Inorganic Chemistry

Article

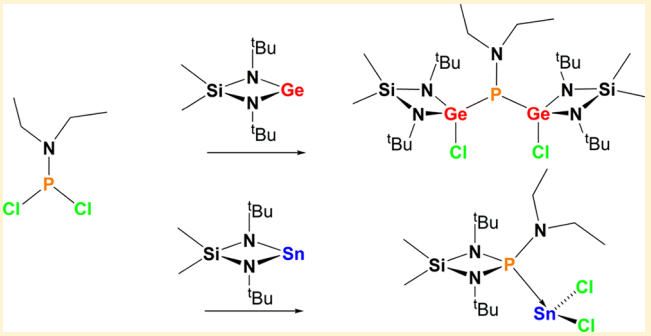
pubs.acs.org/IC

Reactions of Germylenes and Stannylenes with Halo(hydrocarbyl)- and Chloro(amino)phosphines: Oxidative Addition versus Ligand Transfer

Joseph K. West[†] and Lothar Stahl*

Department of Chemistry, University of North Dakota, Grand Forks, North Dakota 58202-9024, United States

ABSTRACT: Oxidative addition (OA) is an important elementary step in chemistry, but it has been studied mainly in the context of transition-metal-catalyzed reactions and mainly with carbon−X substrates (X = halogen, H). Reports of main-group metal compounds undergoing OA are rare by comparison, and those involving phosphorus−halogen substrates are rarer still. Acyclic and cyclic diazagermylenes and -stannylenes react with chloro(hydrocarbyl)phosphines with the intermediacy of oxidative addition products. Stannylenes react faster than germylenes, and these reactions are first-order in both reactants and slowed by steric bulk. Kinetic data and the structures of intermediates and products had suggested an adduct/insertion mechanism for these reactions. To gain further insight into these transformations, the work presented herein was extended to chloro(hydrocarbyl)phosphines with varying organic substituents. These studies confirmed prior conclusions concerning the rate-diminishing effect of steric bulk, and the rate dependence on leaving groups also seems to suggest adduct/insertion or S_N2 mechanisms. Importantly, these new data now also point to associative decomposition pathways. In the course of the investigation, it was discovered that aliphatic chloro(amino)phosphines react differently with the carbene analogues, giving oxidative addition products for germylenes but metathesis reactions for stannylenes.



1. INTRODUCTION

Oxidative addition (hereafter also OA) is a key elementary step in many catalytic cycles because it entails the functionalization of molecules by the controlled breaking of chemical bonds to set up the subsequent formation of new bonds.[1] Although the reaction can principally occur on any metal with two stable oxidation states that are two units apart, it is most often observed for second- and third-row transition metals of Groups 9 and 10, Vaska's complex and Wilkinson's catalyst being classic examples.[2,3]

Main-group metals also undergo oxidative additions, as the reaction of magnesium with hydrocarbyl halides shows.[4] This *s*-block metal, however, does not exhibit the facile two-oxidation state shuttle seen in transition metals. The *p*-block elements, particularly those of Group 14, undergo oxidative additions that more closely resemble those of the transition metals, as, for example, demonstrated by the OA of methyl iodide to stannocene.[5] Studies by Lappert et al. on organic halides adding to tin(II) and germanium(II) carbene analogues revealed the broader scope of such reactions.[6−8] The work was recently expanded by the group of Banaszak Holl, who published the most extensive and potentially most useful series of papers on C−X bond activation by germylenes and stannylenes.[9−13] Of course, silylenes also react with a variety of organic functional groups, but their even greater reactivity comes with loss of selectivity and control.[14,15] Because of the long history of carbene analogues in oxidative additions, these transformations are consistently used as benchmarks for novel carbene analogues in these and related reactions, as recent reports confirm.[16−25]

There is considerable current interest in the generation and manipulation of homo- and heteronuclear bonds between pnictogens, particularly those involving phosphorus,[26−37] for both fundamental studies and the potential use of such compounds in new materials. We are investigating homogeneous reductions of halophosphines by Group 14 carbene analogues for generating phosphorus−phosphorus bonded species. The reductions are usually performed with reactive bulk metals,[38−40] but homogeneous reductions are known.[41,42] These latter transformations also proceed with the intermediacy of OA products, but they are more complex than those of their carbon analogues. This is partly due to phosphorus' ability to exhibit hypervalency in both, intermediates and products, but it is also due to the weaker phosphorus−metal bonds which rarely afford isolable metal-containing species. However, because these reactions are homogeneous, they are amenable to mechanistic investigations, and we initiated such studies to gain insight into OA reactions of soluble Group 14 metal compounds.

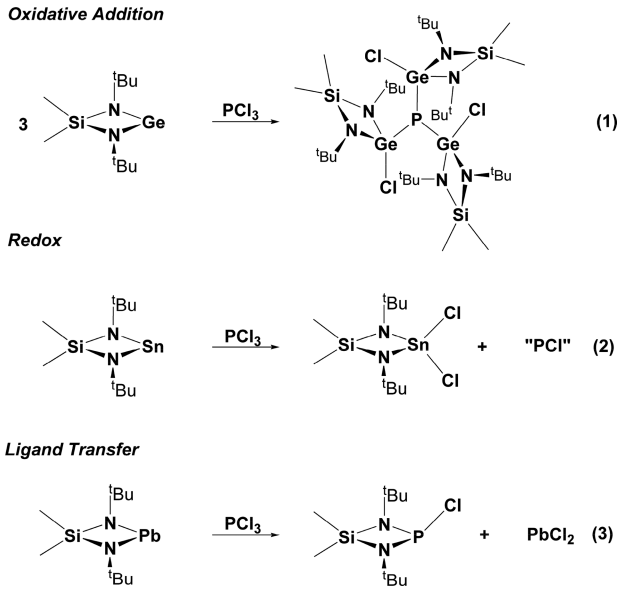
Early work by du Mont and Schumann had suggested that germanium(II) and tin(II) halides insert reversibly into the

Received: May 21, 2017

DOI: 10.1021/acs.inorgchem.7b01275
Inorg. Chem. XXXX, XXX, XXX−XXX

phosphorus−halogen bonds of halo(organo)phosphines.[43−50] These authors also produced strong evidence that these oxidative additions are preceded by adduct formation. Later, Veith et al. reported that phosphorus trichloride reacts with homologous cyclic Group 14 carbene analogues to give three entirely different products, which are depicted in Scheme 1.[51]

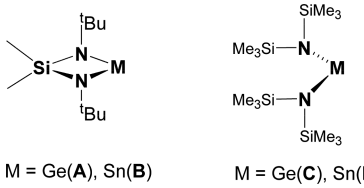
Scheme 1. Homologous Group 14 Carbene Analogues React Differently with PCl_3



All three of the P−Cl bonds of PCl_3 added to three germylenes to furnish a C_3-symmetrical trioxidative addition product. The stannylene, by contrast, underwent a redox reaction (eq 2) and was transformed to a dichlorostannane. Cyclic diazaplumbylene reacted by apparent ligand exchange only, producing $PbCl_2$ and a *P*-chloro-1,3,2λ^3,4-diazaphosphasiletidine, which had been previously accessible only by a much more cumbersome route.[52] Attempts by these authors to isolate intermediates using bulkier chlorophosphines were thwarted, but NMR spectroscopy allowed the identification of a few of these products in the reaction mixtures.[42]

Because chloro(organo)phosphines are less reactive than phosphorus trichloride, we reinvestigated prior work by incorporating these reagents. In addition to cyclic diazagermylenes and -stannylenes, we also tested their acyclic versions, all four of which are shown in Chart 1.

Chart 1



These modifications proved to be fortuitous, as numerous oxidative addition products were isolated and their solid-state structures were determined.[53] The results of our initial study can be summarized as follows:

1. The ultimate products of the reactions between diazagermylenes and -stannylenes and chloro(organo)-phosphines are primarily the corresponding dichlorogermanes and -stannanes and phosphorus−phosphorus coupled products, namely, diphosphines or cyclic oligophosphines.
2. All reactions seem to proceed with the intermediacy of oxidative addition products, which are almost always isolable if M = Ge, but less frequently so when M = Sn. The isolated tin compounds are often the decomposition products of the OA intermediates.
3. Conversion times vary greatly and range from seconds to months. They follow first-order kinetics for both, carbene analogues and chlorophosphines.
4. The reactivities of the carbene analogues follow the order: cyclic stannylene > cyclic germylene ∼ acyclic stannylene > acyclic germylene
5. Steric bulk on either the halophosphines or the carbene analogues hinders the rate of oxidative addition.

Below, we report on the expansion of this work to sterically smaller chloro(alkyl)phosphines, sterically bulkier chloro(aryl)-phosphines, and to chloro(amino)phosphines. These studies not only support earlier mechanistic evidence about the oxidative additions but also provide key insights into the decomposition pathway of the ensuing products. The chloro-(amino)phosphines, which had not been studied previously, showed an unexpected divergence in reactivity, giving oxidative addition products with germylenes but amide-ligand transfer products with stannylenes. These differences, in turn, hint at the subtle kinetic and thermodynamic factors that underlie these reactions.

2. EXPERIMENTAL SECTION

2.1. General Procedures. All manipulations and reactions were done under an atmosphere of argon using standard Schlenk techniques. Solvents were dried over and distilled from Na/benzophenone (toluene) and K/benzophenone (THF and hexanes). $PhPCl_2$ and Ph_2PCl were purchased from Aldrich Chemical Co. and distilled before use. $^tBu_2PCl$ was synthesized using a published procedure,[54] and $^tBuPCl_2$ was synthesized similarly using only 1 equiv of ^{t}BuLi. The chloro(amino)phosphines $Me_2Si(\mu\text{-}N^tBu)_2PCl$,[51] $(Et_2N)_2PCl$,[55] and Et_2NPCl_2[56] were prepared as previously reported. Cyclic $Me_2Si(\mu\text{-}N^tBu)_2E$ [E = Ge (**A**), Sn (**B**)],[57,58] and acyclic $[(Me_3Si)_2N]_2E$ [E = Ge (**C**), Sn (**D**)] were synthesized according to literature procedures.[59] Elemental analyses were conducted by Desert Analytics, Midwest Microlabs, and Columbia Analytical Services. All ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker Avance 500 NMR spectrometer in C_6D_6, THF-d_8, and CD_2Cl_2. ^{119}Sn NMR spectra were acquired on a JEOL ECX-300 NMR spectrometer. The chemical shifts, δ, are relative to the residual solvent peak(s) (e.g., C_6HD_5) for ^1H and ^{13}C spectra and the external standard $P(OEt)_3$ for ^{31}P spectra. Tin spectra are referenced to external $SnCl_4$ at −150.0 ppm. Melting points were obtained on a Mel-Temp apparatus; they are uncorrected.

2.2. Syntheses. *2.2.1. Halophosphines. (2,6-Me$_2$Ph)$_2$PCl.* In a 250 mL, 3-neck flask, fitted with an addition funnel, Et_2NPCl_2 (1.31 mL, 9.00 mmol) was stirred in hexanes (24 mL) at 0 °C. A 1.0 M THF solution of 2,6-Me_2PhMgBr (18.0 mL, 18.0 mmol) was added dropwise over 1 h. After 40 min, the flask was allowed to warm to rt. Volatiles were removed *in vacuo*, and the solid residue was redissolved in hexanes and filtered. Dry HCl was bubbled through this solution for ca. 30 min, and the ammonium salt that formed was removed by filtration. Colorless crystals formed in the filtrate at room temperature. Yield 1.98 g (80%). Mp: 57−59 °C. ^1H NMR (500.1 MHz, C_6D_6, 25 °C): δ 7.04 (t, 2 H, J_{HH} = 15 Hz, *p*-Ph), 6.86 (m, 4 H, *m*-Ph), 2.35 (s, 12 H, *o*-MePh). $^{31}P\{^1H\}$ NMR (202.5 MHz, C_6D_6, 25 °C): δ 82.2 (s).

^{t}Bu(Ph)PI. In a 250 mL, 3-neck flask, ^{t}Bu(Ph)PCl (4.71 mL, 25.0 mmol) and sodium iodide (15.0 g, 100 mmol) were stirred in refluxing toluene for 8 h, while the reaction mixture changed from colorless to

DOI: 10.1021/acs.inorgchem.7b01275
Inorg. Chem. XXXX, XXX, XXX−XXX

pale yellow. The solvent was removed *in vacuo*. This crude product, which was determined by ^{1}H NMR spectrometry to be >95% pure, was found to be of sufficient purity for all studies, Yield 5.23 g (72%). ^{1}H NMR (500.1 MHz, C_6D_6, 25 °C): δ 7.02−7.81 (m, 5 H, Ph), 1.01 (d, 9 H, ^{t}Bu, $^3J_{PH}$ = 15 Hz). ^{31}P{^{1}H} NMR (202.5 MHz, C_6D_6, 25 °C): δ 106.1 (s).

*2.2.2. Group 14 Derivatives. {{[(Me$_3$Si)$_2$N]$_2$Ge(Cl)P(Cl)}$_2$·C$_6$H$_{14}$} (**1**).* A stirred solution of $[(Me_3Si)_2N]_2Ge$ (0.651 g, 1.66 mmol) in hexanes (20 mL) was treated at 0 °C with a 1.0 M hexanes solution of PCl_3 (0.83 mL, 0.83 mmol) all at once. After 1 h, the reaction mixture was allowed to warm to rt. The initially bright-yellow solution, which changed to bright pink after 3.5−5 h, deposited pale-pink crystals as a hexane solvate after standing at 3 °C for several days. Yield: 0.94 g (57%). Mp: 150−153 °C (dec.). Anal. Calcd for $C_{27}H_{79}Cl_4Ge_2N_4P_2Si_8$ (1033.11): C, 31.37; H, 7.70; N, 5.42. Found: C, 30.27; H, 7.33; N, 5.44. ^{1}H NMR (500.1 MHz, C_6D_6, 25 °C): δ 0.48 (s, SiMe). ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6, 25 °C): δ 1.8 (s). ^{31}P{^{1}H} NMR (202.5 MHz, C_6D_6, 25 °C): δ 62.6 (s).

*[(Me$_3$Si)$_2$N)]$_2$SnI$_2$ (**2**).* A solution of $[(Me_3Si)_2N]_2Sn$ (8.21 mmol) in hexanes (10 mL) was treated dropwise with a PI_3 (2.74 mmol) solution in hexanes (10 mL) at 0 °C. The dark-red reaction mixture was stirred overnight, whereupon it took on a bright-orange color, which deposited a black precipitate. A ^{1}H NMR spectrum taken on an aliquot showed a complex product mixture. After the solution had been concentrated *in vacuo* and kept at 3 °C overnight, 0.94 g of colorless crystals formed. Yield: 55%. Mp: 92−94 °C. Anal. Calcd for $C_{12}H_{36}I_2N_2Si_4Sn$ (693.91): C, 20.79; H, 5.23; N, 4.04. Found: C, 20.47; H, 5.33; N, 4.14. ^{1}H NMR (500.1 MHz, C_6D_6, 25 °C): δ 0.424 (s, SiMe). ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6, 25 °C): δ 6.2 (s). ^{119}Sn NMR (111.9 MHz, C_6D_6, 25 °C): δ −669.65 (s).

*{[(Me$_3$Si)$_2$N]$_2$Ge(Cl)PEt$_2$} (**3**).* A stirred solution of $[(Me_3Si)_2N]_2Ge$ (0.389 g, 0.989 mmol) in hexanes (10 mL) was treated dropwise at 0 °C with a Et_2PCl solution (0.99 mL, 0.99 mmol) in hexanes (10 mL). After 10 min, the flask was removed from the cold bath and the reaction mixture was stirred at rt for 7.5 h. All volatiles were removed *in vacuo*, leaving a pale orange-yellow solid, which was redissolved in a minimal amount of hexanes. Crystals formed after the flask had been stored at rt for several days. Yield: 0. 226 g (43%). Mp: 102−105 °C. Anal. Calcd for $C_{16}H_{46}ClGeN_2PSi_2$ (517.96): C, 37.10; H, 8.95; N, 5.41. Found: C, 37.24; H, 8.77; N, 5.09. ^{1}H NMR (500.1 MHz, C_6D_6, 25 °C): δ 2.56 (m, 4 H, PCH_2), 0.85 (t, 6 H, J = 4.5 Hz PCH$_2$CH_3), 0.50 (s, 36 H, SiMe). ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6, 25 °C): δ 18.4 (d, J_{PC} = 20 Hz), 7.9 (s), 6.1 (s, SiMe). ^{31}P{^{1}H} NMR (202.5 MHz, C_6D_6, 25 °C): δ 20.4 (s).

*Me$_2$Si(μ-N^{t}Bu)$_2$Sn(Cl)P(2,6-Me$_2$Ph)$_2$ (**4**).* To a cold (0 °C) benzene solution (5 mL) of (2,6-Me$_2$C$_6$H$_3$)$_2$PCl (0.13 g, 0.47 mmol) was added dropwise a 1.0 M Me$_2$Si(μ-N^{t}Bu)$_2$Sn solution (0.47 mL). After 30 min, the reaction mixture was allowed to warm to rt and all volatiles were removed *in vacuo*. The residue was dissolved in a minimal amount of toluene, and the ensuing solution was kept at 3 °C until it deposited block-shaped, orange crystals. Yield: 0.25 g, 89%. Mp: 135−138 °C. Anal. Calcd for $C_{26}H_{42}ClN_2PSiSn$ (596.16): C, 52.41; H, 7.10; N, 4.70. Found: C, 52.58; H, 7.22; N, 4.96. ^{1}H NMR (500.1 MHz, C_6D_6, 25 °C): δ 6.94 (t, 2 H, J_{HH} = 15 Hz, *p*-Ph), 6.84 (m, 4 H, *m*-Ph), 2.44 (s, 12 H, *o*-MePh), 1.27 (s, 18 H, N^{t}Bu), 0.50 (s, 3 H, SiMe), 0.29 (s, 3 H, SiMe). ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6, 25 °C): δ 53.0 (s, NC(CH$_3$)$_3$), 36.2 (s, NC(*C*H$_3$)$_3$), 8.41 (s, SiMe$_3$), 7.13 (s, SiMe$_3$),. ^{31}P{^{1}H} NMR (202.5 MHz, C_6D_6, 25 °C): δ −26.6 (s) ($^1J_{117/119SnP}$ = 1725/1804 Hz). ^{119}Sn NMR (112.1 MHz, C_6D_6, 25 °C): δ 114.6 (d), ($^1J_{119SnP}$ = 1802 Hz).

*[Me$_2$Si(μ-N^{t}BuSnCl)(μ-N^{t}Bu(P(μ-N^{t}Bu)$_2$SiMe$_2$))] (**5**).* To a stirred toluene solution of Me$_2$Si(μ-N^{t}Bu)$_2$PCl (7.5 mmol) at 0 °C was added 7.5 mL a solution of Me$_2$Si(μ-N^{t}Bu)$_2$Sn (1.0 M in toluene) by syringe. The reaction mixture was stirred at 60 °C for 15 days, and the product was collected as transparent, colorless crystals directly from the reaction mixture by cooling to −15 °C. Several crystal fractions were collected for an overall yield of 1.49 g (34%). Mp: 159−160 °C. Anal. Calcd for $C_{20}H_{48}ClN_4PSi_2Sn$ (585.93): C, 41.00; H, 8.26; N, 9.56. Found: C, 40.74; H, 8.11; N, 9.18. ^{1}H NMR (500.1 MHz, C_6D_6, 25 °C): δ 1.55 (s, 9 H, SnN^{t}Bu), 1.49 (s, 9 H, PN^{t}Bu), 1.33 (s, 18 H, PN^{t}Bu), 0.77 (s, 6 H, SiMe$_2$), 0.24 (s, 3 H, SiMe), 0.17 (s, 3 H, SiMe). ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6, 25 °C): δ 53.3 (s, NC), 36.8 (d, PC, $^1J_{PC}$ = 37.3 Hz), 36.5 (s, N^{t}Bu), 33.7 (d, P^{t}Bu$_2$, $^2J_{PC}$ = 13.5 Hz), 8.52 s, 6 H, SiMe), 7.23 (s, 6 H, SiMe). ^{31}P{^{1}H} NMR (202.5 MHz, C_6D_6, 25 °C): δ 85.95 (s) ($^1J_{119,117SnP}$ = 2022, 1932 Hz). ^{119}Sn NMR (112.1 MHz, C_6D_6, 25 °C): δ 90.34 (d), ($^1J_{119SnP}$ = 2023 Hz).

*[Me$_2$Si(μ-N^{t}BuSnCl)(μ-N^{t}Bu(P(NEt$_2$)$_2$)] (**6**).* To a solution of Me$_2$Si(μ-N^{t}Bu)$_2$Sn (0.720 g, 2.26 mmol), dissolved in hexanes (35 mL), was added at 0 °C neat (Et$_2$N)$_2$PCl (0.47 mL) by syringe over 6 min. Upon addition of the phosphine, the reaction mixture turned from orange to yellow. After 1 h, the flask was removed from the cold bath and allowed to stir overnight at rt. Large, clear, colorless crystals, suitable for X-ray analysis, were obtained after the solution had been stored at 3 °C for several days. Yield: 0.770 g (64%). Mp: 91−93 °C. Anal. Calcd for $C_{18}H_{44}ClN_4PSiSn$ (529.79): C, 40.81; H, 8.37; N 10.58. Found: C, 40.51; H, 7.99; N, 10.71. ^{1}H NMR (500.1 MHz, C_6D_6, 25 °C): δ 2.83 (m, 8 H, NCH_2), 1.53 (s, 9 H, SnN^{t}Bu), 1.26 (s, 9 H, PN^{t}Bu), 0.93 (t, 12 H, NCH$_2$CH_3, J_{HH} = 15 Hz), 0.74 (s, 6 H, SiMe). ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6, 25 °C): δ 56.6 (d, SnNCCH$_3$, J_{PC} = 11 Hz), 55.2 (d, PNCCH$_3$, J_{PC} = 14 Hz), 39.0 (s, NCH$_2$), 37.4 (SnNCCH$_3$, $^3J_{SnC}$ = 52 Hz), 33.3 (s, PNCCH$_3$), 13.9 (NCH$_2$CH$_3$), 12.1 (s, SiMe). ^{31}P{^{1}H} NMR (202.5 MHz, C_6D_6, 25 °C): δ 96.1 (s) ($^1J_{119,117SnP}$ = 2057, 1966 Hz). ^{119}Sn NMR (112.1 MHz, C_6D_6, 25 °C): δ 65.85 (d) ($^1J_{119SnP}$ = 2057 Hz).

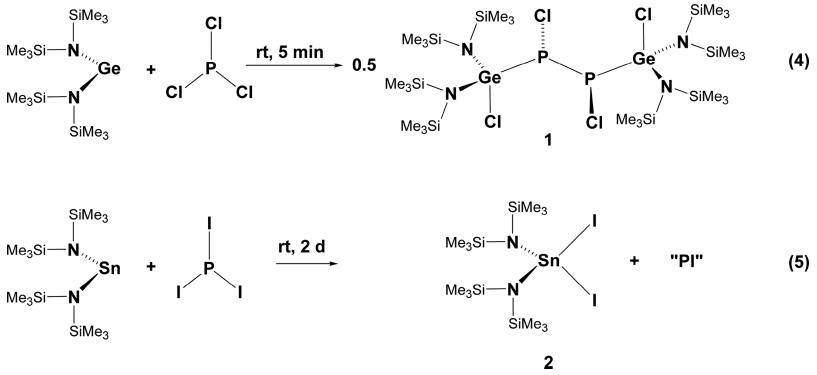
*[Me$_2$Si(μ-N^{t}Bu)$_2$PNEt$_2$]SnCl$_2$ (**7**).* Me$_2$Si(μ-N^{t}Bu)$_2$Sn (150 mg, 0.470 mmol) in hexanes (5 mL) was treated dropwise at −78 °C with a 0.50 M hexanes solution of Et$_2$NPCl (0.94 mL) by syringe. After several minutes, the flask was removed from the cold bath. Upon warming, a white precipitate slowly formed in the yellow solution. The solution was filtered and crystals suitable for X-ray analysis grew after the filtrate had been stored at 3 °C for several days. Yield: 95 mg (41%). Mp: 161−163 °C (dec.). Anal. Calcd for $C_{14}H_{34}Cl_2N_3PSiSn$ (493.12): C, 34.10; H, 6.95; N, 8.52. Found: C, 34.28; H, 7.09; N, 8.79. ^{1}H NMR (500.1 MHz, C_6D_6, 25 °C): δ 2.97 (dq, 4 H, NCH_2CH$_3$, J_{PH} = 165 Hz, J_{HH} = 9 Hz), 1.18 (s, 18 H, N^{t}Bu), 0.91 (dt, 6 H, NCH$_2$CH_3, J_{PH} = 60 Hz, J_{HH} = 9 Hz), 0.32 (s, 6 H, SiMe). ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6, 25 °C): δ 57.6 (d, NCH$_2$CH$_3$, $^2J_{PC}$ = 10.1 Hz), 53.0 (s, NC(CH$_3$)$_3$), 35.1 (s, NC(CH$_3$)$_3$), 15.2 (d, NCH$_2$CH$_3$, $^3J_{PC}$ = 5.0 Hz), 7.32 (s, SiMe$_3$), 6.03 (s, SiMe$_3$). ^{31}P{^{1}H} NMR (202.5 MHz, C_6D_6, 25 °C): δ 105.0 (s), major component. ^{119}Sn NMR (112.1 MHz, C_6D_6, 25 °C): δ −57.7 (d), ($^1J_{119SnP}$ = 2057 Hz), minor component.

*[Me$_2$Si(μ-N^{t}Bu)$_2$Ge(Cl)]$_2$PNEt$_2$ (**8**).* In a two-neck flask, Me$_2$Si(μ-N^{t}Bu)$_2$Ge (0.622 g, 2.28 mmol) was stirred in ca. 1 mL of hexanes at 0 °C. A sample of neat Et_2NPCl_2 (1.1 mmol, 0.23 mL) was added all at once by syringe. Approximately 2 mL of hexanes was added to dissolve the small amount of precipitate which appeared. X-ray quality crystals were obtained from this solution at rt after it had been stored for 3 days. Yield: 0.367 g (72%). Mp: 106−107 °C. Anal. Calcd for $C_{24}H_{58}Cl_2Ge_2N_5PSi_2$ (720.08): C, 40.03; H, 8.12; N, 9.73. Found: C, 40.24; H, 7.89; N, 9.54. ^{1}H NMR (500.1 MHz, C_6D_6, 25 °C): δ 3.28 (dq, 4 H, NCH_2CH$_3$, $^3J_{HH}$ = 14.4 Hz, $^3J_{PH}$ = 2.3 Hz), 1.41 (s, 36 H, N^{t}Bu), 1.12 (t, 6 H, NCH$_2$CH_3, $^3J_{HH}$ = 14.4 Hz), 0.48 (s, 3 H, SiMe$_3$), 0.41 (s, 3 H, SiMe$_3$). ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6, 25 °C): δ 57.6 (d, NCH_2CH$_3$, $^2J_{PC}$ = 10.1 Hz), 53.0 (s, NC(CH$_3$)$_3$), 35.1 (s, NC(*C*H$_3$)$_3$), 15.2 (d, NCH_2CH$_3$, $^3J_{PC}$ = 5.0 Hz), 7.32 (s, SiMe$_3$), 6.03 (s, SiMe$_3$). ^{31}P{^{1}H} NMR (202.5 MHz, C_6D_6, 25 °C): δ 66.3 (s).

2.3. X-ray Crystallography. Suitable single crystals of **1**−**8** were coated with Paratone N oil, affixed to Mitegen crystal holders, and centered on the diffractometer in a stream of cold nitrogen. Reflection intensities were collected with a Bruker Apex diffractometer, equipped with an Oxford Cryosystems 700 Series Cryostream cooler, operating at 173 K. Data were measured with ω scans of 0.3° per frame for 20 s until complete hemispheres of data had been collected. Data were retrieved using SMART software and reduced with SAINT-plus,[60] which corrects for Lorentz and polarization effects and crystal decay. Empirical absorption corrections were applied with SADABS.[61] The structures were solved by direct methods with SHELXS-97 and refined by full-matrix least-squares methods on F^2 with SHELXL-97.[62]

DOI: 10.1021/acs.inorgchem.7b01275
Inorg. Chem. XXXX, XXX, XXX−XXX

Scheme 2. Reactions of Acyclic Group 14 Carbene Analogues with Trihalophosphines



3. RESULTS AND DISCUSSION

3.1. Syntheses and Structures. *3.1.1. Trihalophosphine Substrates.* With the extensive set of data gathered in our first study and aided by our improved ability to identify solution structures, we reinvestigated the reactions between $Me_2Si(\mu\text{-}N^tBu)_2M$ (M = Ge, Sn) and PCl_3 to see if any additional information might be gleaned from these transformations. We confirmed that, when **A** reacted with PCl_3 in a 3:1 ratio, the stable trioxidative addition product $[Me_2Si(\mu\text{-}N^tBu)_2Ge(Cl)]_3P$ was obtained as indicated by a (previously unreported) $^{31}P\{^1H\}$ NMR singlet at δ −78.0 ppm. The 3:1 addition of **B** to PCl_3 allowed the observation of an analogous trioxidative addition product at δ −114.6 ppm with the expected satellites, $^1J_{119/117SnP}$ = 1541/1472 Hz. The formal redox reaction of stannylene **B** (eq 2) thus also proceeds via an intermediate oxidative addition product.

When the bulkier acyclic diazastannylene **D** was allowed to react with PCl_3 in a 3:1 ratio, the ^{31}P NMR spectrum showed that only a dioxidative addition product had formed, although it did so in almost quantitative yield. This intermediate decomposed only very slowly, but it escaped isolation. The reaction of the analogous diazagermylene in a 2:1 ratio (eq 4, Scheme 2), however, afforded an isolable product, namely, **1**, whose solid structure is shown in Figure 1..

The thermal-ellipsoid plot of **1** shows that this compound is not the actual OA product, but rather a decomposition product thereof. On the basis of the solution structure of the dioxidative addition product with acyclic stannylene **D**, we hypothesize that a similar product was formed here. We were unable to detect the remaining product(s) of this reaction by NMR spectroscopy, which, based on stoichiometry and by analogy, should be the digermane $\{[(Me_3Si)_2N]_2(Cl)Ge{-}Ge(Cl)[N(SiMe_3)_2]_2\}$. The reaction mixture was initially orange in color, but it changed to pink, perhaps suggesting homolysis of the Ge−P bonds and the presence of radicals in the decomposition pathway. Compound **1** is a structural analogue of the product formed when the acyclic stannylene **D** reacted with $PhPCl_2$, the main difference being that, in **1**, the phosphorus−phosphorus bond (2.2192(11) Å) is slightly shorter than that of the **D**/$PPhCl_2$ product, but it is virtually isometric with those in similar compounds featuring phosphorus−phosphorus bonds.[63−65] This central linkage is flanked by two Ge−P bonds (2.4086(6) Å) which are comparatively shorter than the corresponding bonds in the above-mentioned stannylene analogue (2.5702(6) Å).

Thus far, only phosphine chlorides had served as substrates in these transformations, and to avoid a bias toward this halide,

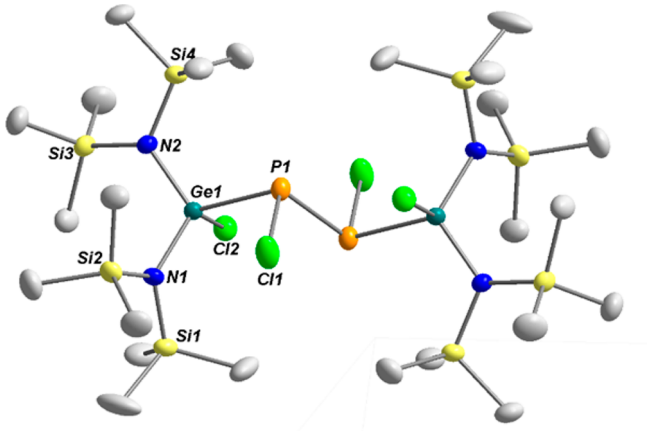


Figure 1. Solid-state structure and partial labeling scheme of inversion-symmetric **1**. Hydrogen atoms and hexane solvent have been omitted, and all non-hydrogen atoms are drawn as 50% probability thermal ellipsoids. Selected bond lengths (Å) and angles (deg). Ge1−P1 2.4086(6), P1−P1′ 2.2192(11), Ge1−Cl2 2.1853(5), P1−Cl1 2.0577(8), Ge1−N1 1.8373(16), Ge1−N2 1.8386(16); Ge1−P1−P1′ 100.57(3), Cl2−Ge1−P1 105.13(2), Ge1−P1−Cl1 96.37(3), P1′−P1−C11 96.69(4), N1−Ge1−N2 114.36(8), N1−Ge1−Cl2 108.10(6), N2−Ge1−Cl2 105.32(5), N1−Ge1−P1 113.51(5), N2−Ge1−P1 109.66(5), Cl2−Ge1−P1 105.13(2).

we investigated phosphorus triiodide as an alternative phosphorus trihalide. The reaction with PI_3, shown in eq 5, was quite complex, however, perhaps due to the weakness of the phosphorus−iodine bonds and the redox sensitivity of this compound. Only the reaction of the acyclic diazastannylene **D** with phosphorus triiodide yielded an isolable compound, namely, the oxidation product $[(Me_3Si)_2N]_2SnI_2$ (**2**). While eq 5 may suggest a direct interaction between PI_3 and cyclic stannylene **B**, the transformation itself is likely more complex. The colorless, crystalline compound obtained showed only one singlet each in the ^1H and ^{13}C NMR spectra, characteristic of a highly symmetrical structure. A single-crystal X-ray study of **2**, depicted in Figure 2, confirmed this assumption by revealing a C_2-symmetric tin bis(hexamethyldisilylazide)-diiodide.

The tin(IV) derivative **2** is a member of a series of compounds of the formula $[(Me_3Si)_2N]_2ElX_2$, El = Ge, Sn, X = amide, acyl, hydrocarbyl, halogen,[6a] whose dichloride analogue had been the only dihalide reported previously.[6b] In the unit cell, the molecules lie on the two-fold axes of space group $C2/c$, the axes bisecting the I−Sn−I angle. The tin atom is in a pseudo-tetrahedral environment, and both Si_2N planes form a dihedral angle of 86.10°. The Sn−I bonds are expectedly

DOI: 10.1021/acs.inorgchem.7b01275
Inorg. Chem. XXXX, XXX, XXX−XXX

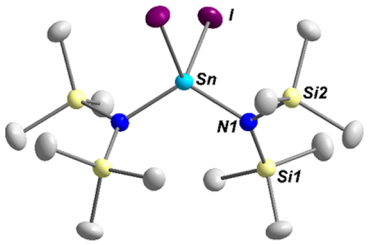


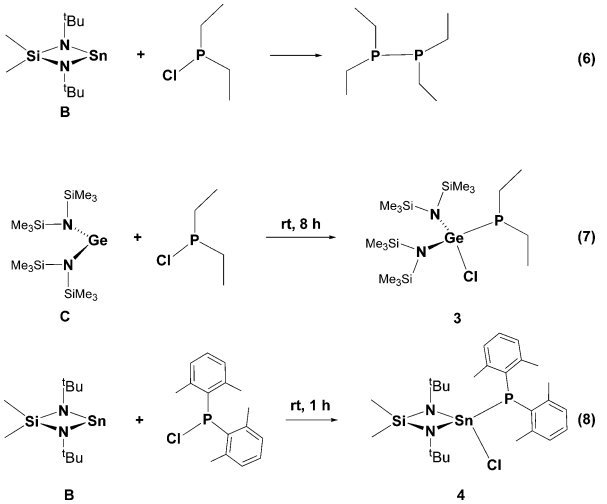
Figure 2. Solid-state structure and partial labeling scheme of C_2-symmetric **2**. Hydrogen atoms have been omitted, and all non-hydrogen atoms are drawn as 50% probability thermal ellipsoids. Selected bond lengths (Å) and angles (deg): Sn1−I1 2.6995(3), Sn1−N1 2.0237(15), N1−Si1 1.7604(16), N1−Si2 1.7654(16); I−Sn−I′ 102.125(13), N1−Sn−I1 104.37(4), N1−Sn−N1′ 117.29(9), Sn−N1−Si1 116.98(8), Sn−N1−Si2 118.54(8), Si1−N1−Si2 122.16(9).

shorter than in the tin(II) derivative Sn(I)(2.6-Trip-C_6H_3), Trip = 2,4,6-^{i}PrC_6H_2,[66] where the lone Sn−I bond was found to be 2.766(2) Å long, but they are also slightly shorter than the Sn−I bonds in a similar tin(IV) species.[67]

3.1.2. Chloro(hydrocarbyl)phosphine Substrates. Our initial study consisted of more than one dozen reactions, involving both cyclic and acyclic germylenes and stannylenes. The chlorophosphine substrates, however, were limited to $PhPCl_2$, Ph_2PCl, ^{t}BuPCl$_2$, and (^{t}Bu)$_2$PCl, the phenylphosphines reacting orders of magnitude faster than their *tert*-butyl counterparts. Phenyl rings are smaller than *tert*-butyl groups, but they are also electron-poorer. The greater reactivity of phenyl-substituted phosphines could thus also be interpreted electronically, namely, that electron-poorer chlorophosphines add faster to the carbene analogues. To separate electronic from steric effects, we compared the compact, electron-richer Et_2PCl with the bulky, electron-poorer (2,6-Me-C_6H_3)$_2$PCl.

Expectedly, Et_2PCl oxidatively added much faster to **A**−**D** than the *tert*-butyl analogues, with the notable difference that all tin-containing intermediates were unstable, furnishing only tetraethyldiphosphine and unidentified tin species, as emblematically shown by eq 6 (Scheme 3). Not only were the stannylene-derived OA products of Et_2PCl unstable but also these intermediates broke down even faster than those of the corresponding chloro(phenyl)phosphines. This suggests that the stability of the tin(IV) products is primarily due to steric shielding of the Sn−P bond and not the electronic properties of the organic substituents.

Scheme 3. Reactions of Chloro(hydrocarbyl)phosphines with Group 14 Carbene Analogues



Acyclic diazagermylene **C**—the least reactive of the carbene analogues—reacted with chloro(diethyl)phosphine (eq 7), to furnish the expected OA product **3** in a 48% yield after a comparatively long 8 h reaction time. This product was isolated as a stable, colorless, crystalline compound and studied by single-crystal X-ray methods. Its solid-state structure is shown in Figure 3, while the caption contains selected bond parameters. The structure confirms that the phosphorus−chlorine bond of the compact chloro(diethyl)phosphine oxidatively added to the bulky diazagermylene, creating an almost perfectly tetrahedral germanium(IV) center. The metalloid is surrounded by two isometric and normal-length Ge−N bonds (1.852(1) Å), which enclose an angle of 114.77(6)°. The Ge−Cl bond length of 2.2093(5) Å is equally unremarkable, while the germanium−phosphorus bond (2.3446(5) Å) is similar in length to some of the Ge−P bonds measured by Izod et al. in low-coordinate germanium compounds. Although, these latter species contain germanium(II) centers whose bond lengths are much more sensitive to bond conformations.[68] Reactions with the sterically small chloro(diethyl)phosphine thus mirrored the results of our earlier studies in that the germylene inserted more slowly, but it produced stable products.

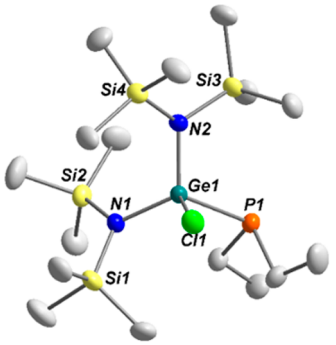


Figure 3. Solid-state structure and partial labeling scheme of **3**. Hydrogen atoms have been omitted, and all non-hydrogen atoms are drawn as 50% probability thermal ellipsoids. Selected bond lengths (Å) and angles (deg): Ge1−Cl1 2.2093(5), Ge1−P1 2.3446(5), Ge1−N1 1.8575(13), Ge−N2 1.8473(14), N1−Si1,2 (avg.) 1.7650(14), N2−Si3,4 (avg.) 1.7646(14); Cl1−Ge1−P1 104.857(19), N2−Ge1−P1 111.51(4), N1−Ge1−N2 114.77(6), N1−Ge1−P1 114.92(5).

Ph$_2$PCl had reacted almost instantly with Me$_2$Si(μ-N^{t}Bu)$_2$Sn to produce solely decomposition products, namely, the distannane [Me$_2$Si(μ-N^{t}Bu)$_2$(Cl)Sn−Sn(Cl)(μ-N^{t}Bu)$_2$SiMe$_2$]$_2$ and the diphosphine Ph_2PPPh_2. The structures of these compounds suggest that the initially generated OA intermediate dissociated at the Sn−P bond and that both moieties then dimerized with like species. By using the bulkier chlorobis(2,6-dimethylphenyl)phosphine, we hoped to ascertain if added steric bulk slowed the reaction. This was indeed observed, but even more important was the discovery that the oxidative addition product of the bulkier chlorophosphine was stable, despite being more sterically congested. This is a strong indication that the unstable tin-containing OA products decompose via an associative, rather than a dissociative, mechanism.

DOI: 10.1021/acs.inorgchem.7b01275
Inorg. Chem. XXXX, XXX, XXX−XXX

The solid-state structure of **4** is shown in Figure 4, while selected bond parameters are listed in the figure caption. In this

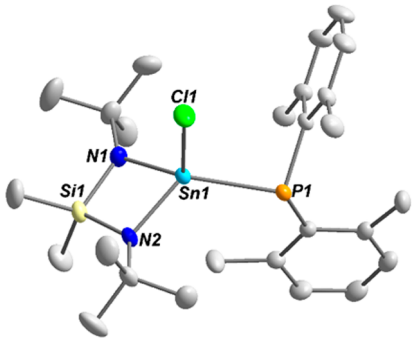


Figure 4. Solid-state structure and partial labeling scheme of **4**. Hydrogen atoms have been omitted, and all non-hydrogen atoms are drawn as 50% probability thermal ellipsoids. Selected bond lengths (Å) and angles (deg): Sn1−Cl1 2.3758(3), Sn1−P1 2.5218(3), Sn1−N1 2.0349(11), Sn1−N2 2.0370(9), Si1−N1 1.7398(11), Si−N2 1.7405(11); Cl1−Sn1−P1 96.378(12), N1−Sn1−P1 142.44(3), N1−Sn1−N2 76.50(4), N1−Sn1−Cl1 115.77(12), N1−Si1−N2 82.41(11).

molecule, a normal-length tin−phosphorus bond, 2.5218(3) Å, connects a pseudo-tetrahedral metal atom to a three-coordinate, pyramidal phosphorus atom. The plane bisecting the heterocycle contains one of the dimethylphenyl ligands, while the second aromatic ring lies perpendicular to that plane. The tin−nitrogen bonds are isometric at 2.0349(11) and 2.0370(9) Å and of normal length, as is the Sn−Cl bond, which is 2.3758(3) Å long. Because tin is part of a heterocycle, the bond angles about this metal differ significantly from tetrahedral values, ranging from 76.50(4)° to 142.44(3)°.

We hoped to gain further insight into the influence of steric bulk on these reactions by synthesizing the mixed chloro(alkyl/aryl)phosphine ^{t}Bu(Ph)PCl and allowing it to react with all four carbene analogues. Although no OA products were isolated, kinetic ^{31}P NMR data indicated that the reactivity of this mixed chlorophosphine was intermediate between those of Ph_2PCl and $^{t}Bu_2PCl$, and that the steric effects are essentially additive. Decomposition rates for the OA products of cyclic and acyclic stannylenes followed the same relative rates as insertions, *viz.*, Ph_2PCl > ^{t}Bu(Ph)PCl ≫ $^{t}Bu_2PCl$. Because steric bulk shields the reactive tin−phosphorus bond, it slows or prevents an associative decomposition pathway.

To investigate possible leaving group effects, the iodo analogue of ^{t}Bu(Ph)PCl, i.e., ^{t}Bu(Ph)PI, was also prepared by halide replacement using a modified literature procedure.[69] As in the case of the mixed chloro(*tert*-butyl)phenylphosphine reactions, no products were isolated, but the oxidative addition reactions were monitored by ^{31}P NMR spectroscopy. The iodophosphines showed an enormous rate increase in their reactions with the carbene analogues, as seen in Table 1, supporting the case for a rate-determining step that is highly sensitive to the nature of the leaving group and pointing to either an S_N2-type mechanism or an adduct/insertion mechanism with a rate-determining 1,2 halide shift.

3.1.3. Chloro(amino)phosphine Substrates. Previous work and that discussed above suggested that reactions of chlorophosphines with diazagermylenes and -stannylenes likely proceed via either an adduct/insertion or an S_N2-type mechanism, but we were unable to isolate potential

Table 1. Kinetic Data for Selected Oxidative Addition Reactions

carbene analogue	halophosphine	temp. (°C)	time (min.) for 99% conversion of reactants
A	(^{t}Bu)PhPCl	25	>1288
A	(^{t}Bu)PhPCl	50	>690
B	(^{t}Bu)PhPCl	25	70−75
D	(^{t}Bu)PhPCl	25	93−98
A	(^{t}Bu)PhPI	50	<15
C	(^{t}Bu)PhPI	50	79−94
C	(^{t}Bu)PhPI	25	178−206

intermediates to support the former. Rather than attempting to confirm our mechanistic hypotheses by isolating such species, if this were indeed possible, we focused on substrates that should be able to undergo the adduct/insertion or S_N2 mechanisms only with great difficulty, or not at all. The *P*-chloro diazasilaphosphetidine produced in eq 3 is a special case of a monochlorophosphine, but it is a cyclic chlorophosphine with little or no conformational flexibility. Notably, no inversion at phosphorus is possible, ruling out an S_N2-type reaction, and even an adduct/insertion mechanism, while feasible, appears very sterically impeded. One would therefore expect this substrate to oxidatively add to the carbene analogues only very slowly, if at all, by these pathways.

Upon combining solutions of **B** and $Me_2Si(\mu\text{-}N^{t}Bu)_2PCl$, no change was observed in either the appearance of the reaction mixture nor in the ^{31}P NMR spectra obtained on aliquots taken from it. Only on heating the solution to 60 °C were the extremely slow disappearance of the signal for the cyclic chlorophosphine and the concomitant appearance of a new signal at δ = 96.1 ppm observed. The slowness of this reaction, which took 15 days at 60 °C to go to complete conversion, seemed to support our hypotheses regarding its mechanism. A free-radical mechanism, similar to the one proposed by West et al.,[14,15] should certainly be feasible for this substrate, but such a reaction would be expected to proceed much faster than the transformation we observed.

Clear, colorless crystals of **5** were isolated in moderate yield from this reaction, and a suitable specimen was subjected to a single-crystal X-ray diffraction analysis. The result of this study may be seen in Figure 5, while selected bond parameters appear in the figure caption. It is apparent from the structure of the

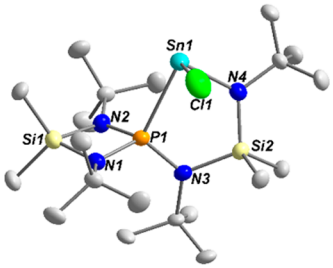


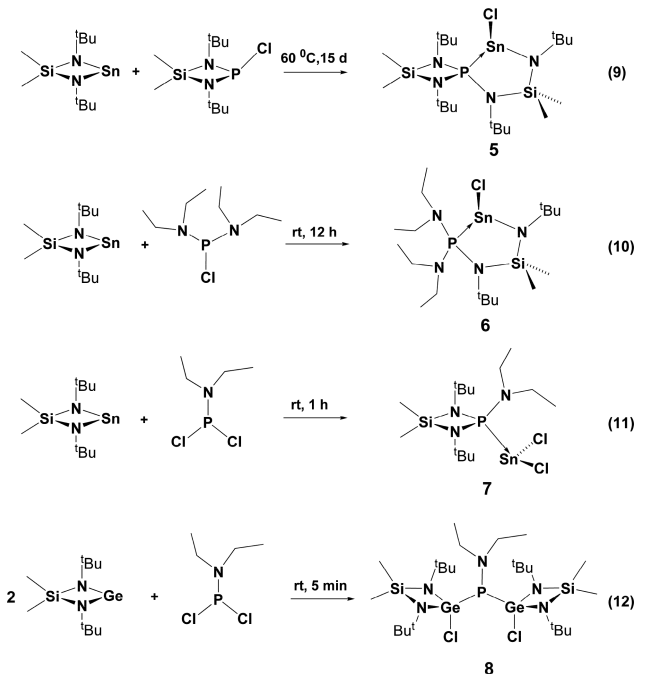
Figure 5. Solid-state structure and partial labeling scheme of **5**. Hydrogen atoms and toluene solvent have been omitted, and all non-hydrogen atoms are drawn as 50% probability thermal ellipsoids. Selected bond lengths (Å) and angles (deg): Sn1−Cl1 2.5109(9), Sn1−P1 2.6322(7), Sn1−N4 2.105(2), P1−N1 1.6673(12), P1−N2 1.6791(12), P1−N3 1.6769(12), Si1−N1,2 (avg.) 1.749(2), Si2−N3 1.820(3), Si2−N4 1.720(3); Cl1−Sn1−P1 101.873), N3−P1−Sn1 108.02(8), N1−P1−N2 85.75(11), N2−P1−N3 115.77(12), N1−Si1−N2 82.41(11), N3−Si2−N4 109.09(11).

DOI: 10.1021/acs.inorgchem.7b01275
Inorg. Chem. XXXX, XXX, XXX−XXX

molecule that the P−Cl bond of the chlorophosphine did not add to the stannylene in a straightforward fashion. Rather, the Sn−N3 bond of the stannylene ruptured, and the *tert*-butylamido group (N3) was transferred to phosphorus, yielding a *spiro*-heterocycle, composed of four- and five-membered rings which share a central phosphorus(III) atom. With the exception of the P−Cl bond, the four-membered ring remained presumably unchanged from the cyclic chlorophosphine, but the five-membered ring was newly formed by the formal insertion of the phosphorus atom into the Sn−N bond. This latter ring has an envelope conformation, featuring a slightly twisted rectangular portion (N3−P1−Sn1−N4) which encloses an angle of 151.00(7)° with the triangular N3−Si2−N4 flap. Because no oxidative addition took place in this reaction, the metal is still a tin(II) ion, and at first glance, this might explain the very long Sn−Cl bond of 2.5109(9) Å. Closer inspection, however, reveals that this bond is too long for even a Sn(II)−Cl bond. It is likely not a conventional covalent bond at all, but it appears that the chloride ion forms a contact-ion pair with a cationic *spiro*-heterocycle.

The second chloro(amino)phosphine tested, namely, chlorobis(diethylamino)phosphine, is also a very bulky substrate, but one that should be able to undergo an adduct/insertion reaction, if not an S_N2 reaction. This substrate, when treated with **B**, as shown in eq 10 (Scheme 4), also reacted

Scheme 4. Reactions of Amino(chloro)phosphines with Group 14 Carbene Analogues



much slower than chloro(hydrocarbyl)phosphines, but the reaction was significantly faster than that shown in eq 9, being complete in 12 h at room temperature. Because the reaction was also much slower than those of the previously observed oxidative additions, a nonstandard transformation was again suggested. This was borne out by the structure of the product, **6**, which is shown in Figure 6.

The thermal-ellipsoid plot (Figure 6) confirms **6** to be a structural analogue of **5**, with an identical five-membered heterocycle, although here it is substituted by two diethylamino

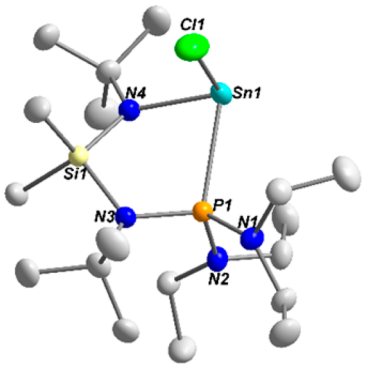


Figure 6. Solid-state structure and partial labeling scheme of **6**. Hydrogen atoms have been omitted, and all non-hydrogen atoms are drawn as 50% probability thermal ellipsoids. Selected bond lengths (Å) and angles (deg): Sn1−Cl1 2.5156(6), Sn1−P1 2.6194(4), Sn1−N4 2.1137(12), P1−N1 1.6673(12), P1−N2 1.6791(12), P1−N3 1.6769(12), Si1−N3 1.8052(12), Si1−N4 1.7279(12); Cl1−Sn1−P1 96.991(15), N3−P1−Sn1 105.36(4), N1−P1−N2 102.19(6), N1−P1−N3 117.00(6), N2−P1−N3 107.35(6), N3−Si1−N4 106.89(6).

groups, rather than a second ring. This heterocycle, however, has a more perfectly shaped envelope conformation, presumably because it is not tethered to another ring. Thus, the nearly planar rectangle, composed of P1, N3, Si1, and N4, encloses an angle of 144.88(3)° with the flap composed of the P1−Sn1−N4 plane. The five bonds within the heterocycle have virtually identical lengths as those in **5**, as does the unusually long Sn−Cl bond, thereby further confirming the close structural relation ship between **5** and **6**.

The two previously discussed reactions did not proceed with the expected oxidative additions, but they resulted in ligand exchange. Both substrates were monochlorophosphines, however, and only a partial ligand exchange was realized in each case because $[Me_2Si(^tBuN)_2]^{2-}$ is bidentate and dinegative. Once it became clear that these reactions proceed via metathesis rather than OA, we tried to generate a product in which the chelating diamide ligand of the stannylene was fully exchanged with the chloride ions. Upon treating Et_2NPCl_2 with 1 equiv of **B**, as shown in eq 11, a decidedly faster transformation took place than those depicted in eqs 9 and 10, and the reaction was judged complete after 1 h of stirring at rt. The $^{31}P\{^1H\}$ NMR spectrum displayed only one singlet peak, with a chemical shift characteristic of a heterocyclic diaminophosphine. A single-crystal X-ray analysis of the product showed that the targeted reaction had indeed taken place. The solid-state structure of **7** is depicted in Figure 7, while selected bond parameters are listed in the figure caption.

The diethylamino group is still bound to the phosphorus atom, and this moiety is chelated by a k^2-*N*-dimethylsila-di-*tert*-butylamido group, thereby forming a triaminophosphine. The endocyclic P−N bonds are isometric and 1.690(1) Å long, while the exocyclic bond is slightly shorter at 1.645(1) Å, as is usual for these heterocycles. The displaced chloride ions now ligate the tin(II) ion (mean distance = 2.456(1) Å) and enclose an angle of 94.42(1)°. Both fragments form a Lewis acid−base adduct, with the longest phosphorus-to-tin bond (2.7274(4) Å) of any species structurally analyzed in these studies. Only a small amount of the adduct **7**, shown in Figure 7, is present in benzene solution, however, the major solution species being free triaminophosphine. This reaction is reminiscent of that

DOI: 10.1021/acs.inorgchem.7b01275
Inorg. Chem. XXXX, XXX, XXX−XXX

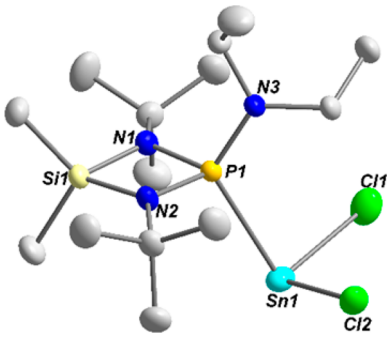


Figure 7. Solid-state structure and partial labeling scheme of **7**. Hydrogen atoms have been omitted, and all non-hydrogen atoms are drawn as 50% probability thermal ellipsoids. Selected bond lengths (Å) and angles (deg): Sn1−Cl1 2.4520(6), Sn1−Cl2 2.4591(5), P1−Sn1 2.7274 (4), P1−N1 1.6862(14), P1−N2 1.6930(14), P1−N3 1.6449(14); Cl1−Sn1−Cl2 94.416(18), N3−P1−Sn1 119.73(5), N1−P1−N2 85.63(7), P1−Sn1−Cl1 95.011(17), P1−Sn1−Cl2 94.282(16), N1−Si−N2 82.11(6).

shown in eq 3, although, there, an adduct was not formed, perhaps due to the lesser Lewis acidity of $PbCl_2$.

While most of the compounds described in this study feature conventional covalent bonds between phosphorus and tetravalent germanium or tin, all products of eqs 9−11, *viz*. **5**, **6**, and **7**, are triaminophosphines with phosphorus-to-tin(II) donor bonds. Those in **5** and **6** are comparatively short intermolecular contacts of ca. 2.62 Å length, which lie at the short end of such bonds.[70−74] The intermolecular bond in **7** is expectedly *ca*. 0.1 Å longer and accordingly weaker, as confirmed by the compound being mainly present in solution in a dissociated form.

Just like the chloro(hydrocarbyl)phosphines had done in our first study, the three chloro(amino)phosphines described above also exhibited vastly different rates in their reactions with stannylene **B**. For example, the formation of **5** required heating at 60 °C for 15 days, while that of **7** took only 1 h at rt. None of these reactions is a formal oxidative addition, however, thereby preventing additional insight into the mechanism(s). The lack of OA products for **B** suggests that such species are thermodynamically unstable with respect to the amino-phosphines that were formed. Because identical five-membered heterocycles are present in both, **5** and **6**, it appears that these compounds went through essentially the same mechanistic steps. They differ in the rate-determining step, which is obviously much slower in **5** than in **6**. The ligation of tin by chloride despite an absent OA product may suggest that adduct formation, followed by a 1,2 chloride shift, is the rate-determining step, and this step would be expected to be much slower for the cyclic chlorophosphine.

The previous three reactions demonstrate that chloro-(amino)phosphines, unlike chloro(hydrocarbyl)phosphines, do not add oxidatively to the tin(II) center, but are either partially or fully aminated by the cyclic stannylene **B**. We wondered if the germanium analogue, **A**, would show the same altered reactivity and allowed it to interact with both acyclic chloro(amino)phosphines, namely, Et_2NPCl_2 and $(Et_2N)_2PCl$. The fast rate of the reaction with Et_2NPCl_2, which is shown in eq 12, immediately signaled an oxidative addition similar to those $PhPCl_2$ and $^tBuPCl_2$ had undergone with this germylene. This was confirmed by the solid-state structure of the product, **8**, which is shown in Figure 8 and whose bond parameters are given in the figure caption.

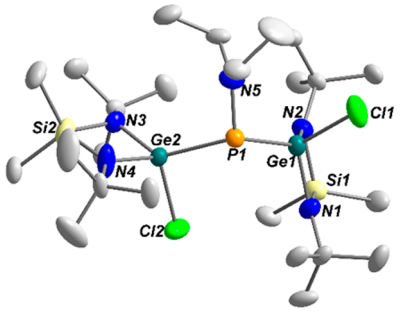


Figure 8. Solid-state structure and partial labeling scheme of **8**. Hydrogen atoms have been omitted, and all non-hydrogen atoms are drawn as 50% probability thermal ellipsoids. Selected bond lengths (Å) and angles (deg): Ge1−P1 2.3526 (7), Ge2−P1 2.3336(7), Ge1−Cl1 2.2103(8), Ge2−Cl2 2.1970(6), Ge1−N (avg.) 1.838(2), Ge2−N (avg.) 1.833(2), P1−N5 1.671(2); Ge1−P1−Ge2 108.00(3), Cl1−Ge1−P1 96.53(3), P1−Ge2−Cl2 100.10(3), Ge1−P1−N5 109.29(5), Ge2−P1−N5 107.11(9).

The molecule is composed of a central diethylaminophosphine unit, which is flanked by two large chlorogermyl moieties. It is the third representative in a series of compounds of the formula $[Me_2Si(\mu\text{-}N^tBu)_2Ge(Cl)]_2PR$, where R is Ph, ^{t}Bu, or NEt_2, syntheses and structures of the phenyl and *tert*-butyl analogues having appeared in our earlier study.[53] The slightly asymmetric P−Ge bonds in **8** are somewhat longer than those of its analogues, perhaps reflecting the greater steric bulk of the diethylamino group. Steric repulsion is also the likely reason for the relatively shallow pyramid which features an angle sum of 324.4° at phosphorus.

Unfortunately, the reaction of **A** with the monochlorophosphine, $(Et_2N)_2PCl$, was less clear-cut, because the product(s) did not crystallize and could thus not be isolated in a pure form. The speed of the transformation and the chemical shift of the phosphorus-containing product, however, strongly suggested an insertion reaction.

3.2. Thermodynamic and Mechanistic Considerations.

The thermodynamic driving force in OAs is the breaking of one bond and concomitant formation of two bonds. In the OA of the P−Cl bond to both **A** and **B**, the same bond is broken, but the Ge−P and Ge−Cl bonds formed are stronger than the Sn−P and Sn−Cl bonds, as reflected in the greater stability of the Ge-containing products. It appears that chloro(amino)-phosphines yield weaker M−P bonds than the corresponding chloro(hydrocarbyl)phosphines, and that, for the cyclic stannylene **B**, such OA intermediates become unstable. In the absence of an oxidative addition, **B** functions as an amine transfer reagent—a not unusual transformation given the polarity of the Sn−N bond.

Oxidative addition reactions proceed by a variety of mechanisms, which are determined by both, the substrates and the molecules, undergoing the additions. Relatively polar substrates, like P−Cl bonds, usually oxidatively add by an S_N2-type mechanism. The faster reactions of stannylenes versus germylenes with these chlorophosphines suggest that the OA reactions discussed above proceed by either S_N2 or adduct/insertion mechanisms, because stannylenes are stronger nucleophiles and stronger Lewis acids than germylenes. If these OAs were to proceed via concerted or radical

DOI: 10.1021/acs.inorgchem.7b01275
Inorg. Chem. XXXX, XXX, XXX−XXX

mechanisms, one would expect the germylenes to react faster, because they undergo both, the +2 to +4 and the singlet-to-triplet transitions, more readily than stannylenes.[75] Mechanistic studies of substitution reactions centered on a third row element, such as phosphorus, present additional problems because of the potential hypervalency of the elements. It is therefore impossible to differentiate between S_N2 and adduct/insertion mechanisms, which are closely related, the latter mechanism implying the presence of a short-lived intermediate, *viz.*, a Lewis acid/base adduct.

4. SUMMARY AND CONCLUSION

The work detailed in the previous pages shows that Group 14 carbene analogues reduce chlorophosphines with the intermediacy of oxidative addition products. These reactions are faster for stannylenes than for germylenes, and they are always faster for the cyclic variant of each. Steric bulk on either the carbene analogue or the chlorophosphine substantially slows these reactions, but the electronic properties of the organic substituents appear to play only a minor role. On the basis of these data and observed leaving group effects, we propose that the oxidative additions proceed via an associative process—either an adduct/insertion or an S_N2 mechanism. The ensuing OA products are almost always stable for germylenes but, because of the weaker Sn−P bond, rarely so for stannylenes, making the isolation of tin-containing products more challenging. An important finding of this study was the discovery that the kinetically unstable OA products of a cyclic stannylene decompose via an associative mechanism.

Our goal to shed more light on the reaction mechanism by using chloro(amino)phosphines substrates was not fully realized. While chloro(amino)phosphines add readily to cyclic germylenes, the OA products of chloro(amino)phosphines to cyclic stannylene (if these indeed form) are apparently unstable. In the absence of such a product, the diazastannylene reacts with ligand transfer to the chlorophosphines. Given the polarity of the Sn−N bond, this outcome is not unexpected, but it does show that the energetics of the oxidative additions described above are delicately balanced. The role of di(*tert*-butylamino)-stannylenes or -plumbylenes as selective amination agents for halophosphines and other nonmetal halides deserves further study, because these reactions are remarkably selective.

■ ASSOCIATED CONTENT

Accession Codes

CCDC 1544260−1544267 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: lothar.stahl@und.edu. Phone: 1-701-777-2242. Fax: 1-701-777-2331.

ORCID

Lothar Stahl: 0000-0003-4482-9673

Present Address

†Department of Chemistry, Winona State University, Winona, MN.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the National Science Foundation (Grant No. EPS-0814442) for financial support of this work.

■ REFERENCES

(1) For modern treatments of oxidative addition reactions, see: (a) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 6th ed.; Wiley: Hoboken, NJ, 2014; pp 163−185. (b) Hartwig, J. *Organotransition Metal Chemistry*; University Science Books: Sausalito, CA, 2010; Chapters 6 and 7.

(2) Vaska, L.; Diluzio, J. W. Activation of Hydrogen by a Transition Metal Complex at Normal Conditions Leading to a Stable Molecular Dihydride. *J. Am. Chem. Soc.* **1962**, *84*, 679−680.

(3) Young, J. F.; Osborn, J. A.; Jardine, F. H.; Wilkinson, G. J. Hydride intermediates in homogeneous hydrogenation reactions of olefins and acetylenes using rhodium catalysts. *Chem. Commun. (London)* **1965**, *0*, 131−132.

(4) Smith, M. B. *Organic Synthesis*, 2nd ed.; McGraw-Hill: New York, 2002; pp 613−614.

(5) Bos, K. D.; Bulten, E. J.; Noltes, J. G. Oxidative additions of some organotin(II) and organic tin(II) compounds. *J. Organomet. Chem.* **1974**, *67*, C13−C15.

(6) (a) Gynane, M. J. S.; Lappert, M. F.; Miles, S. J.; Power, P. P. Ready Oxidative Addition of an Alkyl or Aryl Halide to a Tin(II) Alkyl or Amide; Evidence for a Free-radical Pathway. *J. Chem. Soc., Chem. Commun.* **1976**, 256−257. (b) Lappert, M. F.; Power, P. P. Di-and Trivalent Trimethylsilyl-Substituted Tin Amides and Related Compounds Such as $Sn[(SiMe_3)_2]_2$ or $_3$. *Adv. Chem. Ser.* **1976**, *157*, 70−81.

(7) Gynane, M. J. S.; Lappert, M. F.; Miles, S. J.; Carty, A. J.; Taylor, N. J. Subvalent Group 4B Metal Alkyls and Amides. Part 6. Oxidative Addition of an Alkyl Halide to Bis[bis(trimethylsilyl)methyl]tin(II); Hydrogen-1 Nuclear Magnetic Resonance Data on the Tin(IV) Adducts and a Single-crystal X-Ray Study of Tris[bis(trimethylsilyl)-methyl]chloro-tin(IV). *J. Chem. Soc., Dalton Trans.* **1977**, 2009−2015.

(8) Lappert, M. F.; Misra, M. C.; Onyszchuk, M.; Rowe, R. S.; Power, P. P.; Slade, M. J. Subvalent group 14 metal compounds XI. Oxidative addition reactions of organic halides or acid anhydrides (including $CH_{4-n}Cl_n$, PhBr, $BrN(SiMe_3)_2$, Bu^tCOCl, or $(CF_3CO)_2O$) to some bivalent group 14 metal amides or alkyls. *J. Organomet. Chem.* **1987**, *330*, 31−46.

(9) Kavara, A.; Cousineau, K. D.; Rohr, A. D.; Kampf, J. W.; Banaszak Holl, M. M. A Stannylene/Aryl Iodide Reagent for Allylic CH Activation and Double Bond Addition Chemistry. *Organometallics* **2008**, *27*, 1041−1043.

(10) Miller, K. A.; Bartolin, J. M.; O'Neill, R. M.; Sweeder, R. D.; Owens, T. M.; Kampf, J. W.; Banaszak Holl, M. M.; Wells, N. J. C-H Activation of Ethers and Alkanes by Germylene—Aryl Halide Complexes. *J. Am. Chem. Soc.* **2003**, *125*, 8986−8987.

(11) Walker, R. H.; Miller, K. A.; Scott, A. L.; Cygan, Z. T.; Kampf, J. W.; Banaszak Holl, M. M.; Bartolin, J. M. Silylene- and Germylene-Mediated C−H Activation: Reaction with Alkanes, Ethers, and Amines. *Organometallics* **2009**, *28*, 2744−2755.

(12) Bartolin, J. M.; Kavara, A.; Kampf, J.; Banaszak Holl, M. M. Tin-Mediated CH Activation and Cross-Coupling in a Single Flask. *Organometallics* **2006**, *25*, 4738−4740.

(13) Miller, K. A.; Watson, T. W.; Bender, J. E., IV; Banaszak Holl, M. M.; Kampf, J. W. Intermolecular C−H Insertions and Cyclization Reactions Involving a Stable Germylene. *J. Am. Chem. Soc.* **2001**, *123*, 982−983.

(14) Moser, D. F.; Bosse, T.; Olson, J.; Moser, J. L.; Guzei, I. A.; West, R. Halophilic Reactions of a Stable Silylene with Chloro and Bromocarbons. *J. Am. Chem. Soc.* **2002**, *124*, 4186−4187.

(15) Moser, D. F.; Naka, A.; Guzei, I. A.; Müller, T.; West, R. Formation of Disilanes in the Reaction of Stable Silylenes with Halocarbons. *J. Am. Chem. Soc.* **2005**, *127*, 14730−14738.

DOI: 10.1021/acs.inorgchem.7b01275
Inorg. Chem. XXXX, XXX, XXX−XXX

(16) Dickie, D. A.; Lee, P. T. K.; Labeodan, O. A.; Schatte, G.; Weinberg, N.; Lewis, A. R.; Bernard, G. M.; Wasylishen, R. E.; Clyburne, J. A. C. Flexible coordination of the carboxylate ligand in tin(II) amides and a 1,3-diaza-2,4-distannacyclobutanediyl. *Dalton Trans.* **2007**, 2862−2869.
(17) Wetherby, A. E., Jr.; Samanamu, C. R.; Schrick, A. C.; DiPasquale, A.; Golen, J. A.; Rheingold, A. L.; Weinert, C. S. Synthesis and structures of aryloxo- and binaphthoxogermanium(IV) alkyl iodide complexes. *Inorg. Chim. Acta* **2010**, *364*, 89−95.
(18) Wills, C.; Izod, K.; Clegg, W.; Harrington, R. W. Oxidation reactions of a phosphine-borane-stabilised dialkylstannylene. *Dalton Trans.* **2010**, *39*, 2379−2384.
(19) Sen, S. S.; Hey, J.; Kratzert, D.; Roesky, H. W.; Stalke, D. A Remarkable End-On Activation of Diazoalkane and Cleavage of Both C−Cl Bonds of Dichloromethane with a Silylene to a Single Product with Five-Coordinate Silicon Atoms. *Organometallics* **2012**, *31*, 435−439.
(20) Erickson, J. D.; Vasko, P.; Riparetti, R. D.; Fettinger, J. C.; Tuononen, H. M.; Power, P. P. Reactions of *m*-Terphenyl-Stabilized Germylene and Stannylene with Water and Methanol: Oxidative Addition versus Arene Elimination And Different Reaction Pathways for Alkyl- and Aryl-Substituted Species. *Organometallics* **2015**, *34*, 5785−5791.
(21) Erickson, J. D.; Riparetti, R. D.; Fettinger, J. C.; Power, P. P. Molecular Zinc Species with Ge−Zn and Sn−Zn Bonds: A Reversible Insertion of a Stannylene into a Zinc−Carbon Bond. *Organometallics* **2016**, *35*, 2124−2128.
(22) Wang, X.; Zhu, Z.; Peng, Y.; Lei, H.; Fettinger, J. C.; Power, P. P. Room-Temperature Reaction of Carbon Monoxide with a Stable Diarylgermylene. *J. Am. Chem. Soc.* **2009**, *131*, 6912−6913.
(23) Peng, Y.; Ellis, B. D.; Wang, X.; Power, P. P. Diarylstannylene Activation of Hydrogen or Ammonia with Arene Elimination. *J. Am. Chem. Soc.* **2008**, *130*, 12268−12269.
(24) Peng, Y.; Ellis, B. D.; Zhu, Z.; Fettinger, J. C.; Nagase, S.; Power, P. P.; Guo, J.-D. Diarylstannylene Activation of Hydrogen or Ammonia with Arene Evolution. *J. Am. Chem. Soc.* **2009**, *131*, 16272−16282.
(25) Erickson, J. D.; Fettinger, J. C.; Power, P. P. Reaction of a Germylene, Stannylene, or Plumbylene with Trimethylaluminum and Trimethylgallium: Insertion into Al−C or Ga−C Bonds, a Reversible Metal−Carbon Insertion Equilibrium, and a New Route to Diplumbenes. *Inorg. Chem.* **2015**, *54*, 1940−1948.
(26) Burford, N.; Ragogna, P. J.; Sharp, K.; McDonald, R.; Ferguson, M. J. Arsinophosphonium Cations from Arsenium-phosphine and -bisphosphine Coordination Chemistry. *Inorg. Chem.* **2005**, *44*, 9453−9460.
(27) Burford, N.; Ragogna, P. J. Coordination Chemistry of Phosphorus(III) as a Lewis Acceptor. *ACS Symp. Ser.* **2006**, *917*, 280−292.
(28) MacDonald, E.; Doyle, L.; Burford, N.; Werner-Zwanziger, U.; Decken, A. Stannylphosphonium Cations. *Angew. Chem., Int. Ed.* **2011**, *50*, 11474−11477.
(29) Chitnis, S. S.; Whalen, J. M.; Burford, N. Influence of Charge and Coordination Number on Bond Dissociation Energies, Distances, and Vibrational Frequencies for the Phosphorus−Phosphorus Bond. *J. Am. Chem. Soc.* **2014**, *136*, 12498−12506.
(30) Chitnis, S. S.; Burford, N. Phosphine complexes of lone pair bearing Lewis acceptors. *Dalton Trans.* **2015**, *44*, 17−29.
(31) Bamford, K. L.; Chitnis, S. S.; Stoddard, R. L.; McIndoe, J. S.; Burford, N. Bond fission in monocationic frameworks: diverse fragmentation pathways for phosphinophosphonium cations. *Chem. Sci.* **2016**, *7*, 2544−2552.
(32) Robertson, A. P. M.; Gray, P. A.; Burford, N. Interpnictogen Cations: Exploring Vistas in Coordination Chemistry. *Angew. Chem., Int. Ed.* **2014**, *53*, 6050−6069.
(33) Shah, S.; Protasiewicz, J. D. 'Phospha-variations' on the themes of Staudinger and Wittig: phosphorus analogs of Wittig reagents. *Coord. Chem. Rev.* **2000**, *210*, 181−201.
(34) Shah, S.; Concolino, T.; Rheingold, A. L.; Protasiewicz, J. D. Sterically Encumbered Systems for Two Low-Coordinate Phosphorus Centers. *Inorg. Chem.* **2000**, *39*, 3860−3867.
(35) Smith, R. C.; Gantzel, P.; Rheingold, A. L.; Protasiewicz, J. D. Arsa-Wittig Complexes (ArAs = PMe_3) as Intermediates to Diarsenes. *Organometallics* **2004**, *23*, 5124−5126.
(36) Dutan, C.; Shah, S.; Smith, R. C.; Choua, S.; Berclaz, T.; Geoffroy, M.; Protasiewicz, J. D. Sterically Encumbered Diphosphaalkenes and a Bis(diphosphene) as Potential Multiredox-Active Molecular Switches: EPR and DFT Investigations. *Inorg. Chem.* **2003**, *42*, 6241−6251.
(37) Smith, R. C.; Urnezius, E.; Lam, K.-C.; Rheingold, A. L.; Protasiewicz, J. D. Syntheses and Structural Characterizations of the Unsymmetrical Diphosphene DmpPPMes* (Dmp = 2,6-$Mes_2C_6H_3$, Mes* = 2,4,6-$^tBu_3C_6H_2$) and the Cyclotetraphosphane $[DmpPPPh]_2$. *Inorg. Chem.* **2002**, *41*, 5296−5299.
(38) Cowley, A. H.; Kilduff, J. E.; Newman, T. H.; Pakulski, M. Diphosphenes (RP = PR). Synthesis and NMR Characterization. *J. Am. Chem. Soc.* **1982**, *104*, 5820−5821.
(39) Yoshifuji, M.; Shima, I.; Inamoto, N.; Hirotsu, K.; Higuchi, T. Synthesis and Structure of Bis(2,4,6-tri-*tert*-butylphenyl)diphosphene: Isolation of a True "Phosphobenzene. *J. Am. Chem. Soc.* **1981**, *103*, 4587−4589.
(40) Smith, R. C.; Shah, S.; Protasiewicz, J. D. A role for free phosphinidenes in the reaction of magnesium and sterically encumbered $ArPCl_2$ in solution at room temperature. *J. Organomet. Chem.* **2002**, *646*, 255−261.
(41) Veith, M.; Huch, V.; Majoral, J.-P.; Bertrand, G.; Manuel, G. Stannylene and germylene as powerful dechlorinating reagents: new route to diphosphene. *Tetrahedron Lett.* **1983**, *24*, 4219−4222.
(42) Veith, M.; Gouygou, M.; Detemple, A. Germa-Phosphines and Stanna-Phosphines from the Insertion of Germylenes and Stannylenes into P−Cl Bonds. *Phosphorus, Sulfur Silicon Relat. Elem.* **1993**, *75*, 183−186.
(43) du Mont, W.-W.; Schumann, H. Chloro(di-*tert*-butylphosphino)germanediyl and -stannanediyl: Stable Germanium-(II) and Tin(II) Organophosphorus Compounds. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 368−369.
(44) du Mont, W.-W.; Schumann, H. α-Elimination Reactions at Di-t-Butyl(Trichlorogermyl)phosphine: A Route to Phosphinogermylenes and Triorganophosphino-Dichlorogermylene-Complexes. *J. Organomet. Chem.* **1975**, *85*, C45−C47.
(45) du Mont, W.-W.; Neudert, B.; Schumann, H. Novel Redox Reactions of Tri-*tert*-butylphosphane with Tetrahalides of Germanium and Tin. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 308−309.
(46) Schumann, H.; du Mont, W.-W.; Kroth, H.-J. Organo[chlor-(methyl)stannyl]phosphines and -amines. *Chem. Ber.* **1976**, *109*, 237−245.
(47) Schumann, H.; du Mont, W.-W.; Wöbke, B. Substitution Reactions at Di-*tert*-butyl(chlorodimethylstannyl)phosphine and Di-*tert*-butyl(chlorodimethylgermyl)phosphine. *Chem. Ber.* **1976**, *109*, 1017−1022.
(48) du Mont, W.-W.; Kroth, H.-J.; Schumann, H. Redox Reactions between Tri-*tert*-butylphosphin and Element(IVb)-Tetrachlorides: Tri-*tert*-butylchlorophosphonium-Salts. *Chem. Ber.* **1976**, *109*, 3017−3024.
(49) du Mont, W.-W.; Neudert, B. Organophosphine-substituted Halogenogermylenes and − stannylenes. *Z. Anorg. Allg. Chem.* **1977**, *436*, 270−276.
(50) du Mont, W.-W.; Neudert, B. Synthesis und Vibrational Spectra of Pentacarbonyl[chloro-di-*tert*-butylphosphino)stannio]metal(VI A) Complexes. *Chem. Ber.* **1978**, *111*, 2267−2272.
(51) Veith, M.; Grosser, M.; Huch, V. Cyclic Diazastannylenes. XIX. Reaction of a Bis(amino)germylene, -stannylene, and -plumbylene with Phosphorus Trichloride and 2, 3-Dimethyl-1, 3-butadiene. *Z. Anorg. Allg. Chem.* **1984**, *513*, 89−102.
(52) Scherer, O. J.; Püttmann, M. L.; Krüger, C.; Wolmershäuser, G. Rotamers of Aminophosphanes- and Aminophosphoranes. *Chem. Ber.* **1982**, *115*, 2076−2124.

DOI: 10.1021/acs.inorgchem.7b01275
Inorg. Chem. XXXX, XXX, XXX−XXX

(53) West, J. K.; Stahl, L. Insertions of Cyclic and Acyclic Germanium and Tin Heterocarbenoids into Phosphorus-Chlorine Bonds: Syntheses, Structures, and Reactivities. *Organometallics* **2012**, *31*, 2042−2052.
(54) Schweizer, S.; Becht, J.-M.; Le Drian, C. Highly Efficient and Reusable Supported Pd Catalysts for Suzuki−Miyaura Reactions of Aryl Chlorides. *Org. Lett.* **2007**, *9*, 3777−3780.
(55) Pudovik, M. A.; Mikhailov, Y. B.; Pudovik, A. N. Synthesis and some reactions of cyclic oligomers - derivatives of a 2-coordinate phosphorus atom. *Zh. Obshch. Khim.* **1985**, *55*, 1475−1479.
(56) Amigues, E. J.; Hardacre, C.; Keane, G.; Migaud, M. E. Solvent-modulated reactivity of PCl_3 with Amines. *Green Chem.* **2008**, *10*, 660−669.
(57) Veith, M. Cyclic Nitrogen Derivatives of Tetra- and Divalent Tin. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 263−264.
(58) (a) Veith, M. Cyclic Diazastannylenes, II. Intermolecular Lewis-Acid-Based Adducts of 1,3,2,4λ^2-Diazasilastannetidines. *Z. Naturforsch., B: J. Chem. Sci.* **1978**, *33*, 1−6. (b) Veith, M. Cyclic Diazastannylenes, III. The Crystal and Molecular Structure of the Monoclinic Phase of 1,3-Di-*tert*-butyl-2,2-dimethyl-1,3,2,4λ^2-Diazasilastannetidine. *Z. Naturforsch., B: J. Chem. Sci.* **1978**, *33*, 7−13.
(59) Gynane, M. J. S.; Harris, D. H.; Lappert, M. F.; Power, P. P.; Rivière, P.; Rivière-Baudet, M. Subvalent Group 4B Metal Alkyls and Amides. Part 5. The Synthesis and Physical Properties of Thermally Stable Amides of Germanium(II), Tin(II), and Lead(II). *J. Chem. Soc., Dalton Trans.* **1977**, 2004−2009.
(60) *SMART and SAINT-plus*; Siemens Analytical X-ray Systems: Madison, WI, 1995.
(61) SADABS program for absorption corrections using the Bruker CCD Detector System. Based on: Blessing, R. H. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1995**, *51*, 33−38.
(62) Sheldrick, G. M. A short history of *SHELX*. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2008**, *64*, 112−122.
(63) Dyker, A. C.; Burford, N.; Lumsden, M. D.; Decken, A. Acyclic *catena*-Diphosphinodiphosphonium Dications $[R_3P\text{-}PR'\text{-}PR'\text{-}PR_3]^{2+}$ or Bisphosphine−Diphosphenium Complexes $[R_3P{\rightarrow}PR'\text{-}PR'{\leftarrow}PR_3]^{2+}$: Synthesis by Reductive P−P Coupling of $[R_3P\text{-}PR'Cl]^+$ and Phosphine Ligand Exchange. *J. Am. Chem. Soc.* **2006**, *128*, 9632−9633.
(64) Geier, J.; Harmer, J.; Grützmacher, H. Naked" Phosphanediide Chains and their Fragmentation into Diphosphene Radical Anions. *Angew. Chem., Int. Ed.* **2004**, *43*, 4093−4097.
(65) Stein, D.; Dransfeld, A.; Flock, M.; Rüegger, H.; Grützmacher, H. Lithium Oligophosphanediides in the Li/PhPCl System. *Eur. J. Inorg. Chem.* **2006**, *2006*, 4157−4167.
(66) Pu, L.; Olmstead, M. M.; Power, P. P.; Schiemenz, B. Synthesis and Characterization of the Monomeric Terphenyl-Metal Halides $Ge(Cl)\{C_6H_3\text{-}2,6\text{-}Trip_2\}$ (Trip = C_6H_2-2,4,6-i-Pr_3) and $Sn(I)\{C_6H_3\text{-}2,6\text{-}Trip_2\}$ and the Terphenyl-Metal Amide $Sn\{N(SiMe_3)_2\}\{C_6H_3\text{-}2,6\text{-}Trip_2\}$. *Organometallics* **1998**, *17*, 5602−5606.
(67) Kavara, A.; Kampf, J. W.; Banaszak Holl, M. M. Direct Formation of Propargyltin Compounds via C−H Activation. *Organometallics* **2008**, *27*, 2896−2897.
(68) Izod, K.; Evans, P.; Waddell, P. G.; Probert, M. R. Remote Substituent Effects on Structures and Stabilities of P=E π-Stabilized Diphosphatetrylenes $(R_2P)_2$ (E = Ge, Sn). *Inorg. Chem.* **2016**, *55*, 10510−10522.
(69) Humbel, S.; Bertrand, C.; Darcel, C.; Bauduin, C.; Jugé, S. Configurational Stability of Chlorophosphines. *Inorg. Chem.* **2003**, *42*, 420−427.
(70) Weicker, S. A.; Dube, J. W.; Ragogna, P. J. Synthesis of Zwitterionic Group 14 Centered Complexes: Traditional Coordination and Unusual Insertion Chemistry. *Organometallics* **2013**, *32*, 6681−6689.
(71) Karsch, H. H.; Appelt, A.; Müller, G. Functional trimethylphosphine derivatives. Part 24. Main group element phosphine complexes. 5. Tri- and tetracoordinated, monomeric tin(II) phosphine complexes and x-ray structure of $Sn[C(PMe2)_3]_2$. *Organometallics* **1986**, *5*, 1664−1670.
(72) Krebs, K. M.; Maudrich, J.-J.; Wesemann, L. Reaction of stannylene phosphorus Lewis pairs with dichlorides of germanium, tin and lead − the formation of base stabilized stannyl stannylenes/germylenes and redox reaction with $PbCl_2$. *Dalton Trans.* **2016**, *45*, 8081−8088.
(73) Arras, J.; Eichele, K.; Maryasin, B.; Schubert, H.; Ochsenfeld, C.; Wesemann, L. Intermolecular $^{119}Sn,^{31}P$ Through-Space Spin−Spin Coupling in a Solid Bivalent Tin Phosphido Complex. *Inorg. Chem.* **2016**, *55*, 4669−4675.
(74) Barney, A. A.; Heyduk, A. F.; Nocera, D. G. Synthesis of an anionic tridentate phosphinoborate and its reaction chemistry with Sn(II). *Chem. Commun.* **1999**, 2379−2380.
(75) Su, M.-D. Theoretical Study of Halophilic Reactions of Stable Silylenes with Chloro- and Bromocarbons. *J. Am. Chem. Soc.* **2003**, *125*, 1714−1715.

DOI: 10.1021/acs.inorgchem.7b01275
Inorg. Chem. XXXX, XXX, XXX−XXX