Dalton Transactions

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Journal:	*Dalton Transactions*
Manuscript ID	DT-ART-02-2019-000678.R2
Article Type:	Paper
Date Submitted by the Author:	22-Apr-2019
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Reactivity of the Carbodiphosphorane, $(Ph_3P)_2C$, towards Main Group Metal Alkyl Compounds: Coordination and Cyclometalation[‡]

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Received xxxx xx, 2019.

Abstract: The carbodiphosphorane, $(Ph_3P)_2C$, reacts with Me_3Al and Me_3Ga to afford the adducts, $[(Ph_3P)_2C]AlMe_3$ and $[(Ph_3P)_2C]GaMe_3$, which have been structurally characterized by X-ray diffraction. $(Ph_3P)_2C$ also reacts with Me_2Zn and Me_2Cd to generate an adduct but the formation is reversible on the NMR time scale. At elevated temperatures, however, elimination of methane and cyclometalation occurs to afford $[\kappa^2\text{-}Ph_3PC\{PPh_2(C_6H_4)\}]ZnMe$ and $[\kappa^2\text{-}Ph_3PC\{PPh_2(C_6H_4)\}]CdMe$. Analogous cyclometalated products, $[\kappa^2\text{-}Ph_3P\{CPPh_2(C_6H_4)\}]ZnN(SiMe_3)_2$ and $[\kappa^2\text{-}Ph_3P\{CPPh_2(C_6H_4)\}]CdN(SiMe_3)_2$, are also obtained upon reaction of $(Ph_3P)_2C$ with $Zn[N(SiMe_3)_2]_2$ and $Cd[N(SiMe_3)_2]_2$. The magnesium compounds, Me_2Mg and $\{Mg[N(SiMe_3)_2]_2\}_2$, likewise react with $(Ph_3P)_2C$ to afford cyclometalated derivatives, namely $[\kappa^2\text{-}Ph_3PC\{PPh_2(C_6H_4)\}]MgN(SiMe_3)_2$ and $\{[\kappa^2\text{-}Ph_3PC\{PPh_2(C_6H_4)\}]MgMe\}_2$. While this reactivity is similar to the zinc system, the magnesium methyl complex is a dimer with bridging methyl groups, whereas the zinc complex is a monomer. The greater tendency of the methyl groups to bridge magnesium centers rather than zinc centers is supported by density functional theory calculations.

[‡]Dedicated to F. Geoffrey N. Cloke on the occasion of his 65th birthday. Happy birthday, Geoff!

INTRODUCTION

Carbodiphosphoranes, $(R_3P)_2C$,[1-6] are a class of molecules which feature two-coordinate carbon atoms that are formally zerovalent with two lone pairs (Figure 1).[7] As such, carbodiphosphoranes are distinct from carbenes that are divalent and possess a sextet configuration.[8] The presence of the lone pairs allows carbodiphosphoranes to serve as ligands for metal centers and coordination through either one or both lone pairs is possible (Figure 1).[9-18] Furthermore, consideration of the Tolman electronic parameter[19,20] indicates that carbodiphosphoranes are more strongly electron donating than many PR_3[20] and *N*-heterocyclic carbene ligands.[21,22] In addition to the strong donor properties, analysis of buried volumes indicates that the hexaphenylcarbodiphosphorane, $(Ph_3P)_2C$, is more sterically demanding than many PR_3 and *N*-heterocyclic carbene ligands.[22] Despite these favorable features, however, the majority of studies have focused on the transition metals (and in particular the late transition metals, *e.g.* Pt and Au) rather than main group metals.[23] Therefore, we describe here the application of $(Ph_3P)_2C$ to the organometallic chemistry of magnesium, zinc, cadmium, aluminum, and gallium.

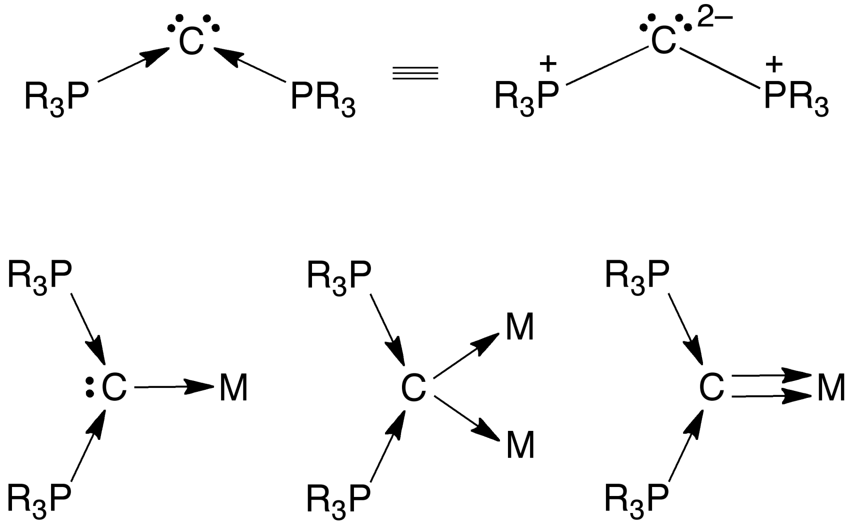
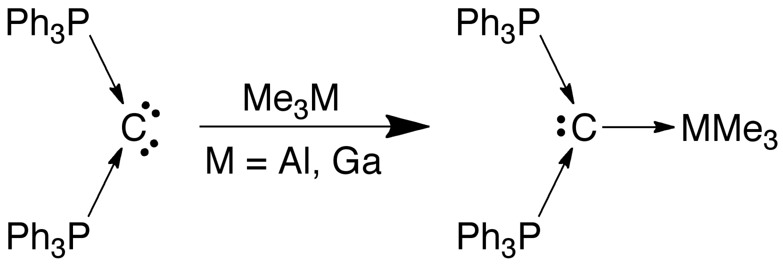


Figure 1. Carbodiphosphoranes and their coordination modes.

RESULTS AND DISCUSSION

1. Reactivity of $(Ph_3P)_2C$ towards Group 13 Metal Compounds

$(Ph_3P)_2C$ reacts readily with Me_3Al and Me_3Ga to afford respectively $[(Ph_3P)_2C]AlMe_3$ and $[(Ph_3P)_2C]GaMe_3$ (Scheme 1), which have been structurally characterized by X-ray diffraction (Figure 2 and Figure 3). The formation of the simple adducts, $[(Ph_3P)_2C]AlMe_3$ and $[(Ph_3P)_2C]GaMe_3$, is noteworthy because the analogous product was not isolated from the corresponding reaction of $(Me_3P)_2C$ with $Me_3Ga(OEt_2)$.[24] Specifically, the latter reaction is accompanied by elimination of methane that is associated with C–H cleavage of the PMe_3 moieties, thereby resulting in the formation of a cyclic compound, $[\kappa^2\text{-}HC(PMe_2CH_2)_2]GaMe_2$, which is devoid of a $C\rightarrow Ga$ dative interaction.[24,25,26] Although $(Ph_3P)_2C$ adducts of trialkyl aluminum and gallium derivatives have not previously been structurally characterized, the molecular structure of the indium counterpart, $[(Ph_3P)_2C]InMe_3$,[27] has been reported, as have the halide derivatives, $[(Ph_3P)_2C]AlBr_3$[27] and $[(Ph_3P)_2C]GaCl_3$.[22] Structural data for these $[(Ph_3P)_2C]MX_3$ compounds are summarized in **Table 1**, which indicate that the metal centers are approximately tetrahedral (with τ_4 and τ_δ parameters[28] close to unity), while the carbon donors are approximately trigonal planar (with the sums of bond angles close to 360°).



Scheme 1.

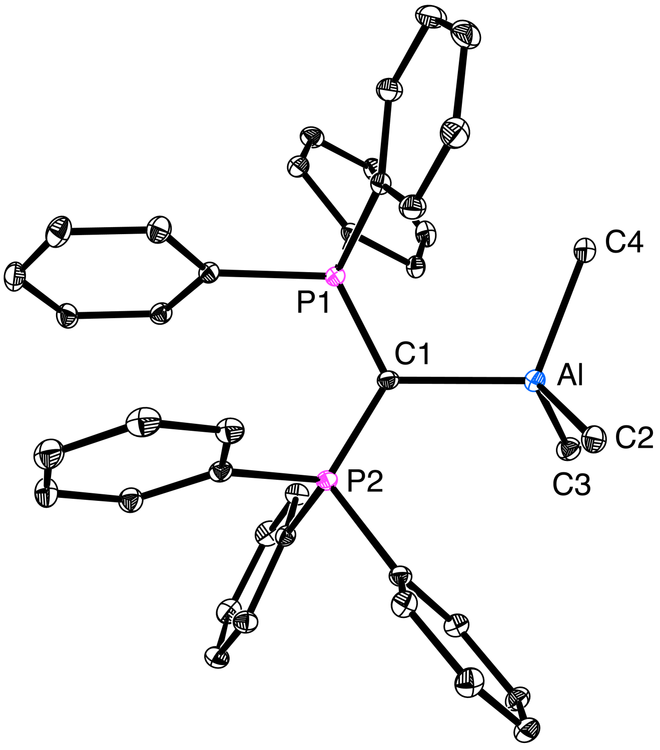


Figure 2. Molecular structure of $[(Ph_3P)_2C]AlMe_3$.

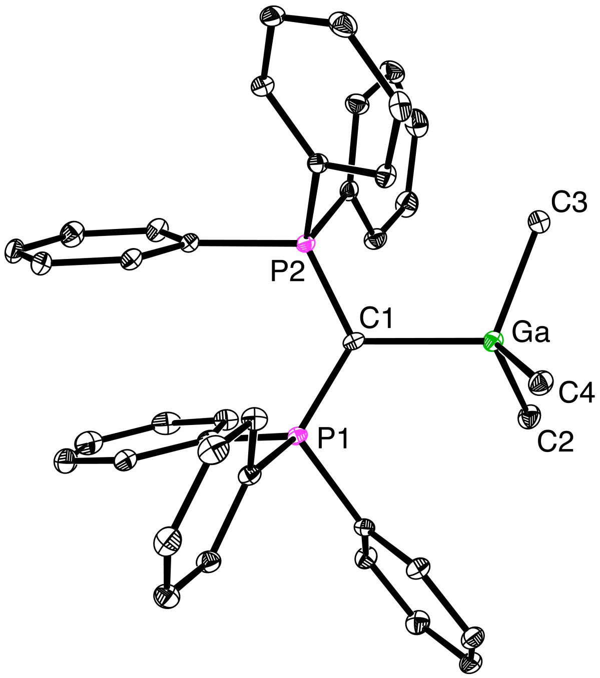


Figure 3. Molecular structure of $[(Ph_3P)_2C]GaMe_3$.

Table 1. Selected metrical data for $[(Ph_3P)_2C]MX_3$ (M = B, Al, Ga, In) and related compounds.

	M–C^a /Å	**M–X^b Avg. /Å**	**P–C–P /°**	**Σ(P–C–Y)^c/°**	**τ_4**	**τ_δ**	**Ref**
$[(Ph_3P)_2C]BH_3$	1.673(4)	1.16(4)	130.5(2)	359.0	0.94	0.93	29
$[(Ph_3P)_2C]AlMe_3$	2.0957(17)	2.006(17)	122.36(9)	360.0	0.97	0.96	this work
$[(Ph_3P)_2C]GaMe_3$	2.1338(19)	2.020(2)	122.85(11)	360.0	0.97	0.94	this work
$[(Ph_3P)_2C]InMe_3$	2.332(3)	2.207(3)	124.2(2)	359.7	0.95	0.92	27
$[(Ph_3P)_2C]AlBr_3$	1.969(3)	2.326(1)	119.5(2)	360.0	0.93	0.92	27
$[(Ph_3P)_2C]GaCl_3$	1.981(1)	2.2062(4)	122.46(7)	360.0	0.93	0.92	22
$[(Ph_2P–(CH_2)_3–PPh_2)C]GaCl_3$	1.947(1)	2.2147(4)	116.70(8)	359.9	0.91	0.88	22

(a) Carbodiphosphorane carbon.

(b) X = H, Me, Cl, or Br.

(c) Y = P or M.

The planarity of the carbodiphosphorane carbon atom suggests the possibility that the lone pair could also participate in π-bonding with the metal centers.[30] However, a π-interaction within $[(Ph_3P)_2C]AlMe_3$ is precluded by the unavailability of a suitable acceptor orbital on the metal center. The M–$C(PPh_3)_2$ bond lengths are thus distinctly longer than the corresponding M–CH_3 bond lengths. For example, the Al–$C(PPh_3)_2$ bond length of $[(Ph_3P)_2C]AlMe_3$ is 2.0957(17) Å whereas the Al–Me bond lengths range from 1.9887(17) to 2.0190(17), with an average value of 2.006 Å. As such, the carbodiphosphorane coordinates *via* a single $(Ph_3P)_2C{\rightarrow}M$ dative covalent bond. Dative covalent bonds are known to be variable and longer than corresponding normal covalent bonds,[31] and a similar trend is observed for *N*-heterocyclic carbene derivatives, $(NHC)MR_3$, for which the $M–C_{NHC}$ bond lengths are longer than the corresponding M–R values.[32,33] As an illustration, bond length data for $(NHC)AlMe_3$ derivatives are listed in Table 2.

Table 2. Comparison of Al–C bond lengths in $[(Ph_3P)_2C]AlMe_3$ and $(NHC)AlMe_3$.

	***d*[Al–C(PPh$_3$)$_2$]/Å**	***d*(Al–Me)$_{av}$/Å**	**Reference**
$[(Ph_3P)_2C]AlMe_3$	2.0957(17)	2.006	this work
$(IPr^{Me})AlMe_3$	2.124(6)	2.001	33a
$(IMes)AlMe_3$	2.097(2)	1.983	34
$(IBu^t)AlMe_3$	2.162(2)	2.000	35

Density functional theory geometry optimization calculations on $[(Ph_3P)_2C]MMe_3$ (Figure 4 and Table 3) support the proposed bonding description of a single dative covalent bond. For example, the calculated $Al–C(PPh_3)_2$ bond length of $[(Ph_3P)_2C]AlMe_3$ (2.161 Å) is longer than the Al–Me bond length (2.022 Å), and analysis of the molecular orbitals indicates that the HOMO is essentially a 2p lone pair on carbon and there is no overlap with an orbital on aluminum (Figure 5).

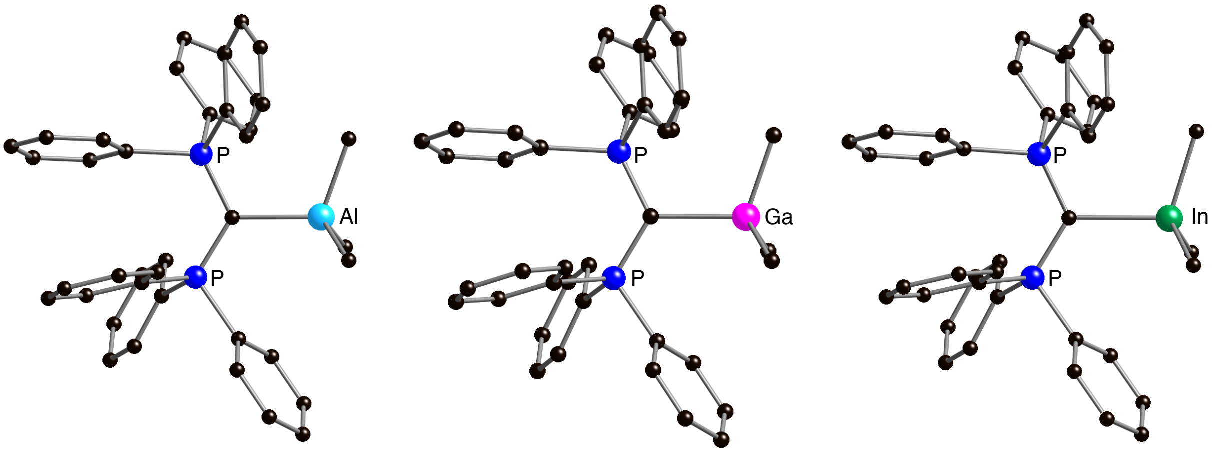


Figure 4. Geometry optimized structures of $[(Ph_3P)_2C]MMe_3$ (hydrogen atoms omitted for clarity).

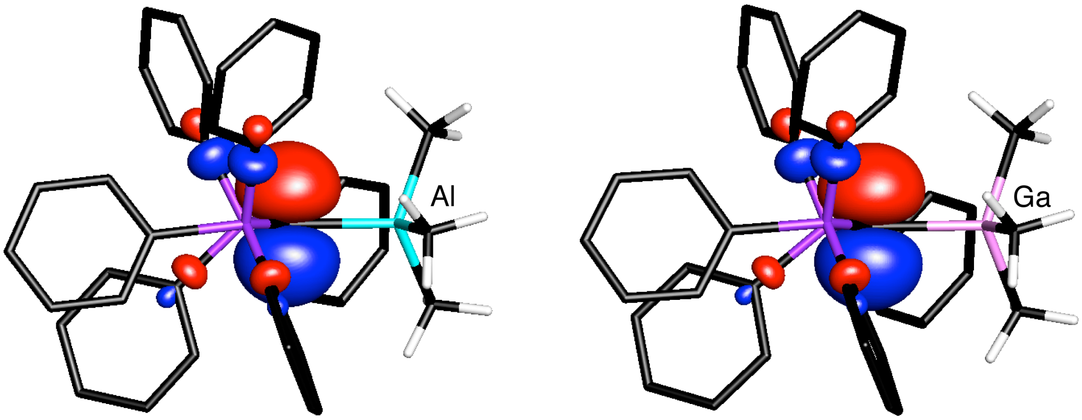


Figure 5. HOMOs of $[(Ph_3P)_2C]AlMe_3$ (left) and $[(Ph_3P)_2C]GaMe_3$ (right). Aromatic hydrogen atoms omitted for clarity.

Table 3. Bond lengths for geometry optimized $[(Ph_3P)_2C]MX_3$.

	$d[M–C(PPh_3)_2]$/Å	$d(M–X)_{av}$/Å
$[(Ph_3P)_2C]AlMe_3$	2.161	2.022
$[(Ph_3P)_2C]AlF_3$	2.014	1.692
$[(Ph_3P)_2C]AlCl_3$	2.020	2.182
$[(Ph_3P)_2C]AlBr_3$	2.018	2.378
$[(Ph_3P)_2C]GaMe_3$	2.239	2.036
$[(Ph_3P)_2C]GaF_3$	2.025	1.735
$[(Ph_3P)_2C]GaCl_3$	2.025	2.236
$[(Ph_3P)_2C]GaBr_3$	2.023	2.458
$[(Ph_3P)_2C]InMe_3$	2.429	2.203
$[(Ph_3P)_2C]InF_3$	2.211	1.866
$[(Ph_3P)_2C]InCl_3$	2.202	2.377
$[(Ph_3P)_2C]InBr_3$	2.204	2.606

In accord with the dative covalent nature of the interaction, the $M–C(PPh_3)_2$ bond lengths of $[(Ph_3P)_2C]MX_3$ depend upon the nature of X.[31] Thus, the $M–C(PPh_3)_2$ bond lengths of the methyl complexes $[(Ph_3P)_2C]MMe_3$ are distinctly longer than the values in the corresponding halide derivatives, $[(Ph_3P)_2C]MX_3$. For example, the $Al–C(PPh_3)_2$ bond length of $[(Ph_3P)_2C]AlMe_3$ [2.0957(17) Å] is 0.13 Å longer than that in $[(Ph_3P)_2C]AlBr_3$ [1.969(3) Å].[27] Similar trends are also observed in *N*-heterocyclic carbene compounds, with $M–C_{NHC}$ bond lengths in halide derivatives, $(NHC)MX_3$, being shorter than those in corresponding alkyl derivatives, $(NHC)MR_3$.[32] Such differences are not restricted to carbon donors and are in accord with other systems that contain dative bonds. For example, the Me_3N–B bond in Me_3NBCl_3 (1.66 Å and 1.65 Å for two independent studies) is shorter than that in Me_3NBMe_3 (1.70 Å).[31] Moreover, the py–B bond in $pyBCl_3$ (38 kcal mol^{-1}) is considerably stronger than that in $pyBMe_3$ (17 kcal mol^{-1}).[31]

Density functional theory geometry optimization calculations on $[(Ph_3P)_2C]MX_3$ reproduce the trends in bond lengths (Table 3). For example, the Al–$C(PPh_3)_2$ bond length of $[(Ph_3P)_2C]AlMe_3$ (2.161 Å) is 0.14 Å longer than that in $[(Ph_3P)_2C]AlBr_3$ (2.018 Å). Furthermore, coordination of $(Ph_3P)_2C$ to the halide derivatives, AlX_3, is computed to be more exothermic than is coordination to $AlMe_3$ (Table 4), which is in accord with the report that $AlCl_3$ is more Lewis acidic than AlR_3.[36,37,38]

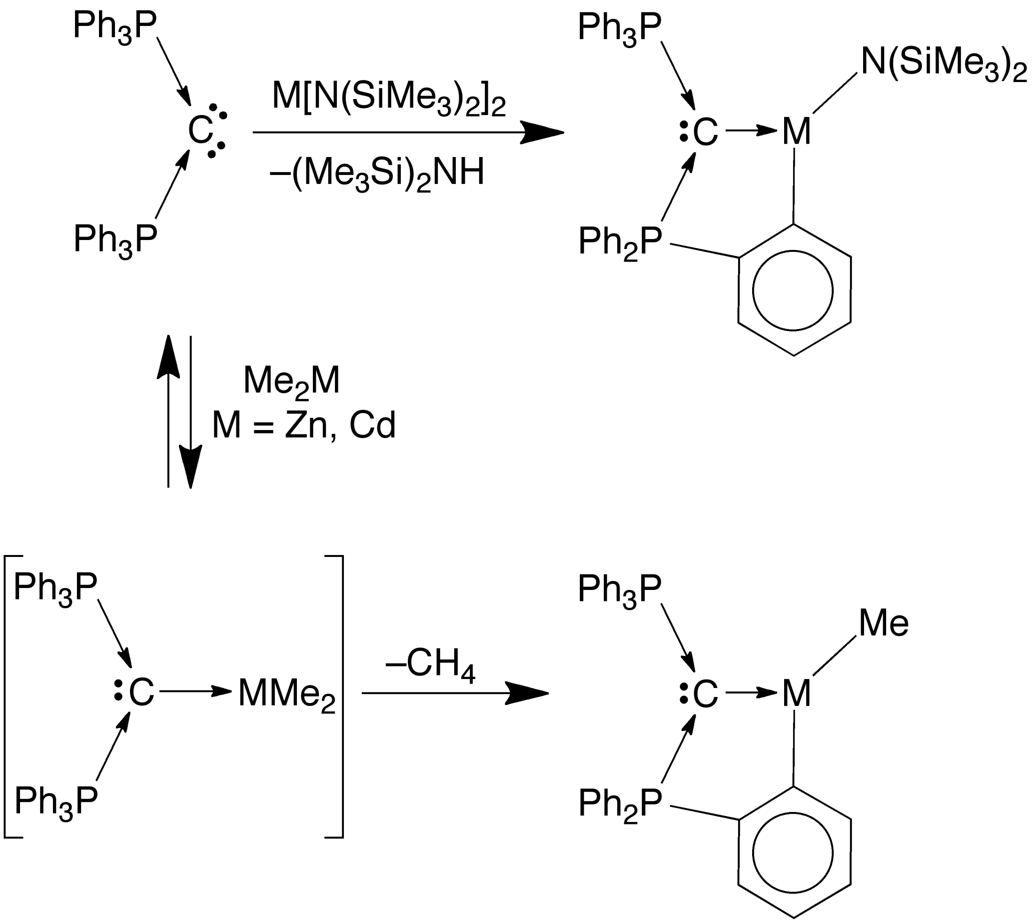
Table 4. ΔE_{SCF} (kcal mol^{-1}) for formation of $[(Ph_3P)_2C]MX_3$ from $(Ph_3P)_2C$ and MX_3.

	Me	**F**	**Cl**	**Br**
Al	–16.9	–60.8	–48.8	–47.7
Ga	–11.5	–61.8	–50.3	–51.4
In	–12.8	–57.8	–49.3	–50.2

Another noteworthy aspect of the molecular structures of $[(PPh_3)_2C]EX_3$ (E = B, Al, Ga, In) is that the increases in both M–$C(PPh_3)_2$ and M–X bond lengths between aluminum and gallium compounds, $[(PPh_3)_2C]AlX_3$ and $[(PPh_3)_2C]GaX_3$, are significantly smaller than the increases between other congeneric pairs (**Table 1**). For example, the increase in M–$C(PPh_3)_2$ bond length between $[(PPh_3)_2C]AlMe_3$ and $[(PPh_3)_2C]GaMe_3$ is only 0.038 Å, whereas the difference between $[(PPh_3)_2C]BH_3$ and $[(PPh_3)_2C]AlMe_3$ is 0.423 Å, and the difference between $[(PPh_3)_2C]GaMe_3$ and $[(PPh_3)_2C]InMe_3$ is 0.198 Å. The corresponding differences in average M–Me bond lengths for $[(PPh_3)_2C]MMe_3$ are 0.014 Å for $[(PPh_3)_2C]AlMe_3$ and $[(PPh_3)_2C]GaMe_3$, and 0.187 Å for $[(PPh_3)_2C]GaMe_3$ and $[(PPh_3)_2C]InMe_3$. These observations are, nevertheless, in accord with the fact that the covalent radii of aluminum and gallium are very similar[39,40] due to the scandide contraction,[41,42] which is a counterpart of the lanthanide contraction. Specifically, the increases in covalent radii[39] between B, Al, Ga and In are irregular: 0.37 Å (B/Al), 0.01 Å (Al/Ga) and 0.20 Å (Ga/In).

2. Reactivity of $(PPh_3)_2C$ towards Group 12 Metal Compounds

In contrast to the reactivity of $(Ph_3P)_2C$ towards Me_3M (M = Al, Ga) to afford isolable adducts, $[(PPh_3)_2C]MMe_3$, $(Ph_3P)_2C$ does not bind effectively to Me_2M (M = Zn, Cd). Thus, whereas $[(Ph_3P)_2C]AlMe_3$ and $[(Ph_3P)_2C]GaMe_3$ can be isolated in the solid state, the coordination of $(Ph_3P)_2C$ to Me_2Zn is readily reversible such that the $^{31}P\{^1H\}$ NMR spectra of solutions composed of a mixture of $(Ph_3P)_2C$ and Me_2M (M = Zn, Cd) vary with the quantities present (Scheme 2). This observation is supported by DFT calculations which indicate that coordination of $(Ph_3P)_2C$ to Me_3Al and Me_3Ga is more thermodynamically favored than is coordination to either Me_2Zn or Me_2Cd (Table 5). The stronger binding of $(Ph_3P)_2C$ to the Group 13 metal centers is also in accord with the greater Lewis acidity of Me_3Al as compared to Me_2Zn and Me_2Cd.[43] Despite the facile reversibility of coordination of $(Ph_3P)_2C$ to Me_2Zn and Me_2Cd, however, adducts of ZnI_2 and CdI_2, namely $[(Ph_3P)_2C]ZnI_2$ and $\{[(Ph_3P)_2C]CdI_2\}_2$, have been reported.[44,45] Furthermore, the cyclic carbodiphosphorane, $H_2C(CH_2PPh_2)_2C$, coordinates to Me_2Zn and Me_2Cd to afford dimeric adducts, $\{[H_2C(CH_2PPh_2)_2C]ZnMe_2\}_2$ and $\{[H_2C(CH_2PPh_2)_2C]CdMe_2\}_2$, although these compounds have not been structurally characterized by X-ray diffraction.[46,47,48]



Scheme 2.

Table 5. ΔE_{SCF} (kcal mol^{-1}) for formation of $[(Ph_3P)_2C]MMe_n$ from $(Ph_3P)_2C$ and Me_nM.

	$[(Ph_3P)_2C]MMe_n$
$AlMe_3$	–16.9
$GaMe_3$	–11.5
$ZnMe_2$	–10.7
$CdMe_2$	–6.5

While the initial interaction between $(Ph_3P)_2C$ and Me_2Zn is reversible, orthometalation and elimination of methane occurs at 80°C, resulting in the formation of the three-coordinate zinc methyl complex, $[\kappa^2\text{-}Ph_3PC\{PPh_2(C_6H_4)\}]ZnMe$ (Scheme 2), which has been structurally characterized by X-ray diffraction (Figure 6). Spectroscopically, [κ^2-$Ph_3PC\{PPh_2(C_6H_4)\}$]ZnMe is characterized by a signal at δ –0.30 ppm in the ^{1}H NMR spectrum attributable to the zinc methyl group, and two doublets at 13.33 and 26.03 ppm for the cyclometalated [κ^2-$Ph_3PC\{PPh_2(C_6H_4)\}$] ligand in the $^{31}P\{^1H\}$ NMR spectrum. NMR spectroscopic studies indicate that $(Ph_3P)_2C$ reacts with Me_2Cd in a similar manner to that of Me_2Zn.

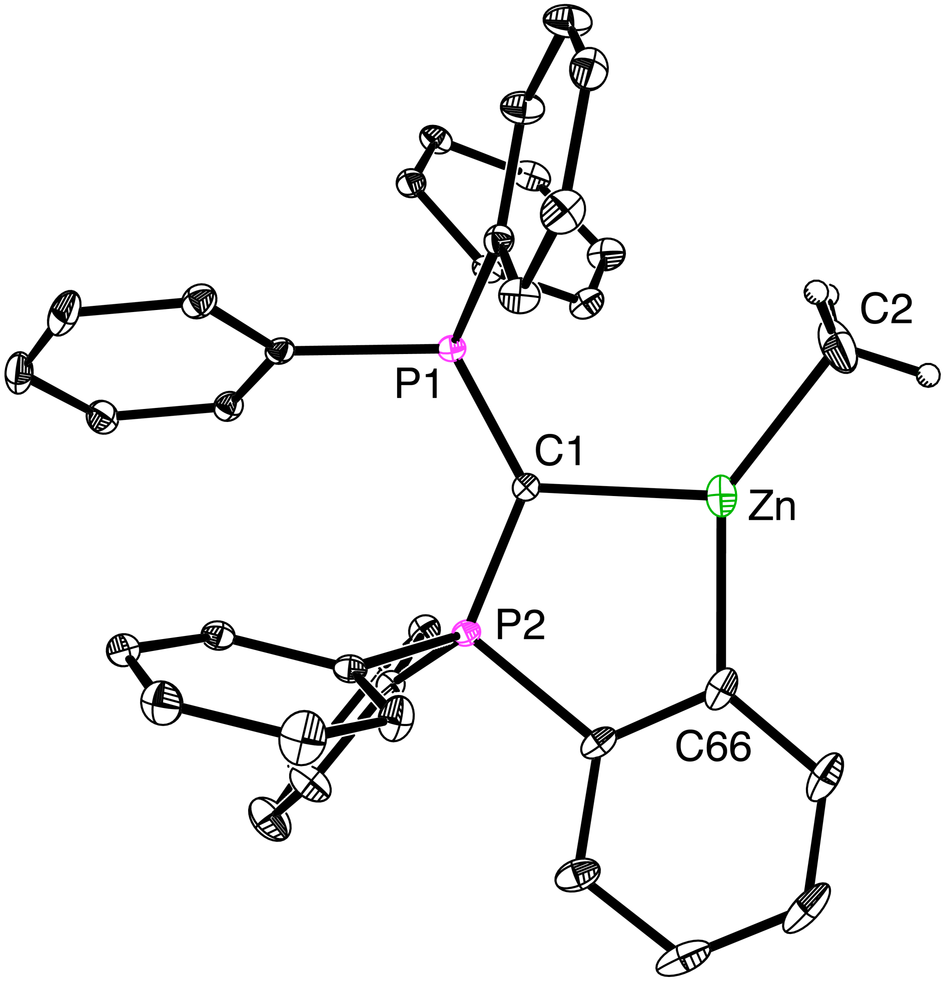


Figure 6. Molecular structure of [κ^2-$Ph_3PC\{PPh_2(C_6H_4)\}$]ZnMe.

[κ^2-$Ph_3PC\{PPh_2(C_6H_4)\}$] is an uncommon example of a bidentate κ^2–*C*,*C* ligand that belongs to the LX covalent bond classification.[49,50] Furthermore, [κ^2-$Ph_3PC\{PPh_2(C_6H_4)\}$]ZnMe is noteworthy because this ligand motif has only previously been structurally characterized for noble metal complexes, and specifically those of Rh, Pd and Pt.[51,52,53] The formation of [κ^2-$Ph_3PC\{PPh_2(C_6H_4)\}$]ZnMe also provides an interesting contrast to the reactivity observed for other carbodiphosphoranes. For example, while the reactions of $(Me_3P)_2C$ with R_2M (M = Zn, Cd; R = Me, Et) are likewise accompanied by elimination of alkane, the transformations involve the transfer of a hydrogen to the carbodiphosphorane carbon atom to afford [κ^2-$HC(PMe_2CH_2)_2]_2M$ (M = Zn, Cd), such that it no longer coordinates to the metal.[24]

With respect to the structure of [κ^2-$Ph_3PC\{PPh_2(C_6H_4)\}$]ZnMe, monomeric three-coordinate zinc methyl compounds with an all-carbon coordination environment are rare, although examples of *(i)* neutral and cationic *N*-heterocyclic carbene derivatives, $(NHC)ZnMe_2$[48c,d] and $[(NHC)_2ZnMe]^+$,[54] and *(ii)* anionic $[R_2ZnMe]^-$ derivatives[55] are known.[56] The coordination geometry of zinc in [κ^2-$Ph_3PC\{PPh_2(C_6H_4)\}$]ZnMe is close to planar ($\Sigma_{C\text{–}Zn\text{–}C} = 359.91^\circ$), but with bond angles of 141.82(12)°, 125.43(12)° and 92.67(9)°, it is severely distorted from trigonal planar. The Zn–C distances for the three different types of interactions range from 1.980(3) Å for the methyl group to 2.079(2) Å for the carbodiphosphorane carbon.[57] The fact that the latter is the longest Zn–C bond in the molecule indicates that there is no associated multiple bond character, despite the fact that the empty 4p orbital on zinc is parallel to the carbon 2p orbital. In this regard, the geometry optimized structure of [κ^2-$Ph_3PC\{PPh_2(C_6H_4)\}$]ZnMe (Figure 7) reproduces the trend in bond lengths and analysis of the molecular orbitals indicates that the HOMO is essentially the carbon 2p lone pair orbital, while the empty 4p orbital on zinc is mainly associated with LUMO+12 (Figure 8).[58,59] The absence of a π-interaction in [κ^2-$Ph_3PC\{PPh_2(C_6H_4)\}$]ZnMe is to be contrasted with that in $Zn(cAAC)_2$, which features a cyclic alkylaminocarbene (cAAC) ligand, and which possesses a Zn–C bond length of 1.8850(17) Å that is shorter than the value of 2.041(4) Å for the alkyl counterpart, $Zn(cAACH)_2$.[60] The bonding within $Zn(cAAC)_2$ has been described as a singlet biradicaloid to refer to the delocalized C–Zn–C π-interaction, in which a 3-center-2-electron bond[61] supplements the two Zn–C σ-bonds.

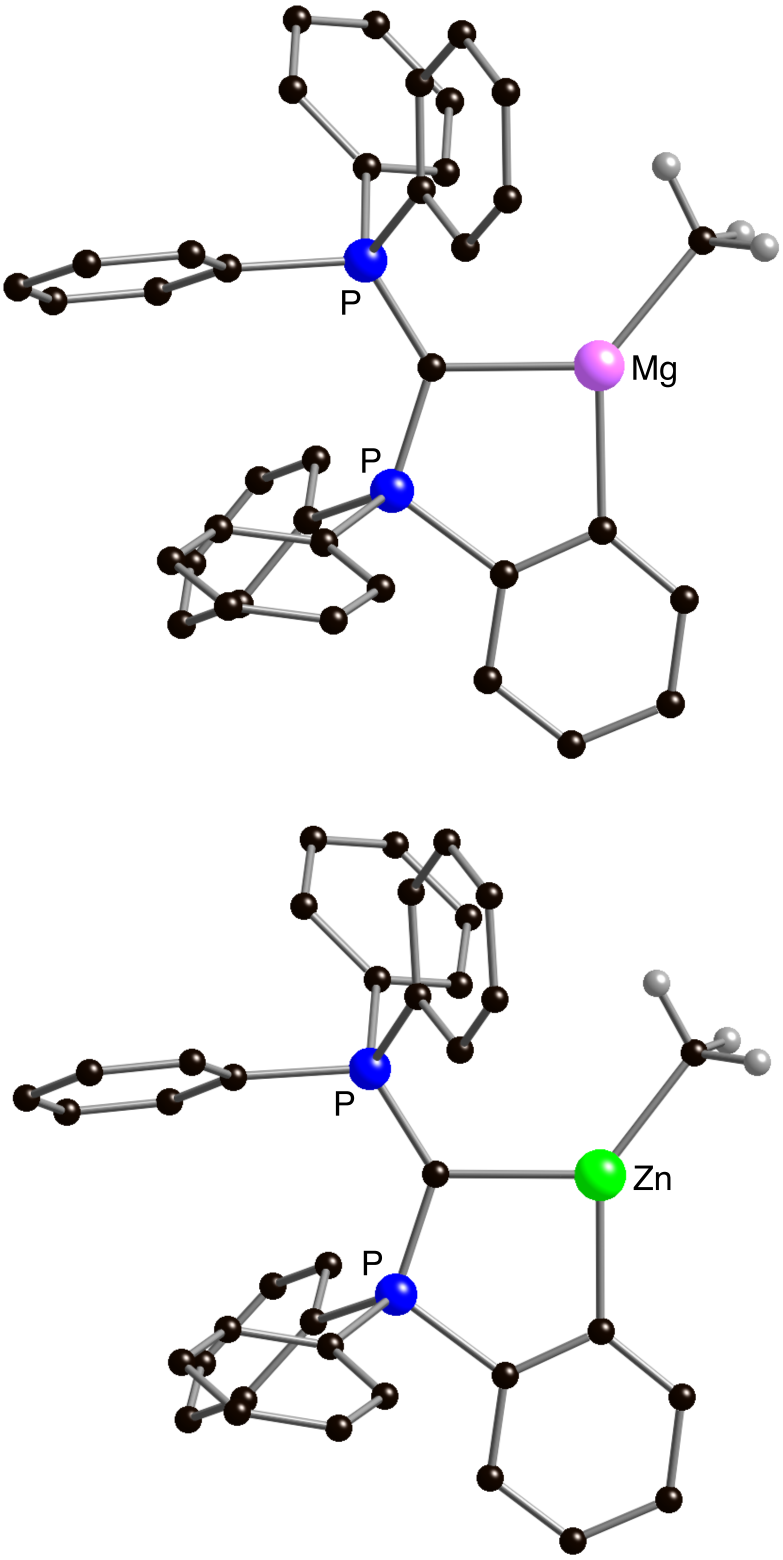
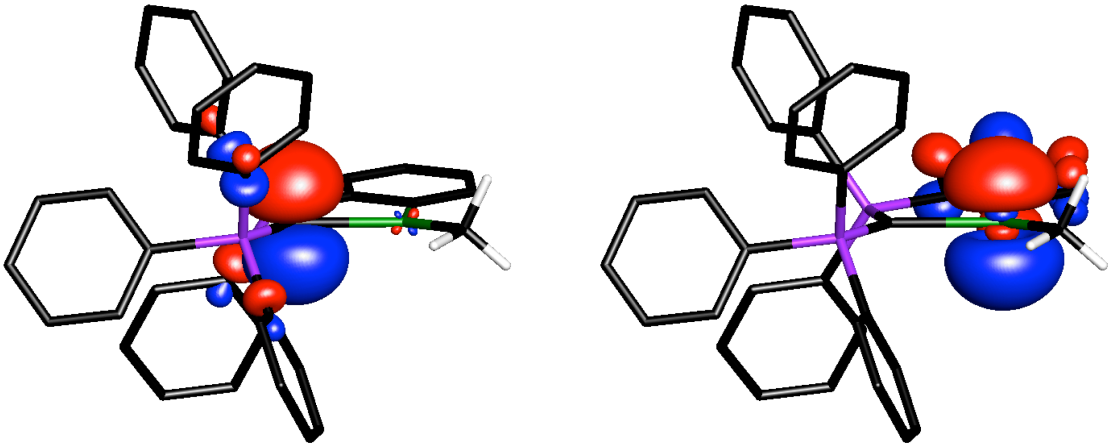


Figure 7. Geometry optimized structures of [κ^2-$Ph_3PC\{PPh_2(C_6H_4)\}$]MgMe and [κ^2-$Ph_3PC\{PPh_2(C_6H_4)\}$]ZnMe (aromatic hydrogen atoms omitted for clarity).



HOMO LUMO+12

Figure 8. HOMO and LUMO+12 of [κ^2-$Ph_3PC\{PPh_2(C_6H_4)\}$]ZnMe.

In addition to achieving orthometalation of $(Ph_3P)_2C$ by reaction with Me_2Zn, a similar product, namely [κ^2-$Ph_3PC\{PPh_2(C_6H_4)\}$]ZnN$(SiMe_3)_2$, is obtained by treatment with Zn[N$(SiMe_3)_2$]$_2$ at 60°C (Scheme 2). The molecular structure of [κ^2-$Ph_3PC\{PPh_2(C_6H_4)\}$]ZnN$(SiMe_3)_2$ has been determined by X-ray diffraction (Figure 9), thereby demonstrating that the compound is mononuclear with a three-coordinate zinc center. Zinc complexes with a Zn[C_2N] coordination environment are not common, but two relevant bis(trimethylsilyamido) derivatives are provided by neutral (NHC)Zn(Et)[N$(SiMe_3)$][62] and anionic {Bu^t_2Zn[N$(SiMe_3)$]}$^-$.[63]

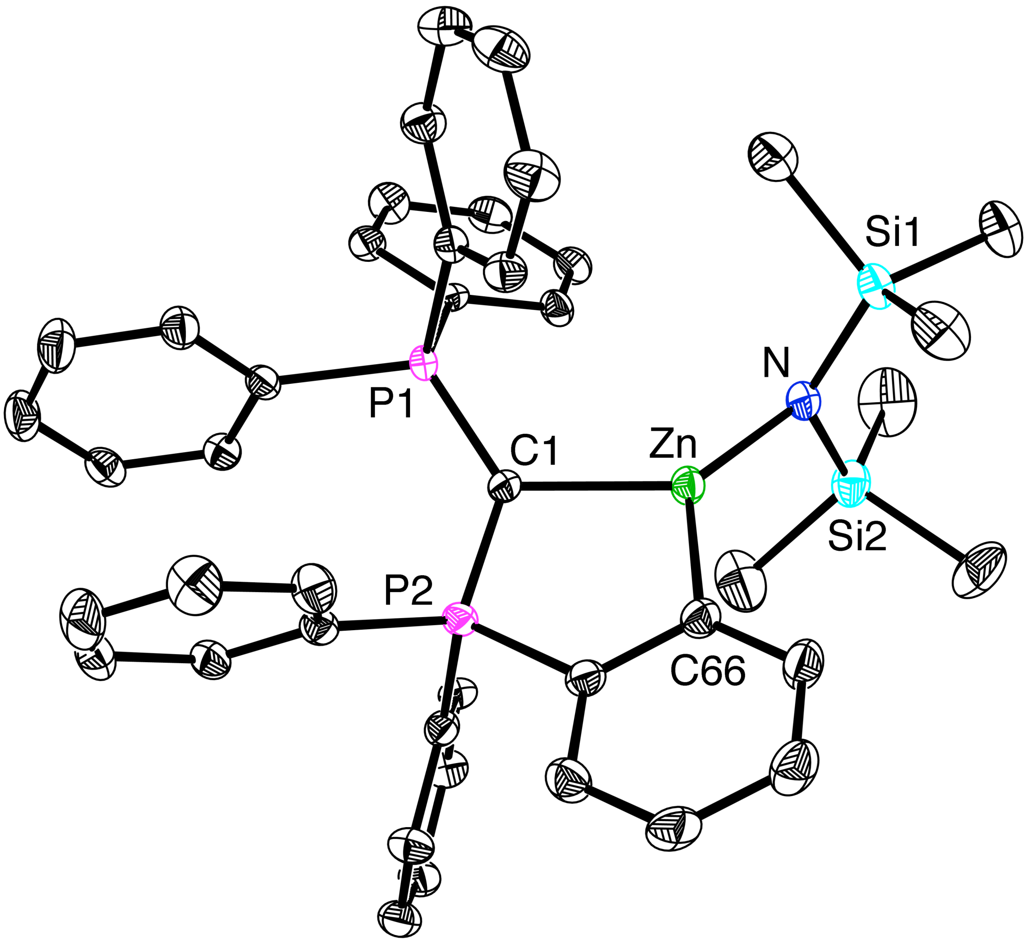
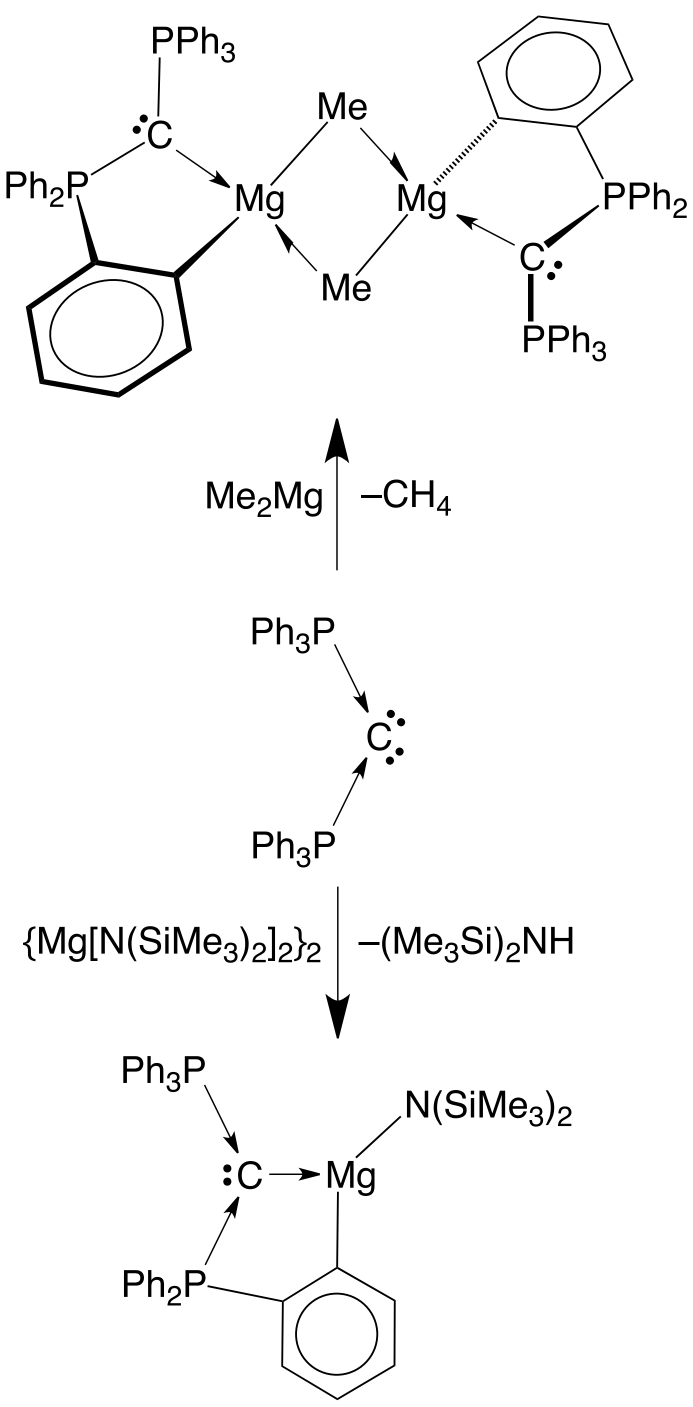


Figure 9. Molecular structure of [κ^2-$Ph_3PC\{PPh_2(C_6H_4)\}$]$ZnN(SiMe_3)_2$.

3. Reactivity of $(PPh_3)_2C$ towards Magnesium Compounds

Similar to the reactivity of $(Ph_3P)_2C$ towards Me_2Zn and $Zn[N(SiMe_3)_2]_2$, $(Ph_3P)_2C$ also reacts with Me_2Mg and $\{Mg[N(SiMe_3)_2]_2\}_2$ to afford cyclometalated derivatives, namely $\{[\kappa^2\text{-}Ph_3PC\{PPh_2(C_6H_4)\}]MgMe\}_2$ and $[\kappa^2\text{-}Ph_3PC\{PPh_2(C_6H_4)\}]MgN(SiMe_3)_2$, as illustrated in Scheme 3.[64]



Scheme 3.

The molecular structures of $\{[\kappa^2\text{-}Ph_3PC\{PPh_2(C_6H_4)\}]MgMe\}_2$ and $[\kappa^2\text{-}Ph_3PC\{PPh_2(C_6H_4)\}]MgN(SiMe_3)_2$ have been determined by X-ray diffraction (Figure 10 and Figure 11), which demonstrates that the latter is monomeric and similar to that of the zinc counterpart, $[\kappa^2\text{-}Ph_3PC\{PPh_2(C_6H_4)\}]ZnN(SiMe_3)_2$. As noted for the zinc counterpart, monomeric three-coordinate magnesium complexes with a Mg[*C*$_2$*N*] motif are also not common, but particularly relevant examples are provided by *N*-heterocyclic carbene derivatives, (NHC)Mg(R)[N(SiMe$_3$)$_2$].[33b,65,66] A particularly interesting difference between the magnesium and zinc systems, however, is that the magnesium methyl complex, {[κ^2-Ph$_3$PC{PPh$_2$(C$_6$H$_4$)}]MgMe}$_2$, is dinuclear with bridging methyl groups (Figure 10).

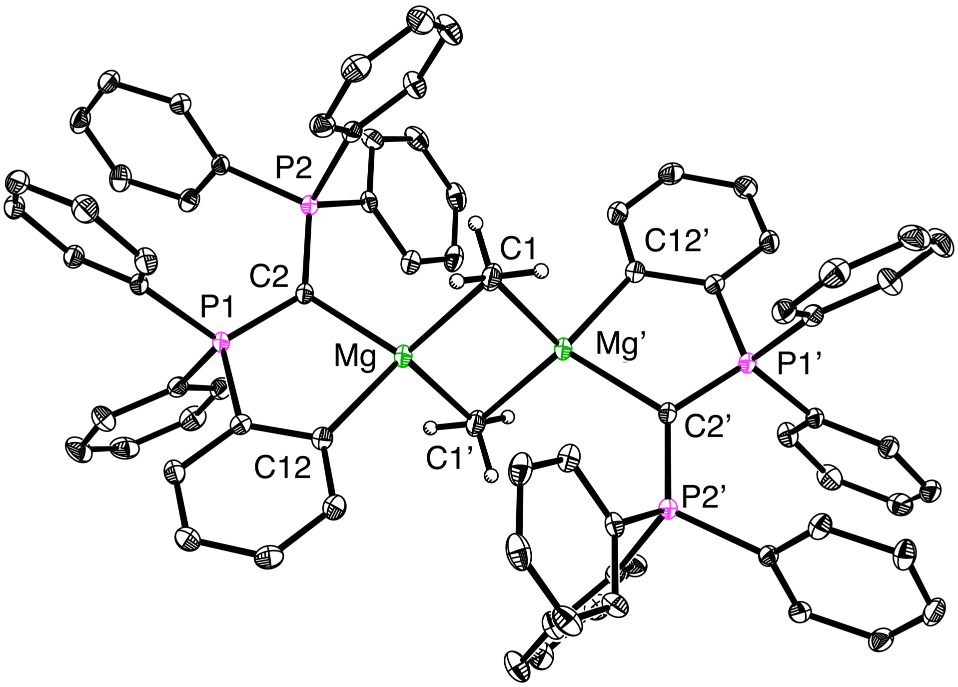


Figure 10. Molecular structure of {[κ^2-Ph$_3$PC{PPh$_2$(C$_6$H$_4$)}]MgMe}$_2$.

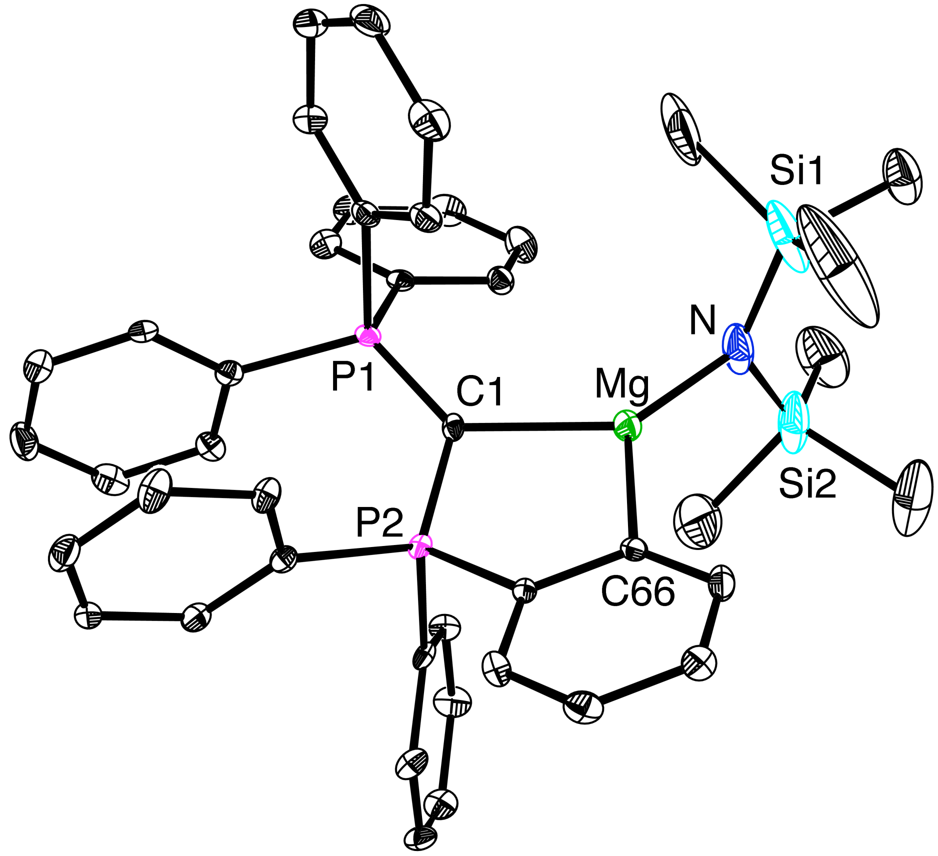
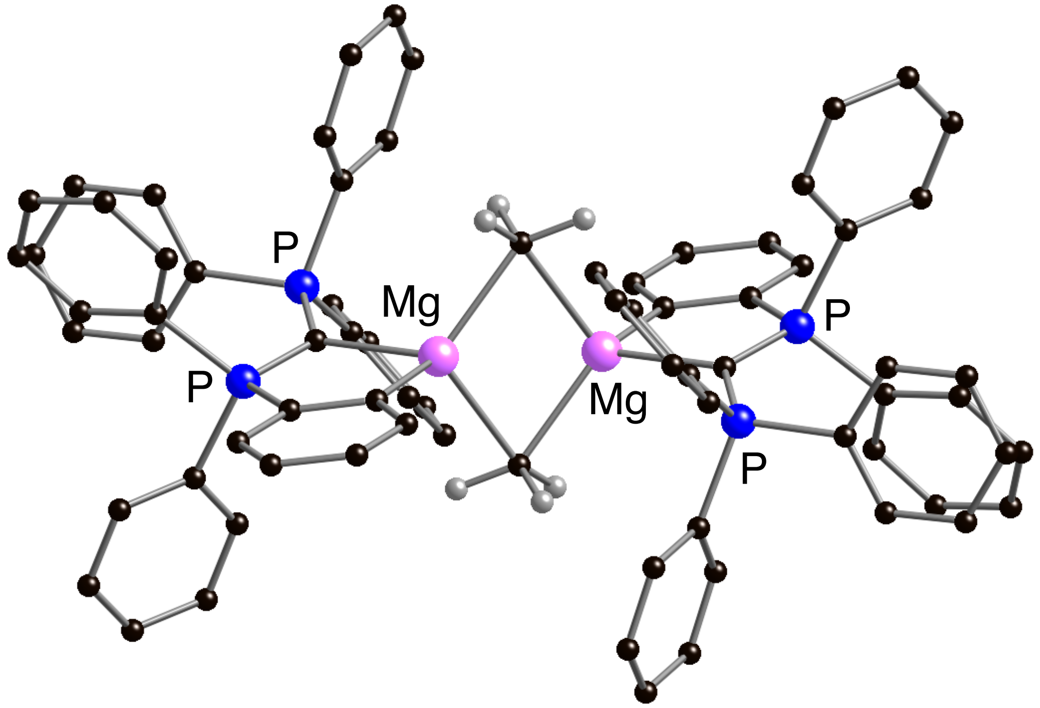


Figure 11. Molecular structure of [κ^2-Ph$_3$PC{PPh$_2$(C$_6$H$_4$)}]MgN(SiMe$_3$)$_2$.

Compounds with bridging methyl groups are known for both main group metals and transition metals, and a variety of coordination modes are possible, which include *(i)* symmetric pyramidal, *(ii)* symmetric trigonal planar, *(iii)* monohapto agostic, *(iv)* dihapto agostic, and *(v)* trihapto agostic.[61,67,68,69] In this regard, the methyl ligands of {[κ^2-Ph$_3$PC{PPh$_2$(C$_6$H$_4$)}]MgMe}$_2$ bridge in a symmetrical pyramidal manner, similar to that in most other dinuclear magnesium methyl compounds.[70,71] Selected metrical data pertaining to the Mg–Me–Mg bridge of {[κ^2-Ph$_3$PC{PPh$_2$(C$_6$H$_4$)}]MgMe}$_2$ are summarized in Table 6 and, as expected, the Mg–Me bond lengths are longer than those in terminal magnesium methyl complexes. For example, the average Mg–CH$_3$ bond length for structurally characterized terminal magnesium methyl compounds listed in the Cambridge Structural Database is 2.149 Å.[72,73,74]

The observed difference between the dinuclear magnesium and mononuclear zinc systems, $\{[\kappa^2\text{-}Ph_3PC\{PPh_2(C_6H_4)\}]MgMe\}_2$ and $[\kappa^2\text{-}Ph_3PC\{PPh_2(C_6H_4)\}]ZnMe$, is in accord with DFT calculations. Specifically, dinuclear $\{[\kappa^2\text{-}Ph_3PC\{PPh_2(C_6H_4)\}]MgMe\}_2$ is 16.8 kcal mol^{-1} more stable than is $\{[\kappa^2\text{-}Ph_3PC\{PPh_2(C_6H_4)\}]ZnMe\}_2$ (Figure 12) relative to dissociation to the mononuclear units, $[\kappa^2\text{-}Ph_3PC\{PPh_2(C_6H_4)\}]MgMe$ and $[\kappa^2\text{-}Ph_3PC\{PPh_2(C_6H_4)\}]ZnMe$ (Figure 7).[75] The lower stability of the geometry optimized dimeric zinc complex $\{[\kappa^2\text{-}Ph_3PC\{PPh_2(C_6H_4)\}]ZnMe\}_2$ is a reflection of the fact that the methyl groups do not bridge the two zinc centers in a symmetric manner, such that there are two pairs of short (2.10 Å) and long (2.90 Å) Zn–Me bonds. In contrast, the methyl groups of geometry optimized $\{[\kappa^2\text{-}Ph_3PC\{PPh_2(C_6H_4)\}]MgMe\}_2$ bridge in a symmetric manner with bond lengths (2.27 Å and 2.32 Å) that are comparable to the experimentally determined structure (2.28 Å and 2.25 Å).



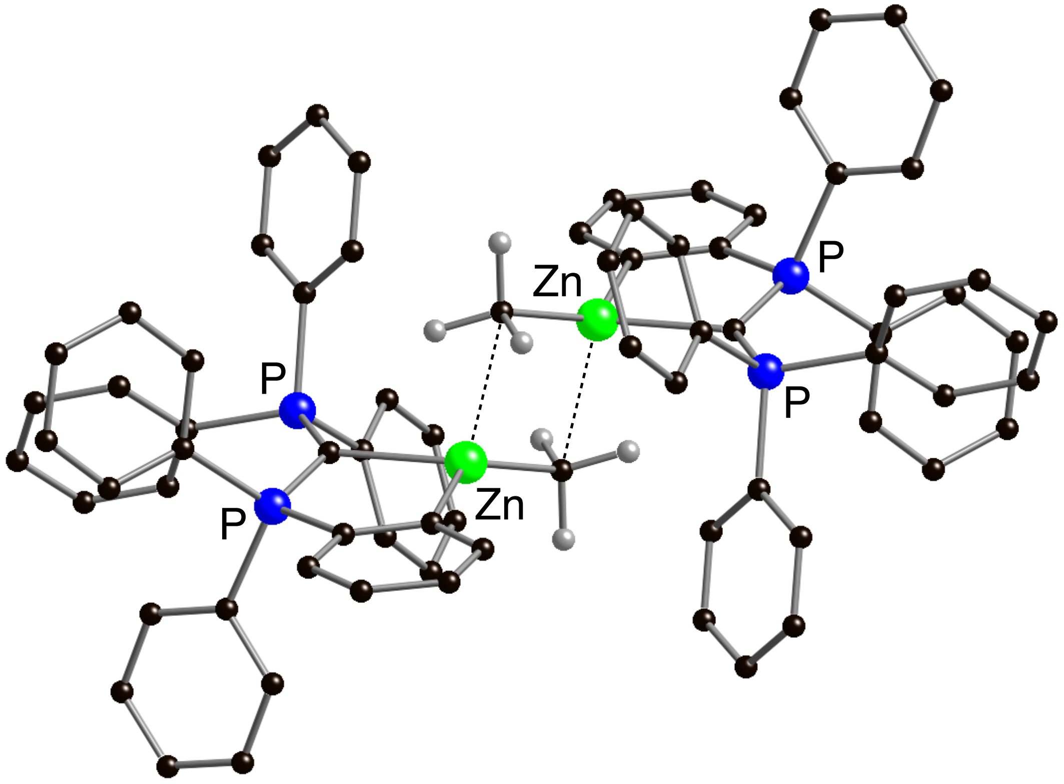


Figure 12. Geometry optimized structures of {[κ^2-Ph$_3$PC{PPh$_2$(C$_6$H$_4$)}]MgMe}$_2$ and {[κ^2-Ph$_3$PC{PPh$_2$(C$_6$H$_4$)}]ZnMe}$_2$ (aromatic hydrogen atoms omitted for clarity)

The greater propensity for alkyl groups to bridge magnesium centers than zinc centers is well known, as illustrated by the monomeric nature of Me_2Zn[76] as compared to the polymeric structure of Me_2Mg.[77] Furthermore, another example of a monomeric three-coordinate zinc methyl compound for which the magnesium counterpart is dinuclear is provided by (BDI)ZnMe[78] and $[(BDI)MgMe]_2$.[70a-c,79] The occurrence of bridged structures with multicenter bonding increases with increasing polarity of the $M^{\delta+}–C^{\delta-}$ bond,[80,81] and so the bridged nature of the magnesium complexes is a reflection of magnesium being more electropositive.[82] Similarly, the greater electropositivity of aluminum relative to gallium correlates with the observation that Me_3Ga is essentially a monomer,[83,84] whereas the aluminum derivative is a dimer with symmetrically bridging methyl groups, *i.e.* $Me_2Al(\mu–Me)_2AlMe_2$.[85,86]

Table 6. Metrical data for dinuclear magnesium compounds with bridging methyl ligands.

	***d*(Mg–C)/Å**	***d*(Mg··Mg)/Å**	**Mg–C–Mg/°**	**C–Mg–C/°**	**Ref.**
$\{[\kappa^2\text{-Ph}_3\text{PC}\{\text{PPh}_2(\text{C}_6\text{H}_4)\}]\text{-MgMe}\}_2$	2.248 2.279	2.756	74.3	105.7	This work
$[\{\text{HC}[\text{C(Me)NAr}']_2\}\text{MgMe}]_2$	2.259 2.296	2.842	77.2	102.8	70a
$[\{\text{HC}[\text{C(Me)NAr}']_2\}\text{MgMe}]_2$	2.220 2.245	2.878	80.3	99.7	70b
$[\{\text{Me}_2\text{Al(NEt}_2)_2\}\text{MgMe}]_2$	2.244 2.296	2.735	74.1	105.6	70c
$[(\text{Cp}^{\text{Me}_4\text{Et}})\text{Mg(THF)Me}]_2$	2.285	2.810	76.2	103.8	70d
$[\text{MeSi(Bu}^t\text{NAlMe}_2)(\text{Bu}^t\text{NH})(\text{Bu}^t\text{NMgMe})]_2$	2.201 2.277	2.836	78.6	101.4	70e
$[\{\text{Bo}^{\text{M}}\text{Cp}^{\text{tet}}\}\text{MgMe}]_2$	2.267 2.271	2.843	77.8	102.2	87
$[(\text{THF})\text{Mg(Me)}(\mu\text{-Me})]_2$	2.262 2.263	2.761	75.2	104.8	88
$[\text{Mg}_2(\mu\text{-Br})_2(\text{trigly})_2][\text{Mg}_2(\mu\text{-Me})_2\text{Br}_4]$	2.280	2.721	73.7	106.3	89
$[(\text{dpp-bian})\text{MgMe}]_2$	2.254 2.314	2.737	73.6	106.4	90
$[(\text{Me}_2\text{Bu}^t\text{Si})_2\text{NMgMe}]_2$	2.212	2.692	74.8	105.2	91
$[(\text{dppmflu})\text{MgMe}]_2$	2.240 2.250	2.739	75.4	104.8	92
$[\{(2,6\text{-Pr}^i_2\text{Ph})\text{BIAN}\}\text{MgMe}]_2$	2.205	2.704	74.5	105.5	93

SUMMARY

In summary, the course of the reaction between the carbodiphosphorane, $(Ph_3P)_2C$, and main group metal alkyls depends on the nature of the metal center. Thus, whereas $(Ph_3P)_2C$ reacts with Me_3Al and Me_3Ga to afford the adducts, $[(Ph_3P)_2C]AlMe_3$ and $[(Ph_3P)_2C]GaMe_3$, which have been structurally characterized in the solid state by X-ray diffraction, coordination to Me_2Zn and Me_2Cd is reversible. At elevated temperatures, however, elimination of methane and cyclometalation occurs to afford $[\kappa^2\text{-}Ph_3PC\{PPh_2(C_6H_4)\}]ZnMe$ and $[\kappa^2\text{-}Ph_3PC\{PPh_2(C_6H_4)\}]CdMe$. $[\kappa^2\text{-}Ph_3PC\{PPh_2(C_6H_4)\}]$ is an uncommon example of a bidentate κ^2–*C*,*C* ligand and this motif has only previously been structurally characterized for noble metal complexes. Analogous cyclometalated products, $[\kappa^2\text{-}Ph_3PC\{PPh_2(C_6H_4)\}]ZnN(SiMe_3)_2$ and $[\kappa^2\text{-}Ph_3PC\{PPh_2(C_6H_4)\}]CdN(SiMe_3)_2$, are, nevertheless, also obtained upon reaction of $(Ph_3P)_2C$ with $Zn[N(SiMe_3)_2]_2$ and $Cd[N(SiMe_3)_2]_2$. Likewise, the cyclometalated magnesium compounds, $\{[\kappa^2\text{-}Ph_3PC\{PPh_2(C_6H_4)\}]MgMe\}_2$ and $[\kappa^2\text{-}Ph_3PC\{PPh_2(C_6H_4)\}]MgN(SiMe_3)_2$, are obtained from the corresponding reactions of Me_2Mg and $\{Mg[N(SiMe_3)_2]_2\}_2$. While this reactivity is similar to the zinc system, the magnesium methyl complex is a dimer with bridging methyl groups, whereas the zinc complex is a monomer. The greater tendency of the methyl groups to bridge magnesium centers rather than zinc centers is supported by density functional theory calculations, and is also in accord with the general observation that the tendency to bridge increases with the polarity of the M–Me bond.

EXPERIMENTAL SECTION

General considerations

All manipulations were performed by using a combination of glovebox, high vacuum, and Schlenk techniques under an argon atmosphere using appropriate safety considerations.[94] Solvents were purified and degassed by standard procedures. NMR spectra were recorded on Bruker AVIII 300 and Bruker AVIII 500 spectrometers. ^{1}H NMR chemical shifts are reported in ppm relative to $SiMe_4$ ($\delta = 0$), and were referenced with respect to the protio solvent impurity ($\delta = 7.16$ for C_6D_5H).[95] $^{31}P\{^1H\}$ NMR spectra are reported in ppm relative to 85% H_3PO_4 ($\delta = 0$) and were obtained by using the Ξ/100% value of 40.480742.[96] Coupling constants are given in hertz. NMR spectra are provided in the Supporting Information, with signals due to impurities indicated by an asterisk, with $(Ph_3P)_2C$ being observed at –4.2 ppm in the $^{31}P\{^1H\}$ NMR spectrum. ^{13}C NMR data are not provided because poor solubility and impurities prevent complete assignment,[97] while the latter also precludes reliable elemental analysis. Infrared data were recorded on a Perkin Elmer Spectrum Two spectrometer in attenuated total reflectance (ATR) mode and are reported in reciprocal centimeters. $(Ph_3P)_2C$,[98] Me_2Mg,[74b] $\{Mg[N(SiMe_3)_2]_2\}_2$,[99] $Zn[N(SiMe_3)_2]_2$[100] and $Cd[N(SiMe_3)_2]_2$[100] were obtained by literature methods and Me_3Al, Me_3Ga, Me_2Zn, and Me_2Cd were obtained commercially.

X-ray Structure Determinations

X-ray diffraction data were collected on a Bruker Apex II diffractometer. The structures were solved by using direct methods and standard difference map techniques, and were refined by full-matrix least-squares procedures on F^2 with SHELXTL (Version 2014/7).[101] Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC 1897055-1897060).

Computational Details

Calculations were carried out using DFT as implemented in the Jaguar 8.9 (release 15) suite of *ab initio* quantum chemistry programs.[102] Geometry optimizations were performed with the B3LYP density functional using the LACVP** basis sets and Cartesian coordinates are provided in the Supporting Information.

Synthesis of $[(Ph_3P)_2C]AlMe_3$

A suspension of $(Ph_3P)_2C$ (12 mg, 0.022 mmol) in benzene (1 mL) was treated with Me_3Al (10 mg, 0.139 mmol) resulting in the formation of a colorless solution, which deposited colorless crystals over a period of 2 days. The solution was decanted and the solid was washed with pentane (1 × 2 mL) to afford $[(Ph_3P)_2C]AlMe_3$ (5 mg, 36%) as colorless crystals. Anal. calcd. for $[(Ph_3P)_2C]AlMe_3$: C, 78.9%; H, 6.5%. Found: C, 77.9%; H, 6.4%. ^{1}H NMR (C_6D_6): –0.52 [s, 9H of $C\underline{H}_3$], 6.94 [m, 18H, $C_6\underline{H}_5$], 7.73 [m, 12H, $C_6\underline{H}_5$]. ^{31}P{^{1}H} NMR (C_6D_6): 19.67 [s, $[(Ph_3\underline{P})_2C]AlMe_3$]. IR (cm^{-1}): 3049 (w), 2908 (w), 1481 (w), 1433 (s), 1308 (w), 1165 (w), 1096 (s), 1082 (s), 1026 (m), 997 (m), 809 (s), 743 (s), 708 (s), 690 (vs), 677 (vs), 613 (m), 574 (m), 500 (vs), 452 (m).

Synthesis of $[(Ph_3P)_2C]GaMe_3$

A suspension of $(Ph_3P)_2C$ (40 mg, 0.075 mmol) in C_6D_6 (0.7 mmol) was treated with Me_3Ga (23 mg, 0.200 mmol), resulting in a colorless solution. After standing for 1 hour, the solution became yellow and off-white solid was deposited. The solid was isolated by decantation, washed with diethyl ether (2 × 1 mL) and pentane (2 × 1 mL), and dried *in vacuo*, to afford $[(Ph_3P)_2C]GaMe_3$ as a crystalline solid suitable for X-ray diffraction (29 mg, 60%). Crystals of $[(Ph_3P)_2C]GaMe_3$ suitable for X-ray diffraction were also obtained from a separate reaction by vapor diffusion of pentane into a solution in benzene. ^{31}P{^{1}H} NMR (C_6D_6): 20.31 [s, $[(Ph_3\underline{P})_2C]GaMe_3$].

Reactivity of $(Ph_3P)_2C$ towards Me_2Zn: Synthesis of $[\kappa^2\text{-}Ph_3PC\{PPh_2(C_6H_4)\}]ZnMe$

(a) A suspension of $(Ph_3P)_2C$ (9 mg, 0.017 mmol) in C_6D_6 (0.7 mL) was treated with Me_2Zn (3 mg, 0.031 mmol), thereby resulting in the formation of a very pale yellow solution which was transferred to an NMR tube equipped with a J. Young valve and analyzed by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. The sample was lyophilized, dissolved in C_6D_6, and analyzed by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. The cycle was repeated several times, thereby demonstrating that Me_2Zn is progressively removed from the sample, which is consistent with adduct formation being reversible.

(b) A solution of $(Ph_3P)_2C$ (5 mg, 0.009 mmol) in C_6D_6 (0.7 mL) in an NMR tube equipped with a J. Young valve was titrated with increasing amounts of Me_2Zn (0.1 equivalents to 7 equivalents) and the solution was analyzed by NMR spectroscopy. The chemical shift of the $^{31}P\{^1H\}$ NMR spectroscopic signal varied with each addition, which is consistent with adduct formation being reversible.

(c) A suspension of $(Ph_3P)_2C$ (10 mg, 0.019 mmol) in C_6D_6 (0.7 mL) was treated with Me_2Zn (15 mg, 0.16 mmol), resulting in the formation of a yellow solution. The mixture was heated at 100°C for 4 days, at which point ^1H and $^{31}P\{^1H\}$ NMR spectroscopy demonstrated formation of $[\kappa^2\text{-}Ph_3PC\{PPh_2(C_6H_4)\}]ZnMe$ and CH_4. The sample was lyophilized, yielding $[\kappa^2\text{-}Ph_3PC\{PPh_2(C_6H_4)\}]ZnMe$ as an off-white solid (8 mg) contaminated with a small quantity of $(Ph_3P)_2C$. ^1H NMR (C_6D_6): –0.30 [s, 3H, $C\underline{H}_3$], 6.79-7.57 [m, 28H, $C_6\underline{H}_5$ and $C_6\underline{H}_4$], 8.54 [d, $^3J_{H\text{-}H} = 7$, 1H, $C_6\underline{H}_4$]. $^{31}P\{^1H\}$ NMR (C_6D_6): 13.33 [d, $^2J_{P\text{-}P} = 43$, 1P, $[\kappa^2\text{-}Ph_3\underline{P}C\{PPh_2(C_6H_4)\}]ZnMe$], 26.03 [d, $^2J_{P\text{-}P} = 43$, 1P, $[\kappa^2\text{-}Ph_3PC\{\underline{P}Ph_2(C_6H_4)\}]ZnMe$]. Crystals suitable for X-ray diffraction were obtained from a separate experiment *via* slow evaporation from a benzene solution.

Reactivity of $(Ph_3P)_2C$ towards Me_2Cd

(a) A solution of $(Ph_3P)_2C$ (9 mg, 0.017 mmol) in C_6D_6 (0.7 mL) was treated with Me_2Cd (3 mg, 0.021 mmol) resulting in the formation of a pale yellow solution which was transferred to an NMR tube equipped with a J. Young valve and analyzed by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy. The sample was lyophilized, dissolved in C_6D_6 and analyzed by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy thereby demonstrating that Me_2Cd is progressively removed from the sample, which is consistent with adduct formation being reversible.

(b) A suspension of $(Ph_3P)_2C$ (10 mg, 0.019 mmol) in C_6D_6 (0.7 mL) was treated with Me_2Cd (15 mg, 0.11 mmol), resulting in the formation of a pale yellow solution. The mixture was heated at 100°C for 3 days and monitored by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy, thereby demonstrating the formation of [κ^2-$Ph_3PC\{PPh_2(C_6H_4)\}$]CdMe and CH_4. The volatile components were removed by lyophilization to afford [κ^2-$Ph_3PC\{PPh_2(C_6H_4)\}$]CdMe as a yellow solid (11 mg), accompanied by partial decomposition to form $(Ph_3P)_2C$. ^{1}H NMR (C_6D_6): -0.38 [s, 3H, $C\underline{H}_3$], 6.83-7.58 [m, 28H, $C_6\underline{H}_5$ and $C_6\underline{H}_4$], 8.43 [d, $^{3}J_{H\text{-}H}$ = 7, 1H, $C_6\underline{H}_4$]. ^{31}P{^{1}H} NMR (C_6D_6): 10.62 [d, $^{2}J_{P\text{-}P}$ = 46, 1P, [κ^2-$Ph_3\underline{P}C\{PPh_2(C_6H_4)\}$]CdMe], 20.96 [d, $^{2}J_{P\text{-}P}$ = 46, 1P, [κ^2-$Ph_3PC\{\underline{P}Ph_2(C_6H_4)\}$]CdMe].

Synthesis of [κ^2-$Ph_3PC\{PPh_2(C_6H_4)\}$]$ZnN(SiMe_3)_2$

A suspension of $(Ph_3P)_2C$ (10 mg, 0.019 mmol) in C_6D_6 (0.7 mL) was treated with $Zn[N(SiMe_3)_2]_2$ (15 mg, 0.039 mmol) and heated at 80°C for 2 days, resulting in the formation of a pale yellow solution at which point ^{1}H and ^{31}P{^{1}H} NMR spectroscopy demonstrated the release of $(Me_3Si)_2NH$ and formation of [κ^2-$Ph_3PC\{PPh_2(C_6H_4)\}$]$ZnN(SiMe_3)_2$. ^{1}H NMR (C_6D_6): 0.37 [s, 18H, $C\underline{H}_3$], 6.75-7.66 [m, 28H, $C_6\underline{H}_5$ and $C_6\underline{H}_4$], 8.46 [d, $^{3}J_{H\text{-}H}$ = 7, 1H, $C_6\underline{H}_4$]. ^{31}P{^{1}H} NMR (C_6D_6): 15.72 [d, $^{2}J_{P\text{-}P}$ = 40, 1P, [κ^2-$Ph_3\underline{P}C\{PPh_2(C_6H_4)\}$]$ZnN(SiMe_3)_2$], 25.66 [d, $^{2}J_{P\text{-}P}$ = 40, 1P, [κ^2-$Ph_3PC\{\underline{P}Ph_2(C_6H_4)\}$]$ZnN(SiMe_3)_2$]. The sample was lyophilized yielding an off-white solid (12 mg) contaminated with a small quantity of $(Ph_3P)_2C$. Crystals of [κ^2-$Ph_3PC\{PPh_2(C_6H_4)\}$]$ZnN(SiMe_3)_2$ suitable for X-ray diffraction were obtained from a separate reaction *via* slow evaporation from a benzene solution.

Synthesis of $[\kappa^2\text{-}Ph_3PC\{PPh_2(C_6H_4)\}]CdN(SiMe_3)_2$

A suspension of $(Ph_3P)_2C$ (10 mg, 0.019 mmol) in C_6D_6 (0.7 mL) was treated with $Cd[N(SiMe_3)_2]_2$ (15 mg, 0.035 mmol) and heated at 60°C for 1 day, resulting in the formation of a yellow solution, at which point ^1H and $^{31}P\{^1H\}$ NMR spectroscopy demonstrated the release of $(Me_3Si)_2NH$ and formation of $[\kappa^2\text{-}Ph_3PC\{PPh_2(C_6H_4)\}]CdN(SiMe_3)_2$. The sample was lyophilized and washed with pentane (1 × 2 mL), yielding $[\kappa^2\text{-}Ph_3PC\{PPh_2(C_6H_4)\}]CdN(SiMe_3)_2$ as an off-white solid (12 mg) contaminated with a small quantity of $(Ph_3P)_2C$. ^1H NMR (C_6D_6): 0.31 [s, 18H, $C\underline{H}_3$], 6.74-7.64 [m, 28H, $C_6\underline{H}_5$ and $C_6\underline{H}_4$], 8.39 [d, $^3J_{H\text{-}H} = 7$, 1H, $C_6\underline{H}_4$]. $^{31}P\{^1H\}$ NMR (C_6D_6): 13.85 [d, $^2J_{P\text{-}P} = 43$, 1P, $[\kappa^2\text{-}Ph_3\underline{P}C\{PPh_2(C_6H_4)\}]ZnN(SiMe_3)_2$], 21.97 [d, $^2J_{P\text{-}P} = 43$, 1P, $[\kappa^2\text{-}Ph_3PC\{\underline{P}Ph_2(C_6H_4)\}]CdN(SiMe_3)_2$]. Crystals of $[\kappa^2\text{-}Ph_3PC\{PPh_2(C_6H_4)\}]CdN(SiMe_3)_2$ suitable for X-ray diffraction were obtained from a separate reaction by vapor diffusion of pentane into a benzene solution.

Synthesis of $\{[\kappa^2\text{-}Ph_3PC\{PPh_2(C_6H_4)\}]MgMe\}_2$

A mixture of $(Ph_3P)_2C$ (8 mg, 0.015 mmol) and Me_2Mg (6 mg, 0.110 mmol) in benzene (0.7 mL) was heated at 80°C for 1 hour and monitored by NMR spectroscopy, thereby demonstrating the release of methane and the formation of $\{[\kappa^2\text{-}Ph_3PC\{PPh_2(C_6H_4)\}]MgMe\}_2$. ^1H NMR (C_6D_6): –0.67 [br s, 6H, bridging $C\underline{H}_3$], 6.78–7.62 [m, 28H, $C_6\underline{H}_5$ and $C_6\underline{H}_4$], 8.55 [m, 1H, $C_6\underline{H}_4$]. $^{31}P\{^1H\}$ NMR (C_6D_6): 13.13 [br, 1P, $\{[\kappa^2\text{-}Ph_3PC\{PPh_2(C_6H_4)\}]MgMe\}_2$], 17.81 [br d, $^2J_{P\text{-}P} = 20$, 1P, $\{[\kappa^2\text{-}Ph_3PC\{PPh_2(C_6H_4)\}]MgMe\}_2$]. Attempts to isolate $\{[\kappa^2\text{-}Ph_3PC\{PPh_2(C_6H_4)\}]MgMe\}_2$ were accompanied by decomposition but colorless crystals of $\{[\kappa^2\text{-}Ph_3PC\{PPh_2(C_6H_4)\}]MgMe\}_2$ suitable for X-ray diffraction were obtained from a separate reaction *via* vapor diffusion of pentane directly into the reaction solution following filtration.

Synthesis of [κ^2-Ph$_3$PC{PPh$_2$(C$_6$H$_4$)}]MgN(SiMe$_3$)$_2$

A suspension of (Ph$_3$P)$_2$C (10 mg, 0.019 mmol) in benzene (0.7 mL) was treated with {Mg[N(SiMe$_3$)$_2$]$_2$}$_2$ (13 mg, 0.019 mmol) resulting in the formation of a colorless solution which was heated at 80°C overnight to form [κ^2-Ph$_3$PC{PPh$_2$(C$_6$H$_4$)}]MgN(SiMe$_3$)$_2$. ^{1}H NMR (C$_6$D$_6$): 0.32 [s, 18H, C$\underline{H}_3$], 6.76-7.55 [m, 28H, C$_6\underline{H}_5$ and C$_6\underline{H}_4$], 8.49 [d, $^3J_{H\text{-}H}$ = 7, 1H, C$_6\underline{H}_4$]. ^{31}P{^{1}H} NMR (C$_6$D$_6$): 14.97 [d, $^2J_{P\text{-}P}$ = 22, 1P, [κ^2-Ph$_3\underline{P}$C{PPh$_2$(C$_6$H$_4$)}]MgN(SiMe$_3$)$_2$], 19.39 [d, $^2J_{P\text{-}P}$ = 22, 1P, [κ^2-Ph$_3$PC$\underline{P}$Ph$_2$(C$_6$H$_4$)]MgN(SiMe$_3$)$_2$]. In addition to [κ^2-Ph$_3$PC{PPh$_2$(C$_6$H$_4$)}]MgN(SiMe$_3$)$_2$, signals due to an impurity are present in both ^{1}H (δ 0.71, s) and ^{31}P NMR spectra (δ 20.32, s; 37.60, s). Colorless crystals of [κ^2-Ph$_3$PCPPh$_2$(C$_6$H$_4$)]MgN(SiMe$_3$)$_2$ suitable for X-ray diffraction were obtained from a separate reaction *via* vapor diffusion of pentane.

Electronic Supplementary Information (ESI) available:

Crystallographic data (CIFs) and NMR spectra. See http://dx.doi.org/10.1039/b000000x/.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements. We thank the National Science Foundation (CHE-1465095) for support of this research.

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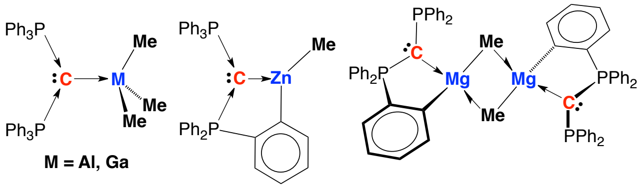
Graphical Abstract



The zerovalent carbodiphosphorane, $(Ph_3P)_2C$, reacts with Me_3Al and Me_3Ga to afford the adducts, $[(Ph_3P)_2C]MMe_3$ (M = Al, Ga), whereas Me_2Zn and Me_2Mg react to afford mononuclear and dinuclear cyclometalated derivatives.