Ring Expansion and Contraction in Reactions of an Alkyne with Stannylplatinum(IV) Metallacycles: Formation of an Alkyl(alkenyl)(alkynyl)platinum(IV) Complex

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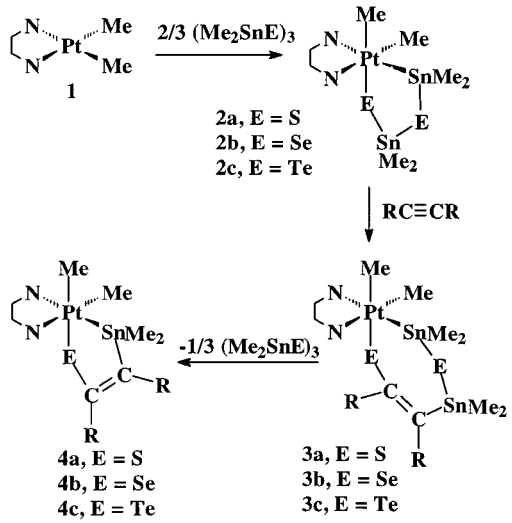
Received September 5, 2001

The five-membered stannylplatinum(IV) metallacycles $[PtMe_2\{SnMe_2ESnMe_2E\}(bu_2bpy)]$, E = S, Se, Te, bu_2bpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine, undergo facile ring expansion by insertion of the electrophilic alkyne RCCR, R = CO_2Me, into the PtE−Sn bond to yield the corresponding seven-membered metallacycles $[PtMe_2\{SnMe_2ESnMe_2CR{=}CRE\}(bu_2bpy)]$. The seven-membered metallacycles slowly eliminate "Me_2SnE" to give new five-membered metallacycles $[PtMe_2\{SnMe_2CR{=}CRE\}(bu_2bpy)]$. When E = Se, reaction with excess RCCR gives the complex $[PtMe_2(CR{=}CRH)(CCR)(bu_2bpy)]$, which contains alkyl, alkenyl, and alkynyl functionalities in the same molecule. In the presence of excess RCCR and $[(Me_2SnSe)_3]$, the products Se(*Z*-CR=CHR)$_2$ and the selenole Se(CR=CRCR=CR) are formed catalytically.

Introduction

Metallacycles are intermediates in a number of catalytic transformations such as metathesis, dimerization, or trimerization of alkenes or alkynes, and so they have attracted considerable interest.[1,2] A key property of metallacyclic compounds is their ability to undergo easy ring expansion and contraction reactions, often with formation or cleavage of metal−carbon and carbon−carbon bonds. Oxidative addition may lead to activation of cyclic compounds, especially those with ring strain, to form metallacycles, and the reverse reductive elimination can lead to cyclic products.[1−3] For example, it has been shown that a Sn−E bond (E = S, Se, Te) of the ring compounds $[(Me_2SnE)_3]$ oxidatively adds to $[PtMe_2(bu_2bpy)]$, **1** (bu_2bpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine), to give organoplatinum(IV) metallacycles $[PtMe_2(Me_2SnE)_2(bu_2bpy)]$, **2** (Scheme 1), which contain five-membered PtSnESnE rings and which exhibit interesting redistribution chemistry and catalytic properties.[4] This article reports the reactions of the electrophilic alkyne RCCR, R = CO_2Me, with these metallacycles, which occur by ring expansion to give the unusual complexes $[PtMe_2\{SnMe_2ESnMe_2CR{=}CRE\}(bu_2bpy)]$, containing reactive seven-membered rings. A preliminary report of parts of this work has been published.[5]

Scheme 1[a]



[a] R = CO_2Me; NN = bu_2bpy.

Results

Formation of Seven-Membered Ring Complexes. The electrophilic alkyne dimethyl acetylenedicarboxylate (RCCR; R = CO_2Me) inserts regioselectively into a Sn−E bond of the five-membered metallacyclic complex $[PtMe_2\{SnMe_2ESnMe_2E\}(bu_2bpy)]$, **2**, to form the cor-

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10.1021/om010800y CCC: $22.00
Publication on Web 02/16/2002

responding seven-membered metallacyclic complex [$PtMe_2${$SnMe_2ESnMe_2CR{=}CRE$}(bu_2bpy)], **3** (Scheme 1). These reactions are complete in 1 h at room temperature in CH_2Cl_2 solution, and the products **3** are yellow and air-stable when E = S or Se, but dark brown and air-sensitive when E = Te. The complexes **2** are unreactive toward less electrophilic alkynes such as PhCCPh, and the similar phenyltin derivatives [$PtMe_2$-{$SnPh_2ESnPh_2E$}(bu_2bpy)] are inert to both RCCR (R = CO_2Me) and PhCCPh.

The new complexes **3** (Scheme 1) were characterized by NMR and, in the case of **3b**, by X-ray structure determination. The ^{1}H NMR spectra of complexes **3** are similar, and only the spectrum of **3a** will be discussed. The complex gives four SnMe, two MePt, and two MeO resonances in the ^{1}H NMR, each corresponding to three protons, thus showing that 1 equiv of alkyne has been added and that the product has no symmetry. One of the SnMe resonances shows coupling to platinum [^3J(PtSnMe) = 4 Hz], and this shows that the Pt−Sn bond is still present in **3a**. The methylplatinum coupling constants ^2J(PtMe) = 59 Hz (Me *trans* to N) and 62 Hz (Me *trans* to E) are similar to those in the precursor complex **2a** and confirm the presence of octahedral platinum(IV).[6] The methoxy resonances occur at δ = 2.80 and 3.41, shifted somewhat from the corresponding value for the free alkyne with δ(MeO) = 3.82. The ^{119}Sn NMR spectrum of **3a** contains two resonances at δ(Sn) = 6.81 and −81.45 [^1J(PtSn) = 11860 Hz], and the observation of the large ^1J(PtSn) coupling clearly shows that the Pt−Sn bond is still present in **3a** and allows easy assignment of the resonances. Both ^{119}Sn resonances exhibit a coupling $^2J(Sn^1SSn^2)$ = 151 Hz, thus showing that the $PtSnMe_2SSnMe_2$ unit was still present. Together, these data define the structure **3a** and show that insertion occurred into the PtS−Sn bond of the precursor complex **2a**.

Complex **3b** was characterized by an X-ray structure determination, and its structure is shown in Figure 1. The structure confirms that RCCR insertion takes place into the PtSe−Sn bond of **2b**. The seven-membered ring in **3b** has a twisted conformation, and this leads to relatively short transannular distances Sn(2)···Se(1) = 3.42 Å and Sn(1)···Se(1) = 3.48 Å, perhaps indicating weak secondary bonding between these atoms. Compared to the five-membered ring of **2b**,[3] the transannular distance between Sn2···Se1 is short (3.42 Å in **3b** vs 3.63 Å in **2b**). The stereochemistry at the C=C bond is *cis*, and one CO_2Me group stacks below the bipyridyl ligand. The Pt−N distance *trans* to tin [2.228(4) Å] is longer than the one *trans* to methyl [2.156(3) Å], as a result of the very high *trans*-influence of tin.[3]

Formation of Five-Membered Ring Complexes. The complexes **3** are sufficiently stable to isolate and characterize, but they decompose in solution over a period of about 8 h at room temperature by elimination of [$(Me_2SnE)_3$] (identified by ^{1}H NMR) to form the corresponding five-membered metallacyclic complexes [$PtMe_2${$SnMe_2ESnMe_2CR{=}CRE$}(bu_2bpy)], **4** (Scheme 1). The complexes **4** were yellow and air-stable when E = S or Se but brown and air-sensitive when E = Te. They were characterized spectroscopically and, for **4b**, by X-ray structure determination. The overall formation of the five-membered ring in **4** from the five-membered ring in **2** involves formal substitution of the alkyne RCCR for a Me_2SnE unit, with the seven-membered ring as intermediate.

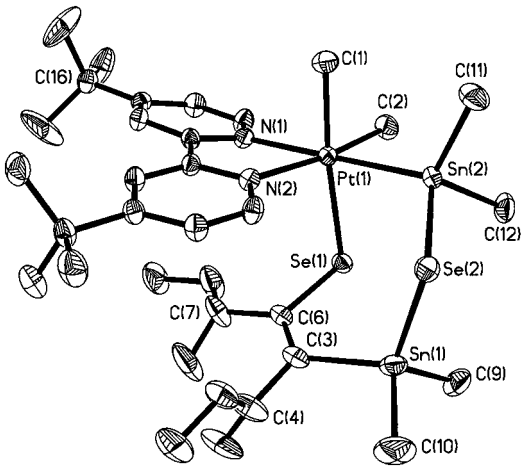

Figure 1. Molecular structure of **3b**. Selected bond distances (Å): Pt−N(2) = 2.156(3), Pt−N(1) = 2.228(4), Pt−C(1) = 2.085(5), Pt−C(2) = 2.065(5), Pt−Sn(2) = 2.5625(4), Sn(2)−Se(2) = 2.5671(6), Se(2)−Sn(1) = 2.5137(6), Sn(1)−C(3) = 2.161(6), C(3)−C(6) = 1.323(7), C(6)−Se(1) = 1.919-(4), Se(1)−Pt = 2.5380(5). Bond angles (deg): Pt−Sn(2)−Se(2) = 114.52(2), Sn(2)−Se(2)−Sn(1) = 103.19(2), Se(2)−Sn(1)−C(3) = 112.4(1), Sn(1)−C(3)−C(6) = 122.2(4), C(3)−C(6)−Se(1) = 121.4(4), C(6)−Se(1)−Pt = 106.4(1), Se(1)−Pt−Sn(2) = 84.12(1). There is disorder of the two CO_2Me groups and of one *tert*-butyl group that is not shown, for clarity.

The ^{1}H NMR of spectrum of complex **4a** exhibits two MeSn, two MePt, and two MeO resonances as expected for the proposed structure (Scheme 1). The MeO resonances occur at δ = 3.65 and 3.61, close to the value for the free alkyne (δ = 3.82). The methylplatinum resonances have coupling constants ^2J(PtMe) = 61 Hz (MePt *trans* to S) and 57 Hz (MePt *trans* to N), similar to those in the corresponding metallacycles **2a** and **3a**, and indicate octahedral platinum(IV).[6] The two MeSn signals each have satellites due to the coupling ^3J(PtSnMe), thus confirming the presence of the Pt−Sn bond, and this is confirmed by the observation of a single resonance in the ^{119}Sn NMR spectrum, with satellites due to the coupling ^1J(PtSn) = 9904 Hz.

The structure of complex **4b** is shown in Figure 2. There are two independent molecules in the unit cell, differing mainly in terms of rotation of one CO_2Me group (Figure 2). The structure confirms the presence of the five-membered PtSnC=CSe ring, which is only slightly distorted from planarity. For example, torsion angles in **4b** are Pt−Se−C=C = −9° and Pt−Sn−C=C = 9°. In contrast, the highly twisted conformation adopted by the seven-membered ring in **3b** gives torsion angles PtSeC=C = −103° and PtSnSeSn = 62.5°, and the envelope conformation of **2b** gives torsion angles PtSeSnSe = −34° and PtSnSeSn = 25°.[4b] The five-membered ring of **4b** contains a relatively short transannular distance Se(1)···Sn(1) = 3.554 Å. The Pt−N distance *trans* to tin [2.244(7) Å] is again longer than that *trans* to methyl [2.144(6) Å] as a result of the very high *trans* influence of tin.

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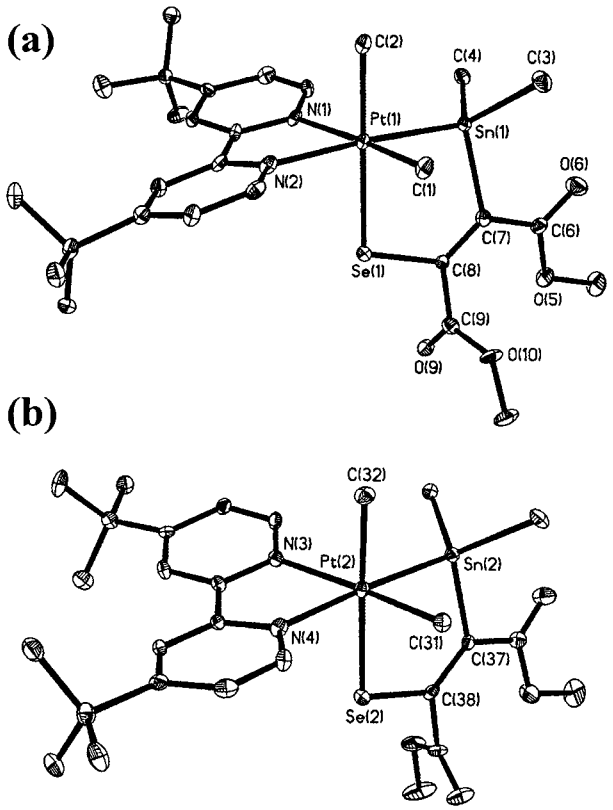
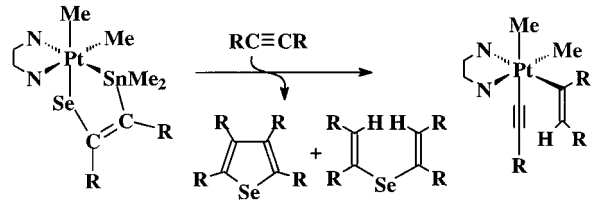


Figure 2. Molecular structures of the two independent molecules of **4b**. Molecules (a) and (b) are related roughly by rotation by about 180° about the bond C(8)−C(9) of molecule (a). Selected bond distances (Å): Pt(1)−C(1) = 2.062(9), Pt(1)−C(2) = 2.091(8), Pt(1)−Sn(1) = 2.5578(7), Pt(1)−Se(1) = 2.5303(9), Pt(1)−N(1) = 2.144(6), Pt(1)−N(2) = 2.244(7). Bond angles (deg): Se(1)−Pt(1)−Sn(1) = 88.60(3), Pt(1)−Sn(1)−C(7) = 99.0(2), Sn(1)−C(7)−C(8) = 120.6(6), C(7)−C(8)−Se(1) = 109.4(5), C(8)−Se(1)−Pt(1) = 104.5(2).

Scheme 2[a]



[a] R = CO_2Me; NN = bu_2bpy.

Reactions with Excess Alkyne. Complex **4b** reacted with excess RCCR to give a mixture of organoselenium compounds, **5** and **6**, an uncharacterized organotin product, **7**, and an unexpected organoplatinum(IV) complex, **8** (Scheme 2). The organoselenium complexes were formed in approximately equal amounts and were separated chromatographically and identified by their ^{1}H NMR and mass spectra as a mixture of the known selenole **5**[7] and the bis(*Z*-alkenyl)selenium compound **6**. The stereochemistry of **6** is deduced from the magnitude of the coupling constant ^3J(SeC=CH) = 5 Hz; the *E*-isomer would be expected to have ^3J(SeC=CH) = ca. 20 Hz.[8] The organotin product, **7**, could be observed by its NMR spectrum in the reaction mixture, but it decomposed on the chromatography column and so was not isolated in pure form or structurally characterized.

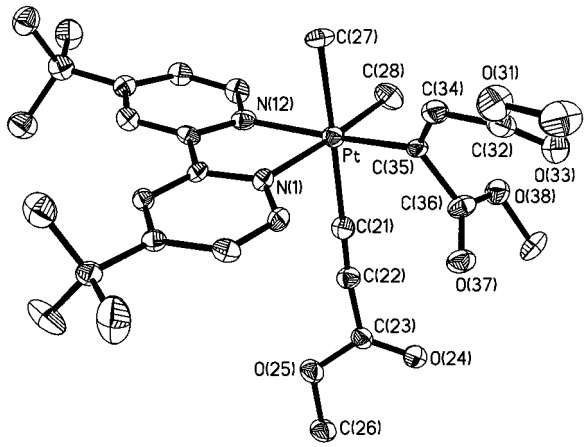


Figure 3. Molecular structure of complex **8**. Selected bond distances (Å): Pt−C(35) = 2.01(1), Pt−C(28) = 2.07(1), Pt−C(21) = 2.09(1), Pt−C(27) = 2.10(1), Pt−N(1) = 2.134(8), Pt−N(12) = 2.114(9). Bond angles (deg): C(21)−Pt−C(27) = 177.4(4), C(22)−C(21)−Pt = 178.3(9), C(34)−C(35)−Pt = 125.6(8).

The organoplatinum product **8** was identified by its ^{1}H and ^{13}C NMR spectra and by an X-ray structure determination. The ^{1}H NMR spectrum contained two PtMe resonances with values of ^2J(PtMe) = 69 Hz [Me *trans* to N] and 51 Hz [Me *trans* to alkynyl]. There were three MeO resonances (δ = 3.79, 3.68, 3.51) of equal intensity, due to the three different groups R in **8** and six aromatic resonances from the bu_2bpy ligand, indicating the absence of a mirror plane in the molecule. The alkenyl =CH resonance was observed at δ = 6.54 and the coupling constant ^3J(PtC=CH) = 80 Hz is consistent with the *Z*-stereochemistry.[9] The ^{13}C NMR spectrum of **8** established the presence of four carbon atoms directly bonded to the platinum center [δ = −5.38, ^1J(PtC) = 575 Hz, PtMe *trans* to N; δ = 3.88, ^1J(PtC) = 477 Hz, PtMe *trans* to C; δ = 119.26, ^1J(PtC) = 780 Hz, PtC(alkenyl *trans* to N); δ = 142.17, ^1J(PtC) = 901 Hz, PtC(alkynyl *trans* to C)]. This gives a dramatic demonstration that the coupling constant ^1J(PtC) follows the series in terms of hybridization at carbon sp > sp^2 > sp^3, even overcoming differences due to *trans*-influence.

The structure of complex **8** is shown in Figure 3. One methyl group and the alkenyl group are *trans* to nitrogen donors, while the other methyl group and the alkynyl group are mutually *trans*. The two Pt−N bond distances [2.134(8) Å, *trans* to Me; 2.114(9) Å, *trans* to alkenyl] are similar and suggest that the methyl and CR=CRH groups have about the same *trans*-influence.

Complex **4b** acted as an inefficient catalyst for the reaction of [$(Me_2SnSe)_3$] and RCCR to give the products **5**, **6**, and **7**, in a 1:1:2 ratio, with a turnover frequency of 0.06 h^{-1} at 40 °C in CH_2Cl_2, as determined by NMR monitoring. Under these conditions, with excess [$(Me_2SnSe)_3$] and RCCR present, complex **4b** was shown to remain as the catalyst resting state, and complex **8** was not formed in detectable amounts. The catalysis is slow, but the catalyst is long-lived and the reaction was monitored through several turnovers.

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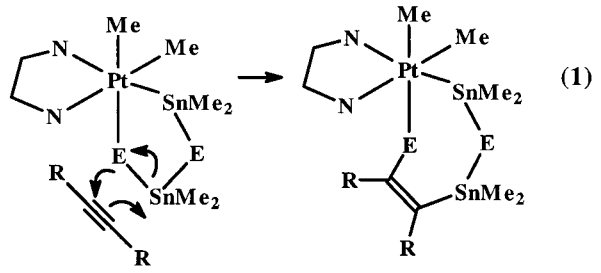
Discussion

The five-membered metallacyclic complexes **2** cannot easily undergo insertion of alkynes at the 18-electron platinum(IV) center, but they can react at a Sn−E bond. It is interesting that the easy ring expansion occurs by regioselective insertion of the electrophilic alkyne dimethyl acetylenedicarboxylate (RCCR) into the shortest, and hence probably the strongest, Sn−Se bond in complex **2b** (Scheme 1). Thus, insertion occurs into the PtSe−Sn bond [Sn−Se = 2.4779(7) Å, ^1J(SnSe) = 1497 Hz], which is shorter and has a higher tin−selenium coupling constant than either the PtSn−Se [Sn−Se = 2.5322(8) Å, ^1J(SnSe) = 841 Hz] or PtSnSe−Sn [Sn−Se = 2.5645(7) Å, ^1J(SnSe) = 1106 Hz]. The observation of the short PtSn−Se bond and high ^1J(SnSe) coupling constant in **2b** was rationalized on the basis that the *trans* methyl group can weaken and polarize the Pt−Se(1) bond, thus leading to enhanced Se−Sn π-bonding. Although it is counterintuitive that the strongest bond would be most reactive, it is likely that the same factors that lead to a shortening of the PtSn−Se bond are also responsible for its high reactivity toward RCCR. Thus, if the insertion reaction is initiated by nucleophilic attack by a lone pair of electrons of selenium on the electrophilic alkyne, the most electron-rich selenium should be most reactive (eq 1). It is interesting that the Sn−E bonds in the precursor molecules [$(Me_2SnE)_3$] are unreactive toward this alkyne, and so the Sn−E bond must be activated within the platinum complex by the polarization effect discussed above. The seven-membered heterocycle ring in complexes [$PtMe_2${$SnMe_2ESnMe_2CR$=CRE}(bu_2bpy)] is well-established and adds plausibility to the suggestion that seven-membered ring intermediates [$PtMe_2(Me_2SnE)_3(bu_2bpy)$] might be formed as transient intermediates in reactions of **1** with [$(Me_2SnE)_3$].[4b]



(1)

In the reaction of seven-membered ring complexes **3** to give the five-membered ring complexes **4** (Scheme 1), it is possible that either the [$Me_2Sn^1E^2$] unit or the [$Me_2Sn^2E^2$] unit (see Figure 1 for labeling) might be eliminated. Both of these routes require cleavage of a Sn−Se bond, but one also requires Sn−C bond cleavage and the other Sn−Pt bond cleavage. It is not obvious which would be preferred.

The reaction of **4b** with excess RCCR is complex, and the mechanism is obscure. The reaction occurs with loss of the Me_2Sn and Se fragments. The selenium forms the selenole **5** and the bis(alkenyl)selenide **6**, while the fate of the dimethyltin fragment is not determined. The most interesting product is the organoplatinum(IV) complex **8**, which contains methyl, alkenyl, and alkynyl ligands at the same metal center (Scheme 2, Figure 3). Complex **8** is stable and fails to react with either excess RCCR or [$(Me_2SnSe)_3$]. The formation of the alkenyl groups present in compounds **5** and **8** requires that an H atom abstraction step must occur, and since the alkenyl proton is still observed in the product formed in reactions in the deuterated solvents CD_2Cl_2 or C_6D_6, the source of the H atom in the CR=CRH group must be one of the reagents used. The formation of **8** also requires cleavage of a R−C bond of RCCR, and the fate of the R = CO_2Me fragment that is eliminated is also unknown. The formation of complex **8** is suppressed when the reaction of complex **4b** is carried out in the presence of [$(Me_2SnSe)_3$] and, under these conditions, the reaction to give **5**, **6**, and **7** (Scheme 2) is catalytic. It had originally been envisioned that the platinum complex **4b** might catalyze the reaction of [$(Me_2SnSe)_3$] with RCCR to give organotin metallacycles of the form {$(Me_2SnSe)_n(RCCR)_m$}, but the actual catalytic reactions are clearly more complex. The nature of the organoselenium products suggests that reaction of **4b** with alkyne may be initiated by nucleophilic attack by selenium on the electrophilic alkyne, but the mechanisms of the subsequent steps are unknown. This work is significant in showing that Sn−E bonds are strongly activated within organoplatinum metallacycles and that easy ring expansion and contraction can occur in reactions with an electrophilic alkyne.

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) or internal $SnMe_4$ (^{119}Sn). ^{1}H NMR spectral assignments are made using the notation where $H^{3,5,6}$ represent signals due to protons on the pyridine ring *trans* to Me, and $H^{3',5',6'}$ will represent signals due to protons on the pyridine ring *trans* to Sn. Unless otherwise specified, quoted couplings to tin are for the ^{119}Sn isotope only.

[$PtMe_2(Me_2SnSSnMe_2C(CO_2Me)$=$C(CO_2Me)S$}($bu_2$bpy)], 3a. To a solution of **2a** (100 mg, 0.117 mmol) in CH_2Cl_2 (5 mL) was added $MeO_2CC{\equiv}CCO_2Me$ (16.6 mg, 0.117 mmol), and the mixture was stirred for 1 h. The yellow product was precipitated by addition of pentane (40 mL) and isolated by filtration. Yield: 88%. Anal. Calcd for $C_{30}H_{48}N_2O_4PtS_2Sn_2$: C, 36.13; H, 4.85; N, 2.81. Found: C, 35.98; H, 4.80; N, 2.70. NMR in CD_2Cl_2: δ(^{1}H) 9.95 [d, 1H, $^3J_{H^{5'}H^{6'}}$ = 6 Hz, $H^{6'}$]; 8.72 [d, 1H, $^3J_{H^5H^6}$ = 6 Hz, $^3J_{PtH^6}$ = 12 Hz, H^6]; 8.16 [d, 1H, $^4J_{H^{3'}H^{5'}}$ = 2 Hz, $H^{3'}$]; 8.11 [d, 1H, $^4J_{H^3H^5}$ = 2 Hz, H^3]; 7.66 [dd, 1H, $^3J_{H^{5'}H^{6'}}$ = 6 Hz, $^4J_{H^{5'}H^{3'}}$ = 2 Hz, $H^{5'}$]; 7.58 [dd, 1H, $^3J_{H^5H^6}$ = 6 Hz, $^4J_{H^5H^3}$ = 2 Hz, H^5]; 3.41 [s, 3H, α-CO_2Me]; 2.80 [s, 3H, β-CO_2Me]; 1.46 [s, 9H, ^{t}bu]; 1.45 [s, 9H, ^{t}bu]; 0.86 [s, 3H, $^2J_{PtH}$ = 59 Hz, Pt−Me]; 0.76 [s, 3H, $^2J_{SnH}$ = 46 Hz, Pt−Sn−Me^a]; 0.59 [s, 3H, $^2J_{SnH}$ = 52 Hz, Pt−S−C=C−Sn−Me^a]; 0.39 [s, 3H, $^3J_{PtH}$ = 4 Hz, $^2J_{SnH}$ = 46 Hz, Pt−Sn−Me^b]; 0.31 [s, 3H, $^2J_{SnH}$ = 55 Hz, Pt−S−C=C−Sn−Me^b]; 0.11 [s, 3H, $^2J_{PtH}$ = 62 Hz, Pt−Me]; δ(^{119}Sn) = 6.81 [$^2J_{SnSn}$ = 151 Hz, Pt−S−C=C−Sn]; −81.45 [$^1J_{PtSn}$ = 11 856 Hz, Pt−Sn].

Similarly were prepared: **[$PtMe_2(Me_2SnSeSnMe_2C(CO_2$-Me)=$C(CO_2Me)Se$}($bu_2$bpy)], 3b**, from **2b**. Yield: 85%. Anal. Calcd for $C_{30}H_{48}N_2O_4PtSe_2Sn_2$: C, 33.02; H, 4.43; N, 2.57. Found: C, 33.00; H, 4.31; N, 2.46. NMR in CD_2Cl_2: δ(^{1}H) 9.99 [br, 1H, $H^{6'}$]; 8.75 [d, 1H, $^3J_{H^5H^6}$ = 6 Hz, $^3J_{PtH^6}$ = 24 Hz, H^6]; 8.15 [d, 1H, $^4J_{H^{3'}H^{5'}}$ = 2 Hz, $H^{3'}$]; 8.10 [d, 1H, $^4J_{H^3H^5}$ = 2 Hz, H^3]; 7.66 [dd, 1H, $^3J_{H^{5'}H^{6'}}$ = 6 Hz, $^4J_{H^{5'}H^{3'}}$ = 2 Hz, $H^{5'}$]; 7.56 [dd, 1H, $^3J_{H^5H^6}$ = 6 Hz, $^4J_{H^5H^3}$ = 2 Hz, H^5]; 3.43 [s, 3H, α-CO_2-Me]; 2.83 [s, 3H, β-CO_2Me]; 1.46 [s, 9H, ^{t}bu]; 1.44 [s, 9H, ^{t}bu];

0.87 [s, 3H, Pt−Sn−Me]; 0.81 [s, 3H, $^2J_{PtH}$ = 59 Hz, Pt−Me]; 0.70 [s, 3H, $^2J_{SnH}$ = 51 Hz, Pt−Se−C═C−Sn−Me[a]]; 0.46 [s, 3H, $^2J_{SnH}$ = 44 Hz, Pt−Sn−Me[b]]; 0.34 [s, 3H, $^2J_{SnH}$ = 53 Hz, Pt−SeC═C−Sn−Me[b]]; 0.20 [s, 3H, $^2J_{PtH}$ = 62 Hz, Pt−Me].

[PtMe$_2$(Me$_2$SnTeSnMe$_2$C(CO$_2$Me)═C(CO$_2$Me)Te}(bu$_2$bpy)], 3c, from **2c**. Yield: 85%. Satisfactory elemental analysis could not be obtained due to air sensitivity. NMR in CD_2Cl_2: δ(^{1}H) 9.94 [br d, 1H, $^3J_{H^{5\epsilon}H^{6\epsilon}}$ = 5 Hz, H$^{6'}$]; 8.82 [d, 1H, $^3J_{H^5H^6}$ = 6 Hz, $^3J_{PtH^6}$ = 14 Hz, H^6]; 8.15 [d, 1H, $^4J_{H^{3\epsilon}H^{5\epsilon}}$ = 2 Hz, H$^{3'}$]; 8.11 [d, 1H, $^4J_{H^3H^5}$ = 2 Hz, H^3]; 7.64 [dd, 1H, $^3J_{H^{5\epsilon}H^{6\epsilon}}$ = 6 Hz, $^4J_{H^{5\epsilon}H^{3\epsilon}}$ = 2 Hz, H$^{5'}$]; 7.52 [dd, 1H, $^3J_{H^5H^6}$ = 6 Hz, $^4J_{H^5H^3}$ = 2 Hz, H^5]; 3.46 [s, 3H, α-CO$_2$Me]; 2.88 [s, 3H, β-CO$_2$Me]; 1.46 [s, 9H, ^{t}bu]; 1.44 [s, 9H, ^{t}bu]; 0.98 [s, 3H, $^2J_{SnH}$ = 56 Hz, Sn−Me]; 0.92 [s, 3H, Sn−Me]; 0.74 [s, 3H, $^2J_{PtH}$ = 60 Hz, Pt−Me]; 0.55 [s, 3H, $^2J_{SnH}$ = 45 Hz, Sn−Me]; 0.41 [s, 3H, $^2J_{SnH}$ = 52 Hz, Sn−Me]; 0.30 [s, 3H, $^2J_{PtH}$ = 61 Hz, Pt−Me].

[PtMe$_2$(Me$_2$Sn{C(CO$_2$Me)═C(CO$_2$Me)S}(bu$_2$bpy)], 4a. To a solution of **2a** (150 mg, 0.175 mmol) in CH_2Cl_2 (5 mL) was added MeO$_2$CC≡CCO$_2$Me (24.9 mg, 0.175 mmol), and the mixture was stirred overnight. The yellow product was precipitated by addition of pentane (40 mL) and isolated by filtration. Yield: 80%. Anal. Calcd for $C_{28}H_{42}N_2O_4PtSSn$: C, 41.19; H, 5.18; N, 3.43. Found: C, 40.74; H, 4.98; N, 3.13. NMR in CD_2Cl_2: δ(^{1}H) 8.75 [d, 1H, $^3J_{H^{5\epsilon}H^{6\epsilon}}$ = 6 Hz, $^3J_{PtH^{6\epsilon}}$ = 20 Hz, H$^{6'}$]; 8.68 [d, 1H, $^3J_{H^5H^6}$ = 5 Hz, $^3J_{PtH^6}$ = 11 Hz, H^6]; 8.19 [d, 1H, $^4J_{H^{3\epsilon}H^{5\epsilon}}$ = 2 Hz, H$^{3'}$]; 8.17 [d, 1H, $^4J_{H^3H^5}$ = 2 Hz, H^3]; 7.67 [dd, 1H, $^3J_{H^{5\epsilon}H^{6\epsilon}}$ = 6 Hz, $^4J_{H^{5\epsilon}H^{3\epsilon}}$ = 2 Hz, H$^{5'}$]; 7.51 [dd, 1H, $^3J_{H^5H^6}$ = 6 Hz, $^4J_{H^5H^3}$ = 2 Hz, H^5]; 3.65 [s, 3H, α-CO$_2$Me]; 3.61 [s, 3H, β-CO$_2$Me]; 1.45 [s, 9H, ^{t}bu]; 1.43 [s, 9H, ^{t}bu]; 0.94 [s, 3H, $^2J_{PtH}$ = 61 Hz, $^3J_{SnH}$ = 6 Hz, Pt−Me]; 0.60 [s, 3H, $^2J_{SnH}$ = 49 Hz, $^3J_{PtH}$ = 6 Hz, Pt−Sn−Me[a]]; 0.34 [s, 3H, $^2J_{SnH}$ = 55 Hz, $^3J_{PtH}$ = 4 Hz, Sn−Me[b]]; 0.29 [s, 3H, $^2J_{PtH}$ = 57 Hz, Pt−Me]; δ(^{119}Sn) = −2.1 [$^1J_{SnPt}$ = 9904 Hz].

Similarly prepared were **[PtMe$_2$(Me$_2$Sn{C(CO$_2$Me)═C(CO$_2$Me)Se}(bu$_2$bpy)]**, **4b**, from **2b**. Yield: 85%. Anal. Calcd for $C_{28}H_{42}N_2O_4PtSeSn$: C, 38.95; H, 4.90; N, 3.24. Found: C, 39.33; H, 5.71; N, 3.84. NMR in CD_2Cl_2: δ(^{1}H) 8.78 [d, 1H, $^3J_{H^{5\epsilon}H^{6\epsilon}}$ = 6 Hz, $^3J_{PtH^{6\epsilon}}$ = 20 Hz, H$^{6'}$]; 8.70 [d, 1H, $^3J_{H^5H^6}$ = 6 Hz, $^3J_{PtH^6}$ = 21 Hz, H^6]; 8.19 [d, 1H, $^4J_{H^{3\epsilon}H^{5\epsilon}}$ = 2 Hz, H$^{3'}$]; 8.16 [d, 1H, $^4J_{H^3H^5}$ = 2 Hz, H^3]; 7.67 [dd, 1H, $^3J_{H^{5\epsilon}H^{6\epsilon}}$ = 6 Hz, $^4J_{H^{5\epsilon}H^{3\epsilon}}$ = 2 Hz, H$^{5'}$]; 7.49 [dd, 1H, $^3J_{H^5H^6}$ = 6 Hz, $^4J_{H^5H^3}$ = 2 Hz, H^5]; 3.66 [s, 3H, α-CO$_2$Me]; 3.62 [s, 3H, β-CO$_2$Me]; 1.45 [s, 9H, ^{t}bu]; 1.43 [s, 9H, ^{t}bu]; 1.03 [s, 3H, $^2J_{PtH}$ = 60 Hz, $^3J_{SnH}$ = 5 Hz, Pt−Me]; 0.58 [s, 3H, $^2J_{SnH}$ = 48 Hz, $^3J_{PtH}$ = 5 Hz, Pt−Sn−Me[a]]; 0.34 [s, 3H, $^2J_{SnH}$ = 54 Hz, $^3J_{PtH}$ = 4 Hz, Pt−Sn−Me[b]]; 0.32 [s, 3H, $^2J_{PtH}$ = 57 Hz, Pt−Me]; δ(^{119}Sn) = −5.8 [$^1J_{SnPt}$ = 10 031 Hz]. **[PtMe$_2$(Me$_2$Sn{C(CO$_2$Me)═C(CO$_2$Me)Te}(bu$_2$bpy)], 4c**, from **2c**. Yield: 82%. Anal. Calcd. for $C_{28}H_{42}N_2O_4PtTeSn$: C, 36.87; H, 4.64; N, 3.07. Found: C, 37.55; H, 5.34; N, 3.56. NMR in CD_2Cl_2: δ(^{1}H) 8.90 [d, 1H, $^3J_{H^5{}'H^6{}'}$ = 6 Hz, $^3J_{PtH^6{}'}$ = 20 Hz, H$^{6'}$]; 8.75 [d, 1H, $^3J_{H^5H^6}$ = 6 Hz, $^3J_{PtH^6}$ = 11 Hz, H^6]; 8.19 [d, 1H, $^4J_{H^3{}'H^5{}'}$ = 2 Hz, H$^{3'}$]; 8.15 [d, 1H, $^4J_{H^3H^5}$ = 2 Hz, H^3]; 7.65 [dd, 1H, $^3J_{H^5{}'H^6{}'}$ = 6 Hz, $^4J_{H^5{}'H^3{}'}$ = 2 Hz, H$^{5'}$]; 7.47 [dd, 1H, $^3J_{H^5H^6}$ = 6 Hz, $^4J_{H^5H^3}$ = 2 Hz, H^5]; 3.65 [s, 3H, α-CO$_2$Me]; 3.62 [s, 3H, β-CO$_2$Me]; 1.45 [s, 9H, ^{t}bu]; 1.43 [s, 9H, ^{t}bu]; 1.03 [s, 3H, $^2J_{PtH}$ = 61 Hz, Pt-Me]; 0.55 [s, 3H, $^2J_{SnH}$ = 48 Hz, $^3J_{PtH}$ = 5 Hz, Pt−Sn-Me[a]]; 0.34 [s, 3H, $^2J_{PtH}$ = 55 Hz, Pt-Me]; 0.32 [s, 3H, $^2J_{SnH}$ = 53 Hz, $^3J_{PtH}$ = 4 Hz, Pt−Sn-Me[b]]; δ(^{119}Sn) = −18.6 [$^1J_{SnPt}$ = 10 009 Hz].

[PtMe$_2${C(CO$_2$Me)═CH(CO$_2$Me)}(C≡CCO$_2$Me)(bu$_2$bpy)], 8. To a solution of **4b** (50 mg, 0.058 mmol) in CH_2Cl_2 (10 mL) was added MeO$_2$CC≡CCO$_2$Me (41 mg, 0.29 mmol), and the mixture was stirred for 40 h at 40 °C. The solvent was removed in vacuo, and the product was purified by chromatography on silica gel using 90:10 CH_2Cl_2/hexanes (v/v) as eluent. Yield: 52%. Anal. Calcd for $C_{30}H_{40}N_2O_6$: C, 50.06; H, 5.60; N, 3.89. Found: C, 50.33; H, 5.91; N, 3.79. NMR in CD_2Cl_2: δ(^{1}H) 9.10 [d, 1H, $^3J_{H^{5\epsilon}H^{6\epsilon}}$ = 6 Hz,$^3J_{PtH^6}$ = 13 Hz, H$^{6'}$]; 8.66 [d, 1H, $^3J_{H^5H^6}$ = 6 Hz, $^3J_{PtH^6}$ = 20 Hz, H^6]; 8.08 [d, 1H, $^4J_{H^{3\epsilon}H^{5\epsilon}}$ = 2 Hz, H$^{3'}$]; 8.10 [d, 1H, $^4J_{H^3H^5}$ = 2 Hz, H^3]; 7.59 [dd, 1H, $^3J_{H^{5\epsilon}H^{6\epsilon}}$ = 6 Hz, $^4J_{H^{5\epsilon}H^{3\epsilon}}$ = 2 Hz, H$^{5\epsilon}$]; 7.52 [dd, 1H, $^3J_{H^5H^6}$ = 6 Hz, $^4J_{H^5H^3}$ = 2 Hz, H^5]; 6.54 [s, 1H, $^3J_{PtH}$ = 80 Hz, Pt−C═C−H]; 3.79 [s, 3H, −CO$_2$Me]; 3.68 [s, 3H, CO$_2$Me]; 3.51[s, 3H, CO$_2$Me]; 1.44 [s, 9H, ^{t}bu]; 1.40 [s, 9H, ^{t}bu]; 1.30 [s, 3H, $^3J_{PtH}$ = 69 Hz, Pt−Me]; −0.04 [s, 3H, $^3J_{PtH}$ = 51 Hz, Pt-Me]. δ(^{13}C) 174.1 [s, J_{PtC} = 18 Hz, CO]; 165.9 [s, J_{PtC} = 95 Hz, CO]; 165.0 [s, $^2J_{PtC}$ = 190 Hz, (MeO$_2$C)C═*C*(H)CO$_2$Me]; 164.2 [s, J_{PtC} = 61 Hz, CO]; 155.6 [s, bipy]; 155.5 [s, bipy]; 153.6 [s, bipy]; 150.5 [s, J_{PtC} = 19 Hz, bipy]; 147.0 [s, J_{PtC} = 17 Hz, bipy]; 142.2 [s, $^1J_{PtC}$ = 900 Hz, (MeO$_2$C)*C*═C(H)CO$_2$Me]; 125.7 [s, bipy]; 125.4 [s, J_{PtC} = 16 Hz, bipy]; 125.2 [s, $^1J_{PtC}$ = 19 Hz, bipy]; 120.7 [s, $^1J_{PtC}$ = 780 Hz, −*C*≡CCO$_2$Me]; 91.8 [s, $^2J_{PtC}$ = 138 Hz, −C≡*C*CO$_2$Me]; 52.0 [s, CO$_2$*Me*]; 51.6 [s, CO$_2$*Me*]; 50.9 [s, CO$_2$*Me*]; 36.1 [s, Me$_3$*C*−; 36.0 [s, Me$_3$*C*′]; 30.5 [s, *Me*$_3$C]; 30.4 [s, *Me*$_3$C′]; 3.88 [s, $^1J_{PtMe}$ = 477 Hz; Me *trans* to −C≡CCO$_2$-Me]; −5.38 [s, $^1J_{PtMe}$ = 575 Hz; Me *trans* to N].

[SeC(CO$_2$Me)═C(CO$_2$Me)-C(CO$_2$Me)═C(CO$_2$Me)],5;[{(Me-O$_2$CCH═C(CO$_2$Me)}$_2$Se], 6; Me$_2$SnX$_2$, 7. A solution of **4b** (50 mg, 0.058 mmol), [(Me$_2$SnSe)$_3$] (120 mg, 0.174 mmol), and MeO$_2$CC≡CCO$_2$Me (82 mg, 0.579 mmol) was stirred in a CH_2Cl_2 solution (10 mL) for 40 h at 40 °C. The solvent was removed in vacuo, and the mixture of products was separated by chromatography on silica gel using 90:10 CH_2Cl_2/hexanes (v/v) as eluent. Data for **5**: Yield: 0.15 mmol. NMR in CD_2Cl_2: δ(^{1}H) 3.88 [s, 6H, CO$_2$Me]; 3.86 [s, 6H, CO$_2$Me]. MS: *m*/*z* 364 (M$^+$). Data for **6**: Yield: 0.17 mmol. NMR in CD_2Cl_2: δ(^{1}H) 6.46 [s, 2H, $^3J_{SeH}$ = 5 Hz, Se−C═C−H]; 3.79 [s, 6H, CO$_2$Me]; 3.74 [s, 6H, CO$_2$Me]. MS: *m*/*z* 366 (M$^+$). Complex **7** decomposed on the column and was partially characterized by its NMR spectrum in the reaction mixture. Estimated yield: 0.3 mmol. NMR in CD_2Cl_2: δ(^{1}H) 0.54 [s, $^2J_{SnH}$ = 66 Hz, MeSn]; no other proton resonances were resolved. A separate reaction was monitored by NMR in CD_2Cl_2 solution until about 3 mol of [(Me$_2$SnSe)$_3$] was decomposed for each mol of **4b** catalyst used.

X-ray Structure Determinations. Crystals of **3b**, **4b**, and **8** were mounted on glass fibers. Data were collected using a Nonius Kappa-CCD diffractometer using COLLECT (Nonius, 1998) software. Crystal cell refinement and data reduction were carried out using the Nonius DENZO package. The data were scaled using SCALEPACK (Nonius, 1998), and no other absorption corrections were applied. The SHELXTL 5.1 (G. M. Sheldrick, Madison, WI) program was used to solve the structure by direct methods, followed by successive difference Fouriers. Crystallographic details are listed in Table 1.

Table 1. Crystal Data and Experimental Details

	3b	4b	8
empirical formula	$C_{30}H_{48}N_2O_4PtSe_2Sn_2$	$C_{28}H_{42}N_2O_4PtSeSn$	$C_{30}H_{40}N_2O_6Pt$
fw	1091.09	863.38	719.73
T/°C	21	−123	−123
λ/Å	0.71073	0.71073	0.71073
space group	*P*1	*Pca*2$_1$	*P*2$_1$/*n*
a/Å	10.8110(3)	30.899(6)	10.2375(6)
b/Å	12.5192(2)	12.156(2)	16.035(1)
c/Å	15.0604(3)	17.311(4)	18.890(1)
α (deg)	78.895(1)	90	90
β (deg)	70.862(1)	90	102.624(3)
γ (deg)	86.72191)	90	90
V/Å^3	1889.60(7)	6502(2)	3025.9(3)
Z	2	8	4
d(c)/g cm^{-1}	1.918	1.764	1.580
μ/mm^{-1}	6.963	6.218	4.680
F(000)	1040	3344	1440
R[*I*>2*σ*(*I*)][a]			
R1	0.0267	0.0293	0.0390
wR2	0.0621	0.0630	0.0959

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

Supporting Information Available: Tables of X-ray data for complexes **3b**, **4b**, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM010800Y