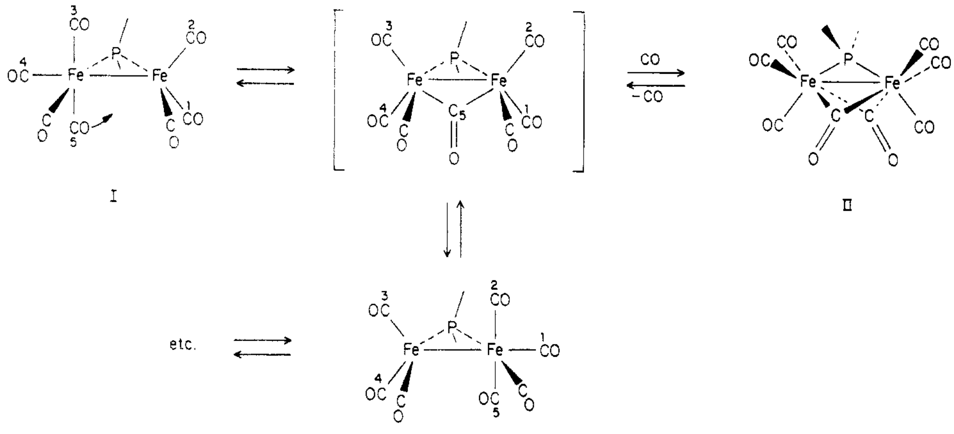
**Scheme II**



ratio [IIB]/[IB] is ca. 0.03 while at −30 °C it is ca. 0.3.

The ESR parameters strongly suggest a symmetric structure for II as shown in Scheme II in which substantial unpaired electron density resides on a pair of equivalent CO ligands. The SOMO in these radicals must have a very small Fe character to account for the narrow line width and a *g* factor close to the "free-spin" value which are more characteristic of organic than metal-centered radicals. Indeed, EHMO calculations on the model compound $Fe_2(CO)_6(\mu\text{-}CO)_2(\mu\text{-}PH_2)$[13] show insignificant unpaired electron density on the two Fe centers (0.2%) and a very substantial one (67.6%) on the two *bridging* CO ligands. The remaining unpaired electron densities are 0.2% for the $PH_2$ group and 31.7% and 0.4%, respectively, for the four cis and two trans terminal CO ligands, in qualitative agreement with the ESR data.[15]

The very rapid CO exchange indicates high substitutional lability for radicals I. Indeed, they react at room temperature with 1 equiv of $P(OMe)_3$ to give isolable, monosubstituted derivatives $Fe_2(CO)_6[P(OMe)_3](\mu\text{-}PR_2)$ (I-$P(OMe)_3$).[16] The ESR spectrum of IA-$P(OMe)_3$ in pentane is quite similar to that of its precursor IA and shows no resolvable hyperfine splitting due to the $P(OMe)_3$ ligand ($a(^{31}P) = 21.77$ G, $g = 2.0507$, −60 °C).[19] Evidently, the "invisible" phosphite ligand occupies one of the two positions trans to the bridging $PR_2$ group where the $^{13}CO$ ligands were also invisible. However, under a CO atmosphere, a new resonance appears at higher field (Figure 1H) due to $Fe_2(CO)_7[P(OMe)_3](\mu\text{-}PEt_2)$[IIA-$P(OMe)_3$] which clearly shows coupling to two $^{31}P$ atoms (8.84 G, 13.66 G, $g = 2.0186$). Under $^{13}CO$, the upfield resonance becomes very complicated and the spectrum of IA-$P(OMe)_3$ acquires additional structure due to five equivalent $^{13}C$ atoms (cf. Figure 1B). The latter observation is consistent with the phosphite ligand being trans to the $PR_2$ bridging group where it does not interfere with the fluxional behavior of the five equatorial CO ligands.

The details of this work and our investigations of the chemical properties (substitution chemistry, photochemical activation of $H_2$, etc.) and catalytic activity[20] of these paramagnetic complexes will be reported elsewhere.

**Acknowledgment.** We thank Professor E. P. Kyba for communicating to us Dr. Osterloh's thesis work prior to publication and for providing samples of $[Et_4N][Fe_2(CO)_n(\mu\text{-}PPh_2)]$ ($n$ = 7, 8). We also acknowledge the fine technical assistance of D. J. Jones (ESR) and S. A. Hill (IR, synthesis).

**Registry No.** I (R = Cy), 102211-01-8; I (R = *t*-Bu), 102211-02-9; IA, 102210-99-1; IB, 102211-00-7; II (R = Cy), 102211-05-2; II (R = *t*-Bu), 102211-06-3; IIA, 102211-03-0; IIA-$P(OMe)_3$, 102211-17-6; IIB, 102211-04-1; III (R = Cy), 102211-09-6; III (R = *t*-Bu), 102211-10-9; IIIA, 102211-07-4; IIIB, 102211-08-5; IV (R = Cy), 102211-13-2; IV (R = *t*-Bu), 102211-14-3; IVA, 102211-11-0; IVB, 102211-12-1; $Fe_2(CO)_7(\mu\text{-}PH_2)$, 102211-15-4; $(CO)_6Fe_2(\mu\text{-}CO)_2(\mu\text{-}PH_2)$, 102211-16-5.

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(12) Roe, D. C. *J. Magn. Reson.* **1985**, *63*, 388. Krusic, P. J.; Jones, D. J.; Roe, D. C. *Organometallics* **1986**, *5*, 456.

(13) The calculations assume that the model compound has the structure of $Fe_2(CO)_9$[14] with one of the bridging CO ligands replaced by a $PH_2$ group [Fe–Fe = 2.523 Å; Fe–P = 2.32 Å; P–H = 1.46 Å; H–P–H = 114.5°].

(14) Cotton, F. A.; Troup, J. M. *J. Chem. Soc., Dalton Trans.* 1984, 800.

(15) The extensive delocalization of the impaired electron on the CO ligands in II is not surprising. The $Fe_2(CO)_8PR_2$ radical species are electronically analogous to $Fe_2(CO)_9$ with an added electron since a bridging $PR_2$ is a three-electron ligand. The unpaired electron in this hypothetical radical anion will wish to reside mostly on the ligands to maintain the desirable 18-electron count at each Fe center existing in $Fe_2(CO)_9$. Our EHMO calculations on $Fe_2(CO)_9^-$ indeed show that the SOMO in this radical anion is made up exclusively of the AO's of the CO ligands (76.4% bridging CO's; 23.6% terminal CO's). A completely analogous situation, judging by similar ESR behavior, obtains with the radical species $Fe_2(CO)_8SR$, isostructural with II, which have a three-electron thiolato group instead of the $PR_2$ group of II (Krusic, P. J., unpublished results).

(16) The ease of this substitution reaction is in contrast with the more severe reaction conditions needed to effect substitution with tertiary phosphines in the isostructural even-electron $(CO)_4Ru(\mu\text{-}PPh_2)Co(CO)_3$ analogue.[17] Greatly enhanced substitutional lability has been associated with odd-electron transition-metal carbonyl systems.[18]

(17) Regragui, R.; Dixneuf, P. H.; Taylor, N. J.; Carty, A. J. *Organometallic* **1986**, *5*, 1.

(18) Cf. Brown, T. L. *Ann. N.Y. Acad. Sci.* **1980**, *333*, 80.

(19) The powder spectra also show coupling to only one P atom: 2.0933 ($g_1$), 2.0325 ($g_2$), 2.0248 ($g_3$), 21.0 G ($A_1$), 26.4 G ($A_2$), 19.1 G ($A_3$).

(20) Menon, R.; Baker, R. T.; Krusic, P. J.; San Filippo, J., Jr., manuscript in preparation.

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# Preparation of Ditungsten Hexakis(2,6-dimethylphenoxide) and Its Reaction with Acetylenes To Give Tungstenacyclobutadiene Complexes

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*Received April 14, 1986*

*Summary:* The reaction between $W_2(O\text{-}t\text{-}Bu)_6$ and excess, fused 2,6-dimethylphenol produces $W_2(DMP)_6$ in high yield (DMP = 2,6-dimethylphenoxide). $W_2(DMP)_6$ re-

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**acts smoothly with 3 equiv of 2-butyne or 3-hexyne to give tungstenacyclobutadiene complexes of the type $W(C_3R_3)(DMP)_3$ virtually quantitatively. The $W(C_3R_3)(DMP)_3$ complexes react smoothly with 3 equiv of HCl in pentane to give the parent trichloride complexes $W(C_3R_3)Cl_3$ virtually quantitatively. A simple large-scale preparation of $W_2(DMP)_6$ consists of the addition of DMPH to $WCl_6$ to give $W(DMP)_3Cl_3$ followed by reduction of $W(DMP)_3Cl_3$ in diethyl ether.**

The only two known compounds of the type $W_2(OR)_6$ [R = $CMe_3$ or $CMe(CF_3)_2$] react with internal acetylenes to give trialkoxytungstenalkylidyne complexes (eq 1).[1]

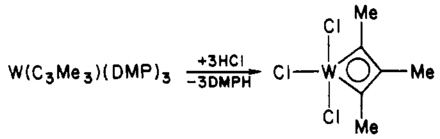
$$W_2(OR)_6 + R'C{\equiv}CR' \rightarrow 2\ W(CR')(OR)_3 \qquad (1)$$

Since some triphenoxide tungsten alkylidyne complexes will metathesize acetylenes via observable tunstenacyclobutadiene complexes[2] and since there appears to be some correlation between acetylene metathesis by alkylidyne complexes and acetylene cleavage by a ditungsten hexaalkoxide complex,[1b] we suspected that if a ditungsten hexaphenoxide complex could be prepared, it would cleave acetylenes. Here we report that this is the case for the 2,6-dimethylphenoxide system. The resulting tungstenacyclobutadiene complexes are extremely useful intermediates for preparing trichlorotungstenacyclobutadiene complexes.

The first synthesis of $W_2(DMP)_6$ was fashioned after the reaction between $Mo_2(O\text{-}i\text{-}Pr)_6$ and DMPH to give $Mo_2(DMP)_6$.[3] A mixture of $W_2(O\text{-}t\text{-}Bu)_6$ and 15 equiv of 2,6-dimethylphenol (DMPH) in toluene was heated in vacuo at 130 °C for a period of 0.5 h until all toluene and liberated *tert*-butyl alcohol were removed. The reaction mixture was cooled, and the excess phenol was sublimed in vacuo onto a −30 °C cold finger. The dark red-brown residue is virtually pure $W_2(DMP)_6$ (~85% yield). Like $Mo_2(DMP)_6$, $W_2(DMP)_6$ is sparingly soluble in hexane but can be recrystallized from toluene.[4a]

A suspension of sparingly soluble $W_2(DMP)_6$ in diethyl ether at 25 °C was treated with 3 equiv of 2-butyne. After 3 h a small amount of poly-2-butyne was removed by filtration, and a red crystalline product with the composition $W(C_3Me_3)(DMP)_3$ was isolated in 90–95% yield.[4b] The $^{13}C$ NMR spectrum of $W(C_3Me_3)(DMP)_3$ showed it to be a tungstenacyclobutadiene complex with a characteristic signal for $C_\alpha$ at 230.9 ppm ($J_{CW}$ = 129 Hz) and $C_\beta$ at 139.0 ppm (cf. $C_\alpha$ at 244.9 ppm ($J_{CW}$ = 124 Hz) and $C_\beta$ at 136.6 ppm in structurally characterized $W(C_3Et_3)$(2,6-diisopropylphenoxide)$_3$[2a]). An analogous reaction between $W_2(DMP)_6$ and 3 equiv of 3-hexyne yields red, pentane-soluble $W(C_3Et_3)(DMP)_3$ in 90–95% yield ($\delta(C_\alpha)$ 236.6; $\delta(C_\beta)$ 141.5). When pyridine, an apparent promoter of the acetylene cleavage reaction by $W_2(O\text{-}t\text{-}Bu)_6$,[1b] is present in the reaction employing $W_2(DMP)_6$, then the products are yellow alkylidyne complexes of the type *cis,mer*-$W(CR)(DMP)_3py_2$ (R = Me, Et).[4c] The same alkylidyne complexes are formed from the $W(C_3R_3)(DMP)_3$ complexes upon treatment with pyridine, a type of reaction with precedent.[2b] The fact that $W(C_3Me_3)(DMP)_3$ will not polymerize 2-butyne rapidly under the reaction conditions is important, as rapid polymerization of 2-butyne so far in our hands has prevented ready isolation of any other trimethyltungstenacyclobutadiene complex.[2b]

When 3 equiv of HCl gas are added to a pentane solution of $W(C_3R_3)(DMP)_3$ (R = Me, Et) at 0 °C, insoluble purple powders are formed essentially quantitatively.[4d] They can be recrystallized from dichloromethane at −30 °C but decompose slowly in this solvent. By analogy with structurally characterized, trigonal-bipyramidal $W[C(t\text{-}Bu)C(Me)C(Me)]Cl_3$,[5,6] we propose that the $W(C_3R_3)Cl_3$ complexes are monomeric, approximately trigonal-bipyramidal trichlorotungstenacyclobutadiene complexes (e.g., eq 2). In the $^{13}C$ NMR spectrum ($CD_2Cl_2$) a signal for the $\alpha$-carbon atom is found at 257.9 ppm and one for the $\beta$-carbon atom at 152.1 ppm (cf. 267.5 ppm for $C_\alpha$, 263.5 ppm for $C_\alpha'$, and 150.7 ppm for $C_\beta$ in $W[C(t\text{-}Bu)C(Me)C(Me)]Cl_3$[6]). One remarkable feature of this reaction is that an $\alpha$-carbon atom is not irreversibly protonated: the nonplanar metallacyclic ring in $W(\eta^5\text{-}C_5H_5)[C_3(t\text{-}Bu)Me_2]Cl_2$ *is* protonated by HCl to give what is believed to be a vinyl-substituted alkylidene complex by opening of the tungstenacyclobutene ring formed by addition of a proton to $C_\alpha$.[7] The second remarkable feature is that the back-reaction between $W(C_3Me_3)Cl_3$ and DMPH is not rapid, at least in pentane where $W(C_3Me_3)Cl_3$ is totally insoluble. $W(C_3Me_3)Cl_3$ has been shown to react with 2-butyne to give a mixture of $[W(\eta^5\text{-}C_5Me_5)Cl_4]_2$ and $W(\eta^5\text{-}C_5Me_5)$(2-butyne)$Cl_2$ virtually quantitatively, a type of reaction that is known for $W[C(t\text{-}Bu)C(Me)C(Me)]Cl_3$.[6] We feel that we will now be able to prepare heterobimetallic complexes in which the metals are linked by a $\eta^5,\eta^5\text{-}Me_4C_5CH_2CH_2C_5Me_4$ ligand system, a simpler analogue of the known $\eta^5,\eta^5\text{-}Et_4C_5CH_2CH_2C_5Me_4$ and $\eta^5,\eta^5\text{-}Et_4C_5CH_2CH_2C_5Et_4$ complexes.[8]



(2)

Once we saw the potential for $W_2(DMP)_6$ as a useful entry into tungsten alkylidyne, metallacyclobutadiene, and cyclopentadienyl chemistry, we set out to try to prepare it straightforwardly on a large scale. *mer*-$W(DMP)_3Cl_3$ can be prepared by adding 3 equiv of DMPH to $WCl_6$ in $CCl_4$ and refluxing the mixture for 18 h.[9,10] Reduction of $W(DMP)_3Cl_3$, on a 20-g scale, in diethyl ether at −55 °C with sodium powder plus a trace of mercury gives 10 g of

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[1] (a) Schrock, R. R.; Listemann, M. L.; Sturgeoff, L. G. *J. Am. Chem. Soc.* **1982**, *104*, 4291. (b) Listemann, M. L.; Schrock, R. R. *Organometallics* **1985**, *4*, 75. (c) Freudenberger, J. H.; Pedersen, S. F.; Schrock, R. R. *Bull. Soc. Chim. Fr.* **1985**, 349. (d) Cotton, F. A.; Schwotzer, W.; Shamshoum, E. S. *Organometallics* **1984**, *3*, 1770. (e) Chisholm, M. H.; Folting, K.; Hoffman, D. M.; Huffman, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 6794. (f) Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C. *Inorg. Chem.* **1983**, *22*, 2903.

[2] (a) Churchill, M. R.; Ziller, J. W.; Freudenberger, J. H.; Schrock, R. R. *Organometallics* **1984**, *3*, 1554. (b) Freudenberger, J. H.; Schrock, R. R.; Churchill, M. R.; Rheingold, A. L.; Ziller, J. W. *Organometallics* **1984**, *3*, 1563.

[3] Coffindaffer, T. W.; Rothwell, I. P.; Huffman, J. C. *Inorg. Chem.* **1983**, *22*, 2906.

[4] (a) Calcd for $WC_{24}H_{27}O_3$: C, 52.66; H, 4.97. Found: C, 52.38; H, 5.14. (b) Calcd for $WC_{30}H_{36}O_3$: C, 57.28; H, 5.7. Found: C, 57.13; H, 5.79. (c) Calcd for $WC_{36}H_{40}N_2O_3$ (R = Me): C, 59.03; H, 5.46; N, 3.82. Found: C, 58.86; H, 5.46; N, 3.86. (d) Calcd for $WC_6H_9Cl_3$ (R = Me): C, 19.39; H, 2.42; Cl, 28.68. Found: C, 19.44; H, 2.49; Cl, 28.34.

[5] Churchill, M. R.; Wasserman, H. J. *J. Organomet. Chem.* **1985**, *279*, 405.

[6] Schrock, R. R.; Pedersen, S. F.; Churchill, M. R.; Ziller, J. W. *Organometallics* **1983**, *4*, 1574.

[7] Churchill, M. R.; Ziller, J. W.; McCullough, L.; Pedersen, S. F.; Schrock, R. R. *Organometallics* **1983**, *2*, 1046.

[8] MacLaughlin, S. A.; Murray, R. C.; Dewan, J. C.; Schrock, R. R. *Organometallics* **1985**, *4*, 796.

[9] Listemann, M. L. Ph.D. thesis, MIT, 1985.

[10] A scale of 50 g of $WCl_6$ in a total volume of 500 mL of $CCl_4$ is convenient. The reaction mixture was taken to dryness in vacuo and the residue washed with pentane. The crude product was recrystallized from dichloromethane to give dark brown microcrystals; yield 65 g (79%). Anal. Calcd for $WC_{24}H_{27}Cl_3O_3$: C, 44.10; H, 4.16. Found: C, 44.33; H, 4.34.[9]

$W_2(DMP)_6$ (60% yield).[11] We believe that this synthesis may be improved even further so that even larger quantities of $W_2(DMP)_6$ can be prepared in two easy steps from $WCl_6$.

**Acknowledgment.** This work has been supported by the National Science Foundation (Grant CHE84-02892) and the Director, Office of Basic Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy, under Contract DE-AC02-78ER04949-A003.

**Registry No.** $W_2(DMP)_6$, 102307-39-1; $W_2(O\text{-}t\text{-}Bu)_6$, 57125-20-9; DMPH, 576-26-1; $CH_3C{\equiv}CCH_3$, 503-17-3; $W(C_3Me_3)(DMP)_3$, 102367-79-3; $W(C_3Et_3)(DMP)_3$, 102307-40-4; $CH_3CH_2C{\equiv}CH_2CH_3$, 928-49-4; *cis,mer*-$W(CMe)(DMP)_3(py)_2$, 102286-60-2; $W(C_3Me_3)Cl_3$, 102342-00-7; $W(C_3Et_3)Cl_3$, 102307-41-5; *mer*-$W(DMP)_3Cl_3$, 102307-42-6; $WCl_6$, 13283-01-7.

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(11) Na powder (2.25 g) was added to a suspension of 20 g of $W(DMP)_3Cl_3$ in 200 mL of diethyl ether that had been cooled to −55 °C. Mercury (10 g) was added, and the mixture was stirred and allowed to warm to 25 °C. After 4 h at 25 °C the crude product was filtered off and recrystallized from THF; yield 10 g (60%).

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# Transition-Metal-Promoted Reactions of Boron Hydrides. 8.[1] Nickel-Promoted Alkyne Insertion Reactions: A New Synthesis of the Four-Carbon Carborane *nido*-4,5,7,8-$R_4C_4B_4H_4$

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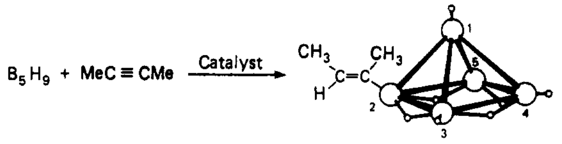
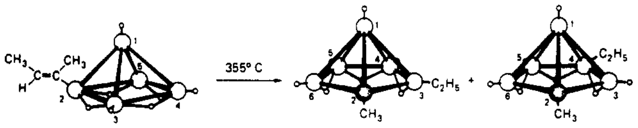
*Summary:* A new type of metal-promoted alkyne/polyhedral borane insertion reaction is reported. The reaction of the carborane *nido*-2,3-$Et_2C_2B_4H_6$ with 2-butyne in the presence of sodium hydride and nickel(II) chloride has been found to result in a two-carbon insertion into the cage system to produce the tetracarbon carborane *nido*-4,5,7,8-$Me_2Et_2C_4B_4H_4$.

We have previously demonstrated that transition-metal reagents can be used to catalyze a variety of reactions of polyhedral boron cage compounds, including acetylene-addition,[2-4] olefin-substitution,[5] dehydrodimerization,[6,7] dehydrocondensation,[1] and cage-growth reactions.[1] We report here the development of a new type of metal-promoted borane/alkyne reaction which leads to direct two-carbon insertion of the acetylenic unit into the polyhedral boron cage system.

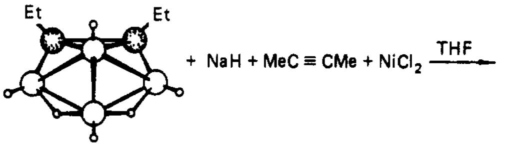
We have already reported[2-4] that various transition-metal reagents, such as $(R_2C_2)Co_2(CO)_6$ and $IrCl(CO)(PPh_3)_2$ catalyze the addition reactions of polyhedral boranes with acetylenes to give boron-substituted alkenylboranes and carboranes.



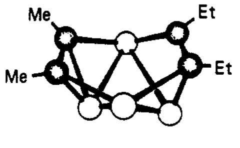
We have also demonstrated that these alkenylpentaboranes are precursors to monocarbon carboranes.



In contrast to the metal-catalyzed acetylene-addition reactions described above, we have now found that Ni(II) salts promote two-carbon acetylene insertions into polyhedral borane anions. For example, the reaction of the carborane *nido*-2,3-$Et_2C_2B_4H_6$ with 2-butyne, in the presence of sodium hydride and nickel(II) chloride has been found to produce the four-carbon carborane *nido*-4,5,7,8-$Me_2Et_2C_4B_4H_4$,[8] as shown.



2,3-$Et_2C_2B_4H_6$



4,5,7,8-$Me_2Et_2C_4B_4H_4$

In a typical reaction, 0.174 g (1.34 mmol) of 2,3-$Et_2C_2B_4H_6$, 0.048 g (2.0 mmol) of sodium hydride, 0.174 g (1.34 mmol) of anhydrous nickel(II) chloride, and 13.4 mmol of 2-butyne were reacted in 5 mL of THF in vacuo. The reaction mixture was initially warmed to −20 °C whereupon 1 equiv of hydrogen gas was generated, indicating the formation of the carborane anion.[9]

$$2,3\text{-}Et_2C_2B_4H_6 + NaH \xrightarrow{-20\ ^\circ C} Na^+[2,3\text{-}Et_2C_2B_4H_5^-]$$

The solution also gradually turned dark green, suggesting the formation of a nickelacarborane complex. The reaction was then allowed to react at 0 °C for 1 h, during which time the solution darkened and an additional 0.30 mmol of $H_2$ was evolved. The solution was stirred for another 18 h at room temperature, resulting in metal reduction and the formation of a black, viscous solution. Vacuum-line fractionation of the contents of the reaction flask gave 76 mg (0.413 mmol, 31% yield) of pure *nido*-4,5,7,8-$Me_2Et_2C_4B_4H_4$ retained in a −23 °C trap.[10]

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(1) For part 7, see: Corcoran, E. W., Jr.; Sneddon, L. G. *J. Am. Chem. Soc.* **1985**, *107*, 7446–7450.
(2) Wilczynski, R.; Sneddon, L. G. *J. Am. Chem. Soc.* **1980**, *102*, 2857–2858.
(3) Wilczynski, R.; Sneddon, L. G. *Inorg. Chem.* **1981**, *20*, 3955–3962.
(4) Wilczynski, R.; Sneddon, L. G. *Inorg. Chem.* **1982**, *21*, 506–514.
(5) Davan, T.; Corcoran, E. W., Jr.; Sneddon, L. G. *Organometallics* **1983**, *2*, 1693–1694.
(6) Corcoran, E. W., Jr.; Sneddon, L. G. *J. Am. Chem. Soc.* **1984**, *106*, 7793–7800.
(7) Corcoran, E. W., Jr.; Sneddon, L. G. *Inorg. Chem.* **1983**, *22*, 182.

(8) The 4,5,7,8-$Me_2Et_2C_4B_4H_4$ carborane has been numbered according to conventional procedures to allow comparisons to previously isolated compounds; however, using the new nomenclature rules recently proposed for polyhedral boranes this compound would be 2,3-$Me_2$-4,5-$Et_2$-tetracarba-1-debor[$C_{2v}$-($1v^6 2v^4 2v^5 2v^5$)-$\Delta^{14}$-*closo*]nonaborane(8). See: Casey, J. B.; Evans, W. J.; Powell, W. H. *Inorg. Chem.* **1983**, *22*, 2228–2235, 2236–2245.
(9) Dunks, G. B.; Onak, T. *Inorg. Chem.* **1966**, *5*, 439–442.