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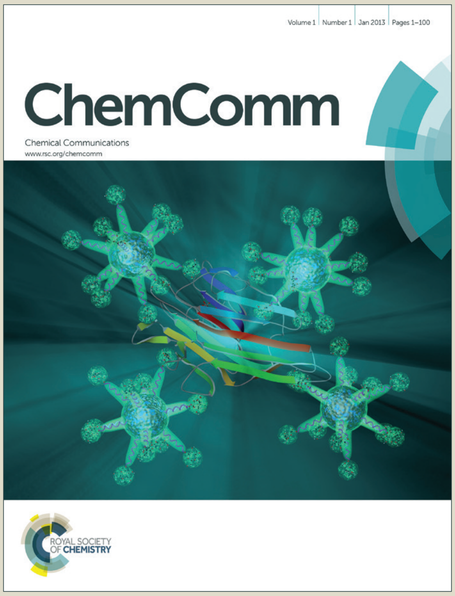

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Platinum catalyzed sequential hydroboration of decaborane: a facile approach to poly(alkenyldecaborane) with decaborane in mainchain

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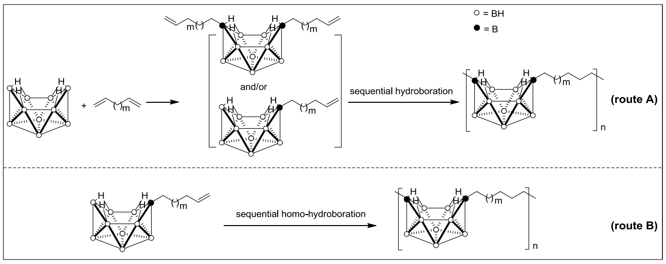
The catalytic sequential hydroboration of decaborane for the synthesis of poly(organodecaborane) with decaborane in mainchain is reported for the first time. Under the platinum catalytic system, the poly(6-hexenyldecaborane) and poly(6-norbornenyldecaborane) were obtained with well-defined structure and moderate yield, thermogravimetric analysis demonstrated the char yields are 73% and 82%, respectively.

Decaborane-containing polymers are a kind of important materials, and have extensive applications in heat-resistance materials and ceramic precursors.[1] Using coordination polymerization and olefin metathesis polymerization, polymers branched with decaborane have been prepared, and display excellent thermo-resistance property as well as high char yield.[2] However, the synthesis of poly(alkenyldecaborane)s with decaborane in mainchain and evaluated their thermal properties have not been reported yet.

As a boron hydride cluster, decaborane displays unique hydroboration reaction activity with olefin unlike other simple boranes (such as diborane, 9-BBN etc.).[3, 4] Pioneering works have demonstrated that either early transition metal (Ti)[4a,e] or late transition metal (Pt)[4d] catalyst could catalyze the hydroboration of decaborane with olefins, which offered an efficient approach for the synthesis of 6-alkyl(alkenyl)decaborane and 6, 9-dialkyldecaborane, respectively. Inspired by these results, we proposed that the direct sequential hydroboration of decaborane with non-conjugated diene or homo-hydroboration of alkenyldecaborane would be a powerful method to poly(alkenyldecaborane) with decaborane in mainchain.

As depicted in Scheme 1, there are two protocols for the synthesis of poly(alkenyldecaborane) with decaborane in mainchain. In our initial studies towards the project, we attempted to prepare poly(alkenyldecaborane) via **route A**. Through many efforts, the desired polymerization could not be realized and gave a complicated mixture. This result indicated that the challenge to get main-chain decaborane-containing polymers lies in the synthesis of compounds with well-defined structures and high purity, and enabling controlled polymerization. To address this problem, we turned our attention to **route B**, which use alkenyldecaborane as polymerizable monomer. The alkenyldecaborane has two advantages. The one is that it can be synthesized with high purity. Another is that its polymerization proceeds via homo-hydroboration, which makes the polymerization more controllable, and thus avoids side reactions.

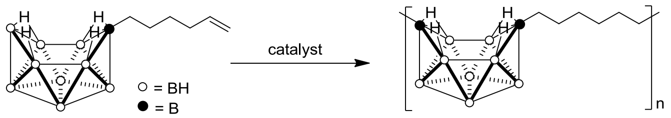


Scheme 1. Sequential hydroboration for the synthesis of poly(alkenyldecaborane)

Sneddon and coworkers have demonstrated the Lewis acidity of decaborane and its derivatives are very significant for hydroboration. The reduced Lewis acidity of monoalkyldecaboranes would hinder the secondary hydroboration to synthesis 6, 9-dialkyldecaboranes except using platinum catalysts.[4d, 5] In this regard, we choose 6-hexenyldecaborane (HD) as model adduct and kinds of platinum catalyst to screen conditions, and the results are summarized in Table 1.

With toluene as solvent, the sequential hydroboration can be proceed at 100°C in the presence of catalytic amount of $PtBr_2$ under nitrogen, and only trace amount of poly(6-hexenyldecaborane)(PHD) was afforded. The reason for this result is that the Friedel-Crafts reaction of toluene with 6-hexenyldecaborane predominant the reaction. (entry 1) To suppress the Friedel-Crafts reaction, we increased the concentration of 6-hexenyldecaborane, and the desired polymer was obtained with 6% yield. (entry 2) Next, we used more inert solvents such as fluorobenzene and chlorobenzene as medium, and found the hydroboration proceeded sluggish. (entry 3 and 4) To our delight,

Table 1. Pt-catalyzed sequential hydroboration of 6-hexyldecaborane[a]

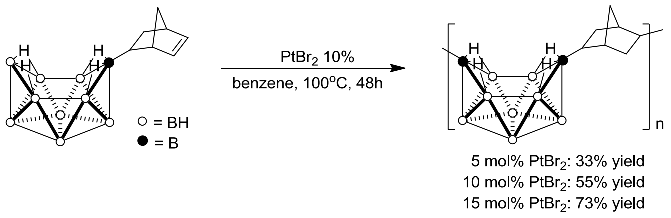


entry	catalyst	solvent	% yield[b]
1	$PtBr_2$	toluene[c]	trace
2	$PtBr_2$	toluene	6
3	$PtBr_2$	fluorobenzene	trace
4	$PtBr_2$	chlorobenzene	trace
5	$PtBr_2$	benzene	35
6	H_2PtCl_6	benzene	5
7	PtO_2	benzene	trace
8	$PtCl_2$	benzene	trace

[a] Reaction conditions: 6-hexyldecaborane (0.485 mmol), catalyst (0.0485mmol) and 0.1 mL solvent at 100°C under N_2 for 48h. [b] yield based on 6-hexyldecaborane. [c] with 0.5 mL toluene.

when the reaction was conducted in benzene, the hydroboration proceeded smoothly and gave the corresponding polymer with 35% yield. (entry 5) Other platinum source such as H_2PtCl_6, PtO_2 and $PtCl_2$ all exhibited lower catalytic activity. (entries 6-8)

Based on the above optimized conditions, (Table1, entry 5) the scope of the reaction was then examined. When 6-norbornenyldecaborane (ND) was employed, the desired poly(6-norbornenyldecaborane) (PND) was afforded with 55% yield. ^1H NMR indicated the hydroboration reaction occurs in 2-position of double bond.[2c,6] Further increasing the loading amount of $PtBr_2$ from 10mol% to 15mol%, the yield of corresponding polymer was improved to 73%, and number average molecular weight was greatly elevated by about two times. When the polymerization was carried out with 5mol% $PtBr_2$, the resulted polymer was obtained with 33% yield, and number average molecular weight was reduced distinctly. (Scheme 2, Table 2) These results imply a step polymerization process.

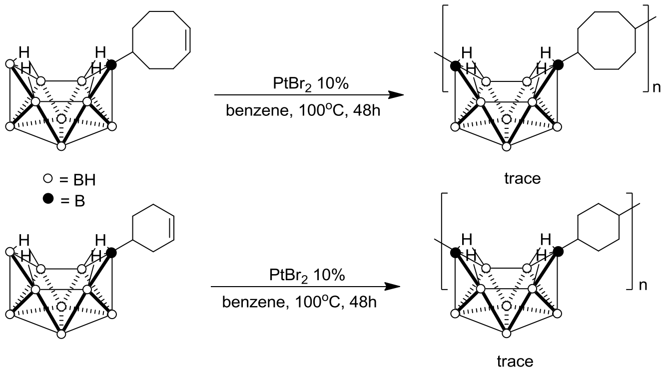


Scheme 2. Polymerization of 6-norbornenyldecaborane

Table 2. Polymerization of HD and ND with $PtBr_2$

monomer	$PtBr_2$ (%)	yield (%)	M_n	M_w	PDI
HD	10	35	4440	9250	2.08
ND	5	33	3130	9700	3.09
ND	10	55	5870	10100	1.72
ND	15	73	11060	19560	1.77

However, when 6-cyclooctenyldecaborane and 6-cyclohexenyldecaborane was subjected to the standard conditions, the polymerization scarcely occurred, and only trace amount of the desired polymer was afforded. (Scheme 3) Unfortunately, many efforts to improving the yield were all failed.



Scheme 3. Polymerization of 6-cyclooctenyldecaborane and 6-cyclohexenyldecaborane

As shown in Figure 1, the thermogravimetric analysis (TGA) studies of PHD and PND (with *Mn* values of 4440Da and 11060Da, respectively) indicated that the weight loss of PND begins at about 50°C and that of PHD near 120°C, and the nearly complete weight loss of PHD at 700°C and of PND at 600°C to give the final char yields with 73% and 82%, respectively. This result demonstrated the poly(organodecaborane) with decaborane in mainchain displays excellent thermal property as well as char yield compare to that of poly(organodecaborane) branched with decaborane.[2a, b]

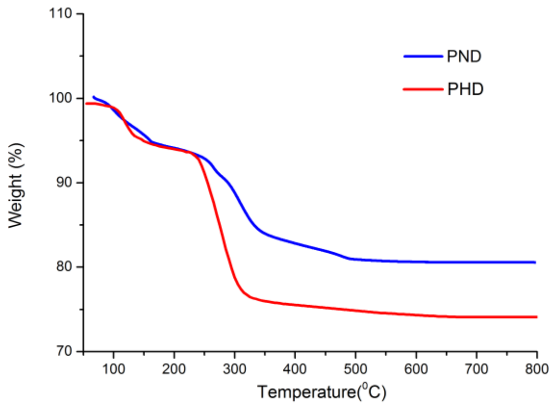


Figure 1. Thermogravimetric analysis (TGA) study of PHD and PND under argon.

Conclusions

In summary, we have developed a new method for the synthesis of poly(alkenyldecaborane) with decaborane in mainchain via platinum catalyzed hydroboration reaction for the first time. The poly(6-hexenyldecaborane) and poly(6-norbornenyldecaborane) were obtained with moderate yield, and the maximum *Mn* of PND reached to 11060Da using 15 mol% $PtBr_2$. TGA studies demonstrated that the char yield of PND was up to 82%. The application of the methodology for synthesis of other poly(organodecaborane)s are ongoing in our group.

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Notes and references

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1 a) P. Jaromir, *Chem. Rev.* **1992**, *92*, 269. b) V. I. Bregadze, *Chem. Rev.* **1992**, *92*, 209. c) M. M. Guron, X. Wei, D. Welna, N. Krogman, M. J. Kim, H. Allcock, L. G. Sneddon *Chem. Mater.* **2009**, *21*, 1708.

2 a) X. Wei, P. J. Carroll, L. G. Sneddon, *Organometallics* **2004**, *23*, 163. b) L. G. Sneddon, M. J. Pender, K. M. Forsthoefel, U. Kusari, X. Wei, *J. Eur. Ceram. Soc.* **2005**, *25*, 91. c) X. Wei, P. J. Carroll, L. G. Sneddon, *Chem. Mater.* **2006**, *18*, 1113.

3 H. C. Brown, *Organic Synthesis via Borane*; Wiley-Interscience: New York, 1975.

4 a) K. Mazighi, P. J. Carroll, L. G. Sneddon, *Inorg. Chem.* **1993**, *32*, 1963. b) D. F. Gaines, A. N. Bridges, *Organometallics* **1993**, *12*, 2015. c) A. N. Bridges, D. R. Powell, J. A. Dopke, J. M. Desper, D. F. Gaines, *Inorg. Chem.* **1998**, *37*, 503. d) M. J. Pender, T. Wideman, P. J. Carroll, L. G. Sneddon, *J. Am. Chem. Soc.* **1998**, *120*, 9108. e) M. J. Pender, P. J. Carroll, L. G. Sneddon, *J. Am. Chem. Soc.* **2001**, *123*, 12222. f) U. Kusari, Y. Li, M. G. Bradley, L. G. Sneddon, *J. Am. Chem. Soc.* **2004**, *126*, 8662. g) U. Kusari, P. J. Carroll, L. G. Sneddon, *Inorg. Chem.* **2008**, *47*, 9203.

5 X. He, J. F. Hartwig, *J. Am. Chem. Soc.* **1996**, *118*, 1696.

6 The ^{1}H NMR is compared with that of 6, 6’-(2,5-Norbornyl)-$(B_{10}H_{13})_2$.