Articles

Contribution from the Institute für Anorganische Chemie der Universität Göttingen, Tammannstrasse 4, D-3400 Göttingen, Federal Republic of Germany

Preparation and Structural Characterization of the Bis[bis(trimethylsilyl)amido]chalcogenides of Selenium and Tellurium

Mår Björgvinsson, Herbert W. Roesky,* Frank Pauer, Dietmar Stalke, and George M. Sheldrick

Received June 11, 1990

The new compounds $Se[N(SiMe_3)_2]_2$ and $Te[N(SiMe_3)_2]_2$ have been prepared in relatively good yields and their crystal structures determined by X-ray crystallography at low temperature. The Se compound crystallizes in the monoclinic system, space group $C2/c$, with $Z = 4$ and unit cell dimensions $a = 1705.4$ (3) pm, $b = 642.2$ (2) pm, $c = 2116.7$ (4) pm, and $\beta = 108.19$ (2)°. The Te compound crystallizes in the triclinic system, space group $P\bar{1}$, with $Z = 2$ and unit cell dimensions $a = 903.9$ (3) pm, $b = 1111.7$ (4) pm, $c = 1241.0$ (4) pm, $\alpha = 88.67$ (2)°, $\beta = 73.68$ (3)°, and $\gamma = 69.10$ (2)°. The crystals of both compounds consist of isolated $Ch[N(SiMe_3)_2]_2$ (Ch = Se, Te) molecules containing V-shaped ChN_2 units with Se-N distances of 186.9 (2) pm and Te-N distances of 205.3 (2) and 204.5 (2) pm. The NChN bond angles were found to be 108.0 (1) and 105.8 (1)° for the Se and Te compounds, respectively. No significant intermolecular Ch···N interactions were found in the two compounds, but an intermolecular Te···Te distance of 377 pm, substantially less than the corresponding van der Waals distance, is present in the Te compound.

Introduction

Over the past few decades a large number of sulfur-nitrogen (S-N) compounds have been prepared, displaying diversity of structures and physical properties.[1] In contrast, few selenium-nitrogen (Se-N) and even fewer tellurium-nitrogen compounds (Te-N) have been structurally characterized. Recently, however, there has been a growing interest in Se-N[2] and Te-N[3] structures. Many of these compounds have novel ring or cage structures such as $(Ph_2C_2N_3Se)_2$,[2c] $[Pt(Se_2N_2H)(PMe_2Ph)_2]Cl$,[2d] $[SeNSeNSe^{2+}][AsF_6^-]_2$,[2e] $(t\text{-BuN})_2Se_6$,[2g] $(t\text{-BuN})_6Se_9$,[2g] and $N(Te(NSN)Cl)_3 \cdot 3DMF$.[3i]

Undoubtedly, one of the main Achilles' heels in the preparation of new Se-N and Te-N compounds has been the lack of suitable stable precursors that can be prepared in good yields. For example, preparations of Se-N and Te-N compounds have often been limited to reactions of amine derivatives with the corresponding chalcogen halogenides or by the use of the explosive Se_4N_4. We therefore wish to report our recent success in preparing and characterizing the new and stable compounds $Se[N(SiMe_3)_2]_2$ (**1**) and $Te[N(SiMe_3)_2]_2$ (**2**). During the preparation of this paper, we learned of a recent report by Haas et al.,[4] which describes a synthesis of **1** comparable to our work.

Results and Discussion

Preparation of 1 and 2. Compounds **1** and **2** were prepared in good yields (50-75%) according to eqs 1 and 2, respectively.

$$2LiN(SiMe_3)_2 + Se_2Cl_2 \xrightarrow[-2LiCl,\ -1/8Se_8]{} \underset{\mathbf{1}}{Se[N(SiMe_3)_2]_2} \quad (1)$$

$$4LiN(SiMe_3)_2 + TeCl_4 \xrightarrow[-LiCl]{} \underset{\mathbf{2}}{Te[N(SiMe_3)_2]_2} \quad (2)$$

As can be seen from eq 1, Se_2Cl_2 reacts as effectively as $SeCl_2$ with $LiN(SiMe_3)_2$ to form **1** with a corresponding formation of Se_8. This is not surprising, as there is evidence from ^{77}Se NMR and Raman studies that Se_2Cl_2 is in equilibrium with $SeCl_2$ and Se_nCl_2 ($n > 2$), indicating relatively labile Se-Cl bonds for these species in solution.[5] Haas et al.[4] recently synthesized **1** by reacting $LiN(SiMe_3)_2$ with Se_2Cl_2. In addition, they report that $Se_2[N(SiMe_3)_2]_2$ is also formed and that $SiMe_3Cl$ forms instead of the expected LiCl. However, as reaction conditions are not reported, we cannot comment on these differences from our work.

The mechanism for the reduction of $TeCl_4$ to **2** is, however, not fully understood. It was found that, in order to minimize substitution reactions of $N\text{-}SiMe_3$ groups with Te-Cl bonds, $LiN(SiMe_3)_2$ must be kept in excess relative to $TeCl_4$ (mole ratio 4:1) in the reaction mixture in order to prevent consequent formation of elemental tellurium. It is conceivable that $Te[N(SiMe_3)_2]_4$ is initially formed, which then decomposes to **2** and $N(SiMe_3)_2$ radicals. The $N(SiMe_3)_2$ radicals so formed could then in turn abstract hydrogen atoms from the solvent (*n*-hexane/toluene mixture). However, irrespective of the initial species formed, the presence of radical reactions are supported by the fact that a relatively large amount of $HN(SiMe_3)_2$ could be identified by ^1H NMR spectroscopy, along with other unidentified species, in the volatile component of the reaction mixture. No $SiMe_3Cl$ was evident in the volatile component.

Compounds **1** and **2** could be isolated and purified by sublimation and were easily characterized by using mass spectroscopy by comparison of the measured and calculated isotopomer mass pattern of their relative intense molecular peaks.

Crystal Structures of 1 and 2. In order to determine the detailed molecular structures of **1** and **2**, their crystal structures were determined by single-crystal X-ray diffraction analysis. The crystal

(1) Sulfur-Nitrogen Compounds. In *Gmelin Handbook of Inorganic Chemistry*; Springer-Verlag: Berlin, 1977, 1985, 1987, 1990; Parts 1-5.
(2) (a) Gieren, A.; Lamm, V.; Haddon, R. C.; Kaplan, M. L. *J. Am. Chem. Soc.* **1980**, *102*, 5070. (b) Haas, A.; Kasprowski, J. *Chimia* **1987**, *41*, 340. (c) Oakley, R. T.; Reed, R. W.; Cordes, A. W.; Craig, S. L.; Graham, J. B. *J. Am. Chem. Soc.* **1987**, *109*, 7745. (d) Kelly, P. F.; Parkin, I. P.; Slawin, A. M. Z.; Williams, D. J.; Woollins, J. D. *Angew. Chem.* **1989**, *101*, 1052; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1047. (e) Awere, E. G.; Passmore, J.; White, P. S.; Klapötke, T. *J. Chem. Soc., Chem. Commun.* **1989**, 1415. (f) Gillespie, R. J.; Kent, J. P.; Sawyer, J. F. *Inorg. Chem.* **1990**, *29*, 1251. (g) Roesky, H. W.; Weber, K. L.; Bats, J. W. *Chem. Ber.* **1984**, *117*, 2686. (h) Roesky, H. W.; Weber, K. L.; Seseke, U.; Pinkert, W.; Noltemeyer, M.; Clegg, W.; Sheldrick, G. M. *J. Chem. Soc. Dalton Trans.* **1985**, 565.
(3) (a) Betini, V.; Dapporto, P.; Lucchesini, F.; Sega, A.; De Munno, A. *Acta Crystallogr.* **1984**, *C40*, 653. (b) Neidlein, R.; Knecht, D.; Gieren, A.; Ruiz-Pérez, C. *Z. Naturforsch.* **1987**, *42B*, 84. (c) Hartl, H.; Huppmann, P.; Lentz, D.; Seppelt, K. *Inorg. Chem.* **1983**, *22*, 2183. (d) Thrasher, J. S.; Nielsen, J. B.; Bott, S. G.; McClure, D. J.; Morris, S. A.; Atwood, J. L. *Inorg. Chem.* **1988**, *27*, 570. (e) Hey, E.; Ergezinger, C.; Dehnicke, K. *Z. Naturforsch.* **1989**, *44B*, 205. (f) Münzenberg, J.; Noltemeyer, M.; Roesky, H. W. *Chem. Ber.* **1989**, *122*, 1915. (g) Johnson, J. P.; MacLean, G. K.; Passmore, J.; White, P. S. *Can. J. Chem.* **1989**, *67*, 1687. (h) Haas, A., Pohl, R. *Chimia* **1989**, *43*, 261 (i) Roesky, H. W.; Münzenberg, J.; Noltemeyer, M. *Angew. Chem.* **1990**, *102*, 73; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 61.
(4) Haas, A.; Kasprowski, J. *Chimia* **1990**, *44*, 57.
(5) Lamouoeux, M.; Milne, J. *Can. J. Chem.* **1989**, *67*, 1936.

0020-1669/90/1329-5140$02.50/0

Table I. Crystallographic Data for **1** and **2**

	1	**2**
formula	$C_{12}H_{36}N_2Si_4Se$	$C_{12}H_{36}N_2Si_4Te$
fw	399.7	448.4
data collcn T, °C	−120	−120
cryst size, mm	0.6 × 0.6 × 0.7	0.7 × 0.7 × 0.8
space group	$C2/c$	$P\bar{1}$
a, pm	1705.4 (3)	903.9 (3)
b, pm	642.4 (2)	1111.7 (4)
c, pm	2116.7 (4)	1241.0 (4)
α, deg	90	88.67 (2)
β, deg	108.19 (2)	73.68 (3)
γ, deg	90	69.10 (2)
cell vol, nm^3	2.203	1.114
formula units/cell (Z)	4	2
calc density ρ, Mg m^{-3}	1.205	1.337
abs coeff μ, mm^{-1}	1.75	1.54
$F(000)$	848	460
measd 2θ range, deg	8–55	8–50
no. of measd rflns	3936	5044
no. of unique rflns	2538	3906
no. of obsd rflns	2261	3857
consistency of equiv rflns (R_{int})	0.0220	0.0202
p ($F > p\sigma(F)$)	3	3
R	0.0281	0.0169
R_w	0.0286	0.0175
goodness-of-fit wtg factor g	1.4843	2.1374
$w = 1/(\sigma^2(F) + \text{abs}(g)\ F^2$	0.0002	0.000 01
no. of refined params	87	172
last diff Fourier synthesis		
highest max, [e$^-$nm^3]:	3.6 × 10^2	7.6 × 10^2
lowest min, [e$^-$nm^{-3}]:	5.3 × 10^2	4.2 × 10^2
abs cor	semiempirical	semiempirical

Table II. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (pm^2 × 10^{-1})[a] for **1**

	x	y	z	U(eq)
Se(1)	5000	5048 (1)	2500	25 (1)
N(1)	5173 (1)	3338 (3)	3245 (1)	25 (1)
Si(1)	6116 (1)	3611 (1)	3881 (1)	28 (1)
C(11)	6900 (1)	5014 (4)	3599 (1)	43 (1)
C(12)	6553 (1)	1027 (4)	4210 (1)	43 (1)
C(13)	5960 (2)	5151 (4)	4581 (1)	43 (1)
Si(2)	4258 (1)	2362 (1)	3348 (1)	27 (1)
C(21)	3560 (1)	4528 (3)	3401 (1)	40 (1)
C(22)	3746 (1)	547 (4)	2662 (1)	41 (1)
C(23)	4491 (1)	816 (4)	4129 (1)	42 (1)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

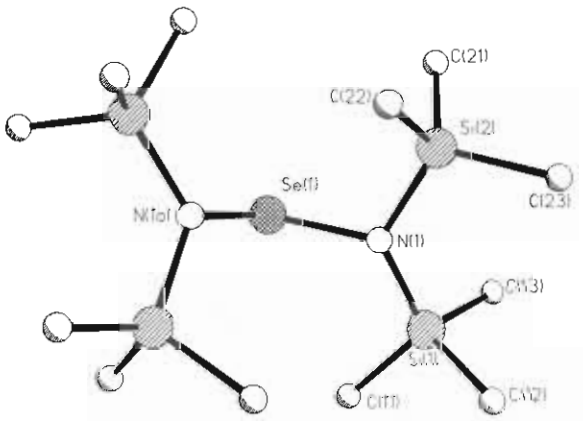

Figure 1. Molecular structure and partial numbering scheme of Se[N(SiMe$_3$)$_2$]$_2$ (**1**). For clarity, the hydrogen atoms have been omitted.

data for **1** and **2** are given in Table I, the fractional coordinates in Tables II (**1**) and III (**2**), and selected bond distances, bond angles, and torsional angles in Table IV (**1** and **2**).

The crystals of **1** and **2** consist of isolated molecules whose structures are shown in Figures 1 (**1**) and 2 (**2**). The average Se–N (187 pm) and Te–N (205 pm) distances for **1** and **2** correspond well to Pauling's single-bond lengths of 186 and 204 pm, respectively.[6] Reported Se–N bond lengths vary from 168 to 190

Table III. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (pm^2 × 10^{-1})[a] for **2**

	x	y	z	U(eq)
Te(1)	5233 (1)	5922 (1)	3707 (1)	22 (1)
N(1)	5551 (2)	4365 (1)	2688 (1)	23 (1)
Si(1)	7401 (1)	3021 (1)	2447 (1)	23 (1)
C(11)	6994 (3)	1670 (2)	3250 (2)	35 (1)
C(12)	8986 (2)	3362 (2)	2948 (2)	35 (1)
C(13)	8342 (3)	2439 (2)	924 (2)	39 (1)
Si(2)	3732 (1)	4338 (1)	2463 (1)	25 (1)
C(21)	2914 (3)	5690 (2)	1623 (2)	37 (1)
C(22)	2164 (3)	4409 (3)	3826 (2)	52 (1)
C(23)	4139 (3)	2841 (2)	1598 (2)	44 (1)
N(2)	4920 (2)	7449 (1)	2732 (1)	22 (1)
Si(3)	3015 (1)	8758 (1)	3090 (1)	23 (1)
C(31)	1313 (2)	8346 (2)	4063 (2)	31 (1)
C(32)	3199 (3)	10125 (2)	3826 (2)	37 (1)
C(33)	2350 (3)	9329 (2)	1807 (2)	41 (1)
Si(4)	6800 (1)	7558 (1)	1926 (1)	25 (1)
C(41)	6445 (3)	8964 (2)	1048 (2)	39 (1)
C(42)	8004 (3)	6097 (2)	921 (2)	38 (1)
C(43)	8025 (3)	7748 (2)	2849 (2)	46 (1)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table IV. Selected Bond Lengths (pm), Bond Angles (deg), and Torsion Angles (deg) for **1** and **2**

Bond Lengths

1		**2**	
Se(1)–N(1)	186.9 (2)	Te(1)–N(1)	205.3 (2)
N(1)–Si(1)	175.3 (1)	Te(1)–N(2)	204.5 (2)
N(1)–Si(2)	175.8 (2)	N(1)–Si(1)	175.3 (1)
		N(1)–Si(2)	175.4 (2)
		N(2)–Si(3)	175.9 (1)
		N(2)–Si(4)	175.7 (2)

Bond Angles

1		**2**	
N(1)–Se(1)–N(1a)	108.0 (1)	N(1)–Te(1)–N(2)	105.8 (1)
Se(1)–N(1)–Si(1)	117.0 (1)	Te(1)–N(1)–Si(1)	118.1 (1)
Se(1)–N(1)–Si(2)	113.7 (1)	Te(1)–N(1)–Si(2)	114.9 (1)
Si(1)–N(1)–Si(2)	125.3 (1)	Si(1)–N(1)–Si(2)	124.6 (1)
		Te(1)–N(2)–Si(3)	119.3 (1)
		Te(1)–N(2)–Si(4)	113.1 (1)
		Si(3)–N(2)–Si(4)	123.9 (1)

Torsion Angles

1		**2**	
N(1a)–Se(1)–N(1)–Si(1)	120.6	N(2)–Te(1)–N(1)–Si(1)	120.4
N(1a)–Se(1)–N(1)–Si(2)	−80.6	N(2)–Te(1)–N(1)–Si(2)	−76.3
		N(1)–Te(1)–N(2)–Si(3)	115.3
		N(1)–Te(1)–N(2)–Si(4)	−85.6

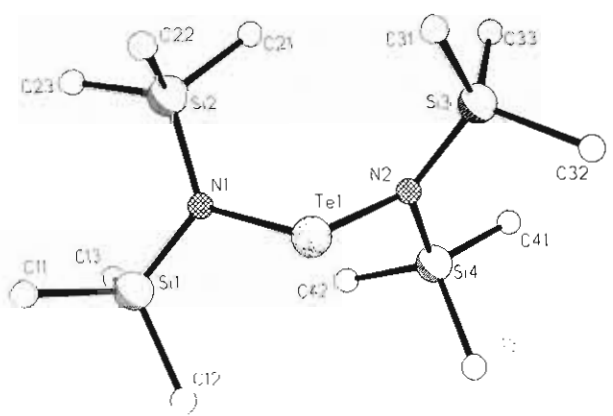

Figure 2. Molecular structure and partial numbering scheme of Te[N(SiMe$_3$)$_2$]$_2$ (**2**). The hydrogen atoms have been omitted for clarity.

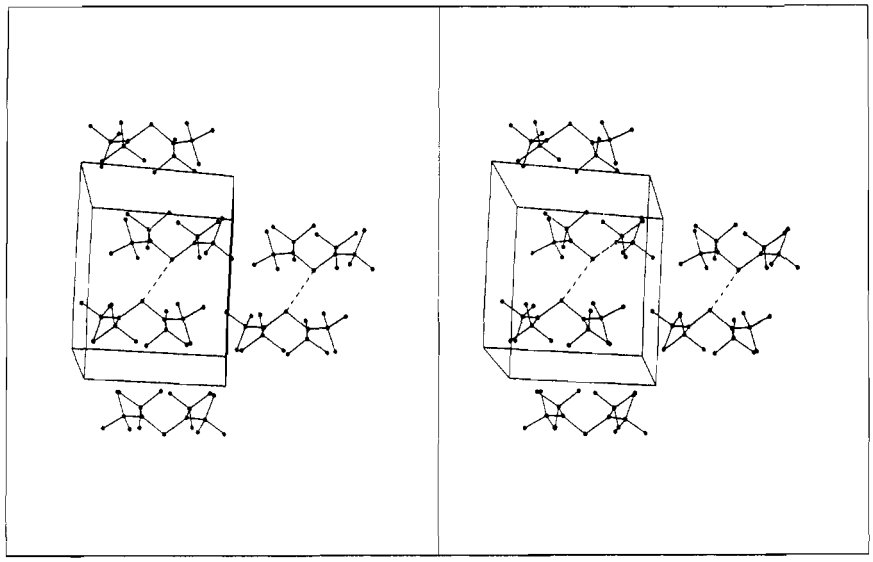

Figure 3. Stereoscopic view of the crystal packing of $Te[N(SiMe_3)_2]_2$ (**2**). The broken lines show the relative short intermolecular Te···Te distances in the crystal (see text).

pm.[2] However, the Se–N distance of **1** corresponds better with the range of 181–190 pm for Se(II)–N bond lengths.[2a,b,g] The Te–N distances of **2** fall within the range of 198–210 pm reported for most other Te–N covalent bonds.[3] The pyramidal NSi_2Ch units of **1** and **2** were found to be relatively flat with nitrogen atoms, on the average, 21 pm (**1**) and 19 pm (**2**) above their respective Si_2Ch planes. The average SiNSi bond angles of 125° (**1**) and 124° (**2**) are larger than the average SiNCh bond angles of 115 and 116° for **1** and **2**, respectively. The NSeN bond angle (108°) of **1** is larger than the NTeN bond angle (106°) of **2**, as expected on the basis of the VSEPR rules,[7] owing to the greater electronegativity of Se relative to that of Te.

Interestingly, even though a large number of compounds containing $N(SiMe_3)_2$ groups as ligands have been structurally characterized,[8] only the structure of $S[N(SiMe_3)_2]_2$ (**3**)[9] has been reported for the group 16 elements. As expected, **3** has the same molecular structure as **1** and **2** and shows similar geometric trends. Thus, the NSi_2S pyramidal units of **3** are also relatively flat with average SiNS (116°) and SiNSi (124°) bond angles similar to those of **1** and **2**. The NSN bond angle (110°) of **3** is significantly larger than the NChN bond angles of **1** and **2**. As above, this could be rationalized on the basis of the VSEPR rules if one assumes Pauling's electronegativity order: S > Se > Te. However, the S–N distances (172 pm) of **3** indicate a small amount of double-bond character by comparison with Pauling's S–N single-bond distance (174 pm)[6] and could therefore also contribute to the observed larger NSN bond angle.

For both compounds **1** and **2** all the intermolecular Se···N and Te···N distances are longer than the corresponding van der Waals distances of 350 and 370 pm, respectively.[6] The melting points of the bis[bis(trimethylsilyl)amido]chalcogenides (Ch = S, Se, Te) are low (64–71 °C) and do not change much with successive substitution of a chalcogen atom. The absence of significant Ch···N intermolecular interactions in **1**–**3** is presumably due to the large size of the $N(SiMe_3)_2$ groups, which hinder their formation. Consequently, only the weaker van der Waals intermolecular interactions are dominant in the crystals of **1**–**3**.

Interestingly, only in the crystals of $Te[N(SiMe_3)_2]_2$ are relatively short intermolecular Ch···Ch distances found in the plane formed by two TeN_2 units (Figure 3). The Te···Te distances of 377 pm are shorter than the van der Waals distances of 440 pm[6] but can be compared with the interhelix chain Te···Te distances of 350 pm in elemental tellurium.[10] This is not surprising if one considers the greater size of the heavier Te atom and the increasing tendency of the heavier main-group elements to exhibit such interactions. However, as the long intermolecular Te···Te distances for **2** are dimeric in nature and do not lead to polymeric network in the crystal, the melting point of **2** is not drastically changed from that of **1** and **3**.

Conclusion

The presence of $SiMe_3$ groups bonded to the nitrogen atoms in **1** and **2** should allow a relatively convenient addition of Se–N or Te–N bonded units into new molecules by simple substitution reactions. Consequently, the relatively high-yield synthesis and isolation of the stable compounds **1** and **2** should render them as important starting materials for the synthesis of new Se–N and Te–N compounds.

Experimental Section

All manipulations were performed under an inert atmosphere of dry nitrogen gas in Schlenk apparatus or in a drybox. The *n*-hexane and toluene solvents were dried over K/Na alloy and sodium metal, respectively, and distilled prior to use. The reagents $LiN(SiMe_3)_2$ and Se_2Cl_2 were prepared according to standard literature methods. The tellurium tetrachloride (Merck) was sublimed prior to use.

Mass spectra (EI) were obtained with a Varian CH-5 MAT instrument. Proton NMR spectra (60 MHz) were recorded for **1** and **2** in CCl_4 at room temperature with external $SiMe_4$ as a reference. Elemental analyses were done by Beller Microanalytical Laboratory, Göttingen, FRG.

Warning! Owing to the relatively volatile nature of **1** and **2** and the toxicity of selenium and tellurium compounds, the following preparations should only be carried out in a well-ventilated fume hood.

$Se[N(SiMe_3)_2]_2$ (1). To a magnetically stirred solution of $LiN(SiMe_3)_2$ (3.08 g, 18.4 mmol) in *n*-hexane (40 mL) was added slowly at −78 °C Se_2Cl_2 (2.11 g, 9.2 mmol). The resulting yellow solution was stirred for 1 h before being allowed to warm to room temperature. After being stirred further for 12 h, the solution was filtered. The volatiles were then pumped off by using a liquid air trap system, and the yellow-orange oily solid residue was finally sublimed at 30–40 °C under dynamic vacuum (<0.1 Torr). Sublimation gave a total of 2.75 g (6.9 mmol, 75% yield) of yellow crystalline product having a melting point of 64–65 °C. Anal. Found (calc for $H_{36}C_{12}N_2Si_4Se$): H, 8.94 (9.08); C, 36.20 (36.06); N, 7.11 (7.01). ^1H NMR (ppm): 0.27. Mass spectrum (EI) [*m*/*z* (^{80}Se peaks, %)]: 400 (M^+, 80), 275 ($M^+ - SeMe_2 - Me$, 45), 239 ($M^+ - HN(SiMe_3)_2$, 40). The yellow crystalline product can be purified further

(6) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; Chapter 7.
(7) Gillespie, R. J. *Molecular Geometry*; van Nostrand Reinhold: London, 1972.
(8) Harris, D. H.; Lappert, M. F. In *Journal of Organometallic Chemistry Library*; Seyferth, D., Davies, A. G., Fischer, E. O., Normant, J. F., Reutov, O. A., Eds.; Elsevier: Amsterdam, 1976; Vol. 2, pp 13–103.
(9) Schubert, G.; Kiel, G.; Gattow, G. *Z. Anorg. Allg. Chem.* **1989**, *575*, 129.
(10) Greenwood, N. N.; Earnshaw, A. Chemistry of the Elements; Pergamon Press: Oxford, U.K., 1984; p 887.

by sublimation, giving colorless crystals having a melting point of 67 °C.

$Te[N(SiMe_3)_2]_2$ (2). The procedure for the preparation of **2** was identical with that of **1** except freshly sublimed $TeCl_4$ was first dissolved in toluene before being added to an $LiN(SiMe_3)_2$/*n*-hexane solution at −78 °C. In a typical preparation using 1.10 g of $LiN(SiMe_3)_2$ (6.57 mmol) and 0.51 g of $TeCl_4$ (1.89 mmol), a total of 0.43 g (0.97 mmol, 50% yield) of orange crystalline material having a melting point of 63–65 °C could be isolated by sublimation from the crude product. However, in order to obtain analytically pure product, the orange crystalline material had to be sublimed again twice (mp 69–71 °C). Anal. Found (calc for $H_{36}C_{12}N_2Si_4Te$): H, 8.17 (8.09); C, 32.48 (32.15); N, 6.28 (6.25). ^1H NMR (ppm): 0.24. Mass spectrum (EI) [*m*/*z* (^{130}Te peaks, %)]: 450 (M^+, 50), 289 ($M^+ - HN(SiMe_3)_2$, 20), 275 ($M^+ - TeMe_2 - Me$, 100).

For analysis of the volatile components from the preparation of **2**, 2.56 g of $LiN(SiMe_3)_2$ (15.3 mmol) and 1.03 g of $TeCl_4$ (3.81 mmol) were each added to separate arms of an H-shaped greaseless reaction vessel. After $LiN(SiMe_3)_2$ and $TeCl_4$ had each been dissolved in *n*-hexane (20 mL) and toluene (20 mL), respectively, the latter solution was decanted in small portions into the former at dry ice/acetone temperature. When the reaction was completed, the volatile components of the reaction mixture (at room temperature) were condensed into the empty ice/water-cooled arm of the vessel. The presence of $HN(SiMe_3)_2$ and absence of $SiMe_3Cl$ in the volatile component were then identified by adding small amounts of them to a sample of the latter and recording their ^1H NMR spectra. A peak intensity enhancement was interpreted as a presence of the compound in the volatile component whereas a new peak indicated the compound's absence.

Crystal Growth and X-ray Measurements of 1 and 2. Crystals of **1** were grown over a period of 2–3 days by slowly condensing the solvent off an *n*-hexane solution of **1**. Crystals of **2** were grown overnight on the colder walls of a dynamically vacuum-pumped (<0.1 Torr) glass tube whose lower end, containing **2**, was kept in warm water (30–40 °C).

Both structures were measured on a Stoe-Siemens four-circle diffractometer with graphite-monochromated Mo Kα radiation (λ = 71.069 pm). Data were collected at −120 °C with a profile-fitting method,[11] 2θ = 8–55° (**1**) and 8–50° (**2**). The structures were solved by Patterson methods and refined by full-matrix least squares, with all non-hydrogen atoms anisotropic. All hydrogen atoms were found by difference Fourier synthesis and refined isotropically. A riding model was employed for the hydrogen atoms with an idealized bond length of 96 pm. A semiempirical absorption correction was applied in both cases. All calculations were performed with SHELX.[12]

Acknowledgment. We wish to thank the Leibniz-Programm der Deutschen Forschungsgemeinschaft and the Fonds der Chemischen Industrie for operating grants and the Alexander von Humboldt Foundation for the award of a fellowship to M.B.

Supplementary Material Available: Tables of bond lengths, bond angles, anisotropic displacement parameters, and H atom coordinates and isotropic displacement parameters (5 pages); listings of observed and calculated structural factors (21 pages). Ordering information is given on any current masthead page. Further details of the X-ray structural investigation can be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, under quotation of the deposit number (CSD-54633), the authors, and the publication.

(11) Clegg, W. *Acta Crystallogr.* **1981**, *A37*, 22.
(12) Robinson, W.; Sheldrick, G. M. In *SHELXS, Crystallographic Computing 4*; Isaacs, N. W., Taylor, M. R., Eds.; Oxford University Press: London, 1988; pp 366–377.

Contribution from the Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A&M University, College Station, Texas 77843

Preparation and Structural Characterization of Two Isomers of Stoichiometry $Re_2Cl_5(PR_3)_3$, Where R = Me or Et

F. Albert Cotton,* Andrew C. Price, and K. Vidyasagar

Received June 25, 1990

The paramagnetic dirhenium compounds of stoichiometry $Re_2Cl_5(PMe_3)_3$ have been prepared from the reactions of $Re_2Cl_4(PMe_3)_4$ with $Cl_2(g)$ or with $PhI{\cdot}Cl_2$. Two isomers have been isolated and their structures determined. In terms of a numbering system to be explained in the text, in one isomer, 1,3,6-$Re_2Cl_5(PMe_3)_3$ (**1**), the two PMe_3 ligands that are coordinated to a Re atom are trans to one another, while in the other isomer, 1,2,7-$Re_2Cl_5(PMe_3)_3$ (**2**), the phosphines are cis. Attempts to convert the 1,2,7-isomer to the 1,3,6-isomer have been unsuccessful. A third compound, 1,3,6-$Re_2Cl_5(PEt_3)_3$ (**3**) was isolated from the reaction between $Re_2Cl_4(PEt_3)_4$ and Ph_4P_2. Pertinent crystal data are as follows: for **1**, monoclinic space group $C2/c$, a = 13.157 (2) Å, b = 12.033 (2) Å, c = 28.197 (4) Å, β = 92.84 (1)°, V = 4459 (1) Å^3, Z = 8; for **2**, monoclinic space group $P2_1/c$, a = 8.973 (2) Å, b = 8.752 (1) Å, c = 28.691 (7) Å, β = 90.21 (2)°, V = 2253 (1) Å^3, Z = 4; for **3**, a = 11.589 (5) Å, b = 14.795 (4) Å, c = 17.942 (6) Å, β = 97.73 (3)°, V = 3048 (3) Å^3, Z = 4.

Introduction

Oxidative addition of halogens, disulfides, and diselenides to multiple metal–metal bonds is an area that has been explored in detail in this laboratory.[1] For example, $Cl_2(g)$ reacts readily with compounds of the type $M_2Cl_4(dppe)_2$ (M = Mo or W) to form the $M_2Cl_6(dppe)_2$ compounds. We carried out reactions of the triply bonded complex $Re_2Cl_4(PMe_3)_4$[2] with $Cl_2(g)$ (or with the use of $PhI{\cdot}Cl_2$, a solid chlorine equivalent) in the hope of obtaining a compound of stoichiometry $Re_2Cl_6(PMe_3)_4$. This target molecule would be of interest with regard to a compound of similar stoichiometry, namely $Re_2Cl_6(dppe)_2$, which was reported several years ago by Walton and co-workers.[3] This compound is quite unusual in that there is no Re–Re bond and hence it would have been interesting to see if $Re_2Cl_6(PMe_3)_4$ could adopt a similar structure. However, we have found that the reaction between $Re_2Cl_4(PMe_3)_4$ and $Cl_2(g)$ yields 1,3,6-$Re_2Cl_5(PMe_3)_3$ (**1**) (an explanation of our numbering system will follow shortly). When the same reaction is carried out in the presence of PMe_3, we obtained a different isomer, namely 1,2,7-$Re_2Cl_5(PMe_3)_3$ (**2**).

The numbering system that we are employing here to distinguish the two isomers is as follows. (1) Place the Re_2 unit within a cube of ligands and number the latter in a clockwise direction as shown below:

(1) (a) Agaskar, P. A.; Cotton, F. A.; Dunbar, K. R.; Falvello, L. R.; O'Connor, C. J. *Inorg. Chem.* **1987**, *26*, 4051. (b) Canich, J. A. M.; Cotton, F. A.; Dunbar, K. R.; Falvello, L. R. *Inorg. Chem.* **1988**, *27*, 804. (c) Cotton, F. A.; Dunbar, K. R. *Inorg. Chem.* **1987**, *26*, 1305.
(2) (a) Ebner, J. R.; Walton, R. A. *Inorg. Chem.* **1975**, *14*, 1987. (b) Root, D. R.; Blevins, C. H.; Lichtenberger, D. L.; Sattelberger, A. P.; Walton, R. A. *J. Am. Chem. Soc.* **1986**, *103*, 953.
(3) Jaecker, J. A.; Robinson, W. R.; Walton, R. A. *J. Chem. Soc., Dalton Trans.* **1975**, 698.

0020-1669/90/1329-5143$02.50/0