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Interaction of 1,3,2,4-Benzodithiadiazines and Their 1-Se Congeners with Ph_3P and Some Properties of the Iminophosphorane Products

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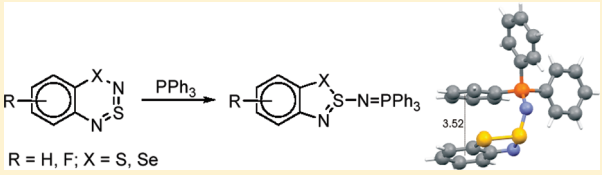
Supporting Information

ABSTRACT: Interaction between Ph_3P and 1,3,2,4-benzodithiadiazine (**1**); its 6,7-difluoro (**2**), 5,6,8-trifluoro (**3**) and 5,6,7,8-tetrafluoro (**4**) derivatives; and 5,6,8-trifluoro-3,1,2,4-benzothiaselenadiazine (**5**) proceeded via a 1:1 condensation to give $Ph_3P{=}N{-}R$ iminophosphoranes (**1a**−**5a**, R = corresponding 1,2,3-benzodichalcogenazol-2-yls), which are inaccessible by general approaches based on the Staudinger and Kirsanov reactions. In contrast, neither Ph_3As nor Ph_3Sb reacted with **1** and **4**. Molecular structures of **1a**−**5a** and **5** were confirmed by X-ray diffraction (XRD). The crystals formed by chiral molecules of **2a**−**5a** were racemic, whereas the crystal of **1a** was formed by a single enantiomer. In all of the $Ph_3P{=}N{-}R$ derivatives, one of the Ph rings is oriented face-to-face to the hetero ring, R. Upon heating to ∼120 °C in squalane (**1a**, **3a**, **4a**) or dissolving in chloroform at ambient temperatures (**1a**, **2a**, **4a**), the $Ph_3P{=}N{-}R$ derivatives generated the 1,2,3-benzodithiazolyls (**1b**−**4b**, respectively) whose identity was confirmed by electron paramagnetic resonance (EPR). 2,1,3-Benzothiaselenazolyls **5b** and **6b** were detected by EPR as the main paramagnetic products of solution thermolysis of **5** and its 5,6,7,8-tetrafluoro congener (**6**), respectively. Passing a chloroform solution of **4a** through silica column unexpectedly gave 5-6-6-6 tetracyclic (**9**) and 6-10-6 tricyclic (**10**) sulfur−nitrogen compounds, which were characterized by XRD.



INTRODUCTION

1,3,2,4-Benzodithiadiazines are 12π-electron, i.e., formally antiaromatic, compounds featuring high and varied heteroatom reactivity of fundamental interest.[1,2] In particular, polyfluorinated 1,3,2,4-benzodithiadiazine (Chart 1, **4**) oxidatively iminates Ph_3P to give $Ph_3P{=}N{-}R$ iminophosphorane (Chart 1, **4a**; R = 4,5,6,7-tetrafluoro-1,2,3-benzodithiazol-2-yl).[3] This reaction is the first example of imination of phosphines with π-heterocycles. As relevant reactions, those between Ar_3X (X = P, As) and inorganic cages S_4N_4 and RCS_3N_5 affording $Ar_3X{=}N{-}R'$ derivatives (R' = S_3N_3 and RCS_3N_4, respectively) can only be mentioned;[4,5] the reaction of S_4N_4 is solvent-dependent, and in MeCN instead of benzene, S_4N_4 and Ph_3P produce $1,5\text{-}(Ph_3P{=}N{-})_2S_4N_4$.[4]

To elucidate the scope of the aforementioned unusual imination, in the present work, an interaction between Ph_3P and 1,3,2,4-benzodithiadiazine (**1**), its 6,7-difluoro (**2**) and 5,6,8-trifluoro (**3**) derivatives, and 5,6,8-trifluoro-3,1,2,4-benzothiaselenadiazine (**5**) (Chart 1) was studied. In all cases, corresponding $Ph_3P{=}N{-}R$ iminophosphoranes were obtained (Chart 1; **1a**−**3a**, **5a**). At the same time, it was found that neither Ph_3As nor Ph_3Sb react with **1** and **4**.

The synthesized $Ph_3P{=}N{-}R$ iminophosphoranes are inaccessible by the standard approaches to this class of compounds based, in particular, on the Staudinger reaction or on the Kirsanov reaction.[6] Their molecules are chiral. Importantly, these iminophosphoranes revealed interesting heteroatom reactivity. It was found that they readily form 1,2,3-benzodithiazolyls R. (Herz radicals) and other uncommon heterocyclic derivatives such as 5-6-6-6 tetracyclic and 6-10-6 tricyclic sulfur−nitrogen compounds (Chart 1, **9** and **10**). Currently, Herz radicals[7] and their heavier chalcogen congeners[8] attract much attention as building blocks in the design and synthesis of molecular magnets and conductors.[9]

EXPERIMENTAL AND COMPUTATIONAL DETAILS

General Procedures. ^1H, ^{13}C, ^{14}N, ^{15}N, ^{29}Si, ^{31}P, and ^{77}Se NMR spectra were measured using $CDCl_3$ solutions on a Bruker DRX-500 machine operating at frequencies of 500.13, 125.76, 36.13, 50.68, 99.36, 202.46, and 95.38 MHz, respectively, and ^{19}F NMR spectra on Bruker AC-200 and Bruker AV-300 instruments at frequencies of 188.28 and 282.4 MHz, respectively. The standards were TMS (^1H, ^{13}C, ^{29}Si), NH_3 (liq.; ^{14}N, ^{15}N), C_6F_6 (^{19}F; δ −162.2 with respect to $CFCl_3$), H_3PO_4 (^{31}P), and Me_2Se (^{77}Se). UV−vis spectra were recorded on a Hewlett-Packard 8453 spectrophotometer. IR spectra were taken on a Bruker

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Chart 1

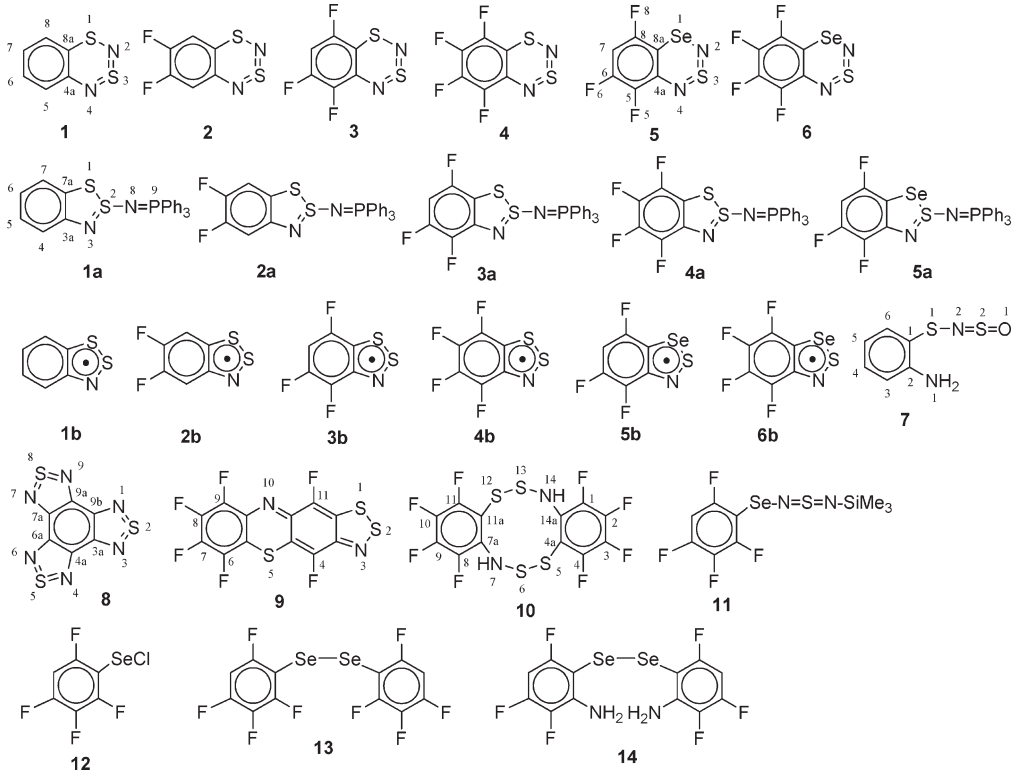

Table 1. Spectral Characterization of Compounds[a]

	NMR, δ				
compound	^{1}H	^{13}C	^{19}F	^{31}P	^{77}Se
1a	7.57, 7.52, 7.39, 7.14, 7.02, 6.90, 6.58	156.6, 132.6, 132.4, 128.4, 126.7, 125.0, 124.9, 119.7, 116.9, 115.3		17.2	
2a	7.60−7.53 (9H), 7.42 (6H), 7.33 (3H, C_6H_6), 6.78 (1H), 6.63 (1H)	153.3, 148.4, 142.6, 132.7,[b] 128.6, 128.1 (C_6H_6), 126.5, 119.8, 107.5, 102.6	18.5, 9.8	19.1	
3a	7.62−7.54 (9H), 7.42 (6H), 6.06 (1H)	150.6, 148.6, 148.5, 137.2, 132.9, 132.8, 128.7, 126.1, 110.1, 92.2	51.9, 19.6, 2.6	20.9	
5[c]	6.55	152.0, 151.2, 138.8, 126.5, 107.2, 90.8	46.8, 30.4, 10.4		758
5a	7.65 (6H), 7.55 (3H), 7.41 (6H), 6.08 (1H)	152.7, 150.5, 149.1, 137.7, 132.9,[b] 128.6, 125.9, 111.0, 92.1	60.1, 20.0, 4.7	21.8	894
7[c]	7.39 (1H), 7.26 (1), 6.77 (2H), 4.24 (2H)	147.2, 133.5, 132.8, 118.8, 116.1, 116.0			
10	5.28		33.8, 15.9, 12.0, 3.2		
11[c,d]	6.91	156.5, 152.6, 150.9, 137.3, 104.6, 101.0, 1.3	59.8, 43.7, 34.0, −1.0		806
12	6.96	158.5, 155.2, 152.7, 138.1, 105.5, 102.3	63.8, 47.6, 38.7, 0.4		805
13	6.85		60.5, 44.7, 34.5, −0.2		360
14[c]	6.28 (2H), 4.62 (4H)	159.1, 151.9, 140.0, 135.3, 98.2, 92.9	60.9, 30.5, 0.0		318

[a] UV−vis, λ_{max}, nm (log ε): **1a** (CH_3CN), 338 (4.65), 307 (3.55), 226 (3.45); **2a** (CCl_4), 317 (3.59); **3a** ($CHCl_3$), 243 (4.53); **5** (heptane), 588 (2.60), 357 (3.43), 265 (4.12); **5a** ($CHCl_3$), 243 (4.37). [b] Two overlapping doublets. [c] δ^{15}N: **5**, 251.0, 241.6. δ^{14}N: **7**, 343, 57; **11**, 325, 302; **14**, 56. [d] δ^{29}Si: 4.6.

Vector 22 spectrometer and Raman spectra on a Bruker IFS 66 spectrometer equipped with Nd/YAG laser with an excitation line of 1064 nm. The NMR and UV−vis data of newly synthesized compounds are given in Table 1.

High-resolution mass-spectra (IE, 70 eV) were obtained using Finnigan MAT MS-8200 and Thermo DFS mass spectrometers. The GLC-MS determinations were performed with a Hewlett-Packard G1800A GDC apparatus.

All utilized solvents were distilled under argon over common drying agents. CsF was calcinated directly before use.

EPR Measurements. EPR spectra of Herz radicals produced in $CHCl_3$ solutions at ambient temperature were acquired using a Bruker ESP-300 spectrometer (MW power, 265 mW; modulation frequency, 100 kHz; and modulation amplitude, 0.005 mT). Simulations of the experimental EPR spectra were performed with the *Winsim 2002*[10] program using the *Simplex* algorithm for many-parametric optimization of hfc values and line widths. The accuracy of the *a* calculation was ±0.001 mT. The *g* values were measured using a MnO standard with an accuracy of ±0.00002. EPR spectra of Herz radicals produced by thermolysis in squalane solutions were acquired using a Bruker EMX

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Table 2. Crystal Data and Structure Refinement for Compounds

compound	1a	2a	3a
empirical formula	$C_{24}H_{19}N_2PS_2$	$C_{24}H_{17}F_2N_2PS_2+ 1/2(C_6H_6)$	$C_{24}H_{16}F_3N_2PS_2$
fw	430.50	505.54	484.50
temperature [K]	293(2)	293(2)	150
wavelength [Å]	0.71073	0.71073	0.71073
cryst syst	monoclinic	monoclinic	monoclinic
space group	*Cc*	$P2_1/n$	*C*2/*c*
unit cell dimensions			
a [Å]	9.715(5)	13.6280(10)	21.8034(12)
b [Å]	16.042(9)	9.2143(7)	9.0335(5)
c [Å]	13.639(7)	19.3762(13)	22.1020(14)
β [deg]	93.66(4)	96.730(5)	98.383(3)
vol [Å ^{3}]	2121.3(18)	2416.4(3)	4306.7(4)
Z	4	4	8
density (calcd) [mg m^{-3}]	1.348	1.390	1.495
abs. coeff [mm^{-1}]	0.340	0.321	0.363
cryst size [mm^3]	0.50 × 0.30 × 0.20	0.50 × 0.44 × 0.26	0.05 × 0.20 × 0.90
reflns collected	2070	5789	21693
independent reflns	1991 ($R_{(int.)}$ = 0.080)	5545 ($R_{(int.)}$ = 0.018)	6258 ($R_{(int.)}$ = 0.059)
final R indices [$I > 2\sigma(I)$]	R1 = 0.0500, wR2 = 0.1020	R1 = 0.0419, wR2 = 0.1036	R1 = 0.0430, wR2 = 0.1076
R indices (all data)	R1 = 0.0801, wR2 = 0.1169	R1 = 0.0604, wR2 = 0.1145	R1 = 0.0570, wR2 = 0.1190

compound	5a	5	7
empirical formula	$C_{24}H_{16}F_3N_2PSSe$	$C_6HF_3N_2SSe$	$C_6H_6N_2OS_2$
fw	531.39	269.11	186.25
temperature [K]	173(2)	150(2)	203(2)
wavelength [Å]	0.71073	0.71073	0.71073
cryst syst	monoclinic	orthorhombic	monoclinic
space group	*C*2/*c*	$Pca2_1$	$P2_1$
unit cell dimensions			
a [Å]	22.3041(15)	25.520(3)	9.106(3)
b [Å]	9.0226(6)	3.8358(5)	4.7383(14)
c [Å]	21.9604(15)	31.309(4)	10.307(3)
β [deg]	98.950(3)		115.677(15)
vol [Å ^{3}]	4365.5(5)	3064.8(7)	400.78(19)
Z	8	16	2
density (calcd) [mg m^{-3}]	1.617	2.333	1.543
abs. coeff [mm^{-1}]	1.930	5.171	0.603
cryst size [mm^3]	0.10 × 0.30 × 0.30	0.38 × 0.06 × 0.04	0.98 × 0.20 × 0.04
reflns collected	21281	27424	1384
independent reflns	6224 ($R_{(int.)}$ = 0.051)	7988 ($R_{(int.)}$ = 0.115)	1312 ($R_{(int)}$ = 0.033)
final R indices [$I > 2\sigma(I)$]	R1 = 0.0364, wR2 = 0.0934	R1 = 0.0430, wR2 = 0.0923	R1 = 0.0437,wR2 = 0.1010
R indices (all data)	R1 = 0.0459, wR2 = 0.0992	R1 = 0.0698, wR2 = 0.1091	R1 = 0.0573,wR2 = 0.1132

compound	8	10
empirical formula	$C_6N_6S_3$	$C_{12}H_2F_8N_2S_4$
fw	252.30	454.40
temp [K]	173(2)	293(2)
wavelength [Å]	0.71073	0.71073
cryst syst	orthorhombic	monoclinic
space group	$Pmn2_1$	$P2_1/n$
unit cell dimensions		
a [Å]	14.2167(8)	12.166(3)
b [Å]	3.6810(2)	5.389(1)
c [Å]	7.8017(4)	12.325(3)

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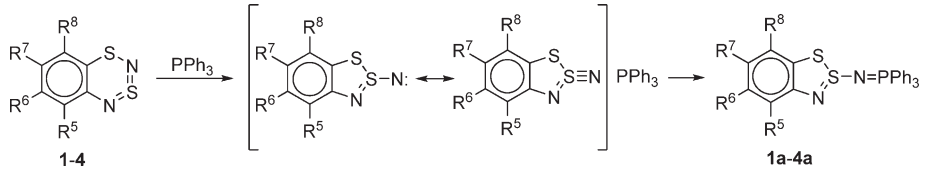
Table 2. Continued

compound	8	10
β [deg]		111.33(1)
vol [Å ^{3}]	408.28(4)	752.7(3)
Z	2	2
density (calcd.) [Mg m^{-3}]	2.052	2.005
abs. coeff [mm^{-1}]	0.873	0.722
cryst size [mm^3]	0.01 × 0.03 × 0.30	0.06 × 0.16 × 1.10
reflns collected	5418	1799
independent reflns	1179 ($R_{(int.)}$ = 0.049)	1722 ($R_{(int.)}$ = 0.036)
final R indices [$I > 2\sigma(I)$]	R1 = 0.0256, wR2 = 0.0600	R1 = 0.0401, wR2 = 0.1024
R indices (all data)	R1 = 0.0280, wR2 = 0.0608	R1 = 0.0580, wR2 = 0.1122

Scheme 1



1-4 1a-4a

1, **1a**, $R^5 = R^6 = R^7 = R^8 = H$;
2, **2a**, $R^5 = R^8 = H$; $R^6 = R^7 = F$;
3, **3a**, $R^7 = H$; $R^5 = R^6 = R^8 = F$;
4, **4a**, $R^5 = R^6 = R^7 = R^8 = F$

spectrometer (MW power 2.07 mW, modulation frequency 100 kHz, and modulation amplitude 0.01 mT). The spectra integration and simulation were performed with the *WIN-EPR* and *Winsim*[10] programs. The accuracy of the *a* calculation was ±0.001 mT. The *g* values were measured using a DPPH standard with an accuracy of ±0.0001.

Crystallographic Analysis. The XRD data (Table 2) for **1a** and **7** were collected on a Syntex $P2_1$ diffractometer, for **2a** and **10** on a Bruker P4 diffractometer, and for **3a**, **5**, **5a**, and **8** on a Bruker Kappa Apex II diffractometer, using Mo Kα (λ = 0.71073 Å) radiation with a graphite monochromator. The structures were solved by direct methods using the SHELXS-97 program[11] and refined by the least-squares method in the full-matrix anisotropic (isotropic for H atoms) approximation using the SHELXL-97 program.[11] The H atom positions were located from difference Fourier maps. The obtained structures were analyzed for exposing shortened contacts between nonbonded atoms with the PLATON[12] and MERCURY[13] programs.

CCDC-769830 (for **1a**), -769831 (for **2a**), -798764 (for **3a**), -769833 (for **5**), -769832 (for **5a**), -769834 (for **7**), -769835 (for **8**), and -769836 (for **10**) contain supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Quantum Chemical Calculations. The DFT/UB3LYP/6-31G-(d) calculations on Herz radicals were performed with the GAMESS program.[14] It should be noted that other tried methods (PBE/6-31G(d), B3LYP/cc-pVDZ and PBE/cc-pVDZ) had worse performance.

Preparations: Improved Synthesis of Compound 4a. At −70 °C and under argon, solutions of 0.240 g (0.001 mol) of **4**[15] and 0.262 g (0.001 mol) of Ph_3P, each in 5 mL of toluene, were simultaneously and dropwise added under stirring, over a period of 0.5 h, to 5 mL of toluene. After an additional 1 h at −70 °C, the reaction mixture was warmed up to 20 °C, and 15 mL of hexane was added to produce a two-layered system. The system was kept at 5 °C until mutual diffusion of solvents ceased. The crystalline precipitate was filtered off. Compound **4a**[3] was obtained in the form of orange crystals, yield 0.305 g (60%), mp 144−145 °C.

Compounds 1a, 2a, 3a, and 5a. At −70 °C and under argon, a solution of 0.262 g (0.001 mol) of Ph_3P in 5 mL of toluene was added, dropwise and over a period of 0.5 h, to a stirred solution of 0.001 mol of **1**,[1] **2**,[16] **3**,[16] or **5** (this work) in 5 mL of the same solvent. After an additional 1 h at −70 °C, the reaction mixture was warmed up to 20 °C, and the solvent was distilled off under reduced pressure. The residue was dissolved in 3 mL of benzene, and 3 mL of hexane was added to produce a two-layered system. The system was kept at 5 °C until mutual diffusion of solvents ceased. The crystalline precipitate was filtered off. Compounds **1a**, **2a** (as **2a**·0.5C_6H_6 solvate), **3a**, and **5a** were obtained in the form of orange crystals. **1a**: yield, 0.070 g (16%); mp, 124−125 °C. **2a**·0.5C_6H: yield, 0.100 g (20%); mp, 122−123 °C (loss of benzene at 68−70 °C). **3a**: yield, 0.254 g (52%); mp, 145−147 °C. **5a**: yield, 0.380 g (72%); mp, 164−166 °C. MS, *m*/*z*, or elemental analyses: **1a**, found 430.0733 (calculated for $C_{24}H_{19}N_2PS_2$, 430.0727); **2a**, found 466.0538 (calculated for $C_{24}H_{17}F_2N_2PS_2$, 466.0538); **3a**, found (calculated for $C_{24}H_{16}F_3N_2PS_2$) C, 59.54 (59.50); H, 3.32 (3.33); N, 5.86 (5.78); F, 11.77 (11.76); P, 6.32 (6.39); S, 13.24 (13.25). **5a**, found 529.9887 (calculated for $C_{24}H_{16}F_3N_2P^{78}Se$, 529.9888).

Compound 5 via Compounds 11−13.

a. At −60 °C and under argon, 50 mL of a 2.0 M solution of *n*-BuLi in hexane was added dropwise over a period of 0.5 h to a stirred solution of 15.0 g (0.1 mol) of 1,2,3,5-tetrafluorobenzene in 150 mL of Et_2O. After an additional 0.5 h, 7.90 g (0.1 mol) of finely powdered elemental selenium was added in small portions. The reaction mixture was warmed up slowly to 20 °C, and 12.7 g (0.1 mol) of elemental iodine was added. The reaction solution was then washed with aqueous sodium thiosulfate and the organic layer separated and dried over $CaCl_2$. The solvent was distilled off under reduced pressure, and the residue was recrystallized from EtOH. 2,2′,3,3′,4,4′,6,6′-Octafluorodiphenyl diselenide (**13**) was obtained in the form of orange-yellow crystals, yield, 13.68 g (60%); mp, 46−47 °C. MS, *m*/*z*, found: 457.8358 (calculated for

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$C_{12}H_2F_8{}^{80}Se_2$, 457.8359). Found (calculated for $C_{12}H_2F_8Se_2$): C, 31.68 (31.60); H, 0.53 (0.44); F, 33.29 (33.33).

b. A mixture of 4.58 g (0.01 mol) of compound **13** and 2.5 g (1.5 mL, 0.02 mol) of SO_2Cl_2 was refluxed for 1 h, the excess of SO_2Cl_2 distilled off, and the residue redistilled under reduced pressure. 2,3,4,6-Tetrafluorophenylselenenyl chloride (**12**) was obtained in the form of dark red oil, yield, 3.90 g (74%); bp, 76−77 °C/3 mm. Found (calculated for C_6HClF_4Se): C, 28.89 (28.35); H, 0.56 (0.38); Cl, 13.02 (13.46); F, 28.79 (28.84).

Table 3. Selected Bond Distances (Å) and Angles (deg) of the Iminophosphoranes

bond/angle	**1a** (X = S)	**2a** (X = S)	**3a** (X = S)	**5a** (X = Se)
X1−S2	2.173(3)	2.1811(8)	2.1933(6)	2.3505(5)
S2−N3	1.582(6)	1.589(2)	1.5980(14)	1.5933(16)
N3−C3a	1.391(9)	1.387(3)	1.367(2)	1.369(2)
C3a−C7a	1.387(10)	1.411(3)	1.412(3)	1.411(3)
C7a−X1	1.753(7)	1.746(2)	1.7419(19)	1.886(2)
S2−N8	1.597(5)	1.597(2)	1.5906(14)	1.5913(16)
N8−P9	1.603(5)	1.607(2)	1.6162(14)	1.6168(16)
C7a−X1−S2	90.7(2)	90.44(7)	90.28(7)	85.70(6)
X1−S2−N3	95.7(2)	96.30(7)	96.65(5)	96.70(6)
S2−N3−C3a	117.7(5)	116.21(14)	116.66(11)	119.37(13)
N3−C3a−C7a	118.5(6)	119.00(17)	120.16(15)	121.67(16)
C3a−C7a−X1	114.9(5)	114.63(14)	114.87(13)	115.46(13)
X1−S2−N8	111.1(2)	107.18(7)	110.15(5)	110.82(6)
N3−S2−N8	113.5(3)	114.92(9)	112.35(7)	111.95(8)
S2−N8−P9	132.8(3)	131.76(11)	129.89(9)	129.53(10)

c. At −30 °C and under argon, a solution of 6.88 g (0.025 mol) of compound **12** in 10 mL of hexane was added dropwise over a period of 1 h to a stirred solution of 5.12 g (0.025 mol) of $(Me_3SiN{=})_2S$[17] in 20 mL of hexane. Over 1 h, the reaction solution was warmed up to 20 °C and then filtered. The solvent was distilled off under reduced pressure. 1-(2,3,4,6-Tetrafluorophenyl)-4-trimethylsilyl-2,4-diaza-1-selena-3-thia-2,3-butadiene (**11**) was obtained in the form of orange oil, yield, 8.57 g (95%). MS, *m/z*, found: 361.9435 (calculated for $C_9H_{10}F_4N_2S^{80}SeSi$, 361.9435). Found (calculated for $C_9H_{10}F_3N_2SSeSi$): C, 29.98 (29.92); H, 3.00 (2.79); F, 20.99 (21.03). Compound **11** was used without further purification since distillation of Ar−Se−N=S=N−$SiMe_3$ derivatives leads to partial decomposition even in high *vacuo*.

d. Under argon, a solution of 1.80 g (0.005 mol) of **11** in 20 mL of MeCN was added for 1 h to a refluxed and stirred suspension of 0.76 g (0.005 mol) of CsF in 80 mL of MeCN. After an additional 1 h, the reaction mixture was cooled to 20 °C and filtered, the solvent distilled off under reduced pressure, and the residue sublimed *in vacuo* and recrystallized from hexane. Compound **5** was obtained in the form of black crystals, yield, 0.67 g (50%); mp, 73−74 °C. MS, *m/z*, found: 269.8978 (calculated for $C_6HF_3N_2S^{80}Se$, 269.8978). IR (KBr), ν (cm^{-1}): 3083 (w), 1602 (s), 1482 (vs), 1413 (vs), 1355 (m), 1268 (w), 1236 (s), 1163 (vs), 1149 (s), 1026 (s), 898 (m), 855 (s), 828 (m), 702 (w), 619 (m), 581 (m), 570 (m), 537 (m), 470 (w). Raman, ν (cm^{-1}): 3085 (w), 1603 (m), 1414 (m), 1356 (vs), 1269 (m), 1230 (m), 1166 (m), 1075 (m), 1041 (s), 1028 (vs), 899 (s), 620 (w), 538 (m), 471 (s), 430 (m), 349 (m), 270 (s), 149 (w).

The residue from sublimation of compound **5** was chromatographed on a silica column with $CHCl_3$ and sublimed *in vacuo*. Compound **8**[18] was obtained in the form of dark needles, yield, 3 mg; mp, 300 °C. The

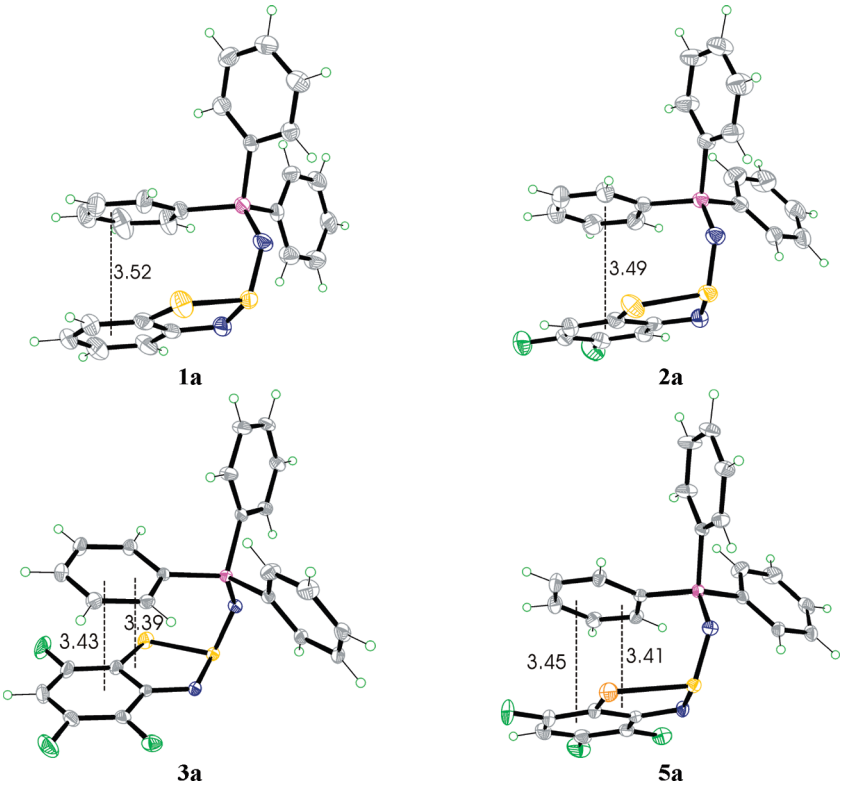

Figure 1. XRD structures of iminophosphoranes **1a**−**3a** and **5a**. Color code: gray, C; light gray, H; green, F; blue, N; brown, P; yellow, S; pink, Se (for **2a** characterized as **2a**·0.5C_6H_6, omitted benzene molecules fill lattice cavities and do not interact with the product). For selected bond distances and angles, see Table 3.

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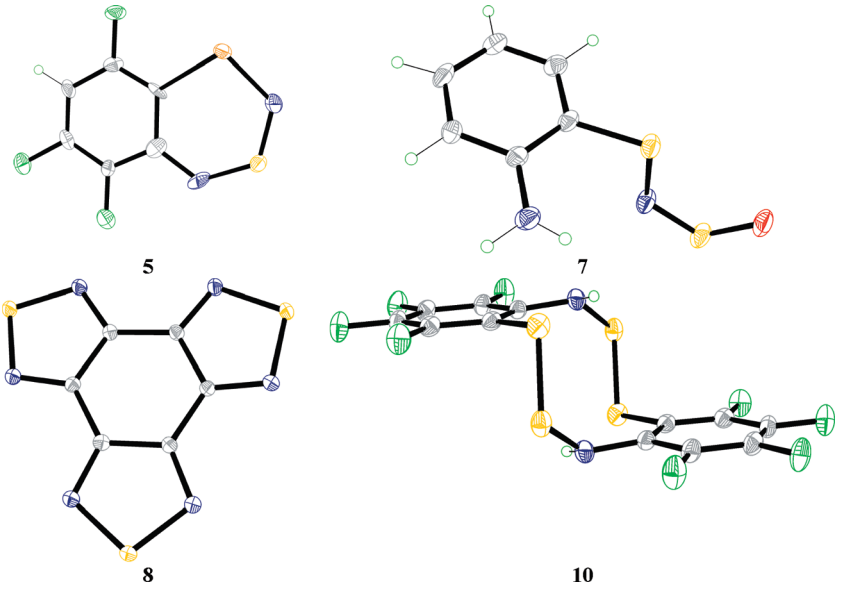


Figure 2. XRD structures of noniminophosphorane products. Color code: gray, C; light gray, H; green, F; blue, N; red, O; yellow, S; pink, Se. Selected bond distances (Å) and angles (deg) (for atom numbering, see Chart 1): **5** (averaged over four crystallographically independent molecules, e.s.d. maximal from refinement or averaging): Se1−N2, 1.851(9); N2−S3, 1.541(7); S3−N4, 1.550(9); N4−C4a, 1.413(15); C4a−C8a, 1.405(11); C8a−Se1, 1.944(9); C8a−Se1−N2, 100.0(3); Se1−N2−S3, 123.9(6); N2−S3−N4, 120.7(6); S3−N4−C4a, 124.4(7); N4−C4a−C8a, 126.0(8); C4a−C8a−Se1, 124.6(7). **7**: C1−S1, 1.772(4); S1−N2, 1.670(4); N2−S2, 1.528(3); S2−O1, 1.450(4); C2−N1, 1.390(5); C1−S1−N2, 99.8(2); S1−N2−S2, 123.9(3); N2−S2−O1, 117.8(2). The S1N2S2O1 fragment is planar within ±0.005 Å; the dihedral angle between S1N2S2O1 and the C1···C6 plane is 77.6(1)°. **8** (molecule symmetry C_s): S1−N2, 1.6321(15); S1−N9, 1.6345(16); S7−N8, 1.6357(14); N2−C2a, 1.338(2); N8−C8a, 1.330(2); N9−C9a, 1.336(2); C8a−C9a, 1.455(2); C2a−C9a, 1.424(2); N2−S1−N9, 100.01(7); S1−N2−C2a, 106.23(12); N6−S7−N8, 99.62(8); S7−N8−C8a, 106.64(10); C9a−N9−S1, 106.19(11). **10** (molecule symmetry C_i): C4a−S5, 1.775(2); S5−S6, 2.0642(11); S6−N7, 1.679(2); C7a−N7, 1.406(3); C4a−S5−S6, 103.10(9); N7−S6−S5, 107.95(9); N7−C7a−C11a, 120.9(2); C7a−N7−S6, 123.96(18).

single crystals suitable for XRD were prepared by slow evaporation of the THF solution.

Generation of Herz Radicals.

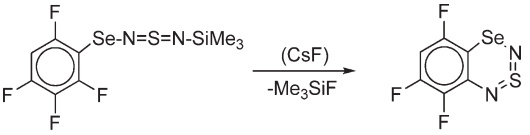
a. At 20 °C, 1 mL of a 1 M solution of compound **1a**, **2a**, or **4a** in $CHCl_3$ was placed into an EPR tube immediately after preparation, and EPR spectra were measured periodically. The concentration of radical **1b**,[19] **2b**, or **4b**[19,20] reached its maximum after ∼24 h and then remained constant for some time, in the case of **2b**, up to ∼2 weeks.

b. A total of 1 mL of a 10^{-3} M squalane solution of compound **1a**, **3a**, or **4a** placed into an EPR tube equipped with a Teflon valve and degassed by three freeze−pump−thaw cycles was heated at 120 °C for 5 min and cooled to 20 °C. The measured EPR spectra were identical to those of radicals **1b**,[19] **3b**, and **4b**,[19,20] respectively.

c. A total of 1 mL of a 10^{-3} M squalane solution of compound **3**,[16] **5**, or **6**[21] placed into an EPR tube equipped with a Teflon valve and degassed by three freeze−pump−thaw cycles was heated at 130−140 °C for 40 min and cooled to 20 °C. The measured EPR spectra revealed radicals **3b**, **5b** (with admixture of **3b**), and **6b** (with admixture of **4b**), respectively.

Hydrolysis of Compound 5. *Compound **14***. The sample of **5** (0.10 g; 0.4 mmol) for the thermolytic experiments was dissolved in Et_2O (5 mL), and the solution formed was added to the solution of H_2O (0.042 g, 2.3 mmol) and 37% aqueous HCl (0.016 g, 0.16 mmol of HCl and 0.56 mmol of H_2O) in Et_2O (10 mL). After 1 day, the blue mixture became yellow. The solution was washed with 3 mL of H_2O and dried with $CaCl_2$. According to GLC-MS, it contained 2,2′-diamino-3,3′,4,4′,6,6′-hexafluorodiphenyl diselenide (**14**; product of hydrolysis of **5**) as the main product and does not contain 2,2′-diamino-3,3′,4,4′,6,6′-hexafluorodiphenyl disulfide (product of hydrolysis of **3**)[22] even at a trace level. The solution was evaporated and the residue sublimed at 140 °C/2 mm and recrystallized from hexane. Compound **14** was obtained in the form of yellow crystals, yield, 74.1 mg (89%); mp, 138−139 °C. MS, *m*/*z*, found (calculated for $C_{12}H_6F_6N_2{}^{80}Se_2$): 451.8767 (451.8766). Found (calculated for $C_{12}H_6F_6N_2Se_2$): C, 31.93 (32.02); H, 1.23 (1.34); N, 6.21 (6.22); F, 25.21 (25.33).

Scheme 2



*Compounds **9** and **10***. A solution of 0.10 g (0.2 mmol) of **4a** in $CHCl_3$ was passed through a silica column (h = 30 cm, d = 1 cm), evaporated under reduced pressure, and the residue was washed with toluene. Compound **10** was obtained in the form of white crystals, yield, 6 mg; mp, 205−207 °C. MS, *m*/*z*, found: 453.8978 (calculated for $C_{12}H_2F_8N_2S_4$, 453.8973). IR (KBr), ν, cm^{-1}: 3268 (m), 1632 (m), 1509 (s), 1482 (s), 1402 (m), 1095 (s), 988 (s), 620 (m).

The toluene solution was evaporated. Compound **9** was obtained in the form of black crystals, yield, 4 mg. The unit cell parameters were identical to previously reported values.[20]

*Compound **7***. A mixture of 0.168 g (1 mmol) of **1** and 0.005 g (1.5×10^{-2} mmol) of Ph_3Sb was exposed to the air. Over 1 min, the deep-blue crystals turned yellow. The product was recrystallized from hexane. Compound **7** was obtained in the form of yellow crystals, yield, 0.119 g (64%); mp, 102−103 °C. MS, *m*/*z*, found: 185.9914 (calculated for $C_6H_6N_2OS_2$, 185.9922).

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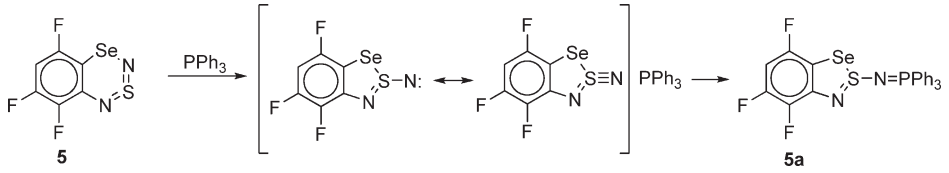
Scheme 3



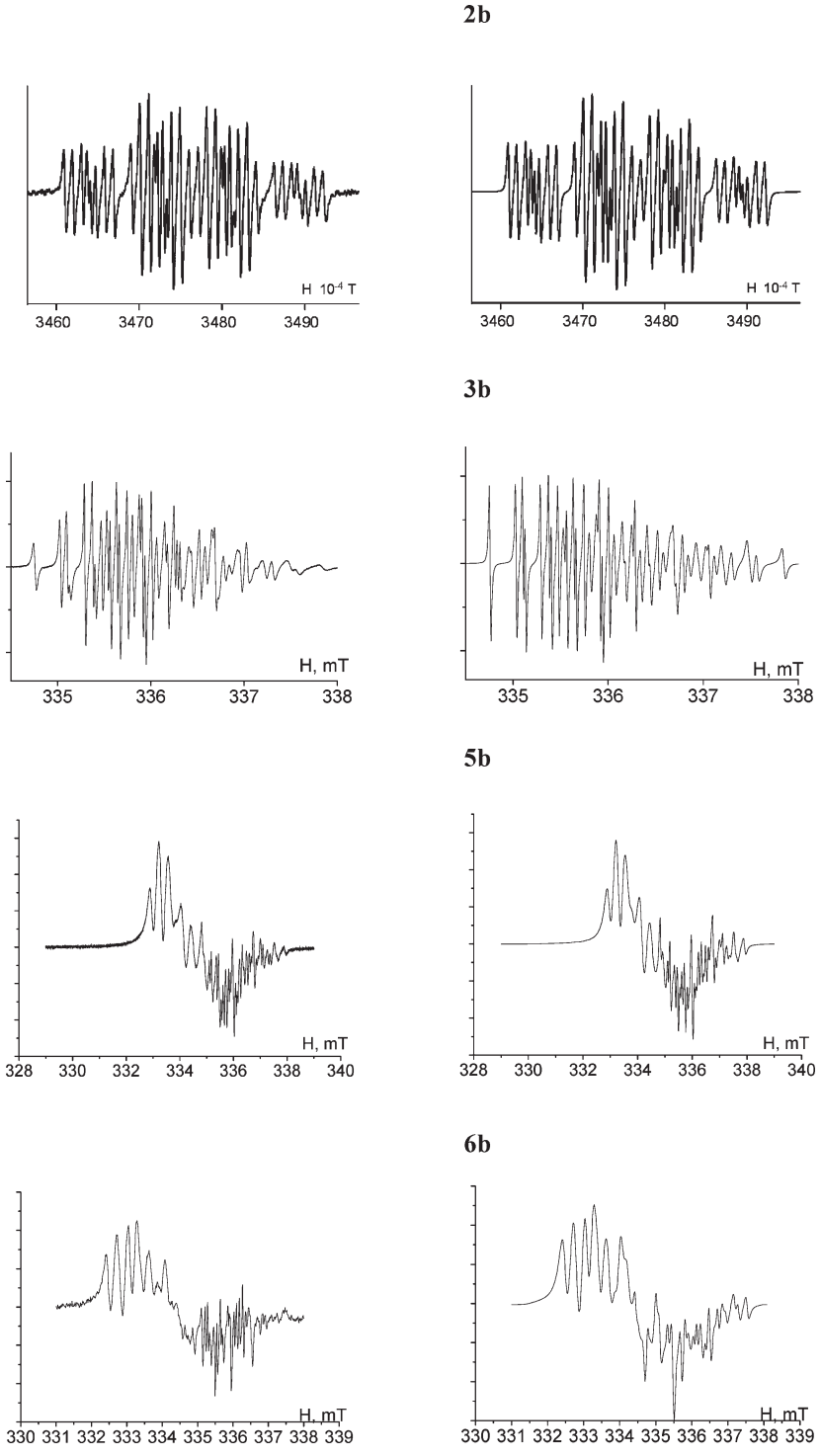


Figure 3. Experimental (left) and simulated (right) EPR spectra of **2b**, **3b**, **5b**, and **6b**.

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Table 4. Experimental (Theoretical from DFT/UB3LYP/6-31G(d) Calculations) hfc Constants ($\times 10^{-4}$ T) and *g* Values of Radicals 2b−6b from Thermolytic Experiments

source/radical(s), a_X	**2**/**2b**	**4**/**4b**[19]	**5**/**5b** (93.8%) and **3b** (6.2%)		**6**/**6b** (93.1%) and **4b** (6.9%)		**3**/**3b**
a_N	8.09 (8.76)	8.2	7.79 (8.00)	7.76 (8.64)	8.00 (8.79)	8.03	7.79 (8.64)
$a_{F(H)}^4$	2.11 (−3.77)	5.7	5.49 (6.91)	5.33 (7.25)	5.89 (7.45)	6.71	5.35 (7.25)
a_F^5	2.75 (−3.37)	2.6	2.85 (−3.89)	2.72 (−4.10)	2.77 (−4.08)	2.35	2.74 (−4.10)
$a_{F(H)}^6$	9.19 (10.36)	10.0	3.88 (−4.27)	3.69 (−4.54)	9.58 (10.22)	10.35	3.73 (−4.54)
$a_{F(H)}^7$	1.03 (1.80)	3.5	3.40 (−4.12)	3.46 (−4.31)	3.51 (−4.63)	3.49	3.46 (−4.31)
g-value	2.0032	2.0078	2.0123	2.0053	2.0140	2.0095	2.0060

RESULTS AND DISCUSSION

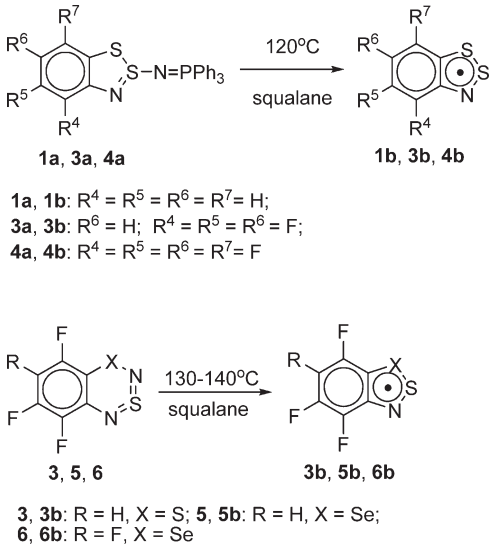
It was reported that compound **4** interacts with Ph_3P in benzene at 20 °C to give iminophosphorane **4a** in an isolated yield of 12%.[3] In this work, the yield of **4a** was increased to 60% by performing the interaction at −70 °C in toluene. Under the same conditions, derivatives **1a**−**3a** were prepared from compounds **1**−**3** (Scheme 1) in isolated yields of 16, 20, and 53%, respectively. The reaction is solvent-dependent and, in hexane instead of toluene, leads to unidentified insoluble products, likely of polymeric structure.

The structures of **1a**−**3a** were confirmed by XRD (Tables 2 and 3, Figure 1), in the case of **2a** as solvate **2a**·0.5C_6H_6 after crystallization from benzene/hexane mixture. Molecules of **1a**−**3a** are chiral. The crystal of **1a** was formed by a single enantiomer, whereas those of **2a** and **3a** were racemic (as in the case of **4a**).[3] For **1a**−**3a** in the crystal, one of phenyl rings of the Ph_3P fragment is oriented practically parallel to the plane of the heterocyclic moiety, with interplanar separations of 3.52, 3.49, and 3.43 Å, respectively (Figure 1). The same structural feature was previously observed for **4a** with an interplanar separation of 3.39 Å.[3] For comparison, the sum of the van der Waals radii of the C atoms is 3.54 Å,[23] and the interplanar distance in graphite is 3.35 Å.[24] In the case of **4a**, the feature was attributed to intramolecular π-stacking interactions of the arene-polyfluoroarene type.[3] Now one can think that the packing effects might be the main driving force behind the discussed structural peculiarity; however, the fact that in the progression **1a**−**4a** the interplanar separation shortens might indicate a contribution from the arene-(poly)fluoroarene π-stacking interactions[25] in the case of fluorinated derivatives.

At the same time, compounds **1** and **4** do not interact with Ph_3As and Ph_3Sb even under refluxing in toluene for 1 h. It was found in these experiments, however, that Ph_3Sb catalyzes a 1:1 addition of atmospheric water to 1,3,2,4-benzodithiadiazines,[26] and compound **7** (Chart 1) was obtained from compound **1** in an isolated yield of 64% (its fluorinated derivatives were described before).[26] The structure of **7** was confirmed by XRD (Table 2, Figure 2).

Previously, the 1-Se analog of compound **4** (Chart 1, **6**) was prepared by the fluoride-induced intramolecular cyclization of C_6F_5−Se−N=S=N−$SiMe_3$, however, in an isolated yield of 7% only.[21] In the present work, it was found that compound **5**, the precursor of iminophosphorane **5a** (Chart 1), can be synthesized in a similar way (Scheme 2) in the isolated yield of 50%. The hetero ring closure (Scheme 2) was highly regioselective since only **5**, one of two possible isomers, was observed in the reaction mixture by ^{19}F NMR. The structure of **5** was confirmed by XRD (Table 2, Figure 2). As minor byproduct, 6-5-5-5 tetracyclic compound (Chart 1, **8**[18]) was identified by XRD (Table 2, Figure 2).[27]

Scheme 4



The interaction between **5** and Ph_3P under the same conditions as above gave iminophosphorane **5a** (Scheme 3) in an isolated yield of 72%. The structure of **5a** was confirmed by XRD (Tables 2 and 3, Figure 1). The racemic crystal of **5a** was isomorphic to that of **3a**. The molecular structure of **5a** revealed the same face-to-face orientation of the hetero ring and one of the hydrocarbon rings that was found for **1a**−**4a**, with an interplanar separation of 3.45 Å.

Thus, the interaction between Ph_3P and 1,3,2,4-benzodithiadiazines which can be classified as the oxidative imination of the former covers both hydrocarbon and fluorocarbon series and, in the later case, 1-Se congeners of the heterocycles as well. As oxidative imination, the interaction of **1**−**5** with Ph_3P should involve an electron lone pair of the P atom (n_P). However, for Ph_3X (X = P, As, Sb), the ability to react with 1,3,2,4-benzodithiadiazines and their 1-Se congeners does not correlate with the $(n_X)^{-1}$ vertical ionization energy from HeI UPS, which is about the same (~ 7.8 eV) in all cases.[28]

It should be noted that Ph_3P=N−R iminophosporanes have found a wide application in chemical synthesis.[6] Generally, they can be prepared from Ph_3P and R−N_3 by performing the Staudinger reaction via phosphazides[6] or from Ph_3PCl_2 and R−NH_2 by the Kirsanov reaction.[6,29] It should be emphasized that the iminophosporanes synthesized in the present work are inaccessible by these approaches.

The reactivity of 1,3,2,4-benzodithiadiazines and 3,1,2,4-benzothiaselenadiazines toward Ph_3P can be associated with RS-N: ↔ RS≡N nitrenoids (RS = corresponding

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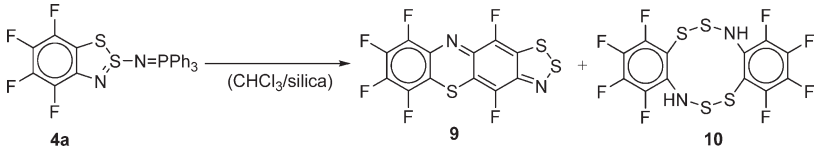
Scheme 5



1,2,3-benzodichalcogenazol-2-yls) detected by matrix isolation techniques among intermediates of photochemical transformations of these heterocycles.[19] It is very likely that RS−N: ↔ RS≡N are also involved in the oxidative imination of SCl_2 with 1,3,2,4-benzodithiadiazines, affording 1,2,3-benzodithiazolium chlorides (Herz salts) after the elimination of NSCl from the initial imination product.[30] A similar intermediate carrying an exocyclic (N)−S≡N group was also observed for photochemical transformations of S_4N_4,[31] which (as well as some other sulfur−nitrogen rings and cages) readily reacts with Ar_3X to give Ar_3X=N−R derivatives (X = P, As).[4,5] The properties of RS−N: ↔ RS≡N species are not studied in detail. At the same time, one can think that the properties of these nitrenoids are different from those of C-bonded nitrenes whose ability to oxidatively iminate P(III) and As(III) atoms is questionable,[6,32,33] whereas nothing definite is known about Sb(III) atoms.

Earlier, it was shown by EPR spectroscopy that in $CHCl_3$ solution (but not in toluene) and at ambient temperatures compound **4a** spontaneously produced Herz radical **4b**. One can suggest a reversible homolytic splitting of the exocyclic S−N bond of **4a** with the formation of **4b** and the Ph_3P=$N^•$ radical, following by fast reaction of the latter with $CHCl_3$ solvent to give Ph_3P=NH. This should shift the first stage toward **4b**. The final product isolated from the solution was 5-6-6-6 tetracyclic compound **9** (Chart 1).[20] It was found in this work that dissolving compounds **1a** and **2a** in the same solvent leads to the generation of radicals **1b**[19] and **2b** (Figure 3, Table 4) detected by EPR. On the other hand, no radicals were detected in a $CHCl_3$ solution of **3a**, which was quantitatively recovered from the solution after 7 days.

Thermolysis of dilute solutions of **1a**, **3a**, and **4a** in squalane at 120 °C affords corresponding Herz radicals **1b**,[19] **3b** (Figure 3, Table 4), and **4b**[19,20] (Scheme 4) identified by EPR. Radical **3b** was also generated by the thermolysis of **3** in squalane at 140 °C (Scheme 4).

The behavior of compound **5a** was different. Upon either dissolving **5a** in $CHCl_3$ at room temperature or heating it in decane up to 170 °C, expected radical **5b** was not detected by EPR. In contrast to **3a**, compound **5a** was not recovered from $CHCl_3$ solution. Instead, a complex mixture of unidentified compounds was observed by ^{1}H and ^{19}F NMR. The reasons for the different behaviors of compounds **1a**−**5a** in $CHCl_3$ solution are not clear.

Meanwhile, previously unknown Herz radicals **5b** and **6b** (Scheme 4, Figure 3, Table 4) were obtained by the thermolysis of compounds **5** and **6** in squalane at 140 °C. In both cases, EPR spectra also revealed the presence of a minor amount of a second radical featuring a lesser *g* value and line widths. The experimental spectra were fairly well simulated as the superposition of those of **5b** (93.8%) and **3b** (6.2%) for the thermolysis of **5** and those of **6b** (93.1%) and **4b** (6.9%) for the thermolysis of **6**.

On the one hand, minor products **3b** and **4b** might arise from trace admixtures of **3** and **4** in **5** and **6**, respectively. On the other hand, the observed ratios of major and minor radicals do not reflect the ratio of the major and minor heterocycles in the staring materials because of a difference in rates of formations and yields of the radicals. Furthermore, compounds **5** and **6** were analytically and NMR pure. However, they were not suitable to more precise GLC-MS analysis. To detect by this method the possible admixture of **3** in the sample of **5** used in the thermolytic experiments, the sample was hydrolyzed by analogy with the hydrolysis of 1,3,2,4-benzodithiadiazines, affording 2,2′-diaminodiphenyl disulfides.[22] No traces of the disulfide corresponding to **3** were observed with GLC-MS. It is known that the thermal behavior of 1,3,2,4-benzodithiadiazines (the 6-6 bicyclic systems) is extremely complex—in particular, giving rise to various 5-6 and 6-7 bi-, 5-5-6 and 5-6-7 tri-, and 5-6-6-6 tetracyclic sulfur−nitrogen systems.[20] The isolation of compound **8** as a byproduct of the synthesis of compound **5** (this work) provides an additional example. Therefore, one can think that precursors of the discussed minor radicals were not admixtures in the starting materials but rather compounds formed in the reaction systems on reaction side routes.

Overall, one can conclude that the discussed iminophosphoranes represent a new promising source of Herz radicals on an EPR scale. A common synthetic approach to these radicals is based on the reduction of Herz salts[8,24] available by the Herz reaction between arylamines and S_2Cl_2[7] and the interaction of *ortho*-aminothiophenols with $SOCl_2$[7] or 1,3,2,4-benzodithiadiazines with SCl_2.[30] On an EPR scale, Herz radicals can also be obtained by the thermolysis or photolysis of various sulfur−nitrogen derivatives,[7] especially 1,3,2,4-benzodithiadiazines[19] and, now, their 1-Se congeners. These methods provide radicals (for example, polyfluorinated)[19] which are inaccessible via Herz salts.[34] An advantage of the iminophosphoranes over the parent 1,3,2,4-benzodithiadiazines is the lower temperature of transformation into Herz radicals since they are better suited structurally to this reaction.

Passing a chloroform solution of **4a** through a silica column unexpectedly gave 5-6-6-6 tetracyclic (**9**) and 6-10-6 tricyclic (**10**) sulfur−nitrogen compounds (Scheme 5). Compound **9** was known before;[20] the structure of compound **10** was confirmed by XRD (Table 1, Figure 2; cf. structure of the hydrocarbon congener[35]).

CONCLUSIONS

The interaction between Ph_3P and 1,3,2,4-benzodithiadiazines affording Ph_3P=N−R iminophosphoranes (R = 1,2,3-benzodithiazol-2-yls) readily proceeds in both the hydrocarbon and fluorocarbon series, in the latter case covering also 1-Se congeners of the heterocycles. It is the first example of imination of phosphines with π-heterocycles. The iminophosporanes obtained are inaccessible by the common procedures based on the Staudinger reaction or on the Kirsanov reaction. Therefore, the new reaction of 1,3,2,4-benzodithiadiazines and their 1-Se congeners described in this work represents

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the new approach to $Ph_3P{=}N{-}R$ iminophosphoranes. In the crystalline state, the synthesized $Ph_3P{=}N{-}R$ derivatives display an interesting structural feature; i.e., one of the Ph rings is oriented face-to-face with the hetero ring R, with the interplanar separation being shorter than the sum of van der Waals radii of two C atoms of 3.54 Å. Overall, they represent a new structural type of the iminophosphoranes. These derivatives also reveal interesting heteroatom reactivity. Particularly, they are a promising new source of 1,2,3-benzodithiazolyls $R^{\bullet}$ (Herz radicals), as well as of uncommon polycyclic compounds hardly accessible by other approaches. These $Ph_3P{=}N{-}R$ iminophosphoranes can also be of interest as chiral ligands in coordination compounds.

■ ASSOCIATED CONTENT

Supporting Information. A crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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