Organometallics **2006,** *25,* 4799−4807

Facile Transformations of a 1,3,5-Triphosphacyclohexadienyl Anion within the Coordination Sphere of Group 13 and 14 Elements: Synthesis of 1,3-Diphosphacyclopentadienyl Complexes and Phosphaorganometallic Cage Compounds

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Received June 26, 2006

The reactivity of the lithium triphosphacyclohexadienyl complex Li[1,3,5-$MeP_3C_3Bu^t_3$] toward a range of group 13 and 14 halide complexes has been investigated. The heterocycle reacts with MX (M = Ga, In, or Tl; X = Cl or I) to give the diphosphacyclopentadienyl (i.e., diphospholyl) complexes [M(η^5-1,3-$P_2C_3Bu^t_3$)] in good yield via phosphinidene, PMe, elimination reactions. One complex, M = Tl, has been structurally characterized and found to exist as a one-dimensional polymer in the solid state. Similarly, the reactions of Li[$MeP_3C_3Bu^t_3$] with MCl_2 (M = Sn or Pb) have given the tetraphosphametallocenes [M(η^5-1,3-$P_2C_3Bu^t_3$)$_2$], which have been structurally characterized. These exhibit fluxional behavior in solution, which has been examined by variable-temperature NMR studies. The monomeric guanidinato−tin chloride complexes [LSnCl] (L = $Cy_2NC(NAr)_2^-$ or (*cis*-2,6-$Me_2C_5H_8N$)C$(NAr)_2^-$, Cy = cyclohexyl, Ar = $C_6H_3Pr^i_2$-2,6) have been prepared, structurally characterized, and treated with Li[$MeP_3C_3Bu^t_3$]. Again, this has yielded diphospholyl complexes [LSn(η^1-1,3-$P_2C_3Bu^t_3$)] via phosphinidene elimination processes. In contrast, the reactions of Ph_3ECl, E = Sn or Pb, do not proceed via phosphinidene elimination reactions, but instead by triphosphacyclohexadienyl rearrangement processes that eventually lead to complexes [Ph_3M(η^2-P,P-$MeP_3C_3Bu^t_3$)], containing five-coordinate metal centers that are P,P-chelated by an anionic bicyclic ligand. In the case of the tin complex, a reaction intermediate has been isolated and shown to contain the first structurally characterized example of a 1,2-diphosphabicyclo[1.1.0]butane fragment. A mechanism for the formation of this intermediate has been proposed.

Introduction

The coordination chemistry of heterocyclic ligand systems containing low-coordinate λ^3-phosphorus centers is a diverse field that has rapidly escalated in recent years. It has become clear that the replacement of one or more carbon centers in classical four-, five-, and six-membered unsaturated ring systems leads to heterocycles that can display both similar and very different coordination chemistry and reactivity compared to their hydrocarbon counterparts.[1]

Our recent activity in this arena[2] has dealt with the transition metal coordination chemistry of the triphosphabenzene, 1,3,5-$P_3C_3Bu^t_3$, and the triphosphacyclohexadienyl complex, Li[1,3,5-$MeP_3C_3Bu^t_3$], **1**, the latter of which is formed by treating the former with MeLi.[3] This work has led to the first examples of transition metal complexes of [$MeP_3C_3Bu^t_3$]$^-$, but has also highlighted the ability of this ligand to undergo metal-mediated transformations. Most notably, in the reaction of **1** with $FeCl_2$, the known tetraphosphaferrocene [Fe(1,3-$P_2C_3Bu^t_3$)$_2$][4] was formed in low yield (among other products), presumably via [Fe(η^5-1,3,5-$MeP_3C_3Bu^t_3$)$_2$], which eliminates 2 equiv of the phosphinidene fragment, PMe, as evidenced by the presence of the known cyclophosphanes, $(PMe)_n$, in the reaction mixture. It seemed to us that p-block complexes of [$MeP_3C_3Bu^t_3$]$^-$ may display a similar facility for phosphinidene elimination, and if so, they could potentially be utilized as sources for the transfer of the phosphinidene, PMe, to other metal or organic fragments. This would be synthetically advantageous, as there are currently few molecular sources of unhindered phosphinidene fragments available to the synthetic chemist.[5] Our efforts to prepare the first group 13 and 14 complexes of [$MeP_3C_3Bu^t_3$]$^-$ are reported herein.

Results and Discussion

Group 13 Element(I) Chemistry. It is now well known that hindered anionic, aromatic ligands, e.g., $C_5Me_5^-$ (Cp*), can stabilize organo-group 13 compounds with the metal in the +1 oxidation state, e.g., the oligomeric metal diyls, [$(MCp^*)_n$], M = Al, $n = 4$; M = Ga, $n = 6$; M = Tl, $n = \infty$. In their monomeric state, these possess metal-based sp-hybridized singlet

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[1] For example: (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) Mathey, F. *Angew. Chem., Int. Ed.* **2003**, *42*, 1578, and references therein.

[2] Francis, M. D.; Holtel, C.; Jones, C.; Rose, R. P. *Organometallics* **2005**, *24*, 4216.

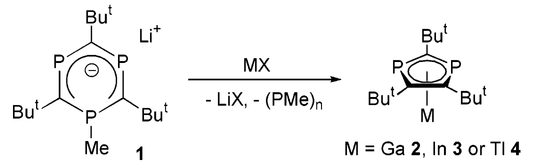
[3] Steinbach, J.; Renner, J.; Binger, P.; Regitz, M. *Synthesis* **2003**, 1526.

[4] Bartsch, R.; Cloke, F. G. N.; Green, J. C.; Matos, R. M.; Nixon, J. F.; Suffolk, R. J.; Suter, J. L.; Wilson, D. J. *J. Chem. Soc., Dalton Trans.* **2001**, 1013.

[5] For example: (a) Lammertsma, K. *Top. Curr. Chem.* **2003**, *229*, 95, (b) Mathey, F.; Tran Huy, N. H.; Marinetti, A. *Helv. Chim. Acta* **2001**, *84*, 2938, and references therein.

10.1021/om0605581 CCC: $33.50

Scheme 1



lone pairs, and accordingly, they are proving very useful as novel Lewis bases in the formation of p-,[6] d-,[7] and even f-block[8] complexes. It occurred to us that the π-system of bulky [MeP$_3$C$_3$Bu$^t_3$]$^-$ may similarly stabilize novel metal diyl complexes of the type [:M(η^5-MeP$_3$C$_3$Bu$^t_3$)]. To this end, the lithium salt **1** was reacted with metal(I) halides, which in all cases led to the diphospholylmetal complexes **2**−**4** (Scheme 1) in good yields after workup. It is apparent that the mechanisms of formation of these complexes involve the initial formation of the target complexes [M(η^5-MeP$_3$C$_3$Bu$^t_3$)], which undergo ring contraction reactions via the elimination of the phosphinidene fragment, PMe. Indeed, the known cyclophosphanes, (PMe)$_n$, are formed in the reactions, as evidenced by the presence of multiplet signals centered at ca. δ 10 ppm in the ^{31}P NMR spectrum of the product mixtures.[9] These phosphinidene elimination reactions are much cleaner than that observed in the formation of [Fe(1,3-P$_2$C$_3$Bu$^t_3$)$_2$], as **2**−**4** were the only observed phosphorus-containing products (other than (PMe)$_n$). The proposed ring contraction reactions must be facile, as following each by ^{31}P{^{1}H} NMR spectroscopy showed they were complete within 3 h and did not reveal any intermediates. It is worthy of note that the lithium salt **1** also eliminates PMe to give the diphosphacyclopentadienyl complex Li[1,3-P$_2$C$_3$Bu$^t_3$], but only on heating in THF at reflux for 3 h.[10] Therefore, it seems that coordination of [MeP$_3$C$_3$Bu$^t_3$]$^-$ to the group 13 metal significantly lowers the energy barrier to this elimination process.

Considering the facility of phosphinidene elimination in the formation of **2**−**4**, the reactions that gave these complexes were carried out in the presence of the alkyne PhC≡CPh in attempts to trap the generated phosphinidene by forming the known phosphirene MeP{C(Ph)}$_2$[11] in [2+1] cycloaddition reactions. These attempts were unsuccessful, as the reactions only afforded **2**−**4** and (PMe)$_n$, without the involvement of the alkyne. Also unsuccessful were reactions of **1** with a variety of metal(III) compounds, MCl$_3$ and Cy$_2$MCl (M = Al, Ga, or In; Cy = cyclohexyl), all of which afforded the known triphosphacyclohexa-1,4-diene MeP$_3$C$_3$Bu$^t_3$(H),[12] presumably via solvent proton abstraction processes.

The spectroscopic data for **2** and **4** are consistent with their formulations. Compound **3** has been previously reported to be formed in the reaction of K[1,3-P$_2$C$_3$Bu$^t_3$] with InI,[13] and its spectroscopic data are identical to those in that report (e.g., ^{31}P{^{1}H} NMR: δ 182 ppm). Most informative of the data for **2** and **4** are their ^{31}P{^{1}H} NMR spectra, which exhibit singlet (δ 189.2 ppm) and doublet (δ 190.8 ppm, $^1J_{\mathrm{PTl}}$ = 159 Hz) resonances, respectively. In addition, the mass spectra of both compounds display molecular ion peaks.

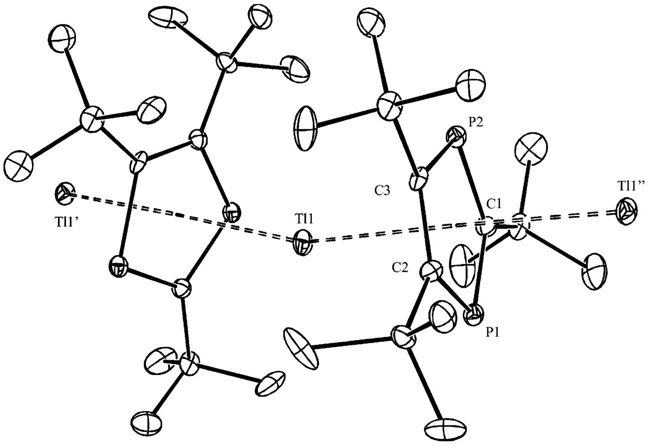


Figure 1. Thermal ellipsoid plot (25% probability surface) of a fragment of one of the crystallographically independent polymeric chains of [Tl(P$_2$C$_3$Bu$^t_3$)] (**4**); hydrogen atoms are omitted for clarity. P(1)−C(1) 1.758(16), C(1)−P(2) 1.762(17), P(2)−C(3) 1.833(16), C(3)−C(2) 1.46(2), C(2)−P(1) 1.800(16), Tl(1)−centroid 2.815(5), Tl(1)″−centroid 2.894(5), centroid−Tl(1)−centroid 162.60(9), Tl(1)−centroid−Tl(1)″ 177.21(10). Symmetry transformation used to generate equivalent atoms ′: *x*, 1−*y*, 1/2+*z*; ″: *x*, 1−*y*, *z*−1/2.

Crystals of **2** suitable for X-ray crystallographic studies could not be obtained, but good quality crystals of **4** were acquired by sublimation. Its structure is depicted in Figure 1 and shows it to exist as infinite one-dimensional polymer strands (NB: only one of the two crystallographically independent strands is shown), as do TlCp*[14] and [Tl(1,2,4-P$_3$C$_2$Bu$^t_2$)].[15] In contrast, the analogous indium complex, [In(η^5-P$_2$C$_3$Bu$^t_3$)], exists as monomeric units in the solid state.[13] The mean thallium−ring centroid distance of 2.84 Å is similar to those in related compounds [e.g., TlCp* 2.91 and 2.99 Å,[14] [Tl(1,2,4-P$_3$C$_2$Bu$^t_2$)] 2.85 and 3.22 Å[15]]. Moreover, the centroid−Tl−centroid angles (166.9° mean) are close to those in the analogous triphospholyl complex, [Tl(1,2,4-P$_3$C$_2$Bu$^t_2$)] (171°), but significantly more obtuse than the angles for TlCp* (145.5° mean). This difference presumably results from the greater steric bulk of the ring in **4**. As is the case for [Tl(1,2,4-P$_3$C$_2$Bu$^t_2$)] and [In(1,3-P$_2$C$_3$Bu$^t_3$)], the intra-ring P−C and C−C bonds in **4** are suggestive of significant delocalization.

Group 14 Element(II) Chemistry. In light of the reactivity that **1** displayed toward low oxidation state group 13 halides, its reactions with a variety of group 14 element(II) halide complexes were carried out with similar results. Treatment of MCl$_2$ (M = Sn or Pb) with **1** afforded the tetraphosphametallocenes **5** and **6** in low isolated yields (Scheme 2). As with **2**−**4**, the mechanism of formation of these complexes most likely involves the initial formation of triphosphacyclohexadienyl complexes, which facilely eliminate phosphinidene (PMe) fragments. Resonances for the proposed intermediates could not be observed when the reactions were followed by ^{31}P NMR spectroscopy, thus suggesting they are short-lived. The spectra did, however, indicate that the formations of **5** and **6** were high yielding. The low isolated yields of these compounds are

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(6) Cowley, A. H. *Chem. Commun.* **2004**, 2369.

(7) Gemel, G.; Steinke, T.; Cokoja, M.; Kempter, A.; Fischer, R. A. *Eur. J. Inorg. Chem.* **2004**, 4161.

(8) Gamer, M. T.; Roesky, P. W.; Konchenko, S. N.; Nava, P.; Ahlrichs, R. *Angew. Chem., Int. Ed.* **2006**, *45*, 4447.

(9) Berger, S.; Braun, S.; Kalinowski, H.-O. *^{31}P NMR-Spektroskopie*; Thieme: Stuttgart, 1991; Vol. 3, p 140.

(10) Steinbach, J.; Binger, P.; Regitz, M. *Synthesis* **2003**, 2720.

(11) Lochschmidt, S.; Mathey, F.; Schmidpeter, A. *Tetrahedron Lett.* **1986**, *27*, 2635.

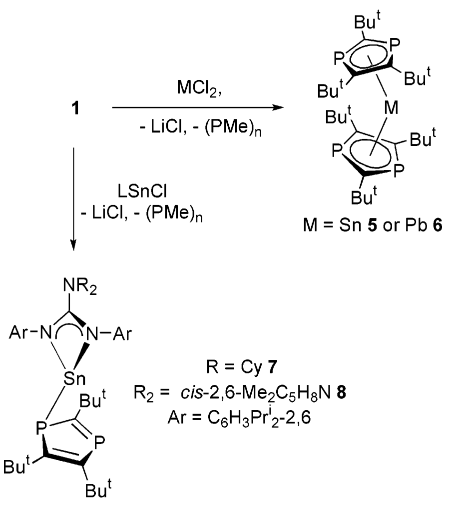
(12) Renner, J.; Bergsträsser, U.; Binger, P.; Regitz, M. *Angew. Chem., Int. Ed.* **2003**, *42*, 1863.

(13) Clentsmith, G. K. B.; Cloke, F. G. N.; Francis, M. D.; Green, J. C.; Hitchcock, P. B.; Nixon, J. F.; Suter, J. L.; Vickers, D. M. *J. Chem. Soc., Dalton Trans.* **2000**, 1715. NB: the authors have become aware that in unpublished work, [Ga(P$_2$C$_3$Bu$^t_3$)] can be prepared via a similar salt elimination reaction, Nixon, J. F. Personal communication.

(14) Werner, H.; Otto, H.; Kraus, H. J. *J. Organomet. Chem.* **1986**, *315*, 57.

(15) Francis, M. D.; Hitchcock, P. B.; Nixon, J. F.; Schnöckel, H. J.; Steiner, J. *J. Organomet. Chem.* **2002**, *646*, 191.

Scheme 2



probably due to their high solubility in organic solvents. In contrast, the 2:1 reaction of **1** with $GeCl_2$(dioxane) led to an intractable mixture of many phosphorus-containing products.

As has been reported for other tetraphosphametallocenes, e.g., [Fe(1,3-$P_2C_3Bu^t{}_3$)$_2$],[4] compounds **5** and **6** display fluxional behavior in solution resulting from the rotation of the two heterocycles with respect to each other. The difference here is that the group 14 metallocenes are most likely bent, as has been proposed for their hexaphospha-analogues, [M(1,2,4-$P_3C_2Bu^t{}_2$)$_2$] (M = Sn[16] or Pb),[17] though the latter have not been crystallographically characterized. At ambient temperature both tetraphosphametallocenes display singlet resonances (**5** δ 196.9 ppm; **6** δ 202.6 ppm) in their $^{31}P\{^1H\}$ NMR spectra, with that of **6** exhibiting a $^1J_{PPb}$ coupling of 215 Hz. Variable-temperature NMR studies were carried out on both complexes, and these showed that upon cooling to −95 °C both spectra resolved into two broad signals (spectra for **6** are shown in Figure 2). The low-temperature spectrum of **5** was sufficiently resolved to allow an intra-ring $^2J_{PP}$ coupling of 34 Hz to be determined, though the magnitude of the $^1J_{SnP}$ coupling could not be accurately assigned. The resolution of the spectra for **5** and **6** can be explained by a slowing of their ring rotations at low temperature to a point where a near eclipsed conformation of the heterocycles is favored, as is seen in the solid state (vide infra). This leads to two chemically inequivalent sets of phosphorus nuclei, P_A and P_B (Figure 2). An analysis of the spectra using the Eyring equation gave values for the free energy of activation ($\Delta G^{\ddagger}$) for the ring rotations of 34.73 kJ mol^{-1} (**5**) and 31.96 kJ mol^{-1} (**6**). The higher value for **5** is likely due to the smaller covalent radius of Sn, relative to Pb, which would restrict ring rotation in that compound. These values can also be compared to the significantly larger barrier to rotation of 59.55 kJ mol^{-1} for [Fe(1,3-$P_2C_3Bu^t{}_3$)$_2$],[4] which results from the smaller covalent radius of Fe relative to the group 14 elements and the fact that the rings in the heteroferrocene are most likely close to parallel.

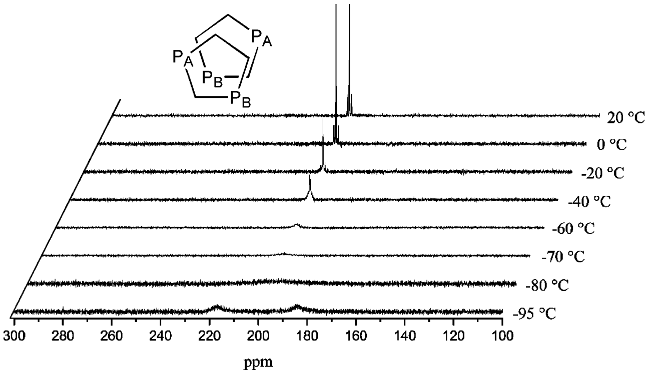


Figure 2. Variable-temperature $^{31}P\{^1H\}$ NMR spectra for [Pb($P_2C_3Bu^t{}_3$)$_2$] (**6**).

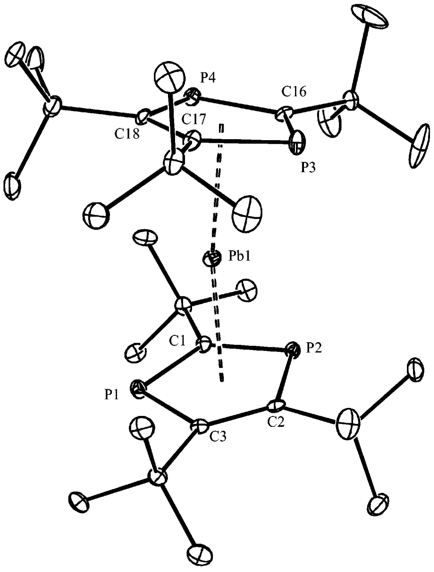


Figure 3. Thermal ellipsoid plot (25% probability surface) of the molecular structure of [Pb($P_2C_3Bu^t{}_3$)$_2$] (**6**); hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): P(1)−C(1) 1.737(5), P(1)−C(3) 1.789(5), P(2)−C(1) 1.743(5), P(2)−C(2) 1.812(5), P(3)−C(16) 1.740(5), P(3)−C(17) 1.814(5), P(4)−C(16) 1.738(5), P(4)−C(18) 1.792(6), C(2)−C(3) 1.414(7), C(17)−C(18) 1.412(7), centroid−Pb(1)−centroid 170.4(3). Selected bond lengths (Å) and angles (deg) for [Sn($P_2C_3Bu^t{}_3$)$_2$] (**5**): P(1)−C(1) 1.735(3), P(1)−C(3) 1.797(3), P(2)−C(1) 1.745(3), P(2)−C(2) 1.809(3), P(3)−C(16) 1.733(3), P(3)−C(17) 1.805(3), P(4)−C(16) 1.740(3), P(4)−C(18) 1.799(3), C(2)−C(3) 1.394(4), C(17)−C(18) 1.407(4), centroid−Sn(1)−centroid 171.3(4).

The X-ray crystal structures of **5** and **6** are isomorphous, and so only that for **6** is depicted in Figure 3, though relevant geometrical parameters for **5** are included in the caption. In both, the heterocycles have approximately η^5-interactions with the metals. They are near eclipsed, and their intra-ring P−C and C−C distances are suggestive of bond delocalization. The metallocenes are bent with centroid−M distances and centroid−M−centroid angles of 2.50 Å (mean) and 171.3(4)° for **5** and 2.56 Å (mean) and 170.4(3)° for **6**. The angles are markedly more obtuse than in, for example, $MCp^*{}_2$ (M = Sn (144.1° mean),[18] Pb (151.0°))[19] and the closely related triphosphaplumbocene, [Pb(1,2,4-$P_3C_2Bu^t{}_2$)(Cp*)] (142.2°),[17] most likely because of the considerable steric bulk of the diphospholyl ligands in **5** and **6**.

To further explore the ability of **1** to undergo metal-mediated phosphinidene elimination reactions, its reaction with compounds of the type RMCl (R = bulky alkyl or aryl, M = Ge, Sn, or Pb) were carried out. In all cases, intractable mixtures of products were obtained. We have had recent success in utilizing

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(16) Elvers, A.; Heinmann, F. W.; Wrackmeyer, B.; Zenneck, U. *Chem. Eur. J.* **1999**, *5*, 3143.

(17) Durkin, J. J.; Francis, M. D.; Hitchcock, P. B.; Jones, C.; Nixon, J. *J. Chem. Soc., Dalton Trans.* **1999**, 4057.

(18) Jutzi, P.; Kohl, F.; Hofmann, P.; Krüger, C.; Tsay, Y. H. *Chem. Ber.* **1980**, *113*, 757.

(19) Atwood. J. L.; Hunter, W. E.; Cowley, A. H.; Jones, R. A.; Stewart, C. A. *J. Chem. Soc., Chem. Commun.* **1981**, 925.

very bulky guanidinate ligands to stabilize monomeric, low oxidation state main group complexes.[20] Accordingly, a range of guanidinato−element halide complexes, [LECl] (L = $Cy_2NC(NAr)_2^-$ or (*cis*-2,6-$Me_2C_5H_8N)C(NAr)_2^-$, Ar = C_6H_3-Pr^i_2-2,6; E = Ge or Sn), were prepared for reaction with **1**. Those reactions with the germanium complexes led to mixtures of unidentified products. The reactions with monomeric [LSnCl] were, however, more successful, and therefore full synthetic, spectroscopic, and structural details for the precursor complexes are included in the Supporting Information. Similar to the formation of **5**, treatment of [LSnCl] with **1** led to phosphinidene elimination and the formation of the tin−diphospholyl complexes **7** and **8** in low to moderate isolated yields (Scheme 2), though the ^{31}P NMR spectra of the total reaction mixtures suggested these were the major products.

The solution state spectroscopic data for **7** and **8** are suggestive of symmetrical structures for these compounds, in which the diphospholyl ring is η^5-coordinated to the tin centers. In particular, their $^{31}P\{^1H\}$ NMR spectra display single resonances (**7**: δ 192.3 ppm; **8**: δ 190.1 ppm) close to where that of **5** was observed. In contrast to **5**, however, cooling solutions of **7** and **8** to −90 °C led only to a broadening of the singlet resonances and no further resolution. This is perhaps surprising, as their solid state structures reveal a less symmetrical coordination of their diphospholyl rings to the tin centers. As both compounds are effectively isostructural, only the molecular structure for **7** is depicted in Figure 4, though relevant geometrical parameters for **8** are included in the figure caption. In each complex, the LSn fragment is within bonding distance of only one P-center in what can be best described as an Sn−heterocycle π-interaction lying somewhere between η^1-P and η^3-CPC ligation (Σangles at P(1): **7**, 256.4°; **8**, 256.7°). An examination of the intra-ring C−P and C−C distances suggests only partial delocalization, and so the former mode could predominate. A similar suggestion of the bonding in the diphosphastannocene [Sn{η^1-PC_4-2,5-Ph_2-3,4-$(SiMe_3)_2\}_2$] (Sn−P 2.76 Å mean) has been previously described.[21] The geometries of the four-membered heterocycles in **7** and **8** are close to those in the tin halide precursors and indicative of delocalization over the guanidinate ligand. Given the solid state structures of **7** and **8**, the solution state NMR spectra of these complexes can be best explained by fluxional migrations of the LSn fragments between the two P-centers of the diphospholyl ligand. It is of note that a similar sigmatropic fluxional migration of the σ-bound Ph_3Sn fragment about the same diphospholyl ring in [$Ph_3Sn^{IV}(\eta^1$-$P_2C_3Bu^t_3)$] (Σangles about the Sn-coordinated P center: 294.4°) has been described by Cloke et al.[22] In **7** and **8**, it is unlikely that the fluxional migrations of the Sn(II) fragments are sigmatropic, and, instead, they could proceed via intermediate η^5-Sn−diphospholyl interactions, especially considering that no $^{117,119}Sn$ satellites were discernible for the resonance in the $^{31}P\{^1H\}$ NMR spectra of each complex (cf. **5**). Whatever the case, these dynamic processes must have low energy barriers and be rapid on the NMR time scale even at −90 °C.

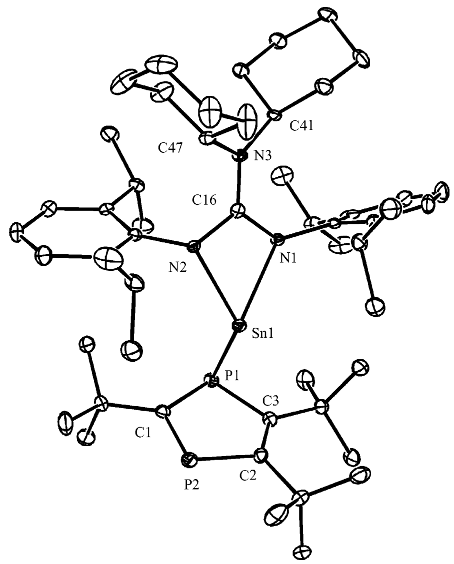

Figure 4. Thermal ellipsoid plot (25% probability surface) of the molecular structure of [{$Cy_2NC(NAr)_2\}Sn(P_2C_3Bu^t_3)$] (**7**); hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Sn(1)−N(2) 2.210(4), Sn(1)−N(1) 2.319(4), Sn(1)−P(1) 2.7595(17), P(1)−C(1) 1.770(5), P(1)−C(3) 1.815(5), P(2)−C(1) 1.706(5), P(2)−C(2) 1.788(5), C(2)−C(3) 1.402(7), N(1)−C(16) 1.361(6), N(2)−C(16) 1.366(6), N(3)−C(16) 1.367(6), N(2)−Sn(1)−N(1) 58.38(13), N(2)−Sn(1)−P(1) 117.92(11), N(1)−Sn(1)−P(1) 111.43(10), C(1)−P(1)−C(3) 96.6(2), C(1)−P(1)−Sn(1) 81.17(17), C(3)−P(1)−Sn(1) 78.66(16), C(16)−N(1)−Sn(1) 92.8(3), C(16)−N(2)−Sn(1) 97.6(3), N(1)−C(16)−N(2) 108.3(4). Selected bond lengths (Å) and angles (deg) for [{(*cis*-2,6-$Me_2C_5H_8N)C(NAr)_2\}Sn(P_2C_3Bu^t_3)$] (**8**): Sn(1)−N(2) 2.212(3), Sn(1)−N(1) 2.357(3), Sn(1)−P(1) 2.7754(12), P(1)−C(1) 1.766(4), P(1)−C(3) 1.829(4), C(1)−P(2) 1.719(4), P(2)−C(2) 1.795(4), C(2)−C(3) 1.405(6), N(1)−C(16) 1.344(5), N(2)−C(16) 1.354(4), N(3)−C(16) 1.372(4), N(2)−Sn(1)−N(1) 57.93(10), N(2)−Sn(1)−P(1) 118.08(8), N(1)−Sn(1)−P(1) 115.16(8), C(1)−P(1)−C(3) 96.98(19), C(1)−P(1)−Sn(1) 80.30(14), C(3)−P(1)−Sn(1) 79.42(13), C(16)−N(1)−Sn(1) 90.7(2), C(16)−N(2)−Sn(1) 96.9(2), N(1)−C(16)−N(2) 110.5(3).

Group 14 Element(IV) Chemistry. As the reactions of group 14 element(II) precursors generally led to the facile formation of diphospholyl complexes via phosphinidene elimination reactions, it was decided to investigate the reactivity of **1** toward group 14 element(IV) compounds for the purpose of comparison. Cloke et al. have found that the reaction of K[1,3-$P_2C_3Bu^t_3$] with Ph_3SnCl leads cleanly to [$Ph_3Sn(\eta^1$-$P_2C_3Bu^t_3)$], which displays unusual fluxional behavior in solution, as described above.[22] Therefore, it seemed worthwhile to react **1** with compounds of the type R_3ECl (E = group 14 element) to see if similar compounds could be formed. The 1:1 reactions with Me_3ECl or Ph_3ECl (E = Si or Ge) were, however, sluggish, and after 24 h only a mixture of unreacted **1** and several unidentified phosphorus-containing products could be observed in the ^{31}P NMR spectra of the reaction solutions. No pure products could be obtained after subsequent workup. In contrast, treating **1** with 1 equiv of Ph_3SnCl in hexane led cleanly, after 2 h, to a high yield of the unusual colorless cage complex **9**, which can be considered as a 1,2-diphosphabicyclo[1.1.0]butane bridged in its *endo*-positions by a P−C fragment (Scheme 3). Subsequently, it was found that when solutions of **9** were left standing at ambient temperature overnight, they took on an orange coloration. This was found to be due to an isomerization of the compound to the novel polycyclic system **10**, which can be drawn as two resonance forms, each containing an ylidic P-center, a phosphaalkene fragment, and a phosphide center. This isomerization was complete after 56 h. It is noteworthy that there was no evidence for the formation of [$Ph_3Sn(P_2C_3Bu^t_3)$] in the reaction that gave **9** and **10**. The corresponding reaction of **1** with Ph_3PbCl was not as clean but did afford a

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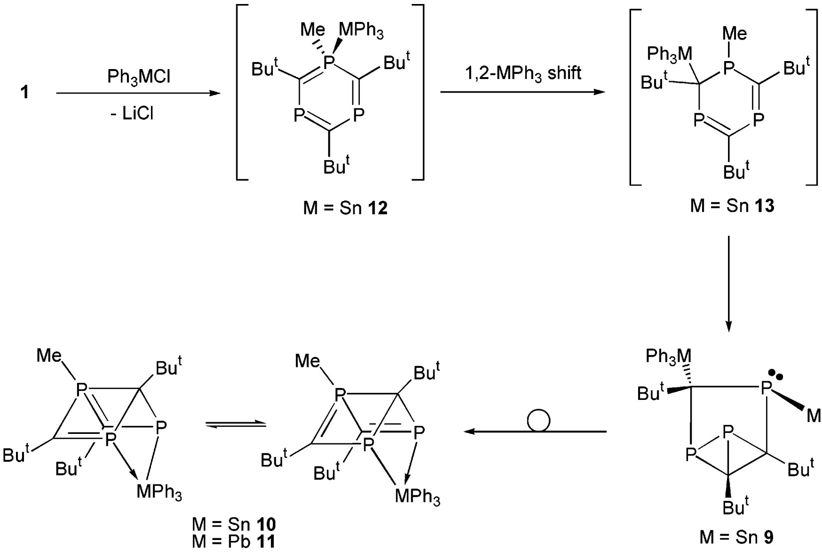
[20] Jones, C.; Junk, P. C.; Platts, J. A.; Stasch, A. *J. Am. Chem. Soc.* **2006**, *128*, 2206.

[21] Westerhausen, M.; Digeser, M. H.; Nöth, H.; Ponikwar, W.; Seifert, T.; Polborn, K. *Inorg. Chem.* **1999**, *38*, 3207.

[22] Cloke, F. G. N.; Hitchcock, P. B.; Nixon, J. F.; Wilson, D. J.; Nyulaszi, L.; Karparti, T. *J. Organomet. Chem.* **2005**, *690*, 3983.

Scheme 3



low yield of the lead analogue of **10**, viz., **11**, among other unidentified products after a reaction time of 4 h at 25 °C. Interestingly, when this reaction was followed by ^{31}P NMR spectroscopy, no signals for an intermediate analogous to **9** were observed. It seems feasible that it is formed but is much more short-lived than its tin counterpart.

It is likely that **9** is formed via an initial stannylation of the methylated P-center of $[\mathrm{MeP_3C_3Bu^t_3}]^-$ to give **12**. In line with this suggestion are theoretical studies on 1,3,5-triphosphacyclohexadienyl anions, which show their negative charge to reside largely on this phosphorus.[3] Indeed, treating triphosphacyclohexadienyl anions with alkyl halides leads to stable 1-λ^5,3-λ^3,5-λ^3-triphosphinines analogous to **12**.[3] A 1,2-stannyl migration could then occur to give **13**, which contains a 1,3-diphosphabutadiene fragment. Compound **13** could then isomerize to give **9**. This proposal seems reasonable, as 1,2-phosphorus to carbon stannyl migrations can be low-energy processes for stannylated unsaturated phosphorus heterocycles, e.g., $[\mathrm{Ph_3Sn(P_2C_3Bu^t_3)}]$.[22] In addition, protonated triphosphacyclohexadienyl anions, cf. **12**, can undergo 1,2-H migrations to give heterocycles related to **13**.[23] With regard to the isomerization that gave **9**, the only other reported 1,2-diphosphabicyclo[1.1.0]butane, $\mathrm{P_2C_2(SiMe_3)_4}$,[24] is similarly formed via a facile isomerization of the corresponding 1,3-diphosphabutadiene. It is not known what the mechanism of isomerization of the, presumably, strained **9** to **10** entails, but valence isomerizations of phospha- and diphosphabicyclo[1.1.0]butanes are now well known to give a variety of unsaturated cyclic and acyclic systems,[25] cf. hydrocarbon bicyclo[1.1.0]butanes.[26]

The spectroscopic data for **9**−**11** are compatible with their proposed structures. Of most note are their $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectra, which in the case of **9** exhibits three resonances. That for the P-center that forms part of the two three-membered rings is at high field (δ −284.7 ppm, $^1J_{\mathrm{PP}} = 184.5$ Hz), in the normal region for 1,3-diphosphabicyclo[1.1.0]butane systems, e.g., δ −268.3 ppm for 1,3-$\mathrm{P_2C_2Bu^t_2GeI_2}$.[27] The resonance for the P-center that forms part of only one three-membered ring is at much lower field (δ −8.4 ppm) than is normally seen for phosphiranes and 2,4-diphosphabicyclo[1.1.0]butanes with *exo*-P substituents.[25b] It is now clear that if the P substituents are in *endo*-positions in such bicycles (as is the case for **9**), such low-field signals are the norm.[25a,28] In concert with the resonance structures proposed for **10** and **11**, the $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectra of each display $\mathrm{AX_2}$ patterns (e.g., **10**: δ $\mathrm{P_A} = 35.3$ ppm; δ $\mathrm{P_X} = 87.1$ ppm, $^1J_{\mathrm{P}^{117}\mathrm{Sn}} = 732$ Hz, $^1J_{\mathrm{P}^{119}\mathrm{Sn}} = 767$ Hz). The $^{119}\mathrm{Sn}\{^1\mathrm{H}\}$ NMR spectrum of **10** also exhibits a triplet resonance at δ −85.5 ppm ($^1J_{\mathrm{PSn}} = 767$ Hz), cf. $[\mathrm{Ph_3Sn(P_2C_3Bu^t_3)}]$ δ −146.2 ppm.

The molecular structures of **9** and **10** are depicted in Figures 5 and 6, respectively. The crystal structure of **11** is isomorphous with that of **10**, and therefore relevant geometrical parameters for that compound can be found in the caption for Figure 6. To the best of our knowledge, **9** contains the first structurally characterized 1,2-diphosphabicyclo[1.1.0]butane fragment. Although this appears strained, its intra-cyclic P−P and P−C distances are all in the normal range.[29] There is a fold angle of 109.1° between the two three-membered rings, which, not surprisingly, is more acute than normally seen for nonbridged *endo,endo*-2,4-diphosphabicyclo[1.1.0]butanes, e.g., 131.6° for $\mathrm{Cy_2P_2C_2Bu^t_2}$.[28] Considering that only one set of signals was observed in the ^{31}P NMR spectrum of the reaction mixture that afforded **9**, this compound must be formed as only one isomer, which its solid state structure shows to have the $\mathrm{SnPh_3}$ fragment *trans* to the phosphorus-bound methyl group of the bridging P−C fragment. The unusual structures of **10** and **11** show them to have distorted square-based pyramidal metal centers that are chelated by two phosphorus centers of an anionic triphosphabicyclic ligand. Although complexes containing five-coordinate $\mathrm{MPh_3}$ (M = Sn or Pb) fragments are well known, there have been no previously structurally characterized examples in which the metal incorporates two P-donors.[29] As a result, the M−P distances in **10** and **11** are much longer than the means for all structurally authenticated examples of such interactions (Sn−P 2.62 Å, Pb−P 2.78 Å),[29] though still within the known ranges. In addition, the P−M interactions in each compound are

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(23) (a) Renner, J.; Bergstässer, U.; Binger, P.; Regitz, M. *Angew. Chem., Int. Ed.* **2003**, *42*, 1863. (b) Heydt, H. *Top. Curr. Chem.* **2003**, *223*, 216.

(24) Niecke, E.; Metternich, H. J.; Streubel, R. *Chem. Ber.* **1990**, *123*, 67.

(25) (a) Slootweg, J. C.; Krill, S.; de Kanter, F. J. J.; Schakel, M.; Ehlers, A. W.; Lutz, M.; Spek, A. L.; Lammertsma, K. *Angew. Chem., Int. Ed.* **2005**, *44*, 6579. (b) Niecke, E.; Fuchs, A.; Nieger, M. *Angew. Chem., Int. Ed.* **1999**, *38*, 3028.

(26) *The Chemistry of the Cyclopropyl Group, Part 2*; Rappoprot, Z., Ed.; Wiley: Chichester, 1987; Chapter 19.

(27) Francis, M. D.; Hitchcock, P. B. *Organometallics* **2003**, *23*, 2891.

(28) Jones, C.; Platts, J. A.; Richards, A. F. *Chem. Commun.* **2001**, 663.

(29) As determined by a survey of the Cambridge Crystallographic Database, June 2006.

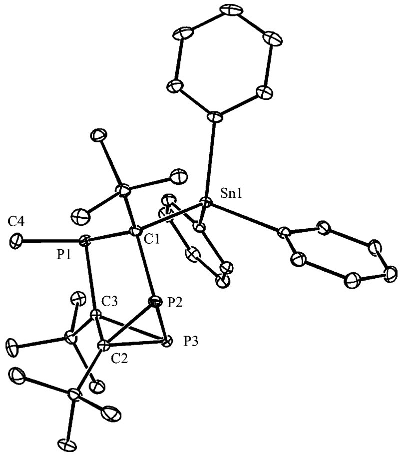

Figure 5. Thermal ellipsoid plot (25% probability surface) of the molecular structure of $[Ph_3Sn(\eta^1\text{-C-MeP}_3C_3Bu^t_3)]$ (**9**); hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Sn(1)−C(1) 2.2371(17), P(1)−C(4) 1.8571(19), P(1)−C(1) 1.8766(18), P(1)−C(3) 1.8965(18), P(2)−C(2) 1.8595(18), P(2)−C(1) 1.8675(18), P(2)−P(3) 2.1547(10), P(3)−C(2) 1.8705(18), P(3)−C(3) 1.9172(18), C(4)−P(1)−C(1) 107.35(9), C(4)−P(1)−C(3) 99.40(8), C(1)−P(1)−C(3) 96.14(8), C(2)−P(2)−C(1) 103.33(8), C(2)−P(2)−P(3) 54.95(6), C(1)−P(2)−P(3) 101.58(6), C(2)−P(3)−C(3) 47.64(7), C(2)−P(3)−P(2) 54.47(6), C(3)−P(3)−P(2) 80.89(6), P(2)−C(1)−P(1) 106.75(9), P(2)−C(1)−Sn(1) 105.97(8), P(1)−C(1)−Sn(1) 100.51(8).

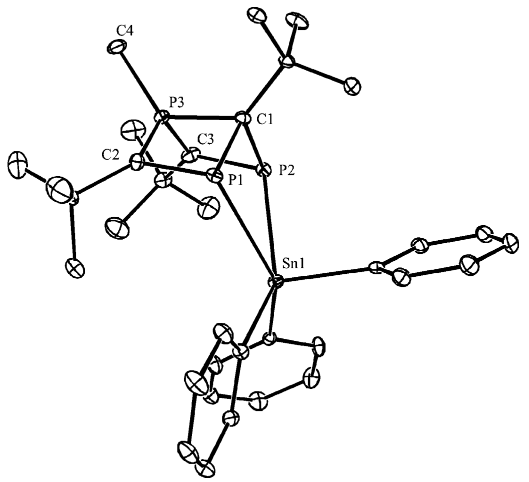

Figure 6. Thermal ellipsoid plot (25% probability surface) of the molecular structure of $[Ph_3Sn(\eta^2\text{-P,P-MeP}_3C_3Bu^t_3)]$ (**10**); hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Sn(1)−P(1) 2.7558(16), Sn(1)−P(2) 2.9265(19), P(1)−C(2) 1.717(7), P(1)−C(1) 1.899(6), P(2)−C(3) 1.728(7), P(2)−C(1) 1.880(6), P(3)−C(3) 1.749(7), P(3)−C(2) 1.773(7), P(3)−C(4) 1.813(6), P(3)−C(1) 1.823(6), P(1)−Sn(1)−P(2) 64.08(4), C(2)−P(1)−C(1) 86.9(3), C(3)−P(2)−C(1) 86.6(3), C(3)−P(3)−C(2) 120.4(3), C(3)−P(3)−C(1) 87.8(3), C(2)−P(3)−C(1) 87.7(3), P(3)−C(1)−P(2) 88.4(2), P(3)−C(1)−P(1) 88.5(3), P(2)−C(1)−P(1) 106.0(3), P(1)−C(2)−P(3) 96.2(3), P(2)−C(3)−P(3) 95.9(3). Selected bond lengths (Å) and angles (deg) for $[Ph_3Pb(\eta^2\text{-P,P-MeP}_3C_3Bu^t_3)]$ (**11**): Pb(1)−P(1) 2.887(3), Pb(1)−P(2) 2.965(3), P(1)−C(2) 1.687(11), P(1)−C(1) 1.881(11), P(2)−C(3) 1.715(13), P(2)−C(1) 1.929(12), P(3)−C(2) 1.740(11), P(3)−C(3) 1.749(12), P(3)−C(4) 1.818(11), P(3)−C(1) 1.834(11), P(1)−Pb(1)−P(2) 63.27(7), C(2)−P(1)−C(1) 86.8(5), C(3)−P(2)−C(1) 86.3(5), C(2)−P(3)−C(3) 120.6(6), C(2)−P(3)−C(1) 86.7(5), C(3)−P(3)−C(1) 88.4(5), P(3)−C(1)−P(1) 88.0(5), P(3)−C(1)−P(2) 87.2(5), P(1)−C(1)−P(2) 107.4(5), P(1)−C(2)−P(3) 97.7(5), P(2)−C(3)−P(3) 97.1(6).

significantly different from each other, as are the intracyclic P−C distances. This suggests that one resonance form of each compound is partially favored in the solid state, i.e., that in which the P(1)−C(2) bond is double.

Conclusions

In summary, reactions of the triphosphacyclohexadienyl anion, $[MeP_3C_3Bu^t_3]^-$, toward a series of group 13 and 14 halide complexes have been investigated. Within the coordination sphere of several group 13 element(I) and group 14 element(II) centers, the triphosphacyclohexadienyl ligand facilely eliminates a phosphinidene fragment, PMe, to give homo- and heteroleptic diphospholyl complexes. These have been structurally characterized and the fluxional behavior of the group 14 complexes explored by variable-temperature NMR studies. In contrast, treating $[MeP_3C_3Bu^t_3]^-$ with Ph_3SnCl does not lead to a phosphinidene elimination process but instead to the first example of a complex containing a structurally characterized 1,2-diphosphabicyclo[1.1.0]butane fragment. This was shown to readily isomerize in solution at room temperature to an unusual five-coordinate tin complex chelated by an unsaturated triphosphabicyclic anion. The lead analogue of this compound has also been reported. This study has highlighted the synthetic versatility of $[MeP_3C_3Bu^t_3]^-$, which has been used as a precursor to the diphospholyl anion, $[1,3\text{-}P_2C_3Bu^t_3]^-$, as a source of the phosphinidene fragment, PMe, and as a reagent for the formation of novel group 14−organophosphorus cage complexes.

Experimental Section

General Methods. All manipulations were carried out using standard Schlenk and glovebox techniques under an atmosphere of high-purity argon. Hexane and THF were distilled over Na/K alloy. ^1H, ^{31}P, and ^{119}Sn NMR spectra were recorded on either Bruker DPX400, Bruker AMX 500, or JEOL Eclipse 300 spectrometers in deuterated solvents and were referenced to the residual ^1H resonances of the solvent used (^1H), external 85% H_3PO_4, δ 0.0 ppm (^{31}P NMR), or external $SnMe_4$, δ 0.0 ppm (^{119}Sn NMR). Mass spectra were recorded using a VG Fisons Platform II instrument operating under APCI conditions or were obtained from the EPSRC National Mass Spectrometric Service at Swansea University. IR spectra were recorded using a Nicolet 510 FT-IR spectrometer as Nujol mulls between NaCl plates. Melting points were determined in sealed glass capillaries under argon and are uncorrected. Microanalyses were obtained from Medac Ltd. $P_3C_3Bu^t_3$[30] and "GaI"[31] were synthesized by literature procedures. All other reagents were used as received.

Preparation of $[Ga(P_2C_3Bu^t_3)]$ (2). To a solution of $P_3C_3Bu^t_3$ (0.15 g, 0.5 mmol) in hexane (20 mL) was added a solution of MeLi (0.5 mmol in 2 mL of diethyl ether) at −78 °C. A color change from yellow to orange was observed. The solution was slowly warmed to ambient temperature and stirred for 2 h. Volatiles were removed in vacuo, and the residue was dissolved in hexane (10 mL). This was added to a suspension of "GaI" (0.13 g, 0.5 mmol) in hexane (10 mL) at − 80 °C. The resultant suspension was warmed to ambient temperature and stirred for 16 h, after which the color changed from orange to brown. Volatiles were removed in vacuo, and the residue was extracted in hexane (5 mL), filtered, and placed at −30 °C overnight to yield **2** as a yellow powder (98 mg, 58%). Mp: 221−226 °C dec. ^1H NMR (300 MHz, C_6D_6, 298 K): δ 1.76 (s, 9H, $PC(Bu^t)P$), 1.79 (s, 18H, $P\{C(Bu^t)\}_2P$). $^{31}P\{^1H\}$ NMR (121.7 MHz, C_6D_6, 298 K): δ 189.2 (s). IR (Nujol)

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(30) Tabellion, F.; Nachbauer, A.; Leininger, S.; Peters, C.; Preuss, F.; Regitz, M. *Angew. Chem., Int. Ed.* **1998**, *37*, 1233.

(31) Green, M. L. H.; Mountford, P.; Smout, G. J.; Peel, S. R. *Polyhedron* **1990**, *9*, 2763.

ν/cm^{-1}: 1457 (s), 1378 (s), 1262 (s), 1201 (s), 1125 (s), 1019 (s), 831 (m). MS EI: *m/z* (%) 339.1 [M$^+$, 15]. Anal. Calc for $C_{15}H_{27}GaP_2$: C 53.14, H 8.03. Found: C 53.01, H 7.98.

Preparation of [Tl($P_2C_3Bu^t_3$)] (4). A solution of Li[$MeP_3C_3Bu^t_3$] (0.5 mmol) in hexane (10 mL) was prepared in-situ as described above. This was added to a suspension of TlCl (0.12 g, 0.5 mmol) in hexane (10 cm^3) at −80 °C. The resultant suspension was warmed to ambient temperature and stirred for 16 h, after which the color changed from orange to green. Volatiles were removed in vacuo, and the residue was extracted in hexane (5 cm^3), filtered, and placed at −30 °C overnight to yield **4** as a yellow powder. Crystals suitable for the X-ray diffraction experiment were grown by sublimation of this powder at reduced pressure (ca. 100 °C, 10^{-5} mmHg) (170 mg, 67%). Mp: 198−200 °C dec. ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 1.42 (s, 9H, PC(Bu^t)P), 1.56 (s, 18H, P{C(Bu^t)}$_2$P). ^{31}P{^{1}H} NMR (121.7 MHz, C_6D_6, 298 K): δ 190.8 (d, $^1J_{PTl}$ = 159 Hz). IR (Nujol) ν/cm^{-1}: 1633 (m), 1455 (s), 1380 (s), 1261 (s), 1095 (s), 1022 (s), 803 (s). MS EI: accurate mass calc for $^{205}TlP_2C_{15}H_{27}$ 474.1327, found 474.1327. Anal Calc for $C_{15}H_{27}TlP_2$: C 38.03, H 5.74. Found: C 37.95, H 5.69.

NB: [In($P_2C_3Bu^t_3$)] (**3**) was prepared by a similar procedure (yield 71%), and its spectroscopic data were found to be identical with that reported in the literature.[13]

Preparation of [Sn($P_2C_3Bu^t_3$)$_2$] (5). A solution of Li[$MeP_3C_3Bu^t_3$] (0.5 mmol) in hexane (10 mL) was prepared in-situ as described above. This was added to $SnCl_2$ (50 mg, 0.26 mmol) suspended in THF (30 mL) at ambient temperature. The resultant mixture was stirred for 4 days, after which volatiles were removed in vacuo. The residue was extracted with hexane (5 mL), filtered, and concentrated to ca. 2 mL. Cooling to −30 °C yielded **5** as a pale yellow crystalline solid (16 mg, 9%). Mp: 174−176 °C dec. ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 1.35 (s, 18H, PC(Bu^t)P), 1.37 (s, 36H, P{C(Bu^t)}$_2$P). ^{31}P{^{1}H} NMR (121.7 MHz, C_6D_6, 298 K): δ 196.9 (s). IR (Nujol) ν/cm^{-1}: 1456 (s), 1363 (s), 1260 (s), 1218 (s), 1098 (s), 937 (w), 868 (m), 797 (s), 722 (m), 668 (m). MS APCI: *m/z* (%) 389.1 [M$^+$ − $P_2C_3Bu^t_3$, 100]. Anal Calc for $C_{30}H_{54}SnP_4$: C 54.81, H 8.28. Found: C 54.55, H 8.26.

Preparation of [Pb($P_2C_3Bu^t_3$)$_2$] (6). A solution of Li[$MeP_3C_3Bu^t_3$] (0.5 mmol) in hexane (10 mL) was prepared in-situ as described above. This was added to $PbCl_2$ (80 mg, 0.29 mmol) suspended in THF (30 mL) at ambient temperature. The resultant mixture was stirred for 4 days, after which volatiles were removed in vacuo. The residue was extracted with hexane (5 mL), filtered, and concentrated to ca. 2 mL. Cooling to − 30 °C yielded **6** as a yellow crystalline solid (24 mg, 13%). Mp: 88−91 °C dec. ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 1.56 (s, 18H, PC(Bu^t)P), 1.58 (s, 36H, P{C(Bu^t)}$_2$P). ^{31}P{^{1}H} NMR (121.7 MHz, C_6D_6, 298 K): δ 202.6 (s, $^1J_{PPb}$ = 215 Hz). IR (Nujol) ν/cm^{-1}: 1644 (m), 1460 (s), 1377 (s), 1260 (s), 1096 (s), 1022 (s), 801 (s). MS EI: accurate mass calc for $C_{30}H_{54}P_4{}^{208}Pb$ 746.2937, found 746.2942. Anal Calc for $C_{30}H_{54}PbP_4$: C 48.31, H 7.30. Found: C 48.23, H 7.28.

Preparation of [{$Cy_2NC(NAr)_2$}Sn($P_2C_3Bu^t_3$)] (7). A solution of Li[$MeP_3C_3Bu^t_3$] (0.5 mmol) in hexane (10 mL) was prepared in-situ as described above. This was added to [{$Cy_2NC(NAr)_2$}SnCl] (350 mg, 0.50 mmol) suspended in hexane (30 mL) at −78 °C. The resultant mixture was stirred for 18 h, after which volatiles were removed in vacuo. The residue was extracted with hexane (10 mL) and filtered, and the filtrate cooled to −30 °C to yield **7** as yellow crystals (98 mg, 21%). Mp: 183−185 °C dec. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ 0.82−1.52 (m, 20H, CH_2), 1.35 (s, 9H, PC(Bu^t)P), 1.48 (d, 12H, $^3J_{HH}$ = 6.7 Hz, CH(C*H*$_3$)$_2$), 1.64 (s, 18H, P{C(Bu^t)}$_2$P), 1.70 (d, 12H, $^3J_{HH}$ = 6.7 Hz, CH(C*H*$_3$)$_2$), 3.52 (m, 2H, NCH), 3.73 (sept., 4H, $^3J_{HH}$ = 6.7 Hz, C*H*(CH$_3$)$_2$), 7.10−7.32 (m, 6H, ArH). ^{31}P{^{1}H} NMR (121.7 MHz, C_6D_6, 298 K): δ 192.3 (br s). IR (Nujol) ν/cm^{-1}: 1612 (m), 1584 (m), 1455 (s), 1377 (s), 1245 (m), 1018 (s). MS APCI: *m/z* (%) 544 [$Cy_2NC(NAr)_2H^+$, 100]. Anal Calc for $C_{52}H_{83}N_3SnP_2$: C 67.09, H 8.99, N 4.51. Found: C 66.70, H 8.95, N 4.50.

Preparation of [{(*cis*-2,6-$Me_2C_5H_8N$)C(NAr)$_2$}Sn($P_2C_3Bu^t_3$)] (8). A solution of Li[$MeP_3C_3Bu^t_3$] (0.5 mmol) in hexane (10 mL) was prepared in-situ as described above. This was added to [{(*cis*-2,6-$Me_2C_5H_8N$)C(NAr)$_2$}SnCl] (330 mg, 0.53 mmol) suspended in hexane (30 mL) at −78 °C. The resultant mixture was stirred for 18 h, after which volatiles were removed in vacuo. The residue was extracted with hexane (10 mL) and filtered, and the filtrate was cooled to −30 °C to yield **8** as yellow crystals (82 mg, 18%). Mp: 177−179 °C dec. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ 0.92−1.55 (m, 6H, CH_2), 0.90 (d, 6H, $^3J_{HH}$ = 6.9 Hz, NC(H)C*H*$_3$), 1.36 (s, 9H, PC(Bu^t)P), 1.42 (d, 12H, $^3J_{HH}$ = 6.7 Hz, CH(C*H*$_3$)$_2$), 1.65 (s, 18H, P{C(Bu^t)}$_2$P), 1.68 (d, 12H, $^3J_{HH}$ = 6.7 Hz, CH(C*H*$_3$)$_2$), 3.75 (sept., 4H, $^3J_{HH}$ = 6.7 Hz, C*H*(CH$_3$)$_2$), 3.95 (m, 2H, NCH), 7.12−7.40 (m, 6H, ArH). ^{31}P{^{1}H} NMR (121.7 MHz, C_6D_6, 298 K): δ 190.1 (br s, $^1J_{PSn}$ = 88 Hz). IR (Nujol) ν/cm^{-1}: 1616 (m), 1585 (m), 1455 (s), 1359 (s), 1236 (m), 1026 (s). MS APCI: *m/z* (%) 476 [($Me_2C_5H_8N$)C(NAr)$_2H^+$, 100]. Anal Calc for $C_{47}H_{75}N_3SnP_2$: C 65.43, H 8.76, N 4.87. Found: C 64.74, H 8.46, N 4.65.

Preparation of [Ph_3Sn(η^1-C-$MeP_3C_3Bu^t_3$)] (9). A solution of Li[$MeP_3C_3Bu^t_3$] (0.5 mmol) in hexane (10 mL) was prepared in-situ as described above. This was added to a solution of Ph_3SnCl (0.19 g, 0.5 mmol) in hexane (20 mL) at −78 °C. The resultant mixture was warmed to 25 °C and stirred for 4 h, after which volatiles were removed in vacuo. The residue was extracted with hexane (10 mL) and filtered, and the filtrate was cooled to −30 °C to yield **9** as colorless crystals (245 mg, 74%). Mp: 134−136 °C dec. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ 0.92 (s, 9H, Bu^t), 1.20 (s, 9H, Bu^t), 1.26 (s, 9H, Bu^t), 1.31 (d, 3H, $^2J_{PH}$ = 11 Hz, PMe), 7.12−7.86 (m, 15H, ArH). ^{31}P{^{1}H} NMR (121.7 MHz, C_6D_6, 298 K): δ −284.7 (dd, $^1J_{PP}$ = 184.5 Hz, $^2J_{PP}$ = 12.0 Hz, P3), −8.4 (d, $^1J_{PP}$ = 184.5 Hz, P2), 22.4 (d, $^2J_{PP}$ = 12.0 Hz, $^2J_{PSn}$ = 193 Hz, P1). IR (Nujol) ν/cm^{-1}: 1461 (s), 1362 (s), 1259 (m), 1197 (m), 1021 (m). MS EI: *m/z* (%) 666 [M$^+$, 8], 315 [$MeP_3C_3Bu^t_3{}^+$, 100]. Anal Calc for $C_{34}H_{45}SnP_3$: C 61.38, H 6.82. Found: C 60.95, H 6.65.

Preparation of [Ph_3Sn(η^2-P,P-$MeP_3C_3Bu^t_3$)] (10). This compound was prepared similarly to **9** except the reaction mixture was stirred at 25 °C for 56 h before workup (284 mg, 86%). Mp: 201−205 °C dec. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ 0.18 (s, 9H, Bu^t), 0.82 (s, 18H, Bu^t), 1.62 (d, 3H, $^2J_{PH}$ = 12 Hz, PMe), 6.89−7.92 (m, 15H, ArH). ^{31}P{^{1}H} NMR (121.7 MHz, C_6D_6, 298 K): δ 35.3 (s, PMe), 87.1 (s, $^1J_{P^{117}Sn}$ = 732 Hz, $^1J_{P^{119}Sn}$ = 767 Hz, P_2Sn). ^{119}Sn{^{1}H} NMR (186.5 MHz, C_6D_6, 298 K): δ −85.5 (tr, $^1J_{P^{119}Sn}$ = 767 Hz). IR (Nujol) ν/cm^{-1}: 1462 (s), 1365 (s), 1260 (m), 1089 (m), 1021 (m), 802 (m). MS EI: *m/z* (%) 666 [M$^+$, 12], 315 [$MeP_3C_3Bu^t_3{}^+$, 100]. MS EI: accurate mass calc for $C_{34}H_{45}SnP_3$ 666.1751, found 666.1753. Anal Calc for $C_{34}H_{45}SnP_3$: C 61.38, H 6.82. Found: C 61.23, H 6.64.

Preparation of [Ph_3Pb(η^2-P,P-$MeP_3C_3Bu^t_3$)] (11). A solution of Li[$MeP_3C_3Bu^t_3$] (0.5 mmol) in hexane (10 mL) was prepared in-situ as described above. This was added to a solution of Ph_3PbCl (0.24 g, 0.5 mmol) in hexane (20 mL) at −78 °C. The resultant mixture was warmed to 25 °C and stirred for 4 h, after which volatiles were removed in vacuo. The residue was extracted with hexane (10 mL) and filtered, and the filtrate was cooled to −30 °C to yield **11** as orange crystals (90 mg, 24%). Mp: 143−145 °C dec. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ 0.23 (s, 9H, Bu^t), 0.87 (s, 18H, Bu^t), 1.64 (d, 3H, $^2J_{PH}$ = 9 Hz, PMe), 7.01−8.12 (m, 15H, ArH). ^{31}P{^{1}H} NMR (121.7 MHz, C_6D_6, 298 K): δ 36.3 (s, $^3J_{PPb}$ = 120 Hz, PMe), 121.0 (s, $^1J_{PPb}$ = 1967 Hz, P_2Pb). IR (Nujol) ν/cm^{-1}: 1462 (s), 1365 (s), 1265 (m), 1013 (m), 915 (m). MS EI: *m/z* (%) 755 [M$^+$, 15], 315 [$MeP_3C_3Bu^t_3{}^+$, 100]. Anal Calc for $C_{34}H_{45}PbP_3$: C 54.17, H 6.02. Found: C 53.89, H 5.98.

X-ray Crystallography. Crystals of **4**−**11** suitable for X-ray structural determination were mounted in silicone oil. Crystal-

Table 1. Summary of Crystallographic Data for Compounds 4−11

	4	**5**	**6**	**7**	**8**	**9**	**10**	**11**
empirical formula	$C_{15}H_{27}P_2Tl$	$C_{30}H_{54}P_4Sn$	$C_{30}H_{54}P_4Pb$	$C_{52}H_{83}N_3P_2Sn$	$C_{47}H_{75}N_3P_2Sn$	$C_{34}H_{45}P_3Sn$	$C_{34}H_{45}P_3Sn$	$C_{34}H_{45}P_3Pb$
fw	473.68	657.30	745.80	930.84	862.73	665.30	665.30	753.80
cryst syst	monoclinic	monoclinic	monoclinic	triclinic	monoclinic	triclinic	monoclinic	monoclinic
space group	$C2/c$	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P2_1/c$
a (Å)	34.278(7)	9.1210(2)	9.1190(2)	13.249(3)	19.036(4)	8.4140(17)	10.548(2)	10.659(2)
b (Å)	18.508(4)	18.1260(3)	18.1130(3)	17.212(3)	14.100(3)	11.287(2)	16.508(3)	16.457(3)
c (Å)	11.287(2)	20.4400(4)	20.6030(4)	22.615(5)	19.674(4)	17.484(4)	19.768(4)	19.767(4)
α (deg)	90	90	90	87.67(3)	90	104.26(3)	90	90
β (deg)	97.78(3)	98.737(1)	98.703(1)	83.94(3)	117.60(3)	90.60(3)	101.65(3)	101.43(3)
γ (deg)	90	90	90	89.49(3)	90	93.64(3)	90	90
vol (Å^3)	7095(2)	3340.08(11)	3363.87(11)	5124.0(18)	4679.9(16)	1605.4(6)	3371.2(12)	3398.9(12)
Z	16	4	4	4	4	2	4	4
ρ(calcd) (g cm^{-3})	1.774	1.307	1.473	1.207	1.224	1.376	1.311	1.473
μ (mm^{-1})	9.271	0.973	5.222	0.596	0.648	0.967	0.921	5.125
F(000)	3648	1376	1504	1984	1832	688	1376	1504
cryst size (mm)	0.10 × 0.05 × 0.05	0.20 × 0.08 × 0.07	0.20 × 0.08 × 0.07	0.15 × 0.10 × 0.08	0.25 × 0.15 × 0.12	0.45 × 0.45 × 0.25	0.20 × 0.18 × 0.08	0.20 × 0.18 × 0.08
θ range (deg)	2.94 to 25.00	3.01 to 27.09	3.00 to 27.09	2.92 to 25.50	3.09 to 27.00	3.04 to 27.45	3.16 to 26.88	3.14 to 26.00
no. of reflns collected	19 355	29 737	31 995	28 902	19 460	20 834	15 150	12 501
R_{int}	0.1065	0.0734	0.0904	0.0551	0.0313	0.0444	0.0431	0.0416
no. of data/restraints/params	6221/0/335	7334/6/334	7397/6/334	18811/0/1079	10167/0/497	7195/0/354	6926/36/354	6630/36/354
goodness of fit on F^2	1.119	1.019	1.022	1.054	1.029	1.013	1.061	1.121
R1 indices [$I > 2\sigma(I)$][a]	0.0854	0.0415	0.0427	0.0693	0.0550	0.0238	0.0678	0.0697
wR2 indices (all data)[b]	0.2077	0.0972	0.1005	0.1158	0.1368	0.0574	0.1614	0.1329
largest peak and hole (e A^{-3})	3.201 (near Tl1) and −2.379 (near Tl2)	0.569 and −1.179	1.169 and −1.289	0.985 and −0.530	2.420 (near Sn1) and −1.429	0.523 and −0.480	2.512 (near Sn1) and −0.989	2.313 (near Pb1) and −1.248

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

lographic measurements were made using a Nonius Kappa CCD diffractometer using a graphite monochromator with Mo Kα radiation ($\lambda = 0.71073$ 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)[32] using all unique data. All non-hydrogen atoms are anisotropic with hydrogen atoms included in calculated positions (riding model). Crystal data, details of data collections, and refinement are given in Table 1.

Acknowledgment. We thank the EPSRC (partial studentship for M.B., studentship for D.P.M., and postdoctoral fellowship for M.D.F.) and the Royal Society (postdoctoral fellowship for G.J.) for financial support. We also gratefully acknowledge the EPSRC Mass Spectrometry Service, Swansea.

Supporting Information Available: Crystallographic data as CIF files for **4**−**11**, [{$Cy_2NC(NAr)_2$}SnCl], and [{(*cis*-$Me_2C_5H_8N$)C-($NAr)_2$}SnCl]; synthetic, spectroscopic, and crystallographic details for [{$Cy_2NC(NAr)_2$}SnCl] and [{(2,6-$Me_2C_5H_8N$)C($NAr)_2$}SnCl]. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0605581

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