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Easy ring expansion and contraction in Pt–Sn bonded metallacycles

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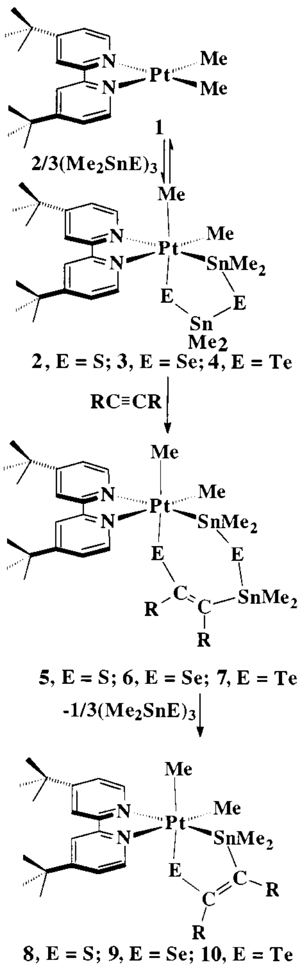
The alkyne RCCR, R = CO_2Me, reacts with 5-membered metallacycles [$PtMe_2\{SnMe_2ESnMe_2E\}(bu_2bpy)$], E = S, Se or Te, bu_2bipy = 4,4′-di-*tert*-butyl-2,2′-bipyridine, yielding the corresponding 7-membered metallacycles [$PtMe_2\{SnMe_2ESnMe_2CR{=}CRE\}(bu_2bpy)$] which slowly eliminate "Me_2SnE" to give new 5-membered metallacycles [$PtMe_2\{SnMe_2CR{=}CRE\}(bu_2bpy)$]; further reaction of which with excess RCCR gives [$PtMe_2(CR{=}CRH)(CCR)(bu_2bpy)$], a complex which contains alkyl, alkenyl and alkynyl functionalities in the same molecule.

A key property of metallacyclic compounds is their ability to undergo easy ring expansion/contraction reactions and these reactions are central to such useful catalytic reactions as alkene or alkyne metathesis, dimerization or trimerization.[1] This article reports that easy ring expansion and contraction can occur in reactions of an alkyne with the metallacycles [$PtMe_2(SnMe_2ESnMe_2E)(bu_2bpy)$]; bu_2bpy = 2,2′-di-*tert*-butyl-4,4′-bipyridine, E = S, **2**; Se, **3**; or Te, **4**, which are easily prepared by reaction of $(Me_2SnE)_3$ with [$PtMe_2(bu_2bpy)$] **1**, as shown in Scheme 1.[2] These appear to be unique examples of such reactions in heteronuclear metallacycles; the closest analogy appears to be the single chalcogen atom abstraction, which converts the 6-membered $Pt^{II}ENC(Ph)NE$ (E = S or Se) ring to a 5-membered ring.[3]

The electrophilic alkyne dimethyl acetylenedicarboxylate inserts regioselectively into a Sn–E bond of the 5-membered metallacycle **2**, **3**, or **4** to form the corresponding 7-membered metallacycle **5**, **6**, or **7**. These reactions are complete in about 1 h at room temperature and the products are yellow and air-stable when E = S or Se, but dark brown and air sensitive when E = Te. They were characterized by their NMR spectra[4] and, for complex **6** by an X-ray structure determination.[5] The ^1H NMR spectra of **5**–**7** contain four MeSn, two MePt and two MeO resonances, each corresponding to three protons, and so demonstrate that one equivalent of alkyne has been added. The ^{119}Sn NMR spectrum of **5** contained two resonances, one of which displayed a coupling $^1J(PtSn) = 11\,860$ Hz, thus showing that the Pt–Sn bond was still present, and both resonances exhibited a coupling $^2J(Sn^1–Sn^2) = 151$ Hz, thus showing that the $PtSnMe_2SSnMe_2$ unit was still present. Final proof that insertion occurred into the remaining PtE–Sn bond of **2**–**4** was obtained from the structure determination for complex **6** (Fig. 1).[5] The conformation of the 7-membered ring leads to relatively short transannular distances Sn2 · · · Se1 = 3.42 Å, Sn1 · · · Se1 = 3.48 Å, perhaps indicating weak secondary bonding between these atoms. The stereochemistry at the C=C bond is *cis* and one CO_2Me group stacks below the bipyridyl ligand. It is interesting that the Sn–E bonds in the precursor molecules $(Me_2SnE)_3$ are unreactive towards this alkyne, and so the Sn–E bond is activated within the platinum complex. We suggest that the reaction is initiated by nucleophilic attack from a lone pair of electrons of the PtE group on the electrophilic alkyne, and that the nucleophilicity of E is increased by donation of electron density from the *trans* MePt group. The complexes **2**–**4** are unreactive towards less electrophilic alkynes such as PhCCPh.



Scheme 1 R = CO_2Me.

The complexes **5**–**7** decompose, over a period of about 8 hours at room temperature in solution in CH_2Cl_2 by elimination of $(Me_2SnE)_3$ (identified by its NMR spectrum)[2,3] to form the 5-membered metallacycles **8**–**10**, Scheme 1. The ^1H NMR of complexes **8**–**10** each contained two MeSn, two MePt and two MeO resonances, and the ^{119}Sn NMR spectra each contain only one resonance with a large coupling due to $^1J(PtSn)$.[4] The structure of **9** is shown in Fig. 2.[5] The 5-membered PtSnC=CSe ring is only slightly distorted from planarity (torsional angle Pt–Se–C=C = −8.6°; Pt–Sn–C=C = 9.3°), in contrast to the twisted conformation adopted by the 7-membered ring in **6** and the envelope conformations of **2**–**4**.[2,3] In both **6** and **9**, the Pt–N distance *trans* to tin is longer than that *trans* to methyl, as a result of the very high *trans* influence of tin.

Complex **9** reacts catalytically with excess $(Me_2SnSe)_3$ and RCCR to give a mixture of products. When reactions were monitored by ^1H NMR, **9** was shown to remain as the catalyst

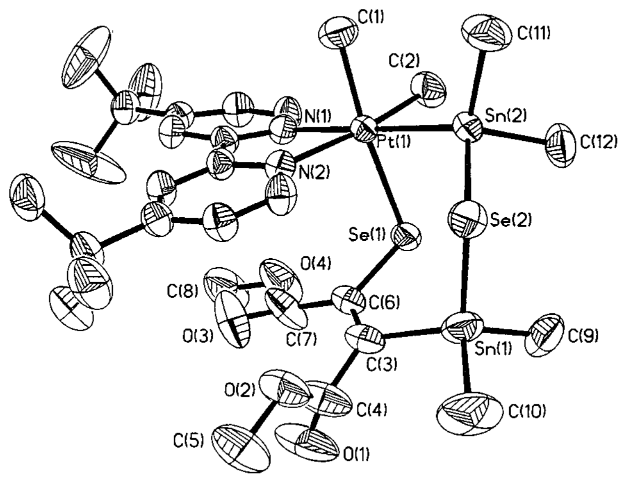


Fig. 1 The molecular structure of **6**. Selected bond distances (Å): Pt–N(2) 2.156(3), Pt–N(1) 2.228(4), Pt–C(1) 2.085(5), Pt–C(2) 2.065(5), Pt–Sn(2) 2.5625(4), Sn(2)–Se(2) 2.5671(6), Se(2)–Sn(1) 2.5137(6), Sn(1)–C(3) 2.161(6), C(3)–C(6) 1.323(7), C(6)–Se(1) 1.919(4), Se(1)–Pt 2.5380(5). Bond angles (°): 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).

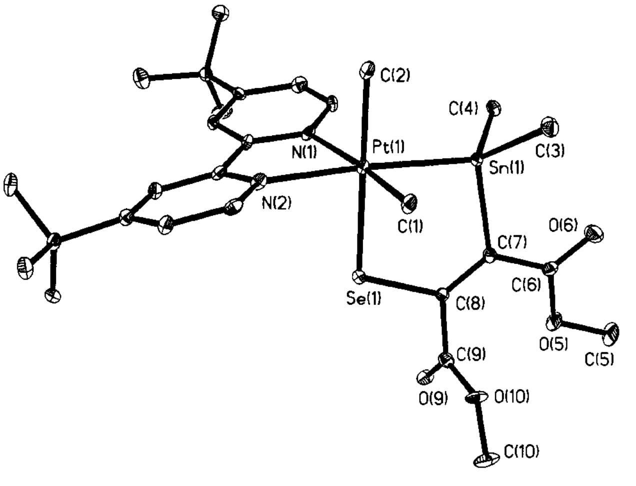


Fig. 2 The molecular structure of **9**. Selected bond distances (Å): Pt–C(1) 2.062(9), Pt–C(2) 2.091(8), Pt–Sn(1) 2.5578(7), Pt–Se(1) 2.5303(9), Pt–N(1) 2.144(6), Pt–N(2) 2.244(7). Bond angles (°): Se(1)–Pt–Sn(1) 88.60(3), Pt–Sn(1)–C(7) 99.0(2), Sn(1)–C(7)–C(8) 120.6(6), C(7)–C(8)–Se(1) 109.4(5), C(8)–Se(1)–Pt 104.5(2).

"resting state". The organoselenium complexes were separated chromatographically and identified as a mixture of the known[6] selenole **11** and the bis(*Z*-alkenyl)selenium compound **12**,[4,7] but an organotin product, **13**, shown to be present in the reaction mixture by its NMR spectra,[4] was decomposed on the column and so was not isolated in pure form or structurally characterized. The same organoselenium and organotin compounds were formed stoichiometrically by reaction of **9** with excess alkyne but, in this case, a new organoplatinum complex **14** was also formed as shown in Scheme 2. Complex **14** is stable and fails to react with either $(Me_2SnSe)_3$ or excess alkyne; it is a unique organoplatinum(IV) complex in that it contains two methyl groups, an alkenyl and an alkynyl group and it has been characterized by its ^1H and ^{13}C NMR spectra and by a structure determination (Fig. 3).[4,5] 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 formation of the alkenyl groups present in compounds **12** and **14** requires that an H-atom abstraction step must occur and, since the alkenyl proton is still observed in the ^1H NMR when the reaction is carried out in deuteriated solvents such as 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 **14** also requires cleavage of a C–C bond of the alkyne and the fate of the CO_2Me fragment that is eliminated is unknown. It had been envisioned that the platinum complex **9** 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 **9** with alkyne may be initiated by nucleophilic attack by selenium on the electrophilic alkyne, but the mechanisms of subsequent steps are still to be determined. This work is significant in showing that Sn–E bonds are strongly activated within organoplatinum metallacycles, that easy ring expansion and contraction can occur in reactions with an electrophilic alkyne, and that catalytic reactions may be developed.

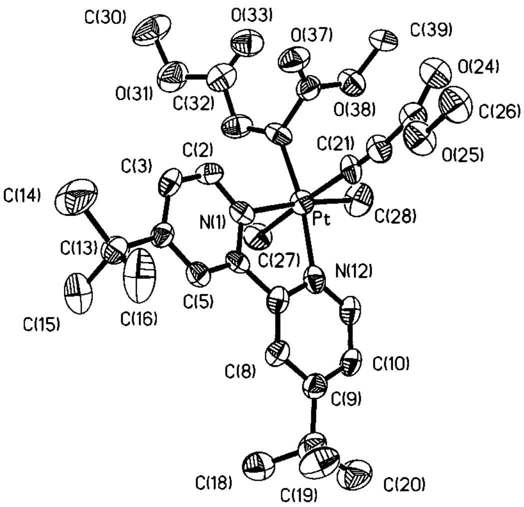
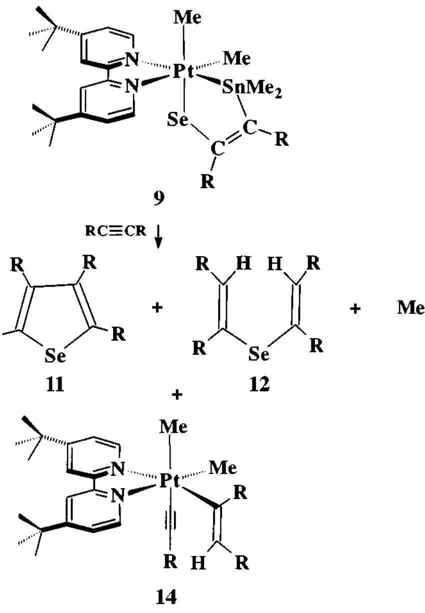


Fig. 3 The molecular structure of **14**. Selected bond distances (Å): Pt–C(35) 2.01(1), Pt–C(28) 2.07(1), Pt–C(21) 2.09(1), Pt–C(27) 2.10(1), Pt–N(1) 2.134(8), Pt–N(12) 2.114(9).



Scheme 2 R = CO_2Me.

Acknowledgements

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Notes and references

1 See for example: P. W. Jennings and L. L. Johnson, *Chem. Rev.*, 1994, **94**, 2241.

2 L. M. Rendina, J. J. Vittal and R. J. Puddephatt, *Organometallics*, 1996, **15**, 1749; M. C. Janzen, H. A. Jenkins, L. M. Rendina, J. J. Vittal and R. J. Puddephatt, *Inorg. Chem.*, in the press.

3 N. Feeder, R. J. Less, J. M. Rawson and J. N. B. Smith, *J. Chem. Soc., Dalton Trans.*, 1998, 4091.

4 Selected spectroscopic data: NMR in CD_2Cl_2 (refs. $SiMe_4$, Me_4Sn, K_2PtCl_4). **5**: $\delta(^{1}\mathrm{H})$ 3.41 [s, 3H, β-CO_2Me]; 2.80 [s, 3H, α-CO_2Me]; 0.86 [s, 3H, $^{2}J(\mathrm{PtH}) = 59$ Hz, Pt–Me]; 0.76 [s, 3H, $^{2}J(\mathrm{SnH}) = 46$ Hz, Pt–Sn–Me$^{\mathrm{a}}$]; 0.59 [s, 3H, $^{2}J(\mathrm{SnH}) = 52$ Hz, Sn–Me$^{\mathrm{a}}$]; 0.39 [s, 3H, $^{3}J(\mathrm{PtH}) = 4$ Hz, $^{2}J(\mathrm{SnH}) = 46$ Hz, Pt–Sn–Me$^{\mathrm{b}}$]; 0.31 [s, 3H, $^{2}J(\mathrm{SnH}) = 55$ Hz, Sn–Me$^{\mathrm{b}}$]; 0.11 [s, 3H, $^{2}J(\mathrm{PtH}) = 62$ Hz, Pt–Me]; $\delta(^{119}\mathrm{Sn})$ 6.81 [$^{2}J(\mathrm{SnSn}) = 151$ Hz, Pt–S–C=C–Sn]; −81.45 [$^{1}J(\mathrm{PtSn}) = 11\,860$ Hz, Pt–Sn]; $\delta(^{195}\mathrm{Pt})$ −1770 [$^{1}J(\mathrm{SnPt}) = 11\,860$ Hz]. **6**: $\delta(^{1}\mathrm{H})$ 3.43 [s, 3H, β-CO_2Me]; 2.83 [s, 3H, α-CO_2Me]; 0.87 [s, 3H, Pt–Sn–Me]; 0.81 [s, 3H, $^{2}J(\mathrm{PtH}) = 59$ Hz, Pt–Me]; 0.70 [s, 3H, $^{2}J(\mathrm{SnH}) = 51$ Hz, Sn–Me$^{\mathrm{a}}$]; 0.46 [s, 3H, $^{2}J(\mathrm{SnH}) = 44$ Hz, Pt–Sn–Me$^{\mathrm{b}}$]; 0.34 [s, 3H, $^{2}J(\mathrm{SnH}) = 53$ Hz, Sn–Me$^{\mathrm{b}}$]; 0.20 [s, 3H, $^{2}J(\mathrm{PtH}) = 62$ Hz, Pt–Me]. **7**: $\delta(^{1}\mathrm{H})$ 3.46 [s, 3H, β-CO_2Me]; 2.88 [s, 3H, α-CO_2Me]; 0.98 [s, 3H, $^{2}J(\mathrm{SnH}) = 56$ Hz, Sn–Me]; 0.92 [s, 3H, Sn–Me]; 0.74 [s, 3H, $^{2}J(\mathrm{PtH}) = 60$ Hz, Pt–Me]; 0.55 [s, 3H, $^{2}J(\mathrm{SnH}) = 45$ Hz, Sn–Me]; 0.41 [s, 3H, $^{2}J(\mathrm{SnH}) = 52$ Hz, Sn–Me]; 0.30 [s, 3H, $^{2}J(\mathrm{PtH}) = 61$ Hz, Pt–Me]. **8**: $\delta(^{1}\mathrm{H})$ 3.65 [s, 3H, CO_2Me]; 3.61 [s, 3H, CO_2Me]; 0.94 [s, 3H, $^{2}J(\mathrm{PtH}) = 61$ Hz, $^{3}J(\mathrm{SnH}) = 6$ Hz, Pt–Me]; 0.60 [s, 3H, $^{2}J(\mathrm{SnH}) = 49$ Hz, $^{3}J(\mathrm{PtH}) = 6$ Hz, Sn–Me]; 0.34 [s, 3H, $^{2}J(\mathrm{SnH}) = 55$ Hz, $^{3}J(\mathrm{PtH}) = 4$ Hz, Sn–Me]; 0.29 [s, 3H, $^{2}J(\mathrm{PtH}) = 57$ Hz, Pt–Me]; $\delta(^{119}\mathrm{Sn})$ −2.1 [$^{1}J(\mathrm{SnPt}) = 9904$ Hz]. **9**: $\delta(^{1}\mathrm{H})$ 3.66 [s, 3H, CO_2Me]; 3.62 [s, 3H, CO_2Me]; 1.03 [s, 3H, $^{2}J(\mathrm{PtH}) = 60.3$ Hz, $^{3}J(\mathrm{SnH}) = 5$ Hz, Pt–Me]; 0.58 [s, 3H, $^{2}J(\mathrm{SnH}) = 48$ Hz, $^{3}J(\mathrm{PtH}) = 5$ Hz, Sn–Me]; 0.34 [s, 3H, $^{2}J(\mathrm{SnH}) = 54$ Hz, $^{3}J(\mathrm{PtH}) = 4$ Hz, Sn–Me]; 0.32 [s, 3H, $^{2}J(\mathrm{PtH}) = 57$ Hz, Pt–Me]; $\delta(^{119}\mathrm{Sn})$ −5.8 [$^{1}J(\mathrm{SnPt}) = 10\,031$ Hz]. **10**: $\delta(^{1}\mathrm{H})$ 3.65 [s, 3H, CO_2Me]; 3.62 [s, 3H, CO_2Me]; 1.03 [s, 3H, $^{2}J(\mathrm{PtH}) = 61$ Hz, Pt–Me]; 0.55 [s, 3H, $^{2}J(\mathrm{SnH}) = 48$ Hz, $^{3}J(\mathrm{PtH}) = 5$ Hz, Sn–Me]; 0.34 [s, 3H, $^{2}J(\mathrm{PtH}) = 55$ Hz, Pt–Me]; 0.32 [s, 3H, $^{2}J(\mathrm{SnH}) = 53$ Hz, $^{3}J(\mathrm{PtH}) = 4$ Hz, SnMe]. **12**: $\delta(^{1}\mathrm{H})$ 6.46 [s, 2H, $^{3}J(\mathrm{SeH}) = 5$ Hz, Se–C=C–H]; 3.83 [s, 6H, CO_2Me]; 3.75 [s, 6H, CO_2Me]; MS: $m/z = 366$. **13**: $\delta(^{1}\mathrm{H})$ 0.54 [s, $^{2}J(\mathrm{SnH}) = 66$ Hz, MeSn]; no other proton resonances. **14**: $\delta(^{1}\mathrm{H})$ 6.54 [s, 1H, $^{3}J(\mathrm{PtH}) = 80$ Hz, Pt–C=C–H]; 3.79 [s, 3H, CO_2Me]; 3.68 [s, 3H, CO_2Me]; 3.51 [s, 3H, CO_2Me]; 1.30 [s, 3H, $^{3}J(\mathrm{PtH}) = 69$ Hz, Pt–Me]; −0.04 [s, 3H, $^{3}J(\mathrm{PtH}) = 51$ Hz, Pt–Me]; $\delta(^{13}\mathrm{C})$ −5.38 [$^{1}J(\mathrm{PtC}) = 575$ Hz, PtMe *trans* to N]; 3.88 [$^{1}J(\mathrm{PtC}) = 477$ Hz, PtMe *trans* to C]; 119.26 [$^{1}J(\mathrm{PtC}) = 780$ Hz, PtC(alkenyl)]; 142.17 [$^{1}J(\mathrm{PtC}) = 901$ Hz, PtC(alkynyl)].

5 Crystal data: **6**: $C_{30}H_{48}N_2O_4PtSe_2Sn_2$, $M = 1091.09$, triclinic, space group $P\bar{1}$, $a = 10.8110(3)$, $b = 12.5192(2)$, $c = 18.975(3)$ Å, $\alpha = 78.895(1)$, $\beta = 70.862(1)$, $\gamma = 86.721(1)°$, $V = 1889.60(7)$ Å^3, $D_c = 1.918$ g cm^{-3}, $Z = 2$, $T = 294$ K, $R = 0.0267$, $R_w = 0.0621$, $\mu = 6.96$ mm^{-1}, 6616 independent reflections. **9**: $C_{28}H_{42}N_2O_4PtSeSn$, $M = 863.38$, orthorhombic, $Pca2_1$, $a = 30.899(6)$, $b = 12.156(2)$, $c = 17.311(4)$ Å, $V = 6502(2)$ Å^3, $D_c = 1.764$ g cm^{-3}, $Z = 8$, $T = 150(2)$ K, $R = 0.0293$, $R_w = 0.0630$, $\mu = 6.22$ mm^{-1}, 6852 independent reflections. **14**: $C_{30}H_{40}N_2O_6Pt$, $M = 719.73$, monoclinic, $P2(1)/n$, $a = 10.2375(6)$, $b = 16.035(1)$, $c = 18.889(1)$ Å, $\beta = 102.624(3)°$, $V = 3025.9(3)$ Å^3, $D_c = 1.580$ g cm^{-3}, $Z = 4$, $T = 150(2)$ K; $R = 0.039$, $R_w = 0.0959$, $\mu = 4.68$ mm^{-1}, 3057 independent reflections. CCDC reference number 186/1434. See http://www.rsc.org/suppdata/dt/1999/1713/ for crystallographic files in .cif format.

6 M. R. J. Dorrity, J. F. Malone, C. P. Morley and R. R. Vaughan, *Phosphorus, Sulfur Silicon Relat. Elem.*, 1992, **68**, 37.

7 The *Z* stereochemistry for **12** is defined from the magnitude of $^{3}J(\mathrm{SeH}) = 5$ Hz; the coupling would be *ca.* 20 Hz in the *E*-isomer. C. Paulmier, *Selenium Reagents and Intermediates in Organic Synthesis*, Pergamon, Toronto, 1986.

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