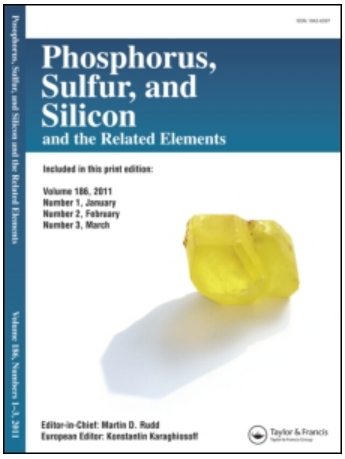

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IR, Proton, and Carbon-13 NMR Spectral Characterization of Some Chiral and Achiral Aminophosphines and Their Selenides

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IR, PROTON, AND CARBON-13 NMR SPECTRAL CHARACTERIZATION OF SOME CHIRAL AND ACHIRAL AMINOPHOSPHINES AND THEIR SELENIDES

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Though aminophosphines have been known for a century, and a large variety of such compounds has been synthesized for different aspects of their chemistry, until now, no examples are available on phosphines containing three different amino substituents. In this study, the first examples of such chiral tris(amino)phosphines and o-phenylenedioxo(amino)phosphines were successfully synthesized using condensation reactions, and they were converted to their respective selenides using a simple oxidative addition reaction. The compounds are characterized by IR, ^{1}H, and ^{13}C NMR spectral techniques, and the spectral aspects are presented. The spectral studies (i) indicated that they are indeed powerful tools for structural elucidation of compounds; (ii) showed the effect of heavier selenium atom on the P–N bond rotation process; and (iii) further supported the fact that dipolar structure predominates over the π-bond structure for the aminophosphine selenides.

Supplemental materials are available for this article. Go to the publisher's online edition of* Phosphorus, Sulfur, and Silicon and the Related Elements *to view the free supplemental file.

Keywords Aminophosphine selenides; aminophosphines; chiral aminophosphine selenides; chiral aminophosphines; dynamic NMR

INTRODUCTION

Aminophosphines are tricoordinate phosphorus compounds containing one to three polar and labile P(III)–N, bonds and they are considered as one of the most intriguing in chemistry. Over the years, aminophosphine research has picked up momentum and has gained paramount importance due primarily to four reasons: (i) their richness in acting as versatile ligands in transition metal coordination chemistry;[1–8] (ii) their specificity in their roles as catalysts for various organic conversions;[9–14] (iii) their ease in being converted

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to chalcogenides, which themselves possess ligating behavior,[15–20] and hence they find applications in catalysis, besides being used as carriers of Group 16 elements in electronic industries;[21] and (iv) their diversity in playing vital roles as effective synthons in realizing newer variety of inorganic heterocycles,[22–28] which has numerous application interests.[29–34] Depending on the substituents attached to phosphorus, drastic changes in catalytic efficiency have been realized,[35–37] and this could possibly be related to the Tolman cone angle, first suggested by Tolman.[38] Hence the tailoring of aminophosphines has become all the more challenging, and many research groups are currently working to design suitable aminophosphines for the synthesis of better catalysts with stereospecific applications. Examples of P-chiral-, C-chiral-, and N-chiral phosphines and partially substituted P-chiral aminophosphines are reported in the literature,[39–48] along with their coordination complexes in some cases, whereas fully substituted P-chiral aminophosphines are not known until we reported[49] the first synthesis, ^{31}P NMR and mass spectral data on chiral, but racemic compounds of the type [(*i*-$C_3H_7)_2$N][(*n*-$C_4H_9)_2$N][R_2N]P (**1**) and (*o*-$C_6H_4O_2$)(R_2N)P (**2**). Earlier, single crystal X-ray structures for the compounds (*o*-$C_6H_4O_2$)[(*c*-$C_6H_{11})_2$N]P and (*o*-$C_6H_4O_2$)(R_2N)PSe, [R = (*i*-$C_3H_7)_2$N; (*c*-$C_6H_{11})_2$N; ($C_6H_5CH_2)_2$N] were determined,[50] which exhibited some interesting structural features, particularly with respect to P—N and P═Se bonds. Common spectral techniques such as IR and multinuclear NMR have been advantageous in elucidating the more precise structures of many of the aminophosphines and their related compounds.[51–55] Aminophosphines also offer interesting examples for the study of their dynamic behavior, especially in solution using NMR as a tool,[56–60] as there exists a possibility of an inversion process occurring at the pyramidal shaped phosphorus and nitrogen and rotation around the P–N bond. Though inversion at phosphorus is possibly less likely an event occurring at room temperature due to the demand of relatively high activation energy barrier, a probing bond rotation process assumes a more complex scenario in many cases, as the substituents on nitrogen influence substantially the inversion process occurring at nitrogen. The substituents on phosphorus as well as nitrogen centers affect the P–N bond rotation process.[61] However, the geometry around nitrogen in almost all of the aminophosphines $R_2P(NR'_2)$ reported so far possess a near planar geometry,[51,62,63] thus reducing the complexity of the scenario. Herein, we report (i) the IR, ^{1}H, and ^{13}C NMR spectral characterization of **1** [R_2N = ($C_2H_5)_2$N (**a**); OC_4H_8N (**b**); C_5H_{10}N (**c**)] and **2** [R_2N = (*i*-$C_3H_7)_2$N (**a**); (*c*-$C_6H_{11})_2$N (**b**); ($C_6H_5CH_2)_2$N (**c**)] along with the corresponding selenides [(*i*-$C_3H_7)_2$N][(*n*-$C_4H_9)_2$N][R_2N]PSe (**3**) [R_2N = ($C_2H_5)_2$N (**a**); OC_4H_8N (**b**); C_5H_{10}N (**c**)] and (*o*-$C_6H_4O_2$)(R_2N)PSe (**4**) [R_2N = (*i*-$C_3H_7)_2$N (**a**); (*c*-$C_6H_{11})_2$N (**b**); ($C_6H_5CH_2)_2$N (**c**)]; and (ii) dynamic ^{1}H NMR behavior of compounds **2a** and **4a**.

RESULTS

IR, ^{1}H, and ^{13}C NMR data for the phosphines **1**(**a**–**c**) and **2**(**a**–**c**) and those of the phosphine selenides **3**(**a**–**c**) and **4**(**a**–**c**) are presented in Tables I and II, respectively. The set of compounds **1**(**a**–**c**) and **3**(**a**–**c**) are the first set of examples containing three different amino substituents on phosphorus.

DISCUSSION

IR Studies

All 12 compounds synthesized exhibited sharp and strong characteristic bands in the region 900–1060 cm^{-1} due to the P–N stretching vibration, which lies well within

Table I IR, ^{1}H, and ^{13}C NMR data for phosphines **1**(**a**–**c**) and **2**(**a**–**c**)

Entry No.	IR (cm^{-1})	^{1}H NMR (δ, ppm)	^{13}C NMR (δ, ppm)
1a	1459(vs), 1370(vs), 1222(w), 1184(vs),1149(w), 1114(m), 1011(vs), 947(s), 915(s), 858(w), 790(m), 691(m), 653(s)	0.86 (t, 6H), 1.00 (t, 6H), 1.10–1.22 (m, 20H), 2.96–3.20 (m, 8H), 3.60–3.76 (m, 2H)	13.6, 18.0, 20.4, 24.1, 29.8, 39.2, 45.4, 46.2
1b	1460(s), 1360(s), 1250(s), 1210(vs), 1180(s), 1110(vs), 1080(vs), 1020(m), 970(s), 930(s), 730(s), 610(m)	0.90 (t, 6H), 1.20 (d, 12H), 1.30–1.70 (m, 8H), 2.94 (m, 10H), 3.65 (t, 4H)	13.9, 20.8, 24.4, 31.0, 43.8, 44.6, 45.4, 67.9
1c	1475(vs), 1370(vs), 1230(s), 1190(vs), 1160(s), 1130(s), 1050(s), 1030(s), 960(vs), 940(vs), 920(s), 870(m), 840(w), 710(vs), 680(m), 640(w)	0.93 (t, 6H), 1.18 (d, 12H), 1.30 (m, 6H), 1.51 (m, 8H), 2.70 (t, 4H), 2.96 (dq, 2H), 3.04 (dt, 4H)	13.9, 20.3, 21.7, 24.8, 26.3, 30.9, 43.9, 45.6, 48.5
2a	1478(vs), 1398(m), 1363(m), 1344(m), 1235(s), 1200(s), 1174(s), 1123(s), 1091(w), 1024(s), 976(s), 912(w), 880(w), 858(m), 829(m), 742(s), 720(w), 678(s), 640(w), 614(w)	1.30 (d, 12H), 3.40 (ds, 2H), 6.90–7.05 (AA′BB′, 4H)	24.5, 45.0, 111.2, 121.5, 147.0
2b	1468(vs), 1360(s), 1344(m), 1232(s), 1165(m), 1149(m), 1110(m), 1094(w), 1062(s), 1027(w), 1002(w), 976(m), 906(w), 890(w), 848(w), 826(vs), 736(vs), 669(m), 627(w)	0.90–1.80 (m, 20H), 2.65–2.80 (m, 2H), 6.75–6.90 (AA′BB′, 4H)	25.3, 26.6, 35.5, 54.3, 111.0, 121.3, 147.1
2c	1476(vs), 1381(vs), 1374(m), 1306(w), 1235(s), 1130(w), 1094(m), 1059(m), 1030(w), 1011(w), 944(vs), 909(m), 896(w), 874(m), 822(vs), 774(m), 739(vs), 698(vs), 605(m)	3.80 (d, 4H) [$^{3}J_{PH}$ = 14.0 Hz], 6.75–6.95 (AA′BB′, 4H), 7.10–7.28 (m, 10H)	47.6, 111.5, 121.8, 127.4, 128.4, 128.5, 136.8, 146.4

the reported range of 780–1100 cm^{-1}.[64] Value as high as 1083 cm^{-1} has been assigned for υ_{PN} in the literature.[65] The substituents on phosphorus do influence the stretching frequency and in some cases substantially, as is evident from Table S1 (available online in the Supplemental Materials). The compounds possessing the dicyclohexylamino group, $(C_6H_{11})_2N$ exhibits a sharp and strong band at 1062 cm^{-1} for the phosphine **2b** and 1053 cm^{-1} for the phosphine selenide **4b**, as reported earlier,[66] and this could be attributed to N–C_{ring} stretching vibration.[67] Each family of compounds, *viz.*, **1**(**a**–**c**), **2**(**a**–**c**), **3**(**a**–**c**) and **4**(**a**–**c**) gave very similar infrared spectra, thus indicating a similar environment around the phosphorus center. For the (*o*-phenylenedioxo)phosphine compounds **2** and **4**, additional bands with regard to *ortho* disubstituted benzene CH wagging vibrations (649–736 cm^{-1}) and *ortho* disubstituted benzene ring bending vibrations (669–698 cm^{-1}); as well as a strong band around 1229–1254 cm^{-1} attributable to P–O_{aryl} stretching frequency could be identified.[67]

Comments on P=Se stretching vibrations. The aminophosphine selenides **3** and **4** exhibited medium to very strong and sharp bands for υ_{PSe} in the range 550–576 cm^{-1}. Compounds with N_3PSe framework showed relatively higher value compared to O_2NPSe framework (563–576 vs. 550–560 cm^{-1}), thus indicating that the contribution of dipolar structure (Figure 1) is more for the latter compared to the former. In fact, variations in P=Se bond length values elucidated from X-ray crystallography in such selenide compounds are generally attributed to the various extent of contribution of dipolar and π-bond structures.[68]

Table II IR, ^{1}H, and ^{13}C NMR data for phosphine selenides **3**(**a**–**c**) and **4**(**a**–**c**)

Entry no.	IR (cm^{-1})	^{1}H NMR (δ, ppm)	^{13}C NMR (δ, ppm)
3a	1459(vs), 1376(vs), 1248(w), 1174(vs), 1117(s), 1094(m), 1018(vs), 973(vs), 922(vs), 867(m), 771(w), 723(m), 672(m), 640(m), 570(s)	0.94 (t, 6H), 1.15 (t, 6H), 1.28 (m, 4H), 1.34 (d, 12H), 1.57 (m, 4H), 3.02 (m, 4H), 3.18 (m, 4H), 3.80 (m, 2H)	13.5, 13.9, 20.5, 23.4, 30.3, 40.3, 46.9, 47.7
3b	1456(vs), 1376(vs), 1251(m), 1174(s), 1155(m), 1114(vs), 1075(m), 1030(m), 973(m), 954(vs), 922(s), 845(m), 752(m), 723(s), 688(w), 640(m), 602(m), 563(s)	1.03 (t, 6H), 1.29 (d, 12H), 1.39–1.81 (m, 8H), 3.04 (m, 10H), 3.69 (t, 4H)	13.9, 21.1, 24.5, 31.2, 45.2, 46.2, 47.1, 68.5
3c	1453(vs), 1379(vs), 1350(vs) 1254(m), 1203(m), 1171(s), 1158(s), 1114(s), 1056(vs), 1027(s), 973(m), 938(s), 717(vs), 688(m), 640(m), 576(vs), 547(m)	0.88–0.98 (t, 6H), 1.22–1.64 (m, 26H), 2.83–3.07 (m, 8H), 3.65–3.84 (m, 2H)	14.1, 20.6, 23.2, 24.8, 26.0, 30.6, 47.0, 47.6, 47.7
4a	1472(vs), 1414(s), 1379(s), 1334(m), 1267(s), 1254(s), 1152(s), 1098(vs), 1040(vs), 982(vs), 896(vs), 851(m), 797(m), 771(m), 736(vs), 694(vs), 624(m), 557(vs), 531(s), 512(s)	1.30–1.34 (d, 12H), 3.91–4.08 (ds, 2H), 6.95–7.10 (AA′BB′, 4H)	22.4, 49.7, 112.4, 123.2, 144.7
4b	1472(vs), 1402(m), 1373(w), 1328(vs), 1270(m), 1254(s), 1226(vs), 1165(s), 1146(s), 1078(vs), 1053(vs), 1005(vs), 976(vs), 890(s), 864(vs), 838(vs), 819(vs), 771(s), 749(vs), 646(vs), 608(m), 550(vs), 518(m), 496(m), 416(m)	1.16–1.30 (m, 4H), 1.54–1.82 (m, 16H), 3.44–3.60 (m, 2H), 6.97–7.06 (AA′BB′, 4H)	25.2, 26.6, 32.9, 59.3, 112.4, 123.1, 144.8
4c	1472(vs), 1450(s), 1354(s), 1328(s), 1229(vs), 1200(m), 1155(w), 1101(vs), 1059(vs), 1027(m), 1008(m), 941(m), 906(s), 848(vs), 787(m), 765(s), 742(s), 694(vs), 643(s), 598(s), 560(m), 496(s), 470(m), 422(s)	4.25 (d, 4H) [$^{3}J_{PH}$ = 14.4 Hz], 7.07–7.13 (AA′BB′, 4H), 7.27–7.39 (m, 10H)	49.5, 112.3, 123.4, 127.9, 128.2, 128.7, 135.6, 145.3

Comments on P–N stretching vibrations. In this study, for the preparation of tris(amino)phosphines **1** and tris(amino)phosphine selenides **3**, the amines used are indicated along with their pK_a values[69] in parentheses: (i) $(i\text{-}C_3H_7)_2NH$ (11.05); (ii) $(n\text{-}C_4H_9)_2NH$ (11.25); (iii) $(C_2H_5)_2NH$ (10.84); (iv) OC_4H_8NH (8.50); and (v) $C_5H_{10}NH$ (11.12). The steric bulk as well as the pK_a values is different for all these amines. This causes different extent of P–N interactions, and as a result, subtle differences in the three P–N bonds arise for **1** and **3**. Moreover, based on single crystal X-ray structural studies,

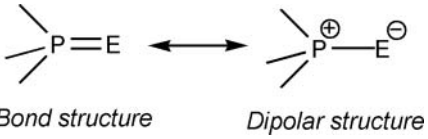


Figure 1 Canonical forms of aminophosphine chalcogenides.

Table III Comparison of δ_C values of N—C carbon for **1** and **3** and **2** and **4**

Compound no.	Groups	Phosphine (1)	Phosphine selenide (3)
	$(i\text{-}C_3H_7)_2N$	45.4	46.9
1a & **3a**	$(n\text{-}C_4H_9)_2N$	46.2	47.7
	$(C_2H_5)_2N$	39.2	40.5
	$(i\text{-}C_3H_7)_2N$	44.6	46.2
1b & **3b**	$(n\text{-}C_4H_9)_2N$	45.4	47.1
	OC_4H_8N	43.8	45.2
	$(i\text{-}C_3H_7)_2N$	45.6	47.6
1c & **3c**	$(n\text{-}C_4H_9)_2N$	48.5	47.7
	$C_5H_{10}N$	43.9	47.0
2a & **4a**	$(i\text{-}C_3H_7)_2N$	45.0	49.7
2b & **4b**	$(c\text{-}C_6H_{11})_2N$	54.3	59.3
2c & **4c**	$(C_6H_5CH_2)_2N$	47.6	49.5

it was reported[70] that in $(R_2N)_3P$, (i) two P–N bonds are short, and the geometry of that nitrogen was found to be planar with reasonable sp^2 character, and the third bond is a longer bond, and the geometry of that nitrogen was found to be pyramidal with sp^3 character; (ii) only two nitrogens (with shorter P–N bond lengths) are accommodated such that their lone pairs are orthogonally placed to that of phosphorus lone pair, and the third nitrogen (with longer P–N bond) then accordingly fits into the remaining space available; and (iii) steric effect of nitrogen substituents is one of the important factors responsible for deciding the geometry of the phosphine. As a result, even for such symmetrically substituted aminophosphines, $(R_2N)_3P$, two types of P–N stretching vibrations were observed and commented.[70] Taking all these arguments along with variations in steric bulk and pK_a values of amines into consideration for the present study, it is very much expected for compounds **1** and **3** to give three sets of P–N stretching vibrations, but to date, no examples of aminophosphines and their selenides containing three different amino substituents are available for comparing and commenting. Indeed, three υ_{PN} values could be identified in the IR spectra of aminophosphines **1** and aminophosphine selenides **3**, which are presented in Table III. The fact that υ_{PN} bands generally appear as sharp and strong bands in most of the cases helped in identifying and presenting them.

^{1}H NMR Studies

In almost all the cases, high resolution ^{1}H NMR spectra of the compounds prepared gave the expected number of proton signals and their intensity, and thus offered valuable assistance in their characterization. The phenyl protons of compounds **2** and **4** gave the characteristic AA'BB' pattern expected of *1,2*-disubstituted benzene. The chiral tris(amino)phosphines and their selenides **1** and **3** exhibit all the signals in the narrow δ-range of 0.9–3.9 ppm, but the splitting patterns were so clear that complete assignment could be made without ambiguity. For example, Figure 2 provides the assignment made for various signals observed for the compounds **1c** and **3a**, respectively. The absence of phosphorus coupling to NCH_2 protons of piperidine ring in **1c** suggests that the ring is puckered. A representative ^{1}H NMR spectrum is given in Figure S1 (available online in the Supplemental Materials) for the compound **3a**.

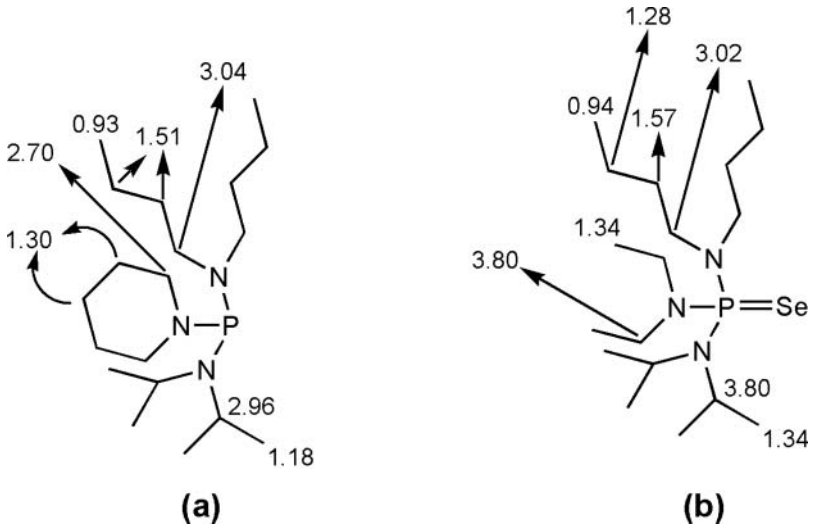


Figure 2 ^{1}H NMR signal assignments for (a) **1c** and (b) **3a**.

^{1}H NMR evidence for the dipolar structure of aminophosphine selenides. Compared to phosphines, the phosphine selenides are found to exhibit slightly downfield proton signals. An interesting observation made is that the lone proton of the cyclohexyl groups in (o-$C_6H_4O_2$)[(c-C_6H_{11})$_2$N]P═E occurs at *ca.* 2.75 ppm for the oxide[71] and *ca.* 3.50 ppm for sulfide[71] and selenide, suggesting the possibility of the dipolar structure (Figure 1) of phosphine chalcogenides predominating for the heavier chalcogen atoms sulfur and selenium, thus supporting the views proposed by Grim and Walton.[72] Our earlier spectral studies (^{31}P, ^{77}Se NMR, and mass) on these compounds have also proven this fact.[49]

Dynamic ^{1}H NMR studies. Dynamic ^{1}H NMR studies of aminophosphines have provided us with the scope to understand different dynamic processes associated with P–N bond(s). In the present study, both an aminophosphine, (o-$C_6H_4O_2$)[(i-C_3H_7)$_2$N]P (**2a**), and its selenide, (o-$C_6H_4O_2$)[(i-C_3H_7)$_2$N]PSe (**4a**) (Figure 3), have been considered for variable temperature NMR investigations. The examples chosen offered the advantage of (i) concentrating on a single trivalent P–N bond as the other two bonds are locked up in a cyclic skeleton; and (ii) evaluating the effect of pentavalent state of phosphorus achieved

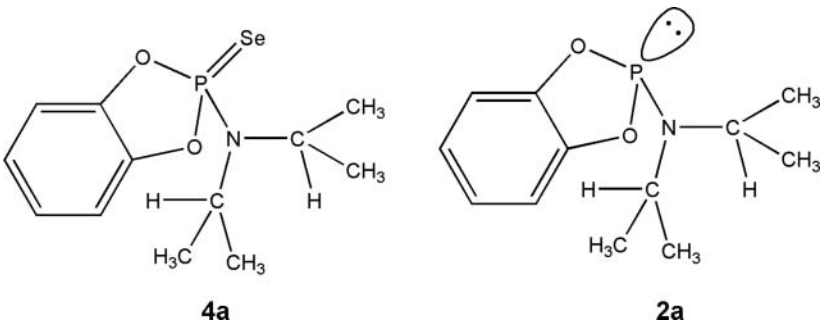


Figure 3 Structures of **4a** and **2a**.

through selenium insertion on the dynamics of phosphorus–nitrogen bond. In addition to these, the chosen isopropyl moiety serves as an excellent candidate for studying and understanding the dynamic features with respect to phosphorus and nitrogen, because the methine proton [$-C\underline{\mathbf{H}}(CH_3)_2$] gives a septet pattern in its ^{1}H NMR spectrum.

In the room temperature ^{1}H NMR spectra, as expected, the lone CH proton of the isopropyl group appears as a 14-line pattern (doublet of septet, *ds*) due to both H–H and P–H coupling interactions. The *ds* pattern for the compound **2a** is shown in Figure S2 (Supplemental Materials). The coupling constant values for the phosphine have been determined to be, $^3J_{HH} = 7.0$ Hz and $^3J_{PH} = 10.0$ Hz, and those for the phosphine selenide to be $^3J_{HH} = 7.0$ Hz and $^3J_{PH} = 8.0$ Hz. The values lie close to the values reported in the literature.[54,73] The methine proton signal of the isopropyl group corresponding to the phosphine selenide shows a relatively lower coupling interaction compared to that of the parent phosphine, especially with respect to $^3J_{PH}$ values (8 and 10 Hz respectively). In an analogous situation, namely, (binaphtholyl)(diisopropylamino)phosphine,[74] the coupling of the methine proton with phosphorus was either not observed or not reported. A careful analysis of the dynamic ^{1}H NMR spectra of both the compounds reveals some salient features.

Cowley et al.[56,57] have observed an eight-line pattern at -50°C for the methyl groups in the chiral chlorophosphine, $(C_6H_5)[(i\text{-}C_3H_7)_2N]PCl$, and this has been rationalized on the basis of restricted rotation about the P–N bond, which renders the four methyl groups anisochronous and each of those that couple to a methine proton to account for four doublets. The same compound gave a four-line pattern at room temperature, and this has been explained on the basis of the diastereotopic nature of the two isopropyl groups of the molecule. However, in the present study, only one set of isopropyl signals is seen for both of the compounds at room temperature, implying their rapid rotation about the P–N bond.

As the temperature is lowered, significant changes are observed with the signals. The dynamic ^{1}H NMR spectra for the isopropyl group of the compounds **2a** and **4a** are presented in Figure S3 (Supplemental Materials). In the case of phosphine, both CH and CH_3 of isopropyl group undergo a significant change simultaneously with the lowering of temperature, whereas only the methine signal (CH) reveals the temperature effect more prominently in the case of phosphine selenide. The coalescence temperature (T_c) is around $-60\ ^\circ$C for the phosphine, and it is around $-40\ ^\circ$C for the selenide. This indicates that the rotation about the P–N bond becomes restricted faster in the case of selenide, which may possibly be due to two factors: (i) the pentavalent phosphorus facilitating a multiple-bond character at the expense of nitrogen lone pair of electrons; and (ii) the increased steric crowding around the phosphorus of the phosphine selenide due to presence of heavier selenium atom, in addition to the other groups. The NMR feature at $-40\ ^\circ$C and below seen for the selenide indicates that the CH signal selectively has become distinguishable while that of CH_3 group has not. This may be the result of the interaction of the bulky selenium atom with one of the CH moieties. Another important observation is, at lower temperature, another doublet at *ca.* 1.40 ppm appears to be growing in intensity for phosphine and the origin of which, though not clearly known, seems to suggest that another conformation for the molecule may become visible at this temperature.

^{13}C NMR Studies

Carbon-13 NMR data acquired on all the compounds both in the proton coupled and decoupled modes helped in unambiguous assignments of the signals. In case of the

phosphines **2**(**a–c**) and their selenides **4**(**a–c**), aromatic carbons of *o*-phenylenedioxo moiety gave the expected number of signals (three numbers) and show practically the same chemical shift values. In these compounds, the most deshielded signal between 144.7 and 147.1 ppm appears as a doublet in the proton decoupled spectrum, which clearly indicates that these carbons (2 numbers in each compound) are the closest to phosphorus, which is coupled ($^2J_{PNC}$ = *ca.* 9 Hz[62]). In the proton-coupled mode, this signal remained unchanged, whereas the other two signals clearly showed a doublet each due to coupling with directly bonded hydrogen ($^1J_{CH}$ = *ca.* 150 Hz[73]). Each line in the doublet at 121 ppm for the phosphine and 123 ppm for the phosphine selenide appears to be further split into a doublet due to coupling to phosphorus compared to 111 and 112 ppm signals, respectively. This further assisted in the spectral assignments.

In the alkyl region, $^2J_{CNP}$ is observable in all the cases in the proton decoupled spectra ($^2J_{CNP}$ = *ca.* 11–25 Hz), and their coupled mode spectra showed the expected multiplet patterns in all the cases. Similarly, compounds **1**(**a–c**) and **3**(**a–c**) showed the expected number of signals and multiplicities in their proton-decoupled spectra, but eluded from calculation of J values due to almost-identical environments and narrow range.

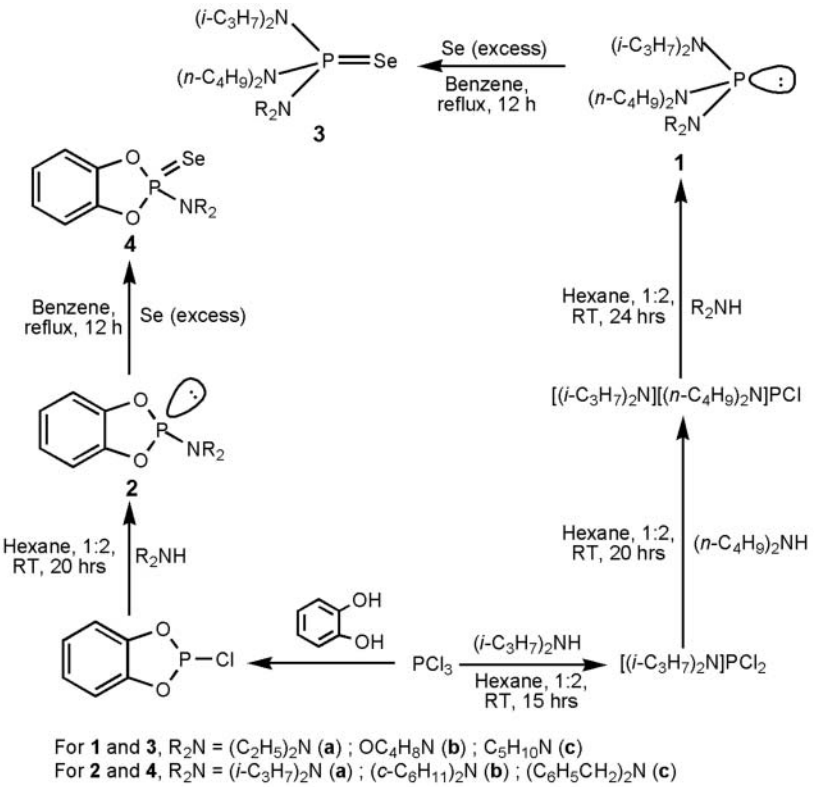
^{13}C NMR evidence for the dipolar structure of aminophosphine selenides. In almost all the cases, compared to the phosphines **1** and **2**, the N–C carbon is deshielded in the phosphine selenides **3** and **4** (Table III). Further, in case of **2b**, that is, (*o*-$C_6H_4O_2$)[(*c*-C_6H_{11})$_2$N]P, compared to its oxide and sulfide (56.4 and 58.4 ppm, respectively),[71] the N–C carbon in the selenide is deshielded the most (59.3 ppm), thus again emphasizing the importance of the dipolar structure over π-bond structure for the heavier chalcogenide (selenide in this case), where a positive sign resides on the phosphorus center (Figure 1).

CONCLUSION

The study has brought out the IR, ^{1}H, and ^{13}C NMR spectral assignments for the first examples of tris(dialkylamino)phosphines and their selenides, containing three different amino substituents on phosphorus center. For such chiral compounds, three different P–N stretching frequencies were identified. Both ^{1}H and ^{13}C NMR data indicated the higher contribution of the dipolar structure for the phosphine selenide compared to the π-bond structure, among the two canonical forms. The dynamic ^{1}H NMR study revealed the effect of the heavier selenium atom and increased multiple bond character of P–N bond on the phosphorus–nitrogen bond rotation. In the free phosphine, T_c occurred at much lower temperature than compared to that of the phosphine selenide.

EXPERIMENTAL

All manipulations were done under inert atmosphere (dry N_2 or Ar gas) conditions. Solvents and amines were purified by standard methods.[75] PCl_3 (Aldrich, 98%) and selenium (CDH) were used as received. Catechol (CDH) was recrystallized from hot toluene before use. Reported procedures[49,76] were employed for synthesizing (*o*-phenylenedioxo)chlorophosphine, (*o*-$C_6H_4O_2$)PCl, and the series of compounds **1**, **2**, **3**, and **4** by employing multistep or one-step condensation reactions between (i) PCl_3 and respective amines and (ii) (*o*-$C_6H_4O_2$)PCl and respective amines; and oxidative addition reactions of **1** and **2** with elemental selenium under benzene reflux conditions (Scheme 1). The yields were found to be between 58–78% for the phosphines



Scheme 1 Synthesis of compounds **1–4**(**a–c**).

and 61–78% for the phosphine selenides. IR spectra were recorded on a Perkin Elmer 1430 spectrophotometer using KBr windows, either as nujol mull (4000–600 cm^{-1}), neat sample (4000–600 cm^{-1}), or KBr disc (4000–400 cm^{-1}). However, only the peaks in the finger print region (1600–600 cm^{-1} for **1** and **2**, and 1600–400 cm^{-1} for **3** and **4**) are presented. ^{1}H NMR spectra (400 MHz) and ^{13}C NMR spectra (100 MHz) were recorded on JEOL JNM GSX-400 spectrometer. The room temperature spectra were recorded as $CDCl_3$ solutions and variable temperature ^{1}H NMR spectra were recorded as acetone-d_6 solution using tetramethylsilane as the internal standard. Upfield shifts are negative. All the chemical shift values (δ) are quoted in ppm.

REFERENCES

1. R. B. King and W.-K. Fu, *Inorg. Chem.*, **25,** 2384 (1986).
2. S. M. Aucott, A. M. Z. Slawin, and J. D. Woollins, *Phosphorus, Sulfur, and Silicon*, **125,** 473 (1997).
3. J. M. Brunel, A. Heumann, and G. Buono, *Angew. Chem., Int. Ed. Engl.*, **39,** 1946 (2000).
4. M. L. Clarke, G. L. Holliday, A. M. Z. Slawin, and J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 1093 (2002).
5. F. Dahan, P. W. Dyer, M. J. Hanton, M. Jones, D. M. P. Mingos, A. J. P. White, D. J. Williams, and A.-M. Williamson, *Eur. J.* Inorg. Chem., 732 (2002).

6. M. P. Magee, W. Luo, and W. H. Hersh, *Organometallics*, **21,** 362 (2002).
7. V. V. Sushev, A. N. Kornev, Y. A. Kurskii, O. V. Kuznetsova, G. K. Fukin, Y. H. Budnikova, and G. A. Abakumov, *J. Organomet. Chem.*, **690,** 1814 (2005).
8. C. Ganesamoorthy, M. S. Balakrishna, P. P. George, and J. T. Mague, *Inorg. Chem.*, **46,** 848 (2007).
9. S. Priya, M. S. Balakrishna, S. M. Mobin, and R. McDonald, *J. Organomet. Chem*., **688,** 227 (2003).
10. J. Cheng, Y. Sun, F. Wang, M. Guo, J. H. Xu, Y. Pan, and Z. A. Zhang, *J. Org. Chem.*, **69,** 5428 (2004).
11. M. L. Clarke and J. D. Woollins, In *Catalysts for Fine Chemical Synthesis*, T. E. Pickett, J. Xiao, J. Whittall, and S. M. Roberts, eds. (John Wiley and Sons, Chichester, UK, 2004), pp. 81–85.
12. M. Alajarin, C. Lopez-Leonardo, and P. Llamas-Lorente, *Top. Curr. Chem.*, **250,** 77 (2005).
13. Z. Fei and P. J. Dyson, *Coord. Chem. Rev.*, **249,** 2056 (2005).
14. B. Punji, J. T. Mague, and M. S. Balakrishna, *Inorg. Chem.*, **45,** 9454 (2006).
15. C. H. Winter, T. S. Lewkebandara, J. W. Proscia, and A. L. Rheingold, *Inorg. Chem.*, **33,** 1227 (1994).
16. P. Bhattacharyya, J. Novosad, J. Phillips, A. M. Z. Slawin, D. J. Woollins, and J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 1607 (1995).
17. J. Anagnostis and M. M. Turnbull, *Polyhedron*, **23,** 125 (2004).
18. C. E. Anderson, A. S. Batsanov, P. W. Dyer, J. Fawcett, and J. A. K. Howard, *J. Chem. Soc., Dalton Trans.*, 5362 (2006).
19. M. C. B. Dolinsky, W. O. Lin, and M. L. Dias, *J. Mol. Catal. A: Chem.*, **258,** 267 (2006).
20. N. Biricik, F. Durap, B. Gümgüm, Z. Fei, and R. Scopelliti, *Transition Met. Chem.*, **32,** 877 (2007).
21. M. Dankowski, In *Chemistry of Organophosphorus Compounds*, Vol. 2, F. R. Hartley, ed. (John Wiley and Sons Ltd, Chichester, UK, 1992), pp. 137–167.
22. H. W. Roesky, J. Lucas, J. Noltemeyer, and G. M. Sheldrick, *Chem. Ber.*, **117,** 1583 (1984).
23. A. J. Elias, M. N. S. Rao, and B. Varghese, *Polyhedron*, **9,** 1433 (1990).
24. C. J. Thomas and M. N. S. Rao, *Z. Anorg. Allg. Chem.*, **619,** 433 (1993).
25. T. Mohan, C. J. Thomas, M. N. S. Rao, G. Aravamudan, A. Meetsma, and J. C. van de Grampel, *Heteroatom Chem*., **5,** 19 (1994).
26. J. Gopalakrishnan, M. N. S. Rao, G. S. Murthy, and J. Srinivas, *Indian J. Chem. Soc. A*, **37A,** 1052 (1998).
27. J. Gopalakrishnan, M. N. S. Rao, G. S. Murthy, and J. Srinivas, *Polyhedron*, **16,** 1089 (1997).
28. J. Gopalakrishnan, A. Doddi, B. Varghese, and M. N. S. Rao, *Appl. Organomet. Chem*., **20,** 880 (2006).
29. H. B. Lamberts, A. Van Der Meer-Kalverkamp, J. C. van de Grampel, A. A. van der Huizen, A. P. Jekel, and N. H. Mulder, *Oncology*, **40,** 301 (1983).
30. S. Rodenhuis, A. H. Scaf, N. H. Mulder, D. T. Sleijfer, M. H. B. Kolmer, D. R. Uges, and J. C. van de Grampel, *Cancer Chemother. Pharmacol.*, **10,** 174 (1983).
31. M. G. L. Mirabelli, A. T. Lynch, and L. G. Sneddon, *Solid State Ionics*, **32–33,** 655 (1989).
32. P. J. Fazen, J. S. Beck, A. T. Lynch, E. E. Remsen, and L. G. Sneddon, *Chem. Mater.*, **2,** 96 (1990).
33. H. R. Allcock and A. M. A. Ambrosio, *Biomaterials*, **17,** 2295 (1996).
34. T. Torroba, *J. Prakt. Chem.*, **341,** 99 (1999).
35. S. Miyano, M. Nawa, A. Mori, and H. Hashimoto, *Bull. Chem. Soc. Jpn.*, **57,** 2171 (1984).
36. M. R. I. Zubiri, M. L. Clarke, D. F. Foster, D. J. Cole-Hamilton, A. M. Z. Slawin, and J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 969 (2001).
37. J. Ansell and M. Wills, *Chem. Soc. Rev*., **31,** 259 (2002).
38. C. A. Tolman, *Chem. Rev.*, **77,** 313 (1977).
39. K. M. Pietrusiewicz and M. Zablocka, *Chem. Rev.*, **94,** 1375 (1994).
40. J. Albert, J. M. Cadena, S. Delgado, and J. Granell, *J. Organomet. Chem.*, **603,** 235 (2000).

41. O. I. Kolodazhnyi, E. V. Gryshkun, N. V. Andrushko, M. Freytag, P. G. Jones, and R. Schmutzler, *Tetrahedron: Asymmetry*, **14,** 181 (2003).
42. O. I. Kolodyazhnyi, N. V. Andrushko, and E. V. Gryshkun, *Zh. Obshch. Khim.*, **74,** 515 (2004).
43. G. Grabulosa, J. I. Muller, A. Ordinas, M. A. Mezzetti, M. Maestro, M. Font-Bardia, and X. Solans, *Organometallics*, **24,** 4961 (2005).
44. E. J. Zijp, J. I. van der Vlugt, D. M. Tooke, A. L. Spec, and D. Vogt, *J. Chem. Soc., Dalton Trans.*, 512 (2005).
45. R. M. Ceder, C. García, A. Grabulosa, F. Karipcin, G. Muller, M. Rocamora, M. Font-Bardía, and X. Solans, *J. Organomet. Chem*., **692,** 4005 (2007).
46. A. Doddi, T. A. Luiz, V. Ramkumar, and M. N. S. Rao, *Acta Cryst*., **E63,** m2727 (2007).
47. T. A. Luiz, B. Varghese, and M. N. S. Rao, *Synth. React. Inorg. Met.–Org. Chem.*, **37,** 669 (2007).
48. K. Wakabayashi, K. Aikawa, S. Kawauchi, and K. Mikami, *J. Am. Chem. Soc.*, **130,** 5012 (2008).
49. J. Gopalakrishnan and M. N. S. Rao, *Bull. Chem. Soc. Ethiop.*, **20,** 207 (2006).
50. J. Gopalakrishnan, T. A. Luiz, B. Varghese, and M. N. S. Rao, Synthesis, Spectral and X-ray Structural Characterization of (Amino)(catecholato)phosphine Selenides. Paper presented in the 9th International Conference on the Chemistry of Selenium and Tellurium (ICCST-9) at the Indian Institute of Technology (IIT), Bombay, India, February 23–27, 2004.
51. G. Bulloch, R. Keat, and D. S. Rycroft, *J. Chem. Soc., Dalton Trans.*, 764 (1978).
52. Z. Liu, X. Li, and J. Zhang, *Phosphorus, Sulfur, and Silicon*, **40,** 215 (1988).
53. M. M. Ben, M. Kossentini, and M. Salem, *Phosphorus, Sulfur, and Silicon*, **181,** 1315 (2006).
54. A. M. Z. Slawin, J. D. Woollins, and Q. Zhang, *J. Chem. Soc., Dalton Trans.*, 621 (2001).
55. R. W. Light and R. T. Paine, *Phosphorus, Sulfur, and Silicon*, **8,** 255 (1980).
56. A. H. Cowley, M. J. S. Dewar, and W. R. Jackson, *J. Am. Chem. Soc.*, **90,** 4185 (1968).
57. A. H. Cowley, M. J. S. Dewar, W. R. Jackson, and W. B. Jennings, *J. Am. Chem. Soc.*, **92,** 5206 (1970).
58. S. Fischer, J. Hoyano, I. Johnson, and L. K. Peterson, *Can. J. Chem.*, **54,** 2706 (1976).
59. R. H. Neilson, R. C.-Y. Lee, and A. H. Cowley, *Inorg. Chem*., **16,** 1455 (1977).
60. J. Anagnostis and M. M. Turnbull, *Polyhedron*, **23,** 125 (2004).
61. M. J. S. Dewar and W. B. Jennings, *J. Am. Chem. Soc.*, **91,** 3655 (1969).
62. R. P. K. Babu, S. S. Krishnamurthy, and M. Nethaji, *Heteroatom Chem*., **2,** 477 (1991).
63. M. D. Wodrich, A. Vargas, P.-Y. Morgantini, G. Merino, and C. Corminboeuf, *J. Phys. Org. Chem*., **22,** 101 (2009).
64. R. A. Chittenden and L. C. Thomas, *Spectrochim. Acta*, **22,** 1449 (1966).
65. T. Q. Ly, A. M. Z. Slawin, and J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 1611 (1997).
66. T. Mohan, Ph.D. Thesis, *Indian Institute of Technology Madras*, Chennai, Tamil Nadu, India (1990).
67. D. H. Williams and I. Fleming, *Spectroscopic Methods in Organic Chemistry*, 5th ed. (McGraw Hill Publ. Co., Berkshire, UK, 1995), Chap. 2, pp. 28–62.
68. K. Maartmann-Moe, C. Romming, and J. Songstad, *Acta Chem. Scand. Ser. A*, **36,** 757 (1982).
69. R. D. Lide, Ed., *CRC Handbook of Chemistry and Physics* (CRC Press, Cleveland, Ohio, 2002), pp. 8:46–8:56.
70. C. Romming and J. Songstad, *Acta Chem. Scand. Ser. A*, **32,** 689 (1978), and refs. cited therein.
71. J. Gopalakrishnan, Ph.D. Thesis, Indian Institute of Technology Madras, Chennai, Tamil Nadu, India (1998).
72. S. O. Grim and E. D. Walton, *Inorg. Chem.*, **19,** 1982 (1980).
73. D. H. Williams and I. Fleming, *Spectroscopic Methods in Organic Chemistry* 5th Ed. (McGraw Hill Publ. Co., Berkshire, England, 1995), Chap. 3, pp. 63–169.
74. A. H. M. de Vries, A. Meetsma, and B. L. Feringa, *Angew. Chem., Int. Ed. Engl*., **35,** 2374 (1996).
75. D. D. Perrin, W. L. F. Armarego, and D. R. Perrin, *Purification of Laboratory Chemicals* (Pergamon Press, Oxford, UK, 1980).
76. B. S. Furniss, A. J. Hannaford, P. W. G. Smith, and A. R. Tatchell, *Vogel's Textbook of Practical Organic Chemistry*, 5th ed. (Longman Scientific and Technical, Essex, UK, 1989), pp. 569–570.