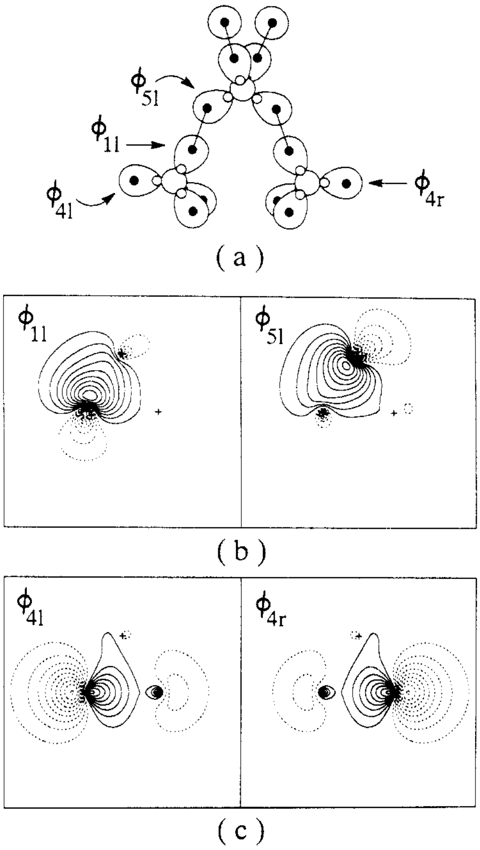

Figure 2. (a) Schematic representation of how the many-electron wave function of [1.1.1]propellane is derived from those of C_2 and three CH_2 groups. (b) Two orbitals forming a bond between a bridgehead carbon and a methylene carbon. There are six equivalent bonds of this form. (c) The two orbitals which form the bond between bridgehead carbon atoms. Note the significant increase in overlap as compared to C_2. There are also six equivalent carbon–hydrogen bonds (orbitals not shown).

overlap with the corresponding orbitals on the right atom to form the Ω-bonds of C_2. Contour plots of one of these bonds (made up of orbitals $\phi_{1\ell}$ and ϕ_{1r}) are shown in Figure 1b. The fourth orbital pair of C_2 is composed of two hybrids which point away from the molecule; the contour plots of these two orbitals are shown in Figure 1c. The overlap of $\phi_{4\ell}$ and ϕ_{4r} is 0.31,[15] while that of the orbitals making up an Ω-bond is 0.82.[16]

From the above description of C_2, the [1.1.1]propellane molecule[17] is related simply by the insertion of a CH_2 species into each of the three Ω-bonds of C_2, such as schematically depicted in Figure 2a for one CH_2 group. Three equivalent C–C bonds (of C_2) are broken, but six equivalent new (and somewhat less strained) C–C bonds are formed. One of these bonds, formed from orbitals $\phi_{1\ell}$ and $\phi_{5\ell}$ (with overlap 0.84), is displayed via the orbital contour plots in Figure 2b. Note that the orbital $\phi_{1\ell}$ of propellane contains less p-character than $\phi_{1\ell}$ of C_2; it is less sp^3-like and more sp^2-like. As a consequence, there is significantly more p-character available for the orbital $\phi_{4\ell}$ (an approximate hybridization of $sp^{4.5}$ as opposed to $sp^{0.8}$ for C_2). The additional p-character in orbitals $\phi_{4\ell}$ and ϕ_{4r} results in a favorable overlap (0.62)[15,16] as shown in the orbital contour plots of Figure 2c. Thus $\phi_{4\ell}$ and ϕ_{4r} of [1.1.1]propellane actually contribute significantly to the bonding and stability of the molecule in contrast to the situation in C_2.[18] This conclusion regarding the bonding is quite different from previous work using uncorrelated wave functions.[6] The use of simple correlated wave functions (GVB-PP) allows a clear physical picture of the bonding to emerge—a picture not unlike that pioneered by Slater and Pauling many years ago.[19]

Acknowledgment. This work was supported in part by the National Science Foundation MRL Program under Grant DMR-8519059 at the Laboratory for Research on the Structure of Matter, University of Pennsylvania.

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[15] The negative relative phase of $\phi_{4\ell}$ and ϕ_{4r} (Figure 1c) in C_2 indicates dominant antibonding character (by examining the natural orbital representation of the pair, 78% antibonding and 22% bonding), detrimental to C–C bonding. For propellane the orbitals are in phase, indicating a positive contribution to the bonding (95% bonding, 5% antibonding).

[16] For reference it is useful to consider H_2 at the same level of theoretical approximation: at $R = 2.0$ Å, the overlap (S) is 0.30 and the binding energy (BE) is 0.47 eV; at $R = 1.25$ Å, $S = 0.62$, and BE = 2.46 eV; at $R = 0.74$ Å (the equilibrium value), $S = 0.80$, and BE = 3.96 eV.

[17] The calculations employed a standard valence double-ζ basis set[13] and used the experimental geometry (Hedberg, L.; Hedberg, K. *J. Am. Chem. Soc.* **1985**, *107*, 7257). The calculated total energy using 13 GVB pairs is −192.789 14 hartree.

[18] The bonding character between the bridgehead carbon atoms inferred from the longer C–C distance in the triplet state as opposed to the singlet[9] is consistent with our conclusion that this pair contributes significantly to the bonding.

[19] Slater, J. C. *Phys. Rev.* **1931**, *37*, 481. Pauling, L. *J. Am. Chem. Soc.* **1931**, *53*, 1367.

Simple and Selective Method for RCHO → (*E*)-RCH=CHX Conversion by Means of a CHX_3-$CrCl_2$ System

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Received June 30, 1986

Many methods are now available for the stereocontrolled preparation of alkenyl halides from acetylenic precursors.[1] However, the one-carbon homologation of an aldehyde to an alkenyl halide is quite limited.[2] For example, treatment of an aldehyde with the Wittig reagent $Ph_3P{=}CHX$ usually gives a mixture of *Z* and *E* isomers and preparation of the ylide is rather complicated.[3] Here we introduce a simple and stereoselective method for the conversion of aldehydes to the corresponding (*E*)-alkenyl halides by an organochromium reagent.[4]

Anhydrous $CrCl_2$[5] (0.74 g, 6.0 mmol) is suspended in THF (10 mL) under an argon atmosphere. A solution of benzaldehyde (0.11 g, 1.0 mmol) and iodoform (0.79 g, 2.0 mmol) in THF (5 mL) is added dropwise to the suspension at 0 °C. After stirring at 0 °C for 3 h, the reaction mixture is poured into water (25 mL) and extracted with ether (3 × 10 mL). The combined extracts are dried over Na_2SO_4 and concentrated. Purification by column chromatography on silica gel (hexane) affords 0.20 g (87%, $E/Z = 94/6$)[6] of β-iodostyrene (**1**) as a colorless oil. The chromium(II)

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[1] For some representative examples, see: (a) Zweifel, G.; Whitney, C. C. *J. Am. Chem. Soc.* **1967**, *89*, 2753. (b) Brown, H. C.; Hamaoka, T.; Ravindran, N. *Ibid.* **1973**, *95*, 5786. (c) Normant, J. F.; Chuit, C.; Cahiez, G.; Villieras, J. *Synthesis* **1974**, 803. (d) Hart, D. W.; Blackburn, T. F.; Schwartz, J. *J. Am. Chem. Soc.* **1975**, *97*, 679. (e) Tamao, K.; Yoshida, J.; Takahashi, M.; Yamamoto, H.; Kakui, T.; Matsumoto, H.; Kurita, A.; Kumada, M. *Ibid.* **1978**, *100*, 290.

[2] Williams, D. R.; Nishitani, K.; Bennett, W.; Sit, S. Y. *Tetrahedron Lett.* **1981**, *22*, 3745.

[3] (a) Seyferth, D.; Heeren, J. K.; Grim, S. O. *J. Org. Chem.* **1961**, *26*, 4783. (b) Koebrich, G. *Angew. Chem.* **1962**, *74*, 33. (c) Koebrich, G.; Trapp, H.; Flory, K.; Drischel, W. *Chem. Ber.* **1966**, *99*, 689. (d) Miyano, S.; Izumi, Y.; Hashimoto, H. *J. Chem. Soc., Chem. Commun.* **1978**, 446. (e) Smithers, R. H. *J. Org. Chem.* **1978**, *43*, 2833. (f) Matsumoto, M.; Kuroda, K. *Tetrahedron Lett.* **1980**, *21*, 4021.

[4] For reactions with organochromium reagents, see: (a) Hiyama, T.; Okude, Y.; Kimura, K.; Nozaki, H. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 561. (b) Takai, K.; Kuroda, T.; Nakatsukasa, S.; Oshima, K.; Nozaki, H. *Tetrahedron Lett.* **1985**, *26*, 5585. See also ref 15.

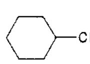
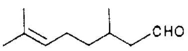
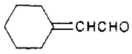
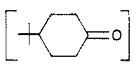
[5] Anhydrous $CrCl_2$ (90% assay) was purchased from Aldrich Chemical Co. and was used without further purification.

[6] The *E/Z* isomer ratios were determined by NMR and/or GLPC.

0002-7863/86/1508-7408$01.50/0

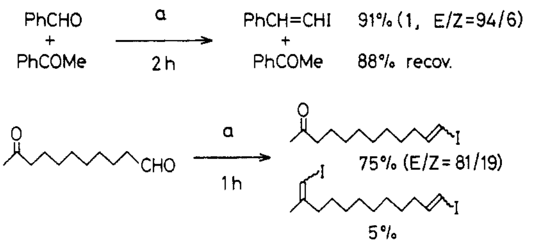
Table I. Conversion of Aldehydes to (*E*)-Alkenyl Halides by Means of the Haloform–CrCl$_2$ System[a]

$$\mathrm{RCHO}\xrightarrow{\mathrm{CHX_3,\ CrCl_2,\ THF}}\mathrm{RCH{=}CHX}$$

run	aldehyde	haloform X	temp, °C	time, h	yield,[b] %	*E*/*Z*[c]
1	PhCHO	I	0	3	87	94/6
2		Br	25	1.5	X = Br, 32	95/5
					X = Cl, 43	95/5
3		Br[d]	50	1	70	95/5
4		Cl	65	2	76	95/5
5	OctCHO	I	0	2	82	83/17
6		Br	25	2	X = Br, 37	89/11
					X = Cl, 32	90/10
7		Br[d]	50	2	61	87/13
8		Cl	65	4	76	94/6
9		I	0	1	78	89/11
10		Br[d,e]	65	4	66	94/6
11		I	0	2.5	84	82/18
12		Br[d]	50	2.5	55[f]	89/11
13		Cl	65	2.5	55[f]	92/8
14		I	0	0.5	76	75/25–55/45[g]
15		Br[d]	50	1	73	81/19
16		I	25	4	75	
17	[$Bu_2O{=}O$]	I	25	21	51 recov 43	

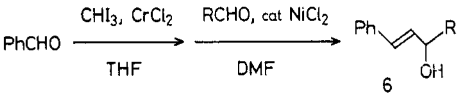
[a] The aldehyde (1.0 mmol) was treated with haloform (2.0 mmol) and CrCl$_2$ (6.0 mmol) in THF. [b] Isolated yields. [c] The isomeric ratios of the alkenyl halides were determined by GLPC or NMR. [d] A combination of CrBr$_3$ and LiAlH$_4$ (1:0.5 molar ratio) was employed instead of CrCl$_2$. [e] Eight millimole of the Cr(II) reagent was used per millimole of the aldehyde. [f] Isopulegol, the ene-reaction product of citronellol, was produced as a byproduct. [g] The *E*/*Z* ratio of the product varies with reaction conditions. Isomerization of the 1-iodo-1,3-butadiene compound took place with a catalytic amount of acid and/or light to yield a thermodynamic mixture (*E*/*Z* ≃ 40/60).

Scheme I



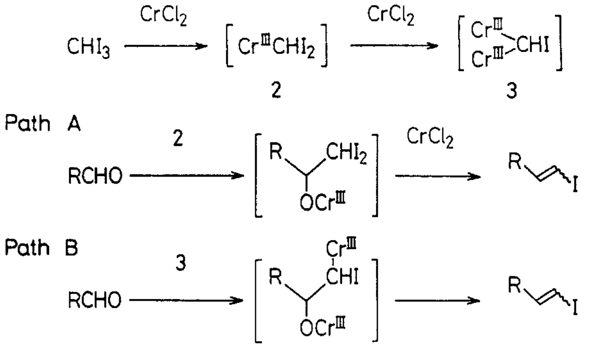
(a) CHI$_3$, CrCl$_2$, THF, 0°C

Scheme II



a: R = Ph 85% (E/Z = >98/<2)
b: Oct 62% (E/Z = >98/<2)

Scheme III



reagent prepared from CrCl$_3$ and LiAlH$_4$ was also effective for the transformation (**1**, 67% (*E*/*Z*=94/6), 25 °C, 1 h).[4a] Treatment of benzaldehyde with iodoform and the other low-valent metals, such as Zn,[7] MnCl$_2$–LiAlH$_4$,[8a] VCl$_3$–LiAlH$_4$,[8b] Sn,[8c] and SnCl$_2$,[8d] gave little or none of the desired iodo olefin **1**.

The results of the preparation of alkenyl halides with haloform and CrCl$_2$ are shown in Table I.[9] Alkenyl halides having an *E* configuration are produced selectively in all but the case of an α,β-unsaturated aldehyde and iodoform (run 14). The *E*/*Z* ratios

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(7) When zinc (copper couple) is employed instead of CrCl$_2$, further reduction leading to a methylenated product is reported to take place. Miyano, S.; Hida, M.; Hashimoto, H. *J. Org. Chem.* **1968**, *12*, 263.

(8) (a) Hiyama, T.; Obayashi, M.; Nakamura, A *Organometallics* **1982**, *1*, 1249. (b) Ho, T.-L.; Olah, G. A. *Synthesis* **1977**, 170. (c) Mukaiyama, T.; Harada, T. *Chem. Lett.* **1981**, 1527. (d) Mukaiyama, T.; Harada, T.; Shoda, S. *Ibid.* **1980**, 1507.

(9) There are two possible reactive species generated from haloform and CrCl$_2$ (Scheme III.) One is a chromium dihalocarbenoid **2** (path A)[10] and the other is a carbodianion species **3** (path B).[11,12] We are tempted to attribute the formation of (*E*)-alkenyl halides to the geminal carbodianion species (path B) due to the following observations. (i) When the reaction was performed with dodecanal, iodoform, and CrCl$_2$ in 1:1:2 molar ratio, the desired 1-iodo-1-tridecene (**5**, 36%) and unchanged dodecanal (38%) were obtained along with a small amount of 1,1-diiodo-2-tridecanol (**4**, 3%). (ii) Treatment of preformed[13] **4** with CrCl$_2$ (or CrCl$_2$–CHI$_3$) did not give **5** at 25 °C but required heating to reflux (THF) to yield a nearly 1:1 mixture of (*Z*)- and (*E*)-**5**.[14] (iii) No cyclopropanes were isolated, which would result from the addition of the chromium carbenoid to the olefinic linkage of an unsaturated aldehyde (runs 11–13).[10]

(10) Castro, C. E.; Kray, W. C., Jr. *J. Am. Chem. Soc.* **1966**, *88*, 4447. Reduction of polyhalomethanes with CrSO$_4$ in aqueous DMF affording carbenoid intermediates is postulated in the above article. The resulting chromium carbenoids react with olefins to give cyclopropane compounds.

(11) For olefination of carbonyl compounds with a geminal carbodianion species, see: (a) Knochel, P.; Normant, J. F. *Tetrahedron Lett.* **1986**, *27*, 1039. (b) Okazoe, T.; Hibino, J.; Takai, K.; Nozaki, H. *Ibid.* **1985**, *26*, 5579, 5581 and references cited therein.

(12) Dichromium species **3** is considered to be present in the reduction of a haloform with CrClO$_4$ in aqueous acetone. Dodd, D.; Johnson, M. D. *J. Chem. Soc. A* **1968**, 34.

(13) Taguchi, H.; Yamamoto, H.; Nozaki, H. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1588.

of the alkenyl halides increase in the order I < Br < Cl and the rates of reaction of the haloform are in the sequence I > Br > Cl. Thus, reaction between an aldehyde and chloroform was conducted in THF at 65 °C (runs 4, 8, and 13). When bromoform was employed, a mixture (approximately 1:1) of an alkenyl chloride and the desired bromide was produced (runs 2 and 6). This difficulty was overcome by using a combination of CrBr$_3$ and LiAlH$_4$ (1:0.5 molar ratio) instead of CrCl$_2$ (runs 3, 7, 10, 12, and 15). Although ketones are also converted into the corresponding alkenyl halides, they are less reactive than aldehydes. As shown in Scheme I, selective conversion of an aldehyde into *E*-iodo olefin was performed without affecting the coexisting ketone group.[4]

Because an alkenyl halide adds to an aldehyde with CrCl$_2$ in the presence of a catalytic amount of NiCl$_2$ in DMF,[15] the new method provides a simple route to *E*-allylic alcohols by addition of three components, i.e., two aldehydes and CHI$_3$ (Scheme II). Iodoform functions as a methine trianion synthon in the reaction sequence.

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(14) (a) Kochi, J. K. *Organometallic Mechanisms and Catalysis*; Academic Press: New York, 1978; pp 258-260. Singleton, D. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1967**, *89*, 6547; **1968**, *90*, 1582. (b) Anet, F. A. L.; Isabelle, E. *Can. J. Chem.* **1958**, *36*, 589. (c) Johnson, C. R.; Kirchhoff, R. A. *J. Am. Chem. Soc.* **1979**, *101*, 3602. (d) Wolf, R.; Steckhan, E. *J. Chem. Soc., Perkin Trans. 1* **1986**, 733.

(15) (a) Takai, K.; Kimura, K.; Kuroda, T.; Hiyama, T.; Nozaki, H. *Tetrahedron Lett.* **1983**, *24*, 5281. (b) Takai, K.; Tagashira, M.; Kuroda, T.; Oshima, K.; Utimoto, K.; Nozaki, H. *J. Am. Chem. Soc.* **1986**, *108*, 6048. (c) Jin, H.; Uenishi, J.; Christ, W. J.; Kishi, Y. *Ibid.* **1986**, *108*, 5644.

(16) Benzaldehyde (0.11 g, 1.0 mmol) was treated at 0 °C with iodoform (0.43 g, 1.1 mmol) and CrCl$_2$ (0.98 g, 8.0 mmol) in THF (15 mL). After the aldehyde was almost consumed (2 h), the THF solvent was replaced by DMF (13 mL). To the mixture was added at 25 °C a solution of nonanal (85 mg, 0.60 mmol) in DMF (2 mL) and then a catalytic amount of NiCl$_2$ (5.2 mg, 0.040 mmol). The resulting dark green mixture was heated at 60 °C for 3 h. The mixture was poured into water and extracted with ether. The combined was poured into water and extracted with ether. The combined extracts were dried (Na$_2$SO$_4$) and concentrated. Purification by preparative TLC (hexane-ethyl acetate, 10:1) afforded the desired allylic alcohol **6b** in 62% yield (92 mg, E/Z = >98/<2). The E/Z ratio was determined by NMR.

Ethylene Polymerization by a Cationic Dicyclopentadienylzirconium(IV) Alkyl Complex

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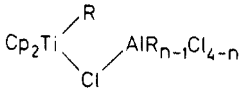
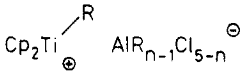
Received May 29, 1986

The mechanism of olefin polymerization by soluble Ziegler–Natta catalysts has been the object of continuous study for over 25 years.[1] As early as 1960 Breslow, Long, and Newburg proposed,[2] on the basis of UV-visible spectroscopic and chemical studies, that the active species in Cp$_2$TiCl$_2$/AlR$_n$Cl$_{3-n}$ model systems is titanium alkyl complex **1** or a species derived therefrom, possibly cationic complex **2** as recently discussed by Eisch and co-workers.[3] The proposed role of the Al cocatalyst is to alkylate Cp$_2$TiCl$_2$ and to activate the resulting Cp$_2$TiRCl complex by Lewis acid complexation to (as in **1**) or complete removal of (as in **2**) a chloride ligand. Polymerization was proposed to involve coordination of olefin to this activated Ti–R species (presumably with concomitant extrusion of [AlR$_{n-1}$Cl$_{5-n}$]$^-$ in the case of **1**) and subsequent insertion into the Ti–R bond (the Cossee–Arlman mechanism[4]). The results of kinetic studies[5] and isotope effect measurements[6] are consistent with this proposed mechanism. Support for the intermediacy of the cationic species **2** or its olefin adduct is provided by (1) the isolation of a cationic complex Cp$_2$TiC(SiMe$_3$)=C(CH$_3$)Ph$^+$ from the reaction of (SiMe$_3$)CCPh with Cp$_2$TiCl$_2$/AlMeCl$_2$,[3] (2) electrochemical experiments[7] and other observations,[8] (3) the observation that (C$_5$Me$_5$)$_2$MR (M = Lu,[9] Sc[10]) and [(C$_5$Me$_5$)$_2$MH]$_2$ (M = La, Nd, Lu)[11] compounds, which in monomeric form are isoelectronic with **2** (neglecting f electrons), are active ethylene polymerization catalysts, and (4) the direct observation of propylene insertion into the Lu–CH$_3$ bond of (C$_5$Me$_5$)$_2$LuCH$_3$.[12] However, cationic Cp$_2$TiR$^+$ (R = alkyl) complexes have never been directly observed in Ziegler–Natta model systems nor isolated and characterized. In view of the complexity of these catalytic systems[1] it is important to demonstrate the existence of cationic Cp$_2$M(IV)R$^+$ complexes and to delineate their chemistry. With these goals in mind we recently reported the synthesis of Cp$_2$Zr(R)(L)$^+$ (L = labile ligand) complexes.[13] Here we report the X-ray structure of a simple member of this series, Cp$_2$Zr(CH$_3$)(THF)$^+$, which polymerizes ethylene in the absence of an Al cocatalyst.



1



2

[Cp$_2$Zr(CH$_3$)(THF)][BPh$_4$] (**3**) was prepared by reaction of Cp$_2$Zr(CH$_3$)$_2$ with 1 equiv of Ag[BPh$_4$] in CH$_3$CN followed by recrystallization from THF as previously described.[13] The structure of this compound has been confirmed by X-ray diffraction and is given in Figure 1 along with important molecular parameters.[14] The Zr–CH$_3$ and average Zr–Cp distances in **3** are ca. 0.02 and 0.04 Å shorter, respectively, than the corresponding distances in Cp$_2$Zr(CH$_3$)$_2$[15] possibly as a result of the greater Lewis acidity of the metal center in the former compound. The THF ligand is oriented nearly perpendicular to the plane defined by the methyl carbon, zirconium, and THF oxygen atoms (dihedral angle C(36)–O–C(39)/(Me–Zr–O = 102.3°). This orientation is more clearly shown in Figure 2. In contrast, in the isoelectronic (neglecting f electrons) lanthanide metal complex,

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(1) (a) Boor, J. *Ziegler-Natta Catalysts and Polymerizations*; Academic: New York, 1979. (b) Sinn, H.; Kaminsky, W. *Adv. Organomet. Chem.* **1980**, *18*, 99. (c) Reichert, K. H. *Transition Metal Catalyzed Polymerizations. Alkenes and Dienes*; Quirk, R. P., Ed.; Harwood Academic: New York, 1983; Part B, p 465.

(2) (a) Long, W. P.; Breslow, D. S. *J. Am. Chem. Soc.* **1960**, *82*, 1953. (b) Breslow, D. S.; Newburg, N. R. *J. Am. Chem. Soc.* **1959**, *81*, 81.

(3) Eisch, J. J.; Piotrowski, A. M.; Brownstein, S. K.; Gabe, E. J.; Lee, F. L. *J. Am. Chem. Soc.* **1985**, *107*, 7219.

(4) (a) Cossee, P. *J. Catal.* **1964**, *3*, 80. (b) Arlman, E. J.; Cossee, P. *J. Catal.* **1964**, *3*, 99.

(5) Fink, G.; Zoller, W. *Makromol. Chem.* **1981**, *182*, 3265.

(6) (a) Soto, J.; Steigerwald, M. L.; Grubbs, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 4479. (b) Clawson, L.; Soto, J.; Buchwald, S.; Steigerwald, M. L.; Grubbs, R. H. *J. Am. Chem. Soc.* **1985**, *107*, 3377.

(7) (a) Dyachkovskii, F. S.; Shilova, A. K.; Shilov, A. E. *J. Polym. Sci., Part C* **1967**, *16*, 2333. (b) For a discussion, see ref 1a, p 349.

(8) For a summary, see ref 3.

(9) Watson, P. L.; Parshall, G. W. *Acc. Chem. Res.* **1985**, *18*, 51.

(10) Thompson, M. E.; Bercaw, J. E. *Pure Appl. Chem.* **1984**, *56*, 1.

(11) Jeske, G.; Lauke, H.; Mauermann, H.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8091.

(12) Watson, P. L. *J. Am. Chem. Soc.* **1982**, *104*, 337.

(13) Jordan, R. F.; Dasher, W. E.; Echols, S. F. *J. Am. Chem. Soc.* **1986**, *108*, 1718.

(14) Suitable crystals were obtained by slow cooling of a hot THF solution. Crystallographic data: a = 13.707 (12) Å, b = 9.469 (6) Å, c = 24.824 (17) Å, α = 89.97 (5), β = 93.87 (6)°, Γ = 90.00 (6°), v = 3214 (4) Å^3, Z = 4 in space group $P2/c$; R_F = 0.0648, R_{wF} = 0.0646 for 1861 unique reflections ($I \geq 3\sigma(I)$). Disorder of the Cp and THF ligands in two equally populated conformers limited the refinement. The disordered Cp rings were treated as rigid bodies with independent thermal parameters for each C atom and C–H distances fixed at 0.96 Å. The positional and thermal parameters for the two disordered THF molecules were refined independently. No attempt was made to constrain distances and angles (except for H atom positions). It was not possible to refine all thermal parameters anisotropically due to the strong correlation between parameters. In the final refinement the C atoms of the THF molecules except C(36') and C(39') of the conformer not shown were assigned isotropic thermal parameters. Anisotropic thermal parameters were used for all C atoms of the Cp rings except for C(5), C(8), C(9), C(5'), C(9'), and C(10'). Bond distances and bond angles quoted in the text and in Figure 1 are for one of the two conformers; parameters for the other are similar. A low-temperature structure determination of **3** is planned.

(15) Hunter, W. E.; Hrncir, D. C.; Bynum, R. V.; Penttila, R. A.; Atwood, J. L. *Organometallics* **1983**, *2*, 750.

0002-7863/86/1508-7410$01.50/0