Inorg. Chem. **2003**, *42*, 6294–6299

Inorganic Chemistry
Article

Synthesis and Characterization of $HN(SP^iPr_2)(SePPh_2)$ and $[Te\{N(SP^iPr_2)(SePPh_2)\}_2]$

Perumal Sekar and James A. Ibers*

Department of Chemistry, Northwestern University, 2145 Sheridan Road,
Evanston, Illinois 60208-3113

Received June 11, 2003

The compound $HN(SP^iPr_2)(SePPh_2)$ has been synthesized from the reaction of $Ph_2P(Se)NH_2$ with $^iPr_2P(S)Cl$ in the presence of NaH in THF. $HN(SP^iPr_2)(SePPh_2)$ crystallizes with eight formula units in space group *Pbca* of the orthorhombic system in a cell of dimensions at –120 °C of $a = 9.9560(6)$ Å, $b = 17.9053(10)$ Å, $c = 22.4156(13)$ Å, and $V = 3995.9(4)$ Å^3. The square-planar Te(II) complex $[Te\{N(SP^iPr_2)(SePPh_2)\}_2]$ has been isolated from the reaction of $Te(tu)_4Cl_2{\cdot}2H_2O$ (tu = thiourea) with the anion $[N(SP^iPr_2)(SePPh_2)]^-$, generated in situ from $HN(SP^iPr_2)(SePPh_2)$ in the presence of KO^tBu. $[Te\{N(SP^iPr_2)(SePPh_2)\}_2]$ is dimorphic, crystallizing with one formula unit in space group $P\bar{1}$ of the triclinic system in a cell of dimensions at –120 °C of $a = 9.8476(9)$ Å, $b = 10.3296(9)$ Å, $c = 11.3429(10)$ Å, $\alpha = 101.903(1)°$, $\beta = 115.471(1)°$, $\gamma = 92.281(2)°$, and $V = 1008.4(2)$ Å^3 and also crystallizing with two formula units in space group $P2_1/n$ of the monoclinic system in a cell of dimensions at –120 °C of $a = 8.7931(5)$ Å, $b = 17.1830(10)$ Å, $c = 14{,}1026(9)$ Å, $\beta = 104.696(1)°$, and $V = 2061.1(2)$ Å^3. In each instance, the $[Te\{N(SP^iPr_2)(SePPh_2)\}_2]$ molecule possesses a center of symmetry, comprising a Te center liganded in a trans manner by two bidentate $N(SP^iPr_2)(SePPh_2)$ groups. However, the ^{31}P, ^{77}Se, and ^{125}Te NMR spectra of $[Te\{N(SP^iPr_2)(SePPh_2)\}_2]$ show two sets of resonances at 25 °C. The ^{31}P VT NMR spectra show two sets of resonances between –50 and +50 °C that coalesce between 80 and 100 °C, consistent with the presence of the cis as well as the trans isomer in solution.

Introduction

A number of bis-S or bis-Se compounds $HN(QPR_2)_2$ (Q = S, Se; R = Me, Et, Ph, ^{i}Pr, ^{n}Bu, OPh) have been synthesized, and the coordination chemistry of their anions $[N(QPR_2)_2]^-$ has been extensively studied with a variety of transition-metal, main-group, and rare-earth systems.[1−38] In addition, the unsymmetrical bis-S compounds $HN(SPR_2)(SPR'_2)$ (R = Ph, R′ = Me, Et, ^{i}Pr, OEt, OPh; R = OPh, R′

---

* Author to whom correspondence should be addressed. E-mail: ibers@chem.northwestern.edu.

(1) Rossi, R.; Marchi, A.; Marvelli, L.; Peruzzini, M.; Casellato, U.; Graziani, R. *J. Chem. Soc., Dalton Trans.* **1992**, 435−437.
(2) Crespo, O.; Gimeno, M. C.; Jones, P. G.; Laguna, A. *Inorg. Chem.* **1994**, *33*, 6128−6131.
(3) Phillips, J. R.; Slawin, A. M. Z.; White, A. J. P.; Williams, D. J.; Woollins, J. D. *J. Chem. Soc., Dalton Trans.* **1995**, 2467−2468.
(4) Cupertino, D.; Keyte, R.; Slawin, A. M. Z.; Woollins, J. D.; Williams, D. J. *Polyhedron* **1996**, *15*, 4441−4445.
(5) Geissinger, M.; Magull, J. *Z. Anorg. Allg. Chem.* **1997**, *623*, 755−761.
(6) Papadimitriou, C.; Veltsistas, P.; Novosad, J.; Cea-Olivares, R.; Toscano, A.; Garcia y Garcia, P.; Lopez-Cardosa, M.; Slawin, A. M. Z.; Woollins, J. D. *Polyhedron* **1997**, *16*, 2727−2729.
(7) Abram, U.; Lang, E. S.; Abram, S.; Wegmann, J.; Dilworth, J. R.; Kirmse, R.; Woollins, J. D. *J. Chem. Soc., Dalton Trans.* **1997**, 623−630.
(8) Ho, E. N.-M.; Wong, W.-T. *J. Chem. Soc., Dalton Trans.* **1997**, 915−916.
(9) Abram, U.; Abram, S.; Schibli, R.; Alberto, R.; Dilworth, J. R. *Polyhedron* **1998**, *17*, 1303−1309.
(10) Laguna, A.; Laguna, M.; Fraile, M. N.; Fernandez, E.; Jones, P. G. *Inorg. Chim. Acta* **1988**, *150*, 233−236.
(11) Ly, T. Q.; Woollins, J. D. *Coord. Chem. Rev.* **1998**, *176*, 451−481.
(12) Gilby, L. M.; Piggott, B. *Polyhedron* **1999**, *18*, 1077−1082.
(13) Parr, J.; Smith, M. B.; Slawin, A. M. Z. *J. Organomet. Chem.* **1999**, *588*, 99−106.
(14) Leung, W.-H.; Chim, J. L. C.; Williams, I. D.; Wong, W.-T. *Inorg. Chem.* **1999**, *38*, 3000−3005.
(15) Birdsall, D. J.; Slawin, A. M. Z.; Woollins, J. D. *Inorg. Chem.* **1999**, *38*, 4152−4155.
(16) Pernin, C. G.; Ibers, J. A. *Inorg. Chem.* **1999**, *38*, 5478−5483.
(17) Béreau, V.; Ibers, J. A. *C. R. Acad. Sci.* **2000**, *IIc*(*3*), 123−129.
(18) Aragoni, M. C.; Arca, M.; Garau, A.; Isaia, F.; Lippolis, V.; Abbati, G. L.; Fabretti, A. C. *Z. Anorg. Allg. Chem.* **2000**, *626*, 1454−1459.
(19) Bereau, V.; Sekar, P.; McLauchlan, C. C.; Ibers, J. A. *Inorg. Chim. Acta* **2000**, *308*, 91−96.
(20) Valderrama, M.; Contreras, R.; Lamata, P. M.; Viguri, F.; Carmona, D.; Lahoz, F. J.; Elipe, S.; Oro, L. A. *J. Organomet. Chem.* **2000**, *607*, 3−11.
(21) Leung, W.-H.; Zheng, H.; Chim, J. L. C.; Chan, J.; Wong, W.-T.; Williams, I. D. *J. Chem. Soc., Dalton Trans.* **2000**, 423−430.

10.1021/ic030194u CCC: $25.00

= Et, ^{i}Pr, OEt) have been prepared and their anions complexed with Co, Zn, Pd, and Pt systems.[39−41]

A few mixed S/Se compounds HN(SPR$_2$)(SePR′$_2$) (R, R′ = Ph; R, R′ = ^{i}Pr; R = OPh, R′ = Ph) have been prepared.[34,40,42−45] We recently reported an improved synthesis of HN(SPPh$_2$)(SePPh$_2$) and some coordination chemistry of its anion.[45] The parent compound as well as the metal complexes of the anion exhibit S/Se disorder in the solid state; the electronic and steric differences between S and Se are not sufficient to prevent this. We have successfully circumvented this problem by introducing different R groups onto the P atoms. Here we report the syntheses, spectroscopic characterization, and crystal structures of HN(SP^{i}Pr$_2$)(SePPh$_2$) and the Te(II) complex, [Te{N(SP^{i}Pr$_2$)(SePPh$_2$)}$_2$], which appears to be the first example of an imidodiphosphinochalcogenido complex that contains all three (S, Se, and Te) chalcogens.

Experimental Section

General Procedures. All manipulations were performed under an inert atmosphere of N$_2$ with the use of standard Schlenk-line techniques or under Ar in a glovebox. Solvents were dried, distilled, and degassed under N$_2$ before use. Anhydrous Et$_2$O and THF were distilled from Na and benzophenone; CH$_2$Cl$_2$ was distilled from P$_2$O$_5$; MeOH was dried over molecular sieves; *n*-hexane was stored over molecular sieves and bubbled with N$_2$ for 10 min prior to use. NaH (60% dispersion in mineral oil) was used as received from Aldrich. The compounds Ph$_2$P(Se)NH$_2$, ^{i}Pr$_2$P(S)Cl, and Te(tu)$_4$Cl$_2$·2H$_2$O (tu = thiourea) were prepared according to literature methods.[40,41,46]

NMR data on CH$_2$Cl$_2$/CD$_2$Cl$_2$ solutions of HN(SP^{i}Pr$_2$)(SePPh$_2$) and [Te{N(SP^{i}Pr$_2$)(SePPh$_2$)}$_2$] were recorded on either a Mercury 400 MHz spectrometer (^{31}P with a 5-mm NMR probe) or an INOVA 400 MHz spectrometer (^{77}Se and ^{125}Te with a 10-mm broad-band NMR probe). The ^{31}P VT NMR spectra were recorded on an INOVA 400 MHz spectrometer with DMF-*d*$_7$/DMF as solvent. ^{31}P chemical shifts, in ppm, were recorded at 166.994 MHz and were referenced to an external standard of 85% H$_3$PO$_4$ (set to 0 ppm). ^{77}Se chemical shifts, in ppm, were recorded at 76.287 MHz and referenced to an external standard of a saturated solution of Ph$_2$Se$_2$ in CD$_2$Cl$_2$ (set to 460 ppm). ^{125}Te chemical shifts, in ppm, were recorded at 126.234 MHz and referenced to an external standard of a saturated solution of Ph$_2$Te$_2$ in CD$_2$Cl$_2$ (set to 422 ppm). Electrospray mass spectra were obtained on a Micromass Quattro II instrument. Elemental analyses were performed by Oneida Research Services, Whitesboro, NY. Melting points were determined with a Mel-Temp device on samples in glass capillaries.

Synthesis of HN(SP^{i}Pr$_2$)(SePPh$_2$). Ph$_2$P(Se)NH$_2$ (5.6 g, 20 mmol) and NaH (1.44 g, 36 mmol) were loaded in separate flasks in an Ar-filled glovebox. A slurry of NaH in THF (20 mL) was added slowly with stirring to a solution of Ph$_2$P(Se)NH$_2$ in THF (40 mL) at −78 °C by means of a cannula. The reaction mixture was allowed to warm to 20 °C. It was stirred for 30 min and cooled again to −78 °C, and then a solution of ^{i}Pr$_2$P(S)Cl (3.69 g, 20 mmol) in THF (20 mL) was added dropwise. The mixture was refluxed for 4 h and stirred overnight at 20 °C. The solvent was removed under vacuum and dilute HCl (15%, 50 mL) was added, producing a cloudy white mixture that was extracted with CH$_2$Cl$_2$ (75 mL). The CH$_2$Cl$_2$ solution was dried over MgSO$_4$ and then filtered. The filtrate was evaporated to dryness to give a yellow oil. The crude product was precipitated with hexane and collected by filtration. The unreacted Ph$_2$P(Se)NH$_2$ was removed by stirring the crude product in MeOH (20 mL) with the addition of excess of K^{t}BuO (2 g, 17.8 mmol). The solvent was removed under vacuum, and the product was washed with Et$_2$O (40 mL). The K$^+$ salt was then converted back to the free ligand by stirring in water (25 mL) with the addition of dilute HCl (15%, 50 mL) and extraction with CH$_2$Cl$_2$ (75 mL). Again, the CH$_2$Cl$_2$ solution was dried over MgSO$_4$ and filtered, and the filtrate was evaporated to dryness to give a yellow oil. The product was recrystallized from CH$_2$Cl$_2$/hexane to give colorless crystals of HN(SP^{i}Pr$_2$)(SePPh$_2$) upon cooling. Yield 3.8 g, 44%. Anal. Calcd for C$_{18}$H$_{25}$NP$_2$SSe: C, 50.47; H 5.88; N 3.27. Found: C, 50.66; H, 5.79; N, 3.12. ^{1}H NMR (CD$_2$Cl$_2$, 25 °C): δ 4.5 (s, NH). ^{31}P{^{1}H} NMR (CH$_2$Cl$_2$/CD$_2$Cl$_2$, 25 °C): δ 99.1 (d,$^2J_{\mathrm{P-P}} = 28$ Hz, PS), 46.3 (d, $^1J_{\mathrm{P-Se}} = 783$ Hz; $^2J_{\mathrm{P-P}} = 28$ Hz, PSe). ^{77}Se{^{1}H} NMR (CH$_2$Cl$_2$/CD$_2$Cl$_2$, 25 °C): δ −224.9 (d, $^1J_{\mathrm{Se-P}} = 782$ Hz, $^2J_{\mathrm{P-P}} = 28$ Hz). ESI-MS (CH$_2$Cl$_2$) {*m*/*z* (%) [assignment]}: 430 (100) [HN(SP^{i}Pr$_2$)(SePPh$_2$) + H]$^+$, 350 (47) [HN(SP^{i}Pr$_2$)(PPh$_2$) + H]$^+$, 265 (47) [SePPh$_2$]$^+$. Mp: 109−111 °C.

[Te{N(SP^{i}Pr$_2$)(SePPh$_2$)}$_2$]. Te(tu)$_4$Cl$_2$·2H$_2$O (0.27 g, 0.50 mmol) dissolved in MeOH (20 mL) was added to a solution of HN(SP^{i}Pr$_2$)(SePPh$_2$) (0.428 g, 1.0 mmol) and KO^{t}Bu (0.112 g, 1.0 mmol) in MeOH (10 mL). After the mixture was stirred for 1 h, the resultant yellow precipitate was filtered off, washed with MeOH and Et$_2$O, and dried under vacuum. Yellow (minor) and yellow-

---

(22) Zhang, Q.-F.; Lau, K.-K.; Chim, J. L. C.; Wong, T. K. T.; Wong, W.-T.; Williams, I. D.; Leung, W.-H. *J. Chem. Soc., Dalton Trans.* **2000**, 3027−3033.

(23) Béreau, V.; Pernin, C. G.; Ibers, J. A. *Inorg. Chem.* **2000**, *39*, 854−856.

(24) Pernin, C. G.; Ibers, J. A. *Inorg. Chem.* **2000**, *39*, 1216−1221.

(25) Pernin, C. G.; Ibers, J. A. *Inorg. Chem.* **2000**, *39*, 1222−1226.

(26) Zhang, Q.-F.; Zheng, H.; Wong, W.-Y.; Wong, W.-T.; Leung, W.-H. *Inorg. Chem.* **2000**, *39*, 5255−5264.

(27) Canseco-Melchor, G.; García-Montalvo, V.; Toscano, R. A.; Cea-Olivares, R. *Z. Anorg. Allg. Chem.* **2001**, *627*, 2391−2396.

(28) Niu, Y.-Y.; Song, Y.-L.; Zheng, H.-G.; Long, D.-L.; Fun, H.-K.; Xin, X.-Q. *New J. Chem.* **2001**, *25*, 945−948.

(29) Haiduc, I. *J. Organomet. Chem.* **2001**, *623*, 29−42.

(30) Canseco-Melchor, G.; García-Montalvo, V.; Toscano, R. A.; Cea-Olivares, R. *J. Organomet. Chem.* **2001**, *631*, 99−104.

(31) Zúñiga-Villarreal, N.; Reyes-Lezama, M.; Espinosa, G. *J. Organomet. Chem.* **2001**, *626*, 113−117.

(32) Valderrama, M.; Contreras, R.; Muñoz, P.; Lamata, M. P.; Carmona, D.; Lahoz, F. J.; Elipe, S.; Oro, L. A. *J. Organomet. Chem.* **2001**, *633*, 182−188.

(33) García-Montalvo, V.; Zamora-Rosete, M. K.; Gorostieta, D.; Cea-Olivares, R.; Toscano, R. A.; Hernández-Ortega, S. *Eur. J. Inorg. Chem.* **2001**, 2279−2285.

(34) Wilton-Ely, J. D. E. T.; Schier, A.; Schmidbaur, H. *J. Chem. Soc., Dalton Trans.* **2001**, 3647−3651.

(35) Simón-Manso, E.; Valderrama, M.; Boys, D. *Inorg. Chem.* **2001**, *40*, 3647−3649.

(36) Wilton-Ely, J. D. E. T.; Schier, A.; Schmidbaur, H. *Inorg. Chem.* **2001**, *40*, 4656−4661.

(37) Silvestru, C.; Drake, J. E. *Coord. Chem. Rev.* **2001**, *223*, 117−216.

(38) Ghesner, I.; Opris, L.; Balazs, G.; Breunig, H. J.; Drake, J. E.; Silvestru, A.; Silvestru, C. *J. Organomet. Chem.* **2002**, *642*, 113−119.

(39) Silvestru, C.; Rösler, R.; Drake, J. E.; Yang, J.; Espinosa-Pérez, G.; Haiduc, I. *J. Chem. Soc., Dalton Trans.* **1998**, 73−78.

(40) Necas, M.; Foreman, M. R. St. J.; Marek, J.; Woollins, J. D.; Novosad, J. *New J. Chem.* **2001**, *25*, 1256−1263.

(41) Birdsall, D. J.; Slawin, A. M. Z.; Woollins, J. D. *Polyhedron* **2001**, *20*, 125−134.

(42) Bhattacharyya, P.; Slawin, A. M. Z.; Smith, M. B. *J. Chem. Soc., Dalton Trans.* **1998**, 2467−2475.

(43) Cupertino, D.; Birdsall, D. J.; Slawin, A. M. Z.; Woollins, J. D. *Inorg. Chim. Acta* **1999**, *290*, 1−7.

(44) Cea-Olivares, R.; Toscano, R. A.; Hernández-Ortega, S.; Novosad, J.; García-Montalvo, V. *Eur. J. Inorg. Chem.* **1999**, 1613−1616.

(45) Sekar, P.; Ibers, J. A. *Inorg. Chim. Acta* **2001**, *319*, 117−122.

(46) Foss, O.; Hauge, S. *Acta Chem. Scand.* **1961**, *15*, 1616−1617.

Table 1. Selected Crystallographic Data for $HN(SP^iPr_2)(SePPh_2)$ and $[Te\{N(SP^iPr_2)(SePPh_2)\}_2]$

		$[Te\{N(SP^iPr_2)(SePPh_2)\}_2]$	
	$HN(SP^iPr_2)(SePPh_2)$	triclinic	monoclinic
formula	$C_{18}H_{25}NP_2SSe$	$C_{36}H_{48}N_2P_4S_2Se_2Te$	$C_{36}H_{48}N_2P_4S_2Se_2Te$
fw	428.35	982.28	982.28
space group	*Pbca*	$P\bar{1}$	$P2_1/n$
a (Å)	9.9560(6)	9.8476(9)	8.7931(5)
b (Å)	17.9053(10)	10.3296(9)	17.183(1)
c (Å)	22.4156(13)	11.3429(10)	14.1026(9)
α (deg)		101.903(1)	
β (deg)		115.471(1)	104.696(1)
γ (deg)		92.281(2)	
V (Å^3)	3995.9(4)	1008.4(2)	2061.1(2)
Z	8	1	2
T (K)	153	153	153
ρ_{calcd} (g/cm^3)	1.424	1.617	1.583
μ(Mo Kα), (cm^{-1})	21.43	28.33	27.72
$R_1(F)^a$	0.045	0.036	0.035
$R_w(F^2)^b$	0.112	0.084	0.082

[a] $R_1(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w(F_o^2) = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (qF_o^2)^2$ for $F_o^2 > 0$; $w^{-1} = \sigma^2(F_o^2)$ for $F_o^2 \leq 0$; $HN(SP^iPr_2)(SePPh_2)$, $q = 0.05$; $[Te\{N(SP^iPr_2)(SePPh_2)\}_2]$, $q = 0.04$.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $HN(SP^iPr_2)(SePPh_2)$ and Related Compounds

				$HN(SP^iPr_2)(SPPh_2)^d$		
	$HN(SP^iPr_2)(SePPh_2)^a$	$HN\{SP(OPh)_2\}(SePPh_2)^b$	$HN(SP^iPr_2)_2$ ^{c}	molecule 1	molecule 2	$HN(SePPh_2)_2$ ^{e}
P(1)−S(1)	1.966(1)	1.915(1)	1.941(1)	1.935(1)	1.941(1)	
P(2)−S(2)			1.949(1)	1.958(1)	1.955(1)	
P(1)−Se(1)						2.101(1)
P(2)−Se(1)	2.0971(8)	2.079(1)				
P(2)−Se(2)						2.085(1)
P(1)−N(1)	1.686(2)	1.626(3)	1.682(3)	1.674(3)	1.668(3)	1.678(4)
P(2)−N(1)	1.686(2)	1.699(3)	1.684(2)	1.683(2)	1.679(3)	1.686(3)
P(1)−N(1)−P(2)	135.58(15)	131.6(2)	131.6(1)	134.9(2)	132.6(2)	132.3(2)
S(1)−P(1)−N(1)	109.23(9)	113.4(1)	114.14(9)	115.7(1)	113.3(1)	
S(2)−P(2)−N(1)			114.76(10)	110.2(1)	109.0(1)	
Se(1)−P(1)−N(1)						114.5(1)
Se(1)−P(2)−N(1)	115.62(9)	113.7(1)				
Se(2)−P(2)−N(1)						116.1(1)

[a] This work, $T = 153$ K. [b] Reference 40, $T = 293$ K. [c] Reference 53, $T = 253$ K. [d] Reference 40, $T = 293$ K. [e] Reference 54, $T = 298$ K

orange (major) crystals of $[Te\{N(SP^iPr_2)(SePPh_2)\}_2]$ were obtained by recrystallization from CH_2Cl_2/*n*-hexane. Yield 0.21 g, 43%. Anal. Calcd for $C_{36}H_{48}N_2P_4S_2Se_2Te$: C, 44.02; H 4.93; N 2.85. Found: C, 44.36; H, 4.72; N, 2.67. $^{31}P\{^1H\}$ NMR (CH_2Cl_2/CD_2Cl_2, 25 °C): δ 66.6, 65.0, 18.8, 17.3 (d,$^2J_{P-P} = 25$ Hz). $^{77}Se\{^1H\}$ NMR (CH_2Cl_2/CD_2Cl_2, 25 °C): δ 83.7 (d, $^1J_{Se-P} = 506$ Hz), δ 60 (d, $^1J_{Se-P} = 537$ Hz). $^{125}Te\{^1H\}$ NMR (CH_2Cl_2/CD_2Cl_2, 25 °C): δ 934.9 ($^1J_{Te-Se} = 1094$ Hz), δ 915.6 ($^1J_{Te-Se} = 937$ Hz). The ^{31}P, ^{77}Se, and ^{125}Te chemical shifts arise from the presence of both cis and trans isomers. ESI-MS (CH_2Cl_2) {*m*/*z* (%) [assignment]}: 556 (100) $[Te\{N(SP^iPr_2)(SePPh_2)\}]^+$. Mp: yellow-orange solid turns red at 202 °C and liquefies between 206 and 208 °C.

Crystallography. Single-crystal X-ray diffraction data were collected on a clear crystal of $HN(SP^iPr_2)(SePPh_2)$ and on yellow (triclinic) and yellow-orange (monoclinic) crystals of $[Te\{N(SP^iPr_2)(SePPh_2)\}]$ with the use of the program SMART[47] on a Bruker Smart 1000 CCD diffractometer[47] at 153 K with the use of monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å). The diffracted intensities generated by a scan of 0.3° in ω were recorded on four sets of 606 frames at φ settings of 0, 90, 180, and 270°, with an additional 50 frames at $\varphi = 0°$ for decay corrections. The exposure times were 15 s/frame. Cell refinement and data reduction were carried out with the use of the program SAINT.[47] Face-indexed absorption corrections were made with the program XPREP.[48] Then the program SADABS was employed to make incident beam and decay corrections.[47] The structure of $HN(SP^iPr_2)(SePPh_2))$ was solved by direct methods and that of $[Te\{N(SP^iPr_2)(SePPh_2)\}])$ was solved from a Patterson function with the program SHELXS, and each was refined by full-matrix least-squares techniques with the program SHELXL in the SHELXTL-97 suite.[48] Hydrogen atoms were generated in calculated positions and constrained with the use of a riding model. The final models involved anisotropic displacement parameters for all non-hydrogen atoms. Selected crystallographic data are listed in Table 1, and selected bond distances and angles are listed in Tables 2 and 3. Further crystallographic details may be found in Supporting Information.

Results and Discussion

Syntheses. Reaction of equimolar amounts of $Ph_2P(Se)NH_2$ and $^iPr_2P(S)Cl$ in the presence of NaH in THF at −78 °C followed by the addition of dilute HCl yields $HN(SP^iPr_2)(SePPh_2)$. This synthesis is based on previously reported routes to related compounds.[41,45] Reaction of $Te(tu)_4Cl_2{\cdot}2H_2O$ with 2 equiv of $HN(SP^iPr_2)(SePPh_2)$ and KO^tBu in MeOH at 20 °C affords $[Te\{N(SP^iPr_2)(SePPh_2)\}_2]$. Both

---

(47) Bruker. *SMART Version 5.054 Data Collection and SAINT-Plus Version 6.22 Data Processing Software for the SMART System*; Bruker Analytical X-ray Instruments, Inc.: Madison, WI, 2000.

(48) Sheldrick, G. M. *SHELXTL DOS/Windows/NT Version 6.12; Bruker Analytical X-ray Instruments, Inc.*: Madison, WI, 2000.

Table 3. Selected Bond Distances (Å) and Angles (deg) for $[Te\{N(SP^iPr_2)(SePPh_2)\}_2]$ and Related Compounds

	$[Te\{N(SP^iPr_2)(SePPh_2)\}_2]$[a]				$[Te\{N(SePPh_2)_2\}_2]$[c]	
	triclinic	monoclinic	$[Te\{N(SP^iPr_2)_2\}_2]$[b]	$[Te\{N(SP^iPr_2)(SPPh_2)\}_2]$[b]	molecule A	molecule B
Te−S(1)	2.6609(8)	2.6845(7)	2.6730(6)	2.678(2)		
Te−S(2)			2.6978(6)	2.684(2)		
Te−Se(1)	2.8278(4)	2.8057(3)			2.7754(8)	2.790(1)
Te−Se(2)					2.807(1)	2.815(1)
P(1)−S(1)	2.050(1)	2.041(1)	2.0354(8)	2.022(2)		
P(2)−S(2)			2.0363(8)	2.032(2)		
P(1)−Se(1)					2.176(1)	2.172(1)
P(2)−Se(1)	2.1837(9)	2.1826(8)				
P(2)−Se(2)					2.178(1)	2.187(1)
P(1)−N(1)	1.591(3)	1.595(2)	1.583(2)	1.589(5)	1.596(4)	1.584(4)
P(2)−N(1)	1.583(3)	1.592(2)	1.584(2)	1.593(5)	1.589(4)	1.583(4)
S(1)−Te−S(2)			87.21(2)	85.69(6)		
Se(1)−Te−Se(2)					87.01(3)	86.43(3)
S(1)−Te−Se(1)	91.23(2)	85.96(2)				
S(1)−Te−Se(1A)	88.77(2)	94.04(2)	92.79(2)	94.31(6)	92.99(3)	93.57(2)
Te−S(1)−P(1)	103.50(4)	102.74(3)	100.84(3)	94.72(9)		
Te−S(2)−P(2)			96.27(3)	101.51(9)		
Te−Se(1)−P(1)					95.99(4)	87.37(5)
Te−Se(1)−P(2)	92.86(2)	88.39(2)				
Te−Se(2)−P(2)					94.82(4)	95.03(4)
S(1)−P(1)−N(1)	117.7(1)	119.35(9)	118.66(7)	119.8(2)		
S(2)−P(2)−N(1)			117.04(7)	118.9(2)		
Se(1)−P(1)−N(1)					118.4(1)	118.8(2)
Se(1)−P(2)−N(1)	117.1(1)	118.70(9)				
Se(2)−P(2)−N(1)					119.5(1)	119.3(1)
P(1)−N(1)−P(2)	139.40(7)	137.9(2)	142.9(1)	138.8(8)	137.2(2)	140.8(2)

[a] This work, $T = 153$ K. [b] Reference 50, $T = 293$ K. [c] Reference 55, $T = 103$ K.

Table 4. Selected NMR Data for $HN(QPR_2)(Q'PR'_2)$ (Q, Q′ = S, Se) and Te Complexes Involving the $[N(QPR_2)(Q'PR'_2)]^-$ Ligand

compound	$^{31}P\{^1H\}$ (δ)	$^1J_{P-Se}$ (Hz)	$^{77}Se\{^1H\}$ (δ)	$^1J_{Se-P}$ (Hz)	$^2J_{P-P}$ (Hz)	$^{125}Te\{^1H\}$ (δ)	$^1J_{Te-Se}$ (Hz)	ref
$HN(SP^iPr_2)(SePPh_2)$	99.1, 46.3	783	−224.9	782	28			*a*
$HN(SPPh_2)(SePPh_2)$	56.9, 52.5	790	−160.2	790	4.6			45
$HN(SP^iPr_2)(SeP^iPr_2)$	92.1, 89.2	747			35.2			43
$HN(SP^iPr_2)(SPPh_2)$	100.0, 51.5				30.8			41
$HN\{SP(OPh)_2\}(SePPh_2)$	55.3, 50.5	805			26.8			40
$[Te\{N(SP^iPr_2)(SePPh_2)\}_2]$	66.6, 65.0, 18.8, 17.3		83.7, 60	537, 506	25	934.9, 915.6	1094, 937	*a*
$[Te\{N(SP^iPr_2)(SPPh_2)\}_2]$	64.3, 63.7, 32.7, 31.8							50
$[Te\{N(SP(OPh)_2)(SPPh_2)\}_2]$	51.1, 43.4, 35.4, 27.2				29			51
$[Te\{N(SP^iPr_2)_2\}_2]$	58.7							50
$[Te\{N(SePPh_2)_2\}_2]$	24.4	586.4						5
$[Te\{N(SeP^iPr_2)_2\}_2]$	58.7	528						50

[a] This work.

compounds are soluble in CH_2Cl_2 and THF; they are reasonably stable in air for a few days and very stable under inert conditions. Crystals suitable for X-ray diffraction studies were grown from CH_2Cl_2/*n*-hexane. Both triclinic and monoclinic crystals of the trans isomer of $[Te\{N(SP^iPr_2)(SePPh_2)\}_2]$ were obtained in the same crystallization. This is another example of concomitant polymorphism, the subject of a recent review.[49]

NMR Spectroscopy. Selected NMR data for the present and related compounds are given in Table 4. The $^{31}P\{^1H\}$ NMR spectrum of $HN(SP^iPr_2)(SePPh_2)$ shows two doublets with the expected ^{77}Se satellite and $^2J_{P-P}$ coupling of 28 Hz. The P−Se coupling constant, $^1J_{P-Se}$, in $HN(SP^iPr_2)(SePPh_2)$ is consistent with values found in other systems containing the $Ph_2P(Se)$ fragment and hence with the presence of a P═Se double bond.[16,45] The $^{31}P\{^1H\}$ NMR spectrum of $[Te\{N(SP^iPr_2)(SePPh_2)\}_2]$ recorded at 25 °C shows two sets of doublets with equal $^2J_{P-P}$ coupling of 25 Hz, indicative of the presence of two isomers (cis and trans). The ^{77}Se NMR spectrum of $[Te\{N(SP^iPr_2)(SePPh_2)\}_2]$ displays two doublets with different $^1J_{Se-P}$ coupling constants. The ^{31}P NMR resonances are shifted to lower frequencies, and the ^{77}Se NMR resonances are shifted to higher frequencies compared to those of $HN(SP^iPr_2)(SePPh_2)$. The $^1J_{Se-P}$ coupling constants are in the typical range reported for metal-coordinated ligands.[16,24,25,45] The ^{125}Te NMR spectrum of $[Te\{N(SP^iPr_2)(SePPh_2)\}_2]$ shows two singlets with broad ^{77}Se satellites. The $^1J_{Te-Se}$ coupling constants are different from each other.

The presence of two species in solutions of Te[50] and Pt[41] square-planar complexes comprising two unsymmetrical bis-S $N(SPR_2)(SPR'_2)^-$ groups has been detected by ^{31}P NMR spectroscopy at room temperature. The NMR evidence is strong, but not incontrovertible, that the species are the cis and trans isomers. Unfortunately, only the trans isomers

---

(49) Bernstein, J.; Davey, R. J.; Henck, J.-O. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 3440−3461.

(50) Birdsall, D. J.; Novosad, J.; Slawin, A. M. Z.; Woollins, J. D. *J. Chem. Soc., Dalton Trans.* **2000**, 435−439.

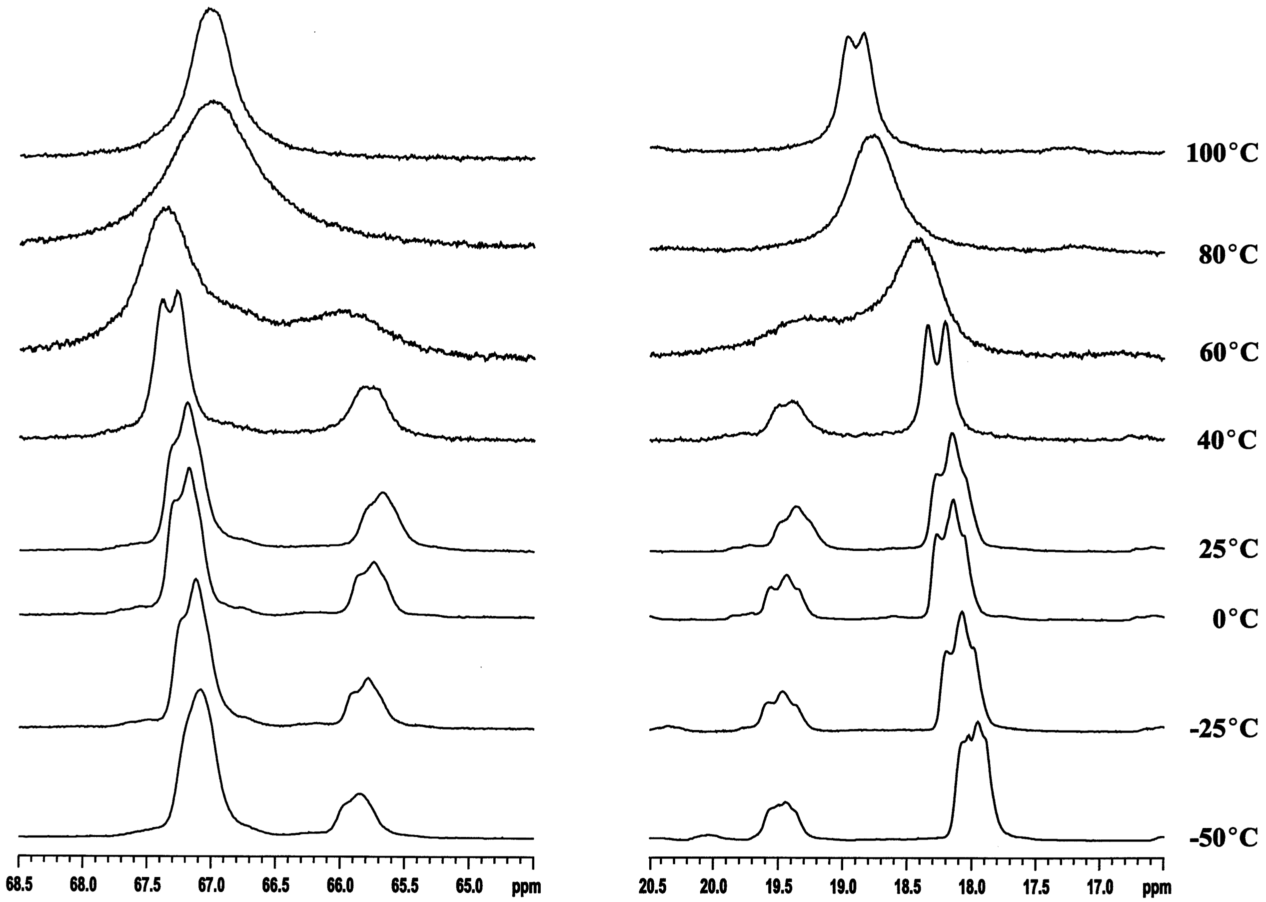

Figure 1. Variable-temperature ^{31}P NMR spectra of $[Te\{N(SP^iPr_2)(SePPh_2)\}_2]$.

were crystallized. In one instance,[51] the pure cis and trans isomers were prepared by different routes and characterized in the solid state but no NMR data from solutions of these compounds were obtained. In the present instance, ^{31}P, ^{77}Se, and ^{125}Te NMR data, especially the ^{31}P VT NMR spectra (Figure 1), clearly indicate the presence of two species in solution. Moreover, a ^{31}P NMR spectrum obtained at 25 °C from a solution in which the yellow and yellow-orange crystals of the trans isomer were redissolved displays the two species. Thus, although cis−trans equilibrium is reached in solution, the trans isomer is less soluble than the cis isomer and crystallizes from solution. We do not know which resonances correspond to the trans isomer obtained by crystallization.

Structure of $HN(SP^iPr_2)(SePPh_2)$. The molecular structure of $HN(SP^iPr_2)(SePPh_2)$ is shown in Figure 2, and selected metrical data are given in Table 2. The molecule possesses a crystallographically imposed center of symmetry. In neither of the present structures, $HN(SP^iPr_2)(SePPh_2)$ and $[Te\{N(SP^iPr_2)(SePPh_2)\}_2]$, is there disorder between S and Se atoms, as was the case in the structures of previously reported mixed S/Se ligands and their complexes.[45] The P−S, P−Se, and P−N bond distances in $HN(SP^iPr_2)(SePPh_2)$ are typical for P=S and P=Se double bonds and P−N single bonds. The P−N−P angle is in the normal range. There is a weak N−H···S intermolecular interaction, with the calculated H···S distance being 2.60 Å and the N−H−S angle being 169°.

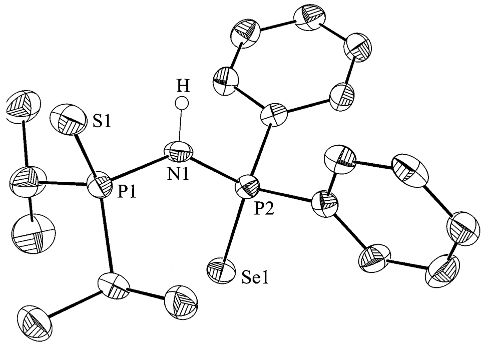

Figure 2. Molecular structure of $[HN(SP^iPr_2)(SePPh_2)]$. Here and in the succeeding figure, anisotropic displacement parameters are drawn at the 50% probability level and H atoms on the phenyl rings have been omitted for the sake of clarity.

Structure of $[Te\{N(SP^iPr_2)(SePPh_2)\}_2]$. This compound is dimorphic, crystallizing as the trans isomer in both a triclinic and a monoclinic space group. The triclinic compound is about 2% more dense. Because of differing crystallographic symmetry elements and cells, the crystal structures differ, displaying different packing patterns and intermolecular interactions. For example, in the triclinic structure, the ^iPr groups face each other whereas in the monoclinic structure they face opposite to each other. In the triclinic structure, there is a possible C−H···S intermolecular

---

(51) Necas, M.; Novosad, J.; Husebye, S. *J. Organomet. Chem.* **2001**, *623*, 124−130.

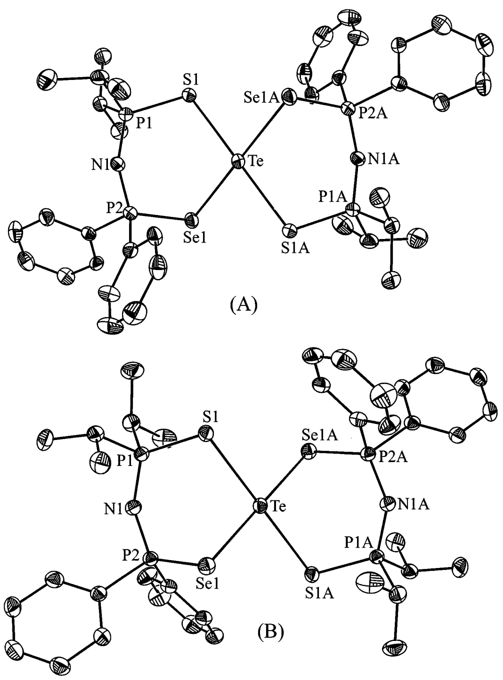

Figure 3. Triclinic (A) and monoclinic (B) structures of the trans isomer of $[Te\{N(SP^{i}Pr_2)(SePPh_2)\}_2]$.

interaction in which the H···S distance is 2.82 Å and the CHS angle is 149° but there are no obvious C−H···Se interactions; in the monoclinic structure, there is a possible C−H···Se intermolecular interaction in which the H···Se distance is 3.10 Å and the CHSe angle is 167° but there are no C−H···S interactions. In the two crystal structures, the molecules of $[Te\{N(SP^{i}Pr_2)(SePPh_2)\}_2]$ consist of two $[N(SP^{i}Pr_2)(SePPh_2)]^-$ ligands coordinated to a Te(II) center in a centrosymmetric square-planar fashion with each six-membered TeSPNPSe ring in a pseudoboat conformation. However, as depicted in Figure 3, there are discernible differences in the orientations of the Ph and ^{i}Pr groups. Although the bond distances in the triclinic and monoclinic structures are in good agreement, some of the angles, particularly the S−Te−Se angles, differ significantly (Table 3); angles should be more sensitive to intermolecular interactions than bond distances.

Table 3 compares the metrical data for $[Te\{N(SP^{i}Pr_2)(SePPh_2)\}_2]$ and related compounds. Once again, comparable bond distances show minimal variation despite the wide range of temperatures of data collection but bond angles show some significant variations. The very different S−Te−Se angles in the triclinic (91.23(2)°) and monoclinic (85.96(2)°) structures may be compared with those in the cis isomers of $[Te(trtu)_2(SeCN)_2]$ (trtu = trimethylenethiourea) (90.29(4)°), $[Te(esu)_2(SCN)_2]$ (esu = ethylenethiourea) (92.17(3)°),[52] $[Te(tu)_2(SeCN)_2]$ (82.65(3)°), and $[Te(su)_2(SCN)_2]$ (su = selenourea) (82.11(4)°).[52] As expected, the P−S and P−Se bond lengths in $[Te\{N(SP^{i}Pr_2)(SePPh_2)\}_2]$ are elongated compared with those in $HN(SP^{i}Pr_2)(SePPh_2)$, indicative of a reduction of bond order.

Acknowledgment. This work was supported by the National Science Foundation (Grant No. CHE-9819385).

Supporting Information Available: Crystallographic data in CIF format for $HN(SP^{i}Pr_2)(SePPh_2)$, triclinic $[Te\{N(SP^{i}Pr_2)(SePPh_2)\}_2]$, and monoclinic $[Te\{N(SP^{i}Pr_2)(SePPh_2)\}_2]$. This material is available free of charge via the Internet at http://pubs.acs.org.

IC030194U

---

(52) Foss, O.; Henjum, J.; Maartmann-Moe, K.; Marjy, K. *Acta Chem. Scand., Ser. A* **1987**, *41*, 77−86.

(53) Cupertino, D.; Keyte, R.; Slawin, A. M. Z.; Williams, D. J.; Woollins, J. D. *Inorg. Chem.* **1996**, *35*, 2695−2697.

(54) Bhattacharyya, P.; Novosad, J.; Phillips, J.; Slawin, A. M. Z.; Williams, D. J.; Woollins, J. D. *J. Chem. Soc., Dalton Trans.* **1995**, 1607−1613.

(55) Novosad, J.; Lindeman, S. V.; Marek, J.; Woollins, J. D.; Husebye, S. *Heteroat. Chem.* **1998**, *9*, 615−621.