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FULL PAPER

Synthesis and crystal structure determination of two monomeric alkali metal phosphide derivatives: [M{P(H)C_6H_2-t-Bu_3-2,4,6}-(18-crown-6)] (M = K or Rb)

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The molecular structures of two crown ether adducts of heavier alkali metal derivatives (M = K or Rb) of the primary phosphane "supermesitylphosphane" [*i.e.* $H_2PC_6H_2$-t-Bu_3-2,4,6] have been determined. The complexes [M{P(H)C_6H_2-t-Bu_3-2,4,6}(18-crown-6)] [M = K **1** or Rb **2**] were obtained in good yield by crystallization of MP(H)C_6H_2-t-Bu_3-2,4,6 from toluene–18-crown-6. A main feature is the crown ether adducts of bent MP(H)C_6H_2-t-Bu_3-2,4,6 moieties, thereby representing rare examples of monomeric complexes of the heavier alkali metals containing a phosphide ligand. Both solution and solid-state NMR data are presented.

Introduction

More than thirty years ago Issleib and co-workers reported synthetic pathways as well as ^{31}P NMR spectroscopic data of 1,4-dioxane adducts of alkali metal derivatives (M = Li to Cs) of diphenylphosphane, thereby representing the first reports on the accessibility of molecular alkali metal phosphide derivatives.[1,2] Since the early eighties numerous reports on molecular structure determinations of lithium phosphide derivatives followed,[3,4] and in the nineties a limited number of examples of molecular sodium and potassium phosphides appeared.[5–13] However, only in recent years the research groups of Driess,[13] Ruhlandt-Senge and Uhlig,[14] and ourselves[15–18] have reported stuctural data on rubidium and caesium derivatives of both primary and secondary phosphanes. This dearth of structural data on heavier congeners of alkali metal derivatives of phosphanes is in sharp contrast to numerous reports on binary M–P solid-state phases of the heavier alkali metals (M = K, Rb or Cs).[19,20]

Crown ether ligands are known to be selective complexing agents for alkali metal cations. Recently, we reported a number of 18-crown-6 adducts of caesium derivatives of two primary phosphanes with molecular structures exhibiting highly restricted dimensionality and, also, representing the first examples of structurally characterized monomeric caesium phosphide derivatives.[21] We here present the synthesis and crystal structural determination of two more crown ether adducts of alkali metal salts of "supermesitylphosphane" (= $H_2PC_6H_2$-t-Bu_3-2,4,6)[22,23] of general composition [M{P(H)C_6H_2-t-Bu_3-2,4,6}(18-crown-6)] [M = K **1**, or Rb **2**], thereby providing more structural data on rare *monomeric* heavier alkali metal phosphide derivatives[12,21] as well as a comparison with our previous reports on the corresponding caesium derivative (**3**·0.5 C_6H_5Me).[21]

Results and discussion

[K{P(H)C_6H_2-t-Bu_3-2,4,6}(18-crown-6)] 1

Crystallization of [KP(H)C_6H_2-t-Bu_3-2,4,6]$_x$ from toluene in the presence of 18-crown-6 produces yellow crystals. The composition of these crystals was determined crystallographically as [K{P(H)C_6H_2-t-Bu_3-2,4,6}(18-crown-6)] **1**. The molecular structure of complex **1** (Fig. 1) features a potassium cation co-ordinated by the six oxygen atoms of the crown ether ligand and the phosphorus atom of the P(H)C_6H_2-t-Bu_3-2,4,6 substituent. The angle between the planes described by the phenyl ring [C(1)–C(6)] and the six oxygen atoms of the crown ether ligand [O(21)–O(26)] is 4.3°. The K–P distance of 3.4822(9) Å is longer than the corresponding distances in [KP(H)C_6H_2-t-Bu_3-2,4,6]$_x$ ranging from 3.181(2) to 3.357(2) Å,[8] and can furthermore be favorably compared with reports on other K–P species.[5,9–12,14] The K(1)–P(1)–C(6) angle of 85.57(7)° in monomeric **1** is significantly smaller than the corresponding angle in

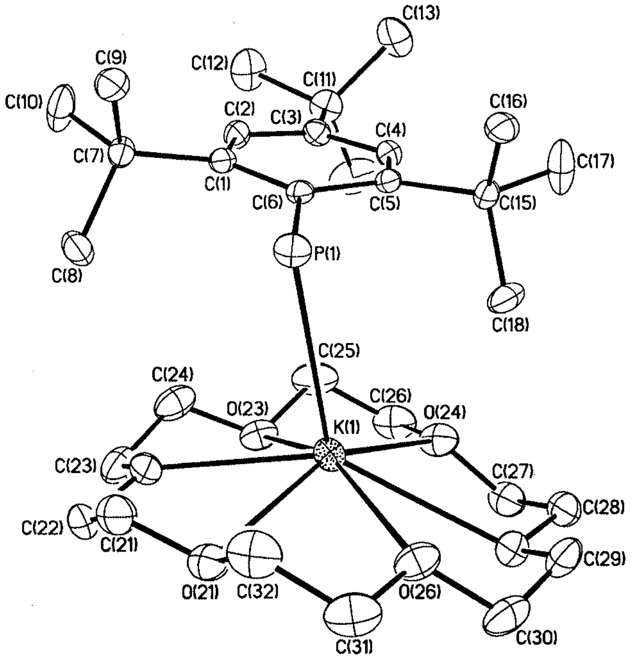

Fig. 1 An ORTEP[24] diagram of [K{P(H)C_6H_2-t-Bu_3-2,4,6}(18-crown-6)] **1**, showing the atom labelling scheme. Thermal ellipsoids are at 30% probability and hydrogen atoms are omitted for clarity.

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Table 1 Significant interatomic separations [Å] and angles [°] for [K{P(H)C_6H_2-t-Bu_3-2,4,6}(18-crown-6)] **1** and [Rb{P(H)C_6H_2-t-Bu_3-2,4,6}-(18-crown-6)] **2** as well as the caesium derivative [Cs{P(H)C_6H_2-t-Bu_3-2,4,6}(18-crown-6)]·0.5C_6H_5Me **3**·0.5C_6H_5Me.[21] Both independent molecules of the latter are listed

	1	**2**	**3**·0.5C_6H_5Me
M–P	3.4822(9)	3.5529(11)	3.847(2)/4.069(3)
M···C(phenyl)	3.810(12) [C(6)]	3.674(3) [C(13)]	3.411(6) [C(6)]/3.405(6) [C(46)]
			3.637(6) [C(5)]/3.494(7) [C(41)]
			3.675(6) [C(1)]/3.605(7) [C(45)]
			3.850(6) [C(4)]/3.644(6) [C(42)]
			3.878(6) [C(2)]/3.721(7) [C(44)]
			3.952(6) [C(3)]/3.756(7) [C(43)]
M–O	2.749(2) [O(22)]	2.853(3) [O(6)]	3.048(5) [O(21)]/3.066(9) [O(64)]
	2.833(2) [O(26)]	2.945(3) [O(4)]	3.127(5) [O(23)]/3.117(8) [O(66)]
	2.874(2) [O(23)]	2.966(3) [O(2)]	3.127(5) [O(25)]/3.202(6) [O(65)]
	2.887(2) [O(21)]	2.986(3) [O(1)]	3.186(5) [O(26)]/3.252(10) [O(62)]
	2.894(2) [O(24)]	3.014(3) [O(5)]	3.273(5) [O(22)]/3.268(9) [O(63)]
	2.990(2) [O(25)]	3.088(3) [O(3)]	3.299(5) [O(24)]/3.448(11) [O(61)]
M–P–C	85.57(7)	78.85(11)	62.4(2)/56.0(2)

polymeric [KP(H)C_6H_2-t-Bu_3-2,4,6]$_x$ [139.5(1)°], an observation which can be explained by the different co-ordination modes of the phosphide moiety in both systems. The shortest non-bonding K···C(phenyl) distance is 3.810(12) Å [K(1)···C(6)]. Additionally, one of the methyl groups of one of the *tert*-butyl groups of the supermesityl ligand, C(18), has a non-bonding K···C contact at a distance of 3.431(3) Å. Furthermore, all of the non-bonding K···C(crown ether) distances are below 4.0 Å, ranging from 3.513(4) [K(1)···C(32)] to 3.818(4) Å [K(1)···C(28)].

Atom K(1) is 0.70 Å above the plane defined by the six oxygen atoms of the crown ether ligand. It does not reside exactly above the center of the crown ether cavity, but shifted towards oxygen atom O(22) and away from O(25), as can be seen from data given in Table 1. Atom C(6), being the *ipso* carbon atom of the phenyl ring, is 0.10 Å below the plane defined by atoms C(1) to C(5).

[Rb{P(H)C_6H_2-t-Bu_3-2,4,6}(18-crown-6)] 2

Complex **2** was prepared and bright yellow crystals were obtained in a similar way to that described for the potassium derivative **1**. The molecular structure of **2** is *in principle* quite similar to the one found for complex **1**. The Rb–P distance of 3.5529(11) Å can be compared, *e.g.*, with our earlier report on the corresponding distances in [RbP(H)C_6H_2-t-Bu_3-2,4,6]$_x$, ranging from 3.381(1) to 3.504(1) Å.[15] The Rb(1)–P(1)–C(13) angle of 78.85(11)° is, as was observed in the case of the potassium derivative **1**, significantly smaller than the corresponding angle of 138.3(2)° in [RbP(H)C_6H_2-t-Bu_3-2,4,6]$_x$. A couple of minor differences between the molecular structures of complexes **1** and **2** need to be discussed. As the alkali metal increases in size (the ionic radius increases 0.14 Å from potassium to rubidium given the formal co-ordination number of six),[25] the metal atom resides further above the oxygen atoms of the crown ether ligand. The rubidium atom in **2** is located 0.93 Å above the plane defined by the six oxygen atoms of the crown ether ligand. The metal center is, as can be seen by looking at the Rb···O distances, shifted towards O(6) and away from O(3), with Rb(1)···O(*n*)···centroid(18-crown-6) angles ranging from 17.1 [O(3)] to 18.9° [O(6)]. The metal center does therefore not reside exactly in the centre of the crown ether cavity. The angle between the two planes forming the bent arrangement, namely the phenyl ring [C(13)–C(18)] and the six oxygen atoms of the crown ether [O(1)–O(6)], is 2.5°. The *ipso* carbon atom C(13) is 0.10 Å below the plane defined by the carbon atoms C(14) to C(18). There is a weak electrostatic interaction between the rubidium cation and the *ipso* carbon atom [C(13)] at a distance of 3.674(3) Å. In addition, there is a relatively short metal–carbon interaction between Rb(1) and one of the methyl groups of a *tert*-butyl group [C(22)] at a distance of 3.486(5) Å. Finally, there are three more close contacts (<4.0 Å) between the metal center and certain carbon atoms of the crown ether ligand, namely Rb···C(1) [3.565(5)], Rb···C(9) [3.655(5)], and Rb···C(12) [3.656(5) Å].

Comparison of the molecular structures of complexes 1, 2, and 3·0.5C_6H_5Me

Different degrees of π co-ordination between the anionic supermesityl ligand and the corresponding metal center are observed in complexes **1**, **2**, and **3**·0.5C_6H_5Me. While a pronounced η^6 bonding mode between the metal center and the phenyl ring as well as a slightly distorted "sandwich-type" structure is found in the case of the caesium derivative (**3**·0.5C_6H_5Me), basically no π interaction is present between the supermesityl ligand and the potassium atom in complex **1**. This trend is accompanied, with the alkali metal decreasing in size, by a stepwise approach of the location of the corresponding metal center towards the crown ether cavity. In parallel, a stepwise increase of the M–P–C angles is observed, thereby prohibiting a higher degree of π interaction between the metal center and the phenyl ring of the supermesityl ligand in the case of **1** and **2**. Further comparison of significant interatomic separations and angles of complexes **1** and **2** with the previously reported caesium derivative **3**·0.5 C_6H_5Me can be derived from Table 1.

Solid-state NMR spectroscopy

We were interested in finding out how solution and solid-state NMR data of complex **1** compare. In particular, we wanted to investigate whether the presence of different M···C distances in the molecular structures of **1** and **2** can further be corroborated using solid-state NMR spectroscopy. As an example, both a ^{13}C CP MAS and a ^{31}P MAS study of **1** were undertaken.

Fig. 2 shows the aromatic region of the ^{13}C CP MAS spectrum of the potassium derivative **1** featuring five signals at δ 157.5, 146.4, 144.9, 135.1, and 120.3. Based on integration data combined with a comparison with the solution spectrum, the signal at δ 157.5, exhibiting a well resolved doublet structure ($^1J_{P-C} = 85$ Hz) due to indirect coupling to the neighboring phosphorus atom, can be assigned to the *ipso* carbon atom. Further comparison with chemical shifts of the signals from the solution spectrum suggests that the remaining signals in the aromatic region correspond to two crystallographically inequivalent *ortho* (δ 146.4 and 144.9) and the *para* (δ 135.1) carbon atoms, while the broad signal at δ 120.3 corresponds to the two *meta* carbon atoms. This relatively broad signal is not resolved into two lines presumably because of residual dipolar coupling to the directly bound hydrogen atoms. Our assignment is further corroborated by integration data. It is noteworthy

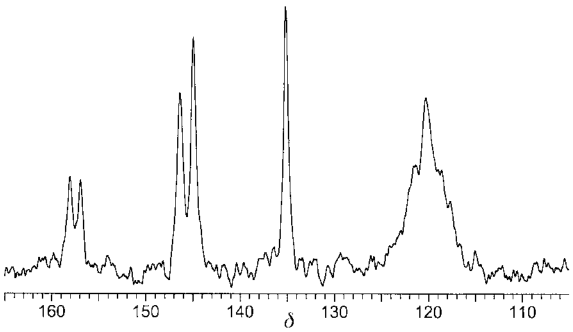

Fig. 2 Aromatic region of the ^{13}C CP MAS NMR spectrum of [K{P(H)C_6H_2-t-Bu_3-2,4,6}(18-crown-6)] **1**.

that the presence of two inequivalent *ortho* carbon atoms could not be detected in the solution NMR spectra.

In addition to the the signals in the aromatic region, six more signals are found in the ^{13}C CP MAS spectrum corresponding to the crown ether carbon atoms (δ 70.7), the tertiary carbon atoms (δ 39.4 and 38.9) and the methyl carbon atoms (δ 34.8, 33.8, and 32.2) of the *tert*-butyl groups of the supermesityl ligand.

With respect to their chemical shifts, all signals from the ^{13}C solid-state NMR spectrum of compound **1** are found at similar positions to those of the corresponding signals from the solution spectra in deuteriated benzene and tetrahydrofuran at room temperature.

The ^{31}P MAS NMR spectrum of the potassium salt **1** exhibits a signal at δ −92.4. A comparison of this signal with the corresponding solution NMR spectra at room temperature reveals an upfield shift for the solid-state spectrum of 6.8 (*vs.* benzene) and 12.3 ppm (*vs.* tetrahydrofuran), respectively. Further comparison can be made with the previously reported ^{31}P MAS spectrum of [KP(H)C_6H_2-t-Bu_3-2,4,6]$_x$ (δ −104).[15]

Given the fact that the solution structure of complex **1** is not known, it is rather difficult at this point to come up with definite conclusions from the presented comparison of solution *vs.* solid-state NMR data.

Conclusion

Our work reports two crown ether adducts of heavier alkali metal phosphide derivatives of general composition [M{P(H)-C_6H_2-t-Bu_3-2,4,6}(18-crown-6)] (M = K or Rb), thereby allowing for a detailed comparison of structural parameters of a series of crown ether adducts of MP(H)R species (M = K, Rb or Cs). We were able to demonstrate that, depending on the size of the alkali metal cation employed, different degrees of π co-ordination between the supermesityl ligand and the metal center are found to be present.

Experimental

The compounds described below were handled under nitrogen using Schlenk double manifold, high-vacuum, and glove-box (M.Braun, Labmaster 130) techniques. Solvents were dried and physical measurements were obtained following typical laboratory procedures. The compounds [KP(H)C_6H_2-t-Bu_3-2,4,6]$_x$[8] and [RbP(H)C_6H_2-t-Bu_3-2,4,6]$_x$[15] were prepared as described previously; 18-crown-6 was purchased from Aldrich and used as received. NMR spectra were recorded on a JMN-GX 400 instrument, the solid-state MAS NMR spectra on a Bruker MSL 300 spectrometer, operating at 121.496 and 75.468 MHz for ^{31}P and ^{13}C, respectively. The ^{13}C CP MAS NMR spectrum was referenced externally using adamantane as a secondary chemical shift standard (the low-frequency signal was set to δ 29.47 relative to TMS). For the ^{31}P MAS NMR spectrum $NH_4H_2PO_4$ (δ 1.1 *vs.* 85% H_3PO_4) was used as an external reference. Approximately 50 mg of [K{P(H)C_6H_2-t-Bu_3-2,4,6}(18-crown-6)] were packed into a 4 mm ZrO_2 rotor with a Kel-F cap. The ^{31}P NMR spectrum was obtained at a spinning speed of 10.0 kHz (recycle delay: 8 s) using proton-high-power decoupling. The ^{13}C CP MAS NMR spectrum was recorded under the following conditions: recycle delay 4 s; contact time 5 ms; spinning speed 10 kHz.

Preparations

[K{P(H)C_6H_2-t-Bu_3-2,4,6}(18-crown-6)] 1. Recrystallization of [KP(H)C_6H_2-t-Bu_3-2,4,6]$_x$ (200 mg, 0.63 mmol) from toluene–18-crown-6, followed by removal of solvent and drying of the crystals under vacuum, gave complex **1** as a yellow powder (220 mg, 60%). Compound **1** is well soluble in toluene, but insoluble in aliphatic hydrocarbons. Calc. for $C_{30}H_{54}KO_6P$: C, 62.04; H, 9.37. Found: C, 61.81; H, 9.02%. ^{1}H NMR (C_6D_6, 400 MHz, 25 °C): δ 1.55 (s, 9 H, *p*-^{t}Bu), 2.23 (s, 18 H, *o*-^{t}Bu), 3.13 (s, 24 H, OCH_2), 3.47 (d, $^1J_{P-H}$ = 166 Hz, 1 H, PH) and 7.46 (s, 2 H). ^{31}P NMR (C_6D_6, 161.9 MHz, 25 °C): δ −85.6 (d, $^1J_{P-H}$ = 166 Hz). ^{13}C NMR (C_6D_6, 100.4 MHz, 25 °C): δ 32.0, 32.1, 32.3, 34.3 (CH_3C), 38.6 (CH_3C), 69.7 (OCH_2), 119.8 (*meta*-C), 135.1 (*para*-C), 145.5 (d, $^2J_{C-P}$ = 6, *ortho*-C) and 157.0 (d, $^1J_{C-P}$ = 75 Hz, *ipso*-C). ^{1}H NMR (C_4D_8O, 400 MHz, 25 °C): δ 1.18 (s, 9 H, *p*-^{t}Bu), 1.67 (s, 18 H, *o*-^{t}Bu), 2.83 (d, $^1J_{P-H}$ = 161 Hz, 1 H, PH), 3.52 (s, 24 H, OCH_2) and 6.75 (s, 2 H). ^{31}P NMR (C_4D_8O, 161.9 MHz, 25 °C): δ −80.1 (d, $^1J_{P-H}$ = 161 Hz). ^{13}C NMR (C_4D_8O, 100.4 MHz, 25 °C): δ 30.6, 30.7, 31.6, 33.7 (CH_3C), 37.8 (CH_3C), 70.1 (OCH_2), 118.4 (*meta*-C), 132.2 (*para*-C), 144.0 (d, $^2J_{C-P}$ = 6, *ortho*-C) and 159.8 (d, $^1J_{C-P}$ = 80 Hz, *ipso*-C). IR (Nujol): 2357s, 1975w, 1748w, 1592m, 1262s, 1209m, 1182w, 1158m, 1108vs, 1028m, 960s, 870m, 835s, 771w, 743s, 627m, 591w, 548w, 528w and 486w cm^{-1}.

[Rb{P(H)C_6H_2-t-Bu_3-2,4,6}(18-crown-6)] 2. Recrystallization of [RbP(H)C_6H_2-t-Bu_3-2,4,6]$_x$ (200 mg, 0.55 mmol) from toluene–18-crown-6, followed by removal of solvent and drying of the crystals under vacuum, gave complex **2** as a bright yellow powder (207 mg, 60%). It is well soluble in toluene, but insoluble in aliphatic hydrocarbons. Calc. for $C_{30}H_{54}O_6PRb$: C, 57.45; H, 8.68. Found: C, 57.24; H, 8.37%. ^{1}H NMR (C_6D_6, 400 MHz, 25 °C): δ 1.51 (s, 9 H, *p*-^{t}Bu), 2.23 (s, 18 H, *o*-^{t}Bu), 3.09 (s, 24 H, OCH_2), 3.67 (d, $^1J_{P-H}$ = 164 Hz, 1 H, PH) and 7.40 (s, 2 H). ^{31}P NMR (C_6D_6, 161.9 MHz, 25 °C): δ −79.4 (d, $^1J_{P-H}$ = 164 Hz). ^{13}C NMR (C_6D_6, 100.4 MHz, 25 °C): δ 31.6, 31.7, 32.1, 34.3 (CH_3C), 38.7 (CH_3C), 69.7 (OCH_2), 119.6 (*meta*-C), 134.4 (*para*-C), 145.3 (d, $^2J_{C-P}$ = 6, *ortho*-C) and 158.5 (d, $^1J_{C-P}$ = 75 Hz, *ipso*-C). ^{1}H NMR (C_4D_8O, 400 MHz, 25 °C): δ 1.21 (s, 9 H, *p*-^{t}Bu), 1.69 (s, 18 H, *o*-^{t}Bu), 2.87 (d, $^1J_{P-H}$ = 163 Hz, 1 H, PH), 3.55 (s, 24 H, OCH_2) and 6.83 (s, 2 H). ^{31}P NMR (C_4D_8O, 161.9 MHz, 25 °C): δ −80.4 (d, $^1J_{P-H}$ = 163 Hz). ^{13}C NMR (C_4D_8O, 100.4 MHz, 25 °C): δ 30.7, 30.8, 31.5, 33.7 (CH_3C), 37.9 (CH_3C), 69.9 (OCH_2), 118.6 (*meta*-C), 133.0 (*para*-C), 144.3 (d, $^2J_{C-P}$ = 6, *ortho*-C) and 158.9 (d, $^1J_{C-P}$ = 80 Hz, *ipso*-C). IR (Nujol): 2360s, 1971w, 1754w, 1592m, 1297m, 1250s, 1209m, 1182w, 1155m, 1108vs, 1026m, 946m, 928m, 865m, 834m, 767w, 745m, 723w, 626m, 590w, 523w and 484w cm^{-1}.

X-Ray data collection, structure determination, and refinement for complexes 1 and 2

Crystal, data collection, and refinement parameters are given in Table 2. Suitable crystals for single-crystal X-ray diffraction were selected and mounted in nitrogen-flushed, thin-walled glass capillaries. The data were collected on a Siemens P4 diffractometer equipped with a SMART CCD detector.

The systematic absences in the diffraction data are consistent with the *C*-centered monoclinic space groups, *Cc* and *C*2/*c*. *E*-statistics suggested the centrosymmetric space group, which yielded chemically reasonable and computationally stable

Table 2 Crystallographic data for [K{P(H)C_6H_2-t-Bu_3-2,4,6}(18-crown-6)] **1** and [Rb{P(H)C_6H_2-t-Bu_3-2,4,6}(18-crown-6)] **2**

	1	2
Formula	$C_{30}H_{54}KO_6P$	$C_{30}H_{54}O_6PRb$
M	580.80	627.17
Space group	*C*2/*c*	*C*2/*c*
Crystal symmetry	Monoclinic	Monoclinic
a/Å	40.7745(2)	40.3994(5)
b/Å	9.0007(2)	9.1640(1)
c/Å	19.1484(3)	19.2861(2)
β/°	106.6551(6)	106.2637(7)
V/Å^3	6732.6(2)	6854.36(13)
Z	8	8
T/°C	−50(2)	−100(2)
μ(Mo-Kα)/cm^{-1}	2.42	15.27
*R*1 (%)	5.72	5.30
*wR*2 (%)	15.09	14.49

results of refinement. The structures were solved using direct methods, completed by subsequent Fourier difference syntheses and refined by full-matrix, least-squares procedures. The two structures are isomorphous. The methyl carbon atoms of one *tert*-butyl group in **1** and **2**, C(12)–C(14) and C(28)–C(30), respectively, were disordered over two positions, 60/40. Carbon atoms C(28)–C(30) and C(28′)–C(30′) were refined isotropically. All other non-hydrogen atoms were refined with anisotropic displacement coefficients. The hydrogen atom on the phosphorus atom of **1** could not be located, and of **2** was located from the difference map and refined with a fixed P–H distance of 1.40 Å. All other hydrogen atoms were treated as idealized contributions.

All software sources of the scattering factors are contained in the SHELXTL (5.3) program.[26]

CCDC reference number 186/1951.

See http://www.rsc.org/suppdata/dt/b0/b000653j/ for crystallographic files in .cif format.

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