Selective and Efficient Syntheses of Perhydro-1,3,5-triazine-2,4,6-triones and Carbodiimides from Isocyanates Using $ZP(MeNCH_2CH_2)_3N$ Catalysts

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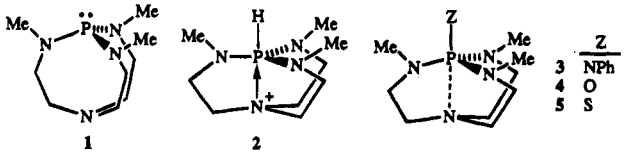
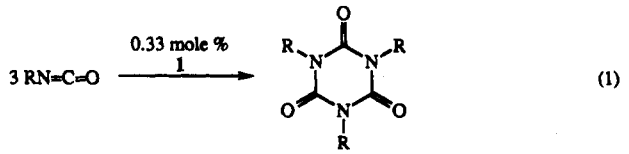
With concentrations as low as 0.0033 mol % $ZP(MeNCH_2CH_2)_3N$ (Z = lone pair, **1**) isocyanates are catalytically trimerized to perhydro-1,3,5-triazine-2,4,6-triones (isocyanurates) at room temperature. This reaction proceeds readily in the presence or absence of solvent, and the catalyst can be recycled at least six times without detectable degradation. Though not as potent a catalyst as **1**, the molecule in which Z = NPh (**3**) also facilitates this reaction, and evidence is adduced that the catalytically active species is the adduct **3**•ArNCO (**6**). In contrast, $Ch{=}P(MeNCH_2CH_2)_3N$ (Ch = O, **4**; Ch = S, **5**) selectively catalyze the transformation of isocyanates to carbodiimides and do so more efficiently than their acyclic analogues $O{=}P(NMe_2)_3$ and $(MeO)_2P(S)Ph$, respectively. The crystal structure of **4** is reported for the first time, and details of the crystal structure of $[PhN{=}C(SMe)P(MeNCH_2CH_2)_3N]I$ reported earlier by us in preliminary form are presented. Both structures support the hypothesis that $P{-}N_{ax}$ transannulation plays a lead role in the catalytic activities of **1** and **3**–**5**.

Introduction

In the course of our synthetic and structural investigations of proazaphosphatrane **1**, its azaphosphatranium derivative **2**, and quasi-azaphosphatrane derivatives such as **3**–**5**,[1–6] we have discovered that **1** is a nonionic



superbase[5] useful in organic synthesis as a deprotonation agent and that it functions as a superior catalyst for the rapid and clean conversion of aryl isocyanates to perhydro-1,3,5-triazine-2,4,6-triones (isocyanurates):[7]



(1)

Isocyanurates, which in some cases are stable to 400 °C,[8] enhance the dimensional and hydrolytic stability of urethane polymer networks and also impart low combustibility.[9] Hence, the efficient trimerization of isocyanates is currently of considerable commercial importance, especially in the production of rigid urethane-modified isocyanurate foams.[10] Triaryl isocyanurates are also useful as activators for the continuous anionic polymerization and postpolymerization of ϵ-caprolactam to nylon-6 possessing a low monomer content and a highly stable melt viscosity.[11] Triallyl isocyanurate is used to make polymers for the preparation of flame-retardant laminating materials for electrical devices.[12a] It is also utilized as a cross-linking agent for plastics[12b] and as a monomer in making copolymer resins that are water-resistant, transparent, and impact-resistant.[12c–f]

Catalysts for the trimerization of isocyanates include a broad range of compound types.[13–19] Among these catalysts are neutral Lewis bases such as amines,[13a,15,17] NO,[13b] a phosphorus ylide,[13c] trialkyl arsenic oxides,[13d] alkoxyalkenes,[14] aminoalkyl silicates,[18] and anions such as cyanate[16] and phenoxide.[19] Metallic compounds such as organotin alkoxides and oxides,[13e,f] an arene manganese tricarbonyl,[13g] alkylzinc amides and alkoxides,[13h]

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and copper(II) and nickel(II) halides[13b] have also been employed, which in some cases could induce a Lewis acid catalyzed pathway.[13b,h]

As part of our continuing exploration of the catalytic properties of **1**, we report here (1) the extension of our catalysis studies to the trimerization of alkyl isocyanates, (2) an investigation of the lifetime of catalyst **1** in trimerization reactions, and (3) how far the catalyst concentration can be reduced without seriously impairing the rate of trimerization. We also report on the catalytic activity and selectivity of **3** in converting isocyanates to isocyanurates and on the greater activity of **4** and **5** in

$$2\mathrm{RNCO} \xrightarrow{\textbf{4 or 5}} \mathrm{RN{=}C{=}NR} + \mathrm{CO_2} \qquad (2)$$

catalytically transforming isocyanates to carbodiimides compared with their acyclic analogues $O{=}P(NMe_2)_3$ and $(MeO)_3P(S)Ph$, respectively. The effect of partial transannulation in **3**–**5** on their catalytic activities will be discussed.

Results and Discussion

Isocyanurate Formation Catalyzed by 1. In the following paragraphs the three major advantages of **1** over a variety of other catalysts for the trimerization of isocyanates will be discussed.

First, a substantial variety of isocyanates can be used as substrates for catalyst **1**. Compound **1** catalyzes the trimerization of phenyl isocyanate quantitatively and in >99% purity within a few minutes (entry 1, Table 1). The IR spectrum of the reaction mixture reveals no band characteristic of the N=C=O group at 2260 cm^{-1}. An electron-donating group on the aromatic ring of an aryl isocyanate renders the carbonyl less electrophilic, and hence more difficult to trimerize, as has been shown to be the case for p-MeC_6H_4NCO, which other catalysts fail to trimerize.[14] Using **1** as the catalyst, we find that even the much stronger electron-donating p-$MeOC_6H_4$ moiety leads to a 99% isolated yield of trimer on extension of the reaction time to 8 min (entry 4 in Table 1).

Few catalysts have been reported to trimerize alkyl isocyanates. In the presence of Et_3N, for example, ethyl isocyanate trimerizes in 65% yield after 20 h at 70 °C and 800 MPa.[15] In contrast, **1** readily catalyzes this transformation with 100% conversion and in 82% isolated yield in 5 min at room temperature (Table 1, entry 7). An earlier preparation of triallyl isocyanurate involves the reaction of allyl chloride and highly toxic potassium cyanate at 150 °C and gives a poor (ca. 30%) yield.[16a] Although improvements in the yield were reported later, the purification procedures were complicated.[16b-f] A two-step synthesis for triallyl isocyanurate includes the initial formation of triallyl cyanurate via the reaction of cyanuric chloride with allyl alcohol followed by thermal rearrangement to the corresponding isocyanurate in toluene containing Cu and $FeCl_2/SnCl_4$[20a] or a salt of Cu[20b] or by employing DMF as a solvent containing a methyl silicate drying agent.[20c] In the present work, **1** quantitatively trimerizes allyl isocyanate (entry 8, Table 1) as shown by the lack of a detectable N=C=O band in the IR spectrum of the reaction mixture. Moreover, the spectrum was identical with that of pure triallyl isocyanurate obtained in 75% yield by distillation of the product.

Table 1. Synthesis of Isocyanurates Catalyzed by 1[a]

entry	RNCO R	RNCO mmol	T (°C)	reactn solvent (mL)	reactn time	isolated yield (%)
1	Ph	150	25	PhH (5)	3 min	97
2	Ph	150	25	none	2 min	94
3	Ph	150	65	PhH (80)	40 h	96
4	p-$MeOC_6H_4$	75	25	PhH (5)	8 min	99
5	p-$MeOC_6H_4$	75	25	none	5 min	94
6	p-$MeOC_6H_4$	150	65	PhH (80)	72 h	95
7	Et	25	25	THF (1)	5 min	82
8	$CH_2{=}CHCH_2$	23	25	THF (1)	3 days	75[b]

[a] Using 0.33 mol % **1**. Conversion was 100% according to the IR and ^1H NMR spectra of the crude product. [b] The yield upon distillation of a small scale reaction.

Secondly, **1** can be used in relatively small quantities for rapid and efficient isocyanate trimerization. Normally, substantial amounts of other catalysts are required to achieve reasonable yields of isocyanurates. For example, triphenyl isocyanurate was obtained in 63% yield in an overnight reaction catalyzed by $Si(OCH_2CH_2NMe_2)_4$.[18] Triphenyl and tris(p-chlorophenyl) isocyanurate was obtained in 66 and 80% yields, respectively, in 24 h using 5% alkoxyalkenes as catalysts.[14] It is noteworthy that such catalysts fail to trimerize the less reactive p-MeC_6H_4NCO or alkyl isocyanates. Triaryl and trialkyl isocyanates were obtained in 22–100% yield after 20 h at 100 °C and 800 MPa in the presence of 10% Et_3N.[15] According to Table 1, however, such catalyses can be accomplished in quite short time periods under very mild conditions with a small amount of **1**.

We were interested in determining how far the catalyst concentration could be reduced while maintaining reasonable catalytic efficiency. As is seen in Table 2, when the concentration of **1** is 0.083 mol % (a 4-fold reduction from entries **1** and **2** in Table 1) the trimerization of phenyl isocyanate reaches completion in 15 min giving the corresponding isocyanurate in 93% isolated yield. After stepwise reduction of this catalyst ratio to 0.0033 mol % (i.e., ~0.3 mg of **1**) a reasonable yield (76%) of the trimer could still be isolated after the reaction mixture was stirred for 24 h.

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Table 2. Room Temperature Synthesis of Triphenyl Isocyanurate with Varying Catalyst (1) Concentration[a]

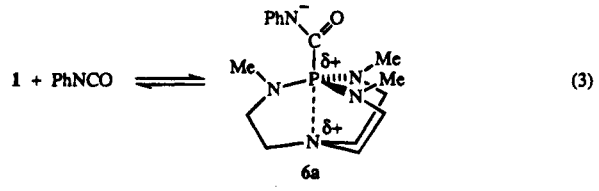
				product yield[b]	
entry	mol % of 1	PhNCO (g)	reactn time	g	%
1	0.083	4.38	15 min	4.90	92.8
2	0.033	5.48	38 min	6.01	91.3
3	0.0066	5.48	15 h	5.97	90.6
4	0.0033	5.48	24 h	5.00	75.9

[a] One mL of THF was used to dissolve the catalyst **1**. [b] The product crystallizes with 1 mol of THF as was shown by integration of its ^{1}H NMR spectrum. THF was removed *in vacuo* at 40–50 °C.

Thirdly, the catalyst survives repeated use. For the first cycle of the catalyst **1** (0.33 mol %) was dissolved in THF (5 mL) and phenyl isocyanate (5.48 g) added to the catalyst solution. After the mixture was stirred for 5 min at room temperature, the solid trimer was filtered *in vacuo*, washed within the filter with pentane (3 × 3 mL), and dried in vacuo to give the corresponding 1:1 isocyanurate•THF complex (as indicated by ^{1}H NMR spectroscopy). The filtrate and washings were combined, concentrated to ~5 mL, and then reused for the second cycle. This procedure was repeated for all six cycles. The yield of product ranged from 82.4% in the first run to 108.0% in the sixth run (the latter owing to incomplete precipitation in the previous run) with an average isolated yield of 97.8%.

A variety of organic solvents lend themselves to these catalytic trimerization reactions, including benzene, THF, toluene, and DMF. In these solvents, catalyst **1** is very soluble whereas the solid trimers are less so, facilitating easy separation by filtration and recycling of the filtrate containing the catalyst. As can be seen from Table 1, large ratios of solvent to substrate lengthen reaction times in part because the reaction is exothermic. Thus, the temperature rise accelerates the reaction when small amounts of solvent are used.

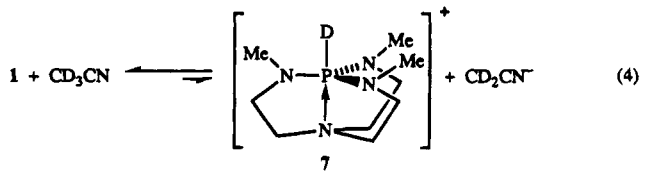
Acetonitrile is not recommended for these trimerizations owing to an interesting side reaction. Compound **1** appears to be stable in CD_3CN for days and at least for 12 h at 50 °C according to ^{31}P NMR spectra for these solutions, which exhibit only a peak for **1** at 119.95 ppm. However, 15 min after PhNCO was added to such a solution at room temperature, a peak at 30.03 ppm had grown to 20 times the intensity of the peak at 119.95 ppm. We tentatively assigned the peak at 30.03 ppm to intermediate **6a** in reaction 3 (*vide infra*). With the



(3)

6a

passage of time, this peak decreased as a 1:1:1 triplet at −9.98 ppm ($^1J_{PD}$ = 73.6 Hz) and the 119.95 ppm peak grew. After 30 h, the peak at 30.03 ppm had disappeared and those at −9.98 and 119.95 ppm remained for weeks in the ratio 1:4.3. Simultaneous with the disappearance of the peak at 30.03 ppm, crystals appeared which upon ^{1}H NMR, ^{13}C NMR, HRMS, and mp analysis were shown to be triphenyl isocyanurate. The 1:1:1 triplet at −9.98 ppm was undoubtedly due to the deuterium analogue of **2** (δ^{31}P −10.6 ppm, $^1J_{PH}$ = 491 Hz[1a]). The observation that it appears only after PhNCO is added suggests that equilibrium 4, though small, may be driven to the right by reaction 5. Apparently the latter reaction can compete



(4)

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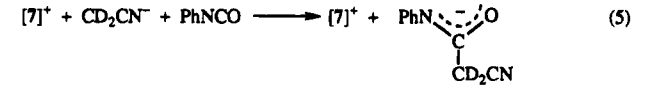
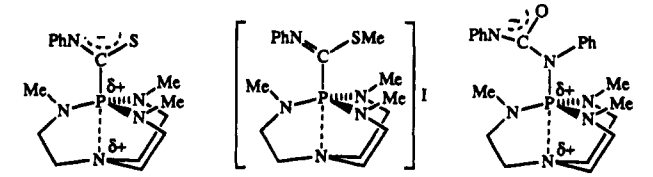


(5)

with the catalytic trimerization reaction for PhNCO. Attempts to isolate **7**(PhNC(O)CD_2CN) failed as did addition of MeI or Me_3OBF_4 for the purpose of isolating the alkylated anion.

Additional evidence for intermediate **6a** in the trimerization of PhNCO has been gathered. Fifteen minutes after 3 equiv of PhNCO was added to a solution of **1** in C_6D_6, ^{31}P NMR peaks at 120.3 ppm (**1**) and 29.46 ppm (presumably **6a**) were observed in a ratio of 1:1.5. After about 7 h, only the downfield peak remained and triphenyl isocyanurate precipitated. Although the ^{1}H spectrum of the reaction mixture after 15 min was complex, the ^{13}C NMR spectrum revealed nonbenzenoid chemical shifts consistent only with the presence of **1**, trimer, and **6a**. Moreover, the doublet at 161.08 ppm ($^1J_{PC}$ = 201.6 Hz) assigned to the carbonyl carbon of **6a** is in the region of the thiocarbonyl carbon of **8** (178.41 ppm, $^1J_{PC}$ = 187.8 Hz) which was isolated and structurally characterized by X-ray means as its derivative **9**(I).[6] The ^{31}P chemical shift of **6a** (29.46 ppm) is close to that of its analogue **8** (29.60 ppm). An attempt to isolate **6a** from a 1:1

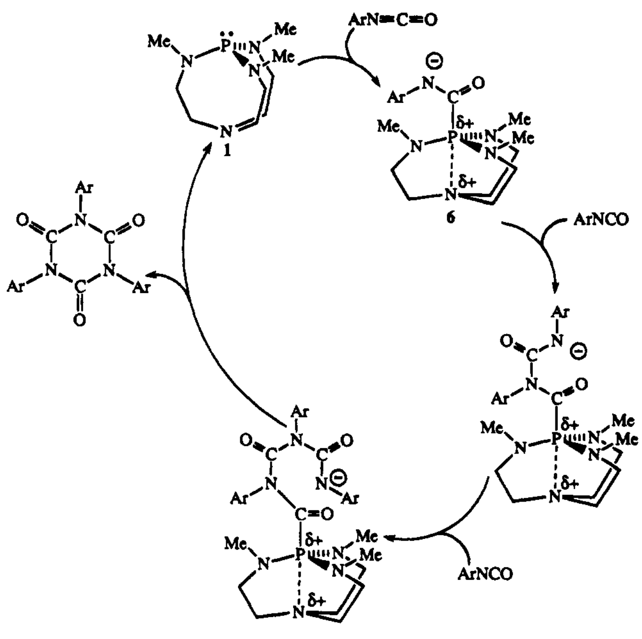


8 **9** **10**

equimolar mixture of **1** and phenyl isocyanate in Et_2O resulted in a precipitate which upon filtration gave a powder whose FAB mass spectrum revealed a strong peak for **6a** at 336.1 Da $(M + H)^+$ (with no detectable peaks of higher mass) and a base peak for **1** at 217.1 Da $(M + H)^+$. Because FAB/MS gave $(M + H)^+$ peaks for analogous species such as zwitterionic **8** and cationic **9**,[4,5] it is likely that **6a** is an intermediate that exists in detectable concentration in this catalytic reaction depicted in Scheme 1. Attempts to purify the precipitate or to trap **6a** as an alkylated cation by adding MeI to the reaction mixture failed. The ^{1}H NMR spectrum of the mixture formed in reaction 3, to which MeI had been added, was complicated and resisted interpretation. ^{31}P NMR spectroscopy also revealed a peak at 29.23 ppm assigned to the intermediate *p*-$MeOC_6H_4NCO$•**1** (**6b**) in the trimerization of *p*-$MeOC_6H_4NCO$ catalyzed by **1**.

The importance of transannulation in the intermediates shown in Scheme 1 can be inferred from the structure of **9**(I) shown in Figure 1. Cation **9** can be

Scheme 1



viewed as a methylated derivative of this analogue of **6a**. The transannular distance in cation **9** is 2.209(6) Å which is 34% shorter than the sum of the P and N van der Waals radii of 3.34 Å. Further evidence for transannulation is the average of the N_{eq}—P—N_{eq} bond angles (118.3(3)°) which is very close to the 120° expected for trigonal bipyramidal phosphorus. While the cationic charge on **9** could be expected to accentuate transannulation over a zwitterionic species such as **6a**, the zwitterionic CS_2 adduct of **1** (i.e., $^-S_2CP^+(MeNCH_2CH_2)_3N$) is also partially transannulated, featuring a P—N_{ax} distance of 3.008 Å[6] which is 10% shorter than the sum of the van der Waals radii.

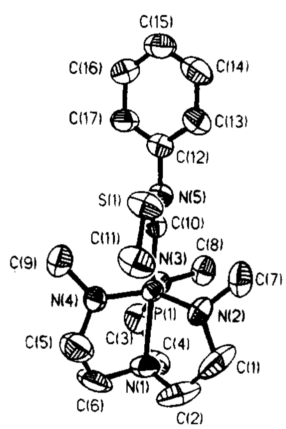
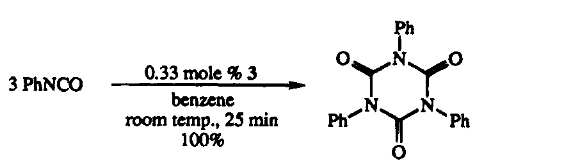


Figure 1. ORTEP drawing of **9**(I). Ellipsoids are drawn at the 50% probability level.

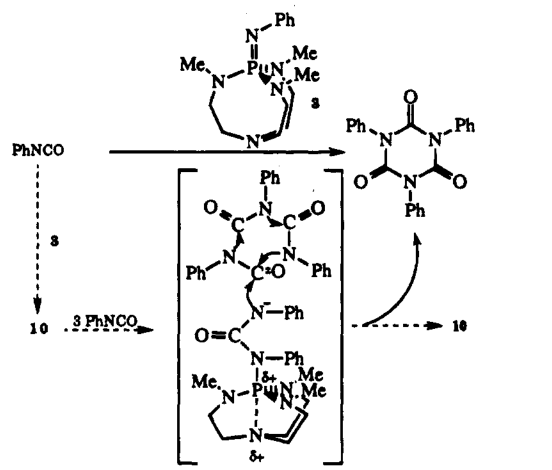
Isocyanurate Formation Catalyzed by 3. Like **1**, **3** is also a strong catalyst for trimerizing phenyl isocyanate:

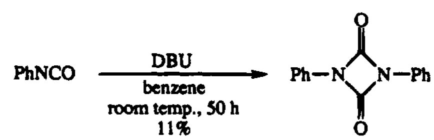


(6)

Quantitative isolation of the trimer followed washing and drying of the precipitated product. By contrast, we found that DBU, though a stronger base than **3**,[5] is a much weaker catalyst, leading to dimeric rather than trimeric product:

Scheme 2





(7)

Earlier[7] we suggested that the much stronger catalytic activity of **1** than its acyclic analog $P(NMe_2)_3$ arises from the stabilization of intermediates of type **6** by transannular interaction. It could be expected that the analogous 1:1 intermediate **10**, arising from **3**, is similarly stabilized, and indeed this seems to be the case. The ^{31}P NMR spectrum taken 10 min after a 1:3 solution of **3** and phenyl isocyanate in C_6D_6 had been made revealed peaks at 21.91 and 13.35 ppm in a ratio of about 1:50. The downfield peak, tentatively assigned to **10**, grows while the upfield resonance due to **3** decreases over time. By the next morning, the peak corresponding to **3** disappeared and only the peak at 21.91 ppm remained. In addition, the ^{13}C NMR spectrum of the reaction mixture displayed a new peak at 154.00 ppm tentatively regarded as stemming from the carbonyl carbon of **10**. After crystals of trimer were isolated from this solution, the solution was added to 2.5 g of phenyl isocyanate. After one day at room temperature, an 85% yield of product was isolated. Since **1** was not regenerated in this reaction and **10** is the only detectable species at the end of the reaction, it is not unreasonable to suggest that adduct **10** is the catalytically active species which initiates the sequential process implied in brackets depicted in Scheme 2.

Carbodiimide Formation Catalyzed by 4 and 5. As a consequence of both their intrinsic interest and their great importance as versatile reagents in organic synthesis, carbodiimides rank as one of the most important classes of compounds in organic chemistry.[21] Of particular significance is their use as condensing agents in the synthesis of peptides and nucleotides. More recently, carbodiimides have been shown to provide an efficient annulation route to highly substituted indoles, quinindolines, and isoquinolines which are pharmacologically active compounds, displaying strong cytostatic antitumor activity.[22]

(21) (a) Mikolajczyk, M.; Kielbasinski, P. *Tetrahedron* **1981**, *37*, 233. (b) Kurzer, T.; Dougrashi-Zadeh, K. *Chem. Rev.* **1967**, *67*, 107.

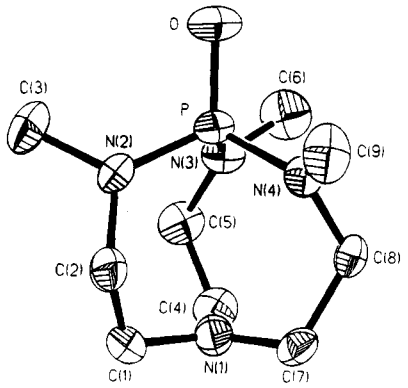
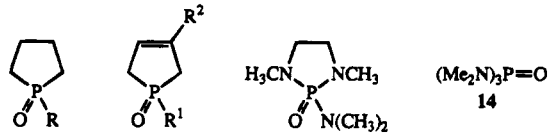


Figure 2. ORTEP drawing of **4**. Ellipsoids are drawn at the 50% probability level. Since the transannular interaction in **4** is only partial (see Discussion) no bond is drawn between P and N(1).

The synthesis of diaryl carbodiimides from aryl isocyanates, using cyclic phospholanes **11**[23a-c] and phospholenes **12**[23d] as catalysts, represents a decided improvement in view of their ease of preparation in high yield and purity by this route over other methods.[21] These preparations are carried out over a range of temperatures (room temperature to 194 °C). Catalyst **12** where R^1 = Ph, R^2 = Me, is most widely used because of its facile synthesis,[23e,f] although **12** wherein R^1 = Et, R^2 = Me is more active.[23d] The stronger catalytic activity of **12** than **11** in these reactions may be associated with some donation of π-electron density from the ring carbons to the P=O moiety. However, these catalysts produce only moderate yields of dialkyl carbodiimides from alkyl isocyanates and they do not catalyze the conversion of strongly sterically hindered isocyanates such as Ph_2CHNCO into carbodiimides.[23a]

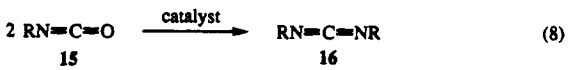


It is well known that the catalytic activity of phosphoryl compounds increases with P=O bond nucleophilicity.[21b] Electron-withdrawing groups bound to the phosphorus atom decrease this nucleophilicity and thus decrease the catalytic activity in the order $R_3P{=}O > R_2(RO)P{=}O > R(RO)_2P{=}O > (R_2N)_3P{=}O \geq (RO)_3P{=}O$,[24a] while electron-donating groups increase P=O nucleophilicity and increase the catalytic activity. Thus, in **12** (R^2 = CH_3, R^1 = p-$R^3C_6H_4$), the increasing catalysis order for R^3 is H < Me < NEt_2.[24b] We have mentioned earlier in this paper that bridgehead P—N transannulation is an important factor in rendering **1** the most effective catalyst thus far discovered for the conversion of isocyanates into isocyanurates. By analogy, we thought that **4**[1b] might be a stronger catalyst for the conversion of isocyanates to carbodiimides than its analogue **13** (which was shown earlier to catalyze carbodiimide formation from isocyanates[25] and is also an analogue of **11**) and its analogue **14** (which lacks the opportunity for transannular bonding). Such enhanced P=O bond nucleophilicity in **4** expected from electron donation of the bridgehead nitrogen lone pair via partial bridgehead P—N transannulation is substantiated by the P—N_{ax} distance (3.137(3) Å) obtained by means of an X-ray diffraction study (Figure 2). This transannular distance is 6% shorter than the sum of the van der Waals radii of the P and N atoms (3.34 Å). Indeed, **4** catalyzes the condensation of both aryl and alkyl isocyanates **15** to their corresponding carbodiimides **16** in high yield (reaction 8, Table 3). Compound **4** is not as strong a catalyst as **11** or **12** as is seen from a comparison of entries 1–3 with 7–9 in Table 3. The possible roles of electronic and steric factors in rationalizing these observations are not clear at this time. On the other hand, the primary reason why **4** is a much stronger catalyst than its analogues **13** and **14** appears to be the lack of opportunity for transannulation in the latter compounds to augment their P=O bond nucleophilicity. The stronger catalytic activity of **4** over **13** and **14** can be seen from comparison experiments (entry 3 versus entries 10 and 11 in Table 3), in which **4** requires a much shorter time than **13** or **14** for the complete conversion of *o*-tolyl isocyanate to di(tolyl) carbodiimide at reflux temperature.

Table 3. Catalytic Synthesis of Carbodiimides

entry	R of **15**, **16**	catalyst	T (°C)	time (h)	isolated yield (%) of **16**
1	Ph	**4**	180–210	5.5	84[a] (**16a**)
2	3-ClC_6H_4	**4**	145–180	6.5	98[b] (**16b**)
3	2-MeC_6H_4	**4**	180–250	12	80 (**16c**)
4	c-C_6H_{11}	**4**	200–230	91	92 (**16d**)
5	n-$C_{18}H_{37}$	**4**	160–230	96	90[b] (**16e**)
6	Ph	**5**	180–210	5.5	81[a] (**16a**)
7	Ph	**12**[c]	50	2.5	94 (**16a**)
8	3-ClC_6H_4	**12**[c]	rt	2	99 (**16a**)
9	2-MeC_6H_4	**12**[c]	50–55	9.5	87 (**16a**)
10	2-MeC_6H_4	**13**	180–250	29	[d] (**16c**)
11	2-MeC_6H_4	**14**	180–250	30	[e] (**16c**)

[a] Distillation gave 65% of monomeric **16a** (R = Ph). The solid residue of the remainder of the yield was dimeric $(PhNC{=}NPh)_2$ (see Experimental Section). [b] The crude product had a very high boiling point and was not purified. [c] R^1 = Et, R^2 = Me. Data taken from ref 22f. [d] 100% conversion as shown by lack of a detectable N=C=O absorption in the IR. [e] After 30 h at 180–250 °C, conversion was not complete according to the IR spectrum and persistent CO_2 evolution.



Compound **5**, described earlier by us,[1b] is also a more effective catalyst than the acyclic sulfide $(CH_3O)_2P(S)Ph$ which at 0.9 mol % provides only a 20% yield of **16a** after 16.5 h at 162 °C. It is no surprise that **5** is nearly as catalytically active as **4** because **5** also exhibits a partial P—N_{ax} transannular bond (although it is only 3% shorter than the sum of van der Waals radii[2]) and **5** may share the same reaction pathway with **4** as shown in Scheme

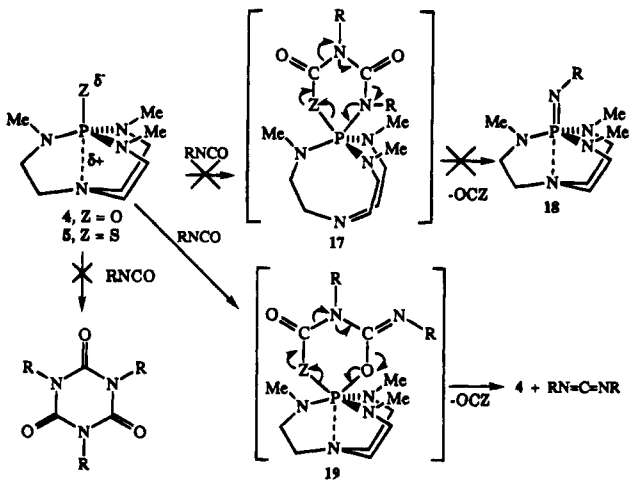
(22) (a) Molina, P.; Alajarin, M.; Vidal, A. *J. Org. Chem.* **1992**, *57*, 6703. (b) Molina, P.; Alajarin, M.; Vidal, A.; Sanchez-Andrada, P. *J. Org. Chem.* **1992**, *57*, 929 and references cited therein.

(23) (a) Neumann, W.; Fisher, P. *Angew. Chem., Int. Ed. Engl.* **1962**, *1*, 621. (b) Balon, W. J. US 2,853,418, 1958; *Chem. Abstr.* **1959**, *53*, 5202b. (c) Campbell, T. W.; Verbanc, J. US 2,853,473, 1958; *Chem. Abstr.* **1959**, *53*, 10126. (d) Campbell, T. W.; Monagle, J. J.; Foldi, V. S. *J. Am. Chem. Soc.* **1962**, *84*, 3673 and references cited therein. (e) Campbell, T. W.; Monagle, J. J. *Org. Synth.* **1963**, *43*, 31. (f) McCormack, W. B. Ibid. 73.

(24) (a) Monagle, J. J. *J. Org. Chem.* **1962**, *27*, 3851. (b) Ostrogovich, G.; Kerek, T.; Buzas, A; Doca, N. *Tetrahedron* **1969**, *25*, 1875.

(25) Ulrich, H.; Tucker, B.; Sayigh, A. A. R. *J. Org. Chem.* **1967**, *32*, 1360.

Scheme 3



3. Unlike the pathway for other O=P compounds,[26] the phosphorimide **18** is not expected as an intermediate in our systems because if it were formed, it would catalyze the trimerization of isocyanates to isocyanurates as discussed earlier. No isocyanurate was detected in the HRMS and IR spectra of the residues obtained upon distillation of the carbodiimides, however. The failure of **18** to form in Scheme 3 can be attributed to the preferential formation of intermediate **19** over **17** owing to greater stability of the P—O bond compared with P—N and less steric encumbrance of the R group proximal to the methyl groups in **19**. The observed reaction is also driven by the evolution of CO_2 (and OCS) which is also favored by **19** since breakage of a P—Z bond is compensated by P=O formation.

Regardless of whether **4** or **5** was used as the catalyst, only **4** was present after reaction completion, as was shown by ^{31}P NMR spectroscopy. Although the evolution of CO_2 was easily demonstrated by the formation of a white precipitate in a solution of $Ca(OH)_2$, no attempt was made to separate and identify the small amount of OCS that probably formed when **5** was used as the catalyst.

Experimental Section

General. All procedures were carried out in an atmosphere of argon or nitrogen. Et_2O, THF, and pentane were dried by refluxing with sodium and were distilled under nitrogen. CD_3CN, CH_3CN, C_6D_6, and benzene were dried with CaH_2 and distilled under argon. NMR spectrometers employed were a Nicolet NT-300 for ^1H spectra, a Bruker WM-200 for ^{31}P spectra, and a Varian VXR-300 for ^{13}C spectra. Standards for the NMR spectra (δ) were TMS (^1H, internal), 85% H_3PO_4 (^{31}P, external), and the δ 118.20 peak of the solvent CD_3CN or the δ 128.00 peak of the solvent C_6D_6 (^{13}C, internal). Infrared spectra were recorded with a Bruker/FS-113 V spectrometer. High-resolution and FAB mass spectra were recorded on a KRATOS MS-50 spectrometer. A solution molecular weight of $(PhNC{=}NPh)_2$ in chloroform and elemental analyses were performed by Desert Analytics. X-ray data collections and structure solutions were carried out at the Iowa State University Molecular Structure Laboratory. The catalysts **1** and **3**–**5** were synthesized by our previously published methods.[1] All melting points are uncorrected.

Triphenyl Isocyanurate. Method A. To a one-necked round bottomed flask (250 mL, filled with N_2 and closed with a septum) containing a solution of **1** (0.11 g, 0.50 mmol) in dry benzene (10 mL) was added by syringe phenyl isocyanate (18.0 g, 99% pure, 150 mmol, Aldrich). After the mixture was stirred at room temperature for 3 min, the white precipitate which had very rapidly formed transformed the reaction mixture into a solid mass in a few seconds. The solid was cooled to room temperature, stirred with 30 mL of dry benzene for 2 h, filtered in vacuo, further washed with 15 mL of dry benzene, and finally dried in vacuo to give 17.2 g (96.6%) of pure (>99%) product as shown by ^1H NMR spectroscopy, TLC (silica gel using hexane:ether = 2:1, or $CHCl_3$, or $CHCl_3$:acetone = 50:1 as eluents), and GC (in $CHCl_3$). Mp: 279.0–279.5 °C (lit.[11b] mp 281–281.5 °C). IR (KBr pellet): 1726 cm^{-1} (C=O). ^1H NMR ($CDCl_3$): δ 7.35–7.51 (m, C_6H_5). ^{13}C NMR (CD_3CN): δ 128.21, 128.74, 129.16, 133.39, 148.46. HRMS (*m/z*) calcd and found for $C_{21}H_{15}N_3O_3$ 357.11134 (54, M^+).

Method B. To 0.11 g (0.50 mmol) of **1** under argon was added by syringe phenyl isocyanate (18.0 g, 99% pure, 150 mmol, Aldrich). The mixture was stirred at room temperature. A white precipitate formed rapidly after 2 min of stirring, and a solid mass appeared in a few seconds thereafter. The solid mass was cooled, ground to a powder, and then stirred with 30 mL of dry benzene, filtered *in vacuo*, further washed with 10 mL of dry benzene, and finally dried at 40–50 °C to give 10.7 g (94.4%) of TLC-pure triphenyl isocyanurate. Mp: 279.0–279.5 °C. IR (KBr pellet): 1726 cm^{-1} (C=O).

Method C. To a solution of **1** (0.11 g, 0.50 mmol) under argon in dry benzene (80 mL) was added by syringe phenyl isocyanate (18.0 g, 99% pure, 150 mmol, Aldrich). The mixture was stirred and heated at 60–70 °C for 40 h and then allowed to stand at room temperature for 10 h. The white precipitate was filtered and dried *in vacuo* to give 16.8 g (94%) of GC-pure (>99%) triphenyl isocyanurate. Mp 279.0–279.5 °C. The mother liquor was concentrated to about 50 mL, filtered, and washed with dry benzene (2 × 5 mL) to give 0.41 g of triphenyl isocyanurate. The total yield was 96%.

Tris(*p*-methoxyphenyl) Isocyanurate. Method A. To a solution of **1** (0.06 g, 0.3 mmol) in dry benzene (5 mL) under argon was added by syringe *p*-methoxyphenyl isocyanate (11.3 g, 99% pure, 75 mmol, Aldrich). After about 3 min of stirring at room temperature, a white precipitate formed gradually and within another 5 min the mixture solidified. The solid was cooled to room temperature and evacuated to remove solvent. The residue was ground to a powder, stirred with 50 mL of dry benzene, filtered *in vacuo*, further washed with 30 mL of dry benzene, and finally dried *in vacuo* at 50 °C to give 11.1 g (99%) of TLC- and GC-pure (>99%) tris(*p*-methoxyphenyl)-isocyanurate. Mp: 261.0–261.5 °C (lit.[11b] mp 261–262 °C). IR (KBr pellet): 1697 cm^{-1} (C=O). ^1H NMR ($CDCl_3$): δ 3.81 (s, 9 H, OCH_3), 6.96 (d, 4 H, C_6H_4, $^3J_{HH}$ = 8.7 Hz), 6.27 (d, 4 H, C_6H_4, $^3J_{HH}$ = 8.7 Hz). HRMS (*m/z*): calcd for $C_{24}H_{21}N_3O_6$, 447.14304, found 447.14358 (M^+, 50).

Method B. To 0.06 g (0.3 mmol) of **1** under argon was added by syringe *p*-methoxyphenyl isocyanate (11.3 g, 99% pure, 75.0 mmol, Aldrich). The mixture was stirred at room temperature. After 5 min of stirring, a white precipitate formed very rapidly and the mixture solidified in a few seconds. The solid was cooled to room temperature, ground to powder, stirred with 50 mL of dry benzene, filtered *in vacuo*, further washed with 30 mL of dry benzene within the filter, and finally dried *in vacuo* at 50 °C to give 10.5 g (94%) of TLC- and GC-pure (>99%) tris(*p*-methoxylphenyl)isocyanurate. Mp: 261.0–261.5 °C. IR (KBr pellet): 1697 cm^{-1} (C=O).

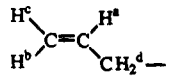
Method C. To a solution of **1** (0.11 g, 0.50 mmol) in dry benzene (80 mL) under argon was added by syringe *p*-methoxyphenyl isocyanate (22.6 g, 99% pure, 150 mmol, Aldrich). The mixture was stirred and heated at 60–70 °C for 72 h and allowed to stand at room temperature for 10 h. The precipitate was filtered *in vacuo*, washed with dry benzene (2 × 15 mL), and dried *in vacuo* at 50 °C to give 21.5 g (95%) of TLC- and GC-pure (>99%) tris(*p*-methoxyphenyl)isocyanurate. Mp: 261.0–261.5 °C. IR (KBr pellet): 1697 cm^{-1} (C=O).

Triethyl Isocyanurate. To a solution of **1** (0.018 g, 0.89 mmol) in pentane (1 mL) under argon was added by syringe EtNCO (1.79 g, 25.3 mmol) at room temperature. The reaction mixture became warm, and a colorless crystalline precipitate formed immediately. After about 5 min, the reaction temperature began to fall and the solid was filtered and dried *in*

(26) Monagle, J. J. Mengehauser, J. V. *J. Org. Chem.* **1966**, *31*, 2321.

vacuo to give triethyl isocyanurate (1.46 g, 81.7%). Mp: 93–94 °C (lit.[27] 95 °C). IR (Nujol mull): 1693 cm^{-1} (C=O). ^1H NMR ($CDCl_3$): 1.21 (t, 9 H, $^3J_{HH}$ = 6.9 Hz, CH_3), 3.91 (q, 6 H, $^3J_{HH}$ = 6.9 Hz, CH_2). ^{13}C NMR ($CDCl_3$): 13.03 (CH_3), 38.07 (CH_2), 148.57 (C=O). HRMS (*m/z*): calcd for $C_9H_{15}N_3O_5$ 213.11030, found 213.11169 (M^+, 100).

Triallyl Isocyanurate. To a stirred solution of **1** (0.016 g, 0.074 mmol) in dry THF (1 mL) under argon was added by syringe allyl isocyanate (1.88 g, 22.6 mmol). There was no obvious change of the reaction mixture after 3 days of stirring at room temperature. The solvent was removed *in vacuo*, and the residue was vacuum distilled to give 1.4 g (75%) of pure triallylisocyanurate. Mp: 23–24 °C (lit.[16b] mp 25–26 °C). IR (neat), 1686 cm^{-1} (C=O). ^1H NMR ($CDCl_3$):



4.45 (ddd, 2 H, H^d, $^3J_{H^aH^d}$ = 6.0 Hz, $^4J_{H^bH^d}$ = $^4J_{H^cH^d}$ = 1.2 Hz); 5.20 (tdd, 1 H, H^c, $^3J_{H^cH^a}$ = 11.1 Hz, $^2J_{H^cH^b}$ = 1.5 Hz, $^4J_{H^cH^d}$ = 1.2 Hz), 5.26 (tdd, 1 H H^b, $^3J_{H^bH^a}$ = 16.2 Hz, $^2J_{H^cH^b}$ = 1.5 Hz, $J_{H^bH^d}$ = 1.2 Hz), 5.80 (tdd, 1 H, H^a, $^3J_{H^aH^b}$ = 16.2 Hz, $J_{H^aH^c}$ = 11.1 Hz, $^3J_{H^aH^d}$ = 6.0 Hz). ^{13}C NMR ($CDCl_3$): 44.88 (CH_2), 118.85 (C=), 130.74 (C=), 148.39 (C=O). MS (*m/z*, EI) 249.1 (6). The IR spectrum of the crude reaction mixture showed complete absence of the band at 2260 cm^{-1} characteristic of N=C=O in the starting material and is identical with the pure trimer obtained upon distillation. Hence the catalytic trimerization was quantitative.

General Procedure for Trimerization of PhNCO in the Presence of Varying Concentrations of 1. To a stirred solution of **1** in THF (1 mL) was added by syringe PhNCO. Upon completion of the trimerization (i.e., when cooling of the exothermic reaction occurred) dry pentane (5 mL) was added to precipitate $(PhNCO)_3$ remaining in solution. The solid was filtered and dried *in vacuo* at room temperature to give $(PhNCO)_3$•THF as confirmed by ^1H NMR spectroscopy. ^1H NMR ($CDCl_3$): 1.82 (t, 4 H, $^3J_{HH}$ = 6.9 Hz, THF), 3.72 (t, 4 H, $^3J_{HH}$ = 6.9 Hz, THF), 7.36–7.60 (m, 15 H, 3 C_6H_5). The relevant data are summarized in Table 2.

General Procedure for Recycling Catalyst 1 in the Trimerization of PhNCO. To a stirred solution of **1** (0.033 g, 0.15 mmol) in THF (5 mL) under argon was added by syringe PhNCO (5.48 g, 99%, 46.4 mmol) at room temperature. A colorless crystalline solid began to separate within 30 s along with evolution of heat which ceased after about 5 min. The solid was then filtered, washed with pentane (3 × 3 mL) within the filter, and dried *in vacuo* at room temperature. The solid was identified as $(PhNCO)_3$•THF by ^1H NMR spectroscopy (see above paragraph). The combined filtrate and washings were concentrated to about 5 mL and reused as the catalyst solution for the second cycle. This procedure was repeated five times.

Detection of the Intermediates 6a and 6b. To a solution of **1** (0.037 g, 0.17 mmol) in 0.8 mL of C_6D_6 in an NMR tube was added PhNCO (0.062 g, 0.52 mmol). The mixture was briefly shaken. Fifteen min after the addition of PhNCO to the solution of **1**, the ^{31}P NMR spectrum was recorded showing peaks at 29.46 (**6a**) and 120.31 (**1**[16b]) ppm, respectively, in the ratio of 1:1.5. The intensity of the peak at 120.3 ppm increased while that at 29.46 ppm decreased with time as indicated by ^{31}P NMR spectra taken every 15 min. After about 7 h, the peak at 24.46 ppm disappeared completely and only the one at 120.31 ppm remained.

In a separate experiment, the reaction mixture was monitored by ^1H NMR spectroscopy 15 min after the addition of 3 equiv of PhNCO to a solution of **1** in C_6D_6 in an NMR tube. The ^1H NMR spectrum showed two sets of signals, namely, those of **1** and those assigned to the NCH_2 and NCH_3 protons of **6a**. The phenyl proton region consisted of overlapping proton signals.

In another experiment, the reaction mixture was monitored by ^{13}C NMR spectroscopy about 10 min after addition of 3 equiv of PhNCO to a solution of **1** in C_6D_6 in an NMR tube. The first spectrum showed a new peak (doublet) at 161.1 ppm ($^1J_{PC}$ = 201.6 Hz) not assignable to carbons in PhNCO, triphenyl isocyanurate, or **1** recorded in the same solvent. This peak disappeared after about 7 h when the reaction was complete and was assigned the chemical shift of the C=O carbon of **6a**.

In another experiment, 1 equiv of PhNCO (0.08 g, 0.7 mmol) was added by syringe to a dilute solution of **1** (0.1 g, 0.5 mmol) in dry diethyl ether (5 mL) under argon to give an immediate colorless precipitate. The precipitate was filtered *in vacuo* about 1 min after the addition of PhNCO, washed with dry ether (2 mL) within the filter, and dried *in vacuo*. The mass spectrum (FAB, CH_3CN as solvent, 3-nitrobenzyl alcohol as matrix) of the solids showed a peak at 217.1 (M + H; for **1**, 100) and a peak at 336.1 (M + H, for **6a**, 50) and no peak higher than mass 336.1. The ^{31}P NMR spectrum (C_6D_6) of this solid showed a peak at 29.46 ppm (**6a**) which disappeared slowly as the peak at 120.31 ppm (**1**) increased.

For the detection of **6b**, 0.094 g (0.79 mmol) of *p*-$MeOC_6H_4$-NCO was added by syringe to a solution of **1** (0.0.57 g, 0.26 mmol) in C_6D_6 (0.7 mL). The ^{31}P NMR spectrum recorded about 15 min after the addition of *p*-$MeOC_6H_5NCO$ showed peaks at 29.21 ppm (**6b**) and 120.31 ppm in the ratio of 3:10. The peak at 29.21 ppm disappeared overnight while the peak at 120.31 ppm remained.

Reaction of PhNCO with 1 in CD_3CN. To **1** (0.020 g, 0.093 mmol) in an NMR tube under N_2 were added CD_3CN (0.6 mL) and PhNCO (0.033 g, 0.28 mmol). The ^{31}P NMR spectrum recorded 15 min later indicated peaks at 30.01 (**6a**) and 119.95 ppm (**1**) in the ratio of 100:5. The peak at 30.01 ppm decreased as peaks at −9.98 (t, $^1J_{PD}$ = 75.0 Hz, **7**) and at 119.95 ppm (**1**) increased. After 8.7 h, the peak at 30.01 ppm disappeared completely and the peaks at −9.98 and 119.95 ppm remained for weeks in the ratio of 1:4.3. After the peak at 30.01 ppm had disappeared, colorless crystals had formed and so the solution was transferred by syringe to another NMR tube for the additional monitoring. These crystals (10 mg) were dried *in vacuo* and identified by ^1H NMR, ^{13}C NMR, and HRMS as triphenyl isocyanurate.

The Zwitterionic Adduct $PhN(CS)P(MeNCH_2CH_2)_3N$, 8. To a solution of **1** (0.14 g, 0.60 mmol) in dry diethyl ether (3 mL) under N_2 was added by syringe PhNCS (0.081 g, 0.60 mmol). The mixture was stirred for 5 min, and the greenish yellowish solid which had formed was collected by vacuum filtration, washed with dry ether (5 mL), and dried *in vacuo* to give **8** (0.22 g, 100%). ^{31}P NMR (CD_3CN): 29.60 ppm. ^1H NMR (CD_3CN): 2.83 (m, 2 H, CH_2), 2.94 (m, 2 H, CH_2), 3.00 (d, 9 H, NCH_3, $^3J_{PH}$ = 9.0 Hz), 6.89–7.27 (m, 5 H, Ph). ^{13}C NMR (CD_3CN): 37.30 (d, $^2J_{PC}$ = 3.2 Hz, NCH_3), 50.14 (s, N_{eq}-CH_2) 52.48 (s, $N_{ax}CH_2$), 122.36 (d, C(2) of Ph, $^4J_{PC}$ = 1.4 Hz), 122.80 (s, C(3) or C(4) of Ph), 120.95 (s, C(4) or C(3) of Ph), 154.59 (d, $^3J_{PC}$ = 37.1 Hz, C(1) of Ph), 178.40 (d, $^1J_{PC}$ = 187.8 Hz, NCS). MS (*m/z*, FAB, CH_3CN as solvent, 3-nitrobenzyl alcohol as matrix): 352.2 (M + H, base peak).

[PhN=C(SMe)P(MeNCH$_2$CH$_2$)$_3$N]I, 9(I). To **8** (0.073 g, 0.20 mmol) in CH_3CN (1 mL) was added by syringe MeI (0.5 g, 3.5 mmol). The exothermic reaction mixture was stirred for 30 min to give a slightly yellowish solution. Volatiles were removed *in vacuo* to give a light yellowish solid (0.14 g, 100%). ^{31}P (CD_3CN): 14.45. ^1H NMR (CD_3CN), 2.18 (d, 3 H, SCH_3, $^4J_{PH}$ = 0.6 Hz), 2.90 (t, $N_{ax}CH_2$, $^3J_{PH}$ = 5.1 Hz), 2.94 (d, 9 H, NCH_3, $^3J_{PH}$ = 11.4 Hz), 3.08 (td, 6 H, $N_{eq}CH_2$, $^3J_{PH}$ = 15.3 Hz, $^3J_{HH}$ = 7.3 Hz), 6.89–7.40 (m, 5 H, Ph). ^{13}C NMR (CD_3N): 16.90 (d, SC, $^3J_{PC}$ = 2.3 Hz), 38.23 (d, NCH_3, $^2J_{PC}$ = 3.3 Hz), 49.69 ($N_{ax}CH_2$), 50.67 (d, $N_{eq}CH_2$, $^2J_{PC}$ = 6.0 Hz), 119.0 (d, $^4J_{PC}$ = 1.4 Hz, C(2) of Ph), 125.69 (C(3) or C(4) of Ph), 130.19 (C(4) or C(3) of Ph), 149.96 (d, $^3J_{PC}$ = 22.5 Hz, C(1) of Ph), 167.30 (d, $^1J_{PC}$ = 186.9 Hz, NCS); MS (*m/z*, base peak): 366.3 (M^+). For elemental and crystal structure analyses, the crude product was dissolved in CH_3CN (0.8 mL). The small flask that contained the above solution was placed in a Dewar flask which was stored in a freezer at about −20 °C. After several days large colorless crystals were formed. The supernatant was removed by syringe and the crystals were dried *in vacuo*.

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Anal. Calcd (found) for $C_{17}H_{29}N_5PSI$: C, 41.35 (40.82); H, 5.93 (5.88); N, 14.19 (13.78).

General Procedure for the Synthesis of Carbodiimides from Isocyanates Using Catalysts 4 or 5. A single-neck round bottom flask containing an isocyanate and a catalyst (0.56 mol % for entries 1, 2, 5, and 6 and 0.37 mol % for entries 3, 7, and 8 in Table 3) was equipped with a condenser. The top of the condenser was closed with a septum through which cannulas were inserted for an argon inlet and a gas outlet. The gas outlet was passed through a saturated $Ca(OH)_2$ solution. The mixture in the flask was heated in an oil bath until no more $CaCO_3$ was precipitated from a fresh saturated $Ca(OH)_2$ solution. At this point an IR spectrum of the reaction mixture was recorded which revealed the complete absence of the characteristic N=C=O band of the starting material. The crude product was then distilled at reduced pressure. The reaction temperatures, times for completing the reactions, and the yields of isolated carbodiimides are summarized in Table 3.

Diphenylcarbodiimide (**16a**) (R = Ph).[23b] Bp: 104–5 °C/0.2 Torr. IR (neat): 2135 cm^{-1} (N=C=N). HRMS (*m/z*): calcd for $C_{13}H_{10}N_2$ 194.08440. Found 194.08476.

Bis(3-chlorophenyl)carbodiimide (**16b**) (R = 3-ClC_6H_4).[23b] IR (neat): 2143 cm^{-1} (N=C=N). HRMS (*m/z*): calcd for $C_{13}H_8Cl_2N_2$ 262.00645, found 262.00662.

Bis(2-methylphenyl)carbodiimide (**16c**) (R = 2-MeC_6H_4).[23a] Bp: 132–134 °C/0.72 Torr. IR (neat): 2138 cm^{-1} (N=C=N). MS (*m/z*): calcd for $C_{15}H_{14}N_2$ 222.11570, found 222.11544.

Dicyclohexylcarbodiimide (**16d**). Bp: 120–122 °C/0.48 Torr. IR (neat): 2117 cm^{-1} (N=C=N). HRMS (*m/z*) calcd for $C_{13}N_2H_{22}$ 206.17830, found 206.17807. IR spectrum was identical with that of an authentic sample (Aldrich).

Dioctadecylcarbodiimide (**16e**).[25] IR (neat): 2137 cm^{-1} (N=C=N). HRMS (*m/z*): calcd for $C_{37}H_{23}N_2$ 545.57737, found 545.57670.

Dimer of Diphenylcarbodiimide (PhNC=NPh)$_2$. Diphenylcarbodiimide subjected to thermal treatment had been suggested[23b] to trimerize and polymerize. In our experiments the residue obtained after distillation of the diphenyl carbodiimide **16a** was shown to be the title dimer which formed in 19% yield. Mp: 163–164 °C. ^1H NMR ($CDCl_3$): 6.86 (m, 10 H, 2 C_6H_5), 7.01 (m, 10 H, 2 C_6H_5). HRMS (*m/z*): calcd for $C_{26}H_{20}N_4$ 388.16880, found 388.16918. MS (CI, NH_3, *m/z*): 389.1 $(M + H)^+$. Solution molecular weight (osmometry, $CHCl_3$): 414.

Detection of Catalysts. (A) A mixture of PhNCO (0.78 g, 6.6 mmol) and O=P($MeNCH_2CH_2$)$_3$N (**4**, 0.26 g, 1.1 mmol) was heated at 200–210 °C until evolution of CO_2 ceased (*ca.* 0.5 h). The ^{31}P NMR ($CDCl_3$) spectrum of the reaction mixture showed a peak at 19.8 ppm corresponding to the catalyst **4**.

(B) A mixture of PhNCO (0.49 g, 4.1 mmol) and S=P($MeNCH_2CH_2$)$_3$N (**5**, 0.17 g, 0.68 mmol) was heated at 200–210 °C until evolution of CO_2 (and presumably OCS) ceased (*ca.* 40 min). The ^{31}P NMR spectrum ($CDCl_3$) of the reaction mixture showed a peak at 19.8 ppm corresponding to catalyst **4**.

PhNCS in the Presence of Catalyst 4. A mixture of PhNCS (27.0 g, 0.20 mol) and **4** (0.26 g, 0.011 mmol) was heated at 160 to 200 °C for 11.5 h following the aforementioned general procedure. The mixture was cooled to room temperature and then subjected to distillation at 25–40 °C/0.14 Torr to give 26.5 g of starting material PhNCS.

Molecular Structures of 4 and 9(I). A colorless crystal of **4**, obtained from a benzene/pentane solution cooled in a freezer, was mounted in a glass capillary tube on the CAD4 diffractometer for a data collection at −50 ± 1 °C graphite-monochromated Mo Kα radiation (0.710 73 Å). Lorentz and polarization corrections were applied. A correction based on a nonlinear decay in the standard reflections was applied to the data. An absorption correction based on a series of ψ-scans was applied. The agreement factor for the averaging of observed reflections was 2.3% (based on F^2). Axial photographs indicated that the lattice was monoclinic. The space group $P2_1/c$ was chosen based on the systematic absences. The crystal structure was solved by direct methods using the SHELXTL-Plus package.[28] Refinement calculations were performed on a Digital Equipment Corp. VaxStation 3100 computer using the same program package. All non-hydrogen atoms were placed directly from the E-map and were refined anisotropically. All methylene hydrogens were generated with ideal positions with C–H distances equal to 0.96 Å and were refined with isotropic thermal parameters as riding atoms. The methyl hydrogens were refined as rigid bodies initially and in the final cycles of least-squares were converted to riding atoms with isotropic thermal parameters. Crystal and structure refinement data are as follows: $C_9H_{21}N_4OP$, 0.40 × 0.40 × 0.35 mm, monoclinic, $P2_1/c$, a = 7.187(2) Å, b = 14.190(4) Å, c = 12.161(3) Å, β = 105.31(2)°, V = 1197.1(5) Å^3, Z = 4, $F(000)$ = 504, d(calcd) = 1.289 g/cm^3, ω scans, $2\theta - \theta$, 1656 observed data ($F \geq 6.0\sigma(F)$), 145 parameters, R = 0.0351, R_w = 0.0598.

Colorless crystals of **9**(I), having a mp of 148–9 °C, were grown from a saturated CH_3CN solution cooled slowly by placing it in a Dewar flask and then storing the Dewar flask in the freezer for several days. A crystal was attached to the tip of a glass fiber and mounted on the CAD4 diffractometer for a data collection at 20 ± 1 °C. The cell constants for data collection were determined from a list of reflections found by an automated search routine. Lorentz and polarization corrections were applied. A correction based on a decay in the standard reflections was required for this data set. An absorption correction based on a series of ψ-scans was applied. The agreement factor for the averaging of observed reflections was 2.6% (based on F). The acentric space group $Pca2_1$ was indicated initially by systematic absences and intensity statistics using the SHELX-86 package.[29] Using the same program package, positions of all the atoms were determined by a Patterson interpretation program. All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were placed at idealized positions as riding atoms with isotropic temperature factors set equal to 1.2 times the isotropic equivalent of that atom. The $Pca2_1$ space group requires two independent molecules per asymmetric unit. The cations are nearly centrosymmetric; however, the iodine anions are clearly noncentrosymmetric. Attempts to refine this structure in *Pbcm* failed. The initial refinement in SDP[30] was converted to SHELXL-93[31] to test for racemic twinning. A twinned crystal was confirmed and refined as such. Difference Fourier maps of the residual peaks revealed the presence of one molecule of H_2O which was added to the refinement. Refinement calculations were performed on a Digital Equipment Corp. MicroVAX II computer using the CAD4-SDP program. Neutral-atom scattering factors and anomalous scattering corrections were taken from the literature.[32] Thermal ellipsoid illustrations were drawn using SHELXTYL-Plus.[33] Crystal and structure refinement data are as follows: $C_{17}H_{29}IN_5P{\cdot}H_2O$, 0.45 × 0.35 × 0.35 mm, $Pca2_1$, a = 16.786(3) Å, b = 10.756(2) Å, c = 24.328(4) Å, $\alpha = \beta = \gamma = 90.0°$, V = 4392.4(13) Å^3, Z = 8, $F(000)$ = 2032, d(calcd) = 1.51 g/mL, ω scans, $\omega - 2\theta$, 6401 observed data ($I \geq 2\sigma(I)$), 463 parameters, R = 0.042, R_w = 0.113.

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(34) The authors have deposited X-ray structural data for **4** and **9**(I) with the Cambridge Crystallographic Data Centre. These data can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.