

# Spectroscopic and Structural Characterization of a Phosphavinylidene Carbenoid, $\text{Mes}^*\text{-P}=\text{C}(\text{Cl})\{\text{Li}(\text{DME})_2\}$ : Stabilization of a Carbenanionic Center by a Cisoid Lone Pair Interaction

Edgar Niecke,<sup>\*,†</sup> Martin Nieger,<sup>†</sup> Olaf Schmidt,<sup>†</sup> Dietrich Gudat,<sup>†</sup> and Wolfgang W. Schoeller<sup>‡</sup>

Contribution from the Institut für Anorganische Chemie der Universität Bonn, Gerhard-Domagk-Strasse 1, D-53121 Bonn, Germany, and Fakultät für Chemie der Universität Bielefeld, Universitätsstr., D-33501 Bielefeld, Germany

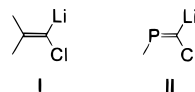
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**Abstract:** Characterization of the phosphavinylidene carbenoid DME-solvate (*Z*)- $\text{Mes}^*\text{-P}=\text{C}(\text{Cl})\{\text{Li}(\text{DME})_2\}$  (**Z-2a**) or the corresponding THF-solvate (**Z-2b**) by low-temperature X-ray diffractometry and multinuclear NMR studies reveals the presence of discrete monomeric molecules with donor-solvated metal atoms both in solution and the solid state. The structural parameters of solid **2a** and the observed intermolecular exchange of  $\text{Li}^+$  between different carbanion fragments in solution suggest a low degree of covalency for the C–Li bond. This is in accord with a theoretical analysis of the bonding which demonstrates that the electronic structure of the model carbenoids (*E/Z*)- $\text{Me-P}=\text{C}(\text{Cl})\{\text{Li}(\text{DME})_2\}$  (**5**) is very similar to that of the carbanions (*E/Z*)- $[\text{Me-P}=\text{C}(\text{Cl})]^-$  (**6**). In particular, the low degree of covalency in the C–Li bond in **5** is confirmed by natural population analyses and an analysis of the Laplacian of the electron density. On the basis of these results, the bonding situation in the phosphavinylidene carbanion system is discussed in terms of an isolobal analogy to  $\text{N}_2\text{F}_2$ .

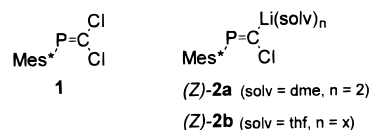
Carbenoids have attracted a great deal of interest because of their potential as synthetic building blocks in organic chemistry,<sup>1</sup> as well as their unique bonding situation.<sup>2</sup> Of particular interest are vinylidene carbenoids **I** which display a  $\text{sp}^2$ -hybridized carbenoid center as part of a  $\pi$ -system and whose intramolecular rearrangement opens a synthetic route to triple bond systems.<sup>3</sup> That these species do not represent only reactive intermediates was recently demonstrated by the first crystal structure determination of an isolable vinylidene carbenoid.<sup>4</sup>

In contrast to **I**, reports on phosphavinylidene carbenoids **II**, which are related to **I** in a manner similar to that of phosphalkenes being related to olefines, are rare, and their existence was so far deduced only from in situ  $^{31}\text{P}$  NMR studies and trapping in subsequent chemical reactions.<sup>5</sup> Here, we report on the first isolation of a representative of type **II**, including its

## Scheme 1



## Scheme 2



full characterization by NMR spectroscopy and single-crystal X-ray diffractometry, as well as an analysis of the bonding properties by means of ab initio model calculations.

## Results

**Syntheses.** Treatment of THF or DME solutions of the aryl-(dichloromethylene)phosphine **1**<sup>5a</sup> with excess *n*-BuLi under conditions similar to those described before<sup>5e,6</sup> afforded cleanly the corresponding phosphavinylidene carbenoid as DME-solvate (**Z-2a**, solv = DME, *n* = 2) or THF-solvate (**Z-2b**, solv = THF, *n* = unknown)<sup>5a–e</sup> (Scheme 2). Crystallization of **2a** from DME at  $-60^\circ\text{C}$  afforded colorless, highly air- and moisture-sensitive crystals which decomposed on warming to room temperature. Thorough NMR investigations were carried out on a sample of  $\{\text{Li}\}$ -**2b** which was prepared analogously from **1** and a stoichiometric amount of  $\{\text{Li}\}$ -*n*-BuLi in THF. **E-2b** was generated analogously by metalation of (*E*)- $\text{Mes}^*\text{-P}=\text{C}(\text{H})\text{Cl}$

<sup>†</sup> Institut für Anorganische Chemie der Universität Bonn.

<sup>‡</sup> Fakultät für Chemie der Universität Bielefeld.

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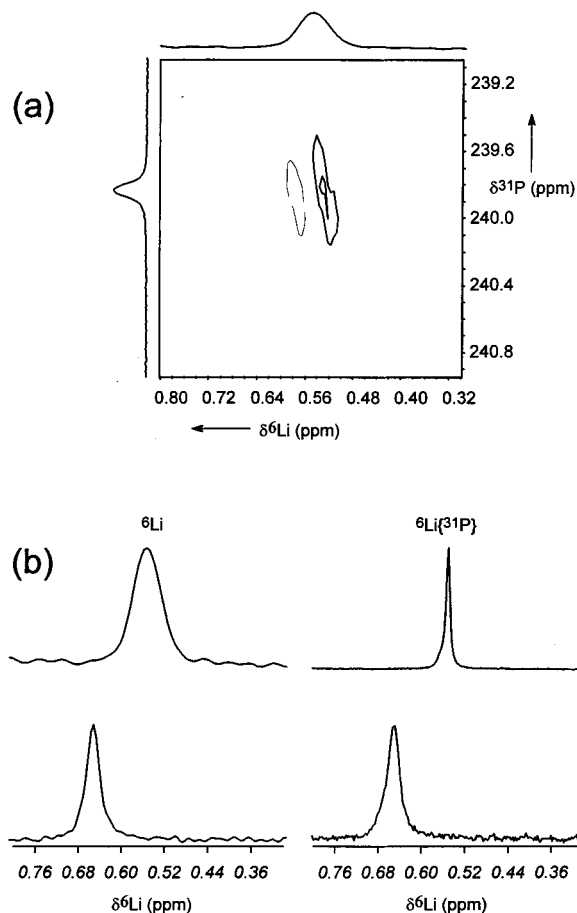
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(*E-3*)<sup>5a,b</sup> with excess *n*-BuLi and identified by <sup>31</sup>P NMR spectroscopy.<sup>5b,d,e</sup> Unlike the *Z*-isomer, *E-2b* was found to be unstable under the reaction conditions and decomposed to give Mes\**C*≡P<sup>5b,d,e</sup> and *n*-BuP=C(Li)Mes\* as main products. The conversion went to completion in a minute time scale and precluded further attempts to spectroscopic characterization of the carbenoid. The identity of the addition product *n*-BuP=C(Li)Mes\* was derived from in situ NMR studies and was further proven by independent generation from reaction of Mes\**C*≡P with 1 equiv of *n*-BuLi under similar conditions. Isolation of the product by low-temperature crystallization failed as a result of the onset of decomposition reactions.

**NMR Spectroscopy.** The molecular constitution of the carbenoid *Z-2b* in solution is unequivocally assigned on the basis of <sup>6</sup>Li, <sup>13</sup>C, and <sup>31</sup>P NMR data. The conservation of the double bond is indicated by the characteristic deshielding of the resonances of both atoms in the central PC unit [ $\delta$  <sup>31</sup>P 240.3,  $\delta$  <sup>13</sup>C 257.4]. The <sup>13</sup>C signal displays at  $-100$  °C splitting due to coupling with the <sup>31</sup>P [ $J$ (P,C) = 99.2 Hz] and <sup>6</sup>Li nuclei [ $J$ (C,<sup>6</sup>Li) = 14.1 Hz]. The multiplicity [1:1:1 triplet] and magnitude of the C,Li coupling, which matches the values of <sup>1</sup> $J$ (C,<sup>6</sup>Li) in monomeric lithium organyls,<sup>7,8</sup> prove the presence of monomeric molecules with direct attachment of the metal at the double-bonded carbon. Further THF-solvation of the metal followed from the result of a 2D <sup>6</sup>Li,<sup>1</sup>H HOESY spectrum. Even if the <sup>2</sup> $J$ (P,<sup>6</sup>Li) coupling is not resolved in the 1D-spectra, its presence is revealed by a cross-peak in a 2D <sup>31</sup>P,<sup>6</sup>Li HMQC spectrum (Figure 1a), and by the comparison of <sup>6</sup>Li and <sup>6</sup>Li{<sup>31</sup>P} spectra obtained at  $-100$  °C (Figure 1b) where the larger line width in the former owes to both the unresolved doublet splitting and additional line broadening due to scalar relaxation of the second kind.<sup>9a</sup> Evaluation of the relaxation contribution by using the relation <sup>9a</sup>  $1/T_{2,sc}(\text{Li}) = T_1(\text{P})\{\pi J(\text{P},\text{Li})\}^2$  with values of  $T_{2,sc}(\text{Li})$  and  $T_1(\text{P})$  obtained from relaxation measurements at  $-100$  °C permitted the computation of the magnitude of <sup>2</sup> $J$ (P,<sup>6</sup>Li) as 0.3 Hz. Comparison of a series of <sup>6</sup>Li and <sup>6</sup>Li{<sup>31</sup>P} spectra of **2b** recorded between  $-100$  and  $-40$  °C revealed that the line broadening associated with  $J$ (P,Li) gradually decreases and eventually disappears (Figure 1b). This suggests that at higher temperatures the P,Li coupling is averaged out by intermolecular exchange of Li<sup>+</sup> between different anion fragments [Mes\**P*=C(Cl)]<sup>-</sup>.

Comparison of the NMR data for the double-bonded atoms in *Z-2b* and the phosphalkene (*Z*)-Mes\**P*=C(H)Cl, **Z-3**,<sup>10</sup> [ $\delta$  <sup>31</sup>P 248.8;  $\delta$  <sup>13</sup>C 160, <sup>1</sup> $J$ (P,C) = 49.9 Hz] reveals that the carbon atom in the carbenoid is considerably deshielded and exhibits a larger magnitude of <sup>1</sup> $J$ (P,C). The extent of the deshielding [ $\Delta\delta$  = 98] notably exceeds the differences between vinylidene carbenoids **I** and the corresponding olefines R<sub>2</sub>C=C(H)Cl [ $\Delta\delta$  60–65]<sup>7</sup> and reflects presumably the larger chemical shift range of P=C as compared to C=C double bond systems. The apparent increase of <sup>1</sup> $J$ (P,C) from **3** to **2b** contradicts at a first glance the finding that <sup>1</sup> $J$ (C,C) in vinylidene systems decreases upon lithiation.<sup>7</sup> However, if one considers that <sup>1</sup> $J$ (C,C) in olefins is generally positive whereas <sup>1</sup> $J$ (P,C) in phos-



**Figure 1.** (a) 2D-<sup>31</sup>P,<sup>6</sup>Li-HMQC spectrum of **Z-2b** at  $-100$  °C; projections denote the corresponding 1D-<sup>6</sup>Li (top) and <sup>31</sup>P{<sup>1</sup>H} NMR spectra (right); (b) <sup>6</sup>Li (left) and <sup>6</sup>Li{<sup>31</sup>P} spectra of **Z-2b** (right) at  $-100$  °C (top row) and  $-50$  °C (bottom row). The observed difference in line widths between the <sup>6</sup>Li and <sup>6</sup>Li{<sup>31</sup>P} spectra at  $-100$  °C owes to the <sup>2</sup> $J$ (P,<sup>6</sup>Li) coupling which produces both an unresolved doublet splitting and additional line broadening due to scalar relaxation of the second kind.<sup>9a</sup>

phorus(III) compounds is negative,<sup>9b</sup> this suggests an algebraic decrease of the reduced couplings in both vinylidene and phosphavinylidene carbenoids, which is presumably attributable to the increased C<sup>δ-</sup>–Li<sup>δ+</sup> bond polarization.

Comparison of the <sup>31</sup>P NMR spectra of **Z-2a** and **Z-2b** revealed only insignificant differences, indicating that the nature of the solvation sphere at the lithium atom has no marked effect on the constitution of the carbenoid.

**Crystal Structure Analysis of Z-2a.** A crystal structure analysis of **Z-2a** reveals that the monomeric constitution persists in the solid state (Figure 2). The sterically demanding aryl substituent and the Li atom occupy *trans*-positions. The Li atom is further coordinated by two DME molecules whose four oxygen atoms occupy the basal positions of a square pyramidal coordination polyhedron. The apical C1–Li1 bond length [2.128(3) Å] matches the corresponding distances in structurally comparable lithium organyls<sup>8</sup> and suggests a weakly bonding interaction between these atoms which is compatible with the presence of a donor–acceptor complex between a phosphavinylidene anion and Li<sup>+</sup>. The P1–C1 [1.677(2) Å] and C1–C11 [1.778(2) Å] distances compare to the corresponding bond lengths in the phosphalkene Mes\**P*=C(Cl)–PCl<sub>2</sub> (**4**)<sup>11</sup> which exhibits the same *Z*-configured C<sub>aryl</sub>–P=C–Cl skeleton as

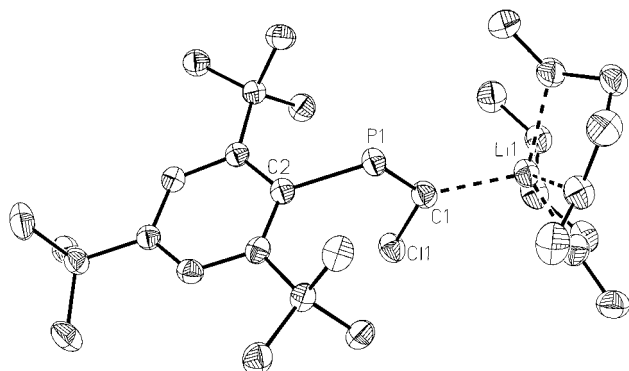
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**Figure 2.** ORTEP view (50% probability ellipsoids, H atoms omitted for clarity) of the molecular structure of **Z-2a** in the crystal. Important bond distances [Å] and angles [deg]: C1–C11 1.7779(15), C1–P1 1.6769(15), C1–Li1 2.128(3), P1–C2 1.8723(14), C1–P1–C2 115.36(7), P1–C1–C11 120.52(8), P1–C1–Li1 122.44(10), C11–C1–Li1 117.01(10).

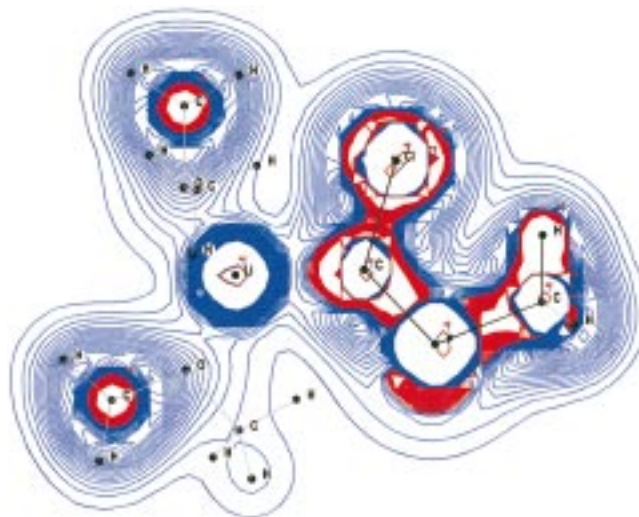
that of **Z-2a**. Interestingly, the C2(aryl)–P1 bond in **Z-2a** [1.872(1) Å] is significantly longer than in other known compounds of the type Mes\*–P=CR<sub>2</sub> [e.g., 1.826 Å in **4**,<sup>11</sup> 1.84 Å in Mes\*–P=CCl<sub>2</sub>]<sup>12</sup>, while at the same time also the C1–P1–C2 bond angle [115.4(3)°] is wider than that in **4** [102.0(3)°<sup>11</sup>]. Further noticeable is the regular trigonal planar coordination of the carbenic C1 atom whose bond angles [P1–C1–Li1 122.4(1)°, P1–C1–C11 120.5(1)°, C11–C1–Li1 117.0(1)°] all fall close to the ideal value of 120°; in contrast, the carbenic centers in the alkylidene and phosphoranylidene carbenoids (*p*-Cl–C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>C=C(Cl){Li(TMEDA)(THF)}<sup>4</sup> [C–C–Li 137.1°, C–C–Cl 112.6°, Cl–C–Li 108.7°] and Mes\*–P{=C(SiMe<sub>3</sub>)<sub>2</sub>}=C(Cl){Li(THF)<sub>3</sub>}<sup>6</sup> [P–C–Li 155.5°, P–C–Cl 109.4°, Cl–C–Li 94.8°] display more T-shaped geometries.

**Quantum Chemical Studies.** To further analyze the bonding situation in phosphavinylidene carbenoids, we performed quantum chemical ab initio calculations<sup>13</sup> on the model carbenoids (*E/Z*)-[H<sub>3</sub>C–P=C(Cl){Li(DME)<sub>2</sub>}] (*E/Z-5*), the carbanions (*E/Z*)-[H<sub>3</sub>C–P=C(Cl)]<sup>–</sup> (*E/Z-6*), and the phosphalkenes (*E/Z*)-[H<sub>3</sub>C–P=C(Cl)H] (*E/Z-7*). A comparison of relevant bonding parameters as obtained from energy optimizations under the constraint of C<sub>s</sub> symmetry at both SCF (HF/6-31+G\*) and density functional level<sup>14</sup> (B3LYP/6-31+G\*, see Table 1) reveals the following trends: (a) The C–P=C–Cl structural units in the carbenoids *E/Z-5* and in the free anions *E/Z-6* are very similar. In other words, addition of a solvated counterion does not change the bonding features (computed for the gas phase) in the phosphavinylidene anion. (b) The C–Cl distances in *E/Z-5*, **6** are substantially longer than in the corresponding phosphalkenes *E/Z-7*; this difference increases upon inclusion of electron correlation (DFT vs SCF). (c) Both P=C–Cl and

**Table 1.** Relevant Geometric Parameters (Bond Lengths in Å, Bond Angles in deg) of **5–7** Obtained by Energy Optimization at the B3LYP/6-31+G\* Level

	C–P	P=C	C–Cl	C–P=C	P=C–Cl
<i>E-5</i> <sup>a</sup>	1.892	1.701	1.883	99.7	108.6
<i>Z-5</i> <sup>b</sup>	1.887	1.691	1.861	112.4	119.7
<i>E-6</i>	1.898	1.718	1.915	97.3	108.4
<i>Z-6</i>	1.914	1.706	1.912	113.8	117.2
<i>E-7</i>	1.874	1.682	1.746	100.2	122.9
<i>Z-7</i>	1.865	1.680	1.750	105.4	130.7

<sup>a</sup> Li–C = 2.119 Å, Li–C–P = 143.0°. <sup>b</sup> Li–C = 2.105 Å, Li–C–P = 131.3°.



**Figure 3.** Laplacian of the electron density<sup>16</sup> of **Z-5** computed at the B3LYP/6-31+G\* level.

C–P=C angles are considerably larger in the *Z*- than in the *E*-isomer of the anion **6**. Despite the presence of the sterically demanding solvated Li atom, this feature is completely preserved in the carbenoids *E/Z-5*, suggesting an electronic rather than a steric origin for this effect. (d) Both the P–C single and double bonds grow increasingly longer in the order phosphalkene < carbenoid < phosphavinylidene anion.

The limited electronic perturbation of the phosphavinylidene anion due to attachment of Li<sup>+</sup> is further reflected in the results of a natural orbital population analysis<sup>15</sup> of the DFT wave function of (*Z*)-**5** which revealed a charge density of –0.91 on the anion fragment, corresponding to a transfer of 0.09 electrons to {Li(DME)<sub>2</sub>}<sup>+</sup>. The spurious covalent interaction between carbon and lithium and the preservation of the multiple bond system is further indicated by the Wiberg bond indexes [C–Li 0.09, C–Cl 0.96, C–P 0.92, C=P 1.95]. Last, but not least, the nature of the carbenoid as a tight ion pair is highlighted by an inspection of the Laplacian of the electron density:<sup>16</sup> the representation in Figure 3 clearly reveals the presence of an electron pair domain at the olefinic carbon atom which points toward the Li atom and documents the anionic character of the phosphavinylidene fragment.

## Discussion

The differences in geometric parameters between *E/Z-5* and **6** and the results of population analyses suggest that the bonding in the carbanion **6** (and the carbenoid **5**) can be perceived in

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terms of an isolobal analogy to  $N_2F_2$ .<sup>17</sup> Of central importance for the stabilization of the phosphavinylidene anion is the remedy of the repulsion between the adjacent lone pairs at the central atoms. This is achieved by both hyperconjugation between the lone pairs and adjacent single bonds which induces the elongation of the latter due to population of  $\sigma^*(P-C)$  and  $\sigma^*(C-Cl)$  orbitals, and rehybridization at the central atoms which causes an opening of  $C-P=C$  and  $P=C-Cl$  angles. Since both effects are more effective in the *Z*- than in the *E*-isomers, the higher stability of *Z-2* as compared to that of *E-2* with respect to rearrangement into a thermodynamically more stable phosphalkyne is attributed to a more pronounced reluctance to decrease the  $C-P=C$  angle, which is a prerequisite for the 1.2-migration of the aryl group.

In conclusion, the results of the experimental and theoretical studies agree in giving a description of the carbenoid *Z-2* as a tightly bound ion pair whose carbenic center behaves predominantly as a cryptocarbion. The discussion of the bonding in *E/Z*-phosphavinylidene carbenoids in terms of an isolobal analogy to  $N_2F_2$  permits the rationalization of the previously noted<sup>5b,d,e</sup> different chemical reactivity of the two stereoisomers. Investigations of further aspects of bonding properties and reactivities of lithiated phosphalkenes are in progress.

### Experimental Section

**General.** All manipulations were carried out under a dry argon atmosphere using standard Schlenk techniques.  $^1H$ ,  $^{31}P\{^1H\}$ ,  $^{13}C\{^1H\}$ ,  $^6Li$ , and  $^6Li\{^{31}P\}$  NMR spectra (121.5, 300.15, 75.5, 44.2 MHz) were recorded on a Bruker AMX 300 instrument equipped with three independent rf channels and a triple resonance probe head.  $^{13}C$  spectra were recorded with solvent suppression, and signal assignment was supported by  $^{31}P$ -based  $^{13}C,^{31}P\{^1H\}$ -INEPT experiments. All experiments involving heteronuclear *X,Y*-polarization transfer were conducted using previously published pulse sequences.<sup>18</sup> Chemical shifts are referenced to external 85%  $H_3PO_4$  ( $^{31}P$ ), TMS ( $^{13}C$ ,  $^1H$ ), or 70% LiBr in  $D_2O$  ( $^6Li$ ). Relaxation measurements for computation of  $^2J(P,^6Li)$  in *Z-2b* were made at  $-100$  °C to slow intermolecular exchange.  $T_1(^{31}P)$  was obtained from an inversion-recovery experiment, and  $T_2(^6Li)$  in both  $^6Li$  and  $^6Li\{^{31}P\}$  spectra was measured with a CPMG pulse sequence.  $^2J(P,^6Li)$  was calculated with neglect of the  $T_{1,sc}(^6Li)$  contribution to the scalar relaxation by using the formula  $^{9a} 1/T_{2,sc}(^6Li) = T_1(^{31}P) \{ \pi J(P,^6Li) \}^2$ , with  $T_{2,sc}(^6Li)$  being computed according to  $1/T_{2,sc}(^6Li) = 1/T_2(^6Li) - 1/T_2(^6Li\{^{31}P\})$ . Using the values of  $T_1(^{31}P, -100$  °C) = 138 ms,  $T_2(^6Li, -100$  °C) = 686 ms,  $T_2(^6Li\{^{31}P\}, -100$  °C) = 735 ms furnished  $^2J(P,^6Li) = 0.3$  Hz.

**Preparation of *Z-2a,b*.** To a stirred solution of 0.18 g (0.5 mmol) of aryl-(dichloromethylene)-phosphine **1**<sup>5a</sup> in 4.5 mL of DME (*Z-2a*) or THF (*Z-2b*) were added at  $-80$  °C 0.55 mL of *n*-BuLi/ $^6Li$ -*n*-BuLi in hexane ( $c = 1.6$  mol  $L^{-1}$ ). The DME solution of *Z-2a* was allowed to warm to  $-60$  °C and stored at this temperature for several days. Colorless crystals of *Z-2a* separated and were isolated by filtration at  $-60$  °C (no yield determined). *Z-2b* was subjected to NMR spectroscopic analysis without further workup. *Z-2b*:  $^1H$  NMR (THF/hexane,  $-90$  °C)  $\delta$  7.16 (2 H,  $CH_{aryl}$ ), 1.45 (18 H, *o*-CCH<sub>3</sub>), 1.23 (9 H, *p*-CCH<sub>3</sub>).  $^6Li$  NMR (THF/hexane,  $-90$  °C)  $\delta$  0.55 (s).  $^{13}C\{^1H\}$  NMR

**Table 2.** Crystal Data and Structure Refinement for **2a**

empirical formula	$C_{27}H_{49}ClLiO_4P$
formula weight	511.02
temperature	123(2) K
wavelength	0.710 73 Å
crystal system, space group	orthorhombic, $P2_12_12_1$ (no. 19)
unit cell dimensions	$a = 11.0677(6)$ Å $b = 14.9657(9)$ Å $c = 17.6931(10)$ Å $\alpha = 90^\circ$ $\beta = 90^\circ$ $\gamma = 90^\circ$
volume	$2930.6(3)$ Å <sup>3</sup>
Z, calculated density	4, 1.158 mg/m <sup>3</sup>
absorption coefficient	$0.213$ mm <sup>-1</sup>
$F(000)$	1112
crystal size	$0.35 \times 0.30 \times 0.15$ mm
theta range for data collection	$2.96-28.55^\circ$
index ranges	$-14 \leq h \leq 14, -19 \leq k \leq 19,$ $-23 \leq l \leq 23$
reflections collected/unique	37989/6626 [ $R_{int} = 0.0506$ ]
absorption correction	none
refinement method	full-matrix least-squares on $F^2$
data/restraints/parameters	6626/0/309
goodness-of-fit on $F^2$	0.938
final $R$ indices [ $I > 2\sigma(I)$ ]	$R1 = 0.0308, wR2 = 0.0704$
$R$ indices (all data)	$R1 = 0.0519, wR2 = 0.0743$
absolute structure parameter	0.52(4); racemic twin
extinction coefficient	0.0050(7)
largest diff. peak and hole	0.228 and $-0.214$ e Å <sup>-3</sup>

(THF/hexane,  $-90$  °C)  $\delta$  257.41 (m,  $^1J(P,C) = 99.2$  Hz,  $^1J(C,^6Li) = 14.1$  Hz,  $P=C$ ), 150.27 (s, *o*-C<sub>aryl</sub>), 145.33 (s, *p*-C<sub>aryl</sub>), 145.26 (d,  $^1J(P,C) = 100.7$  Hz, *ipso*-C<sub>aryl</sub>), 119.79 (s, *m*-C<sub>aryl</sub>), 37.24 (s, *o*-CC<sub>3</sub>), 34.27 (s, *p*-CC<sub>3</sub>), 31.51 (d,  $^4J(P,C) = 5$  Hz, *o*-CC<sub>3</sub>), 30.80 (s, *p*-CC<sub>3</sub>).  $^{31}P\{^1H\}$  NMR (THF/hexane,  $-90$  °C)  $\delta$  240.3 (s).

**Metalation of *E-3*.** To a stirred solution of 0.16 g (0.5 mmol) of *E-3* in 4.5 mL of THF were added at  $-80$  °C 0.55 mL of  $\{^6Li\}$ -*n*-BuLi in hexane ( $c = 1.6$  mol  $L^{-1}$ ). A  $^{31}P\{^1H\}$  NMR spectroscopic assay allowed detection of the resonance of *E-2b* ( $\delta$  331) which was replaced within a couple of minutes by two new singlets at  $\delta$  200.8 (*n*-BuP=C(Li)Mes\*) and 32.0 (Mes\*-C≡P). *n*-BuP=C(Li)Mes\*:  $^6Li$  NMR (THF/hexane,  $-90$  °C)  $\delta$  0.9 (d,  $^2J(P,Li) = 3.8$  Hz).  $^{13}C\{^{31}P\{^1H\}$  INEPT (THF/hexane,  $-90$  °C)  $\delta$  283.5 (m,  $^1J(P,C) = 130$  Hz,  $^1J(C,^6Li) = 12$  Hz,  $P=C$ ), 155.9 (d,  $^2J(P,C) = 26$  Hz, *ipso*-C<sub>aryl</sub>), 32.5 (d,  $^1J(P,C) = 8$  Hz,  $P-CH_2$ ).

**X-ray Crystallographic Study of *Z-2a*.** Crystal data:  $C_{27}H_{49}ClLiO_4P$ , colorless, orthorhombic, space group  $P2_12_12_1$  (no. 19),  $a = 11.0677(6)$  Å,  $b = 14.9657(9)$  Å,  $c = 17.6931(10)$  Å,  $V = 2930.6(3)$  Å<sup>3</sup>,  $Z = 4$ ,  $wR2(F^2) = 0.0743$ . The structure was solved by direct methods (SHELXS-86).<sup>19</sup> Non-hydrogen atoms were refined anisotropically on  $F^2$  (SHELXL-97);<sup>20</sup> H atoms were refined using a riding model. The absolute structure cannot be determined (racemic twin with Flack parameter  $x = 0.52(4)^{21}$ ). An extinction correction was applied. Further details are given in Table 2.

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**Supporting Information Available:** Tables of final atomic coordinates, anisotropic thermal parameters, and bond distances and angles for **2a** (9 pages, print/PDF). An X-ray crystallographic file, in CIF format, for **2a** is available through the Web only. See any current masthead page for ordering information and Web access instructions.

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