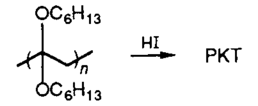
Table I. Physical Properties of PKT

IR (KBr), ν	^{1}H NMR (500 MHz, DMF-d_7), δ	^{13}C NMR (DMF-d_7), δ (ppm)	elem anal.	reduced viscosity (1/g dL), η	UV–vis (DMSO), nm
3700–2000 (br, vs), 1730 (w), 1650 (vs), 1595 (vs), 1400 (s), 1165 (s), 1100 (m), 940 (m), 862 (m)	9.8–11.3 (br m, 0.5 H, enol, phenol), 7.10–5.40 (m, 1.67 H, enol and aromatic CH), 4.69–3.30 (m, 2 H, interketone methylene)	clusters of resonances at 198, 178, 157–163, 136 (br), 113.5–115; peaks at 101.2, 46.0, 36.5	calcd for C_2H_2O: C 57.13; H, 4.80 calcd for $C_{17}H_{16}O_7$: C, 61.44; H, 4.82 found: C, 61.35; H, 5.11	0.1 (c = 0.36% w/w, DMF)	tail to 650, 365 (sh), 285; tail to[a] 820, 430, 355, 285; tail to[b] 720, 425 (sh), 350 (sh), 280, 240[c]

[a] Upon addition of 0.1 mL of 5% ethanolic KOH. The original spectrum is restored upon neutralization with acid. [b] Film on quartz. [c] Absorption too high to measure accurately.

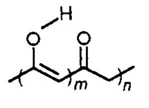
Scheme I



($\bar{M}_w \sim 720000$, poly(styrene) equivalent via GPC),[9] which we converted to the fully characterizable PKT.

Scheme I, below, describes the hydrolytic preparation of PKT in cyclopentanone/water (2:1) with 57% aqueous HI at 80 °C for 5–15 h, depending on the molecular weight of the precursor polymer.

The crude polymer was obtained as reddish-brown solid. Purification by extraction with hexane [to remove incompletely deprotected poly(ketal), hexyl iodide, hexyl alcohol and traces of iodine], followed by repeated reprecipitation from DMF with ether, afforded a dark brown-black solid in 86% yield. The polymer is soluble in DMSO, DMF, TFA, and pyridine, is partially soluble in propylene carbonate and 1:1 acetone/water, and is insoluble in CH_3NO_2, H_2O, Et_2O, MeOH, toluene, and THF. In agreement with the proposed structure, it is also soluble in 5% aqueous and 5% ethanolic KOH. The important characterization properties of this polymer are collected in Table I. As can be seen from the table, all spectroscopic (particularly ^{1}H NMR) data are consistent with the structure of PKT as depicted below, but the



$m \sim 0.63$, $n \sim 0.37$

elemental analysis indicates loss of one molecule of water for every eight monomer units, tantamount to formation of an aromatic ring for every 17 carbon atoms.[10,11] Infrared spectroscopic evidence (3700–2000, 1730, 1650, and 1595 cm^{-1}), which is in excellent agreement with the infrared spectrum (under identical conditions) of 2,4,6-heptanetrione,[12] supports the above keto-enolic structure. There is a dramatic, reversible red shift in electronic absorption with increasing pH (see Table I), a property also exhibited by 2,4,6-heptanetrione.[12] Thermal analysis indicates that the polymer is stable up to $\sim$200 °C. Between 200 and $\sim$850 °C, there is a 43% weight loss (TGA, N_2 atmosphere), in good agreement with loss of one molecule of water/monomer unit. The residue from the TGA measurement exhibits a two-probe room temperature conductivity, σ, of $\sim$2 S cm^{-1}. Graphite has $\sigma \sim 0.2$ S cm^{-1} under the same conditions. The pristine polymer (powder) is an insulator with $\sigma < 10^{-8}$ S cm^{-1}. Exposure of the powder to iodine vapor increases the conductivity by only ca. 4 orders of magnitude ($\sigma \sim 10^{-4}$ S cm^{-1}). The pure polymer has essentially no unpaired spins; two superimposed, weak signals (1 spin/74000 monomer units or 1.3×10^{-5} spins/mol of monomer), $g = 2.0031$, $\Delta H_{pp} = 4.8$ G and $\sim$12 G, indicating a minor spin impurity delocalized and localized, respectively, and located near oxygen.

The polymer forms brittle, dark, transparent thin films when cast from solution but forms flexible, stable, transparent composite films with poly(vinylpyrrolidone) when cast from homogeneous solution in DMF. Nonlinear optical properties as well as other physical properties (in situ spectroscopy, doping, etc.) of these films are being actively investigated.

Acknowledgment. We thank the AFOSR and the ONR for generous support of this work.

Supplementary Material Available: Complete spectroscopic characterization of freshly prepared 2,4,6-heptanetrione including IR (neat and in $CHCl_3$ solution), ^{1}H NMR in DMF-d_7 and $CDCl_3$, ^{13}C NMR in DMF-d_7 and $CDCl_3$, UV–vis, UV–vis as a function of pH, and MS (1 page). Ordering information is given on any current masthead page.

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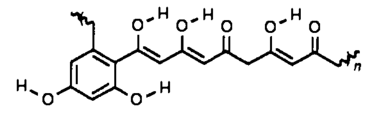
[9] Khemani, K. C.; Askari, S.; Wudl, F., submitted to *Macromolecules*.

[10] A possible structure, which fits the elemental analysis and spectroscopy, is depicted below. The aromatic rings are very likely randomly distributed with extensive runs of conjugated double bonds (electronic absorption in the visible, IR absorption at 1650 and 1595 cm^{-1}) and could be a combination of substituted resorcinols (depicted), trihydroxynaphthalenes, tetrahydroxyanthracenes, etc. Some of the ^{13}C resonances at 113–115 ppm, besides corresponding to enol carbon atoms, also coincide with assignments to aromatic carbon atoms ortho to a hydroxy substituent.



[11] Hydroxy aromatic ring formation from open-chain poly-1,3-ones is well precedented: Gilbreath, S. G.; Harris, C. M.; Harris, T. M. *J. Am. Chem. Soc.* **1988**, *110*, 6172.

[12] Khemani, K. C., unpublished results on spectroscopy of freshly prepared 2,4,6-heptanetrione, available in the form of supplementary material (see Supplementary Material Available).

Glycoconjugated Tetrapyrrolic Macrocycles

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The superstructured models of active site of hemoproteins[1] can allow variation of facial cavity size for synthetic control of the ligand binding.[2] We report the first examples of another class

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[1] (a) Collman, J. P.; Halpert, T. R.; Suslick, K. S. *Metal Ion Activation of Oxygen*; Spiro, T. G.; Ed.; Wiley: New York, 1980; Vol. 1. (b) Traylor, T. G. *Acc. Chem. Res.* **1981**, *14*, 102. (c) Kobayashi, N.; Akiba, U.; Takatoi, K.; Ueno, A.; Osa, T. *Heterocycles* **1982**, *19*, 2011. (d) Eshima, K.; Matsushita, Y.; Sekine, M.; Nishide, H.; Tsuchida, E. *Nippon Kayaku Kaishi* **1983**, 214. (e) Gonzales, M. C.; McIntosh, A. R.; Bolton, J. R.; Weedon, A. C. *Chem. Commun.* **1984**, 1138. (f) Wasielewski, M. R.; Niemczyk, M. P. *J. Am. Chem. Soc.* **1984**, *106*, 5043. (g) Traylor, T. G.; Koga, N.; Dearduff, L. A.; Swepston, P. N.; Ibers, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 5132. (h) Gonzales, M. C.; Weedon, A. C. *Can. J. Chem.* **1985**, *63*, 602. (i) Krishnan, V. *Proc. Indian Natl. Sci. Acad.* **1986**, *52(4)*, 909. (j) Momenteau, M. *Pure Appl. Chem.* **1986**, *58*, 1493. (k) Morgan, B.; Dolphin, D. *Structure and Binding 64*; Buchler, J. W., Ed.; Springer-Verlag: 1987; p 115.

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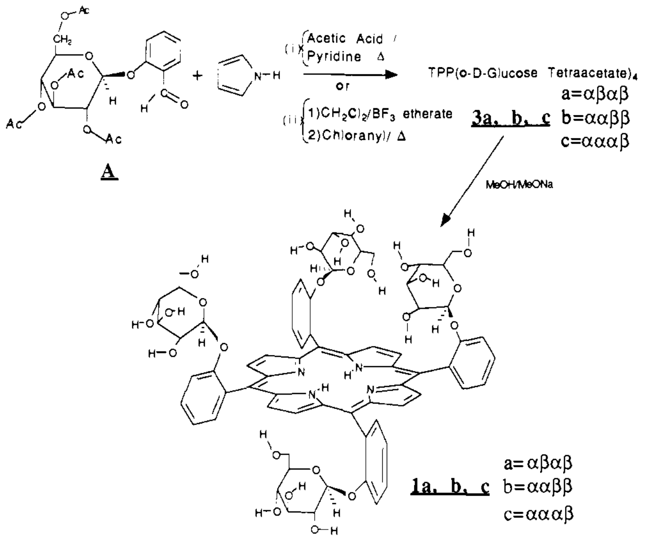
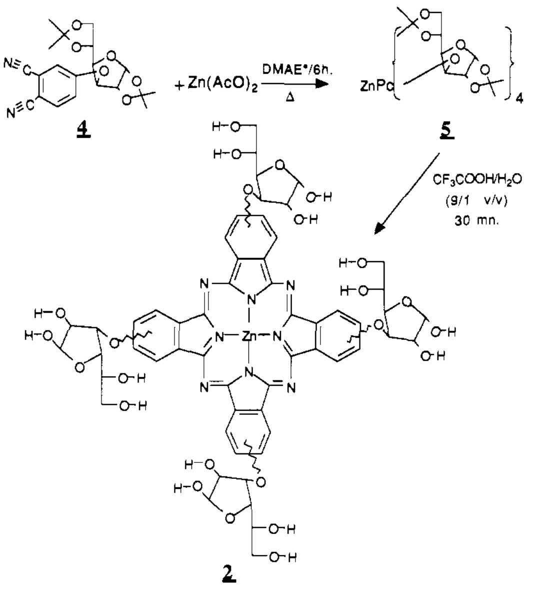
Scheme I



Scheme II[a]



[a] * denotes (dimethylamino)ethanol.

of water-soluble porphyrins **1** and phthalocyanines **2**, in which glycosylated substituents were linked on to the ortho position of meso aryl groups and phthalyl groups, respectively. These nonionizable units protect, by steric hindrance, the face(s) of the porphyrin, prevent the aggregation of the phthalocyanine, and increase their solubility in water.

The condensation of tetraacetyl-β-D-glucose-2-benzaldehyde A (protected helicine) with pyrrole, by two different methods (i)[3] and (ii)[4] shown in Scheme I, give compound **3**: (i) (13% yield) and (ii) (42% yield). The atropisomers of **3** were separated by two successive silica gel chromatographies and identified by ^{1}H NMR spectra (Figure 1). Only three atropisomers, αβαβ **3a**, ααββ **3b**, and αααβ **3c**, are recovered with the relative ratio (1:2:4).

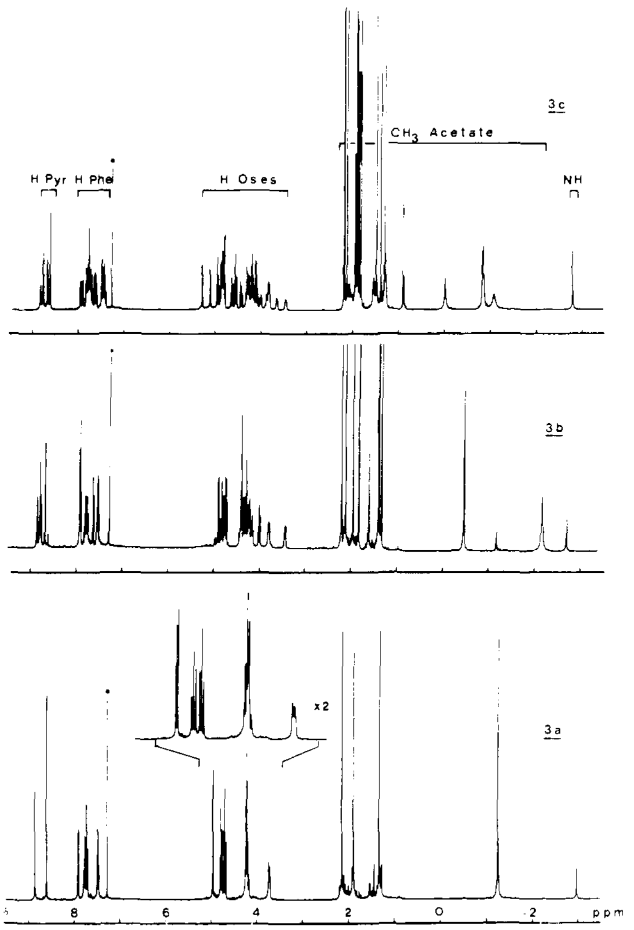


Figure 1. 400 MHz ^{1}H NMR spectra of atropisomers of protected glycosylated porphyrins **3** in $CDCl_3$ at 24 °C.

They were converted to free glycosylated porphyrins **1a**, **1b**, and **1c** by a catalytic amount of sodium methanolate in dry methanol,[5] without a change in both the absolute configuration and the chemical nature of sugars.

The phthalocyanine **5** (Scheme II) was prepared (61% yield), in the presence of zinc acetate, from compound **4** obtained by condensation of 4-nitrophthalonitrile and 1,2:5,6-diisopropylidene-D-glucofuranose[6] (100% yield). Treatment of **5** with trifluoroacetic acid/water (9/1, v/v)[8] gives the unprotected phthalocyanine **2**.

Protected porphyrins **3** (**a**, **b**, and **c**) are soluble in nonpolar solvents. The solubility of **1** (**a**, **b**, and **c**) in water increased in the same order as the protection of the faces (**1c** < **1b** < **1a**) which may be due to the difference in solvation.

Because of the isomer symmetries, each type of protons in the ose meso substituents of **3a** (and **1a**) should be equivalent in the ^{1}H NMR spectra; **3b** (and **1b**) has instead two distinct resonances of two chemically equivalent protons, whilst every proton of **3c** (and **1c**) has its own resonance (Figure 1). The resonance of protons of sugars in **3**, relative to the protected helicine, are shifted upfield between 0.1 and 1.3 ppm for ose and at 4.3 ppm for methyl groups. This suggested the meso substituents bend over the porphyrin ring in spite of the spatial congestion. This motional restriction can explain the tautomerism effect of pyrrolic NH observed on pyrrolic protons with D_2O, at room temperature, as shown with similar molecules.[8]

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(2) (a) Momenteau, M.; Mispelter, J.; Loock, B.; Lhoste, J. M. *J. Chem. Soc., Perkin Trans. 1* **1985**, 61. (b) Momenteau, M.; Mispelter, J.; Loock, B.; Lhoste, J. M. *J. Chem. Soc., Perkin Trans. 1* **1985**, 221. (c) Momenteau, M.; Loock, B.; Tetreau, C.; Lavalette, D.; Croisy, A.; Schaeffer, C.; Huel, C.; Lhoste, J. M. *J. Chem. Soc., Perkin Trans. 2* **1987**, 249. (d) Momenteau, M.; Loock, B.; Huel, C.; Lhoste, J. M. *J. Chem. Soc., Perkin Trans. 1* **1988**, 283. (e) Maillard, Ph.; Schaeffer, C.; Huel, C.; Lhoste, J. M.; Momenteau, M. *J. Chem. Soc., Perkin Trans. 1* **1988**, 3285.

(3) Treibs, A.; Häberle, N. *Liebigs Ann. Chem.* **1968**, *718*, 189.

(4) van der Made, A. W.; Hoppenbrouwer, E. J. H.; Nolte, R. J. M.; Drenth, W. *Recl. Trav. Chim. Pays-Bas* **1988**, *107*, 15.

(5) Zemplen, G.; Gerecs, A.; Hadacsy, I. *Ber.* **1936**, *69*, 1827.

(6) Siegl, W. O. *J. Heterocycl. Chem.* **1981**, *18*, 1613.

(7) Christensen, J. E.; Goodman, L. *Carbohydr. Res.* **1968**, *7*, 510.

(8) (a) Kuroda, Y.; Hiroshige, T.; Sera, T.; Shiroiwa, Y.; Tanaka, H.; Ogoshi, H. *J. Am. Chem. Soc.* **1989**, *111*, 1912. (b) Abraham, R. J.; Hawkes, G. E.; Hudson, M. F.; Smith, K. M. *J. Chem. Soc., Perkin Trans. 2* **1975**, 205.

In order to examine the effect of steric hindrance on the coordination of metallic derivatives of **3**, we have prepared their zinc complexes. Their electronic spectra are much more intense than those of other zinc tetraphenylporphyrins.[9] The formation constants for five-coordinated species with pyridine are very weak, between 14 and 40 L·M^{-1}. A 100-fold reduction in equilibrium constants is observed in comparison to that measured with zinc porphyrins hindered on both faces.[10]

The assignment of the ^{13}C NMR spectra of phthalocyanines **5** and **2** was carried out by analogy of these with **4**. The spectrum of **5** exhibits nine resonances for the aromatic part, 11 for glucose groups, and six for the methyl of isopropylidenes.[11] This multiplicity of peaks could represent some possible environmental interactions present in several isomers. The phthalocyanines **5** and **2** could exist as a mixture of positional isomers around the phthalocyanine ring.

Zinc phthalocyanine **5**, in organic solvents, exhibits a spectrum typical of monomeric metalled phthalocyanine, with a Soret band and Q band.[12] The optical spectra of **2** are characteristic of a dimer in water and of a monomer in DMSO.[12]

In conclusion, our preliminary work has established that the new class of tetrapyrrollic macrocycles on which glucopyranoses or glucofuranoses were linked allows an increase in both their steric hindrance in the vicinity of the metal site and their solubility in water. Futher work, directed on studies of other metal complexes, is now in progress.

Acknowledgment. This work was supported by the Institut National de la Santé et de la Recherche Médicale.

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(9) UV-visible spectra in CHCl$_3$: λ_{max} nm (ϵ/mmol·L^{-1}). **Zn3a**: 404 (40), 425 (517.3), 557 (17.2), 593 (5.5). **Zn3b**: 405 (49.5), 426 (632), 558 (23.2), 595 (5.9). **Zn3c**: 404 (53.2), 425.5 (720.2), 557 (25), 594 (5.8).

(10) The equilibrium constant for the complexation of zinc basket handle porphyrin [a-(C$_{12}$)$_2$-CT]^{2b} was found to be 3.6×10^3 L·M^{-1} in CH$_2$Cl$_2$ at 25 °C.

(11) ^{13}C NMR spectra of phthalocyanines in C$_6$D$_6$ at 24 °C (δ en ppm). **5**: 167.3, 159.4, 125, 124, 120.8, 120.5, 118, 110, 108 (C phthalyl), 106.2, 105.8, 83.4, 82.9, 81.6, 81.1, 73.3, 72.6, 60.7 (C oses), 112.5, 109.6 (C isopropylidene), 27.25, 27, 26.6, 26.3, 25.8, 25.5 (C methyl), 141, 133 (C pyrrolic). **2**: 170.7, 159.3, 158.5, 125.5, 123.5, 118.8, 113.2, 112.2 (C phthalyl), 113.2, 112.3, 98, 94, 86.7, 84.2, 77.7, 75.7, 73.1, 73, 71, 62.7, 62.5 (C oses), 136.4 (C pyrrolic).

(12) UV-visible spectra: λ_{max} nm (ϵ/mmol·L^{-1}). **5** (acetone): 348 (101.7), 611 (34.8), 677 (176.2). **2** (DMSO): 354 (35.4), 618 (14.3), 685.5 (73).

[Cp*(Me)Cr(μ-Me)]$_2$: An Electron-Deficient Chromium(III) Alkyl with Bridging Methyl Groups and a Cr–Cr Bond

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Electron-deficient organometallic compounds of both main-group and transition elements may exhibit bridging alkyl ligands.[1] In the special case of bridging methyl groups, several different binding modes have been observed (featuring symmetric pyramidal, symmetric planar, or agostic μ-CH$_3$ groups).[2] As part of our continuing exploration of the reactivity of paramagnetic chromium(III) alkyls,[3] we have now prepared a complex that displays two methyl groups bridging chromium atoms with 13 electron configurations. Herein we report the full characterization of this compound and some theoretical considerations concerning the metal–metal interaction in this d^3–d^3 system.

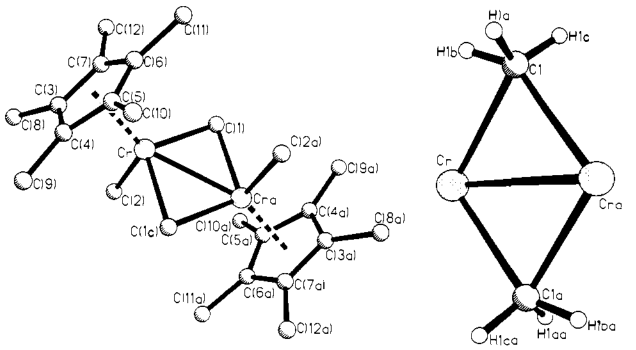
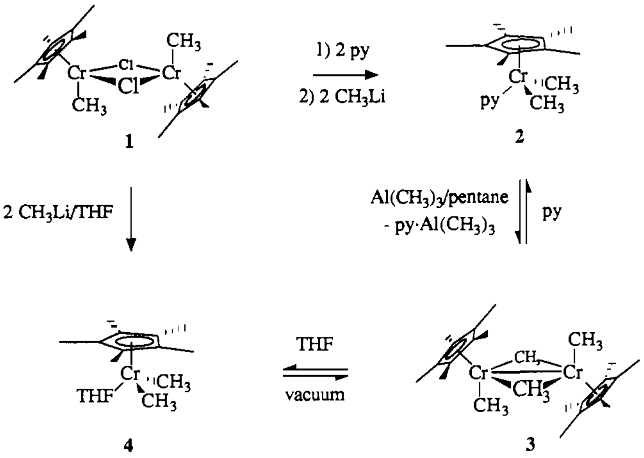


Figure 1. The molecular structure of **3**. Selected bond distances: Cr–Cra, 2.606 (2) Å; Cr–C1, 2.206 (4) Å; Cra–C1, 2.170 (5) Å; Cr–C2, 2.096 (5) Å; Cr–H1b, 2.124 Å; C1–H1a, 0.965 Å; C1–H1b, 0.874 Å; C1–H1c, 0.939 Å. Interatomic angles: Cr–C1–Cra, 73.1 (1)°; C1–Cr–C1a, 106.9 (1)°; Cr–C1–H1b, 73.1°; H1a–C1–H1b, 89.9°; H1a–C1–H1c, 114.3°; H1b–C1–H1c, 104.7°.

Scheme I



Consecutive addition of 2.0 equiv each of pyridine and methyllithium to dimeric [Cp*(Me)Cr(μ-Cl)]$_2$ (**1**) afforded the half sandwich complex Cp*Cr(Py)Me$_2$ (**2**) in 73% yield.[4] Reaction of this compound with 1.0 equiv of trimethylaluminum in pentane followed by rapid workup (evaporation of solvent and recrystallization from pentane at −35 °C) yielded brown crystals of [Cp*(Me)Cr(μ-Me)]$_2$ (**3**) (see Scheme I). Once **3** had been identified, a more direct synthesis was attempted. Addition of 2.0 equiv of methyllithium to a THF solution of **1** resulted in a rapid color change from purple to green. However, upon evaporation of the THF, the solid residue turned brown, and extraction with pentane yielded **3** in 65% isolated yield.[5] **3** was air sensitive,

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(1) (a) Davidson, P. J.; Lappert, M. F.; Pearce, R. *Chem. Rev.* **1976**, *76*, 219. (b) Holton, J.; Lappert, M. F.; Pearce, R.; Yarrow, P. I. W. *Chem. Rev.* **1983**, *83*, 135.

(2) (a) Evans, W. J.; Chamberlain, L. R.; Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1988**, *110*, 6423. (b) Burns, C. J.; Andersen, R. A. *J. Am. Chem. Soc.* **1987**, *109*, 5853. (c) Park, J. W.; Mackenzie, P. B.; Schaefer, W. P.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 6403. (d) For references to earlier papers, see: Bursten, B. E.; Cayton, R. H. *Organometallics* **1986**, *5*, 1051.

(3) (a) Richeson, D. S.; Hsu, S.-W.; Fredd, N. H.; Van Duyne, G.; Theopold, K. H. *J. Am. Chem. Soc.* **1986**, *108*, 8273. (b) Richeson, D. S.; Mitchell, J. F.; Theopold, K. H. *J. Am. Chem. Soc.* **1987**, *109*, 5868. (c) Thomas, B. J.; Mitchell, J. F.; Theopold, K. H. *J. Organomet. Chem.* **1988**, *348*, 333. (d) Thomas, B. J.; Theopold, K. H. *J. Am. Chem. Soc.* **1988**, *110*, 5902. (e) Richeson, D. S.; Mitchell, J. F.; Theopold, K. H. *Organometallics*, in press. (f) Noh, S. K.; Heintz, R. A.; Theopold, K. H. *Organometallics* **1989**, *8*, 2071.

(4) (a) **2**: ^{1}H NMR (C$_6$D$_6$) 25.9 (Cp*), 23.3, −50.5, −59.6 ppm; IR (Nujol) 1599 (s), 1500 (s), 1480 (s) 1383 (s), 1376 (w), 1211 (m), 1062 (m), 757 (s), 697 (s), 640 (m) cm^{-1}. Anal. Calcd for C$_{17}$H$_{26}$CrN: C, 68.89; H, 8.84; N, 4.73. Found: C, 68.71; H, 8.76; N, 4.56. The crystal structure of **2** has been determined by X-ray diffraction and will be reported in a full paper. (b) Related complexes and their NMR spectra have been reported by Grohmann et al.: Grohmann, A.; Köhler, F. H.; Müller, G.; Zeh, H. *Chem. Ber.* **1989**, *122*, 897.

(5) **3**: ^{1}H NMR (C$_6$D$_6$) 88.6 (br, 3 H), 75.8 (br, 3 H), 0.56 (15 H) ppm; IR (Nujol) 2188 (w), 1182 (s), 1108 (m), 1022 (s), 804 (m), 721 (m), 616 (m) cm^{-1}.

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