), 356 (M^+ − Ph − Cp).

Spectroscopic Evidence for $CpCrCl_2$(1,3-dimesitylimidazoline-2-ylidene) (3). Compound **1** was observed to immediately react with $CDCl_3$, changing the color of the solution from purple to blue. Evaporation of the solvent left a blue residue. ^1H NMR (C_6D_6, 200 MHz): δ 219 (br, $\omega_{1/2}$ = 8130 Hz, 5H, Cp), 8.4 (br, $\omega_{1/2}$ = 110 Hz, 4H, *m*-H), 3.70 (br, $\omega_{1/2}$ = 55 Hz, 12H, *o*-CH_3), 2.16 (br, $\omega_{1/2}$ = 55 Hz, 6H, *p*-CH_3), −7.0 (br, $\omega_{1/2}$ = 220 Hz, 2H, NCH). UV/vis (THF, nm (ϵ, M^{-1} cm^{-1})): λ_{max} = 685 (470), 540 (60). MS (EI): *m/e* 491 (M^+). μ_{eff} = 3.39 μ_B (Evan's method).

X-ray Crystallographic Structure Determination of 2. Brown cubic crystals were obtained by cooling a toluene/pentane solution at −35 °C. A crystal of dimensions 0.60 × 0.55 × 0.40 mm was mounted on a glass fiber using paratone oil. X-ray data was collected on a Siemens SMART CCD diffractometer[25] using graphite-monochromated Mo Kα radiation. Data collection method: ω-scan, range 0.6°, crystal-to-detector distance 5 cm; further information is given in Table 1. Data reduction and cell determination were carried out with the SAINT and XPREP programs.[25] Absorption corrections were applied by the use of the SADABS program.[26]

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[23] (a) Aldridge, S.; Shang, M.; Fehlner, T. P. *Acta Crystallogr. C* **1998**, *C54*, 47−49. (b) Arduengo, A. J., III; Gamper, S. F.; Tamm, M.; Calabrese, J. C.; Davidson, F.; Craig, H. A. *J. Am. Chem. Soc.* **1995**, *117*, 572−573.

[24] Arduengo, A. J., III; U.S. Patent 5 077 414, 1991.

[25] *SMART and SAINT Area-detector Control and Integration Software*; Siemens Analytical X-ray intruments Inc.: Madison, WI, 1996.

[26] Sheldrick, G. M. Private communication, 1996.

The structure was determined and refined using the SHELXTL program package.[27] The non-hydrogen atoms were refined with anisotropic thermal parameters; hydrogen positions were calculated from geometrical criteria and given isotropic thermal parameters.

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Supporting Information Available: Complete list of bond angles and distances, as well as atomic coordinates and thermal displacement parameters for **2** (8 pages). Ordering information is given on any current masthead page.

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(27) Sheldrick, G. M. *SHELXTL*, Version 5; Siemens Analytical X-ray Instruments Inc.: Madison, WI, 1996.