1746 *Organometallics* **1994,** *13,* 1746-1750

Bent Metallocenes Containing Ancillary Ligands in Ring-Bridging Chains. Synthesis, Spectroscopy, and X-ray Crystal Structure of [2,6-Pyridinediylbis(methylcyclopentadienyl)]chromium(II)

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Received October 4, 1993[⊗]

$Cr[(\eta^5-C_5H_4CH_2)_2-2,6-C_5H_3N]$ (CrL) has been obtained by metathesis reaction between $CrCl_2$ and $Na_2[(C_5H_4CH_2)_2-2,6-C_5H_3N]$ in THF at room temperature. Low-temperature ^1H NMR studies of CrL are reported. The solid state structure of CrL was determined by single crystal X-ray analysis (monoclinic, $C2/c$, $a = 13.662(3)$ Å, $b = 8.975(2)$ Å, $c = 21.085(3)$ Å, $\beta = 95.11(4)°$, $V = 2575.1(9)$ Å^3, $Z = 8$, $R = 0.041$, $R_w = 0.052$ for 1619 measured reflections with $I > 3\sigma(I)$). The ligand is bound to the metal atom via the two bent cyclopentadienyl rings with distances Cr–Cg(1) (Cg = gravity center) of 1.849(5) Å and Cr–Cg(2) of 1.840(5) Å, with the pyridine nitrogen at a distance Cr–N of 2.521(4) Å, which is the longest Cr–N value yet reported. The effects of the reduction in symmetry of this bent chromocene with respect to the unsubstituted one, which results in the perturbation of the axial ligand field typical of the undistorted metallocenes, are discussed in view of magnetic and optical investigations.

Introduction

The chemistry of bridged ferrocenes, having cyclopentadienyl (Cp) rings tilted with respect to each other, has been significantly explored.[1] The various properties and chemical reactivities of such complexes have been correlated with the structures of different bridges.[2] On the contrary, investigations on organometallic derivatives with linked Cp rings, having the metal different from iron in oxidation state II, are rather scarce,[3] even though the importance of the bending of the Cp rings has been attested by theoretical studies.[4]

Bending of the Cp rings of metallocenes can be achieved by interlinking the two rings by short $(CH_2)_x$ chains, as observed mainly for ferrocene, or by combining the effects of bridging both the Cp rings and additional ligands.[3]

Here, we report the synthesis and molecular structure of $Cr[(\eta^5-C_5H_4CH_2)_2-2,6-C_5H_3N]$ (CrL), the first example of a completely characterized "bent chromocene". In this complex the Cp rings are interlinked by a 2,6-dimethylenepyridine group, which imposes rigidity on the resulting ligand $[(C_5H_4CH_2)_2-2,6-C_5H_3N]$[5] (L), thereby causing tilting of the Cp ring. The consequence of the reduction in symmetry in the molecule, which results in the perturbation of the axial ligand field typical of chromocene, is discussed in the optical and magnetic investigations.

Results and Discussion

Metathesis reaction between $Na_2[(C_5H_4CH_2)_2-2,6-C_5H_3N]$ (Na_2L) and $CrCl_2$ in THF at room temperature gave the dark-blue complex CrL. CrL was isolated and purified from byproducts by extracting the residue obtained after solvent evaporation of the reaction mixture with *n*-hexane.

The extremely air-sensitive CrL was found to be soluble in THF and aromatic solvent but only sparingly soluble in aliphatic hydrocarbons.

Owing to the paramagnetism, the ^1H NMR spectrum (toluene-d_8, $T = 296$ K) of CrL exhibited three widely separated and very broad resonances, devoid of multiplet splitting, whose shifts varied strongly with temperature, at δ 14.76 ($w_{1/2} = 20$ Hz, 3H), 47.53 ($w_{1/2} = 600$ Hz, 8 H), and 43.93 ($w_{1/2} = 300$ Hz, 4 H). On the basis of the broadening of the signals, as a consequence of the distances from the paramagnetic center, the resonance at 14.76 ppm

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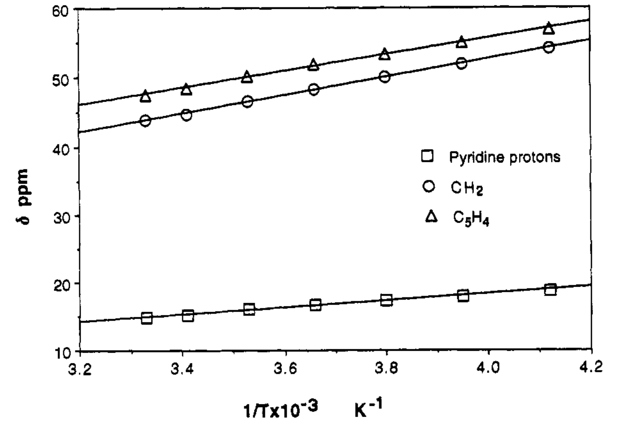
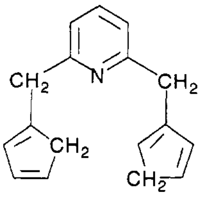


Figure 1. Temperature dependence of the ^{1}H NMR shifts of CrL.

could be tentatively assigned to the pyridine protons and the signals at 47.53 and 43.93 ppm to the Cp and CH_2 protons, respectively. Figure 1 shows that up to room temperature, all the ^{1}H NMR resonances vary inversely with the temperature.

Hydrolysis of the disodium salt Na_2L gave the bis-protonated ligand $[(C_5H_5CH_2)_2\text{-}2,6\text{-}C_5H_3N]$ (LH_2) (see experimental part). It is worth noting that the protonation of Na_2L, instead of a mixture of the six possible isomers, yields only one isomer containing the two cyclopentadiene rings differently protonated, whose structure has been completely determined by NMR spectroscopy[6] as:



The nonequivalence of the two methylene exocyclic protons, giving two multiplets at δ 3.93 and 3.90, is indicative of an asymmetric protonation of the two cyclopentadiene rings, whose methylene protons give rise to two signals at δ 2.98 and 2.93. On the other hand, the remaining six vinyl protons of the cyclopentadiene groups, all magnetically different from one another, give rise to six different signals at δ 6.46 (1 H), 6.43 (1 H), 6.41 (1 H), 6.29 (1 H), 6.20 (1 H), and 6.07 (1 H).

Table 1. Fractional Coordinates and Equivalent Isotropic Displacement Coefficients (Å² × 10³) for CrL

atom	*x*	*y*	*z*	*U*(eq)[a]
Cr	0.38498(5)	0.28548(7)	0.34083(3)	40.5(2)
N	0.5064(3)	0.1013(4)	0.39279(2)	47(1)
C(1)	0.5810(3)	0.1476(5)	0.4332(2)	42(1)
C(2)	0.6401(3)	0.0490(6)	0.4687(2)	57(2)
C(3)	0.6234(4)	−0.1004(6)	0.4611(3)	67(2)
C(4)	0.5468(4)	−0.1511(6)	0.4194(3)	54(2)
C(5)	0.4902(3)	−0.0459(5)	0.3862(2)	44(1)
C(6)	0.4044(5)	−0.0880(6)	0.3394(3)	79(2)
C(7)	0.3450(4)	0.0409(5)	0.3153(3)	56(2)
C(8)	0.3590(4)	0.1240(5)	0.2606(3)	52(2)
C(9)	0.2923(4)	0.2461(6)	0.2571(2)	51(2)
C(10)	0.2369(4)	0.2393(6)	0.3097(3)	55(2)
C(11)	0.2710(4)	0.1125(6)	0.3460(3)	61(2)
C(12)	0.5941(4)	0.3146(6)	0.4374(3)	67(2)
C(13)	0.5117(4)	0.3998(5)	0.4030(2)	52(2)
C(14)	0.5093(4)	0.4482(5)	0.3398(2)	49(2)
C(15)	0.4147(4)	0.5130(5)	0.3230(3)	53(2)
C(16)	0.3597(4)	0.5015(5)	0.3770(3)	55(2)
C(17)	0.4200(4)	0.4289(5)	0.4255(3)	55(2)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for CrL[a]

	Bond Lengths		
Cr–N	2.521(4)	Cr–C(7)	2.314(5)
Cr–C(8)	2.232(5)	Cr–C(9)	2.109(5)
Cr–C(10)	2.112(5)	Cr–C(11)	2.208(6)
Cr–C(13)	2.316(5)	Cr–C(14)	2.242(5)
Cr–C(15)	2.122(5)	Cr–C(16)	2.123(5)
Cr–C(17)	2.219(5)	N–C(1)	1.336(6)
N–C(5)	1.344(6)	C(1)–C(2)	1.374(7)
C(1)–C(12)	1.511(7)	C(2)–C(3)	1.366(8)
C(3)–C(4)	1.382(7)	C(4)–C(5)	1.372(7)
C(5)–C(6)	1.513(8)	C(6)–C(7)	1.477(7)
C(7)–C(8)	1.400(7)	C(7)–C(11)	1.404(8)
C(8)–C(9)	1.423(7)	C(9)–C(10)	1.397(8)
C(10)–C(11)	1.427(8)	C(12)–C(13)	1.494(7)
C(13)–C(14)	1.401(7)	C(13)–C(17)	1.403(8)
C(14)–C(15)	1.433(7)	C(15)–C(16)	1.424(8)
C(16)–C(17)	1.413(7)	Cr–Cg(1)	1.840(5)
Cr–Cg(2)	1.849(5)		
	Bond Angles		
N–Cr–Cg(1)	98.5(2)	N–Cr–Cg(2)	98.3(2)
Cg(1)–Cr–Cg(2)	163.3(2)	C(1)–N–C(5)	118.6(4)
N–C(1)–C(12)	115.2(4)	N–C(1)–C(2)	121.7(4)
C(2)–C(1)–C(12)	123.1(4)	C(1)–C(2)–C(3)	119.0(5)
C(2)–C(3)–C(4)	120.4(5)	C(3)–C(4)–C(5)	117.2(5)
N–C(5)–C(4)	123.0(4)	C(4)–C(5)–C(6)	122.0(4)
N–C(5)–C(6)	115.0(4)	C(5)–C(6)–C(7)	113.5(5)
Cr–C(7)–C(6)	123.5(4)	C(6)–C(7)–C(11)	126.5(5)
C(6)–C(7)–C(8)	126.1(5)	C(8)–C(7)–C(11)	107.0(4)
C(7)–C(8)–C(9)	108.5(4)	C(9)–C(10)–C(11)	106.7(5)
C(7)–C(11)–C(10)	109.4(5)	C(1)–C(12)–C(13)	113.5(4)
C(12)–C(13)–C(17)	126.1(5)	C(12)–C(13)–C(14)	125.0(5)
C(14)–C(13)–C(17)	108.5(4)	C(13)–C(14)–C(15)	107.8(5)
C(14)–C(15)–C(16)	107.6(4)	C(15)–C(16)–C(17)	107.3(5)
C(13)–C(17)–C(16)	108.8(5)		
	Torsion Angles		
C(5)–C(6)–C(7)–C(11)	−81.8(7)	C(1)–C(12)–C(13)–C(14)	−92.4(6)
C(2)–C(1)–C(12)–C(13)	−170.1(5)	C(4)–C(5)–C(6)–C(7)	172.2(5)

[a] Cg, gravity center.

X-ray Crystal Structure. The final parameters with their estimated standard deviations are listed in Table 1. Bond lengths and angles for the non-H atoms are given in Table 2. An ORTEP view of the molecule, together with the atom labeling scheme, is reported in Figure 2. The whole structure consists of well-isolated molecules. The ligand which wraps up the chromium metal ion is rather symmetric, with a pseudomirror plane passing through the C(3) and N atoms of the pyridine moiety and the chromium atom. The cyclopentadienyl terminal branches of the ligand are tilted out around the adjacent C(7)–C(6) and C(12)–C(13) bonds with torsion angles of −81.8(7)° [C(5)–C(6)–C(7)–C(11)] and −92.4(6)° [C(1)–C(12)–C(13)–C(14)] in order to reach the suitable distance for bonding to chromium. While the chromium bond distances to the two Cgs (Cg = ring center of gravity) of the Cp rings are equivalent, Cr–Cg(1) is 1.849(5) Å and Cr–Cg(2) 1.840(5) Å, three types of bond distances can be envisaged to the individual carbon atoms, but in any case the bonds are symmetric with respect to the two ligand arms. The shortest are those with C(9), C(10) on one side (2.11 Å) and those with C(15), C(16) (2.12 Å) on the other side; the medium values are those with C(8), C(11) (2.22

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(6) The complete assignment of all the protons of LH_2 by ^{1}H and ^{13}C NMR homo- and heteronuclear correlated spectroscopy (400 MHz) together with the calculated thermodynamic stabilities of the various isomers will be separately published: Lucchini, V.; Paolucci, G., manuscript in preparation.

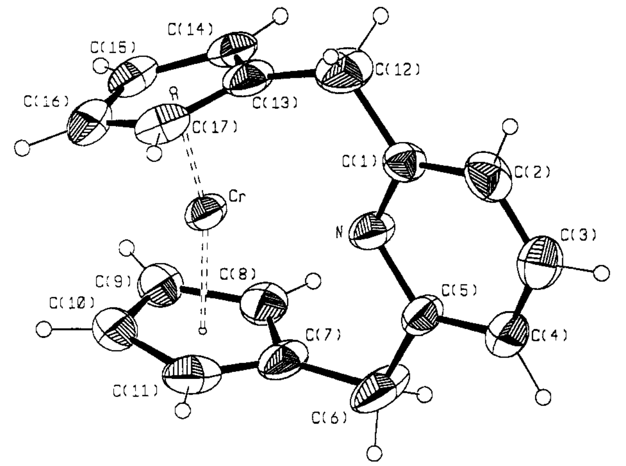

Figure 2. ORTEP drawing of CrL with the atom-numbering scheme. The thermal ellipsoids are drawn in at the 40% probability level.

Å) and C(14), C(17) (2.23 Å), and the longest involves C(7) on one side (2.314(5) Å) and C(13) (2.316(5) Å) on the opposite side. The two Cp rings are bent in the direction of the metal ion with a dihedral angle between the respective mean planes of 29.1(2)°, while the Cp(1)–Cr–Cp(2) angle is 163.3(2)°. These structural features also suggest that the Cp bonding mode to the metal ion is not symmetric considering the difference between the minimum and maximum values of Cr–C bond distances of 0.2 Å, while in $Cr(\eta^5\text{-}C_5H_4CH_3)_2$[7] the range is from 2.125(3) to 2.206(3) Å, with Cr–Cg of 1.778(2) Å. The Cr–N bond distance is 2.521(4) Å, while the literature values for about 20 $Cr–N_{pyridine}$[8] are in the range 2.146–2.178 Å. In addition, the bonding mode of the Cp ligand could be considered as η^5 distorted toward η^4, and the long Cr···N distance seems due to the geometrical position of the nitrogen atom more than to a direct Cr–N bond, also if some type of weak interaction could be present.

If we consider the complex $U[(\eta^5\text{-}C_5H_4CH_2)_2\text{-}2,6\text{-}C_5H_3N]Cl_2$,[5] containing the same ligand, the large ionic radius of uranium, 1.09 vs 0.80 Å for Cr(II), allows a more regular distribution of the bond lengths, with $U–C_{av}$ of 2.70(1) Å and $U–N_{av}$ of 2.62(1) Å. The latter value is comparable to the $U–N_{pyridine}$ value of 2.64(1) Å found in $UCl_2(C_8H_8)(NC_5H_5)$[9] but is also indicative of an actual U–N bond.

Optical and Magnetic Measurements. The electronic absorption spectrum of CrL is composed of a moderately strong broad band centered at 16 000 cm^{-1} (ϵ = 625 L mol^{-1} cm^{-1}), with a steeply rising edge above 25 000 cm^{-1}. This spectrum is significantly different from that of chromocene, which is characterized by a broad band at 21 900 cm^{-1} (ϵ = 175) with stronger absorptions ($\epsilon > 2000$) at about 29 000, 38 000, and 41 000 cm^{-1}.[10] As charge-transfer transitions in metallocene compounds are reported to usually occur above 25 000 cm^{-1},[11] the band at 16 000 cm^{-1} has been assigned to a d–d transition and the absorption edge at 25 000 cm^{-1} to the onset of charge-transfer transitions. In the case of chromocene, the d^4 system may be treated in terms of a purely axial $C_{\infty v}$ field, as a symmetry axis C_n with $n \geq 5$ is present.[12] In the $C_{\infty v}$ point group, the d orbitals span the irreducible representations $\delta(d_{z^2})$, $\pi(d_{xz}\, d_{yz})$, and $\delta(d_{x^2-y^2}, d_{xy})$, with energies $\delta < \sigma << \pi$.[13] The absorption at 21 900 cm^{-1} has been assigned to the group of spin-allowed d–d transitions $^3\Delta(\sigma\delta^3) \rightarrow {}^3\Pi(\pi\delta^3)$, $^3\Phi$, ^3H, $^3\Pi$, and $^3\Pi(\sigma\pi\delta^2)$ on the basis of a Tanabe–Sugano diagram and the magnetic data, which confirmed the $^3\Delta(\sigma\delta^3)$ nature of the ground state.[10] In the case of CrL, the rigidity of the ligand imposes a bent configuration which perturbs the $C_{\infty v}$ symmetry of chromocene, yielding a geometry which can be approximated as C_{2v}. In the lower symmetry, the σ, π, and δ orbitals transform as a_1, $(a_2 + b_1)$, and $(a_1 + b_2)$, respectively. Therefore, on passing from chromocene to CrL, the perturbation introduced by the bent configuration should give rise to splittings of the spin-allowed d–d transition. In our absorption spectrum, these splittings are not resolved, as it is reasonable to assume that the perturbing ligand field is much weaker than the axial one. The 16 000-cm^{-1} band is therefore assigned to the group of bands $^3\Delta(\sigma\delta^3) \rightarrow {}^3\Pi(\pi\delta^3)$, $^3\Phi$, ^3H, $^3\Pi$, and $^3\Pi(\sigma\pi\delta^2)$ in the $C_{\infty v}$ point group, which is analogous to the assignment for $Cr(\eta^5\text{-}C_5H_5)_2$. The triplet nature of the ground state is confirmed by magnetic susceptibility data (see below).

Warren[14] has constructed a Tanabe–Sugano diagram for metal sandwich complexes having a d^4 configuration, assuming the reasonable ratios Dt/Ds = 0.55 and C/B = 4.0. Inspection of this diagram indicates that the sizeable red shift of the spin-allowed transition of CrL with respect to chromocene originates from a reduction of the axial field quantity Dt. This reduction can possibly be explained on the basis of the elongation of the distances between the metal center and the Cp moieties. In fact, for CrL the distances between Cr and the centroids of the Cps are 1.840 and 1.849 Å, longer than those in the case of the normal not-bridged chromocene.[7] This elongation, presumably caused by the rigidity of the ligand, is likely to reduce the overlap between the orbitals of the metal and of the Cp ligands, thus decreasing the axial field.

The increase in intensity of the spin-allowed d–d transition for CrL compared to that of chromocene (ϵ = 625 vs 175) can be explained on the basis of a stronger mixing of the d-based states of Cr with states of opposite parity, induced by the distortion leading to the approximate C_{2v} symmetry.

The χT value at high temperature for CrL is 0.98 emu K mol^{-1} (μ_{eff} = 2.80 μ_B) and decreases steadily on lowering the temperature, reaching a value of 0.33 emu K mol^{-1} (μ_{eff} = 1.62 μ_B) at 4 K. The data follow a Curie–Weiss behavior, and a linear regression analysis of all the data gives $C = 0.987$ and $\theta = -8.2$ K. The parameters do not change significantly by fitting only the data below 50 K, with $C = 1.01$ and $\theta = -8.1$ K. The temperature dependence of χT is shown in Figure 3.

The magnetic behavior of CrL, typical of a $S = 1$ without orbital contribution, is substantially different from that displayed by chromocene. This compound has a large orbital contribution to the magnetic moment, χT being 1.28 emu K mol^{-1} (μ_{eff} = 3.20 μ_B), due to the degeneracy of the δ orbitals.[14,15] In the case of CrL, the bent geometry

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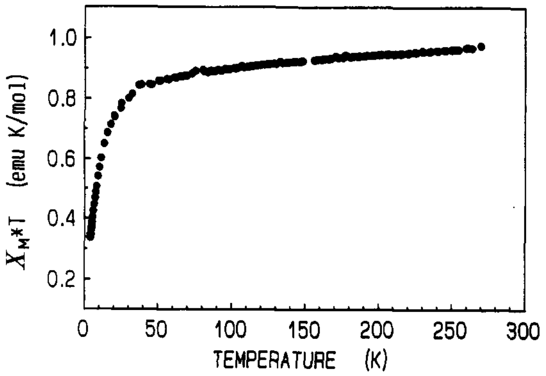

Figure 3. Temperature dependence of χT.

of the molecule removes the degeneracy, and the δ and σ orbitals, which are closer in energy, transform like (a_1 + b_2) and a_1, respectively, in the C_{2v} symmetry. Among the four electrons distributed in these three orbitals, two are unpaired, giving rise to $S = 1$. The (a_2 + b_1) orbitals originating from the π set are too far in energy to be populated, as suggested by the electronic spectra. The C_{2v} distortion leading to a high-temperature value of μ_{eff} close to the spin-only value (2.83 μ_B) is in excellent agreement with the theoretical predictions of Warren.[13]

Experimental Section

General Considerations. All the operations were carried out in nitrogen-filled gloveboxes with the rigorous exclusion of oxygen and moisture. Solvents were purified by standard methods[16] and used immediately after distillation. Na_2L was synthesized according to the literature.[5] Other reagents were commercial products used as supplied.

Elemental analyses were performed by Dornis U. Kolbe Mikroanalytisches Laboratorium, Mulheim/Ruhr, Germany.

Infrared spectra were recorded with a Mattson Galaxy Series FTIR 3000 apparatus; samples were prepared in the glovebox as KBr pellets and sandwiched between KBr plates in an airtight holder.

The electronic absorption spectrum of CrL was measured in toluene solution (1.5×10^{-3} mol L^{-1}) using a Cary 17 D double beam spectrophotometer.

The magnetization was measured in the temperature range 4-270 K with a Metronique MS02 SQUID magnetometer at a field strength of 1 T; due to the air sensitivity of the compound, the sample was sealed in a glass sample holder under nitrogen atmosphere; the contribution of the sample holder was then substracted from the rough data.

The mass spectra were recorded on a double focusing, reverse geometry VG ZAB 2F instrument, operating in EI conditions (70 eV, 200 μA, source temperature 200 °C).

The NMR spectra were recorded with Bruker 200 A and Varian Unity 400 instruments equipped with variable temperature apparatus.

Synthesis of CrL. A solution of Na_2L (840 mg, 3.01 mmol) in THF (50 mL) was added dropwise over 2 h to a suspension of $CrCl_2$ (395 mg, 3.21 mmol) in THF (100 mL), and the resulting deep blue mixture was stirred overnight. The solvent was removed under vacuum and the residue dissolved in hexane. The resulting solution was filtered, the solvent removed under vacuum, and the dark blue residue analyzed and identified as CrL (422 mg, 1.48 mmol, 49% yield). CrL is extremely air sensitive. In fact, when solvents or the glovebox atmosphere is not extremely pure, formation of a green byproduct occurs, presumably a Cr(III) complex; purification of CrL from this species is very easy since the eventual green product becomes insoluble in hexane after 48 h. CrL decomposes at 195–200 °C. EI mass spectrum: m/z (relative intensity) $M^{\bullet+}$ 285 (100), 284 (35), 283 (75), 257 (3), 233 (20), 232 (28), 220 (8), 207 (23), 206 (19), 194 (9), 180 (19), 168 (48), 156 (20), 155 (10), 129 (13), 117 (20), 107 (15), 92 (4), 80 (3), 68 (13), 52 (97). ^1H NMR (toluene d_8, T = 296 K): δ 47.53 (br s, $w_{1/2}$ = 600 Hz, 8 H, Cp), 43.93 (br s, $w_{1/2}$ = 300 Hz, 4 H, CH_2), 14.76 (br s, $w_{1/2}$ = 20 Hz, 3 H, pyridine protons). IR (KBr pellets): ν_{max} 1574 (m), 1453 (s), 1420 (m), 1343 (w), 1211 (w), 1021 (m), 1003 (s), 938 (w), 809 (m), 770 (m), 756 (m), 740 (s), and 632 (m) cm^{-1}. Near-IR–vis λ_{max} (toluene): 625 nm.

Table 3. Summary of Crystallographic Data for CrL

chem formula	$C_{17}H_{15}NCr$
mol wt	285.31
cryst dimens/mm	$0.21 \times 0.12 \times 0.41$
cryst syst	monoclinic
a/Å	13.662(3)
b/Å	8.975(2)
c/Å	21.085(3)
β/deg	95.11(4)
V/Å^3	2575.1(9)
space group	$C2/c$
Z	8
d(calcd)/g cm^{-3}	1.47
temp/°C	22
data collected	$h, k, \pm l$
transm coeff (rel)	0.89–1
F(000)	1184
λ(Mo Kα)/Å	0.71069
μ(Mo Kα)/cm^{-1}	8.1
no. of rflns measd	5768
$2\Theta_{max}$/deg	52
no. of rflns [$I \geq 3\sigma(I)$]	1619
$R(F_o)$	0.041
$R_w(F_o)$	0.052
goodness of fit	1.09

Anal. Calcd for $C_{17}H_{15}NCr$: C, 71.58; H, 5.26; N, 4.91; Cr, 18.25. Found: C, 71.39; H, 5.34; N, 4.86; Cr, 18.35.

Synthesis of LH_2 by Hydrolysis of Na_2L. To Na_2L (420 mg, 1.505 mmol) suspended in anhydrous diethyl ether (50 mL) and maintained at 5 °C was added degassed water (0.5 mL), and the mixture was stirred for 2 h. After addition of anhydrous sodium sulfate, the ethereal solution was evaporated to dryness under vacuum. The residue light-yellow oil was purified by flash chromatography on Silica gel 60 (230–400 mesh ASTM) and eluted by diethyl ether–n-hexane 45–55 (v:v). After solvent evaporation, a colorless residue was isolated (250 mg, 71% yield). EI mass spectrum: m/z (relative intensity) $M^{\bullet+}$ 235 (100), 234 (86), 233 (3), 220 (9), 208 (7), 194 (10), 168 (34), 156 (36), 129 (14), 107 (32), 92 (14), 78 (18). ^1H NMR (400 MHz $CDCl_3$): δ 7.51 (m, 1 H, 4-Py), 6.96 (m, 2 H, 3,5-Py), 6.46 (m, 1 H, HC ring), 6.43 (m, 1 H, HC ring), 6.41 (m, 1 H, HC ring), 6.29 (m, 1 H, HC ring), 6.20 (m, 1 H, HC ring), 6.07 (m, HC ring), 3.93 (m, 2 H, CH_2), 3.90 (m, 2 H, CH_2), 2.98 (m, 2 H, CH_2 cyclopentadiene), 2.93 (m, 2 H, CH_2 cyclopentadiene). Anal. Calcd for $C_{17}H_{17}N$: C, 86.77; H, 7.28; N, 5.95. Found: C, 86.50; H, 7.20; N, 6.30.

X-ray Measurements and Structure Determination of CrL. The crystal and refinement data for CrL are summarized in Table 3. A prismatic air-sensitive (dark blue) crystal was lodged in a Lindemann glass capillary and centered on a four-circle Philips PW1100 diffractometer with graphite monochromated Mo Kα radiation. The orientation matrix and preliminary unit cell dimensions were determined from 25 reflections found by mounting the crystal at random, varying each of the orientation angles χ and ϕ over a range of 120°, with $5 \leq \vartheta \leq 7°$. For the determination of precise lattice parameters, 25 strong reflections with $10 \leq \vartheta \leq 13°$ were considered. Integrated intensities for hkl reflections in the interval h = 0–15 k = 0–11, l = ±24 were measured, and two standard reflections 3,1,–1, and 1,1,4 were measured every 180 min. There were no significant fluctuations of intensities other than those expected from Poisson statistics. The intensity data were corrected for Lorentz–polarization effects

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[16] Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. In *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon: Oxford, 1982.

and for absorption according to the method of North et al.[17] No correction was made for extinction. The structure was solved by using three-dimensional Patterson and Fourier techniques and refined with full matrix least-squares methods, with anisotropic thermal parameters assigned to all the non-hydrogen atoms. The hydrogens were introduced at calculated idealized positions ($d_{C-H} = 0.98$ Å with $U = 0.07$ Å^2) and allowed to ride on the attached carbon atoms. The function minimized was $\sum w\Delta^2$, with $\Delta = (|F_o| - |F_c|)$. The final refinement cycle resulted in the conventional R factors $R = 0.041$ and $R_w = 0.052$ based on the 1619 unique reflections with $I \geq 3\sigma(I)$ and the 173 variables. A final difference Fourier map showed maximum positive and negative peaks of 0.25 and −0.30 e/Å^3, respectively. The anomalous dispersion terms[18] for Cr were taken into account in the refinement. Data processing and computation were carried out by using the SHELX 76 program package,[19] with atomic scattering factors taken from the *International Tables for X-ray Crystallography*.[18] The program for the ORTEP drawing was from ref 20. A list of anisotropic thermal parameters and hydrogen atom coordinates is available as supplementary material.

Acknowledgment. We thank Dr. R. Seraglia for obtaining mass spectra and for her comments and suggestions. Financial support from Progetto Finalizzato "Materiali Speciali per Tecnologie Avanzate" of C.N.R. is gratefully acknowledged.

Supplementary Material Available: Tables of anisotropic thermal parameters for non-hydrogen atoms and fractional coordinates of H-atoms for CrL (2 pages). Ordering information is given on any current masthead page.

OM930682H

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(18) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, 1974; Vol. 4.

(19) Sheldrick, G. M. *SHELX 76: Program for Crystal Structure Determination*; University of Cambridge, 1976.

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