mann[18] and to biological membranes by Tanford[19] and which has more recently been treated in general by Ben Naim[20]. The understanding of the inverse temperature transition is that more-ordered clathrate-like water surrounding the hydrophobic side chains below the transition becomes less-ordered bulk water above the transition as intramolecular and intermolecular contacts involving hydrophobic side chains occur. The decrease in length, which is from the contraction due to the inverse temperature transition at zero load and 40 °C, is to 45% of the 20 °C length,[3] i.e., the length changes by greater than a factor of 2.[21]

Studies on collagen by Katchalsky and colleagues[22,23] are particularly relevant to the present report. Collagen fibers undergo a melting or denaturation of structure with shrinkage in length on raising the temperature, and increasing certain salt concentrations such as LiBr, KSCN, and urea[22] lowers the temperature of the transition. Attending the melting is a contraction to almost one-half of the native length. By using these properties, Katchalsky and co-workers[23] devised a mechanochemical engine which could be driven by a pair of baths, one containing 11.25 M LiBr and the other containing water or dilute (0.3 M) LiBr. This followed work on the contraction of polyelectrolyte (polymethacrylate) fibers where decreased charge–charge repulsion was the mechanism of contraction[24–27] with 50% ionization being required to get the extended state. In the present demonstration, mechanochemical coupling is achieved with a polypeptide containing no charges, and it is the temperature of an inverse temperature transition rather than a regular transition that is being shifted by the charge in chemical potential of the salt solution.

Experimentally modulation of an inverse temperature transition is achievable with smaller changes in chemical potential (less chemical work) which is consistent with the small endothermic heat of the inverse temperature transition, i.e., the heat of polypentapeptide coacervation is about 2 cal/gram (unpublished data). Accordingly, this provides a particularly favorable type of system for free-energy transduction. In principle, of course, desalination could be achieved by driving such a polypentapeptide-based mechanochemical engine backwards. Since the more favored ionic interaction with the polypentapeptide would be cationic interaction with carbonyl oxygens and since this would lead to charge accumulation on the polypeptide with the consequence of charge–charge repulsion, increased cation interaction with polypeptide on raising salt concentration would not seem to be the mechanism with which to bring about contraction. As demonstrated, by carbon-13 NMR spectra, neither does the presence of salt alter the very small amount of Val-Pro cis peptide bond. If the effect of increasing NaCl concentration is not to bind polypeptide as a means of favoring the contracted state of the polymer, then it would seem necessary to consider the effect of increasing ionic strength on the structure of the clathrate-like water which would be to lower the temperature of the transition by destabilizing the clathrate-like water structure of the low-temperature relaxed state.[28]

Acknowledgment. This work was supported in part by National Institutes of Health Grant HL 29578 and the Department of Navy, Office of Naval Research contract N00014-86-K-0402. We also acknowledge the technical assistance of Bryant Haynes and John Jaggard.

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(17) Frank, H. S.; Evans, M. W. *J. Chem. Phys.* **1945**, *13*, 493–507.

(18) Kauzmann, W. *Adv. Protein Chem.* **1959**, *14*, 1–63.

(19) Tanford, C. *The Hydrophobic Effect: Formation of Micelles and Biological Membranes*; J. Wiley and Sons, Inc.: New York, 1973.

(20) Ben-Naim, A. *Hydrophobic Interactions*; Plenum Press: New York, 1980.

(21) In relation to structure, it is of interest to note in Figure 2B that the loss of force on addition of water is a faster process than the development of force on the addition of PBS. A possible explanation for this is that the process is not simply one of solvation swelling and desolvation shrinking, but rather it is an unfolding of structure with solvation while releasing load, and it is a desolvation with folding into the energetically favored helically recurring β-turn structure while developing load. The latter folding can be expected to be slowed by the multiple local minima problem which plagues molecular mechanics and dynamics simulations of protein folding.

(22) Katchalsky, A.; Oplatka, A. *Proc. Forth Intern. Cong. Rheology* **1965**, Part I, 73.

(23) Steinberg, I. Z.; Oplatka, A.; Katchalsky, A. *Nature (London)* **1966**, *210*, 568–571.

(24) Kuhn, W.; Hargitay, B.; Katchalsky, A.; Eisenberg, H. *Nature (London)* **1950**, *165*, 514–516.

(25) Katchalsky, A.; Kunzle, O.; Kuhn, W. *J. Polymer Sci.* **1950**, *5*, 283–300.

(26) Katchalsky, A. *J. Polymer Sci.* **1952**, *1*, 393–412.

(27) Katchalsky, A.; Lifson, S.; Michaeli, I.; Zwick, M. *Size and Shape of Contractile Polymers: Conversion of Chemical and Mechanical Energy*; Wassermann, A., Ed.: Pergamon Press: New York, 1960; pp 1–40.

(28) While this proposed ionic strength modulation of an inverse temperature transition reasonably arises from the well-known salt effect on solubility of hydrophobic solutes,[29,30] the situation with these elastomeric hydrophobic polypeptides is more involved as mechanochemical coupling has recently been demonstrated with cross-linked polypentapeptide, in which there was included four Glu residues per 100 residues at position four. In this case, converting from COOH to ionic COO$^-$ raises the temperature of the inverse temperature transition such that contraction occurs at low pH and relaxation occurs on conversion to the ionic COO$^-$ side chains.[31] The pH driven mechanochemical coupling is polymer-based due to change of polypeptide structure. The mechanochemical coupling demonstrated here may be referred to as solvent-based, as it is achieved without any chemical change in the polypeptide structure.

(29) Nandi, P. K.; Robinson, D. R. *J. Am. Chem. Soc.* **1972**, *94*, 1308–1315.

(30) Hamabata, A.; von Hippel, P. H. *Biochemistry* **1973**, *12*, 1264–1271.

(31) Urry, D. W.; Haynes, B.; Zhang, H.; Harris, R. D.; Prasad, K. U. *Proc. Natl Acad. Sci. U.S.A.* **1988**, in press.

Synthesis of Boron Carbide via Poly(vinylpentaborane) Precursors

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Limitations in traditional ceramic processing have encouraged interest in the development and utilization of polymer pyrolyses as low-temperature synthetic routes to nonoxide ceramic materials.[1,2] Boron carbide is an example of a material where preparation from a polymer precursor might offer advantages[2] over conventional synthetic techniques.[3] Mixed B_4C–SiC ceramics have, in fact, been previously obtained from pyrolysis of poly(carboranesiloxane)[4] polymers; however, a synthesis of pure B_4C from polymeric precursors has heretofore not been developed. We report here that 2-(H_2C=CH)—B_5H_8 will undergo thermal polymerization to vinylpentaborane oligomers and that these species can be converted to pure boron carbide (B_4C) in high ceramic yields under mild conditions.

In a recent paper,[5] we showed that the complex $[\mathrm{Cp^*IrCl_2}]_2$, in the presence of Proton Sponge, catalyzed reactions of pentaborane(9) with acetylenes resulting in the high yield formation of alkenylpentaboranes. Vinyl polymers derived from these compounds would be particularly attractive precursors to boron carbide since they appear to obey several of the criteria previously identified by Wynne and Rice[1] for successful ceramic synthesis from polymers. First, pentaborane(9) has a low decomposition temperature, thus imparting low thermal stability to a polymer and enabling the material to decompose at moderate temperatures. Second, polymer structures containing rings or cages, such as pentaborane(9), should readily undergo a solid-state cross-linking step which is necessary to ensure that molecular fragments are not liberated during pyrolysis.

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(1) Wynne, K. J.; Rice, R. W. *Ann. Rev. Mater. Sci.* **1984**, *14*, 297–334, and references therein.

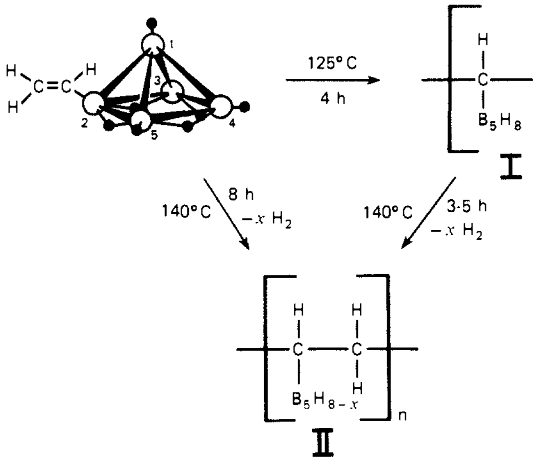
(2) Rice, R. W. *Am. Ceram. Soc. Bull.* **1983**, *62*, 889–892.

(3) For a review of traditional methods of preparation, see: *Gmelin Handbuch der Anorganischen Chemie, Boron*; 1981; Supplement Vol. 2.

(4) Walker, B. E., Jr.; Rice, R. W.; Becher, P. F.; Bender, B. A.; Coblenz, W. S. *Am. Ceram. Soc. Bull.* **1983**, *62*, 916–923.

(5) Mirabelli, M. G. L.; Sneddon, L. G. *J. Am. Chem. Soc.* **1988**, *110*, 449–453.

Scheme I



A soluble polymer was prepared by heating a stirred, neat sample of 2-($H_2C{=}CH$)—B_5H_8 under vacuum at 125 °C for several hours. As the reaction progressed, the liquid became increasingly more viscous until the magnetic stirbar would no longer move. At this point the flask was frozen to −196 °C, and trace amounts of noncondensable gas was removed. The flask was then warmed to room temperature, and the volatile materials were removed in vacuo leaving an air-sensitive, viscous liquid identified as poly[2-(vinyl)pentaborane] (I) in ~91% yield (Scheme I).

The oligomer prepared in this manner is soluble in common organic solvents such as benzene, toluene, and THF and has a broad weight range with fractions up to a molecular weight of ~1000 g/mol (GPC).[6] The ^{11}B NMR spectrum[7] is similar to that of the starting monomer consisting of a low field singlet of intensity 1, attributed to the substituted boron B2, and three doublets with relative intensities of 2:1:1 corresponding to B3,5, B4, and B1, respectively. Upon polymerization the singlet resonance of the monomer at −0.7 ppm[8] is replaced by the new resonance at +3.2 ppm. This is consistent with the formation of a saturated polymer backbone, since the shift of this resonance is similar to that of the substituted boron in 2-(ethyl)pentaborane.[9] The ^{1}H NMR spectrum[7] of I is also in agreement with this interpretation, showing several broad aliphatic proton resonances in the region 1–2 ppm and no vinylic proton resonances between 5 and 6 ppm. The infrared spectrum[7] shows aliphatic C–H stretches from 2940–2820 cm^{-1}, a characteristic B–H stretch at 2590 cm^{-1}, and, most importantly, no evidence for a C=C absorbance. The spectroscopic data are thus consistent with the formulation of I as a pentaborane analogue of known inorganic polyenes of the general formula $(\text{-}CH_2CHX\text{-})_n$ where X is, for example, a pendant carboranyl,[10a,b] ferrocenyl,[10c] or phosphazenyl[10d,e] group.

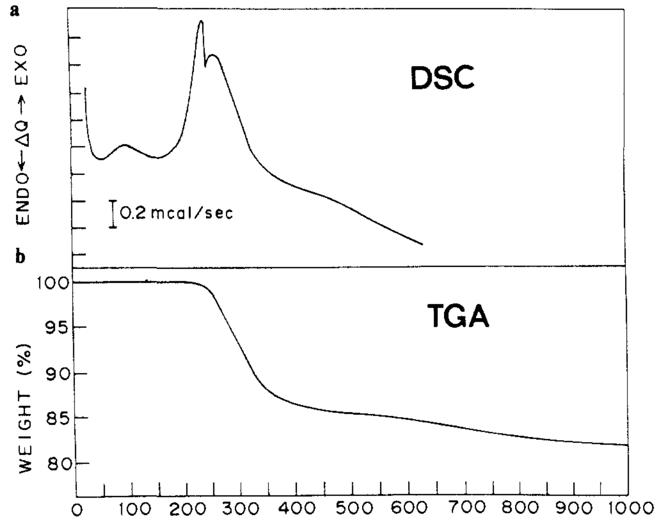
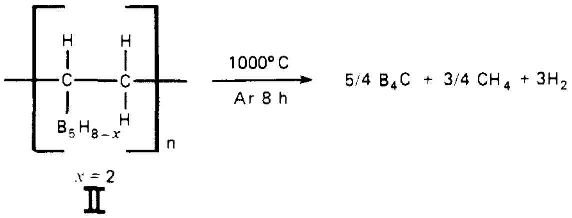


Figure 1. DSC and TGA analysis[12] of polymer II.

Scheme II



Further heating of I at 140 °C for 3–5 h results in loss of ~1.0 mol equiv of H_2 and production of a hard, intractable, cross-linked polymer II. This material is insoluble in acetone, benzene, and THF and decomposes in more polar solvents such as DMF and DMSO. Elemental analysis[11] is consistent with an empirical formula of $C_2B_5H_9$ indicating loss of H_2 and possible formation of B–B linkages. Polymer II can also be formed in high yield (91%) directly from 2-($H_2C{=}CH$)—B_5H_8 by heating the olefin at 140 °C for 8 h.

Thermogravimetric analysis[12] of the cross-linked polymer II (Figure 1a) showed a sharp weight loss in the range 220–375 °C (15%) and a more gradual weight loss (3%) in the region 400–800 °C. A differential scanning calorimetry[12] experiment (Figure 1b) performed on II exhibited a mild exotherm at 100 °C, attributed to residual cross-linking, and, consistent with the TGA results, a large pyrolytic exotherm in the range 200–350 °C.

Bulk pyrolyses were performed by heating a sample of II in a platinum boat in a tube furnace under a flow of argon gas. The sample was heated at ~10 °C/min until a maximum temperature of 1000 °C was achieved, whereupon heating was continued at that temperature for an additional 6.5 h. Boron carbide prepared in this manner was obtained in 77.0% ceramic yield (97.1% of a theoretical yield of 79.3%) consistent with Scheme II.

The resulting material had a black, shiny appearance and retained some of its shape and structural integrity. There were no sharp lines in the X-ray diffraction pattern suggesting a completely amorphous structure. Elemental analysis[13] of the ceramic indicated a B/C ratio of 4.02 with measured levels of hydrogen, nitrogen, and oxygen well below 0.5%. The density of the material

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(6) Gel permeation chromatography was performed on a Waters GPC-2 high-pressure liquid chromatograph equipped with two Waters 100 Å Ultrastyragel columns with tetrahydrofuran as the eluting solvent (flow rate = 1 mL/min). The columns were calibrated with poly(ethylene glycol) and poly(propylene glycol) standards: Mw = 449; Mn = 339; Mw/Mn = 1.33.

(7) ^{11}B NMR (64.2 MHz, ppm, C_6D_6) 3.2 (s, 1, B2), −14.6 (d, 2, J = 139 Hz, B3,5), −19.2 (d, 1, J ~ 131 Hz, B4), −52.4 (d, 1, J = 168 Hz, B1); ^{1}H NMR (200 MHz, δ, C_6D_6) 1.11 (br m, 3, CH), −1.8 (br, 2, BHB), −2.61 (br, 2, BHB); IR (NaCl plates) 2940 s, 2900 vs, 2860 s, 2820 s, 2590 vs, 1820 s vbr, 1400 s vbr, 1150 s vbr, 1020 s, 880 s, 840 s, 790 m, 710 m, 640 s, 600 s, cm^{-1}.

(8) Wilczynski, R.; Sneddon, L. G. *Inorg. Chem.* **1981**, *20*, 3955–3962.

(9) Onak, T.; Dunks, G. B.; Searcy, I. W.; Spielman, J. *Inorg. Chem.* **1967**, *6*, 1465–1471.

(10) (a) Ditter, J. F. In *Gmelin Handbuch der Anorganischen Chemie, Ergaenzungswerk, Vol. 27, Borverbindungen, Part 6*; Springer-Verlag: Berlin, 1975; Chapter 4. (b) Heying, T. L. In *Progress in Boron Chemistry*; Brotherton, R. J., Steinberg, H., Eds.; Pergamon Press: New York, 1970; Vol. 2, Chapter 3. (c) Rausch, M. D.; Macomber, D. W.; Fang, F. G.; Pittman, C. U., Jr.; Jayaraman, T. V.; Priester, R. D., Jr. In *New Monomers and Polymers*; Culbertson, B. M., Pittman, C. U., Jr., Eds.; Plenum Press: New York, 1984; pp 243–267. (d) Dupont, J. G.; Allen, C. W. *Macromolecules* **1979**, *12*, 169–172. (e) Allen, C. W.; Bright, R. P. *Macromolecules* **1986**, *19*, 571–574.

(11) Elemental analysis of polymer II: Found: C, 27.76; H, 10.16; B, 60.46. Anal. Calcd for $C_2B_5H_9$: C, 27.57; H, 10.41; B, 62.02.

(12) TGA (argon atmosphere) and DSC results were obtained by heating a sample of polymer II from room temperature to 1100 °C with a heating rate of 10 °C/min.

(13) Elemental analysis of B_4C prepared from pyrolysis of polymer II: Anal. Calcd for B_4C: C, 21.74; B, 78.26. Found: C, 21.37; B, 77.26; H, 0.21; N, 0.014; 0, <0.3.

was found to be 2.0 g/mL (observed density for hot pressed B_4C, 2.5 g/mL) and compares favorably with the density of B_4C (1.6–1.8 g/mL) prepared from pyrolysis of poly(carborane-siloxanes).[4] Crystalline B_4C, as determined by X-ray diffraction, of higher density (2.3 g/mL) was obtained by heating the amorphous material at 1450 °C for 2 days.

These initial studies clearly demonstrate that oligomeric vinylpentaborane compounds can be prepared in high yield and are excellent low-temperature precursors to B_4C. Furthermore, the fact that polymer I appears to undergo cross-linking at low temperatures indicates that it might be useful for applications where thermosetting behavior is desired. For example, possible applications might involve the synthesis of composite[14] materials or the generation of thin films of B_4C for use as high temperature thermoelectric materials.[15]

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(14) Jamet, J.; Spann, J. R.; Rice, R. W.; Lewis, D.; Coblenz, W. S. *Ceram. Eng. Sci. Proc.* **1984**, *5*, 677–694.

(15) Wood, C. In *Boron Rich Solids*; Edmin, D., Aselage, T., Beckel, C. L., Howard, I. A., Wood, C., Eds.; AIP Conference Proceedings 140; Lerner, R. G., Series Ed.; American Institute of Physics: New York, 1986; pp 362–372.

Diastereoselective Synthesis of the First 2,3,4-Trisubstituted Platina(IV)cyclobutanes

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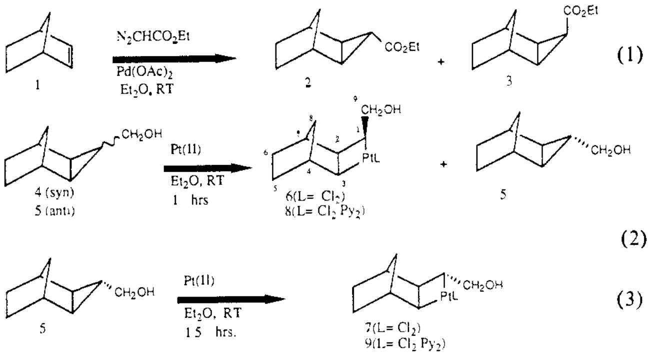
Metallacyclobutane complexes range from proposed transition states to stable entities and are considered to be important pathway components to several organic transformations. Platinacyclobutanes are among the most stable and thus provide a unique opportunity to study metal–carbon ring chemistry. However, until recently the ring-bearing substitutions were simple alkyl and aryl substituents—mostly mono and cis–trans disubstituted.[1-5] There was one trisubstituted example known previously, that being 2,2,3-trimethylplatinacyclobutane.[6] Thus, to explore this area more completely, it seemed reasonable to attempt to expand this group of complexes to more highly substituted examples with more functionality.

We now wish to report (1) the diastereoselective preparation of the first two 2,3,4-trisubstituted platina(IV)cyclobutanes, (2) the crystal structure for one isomer, and (3) the reaction of each diastereomeric cyclobutane complex with diazomethane leading to a *highly stereoselective* preparation of a 1,3-divinylcyclopentane derivative.

Trisubstituted Platinacyclobutanes. Reaction of ethyl diazoacetate with norbornene (**1**) affords the epimeric mixture of cyclopropyl derivatives **2** and **3** in a ratio of 1.7:1, respectively (eq 1).



Reduction with LAH and subsequent treatment of this alcohol mixture (**4** and **5**) with Zeise's dimer, $(C_2H_4)_2Pt_2Cl_4$, in a molar amount equal to or slightly greater than the minor isomer, yields **6** (L = Cl), selectively, as the precipitated complex (eq 2).[5] Filtration of the solid and reaction of the remaining solution with more Pt(II) yields the diastereomeric isomer **7** (eq 3). Subsequent reaction of **6** and **7** with 2 equiv of pyridine gave **8** and **9**, respectively. The yields of platinum insertion are virtually quantitative.

Carbon NMR spectral data for **8** and **9** are listed in Table I. The key features present which typically describe platinacyclobutane structures are the chemical shifts and $J_{\mathrm{Pt,C}}$ constants for C(1), C(2), and C(3).[1,4,5] The values for C(9) are also consistent with structures **8** and **9**.

Although **9** is less stable thermally than **8**, it readily formed quality crystals from chloroform–heptane solutions for X-ray analysis (Figure 1).[7] This result establishes unambiguously that **9** is the correctly assigned isomer of the trisubstituted platinacyclobutane complexes. The pucker angle in the cyclobutane moiety (i.e., the angle generated by the platinum atom being out of the C_1–C_2–C_3 plane) is 17°.

Reactions of 8 and 9. The reason for synthesizing **8** and **9** was to determine the stereochemical result of reacting each with diazomethane. Previous work in our laboratory had revealed the results shown in eq 4.[8] Thus, for extending the future synthetic advantages of this reaction, we wanted to know (a) if we could

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(1) Puddephatt, R. J. *Coord. Chem. Rev.* **1980**, *33*, 149.

(2) Parsons, E. J.; Jennings, P. W. *J. Am. Chem. Soc.* **1987**, *109*, 3973.

(3) Ekeland, R. A.; Jennings, P. W. *J. Organomet.* **1985**, *281*, 397.

(4) Waddington, M. D.; Jennings, P. W. *Organometallics* **1982**, *1*, 1370.

(5) Waddington, M. D.; Jennings, P. W. *Organometallics* **1982**, *1*, 385.

(6) Cushman, B. M.; Brown, D. B. *J. Organomet. Chem.* **1978**, *152*, C42.

(7) X-ray structure determination of complex **9**: tan-colored crystals of **9** were grown by allowing heptane to diffuse into a chloroform solution. A specimen suitable for X-ray analysis (approximately 0.22 × 0.48 × 0.63 mm) was mounted on a glass fiber and coated with a drop of a 3:1 mixture of Paratone-N and mineral oil. Uncoated crystals gradually turned opaque when exposed to air, presumably from loss of lattice solvent, and gave powder diffraction patterns. Data collection was carried out at 25 °C on a Nicolet R3mE automated diffractometer with 96-step ω scans with graphite monochromated Mo Kα radiation (g = 0.71069 Å). Unit cell constants of a = 9.421 (2) Å, b = 11.085 (2) Å, c = 11.399 Å, α = 81.98 (2)°, β = 74.40 (2)°, and q = 73.04 (2)° were determined by least-squares refinement by 25 centered reflections in the range 21° < 2R < 30°. Data reduction, including corrections for Lorentz and polarization effects, gave 7894 unique reflections in the range 3° < 2R < 65°, of which 5197 with I > 3s(I) were used for structure refinement. The space group was assumed to be $P\bar{1}$, on the basis of cell volume and was confirmed by a successful structure solution and refinement. Poor refinement behavior was found in the alternative space group $P1$. The platinum position was obtained from a Patterson synthesis, and difference maps gave the remaining non-hydrogen positions, including one chloroform molecule per two units of complex **9**. The chloroform molecule is disordered between two half-occupied orientations, related by an inversion center halfway between two chlorine atom positions that are shared by both orientations. Calculated density for $C_{19}H_{24}N_2OCl_2Pt\cdot{}^1/_2CHCl_3$, z = 2, is 1.89 g/cm^3. Empirical corrections for absorption were based on azimuthal scans collected for 16 reflections with a transmission factor range of 0.34–0.96 (m = 69.2 cm^{-1}, Mo Kα). All atoms were refined with anisotropic thermal parameters, except hydrogens which were assigned to idealized positions with a common refined isotropic thermal parameter. Statistical weighting was used, and one reflection was excluded from the data set based on evidence of strong extinction. The structure refined to an R value of 0.041 (R_w = 0.040). All crystallographic calculations were performed on a Data General Eclipse computer with the SHELXTL program package by G. M. Sheldrick, Nicolet Instrument Corp., Madison, WI.

(8) Jennings, P. W.; Ekeland, R. E.; Waddington, M. D.; Hanks, T. W. *J. Organomet. Chem.* **1985**, *285*, 429.

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