

Synthesis and Reactivity of a Zwitterionic Palladium Allyl Complex Supported by a Perchlorinated Carboranyl Phosphine

Jess Estrada,[†] David H. Woen,[†] Fook S. Tham,[†] Garret M. Miyake,[‡] and Vincent Lavallo^{*,†}[†]Center for Catalysis, Department of Chemistry University of California—Riverside, Riverside, California 92521, United States[‡]Department of Chemistry and Biochemistry, University of Colorado—Boulder, Boulder, Colorado 80309, United States

S Supporting Information

ABSTRACT: A zwitterionic palladium complex of a phosphine bearing a perchlorinated carba-*closo*-dodecaborate anion as a ligand substituent is reported. A single-crystal X-ray diffraction study reveals that, in the solid state, one of the chlorides of the carborane cage occupies a coordination site of the square-planar complex. However, in solution, the P–carborane bond of the ligand is rapidly rotating at temperatures as low as $-90\text{ }^{\circ}\text{C}$, which demonstrates the carborane substituent's weak coordinative ability even though this anion is covalently linked to the phosphine ligand. The complex is thermally stable and catalyzes the vinyl addition polymerization of norbornene.

The availability of a diverse array of ligand frameworks is critical for the development of effective homogeneous catalysts. One of the most useful classes of ligands is monodentate tertiary phosphines. Such ancillary ligands are typically constructed with combinations of ubiquitous alkyl and aryl groups. An interesting alternative to classical alkyl and aryl ligand R groups is polyhedral carboranes.¹ The most common carboranes used in phosphine design are derived from icosahedral dicarbaborane clusters (C_2B_{10}).^{1a,c,2} Because of its ready availability, the *o*-carborane isomer **1** (Figure 1) of these clusters is most often implemented. While this cluster offers a variety of interesting characteristics, such as an essentially spherical steric profile and the ability to form H–H hydrogen bonds,^{1a} it exhibits reactivity that may not be desirable for catalysis, such as facile B–H cyclometalation and vertex extrusion

reactions to afford *nido*-carboranes **2** (Figure 1). The latter property has been utilized by Teixidor et al.³ to create a family of anionic phosphines, bearing *nido*-carborane substituents, that exhibit unique coordination chemistry. Compared to icosahedral dicarbaboranes, isoelectronic carba-*closo*-dodecaborate clusters **3**^{1b} (CB_{11}^- ; Figure 1) are far more inert, particularly when polyhalogenated. Furthermore, these clusters are among the weakest coordinating anions known and have allowed for the preparation of many exotic cations⁴ and extraordinarily active systems for silylium catalysis.⁵

Recently, we reported the first transition-metal complexes [gold(I) and iridium(I)] of phosphines containing carbon-functionalized carba-*closo*-dodecaborates as ligand substituents.⁶ When these phosphines react with metal precursors, ligand coordination as well as salt metathesis to produce zwitterionic species is observed. The previously reported zwitterionic gold complex,^{6a} which is supported by the phosphine **4** (Figure 1), bearing a perchlorinated carborane anion, catalyzes the hydroamination of alkynes with amines with unprecedented activity. More recently, we have developed the synthetic methodology to access both dianionic symmetrical and monoanionic unsymmetrical carboranyl N-heterocyclic carbenes (NHCs).⁷

One of the applications we envision utilizing such ligands for is the design of single-component late-metal olefin polymerization catalysts analogous to systems supported by phosphine sulfonates **5** (Figure 1).⁸ Initially discovered by Drent et al.^{8b,c} and extensively investigated by Nozaki et al.^{8d–h} and Jordan et al.,^{8i–m} palladium-based olefin polymerization catalysts supported by ligands **5** produce unusual highly linear polyethylene as well as copolymers with high polar monomer content. This unique behavior is proposed to arise from pairing a weakly coordinating sulfonate moiety with a *cis*-binding phosphine. Kim and Jordan⁹ and Piers et al.¹⁰ have independently reported related systems that implement phosphines **6** that contain a tetracoordinate trifluoroborate moiety in lieu of a sulfonate group (Figure 1). The structure of carboranyl phosphine **4** is similar to those of **5** and **6** in that it contains a weakly coordinating anion proximal to the phosphine center. Here we report our initial investigation into the synthesis of a zwitterionic palladium complex supported by **4** and its reactivity with several simple olefin substrates.

For this first investigation, we chose to target the palladium allyl complex **7** (Figure 2) because the allyl moiety should bring stability to the complex, compared to a more reactive metal alkyl.

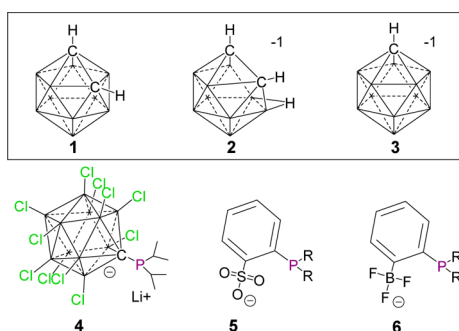


Figure 1. (top) *o*-Carborane **1**, nido anion **2**, and carba-*closo*-dodecaborate anion **3** (unlabeled vertices = B–H). (bottom) Representations of anionic carboranyl phosphine **4** (unlabeled vertices = B), phosphine sulfonates **5**, and trifluoroborate phosphines **6**.

Received: March 12, 2015

Published: May 12, 2015

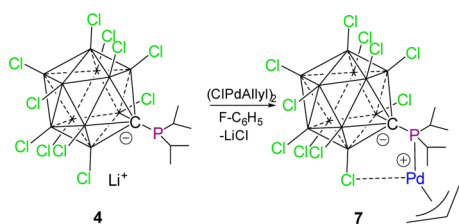


Figure 2. Synthesis of complex 7.

Hence, ligand **4** was reacted with $(\text{CIPd allyl})_2$ in $\text{F-C}_6\text{H}_5$, whereupon a precipitate formed (**7**/LiCl) over 30 min. After the precipitate was collected, the solid was dried and extracted with CH_2Cl_2 (to remove insoluble LiCl) to afford **7** in 97% yield. Analysis of **7** by ^{31}P NMR spectroscopy shows the clean formation of a single new phosphorus-containing species (complex, +117.6 ppm; ligand, +77.3 ppm). At ambient temperature, the ^{11}B NMR spectrum of **7** shows a 1:5:5 ratio of resonances, indicating that the clusters local C_{5v} symmetry is not disrupted. This suggests that the carborane anion is rotating rapidly about the P–carborane bond and is weakly coordinating even though it is projected into the coordination sphere of the metal. Indeed, variable-temperature ^{11}B NMR spectroscopy shows that the cluster is freely rotating down to temperatures as low as -90°C . This behavior is in contrast to a recent report^{6b} of a zwitterionic iridium complex, bearing the parent $\text{CB}_{11}\text{H}_{11}$ ligand substituent, that shows coordinative interactions in solution and in the solid state. The ^1H NMR spectrum of **7** displays the expected signals for diastereotopic isopropyl phosphine substituents as well as three broad resonances for the fluxional allyl group. Variable-temperature NMR analysis (-50°C) allows resolution of the allyl resonances into five distinct multiplets.

A single-crystal X-ray diffraction study of **7** (Figure 3) confirms its identity and reveals that, in the solid state, one of the chlorides

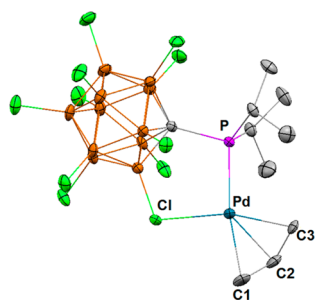


Figure 3. Solid-state structure of complex **7** (hydrogen atoms and disorder about the allyl group omitted for clarity). Color code: brown, B; green, Cl; gray, C; violet, P; blue, Pd.

of the carborane anion is occupying a coordination site of the square-planar palladium center. The Pd–Cl distance [2.401(7) Å] is in the range reported for common Pd–Cl bonds in allyl complexes (terminal Pd–Cl, 2.350–2.410 Å;^{11a,b} bridging Pd–Cl, 2.380–2.420 Å^{11a–c}) and shorter than that reported for palladium complexes with weakly bound chlorocarbons (>2.425 Å).^{11d} Although the metal center interacts with the halogen in the solid state, the B–Cl bond is only slightly elongated [1.794(3) Å; average other B–Cl bonds in the pentagonal belt adjacent to carbon = 1.766(3) Å], indicating little perturbation of this exocuster bond. The P–Pd bond length of **6** [2.354(7) Å] is comparable (2.319–2.363 Å)¹² to that of palladium complexes

containing *o*-carboranyl phosphines. The allyl group is coordinated in an η^3 fashion [Pd–C_{allyl} bond lengths for C1 = 2.206(3) Å, C2 = 2.126(5) Å, and C3 = 2.138(5) Å] and is disordered over two positions.

We next sought to probe the ability of **7** to polymerize simple olefins. Interestingly, complex **7** does not react at all with ethylene (1 atm, 80°C , CD_2Cl_2). However, the addition of 1 mol % complex **7** to a solution of 1-hexene results in very rapid and quantitative isomerization to 2-hexene (Table 1, entry 1). The

Table 1

entry 1	
entry 2	
entry 3	

ability of **7** to isomerize 1-hexene suggests the formation of intermediate palladium hydrides likely formed via facile β -elimination, which likely prevents chain propagation. We next examined the reactivity of **7** with styrene because isomerization is impossible with this substrate. Treatment of a CH_2Cl_2 solution of styrene with 1 mol % **7** at room temperature results in the formation of traces (<1%) of a styrene head-to-tail dimer over 4 h. However, heating the mixture at 50°C for 16 h improves the yield to 75% (Table 1, entry 2). In contrast, at ambient temperature (solvent = C_6H_6 or $\text{F-C}_6\text{H}_5$), the more reactive norbornene instantly polymerizes when contacted with **7**. However, the yield is low (<25%), and the polymer is completely insoluble in all solvents. The insolubility of the polymer also suggests that a very high molecular weight material is formed, which results from poor initiation of the catalyst. In support of this assertion, the primary complex observed in the crude mixture is **7**, as indicated by ^{31}P NMR analysis. Given that the initial insertion step of the polymerization likely occurs via an η^1 -bound allyl species, we reasoned that the addition of the monomer to a heated solution of **7** might improve the performance. Indeed, the addition of norbornene to a solution of **7** (0.1 mol %) at 80°C in $\text{F-C}_6\text{H}_5$ results in a higher yield of the polymer with improved solubility (Table 1, entry 3). Analysis of the material by ^1H NMR shows the absence of olefinic resonances, which suggests that the product forms via a vinyl addition polymerization pathway.¹³ Analysis of the polymer's molecular weight by gel permeation chromatography coupled with light scattering revealed that the polymer had a weight-average molecular weight (M_w) of 44 kDa and a polydispersity index of 1.71. Only a handful of palladium catalysts can produce soluble polynorbornene¹³ because the high reactivity of the monomer usually prohibits controlled polymerization. Monitoring the reaction by ^1H NMR shows that the polymerization is continuous throughout heating of the reaction, which demonstrates that the catalyst is thermally stable. The thermal stability of catalyst **7** is unusual because most palladium olefin polymerization systems begin to rapidly decompose above 70°C .¹⁴

CONCLUSION

This paper introduces a novel approach to the design of zwitterionic olefin polymerization catalysts. Interestingly, the

presence of a carba-*closo*-dodecaborate ligand substituent allows the polymerization of norbornene even though the anion is buried in the coordination sphere of the metal. This highlights the extraordinary weak coordinative ability of these R groups and paves the way for the development of other systems that will be effective for the polymerization of unstrained olefins. We are currently investigating the design of related Pd–Me catalysts, which should display enhanced initiation relative to the allyl system 7.

■ ASSOCIATED CONTENT

■ Supporting Information

Experimental procedures, spectroscopic data, and X-ray crystallographic data in CIF format. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b00576.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: vincent.lavallo@ucr.edu.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. These authors contributed equally.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This material is based on work supported by the NSF (Grant CHE-1455348) and ACS PRF (S2255-DN13). J.E. was supported by the U.S. Department of Education GAANN Award P200A120170.

■ REFERENCES

- (1) For reviews on polyhedral carboranes, see: (a) Popescu, A. R.; Teixidor, F.; Viñas, C. *Coord. Chem. Rev.* **2014**, 269, 54. (b) Douvris, C.; Michl, J. *Chem. Rev.* **2013**, 113, PR179. (c) Spokoyny, A. M. *Pure Appl. Chem.* **2013**, 85, 903. (d) Olid, D.; Nunez, R.; Vinas, C.; Teixidor, F. *Chem. Soc. Rev.* **2013**, 42, 3318. (e) Scholz, M.; Hey-Hawkins, E. *Chem. Rev.* **2011**, 111, 7035.
- (2) For recent examples of complexes of phosphine-containing *o*-carborane substituents, see: (a) Joost, M.; Estévez, L.; Miqueu, K.; Amgoune, A.; Bourissou, D. *Angew. Chem.* **2015**, DOI: 10.1002/ange.201500458. (b) Lugo, C. A.; Moore, C. E.; Rheingold, A. L.; Lavallo, V. *Inorg. Chem.* **2015**, 54, 2094. (c) Joost, M.; Estévez, L.; Mallet-Ladeira, S.; Miqueu, K.; Amgoune, A.; Bourissou, D. *Angew. Chem., Int. Ed.* **2014**, 53, 14512. (d) Joost, M.; Zeineddine, A.; Estévez, L.; Mallet-Ladeira, S.; Miqueu, K.; Amgoune, A.; Bourissou, D. *J. Am. Chem. Soc.* **2014**, 136, 14654. (e) Spokoyny, A. M.; Lewis, C. D.; Teverovskiy, G.; Buchwald, S. L. *Organometallics* **2012**, 31, 8478. (f) Spokoyny, A. M.; Machan, C. W.; Clingerman, D. J.; Rosen, M. S.; Wiester, M. J.; Kennedy, R. D.; Stern, C. L.; Sarjeant, A. A.; Mirkin, C. A. *Nat. Chem.* **2011**, 3, 590.
- (3) (a) Teixidor, F.; Ayllon, J. A.; Vinas, C.; Kivekas, R.; Sillanpää, R.; Casabo, J. J. *Chem. Soc., Chem. Commun.* **1992**, 1281. (b) Teixidor, F.; Vinas, C.; Mar Abad, M.; Lopez, M.; Casabo, J. *Organometallics* **1993**, 12, 3766. (c) Teixidor, F.; Nuñez, R.; Viñas, C.; Sillanpää, R.; Kivekäs, R. *Angew. Chem., Int. Ed.* **2000**, 39, 4290. (d) Nuñez, R.; Farràs, P.; Teixidor, F.; Viñas, C.; Sillanpää, R.; Kivekäs, R. *Angew. Chem., Int. Ed.* **2006**, 45, 1270. (e) Farràs, P.; Teixidor, F.; Rojo, I.; Kivekäs, R.; Sillanpää, R.; González-Cardoso, P.; Viñas, C. *J. Am. Chem. Soc.* **2011**, 133, 16537. (f) Farràs, P.; Olid-Britos, D.; Viñas, C.; Teixidor, F. *Eur. J. Inorg. Chem.* **2011**, 2011, 2525. (g) Popescu, A.-R.; Laromaine, A.; Teixidor, F.; Sillanpää, R.; Kivekäs, R.; Llambias, J. I.; Viñas, C. *Chem.—Eur. J.* **2011**, 17, 4429. (h) Viñas, C.; Nuñez, R.; Teixidor, F.; Kivekäs, R.; Sillanpää, R. *Organometallics* **1996**, 15, 3850. (i) Teixidor, F.; Casabo, J.; Romerosa, A. M.; Viñas, C.; Rius, J.; Miravittles, C. *J. Am. Chem. Soc.* **1991**, 113, 9895.
- (4) For a review on reactive cations stabilized by icosahedral carborane anions, see: Reed, C. A. *Acc. Chem. Res.* **2009**, 43, 121.
- (5) (a) Ramírez-Contreras, R.; Bhuvanesh, N.; Zhou, J.; Ozerov, O. V. *Angew. Chem., Int. Ed.* **2013**, 52, 10313. (b) Douvris, C.; Nagaraja, C. M.; Chen, C.-H.; Foxman, B. M.; Ozerov, O. V. *J. Am. Chem. Soc.* **2010**, 132, 4946. (c) Douvris, C.; Ozerov, O. V. *Science* **2008**, 321, 1188.
- (6) (a) Lavallo, V.; Wright, J. H.; Tham, F. S.; Quinlivan, S. *Angew. Chem., Int. Ed.* **2013**, 52, 3172. (b) El-Hellani, A.; Kefalidis, C. E.; Tham, F. S.; Maron, L.; Lavallo, V. *Organometallics* **2013**, 32, 6887.
- (7) (a) El-Hellani, A.; Lavallo, V. *Angew. Chem., Int. Ed.* **2014**, 53, 4489. (b) Asay, M. J.; Fisher, S. P.; Lee, S. E.; Tham, F. S.; Borchardt, D.; Lavallo, V. *Chem. Commun.* **2015**, 51, 5359.
- (8) (a) Nakamura, A.; Anselment, T. M. J.; Clavier, J.; Goodall, B.; Jordan, R. F.; Mecking, S.; Rieger, B.; Sen, A.; van Leeuwen, P. W. N. M.; Nozaki, K. *Acc. Chem. Res.* **2013**, 46, 1438. (b) Drent, E.; van Dijk, R.; van Ginkel, R.; van Oort, B.; Pugh, R. I. *Chem. Commun.* **2002**, 744. (c) Drent, E.; van Dijk, R.; van Ginkel, R.; van Oort, B.; Pugh, R. I. *Chem. Commun.* **2002**, 964. (d) Ito, S.; Ota, Y.; Nozaki, K. *Dalton Trans.* **2012**, 41, 13807. (e) Nakamura, A.; Munakata, K.; Ito, S.; Kochi, T.; Chung, L. W.; Morokuma, K.; Nozaki, K. *J. Am. Chem. Soc.* **2011**, 133, 6761. (f) Nakamura, A.; Ito, S.; Nozaki, K. *Chem. Rev.* **2009**, 109, 5215. (g) Ito, S.; Munakata, K.; Nakamura, A.; Nozaki, K. *J. Am. Chem. Soc.* **2009**, 131, 14606. (h) Kochi, T.; Noda, S.; Yoshimura, K.; Nozaki, K. *J. Am. Chem. Soc.* **2007**, 129, 8948. (i) Cai, Z.; Shen, Z.; Zhou, X.; Jordan, R. F. *ACS Catal.* **2012**, 2, 1187. (j) Conley, M. P.; Jordan, R. F. *Angew. Chem., Int. Ed.* **2011**, 50, 3744. (k) Shen, Z.; Jordan, R. F. *Macromolecules* **2010**, 43, 8706. (l) Vela, J.; Lief, G. R.; Shen, Z.; Jordan, R. F. *Organometallics* **2007**, 26, 6624. (m) Luo, S.; Vela, J.; Lief, G. R.; Jordan, R. F. *J. Am. Chem. Soc.* **2007**, 129, 8946.
- (9) Kim, Y.; Jordan, R. F. *Organometallics* **2011**, 30, 4250.
- (10) Gutsulyak, D. V.; Gott, A. L.; Piers, W. E.; Parvez, M. *Organometallics* **2013**, 32, 3363.
- (11) For discussions of the structural characteristics of palladium allyl complexes, see: (a) *The Organometallic Chemistry of the Transition Metals*, 5th ed.; Crabtree, R. H., Ed.; John Wiley & Sons Ltd.: Hoboken, NJ, 2009; Vol. 5. For terminal Pd–Cl bond lengths in related allyl complexes, see: (b) Viciu, M. S.; Navarro, O.; Germaneau, R. F.; Kelly, R. A.; Sommer, W.; Marion, N.; Stevens, E. D.; Cavallo, L.; Nolan, S. P. *Organometallics* **2004**, 23, 1629 references cited therein. For bridging Pd–Cl bond lengths in related allyl complexes, see: (c) Szuromi, E.; Shen, H.; Goodall, B. L.; Jordan, R. F. *Organometallics* **2008**, 27, 402 references cited therein. For metrical data for Pd–Cl bond lengths in related allyl complexes containing weakly coordinating chlorocarbon ligands, see: (d) Chernyshova, E. S.; Goddard, R.; Pörschke, K.-R. *Organometallics* **2007**, 26, 3236 references cited therein.
- (12) (a) Fey, N.; Haddow, M. F.; Mistry, R.; Norman, N. C.; Orpen, A. G.; Reynolds, T. J.; Pringle, P. G. *Organometallics* **2012**, 31, 2907. (b) Lee, Y.-J.; Lee, J.-D.; Kim, S.-J.; Keum, S.; Ko, J.; Suh, I.-H.; Cheong, M.; Kang, S. O. *Organometallics* **2004**, 23, 203. (c) Lee, T.; Lee, S. W.; Jang, H. G.; Kang, S. O.; Ko, J. *Organometallics* **2001**, 20, 741.
- (13) (a) Mehler, C.; Risse, W. *Macromol. Rapid Commun.* **1991**, 12, 255. (b) Mehler, C.; Risse, W. *Macromolecules* **1992**, 25, 4226. (c) Seehof, N.; Mehler, C.; Breunig, S.; Risse, W. *J. Mol. Catal.* **1992**, 76, 219. (d) Haselwander, T. F. A.; Heitz, W.; Krügel, S. A.; Wendorff, J. H. *Macromol. Chem. Phys.* **1996**, 197, 3435. (e) Blank, F.; Scherer, H.; Janiak, C. *J. Mol. Catal.* **2010**, 330, 1.
- (14) For discussions on the thermal stability of palladium-based olefin polymerization systems, see: (a) Pan, H.; Zhu, L.; Li, J.; Zang, D.; Fu, Z.; Fan, Z. *J. Mol. Catal.* **2014**, 390, 76. (b) Popeney, C. S.; Rheingold, A. L.; Guan, Z. *Organometallics* **2009**, 28, 4452. (c) Camacho, D. H.; Salo, E. V.; Ziller, J. W.; Guan, Z. *Angew. Chem., Int. Ed.* **2004**, 43, 1821. (d) Tempel, D. J.; Johnson, L. K.; Huff, R. L.; White, P. S.; Brookhart, M. *J. Am. Chem. Soc.* **2000**, 122, 6686.