JOC Article

Diverse Modes of Reactivity of Dialkyl Azodicarboxylates with P(III) Compounds: Synthesis, Structure, and Reactivity of Products Other than the Morrison−Brunn−Huisgen Intermediate in a Mitsunobu-Type Reaction

N. Satish Kumar,[†] K. Praveen Kumar,[†] K. V. P. Pavan Kumar,[†] Praveen Kommana,[†] Jagadese J. Vittal,[‡] and K. C. Kumara Swamy*,[†]

School of Chemistry, University of Hyderabad, Hyderabad 500 046, A.P., India, and Department of Chemistry, National University of Singapore, Science Drive 3, Singapore 117543, Singapore

kckssc@uohyd.ernet.in

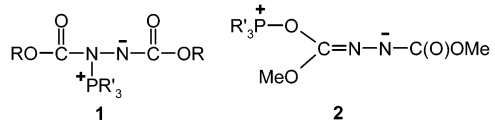
Received November 7, 2003

The reactivity of diethyl azodicarboxylate (DEAD)/diisopropyl azodicarboxylate (DIAD) with P(III) compounds bearing oxygen or nitrogen substituents is explored. Compounds with structures *quite different* from that of Morrison−Brunn−Huisgen intermediate $R'_3P^+N(CO_2R)N^-(CO_2R)$ (**1**), observed in the Mitsunobu reaction, have been established by using X-ray crystallography and NMR spectroscopy. Thus reactions with X(6-*t*-Bu-4-Me-$C_6H_2O)_2$P-NH-*t*-Bu [X = S (**8**), CH_2 (**9**)] or XP(μ-N-*t*-Bu)$_2$P-NH-*t*-Bu [X = Cl (**14**) or NH-*t*-Bu (**15**)] and DEAD/DIAD lead to phosphinimine-carbamate-type of products X{6-*t*-Bu-4-Me-C_6H_2O}$_2$P{N-*t*-Bu}{N(CO_2R)NH(CO_2R)} [X = S, R = Et (**16**); X = CH_2, R = Et (**17**); X = CH_2, R = *i*-Pr (**18**)] or XP(μ-N-*t*-Bu)$_2$P(N-*t*-Bu){N-(CO_2-*i*-Pr)-N(H)(CO_2-*i*-Pr) [X = Cl (**19**), NH-*t*-Bu (**20**)]. Treatment of **19** with 2,2,2-trifluoroethanol afforded the product [(CF_3CH_2O)P(μ-N-*t*-Bu)$_2P^+$(NH-*t*-Bu){N(CO_2-*i*-Pr)(HNCO_2-*i*-Pr)}][Cl^-] (**21**) whose structure is close to one of the intermediates proposed in the Mitsunobu reaction. The isocyanate CH_2-(6-*t*-Bu-4-Me-$C_6H_2O)_2$P-NCO (**10**) underwent 1,3-(P,C) cycloaddition with DEAD/DIAD to lead to CH_2(6-*t*-Bu-4-Me-$C_6H_2O)_2$P{N(CO_2R)N(CO_2R)-C(O)-N} [R = Et (**22**), *i*-Pr (**23**)]. Reaction of **22**−**23** with 1,1′-bi-2-naphthol or catechol leads to novel tetracoordinate CH_2(6-*t*-Bu-4-Me-$C_6H_2O)_2$P(2,2′-$OC_{10}H_6$-$C_{10}H_6$-OH){NC(O)-(CO_2R)NH(CO_2R)} [R = Et (**24**), *i*-Pr (**25**)] or pentacoordinate CH_2(6-*t*-Bu-4-Me-$C_6H_2O)_2$P(1,2-$O_2C_6H_4$){NHC(O)-N(CO_2R)NH(CO_2R)} [R = Et (**26**), *i*-Pr (**27**)] compounds in which the original NCO residue is retained; this mode of reactivity is quite different from that observed for the MBH betaine **1**. In **27**, the nitrogen, rather than the oxygen, occupies an apical position of the trigonal bipyramidal phosphorus violating the commonly assumed preference rules for apicophilicity. It is shown that the previously reported azide derivative **3**, obtained from the reaction of **11** with DIAD, undergoes a Curtius-type rearrangement to lead to the fused cyclodiphosphazane [{CH_2(6-*t*-Bu-4-Me-$C_6H_2O)_2$}P{OC(O-*i*-Pr)NN(CO_2-*i*-Pr)N}]$_2$ (**28**); this compound is in equilibrium with its monomeric form in solution at >300 K. Finally, reaction of S(6-*t*-Bu-4-Me-$C_6H_2O)_2$P(OPh) (**13**) with DIAD gave the hexacoordinate compound S{6-*t*-Bu-4-Me-C_6H_2O}$_2$P-(OPh){N(CO_2-*i*-Pr)NC(O-*i*-Pr)O} (**30**) with an intramolecular S→P bond. X-ray crystallographic evidence for compounds **16**, **19**, **21**, **22**, **25**, **27**, **28**, and **30** has been provided.

Introduction

A combination of the redox couple of a triaryl- or trialkylphosphine and a dialkyl azodicarboxylate [ROOCN=NCOOR, R = Et (DEAD), *i*-Pr (DIAD)] is the key to the success of the Mitsunobu reaction in a wide range of synthetic applications including esterification (eq 1).[1] Although the Morrison−Brunn−Huisgen [MBH] betaine **1** is the proven intermediate in the first step of this reaction, the P−O bonded tetracoordinate species of type **2** was also proposed as another possible intermediate in the earlier literature.[2] Formation of the species **1** has been previously established by multinuclear NMR and FTIR, but not by X-ray.[3]

$$R^1COOH + R^2OH \xrightarrow[-Ph_3PO,\ -EtO_2CNHNHCO_2Et]{Ph_3P + EtO_2CN=NCO_2Et} R^1COOR^2 \quad (1)$$



1 **2**

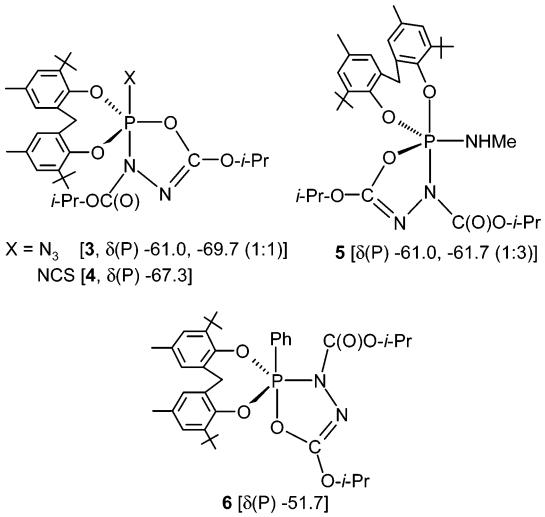
Formation of the betaine **1** occurs through radical cations of type RO_2C-N-(P^+Ph_3)-$N^{\bullet}$-CO_2R as shown by EPR spectroscopy.[2c] Additionally, it is noted that treatment of DIAD with tributylphosphine gives a much weaker EPR signal relative to that with triphenylphosphine, while a much more intense signal could be detected in the reaction of DIAD with tris(dimethylami-

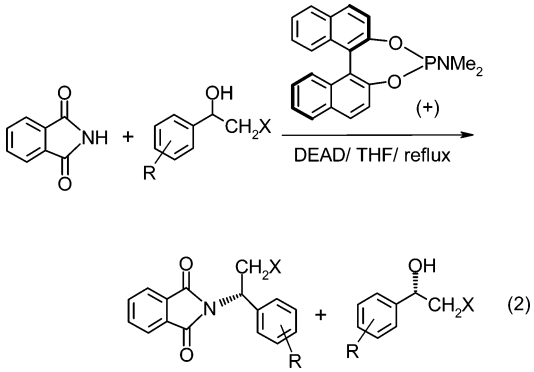
[†] University of Hyderabad.
[‡] National University of Singapore.

10.1021/jo035634d CCC: $27.50
Published on Web 02/14/2004

no)phosphine. These features suggest that the nature of the intermediates in the Mitsunobu reaction could also vary depending upon the P(III) precursor. Indeed it has been observed that in the formation of 2-oxazolidones from CO_2 and ethanolamines with a Mitsunobu protocol, the use of triphenylphosphine and tributylphosphine afforded different isomers.[1c] As regards the esterification with triphenylphosphine/DIAD, it is reported that when the acid is added last, or when a large excess of azodicarboxylate and triphenylphosphine are used, radicals are certainly generated prior to the formation of the betaine **1**.[2c]

A different facet for the reaction of P(III) compounds with DIAD is illustrated by the structural characterization of novel pentacoordinate phosphoranes **3**−**6** showing the "reversed apicophilicity" phenomenon.[4−6] It can be noted that the [4+1] cycloaddition compounds **3**−**6** involve both the N- and O-additions shown in **1** and **2**, suggesting that other modes of reactivity are possible when the electronic environment at phosphorus is altered. Direct reaction of phosphoramidites $(Me_2N)P(2,2'\text{-}O_2\text{-}(C_{10}H_6)_2)$ with DIAD also afforded the pentacoordinate phosphorane $(Me_2N)P[2,2'\text{-}O_2\text{-}(C_{10}H_6)_2][N(CO_2\text{-}i\text{-}Pr)NC(O\text{-}i\text{-}Pr)O]$ [^{31}P NMR: δ −36.7] that could be utilized for the kinetic resolution of alcohols in an asymmetric Mitsunobu reaction, although the details of the mechanism are still not clear.[5d] With use of a similar protocol, enantioselective reaction of racemic secondary alcohols with phthalimide in the presence of $(Me_2N)P(2,2'\text{-}O_2\text{-}(C_{10}H_6)_2)$ could be effected resulting in unreacted, enantiomerically enriched, alcohols (eq 2).[5e] These results also suggest that even when the initial products of the P(III) compound with DEAD/DIAD are different from a betaine of type **1**, Mitsunobu reaction takes place smoothly, thus leaving room to explore other P(III) compounds for specific reactions.





The order of addition of the acid and the alcohol to betaine **1** in the Mitsunobu esterification has a profound effect on the reaction pathway, implying potential duality of the mechanism.[7] Thus different types of phosphorus intermediates could be involved depending upon the order of addition. The intermediate from the reaction between the acid R′COOH and the betaine **1** (obtained from PPh_3) is a species of type $\{RO_2CN\text{-}(P^+Ph_3)\text{-}NH\text{-}CO_2R\}(R'CO_2^-)$ (**7**);[3] the stability of this species may be

(1) Selected references: (a) Mitsunobu, O. *Synthesis* **1981**, 1. (b) Hughes, D. L. *Org. React.* **1992**, *42*, 335. (c) Kodaka, M.; Tomohiro, T.; Okuno, H. (Y) *J. Chem. Soc., Chem. Commun.* **1993**, 81. (d) Dodge, J. A.; Jones, S. A. *Rec. Res. Dev. Org. Chem.* **1997**, *1*, 301. (e) Nikam, S. S.; Kornberg, B. E.; Rafferty, M. F. *J. Org. Chem.* **1997**, *62*, 3754. (f) Saylik, D.; Horvath, M. J.; Elmes, P. S.; Jackson, W. R.; Lovel, C. G.; Moody, K. *J. Org. Chem.* **1999**, *64*, 3940. (g) Barrero, A. F.; Alvarez-Manzaneda, E. J.; Chahboun, R. *Tetrahedron Lett.* **2000**, *41*, 1959. (h) Weissman, S. A.; Rossen, K.; Reider, P. J. *Org. Lett.* **2001**, *3*, 2513. (i) Liu, P.; Jacobson, E. N. *J. Am. Chem Soc.* **2001**, *123*, 10772. (j) Snider, B. B.; Song, F. *Org. Lett.* **2001**, *3*, 1817. (k) Paterson, I.; Savi, C. D.; Tudge, M. *Org. Lett.* **2001**, *3*, 213. (l) Appendino, G.; Minassi, A.; Daddario, N.; Bianchi, F.; Tron, G. C. *Org. Lett.* **2002**, *4*, 3839. (m) Chandrasekhar, S.; Kulkarni, G. *Tetrahedron*: *Asymmetry* **2002**, *13*, 615. (n) Xu, J. *Tetrahedron*: *Asymmetry* **2002**, *13*, 1129. (o) Crimmins, M. T.; Stanton, M. G.; Allwein, S. P. *J. Am. Chem. Soc.* **2002**, *124*, 5958. (p) Kan, T.; Fujiwara, A.; Kobayashi, H.; Fukuyama, T. *Tetrahedron* **2002**, *58*, 6267. (q) Shen, R.; Lin, C. T.; Bowman, E. J.; Bowman, B. J.; Porco, J. A., Jr. *Org. Lett.* **2002**, *4*, 3103. (r) Ahn, C.; Deshong, P. *J. Org. Chem.* **2002**, *67*, 1754. (s) Lan, P.; Porco, J. A., Jr.; South, M. S.; Parlow, J. J. *J. Comb. Chem.* **2003**, *5*, 660.

(2) (a) Brunn, E.; Huisgen, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 513. (b) Huisgen, R.; Knorr, R.; Möbius, L.; Szeimies, G. *Chem. Ber.* **1965**, *98*, 4014. (c) Camp, D.; Hanson, G. R.; Jenkins, I. D. *J. Org. Chem.* **1995**, *60*, 2977.

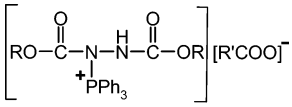
(3) (a) Varasi, M.; Walker, K. A. M.; Maddox, M. L. *J. Org. Chem.* **1987**, *52*, 4235. (b) Hughes, D. L.; Reamer, R. A.; Bergan, J. J.; Grabowski, E. J. J. *J. Am. Chem. Soc.* **1988**, *110*, 6487. (c) Camp, D.; Jenkins, I. D. *J. Org. Chem.* **1989**, *54*, 3045. (d) Camp, D.; Hanson, G. R.; Jenkins, I. D. *J. Org. Chem.* **1995**, *60*, 2977. (e) Hughes, D. L.; Reamer, R. A. *J. Org. Chem.* **1996**, *61*, 2967. (f) Ahn, C.; Correla, R.; deShong, P. *J. Org. Chem.* **2002**, *67*, 1751.

(4) Satish Kumar, N.; Kommana, P.; Vittal, J. J.; Kumara Swamy, K. C. *J. Org. Chem.* **2002**, *67*, 6653.

(5) For earlier literature on the formation of pentacoordinate compounds from the reactions of P(III) species with DEAD/DIAD, see: (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.; Gando M'Pondo, T.; Navech, J. *Tetrahedron Lett.* **1980**, *21*, 1307. (d) Hulst, R.; van Basten, A.; Fitzpatrick, K.; Kellogg, R. M. *J. Chem. Soc., Perkin Trans. 1* **1995**, 2961. (e) Li, Z.; Zhou, Z.; Wang, L.; Zhou, Q.; Tang, C. *Tetrahedron*: *Asymmetry* **2002**, *13*, 145.

(6) For other interesting examples with "reversed apicophilicity", see: (a) Timosheva, N. V.; Prakasha, T. K.; Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1995**, *34*, 4525. (b) Prakasha, T. K.; Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1995**, *34*, 1243. (c) Timosheva, N. V.; Chandrasekaran, A.; Prakasha, T. K.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1996**, *35*, 6552. (d) Kojima, S.; Kajiyama, K.; Nakamoto, M.; Akiba, K.-y. *J. Am. Chem. Soc.* **1996**, *118*, 12866. (e) Kajiyama, K.; Yoshimune, M.; Nakamoto, M.; Matsukawa, S.; Kojima, S.; Akiba, K.-y. *Org. Lett.* **2001**, *3*, 1873. (f) Kobayashi, J.; Goto, K.; Kawashima, T. *The Ninth International Symposium on Inorganic Ring Systems*; Saarbrücken, Germany, July 23−28, 2000; Abstract No. P-115. (g) Kumaraswamy, S.; Muthiah, C.; Kumara Swamy, K. C. *J. Am. Chem. Soc.* **2000**, *122*, 964. (h) Kommana, P.; Kumaraswamy, S.; Vittal, J. J.; Kumara Swamy, K. C. *Inorg. Chem.* **2002**, *41*, 2356. (i) Kojima, S.; Sugino, M.; Matsukawa, S.; Nakamoto, M.; Akiba, K.-y. *J. Am. Chem. Soc.* **2002**, *124*, 7674. (j) Kommana, P.; Satish Kumar, N.; Vittal, J. J.; Jayasree, E. G.; Jemmis, E. D.; Kumara Swamy, K. C. *Org. Lett.* **2004**, *6*, 145.

(7) Paudard-Cooper, A.; Evans, S. A., Jr. *J. Org. Chem.* **1989**, *54*, 2485.

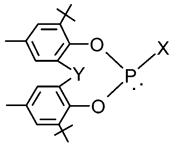


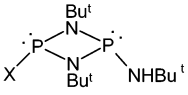
7

enhanced by hydrogen bonding. Oxaphosphorane intermediates, $Ph_3P(OR'')_2$, are formed by the reaction of either **1** or **7** with alcohols. Reaction of **7** with 1 mol equiv of R″OH leads to the phosphonium salt $[Ph_3P^+(OR'')](R'CO_2^-)$; the latter can also be formed from $Ph_3P(OR'')_2$ and $R'CO_2H$.[7] It is possible that some of these intermediates can be stabilized by a suitable choice of the P(III) precursor. This, together with the fact that dialkyl azodicarboxylates ROOCN═NCOOR are electron-poor and hence could participate in other types of cycloadditions [e.g. Diels−Alder, dipolar],[8] has prompted us to look into their behavior toward P(III) compounds possessing reactive functional groups. We also felt that in this process we may be able to isolate compounds of type **7**. Finally, it was also our intention to probe the reactivity of products of types other than **1** that could generate new chemistry.

As P(III) precursors for our studies, we have chosen compounds **8**−**15** (Chart 1). In the original Mitsunobu reaction, triphenylphosphine that contains three carbons attached to phosphorus is utilized. The phosphorus atom in the P(III) compounds used in the present study is bonded to oxygen and/or nitrogen atoms, thus rendering it electronically different from that in Ph_3P.[9] The precursors **14**−**15** have two reactive P(III) centers that facilitate a comparison of their reactivity. All these P(III) compounds can be readily prepared and are inexpensive.[6g−h,10,11] More importantly, they possess a sterically encumbered phosphorus, a feature that could facilitate isolation and structural characterization of the products and study of their reactivity. Since it is shown (cf. eq 2) that Mitsunobu esterification can be effected even with the intermediacy of species other than the betaine **1**, we believe that the data presented here can lead to the extension of related organic methodology.

CHART 1



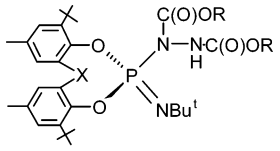


X	Y	
NH-*t*-Bu	S	[**8**, δ(P) 138.2]
NH-*t*-Bu	CH_2	[**9**, δ(P) 141.9]
NCO	CH_2	[**10**, δ(P) 121.2]
N_3	CH_2	[**11**, δ(P) 136.5]
$OCH_2CH_2NMe_2$	CH_2	[**12**, δ(P) 129.0]
OPh	S	[**13**, δ(P) 136.1]

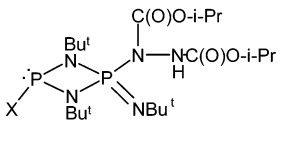
X = Cl [**14**, δ(P) 135.4, 200.3 ^2J(PP) = 44.0 Hz]
= NH-*t*-Bu [**15**, δ(P) 89.4]

In this paper, we highlight the following points (all based on the reaction of P(III) compounds with DEAD/DIAD).

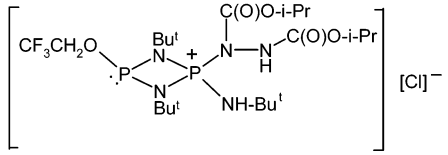
(i) First examples of imino-phosphorus compounds (X-ray evidence) **16**−**20**,[12] that have a structure halfway between the classical MBH betaine **1** and protonated betaine in the Mitsunobu reaction. In addition to posing a unique structural problem, a low-temperature ^{31}P NMR study on compounds **16** and **17** reveals an *unprecedented* solution state behavior wherein *at least four* isomeric phosphoranes are present. While compound **16** is unreactive toward 2,2,2-trifluoroethanol, compound **19** forms the salt **21** that has a structure (X-ray) analogous to *the intermediate* **7** proposed in the Mitsunobu esterification process.[3]



X = S; R = Et (**16**)
X = CH_2; R = Et (**17**)
X = CH_2; R = *i*-Pr (**18**)

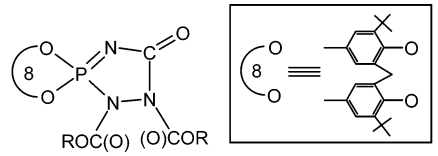


X = Cl (**19**)
X = NH-*t*-Bu (**20**)

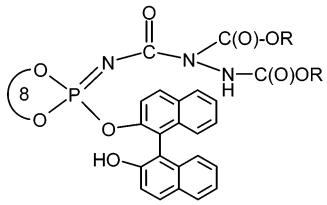


21

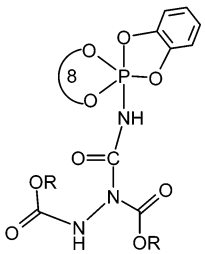
(ii) X-ray structural proof for a previously unknown mode of dipolar cycloaddition involving the P(III) isocyanate **10** and DEAD/DIAD to lead to **22** or **23**.[13] Addition of 1,1′-bi-2-naphthol or catechol to **22**−**23** proceeds by an unusual pathway in which the DEAD/DIAD residue is retained, leading to the respective tetra- and pentacoordinate compounds **24**−**25** and **26**−**27**. In the previously reported general reaction of betaine **1** with diols leading to pentacoordinate phosphorus compounds, the DEAD/DIAD residue was cleaved.[14] Compounds **25** and **27** are characterized by X-ray structure determination.



R = Et (**22**)
R = *i*-Pr (**23**)



R = Et (**24**)
R = *i*-Pr (**25**)

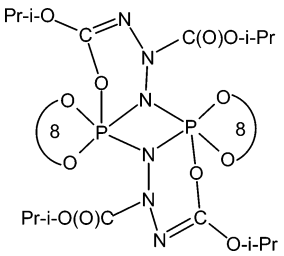


R = Et (**26**)
R = *i*-Pr (**27**)

(iii) A Curtius-type rearrangement of **3** (obtained from the reaction of **11** with DIAD) leading to **28** (X-ray) that is dynamic, with respect to its *monomeric* form, in solution.

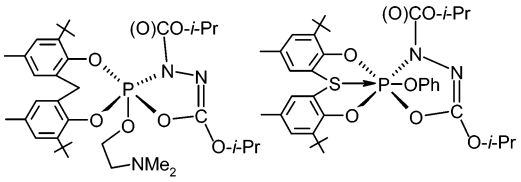
(8) Weinreb, S. M. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Paquette, L. A., Vol. Ed.; Pergamon: Oxford, UK, 1996; Vol. 5, Chapter 4.2, pp 401−449.

(9) Reaction of CH_2(6-*t*-Bu-4-Me-$C_6H_2O)_2$P(*t*-Bu) with DIAD afforded the oxidized product CH_2(6-*t*-Bu-4-Me-$C_6H_2O)_2$P(O)(*t*-Bu) [mp 262−264 °C, δ(P) 27.2] in 72% isolated yield. No other phosphorus product was identified in this case.



28

(iv) Isolation of *penta*- and *hexa*coordinate phosphoranes **29**−**30**, the latter with an S→P coordination (X-ray), from the reaction of **12**−**13** with DIAD. This provides a synthetic route to a new class of hexacoordinate phosphorus compounds.



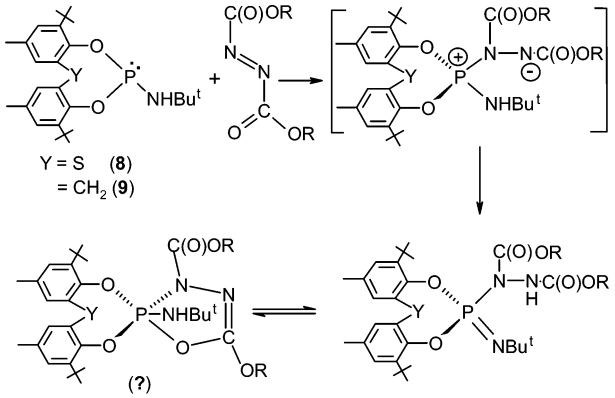
29 **30**

These four points will be discussed in the same order below.

Results and Discussion

(i) Imino Compounds 16−**20 and the Salt 21.** The reaction of **8**−**9** with DEAD or DIAD in toluene leads to compounds **16**−**18**, most likely via betaines analogous to **1** [Scheme 1]. The X-ray structure of **16** (see the Supporting Information for the drawing) clearly shows (i) a strong P═N(*t*-Bu) bond [P−N(3) 1.464(4) Å][15] and (ii) the carbamate-type linkage −NH-C(O)OR that is a hydrogen-bonded dimer through the NH and the C═O moieties. There is no significant S→P interaction in **16**. The IR (KBr) spectra of these compounds showed two ν(NH) bands [for **16** at 3262, 3159 cm^{-1}] consistent with the carbamate−phosphinimine structure;[16] this is different from a single ν(NH) band at 3383 cm^{-1} observed for the

SCHEME 1



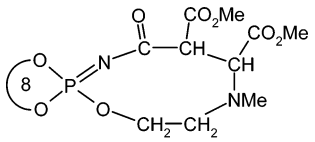
Y = S; R = Et [**16**; δ(P, 298K) -56.3]

Y = CH_2; R = Et [**17**; δ(P, 298K) -56.3]

Y = CH_2; R = *i*-Pr [**18**; δ(P, 298K) -57.6]

pentacoordinate methylamino compound **5**.[4] There is also a fairly strong band at 1211 cm^{-1} ascribable to ν(P═N). For the question as to why the X-ray structure of −NHMe derivative **5** shows pentacoordination, whereas the −NH-*t*-Bu compound **16** shows tetracoordination, the factors responsible could be the bulkiness of the *t*-Bu group resulting in a very strong P═N bond. This together with the hydrogen bonding involving the −NH-C(O) group is the likely driving force for the stability of the phosphinimine−carbamate form compared to the betaine form [cf. Scheme 1]. It is important, however, to note that compounds **16**−**18** can be considered to be tautomeric forms of the corresponding betaines Y{6-*t*-Bu-4-Me-C_6H_2O}$_2$P$^+$-{NH-*t*-Bu}{N(CO_2R)N$^-$(CO_2R)} [Y = CH_2, S].

However, the solution and the solid-state ^{31}P NMR spectra of **16** [Figure 1] appear to be *inconsistent* with the X-ray structure. The δ(P) value of −56.3 [$C_6D_5CD_3$, 298 K, sharpens at higher temperatures] for **16** is clearly in the p*entacoordinate* region (cf. compounds **3**−**6**)[4] and quite upfield to the *tetracoordinate* region [cf. compounds **24**−**25** and **31**]. The solid-state ^{31}P NMR signal [δ −61.1]



31 [δ(P): -13.0, X-ray]

is also in the pentacoordinate region.[6g−h,18] Rather astonishingly, *at least four different signals* could be clearly identified at 255 K [cf. Figure 1]; upon warming to 298 K, the original spectrum was obtained. On the basis of previously available data,[4,18] these signals can be ascribed to pentacoordinate isomers **A**−**D** [Chart 2, the extra low intensity peak at 273 K is perhaps due to a conforma-

(10) Sherlock, D. J.; Chandrasekaran, A.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* **1997**, *119*, 1317.

(11) For the synthesis of cyclodiphosphazane derivatives **14**−**15**, see: Jefferson, R.; Nixon, J. F.; Painter, T. M.; Keat, R.; Stobbs, L. *J. Chem. Soc., Dalton Trans.* **1973**, 1414.

(12) We have also utilized (morpholino)P(N-*t*-Bu)$_2$P(NH-*t*-Bu) wherein the chlorine in **14** is replaced by a morpholino group. Interestingly, we have obtained the analogous compound (morpholino)P(μ-N-*t*-Bu)$_2$P-(N-*t*-Bu){N-(CO_2-*i*-Pr)-N(H)(CO_2-*i*-Pr)} (X-ray) in which only the −NH-*t*-Bu end has reacted. Details are available from the authors.

(13) The corresponding sulfur compound S(6-*t*-Bu-4-Me-C_6H_2O)$_2$P-{N(CO_2-*i*-Pr)N(CO_2-*i*-Pr)-C(O)-N} [mp 58−60 °C; IR (KBr) 2268, 1711, 1660 cm^{-1}; ^{31}P NMR δ 23.6] can also be prepared with S{6-*t*-Bu-4-Me-C_6H_2O}$_2$PNCO [^{31}P NMR δ 129.4]: Pavan Kumar, K. V. P.; Kumara Swamy, K. C. Unpublished results.

(14) Bone, S. A.; Trippett, S. *J. Chem. Soc., Perkin Trans. 1* **1976**, 156.

(15) The P═N bond length in Ph_3P═NC_6H_4Br is 1.57 Å. See: Corbridge, D. E. C. *Phosphorus*—*An Outline of its Chemistry, Biochemistry and Technology*, 4th ed.; Elsevier: Amsterdam, The Netherlands, 1990; p 47.

(16) Generally it is expected that amides show two or more bands for the *NH*-C(O) group due to hydrogen-bonded oligomers; we believe that our compounds also behave similarly. See: Williams, D. H.; Fleming, I. *Spectroscopic Methods in Organic Chemistry*, 4th ed.; Tata McGraw-Hill: New Delhi, India, 1987; pp 60−61 (Figures 2.13a−c).

(17) It is expected that the solution to solid-state difference in δ(P) will be ∼4 ppm [see: Holmes, R. R.; Prakasha, T. K.; Pastor, S. D. In *Phosphorus-31 NMR Spectral Properties in Compound Characterization and Structural Analysis*; Quin, L. D., Verkade, J. G., Eds.; VCH: New York, 1994; p 27], but in **16** this difference is slightly higher.

(18) (a) Said, M. A.; Pülm, M.; Herbst-Irmer, R.; Kumara Swamy, K. C. *J. Am. Chem. Soc.* **1996**, *118*, 9841. (b) Said, M. A.; Pülm, M.; Herbst-Irmer, R.; Kumara Swamy, K. C. *Inorg. Chem.* **1997**, *36*, 2044. (c) Kumaraswamy, S.; Kommana, P.; Satish Kumar, N.; Kumara Swamy, K C. *J. Chem. Soc., Chem. Commun.* **2002**, 40.

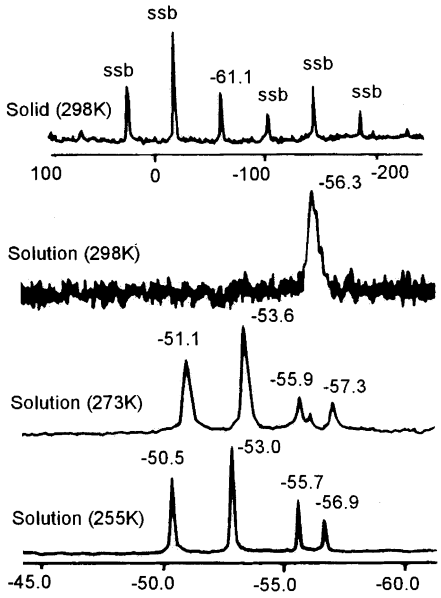
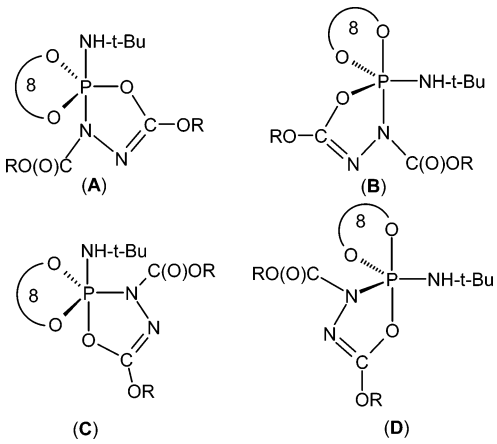


FIGURE 1. Solution (VT) and solid-state (5 kHz) ^{31}P NMR spectra for compound **16**; ssb refers to spinning sidebands. The spinning sidebands were verified by recording the solid-state spectrum at 7 kHz also.

CHART 2

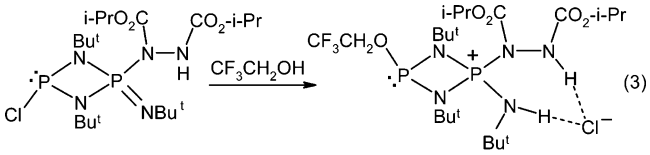


tional isomer involving the eight-membered ring[6g,h]. The bulky −NH-*t*-Bu group may not favor significant hexacoordination via the S→P bond; this assumption is consistent with a similar spectral pattern observed for **17** (see the Supporting Information for details) also. To our knowledge, this is the first ever observation of four distinct isomeric phosphoranes in solution.

It is likely that the formation of cyclophosphazane compounds XP(μ-N-*t*-Bu)$_2$P(N-*t*-Bu){N-(COO-*i*-Pr)-N(H)-(COO-*i*-Pr)} [X = Cl (**19**), NH-*t*-Bu (**20**); see above for drawings] from their precursors **14**−**15** also occurs through a betaine in a manner similar to that for **16**. The electron-rich P-NH-*t*-Bu end of **14** is the reactive center and the P−Cl end remains intact during the reaction. The X-ray structure of **19** (see the Supporting Information) shows (i) a very short P═N bond [P−N 1.488(3) Å] and (ii) a hydrogen-bonded carbamate NH-C(O)OR dimer; these features are analogous to that observed for **16**. The IR spectrum shows a strong band at 1202 cm^{-1} ascribable to ν(P═N). Thus it appears that in reactions of P(III)-NH-*t*-Bu compounds with DEAD/DIAD, the imine−carbamate type of structure is favored.

Compound **19** exhibits broad (solid as well as solution) signals in the ^{31}P NMR in tri-, tetra-, and pentacoordinate regions [major peaks in $C_6D_5CD_3$: 138.6 and 10.5 with ^2J(PP) < 5.0 Hz; 133.6 and −34.6 with ^2J(PP) of ∼16.0 Hz]. There was no significant improvement in the quality of the solution spectra at lower temperatures and the compound could be recovered after removal of solvent from the solution. Thus for **19**, we think that all the three forms, betaine, imine−carbamate, and pentacoordinate structures, are present in solution. Compound **20**, however, exhibited relatively sharp signals [$CDCl_3$: δ 68.9 for P(III) and −28.9 for the tetra-/pentacoordinate P (see above for discussion), ^2J(PP) < 5.0 Hz].

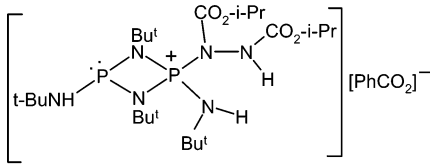
When compound **19** is treated with 1 mol equiv of 2,2,2-trifluoroethanol, the P(III)-Cl end reacts and the proton from the liberated HCl adds to the nitrogen at the P═N-*t*-Bu end to afford **21** (eq 3). This compound can be



19 **21** [δ(P) 11.7, 114.4; ^{2}J = 14.1 Hz]

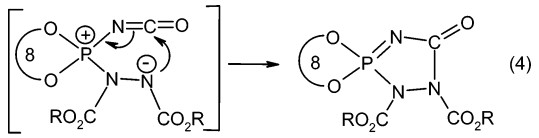
considered to be a protonated form of the betaine (CF_3-CH_2O)P(μ-N-*t*-Bu)$_2$P$^+$(NH-*t*-Bu){N-(CO_2-*i*-Pr)-N$^-$(CO_2-*i*-Pr)}. An X-ray structural analysis (see the Supporting Information) clearly reveals the hydrogen-bonded chloride. This kind of species [cf. structure **7**] is *one of the intermediates proposed in the Mitsunobu reaction*.

Compound **20** did not react with 2,2,2-trifluoroethanol as shown by ^{31}P NMR. However, when benzoic acid was added to a solution of **20** prepared in situ, the ^{31}P NMR of the solid obtained (after removal of all solvent) exhibited two major peaks (∼95%) at δ 80.7 and 1.1 (^2J(PP) < 7.0 Hz) that are quite different from that of **20**, but clearly in the tri- and tetracoordinate region. The ^{1}H NMR spectrum is also different from that of **20** and agrees with structure **E**, which is essentially the type of intermediate [cf. **7** and **21**] proposed in the Mitsunobu reaction. So far, we have not succeeded in obtaining the single crystals of this material.



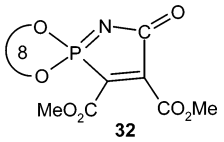
E

(ii) Cycloaddition Compounds 22−23 and Their Reactions with Catechol and 2,2′-Binaphthol To Lead to Addition Compounds 24−27. In the case of the P(III) isocyanate, CH_2(6-*t*-Bu-4-Me-C_6H_2O)$_2$P-NCO (**10**), the reaction with DEAD/DIAD takes an entirely different turn with the formation of the cyclic products **22**−**23**, presumably via betaine (eq 4) in a stepwise pathway.[19] The structure of **22** is proven by X-ray crystallography.[20] The formal P═N bond in this com-



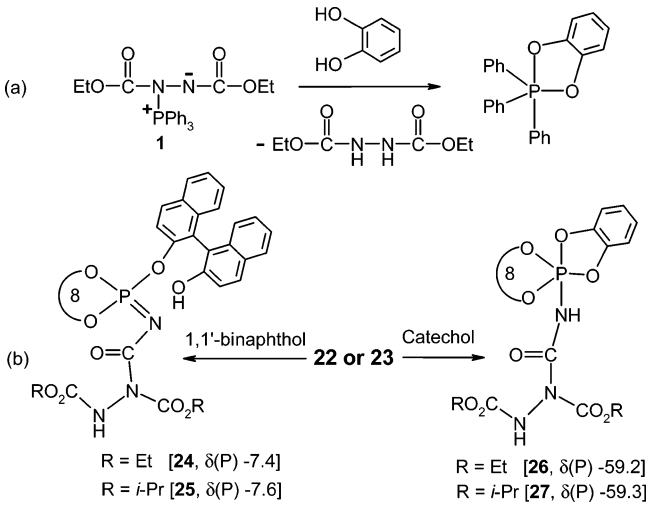
pound [P−N 1.564(4) Å] is significantly longer than that in **16** or **19**, suggesting some phosphonium character in it. Despite having a structure different from that of the betaine **1**, compound **23** *does participate in the Mitsunobu coupling* between ethanol and benzoic acid, suggesting that the five-membered heterocycle is in equilibrium with the betaine.

Previously, we have characterized the pentacoordinate *isothiocyanate* compound **4**, obtained from analogous reaction of CH_2(6-*t*-Bu-4-Me-$C_6H_2O)_2$P-NCS with DIAD;[4] the difference in the reactivity of this *isothiocyanate* from the *isocyanate* **10** probably stems from a better charge separation at the C═O end in the latter compared to the C═S end in the former. Reaction of **10** with DEAD/DIAD affording the heterocycles **22**−**23** can, however, be compared to the 1,3-(P,C) cycloaddition of **10** with $MeO_2CC{\equiv}CCO_2Me$ (DMAD, a dipolarophile) to form the heterocycle **32**.[18c]



In an earlier work, Trippett and co-workers used the betaine **1** (R = Et, R′ = Ph) as a precursor to various pentacoordinate phosphoranes [cf. Scheme 2a].[14] In these reactions, DEAD becomes the hydrazine derivative EtO_2-CNHNHCO$_2$Et and the pentacoordinate compound Ph_3P-[1,2-$O_2C_6H_4$] is formed. Later, this method was utilized for probing the mechanism of the Mitsunobu reaction.[7] In contrast to these, compounds **22**−**23** undergo a two-step addition depending on the diol. First the P−N single bond is cleaved and then addition across the P═N (double) bond takes place. When 1,1′-bi-2-naphthol is used, the reaction stops at the first stage to lead to tetracoordinate compounds **24** and **25**. When catechol is used, the addition across the P═N bond also takes place to lead to the pentacoordinate compounds **26**−**27**. These reactions are shown in Scheme 2b. The structures of **25** and **27** have been confirmed by X-ray crystallography. The P═N bond in **25** [P−N(1) 1.546(3) Å] is slightly shorter than that in **22**, but is still significantly longer than those in **16** or **19**. In the pentacoordinate compound **27** the newly formed −NHC(O)N(CO$_2$-*i*-Pr)NH(CO$_2$-*i*-Pr) and a catecholate oxygen are at the apical positions of trigonal-bipyramidal phosphorus. Thus, this compound

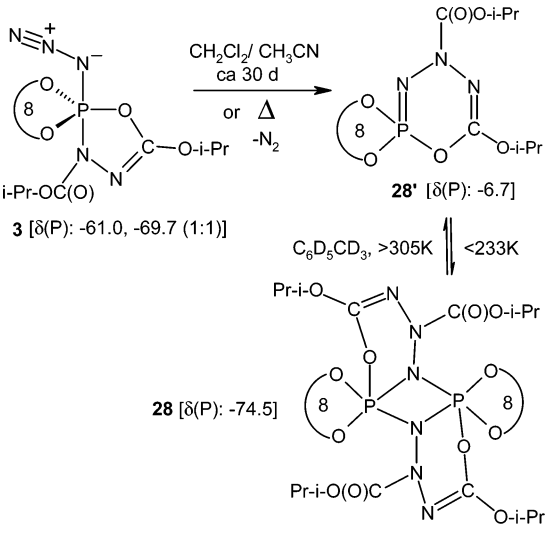
SCHEME 2



also falls into the category of pentacoordinate compounds with *reversed apicophilicity* that was alluded to in the Introduction.

(iii) Curtius-Type Rearrangement of the Azide Product 3 To Lead to 28. The behavior of the P(III) azide **11** compared to the isocyanate **10** toward DEAD/DIAD is different, although the azide (−N_3) group is isoelectronic to isocyanate (N═C═O). Isolation of the pentacoordinate azide CH_2(6-*t*-Bu-4-Me-$C_6H_2O)_2$P(N_3)-{N(CO$_2$-*i*-Pr)N-C(O-*i*-Pr)-O} (**3**) in the reaction of **11** with DIAD has been reported earlier.[4] However, during the process of recrystallization of **3**, it was noticed that a second type of crystals (**28**, rectangular blocks) with morphology much different from **3** (needles) formed at 5 °C over a period of several days. The same compound is also formed when a toluene solution of **3** is heated. The X-ray structure of **28** showed it to be a fused cyclodiphosphazane derivative (Scheme 3) that is *inconsistent with the* ^{31}*P NMR spectrum of* **28** [$C_6D_5CD_3$, δ(P) −6.7] *at room temperature*. A variable-temperature ^{31}P NMR study [see the Supporting Information] reveals that there is a dynamic equilibrium between the monomer (**28′**)[21] and

SCHEME 3



(19) Most of the cycloadditions are assumed to take place in a concerted fashion. However, there are examples in which the cycloaddition takes place stepwise. See: Huisgen, R.; Mloston, G.; Langhals, E. *J. Org. Chem.* **1986**, *51*, 4087.

(20) Previously a weak interaction between the β-nitrogen with isocyanate carbon was envisaged for compound **23** (ref 4), but no proof could be given.

the dimer (**28**) with the former predominating at higher temperatures. Formation of **28′** (and hence **28**) must occur through N_2 elimination from **3** followed by rearrangement; this is analogous to the formation of isocyanates from acid azides via Curtius rearrangement. Thus the identification of the monomer **28′** in addition to the structural characterization of **28** feature gives *firm evidence* for Curtius-type rearrangement involving pentacoordinate phosphorus.[22]

(iv) Formation of Pentacoordinate Product 29 and Hexacoordinate Product 30. In the precursors CH_2(6-*t*-Bu-4-Me-$C_6H_2O)_2$P($OCH_2CH_2NMe_2$) (**12**) and S(6-*t*-Bu-4-Me-$C_6H_2O)_2$P(OPh) (**13**) the phosphorus has three oxygen atoms around it. In addition, there is a possibility of N→P or S→P coordination that could stabilize hypervalent phosphorus. Treatment of **12** with DIAD afforded only the pentacoordinate compound **29** [^{31}P NMR, δ(P) −59.6, −66.7 (1:5)]; it is likely that steric factors have prevented the formation of the additional N→P coordinate bond. Hexacoordination, however, is realized in the product S(6-*t*-Bu-4-Me-$C_6H_2O)_2$P(OPh)[N(CO_2-*i*-Pr)-N-C(O-*i*-Pr)O] [**30**: δ(P) −67.0] obtained by starting with **13**. The S→P distance of 2.794(1) Å is in the range expected for such hexa-coordinate compounds.[10,23] Thus a new range of hexacoordinate phosphoranes can be realized with these reactions.

Summary

What we have shown here is that the naive-looking reaction of DEAD/DIAD with P(III) compounds, the key to the enormous synthetic utility of the Mitsunobu reaction, leads not just to the MBH betaine **1**, but has the potential to open up new frontiers. When electronegative substituents are present on P(III) precursors, one of the preferred pathways is the formation of pentacoordinate derivatives; if a suitable donor site in the substituents is available, hexacoordination is also possible. When reactive functionalities (NCO, N_3, etc.) are present on phosphorus, other pathways including cycloaddition are possible. The molecular formulas of the pentacoordinate (and hexacoordinate) compounds [**3**−**6**, **29**−**30**] or cycloaddition compounds [**22**−**23**] are the same as that of the corresponding betaines, but additional covalent bonding [O−P or N−C] makes them structurally different from the betaines. Finally, if a *tert*-butylamino group is available on the P(III) precursor, the phosphinimine−carbamate compounds [X-ray; e.g. **16**−**19**] are favored. These products are useful in stabilizing some of the intermediates proposed in the Mitsunobu reaction [e.g. **21**]. While compounds **16**−**19** can be considered to be the tautomeric forms of the corresponding betaines, compound **21** is the protonated form of the betaine. Currently, we are exploring this aspect further.

Experimental Section

The precursors CH_2(6-*t*-Bu-4-Me-$C_6H_2O)_2$PCl,[6h] S(6-*t*-Bu-4-Me-$C_6H_2O)_2$PCl,[10] and XP(μ-N-*t*-Bu)$_2$PNH-*t*-Bu [X = Cl (**14**, bp 140 °C/3 mm)[11] and NH-*t*-Bu (**15**)[11]] were prepared by literature procedures and sublimed/crystallized prior to use. The P(III) precursors S(6-*t*-Bu-4-Me-$C_6H_2O)_2$PX [X = NH-*t*-Bu (**8**), OPh (**13**)] or CH_2(6-*t*-Bu-4-Me-$C_6H_2O)_2$PX [X = NH-*t*-Bu (**9**), NCO (**10**),[18c] N_3 (**11**),[6g] $OCH_2CH_2NMe_2$ (**12**)] were prepared by the reaction of the chloro compound with the appropriate reagent from the following: (i) *tert*-butylamine, (ii) phenol + triethylamine, (iii) sodium cyanate, (iv) sodium azide, or (v) 2-(dimethylamino)ethanol.

S{6-*t*-Bu-4-Me-C_6H_2O}$_2$P(N-*t*-Bu){N(CO_2Et)NH(CO_2-Et)} (16). To a stirred solution of **8** [δ(P) 138.2] (1.23 g, 2.68 mmol) in toluene (15 mL) was added diethyl azodicarobxylate (DEAD) (0.46 g, 2.68 mmol) dropwise over a period of 10 min. After being stirred for 24 h, the solution was concentrated (ca. 4 mL) and heptane (ca. 1 mL) was added to obtain **16** as a crystalline solid. Yield: 1.35 g (80%). Mp: 170−171 °C. IR (KBr, cm^{-1}): 3262, 3159, 2965, 2361 (w), 1719, 1422, 1287, 1211, 1098. The two bands at 3262 and 3159 cm^{-1} are indicative of an amide −HNC(O) linkage. IR ($CHCl_3$): 3416, 3250 (vw), 3019, 1736, 1426, 1285, 1215, 1096 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.11 (d, $J \sim 2.0$ Hz, 9 H), 1.24 and 1.46 (2 s, 18 H), 1.32 (t, $J = 7.0$ Hz, 6 H), 2.25 and 2.32 (2 s, 6 H), 4.30 (qrt, $J = 7.0$ Hz, 4 H), 6.45 (br, 1 H), 7.08−7.31 (m, 4 H). ^{13}C NMR ($CDCl_3$): δ 14.7, 20.5, 20.8, 30.1, 31.3, 33.5 (d, $J = 10.2$ Hz), 34.4, 35.9, 51.2 (br), 61.9, 62.8, 120.0, 128.0, 128.5, 130.3, 130.8, 133.1, 133.7, 135.8, 148.0, 155.0 (d, $J \sim 12.0$ Hz), 155.9. ^{31}P NMR ($CDCl_3$): δ −56.2 (br). ^{31}P NMR (solid-state, center band determined by recording the spectra at 5 and at 7 kHz): δ −61.1. Anal. Calcd for $C_{32}H_{48}N_3O_6PS$: C, 60.67; H, 7.58; N, 6.64. Found: C, 60.42; H, 7.46; N, 6.59. This compound did not react with 2,2,2-trifluoroethanol at room temperature [^{31}P NMR].

CH_2(6-*t*-Bu-4-Me-$C_6H_2O)_2$P(N-*t*-Bu){N(CO_2Et)NH(CO_2-Et)} (17). DEAD (0.17 g, 1.0 mmol) was added in one lot to a solution of **9** [mp 116−118 °C, δ(P) 141.9] (0.44 g, 1.0 mmol) in dry toluene (10 mL) and the mixture was stirred for 72 h at room temperature. Removal of all the solvent afforded **17** as a white solid. Crystallization was done with a toluene−heptane mixture [4:3; 0.48 g (76%)]. Mp: 96−98 °C. IR (KBr, cm^{-1}): 3258, 3164, 1719, 1437, 1345, 1279, 1206, 1134, 1062, 933. IR ($CHCl_3$, cm^{-1}): 3407, 3299, 2967, 1738, 1443, 1219. ^{1}H NMR ($CDCl_3$): δ 0.97, 1.32, and 1.45 (3 br s, 33 H), 2.24 and 2.35 (2 s, 6 H), 3.75 (br m, 1 H), 4.17−4.28 (m, 3 H), 4.45 (qrt, $J \sim 4.5$ Hz, 2 H), 6.50 (br s, 1 H), 6.93−7.10 (m, 4 H). ^{13}C NMR ($CDCl_3$, a complex spectrum; for reasons see ^{31}P NMR data): δ 13.5, 14.0, 14.7, 20.8, 20.9, 30.6, 31.3, 31.8, 33.7, 33.8, 34.4, 34.9, 35.4, 36.1, 50.3, 50.5, 61.9, 63.1, 65.3, 126.7, 127.0, 128.9, 129.2, 130.0, 132.6, 132.8, 133.4, 140.2, 140.4, 147.0, 147.2, 154.5, 154.9, 155.6. ^{31}P NMR ($C_6D_5CD_3$): 298 K δ −56.3 (br), 242 K δ −48.0, −50.3 (major), −53.4, −54.2. ^{31}P NMR (solid state, taken at 5 and 7 kHz to determine the center peak): δ −50.2 (>93%), −2.5 (unassigned, minor). Anal. Calcd for $C_{33}H_{50}N_3O_6P$: C, 64.36; H, 8.18; N, 6.82. Found: C, 64.55; H, 8.13; N, 6.90.

CH_2(6-*t*-Bu-4-Me-$C_6H_2O)_2$P(N-*t*-Bu){N(CO_2-*i*-Pr)NH(CO_2-*i*-Pr)} (18). This compound was prepared similarly by using the same molar quantities as the ethyl compound in a yield of 87%. Mp: 174−178 °C. IR (KBr, cm^{-1}): 3346, 1713, 1694, 1601, 1468, 1389, 1302, 1204, 1105, 1028, 949, 916. IR ($CHCl_3$, cm^{-1}): 3418, 3281, 2926, 1744, 1460. ^{1}H NMR ($CDCl_3$): δ 1.32 (d, $J = 6.2$ Hz, 6 H), 1.38 (s, 18 H), 1.42, 1.45, and 1.49 (3 lines, 15 H), 2.33 and 2.35 (2 s, 6 H), 3.42 (dd, $J = 2.7$ and 16.0 Hz, 1 H), 5.17 (m, 3 H), 5.32 (s, 2 H), 7.07−7.20 (m, 4 H). ^{13}C NMR ($CDCl_3$): δ 20.9, 21.1, 21.6, 22.0, 22.6, 30.9, 33.3 (d, $J = 20.7$ Hz), 34.9, 35.3, 35.9, 70.0, 53.4, 74.8, 126.7, 127.1, 128.8, 129.4, 129.5, 133.0, 133.3, 134.6, 134.7, 140.0, 140.2, 147.2, 148.4, 149.1, 153.3. ^{31}P NMR ($CDCl_3$): δ −57.6 (br). Anal. Calcd for $C_{35}H_{54}N_3O_6P$: C, 65.93; H, 8.29; N, 6.40. Found: C, 66.02; H, 8.35; N, 6.48.

(21) The monomeric structure **28′** is consistent with the ^{31}P NMR chemical shifts for similar phosphinimines [e.g. δ(P) −8.3 for $(EtO)_3P{=}NSiMe_3$]. See: Tebby, J. C. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds.; VCH: Deerfield Beach, FL, 1987; pp 1−60.

(22) In the only other reported example in the literature, the structure of a similar dimeric species was assigned based on NMR and the mass spectrum; the monomeric species of type **28′** could not be detected. See: Baceiredo, A.; Bertrand, G.; Majoral, J.-P.; Wermuth, U.; Schmutzler, R. *J. Am. Chem. Soc.* **1984**, *106*, 7065.

(23) Holmes, R. R.; Prakasha, T. K.; Day, R. O. *Inorg. Chem.* **1993**, *32*, 4360.

ClP(μ-N-*t*-Bu)$_2$P(N-*t*-Bu){N-(COO-*i*-Pr)-N(H)(COO-*i*-Pr)} (19). DIAD (0.59 g, 2.92 mmol) in toluene (10 mL) was added dropwise to a stirred solution of **14** (0.91 g, 2.92 mmol) in toluene (20 mL). The mixture was stirred for 24 h at room temperature and concentrated to 2 mL, heptane (2 mL) was added to the residue, and crystals of **19** were obtained at 5 °C after ca. 24 h. Yield: 1.23 g (78%). Mp: 118−120 °C. IR (KBr, cm^{-1}): 3368, 3221, 1759, 1711, 1306, 1202, 899. ^{1}H NMR ($CDCl_3$): δ 1.26−1.56 (many lines, 39 H), 4.92−5.18 (m, 2 H). ^{13}C NMR ($CDCl_3$): δ 21.7, 27.8, 28.1, 30.8, 31.2, 51.8, 52.1, 52.5, 56.1, 57.0, 69.5, 70.1, 70.4, 128.1, 128.9, 153.1, 155.5. The spectra taken in toluene-d_8 were also too complicated to make a detailed assignment. ^{31}P NMR ($CDCl_3$): δ −38.0, 11.8, 133.6, 140.1. Anal. Calcd for $C_{20}H_{42}ClN_5O_4P_2$: C, 46.74; H, 8.23; N, 13.63. Found: C, 46.65; H, 8.32; N, 13.88.

(*t*-BuNH)P(μ-N-*t*-Bu)$_2$P(N-*t*-Bu){N-(COO-*i*-Pr)-N(H)-(COO-*i*-Pr)} (20). The procedure was the same as that for **19** with use of **15** [mp 142−144 °C; δ(P) 89.4] (2.26 g, 7.46 mmol) and DIAD (1.42 g, 7.46 mmol) to yield **20** [3.03 g, 74%]. Mp: 104−106 °C. IR (cm^{-1}): 3380, 3192, 1761, 1720, 1665, 1391, 1308, 1260. ^{1}H NMR ($CDCl_3$): δ 1.22 and 1.24 (2 d, $J \sim 6.0$ Hz, 12 H), 1.28, 1.32, 1.34, 1.38 (4 s, 36 H), 2.70 (d, $J = 10.0$ Hz, 2 H), 4.89−5.00 (m, 2 H). ^{13}C NMR ($CDCl_3$): δ 21.8, 22.1, 22.2, 30.9 (t, $J = 5.0$ Hz), 31.0 (t, $J = 5.0$ Hz), 32.7 (d, $J = 9.0$ Hz), 34.4 (d, $J = 9.0$ Hz), 51.1, 51.5 (t or dd, $J = 3.0$ Hz), 53.0 (d, $J = 9.0$ Hz), 68.8, 69.4, 153.3, (d, $J = 16.0$ Hz), 157.7. ^{31}P NMR ($CDCl_3$): δ −28.9, 68.9 ($^2J_{PNP} \leq 7.0$ Hz). Anal. Calcd for $C_{24}H_{52}N_6O_4P_2$: C, 52.35; H, 9.51; N, 15.26. Found: C, 52.25; H, 9.56; N, 15.41. This compound did not react with 2,2,2-trifluoroethanol.

[(CF$_3$CH$_2$O)P(μ-N-*t*-Bu)$_2$P$^+$(NH-*t*-Bu){N(CO$_2$-*i*-Pr)-(HNCO$_2$-*i*-Pr)}][Cl$^-$] (21). Trifluoroethanol (0.10 g, 0.97 mmol) was added dropwise to a stirred solution of **19** (0.50 g, 0.97 mmol) in toluene (20 mL), the mixture was stirred for 2 d then concentrated to 2 mL, and heptane (2 mL) was added to the residue. Crystals of **21** were obtained at 5 °C after ca. 2 d. Yield: 0.40 g (62%). Mp: 171−173 °C. IR (cm^{-1}): 3086, 1757. ^{1}H NMR ($CDCl_3$): δ 1.22 and 1.40 (2 d, $J \sim 6.0$ Hz, 12 H), 1.28 (s, 9 H), 1.52 (br s, 18 H), 4.25−4.50 (m), 4.89−5.15 (m, 2 H). ^{13}C NMR ($CDCl_3$): δ 21.5, 21.9, 27.7, 30.6, 30.8, 31.0, 55.6, 56.1, 57.5, 58.0, 69.8, 70.5, 73.4, 156.2, 157.0. ^{31}P NMR ($CDCl_3$): δ 11.7, 114.4 ($J \sim 16.0$ Hz). Anal. Calcd for $C_{22}H_{44}N_5O_5ClF_3P_2$: C, 43.08; H, 7.23; N, 11.43. Found: C, 43.12; H, 7.26; N, 11.55.

CH$_2$(6-*t*-Bu-4-Me-C$_6$H$_2$O)$_2$P{N(CO$_2$Et)N(CO$_2$Et)-C(O)-N} (22 as CH$_2$Cl$_2$ solvate). Diethyl azodicarboxylate (1.74 g, 10.0 mmol) was added in one lot to a solution of **10** [mp 124−126 °C] (4.11 g, 9.99 mmol) in dry toluene (20 mL) and the mixture was stirred for 72 h at room temperature. After removing the solvent, compound **22** was obtained as a white solid. This was crystallized (as CH_2Cl_2 solvate) with a dichloromethane−hexane mixture (3:4). Yield: 4.97 g (85%). Mp: 116−120 °C. IR (cm^{-1}): 2266, 1699, 1601, 1443, 1381, 1314, 1206, 1123, 961. Both bands at 1206 and 1314 cm^{-1} are strong, and hence the assignment of ν(P═N) stretch is difficult. ^{1}H NMR ($CDCl_3$): δ 1.25−1.43 (many lines, 24 H), 2.29 (s, 6 H), 3.71 (d, $J = 16.6$ Hz, 1 H), 4.27−4.57 (m, 5 H), 5.30 (s, 2 H), 7.01−7.10 (m, 4 H). ^{13}C NMR ($CDCl_3$): δ 14.0, 14.3, 20.9, 30.6, 34.7, 53.4, 64.4, 64.6, 128.0, 128.9, 130.0, 135.9, 139.7, 139.9, 147.2, 147.5, 152.5. ^{31}P NMR ($CDCl_3$): δ 26.6. Anal. Calcd (after drying in a vacuum for 2 h) for $C_{30}H_{40}N_3O_7P$: C, 61.52; H, 6.88; N, 7.17. Found: C, 61.48; H, 6.80; N, 7.20.

Compound **23** was prepared as described before.[4]

CH$_2$(6-*t*-Bu-4-Me-C$_6$H$_2$O)$_2$P(2,2′-OC$_{10}$H$_6$-C$_{10}$H$_6$-OH){NC-(O)-(CO$_2$Et)NH(CO$_2$Et)} (24). Racemic 1,1′-bi-2-naphthol (0.29 g, 1.00 mmol) was added in one lot to a solution of **22** (0.59 g, 1.00 mmol) in dry THF (10 mL) and the mixture was stirred for 72 h at room temperature. Removal of all the solvent afforded **24** as a white solid. Yield: 0.77 g (89%). Mp: 120−123 °C. IR (cm^{-1}): 3409, 3368, 1765, 1726, 1680, 1593, 1516, 1439, 1354, 1302, 1204, 1132, 1100, 1007. ^{1}H NMR ($CDCl_3$): δ 1.13 and 1.27 (2 t, $J \sim 6.0$ Hz, 6 H), 1.45 (s, 18 H), 2.25 (s, 6 H), 3.48 (d, $J = 15.8$ Hz, 1 H), 4.14 (br m, 4 H), 5.61 (br s, 1 H), 6.54 (br s, 1 H), 6.77−8.14 (m, 16 H). ^{13}C NMR ($CDCl_3$): δ 14.0, 14.3, 20.9, 30.2, 30.5, 34.4, 34.7, 61.8, 62.2, 63.0, 111.8, 114.2, 117.9, 119.2, 120.1, 123.1, 124.5, 125.3, 125.9, 126.1, 126.2, 126.9, 127.1, 127.2, 127.4, 127.9, 128.2, 128.3, 129.0, 129.1, 129.4, 129.9, 131.0, 131.6, 133.7, 133.9, 134.6, 135.0, 140.4, 140.6, 147.6, 152.8, 155.4. ^{31}P NMR ($CDCl_3$): δ −7.4. Anal. Calcd for $C_{50}H_{54}N_3O_9P$: C, 68.89; H, 6.20; N, 4.82. Found: C, 68.63; H, 6.10; N, 4.62.

CH$_2$(6-*t*-Bu-4-Me-C$_6$H$_2$O)$_2$P(2,2′-OC$_{10}$H$_6$-C$_{10}$H$_6$-OH){NC-(O)-(CO$_2$-*i*-Pr)NH(CO$_2$-*i*-Pr)} (25). Racemic 1,1′-bi-2-naphthol (0.29 g, 1.0 mmol) was added in one lot to a solution of **23** [mp: 170−173 °C[4]] (0.61 g, 0.99 mmol) in dry THF (10 mL) and the mixture was stirred for 72 h at room temperature. Crystallization was done with a toluene−heptane mixture (4:3, ca. 5 mL). Yield: 0.68 g (76%). Mp: 145−148 °C. IR (cm^{-1}): 3378, 1732, 1682, 1470, 1385, 1198 (vs), 1101, 1005. The strong band at 1198 cm^{-1} is most likely the ν(P═N) stretch. ^{1}H NMR ($CDCl_3$): δ 1.12, 1.16 (2 d + br s, 21 H), 1.46 (s, 9 H), 2.25 (s, 6 H), 3.50 (d, $J = 14.5$ Hz, 1 H), 4.83−4.95 (m, 2 H), 6.40 (br, 1 H), 6.67−8.11 (m, 16 H). ^{13}C NMR ($CDCl_3$): δ 20.7, 21.3, 21.5, 21.8, 30.1, 30.4, 34.2, 34.6, 69.4, 70.7, 114.9, 118.6, 120.2, 122.9, 124.4, 125.2, 125.6, 126.0, 126.8, 127.1, 127.7, 128.1, 128.9, 129.0, 129.6, 130.0, 130.5, 131.5, 133.6, 134.7, 137.7, 140.2, 146.8, 147.5, 152.4, 152.8, 154.8. ^{31}P NMR ($CDCl_3$): δ −7.6. Anal. Calcd (after drying in a vacuum for 2 h) for $C_{52}H_{58}N_3O_9P$: C, 69.31; H, 6.45; N, 4.66. Found: C, 69.05; H, 6.42; N, 4.58.

CH$_2$(6-*t*-Bu-4-Me-C$_6$H$_2$O)$_2$P(1,2-O$_2$C$_6$H$_4$){NHC(O)-N(COO-Et)NH(COOEt)} (26). The procedure was similar to that for **25** with **22** and catechol (0.11 g, 1.0 mmol). Removal of all the solvent afforded **26** as a white solid. Yield: 0.67 g (82%). Mp: 70−72 °C. IR (cm^{-1}): 3295, 1755, 1490, 1120, 1054. ^{1}H NMR ($CDCl_3$): δ 1.17 (s, 18 H), 1.29 and 1.38 (2 t, $J \sim 6.0$ Hz, 6 H), 2.38 (s, 6 H), 3.58 (d, $J = 14.0$ Hz, 1 H), 4.26 (br m, 4 H), 5.33 (br, 1H), 6.11 (br s, 1 H), 6.74−7.23 (m, 8 H). ^{13}C NMR ($CDCl_3$): δ 14.2, 14.4, 21.1, 30.3, 33.7, 34.5, 62.4, 63.9, 109.2 (d, $J = 13.2$ Hz), 110.4 (d, $J = 16.9$ Hz), 115.2, 119.7, 120.4, 123.3, 125.7, 126.4, 128.3, 129.1, 133.6, 133.8, 139.0, 139.2, 142.0, 144.4, 148.7, 149.0, 151.8, 155.9 (d, $J = 6.9$ Hz). ^{31}P NMR ($CDCl_3$): δ −59.2. Anal. Calcd for $C_{36}H_{46}N_3O_8P$: C, 63.60; H, 6.82; N, 6.18. Found: C, 63.46; H, 6.83; N, 5.98.

CH$_2$(6-*t*-Bu-4-Me-C$_6$H$_2$O)$_2$P(1,2-O$_2$C$_6$H$_4$){NHC(O)-N(CO$_2$-*i*-Pr)NH(CO$_2$-*i*-Pr)} (27). The procedure was similar to that for **25** with catechol (0.11 g, 1.0 mmol). Removal of all the solvent afforded **27** as a white solid. This was crystallized with toluene (ca. 4 mL). Yield: 0.58 g (80%). Mp: 118−120 °C. IR (cm^{-1}): 3290, 1752, 1491, 1375, 1258, 1101, 1034. ^{1}H NMR ($CDCl_3$): δ 1.10 and 1.12 (2 s, 18 H), 1.27 (d, $J = 6.0$ Hz, 6 H), 1.39 (d, $J \sim 6.0$ Hz, 6 H), 2.33 (s, 6 H), 3.55 (d, $J = 13.6$ Hz, 1 H), 4.95−5.18 (m, 3 H), 6.10 (br s, 1 H), 6.64−7.28 (m, 8 H), 9.98 (d, $J \sim 16.0$ Hz, 1 H). ^{13}C NMR ($CDCl_3$): δ 20.9, 21.3, 21.7 (3 s, Ar*C*H$_3$ + CH(*C*H$_3$)$_2$), 30.2 (s, C(*C*H$_3$)$_3$), 33.5 (s, *C*(CH$_3$)$_3$), 34.3 (s, Ar*C*H$_2$), 69.9, 71.9 (2 s, O*C*HMe$_2$), 108.9 (d, $J \sim 8$ Hz), 110.1 (d, $J \sim 8$ Hz), 119.4, 123.0, 125.2, 126.2, 128.1, 128.9, 133.3, 133.7, 138.9, 148.5, 148.8, 151.4, 155.1 (d, $J = 15.3$ Hz). ^{31}P NMR ($CDCl_3$): δ −59.3. Anal. Calcd (after drying in a vacuum for 2 h) for $C_{38}H_{50}N_3O_9P$: C, 63.05; H, 6.96; N, 5.80. Found: C, 63.15; H, 6.92; N, 5.87.

[{CH$_2$(6-*t*-Bu-4-Me-C$_6$H$_2$O)$_2$}P{OC(O-*i*-Pr)NN(CO$_2$-*i*-Pr)N}]$_2$ (28). Compound **3** (3.24 g, 5.28 mmol) was dissolved in CH_2Cl_2 (4 mL) and CH_3CN (∼4 mL) was added and left for crystallization. The first batch of crystals (of **3**) was removed and the mother liquor was left aside. After ∼30 d crystals of **28** were obtained. The same compound was formed upon heating a toluene solution, but other products were present and hence a pure compound could not be obtained by this route. Yield: 0.82 g (27%). Mp: 203−205 °C. ^{1}H NMR: δ 0.80 (d, $J = 6.0$ Hz, 12 H), 1.38 (s, 36 H), 1.41 (d, $J = 6.0$ Hz, 12 H), 2.29 (s, 12 H), 3.70 (br, 2 H), 4.15 (br, 2 H), 4.65−4.80 and

4.95−5.20 (m each, 4 H), 7.05 and 7.20 (2 s, 8 H). Variable-temperature ^{1}H NMR (after evacuation, $C_6D_5CD_3$) at selected temperatures: **243 K**, δ (broad signals) 1.16−1.49 (br) and 1.73, 1.79 (2 br s) [24 and 36 H], 2.30 (br s, 12 H), 3.78 (br, 2 H), 4.53 (br, 2 H), 5.40 and 5.85 (m each, 4 H), 7.21 and 7.27 (2 s, 8 H); **305 K**, δ 1.25 (d, J = 6.2 Hz, 6 H), 1.35 (d, J = 6.2 Hz, 6 H), 1.73 (s, 18 H), 2.28−2.33 (m, 6 H), 3.79 (br, 1 H), 4.25 (br, 1 H), 5.16 and 5.83 (m each, 2 H), 7.20, 7.21, 7.24, and 7.32 (4 s, 4 H). Low-intensity peaks (∼10%) at ca. 1.60 and 2.20 ppm, probably due to the dimer, were also seen. ^{13}C NMR ($C_6D_5CD_3$): 21.4, 21.6, 22.0, 22.1, 30.3, 31.0, 32.0, 34.8, 35.0, 37.8, 68.6, 70.0, 72.0, 72.8, 74.6, 124.5, 125.0, 125.2, 125.4, 126.0, 126.4, 132.4, 133.2, 133.5, 134.3, 135.0, 137.3, 139.3, 140.3, 141.1, 146.8, 151.0, 155.1 [this spectrum was recorded at 294 K where both monomer and dimer are present in solution and hence include many lines]. ^{31}P NMR ($C_6D_5CD_3$): δ at 243 K −74.5; at 294 K −6.5, −74.7 (∼2:1); at 305 K −6.5 [also see the Supporting Information, Figure S10]. ^{31}P NMR ($CDCl_3$): δ 15.8 (∼ 95%), −6.7 (∼ 5%). The peak at δ 15.8 ppm in $CDCl_3$ may perhaps be due to the isomeric phosphonium salt. The ^{31}P NMR spectrum ($C_6D_5CD_3$) recorded immediately after heating compound **28** under neat conditions at 120 °C exhibited two peaks at δ −6.5 (70%) and −10.3 (30%). Anal. Calcd for $C_{62}H_{88}N_6O_{12}P_2$: C, 63.57; H, 7.57; N, 7.17. Found: C, 63.71; H, 7.61; N, 7.20.

CH_2{6-*t*-Bu-4-Me-C_6H_2O}$_2$P($OCH_2CH_2NMe_2$){N(CO_2-*i*-Pr)NC(O-*i*-Pr)O} (29). DIAD (0.20 g, 1.0 mmol) was added in one lot to a solution of CH_2(6-*t*-Bu-4-Me-$C_6H_2O)_2POCH_2CH_2NMe_2$ (**12**) [δ(P) 129.0] (0.46 g, 1.0 mmol) in dry toluene (10 mL) and the mixture was stirred for 72 h at room temperature. After removal of all the solvent, **29** was obtained as white solid. Yield: 0.46 g (70%). Mp: 198−202 °C. IR (cm^{-1}): 1682, 1597, 1510, 1259, 1172, 1109, 1020. ^{1}H NMR ($CDCl_3$): δ 1.35 (br, 30 H), 2.20 and 2.30 (2 s, 12 H), 2.55 (t, J ∼ 6.0 Hz, 2 H), 3.45 (d, J ∼ 14.0 Hz, 1 H), 4.35 (m, 3 H), 5.0 (br m, 2 H), 6.95−7.25 (m, 4 H). ^{13}C NMR ($CDCl_3$): δ 21.0, 22.0, 31.1, 34.1, 35.0, 45.6, 70.5, 72.7, 127.8, 128.8, 132.8, 135.2, 141.1, 144.7, 153.1, 153.5, 155.0. ^{31}P NMR ($CDCl_3$): δ −59.6, −66.7 (1:5). Anal. Calcd for $C_{35}H_{54}N_3O_7P$: C, 63.70; H, 8.25; N, 6.37. Found: C, 63.61; H, 7.98; N, 6.20.

S{6-*t*-Bu-4-Me-C_6H_2O}$_2$P(OPh){N(CO_2-*i*-Pr)NC(O-*i*-Pr)O} (30). To a solution of **13** [δ(P) 136.1] (0.84 g, 1.75 mmol) in toluene (15 mL) was added diisopropylazodicarboxylate (DIAD) (0.35 g, 1.75 mmol) dropwise over a period of 10 min. After being stirred for 1 d, the solution was concentrated to ca. 3 mL and heptane (0.5 mL) was added. Crystals of **30** (0.96 g, 80%) were obtained at 5 °C after a day. These were used for X-ray structure determination. Mp: 179−181 °C. IR (KBr, cm^{-1}): 2961, 1721, 1672, 1593, 1437, 1408, 1277, 1209, 1107, 1049. ^{1}H NMR: δ 1.01, 1.05, 1.07, and 1.43 (d each, 12 H, J ∼ 6.2 Hz), 1.42 and 1.47 (2 s, 18 H), 2.21 and 2.31 (2 s, 6 H), 4.54 and 4.85 (2 m, 2 H), 7.07−7.40 (m, 9 H). ^{13}C NMR: δ 20.8, 21.5, 21.8, 21.9, 29.6, 29.9, 34.8, 34.9, 69.5, 72.5, 118.4, 118.6, 122.2, 122.3, 124.1, 124.3, 129.0, 129.6, 130.0, 130.7, 131.1, 131.4, 131.6, 137.8, 138.0, 138.7, 138.9, 151.8, 152.1, 152.4, 152.6, 153.6, 153.8. ^{31}P NMR ($CDCl_3$): δ −67.0. Anal. Calcd for $C_{36}H_{47}N_2O_7PS$: C, 63.35; H, 6.93; N, 4.10. Found: C, 63.66; H, 7.13; N, 4.29.

Crystal Data. Compound 16: $C_{32}H_{48}N_3O_6PS$, M = 633.76, triclinic, space group $P\bar{1}$, a = 10.681(9) Å, b = 10.761(3) Å, c = 17.409(4), α = 74.34(7)°, β = 72.41(5)°, γ = 71.50(11)°, V = 1775.1(16) Å^3, Z = 2, ρ = 1.186 g cm^{-3}, F_{000} = 680, μ = 0.180 mm^{-1}; data/restraints/parameters 6237/0/405; S(all data) = 1.009; R indices ($I > 2\sigma(I)$) R1 = 0.0629, wR2 (all data) = 0.2057; max/min residual electron density (e Å^{-3}) 0.481/−0.343.

Compound 19: $C_{20}H_{42}ClN_5O_4P_2$, M = 513.98, triclinic, space group $P\bar{1}$, a = 11.439(2) Å, b = 14.028(3) Å, c = 19.909(2) Å, α = 76.23(4)°, β = 75.65(4)°, γ = 80.66(2)°, V = 2987.9(9) Å^3, Z = 4, ρ = 1.143 g cm^{-3}, F_{000} = 1104, μ = 0.265 mm^{-1}; data/restraints/parameters 10535/0/585; S(all data) = 1.044; R indices ($I > 2\sigma(I)$) R1 = 0.0605, wR2 (all data) = 0.2143; max/min residual electron density (e Å^{-3}) 0.526/−0.287.

Compound 21: $C_{22}H_{45}ClF_3N_5O_5P_2$, M = 614.02, monoclinic, space group $P2_1/c$, a = 18.2506(18) Å, b = 9.7929(16) Å, c = 18.982(2) Å, β = 109.54(4)°, V = 3197.2(7) Å^3, Z = 4, ρ = 1.276 g cm^{-3}, F(000) = 1304, μ = 0.275 mm^{-1}; data/restraints/parameters 5628/0/357; S(all data) = 1.572; R indices ($I > 2\sigma(I)$) R1 = 0.1114, wR2 (all data) = 0.2830; max/min residual electron density (e Å^{-3}) 0.680/−0.710 [note: since the data quality is not good, the bond parameters are not used for accurate comparison].

Compound 22·CH_2Cl_2: $C_{31}H_{42}Cl_2N_3O_7P$, M = 670.55, orthorhombic, space group $Pcab$, a = 15.1196(18) Å, b = 17.9591(16) Å, c = 25.632(2) Å, V = 6959.9(12) Å^3, Z = 8, ρ = 1.280 g cm^{-3}, F_{000} = 2832, μ = 0.280 mm^{-1}; data/restraints/parameters 6087/0/415; S(all data) = 1.102; R indices ($I > 2\sigma(I)$) R1 = 0.0614, wR2 (all data) = 0.2077; max/min residual electron density (e Å^{-3}) 0.341/−0.383.

Compound 25·$^3/_2C_6H_5CH_3$: $C_{62.5}H_{70}N_3O_9P$, M = 1038.19, triclinic, space group $P\bar{1}$, a = 12.4123(7) Å, b = 16.2723(10) Å, c = 17.5862(10) Å, α = 63.7960(10)°, β = 70.9040(10)°, γ = 79.2730(10)°, V = 3007.9(3) Å^3, Z = 2, ρ = 1.146 g cm^{-3}, F_{000} = 1106, μ = 0.101 mm^{-1}; data/restraints/parameters 10548/19/684; S(all data) = 1.098; R indices ($I > 2\sigma(I)$) R1 = 0.0759, wR2 (all data) = 0.2170; max/min residual electron density (e Å^{-3}) 0.631/−0.505.

Compound 27·$^3/_2C_6H_5CH_3$: $C_{97}H_{124}N_6O_{18}P_2$, M = 1723.96, triclinic, space group $P\bar{1}$, a = 9.6724(8) Å, b = 11.9518(10) Å, c = 22.0645(19) Å, α = 80.273(2)°, β = 86.782(2)°, γ = 73.459(2)°, V = 2409.9(4) Å^3, Z = 1, ρ = 1.188 g cm^{-3}, F_{000} = 922, μ = 0.113 mm^{-1}; data/restraints/parameters 8496/14/581; S(all data) = 1.019; R indices ($I > 2\sigma(I)$) $R1$ = 0.0691, wR2 (all data) = 0.1325; max/min residual electron density (e Å^{-3}) 0.445/−0.384.

Compound 28: $C_{62}H_{88}N_6O_{12}P_2$, M = 1171.32, monoclinic, space group $P2/n$, a = 17.050(2) Å, b = 10.0336(12) Å, c = 19.816(2) Å, β = 92.216(2)°, V = 3387.5(7) Å^3, Z = 2, ρ = 1.148 g cm^{-3}, F_{000} = 1256, μ = 0.124 mm^{-1}; data/restraints/parameters 5951/44/370; S(all data) = 1.069; R indices ($I > 2\sigma(I)$) R1 = 0.0816, wR2 (all data) = 0.2662; max/min residual electron density (e Å^{-3}) 0.666/−0.550.

Compound 30: $C_{36}H_{47}N_2O_7PS$, M = 682.79, monoclinic, space group $P2_1/c$, a = 20.7843(12) Å, b = 10.6218(6) Å, c = 16.7361(10) Å, β = 99.050(10)°, V = 3648.8(4) Å^3, Z = 4, ρ = 1.243 g cm^{-3}, F_{000} = 1456, μ = 0.181 mm^{-1}; data/restraints/parameters 6433/0/436; S(all data) = 1.008; R indices ($I > 2\sigma(I)$) R1 = 0.0534, wR2 (all data) = 0.1632; max/min residual electron density (e Å^{-3}) 0.486/−0.533.

Additional Comments on the Bond Lengths and Bond Angles in the Structures Reported Here. The P=N(*t*-Bu) bond in **19** is extremely short (similar to that in **16**); even in **21**, the P−NH(*t*-Bu) bond [1.585(7) Å] is shorter than those normally observed for P−N single bonds. The O−P−O bond angle in the eight-membered ring at the X{6-*t*-Bu-4-Me-C_6H_2O}$_2$P [X = CH_2, S] varies between 96.8(2)° and 117.5(2)° and thus allows easy geometry adjustment at phosphorus depending upon the other substituents. In compound **30**, instead of the eight-membered ring as in **16**, two fused five-membered rings are generated because of sulfur coordination to phosphorus. This in turn makes the corresponding O−P−O bond angle approach the expected 90° in a distorted octahedral geometry. Interestingly, the N−P−N angles (in the four-membered cyclodiphosphazane ring) at the phosphorus bearing the DIAD residue in the tetracoordinate compounds **19** and **21** are 83.2(2)° and 85.3(3)°, respectively, whereas it is 75.7(2)° in the pentacoordinate compound **28**. This difference is perhaps due to higher number of substituents on phosphorus in **28** (relative to **19** or **21**) forcing the N−P−N angle at the cyclophosphazane ring to contract.

Acknowledgment. This work was supported by the Department of Science and Technology (DST), New Delhi. We also thank the Council of Scientific and Industrial Research, New Delhi for fellowships to P.K.

and N.S.K., Dr. Sudha Kumaraswamy for useful suggestions, DST (New Delhi) and NUS (Singapore) for Single Crystal Diffractometer facilities, and SIF, Indian Institute of Science (Bangalore) for solid-state ^{31}P NMR.

Supporting Information Available: X-ray structural information for **16**, **19**, **21**, **22**, **25**, **27**, **28**, and **30** as a CIF file; ORTEP drawings for **16**, **19**, **21**, **22**, **25**, **27**, **28**, and **30**; variable-temperature ^{31}P NMR data for **17** (including solid state) and **28**; ^{31}P NMR data with structural drawings. This material is available free of charge via the Internet at http://pubs.acs.org.

JO035634D