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The reaction of allenes with phosphorus(III) compounds bearing a P-NH-(*t*-Bu) group: isolation of both enantiomers in crystalline form from an achiral system

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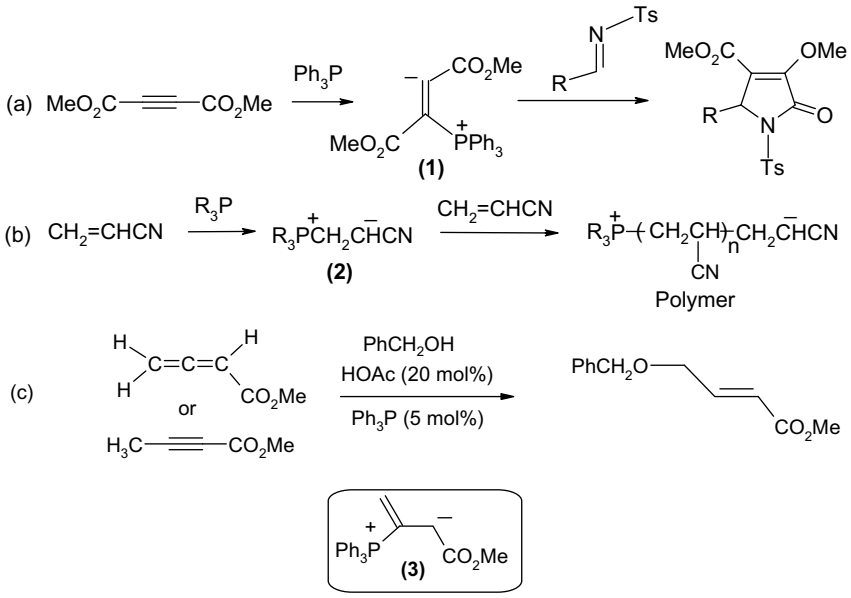
ABSTRACT

Structural characterization of the tautomeric forms of the zwitterions proposed in the phosphine catalyzed transformations of electron-deficient allenes by utilizing a cyclodiphosphazane with a P-NH-*t*-Bu group and Ph_2P(NH-*t*-Bu) is described. Spontaneous resolution of the products (*R* and *S* enantiomers of the crystals) via crystallization is highlighted.

Phosphine activated reactions of electron deficient alkenes/alkynes have found diverse and useful applications for a variety of organic transformations.[1,2] The species $Ph_3P^+C(CO_2Me)=C^-(CO_2Me)$ (**1**) is proposed as an intermediate in the reaction utilizing the Ph_3P–DMAD combination (cf. Scheme 1). This combination also leads to many other products,[3] and to our knowledge, no structural proof for **1** is available. Phosphines also initiate the polymerization of acrylonitrile, wherein the zwitterion $R_3P^+CH_2CH^-CN$ (**2**) is the likely initiator.[4,5] In the umpolung nucleophilic addition to the ester allene $H_2C=C=C(H)CO_2Me$, a species of type **3** is involved as an intermediate; it is possible that an analogous species is involved in the reaction using the isomeric compound $H_3CC\equiv CCO_2Me$.[1a] In



Scheme 1.

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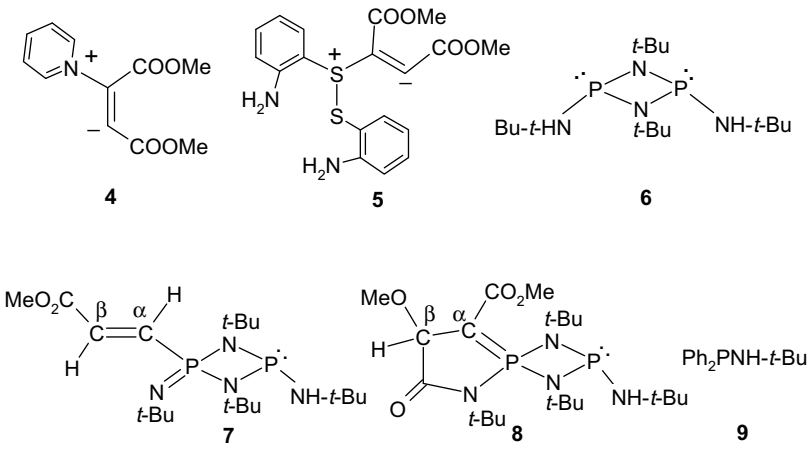
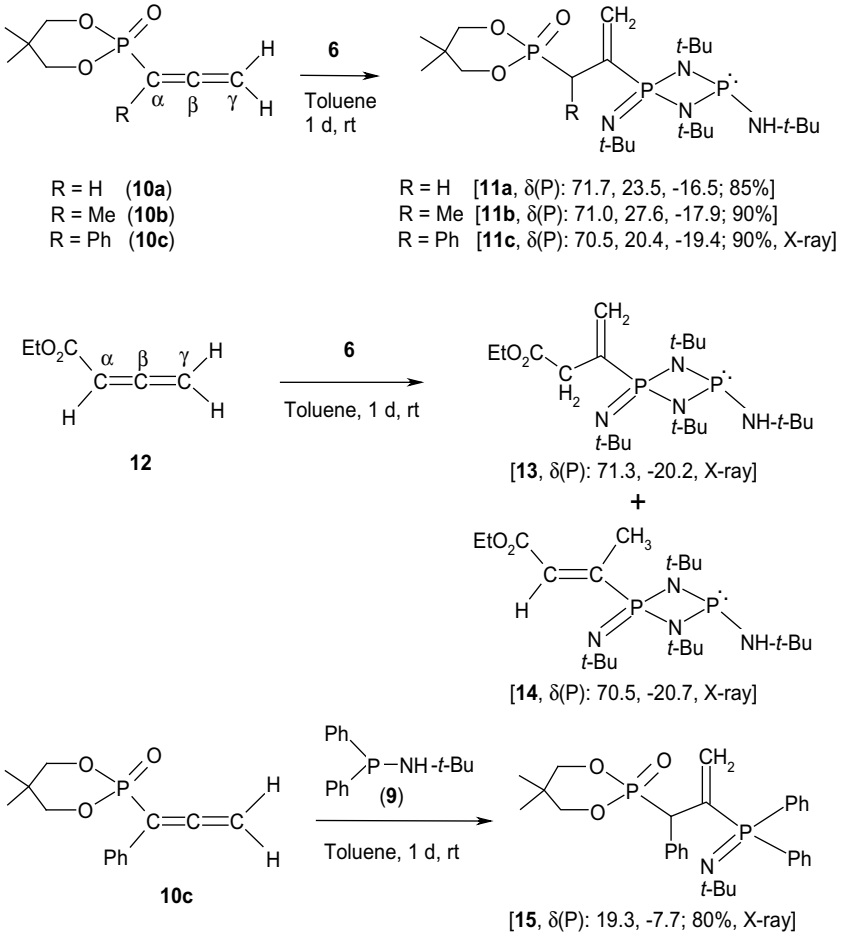


earlier reports on heterocyclic syntheses utilizing pyridine–DMAD or disulfide–DMAD, the involvement of zwitterions **4** and **5** is proposed.[5] One of our interests in this connection is to characterize species such as **1–5** and find utility for them later. Toward this end, we used the P^{III} compound $[t\text{-BuNHPN}(t\text{-Bu})]_2$ (**6**, cyclophosphazane heterocycle) which has a PNH(*t*-Bu) group.[6] Tautomeric forms of the expected zwitterions (e.g., **7**) or novel heterocycles (e.g., **8**) were thus synthesized. The choice of this substrate was dictated by our desire to obtain crystalline materials that will be amenable for conclusive X-ray structural studies. As a continuation of this study, we have explored the reaction of phosphorylated allenes (allenylphosphonates) with **6** and extended it in one case to $Ph_2P(NH\text{-}t\text{-}Bu)$ (**9**). A comparison is made to the reactions with alkynes and acrylates. An interesting case of spontaneous resolution via crystallization is also presented.

Scheme 2 shows the results obtained from the reaction of different allenes with the phosphazane **6**.[7,8] It is clear from these reactions that the P^{III} end of the cyclophosphazane reacts with the β-carbon of the allene. The difference between the proposed intermediate **3** (Scheme 1) and compounds **11a–c** is that in the latter, the



Scheme 2.

proton of the NH-*t*-Bu group from **6** has migrated to the α-carbon. The ^{13}C NMR spectra of compounds **11a–c** show the α-carbon in the expected *aliphatic* region [δ 24.9–41.8] with a ^{1}J(P–C) value of 127 Hz. In compound **11c**, the *ipso*-carbons of the four *C*Me$_3$ groups exhibit separate signals, which could indicate that resolution of the enantiomers may be possible.

In contrast to the above, in the reaction using the ester allene **12**, we obtained the rearranged product **14** by keeping the initially formed normal product **13** in solution over a period of 2 d (for complete conversion).[9] Thus the allenylphosphonates and ester allene differ marginally as regard the nature of the final product. We have also shown in Scheme 2 that the aminophosphine Ph$_2$P(NH-*t*-Bu) **9** leads to a product similar to that from **6** which suggests that the reaction is more general for compounds with a P-NH-*t*-Bu group. Confirmatory structural proof for **11c** (*R* and *S* forms) and **13-14** is given by single crystal X-ray crystallography (Figs. 1–3).[10,11]

It should be noted that in compounds **11c** and **15**, a chiral center is generated at C(22) in each case. Interestingly, in both of these cases, the compounds crystallized in the chiral space groups, *P-na2*$_1$ and *P2*$_1$2$_1$2$_1$, respectively. The absolute configurations at the chiral center as suggested by *checkcif* are *S* and *R*, respectively. In the case of **11c**, we checked the structures of several crystals and were able to obtain the structures of both the *S* and the *R* enantiomers (Fig. 4). Although *a priori* identification of the crystals was not feasible because of similar morphology of the crystals, this feature suggests that there is spontaneous resolution upon crystallization.[12] The CD spectra (Fig. 5) of the crystals showed expected features in the UV region, but in solution we were not able to obtain significant optical rotation. The enantiomeric forms of crystals were detected using the CD spectrum as an indicator. We are exploring this aspect further.

In summary, we have reported structural proof for the attack of a P^{III} center at the β-carbon of allenes. The NH proton of the P-NH-*t*-Bu group migrates to the α- or γ-carbon of the allene resulting in the formation of a phosphinimine.[13] Spontaneous resolution through crystallization has been observed in two cases (**11c** and **15**), wherein a chiral center is generated during the reaction. In the case of **11c**, both the (*R*) and (*S*) enantiomers have been characterized via crystallization in the absence of any chiral agent.

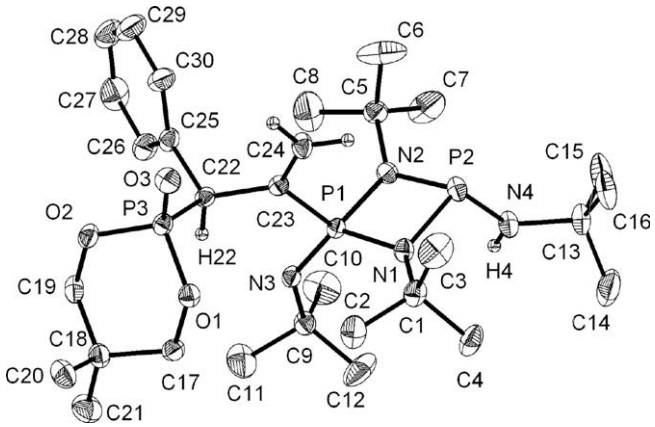


Figure 1. ORTEP diagram (probability ellipsoid 20%) of (*S*)-**11c** [P(1)–C(23) 1.826(3), P(1)–N(1) 1.677(3), P(1)–N(2) 1.688(3), P(1)–N(3) 1.543(3), P(2)–N(1) 1.751(3), P(2)–N(2) 1.742(3) P(2)–N(4) 1.661(3) Å].

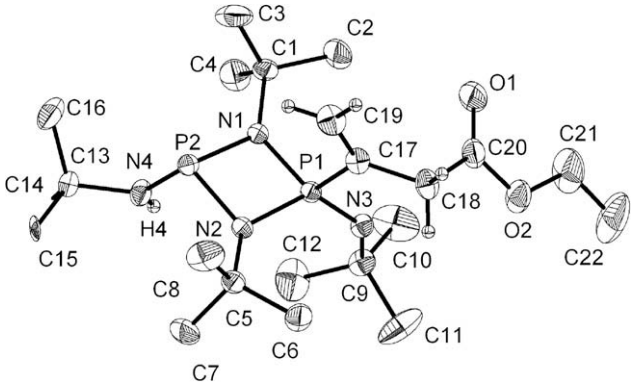


Figure 2. ORTEP diagram (probability ellipsoid 20%) of compound **13** [P(1)–C(17) 1.806(6), P(1)–N(1) 1.683(4), P(1)–N(2) 1.686(4), P(1)–N(3) 1.525(4), P(2)–N(1) 1.735(4), P(2)–N(2) 1.724(4), P(2)–N(4) 1.649(5) Å].

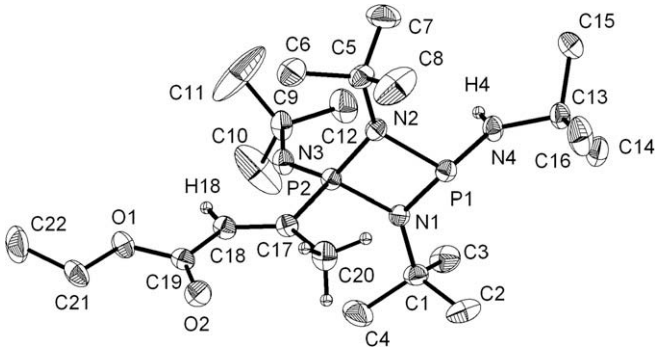


Figure 3. ORTEP diagram (probability ellipsoid 20%) of compound **14** [P(2)–C(17) 1.831(2), P(2)–N(1) 1.672(2), P(2)–N(2) 1.678(2), P(2)–N(3) 1.518(2), P(1)–N(1) 1.739(4), P(1)–N(2) 1.738(2), P(1)–N(4) 1.652(2) Å].

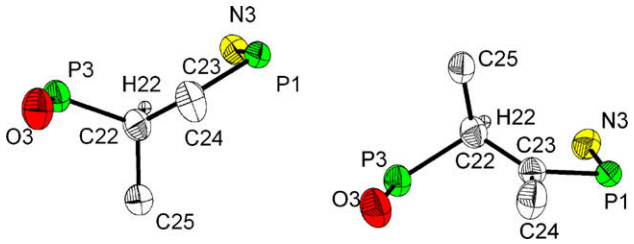


Figure 4. The *R* (left) and *S* (right) configurations at C(22) in the two different crystals of **11c**.

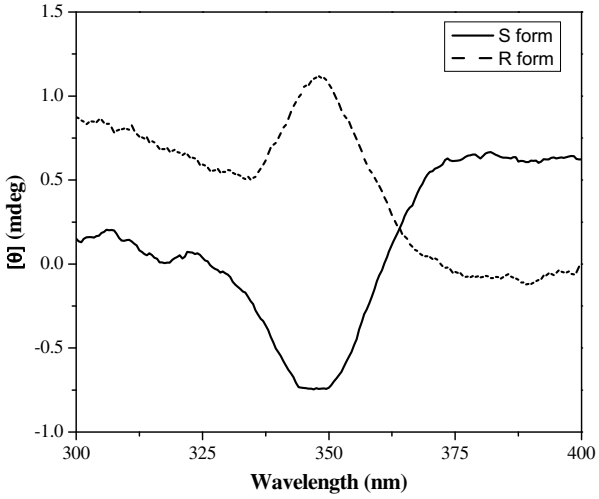


Figure 5. CD spectra of the *R* and *S* forms of crystals of **11c**.

The P=N center in these compounds is attacked readily by acids and even by carbon dioxide/moisture leading to new ionic species.

Acknowledgments

We thank DST (New Delhi) for financial support and for the Single Crystal X-ray diffractometer facility at the University of Hyderabad, and UGC (New Delhi) for equipment under UPE and CAS programs. NNBK thanks CSIR for a fellowship.

Supplementary data

Characterization data for compounds **11a**, **11b** and **15**, an ORTEP drawing of 15 and crystal data (CIF files). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2008.09.153.

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7. *Representative procedure for* **11c**: Allenylphosphonate **10c** (0.20 g, 0.78 mmol) and cyclodiphosphazane **6** (0.27 g, 0.78 mmol) were dissolved in toluene (4 mL), and the mixture was stirred for 1 d. The solution was concentrated in vacuo (to ca. 1.5 cm^3) and cooled for 1 d at −4 °C to obtain large crystals of **11c**. Yield: 0.42 g (90%); mp 152–154 °C. IR (KBr, cm^{-1}): 3310, 2964, 2888, 1599, 1476, 1456, 1366, 1292, 1221, 1063, 1007. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.96, 1.12, 1.25, and 1.37 (4s, 42H, C(*CH*$_3$)$_2$+*t*-Bu-*H*), 2.67 (d, ^2J(P-H) = 7.6 Hz, 1H, N*H*), 3.79–4.33 (m, 4H, O*CH*$_2$), 5.78 (dd, ^3J(P-H) = 22.8 Hz, ^4J(P-H) = 4.0 Hz, 1H, =*CH*$_A$H$_B$, cis to P), 6.04 (dd, ^3J(P-H) = 14.4 Hz, ^2J(P-H) = 18.0 Hz, 1H, P*CH*), 6.80 (d, ^3J(P-H) = 50.4 Hz, 1H, =CH$_A$*H*$_B$, trans to P), 7.18–7.56 (m, 5H, Ar–*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.0 and 22.0 (2s, C(*CH*$_3$)$_2$), 31.0 (dd → t, ^3J(P-C) ∼ 4.9 Hz, C(*CH*$_3$)$_3$), 31.3 (dd → t, ^3J(P-C) ∼ 4.7 Hz, C(*CH*$_3$)$_3$), 32.4 (d, ^3J(P-C) = 6.5 Hz, C(*CH*$_3$)$_2$), 32.9 (d, ^3J(P-C) = 10.0 Hz, C(*CH*$_3$)$_3$), 34.6 (d, ^3J(P-C) = 12.0 Hz, C(*CH*$_3$)$_3$), 41.8 (dd, ^1J(P-C) = 125.5 Hz, ^2J(P-C) = 4.8 Hz, P(O)*C*(Ph)), 51.4 (d, ^2J(P-C) = 14.7 Hz, *C*(CH$_3$)$_3$), 52.2 (d, ^2J(P-C) = 8.4 Hz, *C*(CH$_3$)$_3$), 52.3 (d, ^2J(P-C) = 10.0 Hz, *C*(CH$_3$)$_3$), 52.6 (d, ^2J(P-C) = 8.2 Hz, *C*(CH$_3$)$_3$), 76.5 and 76.6 (2 s, O*CH*$_2$), 127.0, 127.1, 128.2, 128.3, 130.2,130.3, 136.2 (d, ^2J(P-C) = 5.5 Hz, PC=*CH*$_2$), 143.4 (d, ^1J(P-C) = 162.9 Hz, P*C*=CH$_2$). ^{31}P NMR (160 MHz, $CDCl_3$): δ −19.4 (dd, ^3J(P-P) = 34.8 Hz, ^2J(P-P) ∼ 6.6 Hz), 20.4 (d, ^3J(P-P) = 34.8 Hz), 70.5 (d, ^2J(P-P) ∼ 6.6 Hz). LC–MS: *m/z* 613 [M+1]$^+$. X-ray structure was determined for this compound. The enantiomeric forms were detected using the CD spectra as an indicator.
8. (a) Allene preparation: Satish Kumar, N. *Studies on the Synthesis, Reactivity and Utility of Cyclic Phosphorus(III) Compounds and Organophosphonates*, Ph.D. thesis, University of Hyderabad: India, 2004.; (b) Guillemin, J. C.; Savignac, P.; Denis, J. M. *Inorg. Chem.* **1991**, *30*, 2170; (c) Lang, R. W.; Hansen, H.-J. *Organic Syntheses*, *Coll. Vol. 7*, p. 232.
9. In a procedure similar to that for **11c**, compounds **6** (0.33 g, 0.95 mmol) and **12** (0.13 g, 1.14 mmol) were reacted. However, unlike **11c**, isomeric products **13-14** in which the PN*H* proton migrated to the α or γ carbon of the original allene were obtained. Although further purification proved to be difficult, the crystalline material obtained initially contained **13**, predominantly. We were successful in isolating **13** in ca 95% purity and fortunately some crystals suitable for X-ray structure analysis could be obtained. This solution, upon keeping for 2 d, gave **14** which could be purified. Compound **13**: Yield (see above): 0.35 g (80%, purity ca. 95%, remainder was **14**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.27 (t, ^2J(H-H) ∼ 7.2 Hz, 3H, CH$_2$*CH*$_3$), 1.33 and 1.38 (2s, 36H, *t*-Bu-*H*), 2.75 (br, 1H, N*H*), 3.39 (br, 2H, PCC*H*$_2$), 4.14 (q, ^3J(H-H) = 7.1 Hz, 2H, *CH*$_2$CH$_3$), 5.55 (br, 1H, =CH$_A$*H*$_B$, cis to P) 5.70 (d, 1H, ^3J(P-H) = 49.8 Hz, =CH$_A$*H*$_B$, trans to P). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.2 (s, CH$_2$*CH*$_3$), 31.4, 31.4$_5$, 31.4$_7$, 31.5$_0$, 31.5$_4$ and 31.6 (many lines, C(*CH*$_3$)$_3$), 32.9 (dd, ^3J(P-C) = 3.6 Hz and 9.6 Hz, C(*CH*$_3$)$_3$), 34.3 (d, ^3J(P-C) = 12.7 Hz, PCC*H*$_2$), 34.5 (d, ^3J(P-C) = 11.8 Hz, C(*CH*$_3$)$_2$), 51.6, 51.7, 52.3, and 52.4 (4s, *C*(CH$_3$)$_3$), 59.8 (s, O*CH*$_2$CH$_3$), 126.4 (s, PC=*CH*$_2$), 139.6 (d, ^1J(P-C) = 137.5 Hz, P*C*), 163.8 (s, *C*OOEt). Detailed assignment was difficult because, during the time of recording, signals due to **14** also appeared. ^{31}P NMR (160 MHz, $CDCl_3$): δ -20.2, 71.3. X-ray structure was determined for the crystals thus obtained. Compound **14**: Yield (see above); mp 100–103 °C. IR (KBr, cm^{-1}): 3329, 2965, 2874, 1703, 1615, 1460, 1372, 1316, 1190, 1047, 990. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.25 (t, ^2J(H-H) ∼ 7.2 Hz, 3H, CH$_2$*CH*$_3$), 1.32, 1.33, 1.36 and 1.38 (4s, 36H, *t*-Bu-*H*), 2.00 (br d, ^3J(P-H) = 16.0 Hz, 3H, PCC*H*$_3$), 2.87 (d, ^2J(P-H) = 7.2 Hz, 1H, N*H*), 4.17 (q, ^3J(H-H) = 7.2 Hz, 2H, *CH*$_2$CH$_3$), 7.16 (br, 1H, PCC*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.3 (merged s, PCC*H*$_3$ + CH$_2$*CH*$_3$), 31.6 (dd → t, ^3J(P-C) ∼ 5.0 Hz, two of C(*CH*$_3$)$_3$), 33.0 (d, ^3J(P-C) = 10.0 Hz, C(*CH*$_3$)$_2$), 34.5 (d, ^3J(P-C) = 12.0 Hz, C(*CH*$_3$)$_3$), 51.3 (d, ^2J(P-C) = 15.0 Hz, *C*(CH$_3$)$_3$), 51.7 (d, ^2J(P-C) = 7.0 Hz, *C*(CH$_3$)$_3$), 52.3 (d, ^2J(P-C) = 8.0 Hz, two of *C*(CH$_3$)$_3$), 59.9 (s, O*CH*$_2$CH$_3$), 130.1 (s, PC=*CH*), 154.2 (d, ^1J(P-C) = 190.0 Hz, P*C*), 166.7 (d, ^3J(P-C) = 26.0 Hz, *C*O$_2$Et). ^{31}P NMR (160 MHz, $CDCl_3$): δ −20.7, 70.5. LC–MS: *m/z* 461 [M+1]$^+$. X-ray structure was determined for this compound. Anal. Calcd for $C_{22}H_{46}N_4O_2P_2$: C, 57.37; H, 10.07; N, 12.16. Found: C, 57.46; H, 10.05; N, 12.08.
10. X-ray data were collected on a Bruker AXS SMART diffractometer using Mo-Kα (λ = 0.71073 Å) radiation. The structures were solved and refined by standard methods.[11] In some cases, the terminal carbon atoms of the *t*-butyl groups showed high thermals; this was particularly so in the case of (*R*)-**11c** and **13**, where the quality of data was not great.
Crystal data: (***S***)-11 c $C_{30}H_{55}N_4O_3P_3$, *M* = 612.69, orthorhombic, space group *Pna*2(1), *a* = 19.9847(19), *b* = 17.5360(16), *c* = 10.1393(10) Å, *V* = 3553.3(6) Å^3, *Z* = 4, μ = 0.201 mm^{-1}, data/restraints/parameters: 5460/1/379, *R* indices (*I* > 2σ(*I*)): R_1 = 0.0491, wR_2 (all data) = 0.1201. Flack parameter: −0.05(10). CCDC 697359. (***R***)-**11c** $C_{30}H_{55}N_4O_3P_3$, *M* = 612.69, orthorhombic, space group *Pna*2(1), *a* = 19.966(4), *b* = 17.548(4), *c* = 10.131(2) Å, *V* = 3549.4(12) Å^3, *Z* = 4, μ = 0.201 mm^{-1}, data/restraints/parameters: 6231/1/379, *R* indices (*I* > 2σ(*I*)): R_1 = 0.0561, wR_2 (all data) = 0.1332. Flack parameter: 0.02(11). CCDC 697360. Compound **13**: $C_{22}H_{46}N_4O_2P_2$, *M* = 460.57, monoclinic, space group *P*2(1)/*c*, *a* = 9.9107(12), *b* = 36.162(4), *c* = 8.5923(10) Å, β = 114.562 (2)°, *V* = 2800.7(6) Å^3, *Z* = 4, μ = 0.178 mm^{-1}, data/restraints/parameters: 4921/1/287, *R* indices (*I* > 2σ(*I*)): R_1 = 0.0817, wR_2 (all data) = 0.2355. CCDC 697361. Compound **14**: $C_{22}H_{46}N_4O_2P_2$, *M* = 460.57, monoclinic, space group *P*2(1)/*n*, *a* = 9.5893(8), *b* = 18.8492(15), *c* = 15.7060(12) Å, β = 98.2660(10)°, *V* = 2809.4(4) Å^3, *Z* = 4, μ = 0.177 mm^{-1}, data/restraints/parameters: 4959/0/289, *R* indices (*I* > 2σ(*I*)): R_1 = 0.0573, wR_2 (all data) = 0.1681. CCDC 697362. Compound **15**: $C_{30}H_{37}NO_3P_2$, *M* = 521.55, orthorhombic, space group *P*2(1)2(1)2(1), *a* = 9.068(2), *b* = 11.551(3), *c* = 27.114(6) Å, *V* = 2839.9(11) Å^3, *Z* = 4, μ = 0.184 mm^{-1}, data/restraints/parameters: 5598/0/330, *R* indices (*I* > 2σ(*I*)): R_1 = 0.0396, wR_2 (all data) = 0.1015. Flack parameter: −0.03(8). CCDC 697363.
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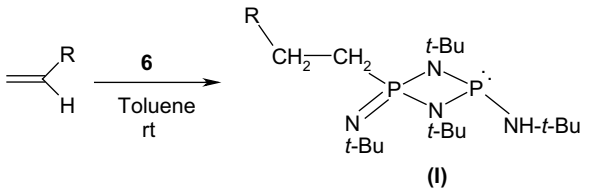
12. (a) Pérez-Garcíaa, L.; Amabilino, D. B. *Chem. Soc. Rev.* **2007**, *36*, 941–967; (b) Jayanty, S.; Radhakrishnan, T. P. *Chem. Eur. J.* **2004**, *10*, 2661–2667. this paper refers to conformationally chiral molecules) and references 7–9 cited therein; (c) Raghavaiah, P.; Supriya, S.; Das, S. K. *Chem. Commun.* **2006**, 2762–2764.
13. We also have corroborative evidence for the regiochemistry in the formation of a species such as **2** by the high yield isolation of compounds of type **I** from the reaction of unsymmetrical alkenes H$_2$C=CHR [R = electron withdrawing group] with **6**. Full characterization data are available from us.



(I)

R = CO_2Me [δ(P): 72.3, -6.4; 87%]
R = CO_2Et [δ(P): 72.8, -6.2; 90%]
R = CO_2-*t*-Bu [δ(P): 72.1, -3.4; 87%]
R = SO_2Et [δ(P): 72.8, -10.4; 82%]