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Double Oxidative Addition of Tin(IV) Halides to Platinum(II): Complexes with Pt−Sn and Pt−Sn−Pt Linkages

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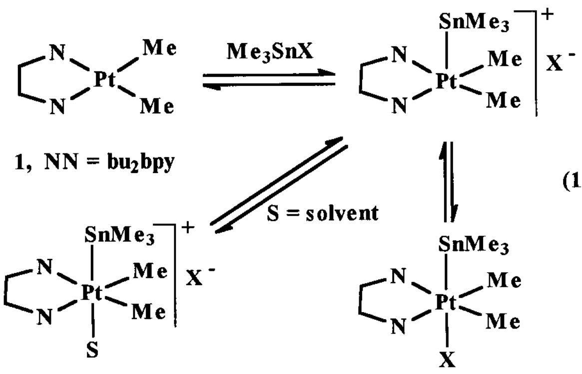
The electron-rich organoplatinum complex [PtMe$_2$(bu$_2$bpy)], **1**, bu$_2$bpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine, undergoes easy oxidative addition of a Sn−Cl bond of Ph$_n$SnCl$_{4-n}$ to give the corresponding stannylplatinum(IV) complexes [PtClMe$_2$(SnPh$_n$Cl$_{3-n}$)(bu$_2$bpy)], **2**, *n* = 0; **3**, *n* = 1; **4**, *n* = 2; **5**, *n* = 3. Further reaction of **1** with **2** or **3** can occur to give the μ-stannylene complexes [{PtClMe$_2$(bu$_2$bpy)}$_2$(μ-SnPh$_n$Cl$_{2-n}$)], **6**, *n* = 0; **7**, *n* = 1, the first time that μ-stannylene complexes have been prepared by oxidative addition of Sn−Cl bonds. In all cases, the oxidative additions of Sn−Cl bonds to platinum(II) occurred with *trans* stereochemistry. The products are characterized by NMR spectroscopy and, in most cases, by X-ray structure determinations. Trends in coupling constants [especially ^1J(PtSn)] and bond distances and angles give insight into structure and bonding in the series of complexes. Complex **2** was cocrystallized with the organotin compound [Me$_2$SnCl$_2$.Me$_2$SnO]$_2$. The oxidative addition of GeCl$_4$ to complex **1** occurs with *cis*-stereochemistry to give [PtClMe$_2$(GeCl$_3$)(bu$_2$bpy)], which does not react with more complex **1** to give a μ-germylene complex.

Introduction

Complexes with Pt−Sn bonds can be important intermediates in homogeneous catalysis, and this has provided a stimulus for research into the chemistry of Pt−Sn bonded complexes.[1,2] Tin(IV)−halogen bonds are known to oxidatively add to platinum(0) to give stannylplatinum(II) complexes, and trichlorostannylplatinum(II) complexes can also be prepared by insertion of tin(II) chloride into Pt−Cl bonds.[1−4] There are fewer stannylplatinum(IV) complexes, but they can be formed by oxidative addition of either Sn−E bonds (E = S, Se, Te)[5] or Sn−X bonds (X = Cl, Br, I)[6−8] to organoplatinum(II) complexes having diimine ligands. For the oxidative addition of Me$_3$SnX (X = Cl, Br, or I) to [PtMe$_2$(bu$_2$bpy)], **1** (bu$_2$bpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine), the reaction has been shown to be easily reversible and to occur by an S$_N$2 mechanism involving a cationic intermediate (eq 1). It was established that both the rate of reaction and the equilibrium constant for the reaction of eq 1 followed the sequence X = I > Br > Cl.[8]



(1)

This paper reports the oxidative addition reactions of Ph$_n$SnCl$_{4-n}$ (n = 0−3) with complex **1**, and for the first time establishes that double oxidative addition can occur to give complexes containing Pt−Sn−Pt units.

Results and Discussion

Complexes Formed by Simple Oxidative Addition. The reactions of the tin(IV) chlorides Ph$_n$SnCl$_{4-n}$ (n = 0−3) with complex **1** occurred by *trans* oxidative addition of the Sn−Cl bonds to platinum(II) to give the corresponding stannylplatinum(IV) complexes [PtClMe$_2$(SnPh$_n$Cl$_{3-n}$)(bu$_2$bpy)], **2**−**5**, according to eq 2. The reactions occurred easily at room temperature, and on the basis of the color change from orange-red to yellow as the reaction proceeded, the rate of reaction followed

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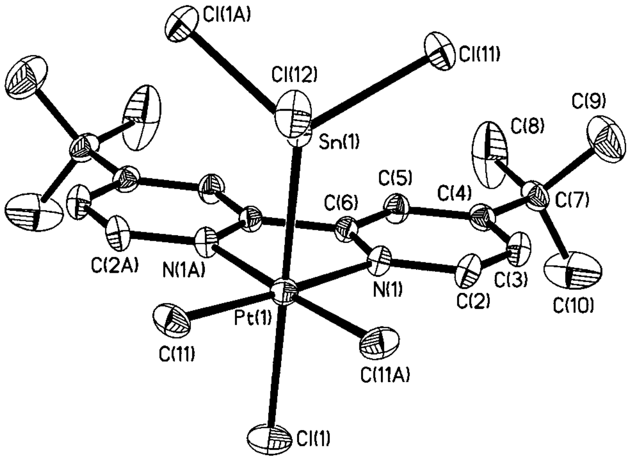
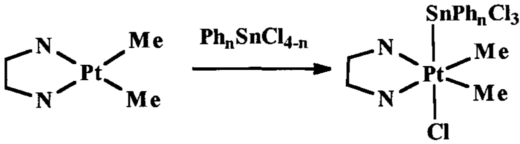


Figure 1. View of the molecular structure of complex **2**.

Table 1. Selected ^{119}Sn NMR Data [δ(Sn) with respect to Me_4Sn reference; *J* in Hz] for Complexes 2−7

	2	3	4	5	6	7
δ(Sn)	−402	−241	−177	−235	−435	−319
^1J(PtSn)	25 864	18 552	14 350	11 681	15 314	12 948

the sequence $n = 0 > 1 > 2 > 3$. For example, the reaction was complete within seconds for $SnCl_4$ and within 10 minutes for Ph_3SnCl. The products were isolated as air-stable pale yellow solids in good yield.



(2)

1, NN = bu$_2$bpy

2, n = 0
3, n = 1
4, n = 2
5, n = 3

The new complexes **2**−**5** were structurally characterized by ^{1}H and ^{119}Sn NMR spectroscopy, and for complexes **2**−**4** by X-ray structure determinations. The ^{1}H NMR spectra each contained a single methylplatinum resonance with satellites due to coupling to ^{195}Pt, with values of ^2J(PtMe) in the range 56−60 Hz, which are typical for similar methylplatinum(IV) complexes.[8] The presence of only three aromatic bu$_2$bpy resonances and only one PtMe and *t*-Bu resonance for complexes **2**−**5** shows that the complexes have mirror symmetry and so that the oxidative addition occurs with *trans* stereochemistry. For complex **2** a small long-range coupling ^3J(SnPtMe) = 11 Hz is resolved and provides evidence for Pt−Sn bonding. The ^{119}Sn NMR spectra of **2**−**5** all show a single resonance with ^{195}Pt satellites, and the coupling constants ^1J(PtSn) are listed in Table 1.[9]

The structures of complexes **2**−**4** are shown in Figures 1−3, and a comparison of relevant bond parameters is given in Table 2. The structures confirm that *trans* addition occurred in each case to give octahedral platinum(IV) complexes and provide an opportunity to compare bond distances within a related series of complexes. In the structure of complex **2** there is a crystallographic mirror plane containing the atoms Cl(12)Sn(1)Pt(1)Cl(1), but the molecules in **3** and **4** have no crystallographically imposed symmetry.

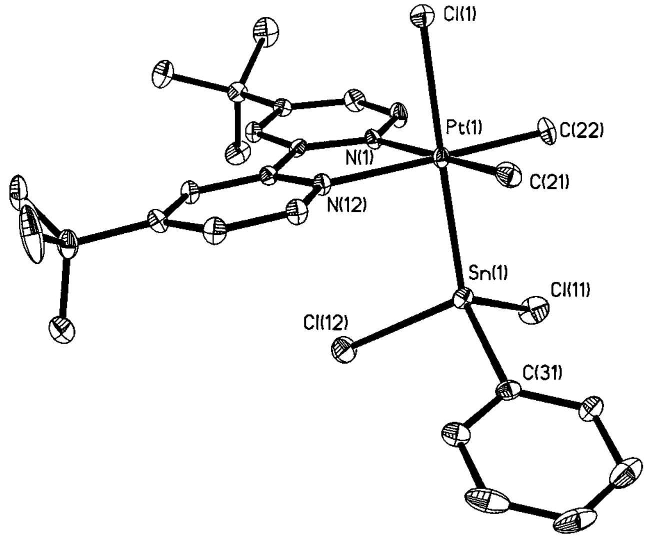


Figure 2. View of the molecular structure of complex **3**.

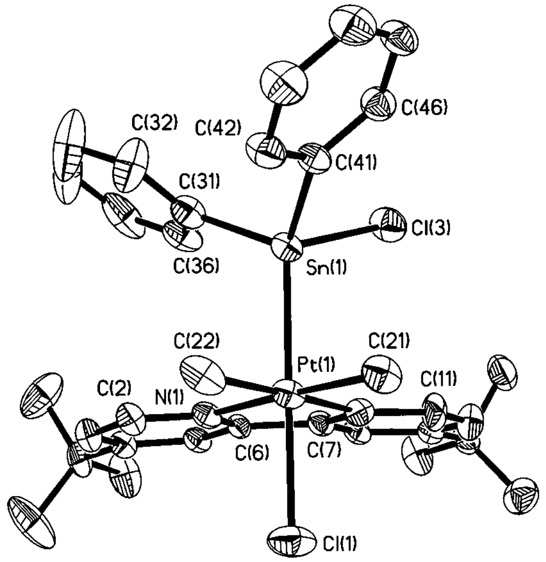


Figure 3. View of the molecular structure of complex **4**.

The Pt−Cl bond distances for complexes **2**−**4** are all longer than the sum of covalent radii for Pt and Cl (2.374 Å)[10] and follow the sequence **2** [2.382(2) Å] < **3** [2.418(3) Å] < **4** [2.476(3) Å]. The Pt−Sn distances also follow the sequence **2** [2.4932(7) Å] < **3** [2.520(2) Å] < **4** [2.5319(7) Å], and they fall in the midrange of published Pt−Sn bond lengths (2.34−2.80 Å).[1] There is a good correlation between the values of *d*(Pt−Sn) and the coupling constants ^1J(Pt−Sn), Table 1. The average Sn−Cl bond length follows the sequence **2** [2.3317(1), 2.348(3) Å] < **3** [2.380(8), 2.336(7) Å] < **4** [2.392(3) Å]. The bond angles Cl−Sn−X (X = Cl, C) for complexes **2**−**4** are all less than the tetrahedral angle and fall in the narrow range 100.5(1)−103.7(3)°, while the angle C−Sn−C for **4** is close to the tetrahedral angle at 110.1(3)°. The bond angles Pt−Sn−Cl follow the order **2** [118.18(7), 115.99(5)°] > **3** [112.8(2)°, 107.7(2)°] > **4**

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(9) Wrackmeyer, B. *Ann. Rep. NMR Spectrosc.* **1985**, *16*, 73.

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Table 2. Selected Bond Distances (Å) and Angles (deg) for Complexes 2, 3, 4, 6, and 7

	2	**3**	**4**	**6**	**7**
Pt−Cl	2.382(2)	2.433(2)	2.476(3)	2.457(2) 2.459(2)	2.493(2) 2.533(2)
Pt−Sn	2.4932(7)	2.5186(6)	2.5319(7)	2.5451(5) 2.5386(6)	2.5715(5) 2.5725(5)
Sn−Cl	2.332(2) 2.332(2) 2.348(3)	2.349(2) 2.380(2)	2.392(3)	2.401(2) 2.424(2)	2.397(2)
Sn−C		2.130(4)	2.149(4) 2.152(6)		2.165(7)
Cl−Sn−Cl	100.5(1) 100.5(1) 103.1(1)	102.71(9)		96.93(9)	
Cl−Sn−C		101.1(1) 103.4(1)	101.1(2) 102.9(2)		97.4(2)
C−Sn−C			110.1(3)		
Pt−Sn−Cl	118.18(7) 115.99(5) 115.99(5)	113.06(7) 108.21(6)	106.35(7)	102.85(6) 104.95(5) 103.64(5) 105.66(6)	107.00(5) 103.73(5)
Pt−Sn−C		125.6(1)	120.6(2) 113.4(2)		112.2(2) 104.0(2)
Pt−Sn−Pt				136.34(2)	128.04(2)

Table 3. Selected Bond Distances (Å) and Angles (deg) for the Compound ($(Me_2SnCl_2{\cdot}Me_2SnO)_2$) that Cocrystallized with Complex 2

Sn(2)−O(20)	2.062(3)	O(20)−Sn(3)	2.020(6)
Sn(2)−C(22)	2.098(9)	Sn(3)−Cl(3)	2.593(2)
Sn(2)−C(21)	2.085(10)	Sn(3)−C(31)	2.094(7)
Sn(2)−Sn(2A)	3.290(1)	Cl(3)−Sn(2)	3.015(2)
C(22)−Sn(2)−C(21)	142.5(5)	O(20)−Sn(3)−Cl(3)	81.33(5)
C(22)−Sn(2)−O(20)	105.0(3)	O(20)−Sn(3)−C(31)	113.1(2)
C(21)−Sn(2)−O(20)	104.6(2)	C(31)−Sn(3)−Cl(3)	94.0(3)
O(20)−Sn(2)−O(20A)	74.2(3)	Cl(3)−Sn(3)−Cl(3A)	162.7(1)
C(31)−Sn(3)−C(31B)	133.7(5)	Sn(2)−O(20)−Sn(3)	127.1(1)
Sn(2)−O(20)−Sn(2A)	105.8(3)		

[106.35(7)°] and the angle Pt−Sn−C for **3** [125.3(4)°] > **4** [120.6(2), 113.4(2)°]. The trends can be understood in terms of the hybridization at tin, with s-character concentrated in the more covalent bonds, and in terms of the steric bulk of the substituents at tin [both following the sequence $PtClMe_2(bu_2bpy)$ > Ph > Cl].[1]

Crystals of complex **2** were grown from a solution containing Me_2SnCl_2, which evidently underwent partial hydrolysis to form $[Me_2SnCl_2{\cdot}Me_2SnO]_2$, **A**, and then this hydrolysis product cocrystallized with **2**. The structure of the organotin compound **A** is shown in Figure 4, and relevant bond parameters are listed in Table 3. Complex **A**, as a pure compound, has been characterized previously, but has a less symmetrical structure than in the mixed crystal studied here; several related compounds are also known.[11,12] In the pure compound **A** there is evidence for weak intermolecular interactions[11,12] which are of course not possible in the present case since the molecules are well separated from each other. It should also be noted that the thermal ellipsoids of the tin atoms in **A** indicate that there may be slight, unresolved disorder of the tin atoms on either side of the mirror plane [Sn(2)] or 2-fold axis [Sn(3)], and so the true molecular symmetry may be lower than indicated.

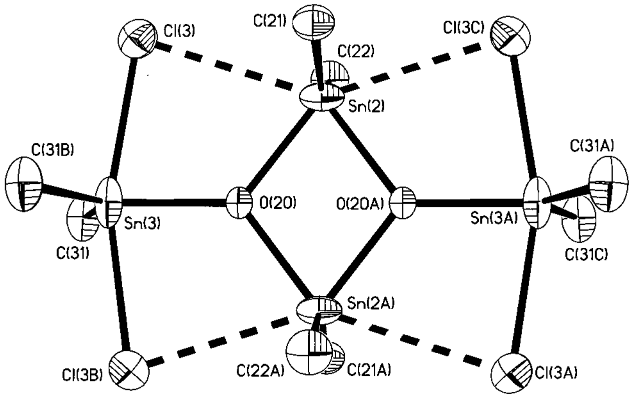
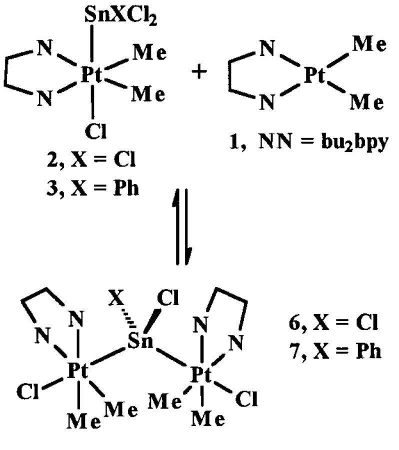


Figure 4. View of the molecular structure of the organotin complex **A**.

Complexes Formed by Double Oxidative Addition. It is clear from the literature that the tin centers in complexes containing $MSnCl_3$ units have much weaker acceptor properties than in compounds such as $SnCl_4$ or $PhSnCl_3$.[1] There are no reports of ligand addition at tin in $MSnCl_3$ units, whereas $PhSnCl_3$ readily adds two donor ligands L to form octahedral $PhSnCl_3L_2$.[12] Since the tin centers in complexes with $MSnCl_3$ units are unreactive toward nucleophiles, they are also expected to have low reactivity toward oxidative addition reactions of the SnCl bonds by the S_N2 mechanism, and there appear to be no examples of such reactions.[1] It was therefore of interest to study the reactivity of complexes **2**−**4** toward further oxidative addition.

Complex **1** reacted with complex **2** or **3** to yield the stannylene-bridged complex **6** or **7**, respectively according to eq 3. The oxidative addition reactions were complete within 10 minutes at room temperature, and the products were isolated as pale yellow solids in high yield. However, complex **1** failed to undergo oxidative addition to the Sn−Cl bond of complex **4** to give the analogous product containing a μ-$SnPh_2$ group and also failed to react with **6** or **7** in reactions that might lead to triply bridging $SnPt_3$ units. The new complexes **6** and **7** were characterized by their ^1H and ^{119}Sn NMR spectra and by X-ray structure determinations.



(3)

The ^1H NMR spectrum of complex **6** contains a single methylplatinum resonance, with coupling constant

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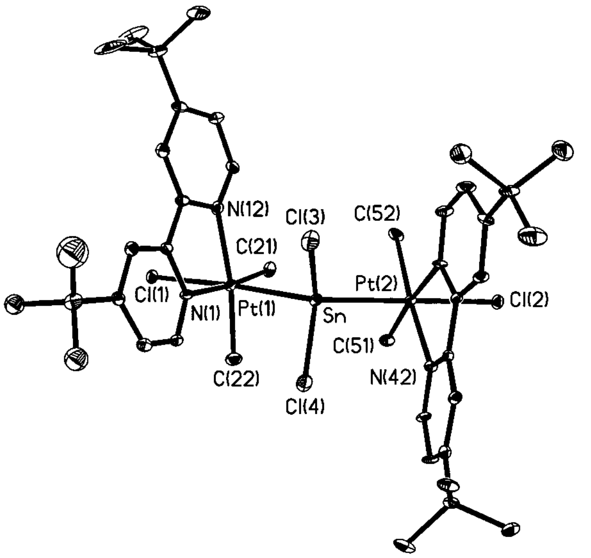

Figure 5. View of the molecular structure of complex **6**.

^2J(PtMe) = 60 Hz, and three aromatic resonances and a single *t*-Bu resonance for the bu$_2$bpy ligand. This indicates that there is an effective mirror plane containing the PtSnPt unit, and so confirms that the second oxidative addition reaction, like the first, occurs with *trans* stereochemistry. In contrast, the ^{1}H NMR spectrum of **7** contains six resonances in the aromatic region and two singlets for the *t*-Bu substituents of the bu$_2$bpy ligands, indicating that there is no mirror plane containing the PtSnPt atoms. This is expected since the molecule contains no mirror plane, due the presence of the unsymmetrical Pt−SnClPh−Pt group, and cannot achieve mirror symmetry by rotation about the Sn−Pt bonds. The spectrum contained only one broad methylplatinum resonance with ^2J(PtMe) = 59 Hz, presumably due to accidental degeneracy of the chemical shifts. The ^{119}Sn NMR spectra of **6** and **7** each exhibit a 1:8:18:8:1 quintet, arising from the coupling ^1J(PtSn). This intensity pattern, arising from overlapping peaks from isotopomers containing zero, one, or two ^{195}Pt atoms, gives clear proof of the presence of a doubly bridging PtSnPt unit. The values of ^1J(PtSn) = 15314 and 12948 Hz for **6** and **7**, respectively, are lower than in the precursor complexes **2** and **3**, respectively (Table 1).[1]

The structures of complexes **6** and **7**, neither of which has crystallographically imposed symmetry, are shown in Figures 5 and 6, and relevant bond parameters are listed in Table 2. The structures confirm the second *trans* oxidative addition and the presence of the novel bridging stannylene units in the products. The Pt−Cl bond lengths for **7** [2.493(2), 2.533(2) Å] are the longest for any of the complexes listed in Table 2, and complex **6** also has long Pt−Cl distances [2.457(2), 2.459(2) Å)]. Complex **7** also has the longest Pt−Sn distances [2.5715(5), 2.5725(5) Å] of all the complexes in Table 2, while the Pt−Sn bond lengths in complex **6** [2.5451(5), 2.5386(6) Å] are only slightly longer than that in complex **4** [2.5319(7) Å]. The angles at tin in complexes **6** and **7** are significantly distorted from ideal tetrahedral geometry. The Pt−Sn−Pt bond angles for **6** [136.34(2)°] and **7** [128.04(2)°] are significantly larger than tetrahedral, while the Cl−Sn−X bond angles for **6** [X = Cl, 96.93(9)°] and **7** [X = Ph, 97.4(2)°] are smaller than tetrahedral. The two bu$_2$bpy rings in each molecule of **6** or **7** are tilted [angles of 49.3° and 39.4°, respectively] and staggered [angles of 44.7° and 78.7°, respectively] with respect to each other. The orientation in **6** appears close to the optimum to minimize steric interactions, while it is likely that the conformation in **7** enhances π-stacking between the phenyltin group and one of the bu$_2$bpy ligands (Figure 6).

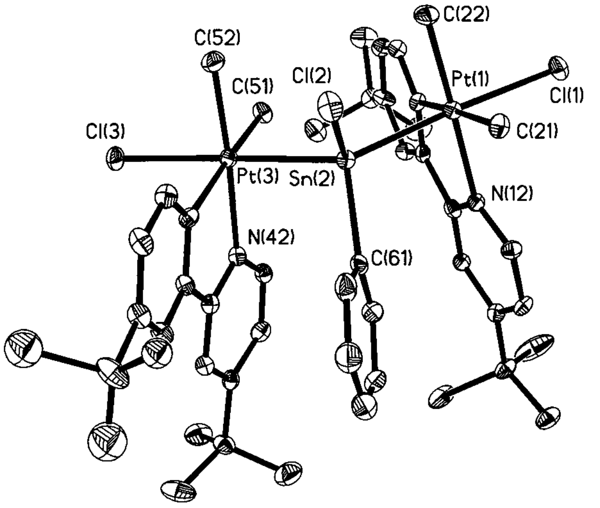

Figure 6. View of the molecular structure of complex **7**.

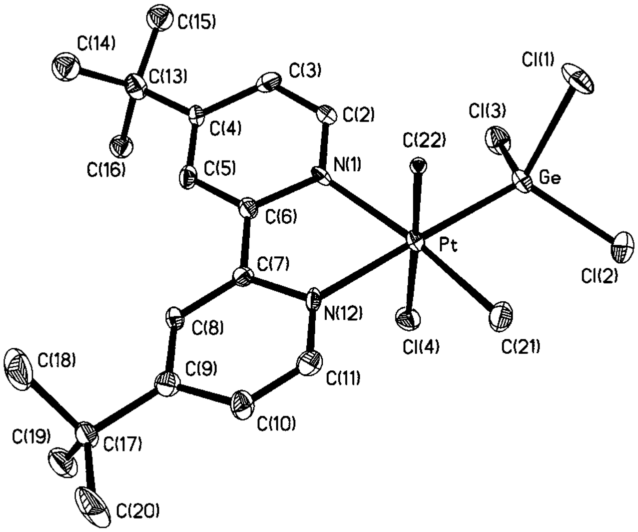

Figure 7. View of the molecular structure of complex **8**.

A Germylplatinum Complex. Germanium tetrachloride reacted with complex **1** to give [PtClMe$_2$(GeCl$_3$)(bu$_2$bpy)], **8**, according to eq 4. However, in this case, the reaction occurred by *cis*-oxidative addition, such that the germyl group is *trans* to a nitrogen donor of the bu$_2$bipy ligand in the product. The stereochemistry was indicated by the ^{1}H NMR spectrum, which contained, for example, two methylplatinum resonances, and was confirmed by X-ray structure determination. The stereochemistry is unexpected since organogermanium halides oxidatively add to platinum(II) with *trans* stereochemistry.[7,8,13] The structure of complex **8** is shown in Figure 7, and selected bond distances and angles are in Table 4. The Pt−Cl distance *trans* to methyl is 2.452(3) Å, and

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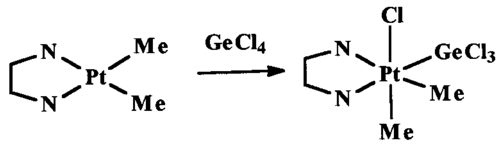
[13] Rankin, D. W. H.; Robertson, A. *J. Organomet. Chem.* **1976**, *105*, 331.

Table 4. Selected Bond Distances (Å) and Angles (deg) for [PtClMe$_2$(GeCl$_3$)(bu$_2$bpy)], 8

Pt−N(1)	2.14(1)	Pt−N(12)	2.10(1)
Pt−C(22)	2.05(3)	Pt−C(21)	2.07(1)
Pt−Cl(4)	2.452(3)	Pt−Ge	2.352(1)
Ge−Cl(1)	2.187(4)	Ge−Cl(2)	2.170(4)
Ge−Cl(3)	2.153(4)		

Pt−Ge−Cl(1)	116.4(1)	Pt−Ge−Cl(2)	119.2(1)
Pt−Ge−Cl(3)	115.6(1)	Cl(1)−Ge−Cl(2)	100.2(2)
Cl(1)−Ge−Cl(3)	102.7(2)	Cl(2)−Ge−Cl(3)	99.8(2)

comparison with the values *trans* to tin in complexes **2**−**4** indicates a *trans*-influence series SnPh$_2$Cl > Me > SnPhCl$_3$ > SnCl$_3$.



(4)

1, NN = bu$_2$bpy **8**

Monitoring the reaction of **1** with GeCl$_4$ in CD$_2$Cl$_2$ at −80 °C showed that the reaction occurred rapidly and that complex **8** was the only product, with no evidence of any long-lived intermediates. The *cis*-stereochemistry of reaction is not expected for the polar S$_N$2 mechanism, and so it is likely that a different mechanism operates. A concerted *cis* oxidative addition mechanism is tentatively suggested. Complex **8** failed to react with **1** to give a complex analogous to **7**.

Discussion

The *trans* oxidative addition of Ph$_n$SnCl$_{4-n}$ ($n = 0-3$) to complex **1** giving the Pt−Sn bonded complexes **2**−**5** suggests that the reactions all occur by the polar S$_N$2 mechanism.[8] The reactions are reversible, with the equilibrium shifted to the product side and with increasing reaction rates in the order Ph$_3$SnCl < Ph$_2$SnCl$_2$ < PhSnCl$_3$ < SnCl$_4$. The values of the coupling constant ^1J(PtSn) listed in Table 1 decrease markedly, and the values of d(Pt−Sn) in Table 2 increase, as the value of n in the PtSnPh$_n$Cl$_{3-n}$ group increases. It follows that a higher degree of s-character in the tin orbital used in forming the Sn−Pt bond leads to a shorter and stronger Pt−Sn bond. The long Pt−Cl bond lengths for complexes **2**−**4** (Table 2) confirm the expected high *trans*-influences of the stannyl groups, and the trend of d(PtCl) in **4** > **3** > **2** shows that the *trans*-influence of the SnPh$_n$Cl$_{3-n}$ group follows the sequence $n = 2 > 1 > 0$. This sequence is readily understood in terms of the σ-donor properties which are highest with the maximum number of phenyl rather than chloro substituents on the stannyl group.[14] The structural and NMR data then indicate that both the Pt−Cl and Pt−Sn bond strengths follow the sequence **2** > **3** > **4**, and it is very likely that **5** has the weakest Pt−Cl and Pt−Sn bonds. It is therefore not surprising that the equilibrium in the oxidative addition reactions to **1** follows the sequence SnCl$_4$ > PhSnCl$_3$ > Ph$_2$SnCl$_2$ > Ph$_3$SnCl. In addition, SnCl$_4$ is expected to react fastest since it is the most electrophilic reagent and offers the least steric effects to approach by the platinum center of **1**.

The average Sn−Cl bond length in the trichlorostannate ligand of **2** is 2.34 Å, which compares to a Sn−Cl bond length of roughly 2.48 Å for an uncoordinated trichlorostannate ion.[15] Coordination of the trichlorostannate to platinum removes electron density from the tin, and there is then contraction of the orbitals at tin, and perhaps enhanced Cl−Sn π-bonding, thus shortening the Sn−Cl bonds. There is also potential for Pt−Sn π-bonding in the Pt−SnCl$_3$ group of **2**, and this would decrease with replacement of chlorotin by phenyltin groups. Both ClSn and PtSn π-bonding will decrease the electrophilic character of the tin center and so reduce the reactivity toward further oxidative addition.

The most interesting aspect of this work is the demonstration that double oxidative addition can occur with complex **1** and SnCl$_4$ or PhSnCl$_3$ to give complexes with bridging stannylene groups. The reactions occur in a stepwise manner and the same products **6** and **7** are formed by reaction of complex **1** with **2** and **3**, respectively. The group 14 tetrahalide compound CCl$_4$ readily reacts with [PtMe$_2$(bpy)] to give [PtClMe$_2$(CCl$_3$)(bpy)],[13] and GeCl$_4$ reacts with [PtMe$_2$(bu$_2$bpy)] to give [PtClMe$_2$(GeCl$_3$)(bu$_2$bpy)], but these products fail to react further with [PtMe$_2$(bpy)] or [PtMe$_2$(bu$_2$bpy)] to give bridging alkylidene or germylene complexes. The large size of the tin nucleus and its high electrophilic nature, compared to carbon and germanium, makes the double oxidative addition possible despite the deactivating effect arising from the first addition. Platinum(0) and platinum(II) complexes containing Pt$_2$(μ-Sn) groups have been prepared earlier by insertion or addition reactions with tin(II) compounds,[1,16] but **6** and **7** are the first platinum(IV) complexes known to contain Pt$_2$(μ-Sn) groups. The syntheses appear to give the first examples of any M$_2$(μ-Sn) group prepared by oxidative addition of Sn−Cl bonds.[1]

In these PtSnPt bonded complexes, the values of the coupling constants ^1J(PtSn) are substantially reduced from their corresponding starting compounds [**6**, 15414 Hz vs **2**, 25864 Hz; **7**, 12948 Hz vs **3**, 18552 Hz], and the Pt−Sn distances are longer [**6**, 2.5451(5), 2.5486(6) Å vs **2**, 2.4932(7) Å; **7**, 2.5715(5), 2.5725(5) Å vs **3**, 2.520(2) Å]. These changes reflect the fact that the tin s-orbital character which was concentrated in a single Pt−Sn bond in **2** and **3** is shared between two platinum centers in **6** and **7**.[1] The large Pt−Sn−Pt bond angles for **6** [136.34(2)°] and **7** [128.04(2)°] and small Cl−Sn−X bond angles for **6** [X = Cl, 96.93(9)°] and **7** [X = Ph, 97.4(2)°] are consistent with the proposed concentration of tin s-character in the Pt−Sn (and to a lesser extent the Sn−Ph) bonds. The Pt−Cl bond lengths for the series of complexes follow the series 7 > 4 > 6 > 3 > 2, reflecting different *trans*-influences of the stannylene and stannyl groups.[14] The trend suggests the inductive donor effect of substituents at tin follows the series [PtClMe$_2$(bu$_2$bpy)] > Ph > Cl.

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Table 5. Crystal Data for Complexes 2, 3, 4, 6, 7, and 8

	2·$Me_4Sn_2Cl_2O$·$C_2H_4Cl_2$	**4**	**3**	**6**·$2CH_2Cl_2$	**7**·$2CH_2Cl_2$	**8**·$1.5CH_2Cl_2$
formula	$C_{26}H_{46}Cl_8N_2OPtSn_3$	$C_{32}H_{40}Cl_2N_2PtSn$	$C_{26}H_{35}Cl_3N_2PtSn$	$C_{42}H_{64}N_{64}Cl_8N_4Pt_2Sn$	$C_{48}H_{65}Cl_7N_4Pt_2Sn$	$C_{21.25}H_{32}Cl_{6.5}GeN_2Pt$
fw	1237.41	837.34	795.69	1417.44	1455.06	813.59
T/K	200	297	200	200	200	200
λ/Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
cryst syst		triclinic	triclinic	triclinic	monoclinic	monoclinic
space group	$C2/m$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2(1)/n$	$P2(1)/c$
a/Å	20.8922(6)	12.8051(5)	11.1975(6)	12.2220(5)	18.5366(5)	14.190(1)
b/Å	14.1144(5)	13.5918(6)	12.1188(6)	14.4755(6)	13.9761(5)	20.061(1)
c/Å	17.0289(6)	21.2123(5)	12.5865(6)	14.7569(7)	21.8945(8)	11.515(1)
α/deg		97.975(2)	102.572(2)	88.164(2)	90	90
β/deg	124.491(2)	96.293(2)	112.859(2)	84.218(2)	90.7519(2)	106.342(2)
γ/deg		110.609(2)	102.488(3)	87.010(3)	90	90
V/Å^3	4138.8(2)	3371.8(2)	1447.7(1)	2593.0(2)	5471.79(3)	3145.6(4)
Z	4	4	2	2	4	4
d(c)/g cm^{-1}	1.986	1.649	1.825	1.815	1.704	1.718
μ/mm^{-1}	5.698	5.065	5.983	6.304	5.722	5.963
F(000)	2352	1632	768	1372	2824	1576
R1[$I > 2\sigma(I)$]^a	0.0454	0.0440	0.0467	0.0438	0.0501	0.0679
wR2(I > 2σ(I)	0.1022	0.1069	0.1214	0.0957	0.1333	0.1807
R1	0.0769	0.0733	0.0538	0.0713	0.0706	0.1204
wR2	0.1103	0.1339	0.1271	0.1019	0.1464	0.2002

Experimental Section

NMR spectra were recorded by using Varian Inova 400 (^1H) or 600 (^{119}Sn) spectrometers. Chemical shifts are quoted with respect to TMS (^1H) or $SnMe_4$ (^{119}Sn).

Solvents were dried and distilled prior to use using standard procedures. [$PtMe_2$(^{t}bu$_2$bpy)] was prepared according to the literature method.[17]

[PtClMe$_2$(SnPh$_3$)(bu$_2$bpy)], 5. To a stirred solution of **1** (100 mg, 0.203 mmol) in CH_2Cl_2 (3 mL) was added Ph_3SnCl (86 mg, 0.223 mmol). After 10 min the solution color had changed from orange to yellow. The solution was filtered through dry Celite, and pentane (40 mL) was added to precipitate the product as a microcrystalline yellow solid, which was isolated by filtration, washed with pentane, and dried in vacuo. Yield: 88%. Anal. Calcd for $C_{38}H_{45}ClN_2PtSn$: C, 51.92; H, 5.16; N, 3.19. Found: C, 51.72; H, 5.08; N, 3.00. NMR in $CDCl_3$: $\delta(^1H) = 8.43$ [d, 2H, $^3J_{H^6H^5} = 6$ Hz, $^3J_{PtH^6} = 13$ Hz, H^6]; 7.96 [d, 2H, $^3J_{H^3H^5} = 1$ Hz, H^3]; 7.24 [dd, 2H, $^3J_{H^5H^6} = 6$ Hz, $^4J_{H^5H^3} = 2$ Hz, H^5], 1.59 [s, 6H, $^2J_{PtMe} = 56$ Hz, Pt-Me]; 1.38 [s, 18H, ^{t}bu]; $\delta(^{119}Sn)$ −235 [s, $^1J_{PtSn} = 11\,681$ Hz, Pt-Sn]. It was not possible to grow single crystals suitable for X-ray structure determination.

[PtClMe$_2$(SnPh$_2$Cl)(bu$_2$bpy)], 4. To a stirred solution of **1** (100 mg, 0.203 mmol) in CH_2Cl_2 (3 mL) was added Ph_2SnCl_2 (70 mg, 0.203 mmol). The solution color changed rapidly from orange to pale yellow. Pentane (40 mL) was added to precipitate the product as a microcrystalline yellow solid, which was isolated by filtration, washed with pentane, and dried in vacuo. Yield: 89%. Anal. Calcd for $C_{32}H_{40}Cl_2N_2PtSn$: C, 45.9; H, 4.81; N, 3.35. Found: C, 45.72; H, 4.77; N, 3.15. NMR in $CDCl_3$: $\delta(^1H)$ 8.60 [d, 2H, $^3J_{H^6H^5} = 6$ Hz, $^3J_{PtH^6} = 14$ Hz, H^6]; 8.00 [d, 2H, $^3J_{H^3H^5} = 1$ Hz, H^3]; 7.44 [dd, 2H, $^3J_{H^5H^6} = 6$ Hz, $^4J_{H^5H^3} = 1.5$ Hz, H^5], 1.53 [s, 6H, $^2J_{PtMe} = 56$ Hz, Pt-Me]; 1.40 [s, 18H, ^{t}bu]; $\delta(^{119}Sn)$ −177 [s, $^1J_{PtSn} = 14\,350$ Hz, Pt-Sn]. Crystals were grown by slow diffusion of pentane into a solution of **4** in CH_2Cl_2 at 5 °C.

[PtClMe$_2$(SnPhCl$_2$)(bu$_2$bpy)], 3. This complex was prepared similarly from **1** and $PhSnCl_3$. Yield: 85%. Anal. Calcd for $C_{26}H_{35}Cl_3N_2PtSn$: C, 39.25; H, 4.43; N, 3.52. Found: C, 39.71; H, 4.58; N, 3.55. NMR in $CDCl_3$: $\delta(^1H)$ 8.76 [d, 2H, $^3J_{H^6H^5} = 6$ Hz, $^3J_{PtH^6} = 14$ Hz, H^6]; 8.15 [d, 2H, $^3J_{H^3H^5} = 2$ Hz, H^3]; 7.64 [dd, 2H, $^3J_{H^5H^6} = 6$ Hz, $^4J_{H^5H^3} = 2$ Hz, H^5], 1.58 [s, 6H, $^2J_{PtMe} = 56$ Hz, Pt-Me]; 1.44 [s, 18H, ^{t}bu]; $\delta(^{119}Sn)$ −241 [s, $^1J_{PtSn} = 18\,552$ Hz, Pt-Sn]. Crystals suitable for X-ray crystallographic study were grown in the same way as for **4**.

[PtClMe$_2$(SnCl$_3$)(bu$_2$bpy)], 2. This complex was prepared similarly from **1** and $SnCl_4$. Yield: 88%. Anal. Calcd for $C_{20}H_{30}Cl_4N_2PtSn$: C, 31.86; H, 4.01; N, 3.71. Found: C, 31.80; H, 3.92; N, 3.59. NMR in $CDCl_3$: $\delta(^1H)$ 8.72 [d, 2H, $^3J_{H^6H^5} = 6$ Hz, $^3J_{PtH^6} = 15$ Hz, H^6]; 8.17 [d, 2H, $^4J_{H^3H^5} = 1$ Hz, H^3]; 7.70 [dd, 2H, $^3J_{H^5H^6} = 6$ Hz, $^4J_{H^5H^3} = 1$ Hz, H^5], 1.70 [s, 6H, $^3J_{SnMe} = 11$ Hz, $^2J_{PtMe} = 60$ Hz, Pt-Me]; 1.45 [s, 18H, ^{t}bu]; $\delta(^{119}Sn)$ −402 [s, $^1J_{PtSn} = 25\,864$ Hz, Pt−Sn]. Attempts to grow crystals for X-ray structure determination were unsuccessful. However, attempted crystallization of **6** in the presence of Me_2SnCl_2 (5 molar excess) from 1,2-$C_2H_4Cl_2$/pentane led to adventitious formation of single crystals of **2**, which cocrystallized with [Me_2SnCl_2·Me_2SnO]$_2$.

[PtClMe$_2$(GeCl$_3$)(bu$_2$bpy)], 8. This complex was prepared similarly from **1** and $GeCl_4$. Yield: 84%. Anal. Calcd for $C_{20}H_{30}Cl_4GeN_2Pt$: C, 33.93; H, 4.27; N, 3.96. Found: C, 33.69; H, 4.01; N, 3.82. NMR in $CDCl_3$: $\delta(^1H)$ 8.78 [d, 1H, $^3J_{H^6H^5} = 6$ Hz, $^3J_{PtH^6} = 24$ Hz, H^6]; 8.67 [d, 1H, $^3J_{H^6H^5} = 6$ Hz, $^3J_{PtH^6} = 17$ Hz, $H^{6'}$]; 8.23 [d, 1H, $^4J_{H^3H^5} = 2$ Hz, H^3]; 8.17 [d, 1H, $^4J_{H^3H^5} = 2$ Hz, $H^{3'}$]; 7.72 [dd, 1H, $^3J_{H^5H^6} = 6$ Hz, $^4J_{H^5H^3} = 2$ Hz, H^5]; 7.63 [dd, 1H, $^3J_{H^5H^6} = 6$ Hz, $^4J_{H^5H^3} = 2$ Hz, $H^{5'}$]; 1.70 [s, 3H, $^2J_{PtMe} = 62$ Hz, Pt-Me *trans* to N]; 1.42, 1.41 [s, each 9H, ^{t}bu]; 1.28 [s, 3H, $^2J_{PtMe} = 66$ Hz, Pt-Me *trans* to Cl].

[{PtClMe$_2$(bu$_2$bpy)}$_2$(μ-SnClPh)], 7. To a stirred solution of **1** (100 mg, 0.203 mmol) in CH_2Cl_2 (3 mL) was added $PhSnCl_3$ (16.7μL, 0.102 mmol). The solution color changed from orange to pale yellow over 10 min. The product was isolated as a pale yellow solid by precipitation with pentane and was isolated by filtration and dried under vacuum. Yield: 90%. Anal. Calcd for $C_{46}H_{65}Cl_3N_4Pt_2Sn$·$2CH_2Cl_2$: C, 37.87; H, 4.49; N, 3.84. Found: C, 37.61; H, 4.28; N, 3.61. NMR in $CDCl_3$: $\delta(^1H)$ 8.68 [d, 2H, $^3J_{H^6H^5} = 6$ Hz, $^3J_{PtH^6} = 16$ Hz, H^6]; 8.53 [d, 2H, $^3J_{H^{6'}H^{5'}} = 6$ Hz, $^3J_{PtH^{6'}} = 16$ Hz, $H^{6'}$]; 7.91 [d, 2H, $^4J_{H^3H^5} = 1$ Hz, H^3]; 7.84 [d, 2H, $^4J_{H^{3'}H^{5'}} = 1$ Hz, $H^{3'}$]; 7.49 [dd, 2H, $^3J_{H^5H^6} = 6$ Hz, $^4J_{H^5H^3} = 1$ Hz, H^5]; 7.33 [dd, 2H, $^3J_{H^{5'}H^{6'}} = 6$ Hz, $^4J_{H^{5'}H^{3'}} = 1$ Hz, $H^{5'}$]; 1.40 [s, 18H, ^{t}bu]; 1.35 [s, 18H, ^{t}bu′]; 1.23 [br s, 12H, $^2J_{PtMe} = 59$ Hz, Pt-Me]; $\delta(^{119}Sn)$ −319 [s, $^1J_{PtSn} = 12\,947$ Hz, (1:8:18:8:1 quintet), Pt-Sn]. Crystals were grown from CH_2Cl_2/pentane by slow diffusion at 5 °C. The same product **7** was formed by reaction of **1** with **3**.

[{PtClMe$_2$(bu$_2$bpy)}$_2$(μ-SnCl$_2$)], 6. This complex was prepared similarly from **1** and $SnCl_4$. Yield: 88%. Anal. Calcd for $C_{40}H_{60}Cl_4N_4Pt_2Sn$·$2CH_2Cl_2$: C, 33.83; H, 4.27; N, 3.95. Found: C, 33.81; H, 4.09; N, 3.79. NMR in $CDCl_3$: $\delta(^1H)$ 8.69 [d, 2H, $^3J_{H^6H^5} = 6$ Hz, $^3J_{PtH^6} = 16$ Hz, H^6]; 8.07 [d, 2H, $^4J_{H^3H^5} = 1$ Hz, H^3]; 7.55 [dd, 2H, $^3J_{H^5H^6} = 6$ Hz, $^4J_{H^5H^3} = 1$ Hz, H^5]; 1.40 [s,

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36H, ^{t}bu]; 1.36 [s, 12H, $^{2}J_{PtMe} = 59$ Hz, Pt-Me]; $\delta(^{119}Sn)$ −436 [s, $^{1}J_{PtSn} = 15\ 317$ Hz, (1:8:18:8:1 quintet), Pt-Sn]. Crystals were grown from CH_2Cl_2/pentane by slow diffusion at 5 °C. The same product **6** was formed by reaction of **1** with **2**.

X-ray Structure Determinations. Crystals were mounted on glass fibers. Data were collected by using a Nonius Kappa-CCD diffractometer using COLLECT (Nonius, 1998) software. Crystal cell refinement and data reduction was carried out using the Nonius DENZO package. The data were scaled using SCALEPACK (Nonius, 1998), and no other absorption corrections were applied. The SHEXTL 5.1 (Sheldrick, G. M., Madison, WI) program was used to solve the structure by direct methods, followed by refinement by successive difference Fouriers. Crystallographic details are shown in Table 5. For complex **2**·$Me_4Sn_2Cl_2O \cdot 2C_2H_4Cl_2$ there was some disorder in the dichloroethane solvent molecules, but all atoms were refined anisotropically. The unusual space group *C*2/*m* was indicated by the e-statistics and confirmed by successful refinement; refinement was also attempted in space group *C*2 but was unsatisfactory. For complex **3**, phenyl groups were constrained to be regular hexagons; all heavy atoms were anisotropic. For complex **4** the unit cell contained two independent molecules; only data for one of them are given in Table 2. The second differs by rotation about the Pt−Sn bond. One of the *tert*-butyl groups was disordered, but all other heavy atoms were refined anisotropically. For complex **6**·$2CH_2Cl_2$ one of the *tert*-butyl groups was disordered, but all other heavy atoms were refined anisotropically. For complex **7**·$2CH_2Cl_2$ one of the *tert*-butyl groups was disordered and was refined isotropically, but all other heavy atoms were refined anisotropically. There was resolved disorder in one of the CH_2Cl_2 molecules of solvation. Complex **8** appears to have some disorder in the mutually *trans* methyl and chloro ligands, but it was not resolved; these atoms are not accurately located.

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Supporting Information Available: Tables of X-ray data for the complexes are available available free of charge via the Internet at http://pubs.acs.org.

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