Probing solid iminobis(diorganophosphine chalcogenide) systems with multinuclear magnetic resonance¹

Bryan A. Demko and Roderick E. Wasylishen

Abstract: A ³¹P and ⁷⁷Se solid-state NMR investigation of the iminobis(diorganophosphine chalcogenide) $HN(R_2PE)_2$ (R = Ph, ⁱPr; E = O, S, Se) systems is presented. The NMR results are discussed in terms of the known $HN(R_2PE)_2$ structures available from X-ray crystallography. The phosphorus chemical shift tensors are found to be sensitive to the nature of the alkyl and chalcogen substituents. The nature of the R group also influences the selenium chemical shift tensors of $HN(R_2PSe)_2$ (R = Ph, ⁱPr), which are shown to be sensitive to hydrogen bonding in the dimer structure of $HN(Ph_2PSe)_2$ and to the presence of disorder in the case of $HN(^iPr_2PSe)_2$. Scalar relativistic ZORA DFT nuclear magnetic shielding tensor calculations were performed yielding the orientations of the corresponding chemical shift tensors. A theoretical investigation into the effect of the *E*-P···P-*E* "torsion" angle on the phosphorus and selenium chemical shift tensors of a truncated $HN(Me_2PSe)_2$ system indicates that the electronic effect of the alkyl group on the respective nuclear magnetic shielding tensors are more important than the steric effect of the *E*-P···P-*E* torsion angle.

Key words: iminobis(diorganophosphine chalcogenide), solid-state NMR, ³¹P NMR, ⁷⁷Se NMR, ZORA DFT.

Résumé : On a effectué une étude basée sur les RMN du ³¹P et du ⁷⁷Se à l'état solide d'iminobis(chalcogénure de diorganophosphine) HN(R_2PE)₂ (R = Ph, ⁱPr; E = O, S, Se). On discute des résultats de la RMN en fonction de structures HN(R_2PE)₂ connues, disponibles à partir de la diffraction des rayons X. On a trouvé que les tenseurs du déplacement chimique du phosphore sont sensibles à la nature du groupe alkyle et des substituants chalcogènes. La nature du groupe R influence aussi les tenseurs du déplacement chimique du sélénium de HN(R_2PSe)₂ (R = Ph, ⁱPr) et on a démontré qu'ils sont aussi sensibles à la liaison hydrogène dans la structure dimère du HN(Ph₂PSe)₂ et à la présence de désordre dans le cas du HN(ⁱPr₂PSe)₂. On a effectué des calculs de théorie de la fonctionnelle de densité ZORA scalaires relativistiques du tenseur de blindage magnétique qui ont permis d'obtenir les orientations correspondantes des tenseurs du déplacement chimique du phosphore et du sélénium d'un système HN(Me₂PSe)₂ tronqué indique que l'effet électronique du groupe alkyle sur les tenseurs respectifs de blindage magnétique nucléaire sont plus importants que l'effet stérique de l'angle de torsion E-P···P-E.

Mots-clés : iminobis(chalcogénure de diorganophosphine), RMN à l'état solide, RMN du ³¹P, RMN du ⁷⁷Se, calculs de théorie de la fonctionnelle de densité ZORA.

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Introduction

The coordination of monoanionic bidentate ligands with metal and non-metal centers continues to provide a vast area

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This paper is dedicated to Professor Richard J. Puddephatt in honour of his outstanding contributions to Canadian chemistry.

B.A. Demko and R.E. Wasylishen.² Department of Chemistry, Gunning–Lemieux Chemistry Centre, University of Alberta, Edmonton, AB T6G 2G2, Canada.

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²Corresponding author (e-mail: roderick.wasylishen@ualberta.ca).

of research interest. Acetylacetonate (acac) and its β diketonate derivatives represent the ideological figurehead of monoanionic bidentate coordination chemistry (1). Recently, β -diketonate precursors have been utilized in the fabrication of metal oxide thin films (2) and other chemical vapor deposition applications (3). Interest in related metal chalcogenide materials has spurred the investigation of monoanionic bidentate ligands possessing the corresponding elements of Group 16. Some sulfur- and seleniumcontaining ligands such as dialkyldichalcogenophosphates, dialkyldichalcogenophosphinates, and dialkyldichalcogenocarbamates have appeared in the literature (4-6); however, their small chalcogen-chalcogen interatomic distances result in the formation of complexes primarily in an anisobidentate fashion (7). The iminobis(diorganophosphine chalcogenide) compounds, the so-called non-carbon (main group) analogues of acetylacetone, offer the opportunity to vary the donor chalcogen atom. Also, variation of the alkyl group in these ligands is more easily accessible than for the organic

Scheme 1. Similarities between the structures of acetylacetone and the iminobis(diorganophosphine chalcogenide) systems.



analogues (8). The fine-tuning available for specific metal complexation permits comparisons between the bonding in organic and inorganic analogues, knowledge widely sought throughout the chemistry community (9). While not isoelectronic, acac and dichalcogenoimidodiphosphinate systems are closely related (Scheme 1). An early example of the Group 10 complexes of [N(Ph₂PSe)₂]⁻ contained heterocyclic MSe₂P₂N rings that were puckered (10), unlike those of acetylacetonate that contain planar six-membered rings (11, 12). This difference has been attributed to the ability of the dichalcogenoimidodiphosphinate ligands to form delocalized systems utilizing low lying d orbitals (10, 13, 14). The structures of these complexes are known to depend on the choice of chalcogen, alkyl group, and metal (13, 15-19). Often, the complexes exhibit symmetrical coordination patterns with the donor chalcogen atoms (8, 20).

Numerous reviews of the versatile dichalcogenoimidodiphosphinate ligands exist in the literature (15, 21–23). In addition to applications as single-source precursors for solidstate metal chalcogenide materials (4–6, 20, 24–29), these bidentate ligands have found uses in the search for stereochemically active lone pairs (10, 19, 30–32), in catalysis (33–35), and in metal extraction processes (15, 36–39), as lanthanide shift reagents (40, 41), luminescent materials (42), and as enzyme mimetics (43–45).

Despite the considerable interest in the properties and chemistry of the complexes of dichalcogenoimidodiphosphinate ligands, relatively little is known about the neutral iminobis(diorganophosphine chalcogenide) $HN(R_2PE)_2$ derivatives (46). Characterization of these systems has predominantly been performed by X-ray crystallography (10, 31, 47-53), often accompanied by IR (31, 54-57), Raman (56, 57), and (or) solution NMR spectroscopy (10, 31, 47, 54, 58). Solid-state NMR, being potentially more informative than solution NMR spectroscopy, would appear to be an appropriate technique for characterizing the $HN(R_2PE)_2$ ligands. Recently, we have demonstrated the use of solid-state NMR spectroscopy in the characterization of the metal(II) complexes of the $[N(^{i}Pr_{2}PSe)_{2}]^{-}$ ligand (59, 60). Herein we present a solid-state ³¹P and ⁷⁷Se NMR investigation of the $HN(R_2PE)_2$ (E = O, S, Se; R = Ph, ⁱPr) systems representing the first solid-state NMR investigation of the iminobis(diorganophosphine chalcogenides). Comparisons of the solidstate NMR results obtained herein with those of the M[N(¹Pr₂PSe)₂]₂ complexes previously investigated are made, where appropriate (59, 60).

Experimental

Sample preparation

The phenyl and isopropyl variants of bis(diorganophosphino)amine $HN(R_2P)_2$ were prepared via the condensation reaction between hexamethyldisilazane $HN(SiMe_3)_2$ and the appropriate chlorodiorganophosphine R_2 PCl (Sigma-Aldrich) (55, 61). Briefly, R_2 PCl in toluene is added dropwise to a hot toluene solution of HN(SiMe₃)₂ and is maintained above 80 °C for at least two hours to remove the chlorotrimethylsilane by-product by distillation. Oxidation to the corresponding iminobis(diorganophosphine chalcogenide) was achieved from the subsequent reaction with hydrogen peroxide in an ice bath (55, 62) and via reflux with either elemental sulfur (55) or elemental selenium (10, 20). X-ray crystal structures from the literature, for each of the investigated iminobis(diorganophosphine chalcogenide) systems, HN(R_2PE_{2} (E = O; R = Ph (50) and ⁱPr (31), E = S; R = Ph(50–52) and ⁱPr (47), E = Se; R = Ph (10) and ⁱPr (31)), have been previously reported.

NMR experiments

Solid-state NMR investigations of powdered samples of $HN(R_2PE)_2]_2$ (E = O, S, Se; R = Ph, ⁱPr) were obtained using 4.70 T, 7.05 T, and 11.75 T NMR spectrometers. The samples were packed in 4 mm (7.05 T and 11.75 T) and 7.5 mm (4.70 T) o.d. zirconium oxide rotors and were placed within probes suitable for magic angle spinning, MAS, NMR experiments. A ramped amplitude cross polarization (RACP) pulse sequence was used to acquire all spectra (63). Two-pulse phase-modulation (TPPM) (64) and proton decoupling fields of approximately 60 kHz were utilized. The ³¹P NMR spectra were referenced with respect to 85% aq. H₃PO₄ by setting the isotropic ³¹P NMR peak of solid (NH₄)H₂PO₄ to 0.81 ppm (65). Selenium-77 NMR spectra were referenced to Me₂Se (1) by setting the isotropic peak of solid ammonium selenate (NH₄)₂SeO₄ to 1040.2 ppm (65, 66).

Solid-state ³¹P NMR experiments were performed at Larmor frequencies of 81.0, 121.6, and 202.5 MHz, and at spinning frequencies ranging from 3.0 to 7.2 kHz. A total of between 64 and 128 scans were acquired per spectrum. Contact times between 1.5 and 6.5 ms, and pulse delays between 600 and 840 s for $HN(Ph_2PE)_2$ systems and between 7 and 18 s for the $HN(Pr_2PE)_2$ systems were employed.

Solid-state ⁷⁷Se NMR measurements were performed at Larmor frequencies of 38.2, 57.3, and 95.4 MHz, and at spinning frequencies ranging from 2.0 to 14.0 kHz. A total of between 384 and 16 384 scans were acquired per spectrum. Contact times between 6.5 and 10.0 ms, and pulse delays between 600 and 840 s for $HN(Ph_2PE)_2$ species and between 5 and 14 s for the $HN(^{i}Pr_2PE)_2$ systems were employed.

The principal components of the respective phosphorus and selenium chemical shift tensors, $\delta_{11} \ge \delta_{22} \ge \delta_{33}$, were determined from the experimental spectra using the procedure of Herzfeld and Berger (67, 68). All experimental solid-state NMR spectra were simulated using the determined values with the program WSOLIDS (69) to assess the quality of the obtained parameters. This procedure results in errors of ± 0.2 ppm in the isotropic chemical shift, $\delta_{iso} = (1/3)(\delta_{11} + \delta_{22} + \delta_{33})$, and errors in the principal components of approximately 1%–3% of the span, $\Omega = \delta_{11} - \delta_{33}$, of the respective chemical shift tensors. Another useful quantity for describing the appearance of chemical shift powder patterns is the skew, $\kappa = 3(\delta_{22} - \delta_{iso})/\Omega$, where axial symmetry is described by $\kappa = +1$ or -1 (70).

DFT computations

Theoretical calculations of NMR parameters were performed on isolated molecules. Cartesian coordinates of the atoms were generated from the reported crystal structures placing hydrogen atoms at idealized locations ($r_{CH} = 1.08$ Å (R = Ph), 1.09 Å (R = Pr)). Magnetic shielding tensors σ were calculated using the NMR module (71-73) of the Amsterdam density functional (ADF) program package (74-78). The Vosko-Wilk-Nusair (79) local density approximation with the Becke88-Perdew86 (80-82) generalized gradient approximation were used for the exchange-correlation functional. Scalar relativistic corrections were carried out based on the implementation of the zero-order regular approximation (ZORA) formalism (83-86). Triple- ζ doubly polarized (TZ2P) Slater-type ZORA basis sets were used for all atoms except for hydrogen, where double- ζ quality (DZ) basis functions were utilized. The corresponding phosphorus and selenium chemical shift tensors were obtained from the magnetic shielding tensors using the relationship,

[1]
$$\delta_{ii}(\text{sample}) = \frac{\sigma_{iso} (\text{ref}) - \sigma_{ii}(\text{sample})}{1 - \sigma_{iso} (\text{ref})}$$

where $\sigma_{iso}(ref)$ is the isotropic shielding of a standard reference. The absolute shielding scale for ³¹P has been determined, and the value of $\sigma_{iso}~(85\%~aq.~H_3PO_4)$ has been established to be 328.35 ppm (87). We have previously investigated the selenium chemical shift tensors in a wide range of selenium-containing compounds and used the value of 1580 ppm determined therein for the isotropic reference shielding of a neat liquid of dimethyl selenide at 23 °C (88).

Results and discussion

A common difference between the R = Ph and $R = {}^{i}Pr$ structures of the $HN(R_2PE)_2$ systems is that while the EPNPE backbones in iminobis(diphenylphosphine chalcogenide) species are oriented *anti*, the $HN(^{i}Pr_{2}PE)_{2}$ (E = O, S,Se) molecules all possess gauche conformations (Fig. 1). X-ray diffraction studies of each of the iminobis(diorganophosphine chalcogenides) investigated here indicate that the crystals contain one molecule in the asymmetric unit. The reported structure for HN(Ph2PO)2 contains an inversion center providing chemical equivalence between the two phosphorus atoms such that only a single phosphorus chemical shift tensor is expected for this sample. The remaining samples investigated, $HN(Ph_2PE)_2$ (E = S, Se) and $HN(^{i}Pr_{2}PE)_{2}$ (E = O, S, Se), do not possess any symmetry elements within their respective molecular structures providing chemical equivalence between the two phosphorus (or two selenium) atoms, thus two distinct phosphorus (or selenium) chemical shift tensors are expected in the experimental NMR spectra. The obtained phosphorus chemical shift tensors for the iminobis(diorganophosphine chalcogenide) systems are presented first, followed by the results of a solid-state ⁷⁷Se NMR study on $HN(R_2PSe)_2$ (R = Ph, ⁱPr). As the syntheses of the phenyl-derivatized species were reported prior to the isopropyl variants, the results for $HN(Ph_2PE)_2$ will precede those for $HN(^{i}Pr_2PE)_2$. The extracted NMR parameters are discussed in terms of the known molecular structures, highlighting the impact in the Fig. 1. Common conformations encountered in iminobis(diorganophosphine chalcogenide), $HN(R_2PE)_2$ (E = O, S, Se), systems.



choice of R group and (or) chalcogen where applicable. DFT computations are used to provide the orientations of the phosphorus and selenium nuclear magnetic shielding tensors.

Solid-state ³¹P NMR The ³¹P NMR parameters obtained for each of the $HN(R_2PE)_2$ (*E* = O, S, Se; *R* = Ph, ⁱPr) samples investigated are given in Table 1, along with theoretical calculations of the corresponding phosphorus chemical shift tensors. Experimental solid-state ³¹P NMR spectra for $HN(R_2PO)_2$, $HN(R_2PS)_2$, and $HN(R_2PSe)_2$ are given in Figs. 2, 5, and 6, respectively.

$HN(R_2PO)_2$ ($R = Ph, {}^{i}Pr$)

For the phenyl derivative, the imidodiphosphinic acid tautomer Ph₂P(OH)NP(O)Ph₂ (50) was found instead of the initially hypothesized HN(Ph₂PO)₂ structure (48, 49), which possesses an acidic N-H proton. As a result, Ph₂P(OH)NP(O)Ph₂ has a considerably different structure from the other iminobis(diorganophosphine chalcogenide) systems investigated that all display acidic N-H protons. Similar to the HN(Ph₂PE)₂ (E = S, Se) molecules that possess a solid-state structure in which the EPNPE backbone adopts an anti conformation, Ph2P(OH)NP(O)Ph2 is trans with an O-P···P-O "torsion" angle of 180° (50). However, unique to the Ph₂P(OH)NP(O)Ph₂ system is a linear P-N-P angle of 180° (50). The solid-state ³¹P NMR spectrum is given, along with its simulation, in Fig. 2a. Contrary to the single phosphorus environment expected from the crystal structure of Ph₂P(OH)NP(O)Ph₂ (50), two phosphorus chemical shift tensors were extracted (Table 1), which possess isotropic chemical shifts and spans that differ by more than 20 ppm despite the two tensors possessing similar skews. As the ³¹P NMR spectrum (not shown) of a chloroform solution of Ph₂P(OH)NP(O)Ph₂ displays only a single peak, the solid sample investigated, as obtained from a methylene chloride - hexanes recrystallization, must be of a different polymorph of Ph₂P(OH)NP(O)Ph₂ than the reported structure from a crystal grown in glacial acetic acid (50).

Phosphorus chemical shift tensors from the DFT computations of a single Ph₂P(OH)NP(O)Ph₂ unit from the reported crystal structure (50) (Table 1) produce comparable values of δ_{iso} , δ_{ii} , Ω , and κ with the experimentally determined parameters; however, they do not predict an equally large difference between the two respective isotropic chemical shifts. This discrepancy is likely a result of using the geometry from the reported crystal structure, which is not entirely representative of the actual solid-state structure of the solid

Table	1.	Solid-state	³¹ P	NMR	parameters	for	$HN(R_2PE)_2$	(E =	О,	S,	Se;	R =	Ph,	ⁱ Pr).	
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			δ_{iso}	δ ₁₁	δ ₂₂	δ ₃₃	Ω		${}^{1}J(\text{Se},\text{P})_{iso}^{a}$
Ε	R		(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	к	(Hz)
0	Ph	(Exptl.)	8.2	79.6	13.3	-68.2	147.8	0.10	
			28.4	109.5	38.6	-62.8	172.3	0.18	
		(Calcd.)	19.0	85.7	35.8	-64.6	150.3	0.34	
			24.4	127.4	51.6	-105.9	233.3	0.35	
	ⁱ Pr	(Exptl.)	52.5	101.8	101.8	-46.0	147.8	1.00	
			57.7	112.7	89.2	-28.8	141.5	0.67	
		(Calcd. a)	62.2	137.9	124.0	-75.2	213.1	0.87	
			68.9	144.3	123.9	-61.4	205.7	0.80	
		(Calcd. b)	59.1	131.1	122.3	-76.2	207.3	0.92	
			69.1	144.7	124.0	-61.4	206.1	0.80	
S	Ph	(Exptl.)	54.7	155.7	77.5	-69.2	224.9	0.30	
			57.1	164.0	92.7	-85.5	249.5	0.43	
		(Calcd.)	75.4	203.9	129.2	-106.9	310.8	0.52	
			76.5	195.3	118.0	-83.8	279.1	0.45	
	ⁱ Pr	(Exptl.)	89.1	155.0	121.7	-9.4	164.4	0.60	
			90.6	163.0	118.5	-9.7	172.7	0.48	
		(Calcd.)	102.2	206.1	142.6	-41.9	248.0	0.49	
			108.2	190.3	164.3	-29.9	220.2	0.76	
Se	Ph	(Exptl.)	48.9	149.5	62.5	-65.2	214.7	0.19	-720
			52.4	160.4	79.9	-83.1	243.5	0.34	-740
		(Calcd.)	98.6	235.0	139.3	-78.6	313.6	0.39	
			101.8	249.3	153.9	-97.8	347.1	0.45	
	ⁱ Pr	(Exptl.)	88.8	152.0	113.7	0.7	151.3	0.49	-740
			91.1	160.4	110.3	2.6	157.8	0.36	-735
		(Calcd. a)	129.8	245.8	170.2	-26.5	272.3	0.44	
			130.3	215.2	192.8	-17.1	232.3	0.81	
		(Calcd. b)	129.9	243.4	170.9	-24.6	268.0	0.46	
			130.5	225.2	184.4	-18.3	243.5	0.66	

"For directly bonded selenium-77 and phosphorus-31 spin pairs; signs of ${}^{1}J({}^{77}\text{Se},{}^{31}\text{P})_{iso}$ are known to be negative for numerous analogous systems (95, 96).

sample investigated, as well as the neglect of intermolecular effects including potential hydrogen bonding between Ph₂P(OH)NP(O)Ph₂ molecules. Additionally, the computations indicate that the phosphorus bearing the hydroxyl group is more shielded than the P=O phosphorus in Ph₂P(OH)NP(O)Ph₂. The calculated orientations of the two phosphorus chemical shift tensors are also different, as shown in Fig. 3a. The computed P-OH phosphorus chemical shift tensor is oriented with δ_{11} perpendicular to the local O-P-N plane, and δ_{33} approximately parallel to the P-N vector with δ_{22} within the O-P-N plane and perpendicular to P-N. The calculated P=O phosphorus chemical shift tensor places δ_{11} perpendicular to the local O-P-N plane, while in contrast δ_{33} is oriented nearly parallel to the P-O vector with δ_{22} within the O-P-N plane and perpendicular to P-O. The orientation of the P=O phosphorus chemical shift tensor is similar to what is consistently found for tris-organophosphine oxides (89).

One of the largest differences between $HN(^{i}Pr_{2}PO)_{2}$ and $Ph_{2}P(OH)NP(O)Ph_{2}$ is that iminobis(diisopropylphosphine oxide) possesses an acidic N-H proton leading to a P-N-P angle of 130° (31). The *gauche* conformation of $HN(^{i}Pr_{2}PO)_{2}$, reflected in a 52° O-P···P-O "torsion" angle, yields a chain-like arrangement of $HN(^{i}Pr_{2}PO)_{2}$ units in its solid state structure (31). The X-ray structure of $HN(^{i}Pr_{2}PO)_{2}$ displays some disorder in that one methyl carbon on one isopropyl

group possesses two 50% occupancy sites (31). There exists three spinning sideband manifolds corresponding to three discernable signals in the ³¹P MAS spectrum of HN(ⁱPr₂PO)₂ given in Fig. 2b; however, as one of the three signals is significantly less intense than the other two it is considered to be a minor impurity in the sample rather than resulting from disorder in the structure. The impurity can be readily identified in Fig. 2b by comparison of the experimental with the simulated spectrum. The two isotropic phosphorus chemical shifts obtained (Table 1) are in good agreement with the ³¹P NMR value from a chloroform solution of HN(¹Pr₂PO)₂, i.e., 55.5 ppm (31). The phosphorus environments are deshielded with respect to those of Ph₂P(OH)NP(O)Ph₂ and possess slightly smaller spans and larger positive skews. The steric or electronic source of this difference will be discussed later. One phosphorus environment indicates an axially symmetric chemical shift tensor despite there being no symmetry reasons for attaining this axial symmetry. Methods for obtaining accurate principal components of the chemical shift tensor from spectra of MAS samples are known to have the greatest difficulty with axially or near axially symmetric species (90).

Calculated phosphorus chemical shift tensors were obtained for both of the 50% occupancy structures (31), labeled "a" and "b" in the Table 1. Both phosphorus chemical shift tensors computed for each of the two structures are in

Fig. 2. (*a*) RACP MAS ³¹P NMR spectrum (lower trace) for $Ph_2P(OH)NP(O)Ph_2$ and its simulation (upper trace). Experimental conditions: 11.75 T, 64 scans, MAS at 3.0 kHz, 10 Hz of line broadening, 3.0 ms contact time, and 900 s recycle delay. (*b*) RACP MAS ³¹P NMR spectrum (lower trace) for $HN(^iPr_2PO)_2$ and its simulation (upper trace). Experimental conditions: 11.75 T, 128 scans, MAS at 3.0 kHz, 10 Hz of line broadening, 3.0 ms contact time, and 900 s recycle delay. (*b*) RACP MAS at 3.0 kHz, 10 Hz of line broadening, 3.0 ms contact time, and 18 s recycle delay. The isotropic peaks are marked with an asterisk (*).



reasonable agreement with the experimental values. The values of δ_{ii} (calcd.) are quite similar for structures "a" and "b", suggesting that the presence of disorder in the methyl group does not significantly affect the phosphorus shielding in HN(ⁱPr₂PO)₂. This is consistent with the solid-state ³¹P NMR spectrum (Fig. 2*b*) where no discernable difference in the obtained line widths or line shapes of the two phosphorus environments was detected. In contrast to the calculated orientations of the phosphorus chemical shift tensors in Ph₂P(OH)NP(O)Ph₂, all phosphorus tensors for HN(ⁱPr₂PO)₂ are oriented similarly (Fig. 3*b*). The computations place δ_{33} approximately along the O-P vector, and δ_{22} perpendicular to the local O-P-N plane, with δ_{11} perpendicular to O-P within the O-P-N plane.

$HN(R_2PS)_2$ ($R = Ph, {}^{i}Pr$)

The *anti* conformation of HN(Ph₂PS)₂, with a S-P···P-S torsion angle of 156° is similar to that of Ph₂P(OH)NP(O)Ph₂, while the P-N-P angle of 133° is consistent with a PNP backbone that possesses a protonated nitrogen (50–52). The solid state structure consists of two HN(Ph₂PS)₂ molecules hydrogen bonded to form dimer pairs (Fig. 4) (50–52). The ³¹P NMR parameters obtained from the RACP MAS spectrum for HN(Ph₂PS)₂ (Fig. 5*a*) are given in Table 1. The isotropic chemical shifts obtained are in good agreement with the solution ³¹P NMR values of 55.1 ppm in THF (54) and 58.2 ppm in CDCl₃ (58). The

phosphorus chemical shift tensors of $HN(Ph_2PS)_2$ describe phosphorus nuclei that are more deshielded, possess larger spans, and have slightly more positive values of κ than those obtained for Ph₂P(OH)NP(O)Ph₂.

The DFT computations were performed on a dimer of $HN(Ph_2PS)_2$ units. The calculated principal components of the respective phosphorus chemical shift tensors slightly overestimate the corresponding experimental values. The orientations of the two calculated phosphorus chemical shift tensors (Fig. 3*c*) are nearly identical and most closely resemble those calculated for the P=O phosphorus of Ph_2P(OH)NP(O)Ph_2, with δ_{33} approximately parallel to the P-S vector, δ_{11} perpendicular to the local S-P-N plane, and δ_{22} nearly within the S-P-N plane perpendicular to P-S. These orientations are consistent with those obtained for tris-organophosphine sulfide systems (89) and similar to those found in tetramethyldiphosphine disulfide (91).

Similar to that of $HN(^{i}Pr_2PO)_2$, the structure of $HN(^{i}Pr_2PS)_2$ contains a 132° P-N-P angle; however, the S-P.··P-S torsion angle is slightly larger at 79° and the X-ray structure reports no evidence of disorder (47). The solid-state ³¹P NMR spectrum of $HN(^{i}Pr_2PS)_2$ is given in Fig. 5*b*. The isotropic chemical shifts for the two phosphorus environments are in good agreement with the value of 91.2 ppm reported for $HN(^{i}Pr_2PS)_2$ in $CDCl_3$ (47). Similar to the chemical shift tensors describing the phosphorus shielding of $HN(Ph_2PS)_2$ and $Ph_2P(OH)NP(O)Ph_2$, the two phosphorus

Fig. 3. Calculated phosphorus chemical shift tensor orientations for (*a*) $Ph_2P(OH)NP(O)Ph_2$, (*b*) $HN(^{1}Pr_2PO)_2$, (*c*) $HN(Ph_2PS)_2$, (*d*) $HN(^{1}Pr_2PS)_2$, (*e*) $HN(Ph_2PS)_2$, (



Fig. 4. Dimer structure of $HN(Ph_2PE)_2$ (E = S, Se).



environments of HN(¹Pr₂PS)₂ are more deshielded and possess larger spans than those for HN(¹Pr₂PO)₂. Solution ³¹P NMR for the mixed chalcogen system ¹Pr₂P(O)NHP(S)¹Pr₂ displays a comparable difference in the values of δ_{iso} (³¹P), 54.8 and 90.9 ppm (31). Additionally, as with the E = O compounds, the phosphorus sites in HN(¹Pr₂PS)₂ are more deshielded and have larger positive skews than the phenyl derivative.

Calculated phosphorus chemical shift tensors for HN(ⁱPr₂PS)₂ are given in Table 1. The computed values of δ_{iso} , δ_{ii} , Ω , and κ are in reasonable agreement with the experimentally obtained parameters. As observed with the calculated orientation of the tensors in HN(ⁱPr₂PO)₂, the two phosphorus chemical shift tensors for HN(ⁱPr₂PS)₂ (Fig. 3*d*) are approximately identical and place δ_{33} nearly parallel to the *E*-P vector; however, the directions of δ_{11} and δ_{22} are essentially reversed in HN(ⁱPr₂PS)₂ with respect to HN(ⁱPr₂PO)₂, with δ_{11} perpendicular to the local S-P-N plane and δ_{22} within the S-P-N plane perpendicular to S-P.

Fig. 5. (*a*) RACP MAS ³¹P NMR spectrum (lower trace) for $HN(Ph_2PS)_2$ and its simulation (upper trace). Experimental conditions: 11.75 T, 64 scans, MAS at 3.0 kHz, 10 Hz of line broadening, 3.0 ms contact time, and 900 s recycle delay. (*b*) RACP MAS ³¹P NMR spectrum (lower trace) for $HN({}^{1}Pr_2PS)_2$ and its simulation (upper trace). Experimental conditions: 11.75 T, 128 scans, MAS at 3.0 kHz, 5 Hz of line broadening, 3.0 ms contact time, and 9 s recycle delay. The isotropic peaks are marked with an asterisk (*).



$HN(R_2PSe)_2$ ($R = Ph, {}^{i}Pr$)

Isomorphous with HN(Ph₂PS)₂, the dimer structure of HN(Ph₂PSe)₂ possesses an *anti* conformation with a Se-P···P-Se torsion angle of 154° and a P-N-P angle of 132° (10). The phosphorus chemical shift parameters, along with an estimation of the one-bond selenium–phosphorus indirect spin–spin coupling constant ${}^{1}J({}^{77}\text{Se},{}^{31}\text{P})_{iso}$ from the MAS ${}^{31}\text{P}$ NMR spectrum (Fig. 6*a*) are reported in Table 1. The values of $\delta_{iso}({}^{31}\text{P})$ and ${}^{1}J({}^{77}\text{Se},{}^{31}\text{P})_{iso}$ obtained are in good agreement with those from ${}^{31}\text{P}$ NMR of methylene chloride and chloroform solutions of HN(Ph₂PSe)₂, 53.0 ppm and (–)793 Hz (10), and 53.2 ppm (58), respectively. The principal components of the phosphorus chemical shift tensors are very similar to those found for HN(Ph₂PS)₂ (Table 1) indicating that the impact of exchanging oxygen for sulfur in HN(Ph₂PE)₂ is larger than exchanging sulfur for selenium.

The phosphorus chemical shift tensors were calculated for a dimer of $HN(Ph_2PSe)_2$ molecules (10). The calculations overestimate the values of δ_{iso} and Ω , indicating that scalar relativistic effects may not be sufficient to accurately describe the shielding environment for $HN(Ph_2PSe)_2$, and that spin–orbit relativistic effects may be important. Similar to those of $HN(Ph_2PS)_2$, the calculated orientations of the phosphorus chemical shift tensors in $HN(Ph_2PSe)_2$ (Fig. 3*e*) place δ_{11} perpendicular to the local Se-P-N plane, δ_{33} approximately along the P-Se vector, and δ_{22} within the Se-P-N plane perpendicular to P-Se. This orientation is similar to that found for tris-organophosphine selenides (89).

The structure of $HN(^{i}Pr_2PSe)_2$ more closely resembles that of $HN(^{i}Pr_2PS)_2$ with an 80° Se-P···P-Se torsion angle and a P-N-P angle of 131° (31). However, similar to the structure of $HN(^{1}Pr_{2}PO)_{2}$, the selenium analogue was refined where the location of one methyl carbon on one isopropyl group contained two 50% occupancy locations (31). The isotropic chemical shifts and ${}^{1}J({}^{77}\text{Se}, {}^{31}\text{P})_{iso}$ values extracted (Table 1) from the simulation of the solid-state ³¹P NMR spectrum of HN(ⁱPr₂PSe)₂ (Fig. 6b) are in good agreement with those from a chloroform solution ³¹P NMR study, 89.5 ppm and (-)757 Hz (31). Similar to the solid-state ³¹P NMR spectrum of $HN(^{i}Pr_{2}PO)_{2}$ (Fig. 2b), no evidence for the disorder in the methyl group was detected in the corresponding spectrum for iminobis(diisopropylphosphine selenide). As with the phosphorus chemical shift tensors of $HN(Ph_2PE)_2$ (E = S, Se), the two tensors for $HN(^{1}Pr_2PSe)_2$ are comparable to those found for HN(¹Pr₂PS)₂ (Table 1). The isotropic phosphorus chemical shifts of the mixed chalcogen compound ⁱPr₂P(S)NHP(Se)ⁱPr₂ from a chloroform solution ³¹P NMR study are also very similar at 89.2 and 92.1ppm (31).

Phosphorus chemical shift tensors were calculated for both of the 50% occupancy structures (31), labeled "a" and "b" in Table 1. The scalar relativistic calculated phosphorus **Fig. 6.** (*a*) RACP MAS ³¹P NMR spectrum (lower trace) for $HN(Ph_2PSe)_2$ and its simulation (upper trace). Experimental conditions: 11.75 T, 64 scans, MAS at 3.0 kHz, 10 Hz of line broadening, 3.0 ms contact time, and 900 s recycle delay. (*b*) RACP MAS ³¹P NMR spectrum (lower trace) for $HN(^{i}Pr_2PSe)_2$ and its simulation (upper trace). Experimental conditions: 11.75 T, 128 scans, MAS at 3.0 kHz, 10 Hz of line broadening, 3.0 ms contact time, and 18 s recycle delay. The isotropic peaks are marked with an asterisk (*).



chemical shift tensors for HN(ⁱPr₂PSe)₂, as with those for HN(Ph₂PSe)₂, overestimate the experimental values. Analogous to those for HN(ⁱPr₂PO)₂, the calculated phosphorus chemical shift tensors for HN(ⁱPr₂PSe)₂ structures "a" and "b" are nearly identical and suggest that evidence for the disorder is unlikely to come from the solid-state ³¹P NMR spectrum. As with the calculated orientations of the phosphorus chemical shift tensors in HN(ⁱPr₂PO)₂, all four tensors for iminobis(diisopropylphosphine selenide) are identical, as shown in Fig. *3f*. They are all oriented similarly to those of HN(ⁱPr₂PS)₂ with δ_{33} near the P-Se vector, δ_{11} perpendicular to the local Se-P-N plane, and δ_{22} within the Se-P-N plane perpendicular to the P-Se vector.

Solid-state ⁷⁷Se NMR

The solid-state ⁷⁷Se NMR spectrum for HN(Ph₂PSe)₂ is given in Fig. 7*a* and the ⁷⁷Se NMR parameters extracted from its simulation are reported in Table 2. The values of ${}^{1}J({}^{77}Se, {}^{31}P)_{iso}$ obtained are in agreement with those from solution ${}^{31}P$ NMR (10) and with our solid-state ${}^{31}P$ NMR values (Table 1) above. Similar to the large difference in isotropic phosphorus chemical shifts observed for Ph₂P(OH)NP(O)Ph₂, there is a significant difference between the two values of $\delta_{iso}(Se)$ in HN(Ph₂PSe)₂. The spans of the selenium chemical shift tensors are both larger than any of the phosphorus chemical shift tensors, which is consistent with the less symmetric environment of selenium in the iminobis(diorganophosphine chalcogenide) systems and the larger chemical shift range of selenium with respect to that of phosphorus (92, 93).

The dimer structure of HN(Ph₂PSe)₂ (Fig. 4) was used to calculate the selenium chemical shift tensors. The computed principal components are in good agreement with the experimental values, particularly in the difference in shielding between the two chemical shift tensors. The calculations indicate that the selenium that participates in hydrogen bonding between the two HN(Ph₂PSe)₂ molecules is less shielded than the selenium that is not involved in hydrogen bonding. The calculated orientations of the two selenium chemical shift tensors are also different (Fig. 8a). For the selenium involved in hydrogen bonding between the dimers, δ_{33} is nearly parallel to the Se-P vector, δ_{11} is perpendicular to the local Se-P-N plane, and δ_{22} is within the Se-P-N plane perpendicular to Se-P. The selenium that is not involved in hydrogen bonding possesses a chemical shift tensor that orients δ_{22} approximately along Se-P, with δ_{11} perpendicular to the local Se-P-N plane, and δ_{33} within the Se-P-N plane perpendicular to Se-P.

The ⁷⁷Se NMR parameters obtained from the solid-state ⁷⁷Se NMR spectrum for $HN(^{i}Pr_2PSe)_2$ (Fig. 7*b*) are given in Table 2. The two $^{1}J(^{77}Se,^{31}P)_{iso}$ obtained are in good agreement with the reported values from solution (31) and solid-

Fig. 7. (*a*) RACP MAS ⁷⁷Se NMR spectrum (lower trace) for $HN(Ph_2PSe)_2$ and its simulation (upper trace). Experimental conditions: 11.75 T, 384 scans, MAS at 3.0 kHz, 50 Hz of line broadening, 10.0 ms contact time, and 840 s recycle delay. (*b*) RACP MAS ⁷⁷Se NMR spectrum (lower trace) for $HN(^{i}Pr_2PSe)_2$ and its simulation (upper trace). Experimental conditions: 11.75 T, 5288 scans, MAS at 6.0 kHz, 50 Hz of line broadening, and 14 s recycle delay. The isotropic peaks are marked with an asterisk (*).



state (above) ³¹P NMR. Unlike those for HN(Ph₂PSe)₂, the two isotropic selenium chemical shifts for iminobis-(diisopropylphosphine selenide) are more shielded and significantly closer together. In contrast to the solid-state ³¹P NMR spectra for HN(ⁱPr₂PE)₂ (E = O, Se), the solid-state ⁷⁷Se NMR spectrum for HN(ⁱPr₂PSe)₂ appears to be sensitive to the disorder of the methyl group in the structure (31). Figure 9 displays the isotropic region of the solid-state ⁷⁷Se NMR spectra for HN(R_2 PSe)₂ (R = Ph, ⁱPr), where one of the two *J*-coupled isotropic peaks for HN(ⁱPr₂PSe)₂ is visibly broader than the other.

The two calculated selenium chemical shift tensors for each of the two 50% occupancy structures also suggest that the impact of the disorder of the methyl group should be more pronounced in the solid-state ⁷⁷Se NMR spectrum; however, the calculations indicate that both selenium environments should be influenced by the disorder. The calculations predict that the selenium environment that is furthest from the methyl group should be affected more than the proximal selenium. The calculated orientations of the selenium chemical shift tensors (Fig. 8b) are identical for structures "a" and "b", yet distinct. The chemical shift tensor for the selenium distal to the methyl disorder is oriented such that δ_{33} is nearly along the Se-P vector, δ_{11} is perpendicular to the local Se-P-N plane, while δ_{22} lies within the Se-P-N plane perpendicular to Se-P. The selenium nearest the methyl disorder possesses a calculated chemical shift tensor that also places δ_{11} approximately perpendicular to the local

Se-P-N plane; however, the P-Se vector nearly bisects the δ_{22} -Se- δ_{33} angle within the Se-P-N plane.

Iminobis(diorganophosphine selenide) vs. diselenoimidodiphosphinato complexes

Upon comparison with the phosphorus and selenium chemical shift tensors of the $M[N(^{i}Pr_2PSe)_2]_2$ complexes previously investigated (59, 60), there are some consistent changes in the calculated orientations of the phosphorus and selenium chemical shift tensors of HN(ⁱPr₂PSe)₂ upon deprotonation and complexation with a cationic center. The phosphorus chemical shift tensors in the diselenoimidodiphosphinato complexes are all oriented similarly, with δ_{33} nearly parallel to the P-N bond vector, δ_{11} perpendicular to the local Se-P-N vector, and δ_{22} within the Se-P-N plane perpendicular to the P-N vector (59, 60). This is in contrast to the majority of the phosphorus chemical shift tensors where δ_{33} is nearly parallel to the P-E vector, and most closely resembles the orientation of the phosphorus chemical shift tensor for the P-OH environment in Ph₂P(OH)NP(O)Ph₂. The change in the orientation of the selenium chemical shift tensor upon complexation is not quite as predictable. When $[N(^{i}Pr_{2}PSe)_{2}]^{-}$ is coordinated with a Group 10 (Pd or Pt) or 12 (Zn, Cd or Hg) metal center, the orientation of the selenium chemical shift tensor remains essentially identical to that found in $HN(^{i}Pr_{2}PSe)_{2}$ with δ_{33} nearly parallel to the P-Se vector, δ_{11} perpendicular to the local Se-P-N plane, and δ_{22} perpendicular to the P-Se vector (59, 60). However, when

		δ_{iso}	δ_{11}	δ ₂₂	δ_{33}	Ω		${}^{1}J(\text{Se},\text{P})_{\text{iso}}^{a}$
R		(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	κ	(Hz)
Ph	(Exptl.)	-184	-41	-219	-291	250	-0.42	-800
		-101	79	-146	-236	317	-0.43	-740
	(Calcd.)	-201	-30	-248	-325	295	-0.48	
		-115	97	-133	-331	408	-0.13	
ⁱ Pr	(Exptl.)	-355	-135	-419	-511	376	-0.51	-760
		-322	-179	-352	-435	256	-0.36	-720
	(Calcd. a)	-495	-140	-609	-735	595	-0.58	
		-436	-222	-512	-575	353	-0.64	
	(Calcd. b)	-518	-307	-608	-638	331	-0.82	
		-465	-265	-528	-603	337	-0.55	

Table 2. Solid-state ⁷⁷Se NMR parameters for $HN(R_2PSe)_2$ (R = Ph, ⁱPr).

^{*a*}For directly bonded selenium-77 and phosphorus-31 spin pairs; signs of ${}^{1}J({}^{77}\text{Se},{}^{31}\text{P})_{iso}$ are known to be negative for numerous analogous systems (95, 96).





coordinated to a Group 16 (Se or Te) center, the orientation of the selenium chemical is significantly different in that δ_{33} is directed nearly parallel to the Se-Se or Te-Se vector, δ_{11} nearly parallel to the Se-P vector, and δ_{22} perpendicular to the Se-Se-P/Te-Se-P plane (60).

The influence of the *E*-P···P-*E* torsion angle on 31 P and 77 Se NMR parameters

From Table 1, it is clear that the phosphorus environments in the HN(Ph₂PE)₂ (E = O, S, Se) systems, which all possess **Fig. 9.** Isotropic region of the ⁷⁷Se NMR spectrum for (*a*) $HN(Ph_2PSe)_2$ and (*b*) $HN(^iPr_2PSe)_2$ (lower traces) and their simulations (upper traces).



anti E-P...P-E torsion angles, are all more shielded than their $HN(^{i}Pr_2PE)_2$ counterparts that have *gauche* torsion angles. Conversely, in Table 2 the selenium nuclei of HN(Ph₂PSe)₂ are both less shielded than those of HN(ⁱPr₂PSe)₂. The consistent differences observed in the isotropic chemical shifts between the phenyl and isopropyl variants of $HN(R_2PE)_2$ (E = O, S, Se) are likely to arise from a combination of the electronic effects of the chosen R group and the common steric differences between the structures. To probe the nature of these differences, nuclear magnetic shielding calculations were performed on a truncated system, HN(Me₂PSe)₂. The HN(Me₂PSe)₂ structure was achieved by replacing the isopropyl groups of one of the two 50% occupancy structures of HN(ⁱPr₂PSe)₂ with methyl groups. Figure 10 displays the effect of rotation about the E-P···P-E torsion angle from an eclipsed orientation of 0° to a *trans* conformation of 180° in 15° increments. For both the computed phosphorus



Fig. 10. Effect of rotation about the *E*-P···P-*E* torsion angle for HN(Me₂PSe)₂ on (*a*) $\delta_{iso}(^{31}P)$ and (*b*) $\delta_{iso}(^{77}Se)$.

and selenium chemical shifts, the calculations predict the opposite effect to what was observed experimentally; that is, the anti structures of HN(Me₂PSe)₂ possess less shielded phosphorus and more shielded selenium environments than any of the gauche structures. The outcome of these calculations suggest that the electronic effect of the chosen R group dominates the impact of the E-P···P-E torsion angle, which is supported by the solution ³¹P NMR reported for the mixed alkyl system Ph₂P(S)NHP(S)ⁱPr₂ (94). The isotropic phosphorus chemical shifts of Ph₂P(S)NHP(S)ⁱPr₂, 100.0 and 51.5 ppm, display an even larger separation than those found between the phenyl and isopropyl compounds studied herein, $HN(R_2PE)_2$ (E = O, S, Se) (Table 1). Rotation of the S-P···P-S angle in solution may effectively average the conformational impact on the phosphorus chemical shift present in the solid state. Thus, the electronic effect of Rgroups on the phosphorus shielding is not opposed to the same extent by the conformation of the EPNPE backbone and the isotropic phosphorus chemical shifts are found to be further apart.

Conclusions

The iminobis(diorganophosphine chalcogenide) systems, HN(R_2PE)₂ (E = O, S, Se; R = Ph, ⁱPr), have been investigated by solid-state ³¹P and ⁷⁷Se NMR spectroscopy and DFT computational chemistry. The phosphorus environments of the HN(Ph₂PE)₂ (E = O, S, Se) systems are all more shielded, with larger spans and smaller skews than the corresponding $HN(^{i}Pr_{2}PE)_{2}$ systems. Aside from Ph₂P(OH)NP(O)Ph₂, the calculated orientations of the two phosphorus chemical shift tensors in each $HN(R_2PE)_2$ system are essentially identical with δ_{33} oriented nearly parallel to the P-E vector as expected from tris-organophosphine chalcogenide systems (89). The experimental and theoretical selenium chemical shift tensors in HN(Ph₂PSe)₂ were found to be sensitive to the presence of hydrogen bonding in its solid state dimer structure, while those of HN(¹Pr₂PSe)₂ were susceptible to the disorder found in its structure. The impact of the conformation of the EPNPE backbone via the $E-P \cdots P-E$ torsion angle was studied by DFT nuclear magnetic shielding calculations on a truncated system, HN(Me₂PSe)₂. The steric impact of the Se-P···P-Se angle on the computed phosphorus and selenium isotropic chemical shifts was found to have the opposite effect to what was observed experimentally, suggesting that the choice of phenyl or isopropyl group is more important than the conformational contributions to the phosphorus and selenium shielding in these systems.

Finally, this study further demonstrates the feasibility of the measurement of phosphorus and selenium chemical shift tensors for these important ligands. Furthermore, the sensitivity of these tensors to subtle structural effects is apparent.

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