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Synthesis of Metallacycles by Oxidative Addition of Sn−S, Sn−Se, Sn−Te, and Ge−Te Containing Precursors to Platinum(II)

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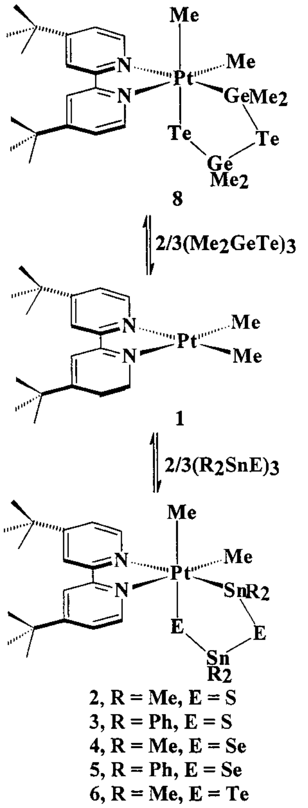
The first metallacycles formed by oxidative addition of tin−sulfur, tin−selenium, tin−tellurium, and germanium−tellurium bonds to platinum(II) are reported. In particular, the ring compounds [$(R_2SnE)_3$], where R = Me, Ph and E = Se, Te, and the new compound [$(Me_2GeTe)_3$], react with [$PtMe_2(bu_2bpy)$] (bu_2bpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine) to give the new organoplatinum(IV) metallacycles [$PtMe_2(R_2SnE)_2(bu_2bpy)$] and [$PtMe_2(Me_2GeTe)_2(bu_2bpy)$], respectively. The tin-containing metallacycles complexes can undergo exchange of either the R_2Sn or the E groups by reaction with [$(R'_2SnE)_3$] or [$(R_2SnE')_3$], respectively, to give the corresponding new metallacycles of general formula [$PtMe_2(R_2SnE-R'_2SnE)(bu_2bpy)$] or [$PtMe_2(R_2SnE-R_2SnE')(bu_2bpy)$]. The isostructural series of complexes [$PtMe_2(Ph_2SnE)_2(bu_2bpy)$] with E = S, Se, and Te have been characterized by X-ray structure determinations. It is shown that ^{119}Sn NMR is a useful method of structure determination for these metallacyclic compounds.

Introduction

There is current interest in the activation of bonds between the elements of groups 14 and 16 by oxidative addition to transition metal complexes, since these reactions constitute a critical step in stoichiometric or catalytic transformations.[1] For example, it has recently been shown that all M−Te bonds (M = C in Ph_2Te; M = Si, Ge, and Sn in Me_3MTePh) oxidatively add to platinum(0) complexes such as [$Pt(PEt_3)_4$].[2,3] In a preliminary communication, it was shown that a Sn−S bond of the ring compounds [$(R_2SnS)_3$][4] adds to [$PtMe_2(bu_2bpy)$], **1**, bu_2bpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine,[5] to give the organoplatinum(IV) metallacycles [$PtMe_2(R_2SnS)_2(bu_2bpy)$] (**2** and **3**, Scheme 1), which contain the new five-membered PtSnSSnS ring.[6] It is now shown that related reactions occur easily for ring complexes containing Sn−Se, Sn−Te, or Ge−Te bonds to give new metallacycles and full details of these and the earlier reactions are now described. The factors affecting reactivity in such reactions have been defined, and the series of complexes [$PtMe_2(Ph_2SnE)_2(bu_2bpy)$] with E = S, Se, or Te have been structurally characterized.

Scheme 1



Results

The synthesis of the metallacycles containing five-membered Pt(SnR_2ESnR_2E) or Pt($GeMe_2TeGeMe_2Te$) rings is depicted in Scheme 1.

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Table 1. Selected ^{119}Sn NMR Data for the Complexes

	δ (Sn^1)	^1J (PtSn)	^1J (SnE)	^2J (SnSn)	δ (Sn^2)	^1J (SnE^1)	^1J (SnE^2)
2	−34.5	12067		223	138.1		
3	−169.1	13344		188	51.9		
9	−32.7	12103		217	51.7		
4	−77.1	11930	841, Se	249	0.2	1106, Se	1497, Se
5	−194.0	13160	921, Se	217	−60.3	1178, Se	1640, Se
10	−72.5	11973	794, Se	250	−57.4	1193, Se	1645, Se
6	−168.1	11600		192	−342.1	2636, Te	3706, Te
7	−244.3	12746	2248, Te	139	−340.3	2892, Te	4112, Te
11	−160.5	11686	1942, Te	181	−334.5	2891, Te	4101, Te
12	−41.3	11951		223	51.6		1501, Se
13	−50.5	11737		214	−128.4		3924, Te
14	−86.0	11686		238	−193.2	1053, Se	3845, Te
15a	−173.1	13237		183	−22.3		1669, Se
15b	−188.6	13253	905, Se	224	23.6	1215, Se	

The preliminary communication[6] reported that the reactions of [PtMe$_2$(bu$_2$bipy)], **1**, with [(R$_2$SnS)$_3$] to give **2** or **3** occur over a period of several hours in refluxing acetone solution. The reactions of **1** with [(R$_2$SnSe)$_3$] (R = Me, Ph)[7] to give **4** and **5**, respectively, were faster, being complete within 0.5 h in refluxing acetone solution, and the products were isolated as air-stable yellow solids (Scheme 1). Similar reactions of **1** with [(R$_2$SnTe)$_3$] (R = Me, Ph)[7] and [(Me$_2$GeTe)$_3$][8] yielded the new PtSn$_2$Te$_2$ metallacycles **6** or **7** and the PtGe$_2$Te$_2$ metallacycle **8** but were faster, being complete within seconds at room temperature in CH$_2$Cl$_2$ solution. These telluride complexes were isolated as air-sensitive purple (**6**, **7**) or red-black (**8**) solids in good yield (Scheme 1). No reaction occurred between **1** and the ring compounds (Me$_2$GeS)$_3$ and (Me$_2$GeSe)$_3$ in refluxing acetone. It has been shown earlier[9] that Ge−X oxidative additions to platinum(II) become more favorable thermodynamically and occur faster kinetically in the sequence X = I > Br > Cl, and it is likely that a similar series with X = Te > Se > S applies in the above reactions. Thus, the oxidative addition of Ge−S or Ge−Se bonds to platinum(II) are probably thermodynamically unfavorable and it is likely that Ge−S addition is both thermodynamically unfavorable and kinetically slow.[9]

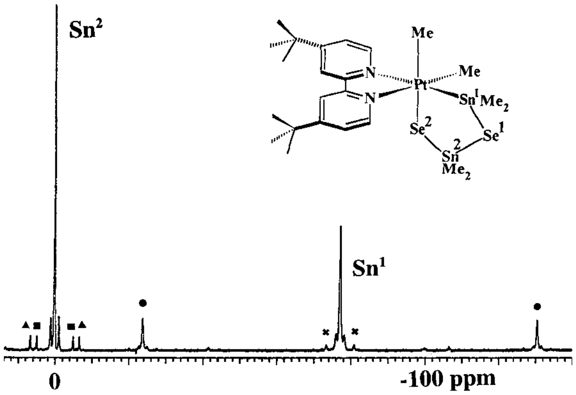

Figure 1. ^{119}Sn NMR spectrum of complex **4** in CD$_2$Cl$_2$. For the Sn^1 resonance, circles indicate ^1J(Sn^{1}Pt) = 11 940 Hz and crosses indicate ^1J(Sn^{1}Se^1) = 841 Hz; for the Sn^2 resonance, trianges and squares indicate the couplings ^1J(Sn^{2}Se^2) = 1497 Hz and ^1J(Sn^{2}Se^1) = 1106 Hz, respectively; the unmarked inner satellites around each resonance are due to ^2J(SnSn) = 249 Hz.

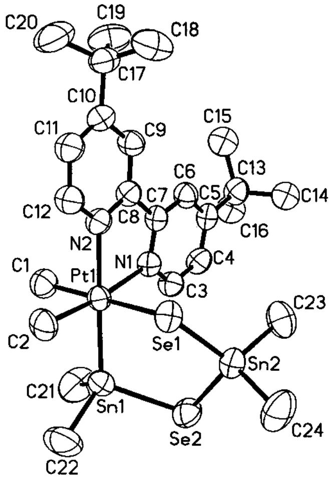

Figure 2. A view of the molecular structure of complex **4**.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Complexes **2** and **4** (E = S, Se)

	2	**4**
Pt(1)−Sn(1)	2.552(1)	2.5548(5)
Pt(1)−E(1)	2.439(3)	2.5493(6)
Pt(1)−N(1)	2.14(1)	2.140(4)
Pt(1)−N(2)	2.21(1)	2.204(4)
Pt(1)−C(1)	2.09(1)	2.072(5)
Pt(1)−C(2)	2.05(1)	2.052(5)
Sn(1)−E(2)	2.435(4)	2.5645(7)
Sn(2)−E(2)	2.416(4)	2.5322(8)
Sn(2)−E(1)	2.355(3)	2.4779(7)
E(1)−Pt(1)−Sn(1)	92.74(9)	92.61(2)
Pt(1)−Sn(1)−E(2)	110.6(1)	112.23(2)
Sn(2)−E(2)−Sn(1)	100.1(1)	97.58(2)
E(1)−Sn(2)−E(2)	108.9(1)	109.00(2)
Sn(2)−E(1)−Pt(1)	108.2(1)	105.91(2)

The new metallacycles have been characterized by ^{1}H and, where appropriate, by ^{119}Sn (Table 1) and ^{195}Pt NMR spectroscopy. The ^{119}Sn NMR data, summarized in Table 1, are particularly useful for structure determination of the new complexes **4**−**7** since the ^{119}Sn resonance of the Pt−Sn unit displays a large value of ^1J(PtSn) in the range 11 599−13 160 Hz and, when E = Se, a single ^1J(SnE) coupling of 841−921 Hz, while the PtESnE unit displays two different ^1J(SnE) couplings when E = Se or Te (E = ^{77}Se, 1106, 1178 in **4** and 1497, 1640 Hz in **5**; E = ^{125}Te, 2636, 2892 in **6** and 3706, 4112 Hz in **7**; Table 1). In addition, the long-range coupling ^2J(*Sn*Te*Pt*) = 66 and 82 Hz was resolved for the β-SnR$_2$ resonance of complexes **6** and **7**, respectively, and the coupling ^2J(SnSn) was also resolved in the metallacyclic compounds (Table 1). A typical ^{119}Sn NMR spectrum is shown in Figure 1. All complexes give two methylplatinum resonances (MePt trans to N or E) and the methyltin complexes give four MeSn resonances as expected for the structures shown in Scheme 1.

The complexes **3**, **4**, **5**, and **7** were characterized by X-ray structure determinations. The structure of **4** is shown in Figure 2 and selected bond distances and angles are in Table 2. The structure of **7**, which is representative of the isostructural series

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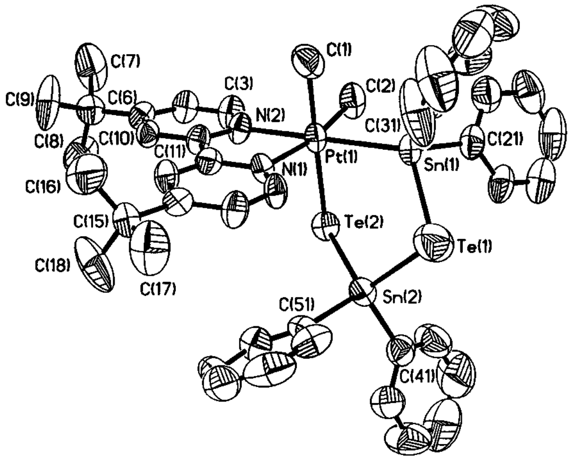


Figure 3. A view of the molecular structure of complex **7**. The structures of complexes **3** and **5** are similar and key bond parameters are compared for the isostructural series in Table 3.

Table 3. Selected Bond Parameters for the Isostructural Complexes **3** (E = S), **5** (E = Se), and **7** (E = Te)

complex	3	5	7
Pt−C(1)	2.081(8)	2.09(1)	2.08(2)
Pt−C(2)	2.070(8)	2.05(1)	2.06(2)
Pt−N(1)	2.142(6)	2.134(8)	2.13(1)
Pt−N(2)	2.192(6)	2.186(8)	2.19(1)
Pt−Sn(1)	2.558(1)	2.566(1)	2.571(1)
Pt−E(2)	2.457(2)	2.570(1)	2.719(1)
Sn(1)−E(1)	2.425(3)	2.556(2)	2.700(2)
Sn(2)−E(1)	2.406(3)	2.528(2)	2.700(2)
Sn(2)−E(2)	2.353(2)	2.484(1)	2.681(2)
E(2)−Pt−Sn(1)	90.06(6)	89.97(4)	89.51(4)
E(1)−Sn(1)−Pt	112.38(6)	114.32(4)	117.63(5)
E(1)−Sn(2)−E(2)	109.73(9)	110.22(5)	110.47(6)
Sn(1)−E(1)−Sn(2)	98.03(9)	95.22(5)	91.65(6)
Sn(2)−E(2)−Pt	107.76(9)	105.56(5)	102.79(4)

3, **5**, and **7**, is shown in Figure 3, and a comparison of selected bond parameters for **3**, **5**, and **7** is given in Table 3. The metallacycles all adopt an envelope conformation with the platinum atom in the "flap" position, but the fold angle follows the sequence E = Te (34°) > Se (32°) > S (30°) for the rare isostructural series **3**, **5**, and **7**. Within the five-membered ring of this series, the angle at E(1) is substantially less than at E(2) and follows the series E = S > Se > Te, while the angle at Sn(1) varies markedly as E = Te > Se > S (Table 3). In contrast to these observations, the five-membered metallacycles [1,3-(t-$Bu_2Sn)_3E_2$] are close to planar.[7f] Of the nonequivalent Sn−E distances in **3**, **5**, and **7**, Sn(2)−E(2) is very short compared to the others and to comparable distances in [$(R_2SnE)_3$], 1,3-(t-$Bu_2Sn)_3E_2$, and related compounds.[7] The short value of Sn(2)−E(2) and the relatively high angle at E(2) may arise since E(2) is trans to a methylplatinum group and hence the Pt−E(2) bond is relatively weak and polar, thus leading to enhanced E(2)Sn-(2) π-bonding. There is a clear correlation of the Sn−E distances and ^1J(SnE) couplings when E = Se or Te, and the values of $^1J(Sn^2E^2)$ appear to be the highest known.[7] The ring folding also leads to a relatively short transannular distance E(2)···Sn(1) (3.55, 3.63, 3.73 Å for E = S, Se, Te respectively), perhaps indicating secondary bonding between these atoms.[7] For the methylplatinum groups trans to E in **3**, **5**, and **7**, the Pt−C distances [2.08(1), 2.09(1), 2.08(2) Å for E = S, Se, Te respectively] and the coupling constants ^2J(PtH) (58, 59, 59 Hz for E = S, Se, Te respectively) are essentially equal, indicating very similar trans influences for E = S, Se, and Te; the Pt−C distances are shorter, and the coupling constants ^2J(PtH) are larger for the methylplatinum groups trans to nitrogen due to the lower trans influence of the nitrogen donor. The Pt−N distances trans to tin are in all cases longer than those trans to methyl, as a result of the very high trans influence of tin. The crystals of **3**, **5**, and **7** are isomorphous, and, as expected, the cell dimensions and volumes follow the sequence E = Te > Se > S (Table 4). Complexes **2**·acetone[6] and **4**·acetone are also isomorphous and isostructural.

There is some evidence for reversibility of the oxidative addition of the Sn−E bonds to platinum(II). Thus, dilute solutions of **2** in acetone gave detectable amounts of **1**, as detected by its UV−visible spectrum,[5] but the degree of dissociation in more concentrated solutions used for NMR studies was too low to measure. However, reaction of **2** with MeI rapidly gave [$PtIMe_3(bu_2bpy)$] and [$(Me_2SnS)_3$], identified in situ by ^1H NMR, again consistent with reversible reductive elimination from **2** to regenerate [$PtMe_2(bu_2bpy)$], **1**, which reacts very rapidly with MeI to give [$PtIMe_3(bu_2bpy)$].

The complexes **2**, **4**, and **6** in dichloromethane solution all give room-temperature emission[6] at 650 nm ($\lambda_{excitation}$ 310 nm) assigned to an n(E)−π*(bipy) excited state but the intensity of the emission follows the series E = S > Se > Te.

New metallacycles **9**, **10**, or **11** could be generated by reaction of **2**, **4**, or **6**, respectively, with $(Ph_2SnE)_3$ according to Scheme 2. These reactions led to selective replacement of the β-$SnMe_2$ group by Ph_2Sn in each case. To obtain complexes **9**, **10**, and **11** in pure form, it was necessary to monitor the reactions carefully since reaction for longer periods also led to replacement of the α-$SnMe_2$ group by Ph_2Sn to give the corresponding complex **3**, **5**, or **7**. Reaction between **3**, **5**, or **7** and $(Me_2SnE)_3$ also gave **9**, **10**, and **11**, respectively, although these reactions occurred more slowly in CH_2Cl_2 solution. Finally, complexes **9**, **10**, and **11** were also formed by a redistribution reaction from equimolar amounts of **2**, **4**, and **6**, with **3**, **5**, and **7**, respectively, but this reaction was very slow at room temperature. The structures of **9**, **10**, and **11** were unambiguously determined from the NMR spectra. In particular, comparison of the parameters from the ^{119}Sn NMR spectra (Table 1) with those of the symmetrical complexes **2**, **4**, **6** and **3**, **5**, **7** is definitive. Thus, both the ^{119}Sn chemical shifts and ^1J(SnPt) coupling constants are very different in analogous complexes containing $PtSnMe_2$ or $PtSnPh_2$ groups (Table 1).

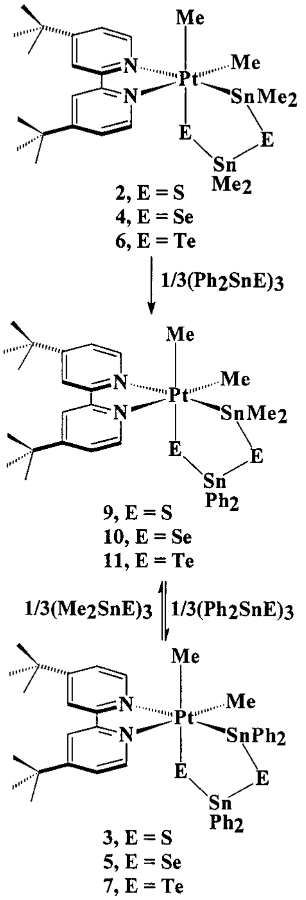
New metallacycles were also formed by reaction of **2**−**6** with $(R_2SnE')_3$ according to Scheme 3. These reactions occur to give overall chalcogenide exchange. In most cases, the product complex contains the heavier, softer chalcogenide directly bonded to the softer platinum atom (Scheme 3), as expected in the thermodynamically more stable product. Thus, for example, complex **13** was formed either from **2** with $(Me_2SnTe)_3$ or from **6** with $(Me_2SnS)_3$; similar observations were made with respect to the formation of the methyltin derivatives **12** and **14**. However, an exception was found in the formation of the diphenyltin derivative **15** since **15a** was formed selectively from **5** with $(Ph_2SnS)_3$ while the isomer **15b** was formed from **3** with $(Ph_2SnSe)_3$; clearly the β-chalcogen atom was replaced as a result of kinetic control in this case at least. Isomers **15a** and **15b** do not interconvert over a period of days at room temperature. Not all possible reactions of this kind were successful. Thus, the reaction of complex **7** with $(Ph_2SnTe)_3$ was unsuccessful since it gave a complex mixture of products over the time (4 days) needed to give complete consumption of the starting material **7**. In general, it was difficult to separate the metallacycles **12**−**14**, containing mixed chalcogenide atoms, from reaction byproducts, and they were not isolated in pure

Table 4. Crystal Data and Experimental Details

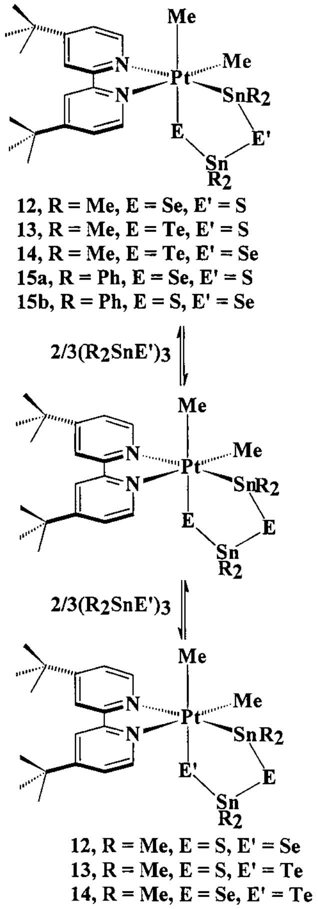
complex	**4**·acetone	**3**	**5**	**7**
empirical formula	$C_{27}H_{48}N_2O_1Pt_1Se_2Sn_2$	$C_{44}H_{50}N_2PtS_2Sn_2$	$C_{44}H_{50}N_2PtSe_2Sn_2$	$C_{44}H_{50}N_2PtTe_2Sn_2$
fw	1007.06	1103.46	1197.25	1294.53
T/°C	27	25	21	21
λ/ Å	0.710 73	0.710 73	0.710 73	0.710 73
space group	$P2_1/n$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a/Å	14.574(1)	12.305(1)	12.372(1)	12.481(3)
b/Å	13.312(1)	16.667(1)	16.702(2)	16.848(4)
c/Å	19.142(2)	20.999(2)	21.113(7)	21.204(5)
β/deg	103.78(1)	92.58(1)	92.26(2)	92.05(2)
V/Å^3	3606.8(5)	4302.3(6)	4359(2)	4456(2)
Z	4	4	4	4
d(c)/g cm^{-3}	1.855	1.704	1.824	1.930
μ/mm^{-1}	7.281	4.524	6.039	5.558
F(000)	1912		2296	2440
R [$I > 2s(I)$][a]				
R1	0.0324	0.0402	0.0481	0.0599
wR2	0.0652	0.0811	0.1036	0.1556

[a] $R1 = \sum(||F_o| - |F_c||)/\sum|F_o|$; $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o4]^{1/2}$.

Scheme 2



Scheme 3



form but were characterized unambiguously by their rich NMR spectra (Table 1) using the principles outlined earlier. For example, in the ^{119}Sn NMR spectrum of complex **12**, the Sn^1-Me$_2$ resonance shows no coupling to selenium while the Sn^2 resonance shows the large coupling ^1J(SnSe) = 1501 Hz expected for a PtSeSnMe$_2$ group (Table 1). Similarly, the isomers **15a** and **15b** are distinguished inter alia by the characteristic values of ^1J(Sn^{2}E) of 1669 Hz in **15a** (PtSeSnS linkage) and 1215 Hz in **15b** (PtSSnSe linkage) (Table 1).

These metallacyclic redistribution reactions also led to formation of mixed cyclic organotin compounds. For example, the reaction of **2** with [(Ph$_2$SnS)$_3$] gives the platinum complex **9** and then **5**, and the dimethyltin groups that are eliminated are incorporated into a mixture of organotin metallacycles including the mixed dimethyltin, diphenyltin derivatives [(Me$_2$SnS)(Ph$_2$SnS)$_2$] and [Ph$_2$SnS(Me$_2$SnS)$_2$], identified in the reaction mixtures by their known NMR spectra.[4,7] Indeed, the complex **2** can act as a catalyst for the redistribution reaction of [(Me$_2$SnS)$_3$] and [(Ph$_2$SnS)$_3$] to give an equilibrium with the mixed trimeric compounds [Ph$_2$SnS(Me$_2$SnS)$_2$] and [(Me$_2$SnS)(Ph$_2$SnS)$_2$]. This reaction reaches equilibrium in less than 5 min in the presence of **2**, whereas, without the platinum catalyst, equilibrium was reached in ca. 2 h under comparable conditions. In a similar way, the reaction of **2** with [(Me$_2$SnSe)$_3$] gives not only **12** but also a mixture of organotin products containing [(Me$_2$SnSe)$_2$(Me$_2$SnS)] and [(Me$_2$SnSe)(Me$_2$SnS)$_2$]. Many of

Table 5. ^{119}Sn Chemical Shifts[a] and Tin−Element Coupling Constants[b] in Compounds $[(Ph_2Sn)_3X_nX'_{3-n}]$ (X = S, Se, Te; n = 2, 3)[c]

X	n	X′	δ (Sn^a)	δ (Sn^b)	^1J (Sn^a−X)	^1J (Sn^b−X)	^1J (Sn^b−X′)	^2J (Sn−X−Sn)	^2J (Sn−X′−Sn)
S	3		14.7					195	
Se	3		−46.5		1318			239	
Te	3		−206		3366			253	
S	2	Te	33.0	−102			3513	212	243
Te	2	S	−246	−73.6	3883	3609		261	216
Se	2	Te	−29.4	−133	1337	1274	3465	250	252
Te	2	Se	−233	−111	3312	3522	1291	255	250
S	2	Se	20.4	−18.9			1332	209	233
Se	2	S	−55.0	−11.9	1309	1342		239	220

[a] In ppm; ref Me_4Sn. [b] ^1J values are for $^1J(^{119}Sn-X)$, ^2J values are for $^2J(^{119}Sn-X-^{119}Sn)$. [c] Unsymmetrical compounds are labeled as follows: Sn^a−X−Sn^b−X′−Sn^b−X.

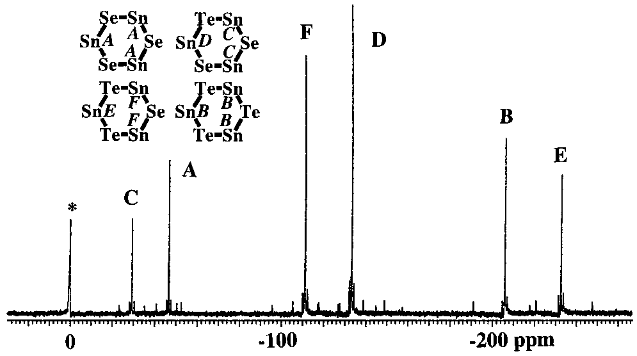


Figure 4. The ^{119}Sn NMR spectrum of the mixture of ring complexes $[(Ph_2Sn)_3Se_nTe_{3-n}]$ formed by equilibration of $[(Ph_2Sn)_3Se_3]$ and $[(Ph_2Sn)_3Te_3]$. Note the distinct chemical shift regions for units containing Ph_2SnSe_2 (A,C), $Ph_2SnSeTe$ (D,F) and Ph_2SnTe_2 (B, E) units. Couplings are not marked but are listed in Table 5.

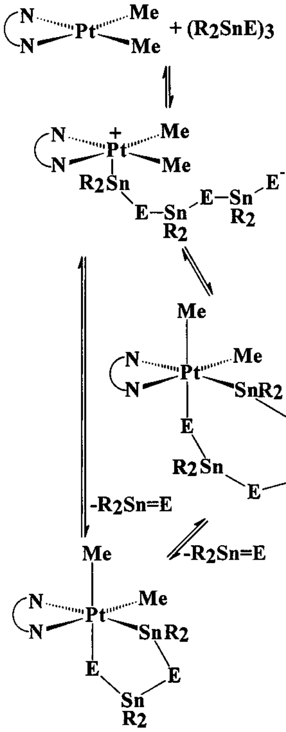
these organotin metallacycles are new, and the characterization data from ^{119}Sn NMR spectra are listed in Table 5, while a typical spectrum is shown in Figure 4.

In principle, it should be possible to extend these redistribution reactions to give unsymmetrical complexes containing Pt-$[SnR_2ESnR'_2E']$ units, with five different groups in the metallacycle, but reactions designed to give such complexes have yielded mixtures too complex to separate or even to analyze by NMR. For example, the reaction of complex **3** with $[(Ph_2SnTe)_3]$, or between complexes **3** and **7**, which might give isomers containing such metallacycles as $PtSnMe_2SeSnPh_2Te$, gave only an intractable mixture of products.

Discussion

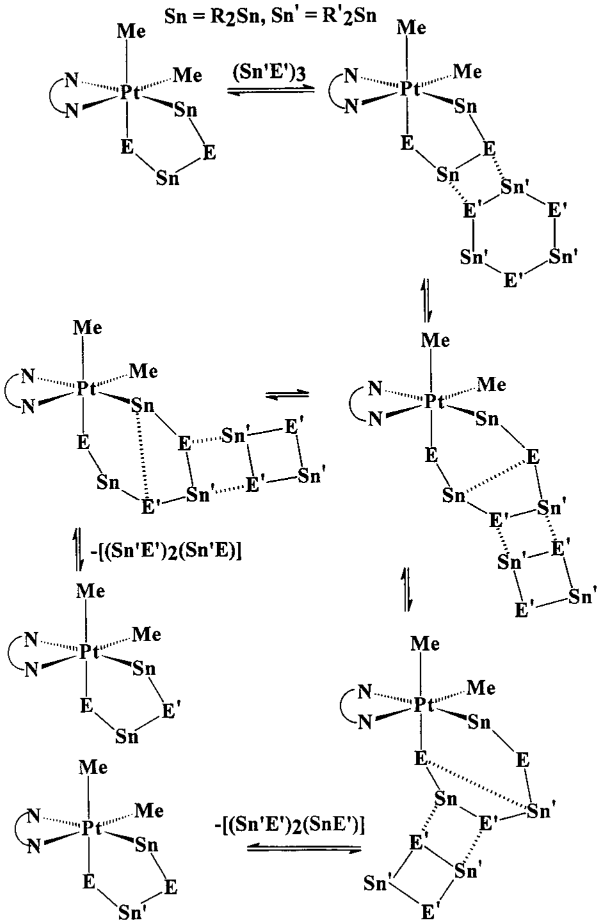
The oxidative addition of Sn−X bonds, where X = halogen, to complex **1** have been shown to occur by the polar S_N2 mechanism,[9] and so it was expected that this mechanism might also apply to the oxidative addition of Sn−E bonds established in the present work. An unexpected feature of the new reactions of Scheme 1 was the formation of five-membered rather than seven-membered rings. No intermediates were detected during these reactions, so it cannot be established if the reactions occur directly with loss of one R_2SnE group or if a seven-membered ring is formed and then undergoes rapid loss of an R_2SnE unit. If the polar mechanism is assumed, these two possibilities are shown in Scheme 4. In either case, $R_2Sn{=}E$ is expected to be very short-lived if formed and would rapidly be incorporated into an $[(R_2SnE)_3]$ trimer.[4,7] Indeed, the extrusion of R_2SnE from a seven-membered ring is likely to occur by a "ladder" intermediate by direct reaction with a free $(R_2SnE)_n$ ring.[7] The five-membered ring is often the optimum chelate ring size in octahedral complexes and so is thermodynamically favored over the seven-membered ring. The evidence does not preclude a concerted *cis*-addition of the Sn−E bond to platinum(II), and this mechanism has the advantage of naturally giving the observed cis stereochemistry of oxidative addition (Schemes 1 and 4). An attempt was made to prepare a six-membered ring by reaction of **1** with the five-membered organotin compound $(Me_2Sn)(Me_2Sn)S(Me_2Sn)S$, but this gave a complex mixture of products in which only the five-membered ring adduct **2** could be charactarized by the NMR spectrum. In this case, the stoichiometry requires oxidative addition with elimination of a single Me_2Sn unit which is presumably incorporated into other unidentified products.

Scheme 4



The new metallacycles are labile and undergo exchange of R_2Sn and/or E groups with reagents $[(R'_2SnE')_3]$, as depicted in Schemes 2 and 3. In most cases studied, the reactions occur to give what is likely the thermodynamically most stable isomer. For mixed complexes, these have the smaller Me_2Sn group α and the bulkier Ph_2Sn group β to platinum; the heavier chalcogenide is directly bonded to the softer platinum center, while the lighter chalcogenide bridges the two harder tin centers. Under these circumstances, no mechanistic insights can be obtained, since it is likely that in some cases these are not the initial products of kinetic control. Only in one case were two isomers formed by such exchange reactions, namely in the formation of **15a** and **15b** according to Scheme 3. These

Scheme 5

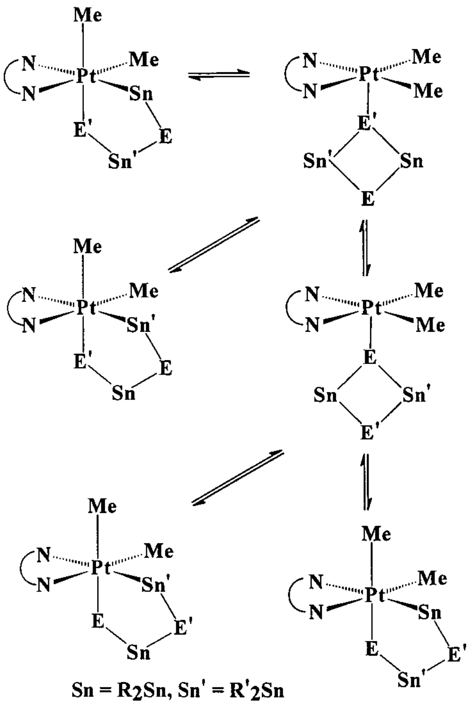


reactions prove that the β-chalcogenide is exchanged selectively at least in this case. Note that this is the chalcogenide having the weaker Sn−E bonds, as shown both by the Sn−E distances and, when E = Se or Te, by the ^1J(SnE) coupling constants. A mechanism is still not defined. In particular, attempts to establish if the reactions occur by exchange of R_2SnE units together or by independent exchange of R_2Sn and E units were not successful. One possible mechanism, involving the "ladder" intermediates commonly proposed in organotin chemistry[7] is shown in Scheme 5. If Scheme 5 is correct, the reactions involve reactivity at the tin rather than at the platinum center, but still appear to be accelerated in the platinacyclic complexes compared to the parent organotin trimers.

The evident ability of these heterometallacycles to undergo skeletal rearrangement is reminiscent of the known chemistry of metallacycloalkanes. In metallacyclopentanes, rearrangement can occur by reversible formation of transient bis(alkene) complexes; an analogous mechanism for these complexes would involve reversible formation of a bis($R_2Sn{=}E$) intermediate but this would be a 20-electron species and thus is improbable. Again the mechanism is not established with certainty, but reversible reductive elimination to give an 18-electron $R_4Sn_2E_2$ complex is one possibility as shown in Scheme 6. These rearrangements are faster in most cases than the reactions by which the metallacycle is formed, so complete reductive elimination of the $(R_2SnE)_2$ unit, which would then rearrange to the more stable trimer $(R_2SnE)_3$, is unlikely in the isomerization mechanism.

In conclusion, the first examples of Sn−S, Sn−Se, Sn−Te, and Ge−Te bond oxidative addition to platinum(II) are established, each giving rise to a new type of metallacycle. The order of reactivity of the group 14-group 16 bonds toward [PtMe$_2$(bu$_2$-bpy)] was Sn−Te, Ge−Te ≫ Sn−Se > Sn−S, while Ge−Se and Ge−S bonds failed to react. These complexes show catalytic properties and undergo interesting redistribution reactions.

Scheme 6



Experimental Section

Reactions were performed under a nitrogen atmosphere using standard Schlenk techniques. Solvents were freshly distilled, dried and degassed prior to use. NMR spectra were recorded by using a Varian Gemini (^{1}H at 300.10 MHz) or Varian XL300 (^{195}Pt at 64.38 MHz; ^{119}Sn at 111.86 MHz) spectrometer. Chemical shifts are reported in ppm with respect to TMS reference (^{1}H), external aqueous K_2PtCl_4 (^{195}Pt), or internal $SnMe_4$ (^{119}Sn). Unless otherwise specified, all quoted couplings to tin are for the ^{119}Sn isotope only. Fluorescence spectra were recorded by using a Fluorolog-3 spectrofluorometer. Elemental analyses were determined by Guelph Chemical Laboratories, Canada.

The complex [PtMe$_2$(bu$_2$bpy)][5] and the compounds [(Me$_2$SnS)$_3$],[7c] [(Ph$_2$SnS)$_3$],[7b] [(Me$_2$SnSe)$_3$],[7i] [(Ph$_2$SnSe)$_3$],[7b] and [(Me$_2$SnTe)$_3$][7a] were synthesized using literature methods.

[(Ph$_2$SnTe)$_3$]. To a stirred mixture of tellurium powder (1.25 g, 9.8 mmol) and distilled water (10 mL) in a Schlenk tube (50 mL) was slowly added $NaBH_4$ (0.75 g, 19.8 mmol) in distilled water (10 mL) to give a solution of Na^+TeH^-. This solution was cooled to 0 °C and Ph_2SnCl_2 (3.37 g, 9.8 mmol) dissolved in ethanol (10 mL) was slowly added. The solution was stirred for 1 h at room temperature, then extracted with CH_2Cl_2 (2 × 40 mL). The extracts were filtered repeatedly to remove suspended material to yield a yellow solution, which was dried over $MgSO_4$. The solution was evaporated to afford a green-yellow precipitate of the product (2.9 g, 74%), which was recrystallized from benzene/hexane. The compound is decomposed slowly by exposure to air. Anal. Calcd for $C_{36}H_{30}Sn_3Te_3$: C, 35.99; H, 2.52. Found: C, 36.03; H, 2.20. NMR in CD_2Cl_2: δ(^{1}H) 7.2−7.7 [m, Ph]; δ(^{119}Sn) −206 [s, $^1J_{\mathrm{Sn}^{125}\mathrm{Te}}$ = 3366 Hz, $^2J_{\mathrm{Sn-Sn}}$ = 253 Hz].

[(Me$_2$GeTe)$_3$]. To a stirred mixture of tellurium powder (3.68 g, 0.029 mol) and distilled water (20 mL) in a Schlenk tube (100 mL) was slowly added $NaBH_4$ (2.19 g, 0.058 mol) in distilled water (20 mL) under an N_2 atmosphere. The aqueous solution was cooled to 0 °C and Me_2GeCl_2 (5 g, 0.028 mol) was added slowly. The solution was stirred for 15 min at room temperature. The green-yellow precipitate which formed was separated, dried, and extracted with petroleum ether (bp 35−60 °C) in a Soxhlet apparatus. Evaporation of the solvent gave

$(Me_2GeTe)_3$ (3.39 g, 53%), which was slowly decomposed on exposure to air. Anal. Calcd for $C_6H_{18}Ge_3Te_3$: C, 10.43; H, 2.63. Found: C, 10.28; H, 2.33. NMR in CD_2Cl_2: $\delta(^1H)$ 1.40 [s, MeGe].

[PtMe$_2$(Me$_2$SnSe)$_2$(bu$_2$bpy)], 4. To a stirred solution of [PtMe$_2$(bu$_2$bpy) (0.50 g, 1.01 mmol) in acetone (10 mL) was added $(Me_2SnSe)_3$ (0.69 g, 1.01 mmol). The solution was heated under reflux for 0.5 h to afford a yellow, microcrystalline solid which was filtered off, washed with acetone and *n*-pentane, and air-dried. Yield 0.75 g (78%). Anal. Calcd for $C_{24}H_{42}N_2PtSe_2Sn_2 \cdot C_3H_6O$: C, 32.20; H, 4.80; N, 2.78. Found: C, 32.19; H, 4.84; N, 2.72. NMR in CD_2Cl_2: $\delta(^1H)$ 9.53 [d, 1H, $^3J_{H^{5'}H^{6'}} = 5.9$ Hz, $^3J_{PtH^{6'}} = 18.6$ Hz, $H^{6'}$]; 8.73 [d, 1H, $^3J_{H^5H^6} = 5.8$ Hz, $^3J_{PtH^6} = 16.6$ Hz, H^6], 8.25 [d, 1H, $^4J_{H^{3'}H^{5'}} = 1.9$ Hz, $H^{3'}$], 8.21 [d, 1H, $^4J_{H^3H^5} = 2.0$ Hz, H^3], 7.67 [dd, 1H, $^3J_{H^{5'}H^{6'}} = 5.8$ Hz, $^4J_{H^{5'}H^{3'}} = 1.9$ Hz, $H^{5'}$], 7.57 [dd, 1H, $^3J_{H^5H^6} = 5.9$ Hz, $^4J_{H^5H^3} = 2.0$ Hz, H^5], 1.47 [s, 9H, ^{t}bu], 1.44 [s, 9H, ^{t}bu], 1.11 [s, 3H, $^2J_{PtH} = 61.2$ Hz, Pt−Me], 0.64 [s, 3H, $^3J_{PtH} = 2.3$ Hz, $^2J_{SnH} = 51.2$ Hz, Pt−SnMe^a], 0.62 [s, 3H, $^2J_{SnH} = 45.7$ Hz, Pt−Se−SnMe^a], 0.60 [s, 3H, $^3J_{PtH} = 4.1$ Hz, $^2J_{SnH} = 44.5$ Hz, Pt−SnMe^b], 0.36 [s, 3H, $^2J_{PtH} = 60.0$ Hz, Pt−Me], 0.10 [s, 3H, $^2J_{SnH} = 55.8$ Hz, Pt−Se−SnMe^b]; $\delta(^{119}Sn)$ 0.2 [s, $^1J_{Sn^{77}Se^2} = 1497$ Hz, $^1J_{Sn^{77}Se^1} = 1106$ Hz, $^2J_{SnSn} = 249$ Hz, Pt−Se−Sn], −77.1 [s, $^1J_{PtSn} = 11\,940$ Hz, $^1J_{Sn^{77}Se^1} = 841$ Hz, $^2J_{SnSn} = 249$ Hz, Pt−Sn]; $\delta(^{195}Pt) = -2240$ [$^1J_{PtSn} = 11\,921$ Hz].

[PtMe$_2$(Me$_2$SnS)$_2$(bu$_2$bpy)], **2**, was similarly prepard (yield 88%). Anal. Calcd for $C_{24}H_{42}N_2PtS_2Sn_2 \cdot C_3H_6O$: C, 35.51; H, 5.30; N, 3.07. Found: C, 35.57; H, 5.29; N, 3.01. NMR in CD_2Cl_2: $\delta(^1H)$ 9.39 [d, 1H, $^3J_{H^{5'}H^{6'}} = 5.9$ Hz, $^3J_{PtH^{6'}} = 18.0$ Hz, $H^{6'}$], 8.72 [d, 1H, $^3J_{H^5H^6} = 5.8$ Hz, $^3J_{PtH^6} = 12.7$ Hz, H^6], 8.24 [d, 1H, $^4J_{H^{3'}H^{5'}} = 1.8$ Hz, $H^{3'}$], 8.21 [d, 1H, $^4J_{H^3H^5} = 1.9$ Hz, H^3], 7.68 [dd, 1H, $^3J_{H^{5'}H^{6'}} = 5.7$ Hz, $^4J_{H^{5'}H^{3'}} = 1.9$ Hz, $H^{5'}$], 7.58 [dd, 1H, $^3J_{H^5H^6} = 5.9$ Hz, $^4J_{H^5H^3} = 2.0$ Hz, H^5], 1.47 [s, 9H, ^{t}bu], 1.45 [s, 9H, ^{t}bu], 1.08 [s, 3H, $^2J_{PtH} = 61.2$ Hz, $^3J_{SnH} = 3.3$ Hz, Pt−Me], 0.56 [s, 3H, $^3J_{PtH} = 4.0$ Hz, $^2J_{SnH} = 45.6$ Hz, Pt−SnMe^a], 0.53 [s, 3H, $^2J_{SnH} = 51.8$ Hz, Pt−S−SnMe^a], 0.46 [s, 3H, $^2J_{SnH} = 58.0$ Hz, Pt−SnMe^b], 0.26 [s, 3H, $^2J_{PtH} = 59.1$ Hz, Pt-Me], −0.06 [s, 3H, $^2J_{SnH} = 58.0$ Hz, Pt−S−SnMe^b]; $\delta(^{119}Sn)$ 138.1 [s, $^2J_{SnSn} = 223$ Hz, Pt−S−Sn], −34.5 [s, $^1J_{PtSn} = 12\,067$ Hz, $^2J_{SnSn} = 223$ Hz, Pt−Sn]; $\delta(^{195}Pt)$ −1486 [$^1J_{PtSn} = 12\,070$ Hz].

[PtMe$_2$(Ph$_2$SnSe)$_2$(bu$_2$bpy)], 5. To a stirred solution of [PtMe$_2$(bu$_2$bpy)] (0.30 g, 0.61 mmol) in acetone (10 mL) was added $(Ph_2SnSe)_3$ (0.64 g, 0.61 mmol). The solution was heated under reflux for 5 min to afford a dark-yellow, microcrystalline solid product, which was filtered off, washed with acetone and *n*-pentane, and air-dried. Yield 82%. The product cocrystallized with free $(Ph_2SnSe)_3$; analytically pure **5** was obtained by extraction from the product by heating with acetone (10 mL) for 2 h. The dark-yellow microcrystalline solid was then collected as described above. Yield 0.46 g (63%). Anal. Calcd for $C_{44}H_{50}N_2PtSe_2Sn_2$: C, 44.14; H, 4.20; N, 2.34. Found: C, 43.84; H, 4.06; N, 2.25. NMR in CD_2Cl_2: $\delta(^1H)$ 9.14 [d, 1H, $^3J_{H^{5'}H^{6'}} = 6.0$ Hz, $^3J_{PtH^{6'}} = 18.3$ Hz, $H^{6'}$], 8.77 [d, 1H, $^3J_{H^5H^6} = 5.7$ Hz, $^3J_{PtH^6} = 14.4$ Hz, H^6], 8.25 [d, 1H, $^4J_{H^{3'}H^{5'}} = 1.5$ Hz, $H^{3'}$], 8.10 [d, 1H, $^4J_{H^3H^5} = 1.5$ Hz, H^3], 7.94−7.14 [m, 20H, C_6H_5], 7.71 [dd, 1H, $^3J_{H^{5'}H^{6'}} = 5.7$ Hz, $^4J_{H^{5'}H^{3'}} = 1.8$ Hz, $H^{5'}$], 6.89 [dd, 1H, $^3J_{H^5H^6} = 5.9$ Hz, $^4J_{H^5H^3} = 2.0$ Hz, H^5], 1.49 [s, 9H, ^{t}bu], 1.32 [s, 9H, ^{t}bu], 1.31 [s, 3H, $^2J_{PtH} = 60.3$ Hz, Pt−Me], 0.49 [s, 3H, $^2J_{PtH} = 59.4$ Hz, Pt−Me]; $\delta(^{119}Sn)$ −60.3 [s, $^1J_{Sn^{77}Se^2} = 1640$ Hz, $^1J_{Sn^{77}Se^1} = 1178$ Hz, $^2J_{SnSn} = 217$ Hz, Pt−Se−Sn], −194.0 [s, $^1J_{Sn^{77}Se^1} = 921$ Hz, $^1J_{SnPt} = 13\,160$ Hz, Pt−Sn]; $\delta(^{195}Pt)$ −1964 [$^1J_{PtSn} = 13\,210$ Hz.

[PtMe$_2$(Ph$_2$SnS)$_2$(bu$_2$bpy)], **3**, was prepared similarly (yield: 84%). Anal. Calcd for $C_{44}H_{50}N_2PtS_2Sn_2$: C, 47.89; H, 4.57; N, 2.54. Found: C, 47.85; H, 4.53; N, 2.49. NMR in CD_2Cl_2: $\delta(^1H)$ 8.92 [d, 1H, $^3J_{H^{5'}H^{6'}} = 5.9$ Hz, $^3J_{PtH^{5'}} = 17.6$ Hz, $H^{6'}$], 8.76 [d, 1H, $^3J_{H^5H^6} = 5.9$ Hz, $^3J_{PtH^6} = 14.5$ Hz, H^6], 8.23 [d, 1H, $^4J_{H^{3'}H^{5'}} = 1.7$ Hz, $H^{3'}$], 8.09 [d, 1H, $^4J_{H^3H^5} = 1.9$ Hz, H^3], 8.00−7.14 [m, 20H, C_6H_5], 7.73 [dd, 1H, $^3J_{H^{5'}H^{6'}} = 5.9$ Hz, $^4J_{H^{5'}H^{3'}} = 1.8$ Hz, $H^{5'}$], 6.86 [dd, 1H, $^3J_{H^5H^6} = 6.0$ Hz, $^4J_{H^5H^3} = 1.8$ Hz, H^5], 1.48 [s, 9H, ^{t}bu], 1.31 [s, 9H, ^{t}bu], 1.27 [s, 3H, $^2J_{PtH} = 60.0$ Hz, $^3J_{SnH} = 4.1$ Hz, Pt−Me], 0.47 [s, 3H, $^2J_{PtH} = 57.9$ Hz, Pt−Me]; $\delta(^{119}Sn)$ 51.94 [s, $^2J_{SnSn} = 188$ Hz, Pt−S−Sn], −169.1 [s, $^1J_{SnPt} = 13\,344$ Hz, Pt−Sn]; $\delta(^{195}Pt)$ −1432 [$^1J_{PtSn} = 13\,340$ Hz].

[PtMe$_2$(Me$_2$SnTe)$_2$(bu$_2$bpy)], 6. To a stirred solution of [PtMe$_2$(bu$_2$bpy)] (0.20 g, 0.41 mmol) in CH_2Cl_2 (2 mL) was added $(Me_2SnTe)_3$ (0.34 g, 0.41 mmol). The solution was stirred for 5 min, and the solvent was then removed in vacuo. The brown-purple microcrystalline solid product was washed with acetone and *n*-pentane. Yield 0.34 g (81%). NMR in CD_2Cl_2: $\delta(^1H)$ 9.66 [d, ^{1}H, $^3J_{H^{5'}H^{6'}} = 6.0$ Hz, $^3J_{PtH^{6'}} = 18.9$ Hz, $H^{6'}$], 8.75 [d, 1H, $^3J_{H^5H^6} = 6.4$ Hz, $^3J_{PtH^6} = 19.5$ Hz, H^6], 8.26 [d, 1H, $^4J_{H^{3'}H^{5'}} = 1.9$ Hz, $H^{3'}$], 8.21 [d, 1H, $^4J_{H^3H^5} = 2.0$ Hz, H^3], 7.66 [dd, 1H, $^3J_{H^{5'}H^{6'}} = 5.8$ Hz, $^4J_{H^{5'}H^{3'}} = 1.92$ Hz, $H^{5'}$], 7.56 [dd, 1H, $^3J_{H^5H^6} = 6.0$ Hz, $^4J_{H^5H^3} = 2.0$ Hz, H^5], 1.47 [s, 9H, ^{t}bu], 1.45 [s, 9H, ^{t}bu], 1.18 [s, 3H, $^2J_{PtH} = 61.8$ Hz, Pt−Me], 0.88 [s, 3H, $^2J_{SnH} = 52.8$ Hz, Pt−Te−SnMe^a], 0.86 [s, $^3J_{PtH} = 3.3$ Hz, 3H, $^2J_{SnH} = 50.1$ Hz, Pt−SnMe^a], 0.67 [s, 3H, $^3J_{PtH} = 4.5$ Hz, $^2J_{SnH} = 42.7$ Hz, Pt−SnMe^b], 0.50 [s, 3H, $^2J_{PtH} = 59.4$ Hz, Pt−Me], 0.42 [s, 3H, $^2J_{SnH} = 53.8$ Hz, Pt−Te−SnMe^b]; δ(Sn) −168.1 [s, $^1J_{SnPt} = 11\,599$ Hz, $^1J_{Sn^{125}Te^1} = 2046$ Hz, Pt−Sn], −342.1 [s, $^2J_{SnSn} = 192$ Hz, $^1J_{Sn^{125}Te^1} = 2636$ Hz, $^1J_{Sn^{125}Te^2} = 3706$ Hz, $^2J_{SnPt} = 66$ Hz, Pt−Te−Sn]; $\delta(^{195}Pt)$ −2209 [$^1J_{PtSn} = 11\,623$ Hz].

[PtMe$_2$(Ph$_2$SnTe)$_2$(bu$_2$bpy)], **7**, was synthesized in a similar way. Yield 81%. Anal. Calcd for $C_{44}H_{50}N_2PtTe_2Sn_2$: C, 40.82; H, 3.27; N, 2.16. Found: C, 40.93; H, 3.39; N, 1.60. NMR in CD_2Cl_2: $\delta(^1H)$ 9.31 [d, 1H, $^3J_{H^{5'}H^{6'}} = 6.3$ Hz, $^3J_{PtH^{6'}} = 18.1$ Hz, $H^{6'}$], 8.81 [d, 1H, $^3J_{H^5H^6} = 5.7$ Hz, $^3J_{PtH^6} = 16.6$ Hz, H^6], 8.25 [d, 1H, $^4J_{H^{3'}H^{5'}} = 1.5$ Hz, $H^{3'}$], 8.13 [d, 1H, $^4J_{H^3H^5} = 1.8$ Hz, H^3], 7.98−7.18 [m, 20H, C_6H_5], 7.69 [dd, 1H, $^3J_{H^{5'}H^{6'}} = 5.7$ Hz, $^4J_{H^{5'}H^{3'}} = 1.8$ Hz, $H^{5'}$], 6.89 [dd, 1H, $^3J_{H^5H^6} = 5.7$ Hz, $^4J_{H^5H^3} = 1.8$ Hz, H^5], 1.49 [s, 9H, ^{t}bu], 1.34 [s, 9H, ^{t}bu], 1.42 [s, 3H, $^2J_{PtH} = 61.4$ Hz, Pt−Me], 0.56 [s, 3H, $^2J_{PtH} = 58.8$ Hz, Pt−Me]; δ(Sn) −340.3 [s, $^1J_{Sn^{125}Te^2} = 4112$ Hz, $^1J_{Sn^{125}Te^1} = 2892$ Hz, $^2J_{SnSn} = 139$ Hz, $^2J_{SnPt} = 82$ Hz, Pt−Te−Sn], −244.3 [s, $^1J_{Sn^{125}Te^1} = 2248$ Hz, $^1J_{SnPt} = 12\,746$ Hz, Pt−Sn]; $\delta(^{195}Pt)$ −2153 [$^1J_{PtSn} = 12\,750$ Hz].

[PtMe$_2$(Me$_2$GeTe)$_2$(bu$_2$bpy)], 8. This complex was synthesized in a similar way. Yield 75%. NMR in CD_2Cl_2: $\delta(^1H)$ 9.72 [d, ^{1}H, $^3J_{H^{5'}H^{6'}} = 6.1$ Hz, $^3J_{PtH^{6'}} = 17.0$ Hz, $H^{6'}$], 8.75 [d, 1H, $^3J_{H^5H^6} = 6.0$ Hz, $^3J_{PtH^6} = 12.5$ Hz, H^6], 8.24 [d, 1H, $^4J_{H^{3'}H^{5'}} = 1.9$ Hz, $H^{3'}$], 8.19 [d, 1H, $^4J_{H^3H^5} = 2.0$ Hz, H^3], 7.62 [dd, 1H, $^3J_{H^{5'}H^{6'}} = 6.1$ Hz, $^4J_{H^{5'}H^{3'}} = 1.9$ Hz, $H^{5'}$], 7.60 [dd, 1H, $^3J_{H^5H^6} = 6.0$ Hz, $^4J_{H^5H^3} = 2.0$ Hz, H^5], 1.46 [s, 9H, ^{t}bu], 1.45 [s, 9H, ^{t}bu], 1.28 [s, 3H, $^2J_{PtH} = 62.5$ Hz, Pt−Me], 1.15 [s, 3H, $^3J_{PtH} = 9.7$ Hz, Pt−GeMe^a], 0.91 [s, 3H, $^3J_{PtH} = 11.2$ Hz, Pt−GeMe^b], 0.77 [s, 3H, Pt−Te−GeMe^a], 0.55 [s, 3H, Pt−Te−GeMe^b], 0.43 [s, 3H, $^2J_{PtH} = 58.5$ Hz, Pt−Me]; $\delta(^{195}Pt) = -2148$ [s].

[PtMe$_2${(SnMe$_2$)Se(SnPh$_2$)Se}(bu$_2$bpy)], 10. To a stirred solution of **4** (0.20 g, 0.21 mmol) in CH_2Cl_2 (2 mL) was added $(Ph_2SnSe)_3$ (0.22 g, 0.21 mmol). The solution was stirred for 1 h at room temperature, and the solvent was removed in vacuo. Recrystallization of the yellow residue from CH_2Cl_2/*n*-pentane at −30 °C gave yellow microcrystals, which were isolated and purified as described for **4**. Yield 0.18 g (81%). Anal. Calcd for $C_{34}H_{46}N_2PtSe_2Sn_2$: C, 38.05; H, 4.32; N, 2.61. Found: C, 37.69; H, 4.15; N, 2.52. NMR in CD_2Cl_2: $\delta(^1H)$ 9.34 [d, 1H, $^3J_{H^{5'}H^{6'}} = 5.7$ Hz, $^3J_{PtH^{6'}} = 18.4$ Hz, $H^{6'}$], 8.77 [d, 1H, $^3J_{H^5H^6} = 6.0$ Hz, $^3J_{PtH^6} = 19.4$ Hz, H^6], 8.24 [d, 1H, $^4J_{H^{3'}H^{5'}} = 1.6$ Hz, $H^{3'}$], 8.10 [d, 1H, $^4J_{H^3H^5} = 1.7$ Hz, H^3], 7.35−7.08 [m, 10H, C_6H_5], 7.70 [dd, 1H, $^3J_{H^{5'}H^{6'}} = 5.7$ Hz, $^4J_{H^{5'}H^{3'}} = 1.8$ Hz, $H^{5'}$], 7.59 [dd, 1H, $^3J_{H^5H^6} = 7.5$ Hz, $^4J_{H^5H^3} = 2.4$ Hz, H^5], 1.48 [s, 9H, ^{t}bu], 1.33 [s, 9H, ^{t}bu], 1.17 [s, 3H, $^2J_{PtH} = 60.9$ Hz, Pt−Me], 0.67 [s, 3H, $^3J_{PtH} = 3.4$ Hz, $^2J_{SnH} = 50.7$ Hz, Pt−SnMe^a], 0.63 [s, 3H, $^3J_{PtH} = 3.8$ Hz, $^2J_{SnH} = 46.1$ Hz, Pt−SnMe^b], 0.31 [s, 3H, $^2J_{PtH} = 59.7$ Hz, Pt−Me]; δ(Sn) −57.4 [s, $^1J_{Sn^{77}Se^2} = 1645$ Hz, $^1J_{Sn^{77}Se^1} = 1193$ Hz, $^2J_{SnSn} = 250$ Hz, Pt−Se−Sn], −72.5 [s, $^1J_{Sn^{77}Se^1} = 794$ Hz, $^1J_{SnPt} = 11\,973$ Hz, Pt−Sn]; $\delta(^{195}Pt)$ −2161 [$^1J_{PtSn} = 11\,968$ Hz]. Prolonged reaction times led to the formation of **5**.

[PtMe$_2${(SnMe$_2$)S(SnPh$_2$)S}(bu$_2$bpy)], **9**, was prepared similarly (yield: 84%). Anal. Calcd for $C_{34}H_{46}N_2PtS_2Sn_2$: C, 41.70; H, 4.73; N, 2.86. Found: C, 41.94; H, 4.61; N, 2.79. NMR in CD_2Cl_2: $\delta(^1H)$ 9.21 [d, 1H, $^3J_{H^{5'}H^{6'}} = 5.9$ Hz, $^3J_{PtH^{6'}} = 18.4$ Hz, $H^{6'}$], 8.77 [d, 1H, $^3J_{H^5H^6} = 5.8$ Hz, $^3J_{PtH^6} = 14.1$ Hz, H^6], 8.23 [d, 1H, $^4J_{H^{3'}H^{5'}} = 1.7$ Hz, $H^{3'}$], 8.10 [d, 1H, $^4J_{H^3H^5} = 1.9$ Hz, H^3], 7.62−7.08 [m, 10H, C_6H_5], 7.72 [dd, 1H, $^3J_{H^{5'}H^{6'}} = 5.9$ Hz, $^4J_{H^{5'}H^{3'}} = 1.7$ Hz, $H^{5'}$], 7.70 [dd, 1H, $^3J_{H^5H^6} = 5.8$ Hz, $^4J_{H^5H^3} = 1.9$ Hz, H^5], 1.48 [s, 9H, ^{t}bu], 1.34 [s, 9H, ^{t}bu], 1.14 [s, 3H, $^2J_{PtH} = 60.7$ Hz, $^3J_{SnH} = 3$ Hz, Pt−Me], 0.60 [s, 3H, $^3J_{PtH} = 3.9$ Hz, $^2J_{SnH} = 45.8$ Hz, Pt−SnMe^a], 0.57 [s, 3H, $^2J_{SnH} = 51.6$ Hz, Pt−SnMe^b], 0.22 [s, 3H, $^2J_{PtH} = 58.7$ Hz, Pt−Me]; δ(Sn) 51.71 [s, $^2J_{SnSn} = 217$ Hz, Pt−S−Sn], −32.67 [s, $^1J_{SnPt} = 12\,103$ Hz, Pt−Sn]; $\delta(^{195}Pt)$ −1479 [$^1J_{PtSn} = 12\,100$ Hz].

[PtMe$_2${SnMe$_2$)Te(SnPh$_2$)Te}(bu$_2$bpy)], **11**, was synthesized in a similar way. Yield 77%. Anal. Calcd for $C_{34}H_{46}N_2PtTe_2Sn_2$: C, 34.89; H, 3.96; N, 2.39. Found: C, 34.51; H, 3.71; N, 2.14. NMR in CD_2Cl_2:

$\delta(^{1}\mathrm{H})$ 9.48 [d, 1H, $^{3}J_{\mathrm{H}^{5'}\mathrm{H}^{6'}} = 6.0$ Hz, $^{3}J_{\mathrm{PtH}^{6'}} = 19.4$ Hz, $\mathrm{H}^{6'}$], 8.78 [d, 1H, $^{3}J_{\mathrm{H}^{5}\mathrm{H}^{6}} = 6.3$ Hz, $^{3}J_{\mathrm{PtH}^{6}} = 15.0$ Hz, H^{6}], 8.25 [d, 1H, $^{4}J_{\mathrm{H}^{3'}\mathrm{H}^{5'}} = 1.8$ Hz, $\mathrm{H}^{3'}$], 8.11 [d, 1H, $^{4}J_{\mathrm{H}^{3}\mathrm{H}^{5}} = 1.8$ Hz, H^{3}], 7.28−7.06 [m, 10H, C_6H_5], 7.66 [dd, 1H, $^{3}J_{\mathrm{H}^{5'}\mathrm{H}^{6'}} = 6.2$ Hz, $^{4}J_{\mathrm{H}^{5'}\mathrm{H}^{3'}} = 1.8$ Hz, $\mathrm{H}^{5'}$], 7.56 [dd, 1H, $^{3}J_{\mathrm{H}^{5}\mathrm{H}^{6}} = 7.7$ Hz, $^{4}J_{\mathrm{H}^{5}\mathrm{H}^{3}} = 1.5$ Hz, H^{5}], 1.48 [s, 9H, ^{t}bu], 1.33 [s, 9H, ^{t}bu], 1.22 [s, 3H, $^{2}J_{\mathrm{PtH}} = 61.2$ Hz, Pt−Me], 0.88 [s, 3H, $^{3}J_{\mathrm{PtH}} = 3.0$ Hz, $^{2}J_{\mathrm{SnH}} = 49.7$ Hz, Pt−SnMe^{a}], 0.68 [s, 3H, $^{3}J_{\mathrm{PtH}} = 4.5$ Hz, $^{2}J_{\mathrm{SnH}} = 43.3$ Hz, Pt−SnMe^{b}], 0.44 [s, 3H, $^{2}J_{\mathrm{PtH}} = 58.8$ Hz, Pt−Me]; δ(Sn) −334.5 [s, $^{1}J_{\mathrm{Sn}^{125}\mathrm{Te}^{2}} = 4101$ Hz, $^{1}J_{\mathrm{Sn}^{125}\mathrm{Te}^{1}} = 2891$ Hz, $^{2}J_{\mathrm{SnSn}} = 181$ Hz, $^{2}J_{\mathrm{SnPt}} = 96$ Hz, Pt−Te−Sn], −160.5 [s, $^{1}J_{\mathrm{Sn}^{125}\mathrm{Te}} = 1942$ Hz, $^{1}J_{\mathrm{SnPt}} = 11\,686$ Hz, Pt−Sn]; $\delta(^{195}\mathrm{Pt})$ −2197 [$^{1}J_{\mathrm{PtSn}} = 11\,681$ Hz].

[PtMe$_2$(Me$_2$SnS)(Me$_2$SnSe)(bu$_2$bpy)], 12. A mixture of **2** (0.070 g, 0.082 mmol) and $(Me_2SnSe)_3$ (0.056 g, 0.082 mmol) in CH_2Cl_2 was stirred for 8 h. The solvent was removed in vacuo, and the solid residue was washed with acetone and *n*-pentane to yield the product in slightly impure form. Yield 0.063 g (85%). The product was always contaminated with small amounts of **2** and **4**, so it could not be isolated in analytically pure form. NMR in CD_2Cl_2: $\delta(^{1}\mathrm{H})$ 1.47 [s, 9H, ^{t}bu], 1.44 [s, 9H, ^{t}bu], 1.09 [s, 3H, $^{2}J_{\mathrm{PtH}} = 61.1$ Hz, Pt−Me], 0.57 [s, 3H, $^{3}J_{\mathrm{PtH}} = 4.0$ Hz, $^{2}J_{\mathrm{SnH}} = 45.8$ Hz, Pt−SnMe^{a}], 0.55 [s, 3H, $^{3}J_{\mathrm{PtH}} = 2.5$ Hz, $^{2}J_{\mathrm{SnH}} = 51.6$ Hz, Pt−SnMe^{b}], 0.51 [s, 3H, $^{2}J_{\mathrm{SnH}} = 51.1$ Hz, Pt−Se−SnMe^{a}], 0.34 [s, 3H, $^{2}J_{\mathrm{PtH}} = 59.5$ Hz, Pt−Me], 0.061 [s, 3H, $^{2}J_{\mathrm{SnH}} = 57.3$ Hz, Pt−Se−SnMe^{b}]; δ(Sn) −41.3 [s, $^{1}J_{\mathrm{SnPt}} = 11\,951$ Hz, $^{2}J_{\mathrm{SnSn}} = 223$ Hz, Pt−Sn], 51.6 [s, $^{1}J_{\mathrm{Sn}^{77}\mathrm{Se}^{2}} = 1501$ Hz, $^{2}J_{\mathrm{SnSn}} = 223$ Hz, Pt−Se−Sn].

[PtMe$_2$(Me$_2$SnS)(Me$_2$SnTe)(bu$_2$bpy)], **13**, was prepared similarly from **6** (0.075 g, 0.072 mmol) and $(Me_2SnS)_3$ (0.039 g, 0.072 mmol) in CH_2Cl_2 for 8 h. Yield 0.053 g (78%). NMR in CD_2Cl_2: $\delta(^{1}\mathrm{H})$ 1.47 [s, 9H, ^{t}bu], 1.44 [s, 9H, ^{t}bu], 1.13 [s, 3H, $^{2}J_{\mathrm{PtH}} = 61.5$ Hz, Pt−Me], 0.68 [s, 3H, $^{2}J_{\mathrm{SnH}} = 51.9$ Hz, Pt−Te−SnMe^{a}], 0.59 [s, 3H, $^{3}J_{\mathrm{PtH}} = 3.9$ Hz, $^{2}J_{\mathrm{SnH}} = 46.1$ Hz, Pt−SnMe^{a}], 0.55 [s, 3H, $^{3}J_{\mathrm{PtH}} = 2.5$ Hz, $^{2}J_{\mathrm{SnH}} = 51.8$ Hz, Pt−SnMe^{b}], 0.47 [s, 3H, $^{2}J_{\mathrm{PtH}} = 59.8$ Hz, Pt−Me], 0.22 [s, 3H, $^{2}J_{\mathrm{SnH}} = 53.3$ Hz, Pt−Te−SnMe^{b}]; δ(Sn) −50.5 [s, $^{1}J_{\mathrm{SnPt}} = 11\,737$ Hz, Pt−Sn^{1}, $^{2}J_{\mathrm{SnSn}} = 214$ Hz, $^{2}J_{\mathrm{SnPt}} = 52$ Hz, Pt−Sn], −128.4 [s, $^{1}J_{\mathrm{Sn}^{125}\mathrm{Te}^{2}} = 3924$ Hz, $^{2}J_{\mathrm{SnSn}} = 214$ Hz, Pt−Te−Sn].

[PtMe$_2$(Me$_2$SnSe)(Me$_2$SnTe)(bu$_2$bpy)], **14**, was also prepared similarly from **3** (0.070 g, 0.074 mmol) and $(Me_2SnTe)_3$ (0.061 g, 0.074 mmol) in CH_2Cl_2 for 8 h. Yield 0.061 g (82%). NMR in CD_2Cl_2: $\delta(^{1}\mathrm{H})$ 1.47 [s, 9H, ^{t}bu], 1.44 [s, 9H, ^{t}bu], 1.15 [s, 3H, $^{2}J_{\mathrm{PtH}} = 61.6$ Hz, Pt−Me], 0.72 [s, 3H, $^{2}J_{\mathrm{SnH}} = 47.8$ Hz, Pt−Te−SnMe^{a}], 0.65 [s, 3H, $^{3}J_{\mathrm{PtH}} = 4.0$ Hz, $^{2}J_{\mathrm{SnH}} = 45.1$ Hz, Pt−SnMe^{a}], 0.61 [s, 3H, $^{3}J_{\mathrm{PtH}} = 2.5$ Hz, $^{2}J_{\mathrm{SnH}} = 44.5$ Hz, Pt−SnMe^{b}], 0.48 [s, 3H, $^{2}J_{\mathrm{PtH}} = 59.5$ Hz, Pt−Me], 0.31 [s, 3H, $^{2}J_{\mathrm{SnH}} = 55.3$ Hz, Pt−Te−SnMe^{b}]; δ(Sn) −86.0 [s, $^{1}J_{\mathrm{SnPt}} = 11\,686$ Hz, $^{2}J_{\mathrm{SnSn}} = 238$ Hz, Pt−Sn], −193.2 [s, $^{1}J_{\mathrm{Sn}^{125}\mathrm{Te}^{2}} = 3845$ Hz, $^{1}J_{\mathrm{Sn}^{77}\mathrm{Se}^{1}} = 1053$ Hz, $^{2}J_{\mathrm{SnSn}} = 238$ Hz, $^{2}J_{\mathrm{SnPt}} = 60$ Hz, Pt−Te−Sn].

[PtMe$_2$(Ph$_2$SnS)(Ph$_2$SnSe)(bu$_2$bpy)], **15a**, was prepared similarly from **2** (0.075 g, 0.068 mmol) and $(Ph_2SnSe)_3$ in CH_2Cl_2 for 4 days. Yield 0.064 g (82%). NMR in CD_2Cl_2: $\delta(^{1}\mathrm{H})$ 1.49 [s, 9H, ^{t}bu], 1.34 [s, 9H, ^{t}bu], 1.30 [s, 3H, $^{2}J_{\mathrm{PtH}} = 58.6$ Hz, Pt−Me], 0.47 [s, 3H, $^{2}J_{\mathrm{PtH}} = 60.0$ Hz, Pt−Me]; δ(Sn) −173.1 [s, $^{1}J_{\mathrm{SnPt}} = 13\,237$ Hz, $^{2}J_{\mathrm{SnSn}} = 183$ Hz, Pt−Sn], −22.3 [s, $^{1}J_{\mathrm{Sn}^{77}\mathrm{Se}^{2}} = 1669$ Hz, $^{2}J_{\mathrm{SnSn}} = 183$ Hz, Pt−Se−Sn].

[PtMe$_2$(Ph$_2$SnSe)(Ph$_2$SnS)(bu$_2$bpy)], **15b**, was prepared similarly from **5** (0.075 g, 0.063 mmol) and $(Ph_2SnS)_3$ (0.058 g, 0.063 mmol) in CH_2Cl_2 for 4 days. Yield 0.058 g, (80%). NMR in CD_2Cl_2: $\delta(^{1}\mathrm{H})$ 1.49 [s, 9H, ^{t}bu], 1.33 [s, 9H, ^{t}bu], 1.31 [s, 3H, $^{2}J_{\mathrm{PtH}} = 58.1$ Hz, Pt−Me], 0.47 [s, 3H, $^{2}J_{\mathrm{PtH}} = 60.0$ Hz, Pt−Me]; δ(Sn) −188.6 [s, $^{1}J_{\mathrm{SnPt}} = 13\,253$ Hz, $^{2}J_{\mathrm{SnSn}} = 224$ Hz, Pt−Sn], 23.6 [s, $^{1}J_{\mathrm{Sn}^{77}\mathrm{Se}^{1}} = 1215$ Hz, $^{2}J_{\mathrm{SnSn}} = 224$ Hz, Pt−S−Sn].

Reaction of 2 with MeI. To a solution of **2**·acetone (0.043 mmol) in CD_2Cl_2 (0.5 mL) in an NMR tube was added MeI (0.043 mmol). There was an immediate color change from bright to pale yellow. The NMR spectrum recorded after 5 min showed the presence of [PtIMe$_3$(bu$_2$bpy)] and [$(Me_2SnS)_3$] only.

X-ray Structure Determinations. Data were collected at room temperature by using a Siemens P4 diffractometer (complex **3**) or an Enraf-Nonius diffractometer fitted with a CCD detector (complexes **4**, **5**, and **7**). Details of the crystal data and experimental parameters are given in Table 4, and selected bond parameters are listed in Tables 2 and 3. In each case, the space group was defined by systematic absences, an empirical absorption correction was applied, and refinement was carried out by full-matrix, least-squares calculations on F^2. Complex **4** was found to contain an acetone molecule in the lattice, while the lattices of the other compounds contained no solvent. Full details of the structures are available in the supporting materials.

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Supporting Information Available: X-ray crystallographic files in CIF format, for the structures of complexes **3**, **4**, **5**, and **7** are available free of charge via the Internet at http://pubs.acs.org.

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