ChemComm

ROYAL SOCIETY OF CHEMISTRY

COMMUNICATION

View Article Online
View Journal | View Issue

Check for updates

Cite this: *Chem. Commun.*, 2023, **59**, 13203

Received 18th August 2023,
Accepted 8th October 2023

DOI: 10.1039/d3cc04014c

rsc.li/chemcomm

Sn(II)–carbon bond reactivity: radical generation and consumption *via* reactions of a stannylene with alkynes†

Wenxing Zou,‡ Kristian L. Mears,‡ James C. Fettinger and Philip P. Power *

Thermal Sn–C cleavage in the diarylstannylene $Sn(Ar^{iPr4})_2$ (Ar^{iPr4} = C_6H_3-2,6-(C_6H_3-2,6-iPr_2)$_2$) was used to generate $^{\bullet}Sn(Ar^{iPr4})$ and $^{\bullet}Ar^{iPr4}$ radicals for alkyne arylstannylation. The radical pair and RCCR′ (R = H, R′ = Ph; R = Ph, R′ = Ph; R = H, R′ = C_4H_9; R = H, R′ = $SiMe_3$) in refluxing benzene generate the aryl vinyl stannylene complexes, $Ar^{iPr4}Sn\{C(C_6H_5)$-$C(H)(Ar^{iPr4})\}$ (1), $Ar^{iPr4}Sn\{C(C_6H_5)$-$C(H)(C_6H_5)\}$ (2) and $Ar^{iPr4}Sn\{C(C_4H_9)$-$C(H)(Ar^{iPr4})\}$ (3) respectively. For $HCCSiMe_3$, the known distannene $\{Sn(CCSiMe_3)Ar^{iPr4}\}_2$ (4) was also generated from this new method.

Structural and theoretical studies of stannylenes, a class of stable, divalent tin carbene analogues,[1–3] have the general formula of SnR_2 where usually, R = bulky organic or related ligand. Stannylenes feature a vacant p-orbital, as well as an orbital occupied by a non-bonding pair of electrons.[4–7] These frontier orbitals define their electron acceptor and donor characteristics. Like other heavier group 14 carbene analogues, stannylenes are highly colored and typically display high reactivity towards small molecules due to their relatively modest HOMO–LUMO gap (*ca.* 2.0–2.5 eV)[8,9] and often well-defined Sn(I) radical character.[10,11] It has been shown that stannylenes react with H_2,[9,12,13] CO_2,[14–16] RNH_2,[9] and ROH (R = Me or H)[17] and ethylene[6] under mild conditions.

In contrast to these studies, investigations of stannylene reactivity with alkynes remain scarce. In late 1980s, Sita and coworkers[18] reported a reversible complexation of a stannylene with a strained cycloheptyne species, which afforded a 1 : 1 complex (Fig. 1a). It is noteworthy that the resulting addition product dissociated to regenerate the corresponding stannylene and free alkyne at elevated temperature, suggesting that this coordination can be understood in terms of a weak π-complex binding.[19] Veith's group[20] reported the synthesis of the first distannacyclobutene, which was prepared from a formal [2+2] cycloaddition reaction of a diamidostannylene (equilibrated with the corresponding distannene) with a strained cyclic alkyne under ambient conditions (Fig. 1b).

In contrast to simple coordination/cycloaddition products mentioned above, Kira *et al.* reported a more complicated reaction of a diaryl stannylene and methyl/ethyl propynoates, which gave a 1 : 2 complex (Fig. 1c).[21] However, treatment of the

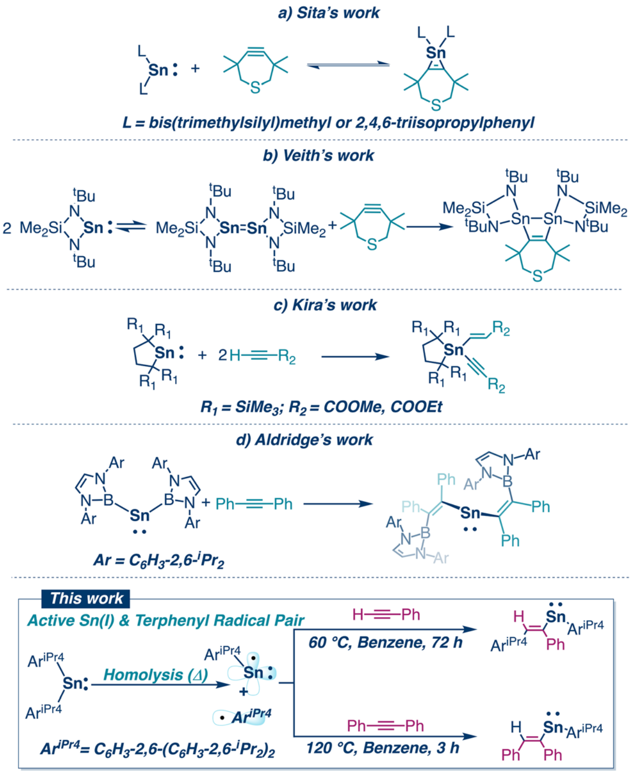


Fig. 1 Previously reported reactions of stannylenes (a–d) with alkynes and the known homolysis exploited for arylstannylation, reported here.[18,20–22]

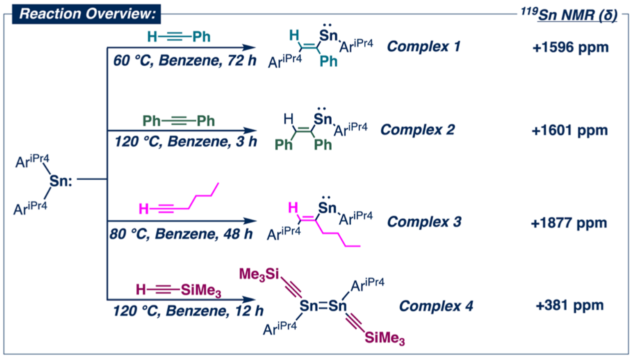
Department of Chemistry, University of California, One Shields Avenue, Davis, 95616, USA. E-mail: pppower@ucdavis.edu

† Electronic supplementary information (ESI) available: Experimental details and characterization methods including multinuclear NMR, UV-vis and IR spectroscopy and SCXRD data. CCDC 2271751 and 2271752. For ESI and crystallographic data in CIF or other electronic format see DOI: https://doi.org/10.1039/d3cc04014c

‡ These authors contributed equally.

same starting reagents with non-terminal alkynes afforded no reaction. A double insertion reaction of bis(boryl)stannylenes and alkynes was reported by Aldridge and co-workers, showing that the treatment of bis(boryl)stannylene with diphenylacetylene yielded a borane-appended (vinyl) Sn(II) compound (Fig. 1d).[22] Previously, we showed that the diarylstannylene $Sn(Ar^{iPr4})_2$ underwent a facile migratory insertion reaction with ethylene, to afford two stannylene species with slightly different terphenyl substituents (Ar^{iPr4} and Ar^{iPr6}, $Ar^{iPr6} = C_6H_3$-2,6-(C_6H_2-2,4,6-$iPr_3)_2$).[6,23] While the use of tin compounds is widespread in organic chemistry[24,25] (*e.g.* Stille coupling),[26] the tin species employed usually have the Sn(IV) oxidation state. However, recent work on radical-based borylstannylations of alkynes using Sn(IV)–B containing compounds[27–29] has provided evidence that a Sn(II) stannylene can accomplish an arylstannylation. By accessing a one-coordinate Sn(I) radical-terphenyl radical pair by thermal homolysis of $Sn(Ar^{iPr4})_2$ at elevated temperatures,[23,30] similar reactivity of this radical pair with alkynes could be envisioned. We herein describe the insertion reactions of the diarylstannylene $Sn(Ar^{iPr4})_2$ and a series of alkynes (Scheme 1).

The reaction of $Sn(Ar^{iPr4})_2$ and 3 equiv. of phenylacetylene in benzene at 60 °C for 3 days resulted in a color change from dark blue to dark red. Benzene was removed under reduced pressure to afford the product, $Ar^{iPr4}Sn\{C(C_6H_5)\text{-}C(H)(Ar^{iPr4})\}$ (**1**), as a dark red residue. Recrystallization from hexane yielded red blocks of **1** which were suitable for single crystal X-ray crystallography (SCXRD). The SCXRD data for **1** (Fig. 2) showed that the $Sn(Ar^{iPr4})_2$ had added across the phenylacetylene molecule to afford monomeric aryl vinyl divalent tin complex (**1**). Complex **1** features a mononuclear two-coordinate tin atom, with an interligand angle of 110.22(15)°, which is significantly narrower than those in the previously reported diaryl stannylene complexes (*cf.* $Sn(Ar^{iPr4})_2 : 117.56(8)°$;[31] $Sn(Ar^{iPr6})_2$ ($Ar^{iPr6} = C_6H_3$-2,6-(C_6H_2-2,4,6-$^iPr_3)_2$):107.61(9)°;[32] $Sn(Ar^{iPr4}\text{-}4\text{-}Cl)_2 : 115.12(8)°$;[33] $Sn(Ar^{iPr4}\text{-}3,5\text{-}^iPr_2)_2 : 123.4(2)°$;[33] $Sn(Ar^{iPr4}\text{-}4\text{-}SiMe_3)_2 : 115.37(9)°$)[33] but considerably wider than those in the related aryl alkyl substituted stannylenes (*cf.* $Ar^{iPr4}SnCH_2CH_2Ar^{iPr4} : 94.7(5)°$;[6] $Ar^{iPr6}SnCH_2CH_2Ar^{iPr6} : 99.22(1)°$).[6] The Sn–C1 and Sn–C9 bond lengths in **1** span the range 2.217(4) to 2.225(16) Å, which slightly exceed the sum of the single bond radii of carbon (0.77 Å) and tin (1.4 Å)[34] but nevertheless can be compared to the Sn–C_{ipso} distances observed in other aryl (alkyl) stannylenes (*cf.* $Sn\{C(Ph) = C(Ph)B(NDipCH)_2\}_2 : 2.2232(19)$ Å;[22] $Sn\{C(Ph) = C(H)B(NDipCH)_2\}\{NDip(SiMe_3)\}$: 2.2298(19) Å;[22] $Ar^{iPr4}SnCH_2CH_2Ar^{iPr4} : 2.192(3)$ Å;[6] $Ar^{iPr6}SnCH_2CH_2Ar^{iPr6} : 2.1992(12)$ Å).[6] C1 and C2 have essentially planar geometry (a sum of interior angles of 359.6(10)° for C1 and 361.0(17)° for C2) which is consistent with their approximate sp^2 hybridization. The ^{119}Sn NMR spectrum of **1** shows two signals, the more downfield signal at +1598.74 ppm corresponding to **1** (the molecular structure of **1** is shown in Fig. 2) and what is likely the corresponding distannene, $[Ar^{iPr4}Sn\{C(C_6H_5)\text{-}C(H)(Ar^{iPr4})\}]_2$ ($\mathbf{1}^{\mathbf{dimer}}$), which displays a more upfield shift of +389.55 ppm. A rapid association/dissociation likely occurs in the solution state leading to the formation of $\mathbf{1}^{\mathbf{dimer}}$ which is also evident by the broad peaks in the ^1H NMR spectrum of **1** indicating high fluxionality. Other distannene compounds also display signals in this region of the ^{119}Sn NMR spectrum.[35,36]



Scheme 1 Overview of insertion reactions of diarylstannylene with alkynes reported here.

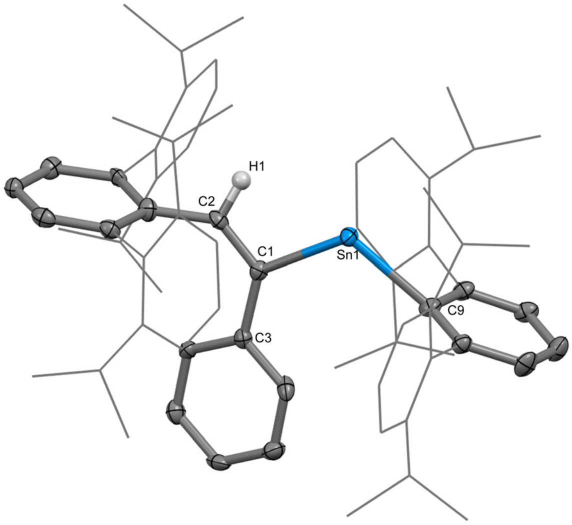


Fig. 2 Molecular structure of complex **1** (ellipsoids shown at 50% probability, most hydrogens not shown and flanking rings shown in wireframe format for clarity). Selected bond lengths (Å) and angles (°) of **1**: C1-C2 1.332(6); C1-C3 1.512(5); C1-Sn1 2.225(16); Sn1-C9 2.217(4); C2-C1-C3 : 125.9(4); C3-C1-Sn1 : 129.5(3); C2-C1-Sn1 : 104.3(3); C1-Sn1-C9 : 110.22(15).

The use of diphenylacetylene, a more sterically demanding alkyne yielded a monomeric organotin species $Ar^{iPr4}Sn\{C(C_6H_5)\text{-}C(H)(C_6H_5)\}$ (**2**) that displays only one terphenyl ligand Ar^{iPr4} at the Sn(II) atom (Fig. 3). The tin atom in **2** (Fig. 3) has a bent two-coordinate configuration with an C1-*Sn*-C15 angle of 98.574(5)°, which is much narrower than that in **1** but is comparable to those in other alkyl substituted arylstannylenes (*cf.* $Ar^{iPr4}SnCH_2CH_2Ar^{iPr4} : 98.59(15)°$,[6] and $^{AriPr6}SnCH_2CH_2{}^{AriPr6} : 99.23(7)°$).[6] The H1, C2, C1 atoms in **2** lie essentially coplanar with the C15-Sn1-C1 plane with a twist angle of 7.04(11)°, while the two phenyl rings on the vinyl substituent are nearly orthogonal to each other (a twist angle of 86.07(6)°).

The ^{119}Sn NMR spectrum of compound **2** revealed a single resonance at +1601 ppm, which falls just upfield of the observed monomeric divalent organotin species (*cf.* $Ar^{iPr4}SnCH_2CH_2Ar^{iPr4}$:

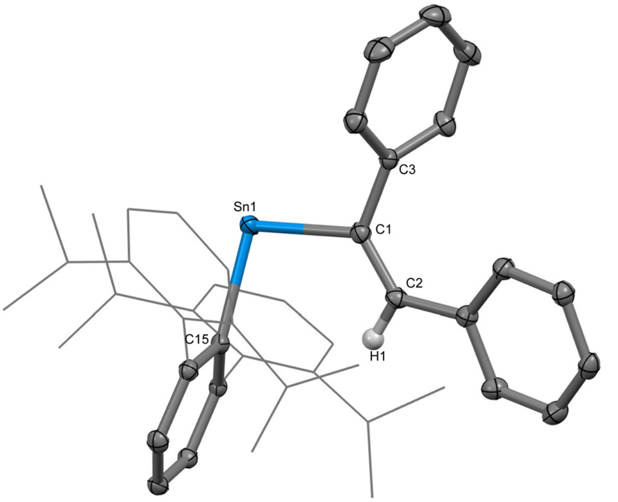
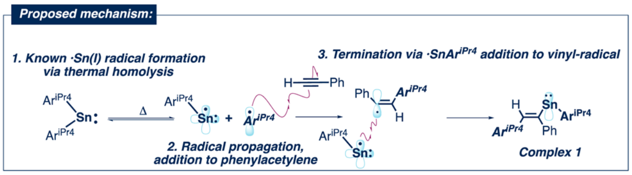


Fig. 3 Molecular structure of complex **2** (ellipsoids shown at 50% probability, most hydrogens not shown, and flanking rings shown in wireframe format for clarity). Selected bond lengths (Å) and angles (°) of **2**: C1-C2 1.3497(17); C1-Sn1 2.1999(13); Sn1-C15 2.2009(12); C1-C3 1.4814(17); C3-C1-Sn1 111.63(8); C2-C1-Sn1 122.34(9); C2-C1-C3 126.03(11); C1-Sn1-C15 98.57(5).



Scheme 2 Proposed mechanism for the formation of complex **1**.

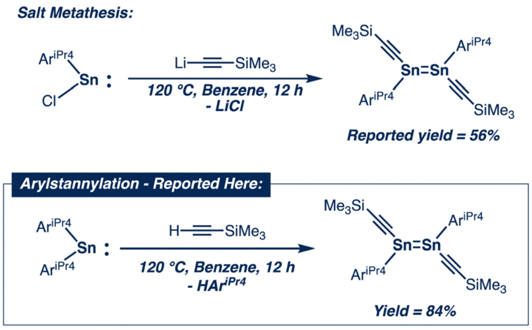


Fig. 4 Comparison of yields obtained for complex **4** by salt metathesis route and arylstannylation route.

+1809 ppm;[6] Ar^{iPr6}SnCH$_2$CH$_2$Ar^{iPr6}: +1946 ppm;[6] Sn{C(Ph) = C(H)B(NDippCH)$_2$}$_2$: +1730 ppm;[22] Sn{C(Ph) = C(Ph)B(NDippCH)$_2$}$_2$: +1670 ppm),[22] which also indicates that **2** is a monomer in solution. The UV-vis spectrum of **2** shows a broad absorption band at 518 nm that tails into visible region. The absorption signal is attributed to n → p transitions which are directly correlated to the HOMO–LUMO energy gap. This value is comparable to those of other monomeric alkyl/aryl stannylene species (*cf.* Ar^{iPr4}SnCH$_2$C$_6$H$_5$: 486 nm;[23] Ar^{iPr4}SnCH$_2$C$_6$H$_4$-3-Me: 490 nm;[23] Ar^{iPr4}SnCH$_2$CH$_2$*t*Bu: 486 nm;[37] Ar^{iPr6}SnCH$_2$CH$_2$*t*Bu: 484 nm;[37] and Ar^{iPr4}SnR (R = norbornyl, 494 nm; norbornenyl, 502 nm) and Ar^{iPr4}Sn(norbornyl)SnAr^{iPr4} (496 nm)).[38]

We then tested reactive aliphatic alkynes with Sn(Ar^{iPr4})$_2$, including 1-hexyne and trimethylsilylacetylene. When Sn(Ar^{iPr4})$_2$ was treated with three molar equivalents of 1-hexyne in benzene at 80 °C for 48 h, the deep blue color of the Sn(Ar^{iPr4})$_2$ gradually became dark purple. Removal of the solvent under reduced pressure afforded a purple powder. This was re-dissolved in diethyl ether (50 mL) and stored in a *ca.* −38 °C freezer to yield the pure compound **3** (68%) as a purple solid. However, attempts to grow crystals of **3** from a variety of other solvents were unsuccessful. A probable structure for **3** based on spectroscopic data is given in Scheme 1. The mechanism (Scheme 2) of the formation of compound **1** is based on known literature precedent.[6,23,30] Homolytic cleavage of a Sn–C bond was initiated upon heating, followed by the formation of a :ṠnAr^{iPr4} radical and a terphenyl carbon radical •Ar^{iPr4}, which can be contrasted with the generation of the radical •Sn{CH(SiMe$_3$)$_2$}$_3$ by heating hydrocarbon solutions of {Sn{CH(SiMe$_3$)$_2$}$_2$}$_2$.[10,11,39] The reaction of the :ṠnAr^{iPr4}/•Ar^{iPr4} radical pair with phenylacetylene yielded the product **1**. In the synthesis of **2**, the •Ar^{iPr4} is not added to the alkyne substrate, likely for steric reasons. We have previously shown that proton abstraction[23] from the most readily available source (solvent) is likely the radical termination step for the generated •Ar^{iPr4} radical.

Interestingly, the addition of Sn(Ar^{iPr4})$_2$ to trimethylsilylacetylene yielded the known distannene [(Ar^{iPr4})Sn(CCSiMe$_3$)]$_2$ (complex **4**) arising from the dimerization of the stannylene monomer [(Ar^{iPr4})Sn(CCSiMe$_3$)] which was previously synthesized *via* the salt metathesis route between [SnCl(Ar^{iPr4})] and LiCCSiMe$_3$ (Fig. 4).[36] The yield obtained for complex **4** was significantly improved using the arylstannylation route reported here (84% compared to 56% obtained for the salt metathesis route). Complex **4** has previously shown to undergo dynamic solution behavior, dissociating from the distannene dimer to the stannylene monomer at room temperature. These fast processes in solution may play a role in the preferential formation of the distannene, rather than the anticipated arylstannylated product, which was not observed.

In summary, the thermal homolysis of an Sn–C bond in Sn(Ar^{iPr4})$_2$ to generate the one-coordinate Sn(I) radical, :ṠnAr^{iPr4} and a terphenyl •Ar^{iPr4} radical has been applied for the first time in the arylstannylations of alkynes at elevated temperature, to afford stable vinylstannylenes (products **1**–**3**). For the case of trimethylsilylacetylene, the known distannene product (**4**) was generated, rather than an arylstannylated alkene product. The structures of **1**, **2** and **4** were confirmed by X-ray crystallography and multinuclear NMR spectroscopy, while **4** was confirmed by ^{1}H, ^{13}C and ^{119}Sn NMR spectroscopy. Further mechanistic investigations are in hand.

Conflicts of interest

There are no conflicts to declare.

Notes and references

1 S. Benet, C. J. Cardin, D. J. Cardin, S. P. Constantine, P. Heath, H. Rashid, S. Teixeira, J. H. Thorpe and A. K. Todd, *Organometallics*, 1999, **18**, 389–398.
2 W. Setaka, K. Sakamoto, M. Kira and P. P. Power, *Organometallics*, 2001, **20**, 4460–4462.
3 H. Arp, J. Baumgartner, C. Marschner and T. Müller, *J. Am. Chem. Soc.*, 2011, **133**, 5632–5635.
4 Y. Mizuhata, T. Sasamori and N. Tokitoh, *Chem. Rev.*, 2009, **109**, 3479–3511.
5 C. Mohapatra, L. T. Scharf, T. Scherpf, B. Mallick, K. Feichtner, C. Schwarz and V. H. Gessner, *Angew. Chem., Int. Ed.*, 2019, **58**, 7459–7463.
6 T. Y. Lai, J.-D. Guo, J. C. Fettinger, S. Nagase and P. P. Power, *Chem. Commun.*, 2019, **55**, 405–407.
7 N. Abedini and M. Z. Kassaee, *Comput. Theor. Chem.*, 2020, **1190**, 112998.
8 S. Banerjee and K. Vanka, *Polyhedron*, 2022, **222**, 115907.
9 Y. Peng, B. D. Ellis, X. Wang and P. P. Power, *J. Am. Chem. Soc.*, 2008, **130**, 12268–12269.
10 A. Hudson, M. F. Lappert and P. W. Lednor, *J. Chem. Soc., Dalton Trans.*, 1976, 2369.
11 K. L. Mears, B. Ruiz, G.-A. Nguyen, W. Zou, J. C. Fettinger and P. P. Power, *Chem. Commun.*, 2023, **59**, 6399–6402.
12 Y. Peng, J.-D. Guo, B. D. Ellis, Z. Zhu, J. C. Fettinger, S. Nagase and P. P. Power, *J. Am. Chem. Soc.*, 2009, **131**, 16272–16282.
13 R. C. Turnell-Ritson, J. S. Sapsford, R. T. Cooper, S. S. Lee, T. Földes, P. A. Hunt, I. Pápai and A. E. Ashley, *Chem. Sci.*, 2018, **9**, 8716–8722.
14 L. A.-M. Harris, M. P. Coles and J. R. Fulton, *Inorg. Chim. Acta*, 2011, **369**, 97–102.
15 L. Ferro, P. B. Hitchcock, M. P. Coles, H. Cox and J. R. Fulton, *Inorg. Chem.*, 2011, **50**, 1879–1888.
16 A. V. Protchenko, M. Á. Fuentes, J. Hicks, C. McManus, R. Tirfoin and S. Aldridge, *Dalton Trans.*, 2021, **50**, 9059–9067.
17 J. D. Erickson, P. Vasko, R. D. Riparetti, J. C. Fettinger, H. M. Tuononen and P. P. Power, *Organometallics*, 2015, **34**, 5785–5791.
18 L. R. Sita and R. D. Bickerstaff, *J. Am. Chem. Soc.*, 1988, **110**, 5208–5209.
19 J. A. Boatz, M. S. Gordon and L. R. Sita, *J. Phys. Chem.*, 1990, **94**, 5488–5493.
20 A. Krebs, A. Jacobsen-Bauer, E. Haupt, M. Veith and V. Huch, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 603–604.
21 J. Xu, X.-Q. Xiao, C. Yan, Z. Li, Q. Lu, Q. Yang, G. Lai and M. Kira, *Organometallics*, 2018, **37**, 2399–2405.
22 A. V. Protchenko, M. P. Blake, A. D. Schwarz, C. Jones, P. Mountford and S. Aldridge, *Organometallics*, 2015, **34**, 2126–2129.
23 T. Y. Lai, J. C. Fettinger and P. P. Power, *J. Am. Chem. Soc.*, 2018, **140**, 5674–5677.
24 A. G. Davies, *Organotin Chemistry*, Wiley-VCH, Weinheim, 2004, pp. 1–77.
25 T. Mukaiyama and S. Kobayashi, *J. Organomet. Chem.*, 1990, **382**, 39–52.
26 J. K. Stille, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 508–524.
27 H. Yoshida, Y. Takemoto and K. Takaki, *Chem. Commun.*, 2015, **51**, 6297–6300.
28 S. Onozawa, Y. Hatanaka, T. Sakakura, S. Shimada and M. Tanaka, *Organometallics*, 1996, **15**, 5450–5452.
29 K. Suzuki, N. Sugihara, Y. Nishimoto and M. Yasuda, *Angew. Chem., Int. Ed.*, 2022, **61**, e202201883.
30 T. Y. Lai, L. Tao, R. D. Britt and P. P. Power, *J. Am. Chem. Soc.*, 2019, **141**, 12527–12530.
31 G. H. Spikes, Y. Peng, J. C. Fettinger and P. P. Power, *Z. Anorg. Allg. Chem.*, 2006, **632**, 1005–1010.
32 M. L. McCrea-Hendrick, M. Bursch, K. L. Gullett, L. R. Maurer, J. C. Fettinger, S. Grimme and P. P. Power, *Organometallics*, 2018, **37**, 2075–2085.
33 P. Wilfling, K. Schittelkopf, M. Flock, R. H. Herber, P. P. Power and R. C. Fischer, *Organometallics*, 2015, **34**, 2222–2232.
34 P. Pyykkö and M. Atsumi, *Chem. – Eur. J.*, 2009, **15**, 186–197.
35 K. W. Zilm, G. A. Lawless, R. M. Merrill, J. M. Millar and G. G. Webb, *J. Am. Chem. Soc.*, 1987, **109**, 7236–7238.
36 C. R. Stennett, M. Bursch, J. C. Fettinger, S. Grimme and P. P. Power, *J. Am. Chem. Soc.*, 2021, **143**, 21478–21483.
37 S. Wang, M. L. McCrea-Hendrick, C. M. Weinstein, C. A. Caputo, E. Hoppe, J. C. Fettinger, M. M. Olmstead and P. P. Power, *J. Am. Chem. Soc.*, 2017, **139**, 6596–6604.
38 H. Lei, J. C. Fettinger and P. P. Power, *Organometallics*, 2010, **29**, 5585–5590.
39 P. J. Davidson, A. Hudson, M. F. Lappert and P. W. Lednor, *J. Chem. Soc., Chem. Commun.*, 1973, 829–830.