# Facile Insertion of Ethylene into a Group 14 Element-Carbon Bond: Effects of the HOMO-LUMO Energy Gap on Reactivity

| | |
|---|---|
| Journal: | *ChemComm* |
| Manuscript ID | CC-COM-10-2018-008488.R1 |
| Article Type: | Communication |
| | |

Journal Name

COMMUNICATION

# Facile Insertion of Ethylene into a Group 14 Element-Carbon Bond: Effects of the HOMO-LUMO Energy Gap on Reactivity

Ting Yi Lai,[a] Jing-Dong Guo,[b,c] James C. Fettinger,[a] Shigeru Nagase[b,c] and Philip P. Power[a*]

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

**www.rsc.org/**

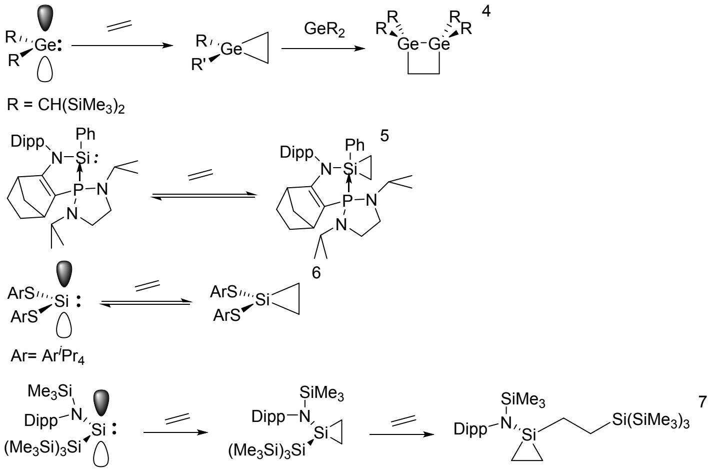
**The diarylstannylenes, Sn(Ar$^{iPr4}$)$_2$ and Sn(Ar$^{iPr6}$)$_2$, (Ar$^{iPr4}$ = $C_6H_3$-2,6-($C_6H_3$-2,6-$^{i}$Pr $_2$)$_2$, Ar$^{iPr6}$ = $C_6H_3$-2,6-($C_6H_2$-2,4,6-$^{i}$Pr$_3$)$_2$), undergo a facile migratory insertion reaction with ethylene at 60 °C to afford the alkyl aryl stannylenes Ar$^{iPr4}$SnCH$_2$CH$_2$Ar$^{iPr4}$ and Ar$^{iPr6}$SnCH$_2$CH$_2$Ar$^{iPr6}$ which were characterized via $^1$H , $^{13}$C and $^{119}$Sn NMR, UV-vis and IR spectroscopy, as well as by X-ray crystallography. Quantum mechanical calculations were performed, and two potential mechanisms were identified, with a migratory insertion reaction pathway being energetically preferred.**

The reactions of heavier divalent group 14 element species (tetrylenes) with unsaturated C-C bonds have attracted increasing interest because of their potential relevance for catalysis involving group 14 molecules.[1] Their relatively low HOMO-LUMO gaps, generate sufficiently high reactivity such that they can often interact with alkenes or alkynes under mild conditions.[2] Several researchers have shown that tetrylenes (ER$_2$; E= Si, Ge, Sn or Pb), tetrlynes (REER) and tetrylenoids (species in which tetrylenes are stabilized by coordination to a donor molecule) react with alkynes affording cycloaddition products.[2] However, examples of direct reactions between olefins and heavier tetrylenes remain relatively rare, in part due to increased HOMO-LUMO energy separations as the atomic number increases, and none has led to insertion into an E-C bond.[3]

In 1994, Ando and coworkers showed that the germylene, (GeR$_2$, R= -CH(SiMe$_3$)$_2$) reacted with ethylene to give a 1,2-digermacyclobutane, probably via a germirane intermediate (Scheme 1, top).[4] More recently, it was shown that a silylene-phosphine complex[5] and a bis(arylthiolato) silylene[6] reacted in a reversible fashion with ethylene (Scheme 1, middle). The silyl silylene, :Si{N($C_6H_3$-2,6-iPr$_2$)SiMe$_3$}{Si(SiMe$_3$)$_3$}, was shown to undergo migratory insertion of ethylene into a Si-Si bond by Rieger and coworkers in 2015 (Scheme 1).[7] However, no examples of a simple insertion of ethylene or other olefins into group 14 element-carbon bonds has been reported.

For stannylenes, calculations on the reaction of SnH$_2$ with ethylene suggest that it involves a two-step mechanism to give, initially, a metallocyclopropane upon binding followed by subsequent insertion into the Sn-H bond having a barrier of 12.66 kcal mol$^{-1}$.[8] In 2008 Banasak-Holl and coworkers[9] reported that a stannylene and a iodobenzene reacted with olefins under mild conditions. The olefin addition products display regioselectivity consistent with a radical induced migratory insertion into a C-H bond.[10]

Nonetheless, the direct reaction of a organostannylene with ethylene or other olefins under ambient or near ambient conditions has remained unknown. Herein we report the direct reaction of the diarylstannylenes Sn(Ar$^{iPr4}$)$_2$ and Sn(Ar$^{iPr6}$)$_2$, (Ar$^{iPr4}$ = $C_6H_3$-2,6-($C_6H_3$-2,6-$^{i}$Pr $_2$)$_2$, Ar$^{iPr6}$ = $C_6H_3$-2,6-($C_6H_2$-2,4,6-$^{i}$Pr$_3$)$_2$) with ethylene at 60°C which afford products in which one equivalent of ethylene is inserted into one of the Sn-C bonds.



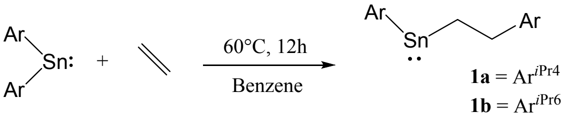
**Scheme** 1. Some Known reactions of tetrylenes with olefins[4-7]

The blue diarylstannylenes, :Sn(Ar$^{iPr4}$)$_2$ (1.00 g, 1.09 mmol),[11] or Sn(Ar$^{iPr6}$)$_2$ (1.00g, 0.924 mmol)[12] in benzene or heptane *ca.* 30 mL

---

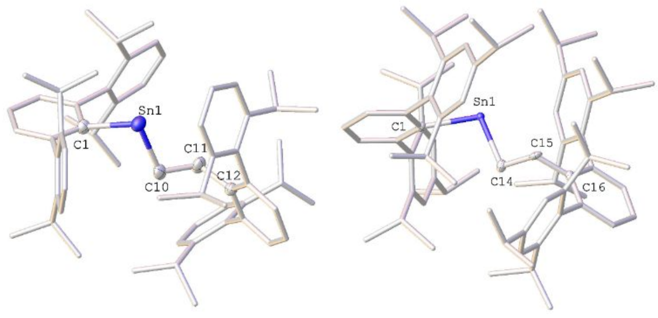
[a] *Department of Chemistry, University of California, One Shields Avenue, Davis, California 95616, United States*
[b] *Institute for Chemical Research, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan*
[c] *Integrated Research Consortium on Chemical Sciences, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan*

*Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x* were treated with an excess of ethylene gas over one hour at 25 °C. The temperature was raised to 60 °C and the mixture was stirred for 12h to give a red solution (Scheme 2). Benzene was removed under reduced pressure and replaced by toluene (*ca.* 20mL). Concentration to ca. 10mL followed by storage at ca. -18 °C afforded red crystals of the stannylenes **1a** and **1b** in moderate yield (0.53g, 51.23%) and (0.42 g, 40.9%). The X-ray crystal structures of compounds **1a** and **1b** are shown in Figure 1.



**Scheme** 2. The reaction of $SnAr_2$ species with ethylene.

The crystal structures illustrate that one ethylene molecule has inserted into one of the Sn-C bonds of each stannylene. The tin atoms have a bent two-coordinate configuration with C-Sn-C angles of 94.7(5)°(**1a**) and 99.06°(**1b**). These are considerably narrower than those in previously reported, related stannylenes which span the range 107.61(9)° to 123.55(14)°.[11-17] In particular, the C-Sn-C angles may be compared to those of the precursor $Sn(Ar^{iPr4})_2$ (112.77(9)°) and $Sn(Ar^{iPr6})_2$ (112.55(6)) which are significantly wider because of the greater steric repulsion between the two large terphenyl substituents. The Sn-C bond lengths in **1a** and **1b** span the range 2.145(4)-2.210(12)Å which is similar to what is found in other stannylenes and distannenes[11-17] (*cf.* sum, 2.17Å, of the single bond radii of carbon, 0.77 Å, and tin ,1.40 Å).[18]



**1a** **1b**

**Figure** 1. X-ray crystal structure of $Ar^{iPr4}SnCH_2CH_2Ar^{iPr4}$ (**1a**, left) and $Ar^{iPr6}SnCH_2CH_2Ar^{iPr6}$ (**1b**, right). Hydrogen atoms and co-crystallized solvent molecules are not shown. Selected bond lengths [Å] and angles [°]: **1a:** C1-Sn1: 2.145(4), Sn1-C10: 2.210(12), C10-C11: 1.542(13), C11-C12: 1.50(17), C1-Sn1-C10: 94.7(5), Sn1-C10-C11: 112.6(12), C10-C11-C12: 119.9(14). **1b**: C1-Sn1: 2.1992(12), Sn1-C14: 2.205(2), C14-C15: 1.549(3), C15-C16: 1.492, C1-Sn1-C14: 99.22(1), Sn1-C14-C15: 109.90(18), C14-C15-C16: 116.224

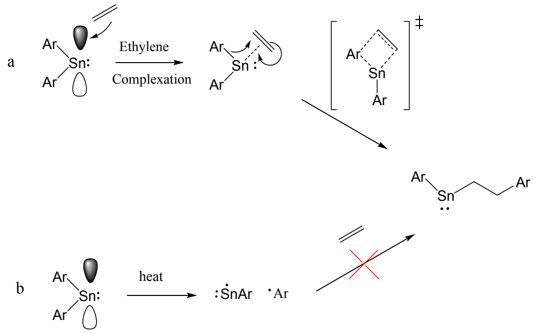
The solution $^{119}Sn\{^1H\}$ NMR spectra of **1a** and **1b** display a single downfield resonance at 1809 and 1946 ppm respectively. These chemical shifts lie within the range (1200-2600ppm) observed for other two-coordinate diorganostannylenes and related species,[19] and may be compared with the $^{119}Sn$ NMR chemical shifts of $Sn(Ar^{Me6})_2$ (1971ppm),[16] $Sn(Ar^{iPr4})_2$ (2245ppm)[17] and $Sn(Ar^{iPr6})_2$ (2129ppm).[12] The UV-vis spectra show one absorption at 482 nm (**1a**) or 489 nm (**1b**), consistent with an n→p transition for alkyl/aryl stannylene species having a monomeric formulation in solution.[11,12,16,20-22] These values may be compared to those of $Ar^{iPr4}SnCH_2C_6H_5$ (486nm),[20] $Ar^{iPr4}SnCH_2C_6H_4$-3-Me (490nm),[20] $Ar^{iPr4}SnCH_2CH_2Bu^t$ (486nm),[21] $Ar^{iPr6}SnCH_2CH_2Bu^t$ (484nm), [21] and $Ar^{iPr4}SnR$ (R= norbornyl, 494nm; norbornenyl, 502nm)[22] and $Ar^{iPr4}Sn(norbornyl)SnAr^{iPr4}$ (496nm) [22] which were prepared by the reactions of the respective olefins with the corresponding aryl tin (II) hydrides.

The reaction of $Sn(Ar^{iPr4})_2$ or $Sn(Ar^{iPr6})_2$ with ethylene to yield **1a** and **1b** was found to be limited to one equivalent of ethylene even in the presence of a large excess of the olefin and extended reaction periods up to 3 days. Cooling the solution to −80°C also afforded no evidence of further ethylene complexation or reaction with **1a** or **1b** on the basis of $^1H$ NMR spectroscopy. We also tested the reactivity of the related tetrylene, $Sn(Ar^{Me6})_2$, where the tin environment is less hindered. However, no reaction with ethylene was observed under identical conditions to those used for **1a** and **1b**. The sterically counter-intuitive reactivity pattern toward ethylene may be compared to the reactions of $Sn(Ar^{Me6})_2$ and $Sn(Ar^{iPr4})_2$ toward $H_2$, where the less bulky $Sn(Ar^{Me6})_2$ was also found to be unreactive toward $H_2$ even at elevated temperature. Inspection of the UV-vis spectra of $Sn(Ar^{Me6})_2$, $Sn(Ar^{iPr4})_2$ and $Sn(Ar^{iPr6})_2$ reveals absorptions at 553, 600 and 612 nm respectively which shows that the absorption maximum is shifted to longer wavelengths, hence lower energies, for the more crowded stannylenes and is consistent with a decreased HOMO-LUMO energy separation as the size of the ligands increase. Attempted reactions of $Sn(Ar^{iPr4})_2$ and $Sn(Ar^{iPr6})_2$ with propene, 2-butene or styrene under similar conditions to those described for ethylene yielded no evidence of reaction, apparently for steric reasons.

In contrast to the UV-vis absorptions mentioned above for $Sn(Ar^{iPr4})_2$ (600nm) and $Sn(Ar^{iPr6})_2$ (612nm), **1a** (482nm) and **1b** (489nm), have the significantly shorter wavelength values indicating a larger HOMO-LUMO separation. They display no further reactivity with ethylene (cf, $Sn(Ar^{Me6})_2$ has an absorption at 553nm and also does not react with ethylene). The initial step of the reaction of $Sn(Ar^{iPr4})_2$ with ethylene is calculated (Figure S7) to involve the approach of the ethylene molecule at an angle to the Sn{C(ipso}$_2$ plane to interact approximately face-on with the Sn 5p-orbital. This is similar to the interactions with other small molecules such as $H_2$, CO or isocyanide[23,24]. This produces a weak ethylene complex (INT-1) (enthalpy of stabilization = -4.7 kcal$^{-1}$) and a slight lengthening of the ethylene C-C double bond. The ethylene is not symmetrically coordinated (the Sn-C distance to the two ethylene differs by over 0.2 Å). The INT-1 complex can further react by two routes involving the transition state TS 1 (ΔH= -2.6 kcal mol$^{-1}$, ΔG= +10.0kcal mol$^{-1}$ ) in which the Sn-C distances to the ethylene become almost equal (2.213 and 2.328 Å) en route to a cyclostannapropane intermediate INT-2 (with equal Sn-C bond lengths to $C_2H_4$ and a single C-C bond of 1.528 Å). This complex has a positive ΔG value and is thus unstable (ΔH= -3.6 kcal mol$^{-1}$, ΔG= +9.0kcal mol$^{-1}$) and does not lead to an inserted product. A somewhat higher energy transition state TS2 (ΔH= +4.8 kcal mol$^{-1}$, ΔG= +15.3kcal mol$^{-1}$) in which the ethylene is displaced toward one of the Sn-C(ipso) bonds which is lengthened to Sn-C1 = 2.601 Å (cf. Sn-C2 = 2.28 Å) and simultaneous initial formation of an Sn-C bond to one of the ethylene carbons (ie Sn--C4 = 2.376Å) and a C-C bond to the other ethylene carbon (C1--C3 = 2.72Å) is also calculated. This leads eventually to the formation of the inserted product (PRO, cf. Figure S7) corresponding to the structurally characterized **1a**. This is enthalpically favoured by 47.4 kcal mol$^{-1}$ (cf ΔG= -34.8 kcal mol$^{-1}$). Attempts to observe experimentally the interaction of ethylene and tin in solution (INT-

1) at *ca*. −80°C were unsuccessful consistent with the calculated instability of INT-2.

The possibility that the reaction might proceed by a different mechanism, involving homolytic cleavage of an Sn-C bond followed by the reaction of the •SnAr$^{iPr4}$/•Ar$^{iPr4}$ or •SnAr$^{iPr6}$/•Ar$^{iPr6}$ radical pairs with ethylene to yield the products as shown (Scheme 3b) was also investigated. The •SnAr$^{iPr4}$ radical has recently been detected in the metathesis reactions of :Sn(Ar$^{iPr4}$)$_2$ with alkyl benzenes in refluxing toluene. However, the calculations at the B3PW91-D3BJ level indicate a quite high activation barrier (*ca.* 44.8 kcal mol$^{-1}$) for such a process shown in Scheme 3b.



**Scheme 3**. Two proposed ethylene insertion mechanisms for the reactions of the diaryl tin with ethylene.

In summary, the reaction of Sn(Ar$^{iPr4}$)$_2$ or Sn(Ar$^{iPr6}$)$_2$ with ethylene at 60°C proceeds via a facile migratory insertion route to afford products **1a** and **1b** The downfield $^{119}$Sn NMR chemical shifts at 1809 and 1946 ppm. X-ray crystallography confirm these monomeric stannylene structures in the solid state and in solution. Further investigation of the reactivity of this open-shell species in underway.

We wish to acknowledge the US Department of Energy, Office of Basic Energy Science (DE-FG02-07ER46475) for support of this work.

## Conflicts of interest

There are no conflicts of interest to declare

## Notes and references

1. R. Jambor and A. Lyčka *Eur. J. Inorg. Chem.***2017**, 4887–4898
2. a) R. Kinjo; M. Ichinohe; A. Sekiguchi; N. Takagi; M. Sumimoto and S. Nagase, *J. Am. Chem. Soc.*, **2007**, *129*, 7766–7767. b) S.J. Han; T. Sasamori; Y. Mizuhata and N. Tokitoh, *Dalton Trans.,* **2010**, *39*, 9238–9240. c) C. Cui; M.M. Olmstead and P.P. Power, *J. Am. Chem. Soc.,* **2004**, *126*, 5062–5063. d) C. Cui; M.M. Olmstead; J.C. Fettinger; G.H. Spikes and P.P. Power, *J. Am. Chem. Soc*., **2005**, *127*, 17530–17541. e) T.J. Hadlington; J. Li; M. Hermann; A. Davey; G. Frenking and C. Jones, *Organometallics*, **2015**, *34*, 3175–3185. f) L. Zhao; C. Jones and G. Frenking, *Chem. Eur. J.,* **2015**, *21*, 12405–12413. g) T. Sasamori; T. Sugahara; T. Agou; J.-D. Guo; S. Nagase; R. Streubel and N. Tokitoh, *Organometallics*, **2015**, *34*, 2106–2109 h) V. Protchenko; M.P. Blake; A.D. Schwarz; C. Jones; P. Mountford and S. Aldridge, *Organometallics,* **2015**, *34*, 2126–2129 i) F. Lips; A. Mansikkamäki; J.C. Fettinger; H.M. Tuononen; P.P Power, *Organometallics* **2014**, *33*, 6253–6258 j) O.T. Summerscales; J.C. Fettinger; P.P. Power, *J. Am. Chem. Soc*. **2011**, *133*, 11960–11963 k) O.T. Summerscales; C.A. Caputo; C.E. Knapp; J.C. Fettinger; P.P. Power, *J. Am. Chem. Soc.* **2012**, *134*, 14595–14603
3. H. Jacobsen; T. Ziegler, *Comments Inorg. Chem.* **1995**, *17*, 301-317
4. H. Ohgaki; Y. Kabe and W. Ando *Organometallics* **1995**, *14*, 2139-2141
5. R. Rodriguez; D. Gau; T. Kato; N. Saffon-Merceron; A. De Cozar; F.P. Cossio; A. Baceiredo, *Angew. Chem., Int. Ed.* **2011**, *50*, 10414-10416
6. F. Lips; J.C. Fettinger; A. Mansikkamäki; H.M. Tuononen; P.P. Power, *J. Am. Chem. Soc.* **2014**, *136*, 634–637
7. D. Wendel; W. Eisenreich; C. Jandl; A. Pöthig; B. Rieger, *Organometallics* **2016**, *35*, 1-4
8. X.H. Lu; L.M. Zhai; Y.X. Wang, *Chin. J. Chem*. **2001**, *19*, 1053-1057
9. A. Kavara; K.D. Cousineau; A.D. Rohr; J.W. Kampf; M.M. Banaszak-Holl, *Organometallics* **2008**, *27*, 1041-1043
10. J. March, *Advanced Organic Chemistry,* 4th ed.; Wiley: New York, **1992**; pp 743–745
11. G.H. Spikes; Y. Peng; J.C. Fettinger; P.P. Power, *Z. Anorg. Allg. Chem.* **2006**, *632*, 1005–1010
12. M. McCrea-Hendrick; M. Bursch; K.L. Gullett; L.R. Maurer; J.C. Fettinger; S. Grimme; and P.P. Power, *Organometallics*, **2018**, *37*, 2075-2085
13. V.Y. Lee; A. Sekiguchi, *Organometallic Compounds of Low-Coordinate Si, Ge, Sn and Pb: From Phantom Species to Stable Compounds*, John Wiley & Sons, Ltd, Chichester, UK, 2010.
14. M. Asay; C. Jones; and M. Driess, *Chem. Rev.* **2011**, *111*, 354-396
15. Y. Mizuhata; T. Sasamori; and N. Tokitoh, *Chem Rev.* **2009**, *109*, 3479-3511
16. P. Wilfling; K. Schittelkopf; M. Flock; R.H. Herber; P.P. Power; R.C. Fischer, *Organometallics* **2015**, *34*, 2222–2232.
17. R.S. Simons; L. Pu; M.M. Olmstead; P.P. Power, *Organometallics* **1997**, *16*, 1920–1925
18. P. Pyykkö; M. Atsumi, *Chem. - Eur. J.* **2009**, *15*, 186-197.
19. a) B. Wrackmeyer, *In Annual Reports on NMR Spectroscopy*; Academic Press: San Diego, CA, 1999; Vol. 38 b) N. Tokitoh; K. Manmaru; R. Okazaki, *Organometallics* **1994**, 13, 167-171 c) M. Weidenbruch; J. Schlaefke; A. Schafer; K. Peters; H.G. von Schnering; H. Marsmann, *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1846-1848.
20. T.Y. Lai; J.C. Fettinger and P.P. Power, *J. Am. Chem. Soc.,* **2018**, *17*, 5674-5677
21. S. Wang; M. McCrea-Hendrick; C.M. Weinstein; C.A. Caputo; E. Hoppe; J.C. Fettinger; M.M. Olmstead; P.P. Power, *J. Am. Chem. Soc*. **2017**, *139*, 6596-6604.
22. S. Wang; M. McCrea-Hendrick; C.M. Weinstein; C.A. Caputo; E. Hoppe; J.C. Fettinger; M.M. Olmstead; P.P. Power, *J. Am. Chem. Soc*. **2017**, *139*, 6586-6595.
23. Y. Peng; J.-D. Guo; B.D. Ellis; Z. Zhu; J.C. Fettinger; S. Nagase; P.P. Power, *J. Am. Chem. Soc*. **2009**, *131*, 16272–16282.
24. Z.D. Brown; P.P. Power, *Inorg. Chem.* **2013**, *52*, 6248-6259