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Contrasting Behavior of Bis[2-(4,4-dimethyl-2-oxazolinyl)phenyl] Chalcogenides (Se/Te) toward Mercuric Chloride: Facile Cleavage of the Te−C Bond

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The reactions of R_2Se (**3**) and R_2Te (**4**) (R = 2-(4,4-dimethyl-2-oxazolinyl)phenyl) with $HgCl_2$ and $Pd(COD)Cl_2$ are described. The reaction of selenoether **3** with $HgCl_2$ affords the expected complex $R_2SeHgCl_2$ (**5**), which is stable in solution. In contrast, the analogous tellurium complex $R_2TeHgCl_2$ (**6**) undergoes slow dismutation in chlorinated solvents to give the fragments RTeCl (**7**) and RHgCl (**8**).

Introduction

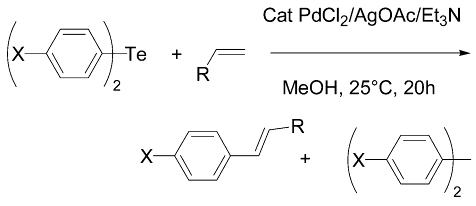
The coordination chemistry of ligands containing heavier chalcogens (Se/Te) is an area of growing interest.[1] Increased interest in this area is due to the application of these ligands in (i) isolation of single-source precursors for MOCVD of group 12 chalcogenides,[2] (ii) better σ-donor capacity of Se/Te ligands compared to the lighter group 16 congeners,[1] and (iii) easy use in stoichiometric/catalytic organic synthesis.[3] Recently Uemura and co-workers reported a palladium-catalyzed Fujiwara−Heck cross-coupling reaction between organic tellurides and alkenes (Scheme 1).[4]

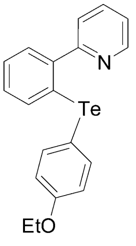
The key step of this coupling reaction was proposed to be the migration of an organic moiety from Te to Pd (transmetalation) in organic telluride−$PdCl_2$ complexes to afford the organopalladium species (eq 1). Such

$$[(R_2Te)PdZ_2]_2 \text{ or } (R_2Te)_2PdZ_2 \rightarrow RPdZ + RTeZ \qquad (1)$$

reverse transmetalation reactions in organotellurium chemistry were discovered for the first time by McWhinnie and co-workers.[5] The reaction of (2-(2-pyridyl)-phenyl)(3-ethoxyphenyl)tellurium (**1**; RR′Te) with $HgCl_2$ afforded [R′HgCl·2RTeCl$_2$]. In a series of papers, McWhinnie and co-workers have established the lability of organic groups from tellurium on reaction with metal compounds.[6] More recently, we have reported a facile C−Te bond cleavage/transmetalation in the reaction of the 22-membered azamacrocycle **2** with $HgCl_2$[7] and Pt(COD)Cl$_2$.[8] The cleavage of the C−Te bond in these cases is facilitated by the strong N→Te intramolecular interactions which involve n−σ* orbital interactions and

Scheme 1





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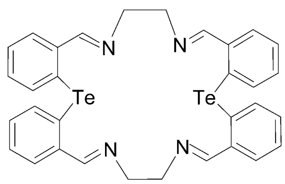

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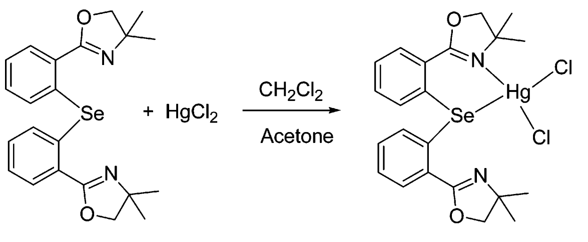
Scheme 2



3 **5**

activate the trans C−Te bond. Intramolecular interactions via n−σ* orbital interactions may be a viable strategy for activating Se−C/Te−C bonds. In this regard, we have begun a systematic study of the cleavage reactions of series of selenides and tellurides which have intramolecular interactions. In this paper we report the reaction of R_2E (E = Se, Te; R = 2-(4,4-dimethyl-2-oxazolinyl)phenyl) with Pd(COD)Cl_2 and $HgCl_2$.

Results and Discussion

Compounds **3** and **4** were synthesized by the reported methods.[9] The reaction of **3** with Pd(COD)Cl_2 in CH_2Cl_2 afforded a yellow-orange solid which was insoluble in all common organic solvents. The elemental analysis indicated the formation of a polymeric complex of the type $(\mathbf{3}\cdot PdCl_2)_n$. However, due to poor solubility, no further characterization could be carried out. Similarly, the reaction of **4** with 1 equiv of Pd(COD)Cl_2 in CH_2Cl_2 afforded a yellow powder which was again insoluble in all organic solvents. Interestingly, slow evaporation of the reaction mixture afforded dark red crystals with an insoluble yellow powder. Unfortunately, on standing for a few days or on recrystallization or precipitation of the CH_2Cl_2 solution by hexane, the dark red crystals convert to the insoluble yellow powder. McWhinnie et al. have also observed the formation of similar complex systems in the reaction of **1** with $PdCl_2$.[6a]

The reaction of selenoether **3** with $HgCl_2$ afforded the expected complex **5** as a white powder (Scheme 2).

The ^1H NMR spectrum of **5** exhibits only one singlet for the methyl protons and another singlet for the methylene protons. This indicates resonances corresponding to half of the molecule, suggesting a symmetric structure for complex **5**. However, in the structure by single-crystal X-ray studies (vide infra), it was found that the two nitrogen atoms are not equivalent in the solid state. The symmetric ^1H NMR spectrum is probably due to a fast exchange between Hg···N(1) and Hg···N(2) bonds in the coordination sphere around Hg. This leads to a dynamic equilibrium between the two structures (**5a** and **5c**) having four-coordinate mercury that may take place via five-coordinate mercury (**5b**) (Scheme 3). The dynamic behavior of the complex has also been confirmed by VT (variable temperature) ^1H NMR studies (Figure 1). When the temperature is lowered, a broadening of the signal for methyl protons was observed, which resolved into two singlets at −55 °C. Also, the singlet corresponding to methylene protons split into a doublet at this temperature. All signals are found to be downfield shifted in the ^1H NMR spectrum compared to the free ligand.[9]

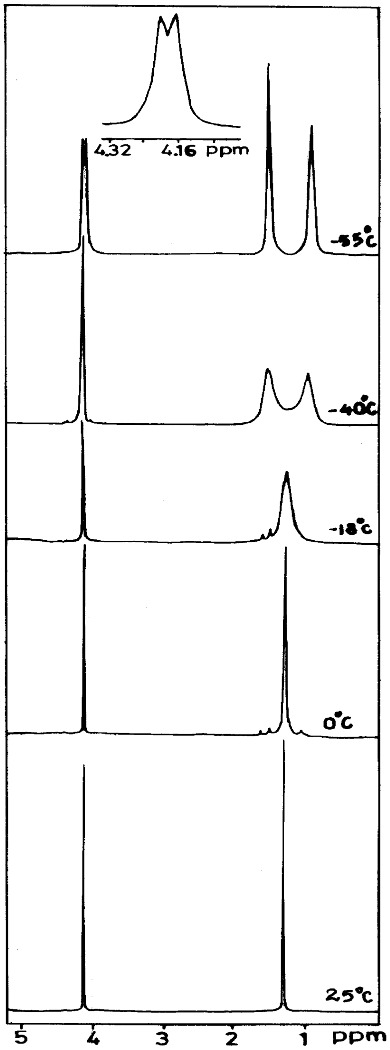
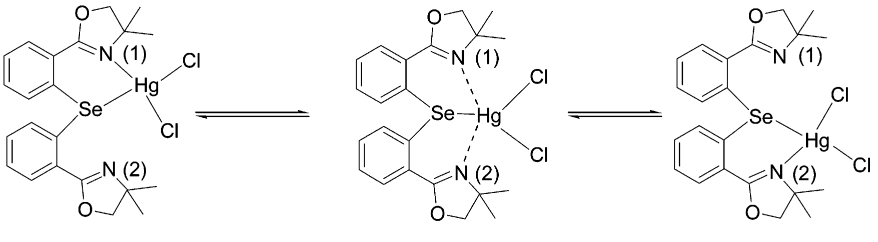


Figure 1. VT (variable temperature) ^1H NMR of **5**.

The ^{77}Se NMR spectrum shows a signal at δ 408.2 which is upfield shifted compared to the free ligand (δ 440.3). This may be due to the strong overlap of the orbitals of Se (where 5s and 4d are unoccupied orbitals) and mercury (where 6s and 5d orbitals are being filled).

Scheme 3



5a **5b** **5c**

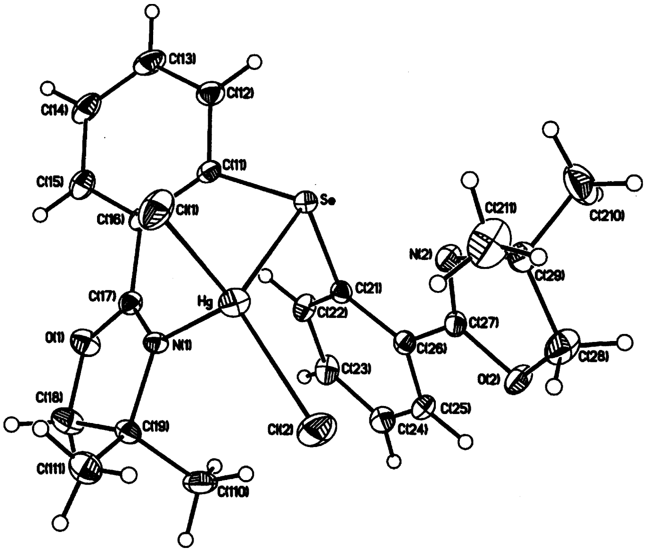
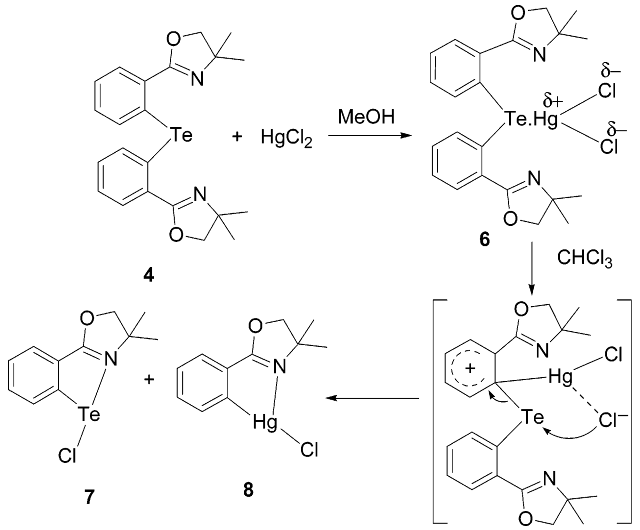


Figure 2. Molecular structure of compound **5**.

Scheme 4



X-ray-quality crystals were obtained by slow evaporation of the concentrated chloroform solution. In the solid state, complex **5** adopts a distorted-tetrahedral geometry around Hg (Figure 2). The Hg−Se distance (2.7501(17) Å) is in close agreement with the reported value in the tetrahedral complexes of Hg with tetraselena crown ether[10a] and selenophene.[10b] The Se−Hg−N angle (82.03(10)°) is much smaller and comparable to the Se−Hg−Se bond angle in the tetraselena crown ether complex with mercury.

Reaction of **4** with $HgCl_2$ in a 1:1 stoichiometric amount also afforded the white complex **6** (Scheme 4), which was sparingly soluble in all organic solvents except DMSO. Complex **6** was characterized by ^1H, ^{13}C, and ^{125}Te NMR and mass spectrometric techniques. The ^1H NMR spectrum of **6** shows an upfield shift for methyl protons but downfield shifts for methylene protons and aromatic protons compared to those of the free ligand **4**. Although the elemental analysis and NMR studies suggest the formation of the 1:1 adduct **6**, unfortunately, the FAB mass spectrum did not show the corresponding molecular ion peak. The highest peaks correspond to $[(R_2Te)_2HgCl]^+$ (*m*/*z* 1189 (28%)) and $[R_2TeHgCl]^+$ (*m*/*z* 713 (39%)).

In $CHCl_3$ or CH_2Cl_2 solution, interestingly, **6** undergoes slow dismutation to give the fragments RTeCl (**7**) and RHgCl (**8**)[11] (Scheme 4). In an attempt to understand the mechanism of the reaction, when the ^{125}Te NMR spectrum for the complex **6** was recorded in DMSO-d_6/$CDCl_3$ (1:1) only one signal at 1185 ppm for the tellurenyl chloride was observed after 10 min. There was no further change in the spectrum, even after 90 min. Mechanistically, this cleavage can be explained through electrophilic substitution by mercury at the ipso carbon of one aromatic ring.[12] It leads to the formation of the σ intermediate, which results in polarization of the Te−C bond (Te^+-C^-). Rearomaticization in the presence of chloride ion generates **7** and **8** with completion of the aryl migration. The Te←N intramolecular nonbonding interactions may be the additional factor facilitating the polarization of the Te−C bond. Compounds **7** and **8** were separated by column chromatography on silica gel and characterized. Crystals of **7** and **8** for single-crystal X-ray studies were obtained by slow evaporation of chloroform/hexane (4:1) solutions.

^1H and ^{125}Te NMR spectra clearly indicate the formation of compound **7**. The ^{125}Te NMR spectrum shows a sharp signal at 1203 ppm, which is shifted upfield compared to values reported for related tellurenyl chlorides having a N···Te−Cl bond (1,6-bis(2-(chlorotelluro)phenyl)-2,5-diazahexa-1,5-diene, 1332.3 ppm;[7] 2-(chlorotellurenyl)-4′-phenylbenzalaniline, 1355.0 ppm[13]) and oxatellurolylium chlorides having an O···Te−Cl bond (3-methyl-5-phenyl-1,2-oxatellurol-1-ium, 1726 ppm; 3,5-diphenyl-1,2-oxatellurol-1-ium, 1692 ppm).[14] In the FAB mass spectrum the base peak corresponds to the molecular ion peak (*m*/*z* 304 (100%)). The peak at *m*/*z* 608 corresponds to the dimer which is in good agreement with the X-ray crystal structure data. In RTeCl (**7**), the geometry around Te is T-shaped with a strong Te···N interaction (Figure 3). The Te···N separation of 2.241(3) Å is much shorter than the sum of van der Waals radii (3.7 Å).[15] The Te−Cl distance (2.5602(10) Å) is significantly larger that the sum of single-bond covalent radii (2.36 Å).[15] The Te···N and Te−Cl bond distances are comparable to the corresponding distances of 1,6-bis(2-(chlorotelluro)phenyl)-2,5-diazahexa-1,5-diene (Te···N, 2.185(8) Å; Te−Cl, 2.597(3) Å),[7] phenylazophenyl(*C*,*N*′)tellurium chloride (Te···N, 2.210(7) and

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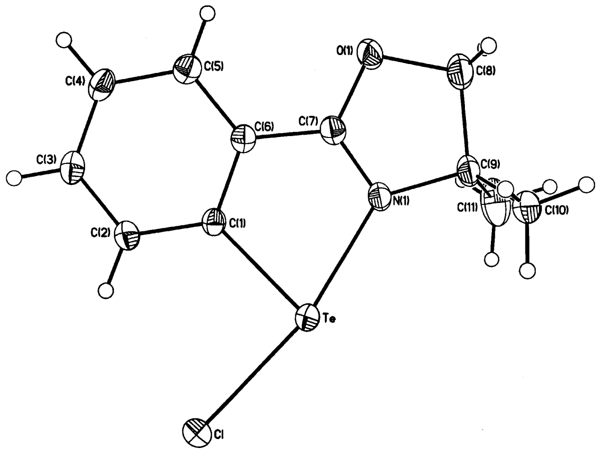

Figure 3. Molecular structure of compound **7**.

2.23(2) Å; Te−Cl, 2.533(3) and 2.552(8) Å),[16] (2-(2-pyridyl)phenyl)tellurium chloride (Te···N, 2.205(11) Å; Te−Cl, 2.606(11) Å),[5b,17] and 2-(chlorotelluronyl)-4′-methylbenzalaniline (Te···N, 2.218(6) and 2.239(6) Å; Te−Cl, 2.582(2) and 2.553(2) Å).[13] The Te−Cl distance is, however, longer than the related distance of 3-phenyl-5-(4-methoxyphenyl)-1,2-oxatellurol-1-ium chloride, where tellurium is intramolecularly coordinated with the oxygen atom by a secondary interaction.[12] The intermolecular distance (3.642 Å) between Te and Cl(A) is considerably shorter than the sum of the van der Waals radii (4.0 Å), indicating a secondary interaction between the molecules.

The unit cell of the molecular structure of RHgCl (**8**) contains two nonsymmetric equivalent molecules. No significant difference between these two molecules was observed. The coordination geometry around Hg is T-shaped, having a weak bonding interaction with nitrogen. Hg−N, Hg−C, and Hg−Cl distances are in close agreement with those reported by Nelson et al.[18] (Figure 4) for related compounds.

In summary, the C−Se bond, even after activation, does not undergo a cleavage reaction. In contrast, the acyclic R_2Te cleaves under very mild conditions. To the best of our knowledge, this is the first structural report of a mercury complex with an (Se, N) type hybrid selenoether ligand and of the isolation and structural characterization of both of the cleaved products in the reaction of an (N, Te, N) type telluroether with $HgCl_2$.

Experimental Section

All reactions were carried out under ambient conditions. Organic solvents were purified by standard procedures and were freshly distilled prior to use. Melting points were recorded in capillary tubes and are uncorrected. ^{1}H, ^{13}C, ^{77}Se, and ^{125}Te NMR spectra were obtained at 299.94, 75.42, 57.22, and 94.72 MHz, respectively, in $CDCl_3$ on a Varian VXR 300S spectrometer and a Bruker 500 spectrometer. Chemical shifts are cited with respect to $SiMe_4$ (^{1}H, ^{13}C) as an internal standard and Me_2Se (^{77}Se) and Me_2Te (^{125}Te) as external standards. Elemental analyses were performed on a Carlo-Erba Model 1106 elemental analyzer. IR spectra were recorded as KBr pellets on a Nicolet Impact 400 FTIR spectrometer. Fast atom bombardment (FAB) mass spectra were recorded at room temperature on a JEOL SX 102 DA-6000 mass spectrometer/data system using xenon (6 kV, 10mV) as a bombarding gas.

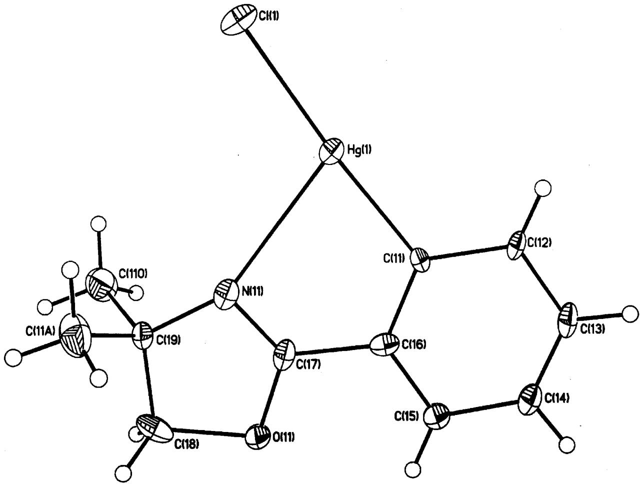

Figure 4. Molecular structure of compound **8**.

Syntheses. $[C_6H_4(C_5H_8NO)]_2SeHgCl_2$ (5). To a stirred solution of selenoether **3** (0.426 g, 1 mmol) in dry CH_2Cl_2 (20 mL) was added a solution of $HgCl_2$ (0.298 g, 1.1 mmol) in acetone (5 mL). Stirring was continued for 0.5 h. The reaction mixture was evaporated to give a white powder. This was dissolved in $CHCl_3$ (50 mL), and the solution was washed repeatedly with water to remove excess $HgCl_2$; the chloroform layer was dried over sodium sulfate and evaporated under vacuum to give a white powder. This was crystallized by slow evaporation of a concentrated chloroform solution (0.67 g, 98%). Mp: 196−198 °C. ^{1}H NMR ($CDCl_3$): δ 8.00−7.97 (m, 2H), 7.51−7.40 (m, 6H), 4.11 (s, 4H), 1.27 (s, 12H). ^{13}C NMR ($CDCl_3$): δ 27.5, 68.7, 79.2, 127.9, 128.9, 131.0, 131.4, 132.1, 133.3, 162.6. ^{77}Se NMR ($CDCl_3$): δ 408.2. MS: *m/z* 713 ($M^+ +$ Me, 34%), 304 (100%), 412 (10%), 478 (31%). IR (KBr, cm^{-1}): 1637 ($\nu_{C=N}$). Anal. Calcd for $C_{22}H_{24}Cl_2HgN_2O_2Se$: C, 37.82; H, 3.46; N, 4.00. Found: C, 37.35; H, 3.43; N, 3.78.

$[C_6H_4(C_5H_8NO)]_2TeHgCl_2$ (6). To a stirred solution of telluroether **4** (0.476 g, 1 mmol) in methanol (20 mL) was added $HgCl_2$ (0.298 g, 1.1 mmol). A white precipitate was obtained immediately. After it was stirred for an additional 10 min, the reaction mixture was filtered and the precipitate was washed with methanol and dried in air to give **6** (0.73 g, 98%). Mp: 134−136 °C. ^{1}H NMR ($(CD_3)_2SO$): δ 7.88 (d, 2H), 7.68 (d, 2H), 7.54 (t, 2H), 7.45 (t, 2H), 4.15 (s, 4H), 1.23 (s, 12H). ^{13}C NMR ($CDCl_3$): δ 28.0, 66.6, 67.0, 67.9, 79.1, 79.9, 82.9, 122.9, 126.9, 127.5, 127.8, 128.5, 131.8, 132.4, 137.2, 153.0, 165.7. ^{125}Te NMR ($(CD_3)_2SO$): δ 533.4. MS: *m/z* 1189 (28%), 713 (39%), 630 (25%), 614 (12%), 585 (16%), 495 (56%), 478 (60%), 304 (79%). IR (KBr, cm^{-1}): 1626, 1643 ($\nu_{C=N}$). Anal. Calcd for $C_{22}H_{24}Cl_2HgN_2O_2Te$: C, 35.36; H, 3.23; N, 3.74. Found: C, 35.92; H, 3.15; N, 3.69.

When complex **6** (0.5 g) was dissolved in $CHCl_3$, an immediate color change to yellow was observed. Two fragments were separated by column chromatography on silica gel using petroleum ether/ethyl acetate (95:5).

$[C_6H_4(C_5H_8NO)TeCl]$ (7): yellow fraction; yield 0.18 g, 80%. Mp: 175−177 °C. ^{1}H NMR ($CDCl_3$): δ 8.58 (d, 1H), 7.88 (dd, 1H), 7.56−7.62 (m, 1H), 7.39−7.45 (m, 1H), 4.57 (s, 2H), 1.58 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 29.0, 66.7, 82.9, 122.9, 126.4, 128.3, 132.3, 133.3, 138.6, 167.9. ^{125}Te NMR ($CDCl_3$): δ 1202.8. MS: *m/z* 339 (M^+, 15%) 304 (100%), 561 (17%), 608 (38%). IR (KBr, cm^{-1}): 1611 ($\nu_{C=N}$). Anal. Calcd for $C_{11}H_{12}ClNOTe$: C,

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Table 1. Crystal Data and Structure Refinement for 5, 7, and 8

	5	**7**	**8**
empirical formula	$C_{22}H_{24}Cl_2HgN_2O_2Se$	$C_{11}H_{12}ClHgNO$	$C_{11}H_{12}ClNOTe$
formula wt	698.88	410.26	337.27
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/m$	$P2_1/n$
a (Å)	12.589(2)	20.2339(16)	11.5638(15)
b (Å)	10.5362(19)	6.9091(8)	9.1432(11)
c (Å)	18.866(3)	8.6311(9)	12.7691(11)
β (deg)	106.010(12)	100.962(8)	113.481(9)
V (Å^3)	2405.3(7)	1184.6(2)	1238.3(2)
Z	4	4	4
D(calcd) (Mg/m^3)	1.930	2.300	1.809
abs coeff (mm^{-1})	8.155	13.191	2.592
no. of obsd rflns ($I > 2\sigma$)	1336	760	648
final $R(F)$ ($I > 2\sigma(I)$)[a]	0.0373	0.0559	0.0272
$R_w(F^2)$ (I > $2\sigma(I)$)	0.0615	0.0745	0.0334
no. of data/restraints/params	5452/0/300	2930/0/192	2840/0/151
goodness of fit on F^2	1.042	1.159	1.105

[a] Definitions: $R(F_o) = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w(F_o^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_c^2)^2]\}^{1/2}$.

39.17; H, 3.58; N, 4.15. Found: C, 38.87; H, 3.47; N, 3.41. HRMS (ES): m/z 304.0000 (calcd for $[C_{11}H_{12}NOTe]^+$ (M − Cl) 303.9981).

$[C_6H_4(C_5H_8NO)HgCl]$ (8): white fraction; yield 0.17 g, 60%. Mp: 169−171 °C. ^{1}H NMR ($CDCl_3$): δ 7.86−7.89 (m, 1H), 7.49−7.52 (m, 1H), 7.33−7.44 (m, 2H), 4.23 (s, 2H), 1.39 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 28.2, 67.3, 80.9, 128.2, 128.4, 132.2, 132.3, 136.9, 166.6. MS: m/z 412 (M$^+$, 49%), 551 (34%), 529 (17%). IR (KBr, cm^{-1}): 1644 ($\nu_{C=N}$). Anal. Calcd for $C_{11}H_{12}ClHgNO$: C, 32.22; H, 2.94; N, 3.41. Found: C, 32.97; H, 2.98; N, 3.40. HRMS (ES): m/z 412.0395 (calcd for $[C_{11}H_{12}NOHgCl]^+$ 412.0392).

X-ray Crystallography. The X-ray diffraction measurements were performed on a Siemens R3m/V diffractometer for compounds **5**, **7**, and **8** and on a Bruker SMART diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.717\ 03$ Å). The structures were solved by direct methods and subjected to full-matrix least-squares refinement on F^2 (program SHELXL-97).[19] The hydrogens were partially located from difference electron-density maps, and the rest were fixed at calculated positions. Scattering factors were taken from common sources. Some details of data collection and refinement are given in Table 1.

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Supporting Information Available: Tables giving crystallographic data for **5**, **7** and **8**; these data are also available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) Sheldrick, G. M. *SHELX 97; Program for Crystal Structure Refinement*; University of Göttingen, Göttingen, Germany, 1997.