^{13}C NMR of **1a** (in CD_2Cl_2) at room temperature showed a single sharp resonance at δ 109.5 (Cp, Cp′); upon cooling to −80 °C two broadened resonances at δ 109.7 and 108.2 are observed, and warming the solution back to room temperature causes coalescence of these two peaks. This fluxional process may involve symmetrical intermediate **3** as shown in Scheme II.

Zirconium "metalloazine" complexes are susceptible to *electrophilic* attack at C as well as at Zr–N, demonstrating an "umpolung" of reactivity with regard to the hydrazones from which they are derived. For example, addition of $(Et_3O)^+BF_4^-$ to a solution of **1a** gave both C-alkylated and N-alkylated hydrazones in approximately equal amounts, yet careful hydrolysis of **1a** leads to $H_2NNCHPh$ as the sole organic product (no attack by H_2O at sp^2 C). Furthermore, the addition of organic carbonyl compounds, such as aldehydes or ketones, gives a mixture of condensation products resulting from attack either at carbon or at nitrogen. Reactions with enones lead to the olefin, exclusively, in good yield. In a typical experiment, to 1.20 g (1.77 mmol) of **1a** in 25 mL of dry THF is added butyraldehyde (1.8 mmol) by syringe. The bright orange reaction mixture slowly fades to yellow over the course of 6 h and is then hydrolyzed with 0.5 mL of dilute aqueous KOH solution, dried over K_2CO_3, and concentrated to a viscous oil. The product mixture is separated by column chromatography (Florisil; hexane). Yield: olefin, 30% (*Z*:*E* = 25:1),[17] and azine, 60%. In similar fashion, **1a** reacted with other representative substrates: cyclohexanecarboxaldehyde [olefin (52%; *Z*:*E* = 16:1); azine (44%)]; 1-acetylcyclohexene [olefin (60%; *Z*:*E* = 3:1); azine (0%)]; *trans*-cinnamaldehyde [olefin 70%; *Z*:*E* = 2.5:1); azine (0%)]; benzaldehyde [olefin (47%; *Z*:*E* = 4.1:1; azine (42%)]; *p*-cyanobenzaldehyde [olefin (62%; *Z*:*E* = 4.2:1; azine (26%)]. Also **1b** reacted with cyclohexanecarboxaldehyde [olefin (57%; *Z*:*E* = 15:1); azine (40%)] and **1c** reacted with *p*-cyanobenzaldehyde [olefin (77%; *Z*:*E* = 1.5:1; azine (0%)]; cyclohexanecarboxaldehyde [olefin (58%; *Z*:*E* = 10:1); azine (13%)].

We are now exploring the scope of synthetic utility of these new complexes.

Acknowledgment. We acknowledge support for this work given by the National Science Foundation and the National Institutes of Health.

Supplementary Material Available: Tables of atom coordinates, anisotropic thermal parameters, bond distances, and bond angles (5 pages); a listing of structure factors (18 pages). Ordering information is given on any current masthead page.

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[14] Crystals of **1b** are orthorhombic of space group $P2_12_12_1$ with a = 8.262 (3) Å, b = 19.441 (7) Å, c = 21.922 (9) Å, V = 3521 (2) Å^3, and d_{calcd} = 1.47 g cm^3 for Z = 4 ($C_{38}H_{40}N_4Zr_2\cdot{}^1/_2C_6H_{14}$, fw = 778.4 g). An orange crystal of dimensions 0.16 × 0.20 × 0.24 mm was mounted on a glass fiber. The intensity data were measured on a Nicolet R3m diffractometer equipped with a graphite monochrometer and Mo Kα radiation (λ = 0.710 69 Å) utilizing an ω scan technique with variable scan rates. The data were corrected for decay but not absorption μ(Mo Kα) = 6.2 cm^{-1}). A total of 3513 independent reflections were measured for $2\theta < 50°$ of which 2996 unique data were considered to be observed [$F_o > 3.0\ \sigma\ (F_o)$]. The structure was solved by conventional heavy-atom methods (Patterson and Fourier) and was refined by blocked-cascade least squares. All calculations were carried out by using the SHELXTL program. In the final stages of refinement, anisotropic thermal parameters were used for the non-hydrogen atoms. The phenyl and Cp hydrogen atoms were located on a difference Fourier map and were entered at idealized positions. The methyl hydrogens were not located. The hydrogen atoms were assigned isotropic temperature factors of $B_H = 1.2B_C$. A hexane molecule of solvation, located on a difference Fourier map and refined with isotropic thermal parameters, is disordered around the 2-fold screw axis in the x direction. At convergence, R = 0.056 and R_w = 0.057 for 2996 data and 409 variables.

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Monomeric, Three-Coordinate Tin(II) and Lead(II) Complexes with a MCP_2 Coordination Sphere: $Sn[CH(PPh_2)_2]_2$ and $Pb[CH(PPh_2)_2]_2$

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Summary: $Li[CH(PPh_2)_2]$ reacts with $SnCl_2$ or $PbCl_2$ in tetrahydrofuran to yield the homoleptic complexes $Sn[CH(PPh_2)_2]_2$ or $Pb[CH(PPh_2)_2]_2$. X-ray crystallographic studies reveal similar structures with a monomeric, pyramidal MCP_2 core and two distinctly different bis(diphenylphosphino)methanide ligands.

Bis(diphenylphosphino)methanide, $CH(PPh_2)_2^-$, is a versatile ligand[1] and building block for the construction of more complex structures, particularly new ligands. Here we report the use of this anion to produce novel, low-coordinate and monomeric tin(II) and lead(II) complexes. There has been considerable recent interest in the chemistry of these species, partly because of their relation to divalent carbon and carbenes.[2a]

Treatment of anhydrous tin(II) chloride over a 1-h period with 2 equiv of lithium bis(diphenylphosphino)methanide, $LiCH(PPh_2)_2$ (**1**),[1a] in dry dioxygen-free tetrahydrofuran followed by 1 h of stirring produces a brown solution from which brown needles of $Sn[CH(PPh_2)_2]_2$ (**2**) (mp 145–148 °C dec) are obtained in 72% yield after evaporation of THF, redissolution in ethyl ether, filtration, and cooling to −10 °C.[2b] Similarly, the reaction between anhydrous lead(II) chloride and **1** produces orange (Pb-$[CH(PPh_2)_2]_2$ (**3**) (mp 141–146 °C dec) in 55% yield.

Characterization through X-ray crystallography reveals that compounds **2**[3] and **3**[4] have similar structures. Perspective drawings of **3** are shown in Figure 1. Compound

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[3] Brown prisms of **2**·$(C_2H_5)_2O$ were obtained by cooling a saturated tetrahydrofuran/ethyl ether (1/9, v/v) solution of **2** to −10 °C. They crystalize in the monoclinic space group $P2_1/c$ with a = 18.124 (5) Å, b = 14.589 (7) Å, c = 18.291 (8) Å, β = 91.50 (3)°, V = 4835 Å^3, and Z = 4 at 130 K. Refinement yielded R = 0.0637 for 1902 relfections with $I > 3\sigma(I)$ and 272 parameters.

[4] Orange parallelepipeds of **3**·$(C_2H_5)_2O$ were obtained by cooling a saturated tetrahydrofuran/ethyl ether (1/9, v/v) solution of **3** to −10 °C. They crystallize in the monoclinic space group $P2_1/c$ (No. 14) with a = 18.075 (8) Å, b = 14.713 (6) Å, c = 18.099 (8) Å, β = 92.29 (4)°, V = 4810 (4) Å^3, and Z = 4 at 130 K which is isomorphic with **2**·$(C_2H_5)O$. Tests for an orthorhombic C-centered cell show it is not present. Refinement yielded R = 0.0571 for 3899 reflections with $I > 3\sigma$(I) and 272 parameters.

Table I. Selected Structural Parameters

	$Sn[CH(PPh_2)_2]_2$ (2)	$Pb[CH(PPh_2)_2]_2$ (3)
	Bond Lengths (Å)	
M–C(1)	2.286 (16)	2.371 (12)
M–P(3)	2.676 (5)	2.782 (4)
M–P(4)	2.659 (5)	2.758 (4)
C(1)–P(1)	1.874 (16)	1.895 (12)
C(1)–P(2)	1.830 (16)	1.775 (13)
C(26)–P(3)	1.733 (16)	1.713 (13)
C(26)–P(4)	1.747 (16)	1.759 (13)
	Bond Angles (deg)	
P(3)–M–P(4)	63.3 (2)	61.5 (1)
P(3)–M–C(1)	99.3 (4)	96.6 (3)
P(4)–M–C(1)	90.3 (4)	88.7 (3)
P(1)–C(1)–P(2)	118.0 (8)	118.2 (7)
P(3)–C(26)–P(4)	107.2 (8)	109.3 (7)
M–P(3)–C(26)	94.6 (5)	94.7 (4)
M–P(4)–C(26)	94.8 (5)	94.5 (4)

2 is similar. Selected bond distances and bond angles for the two compounds are compiled in Table I. The lead (or tin) atoms are three-coordinate with pyramidal geometry. Consequently the lone pair on lead (or tin) appears to be stereochemically active. The ethyl ether molecules are not coordinated; the closest approach of O to Pb is 6.44 (2) Å and to Sn it is 6.57 (2) Å. The two bis(diphenylphosphino)methanide ligands are bound differently. One binds as a monodentate ligand through carbon. Its phosphorus atoms remain uncoordinated. The other binds as a bidentate chelating ligand through two phosphorus atoms. As a consequence, the internal carbon, C(26), is only three-coordinate. The chelate rings are nearly planar: the angles between the MP_2 and CP_2 plane are 2.2° (M = Sn) and 1.8° (M = Pb). This planarity and the shortening of the C(26)–P(3) and C(26)–P(4) bonds relative to the C(1)–P(2) and C(1)–P(1) bonds can be ascribed to delocalization of the lone pair over the P(3)–C(26)–P(4) unit. Comparison of the structural parameters in Table I reveals that the P–M and C–M distances in the lead complex are, as expected, significantly longer than those of the tin complex. Corresponding differences in bond angles in the two materials result largely from these size differences.

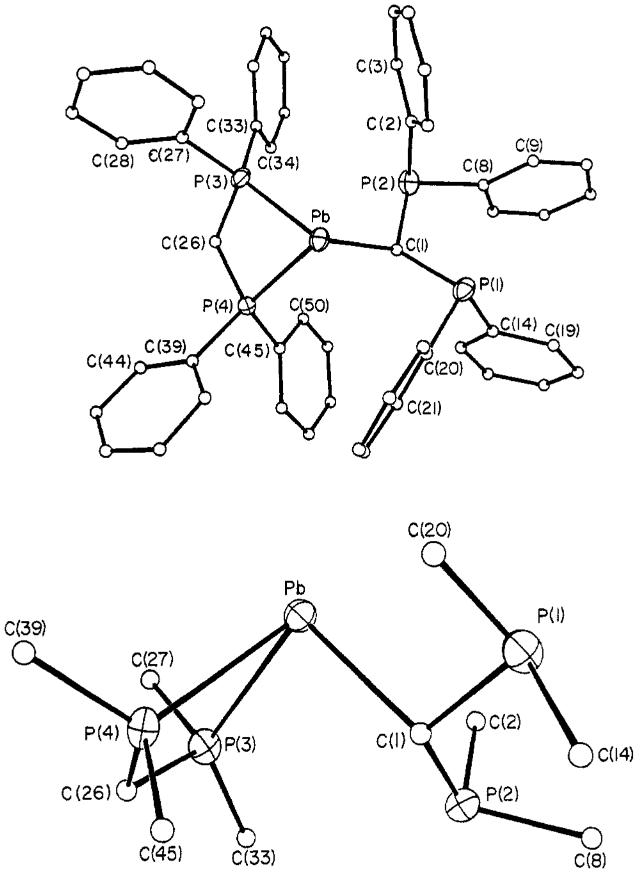

Figure 1. Top: a perspective view of $Pb[CH(PPh_2)_2]_2$ (3) showing the atomic numbering scheme. Bottom: a view of the inner coordination of 3 which emphasizes the pyramidal nature of P(1), P(2), and Pb and the planarity of the chelate ring.

There are a number of noteworthy features of these molecules. They represent the first cases where $CH(PPh_2)_2^-$ acts as a monodentate ligand binding through carbon (i.e., as a very bulky alkyl group). In the homoleptic compounds $Pt[CH(PPh_2)_2]_2$[1g] and $Au_2[CH(PPh_2)_2]_2$,[1h] this ligand acts as a chelating or bridging phosphorus donor, respectively. Even in solid $(CH_3)_2N(CH_2)_2N(CH_3)_2Li[CH(PPh_2)_2]$, the lithium is chelated by the two phosphorus atoms and is not attached to the central carbon.[1i] However, in $Cu_3[CH(PPh_2)_2]_3$ the central carbon participates in bonding to copper in the tridentate form of this ligand while the phosphorus atoms bond other copper ions.[1c] The unprecedented combination of one monodentate and one bidentate $CH(PPh_2)_2^-$ ligand gives the tin and lead ions monomeric three-coordinate geometry which is rare. The availability of two phosphorus donors in the chelating ligand and the steric bulk of the monodentate ligand stabilizes these organotin(II) and organolead(II) complexes in monomeric form. In contrast organotin compounds with SnR_2 stoichiometry have cyclic Sn–Sn bonded structures.[5,6] The exception is bis[bis(trimethylsilyl)methyl]tin(II) (5) which is monomeric in solution and dimeric, Sn–Sn bound in the solid.[7] In 2 the potentially vacant tin orbitals are filled by the phosphorus donors. The C–Sn(II) distance in 2 is nearly identical with that in the solid state, dimeric form of 5 (2.28 (3) Å)[7] and significantly longer than C–Sn(IV) distances which fall in the 2.10–2.17 Å range.[5,6] The structure of 2 is notably different from that of $Sn[C(PMe_2)_3]_2$ which has a pseudo-trigonal-bipyramidal structure with four Sn–P bonds, two uncoordinated PMe_2 groups, and no Sn–C bonds.[8] The steric effects of the eight phenyl groups in 2 are probably responsible for stabilization of its lower coordination number. The Sn–P bonds in 2 are somewhat longer than the equatorial Sn–P bonds (2.602 (2), 2.598 (2) Å) and shorter than the axial bonds (2.790 (2), 2.839 (2) Å) in $Sn[C(PMe_2)_3]_2$. Although a few other compounds containing Sn(II)–P bonds have been described,[9] no other structural data on Sn(II)–P bond lengths are available for comparison. Compounds with structurally characterized σ-Pb(II)–C and Pb(II)–P bonds are, to our knowledge, unknown.[10,11] The Pb(II)–C bond in 3 is longer than the

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Pb(IV)–P bonds in $Pb(CH_3)_4$ (2.238 (9) Å)[12] and $Pb(C_6H_5)_4$ (2.19 (3) Å),[13] and the Pb(II)–P bonds in **3** are slightly longer than the Pb(IV)–P bonds (2.611 Å) in $P_7(PbMe_3)_3$.[11]

For **2** the ^{31}P NMR spectrum at 0 °C (toluene) shows two triplets with ^{119}Sn and ^{117}Sn satellites at δ_1 −10.3 (^3J(P,P) = 25 Hz, ^2J(Sn,P) = 276, 336 Hz (C-bound ligand)) and δ_2 −15.9 (^3J(P,P) = 25 Hz, ^2J(Sn,P) = 1106, 1158 Hz (chelating ligand)). The ^{31}P NMR spectrum of **3** at −20 °C shows two equally intense resonances with ^{207}Pb satellites at δ_1 −4.7 (^1J(Pb,P) = 1970 (chelating ligand)) and δ_2 −11.6 (^2J(Pb,P) = 165 Hz (C-bound ligand)). The complex changes occurring at other temperatures are under investigation. However since the spectrum of **3** at 30 °C consists of a single-bond resonance at −8.0 ppm, it is clear that a path for ligand interchange exists. This mechanism is under study.

We view these substances as potential ligands with the three-coordinate phosphorus atoms, the three-coordinate carbon, and the metal (tin or lead) centers as binding sites. The coordination properties of **2** and **3** toward transition-metal ions are under active investigation.

Acknowledgment. We thank the National Science Foundation (Grants CHE 8217954 and CHE 8519557) for support.

Supplementary Material Available: Listings of the final atomic coordinates, bond distances and angles, and thermal parameters (12 pages); listings of observed and calculated sturcture factors (36 pages). Ordering information is given on any current masthead page.

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Zinc-Promoted Reductive Coupling Reactions. Reaction of Sodium Methoxyalkenyldialkylborates(1−) with Alkenylzinc Chlorides or Zinc Chloride[†]

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Summary: Sodium methoxyalkenyldialkylborates(1−) react with alkenylzinc chlorides or zinc chloride to provide excellent yields of symmetrical 1,3-dienes in an unprecedented reductive coupling process.

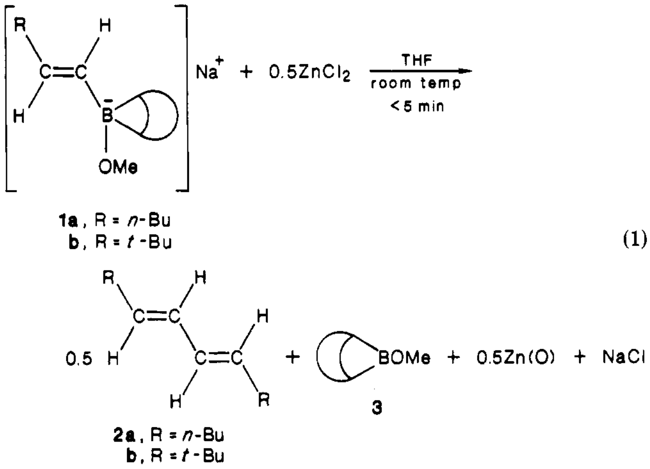
As part of an ongoing synthetic project in our laboratories, we sought entries into alkenylzinc halide reagents which would allow incorporation of a variety of functional groups within the alkenylzinc halide itself. One potential route to alkenylzinc halides we envisioned involved transmetalation from corresponding alkenylboron "ate" complexes.[1] Alkenylboron "ate" complexes can be stereoselectively accessed and utilized in ways permitting incorporation of a number of sensitive functional groups (e.g., halides, esters, and nitriles) within these species.[2] Success of the procedure was expected to greatly expand general routes to functionalized, stereodefined alkenylzinc halides.

Table I. Synthesis of Symmetrical Dienes via Zinc-Promoted Reductive Coupling Reactions[a]

alkyne	% GC yield (isolated) of **2**
1-hexyne	100
3,3-dimethyl-1-butyne	80
5-chloro-1-pentyne	93
phenylacetylene	80 (75)

[a] Reactions performed according to eq 2. Yields are based on 1-alkyne. Satisfactory spectral data were obtained for all compounds.[1c]

In our first attempt, the boron "ate" complex derived by addition of (*E*)-*B*-1-hexenyl-9-borabicyclo[3.3.1]nonane [(*E*)-*B*-1-hexenyl-9-BBN, **1a**] to NaOMe in THF was added to 1 equiv of $ZnCl_2$. To our surprise, an immediate precipitate of Zn(0) appeared. Detailed analysis of the reaction mixture revealed the presence of (*E*,*E*)-5,7-dodecadiene (**2a**) in virtually quantitative yield, along with *B*-methoxy-9-BBN (**3**) and (presumably) NaCl. As suggested by the stoichiometry of the reaction, reductive coupling can be achieved with 0.5 equiv of $ZnCl_2$. This protocol, too, provides quantitative generation of symmetrical dienes. Although similar coupling reactions utilizing copper salts[3] and silver salts[4] are well-known, the present result represents an unprecedented example of zinc-promoted reductive coupling.[5] Synthesis of a number of conjugated dienes can be accomplished without isolation of intermediates by utilizing dicyclohexylborane in THF as the hydroborating agent in conjunction with 1-alkynes.[6] Addition of the (*E*)-1-alkenyldicyclohexylborane solution



(1)

[†] Dedicated to Professor George Zweifel, on the occasion of his 60th birthday.

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