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Pentacoordinate Phosphoranes with Reversed Apicophilicity as Stable Intermediates in a Mitsunobu-Type Reaction

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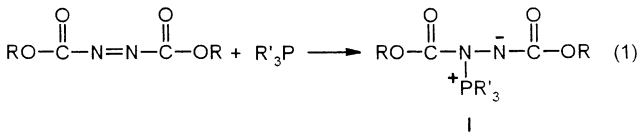
Diisopropyl azodicarboxylate (DIAD) undergoes a cycloaddition reaction with the cyclic phosphites CH_2(6-*t*-Bu-4-Me-$C_6H_2O)_2PX$ (**1**) [X = NCS (**a**), N_3 (**b**), Cl (**c**), NHMe (**d**) and Ph (**e**)] to afford the novel pentacoordinate phosphoranes **2a**−**e** as crystalline solids. This result is different from the reaction of PPh_3 with DIAD used in the well-known Mitsunobu reaction. X-ray crystallography of **2a**, **2b**, and **2d** reveals that the nitrogen, rather than the oxygen, occupies an apical position of the trigonal bipyramidal phosphorus. This is in violation of the commonly accepted preferences for substituents in trigonal bipyramidal phosphorus. In **2e**, although the oxygen of the five-membered ring occupies the expected apical position, the phenyl group also occupies (the other) apical position, forcing the more electronegative oxygen atoms of the eight-membered ring to span equatorial−equatorial positions. In contrast to the above, the isocyanato compound CH_2(6-*t*-Bu-4-Me-$C_6H_2O)_2$-PNCO (**1f**), upon treatment with DIAD, affords compound **3** to which a tetracoordinate structure is assigned.

Introduction

The Mitsunobu reaction, which employs the redox couple of a triaryl- or trialkylphosphine and a dialkyl azodicarboxylate, has proven useful in a wide variety of synthetic applications.[1,2] Several key features of this important reaction have been investigated by various research groups.[3] The Morrison−Brunn−Huisgen betaine **I** is shown to be a key intermediate (eq 1).[1,3j] However,



looking at the same reactants from a different perspective, we note that (i) P(III) compounds undergo facile cycloaddition reactions with a variety of 1,2-diketones (or ketoimines) to afford pentacoordinate phosphoranes of the type **II** (Scheme 1)[4] and that (ii) dialkyl azodicarboxylates **III** are analogous to 1,2-diketones (or the related 1,2-ketoimines). Thus it is possible that in the reaction of P(III) compounds with dialkyl azodicarboxylates **III**, N,O-cycloaddition could take place to give pentacoordinate phosphorus intermediates **II′** that are analogous to **II**.[5−7] Isolation/identification of such a species could support the possible intermediacy of the P−O bonded tetracoordinate intermediate of the type **IV**, mentioned by Brunn and Huisgen,[3b] at least in a few cases.

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(5) Such intermediates have been identified earlier.[6] However, the proposed disposition of the substituents in the five-membered ring is different; see ref 2i.

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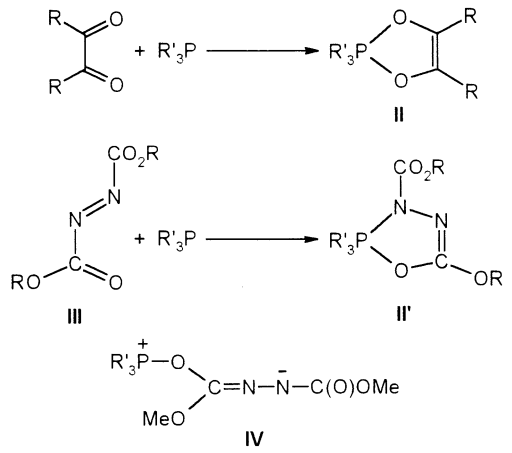
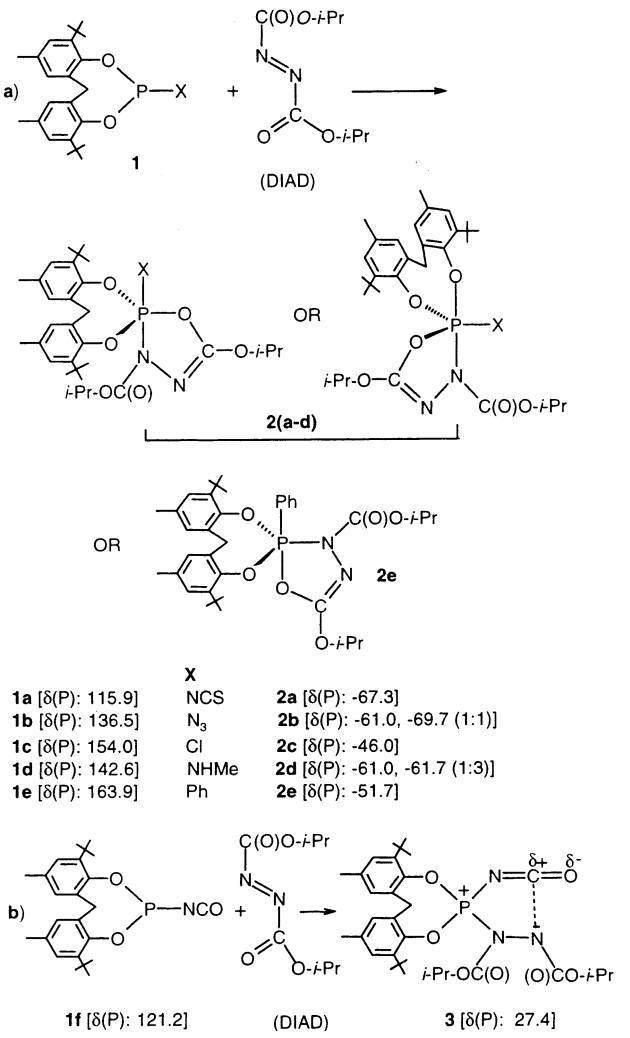
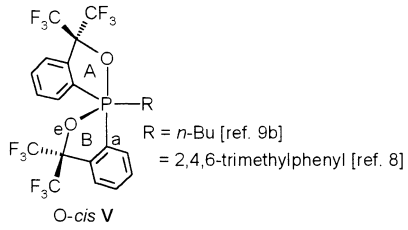
SCHEME 1



SCHEME 2

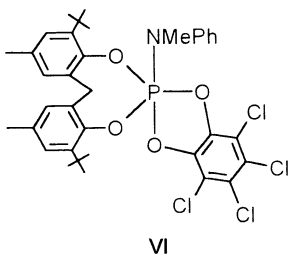


Herein, we report the isolation and first structural characterization of novel pentacoordinate phosphoranes **2a**−**e**, rather than the Morrison−Brunn−Huisgen intermediate of type **I**, from the reaction of the cyclic phosphites **1a**−**e** with diisopropyl azodicarboxylate (DIAD) (Scheme 2, path a). More importantly, it is shown by X-ray crystallographic studies on **2a**, **2b,** and **2d** that these compounds *defy* the steric and electronegativity rules for pentacoordinate phosphorus; we believe that this observation is significant in the context of reactions at a tetrahedral P(V) center. In **2e**, although the oxygen of the five-membered ring is at the apical position, the phenyl group occupies an apical position, pushing the more electronegative oxygen of the eight-membered ring to an equatorial position. These results add another interesting facet to the "reversed apicophilicity" phenomenon that has been reported very recently (cf. Structure **V**).[8,9b] Also presented here is the isolation of the rather unexpected tetracoordinate compound **3** from the reaction of the isocyanate **1f** [**1**; X = NCO] with DIAD (Scheme 2, path b).



Results and Discussion

Compounds **2a**−**e** and **3** are prepared by adding DIAD to a solution of the respective P(III) precursors **1a**−**e** in dry toluene or hexane. The ^{31}P NMR spectra of **2a**−**e** in solution are in the expected pentacoordinate region.[4d,9c,10,11] Compound **2b** exhibits two peaks in the ^{31}P NMR at room temperature, in $CDCl_3$ ($\Delta\delta$ 8.7) as well as $C_6D_5CD_3$ solutions, indicating the presence of isomers with pentacoordinate phosphorus. A similar two-peak pattern was observed for the compound CH_2(6-*t*-Bu-4-Me-$C_6H_2O)_2$P-(NMePh)($O_2C_6Cl_4$) (**VI**) (δ −47.0, −51.7; $\Delta\delta$ 4.7) at 232



VI

(6) For previous examples wherein a pentacoordinate compound is identified/isolated, see ref 2i and (a) Arbuzov, B. A.; Polezhaeva, N. A.; Vinogradova, V. S. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1968**, 2525. (b) Gonclaves, H.; Domroy, J. R.; Chapleur, Y.; Castro, B.; Faudet, H.; Burgada, R. *Phosphorus Sulfur* **1980**, 147. (c) Majoral, J. P.; Kraemer, R.; NGando M'Pondo, T.; Navech, J. *Tetrahedron Lett.* **1980**, *21*, 1307.

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(9) For earlier reports on the greater apicophilicity of aryl carbon relative to oxygen in tetraoxyphosphoranes, see: (a) Timosheva, N. V.; Chandrasekaran, A.; Prakasha, T. K., Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1996**, *35*, 6552. (b) Kojima, S.; Kajiyama, K.; Nakamoto, M.; Akiba, K.-ya *J. Am. Chem. Soc.* **1996**, *118*, 12866. (c) Kumaraswamy, S.; Muthiah, C.; Kumara Swamy, K. C. *J. Am. Chem. Soc.* **2000**, *122*, 964 [This paper also reports the X-ray structure of CH_2(6-*t*-Bu-4-Me-$C_6H_2O)_2$P(NHMe)($O_2C_6Cl_4$) in which the −NHMe group is equatorial].

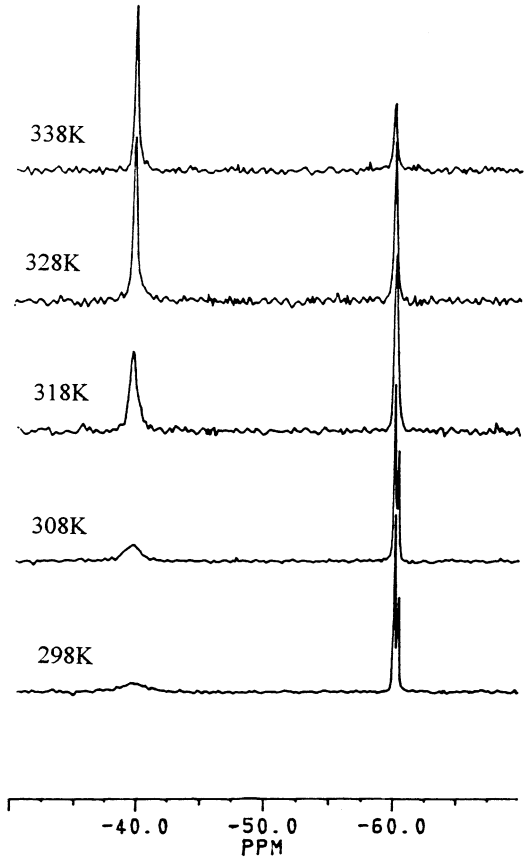
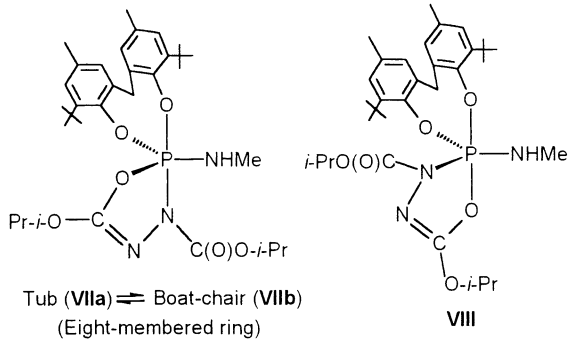


FIGURE 1. Variable temperature ^{31}P NMR spectra for **2d**.

K and were assigned to isomers in which the −NMePh group is apical or equatorial (the eight-membered ring would then be diequatorial or apical−equatorial, respectively).[11] On this basis, for **2b** the two possible isomers are assigned to those in which the $-N_3$ group is apical or equatorial (cf. Scheme 2, path a) in a trigonal bipyramidal arrangement;[12] it is also possible that the two ^{31}P NMR signals reflect equilibrium with N-equatorial/O-apical isomers (see discussion on **2d** and **2e**) while the X-ray data indicate preferences that are unique to the crystal lattice. The ^{31}P NMR spectrum in toluene-d_8 also showed two peaks [δ(P): −60.1, −70.2 (1:2)] at room temperature and below (till 227 K; intensity ratio 1:1). An experiment by dissolving **2b** at −40 °C and recording the ^{31}P NMR spectrum with a spectrometer probe maintained at −40 °C also showed the same two signals, and hence, a clear-cut assignment could not be made. At higher temperatures decomposition occurred (see the Experimental Section).

Compound **2d** also exhibits two peaks (δ −61.0, −61.7; ratio 1:3) that are more closely spaced ($\Delta\delta$ 0.7) in the ^{31}P NMR in $CDCl_3$ solution at room temperature (298 K); however, in toluene-d_8, three peaks at δ −39.5 (br), −60.1, and −60.4 (the intensity ratio of the latter two peaks is 3:2) (Figure 1) are observed in the pentacoordinate region at 298 K. Interestingly, the intensity of the downfield peak (δ −39.5) increases at the cost of the two upfield peaks (which merge eventually) with rise in temperature; at 338 K, the peak at δ −39.5 is the most predominant one.[13] The spectra are reversible with respect to temperature. The large value of $\Delta\delta$ (ca 20.5 ppm) between the downfield signal and the two closely spaced upfield signals suggests a significant change in the ligand arrangement at phosphorus between the isomers corresponding to these. At low temperatures (233 K; toluene-d_8), whether the sample was prepared at 298 or 233 K, the ^{31}P NMR showed only the two closely spaced signals at δ −61.0 and −61.7. The observation of closely spaced upfield signals is reminiscent of the ^{31}P NMR behavior of CH_2(6-*t*-Bu-4-Me-$C_6H_2O)_2$P(NHR)($O_2C_6Cl_4$) (R = Me, δ −52.2, −52.5; R = H, δ −50.6, −50.9);[11] the latter feature was attributed to tub to boat−chair conformational isomerism of the apical−equitorial located eight-membered ring with the −NHR group equatorial.[9c,11] Thus, the closely spaced upfield signals in **2d** can be attributed to **VIIa** and **VIIb**. For the downfield signal,



which is predominant at high temperature, we assign structure **VIII**, in which both the −NHMe and −NC(O)-(O-*i*-Pr) groups are equatorial.

From the X-ray structure of **2a** and **2b** (Figure 2), it can be readily noted that the nitrogen of the five-membered ring, rather than the oxygen, is at the apical position of the trigonal bipyramidal phosphorus although it is less electronegative than oxygen and carries a sterically bulkier group. This feature *contradicts* the well-known preference rule for substituents that "high apicophilicity is favored by high electronegativity and small size".[14] It can be argued that the −C(O)O-*i*-Pr group increases the (group) electronegativity at nitrogen. However, overriding the more electronegative oxygen (which is also certainly sterically less crowded in our system) of the five-membered ring, the nitrogen has occupied the apical position; this was not expected.[5] It can be noted that in Akiba's compounds[8,9b] there is a competition between carbon (aryl) and O−C(CF_3)$_2$ of the five-membered ring, whereas in our compound there is a competition between N(R) and O−C(O-*i*-Pr) of the five-membered ring. In our example, we have a substituent

(10) Muthiah, C.; Said, M. A.; Pülm, M.; Herbst-Irmer, R.; Kumara Swamy, K. C. *Polyhedron*, **2000**, *19*, 63.

(11) Kommana, P.; Kumaraswamy, S.; Vittal, J. J.; Kumara Swamy, K. C. *Inorg. Chem.* **2002**, 41, 2356.

(12) Previous data (refs 9a,c and 11) on the *o*-chloranil system suggests that the isomers are due to the flexibility of the eight-membered ring to occupy either diequatorial or apical−equatorial dispositions in trigonal bipyramidal phosphorus. See the discussion on the structures of **2d** and **2e** also in connection with (equatorial)-NC(O)(O-*i*-Pr).

(13) Because of instrumental limitations the high-temperature limit could not be reached.

(14) Corbridge, D. E. C. *Phosphorus: An Outline of its Chemistry, Biochemistry and Technology*, 4th ed.; Elsevier: Amsterdam, 1990; Chapter 14, pp 994−1007.

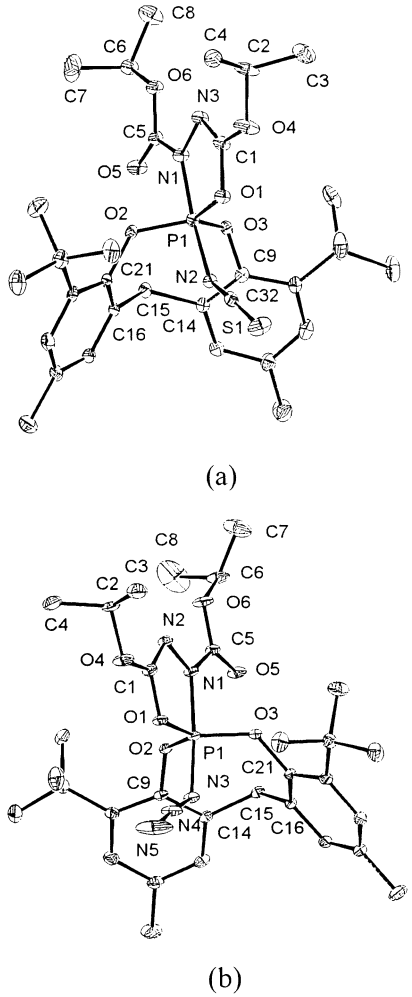


FIGURE 2. (a) Molecular structure of **2a**; only selected atoms are labeled. Important bond distances (Å) and angles (deg): P(1)−O(2), 1.5770(18); P(1)−O(3), 1.5805(19); P(1)−O(1), 1.6400-(18); P(1)−N(1), 1.755(2); P(1)−N(2), 1.770(2); N(2)−C(32), 1.180(3); S(1)−C(32), 1.569(3); N(1)−P(1)−N(2), 170.78(11). (b) Molecular structure of **2b**; only selected atoms are labeled. Important bond distances (Å) and angles (deg): P(1)−O(3), 1.579(2); P(1)−0(2), 1.584(2); P(1)−O(1), 1.645(2); P(1)−N(1), 1.768(3); P(1)−N(3), 1.770(3); N(3)−N(4), 1.186(4); N(4)−N(5), 1.121(5); N(1)−P(1)−N(3), 172.3(14).

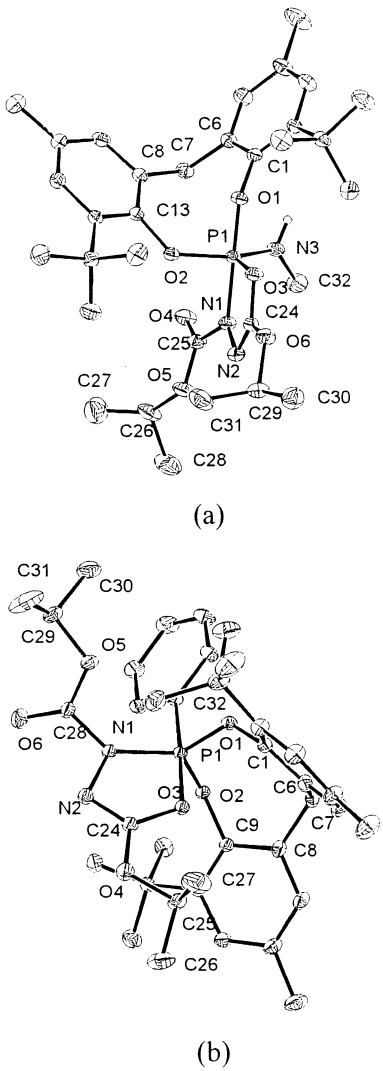


FIGURE 3. (a) Molecular structure of **2d**; only selected atoms are labeled. Important bond distances (Å) and angles (deg): P(1)−O(1), 1.6652(14); P(1)−O(2), 1.6073(14); P(1)−O(3), 1.6452-(14); P(1)−N(1), 1.8123(8); P(1)−N(3), 1.6206(18); O(1)−P(1)−N(1), 171.53(8). (b) Molecular structure of **2e**; only selected atoms are labeled. Important bond distances (Å) and angles (deg): P(1)−O(1), 1.6030(13); P(1)−O(2), 1.6208(12); P(1)−N(1), 1.7005(15); P(1)−O(3), 1.7538(11); P(1)−C(32), 1.8431(17); O(3)−P(1)−C(32), 176.38(7).

on nitrogen; thus, both electronegativity and steric factors are supposed to be unfavorable for this nitrogen to occupy the apical position.

In the structure of **2d** (Figure 3a) also nitrogen of the five-membered ring, rather than the oxygen, is at the apical position. However, the −NHMe group is located equatorial and not apical (cf. **2a** and **2b**); this observation is analogous to that in $CH_2(6\text{-}t\text{-Bu-4-Me-}C_6H_2O)_2P(NHMe)$-$(O_2C_6Cl_4)$ obtained from the reaction of **1d** with *o*-chloranil.[9c,11] The P(1)−N(1)(apical) distance of 1.813 Å in **2d** is longer than that calculated according to the Schomaker−Stevenson empirical expression (1.77 Å).[11]

In contrast to **2a**, **2b**, and **2d**, in compound **2e** (Figure 3b) the expected apical placement of the oxygen and equatorial placement of the nitrogen for the five-membered ring is observed. However, in this case, the phenyl ring is at an apical position, rather than an oxygen of the eight-membered ring, again showing the "reversed apicophilicity" phenomenon.

One may argue that in the above cases the thermodynamically most favored structure is simply not reached. However, a growing body of evidence suggests that at least in our system the steric and electronegativity rules for pentacoordinate phosphorus are often not followed and the products isolated could be the thermodynamically favored ones.[15,16]

Yet another novel feature emanating from this study is the isolation of a tetracoordinate phosphorus species **3** when **1f** (**1**: X = NCO) is used in place of **1a** (**1**: X = NCS) in the reaction with DIAD. Compound **3** exhibits an IR stretch at 2259 cm^{-1} (which is almost the same as in the precursor **1f**), suggesting that the −NCO group is still intact. In the ^{13}C NMR of **3**, the two O*C*HMe$_2$ signals are much closer (δ 72.6, 73.2; $\Delta\delta$ 0.6 ppm) than in the pentacoordinate isothiocyanate derivative **2a** (δ 69.9. 74.7; $\Delta\delta$ 4.8 ppm); this feature suggests that the two

$OCHMe_2$ groups in **3** are in nearly the same environment.[17] However, the δ(P) value of 27.4 ppm for **3** is quite downfield,[18] suggesting that an additional interaction between N and C, leading to a five-membered ring, as shown in Scheme 2 (path b), is possible. Such an interaction could also explain the unexpected difference in reactivity between **1a** and **1f** toward DIAD.[19]

In summary, we have characterized four pentacoordinate phosphoranes with "reversed apicophilicity" by X-ray crystallography, from the reaction of cyclic phosphites with DIAD; these results have a bearing on the extensively studied concept of "apicophilicity" in trigonal bipyramidal phosphorus. The ^{31}P NMR spectra (toluene-d_8) of some of these compounds show more than one signal; a detailed assignment of the resonances has to wait till both the isomers for a particular derivative are isolated. The difference in the types of products obtained by starting with P−NCO and P−NCS compounds suggests that, depending on even subtle change in substituents on the P(III) precursor, the products with DIAD could be different. The results obtained herein could be useful while trying to improve on the original Mitsunobu procedure, wherein removal of the byproduct triphenylphosphine oxide could pose problems in specific cases.

Experimental Section

Synthesis and Characterization of 2a. DIAD (2.02 g, 9.99 mmol) was added in one lot to a solution of **1a** (mp 126−128 °C[11]) (4.27 g, 9.99 mmol) in dry toluene (20 mL) and the mixture was stirred for 72 h at room temperature. Concentration to 2 mL, followed by the addition of heptane (8 mL), afforded crystals of **2a** (5.35 g, 85%) after ca. 24 h: mp 191−193 °C; IR (cm^{-1}) 2024, 1715, 1694; ^{1}H NMR ($CDCl_3$) δ 1.28 (d, ^3J(H−H) = 6.2 Hz, 6 H, CH(C*H*$_3$)$_2$), 1.35 (s, 18 H, *t*-Bu-*H*), 1.42 (d, ^3J(H−H) = 6.2 Hz, 6 H, CH(C*H*$_3$)$_2$), 2.34, 2.35 (2 s, 6 H, ArC*H*$_3$), 3.39 (dd, ^5J(P−H) ∼ 2.7 Hz, ^2J(H−H) = 14.0 Hz, 1 H, ArC*H*$_A$H$_X$), 5.05−5.25 (m, 3 H, ArCH$_A$*H*$_X$ + C*H*Me$_2$), 7.06, 7.19 (2 s, 4 H, Ar-*H*); ^{13}C NMR ($CDCl_3$) δ 21.2, 21.6, 22.0 (3 s, ArC*H*$_3$ + CH(C*H*$_3$)$_2$), 30.6 (s, C(C*H*$_3$)$_3$), 32.7 (s, ArC*H*$_2$), 34.7 (s, *C*(CH$_3$)$_3$), 69.9, 74.7 (2 s, O*C*HMe$_2$), 127.3, 129.3, 129.8, 134.3, 135.2, 136.0, 140.2, 147.2 (d, ^2J(P−C) = 16.8 Hz), 149.2 (^2J(P−C) ∼ 19.0 Hz), 153.1 (^2J(P−C) = 10.1 Hz) (the N*C*S signal is probably merged with those due to others); ^{31}P NMR ($CDCl_3$) δ −67.3 [^{31}P NMR ($C_6D_5CD_3$) δ −66.6]. At 222 K in toluene-d_8 additional low-intensity peaks were observed in the ^{31}P NMR [δ −82.1 (3%) and −76.0 (4%)] in the pentacoordinate region; however, the compound was susceptible to hydrolysis (^{31}P NMR) and hence could not be studied in more detail. Anal. Calcd for $C_{32}H_{44}N_3O_6PS$: C, 61.03; H, 7.04; N, 6.67. Found: C, 61.10; H, 7.06; N, 6.72.

Synthesis and Characterization of 2b. To a stirred solution of **1b** (mp 132 °C[9c]) (**CAUTION**: Although we did not observe any untoward incident in handling the azide **1b**, it is recommended that large-scale operations using this compound be avoided as a safety precaution) (0.673 g, 1.63 mmol) in hexane (10 mL) was added a solution of DIAD (0.33 g, 1.63 mmol) in hexane (5 mL) dropwise over a period of 30 min. After stirring the mixture for 12 h, solvent was removed and the obtained solid was crystallized from a 1:2 $CH_3CN-CH_2Cl_2$ mixture to afford **2b** (0.70 g, 70%): mp 162−164 °C; IR (cm^{-1}) 2141, 1715, 1692; ^{1}H NMR ($CDCl_3$) δ 0.78 (d, ^3J(H−H) ∼ 6.0 Hz, 6 H, CH(C*H*$_3$)$_2$), 1.30−1.38 (m, 6 H, CH(C*H*$_3$)$_2$), 1.36 (s, 18 H, *t*-Bu-*H*), 2.31 (s, 6 H, ArC*H*$_3$), 3.41 (^2J(H−H) ∼ 13 Hz), 3.54 (^2J(H−H) ∼ 13 Hz) and 4.41 (^2J(H−H) ∼ 13 Hz) [total 2 H, all ArC*H*$_A$*H*$_X$], 3.74 (br) and 5.15 (br) [2 H, C*H*Me$_2$], 7.03 and 7.14 (s each, 4 H, Ar-*H*); the spectral pattern is indicative of the presence of more than one isomer (cf. ^{31}P and ^{13}C NMR); ^{13}C NMR ($CDCl_3$) δ 21.0, 21.6, 22.0 (3 s, ArC*H*$_3$ + CH(C*H*$_3$)$_2$), 30.7 (s, C(C*H*$_3$)$_3$), 33.2, 33.7 (2 s, ArC*H*$_2$), 34.8 (s, *C*(CH$_3$)$_3$), 69.7, 72.2, 73.1, 74.3 (4 s, O*C*HMe$_2$), 127.0, 129.0, 133.2, 133.7, 134.3, 134.6, 140.0, 148.0 (d, ^2J(P−C) ∼ 15.0 Hz), 153.0 (br), 153.9 (br); ^{31}P NMR ($CDCl_3$) δ −61.0, −69.7 (1:1). The spectrum in toluene-d_8 also showed two peaks [δ(P): −60.1, −70.2 (1:2)] at room temperature and below (till 227K; intensity ratio 1:1). At 309 K only the broadened upfield peak was observed. On raising the temperature to 343 K, the compound underwent decomposition as well as partial hydrolysis; two major peaks at δ 13.7 (60%) and −6.9 (35%) and a minor peak at δ −10.4 (5%) were observed. The spectrum on returning to room temperature was different from the one taken prior to heating. The peak at δ −10.4 was also observed upon keeping the solution for >1 h. The ^{31}P NMR spectrum of **2b** (or **2d**; see below) dissolved (ca. 20 s for dissolution) in toluene-d_8 in an NMR tube maintained at −40 °C for 1 h and immediately inserted into the NMR spectrometer with the probe maintained at −40 °C also exhibited the same two signals (recording time <10 min). Anal. Calcd for $C_{31}H_{44}N_5O_6P$: C, 60.67; H, 7.22; N, 11.41. Found: C, 60.50; H, 7.12; N, 11.20.

Synthesis and Characterization of 2c. The procedure was the same as that for **2a** using **1c**[11] (4.04 g, 10 mmol). Crystallization was done using dichloromethane to yield 4.85 g (80%): mp 177−180 °C; IR (cm^{-1}) 1755; ^{1}H NMR ($CDCl_3$) δ 1.33−1.47 (many lines, 30 H, CH(C*H*$_3$)$_2$ + *t*-Bu-*H*), 2.33, 2.34, 2.36 (3 s, 6 H, ArC*H*$_3$), 3.35−3.80 (m, 2 H, ArC*H*$_A$H$_X$), 5.10−5.30 (m, 2 H, C*H*Me$_2$), 7.00−7.26 (m, 4 H, Ar-*H*); ^{13}C NMR ($CDCl_3$) δ 21.0, 21.5, 21.9, 30.7, 33.0, 34.7, 69.9, 74.6, 127.0, 128.8, 129.4, 134.4, 134.5, 134.9, 135.0, 139.9, 140.1, 148.0 (d, ^2J(P−C) = 17.0 Hz), 149.1 (d, ^2J(P−C) = 19.1 Hz), 153.0 (d, ^2J(P−C) = 10.5 Hz); ^{31}P NMR ($CDCl_3$) δ −46.0. Anal. Calcd for $C_{31}H_{44}N_2O_6PCl$: C, 61.32; H, 7.30; N, 4.61. Found: C, 61.48; H, 7.36; N, 4.66.

Synthesis and Characterization of 2d. The procedure was the same as that for **2a** using **1d**[9c] (3.99 g, 10 mmol). Crystallization was done using *n*-heptane−toluene (1:1) mixture to yield 5.11 g (85%): mp 140−143 °C; IR (cm^{-1}) 1676; ^{1}H NMR ($CDCl_3$) δ 1.30−1.50 (many lines, 30 H, CH(C*H*$_3$)$_2$ + *t*-Bu-*H*), 2.28, 2.30 (2 s, 6 H, ArC*H*$_3$), 2.63, 2.72 (2 d, ^3J(P−H) = 12.0 Hz each, NHC*H*$_3$), 3.44 (d, ^2J(H−H) = 16.0 Hz, 1 H, ArC*H*$_A$H$_X$), 3.50−3.55 (br, 1 H, −N*H*), 4.55 (d, ^2J(H−H) = 16.0

(15) One of the referees noted "...The authors may well be dealing with kinetic phenomena here. These are awfully hindered structures (isopropyl ester of azodicarboxylate and a half-calixarene ligand protected also by *tert*-butyl groups). In my opinion it is possible that the thermodynamically most favored structure is simply not reached." A referee for one of our earlier papers (ref 11 above) has a different explanation for the observed structures of the products CH_2(6-*t*-Bu-4-Me-$C_6H_2O)_2$P(NRR′)($O_2C_6Cl_4$) where bulkier secondary amino groups preferred apical positions (footnote 16 in ref 11 quoted above) and (less bulkier) primary groups went for an equatorial site. We have also found that the P-*tert*-butyl group in CH_2(6-*t*-Bu-4-Me-$C_6H_2O)_2$P(*t*-Bu)($O_2C_6Cl_4$) is apical while the P-methyl group in CH_2(6-*t*-Bu-4-Me-$C_6H_2O)_2$P(Me)($O_2C_6Cl_4$) is equatorial.[9c,16] In addition, for **2d**, the species observed at higher temperatures reverts back to the low-temperature forms upon cooling (^{31}P NMR). This feature suggests that the initially observed species at room temperature is indeed thermodynamically stable.

(16) Kommana, P.; Vittal, J. J.; Kumara Swamy, K. C. [Synthesis and structure of CH_2(6-*t*-Bu-4-Me-$C_6H_2O)_2$P(*t*-Bu)($O_2C_6Cl_4$)], to be published.

(17) In the pentacoordinate compound **2a**, of the two O*C*HMe$_2$ carbons, one is connected as N=C(O*C*HMe$_2$)O− and the other as −N−C(O)(O*C*HMe$_2$)−.

(18) One of the referees suggested that the δ(P) value of **3** (in relation to the pentacoordinate compounds **2**) can be compared to that of the phosphonium ion $Ph_3P(OCH_2CMe_3)^+(OC(O)Ph)^-$ [δ(P) +61.0]; the latter species is in equilibrium with the phosphorane $Ph_3P(OCH_2CMe_3)_2$ [δ(P) −57.5] in the presence of benzoic acid.[3f,g]

(19) From the reaction of **3** with catechol, we could isolate the pentacoordinate derivative CH_2(6-*t*-Bu-4-Me-$C_6H_2O)_2$P(1,2-$O_2C_6H_4$)-[NHC(O)N(C(O)O−i-Pr−NHC(O)O-*i*-Pr]. In this compound, the carbon of the original NCO group is connected to a nitrogen of the DIAD residue. This would give indirect evidence for the proposed N···C interaction. The quality of the crystals obtained so far is not good, but the X-ray structure (R ∼ 12%) clearly established its authenticity. This and related reactions will be presented in a separate paper.

Hz, 1 H, ArCH$_A$H$_X$), 5.00−5.20 (m, 2 H, CHMe$_2$), 6.80−7.20 (many lines, 4 H, Ar-*H*); ^{13}C NMR ($CDCl_3$) δ 20.8, 21.7, 21.8, 21.9, 22.2, 22.3, 29.8, 30.2, 30.5, 31.1, 34.3, 34.6, 35.1, 35.8, 68.2, 68.3, 71.5, 73.1, 126.2, 127.0, 127.4, 128.4, 129.0, 132.5, 133.0, 133.8, 140.5, 141.0, 147.8, 150.0, 153.1, 153.8 (complexity suggests the presence of isomers); ^{31}P NMR ($CDCl_3$) δ −61.0, −61.7 (1:3). See also the experimental under compound **2b** for further details. Anal. Calcd for $C_{32}H_{48}N_3O_6P$: C, 63.87; H, 8.04; N, 6.98. Found: C, 63.79; H, 8.10; N, 7.08.

Synthesis and Characterization of 2e. To a stirred solution of **1e**[9c] [mp 170−172 °C] (0.406 g, 0.91 mmol) in toluene (5 mL) was added DIAD (0.184 g, 0.91 mmol) in toluene (5 mL) dropwise over a period of 0.5 h. Upon stirring for 2 days and removal of all the solvent, **2e** was obtained as a light yellow solid (0.472 g, 80%): mp 106−108 °C; IR (cm^{-1}) 1742, 1689; ^{1}H NMR ($CDCl_3$) δ 0.69 (d, ^3J(H−H) = 6.0 Hz, 6 H, CH(C*H*$_3$)$_2$), 0.90 (d, ^3J(H−H) = 6.0 Hz, 6 H, CH(C*H*$_3$)$_2$), 1.43 (s, 18 H, *t*-Bu-*H*), 2.32 (s, 6 H, ArC*H*$_3$), 3.50 (d, ^2J(H−H) = 14.4 Hz, 1 H, ArC*H*$_A$H$_X$), 4.30 (dd, ^5J(P−H) = 4.0 Hz, ^2J(H−H) = 16.0 Hz, 1 H, ArCH$_A$*H*$_X$), 3.35−3.50 and 4.50−4.65 (m each, 2 H, C*H*Me$_2$), 7.05 and 7.20 (2 s, 4 H, Ar-*H*), 7.10−7.35 (m, 3 H, Ar-*H*), 8.00−8.20 (m, 2H, Ar-*H*);^{13}C NMR δ 20.9, 21.0, 21.5, 21.9, 30.7, 30.9, 34.0, 34.8, 71.0, 71.8, 126.6, 127.5, 127.8, 128.1, 128.7, 129.0, 130.3, 130.5, 131.7, 133.4, 139.5, 139.6, 144.2, 148.3, 149.0 (^2J(P−C) = 19.0 Hz), 154.6 (^2J(P−C) = 17.0 Hz), 155.3 (^2J(P−C) = 14.9 Hz); ^{31}P NMR ($CDCl_3$) δ −51.8. There was no change in the ^{31}P NMR spectra in toluene-d$_8$, even upon lowering the temperature. Anal. Calcd for $C_{37}H_{49}N_2O_6P$: C, 68.50; H, 7.61; N, 4.31. Found: C, 68.55; H, 7.65; N, 4.38.

Synthesis and Characterization of 3. The procedure was the same as for **2a**, using **1f** (4.11 g, 10 mmol) [mp 124−126 °C; IR (cm^{-1}) 2255 (ν_{NCO}); δ(P) 121.2;[20] ^{13}C NMR ($CDCl_3$) δ 21.1, 30.7, 34.6, 34.7, 126.7 (^2J(P−C) = 9.0 Hz), 127.1, 128.9, 134.3, 135.6, 141.6, 146.8 (Ar-*C*).] and DIAD (2.02 g, 10 mmol) to yield 5.2 g (85%). Unfortunately, the crystals were not suitable for X-ray work: MS (FAB$^+$): *m*/*z* 613 [M$^+$]; mp 170−173 °C; IR (cm^{-1}) 2259, 1714, 1696; ^{1}H NMR ($CDCl_3$) δ 1.33 (d, ^3J(H−H) = 6.0 Hz, 6 H, CH(C*H*$_3$)$_2$), 1.35 (s, 18 H, *t*-Bu-*H*), 1.40 (d, ^3J(H−H) = 6.1 Hz, 6 H, CH(C*H*$_3$)$_2$), 2.30 (s, 6 H, ArC*H*$_3$), 3.70 (d, ^2J(H−H) = 15.9 Hz, 1 H, ArC*H*$_A$H$_X$), 4.53 (d, ^2J(H−H) = 16.1 Hz, 1 H, ArCH$_A$*H*$_X$), 5.03−5.11 (m, 2 H, C*H*Me$_2$), 7.01, 7.10 (2 s, 4 H, Ar-*H*); ^{13}C NMR ($CDCl_3$) δ 20.7, 21.6 (s each, Ar*C*H$_3$ + CH(*C*H$_3$)$_2$), 30.5 (s, CH(*C*H$_3$)$_2$), 30.8 (s, C(*C*H$_3$)$_3$), 34.6 (s, Ar*C*H$_2$ + *C*(CH$_3$)$_3$), 72.6, 73.2 (2 s, O*C*HMe$_2$), 127.2 (d, ^2J(P−C) = 21.0 Hz, N*C*O),[21] 127.8, 128.8, 129.8, 135.7, 139.6, 139.8, 147.1, 147.3, 148.9, 149.0, 152.0 (^3J(P−C) = 6.0 Hz, *C*O$_2$R), 152.7 (^2J(P−C) = 10.0 Hz, *C*O$_2$R)[22] [the ^{13}C NMR spectrum recorded at −20 °C showed broadened resonances, and hence, a satisfactory assignment of the low-intensity P−N*C*O doublet could not be made at this temperature]; ^{31}P NMR ($CDCl_3$) δ 27.4. Anal. Calcd for $C_{32}H_{44}N_3O_7P$: C, 62.63; H, 7.23; N, 6.85. Found: C, 62.79; H, 7.25; N, 6.90.

X-ray Crystallography. X-ray data for **2a**, **2b**, **2d**, and **2e** were collected on a Bruker AXS SMART diffractometer using Mo Kα (λ = 0.71073 Å) radiation and capillary mounting. The structures were solved by direct methods;[23] all non-hydrogen atoms were refined anisotropically. For the hydrogen atoms bonded to carbon, the riding model was used.

Crystal Data for 2a. Empirical formula: $C_{32}H_{44}N_3O_6PS$. Formula weight: 629.73. Crystal system: monoclinic. Space group: $P2_1/c$. a = 19.260(1) Å, b = 9.978(1) Å, c = 19.725(1) Å, β = 114.067(1)°, V = 3461.3(3) Å^3, Z = 4, ρ_{calcd} = 1.208 Mg m^{-3}, μ = 0.184 mm^{-1}, F(000) = 1344. Data/restraints/parameters: 6088/0/388. R indices ($I > 2\sigma(I)$): R1 = 0.0579, wR2 = 0.1112. GOF on F^2 = 1.021. Maximum/minimum residual electron density: 0.275/−0.296 e Å^{-3}.

Crystal Data for 2b. Empirical formula: $C_{31}H_{44}N_5O_6P$. Formula weight: 613.68. Crystal system: monoclinic. Space group: $P2_1/c$. a = 18.037(1) Å, b = 9.735(1) Å, c = 19.082(1) Å, β = 94.674(1)°, V = 3339.5(3) Å^3, Z = 4, ρ_{calcd} = 1.221 Mg m^{-3}, μ = 0.30 mm^{-1}, F(000) = 1312. Data/restraints/parameters: 5896/ 0/ 388. R indices ($I > 2\sigma(I)$): R1 = 0.0797, wR2 = 0.1905. GOF on F^2 = 1.084. Maximum/minimum residual electron density: 0.413/−0.564 e Å^{-3}.

Crystal Data for 2d. Empirical formula: $C_{32}H_{48}N_3O_6P$. Formula weight: 601.70. Crystal system: monoclinic. Space group: $P2_1/c$. a = 16.2599(8) Å, b = 18.4942(9) Å, c = 11.2391(5) Å, β = 101.5380(10)°, V = 3311.5(3) Å^3, Z = 4, ρ_{calcd} = 1.207 Mg m^{-3}, μ = 0.128 mm^{-1}, F(000) = 1296. Data/restraints/parameters: 5832/0/389. R indices ($I > 2\sigma(I)$): R1 = 0.0472, wR2 = 0.1073. GOF on F^2 = 1.012. Maximum/minimum residual electron density: 0.296/−0.324 e Å^{-3}.

Crystal Data for 2e. Empirical formula: $C_{37}H_{49}N_2O_6P$. Formula weight: 648.75. Crystal system: monoclinic. Space group: $P2_1/c$. a = 12.0296(6) Å, b = 16.3575(8) Å, c = 19.1558(10) Å, β = 106.5720(10)°, V = 3612.8(3) Å^3, Z = 4, ρ_{calcd} = 1.193 Mg m^{-3}, μ = 0.122 mm^{-1}, F(000) = 1392, Data/restraints/parameters: 6367/0/426. R indices ($I > 2\sigma(I)$): R1 = 0.0438, wR2 = 0.1326. GOF on F^2 = 1.063. Maximum/minimum residual electron density: 0.421/−0.28 e Å^{-3}.

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Supporting Information Available: X-ray structure determination and crystal data for **2a**, **2b**, **2d**, and **2e** as CIF files. This material is available free of charge via the Internet at http/::pubs.acs.org.

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(20) This precursor was reported by us already: Kumaraswamy, S.; Kommana, P.; Satish Kumar, N.; Kumara Swamy, K. C. *Chem. Commun.* **2002**, 40.

(21) In 4-alkoxy-4-isocyanato-1,2,4(λ^5)diazaphospholes, which have tetracoordinate phosphorus, the P(V)−N*C*O carbon appears at δ 127.8 ± 0.1 ppm with a ^2J(P−C) of 17.6 ± 0.4 Hz. See: Kerth, J.; Werz, U.; Maas, G. *Tetrahedron* **2000**, *56*, 35.

(22) For ^{13}C NMR chemical shift values of P−NCO$_2$CHMe$_2$ compounds, see ref 7b.

(23) SHELX-97, *A package for structure solution and refinement*, Sheldrick, G. M., University of Göttingen, Göttingen, Germany, 1997.