First X-ray Crystal Study and DFT Calculations of Anionic λ^4-Phosphinines

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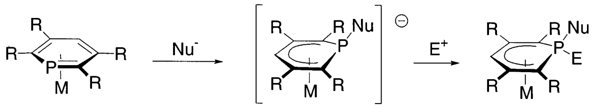
Anionic λ^4-phosphinines **3** and **4** were synthesized via the reaction of the corresponding λ^3-phosphinines **1** and **2** with MeLi. The X-ray structure of [**3**][Li(thf)$_2$] is reported and shows the η^5-coordination of the Li cation to the five carbon atoms of the phosphacyclohexadienyl moiety. Cryptated species [**3**][Li[2.2.2]] and [**4**][Li(thf)$_4$] were also synthesized and analyzed by X-ray diffraction methods, allowing direct comparison with noncryptated species. Anion **5** was obtained by the reaction of **2** with *t*-BuLi. This shows that electronics and sterics can easily be modified on these highly reactive species. The crystal structure of [**5**][Li[2.2.2]] is presented. This study was completed by DFT calculations, which showed the negative charge to be essentially localized on the α carbon atoms of these anions.

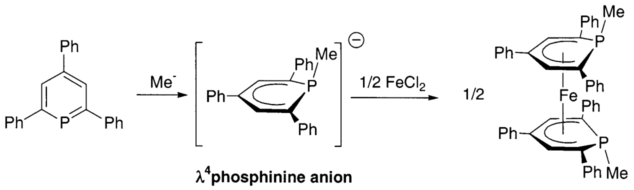
Introduction

The coordination chemistry of λ^3-phosphinines is now well documented. Most of the complexes are found in which the ligand is bound to the metal center in a η^1-fashion (coordination through the lone pair).[1] There are also a significant number of η^6-complexes.[2−5] In these complexes, the lone pair at phosphorus is still available for η^1-coordination, and in fact this "double" coordination, in which the ligand acts as an eight-electron donor, has been observed in a few cases.[5,6] On the other hand, very few η^5-phosphacyclohexadienyl complexes have been reported to date.[7,8] In these complexes, only five of the six atoms of the phosphinine are bound to the metal center. Their synthesis usually involves nucleophilic attack at the electrophilic phosphorus center of a η^6-complex followed by a trapping reaction with an electrophile (Scheme 1).

Scheme 1



Scheme 2



Another way of obtaining η^5-phosphacyclohexadienyl complexes is to attack a λ^3-phosphinine with a nucleophile before reacting it with a suitable metal precursor. This approach was followed by Märkl et al., who reported the synthesis of two bis(1-R-2,4,6-trisubstituted phosphinine)iron complexes.[9] These authors initially claimed the complexes to be bis-η^6-phosphinine complexes, but Dimroth et al. reinvestigated the results in 1985, pointing toward bis-η^5-coordination[10a] (Scheme 2).

This was finally proven by Baum and Massa, who obtained X-ray proof of the bis-η^5-coordination the same year.[10b] On the other hand, the λ^4-phosphinine anions produced after the nucleophilic attack have been used to reach organophosphorus compounds such as 1,1-λ^5-phosphinine, λ^3-1,2-dihydrophosphinine, or λ^3-1,4-dihydrophosphinine.[1b,11]

We felt that it could be of great interest to obtain crystals of these highly reactive anionic species, no X-ray

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[1] For a recent review: (a) Mézailles, N.; Mathey, F.; Le Floch, P. *Prog. Inorg. Chem.* **2001**, *49*, 455−550. (b) Le Floch, P. In *Phosphorus−Carbon Heterocyclic Chemistry: The Rise of a New Domain*; Mathey, F., Ed.; Pergamon: New York, 2001; pp 485−533.

[2] Using co-condensation of ligand and metal(0): (a) Ti: Arnold, P. L.; Cloke, F. G. N.; Khan, K.; Scott, P. *J. Organomet. Chem* **1997**, *528*, 77−81. (b) V: Elschenbroich, C.; Nowotny, M.; Metz, B.; Massa, W.; Graulich, J.; Biehler, K.; Sauer, W. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 547−550, *Angew. Chem.* **1991**, *103*, 601−604. (c) Cr: Elschenbroich, C.; Bär, F.; Bilger, E.; Mahrwald, D.; Nowotny, M.; Metz, B. *Organometallics* **1993**, *12*, 3373−3378. (d) Ho: Arnold, P. L.; Cloke, F. G. N.; Hitchcock, P. B. *J. Chem. Soc., Chem. Commun.***1997**, 481−482.

[3] Vahrenkamp, H.; Nöth, *Chem. Ber.* **1972**, *105*, 1148−1157. (b) J. Deberitz, H. Nöth, *Chem. Ber.* **1973**, *106*, 2222−2226.

[4] (a) Nief, F.; Charrier, C.; Mathey, F.; Simalty, M. *J. Organomet. Chem.* **1980**, *187*, 277−285. (b) Fisher, J.; De Cian, A.; Nief, F. *Acta Crystallogr., Sect. B* **1979**, *35*, 1686−1695.

[5] (a) Knoch, F.; Kremer, F.; Schmidt, U.; Zenneck, U.; Le Floch, P.; Mathey, F. *Organometallics* **1996**, *15*, 2713−2719. (b) Böhm, D.; Geiger, H.; Knoch, F.; Kummer, S.; Le Floch, P.; Mathey, F.; Schmidt, U.; Zenneck, U.; *Phosphorus, Sulfur Silicon* **1996**, *109−110*, 173−176. (c) Le Floch, P.; Knoch, F.; Kremer, F.; Mathey, F.; Scholz, J.; Scholz, W.; Thiele, K.-H.; Zenneck, U. *Eur. J. Inorg. Chem.* **1998**, 119−126.

[6] Nainan, K. C.; Sears, C. T. *J. Organomet. Chem.* **1978**, *148*, C31−C34.

[7] Doux, M.; Ricard, L.; Mathey, F.; Le Floch, P.; Mézailles, N. *Eur. J. Inorg. Chem.* **2003**, 687−698.

[8] (a) Nief, F.; Fischer, J. *Organometallics* **1986**, *5*, 877−883. (b) Dimroth, K.; Kaletsch, H. *J. Organomet. Chem.* **1983,** *247*, 271−285.

[9] Märkl, G.; Martin, C. *Angew. Chem., Int. Ed. Engl.* **1972**, *13*, 408−409.

[10] (a) Dave, T.; Berger, S.; Bilger, E.; Kaletsch, H.; Pebler, J.; Knecht, J.; Dimroth, K. *Organometallics* **1985**, *4*, 1565−1572. (b) Baum, G.; Massa, W. *Organometallics* **1985**, *4*, 1572−1574.

[11] (a) Ashe, A. J., III; Smith, T. W. *Tetrahedron Lett.* **1977**, 407−410. (b) Märkl, G., Merz, A. *Tetrahedron Lett.* **1968**, 3611−3614. (c) Märkl, G.; Merz, A. *Tetrahedron Lett.* **1971**, 1215−1218. (d) Märkl, G.; Martin, C.; Weber W. *Tetrahedron Lett.* **1981**, *22*, 1207−1210. (e) Dimroth, K. *Acc. Chem. Res.* **1982**, *15*, 58−64.

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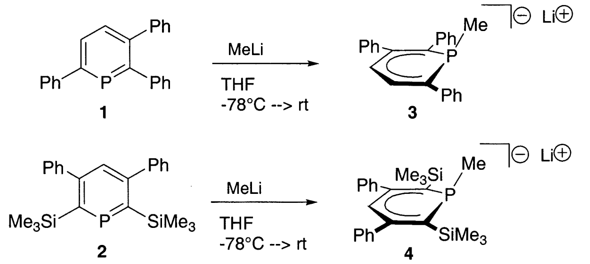
Scheme 3



structure of these being known to date. Their elucidation could allow a better understanding of their electronic properties and reactivity toward metal centers. Having in hand several methods allowing the synthesis of polyfunctional phosphinines,[12] we selected two phosphinines with either phenyl or trimethylsilyl groups at the 2 and 6 positions in order to bring some kinetic stabilization. Herein we report on the first crystal structures of these ligands together with DFT calculations on model species.

Results and Discussion

The two phosphinines chosen for this study are the easily available 2,3,6-triphenylphosphinine **1** and the 3,5-diphenyl-2,6-bistrimethylsilylphosphinine **2**.[12] In a first step, the reaction of these ligands with MeLi was carried out (Scheme 3).

Typically, the phosphinine was dissolved in THF and cooled at −78 °C, and a stoichiometric amount of MeLi in Et_2O was then added via a microsyringe. The solution turned instantaneously from pale yellow to deep blue for **3** or dark red for **4**. The dry ice−acetone bath was then removed and the mixture warmed back to room temperature. As expected, the two anions are highly water sensitive, and samples for NMR characterization were prepared in a drybox. These anions are stable for extended periods of time provided that water is excluded. In ^{31}P NMR, **3** and **4** appear very strongly shifted from **1** and **2** ($\Delta\delta = -258$ ppm for **3** and −333 ppm for **4**). Both signals are singlets at −61 and −64 ppm, respectively, clearly indicating that the aromaticity within the ring has been disrupted. These chemical shifts are in fact very close to PMe_3 ($\delta = -60$ ppm), suggesting a strongly basic phosphorus center and a sp^3 hybridization. Ashe and co-workers observed a strong upfield shift (about 3 ppm) of H_2, H_4, and H_6 in ^{1}H NMR upon reaction of MeLi with the parent phosphinine C_5H_5P.[11a] Here, a comparable upfield shift of 2.36 ppm is measured for H_4 going from **1** to **3**, and 2.2 ppm from **2** to **4**. On the other hand, H_5 in **3** is shifted only by 1.16 ppm. In ^{13}C NMR, the C_2 and C_6 atoms are the most strongly shifted (by 81 ppm from **1** to **3** and by 89 ppm from **2** to **4**), correlated with a strong decrease of the $^1J_{CP}$ from 53 to 4.3 Hz in **3** and from 89 to 36 Hz in **2**. The C_4 is also shifted upfield but to a much lesser extent: $\Delta\delta = -22.3$ ppm. On the other hand, the chemical shifts for C_3 and C_5 are not altered. This already points toward a delocalization of the negative charge mostly on the 2, 4, and 6 positions. To confirm this, an X-ray study was carried out on these species. Crystals of [**3**][Li(thf)$_2$] were obtained in the following manner: a THF solution of anion **3** was taken to dryness and the solid extracted with hexanes. The supernatant was transferred in a tube, which was subsequently sealed. Red crystals deposited within days at −18 °C. Crystals of [**4**][Li(Et_2O)] were obtained by crystallization in a mixture of hexanes and diethyl ether (9:1) of the anion synthesized in hexanes. The solution was transferred in a tube, which was sealed, and yellow crystals appeared within days at −18 °C. An ORTEP view of one molecule of [**3**][Li(thf)$_2$] is presented in Figure 1 together with relevant bond distances and angles.

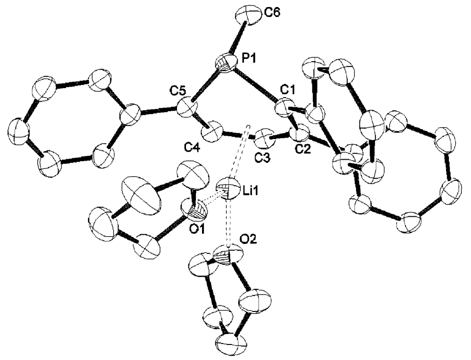


Figure 1. ORTEP view of one molecule of complex [**3**][Li(thf)$_2$]. Ellipsoids are scaled to enclose 50% of the electron density. The numbering is arbitrary and different from that used in the assignment of NMR spectra. Relevant distances (Å) and bond angles (deg): P1−C1, 1.818(2); C1−C2, 1.408(2); C2−C3, 1.417(2); C3−C4, 1.405(2); C4−C5, 1.396(2); C5−P1, 1.815(2); P1−C6, 1.846(2); P1−Li1, 3.140(3); C1−Li1, 2.500(3); C2−Li1, 2.432(3); C3−Li1, 2.463(3); C4−Li1, 2.336(3); C5−Li1, 2.424(3). C1−P1−C5, 96.79(7); P1−C1−C2, 117.9(1); P1−C5−C4, 117.1(1); C1−C2−C3, 122.1(1); C3−C4−C5, 124.1(1); C2−C3−C4, 122.4(1); C1−P1−C6, 101.47(8).

Unfortunately, the structure of [**4**][Li(Et_2O)] is of poor quality and therefore will not be presented, but still allowed us to observe some important points. In both structures the Li cation is coordinated in a η^5-fashion. This is shown by Li−C bond distances, which are in the same range (between 2.336(3) and 2.500(3) Å in [**3**][Li(thf)$_2$] and between 2.21(2) and 2.27(2) Å for [**4**][Li(Et_2O)]), whereas Li−P bond distances are much longer (3.140(3) and 2.89(4) Å, respectively), clearly indicating a lack of Li−P interaction.[13] The phosphorus is now located above the plane of the four central carbon atoms (dihedral angle = 37.2° and 36.4° for [**3**][Li(thf)$_2$] and [**4**][Li(Et_2O)], respectively, angle between plane (C2P1C6) and the plane defined by the four central carbon atoms) and is strongly pyramidalized, as expected for sp^3 hybridization ($\sum$angles = 300.0° for [**3**][Li(thf)$_2$]). The C_4 atom is also shifted above the plane (dihedral angle = 12.1°, angle between plane (C3C4C5) and the plane defined by the four central carbon atoms), giving an overall boat type conformation to the molecule. At this point, it was also interesting to draw a comparison between the bond distances within the ring of **3** and **4** to those of neutral species **1** and **2**, respectively. The structures of **1** and **2** are unknown, but the structure of

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[12] (a) Avarvari, N.; Le Floch, P.; Mathey, F. *J. Am. Chem. Soc.* **1996**, *118*, 11978−11979. (b) Avarvari, N.; Le Floch, P.; Ricard, L.; Mathey, F. *Organometallics* **1997**, *16*, 4089−4098. (c) Charrier, C.; Bonnard, H.; Mathey, F. *J. Org. Chem.*, **1982**, *47*, 2376−2379.

[13] Pfeiffer, M.; Murso, A.; Mahalakshmi, L.; Moigno, D.; Kiefer, W.; Stalke, D. *Eur. J. Inorg. Chem.*, **2002**, 3222−3234.

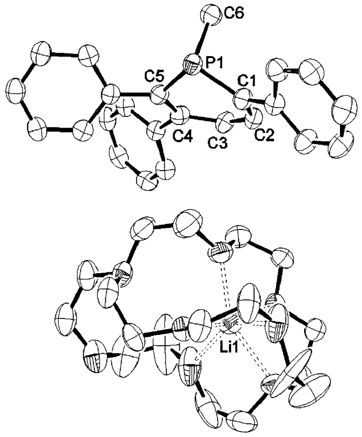


Figure 2. ORTEP view of one molecule of complex [**3**][Li-[2.2.2]]. Ellipsoids are scaled to enclose 50% of the electron density. The numbering is arbitrary and different from that used in the assignment of NMR spectra. Relevant distances (Å) and bond angles (deg): P1−C1, 1.803(3); C1−C2, 1.398(4); C2−C3, 1.398(4); C3−C4, 1.420(4); C4−C5, 1.392(4); C5−P1, 1.816(3); P1−C6, 1.856(4); C1−Si1, 1.845(3). C1−P1−C5, 101.7(2); P1−C1−C2, 117.1(2); P1−C5−C4, 116.3(2); C1−C2−C3, 123.3(3); C3−C4−C5, 124.9(3); C2−C3−C4, 123.9(3); C1−P1−C6, 100.1(2); P1−C1−Si1, 116.0(2).

the macrocycle silacalix-[4]-phosphinines can be taken as a reference for **2** because it contains an analogous subunit.[14] However, the comparison cannot be made with **4** because of the low resolution of the X-ray data. We thus turned our attention to the cryptated species of this anion, which could yield crystals of higher quality. Many attempts using either [2.2.1] or [2.2.2] failed to produce the desired crystals, but a cryptated species was obtained from a solution of the anion in a THF/hexanes mixture (2:1). An ORTEP view of [**4**][Li(thf)$_4$] is presented in Figure 2, and significant bond distances and angles are listed below it.

In the crystal, the Li cation is solvated by four THF molecules. Apparent in the structure is the lack of Li−C bonds. Second, all the C−C bonds in [**4**][Li(thf)$_4$] are nearly equivalent within 3σ (1.394(4)−1.420(4) Å), clearly showing the electronic delocalization between all five carbon atoms. On the other hand, a significant lengthening of the P−C bonds is observed, going from neutral to anionic species: 1.734(5) and 1.746(5) Å (silacalix-[*n*]-phosphinine)[14] increase to 1.803(3) and 1.816(3) Å in [**4**][Li(thf)$_4$]. These latter bond lengths are consistent with Csp^2−Psp^3 bond distances.[15] An internal comparison is given by the P−C$_6$ bond distance (methyl substituent), 1.856(4) Å, which is in turn a Csp^3−Psp^3 bond distance. Last, the phosphorus atom is here also pyramidalized and shifted out of the plane of the carbon atoms of the ring (by 30.7°), as is C4 (by 10.3°).

We felt that it would be interesting to compare the [**3**][Li(thf)$_2$] species, in which the lithium atom is bound to the carbon atoms, to an analogous cryptated species. In fact, it would provide a direct effect of the lithium coordination on the electronic delocalization of the anion. Many attempts using [2.2.1] as cryptand failed, which prompted us to turn to the [2.2.2] cryptand despite its known preference for sodium coordination versus lithium. Several attempts led us to use a mixture of hexanes and THF as solvents and an equimolar amount of anion and cryptand. Deep green crystals deposited in a sealed tube, for which an X-ray structure could be recorded. The ORTEP plot for [**3**][Li[2.2.2]] is presented in Figure 3 together with relevant bond distances and angles.

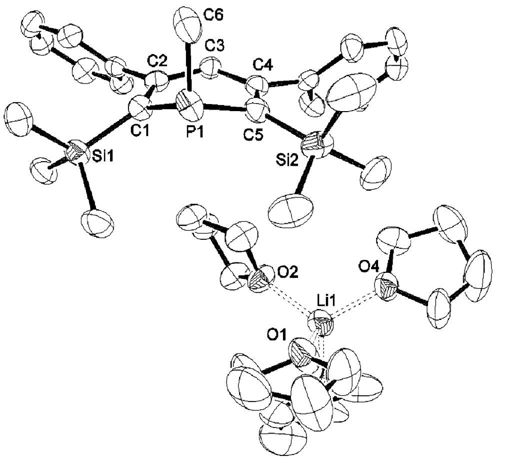
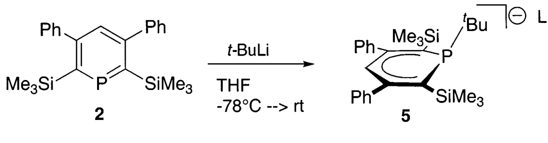


Figure 3. ORTEP view of one molecule of complex [**4**][Li(thf)$_4$]. Ellipsoids are scaled to enclose 50% of the electron density. The numbering is arbitrary and different from that used in the assignment of NMR spectra. Relevant distances (Å) and bond angles (deg): P1−C1, 1.801(4); P1−C5, 1.815(4); C1−C2, 1.396(6); C4−C5, 1.395(6); C2−C3, 1.387(6); C3−C4, 1.410(6); P1−C6, 1.859(4). C1−P1−C5, 99.2(2); P1−C1−C2, 117.8(3); P1−C5−C4, 120.1(3); C1−C2−C3, 125.5(4); C3−C4−C5, 122.3(4); C2−C3−C4, 123.1(4); C1−P1−C6, 101.2(2).

The structure shows an unsymmetrical binding of Li^+ to the cryptand: coordination by five O atoms and one N atom, leaving one O and one N atom unbound. It appears that cryptation neither changes the pyramidalization at phosphorus (302.1° for the [**3**][Li[2.2.2]] species vs 300.0° for [**3**][Li(thf)$_2$]) nor affects the C−C bond distances (1.395(2)−1.419(2) Å in [**3**][Li(thf)$_2$] vs 1.387(4)−1.410(6) Å in [**3**][Li[2.2.2]]). On the other hand, P−C bond distances are also very similar in the two species. It can thus be concluded that cryptation of the cation does not affect the electronic delocalization within the ring.

At this point, two new anionic species with a basic phosphorus atom were available. However, these species contain a small substituent at phosphorus (Me), and we felt that it would be interesting to probe the increase of bulkiness on the stability and reactivity of the anion. Reactions where *t*-BuLi replaced MeLi were thus attempted (eq 1).



(1)

As for the above-mentioned anions **3** and **4**, the solution of **5** is highly sensitive toward moisture. ^{31}P NMR spectroscopy indicates the complete formation of the desired anionic species, the signal of which is

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(14) Avarvari, N.; Mézailles, N.; Ricard, L.; Le Floch, P.; Mathey, F. *Science* **1998**, *280*, 1587−1589.

(15) (a) Baier, F.; Fei, Z.; Gornitzka, H.; Murso, A.; Neufeld, S.; Pfeiffer, M.; Rüdenauer, I.; Steiner, A.; Stey, T.; Stalke, D. *J. Organomet. Chem.* **2002**, *661*, 111−127. (b) Mahalakshmi, L.; Stalke, D. In *Structure and Bonding−Group 13 Elements*; Atwood, D. A., Roesky, H. W., Eds.; Springer-Verlag: Heidelberg, 2002; Vol. 103, pp 85−115.

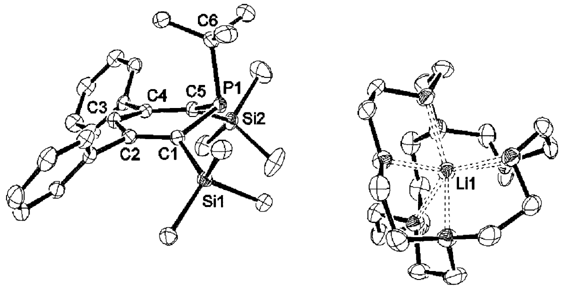
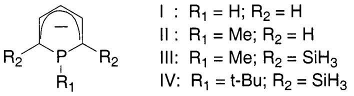


Figure 4. ORTEP view of one molecule of complex [**5**][Li[2.2.2]]. Ellipsoids are scaled to enclose 50% of the electron density. The numbering is arbitrary and different from that used in the assignment of NMR spectra. Relevant distances (Å) and bond angles (deg): P1−C1, 1.821(1); P1−C5, 1.816(1); C1−C2, 1.403(2); C4−C5, 1.401(2); C2−C3, 1.408(2); C3−C4, 1.410(2); P1−C6, 1.912(1); C1−Si1, 1.852(1). C1−P1−C5, 101.16(6); P1−C1−C2, 118.2(1); P1−C5−C4, 118.0(1); C1−C2−C3, 124.5(1); C3−C4−C5, 124.7(1); C2−C3−C4, 123.5(1); C1−P1−C6, 104.50(6); P1−C1−Si1, 114.92(7).

Scheme 4



strongly shifted from **4** ($\delta(5) = -25.9$ ppm, $\Delta\delta = +35$ ppm). This is consistent with the shift from PMe_3 to *t*-$BuPMe_2$ ($\delta = -28.7$ ppm, $\Delta\delta = +33.3$) and already points toward a significant electronic modification of the phosphorus atom.[16] Apart from this, ^{1}H and ^{13}C NMR spectra are very similar to those of **4**, suggesting an analogous electronic delocalization. Here also, both noncryptated [**5**][Li(Et_2O)] and cryptated [**5**][Li[2.2.2]] crystal structures were recorded. As in the case of **3**, they are similar, and only the structure of [**5**][Li[2.2.2]] is presented in Figure 4. Significant bond distances and angles are listed below the drawing.

The cation is unsymmetrically bound to the cryptand. The ORTEP plot clearly shows that the phosphorus atom is pyramidal (∑angles = 310.0°), and it appears quite sterically shielded, as envisioned. The C−C bond distances within the ring (1.401(2)−1.410(2) Å) are similar to those reported above (for [**4**][Li(thf)$_4$]), and the two P−Csp^2 bonds are slightly elongated at 1.816(1) and 1.821(1) Å. The most significant change in this structure is the very long P−C$_6$ bond at 1.912(1) Å, which is about 0.06 Å longer than in the P−Me derivative.

Calculations

To gain information on the charge distribution in these anions, a theoretical study using DFT was undertaken. These calculations were carried out using the Gaussian 98 program with the B3LYP functional and the all-electron 6-311+G* basis set (C, H, P, Si). Four structures were optimized: the parent anion $[C_5H_5PH]^-$ **I**, the P-methylated anion $[C_5H_5PMe]^-$ **II**, and two 2,6-disilyl-substituted anions with either a methyl group, $[2,6\text{-bis}(SiH_3)_2\text{-}C_5H_3PMe]^-$ **III**, or a *t*-Bu group, $[2,6\text{-bis}(SiH_3)_2\text{-}C_5H_3P\text{-}t\text{-Bu}]^-$ **IV**, at phosphorus to assess the effect of substitution at this atom (Scheme 4).

A good correlation was found between experimental and theoretical structures. The most significant bond distances and bond angles are listed in Table 3. Obviously, in compounds **I** and **II**, some discrepancies exist, which are probably due to the absence of substituents on the C2, C6 (α) and C3, C5 (*β*) positions of the ring. The C2−C3 (1.378 Å in **I** and 1.380 Å in **II**) bond distances are always shorter than C3−C4 (1.409 Å in **I** and 1.413 Å in **II**). Introduction of SiH_3 groups at the C2 and C6 positions yields better results, and metric parameters within the ring are close to the experimental values. For example, P−C bond distances in **III** and **IV** are only slightly lengthened compared to those of **4** and **5** (1.834 Å for **III** vs 1.803(3) and 1.816(3) Å in [**4**][Li(thf)$_4$]; 1.834 Å for **IV** vs 1.816(1) and 1.821(1) Å in [**5**][Li[2.2.2]], differences smaller than 1.8% with respect to experimental values). There is also a good fit between calculated C2−C3 bond distances and experimental values (1.390 Å for **III** vs 1.398(4) and 1.392(4) Å in [**4**][Li(thf)$_4$]; 1.392 Å in **IV** vs 1.403(2) and 1.401(2) Å in [**5**][Li[2.2.2]], differences smaller than 0.8% with respect to experimental values). Same conclusions can be drawn for C3−C4 bond distances (1.409 Å for **III** vs 1.398(4) and 1.420(4) Å in [**4**][Li(thf)$_4$]; 1.406 Å in **IV** vs 1.408(2) and 1.410(2) Å in [**5**][Li[2.2.2]], differences smaller than 0.8% with respect to experimental values). Out-of-plane distortion of the phosphorus and the C4 carbon atoms is also apparent but to a lesser extent than in the experimental structure. Whereas the C4 atom deviation from the plane defined by the C2,C3,C5,C6 carbon atoms is well reproduced (9.8° and 8.9° in **III** and **IV**, respectively, vs 10.3° and 8.8° in [**4**][Li(thf)$_4$] and [**5**][Li[2.2.2]], respectively), distortion of the P atom is less

Table 1. Crystal Data and Structural Refinement Details for Compound 3

	[**3**][Li(thf)$_2$]	[**3**][Li[2.2.2]]
cryst color/shape	orange/cube	deep green/cube
cryst size [mm]	0.22 × 0.22 × 0.22	0.22 × 0.18 × 0.18
empirical formula	$C_{128}H_{140}Li_4O_8P_4$	$C_{46}H_{64}LiN_2O_7P$
molecular mass	1958.04	794.90
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
a [Å]	17.130(5)	13.4078(3)
b [Å]	13.084(5)	13.1088(3)
c [Å]	12.611(5)	24.7527(6)
α [deg]	90.00	90.00
β [deg]	105.464(5)	98.6980(10)
γ [deg]	90.00	90.00
V [Å]^3	2724.2(17)	4300.50(17)
Z	1	4
calcd density [g cm^{-3}]	1.194	1.228
abs coeff [cm^{-1}]	0.127	0.116
$2\theta_{max}$ [deg]	28.70	22.21
F(000)	1044	1712
index ranges	−23 23; −17 15; −17 17	−14 14; −13 13; −26 26
no. of reflns collected/ind	12 025/7022	9646/5383
no. of reflns used	5465	4383
(R_{int})	0.0191	0.0213
abs corr	0.9725 min., 0.9725 max.	0.9749 min., 0.9794 max.
no. of params refined	360	525
reflns/param	15	8
final R1[a]/wR2 $[I > 2\sigma(I)]$[b]	0.0512/0.1478	0.0802/0.2396
goodness-of-fit on F^2	1.037	1.032
diff peak/hole [e Å^{-3}]	1.020(0.050)/ −0.424(0.050)	1.269(0.065)/ −0.647(0.065)

[a] $R1 = \sum|F_o| - |F_c|| / \sum|F_o|$. [b] $wR2 = (\sum w||F_o| - |F_c||^2/\sum w|F_o|^2)^{1/2}$.

Table 2. Crystal Data and Structural Refinement Details for Compounds 4 and 5

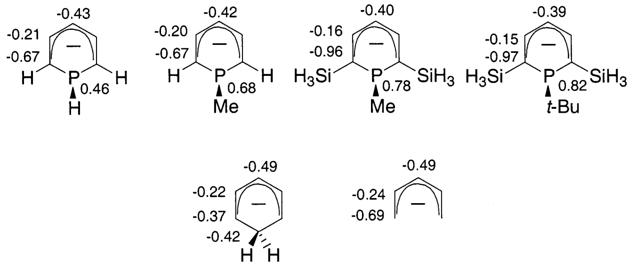
	[**4**][Li(thf)$_4$]	[**5**][Li[2.2.2]]
cryst color/shape	vermilion/plate	red/plate
cryst size [mm]	0.10 × 0.07 × 0.05	0.22 × 0.18 × 0.10
empirical formula	$C_{40}H_{64}LiO_4PSi_2$	$C_{45}H_{74}LiN_2O_6PSi_2$
molecular mass	703.00	833.15
cryst syst	orthorhombic	triclinic
space group	$P2_12_12_1$	$P\bar{1}$
a [Å]	10.842(5)	13.0957(2)
b [Å]	18.047(5)	13.9957(3)
c [Å]	21.942(5))	14.0048(3)
α [deg]	90.000(5)	80.1290(10)
β [deg]	90.000(5)	67.1950(10)
γ [deg]	90.000(5)	86.6090(10)
V [Å]^3	4293(3)	2331.09(8)
Z	4	2
calcd density [g cm^{-3}]	1.088	1.187
abs coeff [cm^{-1}]	0.155	0.157
$2\theta_{max}$ [deg]	22.46	27.47
F(000)	1528	904
index ranges	−11 11; −19 19; −23 23	−17 16; −18 18; −18 18
no. of reflns collected/ind	5581/5581	15745/10631
no. of reflns used	4905	8692
(R_{int})	0.0000	0.0271
abs corr	0.9847 min., 0.9923 max.	0.9663 min., 0.9845 max.
no. of params refined	441	523
refln/params	11	16
final R1^a/wR2 [$I > 2\sigma(I)$]^b	0.0433/0.1128	0.0392/0.1082
goodness-of-fit on F^2	1.042	1.014
diff peak and hole [e Å^{-3}]	0.484(0.039)/ −0.286(0.039)	0.361(0.047)/ −0.327(0.047)

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = (\sum w||F_o| - |F_c||^2/\sum w|F_o|^2)^{1/2}$.

important in calculated structures than in experiment (23.7° and 18.6° in **III** and **IV**, respectively, vs 30.**7**° and 27.2° in [**4**][Li(thf)$_4$] and [**5**][Li[2.2.2]], respectively). These differences are significant, but one must take into account the difference in the substitution scheme of the two compounds. Very probably, the steric crowding effect between $SiMe_3$ and Me or *t*-Bu groups tends to increase the out-of plane distortion of the P atom in the experimental structure. Otherwise pyramidalization of the P atom is comparable in both structures (301° in **III** vs 302° in [**4**][Li(thf)$_4$]; 308° in **IV** vs 310° in [**5**][Li-[2.2.2]]).

But the most significant information is provided by the natural bond orbital (NBO) population analysis. It is 3-fold. First, examination of Wiberg bond indices confirms that no delocalization occurs through the phosphorus atom which is singly bonded to the two α carbons atoms C2 and C6 (P(P−C) between 0.95 and 1.01). A second important piece of data is given by analysis of the P atom lone pair, which reveals that hybridization is close to that of classical phosphines. Thus, in **III** (3s: 47.98%; 3p: 52.02%) and **IV** (3s: 47.90%; 3p: 52.10%) the contribution of the 3s and 3p orbitals is nearly equivalent to that in the Me-P(CH=CH$_2$)$_2$ (3s: 52.60%; 3p: 47.40%) and *t*-Bu-P(CH=CH$_2$)$_2$ (3s: 52.31%; 3p: 47.69%) phosphines (calculated at the same level of theory). All these data confirm that, in these anions, the phosphorus atom behaves as a classical phosphino group. Charge distribution within the ring is the third relevant clue to understand the behavior of the system. As expected, the phosphorus atom bears a positive charge, which can be compared to the charge calculated in classical phosphines: q = 0.79 in **III** vs 0.75 in Me-P(CH=CH$_2$)$_2$ and q = 0.82 in **IV** vs 0.79 in *t*-Bu-P(CH=CH$_2$)$_2$. As can be seen in Scheme 5, in all structures, the amount of charge is more important on the C2 and C6 carbon atoms than on the C4 carbon atom. This effect is obviously enhanced when the C2 and C6 carbon atoms are substituted by silyl groups such as in **III** and **IV**.

Scheme 5



Last, a comparison can be drawn between these phosphacyclohexadienyl anions and carbon-like structures such as cyclohexadienyl $C_6H_7^-$ and pentadienyl $C_5H_7^-$ anions. Contrary to what could be intuitively proposed, analysis of charge distribution in these phosphorus anions suggests that these structures are closer to pentadienyl than to cyclohexadienyl anion (Scheme 5). Indeed, in the pentadienyl anion the amount of negative charge is more important on the terminal carbon atoms than on the middle one. The opposite is observed in the cyclohexadienyl anion. This very likely results from the difference of electronegativity between phosphorus and carbon, phosphorus acting as a σ-donor susbtituent toward the carbocyclic backbone of the anion.

Conclusion

In conclusion, we have synthesized and isolated λ^4-anions of phosphinines. The first crystal structures of noncryptated and cryptated species are also reported. Together with NMR spectroscopy, X-ray data show that the negative charge is delocalized on the five carbon atoms of the ring. The DFT study confirms this delo-

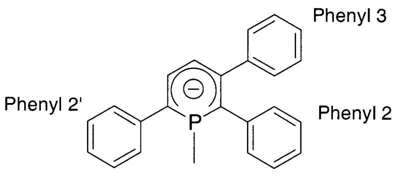
Table 3. Bond Lengths (Å) and Bond Angles (deg) of Theoretical Structures I−IV (Wiberg bond indices are given in parentheses)

	I	**II**	**III**	**IV**
P−C2	1.815 (P=1.01)	1.816 (P=0.96)	1.834 (P=0.95)	1.834 (P=0.96)
C2−C3	1.378 (P=1.61)	1.380 (P=1.60)	1.390 (P=1.54)	1.392 (P=1.53)
C3−C4	1.416 (P=1.35)	1.413 (P=1.35)	1.409 (P=1.36)	1.406 (P=1.36)
P−C2−C3	120.76	122.44	119.13	120.41
C2−C3−C4	125.14	125.44	126.02	126.31
C3−C4−C5	120.03	120.34	121.49	121.29
C6−P−C2	95.15	98.04	100.01	99.94

calization and showed the charge to be mainly on carbons C2 and C6. The analysis of its lone pair also revealed that the phosphorus atom has the same electronic properties as in classical phosphines. In fact, these λ^4-anions can be viewed as a pentadienyl moiety attached to a P sp^3 moiety. We also showed that the bulkiness at phosphorus can be modified, allowing the fine-tuning of the phosphorus properties (electronics and sterics). We are currently studying the coordination of the pentadienyl moiety to various metal fragments, leading to new phosphines. These results will be reported in due course.

Experimental Section

All reactions were routinely performed under an inert atmosphere of argon or nitrogen by using Schlenk and glovebox techniques and dry, deoxygenated solvents. Dry THF, ether, and hexanes were obtained by distillation from Na/benzophenone. Nuclear magnetic resonance spectra were recorded on a Bruker AC-200 SY spectrometer operating at 300.0 MHz for ^{1}H, 75.5 MHz for ^{13}C, and 121.5 MHz for ^{31}P. Solvent peaks are used as internal reference relative to Me_4Si for ^{1}H and ^{13}C chemical shifts (ppm); ^{31}P chemical shifts are relative to a 85% H_3PO_4 external reference. Coupling constants are given in hertz. The following abbreviations are used: s, singlet; d, doublet; t, triplet; m, multiplet. Cryptand [2.2.2] was purchased from Accros organics and [2.2.1] form Aldrich. Methyllithium in ether solution was purchased from Fluka and *tert*-butyl lithium solution in pentane from Aldrich. Phosphinines **1** and **2** were prepared following procedures described in ref 12.



Synthesis of 3. To a THF (2 mL) solution of phosphinine **1** (50 mg, 0.155 mmol) at −78 °C was added 1 equiv of methyllithium in ether (100 μL, 0.155 mmol, 1.6 M). The mixture turned from colorless to dark blue. The solution was warmed to room temperature, and the complete formation of the anion was checked by ^{31}P NMR. The mixture was then taken to dryness to yield quantitatively the title compound as a dark blue solid. ^{1}H NMR (THF-d_8): 0.57 (d, $^2J_{\mathrm{PH}} = 4.91$ Hz, 3 H, $\mathrm{P{-}C}H_3$), 5.25 (dd, $^3J_{\mathrm{HH}} = 7.56$ Hz, $^4J_{\mathrm{PH}} = 0.96$ Hz, 1 H, C_4H of phosphinine), 6.38 (t, $^3J_{\mathrm{HH}} = 7.15$ Hz, 1 H, C_4H of Ph 2), 6.49 (t, $^3J_{\mathrm{HH}} = 7.13$ Hz, 1 H, C_4H of Ph 2′), 6.66 (t, $^3J_{\mathrm{HH}} = 7.7$ Hz, 2 H, C_3H of Ph 2), 6.84 (t, $\sum J = 6.29$ Hz, 1 H, C_3H of phosphinine), 6.93 (pt, $\sum J = 7.49$ Hz, 2 H, C_3H of Ph 2′), 6.95−7.08 (m, 5 H, C_2H of Ph 2 + C_3H of Ph 3 + C_4H of Ph 3), 7.33 (d, $^3J_{\mathrm{HH}} = 8.165$ Hz, 2 H, C_2H of Ph 3), 7.61 (d, $^3J_{\mathrm{HH}} = 8.37$ Hz, 2 H, C_2H of Ph 2′). ^{13}C NMR (THF-d_8): 10.54 (d, $^1J_{\mathrm{PC}} = 24.8$ Hz, $\mathrm{P{-}}CH_3$), 88.68 (d, $^1J_{\mathrm{PC}} = 4.3$ Hz, C_2 of phosphinine), 94.85 (d, $^1J_{\mathrm{PC}} = 3.9$ Hz, C_2' of phosphinine), 109.69 (s, C_4 of phosphinine), 119.82 (s, C_4 of Ph 2 and 2′), 125.51 (d, $^3J_{\mathrm{PC}} = 19.6$ Hz, C_2 of Ph 2′), 126.07 (s, C_4 of Ph 3), 127.70 (d, $^4J_{\mathrm{PC}} = 1.6$ Hz, C_3 of Ph 2), 128.30 (d, $^2J_{\mathrm{PC}} = 5.0$ Hz, C_3H of phosphinine), 128.92 (s, C_3 of Ph 3), 129.34 (d, $^4J_{\mathrm{PC}} = 2.0$ Hz, C_3 of Ph 2′), 131.71 (d, $^3J_{\mathrm{PC}} = 18.4$ Hz, C_2 of Ph 2), 132.51 (s, C_2 of Ph 3), 144.98 (d, $^2J_{\mathrm{PC}} = 4.2$ Hz, $C_3{-}\mathrm{Ph}$), 150.06 (d, $^2J_{\mathrm{PC}} = 52.7$ Hz, C_{ipso} of Ph 2′), 150.48 (d, $^2J_{\mathrm{PC}} = 57.0$ Hz, C_{ipso} of Ph 2), 151.50 (s, C_{ipso} of Ph 3). ^{31}P NMR (THF-d_8): −60.89 ppm.

Synthesis of 4. A solution of 50 mg of phosphinine (0.127 mmol) in 2 mL of THF (respectively hexanes) was prepared. A solution of MeLi in ether (80 μL, 0.127 mmol, 1.6 M) was added at −78 °C. The mixture turned from colorless to bright dark red (respectively yellow). The solution was warmed back to room temperature, and the complete formation of the anion was checked by ^{31}P NMR. The mixture was then taken to dryness to yield quantitatively the title compound as a red (respectively yellow) solid. ^{1}H NMR (THF-d_8): −0.16 (s, 18 H, $\mathrm{Si{-}(C}H_3)_3$), 0.42 (d, $^2J_{\mathrm{HP}} = 5.4$ Hz, 3 H, $\mathrm{P{-}C}H_3$), 5.13 (d, $^4J_{\mathrm{HP}} = 2.3$ Hz, 1 H, H_4), 7.02−7.12 (m, 6 H, C_3H et C_4H of Ph), 7.41 (d, $^3J_{\mathrm{HH}} = 8.04$ Hz, 4 H, C_2H of Ph). ^{13}C NMR (THF-d_8): 5.66 (d, $^3J_{\mathrm{PC}} = 9.8$ Hz, $\mathrm{Si{-}(}CH_3)_3$), 12.81 (d, $^1J_{\mathrm{PC}} = 27.0$ Hz, $\mathrm{P{-}}CH_3$), 77.46 (d, $^1J_{\mathrm{PC}} = 36.2$ Hz, $C_2{-}\mathrm{TMS}$), 111.12 (d, $^3J_{\mathrm{PC}} = 9.8$ Hz, C_4H), 126.55 (s, C_3 of Ph), 128.19 (s, C_4 of Ph), 132.27 (s, C_2 of Ph), 153.09 (d, $^2J_{\mathrm{PC}} = 3.4$ Hz, $C_3{-}\mathrm{Ph}$), 154.55 (d, $^4J_{\mathrm{PC}} = 3.4$ Hz, C_{ipso} of Ph). ^{31}P NMR (THF): −63.92 ppm.

Synthesis of 5. Phosphinine (50 mg, 0.127 mmol) was dissolved in 2 mL of THF (respectively hexanes). A solution of *t*-BuLi in pentane (75 μL, 0.127 mmol, 1.7 M) was added at −78 °C. The solution turned from colorless to bright pink (respectively orange). The solution was warmed back to room temperature, and the complete formation of the anion was checked by ^{31}P NMR. The mixture was then taken to dryness to yield quantitatively the title compound as a pink (respectively orange) solid. ^{1}H NMR (THF-d_8): −0.15 (s, 18 H, $\mathrm{Si{-}(C}H_3)_3$), 0.85 (d, $^3J_{\mathrm{HP}} = 10.5$ Hz, 9 H, $\mathrm{P{-}C{-}(C}H_3)_3$), 5.21 (d, $^4J_{\mathrm{HP}} = 2.2$ Hz, 1 H, H_4), 6.95−7.20 (m, 6 H, C_3H et C_4H of Ph), 7.53 (d, $^3J_{\mathrm{HH}} = 6.7$ Hz, 4 H, C_2H of Ph). ^{13}C NMR (THF-d_8): 6.31 (d, $^3J_{\mathrm{PC}} = 10.3$ Hz, $\mathrm{Si{-}(}CH_3)_3$), 29.40 (d, $^2J_{\mathrm{PC}} = 17.63$ Hz, $\mathrm{P{-}C{-}(}CH_3)_3$), 38.89 (d, $^1J_{\mathrm{PC}} = 31.0$ Hz, $\mathrm{P{-}}C\mathrm{{-}(CH_3)_3}$), 75.11 (d, $^1J_{\mathrm{PC}} = 42.5$ Hz, $C_2{-}\mathrm{TMS}$), 114.83 (d, $^3J_{\mathrm{PC}} = 8.1$ Hz, C_4H), 126.86 (s, C_4 of Ph), 128.37 (s, C_3 of Ph), 132.43 (s, C_2 of Ph), 154.38 (d, $^2J_{\mathrm{PC}} = 2.2$ Hz, C_{ipso} of Ph), 156.92 (d, $^4J_{\mathrm{PC}} = 3.4$ Hz, C_3 of phosphinine). ^{31}P NMR (THF): −25.94 ppm.

Theoretical Methods

Geometry optimizations were carried out by means of a pure gradient-corrected exchange functional and the Lee−Yang−Parr nonlocal correlation functional BLYP as implemented in the Gaussian 98 program.[17,18] A 6-311+G(d) basis set was used for H, C, P, and Si atoms. Vibrational frequencies of the stationary points were calculated at B3LYP with numerical second derivatives of the energy with respect to the coordinates. The structures calculated were located at minima on the potential energy surface. The bonding situation of the optimized structures was analyzed using the natural bond orbital (NBO) method developed by Weinhold.[19]

X-ray Structure Determinations. Crystals of compounds **3**, **4**, and **5** suitable for X-ray diffraction were obtained by slow recrystallization at −18 °C in tubes sealed in vacuo. Orange cubes of [**3**][Li(thf)$_2$] and red-orange plates of [**4**][Li(thf)$_4$] crystallized from a hexanes solution and a hexanes/THF mixture (7:3), respectively. Crystals [**3**][Li[2.2.2]] and [**5**][Li[2.2.2]] were obtained by adding [2.2.2] cryptate (60 mg, 0.155 mmol and 48 mg, 0.127 mmol, respectively) to a THF/ hexanes (1:2) solution of **3** and to a THF/ hexanes (8:2) solution of **5**,

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(16) Mann, B. E. *J. Chem. Soc., Perkin Trans. 2* **1972**, 30−34.

(17) (a) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098−3108. (b) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822−8832.

(18) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, Jr. J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, Revision A.9; Gaussian, Inc.: Pittsburgh, PA, 1998.

(19) Reed, A. E.; Curtis, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899−926.

respectively**.** Data were collected on a Nonius Kappa CCD diffractometer using an Mo Kα (λ = 0.71070 Å) X-ray source and a graphite monochromator at 150 K. Experimental details are described in Tables 1 and 2. The crystal structures were solved using SIR 97[20] and SHELXL-97.[21] ORTEP drawings were made using ORTEP III for Windows.[22] These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Rd., Cambridge CB2 1EZ, UZ; fax: (internat.) +44-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk].

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Supporting Information Available: X-ray structural data on compounds [**3**][Li(thf)$_2$], [**3**][Li[2.2.2]], [**4**][Li(thf)$_4$], and [**5**][Li[2.2.2]]; listings of bond distances, bond angles, and NBO charges for calculated structures **I**−**IV**, pentadienyl anion, cyclohexadienyl anion, Me-P(CH=CH$_2$)$_2$, and *t*-Bu-P(CH=CH$_2$)$_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

OM030023X

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[20] *SIR97*, an integrated package of computer programs for the solution and refinement of crystal structures using single-crystal data: Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R.

[21] Sheldrick, G. M. *SHELXL-97*; Universität Göttingen: Göttingen, Germany, 1997.

[22] *ORTEP-3* program created by Louis J. Farrugia (Department of Chemistry, University of Glasgow).