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

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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.
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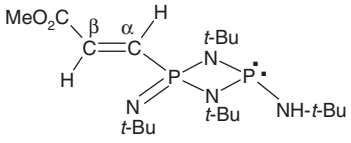
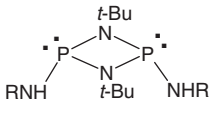
1. Introduction

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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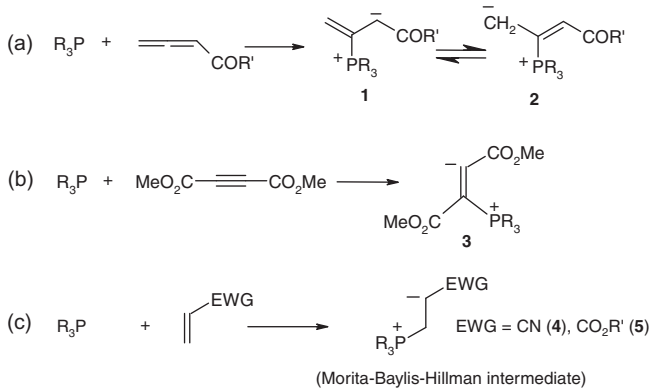

Scheme 1.

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%.

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