3684 *Organometallics* **2003,** *22,* 3684−3690

# Alkali Metal-Mediated Schlenk Dimerization of a Phosphorus-Substituted Alkene. Synthesis and Crystal Structures of Li, Na, and K Derivatives of a Phosphorus-Stabilized Butane-1,4-diide Ligand

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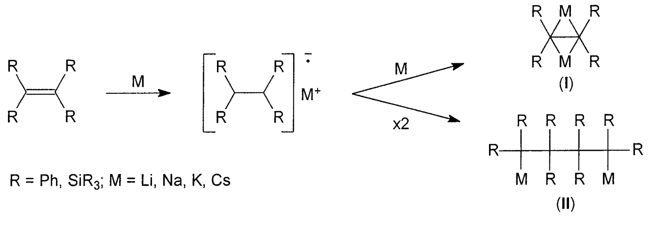
*Received May 27, 2003*

Treatment of the vinylidene phosphine $(Ph_2P)_2C{=}CH_2$ (**1**) with either Li or Na in THF yields the bis(diphosphinomethanide) complexes $\{(THF)_2Li(Ph_2P)_2CCH_2\}_2$ (**2**), $\{(pmdeta)_2Li(Ph_2P)_2CCH_2\}_2{\cdot}(PhMe)_3$ (**6**), and $[\{(tmeda)_{1.5}Na(Ph_2P)_2CCH_2\}_2]_n$ (**3b**), after recrystallization [tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine, pmdeta = *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine]. Treatment of **1** with K under the same conditions results in ligand degradation to give $K(PPh_2)$, which was isolated as the adduct $\{(pmdeta)K(PPh_2)\}_n$ (**4**) after recrystallization from toluene/pmdeta, and unidentified organopotassium products. The potassium bis(diphosphinomethanide) $[\{(Ph_2P)_2CCH_2CH_2C(PPh_2)_2\}_2K_4(pmdeta)(DME)_3{\cdot}(PhMe)_2]_n$ (**5**) may be accessed via a metathesis reaction between **2** and KO-*t*-Bu in ether, followed by recrystallization from toluene/DME in the presence of pmdeta [DME = 1,2-dimethoxyethane]. Compounds **3b**, **4**, **5**, and **6** have been characterized by multielement NMR spectroscopy and X-ray crystallography.

## Introduction

It has been known for many years that certain aryl- or silyl-substituted alkenes undergo reduction upon treatment with alkali metals, ultimately yielding either 1,2- or 1,4-dicarbanions (Scheme 1).[1−3] The formation of 1,4-dicarbanions via the Schlenk dimerization of initially formed radical anions is generally favored for monosubstituted or 1,1-disubstituted alkenes; 1,2-disubstituted and more heavily substituted alkenes typically undergo a second reduction step to yield 1,2-dicarbanions. In these reactions both the radical anion intermediates and the subsequent dicarbanions are stabilized either by extensive charge delocalization into the aromatic rings or by negative hyperconjugation (delocalization of charge into low-lying Si−C $\sigma^*$ orbitals) and/or polarization effects. In the course of our investigations into the chemistry of heteroatom-stabilized carbanions we noted that calculations indicate that silicon- and phosphorus-containing substituents stabilize an adjacent carbanion center to a similar extent; the carbanion stabilization energies of an $SiH_3$ and a $PH_2$ substituent have been calculated as −23.7 and −21.3 kcal/mol, respectively.[4] Thus, we reasoned that phosphorus-substituted alkenes should also undergo Schlenk dimerization to give P-stabilized 1,4-dicarbanions. In this regard, we recently reported that treatment of the vinylidene phosphine $(Ph_2P)_2C{=}CH_2$ (**1**) with lithium in THF gave the butane-1,4-diide complex

### Scheme 1



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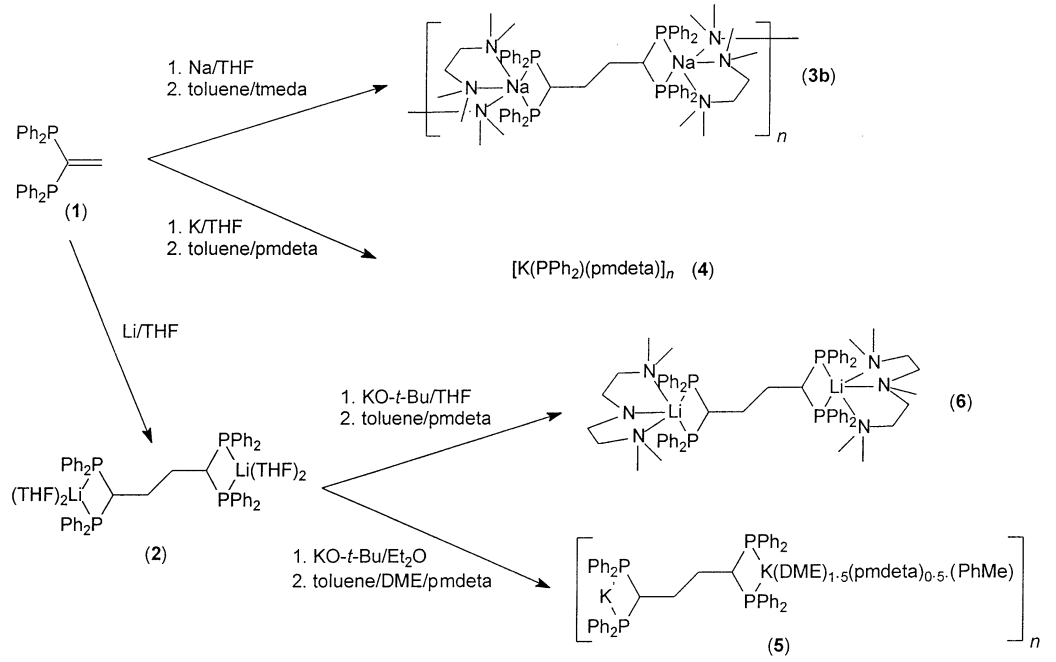
**Scheme 2**



$[(THF)_2Li(Ph_2P)_2CCH_2]_2$ (**2**) in excellent yield via a Schlenk dimerization reaction (Scheme 2).[5]

Phosphorus-stabilized carbanions (phosphinomethanides) exhibit a great variety of coordination modes in their complexes with main group metal cations.[6] The C and P centers in these ligands are valence isoelectronic and have similar electronegativities (the Pauling electronegativities of P and C are 2.19 and 2.55, respectively),[7] and thus may compete as nucleophiles for metal centers. Typically, monophosphinomethanides $[R_2C-PR_2^-]$ adopt $\eta^1$-*C*-, $\eta^1$-*P*-, $\eta^2$-*PC*-, or *PC*-bridging coordination modes, while diphosphinomethanides $[RC(PR_2)_2^-]$ and triphosphinomethanides $[C(PR_2)_3^-]$ adopt bidentate-*PP*, $\eta^3$-heteroallyl-*PCP*, or combined bidentate-*PP*/bridging coordination modes. The coordination mode adopted is highly dependent upon the nature of the metal(s), the steric and electronic properties of the substituents at the P and C centers, and the presence of additional donor ligands such as THF or tmeda (tmeda = *N*,*N*,*N'N'*-tetramethylethylenediamine). Of the many crystallographically characterized alkali metal phosphinomethanides reported to date there are only five examples of heavier alkali metal complexes, the compounds $[\{(Me_3Si)_2CP(C_6H_4\text{-}2\text{-}CH_2NMe_2)_2\}ML_n]_x$ $[ML_n = Na(OEt_2)_{0.5}(DME)_{0.5}$,[8] $x = 1$; K,[9] Rb, $x = \infty$; Cs(PhMe), $x = \infty$;[10] DME = 1,2-dimethoxyethane], isolated in our laboratory, and the ate complex $(Et_2O)Na\{(4\text{-}MeC_6H_4)_2PCHC_6H_4\text{-}2\text{-}OMe\}_3Ca$, reported by Knapp and Müller.[11]

Given the dearth of information regarding the synthesis and structures of heavier alkali metal phosphinomethanides, we wished to explore whether sodium and potassium would also mediate the Schlenk dimerization of **1** and to examine the structures of the resulting complexes. We now report the reactions between **1** and both sodium and potassium and the structural characterization of the first diphosphinomethanide complexes of these elements.

## Results and Discussion

Ultrasonication of a solution of $(Ph_2P)_2C{=}CH_2$ (**1**) in THF over a freshly prepared sodium mirror for 30 min yields the expected Schlenk dimerization product $[(THF)_nNa(Ph_2P)_2CCH_2]_2$ (**3a**) (Scheme 2); $^{31}P$ NMR spectra of the reaction solution indicate that **3a** is by far the major product of this reaction, although a small quantity of the cleavage product $NaPPh_2$ is also produced. Removal of solvent and recrystallization of the resulting sticky, orange solid from toluene in the presence of an excess of tmeda gives the complex $[\{(tmeda)_{1.5}Na(Ph_2P)_2CCH_2\}_2]_n$ (**3b**) as orange blocks in good yield. The $^1H$ NMR spectrum of this complex is consistent with the presence of 1.5 molecules of tmeda per sodium atom and clearly reveals the newly formed $CH_2CH_2$ group of the ligand as a complex multiplet centered at 1.91 ppm.

In contrast to the facile formation of **3a**, ultrasonication of a solution of **1** in THF over a freshly prepared potassium mirror under the same conditions results in rapid cleavage of the P−C(vinyl) bond (Scheme 2). A $^{31}P\{^1H\}$ NMR spectrum of the crude reaction mixture indicates a multitude of phosphorus-containing products from this reaction, including potassium phosphide species, $KPR_2$. Treatment of the resulting orange solution with pmdeta [pmdeta = *N*,*N*,*N'*,*N''*,*N''*-pentamethyldiethylenetriamine], removal of solvent in vacuo, and recrystallization of the resulting sticky, orange solid from toluene gives single crystals of the polymeric complex $[(Ph_2P)K(pmdeta)]_n$ (**4**), the identity of which was confirmed by NMR spectroscopy and X-ray crystallography. The other products from this reaction could

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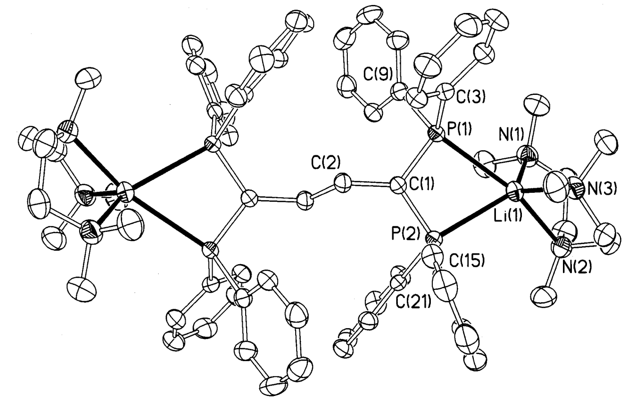
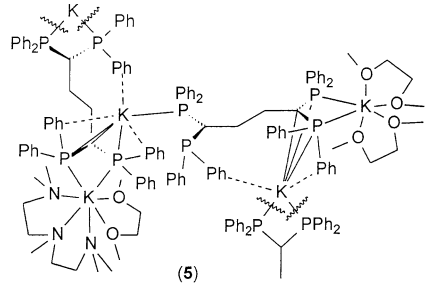


**Figure 1.** Molecular structure of **6** with 50% probability ellipsoids and with H atoms and solvent molecules omitted for clarity.

**Chart 1**



(**5**)

not be isolated but are presumed to be P-substituted vinyl potassium species.

Although the desired potassium butane-1,4-diide complex is apparently not accessible using a Schlenk dimerization protocol, it may readily be prepared via a straightforward metathesis reaction. Metathesis between a suspension of **2** and 2 equiv of KO-*t*-Bu in diethyl ether gives the potassium complex $[(THF)_nK(Ph_2P)_2CCH_2]_2$, after standard workup, as an orange powder in good yield (Scheme 2). This may be recrystallized from a 10:1 mixture of toluene and DME in the presence of pmdeta as orange plates of the polymeric complex $[\{(Ph_2P)_2CCH_2CH_2C(PPh_2)_2\}_2K_4(pmdeta)(DME)_3\cdot(PhMe)_2]_n$ (**5**) (Chart 1); surprisingly, the ratio of pmdeta to potassium atoms in **5** is unaffected by the presence of an excess of pmdeta in the crystallization solution.

Unexpectedly, when the metathesis reaction between **2** and 2 equiv of KO-*t*-Bu is carried out in THF rather than diethyl ether, only the pmdeta complex of the lithium salt $[(pmdeta)Li(Ph_2P)_2CCH_2]_2\cdot(PhMe)_3$ (**6**) is isolated after recrystallization from toluene (Scheme 2). Compounds **3b** and **5** are the first sodium or potassium complexes of a diphosphinomethanide ligand to be crystallographically characterized.

**Solid State Structures of 3b, 4, 5, and 6.** The solid state structure of **6** closely resembles that of **2**; the molecular structure of **6** is shown in Figure 1, and details of bond lengths and angles are given in Table 1. Compound **6** has exact inversion symmetry; the lithium atoms are coordinated at each end of the butane-1,4-diide ligand by the two phosphorus atoms in a bidentate *PP*-coordination mode, typical of diphosphinomethanide ligands. The coordination sphere of each lithium is completed by three nitrogen atoms from a chelating pmdeta molecule, giving an unusual five-coordinate lithium center with a distorted trigonal bipyramidal geometry. The P−Li−P bite angle of 63.26(7)° is slightly smaller than that observed in **2** [67.14(14)°], and the Li−P distances of 2.677(3) and 2.737(3) Å are slightly longer than the Li−P distances in **2** [2.542(6) and 2.559(6) Å], consistent with the greater coordination number of the lithium atoms in **6**. However, the Li−P distances in **6** are similar to Li−P distances in previously reported lithium phosphinomethanides.[12,13]

**Table 1. Selected Bond Distances (Å) and Angles (deg) for 6**[a]

| | | | | | |
|---|---|---|---|---|---|
| Li(1)−P(1) | 2.737(3) | Li(1)−P(2) | 2.677(3) | Li(1)−N(1) | 2.203(4) |
| Li(1)−N(2) | 2.197(4) | Li(1)−N(3) | 2.173(4) | P(1)−C(1) | 1.7511(19) |
| P(1)−C(3) | 1.860(2) | P(1)−C(9) | 1.864(2) | P(2)−C(1) | 1.7507(19) |
| P(2)−C(15) | 1.858(2) | P(2)−C(21) | 1.8629(19) | C(1)−C(2) | 1.535(3) |
| C(2)−C(2′) | 1.546(4) | | | | |

| | | | |
|---|---|---|---|
| P(1)−Li(1)−P(2) | 63.26(7) | P(1)−Li(1)−N(1) | 98.13(13) |
| P(1)−Li(1)−N(2) | 165.86(16) | P(1)−Li(1)−N(3) | 107.19(14) |
| P(2)−Li(1)−N(1) | 130.74(15) | P(2)−Li(1)−N(2) | 105.53(13) |
| P(2)−Li(1)−N(3) | 110.37(14) | N(1)−Li(1)−N(2) | 82.71(13) |
| N(1)−Li(1)−N(3) | 118.80(16) | N(2)−Li(1)−N(3) | 84.39(14) |
| Li(1)−P(1)−C(1) | 93.07(9) | Li(1)−P(1)−C(3) | 116.29(9) |
| Li(1)−P(1)−C(9) | 129.83(9) | C(1)−P(1)−C(3) | 111.32(9) |
| C(1)−P(1)−C(9) | 106.65(9) | C(3)−P(1)−C(9) | 98.95(9) |
| Li(1)−P(2)−C(1) | 95.13(10) | Li(1)−P(2)−C(15) | 115.12(9) |
| Li(1)−P(2)−C(21) | 126.87(9) | C(1)−P(2)−C(15) | 110.99(9) |
| C(1)−P(2)−C(21) | 109.64(9) | C(15)−P(2)−C(21) | 99.04(9) |

[a] Primed atoms are symmetry generated in Tables 1−4.

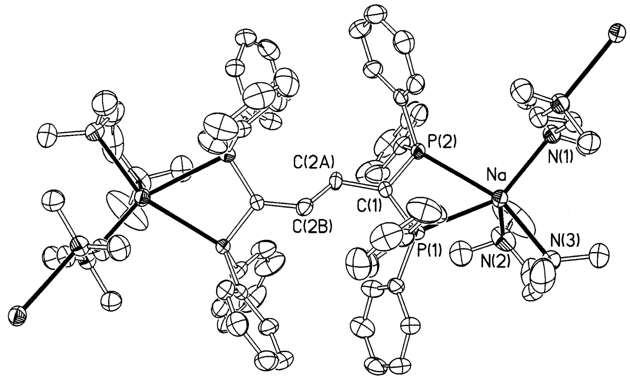


**Figure 2.** Molecular structure of **3b** with 50% probability ellipsoids and with H atoms omitted for clarity.

The carbanion centers in **6** are almost perfectly planar [sum of angles at C(1) = 359.8°], and the C(1)−P(1) and C(1)−P(2) distances of 1.7511(19) and 1.7507(19) Å are significantly shorter than expected for a P−C single bond, consistent with delocalization of charge via negative hyperconjugation into the P−C(aryl) $\sigma^*$ orbitals; there is no contact between the lithium atoms and the carbanion centers. There are three toluene solvent molecules per molecule of **6**, one of them disordered over an inversion center.

The sodium complex **3b** adopts a structure in the solid state similar to that of **2** and **6**; the molecular structure of **3b** is shown in Figure 2, and details of bond lengths and angles are given in Table 2. Each sodium atom is bound by the bis(diphosphinomethanide) ligand in a *PP*-bidentate fashion with a P−Na−P bite angle of 57.55(2)°. The Na−P distances of 2.9285(11) and

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**Table 2. Selected Bond Distances (Å) and Angles (deg) for 3b**

| | | | | | |
|---|---|---|---|---|---|
| Na−N(2) | 2.471(3) | Na−N(3) | 2.500(2) | Na−N(1) | 2.571(2) |
| Na−P(2) | 2.9285(11) | Na−P(1) | 3.0451(11) | P(1)−C(1) | 1.739(2) |
| P(1)−C(9) | 1.858(2) | P(1)−C(3) | 1.863(3) | P(2)−C(1) | 1.743(2) |
| P(2)−C(21) | 1.855(3) | P(2)−C(15) | 1.859(2) | C(1)−C(2A) | 1.561(7) |
| C(2A)−C(2B) | 1.515(6) | | | | |

| | | | |
|---|---|---|---|
| N(2)−Na−N(3) | 75.64(11) | N(2)−Na−N(1) | 108.05(8) |
| N(3)−Na−N(1) | 102.75(8) | N(2)−Na−P(2) | 107.16(8) |
| N(3)−Na−P(2) | 156.55(7) | N(1)−Na−P(2) | 98.46(5) |
| N(2)−Na−P(1) | 104.18(7) | N(3)−Na−P(1) | 99.03(7) |
| N(1)−Na−P(1) | 144.59(6) | P(2)−Na−P(1) | 57.55(2) |
| C(1)−P(1)−C(9) | 111.31(11) | C(1)−P(1)−C(3) | 108.72(12) |
| C(9)−P(1)−C(3) | 99.82(11) | C(1)−P(1)−Na | 93.15(8) |
| C(9)−P(1)−Na | 117.52(8) | C(3)−P(1)−Na | 125.99(9) |
| C(1)−P(2)−C(21) | 109.92(12) | C(1)−P(2)−C(15) | 105.64(11) |
| C(21)−P(2)−C(15) | 100.02(11) | C(1)−P(2)−Na | 97.11(8) |
| C(21)−P(2)−Na | 111.62(8) | C(15)−P(2)−Na | 131.56(8) |
| C(2B′)-C(1)−P(1) | 120.3(3) | C(2A)-C(1)−P(1) | 134.4(3) |
| C(2B′)-C(1)−P(2) | 123.4(3) | C(2A)-C(1)−P(2) | 114.0(3) |
| P(1)−C(1)-P(2) | 111.46(12) | C(2B)-C(2A)−C(1) | 115.4(4) |
| C(2A)-C(2B)−C(1′) | 110.8(4) | | |

3.0451(11) Å in **3b** are substantially longer than the Na−P distance [2.8004(10) Å] in the sodium monophosphinomethanide [{$(Me_3Si)_2CP(C_6H_4\text{-}2\text{-}CH_2NMe_2)_2$}Na$(OEt_2)_{0.5}(DME)_{0.5}$] (although M−P distances in complexes of this latter $PN_2$-tridentate monophosphinomethanide ligand are typically rather short),[8] but are similar to the Na−P distances reported for the calcium ate complex [$(Et_2O)$Na{$(Ph_2P)CHC_6H_4\text{-}2\text{-}OMe$}$_3$Ca] [Na−P = 2.851(2), 2.871(2), and 2.934(2) Å].[11] No other sodium phosphinomethanide complexes are available for comparison. However, the Na−P distances in **3b** fall in the range of previously reported contacts between sodium and a tertiary phosphine center; for example, the Na−P distances in [(DME)Na{$(Ph_2P)C_5H_4$}][14] and tetrameric [Na{(*i*-$Pr_2P$)C(H)═C(O)Ph}]$_4$[15] are 3.056(2) and 2.852(2) Å, respectively.

Each sodium atom in **3b** is further coordinated by the nitrogen atoms of a chelating tmeda molecule and by one nitrogen atom from a molecule of tmeda which bridges between sodium atoms in different $RNa_2$ units, generating a zigzag polymer. Each sodium is thus five-coordinate with a highly distorted trigonal bipyramidal geometry, similar to that observed for the lithium atom in **6**. The Na−N distances of 2.471(3), 2.500(2) (chelating tmeda) and 2.571(2) Å (bridging tmeda) are typical of complexes in which sodium is coordinated by a tertiary amine.[16] The carbanion centers C(1) in **3b** are almost perfectly planar [sum of angles at C(1) = 359.9°], and the C(1)−P distances of 1.739(2) and 1.743(2) Å are shorter than expected for a single P−C bond. The $CH_2$-$CH_2$ link between the two carbanion centers is disordered over two slightly different orientations, only one of which is shown in Figure 2.

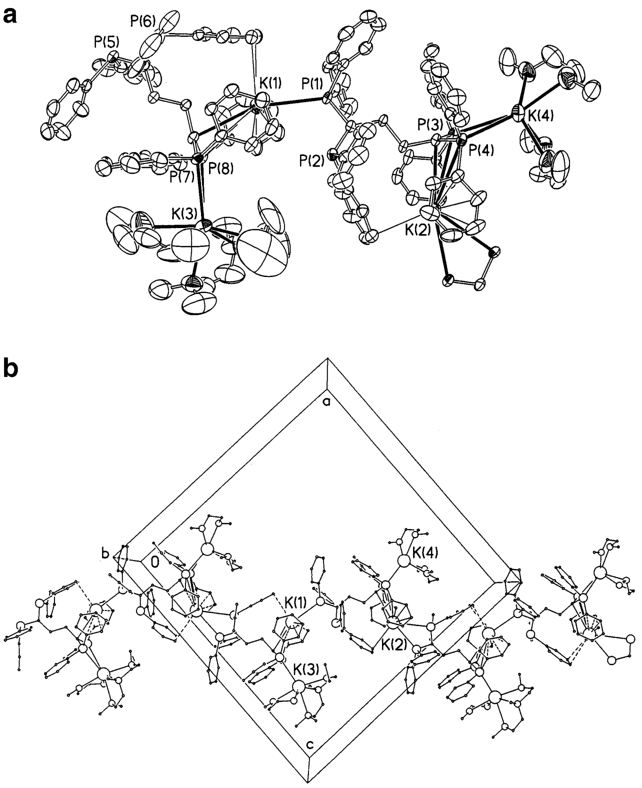

**Figure 3.** (a) Structure of the asymmetric unit of **5** and additional atoms to complete the coordination of K(2), with 50% probability ellipsoids. H atoms, minor disorder components, and toluene of crystallization omitted for clarity. (b) Chain structure of **5**.

Crystals of **5** were obtained from cold toluene/DME solutions containing pmdeta. The molecular structure of **5** is shown in Figure 3, and details of bond lengths are given in Table 3. In contrast to **6** and **3b**, the structure of **5** is rather complex: the asymmetric unit contains four potassium atoms, two bis(diphosphinomethanide) ligands, one molecule of pmdeta, and three molecules of DME; in addition, the asymmetric unit contains two molecules of toluene of crystallization, one of which is disordered over two orientations. The four potassium atoms are in distinct environments, although K(1) and K(2) may be considered as occupying “bridging” positions, whereas K(3) and K(4) may be regarded as occupying “terminal” positions. K(3) and K(4) are each bound by two P atoms from one end of a diphosphinomethanide ligand in an $\eta^2$-*PP* manner; the coordination sphere of K(3) is completed by the oxygen atoms of two chelating molecules of DME (one molecule of which is disordered over two positions), giving a six-coordinate metal center with a distorted trigonal prismatic geometry; the coordination sphere of K(4) is

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[16] For examples see: Smith, J. D. *Adv. Organomet. Chem.* **1999**, *43*, 267.

**Table 3. Selected Bond Distances (Å) for 5**

| | | | | | |
|---|---|---|---|---|---|
| K(1)−P(1) | 3.3727(15) | K(1)−P(7) | 3.8102(16) | K(1)−P(8) | 3.8381(16) |
| K(1)−C(53) | 3.235(4) | K(2)−P(3) | 3.8124(16) | K(2)−P(4) | 3.8887(16) |
| K(2)−P(5′) | 3.3434(15) | K(2)−P(6′) | 3.8124(15) | K(2)−C(4) | 3.281(4) |
| K(3)−P(7) | 3.5515(17) | K(3)−P(8) | 3.3855(17) | K(3)−N(1) | 2.778(9) |
| K(3)−N(2) | 2.847(7) | K(3)−N(3) | 2.888(7) | K(3)−O(1) | 2.798(10) |
| K(3)−O(2) | 2.788(8) | K(4)−P(3) | 3.3992(16) | K(4)−P(4) | 3.2739(16) |
| K(4)−O(3) | 2.738(5) | K(4)−O(4) | 2.725(6) | K(4)−O(5) | 2.671(11) |
| K(4)−O(6) | 2.727(10) | K(4)−O(5A) | 2.818(19) | K(4)−O(6A) | 2.732(17) |
| P(1)−C(1) | 1.755(4) | P(1)−C(5) | 1.854(5) | P(1)−C(11) | 1.864(5) |
| P(2)−C(1) | 1.746(4) | P(2)−C(17) | 1.846(4) | P(2)−C(23) | 1.863(4) |
| P(3)−C(4) | 1.754(4) | P(3)−C(29) | 1.854(5) | P(3)−C(35) | 1.847(4) |
| P(4)−C(4) | 1.761(4) | P(4)−C(41) | 1.856(5) | P(4)−C(46) | 1.862(4) |
| P(5)−C(56) | 1.748(4) | P(5)−C(57) | 1.849(5) | P(5)−C(63) | 1.862(5) |
| P(6)−C(56) | 1.741(5) | P(6)−C(69) | 1.848(4) | P(6)−C(75) | 1.866(4) |
| P(7)−C(53) | 1.764(4) | P(7)−C(81) | 1.858(4) | P(7)−C(87) | 1.863(5) |
| P(8)−C(53) | 1.753(4) | P(8)−C(93) | 1.843(5) | P(8)−C(99) | 1.863(5) |

completed by the two O atoms of a molecule of DME and the three N atoms of a molecule of pmdeta, giving a seven-coordinate metal center. The two remaining K atoms, K(1) and K(2), lie in quite different environments, coordinated solely by the P and C atoms of the diphosphinomethanide ligands. K(1) bridges the two bis(diphosphinomethanide) ligands in the asymmetric unit, binding to ligand A [defined as that containing P(1)−P(4)] in a monodentate $\eta^1$-*P* mode and ligand B [containing P(5)−P(8)] in an $\eta^3$-*PCP*-heteroallyl mode. The coordination sphere of K(1) is completed by K⋯C(aryl) contacts to two of the phenyl rings at the proximal end of ligand B (one $\eta^3$- and one $\eta^2$-interaction) and one of the phenyl rings at the distal end of the same ligand ($\eta^2$). K(2) bridges two bis(diphosphinomethanide) ligands in adjacent asymmetric units, creating a complex polymeric chain. K(2) is bound in an $\eta^3$-*PCP*-heteroallyl fashion to one end of ligand A and in an $\eta^2$-*PP* bidentate fashion to the two P atoms at one end of ligand B′ in the next unit along the chain; the coordination sphere of K(2) is completed by K⋯C(aryl) contacts to two of the proximal phenyl rings in ligand A (two $\eta^3$-interactions) and one of the distal phenyl rings in the same ligand ($\eta^2$). Thus the two ends of each bis(diphosphinomethanide) ligand bind the potassium atoms in very different ways, one end acting as a straightforward bidentate *PP*-$\sigma$-donor, whereas the other end acts as both a *PP*- or *P*-$\sigma$-donor and a bridging ligand via $\eta^3$-*PCP* interactions with the K atoms.

The K−P distances in **5** fall in the range 3.3434(15) Å [K(2)−P(5′) $\eta^2$-*PP* contact] to 3.8887(16) Å [K(2)−P(4) $\eta^3$-*PCP*-heteroallyl contact] and are typical of the few reported contacts between K and a formally tertiary phosphine center. For example, the K−P distance in $[\{(Me_3Si)_2CP(C_6H_4\text{-}2\text{-}CH_2NMe_2)_2\}K]_x$,[9] the only other potassium phosphinomethanide to be crystallographically characterized, is 3.2227(5) Å, the K−P distance in $\{(C_5H_4CH_2CH_2PPh_2)K\}_n$ is 3.3200(7) Å,[17] and the K−P-(tertiary phosphine) distance in $[\{(t\text{-}BuP)_2H\}K(pmdeta)]_2$ is 3.658(3) Å.[18] The K−C(carbanion center) distances in **5** are 3.281(4) Å [K(2)−C(4)] and 3.235(4) Å [K(1)−C(53)]. These are typical of K−C contacts in potassium complexes with heteroatom-stabilized carbanions.[16,19]

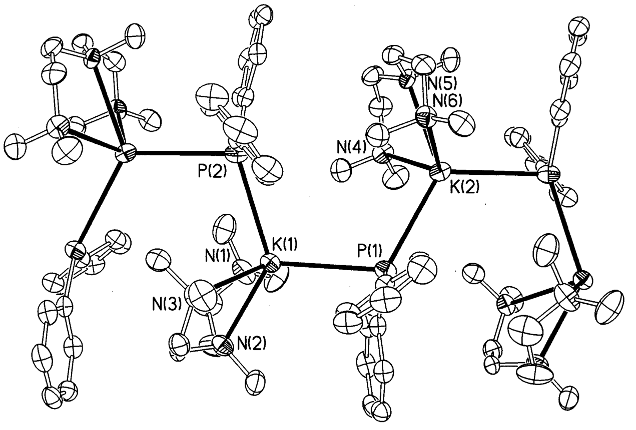

**Figure 4.** Molecular structure of **4** with 50% probability ellipsoids and with H atoms omitted for clarity.

**Table 4. Selected Bond Distances (Å) and Angles (deg) for 4**

| | | | | | |
|---|---|---|---|---|---|
| K(1)−N(1) | 2.901(4) | K(1)−N(2) | 2.844(4) | K(1)−N(3) | 2.985(4) |
| K(1)−P(1) | 3.3286(15) | K(1)−P(2) | 3.3025(14) | K(2)−P(1) | 3.4208(15) |
| K(2)−P(2′) | 3.4084(15) | K(2)−N(4) | 2.866(4) | K(2)−N(5) | 2.897(3) |
| K(2)−N(6) | 2.876(4) | | | | |

| | | | |
|---|---|---|---|
| P(1)−K(1)−P(2) | 108.83(4) | P(1)−K(2)−P(2′) | 121.64(4) |
| K(1)−P(1)−K(2) | 112.86(4) | K(1)−P(2)−K(2′) | 104.70(4) |
| N(1)−K(1)−N(2) | 64.60(11) | N(2)−K(1)−N(3) | 62.73(10) |
| N(1)−K(1)−N(3) | 113.20(11) | N(1)−K(1)−P(1) | 114.91(9) |
| N(2)−K(1)−P(1) | 117.80(9) | N(3)−K(1)−P(1) | 124.44(8) |
| N(1)−K(1)−P(2) | 98.39(9) | N(2)−K(1)−P(2) | 133.31(9) |
| N(3)−K(1)−P(2) | 89.70(7) | N(4)−K(2)−N(5) | 62.30(10) |
| N(5)−K(2)−N(6) | 63.22(10) | N(4)−K(2)−N(6) | 117.46(11) |
| N(4)−K(2)−P(1) | 98.44(8) | N(5)−K(2)−P(1) | 130.98(8) |
| N(6)−K(2)−P(1) | 94.82(8) | N(4)−K(2)−P(2′) | 108.39(9) |
| N(5)−K(2)−P(2′) | 107.36(8) | N(6)−K(2)−P(2′) | 115.10(8) |

Compound **5** represents the first structurally characterized example of a diphosphinomethanide complex of potassium and reveals that such ambidentate ligands may bind to the larger alkali metal cations by a variety of coordination modes; the diphosphinomethanide ligands in **5** adopt monodentate $\eta^1$-*P*, bidentate $\eta^2$-*PP*, and $\eta^3$-*PCP*-heteroallyl coordination modes. This, along with the plethora of K⋯C(aryl) contacts, highlights the tendency of the heavier alkali metals to form multihapto interactions with highly delocalized ligands.

Compound **4** was serendipitously isolated from the reaction between **1** and potassium in THF and was crystallized from toluene/pmdeta; the molecular structure of **4** is shown in Figure 4, and details of bond lengths and angles are given in Table 4. To our knowledge, two potassium salts of the simple diphen-

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ylphosphide anion, unsolvated $[(Ph_2P)K]_n$ (**7**)[20] and the adduct $[(Ph_2P)K(1,4\text{-dioxane})_2]_n$ (**8**),[21] have previously been crystallographically characterized, although several groups, most notably that of Rabe and co-workers, have reported detailed crystallographic investigations into the structures of the heavier alkali metal salts of a range of sterically hindered primary and secondary phosphides such as $(Me_3Si)_2P^-$, (mes*)$PH^-$, (dmp)$PH^-$, and Ph(*t*-Bu)$P^-$ [mes* = 2,4,6-*t*-$Bu_3C_6H_2$; dmp = 2,6-$(2,4,6\text{-}Me_3C_6H_2)_2C_6H_3$].[22,23] In **7** the potassium diphenylphosphide units are linked together by K···C(aryl) $\pi$-interactions to form a complicated polymeric network, whereas in **8** the potassium atoms are in a distorted octahedral environment, coordinated by four dioxane oxygen atoms in the equatorial plane, one P atom from $PPh_2$, and an aryl group from a neighboring $PPh_2$. The dioxane molecules form bridges between the potassium atoms, generating a two-dimensional sheet arrangement, which is further linked into a three-dimensional array by the K···C(aryl) interactions. The solid state structure of the pmdeta adduct **4** is somewhat different from those of **7** and **8**: the structure consists of infinite zigzag chains of alternating potassium cations and $PPh_2$ anions. There are two crystallographically independent potassium atoms alternating along the chain, although these differ significantly only in the conformation of the donor groups of the ligands. The coordination sphere of each potassium in **4** is completed by the three nitrogen atoms from a chelating molecule of pmdeta, conferring a coordination number of five on the metal centers, which adopt highly distorted trigonal bipyramidal geometries. There are no short intra- or intermolecular K···C(aryl) contacts. The K−P distances in **4** range from 3.3025(14) to 3.4208(15) Å and lie within the range of K−P distances in previously reported potassium phosphide complexes;[22,23] the remaining distances and angles in **4** are typical of such complexes and require no further comment.

## Conclusions

The product obtained from the reduction of the vinylidene phosphine $(Ph_2P)_2C{=}CH_2$ (**1**) with alkali metals is highly dependent on the nature of the metal. While treatment of **1** with lithium or sodium furnishes the corresponding Schlenk dimerization product $[(L)_nM(Ph_2P)_2CCH_2]_2$ in good yields, treatment of **1** with potassium results in C−P cleavage and generation of the potassium phosphide $KPPh_2$. The potassium salt of the butane-1,4-diide ligand $[(Ph_2P)_2CCH_2]_2^{2-}$ may be isolated from a metathesis reaction between $[(THF)_2Li(Ph_2P)_2CCH_2]_2$ and 2 equiv of KO-*t*-Bu in diethyl ether. However, when this metathesis reaction is carried out in THF, only the lithium complex $[(pmdeta)Li(Ph_2P)_2CCH_2]_2$ is isolated after recrystallization from toluene/pmdeta. X-ray crystallography reveals that the dicarbanion ligands bind the smaller metals lithium and sodium in a bidentate $\eta^2$-*PP* fashion, but that these ligands bind the larger potassium cation via a combination of $\eta^1$-*P*, $\eta^2$-*PP*, and $\eta^3$-*PCP* interactions supplemented by K···C(aryl) contacts.

## Experimental Section

All manipulations were carried out using standard Schlenk techniques under an atmosphere of dry nitrogen or argon. Ether, THF, toluene, DME, and light petroleum (bp 40−60 °C) were distilled under nitrogen from sodium, potassium, or sodium/potassium alloy. With the exception of THF and DME, which were stored over activated 4 Å molecular sieves, all solvents were stored over a potassium film. Deuterated THF and toluene were distilled from potassium and deoxygenated by three freeze−pump−thaw cycles and were stored over activated 4 Å molecular sieves. All compounds were used as supplied by the manufacturer with the exception of KO-*t*-Bu, which was heated under vacuum at 150 °C/$10^{-2}$ mmHg for 1 h before use, and tmeda and pmdeta, which were freshly distilled from $CaH_2$. The alkene $(Ph_2P)_2C{=}CH_2$ (**1**) was prepared by a previously published method.[24]

$^1H$ and $^{13}C$ NMR spectra were recorded on a JEOL Lambda 500 spectrometer operating at 500 and 125.65 MHz, respectively, or a Bruker Avance 300 spectrometer operating at 300 and 75.47 MHz, respectively; chemical shifts are quoted in ppm relative to tetramethylsilane. $^{31}P$ NMR spectra were recorded on a Bruker WM300 spectrometer operating at 121.5 MHz, and chemical shifts are quoted relative to external 85% $H_3PO_4$. Where possible, elemental analyses were obtained by the Elemental Analysis Service of London Metropolitan University; due to the air-sensitive nature of **3b** and **5** satisfactory elemental analyses of these compounds could not be obtained.

**Preparation of $[(tmeda)_{1.5}Na(Ph_2P)_2CCH_2]_2$ (3b).** Elemental sodium (0.04 g, 1.76 mmol) was sublimed under vacuum to produce a sodium film within a standard Schlenk tube. To this was added a solution of **1** (0.70 g, 1.76 mmol) in THF (30 mL), and the mixture was treated ultrasonically for 30 min. The solution was filtered and the solvent removed in vacuo to give an oily orange solid, which was washed with light petroleum (2 × 5 mL). The solid was treated with tmeda (0.27 mL, 5.28 mmol) and recrystallized from cold (5 °C) toluene as orange blocks of **3b**. Isolated yield: 0.54 g (52%). $^1H$ NMR ($d_8$-THF, 22 °C): $\delta$ 1.91 (m, 4H, $CH_2$), 2.19 (s, 36H, $NMe_2$), 2.35 (s, 12H, $NCH_2$), 6.93−7.54 (m, 40H, Ph). $^{13}C$ NMR ($d_8$-THF, 24 °C): $\delta$ 31.2 (t, $^1J_{PC}$ = 18.6 Hz, $CP_2$), 34.6 ($CH_2$), 46.5 ($NMe_2$), 59.2 ($NCH_2$), 124.9 (*p*-Ph), 127.3 (*m*-Ph), 133.5 (*o*-Ph), 150.0 (*ipso*-Ph). $^{31}P\{^1H\}$ NMR ($d_8$-THF, 24 °C): $\delta$ 20.9.

**Metathesis between 2 and KO-*t*-Bu in Diethyl Ether: Preparation of $[\{(Ph_2P)_2CCH_2CH_2C(PPh_2)_2\}_2K_4(pmdeta)(DME)_3\cdot(PhMe)_2]_n$ (5).** To a solution of **2** (2.09 g, 1.90 mmol) in ether (30 mL) was added a slurry of KO-*t*-Bu (0.43 g, 3.83 mmol) in ether (20 mL). The mixture was stirred for 3 h, after which time the orange precipitate was isolated by filtration and washed with ether (2 × 10 mL). Pmdeta (0.60 mL, 3.00 mmol) was added, and the solid was recrystallized from toluene/DME (10:1 ratio) as orange plates of **5**. Isolated yield: 1.26 g (56%). $^1H$ NMR ($d_8$-THF, 27 °C): $\delta$ 1.91 (m, 8H, $CH_2$),

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**Table 5. Crystallographic Data for 6, 3b, 5, and 4**

| | **6** | **3b** | **5** | **4** |
|---|---|---|---|---|
| formula | $C_{70}H_{90}Li_2N_6P_4\cdot 3C_7H_8$ | $C_{70}H_{92}N_6Na_2P_4$ | $C_{125}H_{135}K_4N_3O_6P_8\cdot 2C_7H_8$ | $C_{21}H_{33}KN_3P$ |
| fw | 1429.6 | 1187.4 | 2363.8 | 397.6 |
| cryst size, mm | 0.50 × 0.30 × 0.20 | 0.40 × 0.40 × 0.30 | 0.10 × 0.10 × 0.10 | 0.78 × 0.58 × 0.52 |
| cryst syst | triclinic | monoclinic | monoclinic | orthorhombic |
| space group | $P\bar{1}$ | $C2/c$ | $P2_1/n$ | $Pna2_1$ |
| $a$, Å | 11.675(2) | 27.3325(12) | 26.756(4) | 18.3415(14) |
| $b$, Å | 14.336(3) | 11.2628(5) | 17.5983(17) | 10.9172(8) |
| $c$, Å | 14.813(3) | 24.0760(11) | 27.040(3) | 22.4764(17) |
| $\alpha$, deg | 112.915(3) | | | |
| $\beta$, deg | 93.433(3) | 111.651(2) | 92.049(11) | |
| $\gamma$, deg | 110.372(3) | | | |
| $V$, Å$^3$ | 2085.3(6) | 6888.7(5) | 12724(3) | 4500.6(6) |
| $Z$ | 1 | 4 | 4 | 8 |
| $\rho_{calcd}$, g cm$^{-3}$ | 1.138 | 1.145 | 1.234 | 1.174 |
| $\mu$, mm$^{-1}$ | 0.138 | 0.166 | 0.269 | 0.317 |
| no. of reflns measd | 12920 | 23554 | 55185 | 20252 |
| no. of unique reflns, $R_{int}$ | 5961, 0.020 | 6063, 0.034 | 22 852, 0.041 | 7811 |
| no. of reflns with $F^2 > 2\sigma(F^2)$ | 5025 | 4916 | 19 555 | 6246 |
| transmn coeff range | 0.934−0.973 | 0.937−0.952 | 0.930−0.971 | 0.580−0.910 |
| $R$, $R_w{}^a$ ($F^2 > 2\sigma$) | 0.039, 0.106 | 0.052, 0.118 | 0.080, 0.224 | 0.055, 0.137 |
| $R$, $R_w{}^a$ (all data) | 0.049, 0.113 | 0.065, 0.126 | 0.092, 0.241 | 0.070, 0.145 |
| $S^a$ | 1.03 | 1.08 | 1.06 | 1.01 |
| parameters | 503 | 379 | 1529 | 480 |
| max., min. diff map, e Å$^{-3}$ | 0.75, −0.25 | 0.47, −0.28 | 1.09, −0.67 | 0.80, −0.43 |

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

2.10 (s, 12H, $NMe_2$), 2.13 (s, 3H, NMe), 2.25 (m, 4H, $NCH_2$), 2.32 (m, 4H, $CH_2N$), 3.24 (s, 18H, OMe), 3.41 (s, 12H, $OCH_2$), 6.66−7.00 (m, 80H, Ph). $^{13}C\{^1H\}$ NMR ($d_8$-THF, 27 °C): $\delta$ 30.3 ($CP_2$, $^1J_{PC}$ = 12.37 Hz), 36.1 ($CH_2$), 43.1 (NMe), 46.3 ($NMe_2$), 57.3 ($NCH_2$), 58.8 ($CH_2N$), 59.3 (OMe), 72.9 ($OCH_2$), 124.6 (*p*-Ph), 127.2 (*m*-Ph), 133.6 (*o*-Ph), 151.1 (*ipso*-Ph). $^{31}P\{^1H\}$ NMR ($d_8$-THF, 23 °C): $\delta$ 19.00.

**Attempted Metathesis between 2 and KO-*t*-Bu in THF: Isolation of [(pmdeta)Li(Ph$_2$P)CCH$_2$]$_2$·(PhMe)$_3$ (6).** To lithium powder (0.12 g, 16.75 mmol) under argon was added a solution of $(Ph_2P)_2C{=}CH_2$ (1.33 g, 3.35 mmol) in THF (10 mL). This mixture was ultrasonically treated for 1 h. Excess lithium was removed by filtration, and solvent was removed in vacuo. The resulting oily solid was washed with light petroleum (2 × 5 mL) and redissolved in THF (30 mL). To this solution was added a solution of KO-*t*-Bu (0.38 g, 3.35 mmol) in THF (10 mL), and the mixture was stirred for 2 h. Solvent was then removed in vacuo to give an orange solid, which was further treated with pmdeta (0.31 mL, 1.51 mmol). The solid was recrystallized from a toluene/THF (95:5) solution at room temperature as yellow plates. Isolated yield: 1.47 g (84%) Anal. Calcd for $C_{70}H_{90}P_4N_6Li_2$ (molecular formula without toluene of solvation, which is readily lost under vacuum): C 70.90; H 7.87; N 7.29. Found: C 72.16; H 7.66; N 6.63. $^1H$ NMR ($d_8$-THF, 27 °C): $\delta$ 1.97 (s, 24H, $NMe_2$), 2.02 (m, 4H, $CH_2CH_2$), 2.16 (m, 8H, $NCH_2$), 2.29 (s, 6H, NMe), 2.31 (m, 8H, $NCH_2$), 6.85−7.23 (m, 40H, Ph). $^{13}C\{^1H\}$ NMR ($d_8$-THF, 27 °C): $\delta$ 29.0 (t, $^1J_{PC}$ = 21.96 Hz, $CP_2$), 35.4 ($CH_2CH_2$), 44.5 (NMe), 45.5 (NMe), 54.9 ($NCH_2$), 57.8 ($NCH_2$), 124.4 (*p*-Ph), 126.6 (*m*-Ph), 132.5 (*o*-Ph), 148.6 (*ipso*-Ph). $^{31}P\{^1H\}$ NMR ($d_8$-THF, 23 °C): $\delta$ 17.3.

**Reaction of 1 with Potassium: Isolation of [(Ph$_2$P)K(pmdeta)]$_n$ (4).** A solution of **1** (1.03 g, 2.60 mmol) in THF (10 mL) was transferred onto a freshly prepared potassium mirror (0.15 g, 3.84 mmol). This mixture was treated ultrasonically for 30 min, and the dark orange solution was filtered to remove unreacted K. Solvent was removed in vacuo to give a sticky, orange-red solid. This solid was recrystallized from cold (−30 °C) toluene containing a small amount of pmdeta as orange blocks of **4**. Isolated yield: 0.46 g (45%) Anal. Calcd for $C_{21}H_{33}N_3PK$: C 63.44; H 8.37; N 10.57. Found: C 63.54; H 8.38; N 10.52. $^1H$ NMR ($d_8$-toluene, 27 °C): $\delta$ 2.56 (s, 8H, $CH_2N$), 2.28 (s, 3H, NMe), 2.31 (s, br, 12H, $NMe_2$), 7.10−8.18 (m, 10H, Ph). $^{13}C\{^1H\}$ NMR ($d_8$-toluene, 27 °C): $\delta$ 42.49 (NMe), 46.14 ($NMe_2$), 57.02 ($CH_2N$), 58.45 ($CH_2N$), 120.73 (br, Ar), 135.74 (br, Ar) [remaining aromatic signals not resolved]. $^{31}P\{^1H\}$ NMR ($d_8$-toluene, 25 °C): $\delta$ −14.9.

**Crystal Structure Determinations of 3b, 4, 5, and 6:** For **3b**, **4**, and **6** measurements were made at 150 K on a Bruker AXS SMART CCD diffractometer using graphite-monochromated Mo Kα radiation ($\lambda$ = 0.71073 Å) and narrow (0.3° in $\omega$) frame exposures. For **5** measurements were made at 120 K on a Bruker SMART 1K CCD diffractometer using a synchrotron X-ray source ($\lambda$ = 0.6948 Å). For all compounds cell parameters were refined from the observed positions of all strong reflections in each data set. Intensities were corrected semiempirically for absorption, based on symmetry-equivalent and repeated reflections. The structures were solved by direct methods and refined on $F^2$ values for all unique data. Table 5 gives further details. All non-hydrogen atoms were refined anisotropically, and H atoms were constrained with a riding model; $U$(H) was set at 1.2 (1.5 for methyl groups) times $U_{eq}$ for the parent atom. Disorder was resolved and refined for one toluene solvent molecule in each of **5** and **6**, for one DME ligand in **5**, and for the ethylene link in the phosphorus ligand of **6**. **4** was found to be a racemic twin, with contributions of 0.67:0.33(5) for the two components, and **5** was a pseudomerohedral twin, resulting from the near-equality of the $a$ and $c$ axis lengths, with 0.909:0.091(7) contributions of the two components. Programs were Bruker AXS SMART (control) and SAINT (integration), and SHELXTL for structure solution, refinement, and molecular graphics.[25]

**Acknowledgment.** The authors thank the EPSRC and the Royal Society for support. The crystal structure of **5** was obtained through the EPSRC-funded national X-ray crystallography service.

**Supporting Information Available:** For **3b**, **4**, **5**, and **6** details of structure determination, atomic coordinates, bond lengths and angles, and displacement parameters. 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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(25) (a) *SMART* and *SAINT* software for CCD diffractometers; Bruker AXS Inc.: Madison, WI, 1997. (b) Sheldrick, G. M. *SHELXTL user manual*, version 6; Bruker AXS Inc.: Madison, WI, 2001.