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Synthesis and Characterization of 1,3-Diphosphapropene and Alkali-Metal 1,3-Diphosphaallyl Complexes and Unexpected 1,3-Rearrangement of a Cesium 1,3-Diphosphaallyl Complex to a Cesium Secondary Phosphanide

Stephen T. Liddle*,† and Keith Izod‡

School of Chemistry, University Park, University of Nottingham, Nottingham NG7 2RD, U.K., and Department of Chemistry, School of Natural Sciences, University of Newcastle upon Tyne, Newcastle upon Tyne NE1 7RU, U.K.

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Protonation of [{*t*-BuC(PMes)$_2$}Li(THF)$_3$] (**2**; Mes = 2,4,6-(CH$_3$)$_3$C$_6$H$_2$) with either *t*-BuCl or H$_2$O yields the 1,3-diphosphapropene (*Z*)-MesP═C(*t*-Bu)P(H)Mes (**3**) after recrystallization; treatment of **3** with *n*-butyllithium at −78 °C in THF regenerates **2**. Metathesis of **2** with MOR (M = Na, K, R = *t*-Bu; M = Rb, Cs, R = CH$_2$CH(Et)CH$_2$CH$_2$CH$_2$CH$_3$) at −78 °C, followed by recrystallization in the presence of crown ethers, allows access to the 1,3-diphosphaallyl complexes [*t*-BuC(PMes)$_2$][M(15-crown-5)$_2$] (M = Na (**4**), K (**5**), Cs (**7**)) and [*t*-BuC(PMes)$_2$]-[Rb(12-crown-4)$_2$] (**6**), the latter of which exhibits a *tert*-butyl CH$_3$···Rb contact in the solid state. An attempt to prepare [*t*-BuC(PMes)$_2$][Cs(12-crown-4)$_2$] (**8**) by metathesis resulted in ligand degradation to give, after recrystallization, the secondary phosphanide complex [Mes$_2$P][Cs(12-crown-4)$_2$] (**9**) in low yield. Studies reveal that the heavier alkali-metal complexes (**5**−**7**) are stable indefinitely in crystalline form under a dry nitrogen atmosphere, but are, as the group is descended, increasingly unstable in solution in the presence of the lithium alkoxide byproduct and may degrade to give mixtures containing secondary phosphanides, the known ditertiary diphosphane (Mes$_2$P)$_2$ (**10**), *t*-BuC≡P (**11**), and other minor unidentified phosphorus-containing compounds. DFT studies at the BL3YP/6-31G* level on the precursor compounds (*Z*)- and (*E*)-MesP═C(*t*-Bu)P(Cl)Mes (**1a,c**) indicate that the *Z* isomer is more stable than the *E* isomer by 47.4 kJ mol^{-1}, confirming the experimentally observed preference for the *Z* configuration of the P═C bond.

Introduction

In recent decades, there has been a considerable drive to design and prepare new ancillary ligands for use in homogeneous catalysis.[1] Among a plethora of established systems, heteroallyl variants, which may easily be tuned sterically and electronically, have emerged as synthetically useful and effective ancillary ligands which may be employed as alternatives to the ubiquitous cyclopentadienyl scaffold. Examples include diiminosulfinates,[2] diiminophosphinates,[3] alkoxysilylamides,[4] guanidates,[5] and amidinates.[6] Arguably the most successful of these are the amidinates; despite this, however, considerably less attention has been paid toward 1,3-heteroallyl systems containing phosphorus (i.e. 1,3-diphosphaallyls). This is particularly surprising, given the prolific development of low-coordinate phosphorus chemistry,[7] but may reflect real, or perceived, difficulties in the preparation and handling of such species. Prior to a recent preliminary contribution to this area by ourselves, describing the preparation and characterization of (*Z*)-MesP═C(*t*-Bu)P(X)Mes (**1**) (X = Cl (**1a**), Br (**1b**); **1a**:**1b** = 0.64:0.36) and its conversion to [{*t*-BuC-(PMes)$_2$}Li(THF)$_3$] (**2**),[8] there were only five structurally characterized 1,3-diphosphaallyl complexes,[9] which are all transition-metal derivatives (Chart 1, **I**−**V**); two related 1-metallo-2,4-diphosphabutadienes have also been reported.[10] In a closely related area, Yoshifuji has demonstrated the potential of neutral 1,3-diphosphapropene ligands in transition-metal coordination chemistry.[11] Niecke and co-workers have also shown that analogous lithium 1,3-diphospha-2-silaallyls can be prepared and characterized.[12] In general, ancillary ligands containing $\lambda^3\sigma^2$ phosphorus centers are proving

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* To whom correspondence should be addressed. E-mail: stephen.liddle@nottingham.ac.uk.

† University of Nottingham.

‡ University of Newcastle upon Tyne.

(1) (a) Elsevier, C. J.; Reedijk, J.; Walton, P. H.; Ward, M. D. *J. Chem. Soc., Dalton Trans.* **2003**, 1869. (b) Gibson, V. C.; Spitzmesser, S. K. *Chem. Rev.* **2003**, *103*, 283. (c) Coates, G. W.; Hustad, P. D.; Reinartz, S. *Angew. Chem., Int. Ed.* **2002**, *41*, 2237. (d) Coates, G. W. *J. Chem. Soc., Dalton Trans.* **2002**, 467. (e) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 428.

(2) (a) Fleischer, R.; Stalke, D. *J. Organomet. Chem.* **1998**, *550*, 173. (b) Wrackmeyer, B.; Klaus, U.; Milius, W. *Inorg. Chim. Acta* **1996**, *250*, 327. (c) Freitag, S.; Kolodziejski, W.; Pauer, F.; Stalke, D. *J. Chem. Soc., Dalton Trans.* **1993**, 3479. (d) Edelmann, F. T.; Knosel, F.; Pauer, F.; Stalke, D.; Bauer, W. *J. Organomet. Chem.* **1992**, *438*, 1. (e) Pauer, F.; Rocha, J.; Stalke, D. *J. Chem. Soc., Chem. Commun.* **1991**, 1477. (f) Pauer, F.; Stalke, D. *J. Organomet. Chem.* **1991**, *418*, 127. (g) Roesky, H. W.; Mainz, B.; Noltemeyer, M. *Z. Naturforsch., B* **1990**, *45*, 53. (h) Knösel, F.; Noltemeyer, M.; Edelmann, F. T. *Z. Naturforsch., B* **1989**, *44*, 1171. (i) Roesky, H. W.; Grunhagen, A.; Edelmann, F. T.; Noltemeyer, M. *Z. Naturforsch., B* **1989**, *44*, 1365. (j) Bats, J. W.; Fuess, H.; Diehl, M.; Roesky, H. W. *Inorg. Chem.* **1978**, *17*, 3031.

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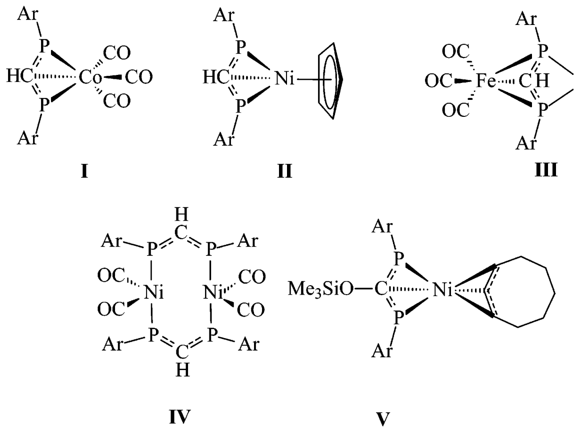
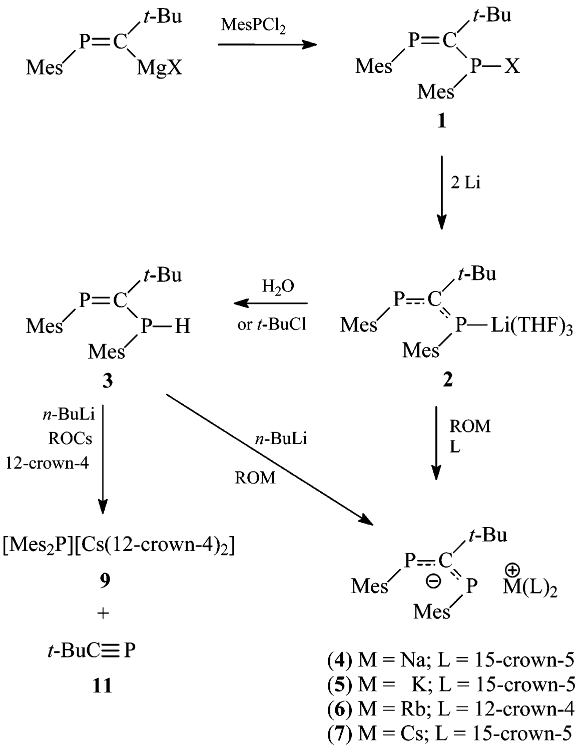
Chart 1[a]



[a] Ar = Mes* = 2,4,6-t-$Bu_3C_6H_2$.

highly valuable in catalytic systems.[13,14] Alkali-metal 1,3-diphosphaallyl complexes are, therefore, of significant interest from a structural point of view and also from a synthetic standpoint for their potential utility as ligand transfer reagents. Herein, we report on the synthesis and characterization of a 1,3-diphosphapropene and a range of alkali-metal 1,3-diphosphaallyl complexes and an unexpected 1,3-rearrangement of a cesium 1,3-diphosphaallyl complex to give a cesium secondary phosphanide.

Scheme 1[a]



[a] X = Cl, Br; Mes = 2,4,6-$(CH_3)_3C_6H_2$. Byproducts from reactions are omitted for clarity.

Results and Discussion

Synthesis and Characterization. Previously, we reported the synthesis of the 1,3-diphosphapropene Z-MesP=C(t-Bu)P(X)Mes (**1**)[8] from the phosphavinyl Grignard reagent [(Z)-MesP=C(t-Bu)MgBr(OEt_2)] (Mes = 2,4,6-$(CH_3)_3C_6H_2$)[15] and $MesPCl_2$, as summarized in Scheme 1. This approach was chosen, as previously reported methods by Appel[9,16a] and Karsch[16b] limit the 2-substituent to H or $OSiMe_3$. Yoshifuji has prepared

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(3) (a) Schultz, M.; Straub, B.; Hofmann, P. *Acta Crystallogr., Sect. C* **2002**, *58*, m256. (b) Wingerter, S.; Pfeiffer, M.; Murso, A.; Lustig, C.; Stey, T.; Chandrasekhar, V.; Stalke, D. *J. Am. Chem. Soc.* **2001**, *123*, 1381. (c) Ackermann, H.; Bock, O.; Muller, U.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **2000**, *626*, 1854. (d) Straub, B. F.; Rominger, F.; Hofmann, P. *Organometallics* **2000**, *19*, 4305 (e) Straub, B. F.; Rominger, F.; Hofmann, P. *Chem. Commun.* **2000**, 1611. (f) Straub, B. F.; Eisentrager, F.; Hofmann, P. *Chem. Commun.* **1999**, 2507. (g) Vollmerhaus, R.; Shao, P.; Taylor, N. J.; Collins, S. *Organometallics* **1999**, *18*, 2731. (h) Boese, R.; Duppmann, M.; Kuchen, W.; Peters, W. *Z. Anorg. Allg. Chem.* **1998**, *624*, 837. (i) Muller, E.; Muller, J.; Olbrich, F.; Bruser, W.; Knapp, W.; Abeln, D.; Edelmann, F. T. *Eur. J. Inorg. Chem.* **1998**, 87. (j) Fleischer, R.; Stalke, D. *Inorg. Chem.* **1997**, *36*, 2413. (k) Muller, E.; Muller, J.; Schmidt, H.-G.; Noltemeyer, M.; Edelmann, F. T. *Phosphorus, Sulfur Silicon Relat. Elem.* **1996**, *1*, 121. (l) Schumann, H.; Winterfeld, J.; Hemling, H.; Hahn, E. E.; Reich, P.; Brzezinka, K.-W.; Edelmann, F. T.; Kilimann, U.; Herbst-Irmer, R. *Chem. Ber.* **1995**, *128*, 395. (m) Kilimann, U.; Noltemeyer, M.; Edelmann, F. T. *J. Organomet. Chem.* **1993**, *443*, 35. (n) Steiner, A.; Stalke, D. *Inorg. Chem.* **1993**, *32*, 1977. (o) Witt, M.; Stalke, D.; Henkel, T.; Roesky, H. W.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1991**, 663. (p) Recknagel, A.; Steiner, A.; Noltemeyer, M.; Brooker, S.; Stalke, D.; Edelmann, F. T. *J. Organomet. Chem.* **1991**, *414*, 327.

(4) (a) Veith, M.; Rammo, A. *Z. Anorg. Allg. Chem.* **2001**, *627*, 662. (b) Preuss, F.; Scherer, M.; Klingshirn, C.; Hornung, G.; Vogel, M.; Frank, W.; Reiss, G. *Z. Naturforsch., B* **1999**, *54*, 1396. (c) Duchateau, R.; Tuinstra, T.; Brussee, E. A. C.; Meetsma, A.; van Duijnen, P. T.; Teuben, J. H. *Organometallics* **1997**, *16*, 3511. (d) Duchateau, R.; Brussee, E. A. C.; Meetsma, A.; Teuben, J. H. *Organometallics* **1997**, *16*, 5506. (e) Dippel, K.; Klingebiel, U.; Schmidt-Base, D. *Z. Anorg. Allg. Chem.* **1993**, *619*, 836. (f) Walter, S.; Klingebiel, U.; Noltemeyer, M. *Chem. Ber.* **1992**, *125*, 783. (g) Recknagel, A.; Steiner, A.; Brooker, S.; Stalke, D.; Edelmann, F. T. *J. Organomet. Chem.* **1991**, *415*, 315. (h) Veith, M.; Bohnlein, J. *Chem. Ber.* **1989**, *122*, 603. (i) Veith, M.; Bohnlein, J.; Huch, V. *Chem. Ber.* **1989**, *122*, 841.

(5) Bailey, P. J.; Pace, S. *Coord. Chem. Rev.* **2001**, *214*, 91 and references therein.

(6) Edelmann, F. T. *Coord. Chem. Rev.* **1994**, *137*, 403 and references therein.

(7) (a) Dillon, K. B.; Mathey, F.; Nixon, J. F. *Phosphorus: The Carbon Copy*; Wiley: Chichester, U.K., 1998. (b) Regitz, M.; Scherer, O. J. *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Thieme, Stuttgart, Germany, 1990.

(8) Liddle, S. T.; Izod, K. *Chem. Commun.* **2003**, 772.

(9) (a) Appel, R.; Schuhn, W.; Nieger, M. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 416. (b) Keim, W.; Appel, R.; Gruppe, S.; Knoch, F. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1012. (c) Appel, R.; Schuhn, W.; Knoch, F. *J. Organomet. Chem.* **1987**, *319*, 345. (d) Appel, R.; Schuhn, W.; Knoch, F. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 420. The preparation and NMR characterization of several lithium 1,3-diphosphaallyls have previously been reported. See: (e) Karsch, H. H. *Synthetic Methods of Organometallic and Inorganic Chemistry*; Thieme, Stuttgart, Germany, 1996; Vol. 3, p 143. (f) Etemad-Moghadam, G.; El-Ouatib, R.; Ballivet-Tkatcherko, D.; Koenig, M. *Phosphorus Sulfur Relat. Elem.* **1993**, *76*, 41. (g) Gouygou, M.; Koenig, M.; Escudié, J.; Couret, C. *Heteroat. Chem.* **1991**, *2*, 221. (h) Gouygou, M.; Tachon, C.; El-Ouatib, R.; Ramarijaona, O.; Etemad-Moghadam, G.; Koenig, M. *Tetrahedron Lett.* **1989**, *30*, 177. A claim of an X-ray structural determination confirming the chemical connectivity of [{$CH_3C(PAr^*)_2$}Li(OEt_2)$_2$] has been made, but the data were reportedly too poor to be publishable. See: (i) Gouygou, M.; Veith, M.; Couret, C.; Escudié, J.; Huch, V.; Koenig, M. *J. Organomet. Chem.* **1996**, *514*, 37. (j) Gouygou, M.; Koenig, M.; Couret, C.; Escudié, J.; Huch, V.; Veith, M. *Phosphorus Sulfur Relat. Elem.* **1993**, *77*, 230.

(10) Karsch, H. H.; Reisacher, H.-U.; Huber, B.; Muller, G.; Jorg, K.; Malisch, W. *New J. Chem.* **1989**, *13*, 319.

(11) (a) Ito, S.; Liang, H.; Yoshifuji, M. *Chem. Commun.* **2003**, 398. (b) Ito, S.; Yoshifuji, M. *Chem. Commun.* **2001**, 1208.

(12) (a) Lange, D.; Klein, E.; Bender, H.; Niecke, E.; Nieger, M.; Pietschnig, R.; Schoeller, W. W.; Ranaivonjatovo, H. *Organometallics* **1998**, *17*, 2425. (b) Niecke, E.; Klein, E.; Nieger, M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 751.

(13) For a review see: Weber, L. *Angew. Chem., Int. Ed.* **2002**, *41*, 563 and references therein.

(14) (a) Ionkin, A.; Marshall, W. *Chem. Commun.* **2003**, 710. (b) Ozawa, F.; Okamoto, H.; Kawagishi, S.; Yamamoto, S.; Minami, T.; Yoshifuji, M. *J. Am. Chem. Soc.* **2002**, *124*, 10968. (c) Daugulis, O.; Brookhart, M.; White, P. S. *Organometallics* **2002**, *21*, 5935. (d) Minami, T.; Okamoto, H.; Ikeda, S.; Tanaka, R.; Ozawa, F.; Yoshifuji, M. *Angew. Chem., Int. Ed.* **2001**, *40*, 4501.

(15) Hibbs, D. E.; Jones, C.; Richards, A. F. *J. Chem. Soc., Dalton Trans.* **1999**, 3531.

1,3-diphosphapropenes from lithium phosphavinyl carbenoids,[11] which afford more flexibility for the nature of the 2-substituent, but the lithium phosphavinyl carbenoids themselves are thermally unstable and present handling difficulties.[17] In contrast, the phosphavinyl Grignard reagents (derived from the stereo- and regioselective 1,2-addition of Grignard reagents across 2,2-dimethylpropylidynephosphine, as reported by Jones[15] and by Binger and Regitz[18]) are thermally stable and, therefore, easier to handle. Compound **1** is routinely isolated as a mixture of chloride and bromide derivatives (X = Cl (**1a**), Br (**1b**); **1a**:**1b** = 0.64:0.36) with $^{31}P\{^1H\}$ NMR spectra exhibiting characteristic signals centered at 259.3 and 93.6 ppm ($^2J_{PP} = 40.0$ Hz, **1a**), and 262.3 and 81.3 ppm ($^2J_{PP} = 47.0$ Hz, **1b**). Crude reaction mixtures often exhibit small amounts (<4%) of the (*E*)-chloride (**1c**) and (*E*)-bromide (**1d**) with signals observed at 279.4 and 89.4 ppm ($^2J_{PP} = 143$ Hz, **1c**) and at 284.1 and 80.9 ppm ($^2J_{PP} = 144$ Hz, **1d**). These values compare with chemical shifts of 322.1 and 63.7 ppm for the previously reported compound Mes*P=C(H)P(X)-Mes* (X = Cl) and 322.7 and 59.9 ppm (X = Br) (no assignment given for the P=C stereochemistry, Mes* = 2,4,6-*t*-$Bu_3C_6H_2$).[16b]

From a coordination chemistry standpoint, formation of the *E* isomer is more desirable than that of the *Z* isomer, since it is preorganized to act as a chelating ligand. Therefore, we were encouraged that small amounts of the *E* isomer were forming during the preparation of **1**. However, we find that thermolysis of THF solutions of crude **1** does not alter the *E*/*Z* ratio. In contrast, photolysis of crude **1** in THF solution with a medium-pressure mercury lamp (100 W) for 24 h results in isomerization of all of the *E* isomer present to the *Z* isomer, resulting in an isomerically pure (with respect to the P=C bond) sample of (*Z*)-**1a**,**b**. This indicated that the *Z* isomer is more stable than the *E* isomer, which prompted us to investigate the relative stabilities of (*Z*)-**1** and (*E*)-**1** using DFT methods (see below).

Previously, Karsch reported that the 1,3-diphosphapropene compound Mes*P=C(H)P(Cl)Mes* could be converted to Mes*P=C(H)P(H)Mes* by reaction with LiH.[16b] In contrast, no reaction was observed between **1** and LiH; reactions between **1** and excess NaH or KH in refluxing THF were also unsuccessful, and only **1** was recovered after workup. However, as we previously disclosed, sonication of a THF solution of **1** with 2 equiv of elemental lithium under an argon atmosphere for 1 h results in a rapid darkening of the yellow solution to dark red. A standard workup affords the 1,3-diphosphaallyl complex [{*t*-BuC(PMes)$_2$}Li(THF)$_3$] (**2**) as an air- and moisture-sensitive red powder (Scheme 1).[8]

Since **1** could not be directly converted to (*Z*)-MesP=C(*t*-Bu)P(H)Mes (**3**), we investigated whether **3** could be accessed from **2**. Excess *t*-BuCl reacts cleanly with **2** in refluxing THF to generate **3** as the sole phosphorus-containing product in essentially quantitative yield (Scheme 1). Compound **3** may also be accessed by reaction of **2** with degassed H_2O in diethyl ether; a simple workup gives **3** as the sole product, with no addition of H_2O across the P=C bond (Scheme 1). A $^{31}P\{^1H\}$ NMR spectrum of crude **3** reveals the presence of one major product (~98%) with doublet signals centered at 263.1 and −64.3 ppm ($^2J_{PP} = 5.8$ Hz) assigned as the *Z* isomer (**3a**). The minor product (~2%) exhibits doublets at 239.6 and −59.5 ppm ($^2J_{PP} = 97.2$ Hz) and is assigned as the *E* isomer (**3b**). These values compare with chemical shifts of 278.8 and −59.5 ppm for the previously reported compound Mes*P=C(H)P(H)Mes* (no assignment given for the P=C stereochemistry).[16b] For each isomer the former (downfield) signal is consistent with a phosphavinyl center, whereas the latter (upfield) signal is commensurate with a secondary phosphane center. This is corroborated by the proton-coupled ^{31}P NMR spectrum of crude **3**; for **3a** two double doublets are observed at 263.1 and −64.3 ppm ($J_{PH} = 254.4$ Hz, $^3J_{PH} = 6.3$ Hz), and for **3b** two double doublets are observed at 239.6 and −59.5 ppm ($J_{PH} = 222.2$ Hz, $^3J_{PH} = 28.1$ Hz). Following recrystallization from diethyl ether, only signals attributable to the *Z* isomer (**3a**) are observed. The ^1H NMR spectrum of pure **3a** exhibits two separate mesityl environments. The phosphavinyl *o*-CH_3 and *m*-CH protons appear as broad singlets, indicating hindered rotation. However, the *o*-CH_3 and *m*-CH protons for the secondary phosphane mesityl group are all magnetically inequivalent, appearing as four separate singlets. The secondary phosphane proton appears as a double doublet centered at 5.36 ppm ($J_{PH} = 254.4$ Hz, $^3J_{PH} = 6.3$ Hz). The inequivalence of the mesityl groups is apparent in the $^{13}C\{^1H\}$ NMR spectrum, with two *p*-CH_3 and three *o*-CH_3 resonances observed. The *tert*-butyl carbons give rise to double doublets at 44.90 ppm ($^2J_{PC} = 8.5$ and 21.1 Hz) and 33.32 ppm ($^3J_{PC} = 5.1$ and 18.3 Hz), and the central phosphavinyl carbon gives rise to a double doublet at 207.26 ppm ($J_{PC} = 58.0$ and 67.8 Hz). Attempts were made to isomerize **3** by thermolysis and photolysis, but, as for **1**, thermolysis was ineffective, and photolysis converted any **3b** present to **3a**.

Reaction of 1 equiv of *n*-butyllithium with **3** in THF at −78 °C cleanly regenerates **2** as the sole product without any addition across the P=C bond (Scheme 1). Access to the heavier alkali-metal salts is then conveniently achieved by metathesis (Scheme 1) of **2** with the corresponding heavier alkali-metal *tert*-butoxide (Na or K) or 2-ethylhexoxide (Rb or Cs). Despite attempts to crystallize the resulting complexes, either on their own or in the presence of a wide variety of neutral Lewis base donors, no solid products could be obtained from any solvent combination. Consequently, attention turned to crown ether complexes, as we have noted in previous studies their propensity to afford crystalline samples of alkali-metal complexes.[19] The resulting compounds [*t*-BuC(PMes)$_2$][M(15-crown-5)$_2$] (M = Na (**4**), K (**5**), Cs (**7**)) and [*t*-BuC(PMes)$_2$][Rb(12-crown-4)$_2$] (**6**) may be recrystallized from THF or THF/petroleum mixtures as

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(16) (a) Appel, R.; Schuhn, W. *J. Organomet. Chem.* **1987**, *329*, 179. (b) Karsch, H. H.; Köhler, F. H.; Reisacher, H.-U. *Tetrahedron Lett.* **1984**, *25*, 3687.

(17) (a) Niecke, E.; Nieger, M.; Schmidt, O.; Gudat, D.; Schoeller, W. W. *J. Am. Chem. Soc.* **1999**, *121*, 519. (b) Köbrich, G. *Angew. Chem.* **1967**, *79*, 15.

(18) Renner, J.; Bergsträsser, U.; Binger, P.; Regitz, M. *Eur. J. Inorg. Chem.* **2000**, 2337.

(19) (a) Liddle, S. T.; Clegg, W.; Morrison, C. A. *J. Chem. Soc., Dalton Trans.* **2004**, 2514. (b) Liddle, S. T.; Clegg, W. *Polyhedron* **2003**, *22*, 3507. (c) Liddle, S. T.; Clegg, W. *Acta Crystallogr., Sect. E* **2003**, *E59*, m1062. (d) Liddle, S. T.; Clegg, W. *Polyhedron* **2002**, *21*, 2451. (e) Liddle, S. T.; Clegg, W. *J. Chem. Soc., Dalton Trans.* **2001**, 3549. (f) Liddle, S. T.; Clegg, W. *J. Chem. Soc., Dalton Trans.* **2001**, 402.

air- and moisture-sensitive red (orange for **6**) crystals. Once isolated in crystalline form, they are indefinitely stable under a dry nitrogen atmosphere. The NMR spectra for **4**−**7** are remarkably similar: in each case a single resonance is observed in the $^{31}P\{^1H\}$ NMR spectrum at approximately 112 ppm; given the X-ray data (see below) and the reluctance of **1** and **3** to isomerize, it seems likely that this signal is due to the anti-anti isomer of the free anion. The ^1H and $^{13}C\{^1H\}$ NMR spectra indicate a symmetrical 1,3-diphosphaallyl anion in solution with only one mesityl environment; the *tert*-butyl carbons and the central carbon of the PCP unit all give rise to triplets at (mean values) 35.07 ppm ($^3J_{PC} = 16.8$ Hz), 42.69 ppm ($^2J_{PC} = 28.3$ Hz), and 214.30 ppm ($J_{PC} = 84.2$ Hz). Given the invariant nature of the NMR spectra, it is almost certain that **4**−**7** exist as separated ion pairs in solution. The essentially identical nature of the NMR spectra of **4**−**7** to that of **2** strongly suggests that **2** exists as a solvent-separated ion pair, of the form $[t\text{-BuC(PMes)}_2][\text{Li(THF)}_4]$, in solution. Interestingly, although we have previously prepared the separated ion pair complex $[\text{Rb(12-crown-4)}_2\text{(THF)}][\text{PyNPh}]$,[19a] crystals of **6** were found to be free of THF.

During the preparation of **4**−**7** it was noted that yields diminished (for **5**−**7**) if solutions of **2** and the LiOR byproduct were stirred for long periods at room temperature. It was also noted that yields for the Cs complex were lower than those of the K or Rb complexes. During the attempted preparation of $[t\text{-BuC(PMes)}_2][\text{Cs(12-crown-4)}_2]$ (**8**) a small crop of orange crystals was obtained, which was subsequently shown by X-ray crystallography (see below) and NMR spectroscopy to be the secondary phosphanide complex $[\text{Mes}_2\text{P}][\text{Cs(12-crown-4)}_2]$ (**9**). The $^{31}P\{^1H\}$ NMR spectrum of **9** exhibits a singlet at −34.4 ppm, which compares with a shift of −42.8 ppm for $[\text{Li(12-crown-4)}_2][\text{PMes}_2]$.[20] The isolation of **9** was surprising; a $^{31}P\{^1H\}$ NMR spectrum of the crude mother liquor from this reaction revealed that the desired complex (**8**) was present, along with **9**, the known ditertiary diphosphane $(\text{Mes}_2\text{P})_2$ (**10**; δ −31.5 ppm),[21] a small quantity of the secondary phosphane Mes_2PH (δ −86.1 ppm),[22] and other minor phosphorus-containing compounds which we were unable to identify. A $^{31}P\{^1H\}$ NMR spectrum of the solvent collected in a cold trap during workup showed the presence of $t\text{-BuC}\equiv\text{P}$ (**11**; δ −69.2 ppm).[23] $^{31}P\{^1H\}$ NMR spectroscopic analysis of the mother liquors from **6** and **7** also revealed small amounts of **10** and **11**, implying that the same process is operating for the K and Rb compounds, although at a lower rate. However, this behavior only occurs with crude mother liquors that contain the lithium alkoxide byproduct (pure **4**−**7** are stable in solution even at elevated temperatures) and this implies that the alkoxide is intimately involved in the decomposition of the 1,3-diphosphaallyl anion; we note that alkali-metal alkoxides have precedent for initiating rearrangements of 1,3-diphosphapropenes.[16b] The exact mechanism of decomposition is clearly complicated and is too rapid to monitor by $^{31}P\{^1H\}$ NMR spectroscopy, but it is evident that a 1,3-rearrangement reaction of the anion is occurring to give Mes_2P^- and **11**. Subsequently, the Mes_2P^- may undergo hydrolysis to form Mes_2PH or oxidatively couple to give **10**. Unexpected rearrangement reactions are a common theme of compounds containing the reactive P═C bond, as exemplified by recent studies by Jones and co-workers[24] and the 1,2-Fritsch−Buttenberg−Wiechell rearrangement of phosphavinyl carbenoids.[25]

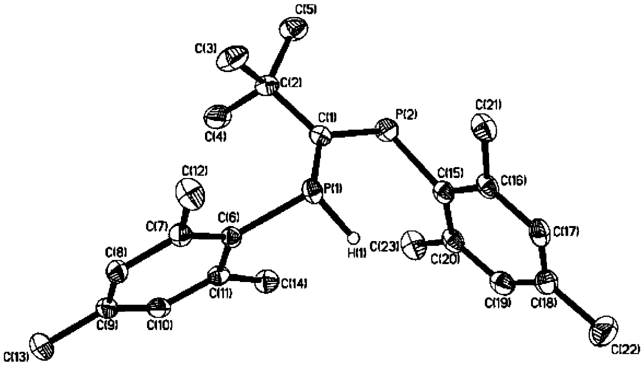

Figure 1. Molecular structure of **3** with 50% probability ellipsoids. Carbon-bound hydrogen atoms are omitted for clarity.

Solid-State Structures. The solid-state structures of (*Z*)-MesP═C(*t*-Bu)P(X)Mes (**1**) and $[\{t\text{-BuC(PMes)}_2\}\text{Li(THF)}_3]$ (**2**) were described in our earlier communication.[8] Yellow crystals of **3** suitable for X-ray crystallography were grown from cold (5 °C) diethyl ether; the molecular structure is illustrated in Figure 1, and selected bond lengths and angles are listed in Table 1. The *Z* configuration of the P═C bond is confirmed, and the two mesityl substituents are no longer syn, as is the case for **1**. Indeed, H(1) is effectively syn to the phosphavinyl mesityl ring, and the H(1)···C(15) distance of 2.546 Å indicates a weak electrostatic point-to-face P−H···π interaction.[26] The C(1)−P(2) and C(1)−P(1) bond lengths of 1.690(2) and 1.827(2) Å, respectively, are significantly different, as befits their double- and single-bond character. Whereas in **2** the corresponding P(1)−C(6) and P(2)−C(15) bond lengths are statistically invariant, in **3** they are significantly different at 1.843(2) and 1.829(2) Å, reflecting the different hybridization of P(2) compared to P(1). The P(1)−H(1) bond length was freely refined to 1.318(3) Å. The C(15)−P(2)−C(1) bond angle of 108.60(6)° is approximately midway between that observed in **1** and **2**; P(1) is trigonal pyramidal (sum of angles 305.50°), and C(1) is essentially planar (sum of angles 359.3°).

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(20) Bartlett, R. A.; Olmstead, M. M.; Power, P. P.; Sigel, G. A. *Inorg. Chem.* **1987**, *26*, 1941.

(21) (a) McFarlane, W.; Rees, N. H.; Constanza, L.; Patel, M.; Colquhoun, I. J. *J. Chem. Soc., Dalton Trans.* **2000**, 4453. (b) Baxter, S. G.; Cowley, A. H.; Davis, R. E.; Riley, P. E. *J. Am. Chem. Soc.* **1981**, *103*, 1699.

(22) Liddle, S. T.; Izod, K. Unpublished results. The value reported in this paper differs from that reported in ref 20 by 6.3 ppm. We attribute this to solvent effects.

(23) Becker, G.; Gresser, G.; Uhl, W. *Z. Naturforsch., B* **1981**, *36*, 1981.

(24) (a) Aldridge, S.; Jones, C.; Junk, P. C.; Richards, A. F.; Waugh, M. *J. Organomet. Chem.* **2003**, *665*, 127. (b) Jones, C.; Richards, A. F. *J. Organomet. Chem.* **2002**, *645*, 256. (c) Jones, C.; Junk, P. C.; Richards, A. F.; Waugh, M. *New J. Chem.* **2002**, *26*, 1209. (d) Jones, C.; Platts, J. A.; Richards, A. F. *Chem. Commun.* **2001**, 663. (e) Jones, C.; Richards, A. F. *J. Organomet. Chem.* **2001**, *629*, 109. (f) Jones, C.; Richards, A. F. *J. Chem. Soc., Dalton Trans.* **2000**, 3233.

(25) (a) Jun, H.; Young, V. G.; Angelici, R. J. *Organometallics* **1994**, *13*, 2444. (b) Romanenko, V. D.; Sanchez, M.; Sarina, T. V.; Mazierès, M.-R.; Wolf, R. *Tetrahedron Lett.* **1992**, *33*, 2981. (c) Yoshifuji, M.; Kawanami, H.; Kawai, Y.; Toyota, K.; Yasunami, M.; Niitsu, T.; Inamoto, N. *Chem. Lett.* **1992**, 1053. (d) Appel, R.; Immenkeppel, M. *Z. Anorg. Allg. Chem.* **1987**, *553*, 7. (e) Yoshifuji, M.; Niitsu, T.; Inamoto, N. *Chem. Lett.* **1988**, 1733.

(26) Janiak, C. *J. Chem. Soc., Dalton Trans.* **2000**, 3885.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 1–4, 6, and 7

	1[a]	**2**[a]	**3**	**4**	**6**	**7**
C(1)–P(1)	1.836(2)	1.760(2)	1.827(2)	1.767(6)	1.758(4)	1.746(7)
C(1)–P(2)	1.694(2)	1.737(2)	1.690(2)	1.735(5)	1.753(4)	1.747(7)
C(1)–C(2)	1.552(3)	1.557(4)	1.547(2)	1.552(8)	1.577(6)	1.582(9)
P(1)-X/Li(1)/H(1)	2.202(2)	2.562(4)	1.318(3)			
P(1)–C(6)	1.832(2)	1.832(2)	1.843(2)	1.835(6)	1.838(5)	1.860(7)
P(2)–C(15)	1.837(2)	1.838(3)	1.829(2)	1.836(6)	1.840(5)	1.843(7)
M–O_{av}		1.946		2.749	2.939	3.139
Rb(1)–C(3)					3.646(3)	
P(1)–C(1)–P(2)	118.05(10)	129.31(15)	123.59(8)	131.2(3)	137.0(3)	132.5(4)
C(2)–C(1)–P(1)	122.85(13)	114.90(16)	118.93(9)	113.2(4)	111.5(3)	114.6(4)
C(2)–C(1)–P(2)	116.49(14)	115.69(17)	116.76(9)	115.6(4)	111.4(3)	112.9(4)
C(6)–P(1)–C(1)	107.82(8)	108.52(11)	108.87(6)	106.7(2)	111.6(2)	107.5(3)
C(6)–P(1)–X/Li/H	97.94(6)	109.20(12)	99.29(7)			
C(1)–P(1)–X/Li/H	109.15(6)	136.22(13)	97.30(8)			
C(1)–P(2)–C(15)	109.18(9)	106.97(11)	108.60(6)	107.8(2)	109.7(2)	107.1(3)

[a] See ref 8.

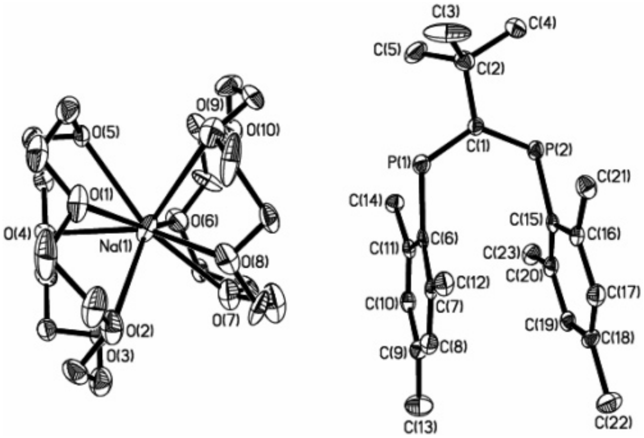

Figure 2. Molecular structure of **4** with 50% probability ellipsoids and with selected labeling. Hydrogen atoms are omitted for clarity.

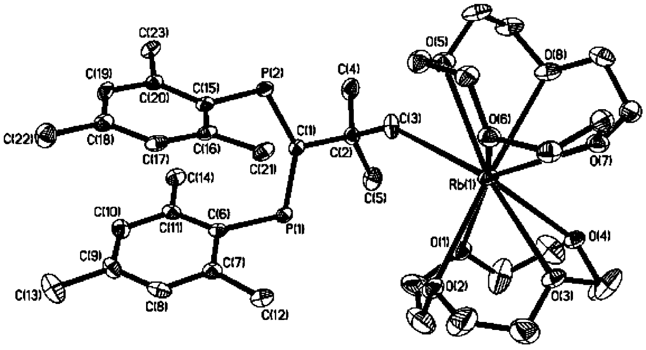

Figure 3. Molecular structure of **6** with 50% probability ellipsoids and with selected labeling. Hydrogen atoms are omitted for clarity.

Dark red crystals of **4** suitable for a single-crystal X-ray study were grown from cold (5 °C) methylcyclohexane/THF; the molecular structure is illustrated in Figure 2, and selected bond lengths and angles are listed in Table 1. The complex crystallizes as a separated ion pair; the anion is in the anti-anti configuration, and the sodium cation is encapsulated by two κ^4 15-crown-5 molecules to give an eight-coordinate sodium center. The Na–O bond lengths span the range 2.621(7)–2.957(7) Å, reflecting the difficulty of sandwiching sodium between two 15-crown-5 molecules (the Na–O nonbonding distances are 3.060 and 3.311 Å). The anion has approximate C_2 symmetry; the C(1)–P(1) and C(1)–P(2) bond lengths of 1.767(6) and 1.735(5) Å are essentially statistically invariant and are within the range observed for delocalized P–C–P systems.[8,9] An intramolecular $\pi\cdots\pi$ slipped stacking interaction[26,27] is observed between the two mesityl rings with C_{ortho}–$ring_{cent}$ distances of 3.323 and 3.377 Å, which are shorter distances than the corresponding distances previously observed in **2**.[8] This has the effect of pushing one P–C_{ipso} bond above the P–C–P plane and the other below, such that C(6) and C(15) reside −0.732 and +0.462 Å below and above the P(1)–C(1)–C(2)–P(2) plane, respectively. The C(1)–P(1)–C(6) and C(1)–P(2)–C(15) angles of 106.7(2) and 107.8(2)° are compressed compared to those in **1** and **3** and are similar to those observed in **2**; C(1) is essentially planar (sum of angles 359.8°).

Dark red needles of **5** were grown from hot THF cooled slowly to room temperature. However, the thin nature of the crystals resulted in weak data of poor quality.[28] Consequently, although the gross structural features are clear, a detailed discussion of bond lengths and angles is not possible. The structure is isomorphous with compound **7**, consisting of a separated ion pair; the potassium cation is sandwiched between two κ^5 15-crown-5 ether molecules, and the anion is in the anti-anti conformation.

Orange crystals of **6** suitable for a single-crystal X-ray study were grown from cold (5 °C) THF; the molecular structure is illustrated in Figure 3, and selected bond lengths and angles are listed in Table 1. The structure consists of a rubidium cation sandwiched between two 12-crown-4 molecules connected to the anion, which is in the anti-anti configuration, via a *tert*-butyl $CH_3\cdots$Rb contact. The Rb–O bond lengths span the range 2.881(3)–3.010(3) Å, resulting in Rb(1) residing a mean distance of 2.141 Å from the mean plane of each crown. The dihedral angle between these two planes is 144.5°, which is remarkably similar to the corresponding angle in [Rb(12-crown-4)$_2$(THF)][PyNPh] (145.5°).[19a] The anion exhibits C(1)–P(1) and C(1)–P(2) bond lengths of

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(27) Hunter, C. A.; Sanders, J. K. M. *J. Am. Chem. Soc.* **1990**, *112*, 5525.

(28) Crystals of **5** were orthorhombic, space group $P2_12_12_1$, with a = 15.552(2) Å, b = 17.140(2) Å, c = 17.246(2) Å, V = 4596.9(8) Å^3, and Z = 4. They were thin red needles giving weak, poor-quality diffraction data (despite repeated recrystallization and data collection), and the structure could not be satisfactorily refined, giving a high R1 value of 0.1496.

1.758(4) and 1.753(4) Å, within the range observed for delocalized P−C−P systems.[8,9] Again, a $\pi\cdots\pi$ slipped stacking interaction is observed, but the mesityl rings are slightly twisted, resulting in C−ring$_{\mathrm{cent}}$ distances of 3.340 (ortho) and 3.493 Å (meta); consequently, the C(6) and C(15) atoms are closer to the P(1)−C(1)−C(2)−P(2) plane, residing −0.024 and +0.406 Å below and above, respectively. This results in a slight distortion of the C(1)−P(1)−C(6) and C(1)−P(2)−C(15) angles to 116.2(2) and 109.7(2)°, respectively. Of considerable interest is the $CH_3\cdots Rb$ contact; **7** crystallizes from neat THF, and it would be anticipated that a molecule of THF would be bound to the Rb center, as observed for [Rb(12-crown-4)$_2$(THF)][PyNPh].[19a] However, in this instance the $CH_3\cdots Rb$ interaction appears to be more favorable than binding to THF; indeed, a growing number of examples of heavier alkali-metal C−H···M interactions have emerged recently,[29] and such interactions are sometimes formed in preference to interactions with more conventional neutral Lewis bases. In a comprehensive study,[30] Klinkhammer has described how alkali-metal C−H···M interactions may be described on electrostatic grounds with a donor−acceptor model between the C−H bonding electron density and the alkali-metal cation; the shortest bonds should therefore be present in linear $CH_3\cdots M$ systems where the number of C−H···M contacts are maximized. In a recent study Kennedy and co-workers noted a correlation between the R−C···M angle and the $CH_3\cdots M$ distance.[31] In **7** the C(3)···Rb(1) distance is 3.646(3) Å (which in the structure exhibits only one C−H···Rb contact) with a C−C···Rb angle of 151.3°; this compares to a range of 3.544−3.626 Å (range of angles 158.0−161.9°) observed for the complexes [Rb(toluene)$_3$][M{N(SiMe$_3$)$_2$}$_3$] (M = Mg, Zn),[31] which may be expected to exhibit shorter contacts, since the only donors in these two systems are C−H···M and M···π-arene interactions, and a range of 3.279−3.772 Å for [{RbC(SiMe$_3$)$_3$}$_\infty$],[29a] which is constrained by geometry limitations of the (Me$_3$Si)$_3$C$^-$ ligand.

Dark red crystals of **7** suitable for a single-crystal X-ray study were grown from cold (−30 °C) THF; the molecular structure is illustrated in Figure 4, and selected bond lengths and angles are listed in Table 1. The complex crystallizes as a separated ion pair; the anion is in the anti-anti configuration, and the cesium cation is encapsulated by two κ^5 15-crown-5 ether molecules to give a 10-coordinate cesium center (pseudo D_{5d} symmetry). The Cs−O bond lengths span the range 3.066(5)−3.232(9) Å, a larger range than in **4**, commensurate with the larger ionic radius of cesium compared to sodium. Consequently, Cs(1) resides a mean distance of 1.994 Å from the mean plane of each crown. The crowns are canted slightly, with a dihedral angle between these two planes at cesium of 171.6°. The anion exhibits C(1)−P(1) and C(1)−P(2) bond lengths of 1.746(7) and 1.747(7) Å, clearly well within the range observed for delocalized P−C−P systems.[8,9] Again, a $\pi\cdots\pi$ slipped stacking interaction is observed (as for **4**), with C$_{\mathrm{ortho}}$−ring$_{\mathrm{cent}}$ distances of 3.390 and 3.367 Å, resulting in C(6) and C(15) residing −0.459 and +0.717 Å below and above the P(1)−C(1)−C(2)−P(2) plane, respectively. The C(1)−P(1)−C(6) and C(1)−P(2)−C(15) angles of 107.5(3) and 107.1(3)° are similar to those observed in **2** and **4**; C(1) is again planar (sum of angles 360.0°).

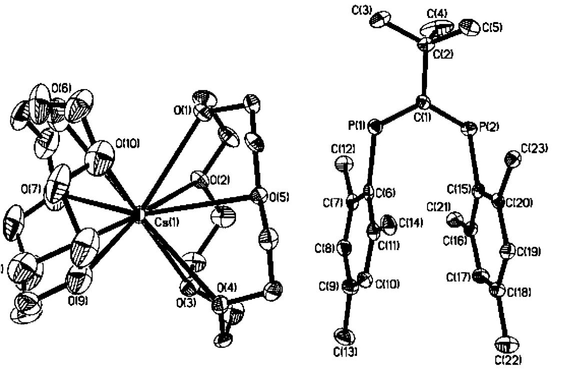

Figure 4. Molecular structure of **7** with 50% probability ellipsoids and with selected labeling. Hydrogen atoms are omitted for clarity. The structure of **5** is essentially identical in appearance.

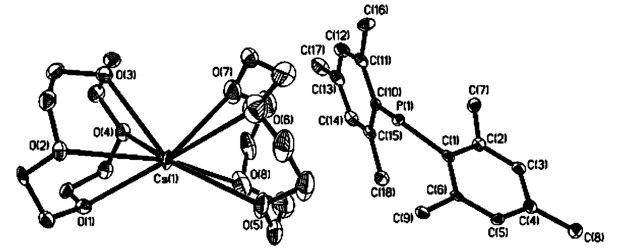

Figure 5. Asymmetric unit of **9** with 50% probability ellipsoids and with selected labeling. Hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 9

P(1)−C(1)	1.858(10)	P(1)−C(10)	1.840(9)
Cs(1)−O(1)	3.052(7)	Cs(1)−O(2)	3.112(7)
Cs(1)−O(3)	3.041(8)	Cs(1)−O(4)	3.149(7)
Cs(1)−O(5)	3.006(9)	Cs(1)−O(6)	3.130(13)
Cs(1)−O(7)	3.016(10)	Cs(1)−O(8)	3.012(11)
Cs(1)···O(2A)	4.835	Cs(1)···O(8A)	4.786
C(1)−P(1)−C(10)		106.2(4)	

Orange crystals of **9** suitable for a single-crystal X-ray study were grown from cold (5 °C) methylcyclohexane/THF; the asymmetric unit is illustrated in Figure 5, and selected bond lengths and angles are listed in Table 2. The complex crystallizes as a separated ion pair; however, the Cs(12-crown-4)$_2$ cations are linked by weak, bridging O−Cs interactions to form infinite 1-dimensional zigzag chains (Figure 6), and the free anion exhibits no intermolecular contacts, residing in voids between the chains. The Cs−O intramolecular bond lengths span the range 3.006(9)−3.149(7) Å, and the two intermolecular bridging contacts are 4.786 and 4.835 Å, which may be regarded as purely electrostatic in nature; examples of 12-crown-4 bridging alkali metals are rare but not unknown.[19a,f,32] Consequently, Cs(1)

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[29] (a) Eaborn, C.; Hitchcock, P. B.; Izod, K.; Smith, J. D. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 687. (b) Eaborn, C.; Hitchcock, P. B.; Izod, K.; Jagger, A. J.; Smith, J. D. *Organometallics* **1994**, *13*, 753. (c) Weiss, E. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1501. (d) Schade, C.; Schleyer, P. v. R. *Adv. Organomet. Chem.* **1987**, 169.

[30] Klinkhammer, K. W. *Chem. Eur. J.* **1997**, *3*, 1418.

[31] Forbes, G. C.; Kennedy, A. R.; Mulvey, R. E.; Roberts, B. A.; Rowlings, R. B. *Organometallics* **2002**, *21*, 5115.

[32] Dietrich, A.; Neumuller, B.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1999**, *625*, 619.

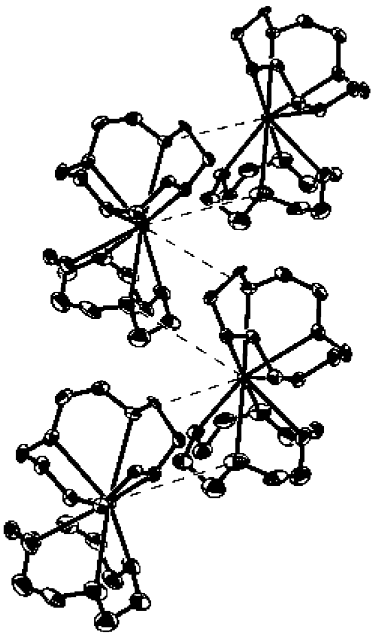
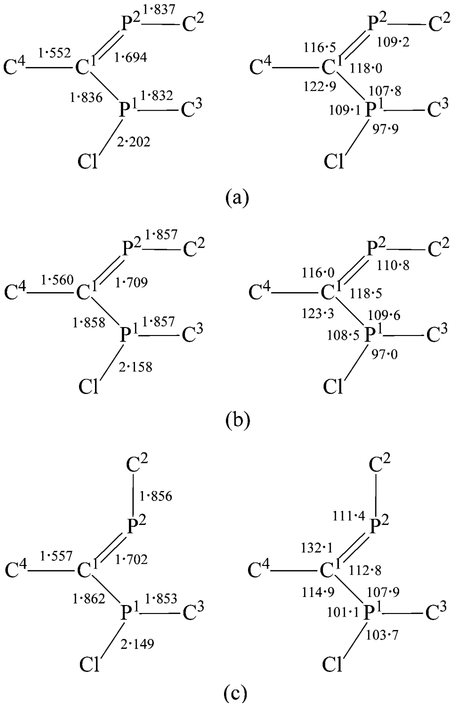


Figure 6. Polymeric cations of **9**. Phosphanide anions, atom labels, and hydrogen atoms are omitted for clarity.

resides a mean distance of 2.326 Å from the mean plane of the crowns. The crowns are canted, with a dihedral angle between the two mean planes of 145.1°, remarkably similar to the corresponding angle observed in **6**. In the phosphanide anion, the P(1)−C(1) and P(1)−C(10) bond lengths are 1.858(10) and 1.840(9) Å; this compares with P−C bond lengths of 1.807 and 1.802 Å in the free phosphanide anion Ph_2P^-.[33] The two mesityl rings adopt a propeller twist motif with torsion angles of 46.9 and 45.9° from the C(1)−P(1)−C(10) plane; these compare with torsion angles of 20.6 and 25.3° in Ph_2P^- and reflect the bulkier nature of the mesityl group compared to phenyl. This increased out-of-plane twisting of the mesityl groups allows the C(1)−P(1)−C(10) bond angle to be 106.2(4)°, comparable to that observed in Ph_2P^- (105.38°).[33] As far as we are aware, the secondary phosphanide anion in **9** is only the third example of a free secondary phosphanide anion.[34]

DFT Calculations. To gain more insight into the experimentally observed stereochemical preference for **1** and **3** to adopt the *Z* configuration, we undertook a theoretical investigation using the Titan program.[35] For calculational simplicity the *Z* and *E* isomers of the chloride of **1** (i.e. **1a**,**c**) were optimized at the BL3YP/6-31G* level of theory. A graphical comparison of experimentally observed (X-ray) and calculated bond lengths and angles for (*Z*)-**1** and **1a**,**c** is illustrated in Chart 2; illustrations of the calculated structures of **1a**,**c** and the HOMO and the LUMO of each are given in the Supporting Information. In general, the calculated structure of **1a** closely matches the bond lengths observed in the crystal structure of (*Z*)-**1**; bond lengths are typically inflated on the order of 0.015−0.025 Å. Calculated bond angles also closely match those observed in the crystal structure of **1**. The calculated conformation of **1a** (which is not subject to solid-state packing forces) closely matches that of (*Z*)-**1**. This may indicate that, in addition to steric repulsion from the *tert*-butyl group, $\pi \cdots \pi$ and $P-H \cdots \pi$ interactions may be important factors to take into consideration regarding the syn arrangement of the two mesityl rings in (*Z*)-**1**, the syn P−H⋯mesityl arrangement in **3** in the solid state, and, consequently, the hindered rotation of the MesP(Cl) and MesP(H) groups of **1** and **3**, respectively, in solution, as evidenced by NMR spectroscopy.

Chart 2. Observed Bond Lengths (Å) and Angles (deg) for the Core Framework: (a) Experimentally Observed Crystal Structure of 1a; (b) Calculated for the *Z* Isomer of 1a; (c) Calculated for the *E* Isomer of 1c



The calculated *E* isomer **1c** compares favorably with the calculated structure of **1a**; however, no crystal structure data for the *E* isomer of **1** are currently available for meaningful comparison. The experimentally observed preference for the *Z* isomer is corroborated by single-point energy calculations of **1a**,**c**. Final energies are calculated to be −2038.0303 au for **1a** and −2038.0122 au for **1c**. This corresponds to the *Z* isomer being more stable than the *E* isomer by 47.4 kJ mol^{-1}.

Summary and Conclusions

Protonation of [{*t*-BuC(PMes)$_2$}Li(THF)$_3$] (**2**; Mes = 2,4,6-$(CH_3)_3C_6H_2$) with either *t*-BuCl or H_2O yields the 1,3-diphosphapropene (*Z*)-MesP=C(*t*-Bu)P(H)Mes (**3**). Metathesis of **2** with heavier alkali-metal alkoxides, in the presence of crown ethers, allows access to the crystalline 1,3-diphosphaallyl complexes [*t*-BuC(PMes)$_2$][M(15-crown-5)$_2$] (M = Na (**4**), K (**5**), Cs (**7**)) and [*t*-BuC(PMes)$_2$][Rb(12-crown-4)$_2$] (**6**). In all instances the anion adopts the anti-anti configuration, probably as a consequence of steric repulsion from the *tert*-butyl group and favorable $\pi \cdots \pi$ slipped stacking interactions. The heavier alkali-metal complexes (K, Rb, Cs) become

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(33) Hope, H.; Olmstead, M. M.; Power, P. P.; Xu, X. *J. Am. Chem. Soc.* **1984**, *106*, 819.

(34) See ref 33 and: Davidson, M. G.; Dillon, K. B.; Howard, J. A. K.; Lamb, S.; Roden, M. D. *J. Organomet. Chem.* **1998**, *550*, 481.

(35) Wavefunction, Inc., Irvine, CA, 2001.

increasingly unstable in the presence of the lithium alkoxide byproduct and decompose to give the ditertiary diphosphane $(Mes_2P)_2$ (**10**) and *t*-BuC≡P (**11**), and in one instance the secondary phosphanide complex $[Mes_2P][Cs(12\text{-crown-}4)_2]$ (**9**) was isolated in low yield. DFT studies at the BL3YP/6-31G* level on the precursor compounds (*Z*)- and (*E*)-MesP=C(*t*-Bu)P(Cl)Mes (**1a,c**) indicate that the *Z* isomer is more stable than the *E* isomer by 47.4 kJ mol^{-1}, confirming the experimentally observed preference for the *Z* configuration of the P=C bond.

Experimental Section

General Comments. All manipulations were carried out using standard Schlenk techniques under, unless stated otherwise, an atmosphere of dry nitrogen. Diethyl ether, THF, methylcyclohexane, and light petroleum (bp 40−60 °C) were distilled from potassium or sodium−potassium alloy under an atmosphere of dry nitrogen and were stored over a potassium film (except THF, which was stored over activated 4 Å molecular sieves). Deuterated solvents were distilled from a potassium mirror, degassed by three freeze−pump−thaw cycles, and stored over activated 4 Å molecular sieves. *t*-BuCl was distilled from CaH_2 and stored over activated 4 Å molecular sieves. Elemental lithium, *n*-butyllithium (2.5 M solution in hexanes), and PCl_3 were purchased from Aldrich and used without any further purification. NaO-*t*-Bu and KO-*t*-Bu were purchased from Aldrich and baked at 120 °C in vacuo for 3 h prior to use. The polydentate crown ethers 12-crown-4 and 15-crown-5 were dried over activated 4 Å sieves and degassed by three freeze−pump−thaw cycles prior to use. $MesPCl_2$ was prepared as described below. The compounds [(*Z*)-MesP=C(*t*-Bu)MgBr(OEt_2)],[15] $MOCH_2CH(CH_2CH_3)CH_2CH_2CH_2CH_3$ (M = Rb, Cs),[36] and $[Mg(2,4,6\text{-}Me_3C_6H_2)_2(THF)_2]$[37] were prepared by modified literature procedures. The synthesis and characterization of compounds **2** and **3** were briefly described in a preliminary communication[8] but are reported here in full.

^1H, ^{13}C, ^7Li, ^{31}P, and ^{133}Cs NMR spectra were recorded on a JEOL Lambda 500 spectrometer operating at 500.16, 125.65, 194.25, 202.35, and 65.48 MHz, respectively; chemical shifts are quoted in ppm and are relative to $Si(CH_3)_4$ (^1H and ^{13}C), external 1 M LiCl, 85% H_3PO_4, and 1 M CsCl, respectively. Elemental microanalyses were carried out by the Microanalysis Service of London Metropolitan University.

Preparation of $MesPCl_2$ (Mes = 2,4,6-$(CH_3)_3C_6H_2$). $[Mg(2,4,6\text{-}Me_3C_6H_2)_2(THF)_2]$ (16.28 g, 40 mmol) in THF (150 mL) was added dropwise over 2 h from a dropping funnel to a cold (−78 °C) mechanically stirred solution of PCl_3 (10.5 mL, 120 mmol) in THF (100 mL). The mixture was warmed slowly to room temperature and was stirred overnight (16 h). Volatiles were removed in vacuo to give a sticky yellow solid. The product was extracted into diethyl ether (200 mL) and filtered and the solid washed with ether (3 × 20 mL). Volatiles were removed from the combined extracts in vacuo to give a pale yellow oil. Distillation (10^{-3} Torr) afforded the product as an essentially colorless oil, which turned pale yellow on standing for several hours. Yield: 12.87 g, 72.8%. ^1H NMR (d_6-benzene, 298 K): δ 2.37 (s, 3H, *p*-CH_3), 2.80 (d, $^4J_{PH}$ = 4.1 Hz, 6H, *o*-CH_3), 6.99 (d, $^4J_{PH}$ = 4.2 Hz, 2H, *m*-C*H*). $^{13}C\{^1H\}$ NMR (d_6-benzene, 298 K): δ 21.35 (*o*-CH_3), 21.70 (*p*-CH_3), 130.66 (*m*-*C*), 131.47 (*p*-*C*), 132.35 (*o*-*C*), 145.53 (d, J_{PC} = 30.6 Hz, *i*-*C*). $^{31}P\{^1H\}$ NMR (d_6-benzene, 298 K): δ 169.9 (s).

Preparation of (*Z*)-MesP=C(*t*-Bu)P(X)Mes (1; X = Cl (1a), Br (1b)). [(*Z*)-MesP=C(*t*-Bu)MgBr(OEt_2)] (16.07 g, 40.42 mmol) in THF (200 mL) was added dropwise to a cold (−78 °C) solution of $MesPCl_2$ (9.8 g, 44.33 mmol) in THF (100 mL). After complete addition, the solution was warmed slowly to room temperature and was stirred for 48 h, during which time the initially red solution became orange. Volatiles were removed in vacuo to give an orange solid, which was warmed in vacuo to remove unreacted $MesPCl_2$. The product was extracted into diethyl ether (3 × 80 mL) and filtered from the resulting white precipitate, and volatiles were removed in vacuo to give a yellow-brown oil. Addition of cold (0 °C) light petroleum/diethyl ether (10:1 mL) resulted in the precipitation of **1** as a bright yellow solid, which was separated from the mother liquor and dried in vacuo. Yield (based upon a Cl to Br ratio of 0.64:0.36): 14.7 g, 88.8%. Yellow crystals of **1** suitable for X-ray crystallography were obtained from a concentrated solution in diethyl ether stored at 5 °C for 2 days. Yield: 9.94 g, 58.4%. Anal. Calcd for $C_{23}H_{31}Br_{0.36}Cl_{0.64}P_2$: C, 65.63; H, 7.42. Found: C, 66.42; H, 7.38. Cl derivative (**1a**): ^1H NMR (d_6-benzene, 298 K) δ 1.42 (s, 3H, *p*-CH_3), 1.51 (s, 9H, C(CH_3)$_3$), 1.70 (s, 3H, *p*-CH_3), 1.79 (s, 3H, P(Cl)Mes *o*-CH_3), 2.13 (s, br, 6H, C=PMes *o*-CH_3), 2.24 (s, 3H, P(Cl)Mes *o*-CH_3), 5.85 (s, 1H, P(Cl)Mes *m*-C*H*), 6.11 (s, br, 2H, C=PMes *m*-C*H*), 6.23 (s, 1H, P(Cl)Mes *m*-C*H*); $^{13}C\{^1H\}$ NMR (d_6-benzene, 298 K) δ 20.89 (*o*-CH_3), 20.95 (*o*-CH_3), 21.05 (*o*-CH_3), 22.15 (*p*-CH_3), 22.36 (*p*-CH_3), 32.61 (s, br, $^3J_{PC}$ not resolved, C(CH_3)$_3$), 47.24 (s, br, $^2J_{PC}$ not resolved, *C*(CH_3)$_3$), 127.81 (*p*-*C*), 128.42 (*p*-*C*), 137.87 (*o*-C), 138.45 (*o*-C), 140.71 (*o*-C), 142.40 (s, br, J_{PC} not resolved, *i*-*C*), 142.53 (s, br, J_{PC} not resolved, *i*-*C*) 206.21 (dd, J_{PC} = 71.2 and 100.3 Hz, P=*C*P, signals for the Mes *m*-*C* were obscured by solvent resonances; $^{31}P\{^1H\}$ NMR (d_6-benzene, 298 K) δ 259.3 (d, $^2J_{PP}$ = 40.0 Hz, *P*=C), 93.6 (d, $^2J_{PP}$ = 40.0 Hz, *P*(Cl)). Br derivative (**1b**): ^1H NMR (d_6-benzene, 298 K) δ 1.40 (s, 3H, *p*-CH_3), 1.53 (s, 9H, C(CH_3)$_3$), 1.73 (s, 3H, *p*-CH_3), 1.83 (s, 3H, P(Br)Mes *o*-CH_3), 2.13 (s, br, 6H, C=PMes *o*-CH_3), 2.25 (s, 3H, P(Br)Mes *o*-CH_3), 5.83 (s, 1H, P(Br)Mes *m*-C*H*), 6.10 (s, br, 2H, C=PMes *m*-C*H*), 6.22 (s, 1H, P(Br)Mes *m*-C*H*); $^{13}C\{^1H\}$ NMR (d_6-benzene, 298 K) δ 20.92 (*o*-CH_3), 21.00 (*o*-CH_3), 21.08 (*o*-CH_3), 22.30 (*p*-CH_3), 23.01 (*p*-CH_3), 32.88 (s, br, $^3J_{PC}$ not resolved, C(CH_3)$_3$), 47.38 (s, br, $^2J_{PC}$ not resolved, *C*(CH_3)$_3$), 127.91 (*p*-*C*), 128.67 (*p*-*C*), 137.78 (*o*-*C*), 138.39 (*o*-*C*), 139.94 (*o*-*C*), 144.03 (s, br, J_{PC} not resolved, *i*-*C*), 144.18 (s, br, J_{PC} not resolved, *i*-*C*), and 204.34 (dd, J_{PC} = 72.1 and 107.9 Hz, P=*C*-P), signals for the mesityl *m*-*C* were obscured by solvent resonances; $^{31}P\{^1H\}$ NMR (d_6-benzene, 298 K) δ 262.3 (d, $^2J_{PP}$ = 47.0 Hz, *P*=C), 81.3 (d, $^2J_{PP}$ = 47.0 Hz, *P*(Br)).

Preparation of [{*t*-BuC(PMes)$_2$}Li(THF)$_3$] (2). A solution of **1** (4.20 g, 10 mmol) in THF (30 mL) was added to a slurry of elemental lithium (0.14 g, 20.2 mmol) in THF (5 mL) under a dry argon atmosphere. The mixture was sonicated for 1 h, during which time the mixture darkened from yellow to dark red. The reaction mixture was stirred for 20 h, and volatiles were removed in vacuo to give a dark red oil. The oil was extracted into diethyl ether (30 mL) and filtered from the resulting white precipitate, and volatiles were removed in vacuo to afford a dark red oil. Addition of cold (0 °C) light petroleum (5 mL) resulted in the precipitation of **2** as a red powder. Yield: 5.80 g, 97.8%. Dark red crystals of **2** suitable for X-ray crystallography were obtained from a concentrated solution in diethyl ether stored at 5 °C for 1 day. Yield: 1.98 g, 33.4%. Anal. Calcd for $C_{35}H_{55}LiO_3P_2$: C, 70.93; H, 9.35. Found: C, 70.89; H, 9.49. ^1H NMR (d_8-THF, 298 K): δ 1.44 (s, 9H, C(CH_3)$_3$), 1.65 (m, 12H, CH_2 thf), 1.86 (s, 6H, *p*-CH_3), 2.21 (s, 12H, *o*-CH_3), 3.48 (m, 12H, OCH_2 thf), 5.96 (s, 4H, *m*-C*H*). $^{13}C\{^1H\}$ NMR (d_8-THF, 298 K): δ 20.21 (*o*-CH_3), 22.22 (*p*-CH_3), 25.37 (CH_2 thf), 34.96 (t, $^3J_{PC}$ = 16.8 Hz, C(CH_3)$_3$), 42.62 (t, $^2J_{PC}$ = 28.2 Hz, *C*(CH_3)$_3$), 67.49 (OCH_2 thf), 125.79 (*m*-*C*), 130.20 (*p*-*C*), 139.38 (*o*-*C*), 144.96 (d, J_{PC} = 25.4 Hz, *i*-*C*), 214.10 (t, J_{PC} = 84.2 Hz, PCP). $^{31}P\{^1H\}$ NMR (d_8-THF, 298 K): δ 109.4 (s). ^7Li NMR (d_8-THF, 298 K): δ −0.69 (s).

Preparation of (*Z*)-MesP=C(*t*-Bu)P(H)Mes (3). Method A. Degassed *t*-BuCl (5.4 mL, 50 mmol) was added neat to a

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(36) Chisholm, M. H.; Drake, S. R.; Naiini, A. A.; Streib, W. E. *Polyhedron* **1991**, *10*, 337.

(37) Waggoner, K. M.; Power, P. P. *Organometallics* **1992**, *11*, 3209.

solution of **2** (2.96 g, 5 mmol) in THF (20 mL), and the reaction mixture was refluxed for 0.5 h, during which time the dark red color rapidly faded to yellow. Volatiles were removed in vacuo, the product was extracted into diethyl ether (3 × 20 mL) and filtered, and the volatiles were removed in vacuo to give a sticky yellow solid. Yield: 1.81 g, 97.8%.

Method B. Degassed distilled H_2O (30 mL) was added to a solution of **2** (2.96 g, 5 mmol) in diethyl ether (30 mL) with stirring. The red solution immediately became yellow. The organic phase was allowed to separate and was decanted from the aqueous phase onto activated 4 Å molecular sieves. The solution was stored for 20 h and filtered, and the volatiles were removed in vacuo to give a sticky yellow solid. Yield: 1.82 g, 98.4%. Yellow crystals of **3** suitable for X-ray crystallography were obtained from a solution in diethyl ether stored at 5 °C for 4 days (0.94 g, 50.8%). Anal. Calcd for $C_{23}H_{32}P_2$: C, 74.57; H, 8.71. Found: C, 73.99; H, 8.54. ^{1}H NMR (d_6-benzene, 298 K): δ 1.53 (s, 9H, C(C*H*$_3$)$_3$), 2.12 (s, 3H, *p*-C*H*$_3$), 2.23 (s, 3H, *p*-C*H*$_3$), 2.57 (s, 6H, C=PMes *o*-C*H*$_3$), 2.58 (s, 3H, P(H)Mes *o*-C*H*$_3$), 2.60 (s, 3H, P(H)Mes *o*-C*H*$_3$), 5.36 (dd, $J_{PH} = 254.4$ Hz, $^3J_{PH} = 6.3$ Hz, 1H, P(*H*)), 6.74 (s, 2H, C=PMes *m*-C*H*), 6.81 (s, 1H, P(H)Mes *m*-C*H*), 6.89 (s, 1H, P(H)Mes *m*-C*H*). ^{13}C{^{1}H} NMR (d_6-benzene, 298 K): δ 21.40 (*o*-*C*H$_3$), 21.52 (*o*-*C*H$_3$), 22.01 (*o*-*C*H$_3$), 24.00 (*p*-*C*H$_3$), 24.19 (*p*-*C*H$_3$), 33.32 (dd, $^3J_{PC} =$ 5.1 and 18.3 Hz, C(*C*H$_3$)$_3$), 44.90 (dd, $^2J_{PC} = 8.5$ and 21.1 Hz, *C*(CH$_3$)$_3$), 138.85 (*o*-*C*), 139.69 (*o*-*C*), 141.60 (*o*-*C*), 144.95 (s, br, J_{PC} not resolved, *i*-*C*), 145.14 (s, br, J_{PC} not resolved, *i*-*C*), 207.26 (dd, $J_{PC} = 58.0$ and 67.8 Hz, P=*C*P), signals for the mesityl *m*-*C* and *p*-*C* were obscured by solvent resonances. ^{31}P{^{1}H} NMR (d_6-benzene, 298 K): δ 263.1 (d, $^2J_{PP} = 5.8$ Hz, *P*=C), −64.3 (d, $^2J_{PP} = 5.8$ Hz, *P*(H)). ^{31}P NMR (d_6-benzene, 298 K): δ 263.1 (dd, $^2J_{PP} = 5.8$ Hz, $^3J_{PH}$ 6.3 Hz, *P*=C), −64.3 (dd, $^2J_{PP} = 5.8$ Hz, $J_{PH} = 254.4$ Hz, *P*(H)).

Preparation of [*t*-BuC(PMes)$_2$][Na(15-crown-5)$_2$] (4). A cold (−78 °C) solution of **3** (0.57 g, 1.54 mmol) in THF (10 mL) was treated with *n*-butyllithium (0.62 mL, 1.54 mmol) to give a red solution. The mixture was warmed to room temperature and was added to NaO-*t*-Bu (0.15 g, 1.54 mmol) and stirred for 18 h. 15-crown-5 (0.61 mL, 3.08 mmol) was added to give a dark red solution. Volatiles were removed in vacuo, and the sticky red solid was extracted into methylcyclohexane/THF (5:7 mL), filtered, and stored at 5 °C for 3 days to afford a crop of dark red crystals of **4** suitable for X-ray crystallography. Yield: 1.02 g, 79.7%. Anal. Calcd for $C_{43}H_{71}NaO_{10}P_2$: C, 62.00; H, 8.59. Found: C, 61.84; H, 8.66. ^{1}H NMR (d_8-THF, 298 K): δ 1.48 (s, 9H, C(C*H*$_3$)$_3$), 1.85 (s, 6H, *p*-C*H*$_3$), 2.23 (s, 12H, *o*-C*H*$_3$), 3.14 (s, 40H, OC*H*$_2$ crown), 5.99 (s, 4H, *m*-C*H*). ^{13}C{^{1}H} NMR (d_8-THF, 298 K): δ 20.20 (*o*-*C*H$_3$), 22.26 (*p*-*C*H$_3$), 35.08 (t, $^3J_{PC} = 16.9$ Hz, C(*C*H$_3$)$_3$), 42.70 (t, $^2J_{PC} = 28.3$ Hz, *C*(CH$_3$)$_3$), 69.35 (O*C*H$_2$ crown), 125.79 (*m*-*C*), 130.10 (*p*-*C*), 139.50 (*o*-*C*), 145.07 (d, $J_{PC} = 25.6$ Hz, *i*-*C*), 214.13 (t, $J_{PC} =$ 84.2 Hz, P*C*P). ^{31}P{^{1}H} NMR (d_8-THF, 298 K): δ 112.3 (s).

Preparation of [*t*-BuC(PMes)$_2$][K(15-crown-5)$_2$] (5). A cold (−78 °C) solution of **3** (0.86 g, 2.32 mmol) in THF (15 mL) was treated with *n*-butyllithium (0.93 mL, 2.32 mmol) to give a dark red solution. The mixture was warmed to room temperature and was added to KO-*t*-Bu (0.26 g, 2.32 mmol), and the mixture was then stirred for 4 h. 15-crown-5 (0.92 mL, 4.63 mmol) was added to give a dark red microcrystalline precipitate. The volume of the solution was reduced to 10 mL in vacuo, and the solution was heated to dissolve the precipitate and then cooled slowly in a warm mineral oil bath to afford a crop of fine dark red needles of **5**. Yield: 1.48 g, 75.1%. Anal. Calcd for $C_{43}H_{71}KO_{10}P_2$: C, 60.83; H, 8.43. Found: C, 60.50; H, 8.10. ^{1}H NMR (d_8-THF, 298 K): δ 1.49 (s, 9H, C(C*H*$_3$)$_3$), 1.85 (s, 6H, *p*-C*H*$_3$), 2.22 (s, 12H, *o*-C*H*$_3$), 3.18 (s, 40H, OC*H*$_2$ crown), 5.97 (s, 4H, *m*-C*H*). ^{13}C{^{1}H} NMR (d_8-THF, 298 K): δ 20.21 (*o*-*C*H$_3$), 22.24 (*p*-*C*H$_3$), 35.07 (t, $^3J_{PC} = 16.8$ Hz, C(*C*H$_3$)$_3$), 42.68 (t, $^2J_{PC} = 28.2$ Hz, *C*(CH$_3$)$_3$), 69.33 (O*C*H$_2$ crown), 125.78 (*m*-*C*), 130.10 (*p*-*C*), 139.47 (*o*-*C*), 145.08 (d, $J_{PC} = 25.6$ Hz, *i*-*C*), 214.12 (t, $J_{PC} = 84.2$ Hz, P*C*P). ^{31}P{^{1}H} NMR (d_8-THF, 298 K): δ 112.7 (s).

Preparation of [*t*-BuC(PMes)$_2$][Rb(12-crown-4)$_2$] (6). A cold (−78 °C) solution of **3** (0.74 g, 2.00 mmol) in THF (15 mL) was treated with *n*-butyllithium (0.80 mL, 2.00 mmol) to give a dark red solution. The mixture was stirred for 0.5 h. Addition of 12-crown-4 (0.65 mL, 4.00 mmol) afforded an orange precipitate. The mixture was then treated with rubidium 2-ethylhexoxide (0.43 g, 2.00 mmol) in THF (5 mL) to give a dark red solution; this was warmed to room temperature and stirred for 1 h. The volume of the solution was reduced to 5 mL in vacuo, and the solution was stored at −30 °C for 24 h to give a crop of orange crystals of **6** suitable for X-ray crystallography. Yield: 1.05 g, 65.2%. Anal. Calcd for $C_{39}H_{63}O_8P_2Rb$: C, 58.02; H, 7.87. Found: C, 59.52; H, 7.75. ^{1}H NMR (d_8-THF, 298 K): δ 1.47 (s, 9H, C(C*H*$_3$)$_3$), 1.83 (s, 6H, *p*-C*H*$_3$), 2.24 (s, 12H, *o*-C*H*$_3$), 3.25 (s, 32H, OC*H*$_2$ crown), 5.87 (s, 4H, *m*-C*H*). ^{13}C{^{1}H} NMR (d_8-THF, 298 K): δ 20.19 (*o*-*C*H$_3$), 22.25 (*p*-*C*H$_3$), 35.07 (t, $^3J_{PC} = 16.7$ Hz, C(*C*H$_3$)$_3$), 42.67 (t, $^2J_{PC} = 28.3$ Hz, *C*(CH$_3$)$_3$), 67.62 (O*C*H$_2$ crown), 125.79 (*m*-*C*), 130.14 (*p*-*C*), 139.48 (*o*-*C*), 145.11 (d, $J_{PC} = 25.7$ Hz, *i*-*C*), 214.80 (t, $J_{PC} =$ 84.1 Hz, P*C*P). ^{31}P{^{1}H} NMR (d_8-THF, 298 K): δ 112.6 (s).

Preparation of [*t*-BuC(PMes)$_2$][Cs(15-crown-5)$_2$] (7). A cold (−78 °C) solution of **3** (0.74 g, 2.00 mmol) in THF (15 mL) was treated with *n*-butyllithium (0.80 mL, 2.00 mmol) to give a dark red solution. The solution was stirred for 0.5 h; 15-crown-5 (0.80 mL, 4.00 mmol) and cesium 2-ethylhexoxide (0.52 g, 2.00 mmol) in toluene (2 mL) were subsequently added. The solution was warmed to room temperature and stirred for 1 h. Volatiles were removed in vacuo to give a red oil. The oil was dissolved in THF (5 mL), filtered, and stored at −30 °C for 48 h to give a crop of dark red crystals of **7** suitable for X-ray crystallography. Yield: 0.49 g, 25.9%. Anal. Calcd for $C_{43}H_{71}CsO_{10}P_2$: C, 54.78; H, 7.59. Found: C, 54.65; H, 7.44. ^{1}H NMR (d_8-THF, 298 K): δ 1.46 (s, 9H, C(C*H*$_3$)$_3$), 1.82 (s, 6H, *p*-C*H*$_3$), 2.22 (s, 12H, *o*-C*H*$_3$), 3.20 (s, 40H, OC*H*$_2$ crown), 5.77 (s, 4H, *m*-C*H*). ^{13}C{^{1}H} NMR (d_8-THF, 298 K): δ 20.21 (*o*-*C*H$_3$), 22.25 (*p*-*C*H$_3$), 35.06 (t, $^3J_{PC} = 16.8$ Hz, C(*C*H$_3$)$_3$), 42.69 (t, $^2J_{PC}$ $= 28.3$ Hz, *C*(CH$_3$)$_3$), 69.62 (O*C*H$_2$ crown), 125.81 (*m*-*C*), 130.15 (*p*-*C*), 139.49 (*o*-*C*), 145.10 (d, $J_{PC} = 25.6$ Hz, *i*-*C*), 214.16 (t, $J_{PC} = 84.3$ Hz, P*C*P). ^{31}P{^{1}H} NMR (d_8-THF, 298 K): δ 112.7 (s). ^{133}Cs NMR (d_8-THF): δ 58.7 (s, br).

Attempted Preparation of [*t*-BuC(PMes)$_2$][Cs(12-crown-4)$_2$] (8) and Isolation of [Mes$_2$P][Cs(12-crown-4)$_2$] (9). A cold (−78 °C) solution of **3** (0.74 g, 2.00 mmol) in THF (15 mL) was treated with *n*-butyllithium (0.80 mL, 2.00 mmol) to give a dark red solution. Addition of 12-crown-4 (0.65 mL, 4.00 mmol) afforded an orange precipitate. The mixture was then treated with cesium 2-ethylhexoxide (0.52 g, 2.00 mmol) in toluene (2 mL) and stirred for 2 h, during which time it was warmed to room temperature, to give a dark red solution. Volatiles were removed in vacuo to give a dark red oil. This was extracted into methylcyclohexane/THF (5:2 mL), filtered, and stored at 5 °C for 72 h to give a small crop of orange crystals of **9** suitable for X-ray crystallography. Yield (based upon Cs): 0.25 g, 16.6%. ^{1}H NMR (d_8-THF, 298 K): δ 1.95 (s, 6H, *p*-C*H*$_3$), 2.24 (s, 12H, *o*-C*H*$_3$), 3.47 (s, 32H, OC*H*$_2$-crown), 6.31 (s, 4H, *m*-C*H*). ^{13}C{^{1}H} NMR (d_8-THF, 298 K): δ 20.35 (*o*-*C*H$_3$), 22.48 (*p*-*C*H$_3$), 68.12 (O*C*H$_2$ crown), 125.27 (*m*-*C*), 130.73 (*p*-*C*), 138.03 (*o*-*C*), 153.41 (s, br, *i*-*C*). ^{31}P{^{1}H} NMR (d_8-THF, 298 K): δ −34.4 (s). ^{133}Cs NMR (d_8-THF): δ −46.8 (s). Analysis of the crude mother liquor by ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopy indicated the presence of **8** (which gave essentially the same spectra as **6**) along with the ditertiary diphosphane (Mes$_2$P)$_2$ (**10**), trace amounts of *t*-BuC≡P (**11**), and other unidentified phosphorus-containing species. Attempts to isolate pure **8** have thus far failed.

Theoretical Calculations. DFT calculations were undertaken using the Titan program.[35] Geometry optimizations and single-point energies were calculated at the BL3YP/6-31G* level of theory.

Table 3. Crystallographic Data for 3, 4, 6, 7, and 9

	3	**4**	**6**	**7**	**9**
formula	$C_{23}H_{32}P_2$	$C_{43}H_{71}NaO_{10}P_2$	$C_{39}H_{63}O_8P_2Rb$	$C_{43}H_{71}CsO_{10}P_2$	$C_{34}H_{54}CsO_8P$
fw	370.43	832.93	807.30	942.85	754.65
cryst size, mm	0.80 × 0.80 × 0.72	0.72 × 0.70 × 0.35	0.42 × 0.18 × 0.12	0.78 × 0.28 × 0.26	0.80 × 0.65 × 0.32
cryst syst	monoclinic	orthorhombic	monoclinic	orthorhombic	orthorhombic
space group	$P2_1/c$	$P2_12_12_1$	$P2_1/c$	$P2_12_12_1$	$Pna2_1$
a, Å	14.9896(6)	15.3088(13)	14.6026(13)	16.2814(6)	10.3690(4)
b, Å	16.1146(7)	17.2665(14)	12.1852(11)	17.0098(6)	15.9375(7)
c, Å	9.2951(16)	17.4201(14)	23.654(2)	17.1196(6)	21.8263(9)
β, deg	106.160(2)		101.095(2)		
V, Å^3	2156.52(16)	4604.6(7)	4130.2(6)	4741.2(3)	3606.9(3)
Z	4	4	4	4	4
ρ_{calcd}, g cm^{-3}	1.141	1.201	1.298	1.321	1.39
μ, mm^{-1}	0.205	0.156	1.324	0.9	1.117
no. of rflns measd	19 164	33 174	28 582	34 739	22 472
no. of unique rflns, R_{int}	5305, 0.0215	8118, 0.0735	7282, 0.0972	8351, 0.0436	5635, 0.0328
no. of rflns with $F^2 > 2\sigma(F^2)$	4477	5998	5057	7436	5419
transmn coeff range	0.853−0.867	0.896−0.947	0.606−0.857	0.540−0.799	0.469−0.716
R, $R_w{}^a$ ($F^2 > 2\sigma$)	0.0371, 0.1061	0.0808, 0.1956	0.0572, 0.1381	0.0496, 0.1250	0.0697, 0.1652
R, $R_w{}^a$ (all data)	0.0455, 0.1128	0.1163, 0.2237	0.0945, 0.1617	0.0597, 0.1332	0.0723, 0.1669
S^a	1.052	1.050	1.015	1.057	1.178
no. of params	238	513	459	514	404
max, min diff map, e Å^{-3}	0.39, −0.22	1.25, −0.34	1.08, −1.01	2.00, −0.81	1.43, −1.55

[a] Conventional $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = [\sum w(F_o{}^2 - F_c{}^2)^2/\sum w(F_o{}^2)^2]^{1/2}$, and $S = [\sum w(F_o{}^2 - F_c{}^2)^2/((\text{no. of data}) - (\text{no. of params}))]^{1/2}$ for all data.

X-ray Crystallography. Crystal data for compounds **3**, **4**, **6**, **7**, and **9** are given in Table 3, and further details of the structure determinations are given in the Supporting Information. Crystal data for compounds **1** and **2** were communicated previously.[8] Bond lengths and angles are listed in Tables 1 and 2. Crystals were examined on a Bruker AXS CCD area detector diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å). Intensities were integrated from a sphere of data recorded on narrow (0.3°) frames by ω rotation. Cell parameters were refined from the observed positions of all strong reflections in each data set. Semiempirical absorption corrections were applied, on the basis of symmetry-equivalent and repeat reflections. The structures were solved variously by heavy-atom and direct methods and were refined by least-squares methods on all unique F^2 values, with anisotropic displacement parameters and with constrained riding hydrogen geometries; U(H) was set at 1.2 (1.5 for methyl groups) times the U_{eq} value for the parent atom. The largest features in final difference syntheses were close to heavy atoms, except for **9**, where residual peaks indicate possible disorder of one of the 12-crown-4 ether molecules, but no chemically sensible interpretation could be modeled. Programs used were Bruker AXS SMART (control), SAINT (integration),[38] and SHELXTL for structure solution, refinement, and molecular graphics.[39]

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Supporting Information Available: For **3**, **4**, **6**, **7**, and **9** details of structure determination, atomic coordinates, bond lengths and angles, displacement parameters, and atomic coordinates, and for **1a**,**c** calculated geometries and energies. This material is available free of charge via the Internet at http://pubs.acs.org. Observed and calculated structure factor details are available from the authors upon request.

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(38) Bruker SMART and SAINT; Bruker AXS Inc., Madison, WI, 2001.

(39) Sheldrick, G. M. SHELXTL version 5; Bruker AXS Inc., Madison, WI, 2001.