Inorganica Chimica Acta 372 (2011) 374–382

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Cyclodiphosph(III)azane chemistry – Ylides from the reaction of $[(RNH)P\text{-}N(t\text{-}Bu)]_2$ [R = *t*-Bu, *i*-Pr] with dimethyl maleate and chiral ansa-type derivatives from reaction of $[ClP\text{-}N(t\text{-}Bu)]_2$ with a substituted BINOL

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ARTICLE INFO

Article history:
Available online 11 January 2011

Dedicated to Prof. S.S. Krishnamurthy on the occasion of his 70th birthday.

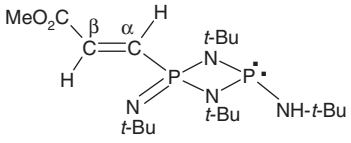
Keywords:
Phosphine activation
BINOL-substituted derivatives
Ylide
Cyclodiphosphazane
Spontaneous resolution
Allene

ABSTRACT

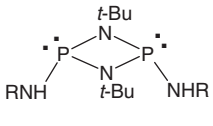
Use of a simple inorganic ring system with the cyclodiphosph(III)azane skeleton [e.g. $[(RNH)P\text{-}N(t\text{-}Bu)]_2$ [R = *t*-Bu (**7**), *i*-Pr (**8**)] to probe some of the intermediates proposed in phosphine mediated organic reactions is highlighted. Thus the reaction of **7–8** with the allenylphosphine oxide $Ph_2P(O)C(Ph)=C=CH_2$ (**9**) affords the *phosphinimines* $[(RNH)P(\mu\text{-}N\text{-}t\text{-}Bu)_2\mathbf{P}(=\mathbf{N}\text{-}R)\text{-}C(=CH_2)CH(Ph)\text{-}P(O)Ph_2]$ [R = *t*-Bu (**10**), *i*-Pr (**11**)], while a similar reaction of **7–8** with dimethyl maleate (or dimethyl fumarate) affords the *ylides* $[(RNH)P(\mu\text{-}N\text{-}t\text{-}Bu)_2\mathbf{P}(NH\text{-}R)=\mathbf{C}(CO_2Me)\text{-}CH_2(CO_2Me)]$ [R = *t*-Bu (**18**), *i*-Pr (**19**)]. The implication of such reactions on phosphine mediated organic transformations including Morita–Baylis–Hillman reaction is mentioned. In a rather rare type of situation, an unusually long phosphoryl (P=O) bond [1.538 (5) Å] as revealed the X-ray structure of $\{(R)\text{-}6,6'\text{-}(t\text{-}Bu)_2\text{-}1,1'\text{-}(C_{10}H_5)_2\text{-}2,2'\text{-}O_2\text{-}\}\{P(O)(N\text{-}t\text{-}Bu)_2\text{-}P(Se)\}$ (**27**) is rationalized by means of crystallographic disorder in packing after comparing the data with that in the literature and $\{1,1'\text{-}(C_{10}H_6)_2\text{-}2,2'\text{-}O_2\}\{P(Se)(N\text{-}t\text{-}Bu)_2\text{-}P(Se)\}$ (**29**). X-ray structures of the new compounds **10–11**, **18–19**, **27** and **29** are discussed. Compound **10** crystallizes in the chiral space group *Pca2(1)* with (*S*)-chirality at the carbon center $[\text{–}C(=CH_2)CH(Ph)\text{-}P]$ suggesting a case of spontaneous resolution through crystallization.

1. Introduction

Cyclodiphosph(III)azanes, $[ClPNR]_n$, and their derivatives constitute well-established examples of inorganic ring systems [1]. The synthetic potential of these compounds as highly versatile ligands, precursors for macrocycles and more recently, probes to explore organic reaction pathways, has been exploited by several groups of workers [2–5]. In addition to these, we have shown that the partial oxidation of some of these compounds leads to crystals that exhibit 'molecular non-stoichiometry' [6]. In the above cyclodiphosph(III)azane precursors, the unshared lone pair on phosphorus takes part in the reactions in a majority of cases. We have been interested in utilizing such a feature in exploring the mechanistic details of traditional organic reactions such as those shown in Scheme 1. The primary intermediates in these reactions are the phosphonium salts (betaines) depicted as $[R'(O)C\text{-}C(H)^-C(=CH_2)\text{-}PR_3^+]$ (**1**), $[R'(O)C\text{–}C(H)=C(CH_2)^-\text{-}PR_3^+]$ (**2**), $[(MeO_2C)C^-=C(CO_2Me)\text{-}PR_3^+]$ (**3**), and $[(EWG)CH^-\text{-}CH_2\text{-}PR_3^+]$ [EWG = CN (**4**), CO_2R (**5**)] in Scheme 1 [7]. One of the most important reactions among those shown in Scheme 1 is the Morita–Baylis–Hillman reaction that leads to a diverse number of functionalized and synthetically useful allylic systems [8]. Our interest in this connection is to identify/isolate compounds analogous to those proposed in such reactions and in this context, we have utilized the cyclodiphosph(III)azane $[(t\text{-}BuNH)P(\mu\text{-}N\text{-}t\text{-}Bu)]_2$, which is an excellent nucleophile. When this P(III) compound was treated with methyl propiolate, it afforded the tautomeric form $(t\text{-}Bu\text{-}NH)P(\mu\text{-}N\text{-}t\text{-}Bu)_2P(=N\text{-}t\text{-}Bu)[CH=CH(CO_2Me)]$ (**6**) of the expected phosphonium salt [7]. Despite the fact that **6** is not a phosphonium salt, the formation of P–C bond vindicated the involvement of the postulated intermediates shown in Scheme 1. In the first part of this paper, we highlight the contrasting reactivity of cyclodiphosphazanes **7–8** with an allenylphosphine oxide and dimethyl maleate. While the former affords a *phosphinimine*, the latter reaction leads to a *phosphorus ylidic species*.



6 [δ(P): -25.7, 70.0]



R = *t*-Bu [**7**, δ(P) 88.8]
i-Pr [**8**, δ(P) 90.7]

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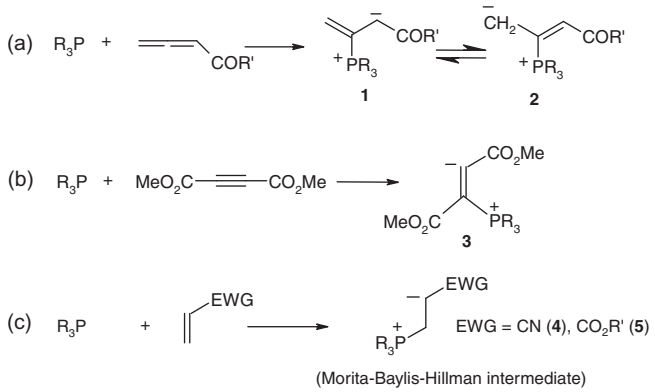
doi:10.1016/j.ica.2010.12.072



Scheme 1.

In the course of our studies on cyclodiphosphazanes, we have also made some new observations related to molecular non-stoichiometry that involves exchange of positions of non-bonded electron pair (on phosphorus) with phosphoryl oxygen in the crystal lattice of cyclodiphosphazane derivatives [6]. An additional interest in such compounds was to prepare chiral-BINOL based cyclodiphosph(V)azanes with a phosphoryl bond for possible use as chiral auxiliaries [9]. In this paper, we report the synthesis and X-ray structures of some of these chiral compounds and also give an example in which there is a rather (unusually) long P=O bond of 1.538 Å [expected range: 1.445–1.460 Å]. A possible rationale based on crystal packing effects is also presented.

2. Experimental

General experimental conditions are described in a recent paper [10]. Cyclophosphazane derivatives [(RNH)P(μ-N-*t*-Bu)]$_2$ [R = *t*-Bu (**7**), *i*-Pr (**8**)] [1d,5,7], 6,6′-di-*t*-butyl-BINOL [11], the allene $Ph_2P(O)C(Ph)=C=CH_2$ (**9**) [12] and [ClP(μ-N-*t*-Bu)]$_2$ (**24**) [13] were prepared by known synthetic routes. Chemicals were procured from Aldrich or Acros Company. IR spectra were recorded on a JASCO FT-IR 5400 spectrophotometer. Elemental analyses were carried out on a Thermo Finnigan EA1112 analyser.

*2.1. Synthesis of [(t-BuNH)P(μ-N-t-Bu)$_2$P(=N-t-Bu)-C(=CH$_2$)CH(Ph)-P(O)Ph$_2$ (**10**)*

Cyclodiphosphazane **7** (0.20 g, 0.57 mmol) and allenylphosphine oxide **9** (0.18 g, 0.57 mmol) were dissolved in dry toluene (5 mL) and the mixture stirred at room temperature for 15 h. The solution was concentrated *in vacuo* (to ca 2 mL) and cooled for 1 d at −4 °C to obtain crystals of **10**. Yield: 0.347 g (91%). Mp: 188–190 °C. IR (KBr, cm^{-1}): 3358, 2963, 2712, 1887, 1597, 1366, 1308, 1030, 887, 693. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.80, 0.94, 1.23, and 1.46 (4s, 36H, C(C*H*$_3$)$_3$), 2.57 (d, ^2J(P–H) = 6.8 Hz, 1H, N*H*), 5.73 (d, ^3J(P–H) ∼ 27.6 Hz, 1H, =C*H*$_A$H$_B$ *cis* to P), 6.16 (dd, ^3J(P–H) ∼ 4.8 Hz, ^2J(P–H) ∼ 13.1 Hz, 1H, P(O)C*H*), 7.00–8.16 (m, 16H, Ar–*H* + =CH$_A$*H*$_B$ *trans* to P). ^{13}C NMR (100 MHz, $CDCl_3$): δ 31.1 (d, ^3J(P–C) = 17.2 Hz, C(*C*H$_3$)$_3$), 32.7 (d, ^3J(P–C) = 9.5 Hz, C(*C*H$_3$)$_3$), 34.4 (d, ^3J(P–C) = 10.9 Hz, C(*C*H$_3$)$_3$), 47.3 (d, ^1J(P–C) ∼ 63.4 Hz, P(O)*C*(Ph)), 51.4 (d, ^2J(P–C) = 14.6 Hz, *C*(CH$_3$)$_3$), 52.2 (d, ^2J(P–C) ∼ 6.5 Hz, *C*(CH$_3$)$_3$), 126.4, 127.6, 127.7, 128.3, 128.4, 129.1, 130.5, 130.8, 130.8, 131.3, 132.1, 132.2, 133.1, 134.4 and 136.2 (d, ^2J(P–C) ∼ 11.2 Hz, (Ar–*C* + PC = *C*H$_2$), 144.5 (d, ^1J(P–C) = 159.9 Hz, PC=CH$_2$). ^{31}P NMR (162 MHz, $CDCl_3$): δ −19.3 (dd, ^3J(P–P) ∼ 24.9 Hz, ^2J(P^{III}–P^{V}) ∼ 8.3 Hz), 31.8 (d, ^3J(P–P) ∼ 24.9 Hz), 69.9 (d, ^2J(P^{III}–P^{V}) ∼ 8.3 Hz). LC–MS: *m*/*z* 665 [M+1]$^+$. *Anal.* Calc. for $C_{37}H_{55}N_4OP_3$: C, 66.85; H, 8.34; N, 8.25. Found: C, 66.75; H, 8.30; N, 8.51%.

*2.2. Synthesis of [(i-PrNH)P(μ-N-t-Bu)$_2$P(=N-i-Pr)-C(=CH$_2$)CH(Ph)-P(O)Ph$_2$ (**11**)*

This compound was prepared by following the procedure for compound **10**. Yield: 0.625 g (88%; using 1.12 mmol of **8**). Mp: 85–88 °C. IR (KBr, cm^{-1}): 3437, 3256, 3059, 2965, 2866, 1597, 1493, 1439, 1366, 1206, 1028, 873. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.74 and 0.87 (2 s,18H, C(C*H*$_3$)$_3$), 1.10 (d, ^2J(H–H) = 6.4 Hz, 3H, CHC*H*$_3$), 1.13 (d, ^2J(H–H) = 6.4 Hz, 3H, CHC*H*$_3$), 1.21 (d, ^2J(H–H) = 6.0 Hz, 3H, CHC*H*$_3$), 1.31 (d, ^2J(H–H) = 6.0 Hz, 3H, CHC*H*$_3$), 2.01 (d, ^2J(P–H) = 8.4 Hz, 1H, N*H*), 3.47–3.64 (br, 2H, NC*H*(CH$_3$)$_2$), 5.80 (d, ^3J(P–H) ∼ 26.4 Hz, 1H, =C*H*$_A$H$_B$ *cis* to P), 6.21 (dd, ^2J(P–H) ∼ 13.2 Hz, ^3J(P–H) ∼ 6.0 Hz, 1H, P(O)C*H*), 7.02–8.22 (m, 16H, Ar–*H* + =CH$_A$*H*$_B$ *trans* to P). ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.2 and 26.6 (2 s, =NCH(*C*H$_3$)$_2$), 28.2 (d, ^3J(P–C) = 6.2 Hz, NCH(*C*H$_3$)$_2$), 28.3 (d, ^3J(P–C) = 8.0 Hz, NCH(*C*H$_3$)$_2$), 30.7 and 31.0 (2 s, C(*C*H$_3$)$_3$), 44.4 (d, ^2J(P–C) = 7.2 Hz, *C*(CH$_3$)$_3$), 46.5 (d, ^1J(P–C) ∼ 63.0 Hz, P(O)*C*(Ph)), 51.8 (d, ^2J(P–C) = 8.5 Hz, *C*(CH$_3$)$_3$), 126.5, 127.6, 127.8, 128.2, 128.4, 130.5, 130.8, 130.9, 131.3, 132.2, 132.3, 133.1, 133.2, 134.2, 136.2 and 136.3 (2 d, ^2J(P–C) ∼ 13.1 Hz, Ar–*C* + PC=*C*H$_2$), 142.5 (d, ^1J(P–C) = 149.1 Hz, PC=CH$_2$). ^{31}P NMR (162 MHz, $CDCl_3$): δ −1.0 (br, *P*=N), 32.0 (d, ^3J(P–P) ∼ 24.5 Hz, *P*=O), 71.9 (br, P-N). LC–MS: *m*/*z* 638 [M+1]$^+$. *Anal.* Calc. for $C_{35}H_{51}N_4OP_3$: C, 66.02; H, 8.07; N, 8.80. Found: C, 66.12; H, 8.15; N, 8.69%.

*2.3. Synthesis of (t-Bu-NH)P(μ-N-t-Bu)$_2$P(NH-t-Bu)=C(CO$_2$Me)CH$_2$(CO$_2$Me) (**18**)*

To a solution of **7** (0.531 g, 1.52 mmol) in toluene (15 mL), dimethyl maleate (0.22 g, 1.52 mmol) was added *via* syringe at room temperature, the mixture was stirred for 3 d and the solution concentrated *in vacuo* (ca 1.5 mL) and kept at −4 °C for 24 h to obtain the crystals of **18**. Yield: 0.66 g (90%). Mp: 138–141 °C. IR (KBr, cm^{-1}): 3380, 2969, 1752, 1603, 1437, 1368, 1327, 1208. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.32, 1.42 and 1.55 (3 s, 36H, C(C*H*$_3$)$_3$), 2.65 (d, ^3J(H–H) = 14.4 Hz, 2H, PCC*H*$_2$), 3.04 (d, ^2J(P–H) = 8.0 Hz, 1H, N*H*), 3.54 and 3.65 (2 s, 6H, OC*H*$_3$), 9.08 (d, ^2J(P–H) = 8.0 Hz, 1H, N*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 30.9, 31.0, 32.2 and 32.8 (d each, ^3J(P–C) = 4.5, 4.5, 3.6 and 9.7 Hz, respectively, C(*C*H$_3$)$_3$), 31.4 (s, PCCH$_2$), 45.2 (d, ^1J(P–C) = 183.0 Hz, P*C*), 49.8, 51.0 (2 s, OCH$_3$), 51.5, 51.8 (2 s, *C*(CH$_3$)$_3$) 52.6 (d, ^2J(P–C) = 6 Hz, *C*(CH$_3$)$_3$), 171.7 (d, ^2J(P–C) = 30.0 Hz, *C*O$_2$Me), 174.9 (d, ^3J(P–C) = 10.0 Hz, *C*O$_2$Me). ^{31}P NMR (162 MHz, $CDCl_3$): δ 23.7, 78.9.

*2.4. Synthesis of (i-Pr-NH)P(μ-N-t-Bu)$_2$P(NH-i-Pr)=C(CO$_2$Me)CH$_2$(CO$_2$Me) (**19**)*

The procedure was similar to that for compound **18** using [(*i*-PrNH)PN-*t*-Bu]$_2$ (**8**) [δ(P) 90.7; 0.315 g, 0.98 mmol] and dimethyl maleate (0.283 g, 0.98 mmol) except that the reaction time was 1 d. Yield: 0.406 g (89%). Mp: 132–136 °C. IR (KBr, cm^{-1}): 3426, 3337, 3100, 2978, 2878, 2288, 2060, 1728, 1609, 1410, 1339, 1277, 1132, 1094, 889. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.14–1.38 (br m, 30H, (C(C*H*$_3$)$_2$ + C(C*H*$_3$)$_3$), 2.23 (m, 1H, N*H*), 2.69 (d, ^3J(H–H) = 14.4 Hz, 2H, PCC*H*$_2$) 3.18–3.52 (br, 2H, NC*H*(CH$_3$)$_2$), 3.49 and 3.61 (2s, 6H, OC*H*$_3$), 8.17–8.23 (m, 1H, =P-N*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.6 (d, ^3J(P–C) ∼ 4.6 Hz, NCH(*C*H$_3$)$_2$), 26.4 (d, ^3J(P–C) = 4.6 Hz, NCH(*C*H$_3$)$_2$), 30.9 (br, C(*C*H$_3$)$_3$), 31.4 (d, ^3J(P–C) ∼ 14.2 Hz, C(*C*H$_3$)$_3$), 41.5 (s, PCCH$_2$), 43.7 (d, ^1J(P–C) ∼ 182.5 Hz, P*C*), 44.4 and 44.7 (2s, N–CH(CH$_3$)$_2$), 49.9 and 51.2 (2s, OCH$_3$), 52.8 (d, ^2J(P–C) ∼ 8.4 Hz, *C*(CH$_3$)$_3$), 171.8 (d, ^2J(P–C) = 31.4 Hz, PC–*C*(O)), 174.9 (d, ^3J(P–C) = 9.2 Hz, PCCH$_2$–*C*(O)). ^{31}P NMR (162 MHz, $CDCl_3$): δ 35.6 (1s, 1P, C=*P*), 79.9 (1s, 1P, NH–*P*). LC–MS: *m*/*z* 465 [M+1]$^+$. *Anal.* Calc. for $C_{20}H_{42}N_4O_4P_2$: C, 51.71; H, 9.11; N, 12.06. Found: C, 51.62; H, 9.18; N, 12.15%.

*2.5. Synthesis of (t-BuNH)P(μ-N-t-Bu)$_2$P(=N-t-Bu){CH_2CH_2R} [R = CO_2Me (**20**), CO_2Et (**21**), CO_2-t-Bu (**22**), SO_2Et (**23**)]*

Compound 20: The procedure was the same as that for **18** using **7** (0.74 g, 2.12 mmol) and methyl acrylate (0.18 g, 2.12 mmol) [reaction time 2 d]. Yield: 0.801 g (87%). Mp: 60–62 °C. IR (KBr, cm^{-1}): 3390, 2967, 1738, 1329, 1206. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.31, 1.39 and 1.44 (3 s, 36H, C(CH_3)$_3$), 2.20–2.32 (many lines, 4H, PCH_2CH_2), 2.92 (br, 1H, N*H*), 3.67 (s, 3H, OCH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 28.2 (d, ^1J(P–C) = 150.0 Hz, P*C*), 28.5 (s, PCCH_2), 31.5–34.2 (many lines, C(CH_3)$_3$), 51.3 (s, OCH_3), 51.0, 51.7, 52.0, 52.1 (4 lines, *C*(CH_3)$_3$), 173.2 (d, ^3J(P–C) = 23.0 Hz, *C*O_2Me). ^{31}P NMR (162 MHz, $CDCl_3$): δ −6.4, 72.3. LC–MS: *m*/*z* 435 $[M+1]^+$.

Compound 21: The procedure was the same as that for **18** using **7** (0.392 g, 1.12 mmol) and ethyl acrylate (0.13 g, 1.12 mmol) [reaction time 2 d]. Yield: 0.466 g (90%). Mp: 68–70 °C. IR (KBr, cm^{-1}): 3356, 2973, 1736, 1464, 1310, 1211. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.24 (t, ^3J(H–H) = 6.8 Hz, 3H, OCH_2CH_3), 1.31, 1.39, 1.44 (3 s, 36H, C(CH_3)$_3$), 2.20–2.31 (many lines, 4H, PCH_2CH_2), 3.05 (br, 1H, N*H*), 4.12 (q, ^3J(H–H) = 6.8 Hz, 2H, OCH_2CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.2 (s, OCH_2CH_3), 27.9 (d, ^1J(P–C) = 134.0 Hz, P*C*), 28.6 (s, PCCH_2), 31.7 (s, C(CH_3)$_3$), 32.8 (d, ^3J(P–C) = 10.0 Hz, C(CH_3)$_3$), 34.2 (d, ^3J(P–C) = 12.0 Hz, C(CH_3)$_3$), 51.1 (d, ^2J(P–C) = 13.0 Hz, *C*(CH_3)$_3$), 51.8 (d, ^2J(P–C) = 9.5 Hz, *C*(CH_3)$_3$), 52.2 (d, ^2J(P–C) = 7.5 Hz, *C*(CH_3)$_3$), 60.4 (s, OCH_2), 172.9 (d, ^3J(P–C) = 23.0 Hz, *C*O_2Et). ^{31}P NMR (162 MHz, $CDCl_3$): δ −6.2, 72.8. LC–MS: *m*/*z* 449 $[M+1]^+$.

Compound 22: The procedure was the same as that for **18** using **7** (1.34 g, 3.83 mmol) and *t*-butyl acrylate (0.13 g, 1.12 mmol) [reaction time 36 h]. Yield: 1.586 g (87%). Mp: 75–78 °C. IR (KBr, cm^{-1}): 3356, 2971, 1732, 1364, 1321, 1219. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.28 (s, 9H, CO_2C(CH_3)$_3$), 1.37, 1.40 and 1.42 (3 s, 36H, NC(CH_3)$_3$), 2.02–2.12 (m, 2H, PCH_2), 2.21–2.32 (m, 2H, PCCH_2), 2.95 (br, 1H, N*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 28.0 (s, OC(CH_3)$_3$), 28.2 (d, ^1J(P–C) = 134.0 Hz, P*C*), 29.9 (br s, PCCH_2), 31.7 (s, C(CH_3)$_3$), 32.8 (d, ^3J(P–C) = 10.0 Hz, NC(CH_3)$_3$), 34.3 (d, ^3J(P–C) = 12.0 Hz, NC(CH_3)$_3$), 51.1 (d, ^2J(P–C) = 15.0 Hz, N*C*(CH_3)$_3$), 51.8 (d, ^2J(P–C) = 10.0 Hz, N*C*(CH_3)$_3$), 52.3 (d, ^2J(P–C) = 13.0 Hz, N*C*(CH_3)$_3$), 80.3 (s, O*C*(CH_3)$_3$), 172.3 (d, ^3J(P–C) = 23.0 Hz, *C*O_2C(CH_3)$_3$). ^{31}P NMR (162 MHz, $CDCl_3$): δ −3.4, 72.1. LC–MS: *m*/*z* 477 $[M+1]^+$.

Compound 23: The procedure was the same as that for **18** using **7** (0.74 g, 2.12 mmol) and ethyl vinyl sulfone (0.28 g, 2.34 mmol) [reaction time 2 d]. Yield: 0.82 g (82%). Mp: 92–97 °C. IR (KBr, cm^{-1}): 3340, 2969, 1647, 1458, 1364, 1209, 1134. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.28, 1.35 and 1.42 (3 s, 36H, C(CH_3)$_3$), 1.36 (br, 3H, CH_2CH_3), 2.42 (br, 2H, PCH_2), 2.95 (br m, 5H, PCH_2CH_2 + SO_2CH_2 + N*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 6.6 (s, CH_2CH_3), 25.8 (d, ^1J(P–C) = 128.6 Hz, P*C*), 31.8 (s, C(CH_3)$_3$), 32.8 and 34.2 (d each, ^3J(P–C) = 9.7, 12.1 Hz, respectively, C(CH_3)$_3$), 46.8 and 47.3 (2 br s, PCH_2CH_2 + SO_2CH_2), 51.5 (d, ^2J(P–C) = 14.0 Hz, *C*(CH_3)$_3$), 52.1 (d, ^2J(P–C) = 8.5 Hz, *C*(CH_3)$_3$), 52.5 (d, ^2J(P–C) = 7.3 Hz, *C*(CH_3)$_3$). ^{31}P NMR (162 MHz, $CDCl_3$): δ −10.4, 72.8. *Anal.* Calc. for $C_{20}H_{46}N_4O_2P_2S$: C, 51.26; H, 9.89; N, 11.96. Found: C, 51.26; H, 9.90; N, 11.87%.

*2.6. Synthesis of (R)-[6,6′-(t-Bu)$_2$$C_{20}H_{10}O_2$][P(μ-N-t-Bu)$_2$P] (**25**)*

This compound was prepared in a manner similar to that for [($C_{20}H_{12}O_2$)[P(μ-N-*t*-Bu)$_2$P] (**28**) [6a] using *R*(−)-6,6′-di-*tert*-butyl-1,1′-binaphthalene-2,2′-diol and [ClP-N(*t*-Bu)]$_2$ (**24**). Yield: 4.80 g (96%, by using 8.3 mmol of **24**). Mp: 140–142 °C. IR (KBr, cm^{-1}): 2959, 1618, 1593, 1505, 1366, 1289, 1204, 951. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.99 and 1.39 (2 s, 36H, *t*-Bu-*H*), 6.65 (2 d, ^3J(H–H) ~ 8.8 Hz, 2H, Ar–*H*), 7.24–7.33 (m, 4H, Ar–*H*), 7.77 (s, 2H, Ar–*H*), 7.89 (2 d, ^3J(H–H) ~ 8.8 Hz, 2H, Ar–*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 30.4, 31.1 and 34.7 (C(CH_3)$_3$), 58.7 (*C*(CH_3)$_3$), 122.7, 123.5, 123.9, 125.9, 126.2, 129.8, 131.2, 132.9, 148.4, 149.2, 149.4. ^{31}P NMR (162 MHz, $CDCl_3$): δ 171.4. LC–MS: *m*/*z* 602 $[M+1]^+$. *Anal.* Calc. for $C_{36}H_{46}N_2O_2P_2$: C, 71.98; H, 7.72; N, 4.66. Found: C, 71.82; H, 7.76; N, 4.55%.

*2.7. Synthesis of (R)-[6,6′-(t-Bu)$_2$$C_{20}H_{10}O_2$][P(μ-N-t-Bu)$_2$P(O)] (**26**)*

To a solution of **25** (1.81 g, 3.0 mmol) in dry tetrahydrofuran (5 mL), diisopropyl azodicarboxylate (DIAD) (1.0 mL, 3.0 mmol) was added. The yellow solution was stirred overnight at 25 °C upon which it became colorless. Removal of the solvent followed by column chromatography (ethyl acetate/hexane) afforded a solid that was crystallized from dichloromethane–hexane mixture (5:2, 7 mL). Yield: 1.56 g (84%). Mp: 240–244 °C(d). IR (KBr, cm^{-1}): 2971, 1622, 1593, 1505, 1385, 1208, 999. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.05, 1.10, 1.20 and 1.21 (4 s, 36H, *t*-Bu-*H*), 6.36 and 6.43 (2 d, ^3J(H–H) ~ 8.8 Hz, 2H, Ar–*H*), 7.11–7.13 (m, 2H, Ar–*H*), 7.40 and 7.46 (2 d, ^3J(H–H) ~ 8.8 Hz, 2H, Ar–*H*), 7.62–7.64 (m, 2H, Ar–*H*), 7.81–7.84 (m, 2H, Ar–*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 30.4_7, 30.5, 30.6, 31.1, 34.6_6 and 34.6_9 (C(CH_3)$_3$), 58.3 and 58.8 (2 *C*(CH_3)$_3$), 122.7, 122.8, 122.9, 123.0, 123.3, 123.4, 125.8, 125.9, 126.3, 126.4, 130.0, 130.2, 131.2, 131.3, 148.5, 148.6. ^{31}P NMR (162 MHz, $CDCl_3$): δ 5.3 and 98.9 (2 d, ^2J(P–P) = 11.3 Hz each). LC–MS: *m*/*z* 618 $[M+1]^+$. *Anal.* Calc. for $C_{36}H_{46}N_2O_3P_2$: C, 70.11; H, 7.52; N, 4.54. Found: C, 70.25; H, 7.47; N, 4.46%. A small amount (ca 5%) of the bis-oxidized material was also there, but no attempt was made to purify the compound further.

*2.8. Synthesis of(R)-[(6,6′-(t-Bu)$_2$$C_{20}H_{10}O_2$][(Se)P(μ-N-t-Bu)$_2$P(O)] (**27**)*

Selenium powder (0.182 g, 2.3 mmol) was added to a solution of **26** (0.712 g, 1.2 mmol) in dry toluene (15 mL). The solution was heated under reflux for 24 h. After cooling, excess selenium was separated by filtration. Toluene was removed in vacuum. The solid residue thus obtained was crystallized from dichloromethane–hexane (1:1) mixture. Yield: 0.61 g (75%). Mp: 154–156 °C. IR (KBr, cm^{-1}): 2963, 1601, 1470, 1294, 1235, 1197. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.16 and 1.18 (2 s, 18H, *t*-Bu-*H*), 1.32–1.37 (m, 18H, N*t*-Bu-*H*), 6.46 and 6.53 (2 d, ^3J(H–H) ~ 8.4 Hz, 2H, Ar–*H*), 7.20–7.25 (m, 2H, Ar–*H*), 7.51 and 7.56 (2 d, ^3J(H–H) ~ 8.4 Hz, 2H, Ar–*H*), 7.75–7.77 (m, 2H, Ar–*H*), 7.93–7.95 (m, 2H, Ar–*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 30.5, 30.5_8, 30.6_2, 31.1, 34.7 and 34.8 (C(CH_3)$_3$), 58.3 and 58.9 (*C*(CH_3)$_3$), 122.8, 122.9, 123.0_0, 123.0_1, 123.4_0, 123.4_2, 125.8_9, 125.9_3, 126.3_7, 126.4_3, 130.0, 130.2, 148.6, 148.7. ^{31}P NMR (162 MHz, $CDCl_3$): δ −1.2 and 36.9 (2 d, ^2J(P–P) = 15.1 Hz each). *Anal.* Calc. for $C_{36}H_{46}N_2O_3P_2Se$: C, 62.15; H, 6.66; N, 4.03. Found: C, 61.95; H, 6.71; N, 4.21%. Satellites due to the ^{77}Se atom were not clear probably due to low S/N ratio. LC–MS (negative mode): *m*/*z* 695 $[M-1]^+$.

*2.9. Synthesis of (S)-($C_{20}H_{10}O_2$)[P(Se)(μ-N-t-Bu)$_2$P(Se)] {alternative formulation: (S)-[(2-O-1-$C_{10}H_6$)$_2$][P(Se)-N-(t-Bu)-P(Se)-N-(t-Bu)]} (**29**)*

Selenium powder (0.152 g, 1.90 mmol) was added to a solution of **28** [6a] (0.471 g, 0.964 mmol) in dry toluene (10 mL). The solution was heated under reflux for 24 h. After cooling, excess selenium was separated by filtration. Toluene was removed in vacuum. The solid residue thus obtained was crystallized from dichloromethane–hexane (1:1) mixture. Yield: 0.45 g (73%). Mp: 246–248 °C. IR (KBr, cm^{-1}): 2971, 1593, 1505, 1368, 1314, 1186, 1030 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.25 (s, 18H, *t*-Bu-*H*), 6.50 (d, 2H), 7.13 (t, 2H) and 7.40 (t, 2H), 7.65 (d, 2H), 7.88 (d, 2H) and 8.06 (d, 2H) (all Ar–*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 30.6 (C(CH_3)$_3$), 59.5 (*C*(CH_3)$_3$), 123.8, 124.0, 124.2, 125.9, 126.0, 127.3, 127.9, 128.4, 131.3, 134. ^{31}P NMR (162 MHz, $CDCl_3$): δ 43.0 (s with broad satellites, ^1J(P–Se) = 981.5 Hz); $[\alpha]_D^{27}$ = −8.65 (*c* = 0.52, $CHCl_3$). X-ray structure was determined for this sample.

2.10. Synthesis of (R)-[(6,6′-(t-Bu)$_2$C$_{20}$H$_{10}$O$_2$)[(Se)P (μ-N-t-Bu)$_2$P(Se)] (30)

Yield: 0.99 g (70%, by using 1.9 mmol of **25**). Mp: 208–212 °C. IR (KBr, cm^{-1}): 2971, 1620, 1593, 1506, 1368, 1260, 1186, 963, 810. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.17 and 1.19, (2 s, 36H, *t*-Bu-*H*), 6.46 (d, ^3J(H–H) = 8.8 Hz, 2H, Ar–*H*), 7.10 (d, ^3J(H–H) = 8.8 Hz, 2H, Ar–*H*), 7.44 (d, ^3J(H–H) = 8.8 Hz, 2H, Ar–*H*), 7.64 (s, 2H, Ar–*H*), 7.80 (d, ^3J(H–H) = 8.8 Hz, 2H, Ar–*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 30.7, 31.1 and 34.7 (C(CH_3)$_3$), 59.5 (*C*(CH_3)$_3$), 122.8, 123.6, 124.1, 126.0, 126.3, 129.9, 131.3, 133.0, 148.6, 149.2, 149.3, 149.4. ^{31}P NMR (162 MHz, $CDCl_3$): δ 44.0 (s with satellites, $^{1,3}J$(P–Se) = 991.5 Hz, ^3J(P–Se) = 17.8 Hz). LC–MS: *m*/*z* 760 [M+1]$^+$. *Anal.* Calc. for $C_{36}H_{46}N_2O_2P_2Se_2$: C, 57.00; H, 6.11; N, 3.69. Found: C, 57.12; H, 6.15; N, 3.75%.

2.11. X-ray crystallography

X-ray data for **10–11**, **18–19**, **27** and **29** were collected on Bruker AXS SMART or OXFORD diffractometer at 296 K using Mo Kα (λ = 0.71073 Å) radiation. The structures were solved by direct methods [14]; all non-hydrogen atoms were refined anisotropically. The hydrogen atoms were fixed by geometry or located by difference Fourier map; subsequently a riding model was used. Some of the methyl carbon atoms of the *t*-butyl groups in these compounds have high thermal parameters, but these do not affect the overall structure around cyclophosphazane skeleton and hence we have not tried to model them rigorously. Crystallographic data are summarized in Table 1. CCDC numbers for compounds **10–11**, **18–19**, **27** and **29** are (respectively) 797416–797421.

3. Results and discussion

3.1. Oxidative addition of [(RNH)P(μ-N-t-Bu)]$_2$ [R = t-Bu (**7**), i-Pr (**8**)] with allenylphosphine oxide Ph$_2$P(O)C(Ph)═C═CH$_2$ (**9**) or dimethyl maleate

Initially, we started with the reaction of cyclodiphosphazanes **7–8** with the allenylphosphine oxide **9**. The reaction afforded compound **10** or **11** (Scheme 2) as essentially a single product formed by the attack of P(III) center on the β-carbon atom of the allenylphosphine oxide. Compound **10** exhibits three signals in the ^{31}P NMR spectrum at δ −19.3 [dd, $^{2,3}J$(PP) = 24.9, 8.3 Hz *P*═N-*t*-Bu], 31.7 [d, *J*(PP) = 24.9 Hz, Ph_2P(O)–] and 69.9 [d, *J*(PP) = 8.3 Hz; *P*(III)-NH-*t*-Bu] as expected. However, the ^{31}P NMR signals corresponding to the cyclodiphosphazane ring of compound **11** showed broad signals at δ 72.0 and −1.0, although the signal for –Ph_2P(O) at δ 32.3 (d) was sharp. This behavior (broad peaks in the ^{31}P NMR spectrum) is probably due to the more pronounced amino-imino (**I–II**) tautomerism or phosphinimine (**11**)-phosphinium salt (**III**) equilibrium in compound **11** compared to compound **10**. However, we have not studied this aspect in detail.

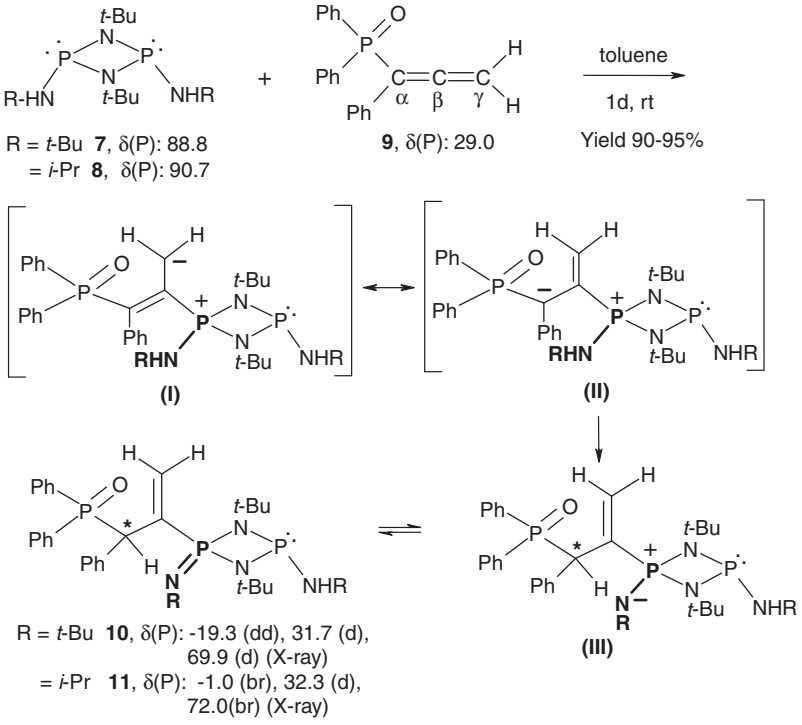
Formation of **10** entails the generation of a chiral center. We have earlier pointed out in an analogous case that it is possible to observe spontaneous resolution by crystallization [15]. Indeed, the samples that we checked crystallized in the chiral space group *Pca2(1)* with (*S*)-chirality at the (Ph)(H)*C*–P carbon center. However, unlike in the earlier example, the other enantiomer of **10** could not be separated although the solid state CD spectrum suggested that the other enantiomeric form may also be present in the bulk. In contrast to this, compound **11** crystallized in the centrosymmetric space group $P\bar{1}$. The structures of **10** and **11** (Fig. 1) clearly show the phosphinimine moiety at P(1) with P-N distances of 1.535(2) and 1.536(2) Å, respectively (cf. Table 2). A comparison of analogous distances in closely related structures **12–17** (Fig. 2) reveals that this distance is comparable to those in **12**–**14**, but longer than that observed in **15**–**17**. Thus it is likely that there is contribution from the phosphonium ion character (cf. structure **III** in Scheme 2) in compounds **10–11** as well as **12–14**, a point that we have not stressed in the earlier work [1d,15,16].

In a second set of reactions, we treated **7–8** with dimethyl maleate and obtained the stable ylides **18–19** (Scheme 3). The IR spectra of **18–19** (also **10–11**) showed the ν(NH) band in the region 3358–3427 cm^{-1}. The ^{31}P NMR spectrum of **18** exhibited two peaks at δ 23.7 and 78.9, with each one essentially as a singlet. The corresponding signals for **19** appeared at δ 35.6 and 79.9, again with negligible ^2J(PP) value. In the ^{13}C NMR spectra, the P–C carbon appears at δ 43–45 with a large ^1J(P–C) of 182–184 Hz. Notably, the ^{13}C NMR chemical shift value is not in the typical alkenic region perhaps because the formal double bond is with phosphorus. The corresponding

Table 1
Crystallographic data for compounds **10**–**11**, **18**–**19**, **27** and **29**.[a]

Compound	**10**[b]	**11**	**18**[c]	**19**	**27**[d]	**29**[e]
Formula	$C_{37}H_{55}N_4OP_3$	$C_{35}H_{51}N_4OP_3$	$C_{22}H_{46}N_4O_4P_2$	$C_{20}H_{42}N_4O_4P_2$	$C_{72}H_{92}N_4O_6P_4Se_2$	$C_{28}H_{30}N_2O_2P_2Se_2$
Formula weightt	664.76	636.71	492.57	464.52	1391.30	646.40
Crystal system	orthorhombic	triclinic	orthorhombic	orthorhombic	monoclinic	orthorhombic
space group	*Pca2(1)*	$P\bar{1}$	*P2(1)2(1)2(1)*	*Pbca*	*P2(1)*	*P2(1)2(1)2(1)*
a (Å)	18.099(2)	9.515(2)	9.002(1)	10.354(1)	14.838(1)	10.328(1)
b (Å)	10.038(1)	10.152(2)	17.788(1)	18.366(2)	13.968(1)	16.448(2)
c (Å)	20.933(2)	19.544(3)	18.124(1)	27.289(3)	23.129(2)	16.971(2)
α (°)	90	79.155(2)	90	90	90	90
β (°)	90	89.058(2)	90	90	96.842(1)	90
γ (°)	90	87.047(2)	90	90	90	90
V (Å^3)	3803.1(6)	1851.7(5)	2901.9(3)	5189.5(8)	4759.5(5)	2881.6(5)
Z	4	2	4	8	2	4
D_{calcd}	1.161	1.142	1.127	1.189	0.971	1.490
μ (mm^{-1})	0.189	0.192	0.181	0.198	0.883	2.705
F(0 0 0)	1432	684	1072	2016	1456	1304
Data/restraints/parameters	6685/7/446	6496/0/398	5076/3/306	4563/0/291	16589/1/816	5065/0/331
Goodness-of-fit (GOF) (S)	1.053	1.044	1.037	1.198	0.960	0.843
R_1	0.0301	0.0543	0.0744	0.0510	0.0638	0.0379
wR_2 (all data)	0.0779	0.1401	0.2087	0.1085	0.1964	0.0675
Max./min. residual electron dens. (e Å^{-3})	0.289/−0.192	0.457/−0.191	0.465/−0.217	0.557/−0.278	0.618/−0.294	0.575/−0.336

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{0.5}$.
[b] Flack parameter: 0.05(5) chiral at C(19) (S).
[c] Flack parameter: 0.15(18), however chirality is not present at the carbon center.
[d] Flack parameter: 0.020(9).
[e] Flack parameter: −0.026(8).



Scheme 2.

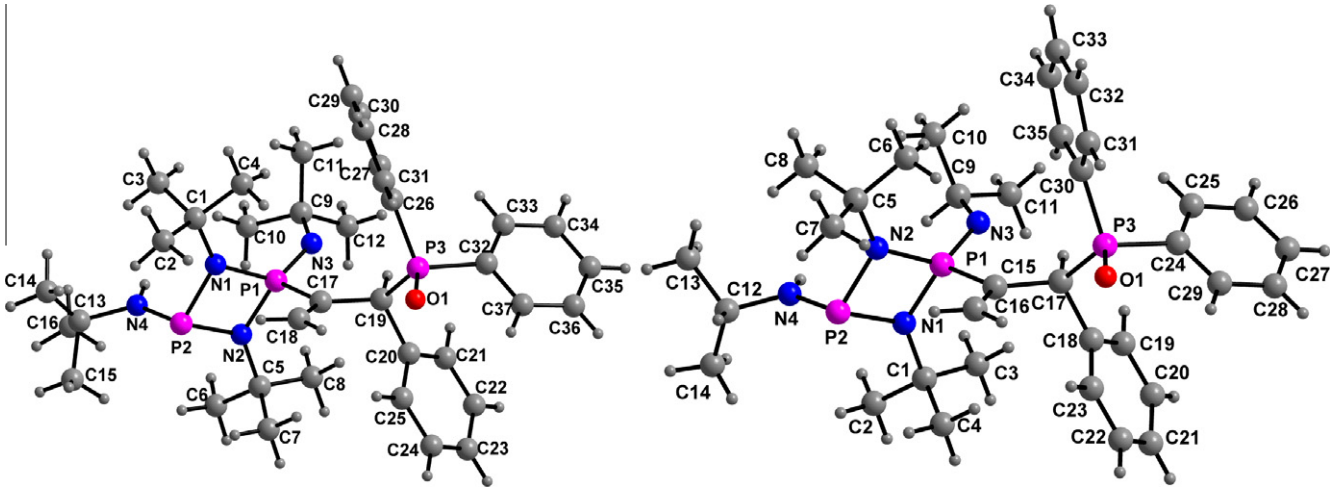


Fig. 1. Molecular structures of compounds **10**–**11**; for **10**, only one position each for C14–C16 is shown. Hydrogen bonding interactions in compound **11** (Å, Å, Å, °): N(4)–H(4D)...O(1) 0.80, 2.35, 3.102(3), 156.9; symm. equiv: $x, -1+y, z$.

^1J(P–C) values [involving the cyclophosphazane phosphorus] in compounds **10–11** are in the range 149–160 Hz at δ(C) 142–145. On the basis of our previous studies, it is expected that the ^1J(P–C) values involving an sp^2 carbon will be significantly higher than that involving a sp^3 carbon [7,17]. As an example, the ^1J(P–C) value in compound **6** (see above) is 168.9 Hz [7]. Thus in solution, the carbon attached to the phosphorus of cyclodiphosphazane skeleton in **18**–**19** has sp^2 character. The up-field chemical shift however, suggests that it does not involve a C=C (double) bond. Observation of a doublet at δ 2.65–2.69 with integrated intensity corresponding to two protons and with a ^3J(P–H) value of 14.4 Hz in the ^{1}H NMR spectra reveals a P=CCH_2 group. All these data are consistent with the structures shown in Scheme 3, but there could be contribution from the phosphonium salt structures **18′**–**19′**. In any case, these are clearly *different from the phosphinimine structures* observed in the case of **6** or **10–11**. It must also be noted that such ylidic structures were *not proposed in the mechanism for Morita–Baylis–Hillman reaction* [8], *but may be involved in specific cases*. Further confirmation of the structures of **18–19** is provided by single crystal X-ray structures as shown in Fig. 3. The shorter P1–C distances [1.715–1.718 Å] and the longer P1–N3 distances [1.599–1.616 Å] in **18–19** when compared to the corresponding distances in **10–11** clearly demonstrate that in compounds **18–19**, the P1–C bond is formally a double bond and the P1–N3 bond is formally a single bond. The presence of intramolecular hydrogen bond between N3 and a carbonyl oxygen atom in both **18** and **19** (Fig. 3) is another proof for the structure as given in Scheme 3.

In the above context, we also treated [(*t*-BuNH)P(μ-N-*t*-Bu)]$_2$ (**7**) with unsymmetrical activated alkenes CH_2=CHR [R = CO_2R, SO_2Et] and obtained compounds **20–23** (Scheme 4) that are tautomeric forms of the expected zwitterionic species **4**. Thus these products are analogous to those with methyl propiolate [cf. compound **6**]

Table 2
Selected bond distances (Å) with su's in compounds **10**–**11** and **18**–**19**.

Compound	**10**	**11**	**18**	**19**
P1–N1	1.682(2)	1.683(2)	1.671(4)	1.660(2)
P1–N2	1.688(2)	1.669(2)	1.654(4)	1.664(2)
P1–N3	1.535(2)	1.536(2)	1.605(5)	1.616(2)
P1–C	1.831(2) (P1–C17)	1.820(2) (P1–C15)	1.717(5) (P1–C17)	1.718(2) (P1–C15)
P2–N1	1.737(2),	1.731(2)	1.727(4)	1.748(2)
P2–N2	1.736(2),	1.740(2)	1.749(4)	1.753(2)
P2–N4	1.662(2)	1.649(2)	1.642(5)	1.649(2)
(P1)C=C	1.326(3) (C17–C18)	1.317(3) (C15–C16)		
(P1)C–C	1.516(2) (C17–C19)	1.518(3) (C15–C17)	1.522(7) (C17–C18)	1.513(3) (C15–C16)

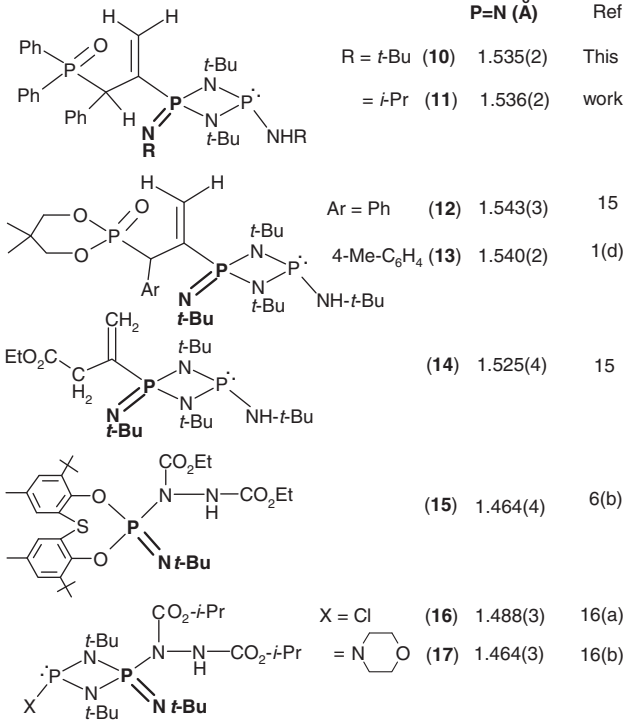


Fig. 2. The P=N distances in closely related phosphinimines.

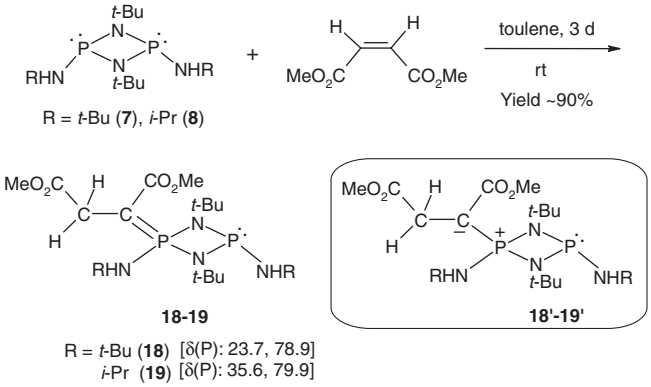
[7] but differ from **18–19**. The PC signal for compounds **20–23** appears as a doublet at δ 25.8–29.0 [^1J(P–C) ~ 128.6–150.0 Hz] in the ^{13}C NMR spectra. A compound analogous to **20–23** from the reaction of acrylonitrile with **7** has been previously characterized by us before [7] and hence this aspect is not elaborated further.

Formation of both the phosphinimine and the ylidic structures in the above reactions may be rationalized by reaction sequences shown in Scheme 5. In the formation of phosphinimine (e.g. **20**), a proton from the –N*H*-*t*-Bu group migrates to the β-carbon while for the formation of ylide (e.g. **18**) the C*H*(CO_2Me) proton migrates to the β-carbon. The presence of an additional electron withdrawing –CO_2Me group on the α-carbon is most likely responsible for the ylidic structure seen in **18–19**.

3.2. Oxidation of P(III) centers in the ansa-type cyclodiphosphazane derivatives with BINOLs-observation of an unusually long P=O (phosphoryl) bond

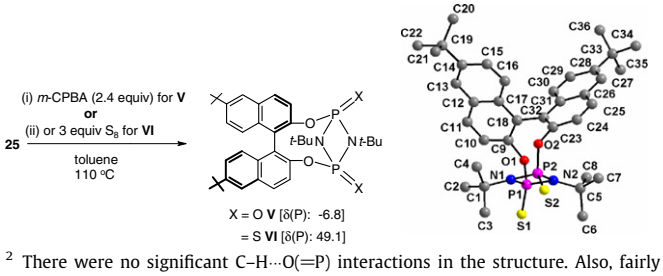
In a second line of study, we have been interested in the synthesis of *chiral* phosphoramidates and related compounds that are based on a cyclodiphosphazane skeleton [6]. Many chiral cyclic phosphoramidates with other substituents are known to show good chiral induction in reactions such as asymmetric reduction [9]. In this direction, we have synthesized a few cyclodiphosphazane compounds bearing a chiral-BINOL residue. The new fairly air-stable chiral cyclodiphosph(III)azane derivative **25** was readily prepared by a known synthetic route using (*R*)-6,6′-di-*t*-butyl-BINOL in good yields [Scheme 6] [6a,11] Analogous derivative **28** using unsubstituted (*S*)-BINOL is known [6a]. There was no indication of the presence of oligomeric products [4a,b] in these reactions. Partial oxidation of **25** by diisopropyl azodicarboxylate (DIAD) to the unsymmetrical phosphazane **26**, followed by treatment with selenium afforded the compound **27** that has P=O group at one end and P=Se at the other end.[1] The *bis*-seleno derivatives **29–30** were readily prepared by treating their respective P(III) precursors **25** and **28** with elemental selenium. The NMR [^{1}H, ^{13}C and ^{31}P] data for these compounds are consistent with the structures shown in Scheme 6.

In addition to being chiral, compound **27** is a rare example in which the two phosphorus atoms of the cyclodiphosphazane are differently oxidized. In order to understand the effect on structural parameters, we have determined the X-ray structure of this compound [Fig. 4]. For comparison, we have obtained the X-ray structure of the diseleno derivative **29** also [Fig. 5]. The ring P-N distances at the tetracoordinate phosphorus in these are normal and comparable to those observed in the compounds **10–11** and **18–19** discussed above. The P=Se distances in **27** and **29** are also nearly the same. However, the P=O distances in **27** [two molecules in the asymmetric unit; P1–O3 1.538(5), P3–O6 1.495(5) Å] are unusually long.[2] For comparison, in analogous compounds **31–32**,



Scheme 3.

[1] We have also prepared compounds the bis-oxidized and bis-sulfurized derivatives **V**–**VI**; X-ray structure of **VI** has also been determined. The disordered solvent (toluene) molecules are present in the structure that could not be modeled satisfactorily. Three molecules are present in the asymmetric unit; only one is shown in the picture below (hydrogen atoms omitted). This structure has also been deposited (CCDC 797421). P–S (mean) ~ 1.906 Å, P–N (mean) ~ 1.677 Å, P–O (mean) ~ 1.607 Å. Further details on **V**–**VI** are available as Supplementary information.



[2] There were no significant C–H···O(=P) interactions in the structure. Also, fairly long P=O distances are found in **10**–**11**, but these are Ph_2P=O distances. The distance found in **27** is much longer.

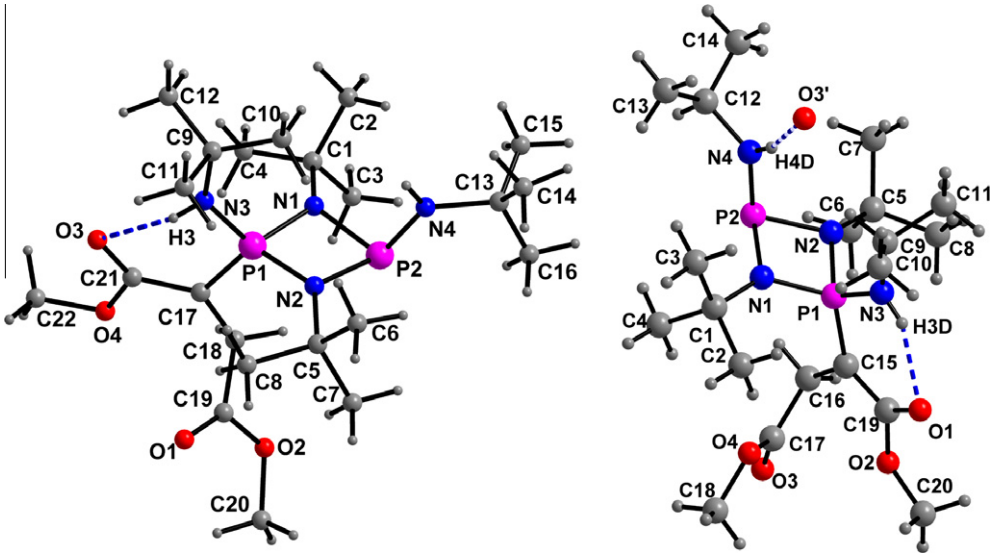
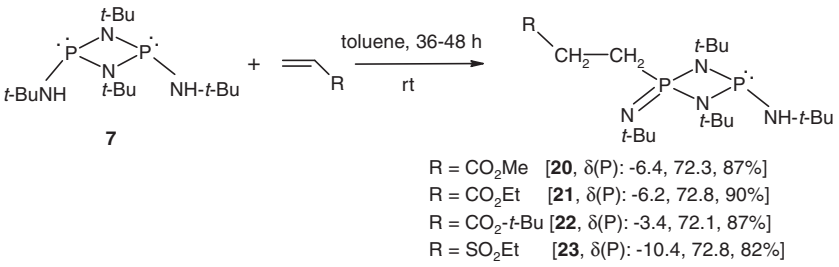
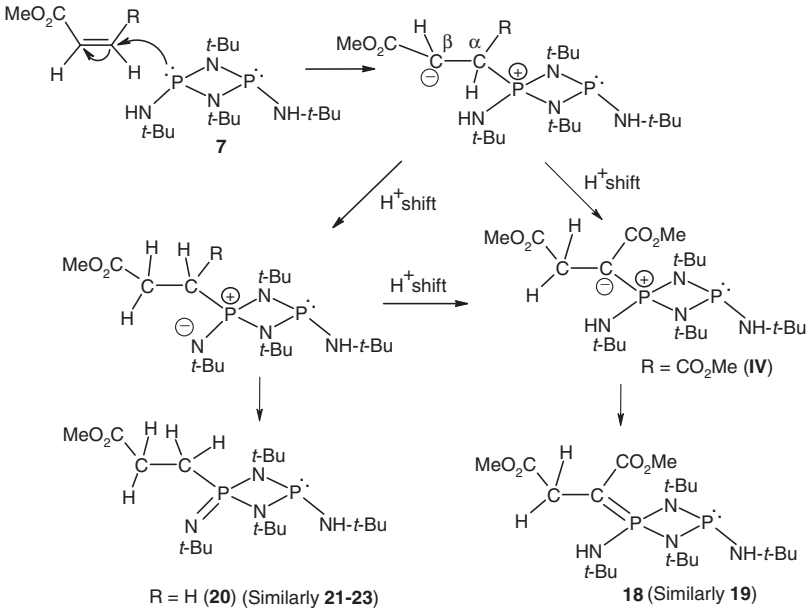


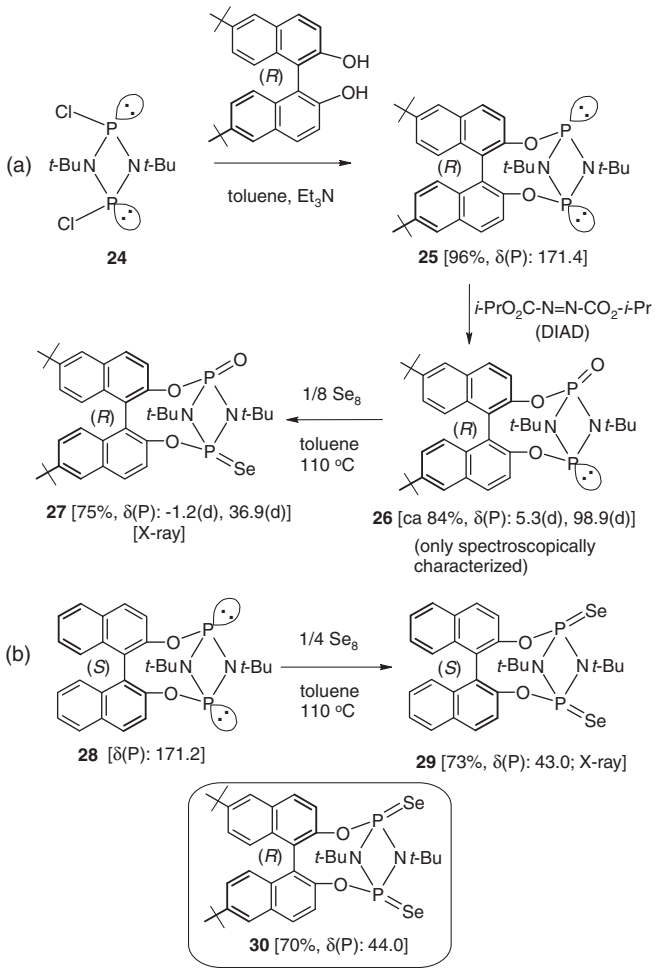
Fig. 3. Molecular structures of compounds **18** and **19**; all the non-hydrogen atoms are labeled. Some of the *t*-butyl carbon atoms are disordered. Only selected bond distances (Å) are given here. Hydrogen bond parameters in compound **18** (Å, Å, Å, °): N(3)–H(3)...O(3) 0.71(4), 2.20(5), 2.676(7), 126(5). Hydrogen bond parameters in compound **19** (Å, Å, Å, °): N4–H4D...O3′ 0.83(3), 2.27(3) 3.067(3), 161(2); N3–H3D...O1 0.80(3), 2.01(3), 2.718(2), 147(3). Symm equiv: 0.5 − *x*, 0.5 + *y*, *z*.



Scheme 4.

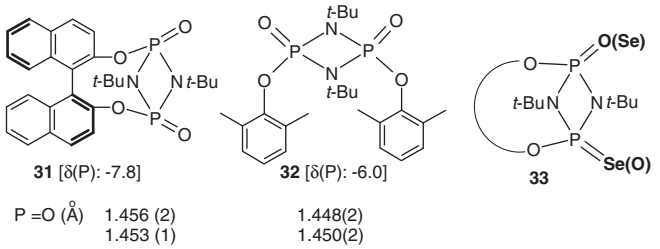


Scheme 5.



Scheme 6.

the corresponding P=O distances are in the range 1.445–1.460 Å. Like what was observed before for crystals of species **33** [6], it is possible that in the crystal there could be exchange of positions of P=O and P=Se that could make P=O bond look longer crystallographically, but as of now, we do not have evidence to corroborate this assertion.



4. Summary

Two structurally different types of products, one a *phosphinimine* and the other a *phosphorus ylide*, respectively, are formed in the reaction of $[(RNH)P\text{-}N(t\text{-}Bu)]_2$ (R = *t*-Bu (**7**), *i*-Pr (**8**)], with the allenylphosphine oxide $Ph_2P(O)C(Ph)=C=CH_2$ (**9**) or dimethyl maleate. The latter result shows that in addition to the proposed interemdiates in phosphine mediated reactions including Morita–Baylis–Hillman reaction, other intermediates may also be involved. One

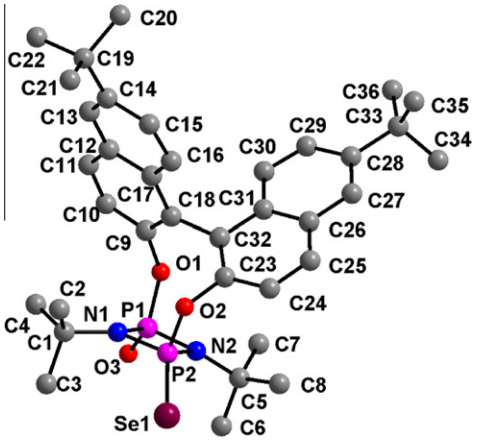


Fig. 4. Molecular structure of compound **27**; only one molecule in the asymmetric unit is shown. Hydrogen atoms are omitted for clarity. Selected bond distances (Å): *Molecule 1* P1–O1 1.591(4), P1–O3 1.538(5), P1–N1 1.656(5), P1–N2 1.681(5), P2–O2 1.601(4), P2–N1 1.695(4), P2–N2 1.650(4), P2–Se1 2.046(2). *Molecule 2* P3–O4 1.594(4), P3–O6 1.495(5), P3–N3 1.647(6), P3–N4 1.657(5), P4–O5 1.618(5), P4–N4 1.668(6), P4–N3 1.682(6), P4–Se2 2.057(2).

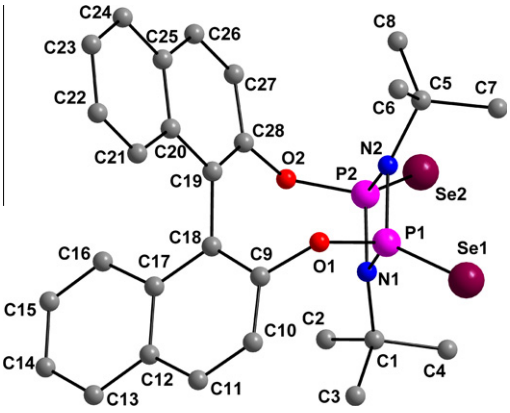


Fig. 5. Molecular structure of compound **29**. Selected bond parameters (Å): P1–N1 1.674(3), P1–N2 1.681(3), P1–O1 1.597(3), P1–Se1 2.049(1), P2–N1 1.678(3), P2–N2 1.667(3), P2–O2 1.606(3), P2–Se2 2.061(1).

of these compounds crystallizes in the chiral space group *Pca2(1)* with (*S*)-chirality at a carbon center [–C(=CH_2)*C*H(Ph)-P] suggesting a case of spontaneous resolution through crystallization. New ansa-type cyclodiphosphazanes with a chiral BINOL residue, that may be useful as chiral auxiliaries, are synthesized. In one of these, an unusually long phosphoryl (P=O) bond [1.538(5) Å] is observed.

Acknowledgements

This work was supported by the Department of Science and Technology (DST), New Delhi. The National Single Crystal Diffractometer Facility at the University of Hyderabad funded by DST (New Delhi), and the UPE and the CAS programs of the UGC for other equipment are gratefully acknowledged. GG, VS, NNBK, EB and MC thank CSIR for fellowships.

Appendix A. Supplementary material

CCDC 797416, 797417, 797418, 797419, 797420, and 797421 contain the supplementary crystallographic data for **10**–**11**, **18**–**19, 27** and **29**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via

www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2010.12.072.

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