density from the affected Si–O bonds.[10] A similar situation apparently applies here.

The five-coordinated anionic phenylgermanates represent new substances. Their synthesis was accomplished by following the reaction used in obtaining analogous methylgermanates reported in the accompanying paper[2] and represents the first comprehensive study of phenyl-containing pentacoordinated germanates. These substances are among the most stable five-coordinated germanates. The derivatives **1–3** all maintain their integrity in contact with water. However, in forming **4**, it was necessary to change the cation from Et_3NH^+ to Ph_4As^+ to achieve hydrolytic stability. It was unfortunate that neither the mixed-ligand derivative **4** nor **5**, containing a saturated thio ring system, was amenable to X-ray analysis. The latter would have provided an example of the influence of structural effects due to ring saturation. So far, all X-ray structures of anionic five-coordinated germanates encompass only unsaturated rings.[16]

Comparisons with Related Main-Group 4 (14) and 5 (15) Element Compounds. Table VI lists phenyl-substituted five-coordinated spirocyclic derivatives of main-group 4 (14) and 5 (15) elements and their structural displacement from the TBP toward the RP.

It is seen that the heavier element in each main group resides in a more RP structure when the ligand environment is the same, i.e., comparing germanate, **1**, with silicate, **6**, and arsorane, **9**, with phosphorane, **8**. This trend has been observed more generally with main group 5 (15) five-coordinated compounds,[6,7] i.e., that the displacement toward the RP structure follows the order Sb > As > P for like ligands. The latter displacement in the group 4 (14) series[34,35] has been discussed in terms of the relaxation of bond electron pair repulsions associated with less electronegative central atoms, a factor that favors the relatively higher energy RP.

Comparison of the structural displacements of the phenyl derivatives containing the tetrachlorocatecholate ligand (**3**, **10–13**) in Table VI shows a leveling effect. They all are nearly RP, ranging from a displacement of 85.2% for the germanium derivative, **3**, to 94% for the phosphoranes, **11** and **12**. Apparently, the electron-withdrawing effect associated with the presence of multiple ring chlorine atoms sufficiently reduces central atom–ligand bond electron pair repulsions to allow a near-RP structure in each case.

The most TBP structure listed, the silicate, **14**, exhibits hydrogen bonding between the Si–O bonds and the Et_3NH^+ group, a factor favoring the RP.[9,10,12,23] However, it is felt that the presence of the electron-donating[9,10] and steric properties[10] of the *tert*-butyl groups residing on the ring, both factors conducive to the formation of a TBP, is causative in leading to its structural form.[10]

Acknowledgment. The support of this research by the National Science Foundation (Grant No. CHE8205411) is gratefully acknowledged. We also thank the University of Massachusetts Computing Center for generous allocation of computer time.

Registry No. 1, 99901-34-5; 2, 99901-36-7; 3, 99901-38-9; 4, 99901-40-3; 5, 99901-42-5; $PhGeCl_3$, 1074-29-9; $[Et_4N]Cl$, 56-34-8; $Ph_3P{=}O{\cdot}C_6Cl_4(OH)_2$, 22400-36-8; $[Ph_4As]Cl$, 507-28-8; disodium ethanedithiolate, 23851-16-3.

Supplementary Material Available: Listings for **1–3**, respectively, of anisotropic thermal parameters (Tables S1–S3), hydrogen atom parameters (Tables S4–S6), additional bond lengths and angles (Tables S7–S9), and observed and calculated structure factors (44 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry,
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Synthesis and Characterization of Pd(II) and Pt(II) Complexes of Me_3MCH_2SeR (M = Si, Ge; R = Me, Ph) and Crystal Structures of *trans*-$(Me_3SiCH_2SeMe)_2PdCl_2$ and *trans*-$(Me_3GeCH_2SeMe)_2PtCl_2$

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Six complexes of the general formula $(Me_3MCH_2SeR)_2M'Cl_2$ (M = Si, Ge; R = Me, Ph; M′ = Pd, Pt) have been prepared. Spectroscopic results suggest that the complexes have trans geometry, which is confirmed by the single-crystal X-ray structure determination of two of them. The crystals of $(Me_3SiCH_2SeMe)_2PdCl_2$ (**1**) are orthorhombic, *Pbca*, with $a = 6.492$ (4) Å, $b = 11.438$ (7) Å, $c = 27.247$ (15) Å, $Z = 4$, and $R = 0.0249$. The crystals of $(Me_3GeCH_2SeMe)_2PtCl_2$ (**2**) are also orthorhombic, *Pbca*, with $a = 6.451$ (1) Å, $b = 11.543$ (2) Å, $c = 27.457$ (5) Å, $Z = 4$, and $R = 0.0431$. Compounds **1** and **2** are isostructural, and the configuration around selenium is pyramidal while around palladium or platinum it is square-planar. In solution, the molecules display pyramidal inversion at selenium.

Introduction

The neopentyl groups Me_3MCH_2 (M = C, Si, Ge, Sn) have been used as ligands in transition-metal complexes.[1] Their reactivities toward iodide and ethoxide ions,[2] their electronic effects in organometallic sulfides,[3] and their group VA (group 15[38]) compounds have been investigated.[4] Many palladium(II) and platinum(II) complexes have been prepared for the primary purpose of studying the pyramidal inversion at sulfur or selenium by dynamic NMR spectroscopy.[5-7] Recently, this work has been extended to include complexes of selenium carbonyls.[8-10] In a previous paper[11] we described the synthesis and characterization

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Table I. Far-Infrared and Raman Spectra (cm^{-1}) of *trans*-$(Me_3MCH_2SeR)_2M'Cl_2$ Species (M = Si, Ge; R = Me, Ph; M′ = Pd, Pt)

complex	M′–Cl(sym) (Raman)	M′–Cl(asym) (IR)	M′–Se(sym) (Raman)	M′–Se(asym) (IR)
$(Me_3SiCH_2SeMe)_2PdCl_2$	297 vs	352 vs	169 m	240 m
$(Me_3SiCH_2SePh)_2PdCl_2$	305 vs	345 vs	164 m	223 m
$(Me_3GeCH_2SePh)_2PdCl_2$	295 vs	347 s	163 w	213 m
$(Me_3SiCH_2SeMe)_2PtCl_2$	327 s (331)[b]	337 vs (340)[b]	175 m (176)[b]	240 m (225)[b]
$(Me_3SiCH_2SePh)_2PtCl_2$	319 m	321 vs	165 mw	238 m
$(Me_3GeCH_2SeMe)_2PtCl_2$	320 m	338 s	*c*	246 m

[a] Symmetric vibrations are Raman-active while asymmetric vibrations are infrared-active. Key: s, strong; vs, very strong; m, medium; mw, medium weak; w, weak. [b] Data for *trans*-$(Me_3Se)_2PtCl_2$ taken from ref 17 shown in parentheses. [c] Not observed.

Table II. ^{13}C, ^{77}Se, and ^{195}Pt NMR Data[a] for the Complexes $(Me_3MCH_2SeR)_2M'Cl_2$ (M = Si, Ge; R = Me, Ph and M′ = Pd, Pt)

	$\delta(^{13}C)$						
complex	Me–M	CH	SeMe	SePh	$\delta(^{77}Se)$	$J_{^{77}Se-^{195}Pt}$, Hz	$\delta(^{195}Pt)$
$(Me_3SiCH_2SeMe)_2PdCl_2$	−0.74	15.46	18.22		138.01, 138.36		
$(Me_3SiCH_2SePh)_2PdCl_2$	−0.82	18.27		129.43, 132.09[b]	266.75, 269.43		
$(Me_3GeCH_2SePh)_2PdCl_2$	−0.90	17.65		129.44, 132.12[b]	275.21, 277.84		
$(Me_3SiCH_2SeMe)_2PtCl_2$	−0.77	15.20	17.74		136.62, 137.28	355.19, 354.23	1379.78, 1381.87
$(Me_3SiCH_2SePh)_2PtCl_2$	−0.97	20.16		127.38, 129.42, 130.24, 131.98	264.91, 265.26	578.26, 570.61	1219.22, 1220.39
$(Me_3GeCH_2SeMe)_2PtCl_2$	−0.99	15.08	17.02		145.91, 146.43	354.18, 352.22	1371.26, 1374.01

[a] The chemical shifts are to low field of Me_4Si, high field of Me_2Se, and high field of 64.200 MHz for the ^{13}C, ^{77}Se, and ^{195}Pt NMR spectra, respectively. [b] Peaks are slightly broad because two peaks are close together in these positions.

Table III. Crystallographic Data for Compounds **1** and **2**

	1	**2**
a, Å	6.492 (4)	6.451 (1)
b, Å	11.438 (7)	11.543 (2)
c, Å	27.274 (15)	27.457 (5)
V, $Å^3$	2025 (2)	2044.6 (6)
cryst syst	orthorhombic	orthorhombic
space group	*Pbca*	*Pbca*
M_r	539.4	717.09
mol formula	$PdSe_2Cl_2Si_2C_{10}H_{28}$	$PtSe_2Ge_2Cl_2C_{10}H_{28}$
Z	4	4
ρ_c, g cm^{-3}	1.769	2.329
ρ_o, g cm^{-3}	1.773	
color	orange-brown	yellow
cryst dimens, mm	0.18 × 0.18 × 0.30	0.11 × 0.17 × 0.20
abs coeff μ, cm^{-1}	43.99	131.18
min abs cor	1.961	3.727
max abs cor	2.138	7.901
total no. of reflcns measd	2112 (+*h*,+*k*,+*l*)	2140 (+*h*,+*k*,+*l*)
no. of unique data used	1220 [$I > 3\sigma(I)$]	1016 [$I > 3\sigma(I)$]
no. of params (NP)	79	79
$R = \sum \lvert\lvert F_o\rvert - F_c\rvert\rvert / \sum\lvert F_o\rvert$	0.0249	0.0431
$R_{wF} = [\sum w\Delta^2/\sum wF_o^2]^{1/2}$	0.0301	0.0457
max, shift/error in final cycle	0.05	0.08
$\nabla\rho(\max)$, e $Å^{-3}$	0.3	1.2

of asymmetric selenides of the type Me_3MCH_2SeR, where M = Si, Ge, or Sn and R = Me or Ph. We now report on the synthesis and low-frequency infrared, Raman, and ^1H, ^{13}C, ^{77}Se, and ^{195}Pt NMR spectroscopy of complexes formed with platinum and palladium as well as the X-ray crystal structure determination of two of the complexes. Although similar compounds are known, no X-ray structure determination of Pt(II) complexes with selenium ligands has been reported. The only structure found was that of a bridging dimethyl diselenide complex with two octahedral platinum centers.[12]

Experimental Section

Starting Materials. All of the $(CH_3)_3MCH_2SeR$ ligands were prepared as previously described.[11] The compounds Na_2PdCl_4 (Alfa) and K_2PtCl_4 (Aldrich) were available commercially. All solvents were dried by conventional methods.

Preparations. Typically, the ligand $(CH_3)_3MCH_2SeR$ (ca. 4 mmol) and Na_2PdCl_4 or K_2PtCl_4 (ca. 2 mmol) were placed in a 50-mL round-bottom flask along with a 1:1 solution of ethanol and water (ca. 20 mL) and then warmed and stirred for 2 h. The solvent was removed in vacuo, and the residue was washed with water and filtered. The product was then dissolved in CH_2Cl_2 and filtered. After evaporation of the solvent the product was redissolved in ethanol and crystals formed by slow evaporation. The complexes were soluble in nonpolar solvents such as hexane and methylene chloride and only slightly soluble in polar solvents such as ethanol. The compounds so formed are as follows: **$(Me_3SiCH_2SeMe)_2PdCl_2$ (1)**: orange-brown; mp 97 °C; 55% yield. Anal. Calcd: C, 22.24; H, 5.19. Found: C, 22.29; H, 5.31. **$(Me_3SiCH_2SePh)_2PdCl_2$**: red-brown; mp 92 °C; 74% yield. **$(Me_3GeCH_2SePh)_2PdCl_2$**: brown; mp 84 °C; 66% yield. **$(Me_3SiCH_2SePh)_2PtCl_2$**: yellow; mp 93 °C; 63% yield. Anal. Calcd: C, 19.11; H, 4.49. Found: C, 19.20; H, 4.55. **$(Me_3SiCH_2SePh)_2PtCl_2$**: yellow; mp 143 °C; 96% yield. Anal. Calcd: C, 31.92; H, 4.29. Found: C, 32.27; H, 4.45. **$(Me_3GeCH_2SeMe)_2PtCl_2$ (2)**: yellow; mp 91 °C; 90% yield.

Attempts to prepare the corresponding tin analogues by the same method resulted in the mixture turning black even when the reaction was carried out at 0 °C. The reduction to Pt metal was confirmed by the formation of the red ketoxime complex L_2Pt where L = 2-pyridyl 2-thienyl ketoxime.[13]

The density of **1** was measured by the flotation method in aqueous $ZnCl_2$. Compound **2** was found to sink in MeI before dissolving, thus indicating a density greater than 2.279 g cm^{-3}.

Spectra. The far-infrared spectra (525–32 cm^{-1}) were recorded as Nujol mulls with the complexes squeezed between polyethylene plates on a Perkin-Elmer 180 spectrometer. The Raman spectra (500–100 cm^{-1}) were recorded on solid samples with the 488 nm argon line of a Model 164 argon ion laser in conjunction with a Spectra-Physics Model 700 spectrometer. The vibrational spectroscopic data obtained for the $M'Se_2Cl_2$ moieties along with the assignments are listed in Table I.

The ^1H NMR spectra were recorded on a Bruker CPX100 spectrometer. The ^{77}Se and ^{13}C NMR spectra were obtained at 57.237 and 75.648 MHz, with Me_2Se and Me_4Si used as external standards, respectively. The ^{195}Pt NMR spectra were obtained for three of the complexes at 64.26264 MHz by using an arbitrary frequency reference at 64.200 MHz. $CDCl_3$ was used as a solvent and served as an internal deuterium lock and as an internal reference at 77 ppm from Me_4Si for ^{13}C NMR spectra. All spectra were recorded on a General Electric GN 300 spectrometer at Wayne State University. The multinuclear NMR data are listed in Table II.

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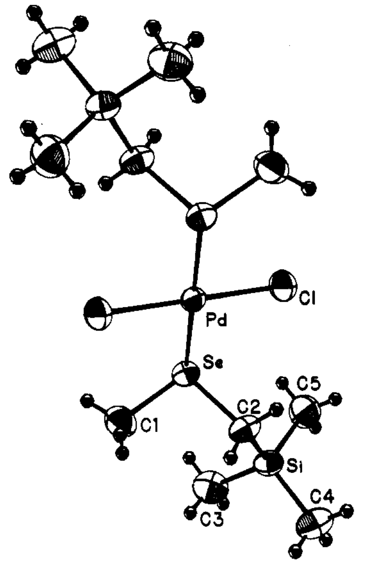

Figure 1. ORTEP drawing of $(Me_3SiCH_2SeMe)_2PdCl_2$. The thermal ellipsoids are drawn at 50% probability except for H atoms, which are at an arbitrary level. Unlabeled atoms are related to the labeled ones by a center of inversion.

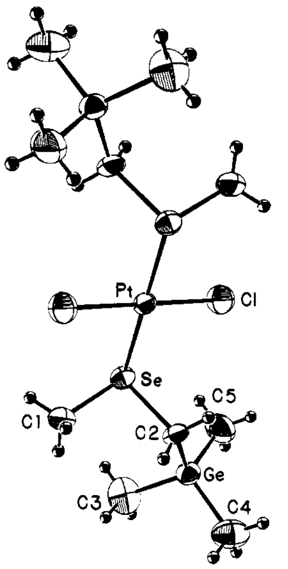

Figure 2. Perspective view of $(Me_3GeCH_2SeMe)_2PtCl_2$.

Table IV. Final Fractional Coordinates and Isotropic Thermal Parameters for Non-Hydrogen Atoms of Compounds **1** and **2** with Standard Deviations in Parentheses

atom	x	y	z	10^3U_{eq},[a] Å^2
		Compound **1**		
Pd	0.0	0.0	0.0	36.0 (3)
Se	−0.21950 (8)	0.07759 (4)	0.06435 (2)	41.2 (3)
Cl	0.2142 (2)	−0.0528 (1)	0.0632 (1)	56 (1)
Si	−0.1224 (2)	0.2241 (1)	0.1613 (1)	46 (1)
C(1)	−0.4246 (9)	0.1785 (5)	0.0338 (2)	62 (4)
C(2)	−0.0536 (8)	0.1998 (4)	0.0950 (2)	48 (3)
C(3)	−0.4043 (9)	0.2424 (6)	0.1679 (2)	68 (3)
C(4)	0.0124 (10)	0.3598 (5)	0.1811 (2)	50 (4)
C(5)	−0.0303 (10)	0.0938 (5)	0.1966 (3)	52 (4)
		Compound **2**		
Pt	0.0	0.0	0.0	33.6 (4)
Se	−0.2199 (3)	0.0766 (2)	0.0636 (1)	38 (1)
Cl	0.2109 (8)	−0.0556 (4)	0.0636 (2)	56 (3)
Ge	−0.1263 (3)	0.2254 (2)	0.1617 (1)	41 (1)
C(1)	−0.4277 (28)	0.1772 (15)	0.0340 (7)	56 (12)
C(2)	−0.0571 (26)	0.2025 (14)	0.0929 (7)	52 (11)
C(3)	−0.4291 (29)	0.2391 (21)	0.1695 (7)	76 (15)
C(4)	−0.0055 (31)	0.3672 (16)	0.1821 (8)	75 (14)
C(5)	−0.0293 (31)	0.0910 (22)	0.1984 (8)	82 (16)

[a] U_{eq} for non-hydrogen atoms is calculated from the refined anisotropic thermal parameters: $U_{eq} = {}^1/_3 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$.

Table V. Bond Lengths (Å) and Angles (deg) for Compounds **1** and **2**, with Standard Deviations in Parentheses

bond lengths		bond angles[a,b]	
		Compound **1**	
Pd–Se	2.429 (1)	Cl–Pd–Cl′	180.0
Pd–Cl	2.295 (1)	Se–Pd–Se′	180.0
Se–C(1)	1.949 (5)	Se–Pd–Cl	84.8 (1)
Se–C(2)	1.952 (4)	C(1)–Se–Pd	108.0 (2)
Si–C(2)	1.884 (5)	C(2)–Se–Pd	104.3 (1)
Si–C(3)	1.851 (5)	C(1)–Se–C(2)	97.8 (2)
Si–C(4)	1.868 (5)	Se–C(2)–Si	112.7 (2)
Si–C(5)	1.872 (6)	C(2)–Si–C(3)	110.1 (2)
		C(2)–Si–C(4)	107.5 (2)
		C(2)–Si–C(5)	107.5 (3)
		C(3)–Si–C(4)	109.5 (3)
		C(3)–Si–C(5)	110.8 (3)
		C(4)–Si–C(5)	111.0 (3)
		Compound **2**	
Pt–Se	2.418 (2)	Cl–Pt–Cl′	180.0
Pt–Cl	2.305 (5)	Se–Pt–Se′	180.0
Se–C(1)	1.952 (17)	Se–Pt–Cl	84.3 (1)
Se–C(2)	1.966 (16)	C(1)–Se–Pt	108.6 (6)
Ge–C(2)	1.959 (19)	C(2)–Se–Pt	104.6 (5)
Ge–C(3)	1.972 (19)	C(1)–Se–C(2)	95.6 (8)
Ge–C(4)	1.928 (20)	Se–C(2)–Ge	111.9 (9)
Ge–C(5)	1.953 (23)	C(2)–Ge–C(3)	110.0 (8)
		C(2)–Ge–C(4)	107.1 (8)
		C(2)–Ge–C(5)	108.5 (9)
		C(3)–Ge–C(4)	109.7 (10)
		C(3)–Ge–C(5)	109.0 (10)
		C(4)–Ge–C(5)	112.5 (10)

[a] Primes denote the symmetry equivalent positions $-x, -y, -z$. [b] Cl–M′–Cl′ and Se–M′–Se angles are symmetry-fixed at 180.0°.

Structure Determination

X-ray diffraction results for $(Me_3SiCH_2SeMe)_2PdCl_2$ (**1**) and $(Me_3GeCH_2SeMe)_2PtCl_2$ (**2**) were collected on a Syntex $P2_1$ diffractometer using a highly oriented graphite monochromator by the procedures already described.[14] A summary of crystal data is given in Table III. The following parameters were common in each case: Mo Kα radiation, $\lambda = 0.71069$ Å; 2θ range 4–50°; scan speed 2.02–4.88° min^{-1}; scan width from K$\alpha_1 - 1°$ to K$\alpha_2 + 1°$; background time/scan time 0.5; data collection temperature 22 °C.

Well-shaped prismatic crystals of **1** and **2** were mounted on a glass fiber. During data collection, the intensity of the three monitor reflections decreased by approximately 0.5 and 3.5% for **1** and **2**, respectively, and appropriate scaling factors were applied. Each set of data was corrected for Lorentz and polarization effects, and analytical absorption corrections were applied.

For both **1** and **2**, the space group *Pbca* (No. 61) was established from the systematic absences ($0kl$, $k = 2n + 1$; $h0l$, $l = 2n + 1$; $hk0$, $h = 2n + 1$). The similar crystal morphologies, cell dimensions, and identical space groups suggested that the two compounds might have isomorphous structures, and this was confirmed by the final refinements. $Z = 4$ in the space group *Pbca* required the M′ atom to be present at the center of inversion. In the case of **1**, the position of the selenium atom was obtained from a sharpened Patterson synthesis, and the remaining atoms were revealed by refinement and a subsequent difference map. The same set of coordinates was used for **2**, because the two structures are isomorphous. Complete anisotropic refinement minimizing $\sum w(|F_o| - |F_c|)^2$ converged at $R = 0.0291$ and $R_{wF} = 0.0352$ for **1** and $R = 0.0489$ and $R_{wF} = 0.0499$ for **2**. The hydrogen atoms were subsequently included in idealized positions with C–H = 0.95 Å, and thermal parameters were assigned values exceeding those for the appropriate carbon atoms by $0.01U$ (Å^2). The structures were then refined to convergences with the final values $R = 0.0249$ and $R_{wF} = 0.0301$ for **1** and $R = 0.0431$ and $R_{wF} = 0.0457$ for **2** for 1220 and 1016 unique "observed" reflections, respectively. A weighting scheme of the form $w = 1/[\sigma^2(F) + pF^2]$ was

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utilized with final *p* values of 0.002 and 0.0001 for **1** and **2** respectively. Computer programs and sources of scattering factors were as referred to elsewhere.[14] The final atomic coordinates and isotropic thermal parameters for non-hydrogen atoms are listed in Table IV with the important bond lengths and angles in Table V. The molecular structures of the two compounds are displayed in Figures 1 and 2.

Results and Discussion

The above reactions are represented by

$$2Me_3MCH_2SeR + \underset{\displaystyle K_2PtCl_4}{\overset{}{Na_2PdCl_4}}\ \text{or} \xrightarrow{EtOH/H_2O} (Me_3MCH_2SeR)_2M'Cl_2 + 2NaCl \ \text{or}\ 2KCl$$

$$M = Si, Ge;\ R = Me, Ph;\ M' = Pd, Pt$$

When M = Sn the corresponding complexes are not obtained. It is reasonable to assume that the Sn–C bond is cleaved because similar cleavage occurs in the reactions of Me_2SnCH_2I with the sodium salts of transition-metal carbonyls.[15,16]

The high-frequency regions of the infrared and Raman spectra are not of great interest except to confirm that they are consistent with those of the free ligands. The low-frequency region (below 500 cm^{-1}) can be utilized to describe the geometry of coordination at the central metal atom.[17] For cis molecules (C_{2v}), all modes are active in both the infrared and Raman effects, while for trans molecules (D_{2h}), the symmetric modes are only Raman-active and the asymmetric modes are only infrared-active. The metal–ligand and metal–chlorine vibrations are listed in Table I. The results are in agreement with data obtained for the trans Me_2Se and Me_2S complexes of palladium and platinum(II) halides.[17] In general, the M′–Se symmetric stretch is observed with difficulty because of considerable background noise. However, it is clear that the expected exclusivity is observed, and there is little change in the positions of the M′–Cl and M′–Se frequencies as a result of the presence of silicon or germanium in the ligands.

The single-crystal X-ray structure determination confirms the trans structure of $[(CH_3)_3SiCH_2SeCH_3]_2PdCl_2$ (**1**) and $[(CH_3)_3GeCH_2SeCH_3]_2PtCl_2$ (**2**). The two compounds exist as discrete and centrosymmetric molecules as shown in Figures 1 and 2. The bonding at M′ (Pd or Pt) is approximately square-planar[18] with a Se–M′–Cl angle of 84.8 (1) and 84.3 (1)° for **1** and **2**, respectively, and with the $M'Se_2Cl_2$ group lying in one plane. The asymmetry in the groups attached to selenium in the ligand may have contributed to the rather chainlike character of the molecule, which is reflected in the fact that one of the cell dimensions *c* is much larger than *a* or *b*.

The pyramidal coordination about selenium is very similar in both compounds and indicates a pseudotetrahedral arrangement with a stereochemically active lone pair occupying the fourth position. The angles C(1)–Se–Pd = 108.0 (2)°, C(2)–Se–Pd = 104.3 (1)°, and C(1)–Se–C(2) = 97.8 (2)° for compound **1** and the angles C(1)–Se–Pt = 108.6 (6°), C(2)–Se–Pt = 104.6 (5)°, and C(1)–Se–C(2) = 95.6 (8)° for compound **2** are all less than the tetrahedral angle of 109.5° but on average are much closer to it than to 90°. This indicates that the repulsive forces between the lone pair and bonding pairs of electrons result in the observed reduction of these angles, which would be in agreement with VSEPR (valence shell electron pair repulsion) theory.[19]

The Pd–Se bond length of 2.429 (1) Å is only slightly less than the sum (2.45 Å) of the Pauling covalent radii, which are 1.31 (for square-planar[19] Pd(II)) and 1.14 Å (for tetrahedral Se), and suggests therefore that π-bonding is not significant. Other Pd–Se bond lengths have been determined to be 2.429 (7) Å in *trans*-dichlorobis(diethyl selenide)palladium(II)[21] and 2.40 (1) Å in *cis*-dichloro-(1,2-bis(isopropylseleno)ethane)palladium (II).[22] This Pd–Se bond length falls between reported bond lengths of Pd–S = 2.310 (3) Å and Pd–Te = 2.606 (1) Å.[23] The determined Pd–Cl bond length of 2.295 (1) Å is close to the sum (2.30 Å) of the Pauling covalent radii,[20] (0.99 Å for chlorine) and agrees well with the values of 2.266 (9) Å in $(Et_2Se)_2PdCl_2$[21] and 2.29 Å in $(Me_2SO)_2PdCl_2$.[24] The Se–C bond lengths[21] and the Si–C distances are in good agreement with determined values.[23,25–27]

The Pt–Se bond length of 2.418 (1) Å is also slightly less than that of the sum (2.45 Å) of the Pauling covalent radii (1.31 Å for square-planar[20] Pt(II)), so π-bonding is again probably not important. As mentioned earlier, the only crystallographically determined Pt–Se bond length was of a bridging diselenide to two platinum centers[12] (Pt–Se = 2.590 (7) Å). However, the determined Pt–Se bond length (2.418 (1) Å) is slightly longer as expected than that reported for the Pt–S bond (2.32,[28] 2.327 (5), 2.408 (4),[29,30] and 2.355 (2) Å[31]) and slightly shorter than the only determined Pt–Te bond length of 2.575 (1) Å in the double salt $[Pt\{PhTe(o\text{-}PPh_2(C_6H_4)\}_2][Pt(SCN)_4]\cdot 2DMF$.[32] The determined Pt–Cl bond length of 2.305 (5) Å is close to the sum of the Pauling covalent radii[20] and agrees well with the literature value of 2.33 (1) Å in *trans*-$[(PEt_3)_2PtCl_4]$.[34] The Se–C bond lengths agree with those determined for the palladium complex and with those determined for *trans*-$(Et_2Se)_2PdCl_2$.[21] The Ge–C bond lengths agree well with a recently determined Ge–C bond length of 1.92 (2) Å in CH_3GeI_3.[35]

It is interesting to note that there is a "tilt" in the C(1)–Se–C(2) moiety with the C(1) atom close to the plane of the $M'Se_2Cl_2$ group. It would be convenient to relate this to a packing effect resulting from the asymmetric substitution on Se. However, there is essentially the same "tilt" in the $(Et_2Se)_2PdCl_2$ structure,[21] where the substitution is symmetric, as well as the related tellurium compound, *trans*-$[(Me_3SiCH_2CH_2CH_2)_2Te]_2Pd(SCN)_2$. In this latter compound[23] it was suggested that the degree of tilt was in some way associated with a repulsive interaction between tellurium and the carbon atom of the SCN group. This obviously cannot be the case in **1** or **2**.

A common factor in all of these structures is the clear evidence of a stereochemically active lone pair on selenium (or tellurium). If it is assumed that the M′–Se bond is along the *x* axis, then maximum separation between the Se lone pair and the chlorine lone pairs is achieved by a configuration in which the selenium lone pair is in the *xz* plane below the *xy* plane with the two carbon atoms above the *xy* plane. This is approximately the chosen configuration with the exception of the slight tilt. The position of the selenium lone pair in the *xz* plane places it in closest proximity to any electron density about M′ associated with the d_{z^2} orbital. Any shift out of the plane will increase this distance, and a simple model suggests that a tilt of 20–30° would lead to a reasonable compromise that would minimize all lone-pair repulsions. The tilt brings the CH_3 group (or one of the CH_2 groups in the case of the other two structures) into closer proximity with one of the Cl atoms, which as a result is bent away from 90°. The

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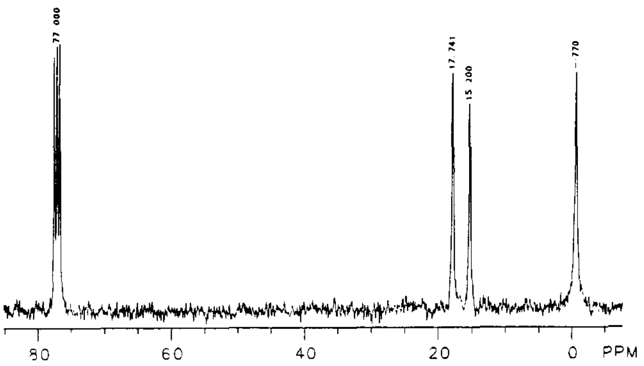

Figure 3. ^{13}C NMR spectrum of $(Me_3SiCH_2SeMe)_2PtCl_2$.

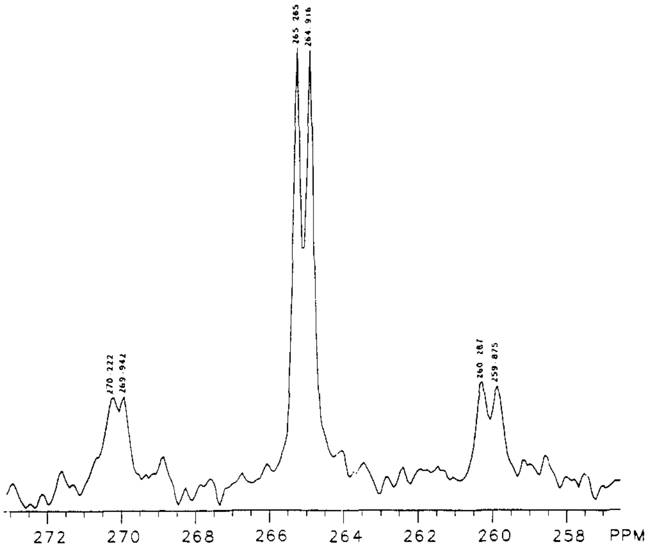

Figure 4. ^{77}Se NMR spectrum of $(Me_3SiCH_2SePh)_2PtCl_2$.

observed Cl′–M′–Se angle (Cl′ is generated from Cl by inversion) is 95.2 (1) and 95.7 (1)° when M′ = Pd and Pt, respectively. In compounds **1** and **2** the tilt is such as to bring the less bulky group towards a Cl atom. For example in compound **1** the C(1)–Cl′ nonbonding distance is 3.307 Å and the C(2)–Cl distance is 3.480 Å. Thus, even though the Cl′ atom is moving away from the CH_3 group and Cl is forced toward the CH_2 group of $CH_2M'Me_3$, the C–Cl distance is still longer to the bulky group.

The above solid-state data from vibrational spectroscopy and X-ray crystallography clearly indicate the trans structure of these complexes. To confirm their structure in solution, the ^1H, ^{13}C, ^{77}Se, and ^{195}Pt NMR spectra were recorded, and data are listed in Table II. A nuclear magnetic resonance study of inversion at sulfur and selenium atoms in similar complexes of Pd(II) and Pt(II) has been reported.[5] Variable-temperature studies of the methylene region of the ^1H NMR spectra were combined with line shape computations to not only establish the existence of interconversion between the (±) isomers and the meso form but also to obtain Arrhenius and activation parameters.[5] The variable-temperature spectra of the complexes studied herein were consistent with those reported earlier.[5] The ^{13}C NMR spectra are very similar to those of the free ligand,[11] while the ^{77}Se NMR spectra show doublets consistent with the presence of the two isomeric forms. With the platinum compounds, the satellites arising from $J_{^{77}Se-^{195}Pt}$ coupling are also observed. Figures 3 and 4 display the ^{13}C and ^{77}Se NMR spectra of $(Me_3SiCH_2SeMe)_2PtCl_2$ and $(Me_3SiCH_2SePh)_2PtCl_2$ as typical examples. Similarly the ^{195}Pt NMR spectra show the existence of two conformers in solution by the presence of closely placed doublets with an average splitting of 2 ppm. The values of the $^{77}Se-^{195}Pt$ coupling constants are the first we can find reported for trans complexes. Values in the range 33.5–291.4 Hz have been reported for a series of *cis* complexes containing bidentate selenium ligands,[36] while values in the range 234–607 Hz were reported for $[PtX_3SeMe_2]^-$ species, where X = I, Br, and Cl.[37] The large shift when a phenyl group replaces a methyl group in the selenium-containing ligand contrasts with the relatively unchanged value when germanium replaces silicon.

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Registry No. **1**, 100020-00-6; **2**, 100020-04-0; $(Me_3GeCH_2SePh)_2PdCl_2$, 100020-01-7; $(Me_3SiCH_2SeMe)_2PtCl_2$, 100020-02-8; $(Me_3SiCH_2SePh)_2PtCl_2$, 100020-03-9; $(Me_3SiCH_2SePh)_2PdCl_2$, 62482-95-5; Na_2PdCl_4, 13820-53-6; K_2PtCl_4, 10025-99-7.

Supplementary Material Available: Tables of anisotropic thermal parameters, hydrogen atom coordinates and isotropic thermal parameters, and observed and calculated structure factors and a unit cell packing diagram (17 pages). Ordering information is given on any current masthead page.

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