

Unusual Reactivity of Methylphosphaalkyne ($P\equiv CMe$) toward Digermenes and Distannenes: Stepwise Formations of Bridged 2,3,5,6-Tetraphospha-1,4-dimethylidenecyclohexanes

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Reactions of methylphosphaalkyne, $P\equiv CMe$, with a digermene, $R''_2Ge\equiv GeR''_2$ ($R'' = -CH(SiMe_3)_2$), and two distannenes, $R''_2Sn\equiv SnR''_2$ and $Ar'_2Sn\equiv SnAr'_2$ ($Ar' = C_6H_2Pr_{3-2,4,6}$), have given moderate to high yields of the first bridged 2,3,5,6-tetraphospha-1,4-dimethylidenecyclohexanes, $[R_2E\{C(Me)(H)PC(\equiv CH_2)P\}]_2$ ($R = R''$ or Ar' , $E = Sn$ or Ge), all of which have been structurally characterized. Their mechanisms of formation are thought to involve successive $[2 + 1]$ and $[2 + 2]$ phosphaalkyne cycloaddition, heterocycle rearrangement, phosphaalkene/vinylphosphine tautomerization, and intermolecular hydrophosphination reactions. In one reaction, two intermediates have been spectroscopically observed and one trapped by coordination to one or two $W(CO)_5$ fragments, yielding the first diphosphagermole complexes, $\{[W(CO)_5]_{10/2}\{R''_2Ge[C(Me)PC(Me)P]\}$, which have been structurally characterized. Differences between the reactivities of $P\equiv CMe$ and $P\equiv CMe^t$ are highlighted.

Introduction

The low coordination chemistry of phosphorus has been extensively developed over the past two decades. Compounds containing P(III)–C multiple bonds are now readily prepared, and their metal complexes have found a variety of applications.¹ Generally, however, bulky substituents are required to stabilize such unsaturated organophosphorus systems toward oxidation, hydrolysis, and cycloaddition reactions. In this area, phosphaalkynes, $P\equiv CR$, have been particularly well investigated and over 450 papers describing their chemistry have appeared.² By far the most studied phosphaalkyne is $P\equiv CMe^t$, which has a diverse coordination chemistry and has been utilized as a building block in the synthesis of numerous organophosphorus cage, heterocyclic, and acyclic compounds.¹ Throughout this work phos-

phaalkynes have proven to be much more alkyne than nitrile like in their reactivity because of the polarization of their $\delta^+P\equiv C\delta^-$ bonds, and the high energy of their π -bonding HOMOs relative to that of their P lone pair.¹

Recent theoretical studies have suggested that the steric (and electronic) properties of the substituents of phosphaalkynes (and other low coordination phosphorus compounds) could have an important bearing on their chemistry.³ Accordingly, we have initiated a study of the previously unexplored reactivity of the unhindered phosphaalkyne, $P\equiv CMe$, to compare it to that of $P\equiv CMe^t$. This is also of interest as $P\equiv CMe$ is the phosphorus analogue of acetonitrile and propyne. Our preliminary results suggest that the chemistry of $P\equiv CMe$ will not mirror that of $P\equiv CMe^t$, as the two phosphaalkynes can yield different product types from cyclodimerization, cycloaddition, and transition metal coordination reactions.⁴ In general, the smaller phosphaalkyne appears to be significantly more reactive than its bulkier counterpart.

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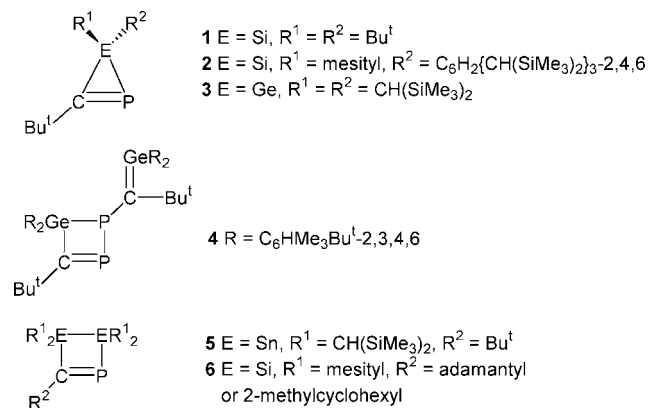
(1) For example, see: (a) Dillon, K. B.; Mathey, F.; Nixon, J. F. In *Phosphorus: The Carbon Copy*; Wiley: Chichester, 1998. (b) *Phosphorus–Carbon Heterocyclic Chemistry: The Rise of a New Domain*; Mathey, F., Ed.; Pergamon: Amsterdam, 2001. (c) Ozawa, F.; Yoshifuji, M. *Dalton Trans.* **2006**, 4987. (d) Breit, B.; Winde, R.; Mackewitz, T.; Paciello, R.; Harms, K. *Chem. Eur. J.* **2001**, *7*, 3106. (e) Mathey, F. *Angew. Chem., Int. Ed.* **2003**, *42*, 1578 and references therein.

(2) Results of a literature survey using SciFinder Scholar, May, 2007.

(3) For example, see: (a) Nyulaszi, L. *J. Organomet. Chem.* **2005**, *690*, 2597. (b) Mo, O.; Yanez, M.; Guillemain, J.-C.; Riague, E. H.; Gal, J.-F.; Maria, P.-C.; Poliart, C. D. *Chem. Eur. J.* **2002**, *8*, 4919. (c) Hltzl, T.; Szieberth, D.; Nguyen, M. T.; Veszpremi, T. *Chem. Eur. J.* **2006**, *12*, 8044 and references therein.

(4) (a) Jones, C.; Schulten, C.; Stasch, A. *Dalton Trans.* **2007**, 1929. (b) Jones, C.; Schulten, C.; Stasch, A. *Dalton Trans.* **2006**, 3733.

Chart 1



As an extension of this preliminary work, we believed it would be of interest to compare the reactivity of the two phosphalkynes toward the heavier Group 14 analogues of carbenes and alkenes, viz. :ER₂ and R₂E≡ER₂ respectively (E = Si, Ge, and Sn), which normally exist in equilibrium in solution. In this respect, P≡CBu^t has been shown to undergo [2 + 1] cycloaddition reactions with silylene or germylene fragments to give the three-membered heterocycles, **1–3**.^{5–7} A germaidiphosphacyclobutene, **4**, has also been prepared and is thought to result from ring opening and a subsequent dimerization reaction of a phosphagermirene similar to **3**.⁸ In addition, the reaction of a distannene with P≡CBu^t has given the phosphadistannacyclobutene, **5**,⁹ via a [2 + 2] cycloaddition. Moreover, a silicon analogue of this, **6**, has been reported to be formed from the stepwise addition of two silylene fragments to two other hindered phosphalkynes, P≡CR (R = adamantyl or 2-methylcyclohexyl).¹⁰ The very different reactivity of P≡CMe toward germylene, stannylene, and related fragments is described herein.

Experimental Section

General Methods. All manipulations were carried out using standard Schlenk and glovebox techniques under an atmosphere of high-purity argon. Diethyl ether, hexane, and toluene were distilled over Na/K alloy. ¹H NMR spectra were recorded on a Bruker DPX400 spectrometer operating at 400.13 MHz and were referenced to the residual ¹H resonances of the solvent used. ³¹P{¹H} NMR spectra were acquired using a Jeol Eclipse 300 spectrometer operating at 121.6 MHz and were referenced to external 85% H₃PO₄. EI mass spectra and accurate mass spectra were obtained from the EPSRC National Mass Spectrometric Service at Swansea University. Although molecular ion peaks displaying correct isotopic distribution patterns were observed for all new complexes, only the accurate mass data for **14** are

reported. All other compounds have masses greater than 1000 Da, and as such, their accurate mass data are not considered meaningful. IR spectra were recorded using a Nicolet 510 FT-IR spectrometer as Nujol mulls between NaCl plates. Reproducible microanalyses could not be obtained for the complexes due to solvent of crystallization (**9**) or their air- and/or moisture-sensitive nature. Their NMR spectra, however, suggested purities of >97% in each case. P≡CMe,¹¹ [Ge{CH(SiMe₃)₂}₂]₂,¹² [Sn{CH(SiMe₃)₂}₂]₂,¹² and [Sn(Ar')₂]₃¹³ were synthesized by literature procedures. All other reagents were used as received.

Preparation of [R'₂Ge{C(Me)(H)PC(≡CH₂)P}]₂ (7**).** P≡CMe (1.2 mL of a 0.52 M solution in diethyl ether, 0.62 mmol) was added to a solution of [Ge{CH(SiMe₃)₂}₂]₂ (100 mg, 0.13 mmol) in toluene (20 mL) at −80 °C. The resultant solution was warmed to 20 °C and stirred for 48 h, during which time **7** deposited as a colorless crystalline solid. The solid was isolated by filtration and dried under a stream of argon (110 mg, 85%). mp = 197–199 °C. ¹H NMR (400 MHz, CD₂Cl₂, 298 K): δ 0.14 (s, 2H, CHSiMe₃), 0.15 (s, 2H, CHSiMe₃), 0.19 (s, 18H, SiMe₃), 0.21 (s, 18H, SiMe₃), 0.27 (s, 18H, SiMe₃), 0.30 (s, 18H, SiMe₃), 1.59 (dd, ³J_{HH} = 7.8 Hz, ³J_{PH} = 23.4 Hz, 6H, CH₃), 2.99 (br. m, 2H, CH), 6.25 (dd, 2H, ³J_{PH} = 46 and 10 Hz, ≡CHH), 6.52 (dd, 2H, ³J_{PH} = 33 and 16 Hz, ≡CHH); ³¹P{¹H} NMR (121.6 MHz, THF-*d*₈, 298 K): δ −13.7 (br. d, ¹J_{PP} = 303.1 Hz, PGe), 31.7 (br. d, ¹J_{PP} = 303.1 Hz, PCCCH₂); IR ν/cm^{−1} (Nujol): 1570w, 1377m, 1307m, 1250s, 1169m, 1087m, 1056m, 1025m; (MS/EI) *m/z* (%): 1014 [M⁺, 55], 855 [M⁺ − CH(SiMe₃)₂, 25], 624 [M⁺ − Ge{CH(SiMe₃)₂}₂, 56].

Preparation of [R'₂Sn{C(Me)(H)PC(≡CH₂)P}]₂ (8**).** P≡CMe (3.3 mL of a 0.25 M solution in diethyl ether, 0.82 mmol) was added to a solution of [Sn{CH(SiMe₃)₂}₂]₂ (120 mg, 0.14 mmol) in toluene (20 mL) at −80 °C. The resultant solution was warmed to 20 °C and stirred for 48 h, during which time **8** deposited as a colorless crystalline solid. The solid was isolated by filtration and dried under a stream of argon (122 mg, 81%). mp = 240–245 °C. ¹H NMR (400 MHz, CD₂Cl₂, 298 K): δ 0.00 (s, 2H, CHSiMe₃), 0.02 (s, 2H, CHSiMe₃), 0.08 (s, 18H, SiMe₃), 0.19 (s, 18H, SiMe₃), 0.27 (s, 18H, SiMe₃), 0.29 (s, 18H, SiMe₃), 1.53 (dd, ³J_{HH} = 8.0 Hz, ³J_{PH} = 15.5 Hz, 6H, CH₃), 2.76 (br. m, 2H, CH), 6.18 (dd, 2H, ³J_{PH} = 43 and 11 Hz, ≡CHH), 6.65 (dd, 2H, ³J_{PH} = 32 and 19 Hz, ≡CHH); ³¹P{¹H} NMR (121.6 MHz, CD₂Cl₂, 298 K): δ −63.2 (br. d, ¹J_{PP} = 311.2 Hz, ¹J_{SnP} = 621.2 Hz, PSn), 16.5 (br. d, ¹J_{PP} = 311.2 Hz, PCCCH₂); IR ν/cm^{−1} (Nujol): 1564w, 1376m, 1246m, 1026m, 996m, 982m; (MS/EI) *m/z* (%): 1107[M⁺, 6], 948 [M⁺ − CH(SiMe₃)₂, 28], 670 [M⁺ − Sn{CH(SiMe₃)₂}₂, 12].

Preparation of [Ar'₂Sn{C(Me)(H)PC(≡CH₂)P}]₂ (9**).** P≡CMe (1.0 mL of a 0.51 M solution in diethyl ether, 0.51 mmol) was added to a toluene solution (50 mL) of [Sn(Ar')₂]₂ (120 mg, 0.13 mmol) at −80 °C (which had been generated in situ by UV irradiation (λ = 254 nm) of [Sn(Ar')₂]₃ at −80 °C). The resultant solution was warmed to 20 °C and stirred for 48 h, during which time **9** deposited as a colorless crystalline solid. The solid was isolated by filtration and dried under vacuum (50 mg, 31%). mp = 210–215 °C (dec). ¹H NMR (400 MHz, C₆D₆, 298 K): δ 0.83 (2 overlapping br., 24H, CH(CH₃)₂), 1.30 (br. overlapping m, 48H, CH(CH₃)₂), 1.60 (br. m, 6H, CH₃), 2.72, 2.93 (2 × br., 2 × 4H, CH(CH₃)₂), 2.92 (br. m, 2H, PCH(CH₃)), 3.25, 3.46 (2 × br., 2 × 2H, CH(CH₃)₂), 5.80 (dd, 2H, ³J_{PH} = 35 and 18 Hz, ≡CHH), 6.19 (dd, 2H, ³J_{PH} = 46 and 12 Hz, ≡CHH), 7.03 (br., 8H, ArH);

(5) Schäfer, A.; Weidenbruch, M.; Saak, W.; Pohl, S. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 776.

(6) Tokitoh, N.; Suzuki, H.; Takeda, N.; Kajiwara, T.; Sasamori, T.; Okazaki, R. *Silicon Chem.* **2002**, *1*, 313.

(7) Cowley, A. H.; Hall, S. W.; Nunn, C. M.; Power, J. M. *J. Chem. Soc., Chem. Commun.* **1988**, 753.

(8) Meiners, F.; Saak, W.; Weidenbruch, M. *Chem. Commun.* **2001**, 215.

(9) Cowley, A. H.; Hall, S. W.; Nunn, C. M.; Power, J. M. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 838.

(10) Weidenbruch, M.; Olthoff, S.; Peters, K.; von Schnering, G. *Chem. Commun.* **1997**, 1433.

(11) Guillemin, J.-C.; Janati, T.; Denis, J.-M. *J. Org. Chem.* **2001**, *66*, 7864.

(12) Fjeldberg, T.; Haaland, A.; Schilling, B. E. R.; Lappert, M. F.; Thorne, A. J. *J. Chem. Soc., Dalton Trans.* **1986**, 1551 and references therein.

(13) Weidenbruch, M.; Schäfer, A.; Kilian, H.; Pohl, S.; Saak, W.; Marsmann, H. *Chem. Ber.* **1992**, *125*, 563.

Table 1. Summary of Crystallographic Data for Compounds **7–9**, **14**, and **15**

	7	8	9 (toluene)	14	15
empirical formula	C ₃₆ H ₈₈ Ge ₂ P ₄ Si ₈	C ₃₆ H ₈₈ P ₄ Si ₈ Sn ₂	C ₇₅ H ₁₁₂ P ₄ Sn ₂	C ₂₃ H ₄₄ GeO ₅ P ₂ Si ₄ W	C ₂₈ H ₄₄ GeO ₁₀ P ₂ Si ₄ W ₂
fw	1014.84	1107.04	1374.91	831.32	1155.22
cryst syst	monoclinic	monoclinic	triclinic	triclinic	orthorhombic
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>a</i> (Å)	13.580(3)	13.726(3)	10.727(2)	9.836(2)	11.323(2)
<i>b</i> (Å)	16.645(3)	16.959(3)	12.633(3)	11.780(2)	18.487(4)
<i>c</i> (Å)	11.978(2)	11.860(2)	14.198(3)	16.021(3)	20.297(4)
α (deg)	90	90	71.70(3)	99.46(3)	90
β (deg)	97.60(3)	96.38(3)	80.66(3)	100.06(3)	90
γ (deg)	90	90	83.61(3)	100.66(3)	90
<i>V</i> (Å ³)	2683.6(9)	2743.5(9)	1798.7(6)	1758.9(6)	4284.7(15)
<i>Z</i>	2	2	1	2	4
ρ (calcd) (gcm ⁻³)	1.256	1.340	1.269	1.570	1.806
μ (mm ⁻¹)	1.442	1.225	0.822	4.377	6.337
<i>F</i> (000)	1080	1152	722	828	2232
cryst size (mm ³)	0.30 × 0.20 × 0.15	0.08 × 0.05 × 0.02	0.25 × 0.20 × 0.15	0.35 × 0.25 × 0.15	0.25 × 0.25 × 0.22
θ range (deg)	2.99–26.00	2.96–25.00	2.93–26.50	3.03–28.00	2.91–27.00
reflns collected	10 263	8895	13 448	15 783	34 743
<i>R</i> _{int}	0.0224	0.0610	0.0265	0.0224	0.0794
data/restraints/params	5273/0/239	4766/0/239	7362/6/375	8421/0/339	9211/0/438
GOF on <i>F</i> ²	1.032	1.035	1.034	1.025	1.048
<i>R</i> 1 indices [<i>I</i> > 2 σ (<i>I</i>)] ^a	0.0280	0.0506	0.0312	0.0233	0.0246
w <i>R</i> 2 indices (all data) ^a	0.0690	0.0879	0.0723	0.0513	0.0538
largest peak and hole (e·Å ⁻³)	0.305 and -0.334	0.652 and -0.447	0.708 and -0.422	0.572 and -1.282	0.784 and -1.406

^a $R1(F) = \{\sum(|F_o| - |F_c|)/\sum|F_o|\}$ for reflections with $F_o > 4\sigma(F_o)$. $wR2(F^2) = \{\sum w(|F_o|^2 - |F_c|^2)^2/\sum w|F_o|^2\}^{1/2}$ where *w* is the weight given for each reflection.

³¹P{¹H} NMR (121.6 MHz, C₆D₆, 298 K): δ -76.3 (d, ¹*J*_{PP} = 320 Hz, ¹*J*_{SNP} = 614 Hz, PSn), 15.8 (d, ¹*J*_{PP} = 320 Hz, PP); IR ν /cm⁻¹ (Nujol): 1594w, 1377m, 1260m, 1154m, 1096m, 1018m; (MS/EI) *m/z* (%): 1283 [M⁺, 7], 1079 [M⁺ - Ar', 10], 758 [M⁺ - Sn(Ar')₂, 20].

Preparation of [{W(CO)₅}{R''₂Ge[C(Me)PC(Me)P]}] (14**) and [{W(CO)₅]₂{R''₂Ge[C(Me)PC(Me)P]}] (**15**).** P≡CMe (1.2 mL of a 0.52 M solution in diethyl ether, 0.62 mmol) was added to a solution of [Ge{CH(SiMe₃)₂]₂ (100 mg, 0.13 mmol) in toluene (20 mL) at 20 °C. After 5 min [W(CO)₅(THF)] (198 mg, 0.501 mmol) in THF (50 mL) was added to the solution. After stirring for 24 h, volatiles were removed in vacuo and the residue extracted with hexane (5 mL). The extract was chromatographed (silica gel/hexane) and yellow and red bands collected. Both bands were concentrated in vacuo, yielding yellow **14** and red **15** as crystalline solids. **14**: (38 mg, 13%) mp = 83–85 °C; ¹H NMR (400 MHz, C₆D₆, 298 K): δ 0.05 (br s, 2H, CHSiMe₃), 0.22 (br, 18H, SiMe₃), 0.25 (br, 18H, SiMe₃), 2.56 (d, ³*J*_{PH} = 31 Hz, 3H, GeC(CH₃)P), 2.71 (v. tr, ³*J*_{PH} = ³*J*_{PH} = 20 Hz, 3H, P₂C(CH₃)); ³¹P{¹H} NMR (121.6 MHz, C₆D₆, 298 K): δ 247.5 (d, ²*J*_{PP} = 53.8 Hz, ¹*J*_{PW} = 257 Hz, PCMe), 342.0 (d, ²*J*_{PP} = 53.8 Hz, GePCMe); IR ν /cm⁻¹ (Nujol): 2072s, 1977s, 1948s (CO str.); (MS/EI) *m/z* (%): 831 (M⁺, 16), 803 (M⁺ - CO, 12), 392 (R''₂GeH⁺, 46); EI Acc. Mass. on M⁺: calcd for C₂₃H₄₄O₅⁷⁰Ge₁P₂Si₄¹⁸²W₁: 826.0460, found 826.0462. **15**: (32 mg, 15%) mp = 55–58 °C; ¹H NMR (400 MHz, C₆D₆, 298 K): δ 0.05 (br, 2H, CHSiMe₃), 0.28 (br, 18H, SiMe₃), 0.33 (br, 18H, SiMe₃), 2.40 (dd, ³*J*_{PH} = 35 Hz, ⁴*J*_{PH} = 8 Hz, 3H, GeC(CH₃)P), 2.68 (dd, ³*J*_{PH} = 29 Hz, ³*J*_{PH} = 20 Hz, P₂C(CH₃)); ³¹P{¹H} NMR (121.6 MHz, C₆D₆, 298 K): δ 251.0 (d, ²*J*_{PP} = 66 Hz, ¹*J*_{PW} = 245 Hz, CPCMe), 287.5 (d, ²*J*_{PP} = 66 Hz, ¹*J*_{PW} = 256 Hz, GePCMe); IR ν /cm⁻¹ (Nujol): 2068s, 1982sh, 1966s, 1955s (CO str.); (MS/EI) *m/z* (%): 1155 [M⁺, 2], 392 [R''₂GeH⁺, 86%].

X-ray Crystallography. Crystals of **7–9**, **14**, and **15** suitable for X-ray structural determination were mounted in silicone oil. Crystallographic measurements were made using a Nonius Kappa CCD diffractometer using a graphite monochromator with Mo K α radiation (λ = 0.710 73 Å). The data were collected at 150 K, and the structures were solved by direct methods and refined

on *F*² by full matrix least-squares (SHELX97)¹⁴ using all unique data. All non-hydrogen atoms are anisotropic (except the carbon atoms of the toluene of crystallization in the structure of **9**) with H atoms included in calculated positions (riding model). The Flack parameter for the structure of **15** is -0.004(5). Crystal data, details of data collections, and refinement are given in Table 1.

Results and Discussion

Reactions of P≡CMe with examples of sources of the heavier carbene analogues, :ER₂ (E = Si, Ge, Sn, or Pb), were attempted. Treatment of the disilene, Mes₂Si≡SiMes₂ (Mes = mesityl), the diplumbene, Ar'₂Pb≡PbAr'₂ (Ar' = C₆H₂Prⁱ₃-2,4,6), or the plumbylene, :Pb{CH(SiMe₃)₂]₂ (which is monomeric in the solid state), with P≡CMe in 1:1, 1:2, and 1:4 stoichiometries all led to intractable mixtures of phosphorus containing products. As the disilene is known not to significantly dissociate to the corresponding silylene in solution,¹⁵ UV irradiation (λ = 254 nm) of a 1:1 mixture of P≡CMe and Mes₂Si(SiMe₃)₂ in THF at -80 °C was attempted. Although irradiation of the trisilene is known to generate the silylene, :SiMes₂, in situ,¹⁶ many phosphorus containing products again resulted from this reaction, none of which could be isolated. It is of note that P≡CMe failed to react with monomeric :Sn{N(SiMe₃)₂]₂, which Cowley et al. have shown to be the case when it is treated with P≡CBu.⁹

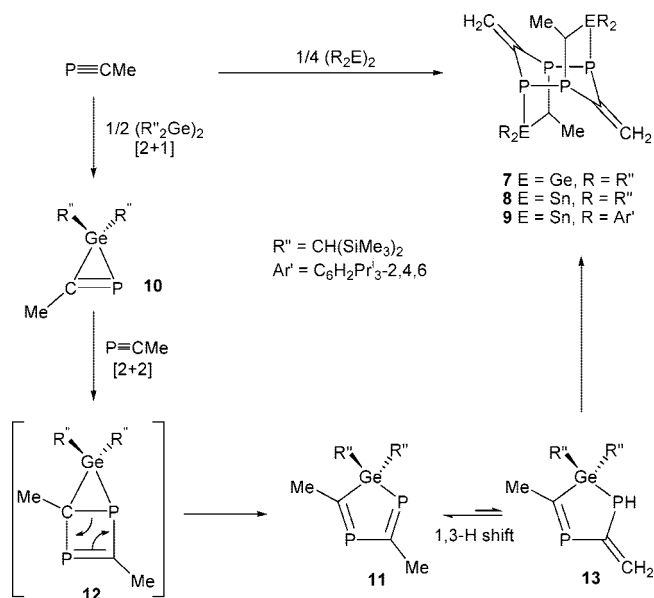
More success was had in the reactions of R''₂E≡ER''₂ (E = Ge or Sn, R'' = -CH(SiMe₃)₂) with P≡CMe which, under 1:4 stoichiometries of reactants, led to the deposition of high yields of colorless crystals of **7** or **8** upon warming the reaction mixtures from -80 °C to ambient temperature and stirring for 18 h (Scheme 1). Similarly, reactions of

(14) Sheldrick, G. M. *SHELX-97*; University of Göttingen: Göttingen, Germany, 1997.

(15) Okazaki, R.; West, R. *Adv. Organomet. Chem.* **1996**, *39*, 231.

(16) West, R.; Fink, M. J.; Michl, J. *Science* **1981**, *214*, 1343.

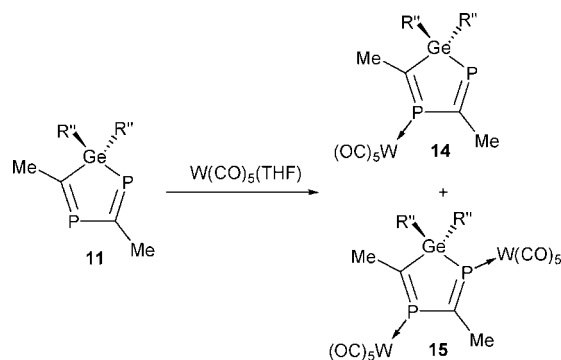
Scheme 1



the in-situ-generated distannene, $\text{Ar}'_2\text{Sn}\equiv\text{SnAr}'_2$, with $\text{P}\equiv\text{CMe}$ yielded the related bridged 2,3,5,6-tetraphospha-1,4-dimethylidencyclohexane, **9**, but in lower yield (31%). In contrast, no reaction occurred with the digermene, $\text{Ar}'_2\text{Ge}\equiv\text{GeAr}'_2$. This difference probably results from the fact that $\text{R}''_2\text{E}\equiv\text{ER}''_2$ and $\text{Ar}'_2\text{Sn}\equiv\text{SnAr}'_2$ significantly dissociate into germylene or stannylene fragments in solution, while $\text{Ar}'_2\text{Ge}\equiv\text{GeAr}'_2$ remains largely intact¹⁷ and is, therefore, less reactive toward $\text{P}\equiv\text{CMe}$. It is also of interest that $\text{R}''_2\text{Ge}\equiv\text{GeR}''_2$ is known to react in a completely different fashion with $\text{N}\equiv\text{CMe}$, in that upon dissociation of the digermene, the germanium center of the monomeric germylene inserts into one C–H bond of the nitrile to give $\text{R}''_2\text{Ge}(\text{H})\text{CH}_2\text{C}\equiv\text{N}$, which has been structurally characterized.¹⁸

It is clear from the products of the reactions reported here that they proceed via different pathways than those that gave **1–6**. In order to shed light on their mechanisms, the reaction that gave **7** (with $\text{P}\equiv\text{CMe}$ in excess) was monitored by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. In toluene- d_8 a reaction occurred immediately at -80°C , as evidenced by the appearance of a singlet resonance at δ 436.6 ppm. This completely disappeared within 5 min, giving rise to an AB spin system (δ P_A 319.8, P_B 308.5 ppm; $^2J_{\text{PAPB}} = 29.8$ Hz) with the concomitant consumption of the $\text{P}\equiv\text{CMe}$ reactant (δ -61.1 ppm). We attribute the low-field singlet resonance to the [2 + 1] cycloaddition product, **10** (cf. **3**: δ 315 ppm⁷), which rapidly reacts with excess $\text{P}\equiv\text{CMe}$ to give the 2,4-diphosphagermole, **11**, which gives rise to the AB spin pattern (cf. the 2,4-diphosphatellurole, $\text{TeP}_2\text{C}_2\text{Bu}'_2$: δ 299, 302 ppm; $^2J_{\text{PP}} = 50.8$ Hz¹⁹). Although there is no spectroscopic evidence, the formation of **11** from **10** could involve a [2 + 2] cycloaddition of **10** with

Scheme 2



$\text{P}\equiv\text{CMe}$ to give intermediate, **12**, which rapidly rearranges. Once formed, **11** persists in solution at -80°C but on warming to ambient temperature it converts into **7**, which has low solubility and precipitates from the reaction mixture over ca. 12 h. It should be noted that spectroscopic monitoring of the reactions that gave **8** and **9** revealed them to be more rapid than that which gave **7** and no long-lived intermediates could be identified.

A plausible mechanism for the conversion of **11** to **7** involves the former being in equilibrium with **13** via a 1,3-hydrogen migration. Two molecules of **13** then react via hydrophosphination of the $\text{P}\equiv\text{C}$ bonds of each other to give **7**. This proposal seems reasonable, as a precedent exists for phosphalkene/vinylphosphine tautomerizations.²⁰ The absence of any observable signals corresponding to **13** in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction mixture suggest that **11** is heavily favored in the equilibrium. Despite this, the formation of **7** and its precipitation from solution both conspire to fully consume **11** in the reaction.

Given that **10** and **11** are long-lived enough to be spectroscopically observable, attempts were made to isolate them and/or complexes of them from reactions of $\text{P}\equiv\text{CMe}$ with $\text{R}''_2\text{Ge}\equiv\text{GeR}''_2$. When an excess of the digermene was employed, the proposed phosphagermirene intermediate, **10**, persisted in solution for hours below -50°C but on warming to ambient temperature decomposed to unidentified products. In order to trap a stable complex of **11**, the reaction was repeated with an excess of $\text{P}\equiv\text{CMe}$ at 20°C . After 5 min, a THF solution of $[\text{W}(\text{CO})_5(\text{THF})]$ was added to the reaction mixture. After chromatographic workup, low yields of the 1:1 and 1:2 adducts of the heterocycle with the $\text{W}(\text{CO})_5$ fragment, viz. **14** and **15**, were obtained as crystalline solids (Scheme 2). The isolation of these compounds gives strong support to the proposed structure of **11**. Both compounds are indefinitely stable in solution, as they are presumably prohibited from further intermolecular reactions to give tungsten carbonyl complexes of **7** or related species.

The low solubility of **7–9** leads to them precipitating from their toluene reaction solutions. It is difficult to redissolve these compounds in most deuterated solvents, but **6** and **7** have sufficient solubility in CD_2Cl_2 or THF- d_8 to obtain their ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra. Similarly, these spectra can be acquired for weak saturated C_6D_6

(17) Schäfer, H.; Saak, W.; Weidenbruch, M. *Organometallics* **1999**, *18*, 3159.

(18) Miller, K. A.; Watson, T. W.; Bender, J. E., IV; Banaszak, H.; Kampf, J. W. *J. Am. Chem. Soc.* **2001**, *123*, 982.

(19) Francis, M. D.; Jones, C.; Morley, C. P. *Tetrahedron Lett.* **1999**, *40*, 3815.

(20) (a) Yam, M.; Tsang, C.-W.; Gates, D. P. *Inorg. Chem.* **2004**, *43*, 3719.
 (b) Chuang, C.-H.; Lien, M.-H. *J. Phys. Chem. A* **2004**, *108*, 1790.

solutions of **9**, but meaningful $^{13}C\{^1H\}$ NMR spectra could not be obtained for any complex and the NMR samples of **8** and **9** were too dilute for signals to be observed in their $^{119}Sn\{^1H\}$ NMR spectra. The 1H and $^{31}P\{^1H\}$ NMR spectra of **7–9** show that they are formed completely diastereoselectively. Four trimethylsilyl methyl singlets were observed in the 1H NMR spectra of **7** and **8**, while the spectra of all three complexes display two inequivalent alkenic proton signals, each split into a doublet of doublets by two $^3J_{PH}$ couplings (N.B.: geminal $^2J_{HH}$ couplings for these signals were not observable). The $^{31}P\{^1H\}$ NMR spectra of **7–9** are similar, and each consists of two doublet signals with characteristic $^1J_{PP}$ couplings. In addition, $^1J_{SnP}$ satellites of typical magnitudes flank the high-field signals of the tin complexes, **8** and **9**. Moreover, the doublets in each spectrum are broadened, presumably because of unresolved second-order J_{PP} couplings. Molecular ion signals exhibiting the expected isotopic abundance patterns are present in the EI mass spectra of **7–9**.

The spectroscopic data for the tungsten carbonyl complexes, **14** and **15**, are consistent with their structures. Most informative are their $^{31}P\{^1H\}$ NMR spectra which each display two low-field doublet signals related by mutual $^2J_{PP}$ couplings. Both resonances in the spectrum of **15** possess $^1J_{WP}$ satellites, while only the higher-field signal in the spectrum of **14** does. It is of note that although the phosphalkenic resonances for **14** and **15** are in the normal low-field range,¹ those associated with the tungsten-coordinated P centers are at significantly higher field than seen in the spectrum of the uncoordinated intermediate, **11**. Similar upfield shifts for peaks in the $^{31}P\{^1H\}$ NMR spectra of phosphalkenes upon P-center metal coordination are common.¹

The X-ray crystal structures of **7–9**, **14**, and **15** were determined. Complexes **7** and **8** are isomorphous, so only the molecular structure of **7** is depicted in Figure 1, though relevant geometrical parameters for **8** are included in the figure caption. Compound **9** has a near identical core structure to those of **7** and **8**, and its molecular structure is shown in Figure 2. As the heterocycle geometries of **14** and **15** are not significantly different, only the molecular structure of **14** is highlighted in Figure 3. That for **15** can be found in the Supporting Information.

The geometries of the heterocyclic cores of **7–9** are very similar, and their structural characterizations represent the first for tetraphospha-1,4-dimethylidencyclohexanes. Each contains a P_4C_2 six-membered ring adopting a chair configuration with two fused P_2C_2E ($E = Ge$ or Sn) rings. All of the interatomic distances within the polycyclic systems are normal for single-bonded interactions,²¹ with the exception of that between the methyldiene carbon, C(4), and C(3). Compounds **14** and **15** are the first structurally elucidated diphosphagermole complexes. Each has a near-planar heterocyclic core with two largely localized P–C double bonds. Their intracyclic Ge–C bond lengths are in the normal range for germole heterocycles

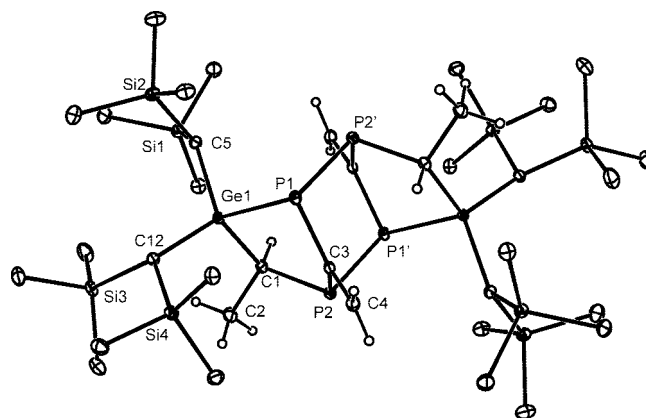


Figure 1. Thermal ellipsoid plot (25% probability surface) of the molecular structure of $[R''_2Ge\{C(Me)(H)PC(=CH_2)P\}_2]$ (**7**) (hydrogen atoms on the R'' substituents are omitted for clarity). Selected bond lengths (Å) and angles (deg): Ge(1)–C(1) 2.020(2), Ge(1)–P(1) 2.3715(7), P(1)–C(3) 1.832(2), P(1)–P(2)' 2.2298(8), P(2)–C(3) 1.830(2), P(2)–C(1) 1.875(2), C(3)–C(4) 1.335(3), C(1)–Ge(1)–P(1) 98.30(6), C(3)–P(1)–P(2)' 100.81(7), C(3)–P(1)–Ge(1) 91.21(7), P(2)'–P(1)–Ge(1) 105.36(3), C(3)–P(2)–C(1) 101.78(9), C(3)–P(2)–P(1)' 105.21(7), C(1)–P(2)–P(1)' 97.76(7), P(2)–C(1)–Ge(1) 112.51(10), P(2)–C(3)–P(1) 121.22(11). Symmetry operation: $'-x + 2, -y, -z + 2$. Selected bond lengths (Å) and angles (deg) for $[R''_2Sn\{C(Me)(H)PC(=CH_2)P\}_2]$ (**8**): Sn(1)–C(1) 2.198(5), Sn(1)–P(1) 2.5388(15), P(1)–C(3) 1.842(5), P(1)–P(2)' 2.2079(19), P(2)–C(3) 1.845(5), P(2)–C(1) 1.873(6), P(2)–P(1)' 2.2079(19), C(3)–C(4) 1.335(7), C(1)–Sn(1)–P(1) 95.07(14), C(3)–P(1)–P(2)' 102.29(17), C(3)–P(1)–Sn(1) 90.83(17), P(2)'–P(1)–Sn(1) 103.41(6), C(3)–P(2)–C(1) 103.9(2), C(3)–P(2)–P(1)' 105.73(16), C(1)–P(2)–P(1)' 97.69(18), P(2)–C(1)–Sn(1) 111.9(2), P(1)–C(3)–P(2) 123.4(3). Symmetry operation: $'-x + 2, -y, -z + 2$.

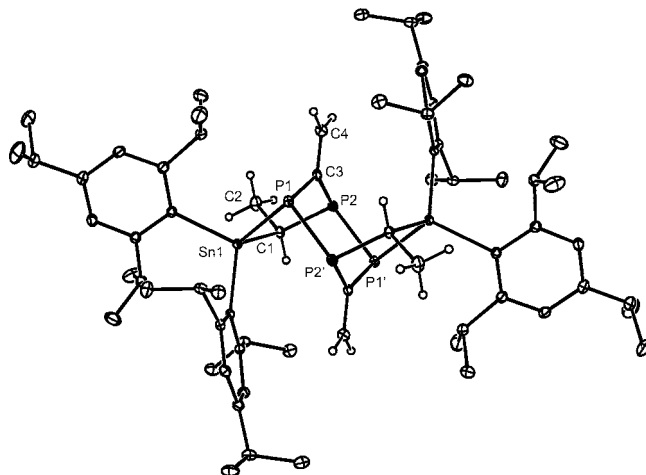


Figure 2. Thermal ellipsoid plot (25% probability surface) of the molecular structure of $[Ar'_2Sn\{C(Me)(H)PC(=CH_2)P\}_2]$ (**9**) (hydrogen atoms on the Ar' substituents are omitted for clarity). Selected bond lengths (Å) and angles (deg): Sn(1)–C(1) 2.202(2), Sn(1)–P(1) 2.5565(9), P(1)–C(3) 1.843(3), P(1)–P(2)' 2.2097(12), P(2)–C(3) 1.833(3), P(2)–C(1) 1.863(2), P(2)–P(1)' 2.2097(12), C(3)–C(4) 1.338(3), C(1)–Sn(1)–P(1) 94.78(7), C(3)–P(1)–P(2)' 107.75(9), C(3)–P(1)–Sn(1) 90.23(8), P(2)'–P(1)–Sn(1) 98.91(3), C(3)–P(2)–C(1) 100.00(11), C(3)–P(2)–P(1)' 106.71(8), C(1)–P(2)–P(1)' 103.52(8), P(2)–C(1)–Sn(1) 112.13(12), P(2)–C(3)–P(1) 123.11(13). Symmetry operation: $'-x + 2, -y, -z + 1$.

(1.92–2.02 Å²¹), and their Ge–P distances are unexceptional. The fact that in **14** the $W(CO)_5$ group is coordinated by the P center in the 4 position of the heterocycle suggests that the lone pair of this phosphorus is more sterically accessible than the P center in the 2 position. Despite this, the lone pair of the latter is available for bonding, as seen in complex **15**.

(21) As determined by a survey of the Cambridge Crystallographic Database, May, 2007.

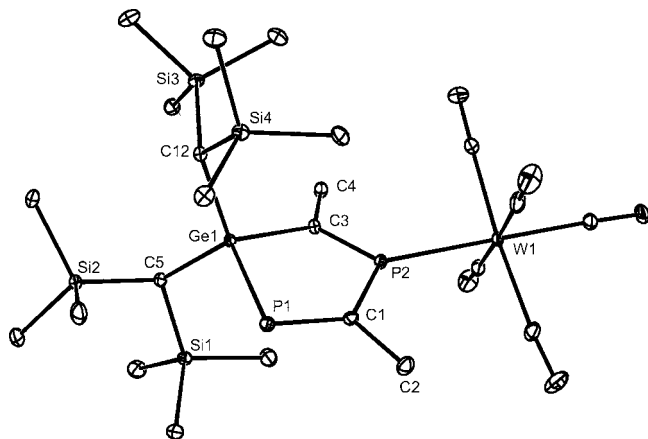


Figure 3. Thermal ellipsoid plot (25% probability surface) of the molecular structure of $[\{W(CO)_5\}\{R'_2Ge[C(Me)PC(Me)P]\}]$ (**14**) (hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (deg): W(1)–P(2) 2.4848(12), Ge(1)–C(3) 1.975(3), Ge(1)–P(1) 2.3403(9), P(1)–C(1) 1.691(3), P(2)–C(3) 1.674(2), P(2)–C(1) 1.813(2), C(1)–P(1)–Ge(1) 96.10(8), C(3)–P(2)–C(1) 106.85(12), C(3)–P(2)–W(1) 128.08(9), C(1)–P(2)–W(1) 124.85(9), P(1)–C(1)–P(2) 124.09(14), P(2)–C(3)–Ge(1) 114.25(12).

Conclusion

In summary, reactions of the unhindered phosphalkyne, $P\equiv CMe$, with a digermene and two distannenes have afforded the first examples of bridged 2,3,5,6-tetraphospha-

1,4-dimethylidenecyclohexanes, all of which have been structurally characterized. The mechanisms for the formation of these products are thought to involve successive [2 + 1] and [2 + 2] phosphalkyne cycloaddition, heterocycle rearrangement, phosphalkene/vinylphosphine tautomerization, and intermolecular hydrophosphination reactions. Two intermediates in one reaction were spectroscopically observed. One of these has been trapped by coordination to one or two $W(CO)_5$ fragments to give crystallographically characterized diphosphagermole complexes. This work further highlights significant differences in the reactivity of $P\equiv CMe$ compared to that of more sterically protected phosphalkynes, e.g., $P\equiv C^tBu$. We continue to explore these differences which will be reported on in future publications.

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Supporting Information Available: Crystallographic data as CIF files for **7–9**, **14**, and **15**, and ORTEP diagrams of **8** and **15**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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