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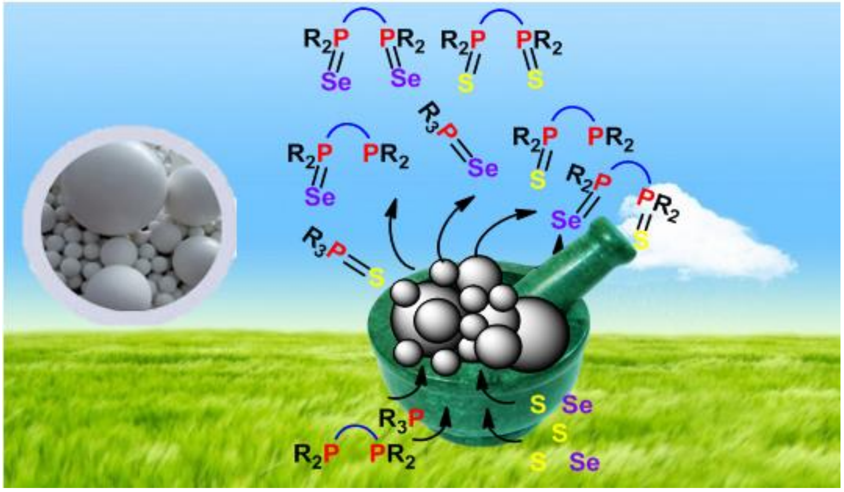
This paper describes the prepartion of chalcogenides and partially oxidized derivatives of tertiary phosphines, amino- and a vareity of bisphosphines in almost quantitative yields under solvent free conditions using rotary ball mill. The scope of this methodology was shown by ployphosphines and also in scaled up reactions. The short duration, absence of solvents and lower rotation frequency makes it a environmentaly benign and energy saving method.



Synthesis of Phosphine-chalcogenides under Solvent-free Conditions using Rotary Ball Mill

Rajnish Kumar, Saurabh Kumar, Madhusudan K. Pandey, Vitthalrao S. Kashid, Latchupatula Radhakrishna and Maravanji S. Balakrishna*

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Abstract: The mechanochemical technique of ball milling has been applied to the solvent-less and eco-friendly synthesis of chalcogenides (sulfide and selenide) of a variety of tertiary and amino-phosphines. In most of the cases, the products are obtained in almost quantitative yields with high purity by applying a simple workup procedure without using chromatographic techniques or any other purification methods. The scope of this methodology was explored by using a range of phosphines (mono, di and tetra) to synthesize partial as well as mixed-chalcogenides. The use of almost equimolar amounts of starting materials and absence of any by-product significantly simplifies the product isolation compared to the standard solution state reactions, thus providing a highly atom economic (100%) method with an ideal E-factor (E = 0). The solid state reactions were monitored by $^{31}P\{^{1}H\}$ NMR spectroscopy. The structures of some of the products are also confirmed by single crystal X-ray analyses. Although most of the reactions were carried out in ~100 mg scale, the scaling up of the reaction did not affect the course of the reaction.

Keywords: Ball Mill; Solid State; Phosphines; Chalcogenides; Oxidation.

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Introduction

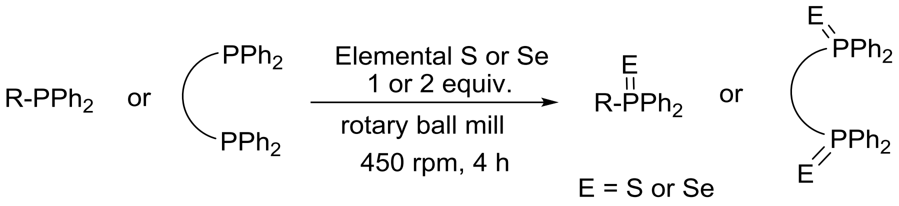
In recent years, synthetic chemists have given much attention towards developing the methodologies which are inexpensive, eco-friendly and recyclable, mainly due to the growing environmental concerns. A reaction under solvent free condition or solid support provides many advantages over the conventional solution phase synthesis[1] in terms of product yield, reaction time, benign condition, ease of purification, and recyclability of the support,[2] minimizing the generation of toxic and nontoxic waste and disposal of the solvents. Another emerging field of research in this respect is the employment of techniques such as mixing, grinding, or ball milling, to carry out chemical reactions in the absence of a solvent,[3] which considerably decreases the E-factor[4] of the reactions. Exploring the low cost eco-friendly methods for the ease and simple preparation of compounds by ball milling, also known as mechanochemistry,[5] is a challenging task especially to reduce the reaction time, the temperature and simplifying the workup procedures. Mechanochemistry has been exploited for the derivatization of biological molecules, for example, synthesis of amino acids,[6] amino esters,[7] peptides,[8] functionalization of nucleosides or carbohydrates.[9] Reactions such as anhydride opening,[10] oxidative 2-naphthol dimerizations,[11] Heck-type cross-couplings,[12] the protection of diamines,[13] the preparation of phosphorus ylides,[14] cyclodiphosphazane derivatives,[15] the metal free reductive benzylization of malononitrile,[16] the functionalization of fullerenes[17] and catalysis[18] have also been carried out using ball milling method which involves lesser reaction time, high yield and simplified workup procedures compared to the conventional solution phase reactions. Synthesis of chalcogenides, in particular sulfides and selenides of phosphines and bisphosphines, is carried out often at high temperature, using high boiling solvents such as benzene, toluene or xylene which are considered as hazardous.[19] In addition, reaction time also varies between 3 to 18 hours depending on the substrate. Further, isolation and purification in the case of partially oxidized bisphosphines is a tedious task owing to the formation of bischalcogenides and the presence of unreacted bisphosphines in the reaction product. In view of this, we sought to develop a more convenient and environmentally benign method for the synthesis of chalcogenides. Ball milling has been proven to be an excellent alternative for the green synthesis of many organic compounds[20] but never employed in the synthesis of phosphorus-chalcogenides despite their utility in coordination chemistry. Herein, we report the solid state synthesis of phosphorus-chalcogenides using rotary ball mill, which does not require any solvent for the synthesis, and the products formed also do not need any further purification as the yields were almost quantitative in most of the cases. The absence of by-products in the reaction makes it a highly atom economic (100%) method with an ideal E-factor of zero and can be termed as a green chemical method.

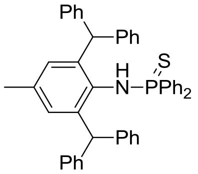
Results and discussion

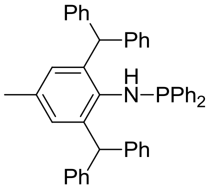
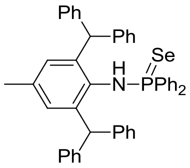
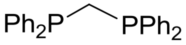
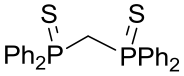
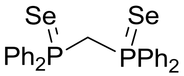
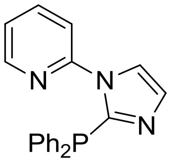
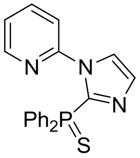
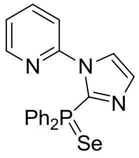
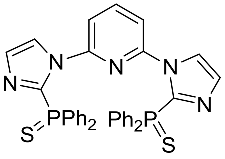
Synthesis of the chalcogenides

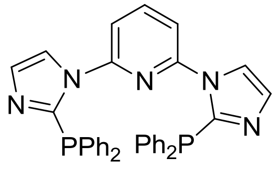
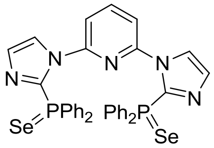
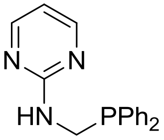
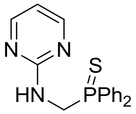
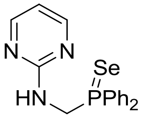
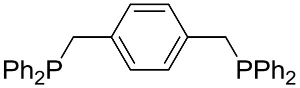
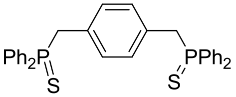
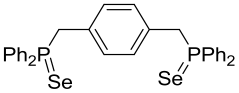
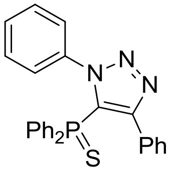
The syntheses of chalcogenides of phosphorus compounds were carried out using a rotary ball mill without using any solvent. The solid phosphines were mixed with stoichiometric amounts of elemental sulfur or selenium in a jar and rotated in the rotary ball mill containing a set of different sized ceramic balls (1 x 15 mm, 2 x 12 mm, 7 x 10 mm, 12 x 8 mm and 40 x 5 mm) for 4 h at a frequency of 450 rpm. Use of different sized balls will ensure effective grinding and hence better yields. To begin with, the reactions of triphenylphosphine were carried out with elemental sulfur and selenium for 4 h and the reaction mixtures were characterized by $^{31}P\{^{1}H\}$NMR spectra which showed single resonances at 43.3 and 35.3 ppm ($^{1}J_{PSe}$ = 728 Hz), respectively, for $Ph_3P{=}S$ (**1a**) and $Ph_3P{=}Se$ (**1b**), indicating the quantitative conversions. In another attempt, the same reaction under identical conditions yielded the chalcogenides **1a** and **1b** within 2 h. However, the reaction of PPh_3 with elemental tellurium did not give Ph_3P=Te even after 6 h, instead yielded a small quantity of Ph_3P=O (δ_P = 29.9 ppm) as confirmed from its $^{31}P\{^1H\}$ NMR data. These results prompted us to explore the oxidation of a variety of phosphines with sulfur and selenium using rotary ball mill and the details are given in Table 1.

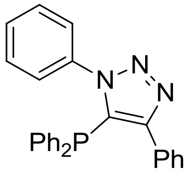
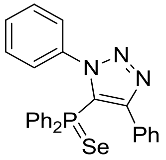
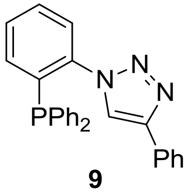
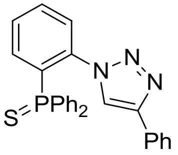
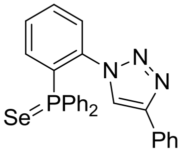
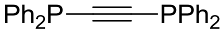
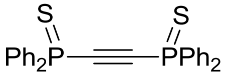
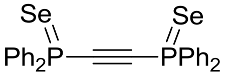
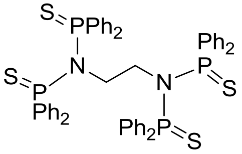
Table 1. Synthesis of sulfide and selenide of phosphines using ball milling

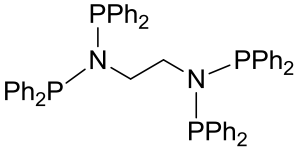
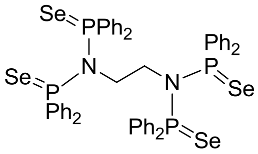


S. No.	Phosphine	Chalcogenide	$^{31}P\{^{1}H\}^{a}$ NMR Shift	% Conversion^{b} (Isolated yield)	Details of conventional synthesis
1	PPh_3 **1**	$Ph_3P{=}S$ **1a**	43.3 (s)	100(95)	Reaction in benzene under N_2 at r.t. for 7 days, yield not mentioned (ref 18c, d)
2		$Ph_3P{=}Se$ **1b**	35.3 (s, $J_{P\text{-}Se}$ = 728)	100(97)	Reflux in $CDCl_3$ (60-70 °C) for 3-16 h, yield not mentioned (ref 18g, h)
3		 **2a**	55.4 (s)	100(93)	NR

4	 **2**	 **2b**	55.3 (s, $J_{P\text{-}Se}$ = 778)	100(94)	NR
5	 **3**	 **3a'**	35.3 (s)	100(96)	Reflux in benzene under N_2 for 30-60 min, 65% yield (ref 18b)
6		 **3b'**	25.1 (s, $J_{P\text{-}Se}$ = 724)	100(94)	Reflux in deoxygenated toluene under N_2 for overnight, 82% yield (ref 18a)
7	 **4**	 **4a**	32.3 (s)	100(96)	NR
8		 **4b**	22.4 (s, $J_{P\text{-}Se}$ = 750)	100(92)	NR
9		 **5a'**	32.5 (s)	100(92)	NR

10	 **5**	 **5b'**	22.0 (s, $J_{P\text{-}Se}$ = 750)	100(90)	NR
11	 **6**	 **6a**	40.8 (s)	100(92)	NR
12		 **6b**	32.7 (s, $J_{P\text{-}Se}$ = 736)	100(90)	NR
13	 **7**	 **7a**	41.9 (s)	100(92)	Reflux in toluene for 24 h, 87% yield (ref 25b)
14		 **7b**	34.1 (s, $J_{P\text{-}Se}$ = 732)	100	NR
15		 **8a**	26.0 (s)	40	NR

16	 **8**	 **8b**	17.5 (s, $J_{P\text{-}Se}$ = 770)	92	NR
17	 **9**	 **9a**	40.5 (s)	100(94)	NR
18		 **9b**	32.0 (s, $J_{P\text{-}Se}$ = 740)	53	NR
19	 **10**	 **10a'**	21.6 (s)	100(93)	Reflux in THF for 2 h, 86% yield (ref 18f)
20		 **10b'**	7.6 (s, $J_{P\text{-}Se}$ = 772)	100(97)	Reaction in benzene at 20 °C for 12 h, yield not reported (ref 18e)
21		 **11a**	69.6 (s)	100	Reflux in THF for 6 h, 57% yield (ref 25d)

22	 **11** (4 equiv. of E)	 **11b**	68.8 (s, $J_{\text{P-Se}}$ = 800)	100	Reflux in THF for 6 h, 55% yield (ref 25d)

$^{a}\delta$ in ppm and J in Hz, ^{b} Based on ^{31}P{^{1}H} NMR. NR = Not Reported

After the completion of the reaction, in each case, the product was isolated by dissolving the reaction mixture in ethyl acetate (5-10 mL) followed by solvent removal under reduced pressure. The product formation was analyzed by $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture, which showed the formation of the corresponding sulfides and selenides in almost quantitative yield. Only in the case of **8a**, **8b** and **9b** the respective yields were 40%, 92% and 53% (Table 1, entry 15, 16 and 18). The reaction of bis(diphenylphosphino)methane (**3**) with two equivalents of elemental sulfur or selenium yielded bischalcogenides (**3a′** and **3b′**) (Table 1, entry 5 and 6). These reaction conditions are also suitable for amino phosphines (secondary phosphines) where the corresponding chalcogenides were obtained in quantitative yields (Table 1, entry 3, 4, 21 and 22). The reaction of Ph_2PH under identical conditions resulted in $Ph_2P(S)H$ and $Ph_2P(Se)H$ in 75% and 71%, respectively and the formation of $Ph_2P(O)H$ was observed in both the cases due to the oxidation by the moisture present in the system. However, quantitative formation of both the chalcogenides can be observed if the reaction is carried out in an inert atmosphere. These results suggest that ball milling is a very useful and efficient method for the synthesis of chalcogenides of most of the phosphines.

Partial oxidation of bisphosphines with O, S, Se or N_3R (Staudinger reaction) to form bisphosphine-monochalcogenides is an important method for generating the heterodifunctional ligands which find application in homogeneous catalysis.[21] Due to the presence of both hard- and soft-donor atoms, these ligands when bound to low-valent soft platinum metals *via* chelation, can readily cleave metal–hetero donor atom bond during oxidative addition to form 14 or 16 e^- species, an important step in homogeneous catalysis. In view of this, there is a scope to generate heterodifunctional ligands using a simple strategy such as controlled oxidation of bisphosphines. Balakrishna *et al*. reported the formation of monosulfide and monoselenide derivatives of aminobisphosphines by refluxing the bisphosphine and elemental sulfur or selenium in hexanes as solvent, in which both bisphosphine and their monochalcogenides are insoluble, in almost quantitative yield.[22] These reactions, which appear to proceed *via* solid-surface interactions, prompted us to employ a ball mill strategy for the generation of sulfide and selenide derivatives of various bi-, tri- or polyphosphines. Reaction of bis(diphenylphosphino)methane (**3**) with one equivalent of elemental sulfur or selenium resulted in the formation of monosulfide (**3a**) and monoselenide (**3b**) in 55% and 90% yields, respectively (Table 2, entry 1 and 2). A similar trend was observed in the case of bisphosphines **5** and **10**, wherein monochalcogenides **5a**, **5b**, **10a** and **10b** were major products and dichalcogenides obtained as minor products (Table 2, entry 3-6). Scaled up reactions in the case of **5** (1.5 g) with sulfur and selenium did not affect the yields Interestingly, in some of the cases, the yields of monosulfides were less than the corresponding monoselenide derivatives indicating the influence of atomic size of reactants on the product formation.[23] In the case of bisphosphines, wherever a mixture of both mono- and bischalcogenides were formed, the products were separated by column chromatography, which is in contrast to the solution state reactions, where isolation and purification, especially in the case of partially oxidized bisphosphines is a tedious task owing to the formation of bischalcogenides and due to the presence of unreacted bisphosphines in the reaction mixture. The $^{31}P\{^1H\}$ NMR spectral data of isolated products are listed in Table 2. The formation of chalcogenides was also supported by various spectroscopic data (see ESI Figures S39 – S53).

An alternative method for the preparation of monochalcogenides is through redistribution method which involves the interaction of equimolar quantities of bisphosphines and the corresponding bischalcogenides through chalcogen exchange mechanism.[24] In order to examine this method, bisphosphine **10** was treated with bischalcogenides **10a′** and **10b′,** which resulted in the formation

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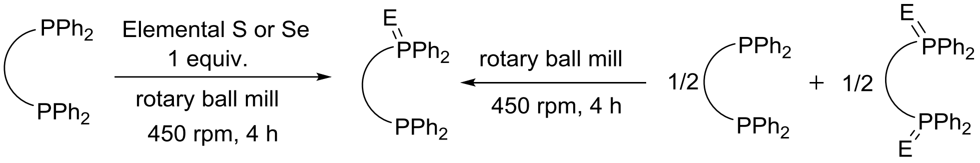
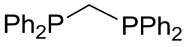
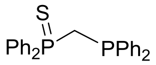
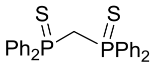
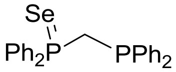
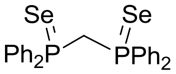
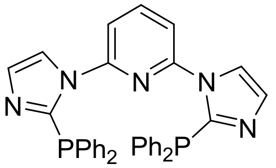
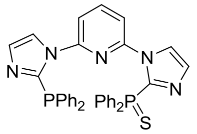
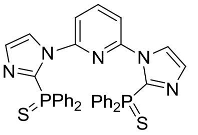
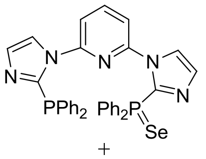
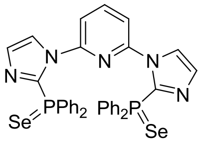
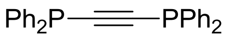
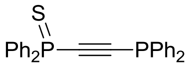
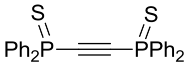
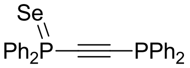
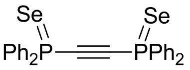
of monosulfide (**10a**) and monoselenide (**10b**) derivatives in 14% and 74% yield, respectively (Table 2). To check the reproducibility, the reactions of bisphosphine **10** and disulfide **10a′** were repeated and exactly the same results were obtained. These results suggest that the selenide derivatives react faster compared to the sulfide derivatives.[23]

Table 2. Synthesis of monosulfide and monoselenide of bisphosphines using ball milling



E = S or Se

S. No.	Phosphine	Chalcogenide	$^{31}P\{^1H\}$ NMR Shift[a]	% Conversion[c] (Isolated yield)
1	 **3**	 3a +  3a'	40.2 (d, $^2J_{PP}$ = 76) & −28.0 (d, $^2J_{PP}$ = 76) + 35.3 (s)	55(52) + 45(40)
2		 **3b** +  **3b'**	30.7 (d, $^2J_{PP}$ = 83, $J_{P\text{-}Se}$ = 728) & −26.9 (d, $^2J_{PP}$ = 83) + 25.1 (s, $J_{P\text{-}Se}$ = 726)	90(85) + 10(7)

3	 **5**	 **5a** +  **5a'**	32.2 (s) & −21.9 (s) 32.5 (s)	60(56) + 40(33)
4		 **5b** +  **5b'**	22.3 (s, $J_{P\text{-}Se}$ = 748) & −22.4 (s) + 22.0 (s, $J_{P\text{-}Se}$ = 750)	54 + 28
5	 **10**	 **10a** +  **10a'**	20.0 (s) & −33.2 (s) + 21.6 (s)	43 (14)^b + 38
6		 **10b** +  **10b'**	5.8 (d, $^3J_{PP}$ = 40, $J_{P\text{-}Se}$ = 772) & −33.1 (d, $^3J_{PP}$ = 40) + 7.6 (s, $J_{P\text{-}Se}$ = 772)	77 (74)^b + 16

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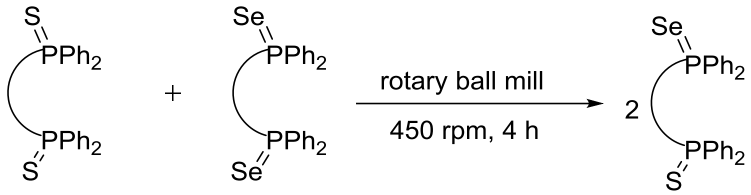
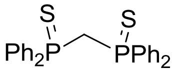
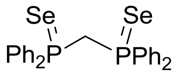
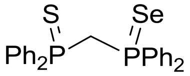
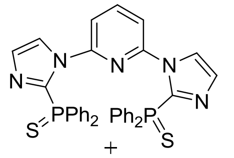
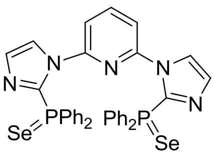
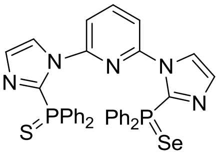
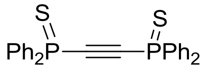
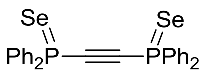
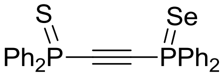
[a] δ in ppm and *J* in Hz. [b] Yield of the reaction between the bisphosphine and its bischalcogenide. [c] conversion based on $^{31}P\{^1H\}$ NMR.

Table 3. Synthesis of mixed chalcogenide of bisphosphines using ball milling



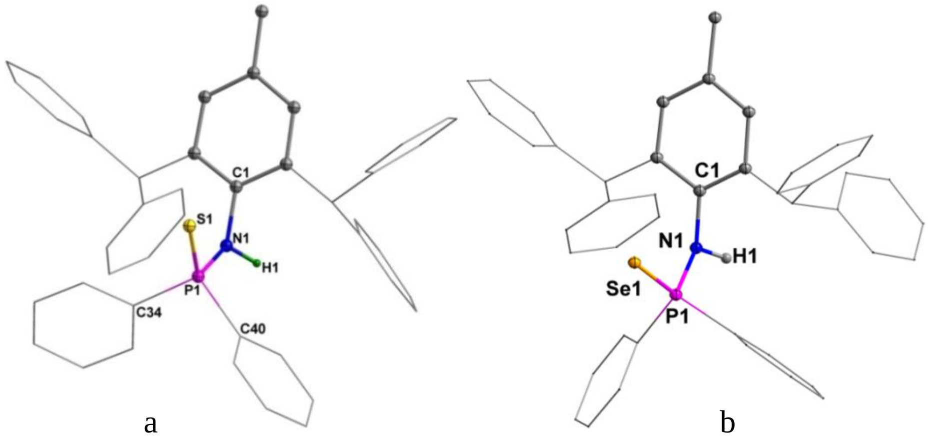
S. No.	Bischalcogenides	Mixed Chalcogenide	$^{31}P\{^1H\}$ NMR Shift[a]	Isolated yield (%)
1	 **3a'** +  **3b'**	 **3c**	35.3 (s) + 25.1 (s, J_{P-Se} = 726)	93
2	 **5a'** +  **5b'**	 **5c**	32.5 (s) + 21.9 (s, J_{P-Se} = 750)	95
3	 **10a'** +  **10b'**	 **10c**	21.6 (s) + 7.6 (s, J_{P-Se} = 772)	92

[a] δ in ppm and *J* in Hz.

Chalcogen exchange reactions can also be used to synthesize mixed chalcogenides by reacting disulfides and diselenides in 1:1 molar ratios. Reactions between disulfides (**3a′**, **5a′** and **10a′**) and diselenides (**3b′**, **5b′** and **10b′**) under ball mill conditions resulted in the formation of the corresponding monosulfide-monoselenide derivatives (**3c**, **5c** and **10c**) in quantitative yields (Table 3). Although the $^{31}P\{^{1}H\}$ NMR spectra did not show any appreciable change in the chemical shifts due to the sulfide- and selenide-P moieties in the mixed chalcogen derivatives compared to the corresponding dichalcogenides, the formation of the product was confirmed by the HRMS analysis where peaks at 503.0203 (calcd. 503.0238, M+Li), 714.0521 (calcd. 714.0522, M+Na), and 513.0805 (calcd. 513.0086, M+Li) were observed for **3c**, **5c** and **10c**, respectively (see ESI).

The reactions of PPh_3 and bisphosphine **5** with elemental sulfur or selenium were scaled up to 3 g and 1.5 g scale, respectively, and it did not affect the course of the reaction and in both the cases the corresponding products **1a**, **1b** and **5a**, **5b** were obtained in quantitative yield. However, in the case of **5** the reaction time was extended by an hour to ensure the completion of the reaction although it was not necessary.

Structural characterization of the chalcogenides



a b

Figure 1. Molecular structure of (a) **2a** and (b) **2b** with 50% ellipsoid probability. Most of the H-atoms and co-crystallized water molecule for **2b** are omitted for clarity. Selected bond distances (Å) and bond angles (deg): for **2a**: N1–C1 1.446(5), N1–P1 1.684(3), P1–S1 1.936(16), P1–C34 1.811(5), P1–C40 1.820(4), C1–N1–P1 123.1(3), N1–P1–S1 111.98(13), C34–P1–S1 114.10(15), C40–P1–S1 113.53(14); for **2b**: N1–C1 1.444(6), N1–P1 1.674(4), P1–Se1 2.0906(14), P1–C34 1.813(6), P1–C40 1.825(5), C1–N1–P1 125.9(3), N1–P1–Se1 113.65(16), C34–P1–Se1 114.59(19), C40–P1–Se1 112.93(18).

The molecular structures of **2a-b** and **4b** are presented in Figure 1 and Figure 2 and the crystallographic details are listed in Table 4. Compound **2a** crystallizes in the orthorhombic system with *Pbca* space group while compounds **2b** and **4b** crystallize in the monoclinic system with *Cc* and *I2/a* space groups, respectively. Their asymmetric unit consists of one molecule and that of **2b** additionally contains one molecule of water as the solvent of crystallization. As expected, the geometry around phosphorus in **2a-b** is distorted tetrahedral where the P–S and P–Se distances are 1.936(16) and 2.0906(14) Å, respectively, which lies in the reported range of P–S (1.919(1)–1.9505(10) Å) and P–Se (2.0563(14)–2.1115(7) Å) distances.[25] The P–Se bond length in **4b** is 2.1179(13) Å which is slightly longer than that found in **2b** and $[\{(Se)P(\mu\text{-N}^{t}Bu)\}_2\{1,3\text{-}(O)_2\text{-}C_6H_4\}]_2$ (2.0670(4) Å) but is similar to that observed for $\{^{t}BuHN(^{t}BuNP(Se))_2\text{-}OCH_2\}_2$ (2.1115(7) Å).[25]

10.1002/ejic.201701414

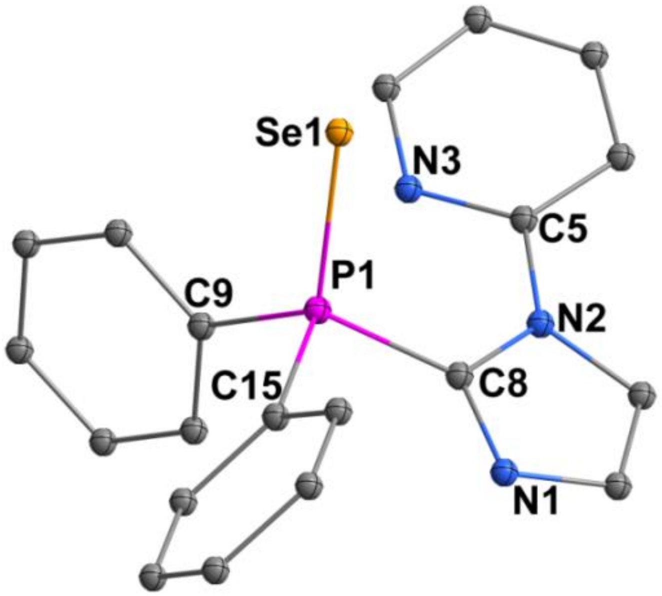


Figure 2. Molecular structure of **4b** with 50% ellipsoid probability. H-atoms are omitted for clarity. Selected bond distances (Å) and bond angles (deg): C8–P1 1.825(5), P1–Se1 2.117(13), P1–C9 1.812(5), P1–C15 1.836(5), C8–P1–Se1 112.96(16), C9–P1–Se1 114.88(16), C15–P1–Se1 111.12(17).

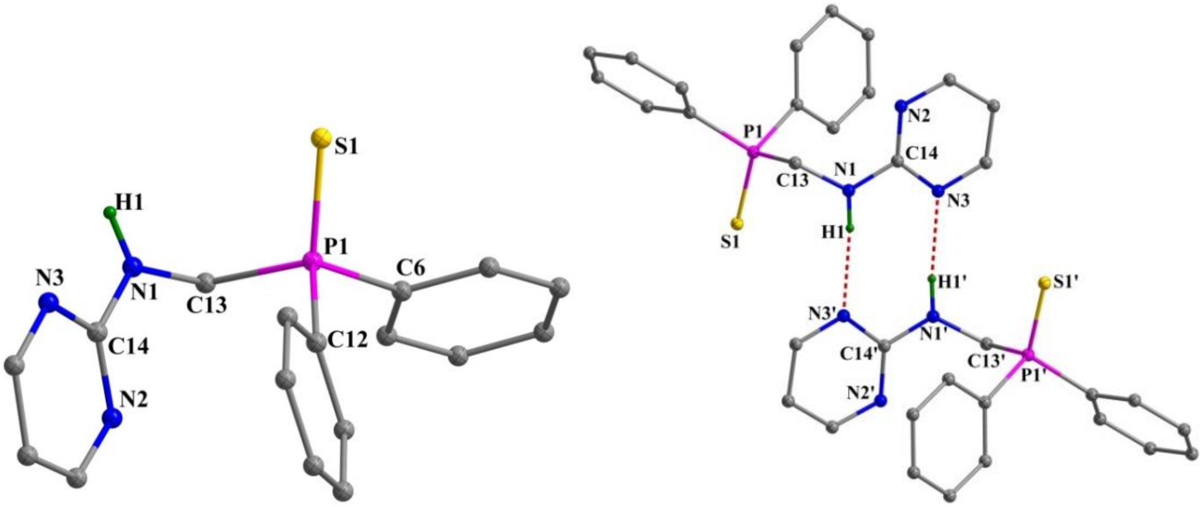


Figure 3. Molecular structure of **6a** with 50% ellipsoid probability and its dimeric form showing intermolecular H-bonding. Most of the H-atoms are omitted for clarity. Selected bond distances (Å) and bond angles (deg): N1–C13 1.4474(18), N1–C14 1.3627(19), C13–P1 1.8384(15), P1–S1

1.9539(6), P1–C6 1.845(15), P1–C12 1.8109(15), N1···N3 2.995, N1–C13–P1 109.29(10), C13–P1–S1 112.36(5), C6–P1–S1 113.35(5), C12–P1–S1 112.17(5), N1–H1···N3 164.28.

The molecular structures of compounds **6a** and **6b** are shown in Figures 3 and 4 respectively, and their crystallographic details are listed in Table 5. Both the compounds crystallize in monoclinic system with *P*2(1)/*c* space group. Molecule **6a** contains one while **6b** contains two molecules in the asymmetric unit. The presence of H-bond donor and acceptor within the molecule resulted in their dimerization in the solid state by virtue of intermolecular N–H···N H–bonding (Figures 3 and 4). The P–S distance of 1.9539(6) Å is longer than that found in **2a** while the P–Se distance of 2.1084(6) Å is slightly longer than that found in **2b** [2.0906(14) Å] but is marginally shorter than that in **4b** [2.1179(13) Å].

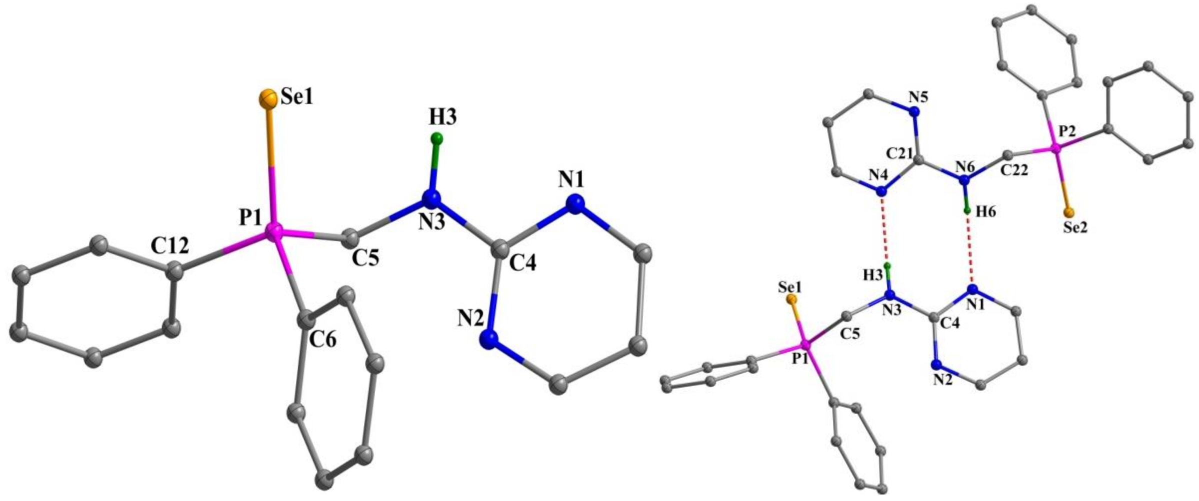


Figure 4. Molecular structure of **6b** with 50% ellipsoid probability and its dimeric form showing intermolecular H-bonding. Most of the H-atoms are omitted for clarity. Selected bond distances (Å) and bond angles (deg): N3–C4 1.355(3), N3–C5 1.440(3), C5–P1 1.846(2), P1–Se1 2.1084(6), P1–C6 1.817(2), P1–C12 1.818(2), N1···N6 3.004, N3···N4 2.988, N3–C5–P1 112.90(15), C5–

P1–Se1 112.67(8), C6–P1–Se1 113.27(7), C12–P1–Se1 114.27(7), N6–H6···N1 145.51, N3–H3···N4 169.43.

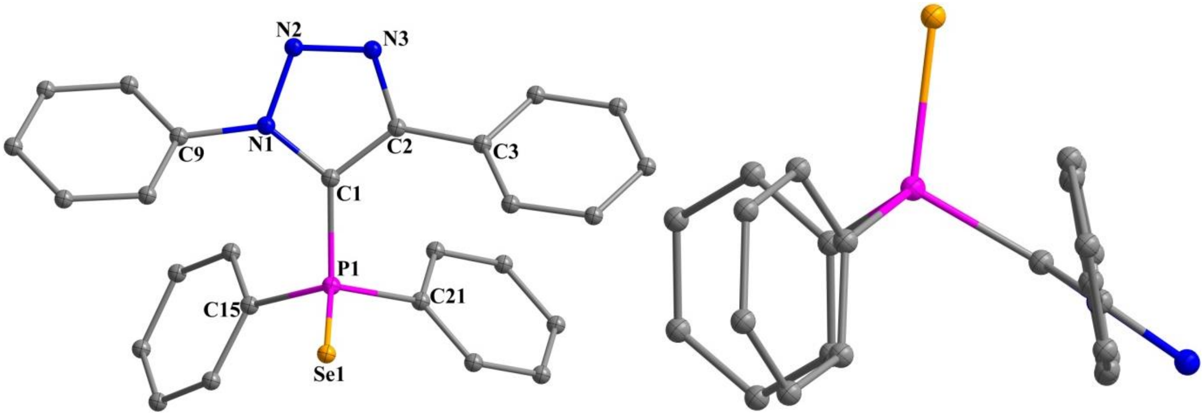


Figure 5. Molecular structure (top view and side view) of **8b** with 50% ellipsoid probability. H-atoms are omitted for clarity. Selected bond distances (Å) and bond angles (deg): C1–P1 1.817(3), P1–Se1 2.1020(8), P1–C15 1.819(3), P1–C21 1.810(3), C1–P1–Se1 113.39(10), C15–P1–Se1 115.52(10), C21–P1–Se1 114.01(10).

Figure 5 and Figure 6 show the molecular structures of compounds **8b** and **11a**, respectively, and their crystallographic details are listed in Table 5. Both the molecules crystallize in the monoclinic system with *P*2(1)/*n* and *P*2(1)/*c* space groups, respectively. The structure of **8b** shows that the phenyl substituents on the triazole ring makes an angle of around 45 (deg.) with the plane of the triazole core. The asymmetric unit of **11a** contains half of the molecule. The sulfur atoms are pointed in opposite directions to accommodate the substituents on the N atoms. The P1–S1 (1.9529(9) Å) and P2–S2 (1.9440(8) Å) bond distances vary slightly and are longer than those found in **2a** but are similar to those of **6a**.

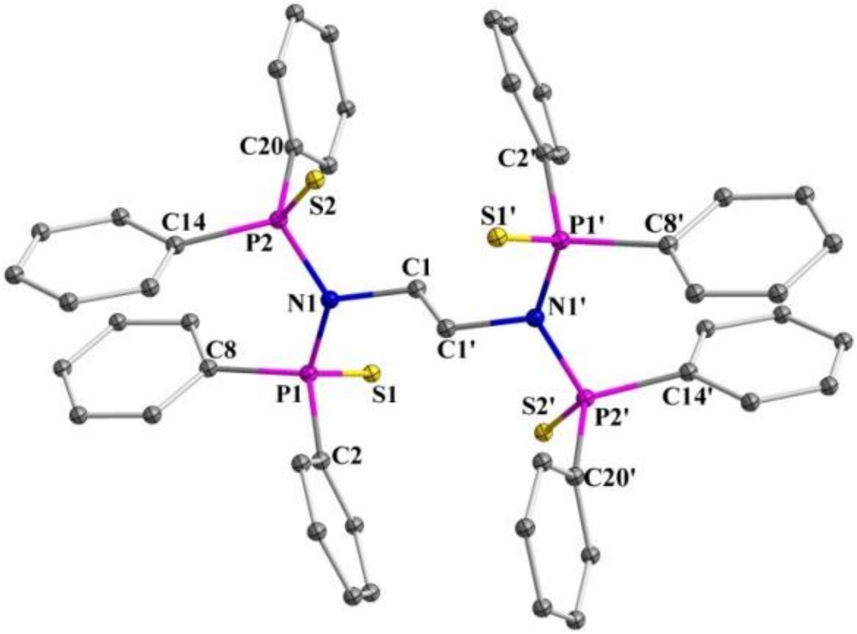


Figure 6. Molecular structure of tetrasulfide **11a** with 50% ellipsoid probability. H-atoms are omitted for clarity. Selected bond distances (Å) and bond angles (deg): N1–P1 1.7188(19), N1–P2 1.7060(19), P1–S1 1.9529(9), P1–S2 1.9440(8), P1–C2 1.812(2), P1–C8 1.818(3), P2–C14 1.809(3), P2–C20 1.814(3), P1–N1–P2 133.31(12), N1–P1–S1 113.97(8), C2–P1–S1 112.85(8),C8–P1–S1 109.51(8),N1–P2–S2 112.13(7), C14–P2–S2 109.21(8), C20–P2–S2 110.38(8).

Table 4. Crystallographic information for compounds **2a**, **2b** and **4b**

	2a	**2b**	**4b**
Empirical formula	$C_{45}H_{38}NPS$	$C_{45}H_{40}NOPSe$	$C_{20}H_{16}N_3PSe$
Formula weight	655.79	720.74	408.29
Wavelength (Å)	0.71075	0.71075	0.71075
Temperature (K)	150(2)	150(2)	150(2)
Crystal system	orthorhombic	Monoclinic	Monoclinic
Space group	*Pbca*	*Cc*	*I2/a*
a/Å	20.246(7)	9.703(3)	18.860(15)
b/Å	15.490(6)	43.815(14)	8.069(5)
c/Å	23.316(9)	9.179(3)	24.696(15)
β/degree	90	107.724(4)	106.90(5)
Volume (Å^3)	7343.5(9)	3717(2)	3596(4)
Z	8	4	8
D_{calcd}, g cm^{-3}	1.186	1.284	1.508
μ/mm^{-1}	0.164	1.088	2.184
F(000)	2768	1488	1648
Crystal size/mm	0.21x0.11x0.09	0.18x0.07x0.04	0.21x0.16x0.08
θ range (degree)	4.8 to 48.99	3.01 to 24.99	3.08 to 25.00
Total/ unique no. of reflns.	32846/6442	22530/6330	17665/3164
R_{int}	0.1924	0.0517	0.1054
GOF (F^2)	1.049	1.026	1.127
$R1$, $wR2$	0.0801, 0.1836	0.0482, 0.1264	0.0939, 0.2305

Table 5. Crystallographic information for compounds **6a**, **6b, 8b** and **11a**

	6a	**6b**	**8b**	**11a**
Empirical formula	$C_{17}H_{16}N_3PS$	$C_{17}H_{16}N_3PSe$	$C_{26}H_{20}N_3PSe$	$C_{50}H_{44}N_2P_4S_4$
Formula weight	325.36	372.26	484.38	924.99
Wavelength (Å)	0.71075	0.71075	0.71075	0.71075
Temperature (K)	150(2)	150(2)	150(2)	150(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*P*2(1)/*c*	*P*2(1)/*c*	*P*2(1)/*n*	*P*2(1)/*c*
a/Å	15.790(3)	17.848(3)	13.5392(9)	12.8507(7)
b/Å	10.787(19)	9.6365(16)	8.0627(5)	10.3146(5)
c/Å	9.819(18)	19.572(4)	20.6916(16)	17.7617(9)
β/degree	102.512(13)	99.183(2)	97.374(7)	109.162(6)
Volume (Å^3)	1632.8(5)	3323.1(10)	2240.1(3)	2223.9(2)
Z	4	8	4	2
D_{calcd}, g cm^{-3}	1.324	1.488	1.436	1.381
μ/mm^{-1}	0.296	2.355	1.766	0.397
F(000)	680	1504	984	964
Crystal size/mm	0.23x0.20x0.19	0.26x0.24x0.06	0.18x0.14x0.06	0.19x0.07x0.05
θ range (degree)	3.25 to 25.00	3.08 to 25.00	1.99 to 24.99	2.30 to 24.99
Total/ unique no. of reflns.	13966/2869	16312/5825	11568/3945	14539/3916
R_{int}	0.0265	0.0341	0.0705	0.0580
GOF (F^2)	1.056	1.039	1.054	1.047
R1, *wR2*	0.0306, 0.0777	0.0324, 0.0751	0.0494, 0.1164	0.0411, 0.0898

10.1002/ejic.201701414

Conclusions

A fast, efficient and green route for the syntheses of sulfides and selenides of tertiary phosphines, aminophosphines and a variety of bisphosphines using a rotary ball mill has been successfully developed. The method is highly attractive due to the solvent-free nature, short reaction time and quantitative product formation, which makes this green chemistry protocol a real alternative to the conventional method. The scope of application was shown by using mono-, bis- and tetraphosphines and also in scale up reactions. Further, the short reaction time and lower rotation frequency results in energy saving. We are currently exploring this method in making sulfur derivatives of organic molecules and also in thiolation reactions.

Experimental Section

Unless otherwise specified, all reagents were purchased from commercial suppliers and used without further purification. Sulphur powder (S_8) (99.5 %) was purchased from Merck Chemicals and black selenium powder (Se_8) (99.5 %) was obtained from Loba chemicals and used as such without further purification. The phosphines were synthesized according to the literature procedures.[26] The ball-milling experiments were performed using a Vertical Planetary Ball Mill model “XQM-0.4A” with four 45-mL grinding bowls and 5-15 mm diameter grinding balls made of zirconium oxide. The NMR spectra were recorded at 500 MHz (^{1}H) and 202 MHz ($^{31}P\{^{1}H\}$) or 400 MHz (^{1}H) and 162 MHz ($^{31}P\{^{1}H\}$) (δ in ppm) using Bruker AV 500/400 spectrometer. The spectra were recorded in $CDCl_3$ solution with $CDCl_3$ as an internal lock; TMS and 85% H_3PO_4 were used as external standards for ^{1}H and $^{31}P\{^{1}H\}$ NMR, respectively. Positive shifts lie downfield to the standard in all of the cases. Mass spectra were recorded using a Bruker Maxis Impact LC-q-TOF Mass Spectrometer.

Representative procedure for the solid state synthesis of chalcogenides

Triphenylphosphine (0.525 g, 2.000 mmol) and elemental sulfur (0.064, 2.000 mmol) were both taken in a jar and one set of ceramic balls (1 x 15 mm, 2 x 12 mm, 7 x 10 mm, 12 x 8 mm and 40 x 5 mm) were added to it. The jar was then fixed in the rotary ball mill and was rotated at a frequency of 450 rpm for 4 h. Extraction of compound by ethyl acetate (10 mL) and subsequent removal of the solvent yielded $Ph_3P=S$, **1a** as a white crystalline solid. Yield: (0.560 g, 95 %). $^{31}P\{^1H\}$NMR (202 MHz, $CDCl_3$, 25 °C, ppm): δ 43.3 (s).

Chalcogenides of all other phosphines were synthesized using the exact same procedure and the results are listed in tables 1-3.

Representative procedure for the preparation of mono chalcogenides

Bis(diphenylphosphino)methane (0.20 g, 0.520 mmol) and elemental sulfur (0.017 g, 0.520 mmol) were both taken in a jar and one set of ceramic balls (1 x 15 mm, 2 x 12 mm, 7 x 10 mm, 12 x 8 mm and 40 x 5 mm) were added to it. The jar was then fixed in the rotary ball mill and was rotated at a frequency of 450 rpm for 4 h. Extraction of compound by ethyl acetate (5 mL) and subsequent removal of the solvent yielded mixture of mono as well as dichalcogenide products, which was separated by column chromatography using petroleum ether/ethyl acetate (1:9) ratio as eluent. Yield: dppmS (**3a)** 0.113 g (52 %) and $dppmS_2$ (**3a′**) 0.087 g (40 %). $^{31}P\{^1H\}$NMR (162 MHz, $CDCl_3$, 25 °C, ppm): δ dppmS (**3a**) 40.4 and 27.88 (d, $^1J_{PP}$ = 76.1 Hz) and $dppmS_2$ 35.31 (s).

X-ray crystallography

Suitable single crystals of **2a-b**, **4b**, **6a-b**, **8b** and **11a** for X-ray diffraction studies were obtained by slow evaporation of their solution in dichloromethane/petroleum ether (v/v 2/1). A crystal of each of these compounds suitable for single crystal X-ray diffraction was mounted in a cryoloop with a drop of paratone oil and placed in the cold nitrogen stream of the kryoflex attachment of the Rigaku Saturn 724+ (4×4 bin mode) diffractometer. Data were collected at 150 K using graphite-monochromated Mo$K\alpha$ radiation (λ = 0.71073 Å) with the ω-scan technique. The data were reduced by using CrysalisPro Red 171.38.43 software. The structures were solved by ShelXT[27] using OLEX2[28] by direct methods and refined by least-squares against F^2 utilizing the software package ShelXL-97[29]. All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were refined isotropically on calculated positions using riding models. Crystallographic refinement data are given in Table 4 and Table 5. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1563578 (**2a**), 1563579 (**2b**), 1563580 (**4b**), 1563581 (**6a**), 1563582 (**6b**), 1563583 (**8b**), and 1563584 (**11a**).

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Supplementary information

Electronic supplementary information (ESI) available. CCDC 1563578–1563584. For ESI and crystallographic data in CIF or other electronic format see DOI:10.1039/x0xx00000x.

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