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Carborane as a Tunable Tag for Ru Catalysts: Generating an Anion-Appended Recyclable and Robust Catalyst Suitable for the Noncovalent Binding Concept

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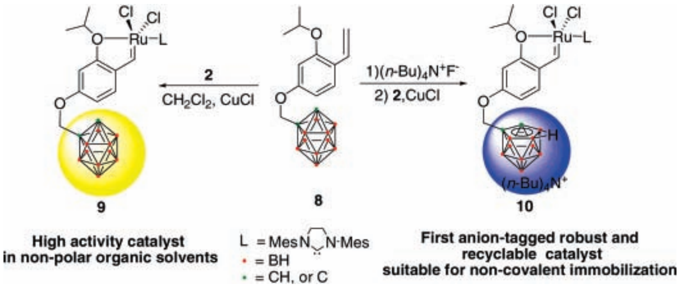
ABSTRACT



Ruthenium carbene complexes 9 with a *closo*-1,2-$C_2B_{10}H_{11}$ tag and 10 with an ionic [*nido*-7,8-$C_2B_9H_{11}$]$^-$ tag were synthesized. Both 9 and 10 are highly reactive catalysts for olefin metathesis reactions. Importantly, 10 is a robust and recyclable anion-appended catalyst that was suitable for noncovalent binding with many cationic resins. At least ten recycles were achieved for RCM of the selected substrate using 10 as the catalyst in ionic liquids.

Immobilization of homogeneous catalysts on support materials is very attractive, as it could offer more practical advantages for such types of catalysts.[1] Compared to the traditional covalent-binding immobilizations, the recently developed noncovalent method via electrostatic interactions is simpler, is more convenient for recycling and reuse of the support materials, and is quite apt for industrial continuous-flow processes.[2] However, it requires cation- or anion-appended homogeneous catalysts or catalysts with precursors for appending anions or cations.

Since the discovery of well-defined modern ruthenium catalysts **1**−**4**,[3] olefin metathesis has gained a position of interesting significance.[4] Various strategies have been employed to reuse and recycle these catalysts.[5] One such

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(2) (a) Horn, J.; Michalek, F.; Tzschucke, C. C.; Bannwarth, W. *Top. Curr. Chem.* **2004**, *242*, 43−77. (b) Kirschning, A.; Jas, G. *Top. Curr. Chem.* **2004**, *242*, 209−241. (c) Jas, G.; Kirschning, A. *Chem.−Eur. J.* **2003**, *9*, 5708−5723. (d) Fletcher, P. D. I.; Haswell, S. J.; Pombo-Villar, E.; Warrington, B. H.; Watts, P.; Wong, S. Y. F.; Zhang, X. *Tetrahedron* **2002**, *58*, 4735−4757. (e) Kirschning, A.; Solodenko, W.; Mennecke, K. *Chem.−Eur. J.* **2006**, *12*, 5972−5990.

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(4) (a) Grubbs, R. H., Ed. *Handbook of Metathesis*; Wiley-VCH: Weinheim, Germany, 2003; Vols. 1−3. (b) Schrock, R. R.; Hoveyda, A. H. *Angew. Chem., Int. Ed.* **2003**, *42*, 4592−4633. (c) Trnka, T. M.; Grubbs, R. H. *Acc. Chem. Res.* **2001**, *34*, 18−29. (d) Furstner, A. *Angew. Chem., Int. Ed.* **2000**, *39*, 3012−3043. (e) Grubbs, R. H.; Chang, S. *Tetrahedron* **1998**, *54*, 4413−4450. (f) Schuster, M.; Blechert, S. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2037−2056.

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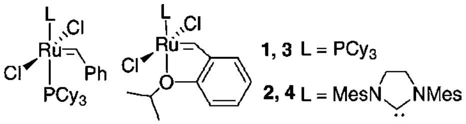
strategy is to introduce a cation-appended ligand on the ruthenium metal center, which is being intensively used for immobilization of transition metal catalysts.[6] For example, Ru carbene complexes can be made soluble in the aqueous phase using cationic phosphine ligands.[7] Introduction of a cationic imidazolium to Hoveyda's boomerang ligand to make the catalyst suitable for use in ionic liquids (ILs)[8] and binding the ammonium-substituted Hoveyda−Grubbs catalyst to commercial resins[9] are the other methods adopted for reuse and recycle. However, reports on anion-appended Ru carbene complexes are rare. In view of the fact that many polymers are cationic resins, there is a strong desire for synthesizing Ru carbene complexes incorporating anion-appended ligands for anchoring the complexes to such cationic resins through noncovalent binding. But, this remained a challenging issue, partially due to the high sensitivity of the ruthenium carbene to many different anions via ligand exchange protocol.[10]

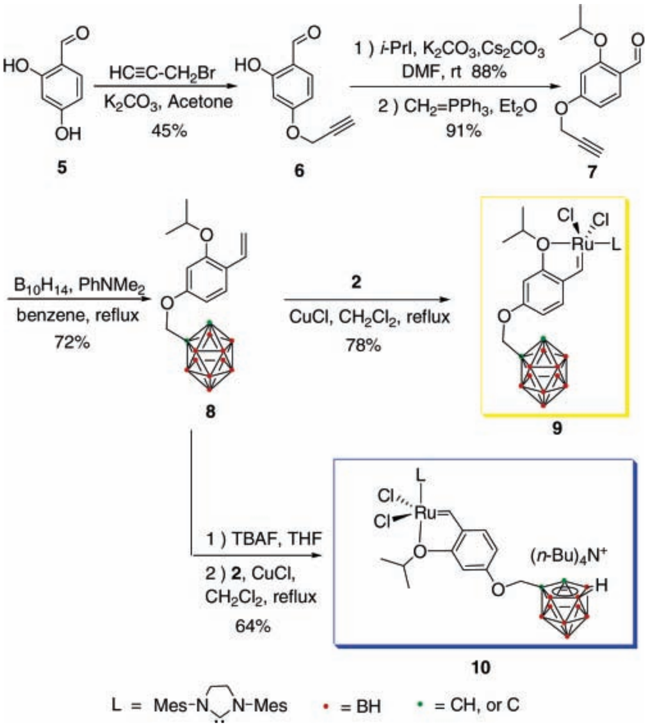


1, 2 **3, 4**

Carborane of formula o-$C_2B_{10}H_{12}$, a commercially available derivative of boron hydrides, has been intensively used for pharmaceutical purposes,[11] in material chemistry,[12] and in metallocarborane chemistry.[13] Under strong basic conditions or in the presence of n-$Bu_4N^+F^-$, a formal $\{BH\}^-$ vertex can be removed selectively from the neutral o-$C_2B_{10}H_{12}$ to form $[nido\text{-}7,8\text{-}C_2B_9H_{12}]^-$ (named the carbollide anion).[14] It is thought worthwhile to make use of this stable anion for the noncovalent immobilization of the ruthenium carbene catalyst to the cationic supports.

With this objective in mind, we have designed and synthesized a carborane-tagged isopropoxy styrene ligand, which on binding to the Ru carbene complex would render it with some different and useful properties, and more importantly, it may potentially offer a robust and recyclable catalyst incorporating anion-appended ligands suitable for noncovalent binding to cationic support materials. Herein, we report the synthesis and the activity of carborane-tagged ruthenium catalyst **9** and the carbollide-tagged ruthenium catalyst **10** in the ring-closing metathesis reaction (Scheme 1).

Scheme 1. Synthesis of Ruthenium Catalysts **9** and **10**



As illustrated in Scheme 1, commenced from the commercially available 2,4-dihydroxybenzaldehyde **5**, the synthesis of *closo*-1,2-carborane-tagged ligand **8** was prepared in a straightforward manner in good yield. Treatment of **8** with **2** in the presence of CuCl in CH_2Cl_2 at 40 °C, as described by Hoveyda and co-workers,[4c] resulted in the exchange of the styrene group to give neutral *closo*-1,2-carborane-tagged ruthenium complex **9** in good yield (78%). Reaction of **8** with tetrabutylammonium fluoride (TBAF) in mixture solvents of THF and water opens the carborane cage to give an intermediate, followed by ligand exchange with **2** which afforded the anionic $[nido\text{-}7,8\text{-}C_2B_9H_{11}]^-$-tagged ruthenium complex **10** in 64% yield as greenish crystalline solid.

Interestingly, **9** and **10** have very different solubility due to the different properties of the carborane tag, which could be used for different tasks. Compound **9** exhibits very good solubility in nonpolar solvents, such as benzene, toluene, and hexanes, while **10** is very soluble in polar solvents, such as alcoholic solvents, acetone, and acetyl acetate.

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(5) Reviews: (a) Kingsbury, J. S.; Hoveyda, A. H. In *Polymeric Materials in Organic Synthesis and Catalysis*; Buchmeiser, M. R., Ed.; Wiley-VCH: Weinheim, 2003; p 467. (b) Buchmeiser, M. R. *New J. Chem.* **2004**, *28*, 549−557. (c) Clavier, H.; Grela, K.; Kirschning, A.; Mauduit, M.; Nolan, S. P. *Angew. Chem., Int. Ed. Engl.* **2007**, DOI: 10.1002/anie 200605099.

(6) Miao, W.; Chan, T. H. *Acc. Chem. Res.* **2006**, *39*, 897−908.

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(9) Michrowska, A.; Mennecke, K.; Kunz, U.; Kirschning, A.; Grela, K. *J. Am. Chem. Soc.* **2006**, *128* (40), 13261−13267.

(10) (a) Tanaka, K.; Bohm, V. P. W.; Chadwick, D.; Roeper, M.; Braddock, D. C. *Organometallics* **2006**, *25*, 5696−5698. (b) Monfette, S.; Fogg, D. E. *Organometallics* **2006**, *25*, 1940−1944. (c) Vygodskii, Y. S.; Shaplov, A. S.; Lozinskaya, E. I.; Filippov, O. A.; Shubina, E. S.; Bandari, R.; Buchmeiser, M. R. *Macromolecules* **2006**, *39*, 7821−7830.

(11) For an excellent review, see: Hawthorne, M. F. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 950−984.

(12) Wei, X.; Carroll, P. J.; Sneddon, L. G. *Organometallics* **2006**, *25*, 609−621.

(13) (a) Xie, Z. *Coord. Chem. Rev.* **2006**, *250*, 259−272. (b) Xie, Z. *Acc. Chem. Res.* **2003**, *36*, 1−9. (c) Saxena, A. K.; Hosmane, N. S. *Chem. Rev.* **1993**, *93*, 1081−1124.

Both the *closo*-1,2-carborane-tagged Ru carbene **9** and the anionic [*nido*-7,8-$C_2B_9H_{11}$]$^-$-tagged **10** are highly active catalysts for ring-closing metathesis (RCM) reactions. Diethyl diallymalonate **11** was chosen as the test diene to investigate the catalytic activity of **9** and **10** in its RCM. The relative conversion rates for RCM by **9** and **10** under different conditions are illustrated in Figure 1. At 0 °C, **9** exhibits better performance than **10**, showing that the *closo*-1,2-carborane motif has less effect on the Ru metal center than [*nido*-7,8-$C_2B_9H_{11}$]$^-$. This could be due to the competitive coordination to the nearby Ru center of the anionic [*nido*-7,8-$C_2B_9H_{11}$]$^-$ tag with the vinyl group of **11**. Nevertheless, at 30 °C the RCM activity of **9** and **10** was enhanced and high conversions were achieved (>98%) after 2 h, which is comparable with those of **4** under similar reaction conditions.[15]

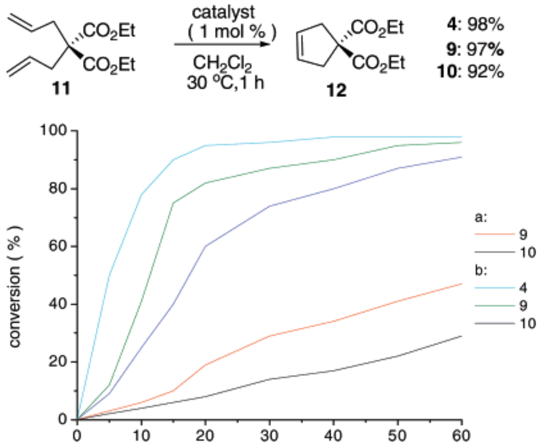
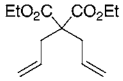
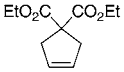
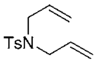
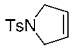
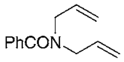
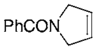
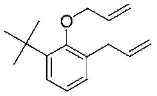
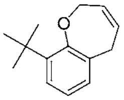
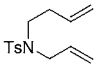
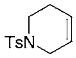
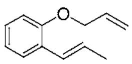
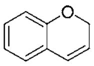
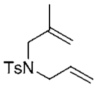
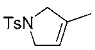
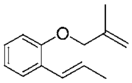
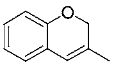
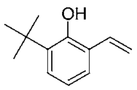
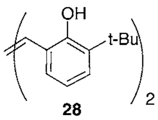
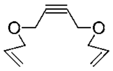
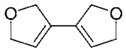


Figure 1. Relative conversion rates of **9** and **10** using 1 mol % of catalyst in CH_2Cl_2: (a) at 0 °C; (b) at 30 °C.

Although the Ru carbene complex bearing an anionic phosphine ligand has been reported,[7a] to the best of our knowledge, ***10*** *is the first anion-appended Ru carbene catalyst that possesses high activity to RCM reaction.* Further study showed that ring closure of N-protected substrates or oxygen-containing substrates leading to either a five-, six-, or seven-membered structure with a di- or trisubstituted double bond was obtained in high conversions (>95%) by either **9** or **10**. Even the cross metathesis of steric bulk-substituted vinyl phenol **25** was also achieved in good conversion for both **9** and **10** (see Table 1).

Moreover, the anionic [*nido*-7,8-$C_2B_9H_{11}$]$^-$-tagged **10** is a robust and recyclable RCM catalyst. Both **9** and **10** were evaluated for their performance toward the RCM of **13** in 1-butyl-3-methylimidazolium hexafluorophosphate (BMI·PF_6) ionic liquids (ILs). As shown in Table 2, with low catalyst loading (2.5%), the anionic [*nido*-7,8-$C_2B_9H_{11}$]$^-$-tagged catalyst **10** can be recycled and reused at least 10 times with only a slight decrease in activity with respect to the activity for the first run, which is comparable to those of the cation-appended ruthenium carbene catalysts. In contrast, a dramatic decrease in the conversion of **13** was found after the first run when **9** was used to promote RCM in ILs. The result clearly indicates that **10** was binding into the ILs via electrostatic interactions though the anionic [*nido*-7,8-$C_2B_9H_{11}$]$^-$ tag and thus solves the leaching problem that has happened for **9** during the recycle and reuse of the catalyst.

Table 1. Application of Catalyst **9** and **10** on Different Substrates[a]

entry	substrate	product	cat.	time	f. convn.
1	 **11**	 **12**	**9**	4 h	> 99%
			10	4 h	> 99%
2	 **13**	 **14**	**9**	12 h	> 99%
			10	12 h	94%
3	 **15**	 **16**	**9**	4.5 h	> 99%
			10	2.5 h	> 99%
4	 **17**	 **18**	**9**	12 h	98%
			10	12 h	94%
5	 **19**	 **20**	**9**	12 h	96%
			10	8.5 h	96%
6	 **21**	 **22**	**9**	24 h	91%
			10	24 h	> 99%
7	 **23**	 **24**	**9**	5 h	> 99%
			10	5.5 h	98%
8	 **25**	 **26**	**9**	20 h	> 99%
			10	5 h	> 99%
9	 **27**	 **28**	**9**	3 h	75%
			10	2 h	73%
10	 **29**	 **30**	**9**	5 h	> 98%
			10	5 h	> 98%

[a] Reactions were conducted at 30 °C using 0.5 mol % of catalyst in CH_2Cl_2.

In summary, we have developed *closo*-1,2-carborane-tagged Ru carbene **9** and robust and recyclable [*nido*-7,8-

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(14) (a) Wiesboeck, R. A.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1964**, *86*, 1642−1643. (b) Garrett, P. M.; Tebbe, F. N.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1964**, *86*, 5016−5017. (c) Hawthorne, M. F.; Young, D. C.; Garrett, P. M.; Owen, D. A.; Schwerin, S. G.; Tebbe, F. N.; Wegner, P. A. *J. Am. Chem. Soc.* **1968**, *90*, 862−868. (d) Fox, M. A.; Gill, W. R.; Herbertson, P. L.; MacBride, J. A. H.; Wade, K.; Colquhoun, H. M. *Polyhedron* **1996**, *15*, 565−571. (e) Tomita, H.; Luu, H.; Onak, T. *Inorg. Chem.* **1991**, *30*, 812−815.

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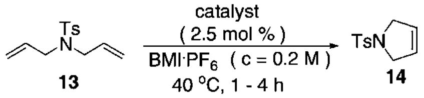
Table 2. Comparative Recycling and Reuse of **9** and **10** in BMI·PF_6



	cycle (% convn.)									
catalyst	1	2	3	4	5	6	7	8	9	10
9	>98	30	–	–	–	–	–	–	–	–
10	>98^a	>98^a	>98^a	>98^a	>97^a	>97^a	>97^a	>97^a	>97^b	>95^c

Reaction time for each run: [a] 1 h; [b] 2 h; [c] 4 h.

$C_2B_9H_{11}]^-$-tagged **10** which is suitable for the noncovalent binding concept. Given the growing interest in the development of immobilization of catalyst via electrostatic interactions for different tasks in organic synthesis, the anionic [*nido*-7,8-$C_2B_9H_{11}]^-$ tagging strategy described here could be applied to design other transition-metal-based catalysts. Studies on the application of **10** with other cationic support materials are currently underway in this lab.

Acknowledgment. This work was supported by Tianjin University.

Supporting Information Available: Experimental details and analytical data for this work described (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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