

was highly air sensitive. Oxygen absorption of II in CCl_4 under identical conditions as for III gave a rate of endoperoxide formation of $k = 4.8 \times 10^{-4} \text{ s}^{-1}$, with $t_{1/2} = 0.4 \text{ h}$, approximately 30 times faster than III. But most interesting was the observation that II did not form a single endoperoxide but two isomers A and B (see Scheme II) in a ratio of 2:1. They were separated by chromatography on silica gel. Both formed colorless crystals analyzing correctly for the oxygen addition products.⁸ The spectral data suggest that A in analogy to endoperoxide VI obtained from semibullvalene III has the *trans*-dioxaperhydroindane structure, while B has the unique dioxatriquinacene structure, based upon the lack of symmetry in the carbon NMR spectrum with three different signals for the quaternary carbons and three different carbon resonances for the cyclopentane section of the molecule. A on the other hand has a center of symmetry as documented in the carbon NMR spectrum. The X-ray analysis of both isomers confirms these assignments.⁹

1,5-Dimethyl-2,4,6,8-tetracarboxymethoxysemibullvalene⁶ does not react with oxygen, neither at room temperature nor at 78 °C. Instead, it isomerizes thermally to 1,5-dimethyl-2,4,6,8-tetracarboxymethoxycyclooctatetraene.^{7,8,10} The oxygenation data suggest that semibullvalenes II and III reversibly open to the respective singlet bicyclo[3.3.0]octadienyl diradicals, e.g., VIIs, ring opening of which to a highly strained cyclooctatetraene is energetically disfavored.¹⁴ Singlet VIIs can undergo spin inversion to triplet VIII which adds triplet oxygen to positions 2 and 6 or 2 and 8 giving endoperoxides A and B.¹² A similar behavior was observed by W. R. Roth et al.¹¹ for the two states of the 2,3-dimethylene-1,4-cyclohexadiyl diradical. However, a direct attack of oxygen on semibullvalene II or III cannot be ruled out especially since III is characterized by an extremely long (weak) $\text{C}_2\text{-C}_8$ bond (1.828 Å).^{7,15} Oxygenation of semibullvalene III occurred only across positions 2 and 6 to endoperoxide VI with a more stable, less strained *trans*-4,5-dioxadecalin structure. In no case did we observe the formation of 3,7-endoperoxides, trapping products of the theoretically possible 1,4-cyclohexadiyl diradical.⁵ It should be noted that octamethylsemibullvalene has been reported by Criegee and Askani in 1968 to react with oxygen forming a peroxide for which the dioxatriquinacene structure was assigned based on its proton NMR spectrum.^{13a,b} The results obtained for the dimethyl compound suggest that the singlet bicyclooctadienyl diradical rearranges much faster into the corresponding cyclooctatetraene than undergoing spin inversion into the triplet.

Neither cycloheptano- nor cyclooctano-2,4,6,8-tetracarboxymethoxysemibullvalene (IV) and (V) reacted with oxygen. The

structural and spectroscopic studies of the 1,5-annulated-2,4,6,8-tetracarboxymethoxysemibullvalenes will be reported in a subsequent paper.¹⁵ Further experiments are under way in order to unravel the surprising behavior of these amazing molecules.

Acknowledgment. We thank Drs. R. Franck, J. Schulman, W. Berkowitz, and J. Dannenberg for helpful discussions. This work was supported through a CUNY-FRAPP Grant no. 66358 and an NIH-MARC Grant no. GM 07823 for R.P. Special acknowledgment goes to Hoffman-La Roche Inc., Nutley, NJ for their generous support of this study.

Registry No. II, 113451-36-8; III, 113451-35-7; VI, 113430-99-2; A, 113431-00-8; B, 113431-01-9.

Supplementary Material Available: NMR and mass spectral data, ORTEP drawings, and tables of crystal data, final atomic parameters, temperature factors, and bond lengths and bond angles for endoperoxide VI, EP-5A, and EP-5B (18 pages); table of observed and calculated structure factors for endoperoxide VI (6 pages). Ordering information is given on any current masthead page.

Electrophilic Activation of Benzene in $[\text{Cr}(\eta^4\text{-C}_6\text{H}_6)(\text{CO})_3]^{2-}$

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It is well established that arenes are activated toward nucleophiles by coordination to the $[\text{Cr}(\text{CO})_3]$ moiety.³ The cyclohexadienyl products⁴ may eliminate substituent anions to give nucleophilic arene substitution^{3b,5} or may be oxidized or protonated to release a substituted arene or cyclohexadiene, respectively.^{3,4} In the case of $[\text{Cr}(\eta\text{-C}_6\text{H}_6)(\text{CO})_3]$, the parent benzene complex, the range of addends is, however, restricted to stabilized carbanions which are more nucleophilic than ester enolates but which do not metalate the arene^{3a} (MeLi and BuLi metalate, for example). We now wish to report that cyclohexadienyl complexes can be prepared in a complementary manner by *electrophilic* addition to the activated η^4 -arene in the dianionic reduction product of $[\text{Cr}(\eta\text{-C}_6\text{H}_6)(\text{CO})_3]$ (Scheme I).

We have previously reported that $[\text{Cr}(\eta\text{-C}_6\text{H}_6)(\text{CO})_2]^{2-}$ can be prepared by naphthalenide reduction of $[\text{Cr}(\eta\text{-C}_6\text{H}_6)(\text{CO})_2\text{(pyridine)}]$,⁶ and the possibility of more convenient access to the dianion led us to examine naphthalenide reduction of the readily available⁷ precursor $[\text{Cr}(\eta\text{-C}_6\text{H}_6)(\text{CO})_3]$ (1). Dropwise addition

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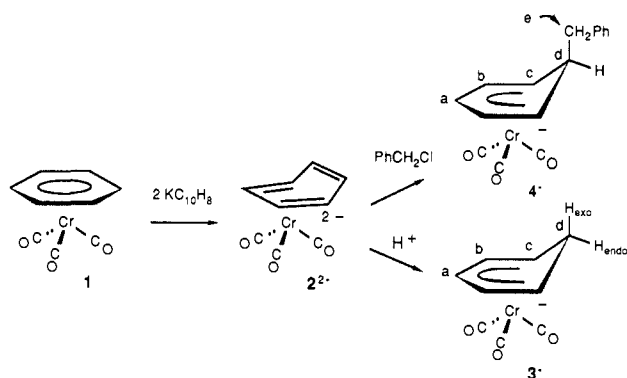
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Scheme I

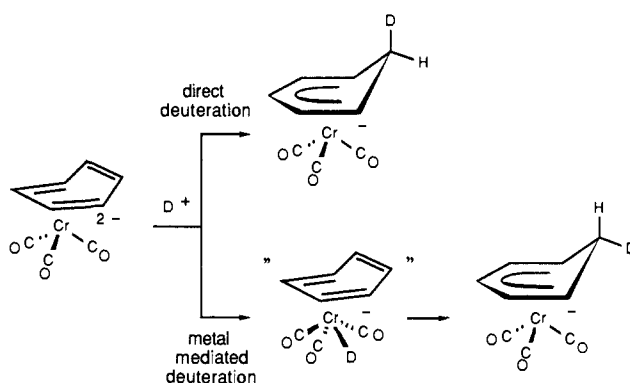


of 7.8 mL of a 0.18 M solution of potassium naphthalenide in tetrahydrofuran (THF)⁸ (2 equiv) to a solution of **1** (0.15 g, 0.7 mmol) in 40 mL of THF at $-78\text{ }^{\circ}\text{C}$ resulted in color changes from yellow through orange to a dark brown just before the naphthalenide green persisted. The loss of CO absorptions at 1965 s and 1885 cm^{-1} showed that **1** had been consumed, but the new bands at 1810 s and 1690 vs br cm^{-1} were not those of $[\text{Cr}(\eta\text{-C}_6\text{H}_6)(\text{CO})_2]^{2-}$. The broad 1690- cm^{-1} band probably corresponds to two absorptions, as indicated by the Nujol mull spectrum of the precipitate obtained by addition of 2 equiv of dibenzo-18-crown-6.⁹ This contained three bands at 1805 s, 1692 s, and 1660 s cm^{-1} , suggesting formulation of the anion as $[\text{Cr}(\eta^4\text{-C}_6\text{H}_6)(\text{CO})_3]^{2-}$ (**2²⁻**, Scheme I), a tricyarbonyl complex with an η^4 -arene ligand.

This formulation is supported by the reactivity of **2²⁻** and by Rieke's demonstration¹⁰ that the dianion produced by Na/Hg reduction (or pseudoreversible 2- e^- electrode reduction) of $[\text{Cr}(\eta^6\text{-C}_{10}\text{H}_8)(\text{CO})_3]$ contains η^4 -naphthalene. Although its instability precluded earlier speculation about the electrode-generated 2- e^- reduction product of **1** and its toluene analogue,¹¹ it is not unreasonable that **1** also forms a dianion containing an η^4 -arene.¹² Dianion **2²⁻** is more stable when generated by naphthalenide reduction¹³ than it appears to be under electrochemical conditions, and, although solutions decompose to **1** instantly on exposure to air, IR spectra suggest that the dianion is stable in an inert atmosphere.¹⁴ The facile aerial oxidation of **2²⁻** to **1** argues against alternative formulations involving an η^6 -benzene and an acetylene diolate ligand formed by reductive coupling of two carbonyls.

Distortion to the η^4 bonding mode should activate the benzene in **2²⁻**, and we have observed that the **K₂**2 (freshly prepared from 0.15 g, 0.7 mmol of **1**) reacts with 1 equiv of H_2O ¹⁵ (13 μL , added

Scheme II



at $-78\text{ }^{\circ}\text{C}$) to give, at room temperature, a new species characterized by carbonyl absorptions at 1890 vs, 1790 s, and 1740 cm^{-1} . Et_4NBr (0.15 g, 0.7 mmol) was added, the solvent was removed from the suspension under vacuum, and the solid washed with diethyl ether ($2 \times 50\text{ mL}$), redissolved in THF (10 mL), and crystallized by addition of diethyl ether (50 mL) to the filtered solution. The dried yellow flakes were shown to be (Scheme I—the nomenclature used to report ^1H and ^{13}C NMR data is indicated) the η^5 -cyclohexadienyl salt $[\text{NET}_4][\text{Cr}(\eta^5\text{-C}_6\text{H}_7)(\text{CO})_3]$ ($[\text{NET}_4]\mathbf{3}$ —0.12 g, 0.35 mmol \equiv 50%).¹⁶ The spectroscopic characteristics of the salt are similar to those of other well characterized cyclohexadienyl complexes,^{4,10,17} and assignment of the multiplets at δ 2.56 and 2.30 to H_{endo} and H_{exo} , respectively, was established by the characteristic 6-Hz coupling observed between H_{endo} and the hydrogen on the neighboring carbon and the absence of coupling between H_{exo} and this hydrogen.^{4f,10a,17b,c,h}

Protonation of **2²⁻** could be direct or metal-mediated, and we conducted two labeling studies to distinguish these possibilities. The first (Scheme II) involved deuteration (D_2O) to give $[\text{NET}_4]\mathbf{3}\text{-}d_1$ ¹⁸ in which the presence of the H_{exo} ^1H resonance and the absence (<1%) of the H_{endo} ^1H resonance suggested metal deuteration followed by deuterium migration to the arene. The second and complementary experiment, which established that the site of protonolysis is kinetically controlled, involved H_2O addition to the dianion generated from $[\text{Cr}(\eta\text{-C}_6\text{D}_6)(\text{CO})_3]$ to give, after metathesis, $[\text{NET}_4][\text{Cr}(\eta^5\text{-C}_6\text{D}_6\text{H})(\text{CO})_3]$ ($[\text{NET}_4]\mathbf{3}\text{-}d_6$) in which (^1H NMR¹⁹) the proton was exclusively in the endo position. IR spectra of $[\text{NET}_4]\mathbf{3}\text{-}d_1$ and $[\text{NET}_4]\mathbf{3}\text{-}d_6$ confirmed the locations of the labels—the medium intensity, low-energy absorption at 2790 cm^{-1} in KBr spectra of $[\text{NET}_4]\mathbf{3}$, assigned to the characteristically low-energy stretches of the exo-C-H bonds of the η^5 -cyclo-

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(13) Sodium naphthalenide can also be used to prepare **2²⁻**. IR spectra of the $\text{Na}_2\mathbf{2}$ contain absorptions at 1895 s, 1830 s, 1810 s, and 1730 vs br^{-1} —the additional bands may reflect counterion effects or may indicate contamination by a cyclohexadienyl complex (see below).

(14) It is interesting to note that, unlike $[\text{Cr}(\eta\text{-C}_6\text{H}_6)(\text{CO})_2]^{2-}$,⁶ **2²⁻** has no tendency to abstract a proton from THF.

(15) Acetic acid can also be used as a proton source.

(16) ν_{CO} (THF) 1890 vs, 1790 s, 1760 s cm^{-1} ; ^1H NMR (500 MHz, acetone- d_6 —see Scheme I for nomenclature) δ 5.07 (t of t, $J_{\text{H}_1\text{-H}_b} = 5.2\text{ Hz}$, $J_{\text{H}_a\text{-H}_c} = 1.4\text{ Hz}$, 1, H_a), 4.38 (d of d, $J_{\text{H}_b\text{-H}_a} = 5.2\text{ Hz}$, $J_{\text{H}_b\text{-H}_c} = 7.0\text{ Hz}$, 2, H_b), 2.10 (d of d, $J_{\text{H}_c\text{-H}_b} = 7.0\text{ Hz}$, $J_{\text{H}_c\text{-H}_{\text{endo}}} = 5.8\text{ Hz}$, 2, H_c), 2.56 (d of t of t, $J_{\text{H}_{\text{endo}}\text{-H}_{\text{exo}}} = 11.0$, $J_{\text{H}_{\text{endo}}\text{-H}_c} = 5.8\text{ Hz}$, $J_{\text{H}_{\text{endo}}\text{-H}_b} = 1.0$, 1, H_{endo}), 2.30 (d, $J_{\text{H}_{\text{exo}}\text{-H}_{\text{endo}}} = 11\text{ Hz}$, 1, H_{exo}); ^{13}C NMR (125 MHz, CD_3CN , gated ^1H decoupling) δ 244.7 (s, CO), 99.10 (d, $J = 156\text{ Hz}$, C_b), 76.60 (d, $J = 169\text{ Hz}$, C_a), 46.71 (d, $J = 163\text{ Hz}$, C_c), 27.67 (t, $J = 129\text{ Hz}$, CH_2). NMR spectra also contained resonances, with the appropriate intensity, characteristic of the tetraethylammonium counterion. Anal. Cald for $\text{C}_{17}\text{H}_{27}\text{CrNO}_3$: C, 59.11; H, 7.88; N, 4.05. Found (Multichem, Lowell, MA): C, 59.10; H, 7.91; N, 3.98.

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(18) ^1H NMR (500 MHz, acetone- d_6) δ 5.07 (t, $J_{\text{H}_1\text{-H}_b} = 5.2\text{ Hz}$, 1, H_a), 4.38 (d of d, $J_{\text{H}_b\text{-H}_a} = 5.2\text{ Hz}$, $J_{\text{H}_b\text{-H}_c} = 7.0\text{ Hz}$, 2, H_b), 2.27 (s, br, 1, H_{exo}), 2.12 (d, br, $J_{\text{H}_c\text{-H}_b} = 7.0\text{ Hz}$, 2, H_c). The C-D_{endo} stretch was observed at 2175 cm^{-1} .

(19) ^1H NMR (500 MHz, acetone- d_6) 2.50 (s, br, H_{endo}).

hexadienyl ligand,^{17a,b,d-8} were present in spectra of [NEt₄]₃-d₁ and absent from those of [NEt₄]₃-d₆.²⁰

It was initially unclear whether electrophilic addition to 2²⁻ could be extended to carbon-based electrophiles. We have, however, observed that K₂2 (freshly prepared from 0.15 g, 0.7 mmol of 1) reacts with 1 mol-equiv of PhCH₂Cl (80 μL) in THF at -78 °C (Scheme I) to give, at room temperature, a species with carbonyl absorptions at 1890 vs, 1792 s, and 1742 s cm⁻¹ similar to those of 3⁻. Addition of [Et₄N]Br (0.15 g, 0.7 mmol) at room temperature gave, after 30 min, a suspension from which yellow flakes of the η⁵-cyclohexadienyl salt [NEt₄][Cr(η⁵-C₆H₆CH₂Ph)(CO)₃] ([NEt₄]₄-0.12 g, 0.27 mmol = 40%)²¹ were obtained after the solvent was removed under vacuum, the solid was washed with diethyl ether (2 × 50 mL) and redissolved in THF (10 mL), and diethyl ether (50 mL) was added to the filtered solution to crystallize the product.

The spectroscopic characteristics of 4⁻ establish that the benzyl group is exo, suggesting that the electrophilic carbon reacted directly with the free double bond of 2²⁻. Thus the ¹H NMR spectrum contains a δ 2.45 absorption with the 6-Hz coupling to the vicinal proton characteristic of an endo cyclohexadienyl proton, and the IR spectrum of a KBr pellet of [NEt₄]₄ did not contain a C-H_{exo} band at 2790 cm⁻¹. Conversely, the IR spectrum of [NEt₄][Cr(η⁵-C₆D₆CH₂C₆H₅)(CO)₃] (obtained by addition of benzyl chloride to [Cr(η⁵-C₆D₆)(CO)₃]²⁻) contained a C-D_{endo} absorption at 2175 cm⁻¹ (see data in footnote 18). Although it is reasonable that indirect addition should be unique to the sterically undemanding proton, the observation of both endo and exo addition contrasts with results for isoelectronic Mn complexes: both protonation and electrophilic alkylation of dienes and arenes in [Mn(CO)₃]⁻ complexes are metal mediated and give endo products,²² while protonation and methylation of [Mn(cyclooctatetraene)(CO)₃]⁻ give exo adducts.²³

Although 3⁻ is the parent of a large class of cyclohexadienyl complexes of [Cr(CO)₃], neither this nor 4⁻ have been previously reported, and neither can be prepared by nucleophilic attack on 1. The generality of the alkylation reaction remains to be established, but our results do establish that electrophilic addition to 2²⁻ provides an alternative route to cyclohexadienyl complexes of [Cr(CO)₃] which may significantly extend the established utility of these species as intermediates in organic synthesis.

Acknowledgment. We thank the National Science Foundation for financial support and Dr. Gary Lee for preliminary experiments.

Registry No. 1, 12082-08-5; 1-d₆, 38095-88-4; K₂2, 113303-46-1; K₂2-d₆, 113303-56-3; [NEt₄]₃, 113303-47-2; K₃, 113303-48-3; [NEt₄]₃-d₁, 113303-50-7; [NEt₄]₃-d₆, 113303-52-9; K₄, 113303-53-0; [NEt₄]₄, 113350-90-6; [NEt₄]₄-d₆, 113303-55-2; C₆H₆, 71-43-2.

(20) A three band pattern at 2105 m, 2080 m, 2050 m cm⁻¹ was observed in spectra of [NEt₄]₃-d₆. The 2080-cm⁻¹ absorption would correspond to ν_{CH}/ν_{CD} = 1.34, in agreement with expectations. The complexity of the absorptions may reflect activation of combination or overtone bands by Fermi resonance.

(21) ν_{CO} (THF) 1890 vs, 1792 s, 1763 s cm⁻¹; ¹H NMR (500 MHz CD₃CN) δ 7.15-6.98 (m, 5, phenyl), 5.08 (t of t, J_{H_a-H_b} = 5.5 Hz, J_{H_a-H_c} = 1.2 Hz, 1, H_a), 4.48 (d of d, J_{H_b-H_a} = 5.5 Hz, J_{H_b-H_c} = 6.5 Hz, 2, H_b), 2.47 (d of d, J_{H_c-H_b} = 6.5 Hz, J_{H_c-H_{endo}} = 5.7 Hz, 2, H_c), 2.43 (t of t of t, J_{H_{endo}-H_c} = 6.7 Hz, J_{H_{endo}-H_e} = 5.7 Hz, J_{H_{endo}-H_b} = 1.0 Hz, 1, H_{endo}), 1.85 (d, J_{H_e-H_{endo}} = 6.7 Hz, 2, H_e); ¹³C NMR (125 MHz, CD₃CN, gated ¹H decoupling) δ 224.1 (s, CO), 140.9, 130.2, 128.9, 126.1 (phenyl), 96.7 (d, J = 156 Hz, C₆), 76.9 (d, J = 170 Hz, C₆), 53.9 (d, J = 163 Hz, C₆), 50.4 (t, J = 129 Hz, CH₂), 40.3 (d, J = 135 Hz, C₆). NMR spectra contain resonances, with appropriate intensity, characteristic of the tetraethylammonium counterion. Anal. Calcd for C₂₄H₃₃CrNO₃: C, 66.20; H, 7.58. Found (Dornis und Kolbe, West Germany): C, 65.84; H, 7.73.

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Highly Oxidizing Organometallics: The Preparation of Magnetic Charge Transfer Salts Derived from (MeCp)VCl₃

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High oxidation state organometallic compounds have recently commanded much attention because of their structural properties, their catalytic applications, and their stabilization of bare main group ligands. It is striking, however, that few high oxidation state organometallics are oxidizing. This is due to the fact that the most actively studied species feature third-row metals and strong π-donor oxo ligands.¹ The complex (MeCp)VCl₃ is unusual in this regard as it is indeed a rare example of a highly oxidizing organometallic complex. In this paper we describe the exploitation of the oxidizing power of (MeCp)VCl₃ for the preparation of some unusual organometallic charge transfer salts.²

The compound, (MeCp)VCl₃, **1**, has the remarkably positive reduction potential of +425 mV (versus Ag/AgCl).^{3,4} Under strictly anhydrous conditions this couple is reversible as is the (MeCp)VCl₃^{0/+} couple at 1690 mV.⁵ Compound **1** appears to be among the most strongly oxidizing neutral organometallic complexes known.

The interaction of **1** with the organic donor tetramethyltetrathiafulvalene⁶ (TmTTF) was studied. When this reaction is conducted at 1:1 stoichiometry in CH₂Cl₂ solution, we observed the precipitation of black microcrystalline [TmTTF]_x[(MeCp)VCl₃]. Slow recrystallization of this material from CH₂Cl₂ gave two pure species. The less soluble material analyzes as [TmTTF][(MeCp)VCl₃] (**2**).⁷ The cyclic voltammogram of **2** in CH₂Cl₂ consists of several reversible processes and is not the superposition of the CVs for **1** and TmTTF.⁸ These results will be described in detail in the full report.

A single-crystal X-ray diffraction study⁹ of **2** reveals that the TmTTF⁺ subunits assemble as a zigzag chain of TmTTF pairs (Figure 1). The interlamellar distances are extremely short at ca. 3.35 Å (cf. α-graphite, 3.354 Å¹⁰) and are substantially shorter

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(8) Cyclic voltammetry data (E₀ (mV) versus Ag/AgCl, 10⁻¹ M TBAHFP, 10⁻³ M complex, n(e⁻) from i_p versus ν^{1/2}): (MeCp)VCl₃^{0/+}, E^{ox} ≈ 455, E^{red} ≈ 395; TmTTF^{0/+}, E^{ox} ≈ 320, E^{red} ≈ 260; **2**, E^{ox} ≈ 315 (n = 1), E^{ox} ≈ 435 (n = 1), E^{red} ≈ 255 (n = 2).

(9) [TmTTF][(MeCp)VCl₃]: opaque plate 0.1 × 0.2 × 0.4 mm, P2₁/c, a = 8.310 (2) Å, b = 10.112 (8) Å, c = 24.035 (5) Å, β = 91.90 (2)°, V = 2018 (2) Å³, and ρ_{calcd} = 1.635 g/cm³ for Z = 4. Enraf-Nonius CAD4 automated κ-axis diffractometer, 25 °C, Mo Kα 3.0 < 2θ < 46.0° (±h-k-l), 3206 reflections (2802 unique, R_i = 0.024, 1343 observed, I > 2.581(I)); corrected for anomalous dispersion, absorption (maximum and minimum numerical transmission factors, 0.926 and 0.766, for μ = 12.73 cm⁻¹), Lorentz and polarization effects. Solution SHELXS-86 (all but Cp ring atoms) and difference Fourier syntheses. H atoms were fixed in "idealized" positions, but the remaining atoms were independently refined (SHELX). R = 0.058 and R_w = 0.061.

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