# **ORGANOMETALLICS**

# Formation and Reactivity of Gold Carbene Complexes in the Gas Phase

Christopher A. Swift and Scott Gronert\*

Department of Chemistry, Virginia Commonwealth University, Richmond, Virginia 23824 United States

**Supporting Information** 

**ABSTRACT:** A series of ligated gold(I) carbenes (where the ligand is  $Ph_3P$ ,  $Me_2S$ , or an N-heterocyclic carbene, NHC) were formed in the gas phase by a variety of methods. Gold(I) benzylidenes could be formed using Chen's method of dissociating an appropriate



phosphorus ylide precursor. The resulting carbene undergoes an addition reaction with olefins to give an adduct. The adduct undergoes a second gas-phase reaction with an olefin, where presumably a cyclopropanation product is displaced by the second olefin molecule. Both steps in the process were analyzed with linear free energy relationships (i.e., Hammett plots). Under collision-induced dissociation conditions, the adduct undergoes competing processes: (1) dissociation of the cyclopropanation product to give ligated gold(I) species and (2) metathesis to give a more stable gold(I) carbene. Attempts to form less stable gold(I) carbenes in the gas phase by Chen's approach or by reactions of diazo species with the ligated gold(I) cations were not successful—processes other than carbene formation are preferred or the desired carbene, after formation, rearranges rapidly to a more stable species. In accord with other recent work, the data suggest that coordination to a ligated gold(I) cation in the gas phase may not offer sufficient stabilization to carbenes to prevent competition from rearrangement processes.

# INTRODUCTION

Gas-phase studies have become a useful tool in examining intermediates in condensed-phase reactions catalyzed by organometallic species.<sup>1-4</sup> The key advantage of the gas phase is that short-lived intermediates can be isolated in the inert environment of a mass spectrometer and probed in the absence of side reactions with solvent and other components in reaction mixtures.<sup>5,6</sup> Transition-metal-stabilized carbenes have been incorporated in many important catalytic cycles, including cyclopropanation and metathesis processes.<sup>7-10</sup> Gold catalysis has become of great interest, due to the unique reactivity that gold exhibits.<sup>11</sup> Previously, we have reported the gas-phase synthesis of iron and cobalt carbene complexes by the reaction of a ligated metal with diazoacetate esters.<sup>12,13</sup> In those cases, the metal carbenes were prone to rearrangement processes, particularly metal-ligand insertions that converted the carbene to an ylide. Here we apply a variety of approaches to prepare and explore the reactivity of gold(I) carbene complexes in the gas phase.

Chen and co-workers have presented several papers focused on the gas-phase formation and reactions of gold(I) benzylidene complexes of the general form LAuCHPh<sup>+</sup>, where L is an N-heterocyclic carbene (NHC).<sup>14–17</sup> The carbenes were not generated directly by electrospray ionization but were formed by the collision-induced dissociation of an ylide precursor (Scheme 1). In their studies, they have shown that the gold(I) benzylidene reacts with alkenes to give addition products and that under collision-induced dissociation conditions (CID) the addition product decomposes either by loss of a cyclopropanation product (combined elements of the benzylidene and alkene) or by metathesis to produce a new gold(I) carbene complex. In the current study, we have tested Scheme 1. Chen's Method of Gold(I) Carbene Formation from Ylide Fragmentation

$$L \xrightarrow{\oplus}_{R} \xrightarrow{O}_{PPh_{3}} \xrightarrow{CID}_{PPh_{3}} \xrightarrow{L-Au}_{R} \xrightarrow{\oplus}_{R}$$

the generality of this approach for forming gold(I) carbenes and explored the kinetics of the bimolecular reactions of the gold(I) benzylidenes. The results are supported by density functional theory (DFT) calculations and highlight the important intermediates on the reaction surface.

## RESULTS AND DISCUSSION

**Gold(I) Benzylidenes.** Chen and co-workers have focused considerable attention on gold(I) benzylidenes that bear an NHC on the gold as the second ligand.<sup>14–17</sup> As noted above, they can be formed by the fragmentation of a phosphorus ylide (Scheme 1). They have shown that these gold carbenes react with alkenes to give addition products, which under CID yield cyclopropanes as well as metathesis products.<sup>15</sup> Given the nature of their apparatus, it was not possible to examine the kinetics of the addition or the subsequent bimolecular reactions of the addition products. In our quadrupole ion trap, we can complete MS<sup>n</sup> experiments and therefore can probe each step in the complex reaction process. In the current study, we have adopted Chen's methodology with triphenylphosphine as the second ligand on gold. When it is subjected to CID, the ylide precursor (Scheme 2) readily loses triphenylphosphine and

Received: September 8, 2014

#### Scheme 2. Gold(I) Benzylidene Precursor



produces a species with characteristic carbene reactivity. The gold(I) benzylidene was isolated in the ion trap and allowed to react with four olefins: cyclohexene, ethyl vinyl ether, 2,3-dihydrofuran, and 1,1-dichloroethylene. It gave addition complexes with each of the olefins, except the most electron-deficient one, 1,1-dichloroethene. The bimolecular rate constants for the olefin reactions are presented in Table 1.

Table 1. Rate Constants for the Reaction of the  $Ph_3PAu^+$ Benzylidene Complex with Olefins<sup>*a*</sup>

| olefin               | k        | efficiency <sup>c</sup> |
|----------------------|----------|-------------------------|
| 1,1-dichloroethylene | $NR^{b}$ | $NR^{b}$                |
| cyclohexene          | 3.34     | 39                      |
| 2,3-dihydrofuran     | 7.75     | 62                      |
| ethyl vinyl ether    | 10.10    | 76                      |

<sup>*a*</sup>Rate constants in units of  $10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> and efficiencies in units of %. <sup>*b*</sup>Reaction too slow to characterize:  $<10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. <sup>*c*</sup> $k/k_{colv}$  where the collision rate is calculated by the method of Su and Bowers.<sup>18</sup>

With the electron-rich olefins ethyl vinyl ether and 2,3dihydrofuran, the rate constants approach the estimated collision-controlled limit, indicating a relatively facile process.<sup>18</sup> With dichloroethylene, the rate is too slow to characterize accurately in our system. The correlation between olefin nucleophilicity and reactivity is consistent with a Fisher carbene electronic structure.

When it is held in the ion trap for an extended time period, the adduct from this reaction undergoes a second reaction with the olefin, leading to displacement of the benzylidene/olefin components of the adduct and formation of a new Ph<sub>3</sub>PAu<sup>+</sup>/ olefin complex. We assume that this reaction is the completion of a cyclopropanation process (Scheme 3). DFT calculations with the M06 functional suggest that the gold coordinates with the cyclopropane rather than forming a metallocyclobutane. Chen and co-workers came to the same conclusion with calculations at the B3LYP level and identified a strong interaction between the gold and the benzene ring of the former benzylidene unit.<sup>15</sup> The reaction exhibits strict secondorder kinetics and is best interpreted as a substitution reaction, with the olefin replacing the cyclopropane in the addition complex.<sup>19</sup> The rate constants for this substitution process are well below those for the addition of the olefin to the gold(I)benzylidene; thus, the addition product can be observed and isolated as an intermediate in the ion trap and there is sufficient

### Scheme 3. Reactions of Gold(I) Benzylidene with Olefins



Kinetic data for the substitution reactions are presented in Table 2. The rate constants for the reactions of the adducts

Table 2. Rate Constants for the Reaction of the Addition Complexes with Olefins (Scheme 3)<sup>a</sup>

| olefin            | k    | efficiency <sup>b</sup> |
|-------------------|------|-------------------------|
| cyclohexene       | 1.40 | 1.66                    |
| 2,3-dihydrofuran  | 0.70 | 0.56                    |
| ethyl vinyl ether | 1.50 | 1.14                    |
|                   |      |                         |

"Rate constants in units of  $10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> and efficiencies in units of %.  ${}^{b}k/k_{colb}$  where the collision rate is calculated by the method of Su and Bowers.<sup>18</sup>

with the olefins are 30–100-fold lower than those that were observed in the reactions of the gold(I) benzylidene. Analyzing the rate data is more complicated in the substitution reactions because features that make the olefin more nucleophilic will also enhance the binding of the cyclopropane to the gold and attenuate the impact of the substituent. In order to achieve a greater understanding of the electronic effects, we used parasubstituted styrenes to establish linear free energy relationships with the kinetics of the olefin reactions. Styrene, 4fluorostyrene, 4-chlorostyrene, 4-methylstyrene, and 4-methoxystyrene were used in the study. The kinetics are presented in Figure 1. As with the other olefins, the styrenes give addition



Figure 1. Hammett plot of the reactions of para-substituted styrenes with the  $Ph_3PAu^+$  benzylidene complex (addition process) and its adducts (substitution process).

rates that are generally fast and approach the collisioncontrolled limit. The Hammett plot illustrates the correlation between the electron-donating capability of the substituent (nucleophilicity of the olefin) and the rate constant of the reaction. In the reaction of the gold(I) benzylidene with the styrenes, the slope gives  $\rho = -0.9$ , which is a modest value for a gas-phase process. Systems such as substituted benzoic acids give  $\rho$  values greater than 10 in the gas phase.<sup>21</sup> The value suggests that relatively little positive charge is developing on the olefin and points to an early transition state. To probe this system in the absence of substituents, we allowed the benzylidene to react with a mixture of styrene and  $d_8$ -styrene. As expected for a fast reaction, the secondary kinetic isotope effect is small  $(k_{\rm H}/k_{\rm D} = 1.13)$ . In the subsequent substitution reactions of the adducts, the  $\rho$  value triples in magnitude to -2.9, indicating that the process is much more sensitive to the electron density of the olefin's  $\pi$  system. These reactions are slower and should have later transition states than the addition reactions-it is likely that there is more charge on the olefin in the transition state. Using a trimethylphosphine complex as a model, the substitution reaction with styrene is computed to be exothermic by about 10 kcal/mol.<sup>22,23</sup> The large  $\rho$  value is also consistent with a metal/cyclopropane structure, because if the addition product were a metallacycle, the electron-donating substituents on the metallocycle should be strongly stabilizing and attenuate the impact of electron-donating substituents on the incoming olefin.

It was also possible to probe the CID behavior of the addition products. Under CID, two pathways are apparent. One involves the loss of the cyclopropane followed by the addition of an olefin. The olefin used to prepare the addition complex is still in the ion trap during the CID experiment in our system and can react very readily with the ligated gold(I) cation that is formed after cyclopropane loss. This represents an activated, two-step version of the substitution process described above. The other pathway is a metathesis and leads to a new carbene. This is illustrated in Figure 2 for the reaction of 4methoxystyrene with the gold(I) benzylidene complex. For comparison, a spectrum obtained without CID is also included. CID mainly produces a 4-methoxybenzylidene complex (m/z)579), which results from the loss of styrene in the fragmentation process. This outcome indicates that, under activated conditions, the addition product can access a metallacycle or related ring-opened intermediate, which is consistent with Chen's observations in the reactions of substituted cyclopropanes with gold(I) complexes.<sup>15</sup> As expected, the reaction shows a strong preference for forming the more stable, methoxy-substituted carbene, as opposed to the original benzylidene (m/z 549). A similar metathesis process also occurs in the CID of the addition product of ethyl vinyl ether with the gold(I) benzylidene.

**Other Gold(I) Carbenes.** Using the same ylide decomposition strategy, we attempted to synthesize other gold(I) carbene complexes. Metal-stabilized, ester-substituted carbenes are widely used in synthesis, in part because they can be generated by the decomposition of relatively stable dizaoacetate (or other ester) precursors.<sup>20,24–28</sup> To probe these species, a phosphorus ylide complex was synthesized that could produce an ester-substituted gold(I) carbene by the loss of triphenyl-phosphine (Scheme 4). However, during CID, methanol was lost rather than triphenylphosphine. Similar structures have been observed in the condensed phase.<sup>29</sup> Subsequent CID of the product led to the free triphenylphosphine-ligated gold



**Figure 2.** Spectra of the reactions of the 4-methoxystyrene adducts of the gold(I) benzylidene phosphine complex (a) with CID applied (30 ms reaction time) and (b) with no CID applied (1800 ms reaction time). The peaks at m/z 579 and 549 are the methoxy and unsubstituted benzylidene complexes, respectively. The peaks at m/z 459 and 477 are Ph<sub>3</sub>Au<sup>+</sup> and its H<sub>2</sub>O adduct (from adventitious water in the ion trap). The parent ion is at m/z 683.

Scheme 4. Fragmentation of the Ylide Precursor of an Ester-Substituted Carbene



cation. Ester-substituted carbenes are destabilized relative to simple carbenes, and apparently, this factor is sufficient to inhibit triphenylphosphine loss and allow the alcohol dissociation channel to dominate. In this case, ylide dissociation is not a viable approach to forming the carbene. As an alternative route to an ester-substituted gold carbene, we also investigated the reaction of a ligated gold(I) cation with ethyl and tert-butyl diazoacetate in the gas phase. As noted earlier, this is a common route to metal carbenes in the condensed phase. We employed triphenylphosphine gold(I), dimethyl sulfide gold(I), and 1,3-diisopropylimidizolium gold(I) in order to explore the impacts of these three general classes of ligands. In these gas-phase reactions of diazoacetates with ligated gold cations, the products indicate the combined loss of N<sub>2</sub> and CO. The likely explanation is that the initial carbene intermediate formed by the loss of N2 spontaneously undergoes a Wolff rearrangement followed by CO loss to give an alkoxy carbene (Scheme 5). It should be noted that Beauchamp and coworkers saw similar rearrangements in the gas-phase reactions of diazomalonates with silver and copper cations.<sup>30</sup> More recently, Roithova and co-workers presented an elegant gasphase study aimed at closely related gold carbenes.31 They observed and carefully characterized this pathway. In our experiments, there is no evidence of adducts with the diazoacetates or the desired carbene product; thus, it appears that the rate-limiting step is the initial addition of the diazo compound to the metal. All three ligand systems afforded the same reactivity with the diazoacetates, indicating that the

Scheme 5. Wolff Rearrangement and CO Loss from Ester-Substituted Carbene



electronic characteristics of the ligand do not control the reactivity in these reactions. Application of CID to the products of the Wolff rearrangement/CO loss leads back to the initial ligated gold cation. This could be the result of a direct cleavage of the gold–carbene bond or a rearrangement of the alkoxy carbene to an aldehyde followed by dissociation (Scheme 6).

Scheme 6. Alkoxy Carbene Rearrangement To Form Aldehyde



DFT computations on a model system (Me<sub>3</sub>P–Au–CH– OMe) using the M06 functional (see the Experimental Section for details) indicate that the gold–carbene bond is relatively weak (~66 kcal/mol) and is not much greater than the computed barrier to the rearrangement in Scheme 6 (~57 kcal/ mol); thus, it is possible that an alkoxy carbene is directly lost during CID rather than rearranging to the acetaldehyde complex before dissociation. The weak gold–carbene bond suggests that this species is best described as a gold–ylide complex with limited back-bonding from the metal (Scheme 7).

Scheme 7. Resonance Forms for Gold Carbene Complex



To explore their reactivity, the putative alkoxy carbenes from the decomposition of the diazoacetate esters (Scheme 5) were allowed to react with four olefins having varying structural and electronic properties: cyclohexene, ethyl vinyl ether, 2,3dihydrofuran, and 1,1-dichloroethylene. No reactions were observed with any of the olefins. We had anticipated typical carbene reactivity such as cyclopropanation or metathesis, but apparently the alkoxy-substituted gold(I) carbene is sufficiently stabilized to inhibit any reactivity, even adduct formation. Of course, there is ample evidence that alkoxy groups greatly stabilize free carbenes.<sup>32</sup> To examine this effect in the gold carbenes, we have used the isodesmic reaction in Scheme 8 as a

Scheme 8. Isodesmic Reaction for Evaluating Carbene Stability



Article

model. Employing DFT calculations with the M06 functional, the methoxy group stabilizes the gold carbene by about 28 kcal/mol relative to an alkyl carbene. This is a large energetic effect and is the likely reason these complexes are unreactive in the gas phase with olefins. The stabilization of the gold carbene is similar to what is seen in free carbenes (32 kcal/mol at the same level of theory), which indicates that the gold has a limited impact on the electronic structure of the carbene. Again, these results suggest that the alkoxy carbene behaves more like an ylide in this system.

To further probe the alkoxy carbenes, we utilized a phosphorus ylide that, when dissociated, would form a methoxy-substituted gold(I) carbene. This is an alternative route to these gold carbenes and allows us to confirm the reactivity patterns seen in the decomposition products of diazoacetates. Upon electrospray ionization and isolation of this ylide, the triphenylphosphine group was disassociated by CID, providing a product with a mass to charge ratio (m/z) that corresponds to the methoxy-substituted gold carbene (Scheme 9). Further CID of this complex led to the ligated gold

Scheme 9. Alkoxy Carbene Generation by Ylide Degradation



complex, as was seen with the products from the diazoacetate decompositions. When this complex was allowed to react with the same set of olefins, no reactions occurred. This behavior suggests that identical species were formed in both proposed pathways to alkoxy-substituted carbenes. The lack of reactivity in the alkoxy carbenes is consistent with computations presented by Chen.<sup>15</sup> They showed that, in related systems, intermediates in the reaction of an alkoxy carbene with an olefin are bound by less than 20 kcal/mol, which is the working threshold for observing them in our ion trap system.

To complete our investigation of the generality of Chen's ylide dissociation synthesis of gold(I) carbenes, we prepared a phosphorus ylide precursor that would yield a gold(I) methylene complex (Scheme 10). The obvious advantage of

Scheme 10. Fragmentation Pathways of Gold(I) Methylene Precursor



this system is that the carbene is not capable of internal rearrangements. The ylide loses triphenylphosphine during CID, but the product did not have reactivity with olefins. This suggested that the triphenylphosphine loss might be from the gold center rather than from the ylide. To avoid this complication, an ylide with a 1,3-diisopropylimidizolium ligand was synthesized (Scheme 11). Under CID, this complex Scheme 11.  $CH_2$  Carbene Precursor using 1,3-Diisopropylimidizolium as the Ligand on Gold



undergoes fragmentations related to the 1,3-diisopropylimidizolium ligand. Specifically, propyl loss and ligand loss are observed. This behavior was not seen in the CID reactions of the precursors to the NHC gold(I) benzylidenes. These results again suggest that the ylide dissociation pathway is best suited for the formation of stabilized carbenes. In the absence of stabilization, other pathways dominate and useful yields of carbenes are not possible. This is consistent with the conclusions from Roithova's recent study.<sup>31</sup>

#### CONCLUSIONS

Ligated gold(I) carbene complexes can be formed in the gas phase by several pathways, including reactions with diazo species and dissociations of phosphorus ylide precursors. Gold(I) benzylidenes react with olefins to give addition products, with rates that are sensitive to the electron density of the olefin's  $\pi$ -system and that increase to near the collisioncontrolled limit for olefins with electron-donating groups (e.g., ethyl vinyl ether). Chen has previously shown that the addition products of the gold(I) benzylidenes complete what appear to be cyclopropanation and metathesis reactions during CID.<sup>15</sup> Here, we show that they have bimolecular reactivity with olefins and secondary substitution reactions occur (olefin displacing cyclopropane). These substitution reactions are slower than the addition reactions of the gold(I) benzylidenes. A Hammett plot analysis shows that the ligand-swapping process is more sensitive to the electron density of the olefin's  $\pi$  system and is consistent with a later transition state and greater positive charge on the olefin unit.

The gas-phase syntheses of gold(I) carbenes tend to have limited scopes. When the carbene is not stabilized, the ylide dissociation pathway produces other decomposition products. This limitation can be overcome by employing diazo precursors in bimolecular reactions, but in the case of ester-substituted carbenes, the desired carbene undergoes a spontaneous Wolff rearrangement followed by CO loss. The product is a gold(I) complex of an alkoxy carbene, which is highly stabilized and does not give reactivity with olefins. Future work will focus on alternative, more general avenues to gold(I) carbene formation.

#### EXPERIMENTAL SECTION

All experiments were conducted in a modified ThermoFinnigan LCQ. Deca XP Plus quadrupole ion trap mass spectrometer equipped with electrospray ionization (ESI). Gold(I) salts and carbene precursors were dissolved in methanol at  $10^{-4}-10^{-5}$  M. Typical ESI conditions involved flow rates of  $3-5 \,\mu$ L/min with needle potentials between 3.5 and 6 kV and heated capillary temperatures from 125 to 200 °C. A notched waveform is used for isolating the cationic gold(I) species at room temperature.<sup>33</sup> When a stable signal is obtained, neutral reagents can be spiked into the helium via a custom gas-handling system which has been previously described.<sup>34</sup>

Kinetic measurements were completed by establishing an appropriate flow rate for the neutral reagent and varying the time between the isolation of the ion and the expulsion of all the ions to obtain a mass spectrum. Ten different time delays were used in each reaction. Reagent flows and time delays were varied to obtain plots that cover 2–3 half-lives of the ionic reagent. Data were obtained over at least 2 days with multiple neutral and ionic solution preparations. Kinetic plots showed sufficient linearity with correlation coefficients  $(r^2)$  of 0.98 or greater.

All neutral reagents were obtained from commercial sources in the highest purity available and used without further purification. As needed, neutral reagents were diluted in cyclohexane. Gold salts, triphenylphosphine gold(I) chloride, and dimethyl sulfide gold(I) chloride were obtained from commercial sources and used without further purification. 1,3-Diisopropyimidizolium gold(I) chloride was synthesized following a previously reported synthesis by Taton et al.<sup>35</sup> Gold ylide compounds of the form PPh<sub>3</sub>RCHAu<sup>+</sup>L (where R = H, Ph, OMe, COOMe and L = PPh<sub>3</sub>, 1,3-diisopropylimidizolium) were synthesized by a ligand exchange procedure that has been reported by Chen et al.<sup>17</sup>

Computational data were obtained using the Gaussian09 suite of quantum mechanical codes.<sup>36</sup> A density functional approach was taken using the M06 functional and the QZVP basis set. The energetic data are estimated enthalpies at 298 K, with no corrections to the zeropoint energies or harmonic frequencies. The data are consistent with preliminary results using the LANL2DZ basis set on gold and 6-311+G\*\* basis set on second-row atoms.

# ASSOCIATED CONTENT

# **Supporting Information**

Text, figures, tables, and an xyz file giving experimental procedures, computational data and the complete citation for ref 36. This material is available free of charge via the Internet at http://pubs.acs.org.

#### AUTHOR INFORMATION

#### **Corresponding Author**

\*E-mail for S.G.: sgronert@vcu.edu.

#### Notes

The authors declare no competing financial interest.

### ACKNOWLEDGMENTS

The authors thank Professor Donald Aue for helpful suggestions with respect to the computational methodology. Support from the National Science Foundation (CHE-1011771 and CHE-1300886) is acknowledged.

#### REFERENCES

(1) Robinson, P. S. D.; Khairallah, G. N.; Silva, G.; Lioe, H.; O'Hair,

- R. A. J. Angew. Chem. Int. Ed. 2012, 51, 3812-3817.
- (2) Rijs, N. J.; O'Hair, R. A. J. Organometallics 2009, 28, 2684–2692.
  (3) Henderson, M. A.; Kwok, S.; Mcindoe, J. S. J. Am. Soc. Mass Spectrom. 2009, 20, 658–666.

(4) Vikse, K.; Khairallah, G. N.; Mcindoe, J. S.; O'Hair, R. A. J. Dalton Trans 2013, 42, 6440–6449.

- (5) Gronert, S. Chem. Rev. 2001, 101, 329-360.
- (6) Gronert, S. Mass Spectrom. Rev. 2005, 24, 100-120.

(7) Bourissou, D.; Guerret, O.; Gabbai, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39–91.

(8) Davies, H. M. L.; Beckwith, R. E. J. Chem. Rev. 2003, 103, 2861–2904.

(9) Díez-González, S.; Marion, N.; Nolan, S. P. *Chem. Rev.* **2009**, *109*, 3612–3676.

(10) Lin, J. C. Y.; Huang, R. T. W.; Lee, C. S.; Bhattacharyya, A.; Hwang, W. S.; Lin, I. J. B. *Chem. Rev.* **2009**, *109*, 3561–3598.

(11) Hashmi, A. S. K. Chem. Rev. 2007, 107, 3180-3211.

(12) Aldajaei, J. T.; Gronert, S. Int. J. Mass Spectrom. 2012, 316-318, 68-75.

(13) Koehn, S. K.; Gronert, S.; Aldajaei, J. T. Org. Lett. 2010, 12, 676–679.

(14) Ringger, D. H.; Chen, P. Angew. Chem. Int. Ed. 2013, 52, 4686–4689.

- (15) Fedorov, A.; Batiste, L.; Bach, A.; Birney, D. M.; Chen, P. J. Am. Chem. Soc. **2011**, 133, 12162–12171.
- (16) Fedorov, A.; Chen, P. Organometallics 2009, 28, 1278-1281.

(17) Fedorov, A.; Moret, M.-E.; Chen, P. J. Am. Chem. Soc. 2008, 130, 8880-8881.

(18) Su, T.; Bowers, M. T. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1979; p 83.

(19) Although a transition state was not computed for this reaction, it is anticipated to be exothermic (see ref 22).

(20) Díaz-Requejo, M. M.; Pérez, P. J. J. Organomet. Chem. 2005, 690, 5441-5450.

(21) Nakata, K.; Fujio, M.; Nishimoto, K.; Tsuno, Y. ChemPlusChem. 2013, 78, 1099–1108.

(22) The binding to styrene is computed to be 40.3 kcal/mol, and that to *trans*-1,2-diphenylcyclopropane is computed to be 30.1 kcal/mol at the M06/QZVP level with enthalpy corrections at the Lanl2dz level—the largest system exceeded our computational limits for QZVP frequencies. The styrene value is consistent with earlier studies on related systems.<sup>23</sup>

(23) Jašikova, L.; Roithova, J. Organometallics 2012, 31, 1935–1942.
(24) Fructos, M. R.; de Fremont, P.; Nolan, S. P.; Díaz-Requejo, M. M.; Perez, P. J. Organometallics 2006, 25, 2237–2241.

(25) Ungvári, N.; Fördős, E.; Kégl, T.; Ungváry, F. Inorg. Chim. Acta 2010, 363, 2016–2028.

(26) Chattopadhyay, P.; Matsuo, T.; Tsuji, T.; Ohbayashi, J.; Hayashi, T. Organometallics **2011**, 1869–1873.

(27) Delgado-Rebollo, M.; Beltrán, Á.; Prieto, A.; Díaz-Requejo, M. M.; Echavarren, A. M.; Pérez, P. J. *Eur. J. Inorg. Chem.* **2012**, 2012, 1380–1386.

(28) Qian, Y.; Zavalij, P. J.; Hu, W.; Doyle, M. P. Org. Lett. 2013, 15, 1564–1567.

(29) Johnson, A.; Laguna, A.; Gimeno, M. C. J. Am. Chem. Soc. 2014, 3-6.

(30) Julian, R. R.; May, J. A.; Stoltz, B. M.; Beauchamp, J. L. J. Am. Chem. Soc. 2003, 125, 4478-4486.

(31) Schulz, J.; Jašíková, L.; Skríba, A.; Roithová, J. J. Am. Chem. Soc. 2014, 11513–11523.

(32) Gronert, S.; Keeffe, J. R. J. Phys. Org. Chem. 2013, 26, 1023-1031.

(33) Gronert, S. J. Am. Soc. Mass Spectrom. 1998, 9, 845-848.

(34) Nettey, S.; Swift, C. A.; Joviliano, R.; Noin, D. O.; Gronert, S. J. Am. Chem. Soc. **2012**, 134, 9303–9310.

(35) Fèvre, M.; Pinaud, J.; Leteneur, A.; Gnanou, Y.; Vignolle, J.; Taton, D.; Miqueu, K.; Sotiropoulos, J.-M. *J. Am. Chem. Soc.* **2012**, 134, 6776–67784.

(36) Frisch, M. J., et al. *Gaussian 09*; Gaussian Inc.: Wallingford, CT, 2009.