Preparation and Reactions of 1,3-Diphosphacyclobutane-2,4-diyls That Feature an Amino Substituent and/or a Carbonyl Group

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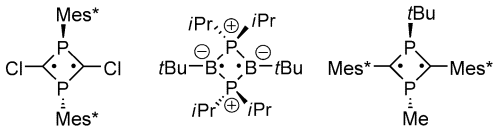
Abstract: The preparation and properties of a 1-amino-1,3-diphosphacyclobutane-2,4-diyl and a 1-benzoyl-1,3-diphosphacyclobutane-2,4-diyl, which can be regarded as functionalized cyclic biradical derivatives, were investigated. Hydrolysis of 1-diisopropylamino-3-methyl-2,4-bis(2,4,6-tri-*tert*-butylphenyl)-1,3-diphosphacyclobutane-2,4-diyl (**7**), which is formed by reaction of Mes*C≡P (**4**; Mes* = 2,4,6-$tBu_3C_6H_2$) with lithium diisopropylamide and iodomethane, resulted in ring-opening of the 1,3-diphosphacyclobutane-2,4-diyl skeleton, as well as de-aromatization of one of the Mes* rings. 3-Oxo-1,3-diphosphapropene **8** and 7-phosphabicyclo[4.2.0]octa-1(8),2,4-triene **9** were the resultant products, and these were subsequently characterized. Isomerization and oxidation of **7** occurred in the presence of TEMPO (2,2,6,6-tetramethyl-1-piperidinoxy) to give the first example of a cyclic dimethylenephosphorane derivative, namely 3-oxo-1,3-diphospha-1,4-diene **10**. 1-Benzoyl-3-*tert*-butyl-2,4-bis(2,4,6-tri-*tert*-butylphenyl)-1,3-diphosphacyclobutane-2,4-diyl (**12**) was isolated and characterized from the reaction of **4** with *tert*-butyllithium and benzoyl chloride. Compound **12** was subsequently heated and underwent rearrangement of the benzoyl group and ring-expansion to afford 1-oxo-1*H*-[1,3]diphosphole **13**. Reaction of **4** with lithium diisopropylamide and benzoyl chloride afforded the 2*H*-[1,2,4]oxadiphosphinine **15**, which was probably formed through the 1,3-diphosphacyclobutane-2,4-diyl intermediate **14**. Thermolysis of **15** afforded 1-oxo-1*H*-[1,3]diphosphole **16** in an Arbuzov-type rearrangement.

Keywords: heterocycles · phosphaalkenes · phosphaalkynes · protecting groups · radicals

Introduction

In recent years, the general character of radicals, which are described as highly reactive and short-lived, has not been found to apply to several biradicals, in particular, the heavier main group elements such as phosphorus.[1] Niecke and co-workers described the synthesis of an isolable, phosphorus-containing, four-membered cyclic biradical species, 2,4-dichloro-1,3-diphosphacyclobutane-2,4-diyl **1**, and its reactions to afford several intriguing compounds.[2–4] For example, ring-opening of the 1,3-diphosphacyclobutane-2,4-diyl and formation of a diphosphabicylo[1.1.0]butane were reported,[2,3,5] and very recently, the aniomesolytic cleavage of a P–C(aryl) bond to afford the 1,3-diphosphacyclobutadienediide was described.[6] On the other hand, Bertrand and co-workers reported the synthesis of a boron-centered biradical **2**,[7,8] and recently, interest has been shown with regard to the latest results of its radical-type reactivity[9] and the structural conversion of the B_2P_2 biradical.[10] These attempts to obtain stable biradicals have had an impact on both main group chemistry, as well as the chemistry of reaction intermediates.



Very recently, we reported the formation of 1,3-diphosphacyclobutane-2,4-diyl **3** in the reaction of a bulky phosphaalkyne (Mes*C≡P (**4**)) with *tert*-butyllithium and iodomethane. Compound **3** was stable at room temperature and did not decompose up to a few days even in air.[11] Moreover, our method enables various kinds of nucleophiles and electrophiles to be employed in the reaction of **4**. Therefore, we thought that it might be possible to prepare a number of 1,3-diphosphacyclobutane-2,4-diyl derivatives.

Herein we report the preparation and reactions of some functionalized 1,3-diphosphacyclobutane-2,4-diyls prepared from **4**. We chose lithium diisopropylamide (LDA) and *tert*-butyllithium as nucleophiles, while iodomethane and benzo-

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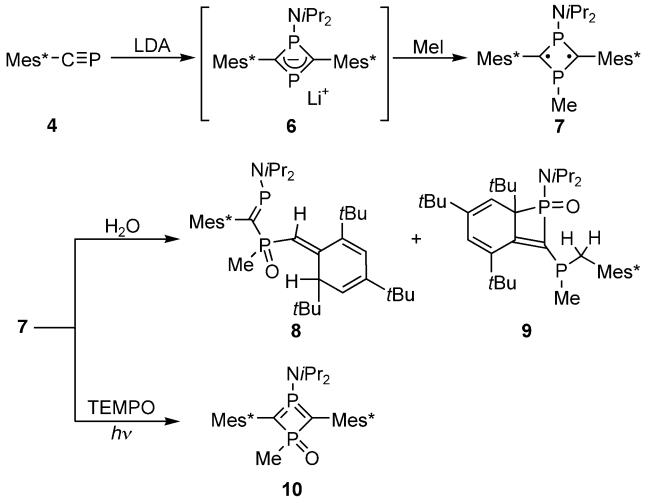
yl chloride were employed as electrophiles. Benzoyl chloride was used in the hope that the carbonyl moiety would act as an electron-withdrawing group that would interact with the P_2C_2 biradical skeleton. Moreover, we anticipated that the amino group on the phosphorus might affect the 1,3-diphosphacyclobutane-2,4-diyl moiety in such a way that it would undergo a number of novel reactions. We found that 1,3-diphosphacyclobutane-2,4-diyls that bear an amino group undergo isomerization and ring-opening, while the 1,3-diphosphacyclobutane skeleton that bears a benzoyl group undergoes ring-expansion.

Results and Discussion

Preparation of phosphaalkyne[12] 4 and its precursor: Phosphaalkyne **4** was prepared by a Fritsch–Buttenberg–Wiechell-type [1,2] rearrangement using 2,2-dibromo-1-(2,4,6-tri-*tert*-butylphenyl)-1-phosphaethene (Mes*P=CBr_2 (**5**)) and a nickel catalyst in the manner previously described,[11,13] while dibromophosphaethene **5**[14] was prepared from (2,4,6-tri-*tert*-butylphenyl)phosphonous dichloride (Mes*PCl_2)[15] and bromoform in the presence of LDA.[16]

Formation and reactions of 1-diisopropylamino-3-methyl-1,3-diphosphacyclobutane-2,4-diyl (7): Phosphaalkyne **4** was allowed to react with 0.5 equivalents of LDA to give the resultant intermediate **6**, the structure of which was determined by ^{31}P NMR spectroscopy ($\delta_P = 258$, 56 ppm; $^2J(P,P) = 102$ Hz) (Scheme 1).[11,17] The reaction mixture was



Scheme 1.

then treated with iodomethane to afford **7** as a deep blue compound in almost quantitative yield. In contrast to **3**, compound **7** was found to decompose in air probably because of the instability of the P–N bond. In addition, **7** underwent slow decomposition in solution even at −20 °C. In the ^{31}P NMR spectrum, the P–N(iPr$_2$)$_2$ phosphorus atom displayed a higher chemical shift than that of the PMe moiety and a larger coupling constant ($^2J(P,P) = 433.7$ Hz) than that observed for **3**.[11] This might indicate that a considerable interaction arises between the phosphorus atoms and the amino group as a result of a π-donating effect.

Attempts to isolate **7** for X-ray crystallographic studies were unsuccessful. However, in the course of these studies several derivatives of **7** were isolated and characterized. In particular, when compound **7** was kept for 0.5 h in a benzene/water mixture, the subsequent ^{31}P NMR spectrum displayed eight major peaks that corresponded to new products, some of which were not able to be identified. The two major products **8** and **9** were isolated by chromatographic purification, each as a mixture of two diastereomers, and these were then recrystallized and analyzed by X-ray crystallography. Figure 1 shows an ORTEP drawing of the molecular structure of **8**, which corresponds to the product of a ring-opening reaction of the 1,3-diphosphacyclobutane skeleton followed by addition of water. The six-membered ring (C3–C8) is not aromatic. It contains two double bonds at C5=C6 and C7=C8 and an *exo* double bond at C3, two single bonds at C3–C4 and C4–C5, and two additional single bonds at C6–C7 and C3–C8 whose bond lengths are characteristic of the central C–C diene bond. The nitrogen atom is planar (Σ(angles) = 360°) and the N–P1–C1–P2 skeleton is coplanar ($\Theta = 2.2(5)°$). Figure 2 displays an ORTEP drawing of **9**. Although the structure of **9** suggests that it is also the product from the ring-opening of **7**, in contrast to **8**, the P(NiPr$_2$) phosphorus is bonded to C3 to form a bicyclic structure.[18] As in compound **8**, the six-membered ring (C2–C7) is not aromatic. Three asymmetric centers are present in **9**, and the diisopropylamino group is *trans* to the C3 *t*Bu group so that steric congestion is minimized. It is likely that compounds **8** and **9** are formed by ring-opening

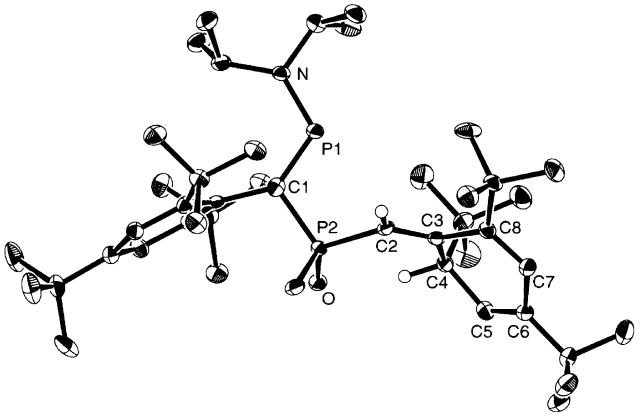


Figure 1. Molecular structure of **8**. All hydrogen atoms except for H1 and H2, and those found in the solvent (dichloromethane), are omitted for clarity. Selected bond lengths [Å] and angles [°]: P1–N 1.646(4), P1–C1 1.670(5), P2–O 1.486(3), P2–C1 1.820(4), P2–C2 1.798(4), P2–Me 1.804(5), C1–Mes* 1.508(6), C2–C3 1.357(6), C3–C4 1.521(6), C4–C5 1.500(6), C5–C6 1.338(6), C6–C7 1.470(6), C7–C8 1.346(6), C3–C8 1.487(6); N-P1-C1 115.5(2), O-P2-C1 114.9(2), O-P2-C2 116.2(2), O-P2-Me 109.8(2), C1-P2-C2 108.0(2), C1-P2-Me 105.6(2), C2-P2-Me 101.0(2), P1-C1-P2 110.3(2), P1-C1-Mes* 138.2(3), P2-C1-Mes* 111.3(3), P2-C2-C3 130.9(4), C2-C3-C4 122.2(4), C2-C3-C8 122.0(4), C4-C3-C8 115.6(4), C3-C4-C5 109.6(4), C3-C4-*t*Bu 115.2(4), C5-C4-*t*Bu 110.4(4), C4-C5-C6 123.0(4), C5-C6-C7 117.4(4), C6-C7-C8 124.1(4), C3-C8-C7 116.1(4).

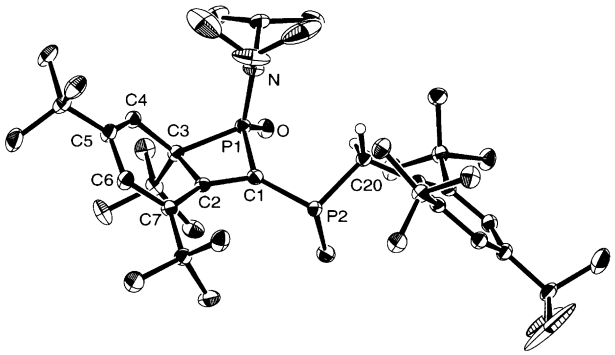
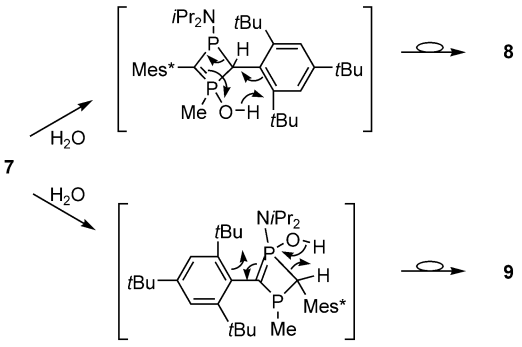


Figure 2. Molecular structure of **9**. All hydrogen atoms except for those in the methylene group (C20) and the solvent (dichloromethane) are omitted for clarity. Selected bond lengths [Å] and angles [°]: P1–O 1.482(3), P1–N 1.646(4), P1–C1 1.790(5), P1–C3 1.877(5), P2–C1 1.828(5), P2–C20 1.860(5), P2–Me 1.847(6), C20–Mes* 1.521(6), C1–C2 1.375(6), C2–C3 1.531(6), C2–C7 1.464(6), C3–C4 1.501(7), C4–C5 1.347(5), C5–C6 1.465(7), C6–C7 1.354(7); O-P1-N 109.8(2), O-P1-C1 121.0(2), O-P1-C3 118.8(2), N-P1-C1 111.5(2), N-P1-C3 114.9(2), C1-P1-C3 77.7(2), C1-P2-C20 100.1(2), C1-P2-Me 99.3(2), C20-P2-Me 98.8(2), P1-C1-P2 133.1(3), P1-C1-C2 92.1(3), P2-C1-C2 134.6(4), C1-C2-C3 104.6(4), C1-C2-C7 137.3(4), C3-C2-C7 117.5(4), P1-C3-C2 84.1(3), P1-C3-C4 120.7(4), P1-C3-*t*Bu 113.0(3), C2-C3-C4 111.6(4), C2-C3-*t*Bu 115.4(4), C4-C3-*t*Bu 110.0(4), C3-C4-C5 119.8(4), C4-C5-C6 119.1(4), C5-C6-C7 125.9(5), C6-C7-C2 113.7(4).

of a 1,3-diphosphacyclobutene intermediate upon hydrolysis of **7** in the manner displayed in Scheme 2. Hydrolysis of the C_2P_2 four-membered ring might occur to generate the corresponding intermediary 1-hydroxy-1λ^5,3λ^3-diphosphacyclobu-



Scheme 2.

tenes, and then these subsequently undergo rearrangement and de-aromatization of the Mes* ring to give **8** and **9**. Although the reason for this facile hydrolysis and ring-opening is unclear, the increased reactivity of the aromatic ring might arise as a result of steric hindrance caused by distortion. Under similar conditions, compound **3** did not undergo this kind of hydrolysis; this suggests that the electronic effect of a diisopropylamino group in the C_2P_2 system facilitates these ring-opening reactions.

Reaction of **7** with 2,2,6,6-tetramethyl-1-piperidinoxy (TEMPO) gave rise to markedly different results than those mentioned above. When a solution of **7** and TEMPO in THF was irradiated with light, the color of the solution turned from blue to red. Subsequent recrystallization of the residue obtained upon removal of the solvent afforded cyclodimethylenephosphorane **10** as a red solid (Scheme 1). The ^{31}P and ^{13}C NMR data were similar to those of a previously reported aminodimethylenephosphorane (Me_2N–$P(=CTMS_2)_2$: TMS = $SiMe_3$: $\delta_P = 167$ ppm; $\delta_{C(P=C)} = 55.6$ ppm, $^1J(P,C) = 71.3$ Hz).[19] The molecular structure of **10** (Figure 3) reveals that the four-membered ring is almost

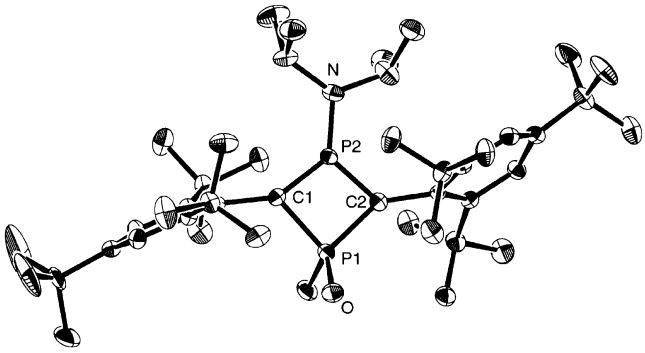
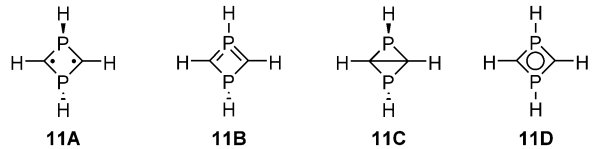


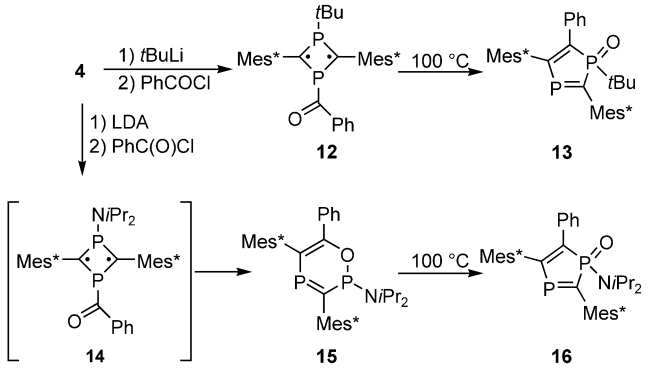
Figure 3. Molecular structure of **10**. All hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: P1–O 1.479(3), P1–C1 1.837(4), P1–C2 1.822(4), P1–Me 1.814(4), P2–N 1.612(4), P2–C1 1.656(4), P2–C2 1.669(4), C1–Mes* 1.497(5), C2–Mes* 1.499(5); C1-P1-C2 88.3(2), C1-P2-C2 100.1(2), P1-C1-P2 85.7(2), P1-C2-P2 85.8(2), P1-C1-Mes* 125.3(3), P2-C1-Mes* 146.5(3), P1-C2-Mes* 143.9(3), P2-C2-Mes* 128.8(3).

planar (Θ(C1-P1-C2-P2) = 1.6(2)°), and the nitrogen atom also has an almost planar coordination (Σ(angles) = 359.9°). The P2–C1 and P2–C2 distances indicate that these are phosphorus–carbon double bonds, while the sum of the angles around P2 (359.8°) suggests that it has a $\lambda^5\sigma^3$ coordinating mode.[12,19] Although the mechanism of formation for compound **10** is still uncertain, irradiation may induce the 1,3-diphosphacyclobutane-2,4-diyl moiety in **7** to undergo valence isomerization, while the P=O group generated by subsequent TEMPO oxidation stabilizes the dimethylenephosphorane[12b] structure. Indeed, compound **10** was not formed when a mixture of **7** and TEMPO were stirred in the dark or when a solution of **7** was irradiated in the absence of TEMPO.[20] Theoretical calculations predicted that the cyclic phosphorane compound **11B**, which is a possible



valence isomer of 1,3-diphosphacyclobutane-2,4-diyl, is slightly less stable than structure **11A**, but is much more stable than bicyclo[1.1.0]butane **11C** or the planar isomer **11D**.[4] In contrast to what was observed for **7**, compound **3** did not react in the presence of TEMPO upon irradiation, and only **3** was recovered.

Preparation and reactions of 1-benzoyl-1,3-diphosphacyclobutane-2,4-diyls: We allowed **4** to react with 0.5 equivalents of *tert*-butyllithium and benzoyl chloride, in a manner similar to that employed for **3**, to afford the corresponding 1-benzoyl-1,3-diphosphacyclobutane-2,4-diyl **12** as a dark-green solid (Scheme 3). Compound **12** did not decompose



Scheme 3.

below 20 °C and could be handled in air for several minutes. The structure of **12** was determined from spectroscopic data. In the ^{13}C NMR spectrum, a peak for the ring carbon atom was observed at $\delta_C = 97.7$ ppm. In the UV/Vis spectrum, **12** displayed an absorption at 664 nm; this constitutes a bathochromic shift, and indicates that the HOMO–LUMO gap is smaller than that for **3**.[11]

When **12** was heated at 100 °C for 10 min, 1-oxo-1*H*-[1,3]diphosphole **13** was obtained in 39% yield as a yellow solid. The structure of **13** (Figure 4) reveals that the C_3P_2

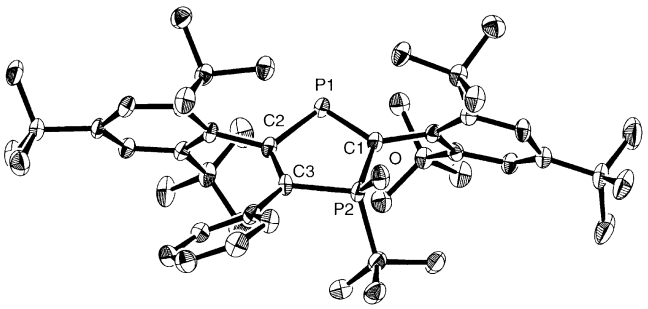


Figure 4. Molecular structure of **13**. All hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: P1–C1 1.680(2), P1–C2 1.856(3), P2–O 1.486(2), P2–C1 1.836(3), P2–C3 1.838(2), P2–*t*Bu 1.862(3), C2–C3 1.346(3), C1–Mes* 1.510(3), C2–Mes* 1.517(3), C3–Ph 1.488(3); C1-P1-C2 99.5(1), O-P2-C1 111.6(1), O-P2-C3 113.2(1), O-P2-*t*Bu 109.2(1), C1-P2-C3 98.0(1), P1-C1-P2 111.5(1), P1-C2-C3 116.2(2), P2-C3-C2 113.7(2), P1-C1-Mes* 129.5(2), P2-C1-Mes* 118.4(2), P1-C2-Mes* 119.7(2), C3-C2-Mes* 123.7(2), P2-C3-Ph 119.6(2), C2-C3-Ph 126.3(2), C1-P2-*t*Bu 115.0(1), C3-P2-*t*Bu 109.5(1).

five-membered ring is almost planar, the largest deviation being 0.132 Å, and the P1–C1 distance indicates the presence of a phosphorus–carbon double bond.[12] The structure of **13** is similar to the calculated structure of 1,3-diphosphole,[21] which has not as yet been synthesized experimentally.[22]

Compound **4** was also allowed to react first with 0.5 equivalents of LDA and then benzoyl chloride at −78 °C to give 2*H*-[1,2,4]oxadiphosphinine **15**. Although the color of the reaction mixture turned deep blue when LDA was allowed to react with **4**, and indicates that compound **14** is being generated, the biradical **14** was not observed in the spectra (Scheme 3). Furthermore, upon addition of benzoyl chloride to the reaction, the mixture turned deep red in several seconds. The isolated product was subsequently recrystallized and suitable crystals were used for X-ray crystallographic studies. Figure 5 displays the molecular structure of

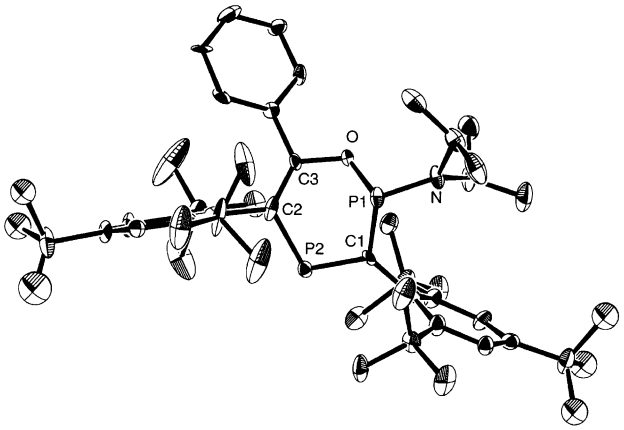


Figure 5. Molecular structure of **15**. Hydrogen atoms and the solvents (dichloromethane) are omitted for clarity. As the *p*-*t*Bu groups are disordered, only the atoms with predominant occupancy factors (0.58 for C1–Mes*, 0.52 for C2–Mes*) are displayed. Selected bond lengths [Å] and angles [°]: P1–O 1.724(8), P1–N 1.639(9), P1–C1 1.85(1), P2–C1 1.708(10), P2–C2 1.81(1), O–C3 1.36(1), C2–C3 1.38(2), C1–Mes* 1.53(1), C2–Mes* 1.51(1), C3–Ph 1.51(2); O-P1-N 100.7(5), O-P1-C1 96.3(5), N-P1-C1 110.2(5), C1-P2-C2 107.0(5), P1-O-C3 113.4(7), P1-C1-P2 110.4(6), P1-C1-Mes* 125.4(7), P2-C1-Mes* 124.0(8), P2-C2-C3 121.4(8), P2-C2-Mes* 113.7(9), C3-C2-Mes* 122.8(9), O-C3-C2 121.1(9), O-C3-Ph 109.7(10), C2-C3-Ph 129.1(9).

15, and reveals a six-membered ring, namely the 2*H*-[1,2,4]oxadiphosphinine skeleton. The six-membered ring displays a boat-type conformation in which the P1 atom is located at the "bow" position (Θ(C1–P1–O–C3) = 76.0(7)°). The sum of the angles around the nitrogen atom is 356.6°. The sp^2 phosphorus atom, the phosphino group, and the sp^2 carbon atom were identified by NMR spectroscopy.

Upon being heated, **15** underwent an Arbuzov-type rearrangement to afford 1-oxo-1*H*-[1,3]diphosphole **16** (Scheme 3), and indicates that a stability difference arises between **15** and **16**. In contrast, the formation of 1-oxo-1*H*-[1,3]diphosphole **13** from **12** was probably the result of a *t*Bu group substituent effect. The structure of **16** was unambiguously determined by X-ray crystallography (Figure 6).

Although several mechanisms for the reactions described in Scheme 4 are feasible, it is plausible that the isomerizations that afford compounds **13**, **15**, and **16** include a [1,2] rearrangement of the benzoyl group, in a manner similar to the Fries-type rearrangement.[23] Subsequently, the carbonyl group might play a role in the 1,3-diphosphacyclobutane skeleton undergoing expansion to afford a five- or six-mem-

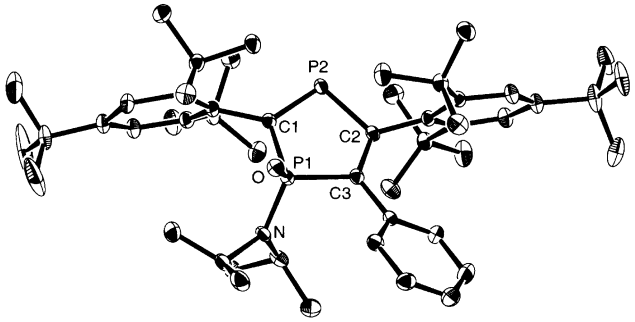
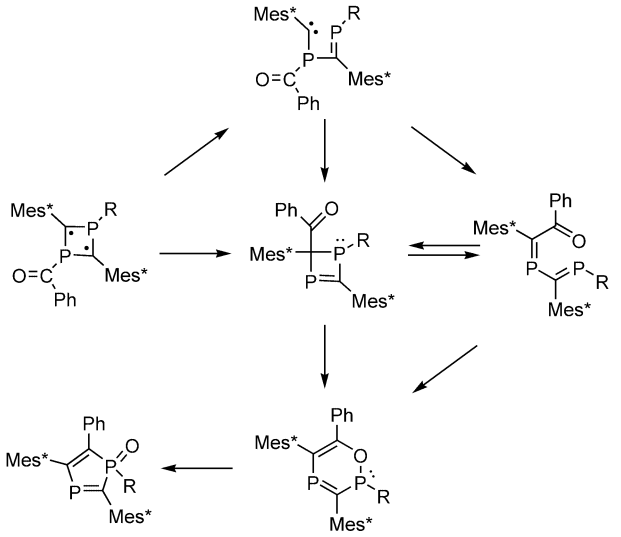


Figure 6. Molecular structure of **16**. Hydrogen atoms and the solvents (benzene) are omitted for clarity. Selected bond lengths [Å] and angles [°]: P1–O 1.482(3), P1–N 1.658(3), P1–C1 1.839(3), P1–C3 1.843(4), P2–C1 1.679(3), P2–C2 1.875(3), C2–C3 1.353(5), C1–Mes* 1.514(4), C2–Mes* 1.512(4), C3–Ph 1.491(5); O-P1-N 110.8(1), O-P1-C1 109.9(2), O-P1-C3 112.7(2), N-P1-C1 116.2(2), N-P1-C3 109.0(2), C1-P1-C3 97.8(2), C1-P2-C2 99.5(2), P1-C1-P2 111.5(2), P1-C1-Mes* 118.0(2), P2-C1-Mes* 130.1(3), P2-C2-C3 115.6(3), P2-C2-Mes* 118.8(2), C3-C2-Mes* 125.3(3), P1-C3-C2 113.8(3), P1-C3-Ph 119.0(2), C2-C3-Ph 126.7(3).



Scheme 4.

bered heterocyclic system. Alternatively, as is the case for **1**, ring-opening of the four-membered ring in compound **12** or **14** by cleavage of the P–C bond might occur to generate a nucleophilic phosphinocarbene intermediate.[2] Migration of the benzoyl group then takes place, and allows the residual 5-oxo-1,3-diphosphapropene derivatives that bear a P=C–P=C–C=O skeleton to undergo cyclization to give a 2*H*-[1,2,4]oxadiphosphinine ring. Studies are in progress to clarify the reaction mechanism for the ring-expansion of **12** and intermediary **14**.

Conclusion

In summary, we have prepared some functionalized 1,3-diphosphacyclobutane-2,4-diyls that bear a diisopropylamino and benzoyl group on the four-membered biradical skeleton, and showed the first examples of these diyls undergoing ring-opening, valence isomerization, and ring-expansion reactions to afford novel organophosphorus compounds. Incorporation of functional groups in the 1,3-diphosphacyclobutane-2,4-diyl moiety is a useful manner by which to tune the properties of the C_2P_2 ring, as well as to construct novel heterocyclic structures.

Experimental Section

General: All the experiments described here were carried out under an atmosphere of argon using dry solvents, unless otherwise specified. Melting points were determined with a Yanagimoto micro melting-point apparatus MP-J3, and are not corrected. Microanalyses were performed at the Instrumental Analysis Center of Chemistry, Graduate School of Science, Tohoku University. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE400 spectrometer and ^{31}P NMR spectra were obtained with a Bruker AC200P or AVANCE400 spectrometer using 85% H_3PO_4 as an external standard. NMR spectra were recorded at 25 °C unless otherwise noted. MS spectra were taken on a JEOL HX-110 or a Hitachi M-2500S spectrometer. FT-IR and UV/Vis spectra were taken on a Horiba FT-300 and a Hitachi U-3210 spectrometer, respectively.

Compound 5: LDA (ca. 36 mmol, prepared from diisopropylamine and butyllithium in THF at 0 °C) was added to a stirred solution of Mes*PCl_2 (5.2 g, 15 mmol) and bromoform (17 mmol) in THF (60 mL) at −78 °C. The reaction mixture was stirred at −78 °C for 15 min and was then allowed to warm to room temperature. The solvent was removed under vacuum, the residue was dissolved in hexane (200 mL), and the organic layer was washed with water. The solution was dried with $MgSO_4$ and concentrated. The residual solid was recrystallized from ethanol to afford **5** (4.6 g, 67%). The spectroscopic data were identical to those from the literature.[14]

Compound 7: LDA (ca. 0.56 mmol) was added to a solution of **4** (300 mg, 1.04 mmol) in THF (6 mL) at −78 °C. The reaction mixture was stirred at −78 °C for 15 min and was then stirred for 1 h at room temperature. Iodomethane (0.64 mmol) was added to the mixture and the solvent was removed under vacuum. The residue was extracted with hexane and the solution was concentrated to afford almost pure **7** as a deep blue solid in almost quantitative yield (0.36 g). Attempts to crystallize **7** were not successful because of its slight instability. The sp^2 radical center could not be identified in the ^{13}C NMR spectrum as a result of slow decomposition. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = 15.1 (d, ^2J(P,P) = 433.7 Hz; PMe), −18.4 ppm (d, ^2J(P,P) = 433.7 Hz; PN*i*Pr$_2$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54 (s, 2H; *m*-Mes*), 7.36 (s, 2H; *m*-Mes*), 3.11 (sept, ^3J(H,H) = 6.6 Hz, 2H; $CHMe_2$), 1.84 (d, ^2J(P,H) = 10.0 Hz, 3H; PMe), 1.73 (s, 18H; *o*-*t*Bu), 1.72 (s, 18H; *o*-*t*Bu), 1.40 (s, 18H; *p*-*t*Bu), 0.68 ppm (d, ^3J(H,H) = 6.6 Hz, 12H; $CHMe_2$).

Reaction of 7 with water: A solution of **7** (0.36 g, 0.52 mmol) in wet benzene (10 mL) was stirred in air at room temperature for 0.5 h. The solvent was then removed under vacuum and the residue was purified by silica-gel column chromatography (hexane/EtOAc) to afford **8** (177 mg, 48%) and **9** (156 mg, 42%), respectively, each as a mixture of two isomers. Recrystallization of each isolated compound from dichloromethane at 0 °C afforded single isomers of **8** and **9**.

Compound 8: (Isomer A): Colorless plates, m.p. 127–129 °C (decomp); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = 282.3 (d, ^2J(P,P) = 174.4 Hz; P=C), 31.6 ppm (d, ^2J(P,P) = 174.4 Hz; P=O); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48 (d, ^4J(H,H) = 2.0 Hz, 1H; *m*-Mes*), 7.39 (d, ^4J(H,H) = 2.0 Hz, 1H; *m*-Mes*), 6.06 (dd, ^2J(P,H) = 21.7 and ^5J(H,H) = 1.2 Hz, 1H; P(O)CH), 6.04 (pseudo-t, [^5J(H,H) + ^5J(H,H)]/2 = 2.6 Hz, 1H; =CH), 5.78 (dd, ^3J(H,H) = 5.8 and ^5J(H,H) = 2.6 Hz, 1H; =CH), 4.58 (d, ^3J(H,H) = 5.8 Hz, 1H; CH), 4.45 (sept, ^3J(H,H) = 6.3 Hz, 1H; NCH), 3.56 (sept, ^3J(H,H) = 7.0 Hz, 1H; $CHMe_2$), 1.65 (s, 9H; *o*-*t*Bu), 1.54 (s, 9H; *o*-*t*Bu), 1.37 (d, ^3J(H,H) = 7.0 Hz, 6H; $CHMe_2$), 1.32 (s, 9H; *t*Bu), 1.31 (s, 9H; *p*-*t*Bu), 1.13 (d, ^2J(P,H) = 12.6 Hz, 3H; PMe), 1.07 (s, 9H; *t*Bu), 1.07 (m, 6H; $CHMe_2$), 0.99 ppm (s, 9H; *t*Bu); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 160.2 (d, ^3J(P,C) = 4.6 Hz; C=C), 149.7 (pseudo-t, [^3J(P,C) + ^4J(P,C)]/2 = 4.9 Hz; *o*-Mes*), 147.5 (pseudo-t, [^3J(P,C) + ^4J(P,C)]/2 = 4.9 Hz; *o*-Mes*),

147.1 (d, ^4J(P,C) = 2.8 Hz; C=C), 145.1 (d, ^2J(P,C) = 16.7 Hz; C=C), 144.0 (s; *p*-Mes*), 132.4 (dd, ^1J(P,C) = 81.7 and 53.8 Hz; P=C), 130.2 (s; C=C), 130.1 (s; C=C), 126.2 (dd, ^2J(P,C) = 39.0 and 2.7 Hz; *ipso*-Mes*), 125.3 (dd, ^1J(P,C) = 101.2 and ^3J(P,C) = 5.6 Hz; P(O)*C*=C), 123.1 (s; *m*-Mes*), 122.8 (s; *m*-Mes*), 51.7 (d, ^4J(P,C) = 12.9 Hz; *o*-*C*Me$_3$), 47.2 (d, ^4J(P,C) = 24.1 Hz; *o*-*C*Me$_3$), 46.3 (d, ^4J(P,C) = 5.6 Hz; *C*Me$_3$), 40.1 (s; *C*Me$_3$), 39.6 (s; *C*Me$_3$), 38.7 (d, ^2J(P,C) = 4.5 Hz; NCH), 38.7 (d, ^2J(P,C) = 5.6 Hz; NCH), 36.0 (s; *o*-C*Me*$_3$), 35.8 (s; *p*-C*Me*$_3$), 35.6 (s; *o*-C*Me*$_3$), 34.4 (s; C*Me*$_3$), 32.6 (s; C*Me*$_3$), 31.6 (s; *p*-C*Me*$_3$), 29.7 (s; C*Me*$_3$), 28.7 (s; NCH*Me*$_2$), 28.7 (s; NCH*Me*$_2$), 27.3 (d, ^3J(P,C) = 15.8 Hz; CH), 20.1 ppm (dd, ^1J(P,C) = 80.2 and ^3J(P,C) = 9.7 Hz; P(O)Me); IR (KBr): $\tilde{\nu}$ = 1174 and 1159 cm^{-1} (P=O); elemental analysis calcd (%) for $C_{45}H_{77}NOP_2 \cdot 1.5\,CH_2Cl_2$: C 66.69, H 9.63, N 1.67; found: C 67.08, H 10.25, N 1.77. (Isomer B): $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ = 287.8 (d, ^2J(P,P) = 156.4 Hz; P=C), 33.8 ppm (d, ^2J(P,P) = 156.4 Hz; P=O).

Compound 9: (Isomer A): Pale yellow powder, m.p. 164–165 °C (decomp); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 35.4 (d, ^2J(P,P) = 5.0 Hz; P=O), −24.6 ppm (d, ^2J(P,P) = 5.0 Hz; PMe); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31 (s, 1H; *m*-Mes*), 7.26 (s, 1H; *m*-Mes*), 6.34 (d, ^5J(P,H) = 2.2 Hz, 1H; =CH), 6.10 (d, ^3J(P,H) = 14.5 Hz, 1H; =CH), 4.40 (dd, ^2J(P,H) = 13.4 and ^3J(P,H) = 7.4 Hz, 1H; C*H*H), 3.78 (pseudo-t, [^2J(P,H) + ^3J(P,H)]/2 = 12.9 Hz, 1H; CH*H*), 3.27 (sept, ^3J(H,H) = 6.9 Hz, 2H; CHMe$_2$), 1.58 (s, 9H; *o*-*t*Bu), 1.42 (m, 12H; CH*Me*$_2$), 1.38 (s, 9H; *t*Bu), 1.31 (s, 9H; *o*-*t*Bu), 1.15 (s, 9H; *t*Bu), 1.07 (s, 9H; *t*Bu), 0.71 ppm (d, ^2J(P,H) = 5.7 Hz, 3H; PMe); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, selected data): δ = 165.5 (dd, ^2J(P,C) = 17.6 and 12.1 Hz; C=C), 150.1 (dd, ^1J(P,C) = 61.7 and 46.9 Hz; C=C), 145.0 (dd, ^2J(P,C) = 43.6 and ^4J(P,C) = 2.8 Hz; C=C), 144.3 (d, ^3J(P,C) = 12.0 Hz; C=C), 132.3 (d, ^4J(P,C) = 7.4 Hz; C=C), 125.6 (d, ^3J(P,C) = 13.0 Hz; C=C), 78.3 (dd, ^1J(P,C) = 64.0 and ^3J(P,C) = 3.7 Hz; PC), 24.0 ppm (m; CH_2); IR (KBr): $\tilde{\nu}$ = 1153 and 1126 cm^{-1} (P=O); elemental analysis calcd (%) for $C_{45}H_{77}NOP_2 \cdot 0.4\,CH_2Cl_2$: C 73.29, H 10.53, N 1.88; found: C 73.80, H 10.86, N 1.83. (Isomer B): $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 33.8 (d, ^2J(P,P) = 7.0 Hz; P=O), −26.9 ppm (d, ^2J(P,P) = 7.0 Hz; PMe).

Compound 10: A mixture of **7** (ca. 0.52 mmol) and TEMPO (0.52 mmol) in THF (25 mL) was irradiated with a medium-pressure Hg lamp (100 W) at −10 °C for 1 day. The mixture was then warmed to room temperature and the solvent was removed under vacuum. The residue was purified by silica-gel column chromatography (hexane/EtOAc) to afford **10** (79 mg, 45 %). Recrystallization from hexane/dichloromethane at 0 °C afforded single crystals of dark orange plates. M.p. 192–194 °C; ^{31}P NMR (162 MHz, $CDCl_3$): δ = 121.8 (dt, ^2J(P,P) = 183.2 and ^3J(P,H) = 12.6 Hz; PN*i*Pr$_2$), 25.4 ppm (dq, ^2J(P,P) = 183.2 and ^3J(P,H) = 12.9 Hz; PMe); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42 (s, 2H; *m*-Mes*), 7.34 (s, 2H; *m*-Mes*), 3.22 (sept, ^3J(H,H) = 6.8 Hz, 2H; CHMe$_2$), 2.00 (d, ^2J(P,H) = 12.9 Hz, 3H; PMe), 1.74 (s, 18H; *o*-*t*Bu), 1.60 (s, 18H; *o*-*t*Bu), 1.32 (s, 18H; *p*-*t*Bu), 1.11 ppm (d, ^3J(H,H) = 6.8 Hz, 12H; CH*Me*$_2$); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 155.6 (dd, ^3J(P,C) = 10.0 and 3.9 Hz; *o*-Mes*), 152.5 (dd, ^3J(P,C) = 8.7 and 4.3 Hz; *o*-Mes*), 147.4 (dd, ^5J(P,C) = 3.9 and 2.2 Hz; *p*-Mes*), 126.8 (dd, ^2J(P,C) = 3.4 and 1.7 Hz; *ipso*-Mes*), 123.3 (dd, ^4J(P,C) = 3.4 and 1.7 Hz; *m*-Mes*), 123.2 (dd, ^4J(P,C) = 3.4 and 1.7 Hz; *m*-Mes*), 56.0 (dd, ^1J(P,C) = 110.7 and 68.4 Hz; P(=C)$_2$), 51.4 (s; *o*-*C*Me$_3$), 51.4 (s; *o*-*C*Me$_3$), 39.0 (d, ^2J(P,C) = 25.0 Hz; *C*HMe$_2$), 35.0 (s; *p*-*C*Me$_3$), 34.8 (s; *o*-C*Me*$_3$), 34.5 (s; *p*-C*Me*$_3$), 31.7 (s; *o*-C*Me*$_3$), 24.5 (d, ^3J(P,C) = 3.4 Hz; CH*Me*$_2$), 20.6 ppm (dd, ^1J(P,C) = 77.4 and ^3J(P,C) = 24.7 Hz; PMe); IR (KBr): $\tilde{\nu}$ = 1186 cm^{-1} (P=O); elemental analysis calcd (%) for $C_{45}H_{75}NOP_2$: C 76.34, H 10.68, N 1.98; found: C 76.17, H 10.90, N 1.86.

Compound 12: To a solution of **4** (300 mg, 1.04 mmol) in THF (8 mL) at −78 °C was added *tert*-butyllithium (0.52 mmol, 1.6 M solution in pentane). The mixture was warmed to room temperature, benzoyl chloride (0.52 mmol) was added, and after several minutes the solvent was removed under vacuum. The residue was extracted with hexane and the solution was concentrated. The residual solid was washed with ethanol to obtain **12** (257 mg, 67 %) as deep green crystals. M.p. 134–136 °C; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 73.2 (d, ^2J(P,P) = 215.1 Hz; P*t*Bu), 25.2 ppm (d, ^2J(P,P) = 215.1 Hz; PC(O)Ph); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46 (s, 2H; *m*-Mes*), 7.44 (s, 2H; *m*-Mes*), 7.42 (m, 2H; *o*-Ph), 7.31 (t, ^3J(H,H) = 7.5 Hz, 1H; *p*-Ph), 7.04 (pseudo-t, [^3J(H,H) + ^3J(H,H)]/2 = 7.5 Hz, 2H; *m*-Ph), 1.70 (brs, 18H; *o*-*t*Bu), 1.45 (brs, 18H; *o*-*t*Bu), 1.37 (s, 18H; *p*-*t*Bu), 1.05 ppm (d, ^3J(P,H) = 15.4 Hz, 9H; P*t*Bu); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, selected data): δ = 207.1 (dd, ^1J(P,C) = 94.2 and ^3J(P,C) = 31.1 Hz; C=O), 97.7 ppm (dd, ^1J(P,C) = 25.0 and 16.7 Hz; CP_2); IR (KBr): $\tilde{\nu}$ = 1637 cm^{-1} (C=O); UV/Vis (hexanes) $\lambda_{max}(\varepsilon)$ = 664 (1500), 370 (13200), 329 nm (17600).

Compound 13: A solution of **12** (ca. 1.04 mmol) in toluene (8 mL) was heated at 100 °C for 10 min, after which time it was cooled to room temperature and the solvent was removed under vacuum. The residue was purified by silica-gel column chromatography (hexane/EtOAc) and the resultant solid was recrystallized from a mixture of hexane and dichloromethane at 0 °C to give **13** (150 mg, 39 %) as orange prisms. M.p. 199–201 °C; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 313.7 (d, ^2J(P,P) = 36.9 Hz; P=C), 75.7 ppm (d, ^2J(P,P) = 36.9 Hz; P=O); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54 (brs, 1H; *m*-Mes*), 7.52 (d, ^4J(H,H) = 2.0 Hz, 1H; *m*-Mes*), 7.44 (d, ^3J(H,H) = 7.1 Hz, 2H; *o*-Ph), 7.35 (brs, 1H; *m*-Mes*), 7.24 (d, ^4J(H,H) = 2.0 Hz, 1H; *m*-Mes*), 7.05 (t, ^3J(H,H) = 7.1 Hz, 1H; *p*-Ph), 6.99 (pseudo-t, [^3J(H,H) + ^3J(H,H)]/2 = 7.1 Hz, 2H; *m*-Ph), 1.72 (s, 9H; *o*-*t*Bu), 1.71 (s, 9H; *o*-*t*Bu), 1.60 (s, 9H; *o*-*t*Bu), 1.34 (s, 9H; *p*-*t*Bu), 1.32 (s, 9H; *p*-*t*Bu), 1.20 (s, 9H; *o*-*t*Bu), 0.54 ppm (d, ^3J(P,H) = 15.0 Hz, 9H; P*t*Bu); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 179.9 (dd, ^1J(P,C) = 52.5 and ^1J(P,C) = 44.5 Hz; P=C), 155.1 (dd, ^1J(P,C) = 46.4 and ^3J(P,C) = 33.4 Hz; C=C), 152.4 (dd, ^2J(P,C) = 10.2 and ^3J(P,C) = 5.6 Hz; *ipso*-Mes*), 149.7 (s; *o*-Mes*), 149.4 (brs; *o*-Mes*), 149.3 (s; *o*-Mes*), 148.3 (d, ^3J(P,C) = 2.8 Hz; *o*-Mes*), 146.9 (pseudo-t, [^2J(P,C) + ^2J(P,C)]/2 = 7.0 Hz; *ipso*-Mes*), 143.9 (d, ^5J(P,C) = 2.7 Hz; *p*-Mes*), 143.1 (d, ^5J(P,C) = 2.8 Hz; *p*-Mes*), 132.1 (dd, ^2J(P,C) = 21.3 and 14.8 Hz; C=C), 129.3 (d, ^4J(P,C) = 4.6 Hz; *o*-Ph), 128.7 (d, ^3J(P,C) = 13.0 Hz; *ipso*-Ph), 127.4 (s; *m*-Ph), 125.5 (d, ^4J(P,C) = 1.9 Hz; *m*-Mes*), 125.5 (s; *m*-Mes*), 122.2 (s; *m*-Mes*), 122.1 (d, ^4J(P,C) = 2.1 Hz; *m*-Mes*), 41.7 (s; *o*-*C*Me$_3$), 39.4 (s; *o*-*C*Me$_3$), 38.8 (d, ^1J(P,C) = 8.3 Hz; P*C*Me$_3$), 37.0 (s; *o*-*C*Me$_3$), 36.4 (s, *o*-*C*Me$_3$), 36.0 (s; *o*-C*Me*$_3$), 35.6 (s; *o*-C*Me*$_3$), 35.5 (s; *o*-C*Me*$_3$), 35.3 (s; *o*-C*Me*$_3$), 35.1 (s; *p*-*C*Me$_3$), 34.9 (s; *p*-*C*Me$_3$), 31.8 (s; *p*-C*Me*$_3$), 31.8 (s; *p*-C*Me*$_3$), 25.5 ppm (s; PC*Me*$_3$); IR (KBr): $\tilde{\nu}$ = 1161 cm^{-1} (P=O); elemental analysis calcd (%) for $C_{49}H_{72}OP_2$: C 79.63, H 9.82; found: C 79.67, H 9.91.

Compound 15: LDA (0.52 mmol) was added to a solution of **4** (300 mg, 1.04 mmol) in THF (8 mL) at −78 °C. The mixture was warmed to room temperature, benzoyl chloride (0.52 mmol) was added, and the solvent was removed under vacuum. The residue was extracted with hexane and the solution was concentrated. The resultant solid was recrystallized from dichloromethane at 0 °C to give **15** (253 mg, 62 %, based on **4**) as orange crystals. M.p. 102–104 °C (decomp); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 294.7 (d, ^2J(P,P) = 46.9 Hz, P=C), 122.3 ppm (d, ^2J(P,P) = 46.9 Hz, PN*i*Pr$_2$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.62 (brs, 1H; *m*-Mes*), 7.56 (brs, 1H; *m*-Mes*), 7.54 (brs, 1H; *m*-Mes*), 7.49 (brs, 1H; *m*-Mes*), 7.34 (d, ^3J(H,H) = 7.0 Hz, 2H; *o*-Ph), 7.20 (t, ^3J(H,H) = 7.0 Hz, 1H; *p*-Ph), 7.13 (pseudo-t, [^3J(H,H) + ^3J(H,H)]/2 = 7.0 Hz, 2H; *m*-Ph), 3.48 (m, 2H; C*H*Me$_2$), 1.72 (s, 9H; *o*-*t*Bu), 1.61 (s, 9H; *o*-*t*Bu), 1.52 (s, 9H; *o*-*t*Bu), 1.41 (s, 9H; *o*-*t*Bu), 1.40 (s, 9H; *p*-*t*Bu), 1.35 (s, 9H; *p*-*t*Bu), 0.68 ppm (m, 12H; CH*Me*$_2$); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, selected data): δ = 179.5 (dd, ^1J(P,C) = 77.2 and 53.7 Hz, P=C), 153.1 (m, C=C), 123.0 ppm (pseudo-t, [^1J(P,C) + ^1J(P,C)]/2 = 25.4 Hz, C=C).

Compound 16: A solution of **15** (0.36 mg, 0.52 mmol) in toluene (10 mL) was heated at 100 °C for 12 h, and was then cooled to room temperature and concentrated. The residue was purified by silica-gel column chromatography (hexane/EtOAc) to give **16** (400 mg, ca. 100 %) as an orange amorphous solid. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 281.2 (d, ^2J(P,P) = 36.6 Hz; P=C), 56.0 ppm (d, ^2J(P,P) = 36.6 Hz; PN*i*Pr$_2$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.62 (brs, 1H; *m*-Mes*), 7.61 (brs, 1H; *m*-Mes*), 7.51 (brs, 1H; *m*-Mes*), 7.42 (brs, 1H; *m*-Mes*), 7.40 (d, ^3J(H,H) = 7.0 Hz, 2H; *o*-Ph), 7.05 (brs, 1H; *p*-Ph), 7.04 (brs, 2H; *m*-Ph), 3.14 (m, 2H; C*H*Me$_2$), 1.77 (s, 9H; *o*-*t*Bu), 1.74 (s, 9H; *o*-*t*Bu), 1.70 (s, 9H; *o*-*t*Bu), 1.40 (s, 9H; *o*-*t*Bu), 1.39 (s, 9H; *p*-*t*Bu), 1.26 (s, 9H; *p*-*t*Bu), 0.77 ppm (dd, ^3J(P,H) = 7.0 and ^3J(H,H) = 7.0 Hz, 12H; CH*Me*$_2$); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, selected data): δ = 182.8 (dd, ^1J(P,C) = 71.2 and 48.5 Hz; P=C), 151.5 (pseudo-t, [^1J(P,C) + ^1J(P,C)]/2 = 29.3 Hz; C=C), 122.1 ppm (d, ^1J(P,C) = 28.8 Hz; C=C); IR (KBr): $\tilde{\nu}$ = 1159 cm^{-1} (P=O); elemental analysis calcd (%) for $C_{51}H_{77}NOP_2 \cdot 2\,C_6H_6$: C 80.64, H 9.56, N 1.49; found: C 80.50, H 9.86, N 1.48.

X-ray crystallography: Single crystals were obtained by recrystallization from a mixture of hexane and dichloromethane at 0 °C. A Rigaku RAXIS-IV imaging plate detector (for **8**, **9**, **10**, **15**, and **16**) or a Rigaku MSC Mercury CCD detector (for **13**) with graphite-monochromated

$Mo_{K\alpha}$ radiation ($\lambda = 0.71070$ Å) was used. The structures were solved by direct methods (SIR92),[24] expanded by using Fourier techniques (DIRDIF94),[25] and then refined by full-matrix least squares. The data were corrected for Lorentz polarization effect. Structure solution, refinement, and graphical representation were carried out using the teXsan package.[26]

Compound ***8***: $C_{45}H_{75}NOP_2 \cdot CH_2Cl_2$, $M_r = 794.99$, pale yellow prisms, $0.15 \times 0.15 \times 0.10$ mm^3, triclinic, $P\bar{1}$ (no. 2), $a = 16.040(2)$, $b = 16.570(1)$, $c = 9.689(1)$ Å, $\alpha = 100.729(1)$, $\beta = 101.232(2)$, $\gamma = 102.225(5)°$, $V = 2398.1(4)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.101$ g cm^{-3}, $F(000) = 868$, $\mu = 0.234$ mm^{-1}, $T = 150$ K, 17793 reflections measured ($2\theta_{max} = 55.0°$), 9882 observed ($R_{int} = 0.041$), $R_1 = 0.074$ [$I > 3.0\sigma(I)$], $R_w = 0.095$ (all data), $S = 1.79$ (785 parameters).

Compound ***9***: $C_{45}H_{75}NOP_2 \cdot 1.5\,CH_2Cl_2$, $M_r = 879.92$, pale yellow prisms, $0.25 \times 0.25 \times 0.20$ mm^3, triclinic, $P\bar{1}$ (no. 2), $a = 12.344(1)$, $b = 22.569(2)$, $c = 9.856(1)$ Å, $\alpha = 101.930(6)$, $\beta = 92.154(2)$, $\gamma = 105.444(6)°$, $V = 2576.9(4)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.134$ g cm^{-3}, $F(000) = 952$, $\mu = 0.324$ mm^{-1}, $T = 150$ K, 19257 reflections measured ($2\theta_{max} = 55.0°$), 10635 observed ($R_{int} = 0.037$), $R_1 = 0.089$ [$I > 3.0\sigma(I)$], $R_w = 0.238$ (all data), $S = 1.89$ (496 parameters).

Compound ***10***: $C_{45}H_{75}NOP_2$, $M_r = 708.04$, red prisms, $0.30 \times 0.20 \times 0.15$ mm^3, orthorhombic, $P2_12_12_1$ (no. 19), $a = 9.7452(7)$, $b = 17.211(1)$, $c = 25.8268(9)$ Å, $V = 4331.8(5)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.086$ g cm^{-3}, $F(000) = 1560$, $\mu = 0.133$ mm^{-1}, $T = 130$ K, 36734 reflections measured ($2\theta_{max} = 55.0°$), 5099 observed ($R_{int} = 0.047$), $R_1 = 0.051$ [$I > 3.0\sigma(I)$], $R_w = 0.130$ (all data), $S = 1.35$ (443 parameters).

Compound ***13***: $C_{48}H_{72}OP_2$, $M_r = 727.04$, yellow prisms, $0.20 \times 0.20 \times 0.05$ mm^3, monoclinic, $P2_1/n$ (no. 14), $a = 18.864(2)$, $b = 13.344(4)$, $c = 19.525(6)$ Å, $\beta = 115.370(4)°$, $V = 4440(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.087$ g cm^{-3}, $F(000) = 1592$, $\mu = 0.130$ mm^{-1}, $T = 173$ K, 34457 reflections measured ($2\theta_{max} = 55.0°$), 9769 observed ($R_{int} = 0.035$), $R_1 = 0.038$ [$I > 3.0\sigma(I)$], $R_w = 0.041$ (all data), $S = 0.81$ (469 parameters).

Compound ***15***: $C_{51}H_{77}NOP_2 \cdot 2\,CH_2Cl_2$, $M_r = 951.99$, yellow prisms, $0.25 \times 0.25 \times 0.20$ mm^3, monoclinic, $P2_1/n$ (no. 14), $a = 9.7433(9)$, $b = 18.122(1)$, $c = 30.773(5)$ Å, $\beta = 94.431(4)°$, $V = 5417.2(8)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.167$ g cm^{-3}, $F(000) = 2048$, $\mu = 0.313$ mm^{-1}, $T = 120$ K, 39325 reflections measured ($2\theta_{max} = 55.0°$), 12276 observed ($R_{int} = 0.152$), $R_1 = 0.098$ [$I > 3.0\sigma(I)$], $R_w = 0.137$ (all data), $S = 2.12$ (546 parameters).

Compound ***16***: $C_{51}H_{77}NOP_2 \cdot 2\,C_6H_6$, $M_r = 938.35$, orange prisms, $0.30 \times 0.20 \times 0.20$ mm^3, triclinic, $P\bar{1}$ (no. 2), $a = 14.526(1)$, $b = 15.555(1)$, $c = 14.349(1)$ Å, $\alpha = 114.314(4)$, $\beta = 89.923(4)$, $\gamma = 100.728(6)°$, $V = 2892.7(4)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.077$ g cm^{-3}, $F(000) = 1024$, $\mu = 0.114$ mm^{-1}, $T = 223$ K, 20616 reflections measured ($2\theta_{max} = 55.0°$), 11662 observed ($R_{int} = 0.040$), $R_1 = 0.071$ [$I > 3.0\sigma(I)$], $R_w = 0.098$ (all data), $S = 1.81$ (604 parameters).

CCDC-223665 (**8**), 223666 (**9**), 222766 (**10**), 222765 (**13**), 222764 (**15**), and 224391 (**16**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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