Contribution from the Research Laboratories,
Eastman Kodak Company, Rochester, New York 14650

New Dialkyl Tellurides. Synthesis and Ligand Properties of $Te((CH_2)_nSi(CH_3)_3)_2$ ($n = 1, 3$) and Crystal Structure of *trans*-$Pd(SCN)_2[Te(CH_2CH_2CH_2Si(CH_3)_3)_2]_2$

HENRY J. GYSLING,* HENRY R. LUSS, and DOUGLAS L. SMITH

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The dialkyl tellurides $Te((CH_2)_nSi(CH_3)_3)_2$ ($n = 1, 3$) have been prepared by alkylation of Na_2Te with the corresponding alkyl chlorides. Coordination complexes of these two new, somewhat air-sensitive, liquid ligands with palladium chloride and thiocyanate (i.e., $PdX_2[Te((CH_2)_nSi(CH_3)_3)_2]_2$) have been prepared. The complexes have a trans geometry on the basis of their infrared and Raman spectra. Infrared and ^1H NMR spectra support Pd–SCN bonding modes for the thiocyanate complexes in the solids and $CHCl_3$ solutions. A single-crystal X-ray structure determination has confirmed the proposed structure of *trans*-$Pd(SCN)_2[Te(CH_2CH_2CH_2Si(CH_3)_3)_2]_2$. The square-planar complex contains two sulfur-bonded thiocyanates in a trans arrangement. The configuration at tellurium is pyramidal with a stereochemically active lone pair of electrons at the fourth corner of a tetrahedron. There is probably some π bonding between sulfur and palladium but not between tellurium and palladium. The crystals are monoclinic, $P2_1/c$ with $a = 14.385$ (9) Å, $b = 13.122$ (4) Å, $c = 11.678$ (4) Å, $\beta = 91.34$ (2)°, $Z = 2$, and $d_m = 1.40$ g/cm^3. The structure was solved by the heavy-atom method and refined by block-diagonal least squares to $R = 0.082$ for 3173 observed reflections. The thiocyanate complexes retain the sulfur-bonding mode in $CHCl_3$ solution, but formation of some cis isomers is suggested by their infrared spectra.

Introduction

Although the organic chemistry of sulfur[1] and selenium[2] has been the subject of extensive investigation, the scope of reported organotellurium compounds is considerably less diverse.[3-5] Diaryl tellurides are generally quite stable solids (diphenyl telluride is, however, a liquid), but the lower dialkyl tellurides which have been reported are generally air-sensitive, foul-smelling liquids.[3-5] We have been interested in the synthesis of diorganotellurides and their use as ligands for various class b transition-metal ions. Coordination complexes with diaryl tellurides [e.g., $CuX(TeAr_2)_n$ (X = Cl, Br, I; n = 1–3),[6] $(TePh_2)Fe(CO)_3Br_2$,[7] $(TePh_2)_2Mn(CO)_3X$ (X = Cl, Br, I),[7] $HgX_2(TeAr_2)$,[8] $MX_2(TeAr_2)_2$ (M = Pd, Pt; X = Cl, Br)[9]], lower dialkyl tellurides [e.g., $MX_2(TeR_2)_2$ (X = Cl, Br, I; M = Pd, Pt; $R = CH_3, C_2H_5$),[10-14] $[HgX_2(Te(C_2H_5)_2)]_2$ (X = Cl, Br),[14] $TaX_5(Te(CH_3)_2)$ (X = Cl, Br),[15] $Ir(CO)_2Cl(Te(C_2H_5)_2)$,[16] $AgI(Te(CH_3)_2)_2$,[17] $(AgI)_2(Te(CH_3)_2)$[17]], aryl tellurides [e.g., $(\pi\text{-}C_5H_5)Ni[P(n\text{-}C_4H_9)_3](TeAr)$,[18] $(\pi\text{-}C_5H_5)M(TeAr)_2$ (M = Ti,[19] Zr,[19] Nb,[20] W[20])], and dimeric complexes with organotelluride bridges [e.g., $(\eta^7\text{-}C_7H_7)(CO)Mo(\mu\text{-}TeC_6H_5)_2Mo(CO)(\eta^7\text{-}C_7H_7)$,[21] $(\pi\text{-}C_5H_5)Ti(\mu\text{-}TeC_6H_5)_2Fe(NO)(CO)$,[22] $(\pi\text{-}C_5H_5)Nb(\mu\text{-}TeC_6H_5)Co(NO)_2$[22]] have been reported.

We report here the synthesis of two new dialkyl tellurides ($Te((CH_2)_nSi(CH_3)_3)_2$; n = 1,3), their incorporation as ligands in Pd(II) complexes, and the crystal structure of one of these new complexes, *trans*-$Pd(SCN)_2[Te(CH_2CH_2CH_2Si(CH_3)_3)_2]_2$.

Experimental Section

Reagents. (Chloromethyl)trimethylsilane (Pfaltz and Bauer), (3-chloropropyl)trimethylsilane (PCR Inc.), tellurium powder (Alfa/Ventron), and Na_2PdCl_4 (Alfa/Ventron) were purchased from the indicated commercial sources. $PdCl_2(NCC_6H_5)_2$[23] and $K_2Pd(SCN)_4$[24] were prepared by literature methods. Dichloromethane and chloroform were freshly distilled over phosphorus pentoxide. DMF was dried over $MgSO_4$ and then vacuum distilled. All other reagents were obtained from Eastman Organic Chemicals and used as received.

Preparation of $Te(CH_2CH_2CH_2Si(CH_3)_3)_2$. A suspension of 42.2 g (0.33 g-atom) of tellurium powder in a solution of 44.7 g (0.83 mol) of KBH_4 dissolved in 700 mL of 20% aqueous NaOH was refluxed in an argon atmosphere for 3 h in a two-neck round-bottomed Schlenk flask fitted with a reflux condenser and a dropping funnel, giving a pale yellow solution. To this solution (Na_2Te) was added a deaerated solution of 100 g (0.66 mol) of $ClCH_2CH_2CH_2Si(CH_3)_3$ in 800 mL of methanol, and the solution was refluxed for 20 h. The alcohol was then distilled off and the residual solution was extracted with three 500-mL portions of ethyl ether. The combined extracts were washed with water and dried over anhydrous $MgSO_4$, and the ether was distilled off, giving a pale orange liquid (113 g, 95.6%). The crude telluride was purified by vacuum distillation (bp 51 °C (3×10^{-3} mm)). Anal. Calcd for $C_{12}H_{30}Si_2Te$: C, 40.2; H, 8.4; Te, 35.6. Found: C, 40.2; H, 8.7; Te, 35.9.

The derivative $Te(CH_2Si(CH_3)_3)_2$ (bp 66–68 °C (3 mm)) was prepared by an analogous reaction with $ClCH_2Si(CH_3)_3$. Anal. Calcd for $C_8H_{22}Si_2Te$: C, 31.8; H, 7.3; Te, 42.2. Found: C, 31.5; H, 6.9; Te, 42.3.

Preparation of $PdCl_2[Te(CH_2CH_2CH_2Si(CH_3)_3)_2]_2$. To a solution of 1.6 g of Na_2PdCl_4 (5.0 mmol) in 75 mL of water was added a solution of 3.6 g (10.0 mmol) of $Te(CH_2CH_2CH_2Si(CH_3)_3)_2$ dissolved in 75 mL of methanol. The reaction solution was stirred at room temperature for 0.5 h, and the precipitated product was filtered, washed well with water, air-dried, and recrystallized from 1:1 hexane–methanol, giving 3.2 g (71.6%) of red needles (mp 70 °C). Anal. Calcd for $C_{24}H_{60}Cl_2PdSi_4Te_2$: C, 32.3; H, 6.8; Cl, 7.8; Pd, 11.9. Found: C, 32.3; H, 6.8; Cl, 7.8; Pd, 11.7.

Preparation of $PdCl_2[Te(CH_2Si(CH_3)_3)_2]_2$. To a solution of 2.3 g (6 mmol) of $PdCl_2(NCC_6H_5)_2$ in 150 mL of benzene was added 3.6 g (12.0 mmol) of $Te(CH_2Si(CH_3)_3)_2$. The solution color immediately lightened. The solution was stirred at room temperature for 0.5 h, and the solvent was removed under vacuum. Recrystallization of the residue from 1:1 hexane–methanol gave 2.6 g (56%) of red needles (mp 99 °C). Anal. Calcd for $C_{16}H_{44}Cl_2PdSi_4Te_2$: C, 24.6; H, 5.7; Cl, 9.1; Pd, 13.6. Found: C, 24.3; H, 5.5; Cl, 9.4; Pd, 13.3.

Preparation of $Pd(SCN)_2[Te(CH_2CH_2CH_2Si(CH_3)_3)_2]_2$. To a solution of 2.6 g (6.0 mmol) of $K_2Pd(SCN)_4$ in 250 mL of methanol was added 4.3 g (12.0 mmol) of $Te(CH_2CH_2CH_2Si(CH_3)_3)_2$. The reaction solution was stirred at room temperature for 0.5 h and then concentrated to 50 mL under vacuum and cooled to 0 °C, giving orange-red crystals which were recrystallized from 75 mL of 1:1 hexane–methanol (4.3 g (76%); mp 64 °C). Anal. Calcd for $C_{26}H_{60}N_2PdS_2Si_4Te_2$: C, 33.3; H, 6.4; N, 3.0; Pd, 11.3. Found: C, 33.3; H, 6.1; N, 2.9; Pd, 11.1. The derivative $Pd(SCN)_2[Te(CH_2Si(CH_3)_3)_2]_2$ was prepared by an analogous reaction, giving 4.4 g (88.7%) of red crystals (mp 143 °C). Anal. Calcd for $C_{18}H_{44}N_2PdS_2Si_4Te_2$: C, 26.2; H, 5.4; N, 3.4; Pd, 12.9; Te, 30.9. Found: C, 26.1; H, 5.4; N, 3.5; Pd, 12.7; Te, 31.0.

Physical Measurements. Microanalyses were done by the Analytical Sciences Division of the Kodak Research Laboratories. Infrared spectra were recorded on a Perkin-Elmer Model 621 spectrometer and calibrated with a polystyrene film. Solution integrated absorption intensities of the ν_{CN} bands were determined by Ramsay's method of direct integration.[25] Matched NaCl cells (0.15 mm) were used for these measurements with a fourfold wavenumber scale expansion. Spectra in the far-infrared region were recorded on a Nicolet Series 7000 Fourier transform infrared spectrometer.

Proton NMR spectra were recorded on a Bruker Model HX-90 spectrometer. Spectra of solutions containing $[Pd(SCN)_2(TeR_2)_2]$ complexes and the europium shift reagent $Eu(fod)_3\text{-}d_{27}$ (fod = 7,7-dimethyl-1,1,1,2,2,3,3-heptafluorooctane-4,6-dionato) were re-

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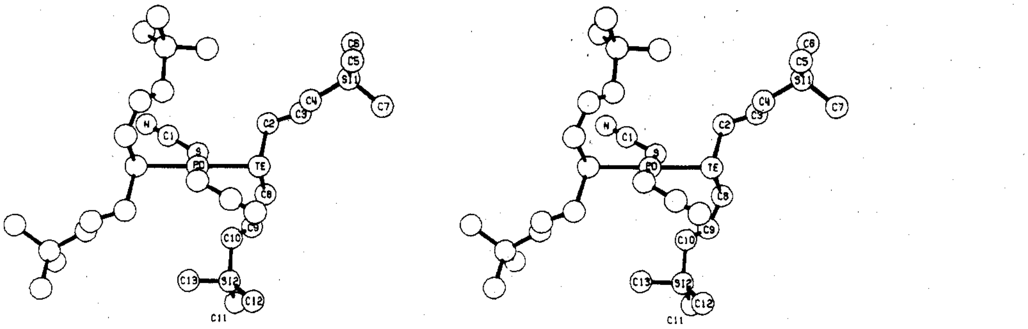

Figure 1. Stereoscopic view of the molecule with atomic labeling. C(X) is not shown but is located 1.25 Å to the right of C(10).

Table I. Summary of Crystal Data

$C_{26}H_{60}N_2PdS_2Si_2Te_2 = Pd(SCN)_2[Te(CH_2CH_2CH_2Si(CH_3)_3)_2]_2$
fw 938.9
monoclinic (λ(Mo Kα_1) 0.709 26 Å), 25 ± 2 °C

$a = 14.385\ (9)$ Å	$Z = 2$
$b = 13.122\ (4)$ Å	$d_m = 1.40$ g cm^{-3}
$c = 11.678\ (4)$ Å	$d_c = 1.414$ g cm^{-3}
$\beta = 91.34\ (2)°$	μ(Mo Kα) = 2.0 mm^{-1}
$V = 2204\ (2)$ Å^3	$F(000) = 936$

systematic absences: $h0l$, l odd; $0k0$, k odd
space group: $P2_1/c$ (C_{2h}^5)

corded by using a 1:2 molar ratio of Pd complex to Eu(fod)$_3$-d_{27}.

X-ray Measurements. Unit cell parameters and other pertinent data are given in Table I. The cell constants were determined by a least-squares refinement of 18 reflections at moderately high Bragg angles (Mo Kα_1) which were manually centered through very narrow vertical and horizontal slits on a Picker diffractometer.

Intensity data were collected by the θ–2θ scan technique with Zr-filtered Mo radiation on a card-controlled Picker four-circle diffractometer. The crystals were unstable to X-rays, and one crystal, 0.33 × 0.41 × 0.56 mm, was used to collect the intensities for $2\theta < 40°$ and a second crystal, 0.28 × 0.38 × 0.46 mm, was used for the interval $40° \leq 2\theta \leq 50°$. For the first crystal, the net intensity loss of a standard reflection after 2100 reflections was 45%. To check the uniformity of decomposition, we remeasured 79 reflections in the shell $10° \leq 2\theta \leq 15°$ which had originally been measured very early in the data collection. Comparison of the two sets of intensities indicated two populations of reflections—a set of 12 which, like the standard, had decreased about 45% and a larger set of 67 which had decreased only 27%. For the second crystal, the original standard decreased by 20% and a second standard decreased by 9% during the collection of about 1900 reflections. We were unable to determine a rule which would assign a given reflection to one of the standard reflection classes. Therefore, the observed variation of the standard reflections, weighted heavily toward the standard which represented the larger population, was used directly to place the data on an approximately common scale. The scaled intensities were corrected for background, attenuator, Lorentz, and polarization effects but not for absorption. The maximum possible error which could arise from the neglect of absorption is approximately 13%, but most errors are considerably less than this. The decomposition of the crystals and the neglect of absorption both introduce systematic error into the data. Of the 3890 unique reflections measured, 717 with $I < \sigma(I)$ were considered unobserved and were not used in further calculations.

Structure Determination. The structure was solved by the heavy-atom technique and refined by block-diagonal least squares[26] in which 4 × 4 and 9 × 9 blocks were used for atoms with isotropic and anisotropic thermal parameters, respectively. The function minimized was $\sum w(|F_o| - K|F_c|)^2$. The weights were defined as $w^{-1} = \sigma^2(F_o) + (0.03F_o)^2$ where $\sigma(F_o) = [(I + \sigma(I))/(Lp)]^{1/2} - F_o$. The usual agreement indices are $R = \sum||F_o| - K|F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - K|F_c|)^2/\sum wF_o^2]^{1/2}$. Atomic scattering factors were for neutral atoms.[27]

Initially, the presence of the heavy elements Pd and Te led us to assume a plausible density of 2.83 g cm^{-3} for four molecules per unit cell. We did not measure the density at that time because of the necessity to use organic solvents in which the crystals are very soluble. We were unable to obtain a satisfactory structure for $Z = 4$ and were led to postulate a different molecular species which would have a density of 1.75 g cm^{-3} for $Z = 4$. Since this was attainable with aqueous ZnCl$_2$, we measured the density and found it to have the amazingly low value of 1.40 g cm^{-3}. This meant that there were two centrosymmetric, trans molecules of the original species per unit cell and led to the successful solution of the structure.

Table II. Positional Parameters with Estimated Standard Deviations[a]

	10^4x	10^4y	10^4z
Pd	0	0	0
Te	220.3 (5)	903.8 (4)	1975.2 (5)
S	−107 (3)	−1509 (2)	1009 (3)
Si(1)	3140 (2)	1761 (3)	4652 (4)
Si(2)	−3250 (3)	1491 (3)	924 (5)
N	352 (8)	−3147 (10)	−311 (12)
C(1)	181 (8)	−2439 (10)	232 (11)
C(2)	1230 (8)	−119 (8)	2888 (10)
C(3)	1704 (9)	400 (10)	3877 (11)
C(4)	2342 (10)	1218 (11)	3550 (13)
C(5)	3919 (14)	2671 (17)	3867 (21)
C(6)	3941 (15)	860 (14)	5362 (18)
C(7)	2474 (14)	2434 (19)	5759 (22)
C(8)	−949 (8)	316 (9)	2902 (11)
C(9)	−1912 (17)	535 (19)	2323 (20)
C(10)	−2117 (20)	834 (20)	1280 (25)
C(X)	−2049 (18)	1425 (21)	2117 (24)
C(11)	−4226 (14)	1031 (14)	1670 (18)
C(12)	−3343 (15)	2840 (19)	1011 (25)
C(13)	−3330 (17)	953 (18)	−468 (22)

[a] Positional parameters are given as fractions of the unit cell. The occupancy parameters are 0.5 for C(10) and C(X).

The Patterson map was reinterpreted with Pd on the inversion center at the origin to yield the Te position. Electron density maps readily gave the positions of the S and Si atoms but only slowly revealed the locations of the remaining nonhydrogen atoms. In general, the electron densities of the lighter atoms were unusually low. These difficulties probably arose from a combination of factors, chief of which were the decomposition of the crystal during data collection, the low density of the crystal and consequent high thermal motion and disorder, and the domination of the scattering by Pd and Te which constituted about 75% of the scattering power of the crystal.

Refinement of the 19 atoms with isotropic temperature factors only reduced R to 0.19. Continued refinement with anisotropic temperature factors for the five heavy atoms and isotropic temperature factors for the lighter atoms quickly reduced R to 0.085. Some of the temperature factors were very large, and there were unreasonable bond lengths at C(9) and C(10) (atomic labeling is given in Figure 1). In addition, difference electron density maps had been consistently showing a residual peak in the C(9)–C(10) region. We have interpreted this as a disorder of the ligand, with C(10) resolved into two half-atoms, C(10) and C(X). This would also require alternative positions for other atoms, particularly for C(11), C(12), and C(13), but these were not resolvable. Refinement was concluded with 5 anisotropic heavy atoms, 18 isotropic light atoms, and 2 isotropic half-atoms.

The final agreement indices are $R = 0.082$ and $R_w = 0.102$ for 3173 observed reflections. All parameter shifts were less than 0.2σ in the final refinement cycle. A final difference map showed no particular detail with residual electron density between −0.84 and +0.90 e/Å^3. The final positional and thermal parameters with standard deviations estimated from the least-squares process are given

Table III. Thermal Parameters with Estimated Standard Deviations

Anisotropic Atoms[a]

atoms	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Pd	7.62 (6)	4.12 (4)	5.06 (4)	−1.05 (4)	−0.63 (4)	0.14 (3)
Te	8.65 (4)	4.87 (3)	5.34 (3)	−0.72 (3)	−1.26 (3)	−0.36 (2)
S	20.7 (4)	4.4 (1)	6.0 (2)	−1.8 (2)	0.9 (2)	0.4 (1)
Si(1)	7.9 (2)	9.2 (2)	9.5 (2)	−0.3 (2)	−2.0 (2)	−1.6 (2)
Si(2)	9.6 (2)	9.3 (2)	14.5 (4)	1.2 (2)	−1.4 (2)	2.5 (3)

Isotropic Atoms

atoms	B	atoms	B	atoms	B
N	12.7 (4)	C(5)	16.6 (7)	C(10)	9.7 (7)
C(1)	8.3 (3)	C(6)	15.6 (7)	C(X)	9.6 (7)
C(2)	7.8 (3)	C(7)	17.3 (7)	C(11)	14.3 (6)
C(3)	8.8 (3)	C(8)	7.8 (3)	C(12)	19.3 (9)
C(4)	10.4 (4)	C(9)	17.9 (8)	C(13)	18.6 (8)

[a] The anisotropic thermal parameters are of the form $\exp[-0.25(h^2a^{*2}B_{11} + \ldots + 2klb^*c^*B_{23})]$.

in Tables II and III, respectively. A compilation of observed and calculated structure factors is available as supplementary material.

Results and Discussion

The new dialkyl tellurides $Te((CH_2)_nSi(CH_3)_3)_2$ (n = 1, 3) have been prepared in high yields by the alkylation of sodium telluride with the appropriate alkyl chloride.

$$\mathrm{Te(0) + KBH_4 \xrightarrow{NaOH/H_2O} Na_2Te}$$

$$\mathrm{Na_2Te + 2RCl \xrightarrow{H_2O/CH_3OH} TeR_2 + 2NaCl}$$

The reduction of elemental tellurium to Te(−II) can be effected by Na/NH_3 as well as by a variety of reducing agents in aqueous solution (e.g., sodium formaldehyde sulfoxylate, NaH_2PO_2, Al, Zn, sodium dithionite).[28] We have found that 2.5 equiv of KBH_4 in 20% aqueous sodium hydroxide completely reduces elemental tellurium to a colorless, very air-sensitive solution of Te(−II) after 3–5 h at reflux temperature. Subsequent treatment of this solution with a solution of 2 equiv of the alkyl halide in an equal volume of deaerated methanol gives an essentially quantitative yield of the dialkyl telluride. Complete alkylation generally requires several hours at reflux temperature. The reaction can be conveniently monitored by removing small aliquots of the reaction solution, formation of black colloidal tellurium by air oxidation of Te(−II) indicating incomplete reaction. The workup may be done in air without any significant decomposition. The purified diorganotellurides are, however, stored under argon since they do slowly deposit elemental tellurium on prolonged storage in air.

The dialkyl tellurides can be converted into solid derivatives by halogen oxidation (i.e., TeR_2X_2 (X = Cl, Br, I))[29] and complexation with soft transition-metal ions such as Pd(II).

$$\mathrm{K_2PdCl_4 + 2TeR_2 \rightarrow PdCl_2(TeR_2)_2}$$

$$\mathrm{PdCl_2(NCC_6H_5)_2 + 2TeR_2 \rightarrow PdCl_2(TeR_2)_2}$$

$$\mathrm{K_2Pd(SCN)_4 + 2TeR_2 \rightarrow Pd(SCN)_2(TeR_2)_2}$$

The palladium complexes, isolated in good yields as crystalline red solids, showed no sign of decomposition on prolonged storage in air. However, exposure of $Pd(SCN)_2[Te(CH_2CH_2CH_2Si(CH_3)_3)_2]_2$ to X-rays in air did cause some degradation of the crystals.

These complexes are very soluble in nonpolar solvents such as dichloromethane, hexane, and ethyl ether but only moderately soluble in polar solvents such as methanol.

The use of the (trimethylsilyl)methyl radical to produce transition-metal alkyls with high solubility in nonpolar solvents was reported by Lappert and co-workers.[30,31] This radical has also been used to stabilize transition-metal alkyls by precluding the β-hydride elimination decomposition pathway.[30] The stability of $Te(CH_2CH_2CH_2Si(CH_3)_3)_2$ and other $Te(alkyl)_2$ derivatives[29] which contain β-hydrogen atoms suggests that a hydrogen elimination reaction is not operative in the decomposition of these derivatives. The hypothetical intermediates in such a decomposition pathway, alkyl tellurols (RTeH), are extremely unstable.[32]

The far-infrared and Raman spectra of both chloro complexes support trans configurations.[9,23] Both exhibit one ν_{Pd-Cl} band in the far-infrared region, as expected for D_{2h} symmetry (i.e., $PdCl_2[Te(CH_2Si(CH_3)_3)_2]_2$, 348 cm^{-1}; $PdCl_2[Te(CH_2CH_2CH_2Si(CH_3)_3)_2]_2$, 352 cm^{-1}). These bands are absent in the Raman spectra of the complexes, as expected for trans geometry. The recently reported complexes $PdX_2(TeAr_2)_2$ (X = Cl, Br; Ar = C_6H_5, p-$C_2H_5OC_6H_4$) have also been formulated as trans complexes on the basis of their far-infrared spectra.[9]

The bonding mode of the ambidentate thiocyanate ligand in Pd(II) complexes has been the subject of considerable interest in the recent literature.[34] A variety of spectroscopic techniques (IR,[34] NMR,[34-36] NQR[34,37]) have been employed as diagnostic tools for the elucidation of the thiocyanate bonding mode. Solid-state spectra of the two palladium thiocyanate complexes suggest sulfur bonding modes in both cases.

Although the ν_{CS} and δ_{SCN} bands are obscured by ligand absorptions, the appearance of very sharp ν_{CN} bands slightly above 2100 cm^{-1} is characteristic of M–SCN bonding[34] ($Pd(SCN)_2[Te(CH_2Si(CH_3)_3)_2]_2$, 2107 cm^{-1}; $Pd(SCN)_2[Te(CH_2CH_2CH_2Si(CH_3)_3)_2]_2$, 2106 cm^{-1}). Solution infrared measurements in $CHCl_3$ of the CN stretching frequency show bands shifted very slightly to longer wavenumbers but with pronounced asymmetry on the low-energy side. The $Te(CH_2Si(CH_3)_3)_2$ complex gives a distinct shoulder (2112 (s, sp) and 2095 cm^{-1} (sh, br)) whereas the $Te(CH_2CH_2CH_2Si(CH_3)_3)_2$ derivative gives only a pronounced broadening on the low-energy side of the 2113-cm^{-1} band.

Integrated intensity measurements of these solutions (ν_{CN}) gave values [2.8 × 10^4 M^{-1} cm^{-2} ($Te(CH_2Si(CH_3)_3)_2$ complex); 3.2 × 10^4 M^{-1} cm^{-2} ($Te(CH_2CH_2CH_2Si(CH_3)_3)_2$ complex)] generally found for M–SCN complexes (e.g., (1–3) × 10^4 M^{-1} cm^{-2}).[34] The asymmetry of the ν_{CN} bands in solution suggests the presence of a small amount of either M–NCS isomers or *cis*-$Pd(SCN)_2L_2$ isomers in solution. Since the intensity of M–NCS isomers is generally an order of magnitude higher than that of M–SCN isomers, the possible amount of the former in these solutions must be considered to be small. Indeed the NMR spectra of the complexes in the presence of $Eu(fod)_3$-d_{27} showed a downfield shift of ca. 0.7 ppm compared to the spectra of the complex alone, a value indicative of M–SCN isomers.[35] The proximity of the

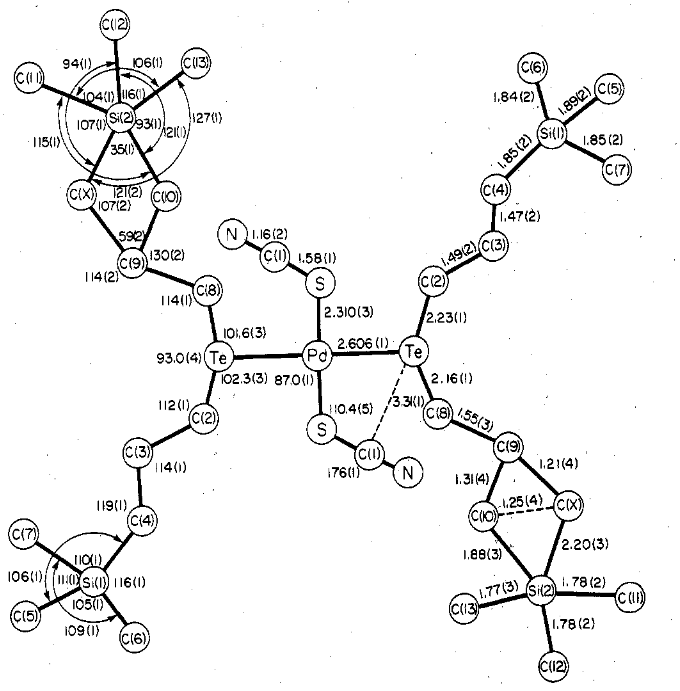

Figure 2. Bond lengths and angles with standard deviations in parentheses.

shoulders to the main component of the ν_{CN} bands is also more consistent with a cis splitting of this vibration than the presence of the N-bonded isomers (for which larger shifts to low energy would be expected).[34] The infrared spectra of the chloroform solutions containing the thiocyanate complexes and the shift reagent were identical with the solution spectra of the thiocyanate complexes alone except for the appearance of a weak ionic thiocyanate band at 2055 cm^{-1}. Heating the thiocyanate complexes at 75 °C for 5 h resulted in no spectral changes in the solid state.

The ^{13}C chemical shifts of the thiocyanate carbons of the complexes ($CDCl_3$ solutions) are both shifted upfield [$Te(CH_2CH_2CH_2Si(CH_3)_3)_2$ complex, 117.6 ppm; $Te(CH_2Si(CH_3)_3)_2$ complex, 118.1 ppm] compared to the case of ionic thiocyanate (ca. 133 ppm[36]), a result consistent with Pd–SCN bonding modes.[36]

The single-crystal X-ray structure determination has confirmed the trans S-bonded structure of $Pd(SCN)_2[Te(CH_2CH_2CH_2Si(CH_3)_3)_2]_2$. The complex exists as discrete, centrosymmetric, $Pd(SCN)_2(TeR_2)_2$ molecules, shown stereoscopically[38] in Figure 1. The angle Te–Pd–S is 87.0 (1)°, and the PdS_2Te_2 group of atoms is strictly planar by symmetry. Thus the bonding at Pd is square planar, the usual dsp^2 configuration of Pd(II) compounds.[39] Since Pd(II) is considered a class b or "soft" metal,[40] bonding of the ambidentate thiocyanate group is expected to be through S, and the exceptions to this have been explained on electronic[34] or steric grounds.[33,41]

From Figure 1 it is apparent that Te is pyramidally coordinated to Pd and two organic ligands. The coordination can best be described as tetrahedral with the fourth sp^3 orbital occupied by a stereochemically active lone pair of electrons. According to the VSEPR (valence shell electron pair repulsion) theory,[42] the repulsive forces between the lone pair of electrons and the bonding pairs of electrons should reduce the angles between the bonded atoms to less than the tetrahedral angle (109.5°). The angles observed are C–Te–C = 93.04 (4)° and C–Te–Pd = 102.3 (3)° and 101.6 (3)°. The orientation of the lone pair of electrons makes π bonding of Te with Pd unlikely. Alternative descriptions of the bonding in terms of sp^2 hybridization or no hybridization at all (with bonding through p_x, p_y, and p_z orbitals) are less satisfactory.

There is a close intramolecular contact of 3.31 Å between Te and C(1) of the thiocyanate group. This is much larger than the usual range of 2.01–2.18 Å for Te–C single bonds[4,5] but is considerably less than the sum, 3.8 Å, of the van der Waals radii. It is possible that there is some p_π–d_π bonding between the filled π orbitals of C(1) and the empty 5d orbitals of Te, although it is also possible that the interaction is repulsive (vide infra).

Bond lengths and angles are shown in Figure 2. The Pd–Te distance, 2.606 (1) Å, is slightly less than the sum (2.63 Å) of the covalent radii, 1.31 Å for square-planar Pd(II) and 1.32 Å for tetrahedral Te,[43] so that π bonding does not appear to be important. We are not aware of other determinations for organometallic compounds of the Pd–Te bond length, but Pd–Se in *trans*-dichlorobis(diethyl selenide)palladium(II)[44] is 2.424 (7) Å. This is 0.18 Å shorter than our Pd–Te bond, which is just the difference in the tetrahedral radii of Se and Te.[43] Numerous structures with Pd–SCN groupings have been determined and the dimensions have been tabulated.[41,45] The angles at S and C(1) and the S–C(1) and C(1)–N distances appear normal. The Pd–S distance, 2.310 (3) Å, ranks among the shorter Pd–S distances and is somewhat shorter than the sum, 2.36 Å, of the covalent radii,[43] which indicates the possibility of π bonding between the filled p_z orbitals of the sulfur atoms and the empty p_z orbital of palladium. The dihedral angle between the PdS_2Te_2 and $Pd(SCN)_2$ planes is 24°, and the SCN group itself is tilted 22° from the PdS_2Te_2 plane. There is no steric reason why the tilt could not be larger. However, the close Te–C(1) contact (3.31 (1) Å) mentioned above could be repulsive, which could prevent the tilt of the SCN group from becoming smaller than 22°. Thus, the orientation of the SCN group could represent a balancing of Pd–S π-bonding forces trying to reduce the tilt and Te–C(1) repulsive forces trying to increase the tilt.

Because of the disorder, the high thermal motion, and the domination of the X-ray scattering by the heavier atoms, the positions of the carbon atoms are not well determined. The Te–C bonds (2.16 (1) and 2.23 (1) Å) and the C–Te–C angle (93.0 (4)°) are within the range of previously tabulated values[4,5] and agree well with values determined from several acetylacetone tellurium(II) compounds.[46] The Si(1)–C distances average 1.856 (11) Å, in good agreement with recently determined values.[47] The Si(2)–C distances are not well determined because of the disorder at C(10).

We are continuing our investigations of the ligand properties of diorganotellurides in $MX_2(TeR_2)_2$ (M = Pd, Pt; X = halide, pseudohalide) complexes.

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Registry No. $PdCl_2[Te(CH_2CH_2CH_2Si(CH_3)_3)_2]_2$, 71032-48-9; $PdCl_2[Te(CH_2Si(CH_3)_3)_2]_2$, 71032-49-0; $Pd(SCN)_2[Te(CH_2CH_2CH_2Si(CH_3)_3)_2]_2$, 71032-50-3; $Te(CH_2CH_2CH_2Si(CH_3)_3)_2$, 71010-00-9; $Te(CH_2Si(CH_3)_3)_2$, 71010-01-0; $ClCH_2CH_2CH_2Si(CH_3)_3$, 2344-83-4; $ClCH_2Si(CH_3)_3$, 2344-80-1; Na_2Te, 12034-41-2.

Supplementary Material Available: A listing of observed and calculated structure factors (24 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry,
The University of Alberta, Edmonton, Alberta, Canada, T6G 2G2

Structure of $[Rh_2(CO)_2(\mu\text{-}Cl)((C_6H_5)_2PCH_2P(C_6H_5)_2)_2][BF_4]$. A Binuclear "A-Frame" Complex Showing the Open "Active" Site

MARTIN COWIE* and STEPHEN K. DWIGHT

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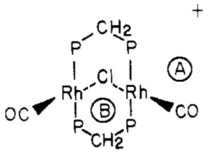
The structure of the complex $[Rh_2(CO)_2(\mu\text{-}Cl)((C_6H_5)_2PCH_2P(C_6H_5)_2)_2][BF_4]$ has been determined by X-ray crystallography, verifying that it is an "A-frame" type species. The structural parameters are similar in most aspects to those of the closely related species $[Rh_2(CO)_2(\mu\text{-}S)((C_6H_5)_2PCH_2P(C_6H_5)_2)_2]$, with the significant difference that the "active" site, bridging the two metal centers, is more open to attack by small molecules in the present complex. The title complex crystallizes in the space group $C_i^1\text{-}P\bar{1}$ from an acetone solution containing as the only anions PF_6^- and $B(C_6H_5)_4^-$. Evidence suggests that the BF_4^- anion results from the leaching of boron from the glass by HF. The reduced unit cell has dimensions a = 13.044 (1) Å, b = 14.962 (2) Å, c = 12.800 (2) Å, α = 96.20 (1)°, β = 92.56 (1)°, and γ = 86.42 (1)° with Z = 2. On the basis of 5729 unique, observed reflections the structure was refined by full-matrix, least-squares techniques to agreement indices of R = 0.046 and R_w = 0.064. Some relevant metrical parameters are Rh–P(av) = 2.321 (2) Å, Rh–C = 1.794 (7) and 1.807 (7) Å, Rh–Cl = 2.380 (2) and 2.406 (2) Å, C–O = 1.184 (8) and 1.202 (8) Å, Rh–Rh = 3.1520 (8) Å, C–Rh–Cl = 170.9 (2) and 172.6 (3)°, and Rh–Cl–Rh = 82.38 (5)°.

Introduction



1

The reactions of small molecules with binuclear metal complexes and the subsequent coordination modes of these molecules are of considerable current interest owing to the obvious implications regarding homogeneous catalysis by metal systems.[1] As part of our continuing investigations in this area[2-6] we have been studying the chemistry of the binuclear cationic species $[Rh_2(CO)_2(\mu\text{-}Cl)(DPM)_2]^+$ (**1**),[7] assumed to be an "A-frame" type complex based on spectral data and the structural characterization of its carbonyl adduct $[Rh_2(CO)_2(\mu\text{-}CO)(\mu\text{-}Cl)(DPM)_2]^+$ (**2**).[2,3] The "A-frame" complex **1** reacts reversibly with CO[2,8] and SO_2[4,5,8] and undergoes facile reactions with several other small molecules, including NO, N_2Ph^+, CS_2,[9] and TCNE.[10] The reactions with CO and SO_2 contrast the two possible modes of attack of small molecules

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