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Luminescent Platinum−Tin-Bonded Metallacycles: First Oxidative Addition of Sn−S Bonds

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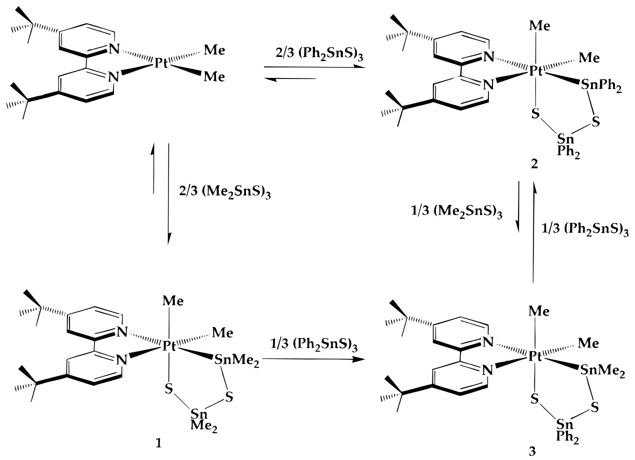
Summary: In the first examples of oxidative addition of tin−sulfur bonds to a transition-metal complex, the ring compounds $(R_2SnS)_3$ *(R = Me, Ph) react with* $[PtMe_2(^tbu_2bpy)]$ *(*$^tbu_2bpy$ *= 4,4′-di-tert-butyl-2,2′-bipyridine) to give the new luminescent organoplatinum(IV) complexes* $[PtMe_2(R_2SnS)_2(^tbu_2bpy)]$ *(**1** and **2**; R = Me and Ph, respectively), which contain the new five-membered PtSnSSnS ring. The complex* $[PtMe_2\{(SnMe_2)S(SnPh_2)S\}(^tbu_2bpy)]$ *(**3**) is formed selectively by any of the redistribution reactions between **1** and* $(Ph_2SnS)_3$*, **2** and* $(Me_2SnS)_3$*, or **1** and **2**.*

Diorganotin sulfides, which usually occur as the six-membered-ring compounds $(R_2SnS)_3$ (e.g., R = Me, Et, Ph), show interesting organometallic reactivity[1] and find applications in both catalytic and stoichiometric organic synthesis,[2] but no oxidative-addition reactions with transition-metal complexes have been explored. This paper reports the first such reactions in which the unusual oxidative addition of two R_2SnS units from $(R_2SnS)_3$ (R = Me, Ph) to $[PtMe_2(^tbu_2bpy)]$[3] ($^tbu_2bpy$ = 4,4′-di-*tert*-butyl-2,2′-bipyridine) yields the luminescent organoplatinum(IV) complexes $[PtMe_2(R_2SnS)_2(^tbu_2bpy)]$ (**1** and **2**) (Scheme 1), containing the new five-membered PtSnSSnS ring.

Scheme 1



The reactions to form **1** and **2** (Scheme 1) were

[⊗] Abstract published in *Advance ACS Abstracts,* March 15, 1996.

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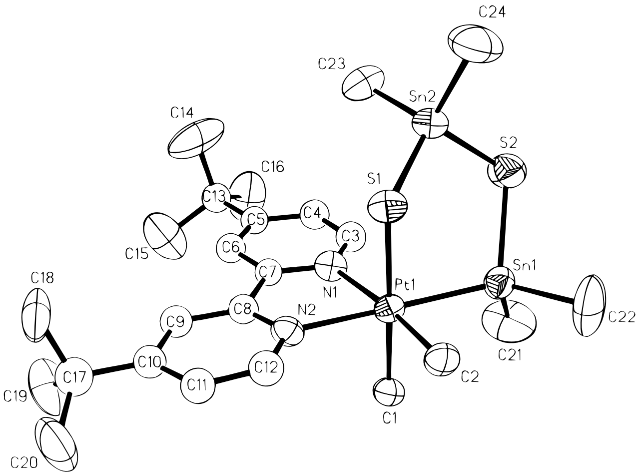


Figure 1. Molecular stucture of **1**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are represented at the 50% level. Selected bond distances (Å) are Pt−Sn(1) = 2.552(1), Pt−S(1) = 2.439(3), Pt−C(1) = 2.09(1), Pt−C(2) = 2.05(1), Pt−N(1) = 2.14(1), Pt−N(2) = 2.21(1), Sn(1)−S(2) = 2.435(4), Sn(2)−S(1) = 2.355(3), and Sn(2)−S(2) = 2.416(4). Selected bond angles (deg) are S(1)−Pt−Sn(1) = 92.74(9), S(2)−Sn(1)−Pt = 110.6(1), S(1)−Sn(2)−S(2) = 108.9(1), Sn(2)−S(1)−Pt = 108.2(1), and Sn(2)−S(2)−Sn(1) = 100.1(1).

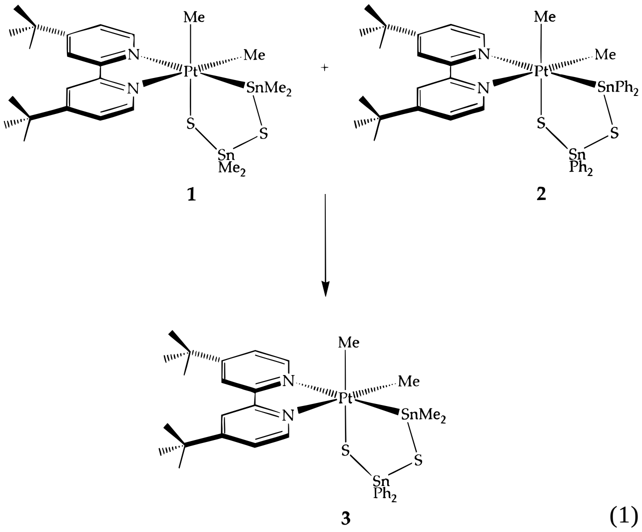
complete in 0.5 h in refluxing acetone solution, and the products were isolated as air-stable bright yellow and pale yellow solids, respectively, in high yield (>88%). They have been characterized by ^{1}H, ^{119}Sn, and ^{195}Pt NMR spectroscopy[4] and, for **1**·acetone, by an X-ray structure determination. The structure of the new five-membered PtSnSSnS ring is illustrated in Figure 1.[5]

Complex **3**, which contains both Me_2Sn and Ph_2Sn groups, was formed by reaction of $(Ph_2SnS)_3$ with **1** in CH_2Cl_2 solution for 1 h and could be isolated in 85% yield.[6] The reaction involves the very selective replacement of one Me_2Sn group of **1** by Ph_2Sn (Scheme 1). Longer reaction times led to displacement of the second Me_2Sn group by Ph_2Sn to give **2**. Similarly, reaction between **2** and $(Me_2SnS)_3$ also yields **3** selectively, although this reaction is much slower (*ca.* 50% conversion after 24 h). Finally, complex **3** is formed slowly by a redistribution reaction from equimolar amounts of **1** and **2** in CH_2Cl_2 solution (eq 1). The structure of **3** was deduced from its NMR spectra. The Me_2Sn and Ph_2Sn groups have very different ^{119}Sn chemical shifts, and only the directly bonded diorganotin moiety gives a large coupling $^1J_{PtSn}$ (Table 1).[7] It is then immediately apparent from the ^{119}Sn NMR spectrum of **3** (Table 1) that the dimethyltin rather than the diphenyltin unit is coordinated to the platinum center.

Table 1. ^{119}Sn NMR Data for $PtSn^1R^1{}_2SSn^2R^2{}_2S$ Rings, Establishing the Structure of 3^a

complex	δ(Sn^1)	$^1J_{PtSn^1}$ (Hz)	δ(Sn^2)
1, R^1 = R^2 = Me	−34.45	12 067	138.13
2, R^1 = R^2 = Ph	−169.10	13 344	51.94
3, R^1 = Me, R^2 = Ph	−32.67	12 103	51.71

^{a} Measured in CD_2Cl_2.



(1)

Complexes **1**−**3** luminesce strongly in CH_2Cl_2 solution at room temperature.[8] A characteristic band at *ca.* 650 nm in the emission spectrum ($\lambda_{excitation}$ = 431 nm for **1** and 410 nm for **2** and **3**) is tentatively assigned to the n(S)−π*(^{t}bu$_2$bpy) excited state, while a weaker band at 450−500 nm is attributed to a π−π* excited state of the ^{t}bu$_2$bpy ligand.[9] The presence of both tin and thiolate seems important for luminescence, since related (bipyridine)platinum(IV) complexes containing thiolate or Pt−Sn bonds alone do not luminesce at room temperature.[10]

In dilute solution, complex **1** dissociates slowly to give an equilibrium with dimethyltin sulfide and [PtMe$_2$-

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(4) **1**·acetone data are as follow. NMR in CD_2Cl_2: $\delta(^1H)$ 9.39 [d, ^{1}H, $^3J_{H^{5'}H^{6'}} = 5.9$ 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, $^3J_{^{119,117}SnH} = 3.3$ Hz, Pt−Me], 0.56 [s, 3H, $^3J_{PtH} = 4.0$ Hz, $^2J_{^{119}SnH} = 45.6$ Hz, $^2J_{^{117}SnH} = 43.6$ Hz, Pt−SnMe^a], 0.53 [s, 3H, $^3J_{PtH} = 2.5$ Hz, $^2J_{^{119}SnH} = 51.8$ Hz, $^2J_{^{117}SnH} = 49.5$ Hz, Pt−SnMe^b], 0.46 [s, 3H, $^2J_{^{119}SnH} = 58.0$ Hz, $^2J_{^{117}SnH} = 55.4$ Hz, Pt−S−SnMe^a], 0.26 [s, 3H, $^2J_{PtH} = 59.1$ Hz, Pt−Me], −0.06 [s, 3H, $^2J_{^{119}SnH} = 58.0$ Hz, $^2J_{^{117}SnH} = 55.5$ Hz, Pt−S−SnMe^b] (referenced to TMS); $\delta(^{119}Sn)$ 138.13 [$^2J_{^{119}Sn^{117}Sn} = 222.7$ Hz, Pt−S−Sn]; −34.45 [$^1J_{Pt^{119}Sn} = 12\,067$ Hz, Pt−Sn] (referenced to $SnMe_4$); $\delta(^{195}Pt)$ −1486 [$^1J_{^{119}SnPt} = 12\,074$ Hz, $^1J_{^{117}SnPt} = 11\,543$ Hz] (referenced to external $K_2[PtCl_4]$ in D_2O). 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. **2** data are as follows. NMR in CD_2Cl_2: $\delta(^1H)$ 8.92 [d, ^{1}H, $^3J_{H^{5'}H^{6'}} = 5.9$ Hz, $^3J_{PtH^{6'}} = 17.6$ 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, $^3J_{^{119,117}SnH} = 4.1$ Hz, Pt−Me], 0.47 [s, 3H, $^2J_{PtH} = 57.9$ Hz, Pt−Me]; $\delta(^{119}Sn)$ 51.94 [$^2J_{^{119}Sn^{117}Sn} = 188.1$ Hz, Pt−S−Sn]; −169.10 [$^1J_{Pt^{119}Sn} = 13\,344$ Hz, Pt−Sn]; $\delta(^{195}Pt)$ −1432 [$^1J_{^{119}SnPt} = 13\,348$ Hz, $^1J_{^{117}SnPt} = 12\,752$ Hz]. 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.

(5) Crystallographic data for **1**·acetone: MW = 913.26; crystal system monoclinic, space group $P2_1/n$; $a = 14.597(3)$ Å, $b = 13.196(3)$ Å, $c = 18.975(3)$ Å, $\beta = 104.41(1)°$; $V = 3540(2)$ Å^3; $d_{calcd} = 1.714$ g cm^{-3} for $Z = 4$ at 23 ± 1 °C; $R = 0.0473$, $R_w = 0.1034$. Details of data collection and refinement are given in the Supporting Information.

(6) **3** data are as follows. NMR in CD_2Cl_2: $\delta(^1H)$ 9.21 [d, ^{1}H, $^3J_{H^{5'}H^{6'}} = 5.9$ 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, $^4J_{H^3H^5} = 1.95$ Hz, H^3], 7.72 [d, 1H, $^3J_{H^{5'}H^{6'}} = 5.9$ Hz, H$^{5'}$], 7.70 [d, 1H, $^3J_{H^5H^6} = 5.8$ Hz, H^5], 7.62−7.08 [m, 10H, Pt−S−SnPh$_2$], 1.48 [s, 9H, ^{t}bu], 1.34 [s, 9H, ^{t}bu], 1.14 [s, 3H, $^2J_{PtH} = 60.7$ Hz, $^3J_{^{119,117}SnH} = 3.1$ Hz, Pt−Me], 0.60 [s, 3H, $^3J_{PtH} = 3.9$ Hz, $^2J_{^{119}SnH} = 45.8$ Hz, $^2J_{^{117}SnH} = 43.8$ Hz, Pt−SnMe^a], 0.57 [s, 3H, $^2J_{^{119}SnH} = 51.6$ Hz, $^2J_{^{117}SnH} = 49.4$ Hz, Pt−SnMe^b], 0.22 [s, 3H, $^2J_{PtH} = 58.7$ Hz, Pt−Me]; $\delta(^{119}Sn)$ 51.71 [$^2J_{^{119}Sn^{117}Sn} = 217.0$ Hz, Pt−S−Sn], −32.67 [$^1J_{Pt^{119}Sn} = 12\,103$ Hz, Pt−Sn]; $\delta(^{195}Pt)$ −1479 [$^1J_{^{119}SnPt} = 12\,104$ Hz, $^1J_{^{117}SnPt} = 11\,566$ Hz]. 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.

(7) Wrackmeyer, B. *Annu. Rep. NMR Spectrosc.* **1985**, *16*, 73.

(8) Complexes **1** and **3** also exhibit intense solid-state luminescence on irradiation with UV light (λ = 254 nm).

(9) Chan, C.-W.; Cheng, L.-K.; Che, C.-M. *Coord. Chem. Rev.* **1994**, *132*, 87.

(^{t}bu$_2$bpy)], as indicated by UV−visible spectroscopy, but the equilibrium is shifted toward the platinum(IV) complex compared to related reactions of organotin halides[10a] and no platinum(II) complex is detectable at the higher concentrations used in NMR spectroscopy.

It is reasonable to predict that the oxidative addition with Sn−S bond cleavage of the diorganotin sulfides to [PtMe$_2$(^{t}bu$_2$bpy)] to give **1** and **2** proceeds by a polar S$_N$2 mechanism, as described elsewhere for the oxidative addition of organotin halides to related organoplatinum(II) complexes.[3,10] However, the way in which only two of the three R$_2$SnS units of (R$_2$SnS)$_3$ are incorporated remains uncertain. It is known that redistribution of R$_2$SnS units occurs easily in the trimers (R$_2$SnS)$_3$; the mechanism is probably associative, perhaps with a “ladder” intermediate, though the detailed mechanism is difficult to establish.[1a] Clearly, the redistribution reactions observed for the five-membered PtSnSSnS ring compounds could occur in a similar way, but it is also possible that they could occur by reductive elimination of the diorganotin sulfide fragment, as established above, followed by scrambling within the diorganotin sulfide oligomers and then oxidative addition to re-form a new PtSnSSnS ring. The selectivity for formation of the unsymmetrical **3** rather than its isomer containing a Pt(SnPh$_2$)S(SnMe$_2$)S ring is remarkable. Complex **3** must be the product of thermodynamic control, since it is formed selectively by three different routes, but molecular mechanics calculations indicate that steric energies are similar for the two isomers, and most redistribution reactions in organometallic chemistry lead to all possible isomers (see for example ref 1a).

In conclusion, the first Sn−S bond oxidative additions lead to interesting new five-membered PtSnSSnS metallacycles which display unusual reactivity and luminescence properties. The ease of formation of the metallacycles, coupled with the known reactivity of Pt−Sn bonds, suggests that transition-metal catalysis could widen the scope of the use of (R$_2$SnS)$_3$ in organic synthesis.[1,2,10]

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Supporting Information Available: Text giving a description of the data collection and structure solution and tables of crystal data, complete interatomic distances and angles, atomic anisotropic displacement parameters, positional parameters for the hydrogen atoms, torsion angles for nonhydrogen atoms, and selected weighted least-squares planes (12 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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