Organometallics **2003,** *22,* 2891−2896

Studies of the 24-Electron *nido*-5-Vertex Clusters $[M(\eta^4\text{-}P_2C_2Bu^t{}_2)]$ (M = Ge, Pb, Sn): Synthesis and Characterization of $[M(\eta^4\text{-}P_2C_2Bu^t{}_2)]$ (M = Ge, Pb), $[Sn(\eta^4\text{-}P_2C_2Bu^t{}_2)\{W(CO)_5\}_n]$ (*n* = 1, 2), and $[I_2GeP_2C_2Bu^t{}_2]$ and the Mössbauer Spectrum of $[Sn(\eta^4\text{-}P_2C_2Bu^t{}_2)]$

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The group 14 1,3-diphosphacyclobutadienyl complexes $[M(\eta^4\text{-}P_2C_2Bu^t{}_2)]$ (M = Ge, Pb) have been synthesized by the reaction of $[Zr(\eta^5\text{-}C_5H_5)_2(PCBu^t)_2]$ with $GeCl_2{\cdot}$(dioxane) or PbI_2 and fully characterized by multinuclear NMR spectroscopy and single-crystal X-ray diffraction studies. Structurally they can be viewed as 24-electron *nido*-5-vertex clusters. The significant solvent dependence of the ^{207}Pb chemical shift of $[Pb(\eta^4\text{-}P_2C_2Bu^t{}_2)]$ suggests the possibility of formation of an adduct with Lewis bases. The oxidative addition of $[Ge(\eta^4\text{-}P_2C_2Bu^t{}_2)]$ with I_2 has been studied as well as the reactivity of the previously reported tin analogue $[Sn(\eta^4\text{-}P_2C_2Bu^t{}_2)]$ with $[W(CO)_5(THF)]$ in which it coordinates via its P lone pairs. The Mössbauer spectrum of $[Sn(\eta^4\text{-}P_2C_2Bu^t{}_2)]$ is reported and shows an isomer shift consistent with it being an organo tin(II) complex.

Introduction

In 1986 Nixon and Binger independently reported the first examples of the cyclodimerization of phosphaalkynes (P≡CR) within the coordination sphere of cobalt, rhodium, and iridium, yielding complexes of the previously unknown 1,3-diphosphcycloabutadienyl ring.[1−4] Further examples subsequently appeared containing zerovalent nickel, iron, and molybdenum.[5−7] The usual route to such complexes has been via displacement, by phosphaalkynes, of a labile transition metal bound substitutent such as ethylene followed by a [2+2] cycloaddition of the two phosphaalkyne units or by co-condensation of metal atoms with phosphaalkynes by the metal vapor synthesis (MVS) technique. In contrast, main group compounds of the 1,3-diphosphacyclobutadienyl ring were unknown until recently. Furthermore, it could be anticipated that such compounds would not be readily accessible via straightforward cyclodimerization of phosphaalkynes. Recently, however, we described the synthesis of the first non transition metal diphosphacyclobutadienyl complex, namely, $[Sn(\eta^4\text{-}P_2C_2Bu^t{}_2)]$ (**1**) from the reaction between $SnCl_2$ and the 1,3-diphosphabicyclo[1.1.0]butane zirconium complex $[Zr(\eta^5\text{-}C_5H_5)_2(PCBu^t)_2]$ (**2**).[8] We have now extended this preliminary study, and in this paper we wish to present (i) the synthesis and characterization of the germanium, $[Ge(\eta^4\text{-}P_2C_2Bu^t{}_2)]$ (**3**), and lead, $[Pb(\eta^4\text{-}P_2C_2Bu^t{}_2)]$ (**4**), analogues of **1**, (ii) tentative evidence for the formation of a weakly interacting adduct of $[Pb(\eta^4\text{-}P_2C_2Bu^t{}_2)]$ with pyridine, and (iii) oxidative addition of iodine to **3** and the formation of $W(CO)_5$ adducts of **1** as well as its Mössbauer spectrum. It is of interest to note that the complexes $[M(\eta^4\text{-}P_2C_2Bu^t{}_2)]$ can be regarded as 24-electron *nido*-5-vertex clusters, similar to the recently reported phosphacarba-*nido*-pentaborane $2Bu^t$-1,2-PCB_3H_5.[9] Photoelectron spectroscopic studies of $[M(\eta^4\text{-}P_2C_2Bu^t{}_2)]$ (M = Ge, Sn) and a full analysis of the bonding (M = Ge, Sn, Pb) have been carried out, and these results are reported in a contemporary publication.[10]

Results and Discussion

Treatment of $[Zr(\eta^5\text{-}C_5H_5)_2(PCBu^t)_2]$ (**2**) with $GeCl_2{\cdot}$(1,4-dioxane) in THF at 70 °C led to the 1,3-diphosphacyclobutadienyl germanium complex $[Ge(\eta^4\text{-}P_2C_2Bu^t{}_2)]$ (**3**) in an isolated yield of 81%. A similar reaction of **2** and $PbCl_2$ led to some formation of the corresponding lead complex $[Pb(\eta^4\text{-}P_2C_2Bu^t{}_2)]$ (**4**), as evidenced by $^{31}P\{^1H\}$ NMR spectroscopy, but the conversion was never above 30% even with a large excess of $PbCl_2$. This problem was overcome by using PbI_2, in which case

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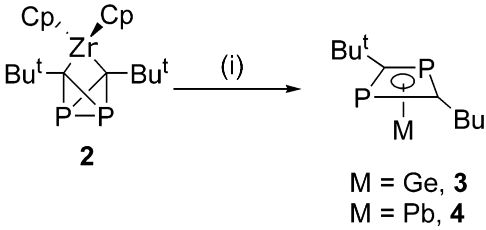
Scheme 1[a]



[a] Reagents and conditions: (i) $GeCl_2$•(1,4-dioxane), 70 °C, 48 h in THF; PbI_2, 70 °C, 72 h in THF.

NMR monitoring indicated complete conversion and the product could be isolated pure in 30% yield by recrystallization from toluene (Scheme 1). Both **3** and **4** show reasonable thermal stability, with **3** melting at 107−110 °C without decomposition and **4** melting with gradual decomposition from 120 °C.

The $^{31}P\{^1H\}$ NMR spectra (in C_5D_5N) of **3** and **4** show singlets at 142.2 and 159.3 ppm, respectively, which are similar to the value of 144.9 recorded for the related tin complex **1**. In addition, the spectrum of **4** shows clearly defined ^{207}Pb satellites. Interestingly, although the $^{31}P\{^1H\}$ chemical shift in **4** is almost insensitive to changes in solvent (it varies by less than ±2 ppm), the $^1J_{Pb-P}$ coupling changes significantly: in C_6D_6 the coupling is 286.6 Hz, and this drops to 236.3 Hz when the spectrum is recorded in C_5D_5N. We tentatively suggest that this may be a result of the formation of an adduct between **4** and pyridine in solution, although we have not yet been able to isolate and characterize such a species despite attempts with a variety of nitrogen donor Lewis bases such as tmeda and 2,2′-bipy. This suggests that **4** shows a degree of Lewis acidity, which is further supported by the fact that no changes in the NMR parameters of **4** are seen upon treatment with strong Lewis acids such as $B(C_6F_5)_3$. The formation of an adduct is perhaps not completely without precedent since Wright and co-workers have shown that both plumbocene and stannocene form weakly interacting adducts with Lewis bases such as bipy and tmeda.[11] In light of these observations we decided to reexamine the solvent effect of the $^1J_{Sn-P}$ coupling in **1**. In this case, however, the effect was much less pronounced, with a reduction in the coupling constant of only approximately 10 Hz on going from C_6D_6 to C_5D_5N (i.e., 296 to 286 Hz). Like the $^1J_{Pb-P}$, the $^{207}Pb\{^1H\}$ NMR spectrum of **4** shows a significant solvent dependence. In C_5D_5N the shift is −4522.6 ppm, and in C_6D_6 it is −5325.4 ppm. Both of these high-field resonances are in the same spectral region as that seen for plumbocenes, which span from around −4390 ppm in $Pb(\eta^5\text{-}C_5Me_5)_2$ to −5030 ppm in $Pb(\eta^5\text{-}C_5H_5)_2$.[12,13]

The other spectroscopic data for **3** and **4** were as expected, their ^1H and ^{13}C NMR spectra being consistent with the presence of two equivalent *tert*-butyl groups. Additionally both show strong molecular ions in their EI mass spectra.

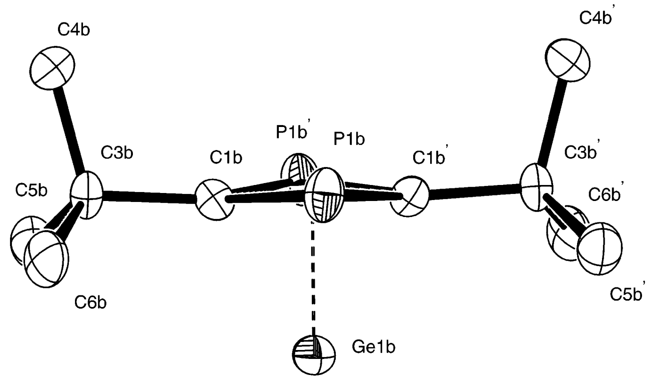


Figure 1. Molecular structure of $[Ge(\eta^4\text{-}P_2C_2Bu^t{}_2)]$, **3**.

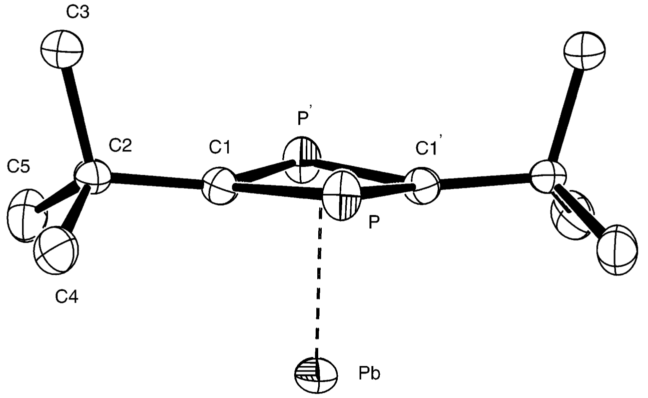


Figure 2. Molecular structure of $[Pb(\eta^4\text{-}P_2C_2Bu^t{}_2)]$, **4**.

The solid state structures of **3** and **4** were confirmed by single-crystal X-ray diffraction studies and are shown in Figures 1 and 2, respectively, along with important bond angles and distances in Table 1. Compound **3** contains two independent molecules in the asymmetric unit, one in a general position and one on a 2-fold rotation axis, although there are no significant geometric differences between them and the parameters in the following discussion pertain to the latter. In both **3** and **4** the P−C bond lengths are essentially equivalent, suggesting delocalization, 1.794(6) and 1.790(6) Å in **3** and 1.807(5) and 1.802(6) Å in **4**. These distances are very similar to those seen in the related tin compound **1**, cf. 1.796(3) and 1.800(3) Å. Furthermore, the angles within the P_2C_2 rings in **3** and **4** are similar to those seen in **1**. In **3** and **4** the CPC angles are 81.1(3)° and 82.9(3)°, respectively, while the PCP angles are 98.3(3)° and 96.7(3)°. For comparison, the corresponding values in **1** are 82.11(17)° and 97.47(17)°.[8] The P_2C_2 rings in both **3** and **4** deviate somewhat from planarity and indeed more so than in **1** (dihedral angle = 5.9°). In **4**, the dihedral angle between the planes defined by P−C1−P′ and P−C1′−P′ is 9.43°, and the corresponding angle in **3** is 12.7(2)°. A similar but even more pronounced folding of the rings has been seen in the zerovalent molybdenum complex $[Mo(\eta^4\text{-}P_2C_2Bu^t{}_2)_3]$, in which the fold angles of the three individual rings are 10.66°, 19.91°, and 25.34°.[7] As a consequence of this deviation from planarity, we believe it is more informative to comment on the individual metal−phosphorus and metal−carbon distances rather than to compare the metal−centroid distances. As expected, the distances increase steadily with increasing size of the metal. The metal−ring carbon distances increase from 2.204(6) Å

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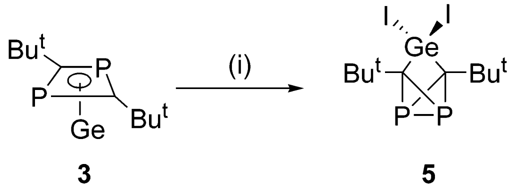
Table 1. Bond Angles (deg) and Distances (Å) in Compounds 3, 4, and 5[a]

3	P(1b)′−C(1b) 1.790(6)	Ge(1b)−C(1b) 2.204(6)	C(1b)′−P(1b)−C(1b) 81.1(3)
	P(1b)−C(1b) 1.794(6)	Ge(1b)−P(1b)′ 2.416(3)	P(1b)−C(1b)−P(1b) 98.3(3)
4	Pb−C(1) 2.544(6)	P−C(1) 1.802(6)	C(1)′−P−C(1) 82.9(3)
	Pb−P 2.704(2)	P−C(1)′ 1.807(5)	P(1)′−C(1)−P(1)′ 96.7(3)
	Ge−I(1) 2.5512(5)	C(1)−Ge 1.948(4)	C(2)−Ge−C(1) 74.78(16)
5	Ge−I(2) 2.5394(5)	C(2)−Ge 1.958(4)	P(2)−C(2)−P(1) 69.04(15
	P(1)−P(2) 2.1435(16)	I(2)−Ge−I(1) 106.560(18)	P(2)−C(1)−P(1) 69.11(14)

[a] Symmetry transformations used to generate equivalent atoms in **3** and **4**: $-x, y, -z + 1/2$.

Scheme 2[a]



[a] Reagents and conditions: (i) I_2, toluene −30 to 25 °C, 18 h.

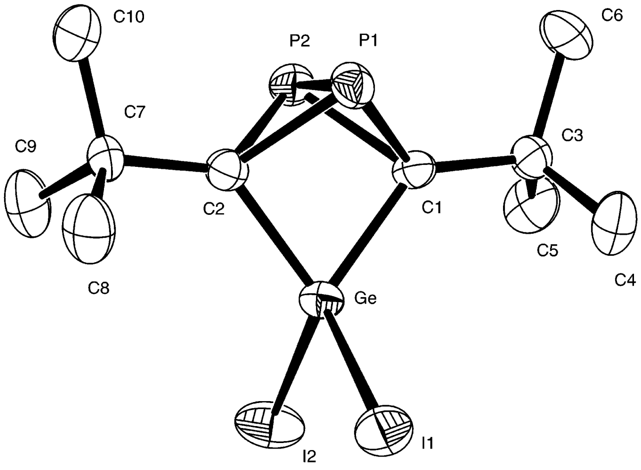


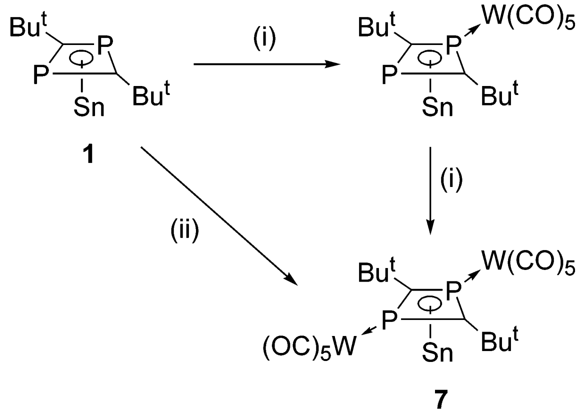
Figure 3. Molecular structure of [$Ge(P_2C_2Bu^t{}_2)I_2$], **5**.

in **3** to 2.432(3) Å in **1** to 2.544(6) Å in **4**, while the metal−phosphorus distances increase from 2.416(3) Å in **3** to 2.611(1) Å in **1** to 2.704(2) Å in **4**.

Treatment of **3** with 1 equiv of I_2 in toluene at −30 °C led to the immediate disappearance of the purple color of the iodine. A $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture showed complete disappearance of the resonance for **3** at ca. 142 ppm and emergence of a single peak at −268.3 ppm for the oxidative addition product **5** (Scheme 2). The high-field resonance in the $^{31}P\{^1H\}$ NMR spectrum of **5** is characteristic of a folded $P_2C_2Bu^t{}_2$ moiety, a feature present in **2** and whose presence in **5** was subsequently confirmed by a single-crystal X-ray diffraction study (vide infra).

The molecular structure of **5** is shown in Figure 3, and important bond distances and angles are collected in Table 1 with those of compounds **3** and **4**. The structure contains a central distorted tetrahedral germanium bonded to the two iodine centers and the two carbons of the $P_2C_2Bu^t{}_2$ framework. Interestingly, a survey of the Cambridge Crystallographic Database reveals that this is only the third structurally characterized Ge(IV) organometallic species in which the germanium center is bonded to two iodine and two carbon centers, the other two examples being $(C_6Cl_5)_2GeI_2$[14] and the germacycle *cyclo*-$(GeI_2CHCH)_2$ (**6**).[15] The two Ge−I bond distances in **5** of 2.5394(5) and 2.5512(5) Å differ marginally from each other but are similar to those of 2.498 and 2.519 Å in **6**. The constrained geometry of the $P_2C_2Bu^t{}_2$ frame results in the C(1)−Ge−C(2) angle being 74.78(16)°, which is markedly smaller than the C−Ge−C angle of 108.703° in **6**, in which no such geometric constraint exists. The I−Ge−I angles in **5** and **6** show less of a difference, being 106.560(18)° and 101.969°, respectively. In the structures of **1**, **3**, and **4** the $P_2C_2Bu^t{}_2$ ring is distorted slightly from planarity. The structure of **5** can be viewed as an extreme example of this situation in which the ring has been distorted to a point where the phosphorus centers are too far to bond to the germanium and instead form a P−P bond. The P−P bond distance of 2.1435(16) Å is close to that of 2.147 Å in **2**. The dihedral angle in **5** between the planes defined by C(2)−P(2)−P(1) and C(1)−P(1)−P(2) is 99.2°.

Scheme 3[a]



[a] Reagents and conditions: (i) [$W(CO)_5(THF)$], 25 °C, 48 h; (ii) [$W(CO)_5(THF)$] 2 equiv, 25 °C, 48 h.

Treatment of **1** with a THF solution of [$W(CO)_5(THF)$] in stoichiometric quantity or excess enabled coordination of a $W(CO)_5$ fragment to one and both of the phosphorus centers, respectively (Scheme 3). The 1:1 adduct was not isolated but was characterized in solution by its characteristic $^{31}P\{^1H\}$ NMR spectrum. The spectrum consists of two doublets at 92.9 and 74.3 ppm with a $^2J_{PP}$ coupling of 9.7 Hz. This coupling is similar to that seen in transition metal complexes of the $P_2C_2Bu^t{}_2$ ring in which the two phosphorus centers have been made nonequivalent by coordination of one of them to another metal fragment, e.g., [$Co(\eta^5$-$C_5Me_5)(\eta^4$-$P_2C_2Bu^t{}_2)\{Pt(PPh_3)_2\}$] (9.5 Hz).[16] Furthermore, the lower field doublet shows satellites due to coupling to both $^{119/117}Sn$ and ^{183}W. The $^1J_{P-W}$ value of 214 Hz is typical for this type of coordination.[17] Unfortunately the ^{119}Sn

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and ^{117}Sn satellites were poorly defined, and only a mean $^1J_{P-Sn}$ coupling of 274 Hz could be measured.

Treatment of the solution with a further equivalent of [W(CO)$_5$(THF)] in THF led to disappearance of the doublets and emergence of a single resonance at 44.7 ppm corresponding to coordination of the other phosphorus lone pair and formation of the bis-W(CO)$_5$ adduct **7**, in which both phosphorus centers are again equivalent. This compound could also be directly synthesized by treatment of **1** with an excess of [W(CO)$_5$(THF)] in THF solution. Unfortunately crystals of **7** suitable for an X-ray diffraction study could not be obtained despite numerous attempts with a variety of solvents, but its structure has been elucidated by multinuclear NMR spectroscopy and IR and mass spectrometry. The ^{31}P-{^{1}H} NMR spectrum of **7** consists of a single resonance at 44.7 ppm with clearly defined tin satellites from which the respective $^1J_{P-Sn(117)}$ and $^1J_{P-Sn(119)}$ couplings of 332.8 and 348.1 Hz could be measured; the $^1J_{P-W}$ coupling is 228.3 Hz. The $^1J_{P-Sn(119)}$ coupling is reflected in the ^{119}Sn NMR spectrum, which consists of a triplet at −2278.2 ppm, the latter shift being very similar to that of −2128.9 ppm in the parent complex **1**. The presence of the W(CO)$_5$ fragments was confirmed by infrared spectroscopy. A sharp medium-intensity band was observed at 2070 cm^{-1}. The other two stronger bands, which overlap, occur at ca. 1955 cm^{-1}, the lower energy band being seen as a shoulder on the higher energy one. These observations are consistent with theory which suggests that an M(CO)$_5$ fragment of local symmetry C_{4v} should show three IR-active CO bands (2A$_1$ + E).[18,19] The EI mass spectrum of **7** shows a weak molecular ion at $m/z = 966$ with the expected isotopic distribution pattern as well as clusters corresponding to loss of CO groups. Despite the lack of an X-ray crystal structure, we believe these data show beyond all reasonable doubt that **7** is formed by addition of two W(CO)$_5$ units to **1** via the P lone pairs, an assertion that is supported by a parallel theoretical study which indicates the P lone pairs to be more basic than the lone pair at the Sn center.[10]

The ^{119}Sn Mössbauer spectrum of **1** is shown in Figure 4. The spectrum shows an isomer shift of 3.02 mm s^{-1} but no resolvable quadrupole splitting. Although in the region normally seen for organotin(II) compounds (typically 2.5−4.3 mm s^{-1}),[20] this isomer shift is unusually low when compared with other divalent organotin compounds bearing π-bonded ligands, e.g., stannocenes, which show isomer shifts between 3.53 for Sn(C$_5$Me$_5$)$_2$[21] and 3.83 for Sn(C$_5$MeH$_4$)$_2$,[22] with stannocene itself coming at 3.74.[23]

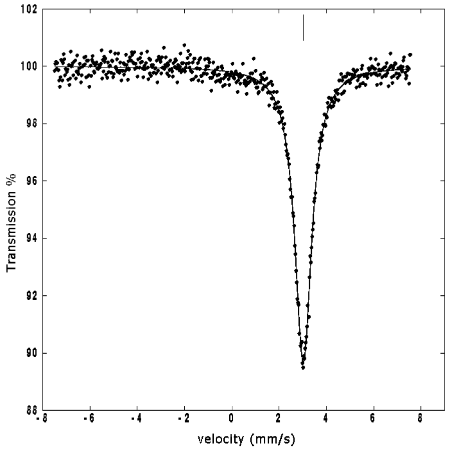

Figure 4. Mössbauer spectrum of [Sn(η^4-P$_2$C$_2$Bu$^t_2$)], **1**.

The absence of a quadrupole splitting suggests that there is coincidentally an almost zero electric field gradient at the tin center despite the apparent asymmetry of the molecule. This is not without precedent, however, and in a review, Zuckermann highlighted almost 161 asymmetric compounds with no resolvable quadrupole splitting.[24]

Conclusion

We have described the synthesis and characterization of a new series of stable compounds bearing a 1,3-diphosphacyclobutadienyl ring, namely, [M(η^4-P$_2$C$_2$-Bu$^t_2$)] (M = Ge, Sn, Pb). These are the first examples of non transition metal compounds bearing such a ligand. The Mössbauer spectrum of **1** as well as the similarity of the ^{119}Sn and ^{207}Pb NMR spectra of **1** and **4** with those of stannocene and plumbocene leads us to view **1**, **3**, and **4** as a series of divalent group 14 compounds in which the 1,3-diphosphacyclobutadienyl ring can be thought of as accepting two electrons from the group 14 element and existing as a six π-electron dianion. Complex **3** can be easily oxidized to its related Ge(IV) compound with iodine, and we have shown that **1** forms simple adducts with W(CO)$_5$ by donation of one or both of the phosphorus lone pairs.

Experimental Section

General Considerations. All procedures were conducted using conventional Schlenk and glovebox techniques under an atmosphere of high-purity argon or nitrogen in flame-dried glassware. The solvents toluene, hexane, and THF were dried by heating to reflux over sodium−potassium alloy for at least 12 h and were distilled and freeze−thaw degassed prior to use. C$_6$D$_6$ and C$_5$D$_5$N were dried over molten potassium and were vacuum transferred into ampules fitted with greaseless taps and stored in the glovebox. ^{31}P{^{1}H} and ^{1}H NMR spectra were recorded on a Bruker DPX-300 or AMX-500 spectrometer and were referenced to external 85% H$_3$PO$_4$ and the residual ^{1}H resonances of the solvent, respectively. ^{13}C, ^{119}Sn, and ^{207}Pb spectra were recorded on a Bruker AMX-500 spectrometer and were referenced to the ^{13}C resonances of the deuterated solvent, external SnMe$_4$, and PbMe$_4$, respectively. EI mass spectra were recorded on a VG Autospec instrument at 70 eV. Microanalyses were performed by Medac Ltd, Surrey, England. Details of the Mössbauer spectrometer and related experimental procedures are given elsewhere.[25] PbI$_2$ and W(CO)$_6$

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Table 2. Crystallographic Data for 3, 4, and 5

	3	4	5
chemical formula	$C_{10}H_{18}GeP_2$	$C_{10}H_{18}PbP_2$	$C_{10}H_{18}GeI_2P_2$
M	272.77	407.37	526.57
cryst syst	monoclinic	monoclinic	monoclinic
space group	$C2/c$ (No. 15)	$C2/c$ (No. 15)	$P2_1/n$
λ/Å	0.71073	0.71073	0.71073
lattice params	a = 31.926(3) Å b = 6.0639(5) Å c = 21.460(2) Å β = 113.481(5)°	a = 19.8240(19) Å b = 6.0564(6) Å c = 10.6501(7) Å β = 96.014(5)°	a = 8.9736(2) Å b = 19.2898(5) Å c = 9.9627(2) Å β = 101.919(1)°
V/Å^3	3810.6(6)	1271.6(2)	1687.35(7)
T/K	173(2)	173(2)	173(2)
Z	12	4	4
D_{calc}/Mg m^{-3})	1.43	2.13	2.07
F_{000}	1680	760	984
μ/mm^{-1}	2.62	13.48	5.64
T_{max}/T_{min}	0.6221/0.5068	0.384/0.291	0.360/0.288
θ range/deg	3.81 to 22.94	4.13 to 27.86	3.93 to 25.04
no. of reflns collected	7563	3237	7857
no. of ind reflns	2551	1495	2932
R_{int}	0.091	0.054	0.036
final R indices [$I > 2\sigma(I)$]	R_1 0.065; wR_2 0.171	R_1 0.039; wR_2 0.100	R_1 0.028; wR_2 0.063
R indices (all data)	R_1 0.089; wR_2 0.192	R_1 0.044; wR_2 0.105	R_1 0.035; wR_2 0.067
Goodness-of-fit of F^2	1.072	0.961	1.096

were commercial samples and were used as received. [Zr(η^5-C_5H_5)$_2$($PCBu^t$)$_2$][26] and $GeCl_2$·(1,4-dioxane)[27] were prepared as described in the literature. The preparation and characterization of [Sn(η^4-$P_2C_2Bu^t{}_2$)] were described in our recent preliminary communication.[8]

Synthesis of [Ge(η^4-$P_2C_2Bu^t{}_2$)], 3. $GeCl_2$·(1,4-dioxane) (357 mg, 1.54 mmol) and [Zr(η^5-C_5H_5)$_2$($PCBu^t$)$_2$] (650 mg, 1.54 mmol) were placed in an ampule, THF (15 mL) was added, and the ampule was evacuated. The resultant mixture was stirred at 70 °C for 48 h, whereupon it turned from deep red to orange. Volatiles were removed from the resultant solution, and the residue was extracted with hexane (2 × 50 mL) and filtered to give a yellow solution. The hexane was removed in vacuo to yield [Ge(η^4-$P_2C_2Bu^t{}_2$)] as a bright yellow crystalline solid (340 mg, 81%), which was spectroscopically and analytically pure. Mp: 107−110 °C. NMR (C_5D_5N, 298 K): δ_H (300 MHz) 0.98 (s, 18H, Bu^t); δ_P (121.68 MHz) 142.2 (s); δ_C (125.72 MHz) 32.9 (tr, $^3J_{PC}$ = 3.98 Hz, −C(CH_3)$_3$), 33.6 (tr, $^2J_{PC}$ = 6.21 Hz, −C(CH_3)$_3$), 124.2 (tr, $^1J_{PC}$ = 47.4 Hz, PCP). EI mass spectrum (main peaks) (70 eV) m/z (%): 273 (91) M$^+$, 258 (100) [M − CH_3]$^+$. Anal. Found: C 43.98, H 6.64. $C_{10}H_{18}P_2Ge$ requires: C 44.03, H 6.65.

Synthesis of [Pb(η^4-$P_2C_2Bu^t{}_2$)], 4. PbI_2 (287 mg, 0.62 mmol) and [Zr(η^5-C_5H_5)$_2$($PCBu^t$)$_2$] (175 mg, 0.42 mmol) were placed in an ampule, THF (15 mL) was added, and the ampule was evacuated. The resultant mixture was stirred at 70 °C for 72 h. Volatiles were removed from the resultant orange-brown solution, and the residue was extracted with hexane (80 mL) and filtered to give an orange-yellow solution. The hexane was removed in vacuo and the residue recrystallized from toluene at −85 °C to afford [Pb(η^4-$P_2C_2Bu^t{}_2$)] as a orange-red crystalline solid (50 mg, 30%). The crystals were suitable for the X-ray diffraction study. The compound begins to darken slowly at ca. 120 °C, with rapid decomposition at 175 °C. NMR (C_5D_5N, 298 K): δ_H (300 MHz) 1.19 (s, 18H, Bu^t); δ_P (121.68 MHz) 159.3 (s, $^1J_{PPb}$ = 236.3 Hz, from satellites); δ_C (125.72 MHz) 36.2 (tr, $^3J_{PC}$ = 4.51 Hz, −C(CH_3)$_3$), 33.5 (tr, $^2J_{PC}$ = 6.78 Hz, −C(CH_3)$_3$), 139.7 (tr, $^1J_{PC}$ = 48.9 Hz, poorly defined satellites give $^1J_{CPb}$ ≈ 27 Hz, PCP), δ_{Pb} (104.60 MHz, C_6D_6) −5325.4 (tr, $^1J_{PPb}$ = 286.6 Hz); δ_{Pb} (C_5D_5N) −4522.6 (tr, $^1J_{PPb}$ = 236.3 Hz). EI mass spectrum (main peaks) (70 eV) m/z (%): 408 (85) M$^+$, 393 (38) [M − CH_3]$^+$, 207 (100) Pb$^+$. Anal. Found: C 29.53, H 4.48. $C_{10}H_{18}P_2Pb$ requires: C 29.48, H 4.45.

Synthesis of [Ge($P_2C_2Bu^t{}_2$)I_2], 5. To a solution of [Ge(η^4-$P_2C_2Bu^t{}_2$)] (150 mg, 0.55 mmol) in toluene (5 mL) at −30 °C was added dropwise an iodine (140 mg, 1.1 mmol) solution in toluene (5 mL) with rapid stirring. The purple color of the iodine solution immediately disappeared. The solution was gradually warmed to room temperature, becoming first orange then yellow in color. After stirring for 18 h at ambient temperature volatiles were removed in vacuo. The resultant residue was difficult to purify in good yield because of its high solubility in hydrocarbon solvents, but NMR data suggest that the reaction is quantitative and with no side-products. A small amount of pure crystalline material suitable for analysis was obtained from a concentrated toluene solution kept for several days at −85 °C (60 mg, 21%). Mp: decomposes gradually from 110 °C. NMR (C_6D_6, 298 K): δ_H (300 MHz) 0.81 (s, 18H, Bu^t); δ_P (121.68 MHz) −268.3 (s); δ_C (125.72 MHz) 31.0 (tr, $^3J_{PC}$ = 3.1 Hz, −C(CH_3)$_3$), 34.9 (tr, $^2J_{PC}$ = 4.5 Hz, −C(CH_3)$_3$), 79.6 (tr, $^1J_{PC}$ = 51.9 Hz, PCP). EI mass spectrum (largest peak of cluster is quoted) (70 eV) m/z (%): 528 (6) M$^+$, 403 (54) [M − I]$^+$, 273 (30) [M − 2I]$^+$, 169 (100) [$PC_2Bu^t{}_2$]$^+$. Anal. Found: C 22.93, H 3.47. $C_{10}H_{18}P_2GeI_2$ requires: C 22.81, H 3.45.

Synthesis of [Sn(η^4-$P_2C_2Bu^t{}_2$){W(CO)$_5$}$_2$], 7. [W(CO)$_6$] (385 mg, 1 mmol) in THF (100 mL) was irradiated (254 nm) for 6 h with a mercury vapor UV lamp. To the resultant yellow solution was added a solution of **1** (150 mg, 0.47 mmol) in THF (5 mL). The mixture was stirred at room temperature for 48 h and became orange in color. Volatiles were removed in vacuo, and the residue was purified by chromatography (Kieselgel, toluene). A single orange band was eluted. Removal of volatiles from this band afforded **7** as an orange solid (ca. 50 mg, 11%). A reproducible microanalysis could not be obtained due to the presence of a small and unidentified persistent impurity peak in the $^{31}P\{^1H\}$ NMR spectrum, although the $^{31}P\{^1H\}$ and ^1H NMR spectra both suggested the purity to be >90%. NMR (C_6D_6, 298 K): δ_H (300 MHz) 1.08 (s, 18H, Bu^t); δ_P (121.68 MHz) 44.7 (s, $^1J_{P-Sn(117)}$ = 332.8 Hz, $^1J_{P-Sn(119)}$ = 348.1 Hz, $^1J_{P-W}$ = 228.3 Hz), δ_{Sn} (186.36 MHz) −2278.2 (t, $^1J_{P-Sn}$ = 348.0 Hz). IR ν/cm^{-1} (CO): 2070 m (sh), 1955 s (br, two overlapping bands) (Nujol). EI mass spectrum (main peaks) (70 eV) m/z (%): 966 (4) M$^+$, 863 (8) [M − 4CO]$^+$, 769 (6) [M − 7CO]$^+$, 642 (60) [M − W(CO)$_5$]$^+$, 587 (22) [M − W(CO)$_7$]$^+$, 531 (24) [M − W(CO)$_9$]$^+$, 503 (27) [M − W(CO)$_{10}$]$^+$.

X-ray Structure Determinations. Crystals of **3** suitable for the X-ray diffraction study were grown by slow sublimation in a tube sealed in vacuo (ca. 10^{-6} mmHg) over a small temperature gradient (furnace temperature 45 °C), while those of **4** and **5** were grown by recrystallization from toluene at −85

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°C. Intensity data for all compounds were collected on a KappaCCD diffractometer. The structures were solved by direct methods and refined on F^2 using full matrix least squares with SHELX-97.[28] An empirical absorption correction was applied in each case. Details of each data collection, structure solution, and refinement are collected in Table 2.

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Supporting Information Available: Crystal structure data for **3**, **4**, and **5** including tables of bond angles and distances, thermal parameters, and structure refinement details. This material is available free of charge via the Internet at http://pubs.acs.org.

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