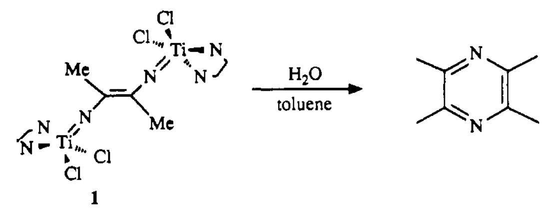
Scheme II



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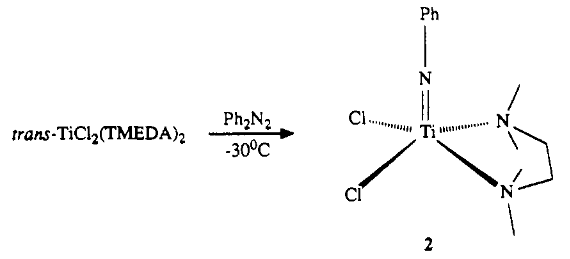
Scheme III



2

the final product via either direct dimerization or reaction with a second molecule of acetonitrile and unreacted starting Ti(II) complex. The solution NMR data, consistent with the solid-state formulation, suggest that the reaction cannot be reversed. There was no evidence for the presence of the cis isomer either in the pure sample or in the mother liquor. We find this selectivity remarkable, when one considers that no significant steric hindrance is present in complex **1**. This complex provides the first case where the four-electron reductive coupling of acetonitrile takes place on a mononuclear system, this kind of transformation having so far been observed only with multiply bonded di- or polymetallic systems.[14,15]

Attempts to demetalate the organic fragment via hydrolysis gave moderate yield (47%) of tetramethylpyrazine (TMP) as a colorless crystalline material (Scheme II).[17] This compound could be isolated only when the hydrolysis was carried out under inert atmosphere with the use of 4 equiv of water. Intractable mixtures have been obtained in all the other cases. It is difficult to rationalize the unexpected formation of this heterocyclic compound during the hydrolysis since the cyclic structure imply rearrangement of the $[\mathrm{N{-}C(Me){=}C(Me){-}N}]^{4-}$ moiety from the trans to the cis configuration. Attempts to isolate and identify the inorganic residue failed.

The stability of the Ti–N multiple bond, as suggested by the very short Ti–N distance, is probably high and is likely the thermodynamic driving force for the preliminary reduction of CH_3CN. In agreement with this hypothesis, the Ti-imido function can be easily formed with other organic precursors. The reaction of $(TMEDA)_2TiCl_2$ with azobenzene for example, proceeds at −30 °C in THF to form the corresponding $(TMEDA)Cl_2Ti{=}NPh$ (**2**) in good yield (Scheme III). The ease of this reaction is in contrast to the hard pyrolitic conditions employed for the preparation of $(ArO)_2Ti(NPh)py_2$,[16] underlying the versatility of $TiCl_2(TMEDA)_2$ as a synthetic tool. Furthermore, the presence of two "reactive" chlorine atoms in **1** and **2** is especially desirable for further reactivity studies, including toward reduction and alkylation reactions. The structure of **2**, as demonstrated by X-ray analysis, shows the monomeric complex basically isostructural with the monomeric fragment of **1** forming comparable bond distances and angles (Figure 2). The Ti=N distance [Ti—N = 1.702 (6) Å] is slightly shorter than in the previously reported $(ArO)_2Ti(NPh)(py)_2$,[16a] probably as a result of decreased steric hindrance. There is no prohibitive steric hindrance in complex **2**; therefore, we suggest that the unusual pyramidal geometry, generally observed among group 4 metal imidates,[16] may be determined by electronic factors.

Finally the reaction of $(TMEDA)_2TiCl_2$ with Me_3SiN_3 led to the formation in low yield of the thermally unstable $(TMEDA)TiCl_2N_3$ as a light blue crystalline solid. The characteristic absorption at ν = 1980 cm^{-1} of the IR spectrum suggested the presence of a bent terminally bonded azido group.

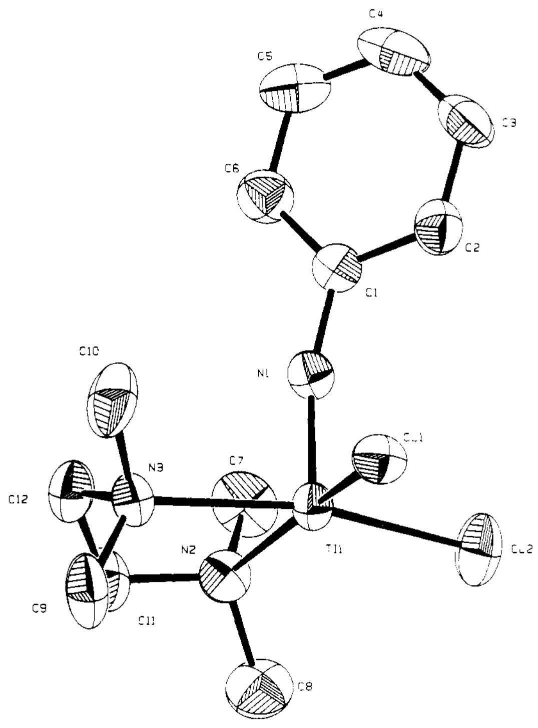


Figure 2. ORTEP drawing of **2** showing the labeling scheme. Thermal ellipsoids are drawn at the 50% probability level.

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Supplementary Material Available: Tables listing atomic positional parameters, anisotropic thermal parameters, and complete bond distances and angles for **1** and **2** (21 pages); tables listing observed and calculated structure factors for **1** and **2** (24 pages). Ordering information is given on any current masthead page.

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Simple Syntheses and Alkylation Reactions of 3-Iodo-*o*-carborane and 9,12-Diiodo-*o*-carborane[1]

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Although 3-chloro-,[2a,b] 3-bromo-,[2c] and 3-fluoro-*o*-carborane[2b] are all known, 3-iodo-*o*-carborane (**1**) is not. In this note, we first describe a modification of our recent recipe for 3-bromo-*o*-carborane[2c] that produces **1** in good yield and purity. Next, we report an extension of our route to 9-iodo-*o*-carborane[3] to give

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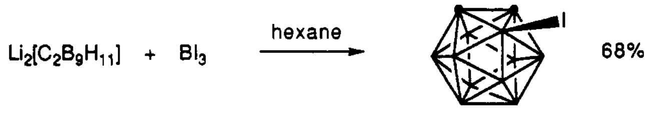
Table I. Coupling of 9,12-Diiodo-*o*-carborane (**2**) with Allylmagnesium Chloride (C_3H_5MgCl) Catalyzed by $(Ph_3P)_2PdCl_2$[a]

amt, mmol				yield,[c] %		
9,12-$I_2C_2B_{10}H_{10}$	C_3H_5MgCl	solvent[b]	time, h	**5b**	**6**	**2**
10	50	Et_2O	72	17.5	10.1	59.4
10	50	Et_2O/THF	40	81.5	3.0	14.2
10	50	THF	30	96.8	2.8	0.1
10	30	Et_2O	48	5.9	25.4	64.8
10	30	THF	10	47.6	1.7	50.6

[a] Catalyst 0.2 mmol; bath temperature 40–45 °C. [b] Solvent 50 mL, or Et_2O/THF 25 mL/25 mL. [c] Determined by analytical GC.

9,12-diiodo-*o*-carborane (**2**) without complicating side products. Finally, we show that the palladium-catalyzed coupling of Grignard reagents[4] is effective in converting these iodo compounds into B-alkylated *o*-carboranes, thus providing a convenient synthesis of 3-alkyl-*o*-carboranes and 9,12-dialkyl-*o*-carboranes.

3-Iodo-*o*-carborane (1). The overall strategy is to use the double displacement of iodide from boron triiodide by $Li_2[C_2B_9H_{11}]$ (**3**). As BI_3 would surely cleave the diethyl ether in which **3** is generated, the diethyl ether is removed after generation of **3** and, replaced with hexane. This is necessary to avoid formation of 3-ethoxy-*o*-carborane by reaction of **3** with I_2BOEt formed in the ether cleavage reaction.[2c] Addition of a hexane solution of BI_3 to the hexane solution of **3** gives **1** in 68% yield after a single crystallization from hexane.



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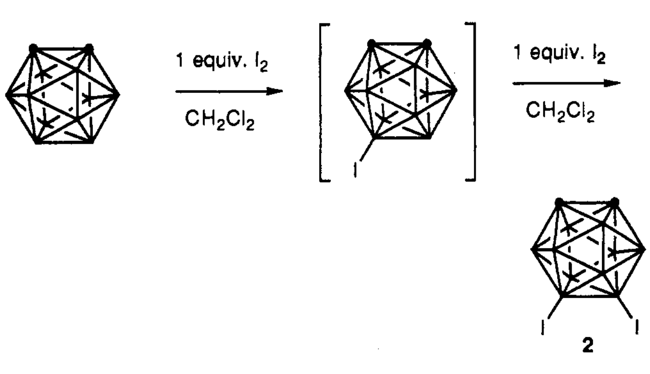
9,12-Diiodo-*o*-carborane (2). An extension of our method for making 9-iodo-*o*-carborane without complicating side products serves to generate 9,12-diiodo-*o*-carborane from this compound. The introduction of a single iodine at the 9-position does not sterically deactivate the adjacent 12-position to the point that substitution at other positions becomes competitive. Nor is the 9-iodine sufficiently electron-withdrawing so as to deactivate the adjacent 12-position. The 12-position remains the most active position in aromatic substitution, even with the 9-position occupied.[3a,5] In practice, 9-iodo-*o*-carborane need not be isolated. The procedure for producing 9-iodo-*o*-carborane is followed, in which *o*-carborane is refluxed in methylene chloride in the presence of 1 equiv of iodine for 4 h. At that time, an additional equivalent of iodine is added. This procedure produces pure **2** without overiodination.



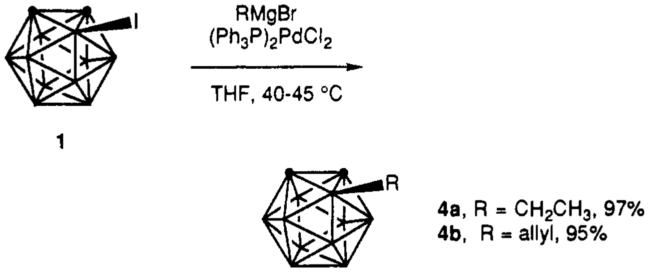
2

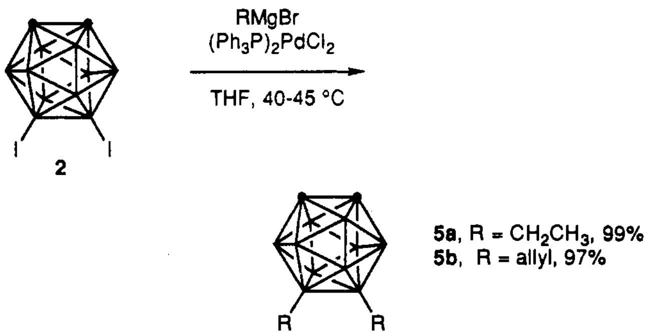
Table II. Solvent Effects on the Coupling of 3-Iodo-*o*-carborane with Allylmagnesium Chloride Catalyzed by $(Ph_3P)_2PdCl_2$[a]

solvent[b]	time, h	yield of 3-allyl-*o*-carborane,[c] %
ether	48	32.1
THF	24	94.6

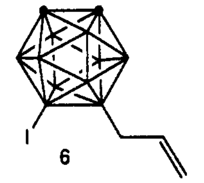
[a] 10 mmol of 3-iodo-*o*-carborane, 35 mmol of allylmagnesium chloride, and 0.2 mmol of $(Ph_3P)_2PdCl_2$. [b] Solvent 50 mL. [c] Isolated by column chromatography on silica gel.

Alkyl-*o*-carboranes. It has been shown that 9-iodo-*o*-carborane can be alkylated by Grignard reagents in a reaction catalyzed by phosphine complexes of palladium.[4] However, it has also been noted that bromo and chloro compounds are inert to these and other conditions.[4,6] Currently, 3-substituted *o*-carboranes are best synthesized through the reaction of **3** with alkyldichloroboranes.[7] With an easy route to **1** available, 3-alkyl compounds such as **4a** and **4b** can be simply made in over 95% yield using the procedure developed by the Zakharkin group[4] for other iodo carboranes. In similar fashion we have produced 9,12-dialkyl-*o*-carboranes **5a** and **5b** from **2** in over 97% yield.





Tables I and II show that tetrahydrofuran (THF) is a better solvent than ether for the reaction, even though the opposite is true for catalytic carbon–carbon coupling.[8] Further, gas chromatographic analysis of the reaction progress shows that 9-iodo-12-allyl-*o*-carborane (**6**) does not build up during the reaction.



6

The regiospecificity of the cross-coupling reaction rests on the analogy to the related reaction of aryl halides[8] first drawn by Zarharkin and co-workers.[4] In all our cases, the ^{13}C and ^{11}B NMR spectra are consistent with a regiospecific replacement of iodine for carbon, as the mechanistic analogy would demand.[4,8]

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Experimental Section

3-Iodo-*o*-carborane (1). $[Me_3NH][C_2B_9H_{12}]$ (5.0 g, 26 mmol) was placed in 50 mL of anhydrous ethyl ether in a 250-mL three-necked flask equipped with a magnetic stirrer, reflux condenser, and gas inlet and outlet. The system was slowly flushed with argon while the reaction was in progress. A solution of 2.5 M butyllithium in hexane (21.5 mL, 52 mmol) was added dropwise to the mixture with stirring at 0 °C. After the addition was completed, the reaction mixture was stirred at room temperature for an additional 2 h and then refluxed for 4 h. After the reaction mixture cooled to room temperature, all solvent was removed at the water pump. Anhydrous hexane (100 mL) was added with a syringe to the remaining solid. A solution of BI_3 in hexane was prepared from $LiBH_4$ (1.25 g, 67 mmol) and iodine (22.5 g, 88 mmol) in 50 mL of hexane by following Renner's procedure[9] and was added dropwise with stirring at 0 °C. The stirring was continued for another 6 h at room temperature after the addition was finished. The reaction mixture was hydrolyzed with 10 mL of water to decompose the excess boron triiodide. The organic layer was separated from the mixture in a separatory funnel, dried over $MgSO_4$, and then concentrated at the water pump. The resulting solid was purified by recrystallization from hexane to give 3-iodo-*o*-carborane (4.78 g, 68% yield). Mp: 82.5-83 °C. ^1H NMR (δ, $CDCl_3$): 3.87 (s, 2 H), 3.60-1.29 (m, 9 H). ^{13}C NMR (δ, $CDCl_3$): 59.66. MS [*m*/*e* (relative intensity)]: 272 (32), 271 (79), 270 (100), 269 (74), 268 (47), 267 (25), 144 (18). ^{11}B NMR (δ relative to $BF_3{\cdot}OEt_2$ = 0; positions quoted from hydrogen-decoupled spectra, multiplicities from hydrogen-coupled spectra): −1.44 (d, 2 B), −7.31 (d, 3 B), −11.19 (d, 3 B), −12.65 (d, 3 B), −29.47 (s, 1 B). Precise mass: calc for $C_2B_{10}H_{11}I$, 272.0838; found, 272.0845. Anal. Calc for $C_2B_{10}H_{11}I$: C, 8.89; H, 4.10; B, 40.04; I, 46.96. Found: C, 9.01; H, 4.28; B, 40.20; I, 46.92.

9,12-Diiodo-*o*-carborane (2). A. From 9-Iodo-*o*-carborane. A mixture of 9-iodo-*o*-carborane, produced by the procedure of Andrews[3] (1.08 g, 4 mmol), and I_2 (1.02 g, 4 mmol) in 30 mL of methylene chloride was stirred with a catalytic amount of $AlCl_3$ at 35 °C for 3.5 days. The mixture was poured into distilled water, and the water layer was extracted with 15 mL of ether. The organic layers were washed with 3 × 10 mL of aqueous $Na_2S_2O_3$ to remove the remaining I_2 and dried over $MgSO_4$. The filtered solvent was removed at the water pump. ^1H NMR spectroscopy of the resulting solid showed two components, starting material and **2** in the ratio 1:4.5. The crude product was purified by recrystallization from hexane to give pure **2** (1.27 g, 80.3% yield). Mp: 184.5-185.5 °C (lit.[5] 185-186 °C). ^1H NMR (δ, $CDCl_3$): 3.98 (s, 2 H), 3.90-1.40 (m, 9 H). ^{13}C NMR (δ, $CDCl_3$): 52.50. ^{11}B NMR (δ relative to $BF_3{\cdot}OEt_2$ = 0; positions quoted from hydrogen-decoupled spectra, multiplicities from hydrogen-coupled spectra): −5.99 (d, 2 B), −13.24 (d, 4 B), −14.50 (s, 2 B), −14.60 (d, 2 B).

B. From *o*-carborane. A mixture of *o*-carborane (10.35 g, 71 mmol), iodine (18.2 g, 71 mmol), and 0.53 g of $AlCl_3$ in 250 mL of CH_2Cl_2 was gently refluxed for 4 h. Iodine (18.2 g) was added slowly to this mixture. After the addition was completed, the reaction mixture was stirred at 45 °C for an additional 14 h. The reaction mixture was then poured into 20 mL of ice-cold water and the organic layer separated from the mixture. The water layer was extracted once with 50 mL of ether; the organic layers were washed with 5% aqueous Na_2CO_3 and distilled water and were dried over $MgSO_4$. The filtered solvent was removed under vacuum. Recrystallization of the crude product from a 6:1 hexanes:$CHCl_3$ mixture gave 25.8 g (91.8% yield) of **2**.

General Procedure for Cross-Coupling. To a stirred mixture of 10 mmol of 3-iodo-*o*-carborane (or 9,12-diiodo-*o*-carborane) and 0.2 mmol of L_2PdCl_2 in 25 mL of anhydrous THF at 0 °C was added 40 mmol (50 mmol in the case of 9,12-diiodo-*o*-carborane) of the appropriate Grignard reagent in 25 mL of THF. After the addition was completed, the reaction mixture was stirred at 40-45 °C (bath temperature) for 20-40 h. The reaction was checked by gas chromatography and was stopped when starting material was almost gone. The reaction mixture was then cooled to room temperature. An additional 100 mL of ether was added, and the excess Grignard reagent was destroyed by the dropwise addition of water. The water layer was washed with ether (3 × 15 mL). The combined organic layers were washed with 3 × 15 mL of 3% HCl solution and then water and dried over $MgSO_4$. The solvent was removed at the water pump. The crude product could be purified on a silica gel column, using hexane as eluting solvent.

3-Ethyl-*o*-carborane. After 16 h, a colorless liquid was produced in 97% yield. ^1H NMR (δ, $CDCl_3$): 3.41 (s, 2 H), 3.18-1.20 (m, 11 H), this signal including 1.54 (s, 2 H) and 1.07 (s, 3 H). ^{13}C NMR (δ, $CDCl_3$): 56.9, 12.5. MS [*m*/*e* (relative intensity)]: 174 (6.5), 173 (13), 172 (28), 171 (41), 170 (42), 169 (32), 83 (100). ^{11}B NMR (δ relative to $BF_3{\cdot}OEt_2$ = 0; positions quoted from hydrogen-decoupled spectra, multiplicities from hydrogen-coupled spectra): −2.35 (d, 3 B), −6.81 (s, 1 B), −8.66 (d, 2 B), −12.47 (d, 3 B), −13.87 (d, 2 B). Precise mass: calc for $C_4B_{10}H_{16}$, 174.2183; found, 174.2181.

3-Allyl-*o*-carborane. After 30 h, a colorless liquid was produced in 94.6% yield. ^1H NMR (δ, $CDCl_3$): 5.77 (m, 1 H), 4.99-4.93 (m, 2 H), 3.42 (s, 2 H), 3.20-1.02 (m, 11 H). ^{13}C NMR (δ, $CDCl_3$): 136.3, 116.4, 56.6, 14.0. MS [*m*/*e* (relative intensity)]: 186 (36), 185 (86), 184 (100), 183 (79), 182 (60), 169 (32), 156 (26). ^{11}B NMR (δ relative to $BF_3{\cdot}OEt_2$ = 0; positions quoted from hydrogen-decoupled spectra, multiplicities from hydrogen-coupled spectra): −2.57 (d, 3 B), −6.77 (s, 1 B), −8.72 (d, 2 B), −12.59 (d, 2 B), −13.66 (d, 2 B). Precise mass: calc for $C_5B_{10}H_{16}$, 184.2255; found, 184.2259.

9,12-Diethyl-*o*-carborane. After 24 h, a low-melting crystal (mp 41.5-42.5 °C) was obtained in 99% yield. ^1H NMR (δ, $CDCl_3$): 3.38 (s, 2 H), 3.20-1.05 (m, 9 H), 0.86 (d, 3 H), 0.70 (s, 2 H). ^{13}C NMR (δ, $CDCl_3$): 48.2, 14.0. MS [*m*/*e* (relative intensity)]: 202 (20), 201 (48), 200 (56), 185 (31), 171 (100), 143 (93). ^{11}B NMR (δ relative to $BF_3{\cdot}OEt_2$ = 0; positions quoted from hydrogen-decoupled spectra, multiplicities from hydrogen-coupled spectra): 9.28 (s, 2 B), −8.66 (d, 2 B), −14.75 (d, 4 B), −16.74 (d, 2 B). Precise mass: calc for $C_6B_{10}H_{20}$, 202.2568; found, 202.2574.

9,12-Diallyl-*o*-carborane. After 32 h, a slightly yellow liquid was obtained in 96.8% yield. ^1H NMR (δ, $CDCl_3$): 5.79 (m, 1 H), 4.83-4.76 (m, 2 H), 3.41 (s, 2 H), 3.20-1.05 (m, 10 H). ^{13}C NMR (δ, $CDCl_3$): 140.8, 112.4, 48.8. MS [*m*/*e* (relative intensity)]: 226 (11), 225 (28), 224 (33), 210 (90), 201 (100), 194 (99), 179 (48). ^{11}B NMR (δ relative to $BF_3{\cdot}OEt_2$ = 0; positions quoted from hydrogen-decoupled spectra, multiplicities from hydrogen-coupled spectra): 7.19 (s, 2 B), −8.91 (d, 2 B), −14.61 (d, 4 B), −16.59 (d, 2 B). Precise mass: calc for $C_8B_{10}H_{20}$, 225.2532; found, 225.2529.

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Oligomeric Gallium Amide/Hydride Complexes, $[H_2Ga_2\{(NPr^iCH_2)_2\}_2]$ and $[H_5Ga_3\{(NMeCH_2)_2\}_2]$, via Hydrometalation and Metalation

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and Colin L. Raston*[,1b]

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There has been recent interest in the chemistry of gallane.[2-5] This includes the utility of tertiary amine adducts, such as H_3GaNMe_3, as precursors for the formation of gallium nitride using vapor deposition technology with nitrogen as a carrier gas[6] and also for the formation of the simple gallium amide $[\{H_2GaNH_2\}_3]$ from H_3GaNMe_3 and ammonia, which can be converted to gallium nitride.[4] We report the synthesis and characterization (X-ray, NMR) of some new gallium/hydride/amide complexes derived from reactions of H_3GaNMe_3 with a bis(imine) and a bis(secondary amine); 1,4-diisopropyl-1,4-diazabutadiene (= Pr^{i}DAB) undergoes dihydrogallation yielding a dimeric species,

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