

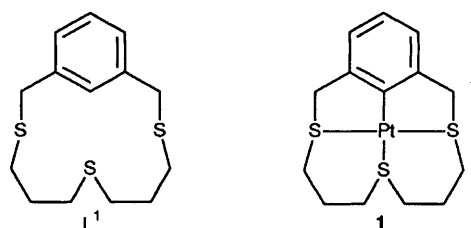
Metallation of a Crown Thioether Ligand. Synthesis, Structure and Reactivity of $[\text{Pt}(\text{L}^1)][\text{BF}_4]$ and Structure of $[\text{Pt}_2(\text{L}^1)][\text{BF}_4]$ ($\text{L}^1 = 2,6,10\text{-Trithia}[11]\text{-}m\text{-benzenophane}$)

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Metallation of L^1 results in formation of the square-planar, crown thioether complex $[\text{Pt}(\text{L}^1)][\text{BF}_4]$ **1**; the versatility of this S_3C donor ligand is demonstrated by substitution for the central S donor and oxidative-addition to octahedral complexes of Pt^{IV} .

A wide variety of crown thioether complexes have been reported recently and the stability and redox properties of these complexes appear to be partly dependent on the sulphur coordination sphere.¹⁻⁴ The functionalization or derivatization of these thioether macrocycles must certainly be one of the next steps in the evolution of their chemistry.^{5,6} We report herein the first example of a metallated crown thioether and a rare example of a macrocyclic complex containing a direct M-C bond.



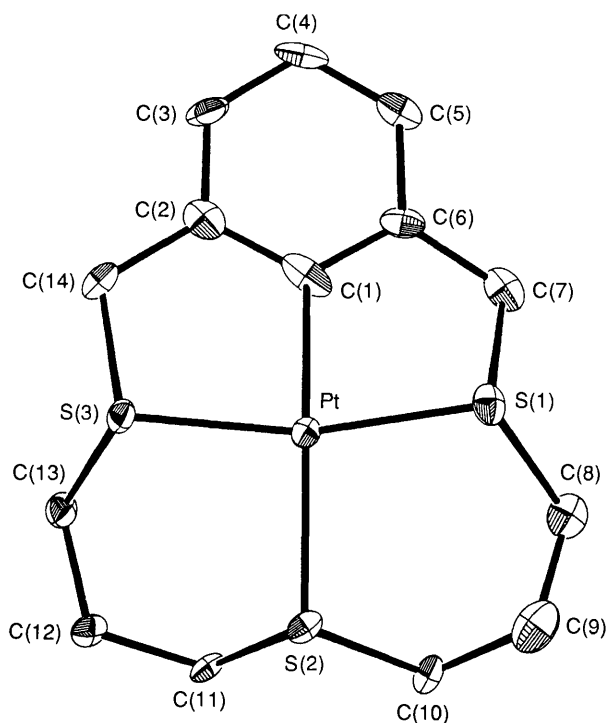
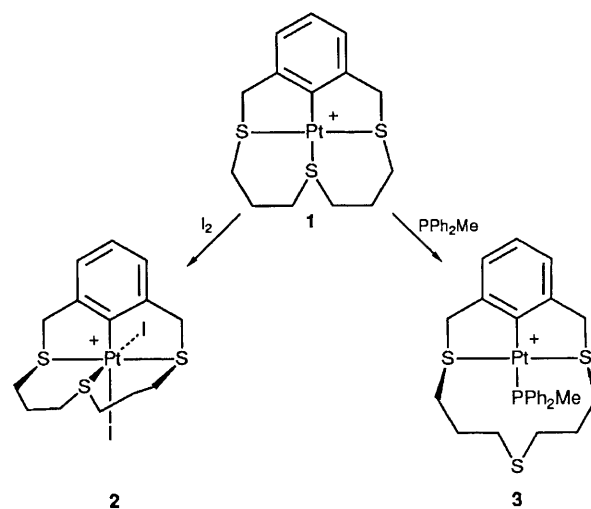


Fig. 1. Perspective ORTEP drawing of the $[\text{Pt}(\text{L}^1)]^+$ cation of **1** showing the atom numbering scheme. Significant bonding parameters are Pt-S(1) 2.255(6), Pt-S(2) 2.365(5), Pt-S(3) 2.266(6), Pt-C(1) 1.99(3) Å; S(1)-Pt-S(2) 98.2(2), S(2)-Pt-S(3) 94.3(2), S(1)-Pt-C(1) 83.0(9), S(3)-Pt-C(1) 86.4(9), S(1)-Pt-S(3) 163.6(2), S(2)-Pt-C(1) 170.4(6)°.

The reaction of equimolar amounts of L^1 and $[\text{PtCl}_2(\text{cod})]$ (cod = cycloocta-1,5-diene) in the presence of AgBF_4 , in refluxing MeCN, yields $[\text{Pt}(\text{L}^1)][\text{BF}_4]$ **1**, as a colourless crystalline solid.† ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy indicate that metallation of the aromatic ring of L^1 has occurred.‡ In particular, the absence of a ligand proton resonance (δ 7.43) and the presence of a large ^{195}Pt coupling (854.6 Hz) to a

† The crown thioether ligand 2,6,10-trithia[11]-*m*-benzenophane was prepared by the Cs^+ mediated cyclization⁷ of either α,α' -dibromo-*m*-xylene and 4-thia-heptane-1,7-dithiol or *m*-xylene- α,α' -dithiol and 4-thia-heptane-1,7-ditosylate. Both reactions produced ligand in 60–75% yield.

‡ *Spectroscopic data*, NMR (δ in ppm, J/Hz). L^1 (CDCl_3 , 300 K), ^1H : 7.43 (s, 1H, Ar), 7.17–7.25 (m, 3H, Ar), 3.70 (s, 4H, benzylic), 2.48 (t, 4H, 2J 7.1, SCH_2), 2.38 (t, 4H, 2J 7.0, SCH_2), 1.58 (m, 4H, CH_2); $^{13}\text{C}\{^1\text{H}\}$: 139.49, 129.35, 128.75, 127.74 (Ar), 36.88 (benzylic), 31.24 (CH_2S), 30.25, (CH_2S), 29.88 (CH_2). **1**: (CD_3CN , 300 K), ^1H : 7.12 (m, 3H, Ar), 4.91 (d, 2H, 2J 15.9, 3J 70.4, benzylic), 4.41 (d, 2H, 2J 15.9, benzylic), 3.67 (m, 2H, $^3J_{\text{PtH}}$ 81.1, SCH_2), 3.12–3.33 (m, 4H, SCH_2), 2.89 (m, 2H, SCH_2), 2.60 (m, 2H, CH_2), 2.00 (m, 2H, CH_2); $^{13}\text{C}\{^1\text{H}\}$: δ 157.9 ($^1J_{\text{PtC}}$ 854.6), 147.36 ($^2J_{\text{PtC}}$ 111.1), 126.57, 122.08 ($^3J_{\text{PtC}} < 30$, Ar), 52.50 ($^3J < 30$, benzylic), 38.59 ($^3J_{\text{PtC}}$ 23.5, SCH_2), 35.75 ($^3J < 20$, SCH_2), 28.22 ($^3J_{\text{PtC}}$ 29.9, CH_2). **2**: (CH_3CN , 300 K), ^1H : 7.27 (m, 2H, Ar), 7.11 (m, 1H, Ar), 4.93 (m, 4H, benzylic), 3.45 (m, 2H, SCH_2), 3.37 (m, 4H, SCH_2), 3.10 (m, 2H, SCH_2), 2.89 (ddd, 2H, $^3J_{\text{PtH}}$ 60.0 CH_2), 2.41 (m, 2H, CH_2); $^{13}\text{C}\{^1\text{H}\}$: δ 149.61 ($^1J_{\text{PtC}}$ 634.0), 144.79 ($^2J_{\text{PtC}}$ 51.8), 132.70, 128.40 ($^3J_{\text{PtC}} < 30$, Ar), 48.33 ($^3J_{\text{PtC}} < 20$, benzylic), 34.30, (SCH_2), 32.74 (SCH_2), 21.99 ($^3J_{\text{PtC}}$ 19.5, CH_2). **3**: (CD_3CN , 300 K), ^1H : 7.67 (m, 4H, PPh_2Me), 7.53 (m, 6H, PPh_2Me), 7.17 (m, 3H, L^1 Ar), 4.92 (d, 2H, 2J 17.0, benzylic), 4.43 (d, 2J 17.0, $^3J_{\text{PtH}}$ 37.0 benzylic), 3.14 (m, 2H, SCH_2), 2.54 (m, 6H), 2.32 (m, 4H), 1.77 (br s, 3H, PMe); $^{13}\text{C}\{^1\text{H}\}$: δ 169.1 ($^1J_{\text{PtC}}$ 904.8, $^2J_{\text{PtC}}$ 103.3, L^1), 150.10 ($^2J_{\text{PtC}}$ 105.6, L^1), 133.43 (d, $^1J_{\text{PC}}$ 48.3, PPh_2Me), 133.45 ($^2J_{\text{PC}}$ 10.6, PPh_2Me), 132.38 (PPh_2Me), 126.97 (L^1), 122.21 (L^1), 52.65 (benzylic), 40.27 (SCH_2), 29.37 (SCH_2), 28.59 ($^3J_{\text{PtC}}$ 38.1, CH_2); $^{31}\text{P}\{^1\text{H}\}$: -0.34 ($^1J_{\text{PtP}}$ 1950.4).



Scheme 1

downfield shifted ^{13}C resonance (δ 157.9) are consistent with the formation of a Pt–C bond at the 2-position of the aromatic ring. Recrystallization from MeCN affords crystals suitable for X-ray diffraction.§ The X-ray structure verifies (Fig. 1) that the Pt atom is in a square-planar PtS_3C environment. The Pt–S distances to the mutually *trans* S atoms are Pt–S(1), 2.255(6) and Pt–S(3), 2.266(6) Å but the Pt–S(2) distance *trans* to the Pt–C(1) bond is significantly longer, 2.365(5) Å, owing to the strong *trans* influence of the aromatic group. The Pt–C(1) distance is 1.99(3) Å.

Although the Pt^{II} centre is contained in a macrocycle with a relatively rigid $-\text{SCH}_2(\text{C}_6\text{H}_4)\text{CH}_2\text{S}-$ fragment, a pathway for reaction chemistry is available *via* labilization of the Pt–S(2) bond and the flexibility of the $-\text{SCH}_2\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{CH}_2\text{S}-$ linkage. Simple substitution reactions were attempted with two-electron donor molecules such as CO, C_2H_4 , $\text{RC}\equiv\text{CR}$ ($\text{R} = \text{Ph}$ or CO_2Me), and PPh_2Me . The results of these reactions indicate that formation of adducts of the type $[\text{Pt}(\text{Y})(\text{L}^1)]^+$ are possible, but only strong donors such as $\text{Y} = \text{PPh}_2\text{Me}$ can successfully compete with S(2) for the coordination site, allowing isolation of the adduct. $^{13}\text{C}\{^1\text{H}\}$ NMR chemical shifts for the $-\text{SCH}_2\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{CH}_2\text{S}-$ chain atoms of $[\text{Pt}(\text{PPh}_2\text{Me})(\text{L}^1)][\text{BF}_4]$ **3** suggest that the phosphine ligand substitutes for S(2) resulting in a square-planar complex in which the central S(2) atom is exodentate and the methylene chain is folded away, perpendicular to the PtS_2P plane (Scheme 1).‡

This demonstrated flexibility of L^1 suggests that **1** might also accommodate the necessary structural changes required for oxidative addition to complexes of Pt^{IV} with either *cis*- or *trans*-addition geometry. Reaction of **1** with one equivalent of I_2 yielded the Pt^{IV} oxidative-addition product *cis*- $[\text{PtI}_2(\text{L}^1)]^+[\text{BF}_4]^-$ **2**.‡ Recrystallization of **2** from MeCN affords crystals suitable for X-ray diffraction.§ The X-ray structure shows

§ *Crystal data* for **1**, $[\text{C}_{16}\text{H}_{19}\text{PtS}_3][\text{BF}_4]$: monoclinic, $P2_1/c$, $a = 8.373(1)$, $b = 21.784(7)$, $c = 9.517(4)$ Å, $\beta = 95.09(2)^\circ$, $U = 1729.1(16)$ Å³, $Z = 4$, $D_c = 2.172$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 85.79$ cm⁻¹. Rigaku AFC6 diffractometer; 1885 unique reflections with $F_o^2 > 3\sigma F_o^2$, $R = 6.93\%$, $R_w = 6.99\%$.

Crystal data for **2**, $[\text{C}_{16}\text{H}_{19}\text{I}_2\text{PtS}_3][\text{BF}_4]$: monoclinic, $P2_1/n$, $a = 11.253(4)$, $b = 11.120(2)$, $c = 16.558(4)$ Å, $\beta = 99.53(3)^\circ$, $U = 2043(2)$ Å³, $Z = 4$, $D_c = 2.662$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 102.56$ cm⁻¹. Rigaku AFC6 diffractometer; 2464 unique reflections with $F_o^2 > 3\sigma F_o^2$, $R = 6.50\%$, $R_w = 6.95\%$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

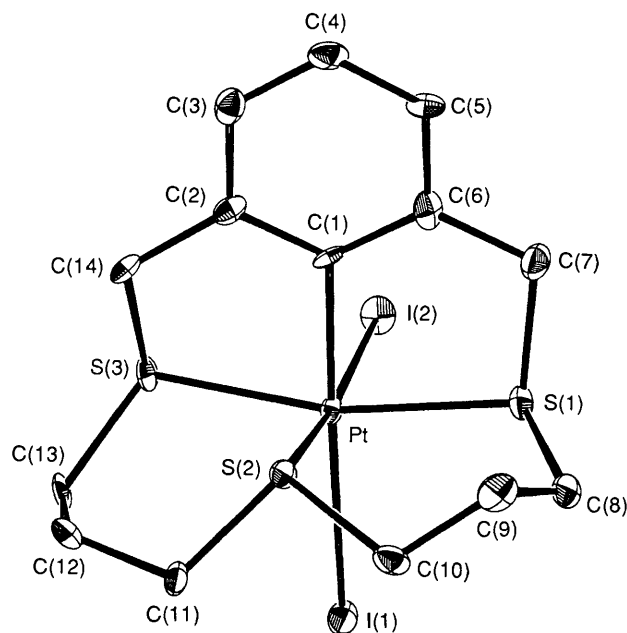


Fig. 2 Perspective ORTEP drawing of the $[\text{PtI}_2(\text{L}^1)]^+$ cation of **2** showing the atom numbering scheme. Significant bonding parameters are Pt-I(1) 2.739(2), Pt-I(2) 2.681(2), Pt-S(1) 2.325(5), Pt-S(2) 2.346(5), Pt-S(3) 2.331(5), Pt-C(1) 2.04(2) Å; S(1)-Pt-S(2) 99.0(2), S(2)-Pt-S(3) 89.4(02), S(1)-Pt-C(1) 86.1(6), S(3)-Pt-C(1) 83.8(6), S(1)-Pt-S(3) 166.2(2), S(2)-Pt-C(1) 84.6(5)°.

(Fig. 2) that addition of I_2 to Pt has occurred to produce an octahedral Pt^{IV} species with a $\text{PtI}_2\text{S}_3\text{C}$ coordination sphere in which the I atoms are mutually *cis* and L^1 is folded such that S(2) is coordinated perpendicular to the PtIS_2C plane. The Pt-S distances to the mutually *trans* S atoms are Pt-S(1), 2.325(5) and Pt-S(3), 2.331(5) Å and the Pt-S(2) distance *trans* to I(2) is 2.346(5) Å. The Pt-I distances are Pt-I(1) 2.739(2) and Pt-I(2) 2.681(2) Å with the former reflecting the *trans*-influence of the aromatic group similar to that observed for S(2) in **1**. The Pt-C(1) distance of 2.04(2) Å is only slightly longer than that found for **1**.

There are a number of open-chain ligand systems of the type $\text{XCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{X}$ in which X = NMe_2 ,⁸ SMe ⁹ and P^+Bu_2 .¹⁰

These systems have incorporated metallation of the central aromatic ring carbon and each displays some interesting chemistry related to the unique X_2C donor set. The incorporation of this type of framework into a thioether macrocycle has great potential for reaction chemistry as demonstrated by **1**. The substitution and oxidative addition reactions outlined herein, for **1**, can be thought of as models for essential reaction pathways required in catalytic chemistry. For a square-planar 16-electron complex to participate in a catalytic cycle there must be reaction pathways that allow for a single-site dissociation and substrate binding as well as *cis*-oxidative addition and reductive-elimination.¹¹ The formation of **2** and **3** from **1** demonstrates that complexes of L^1 can accommodate these pathways. Complexes of L^1 with more active metals such as Rh^{I} , Ru^{II} and Ir^{I} have the potential for exhibiting catalytic chemistry employing a thioether macrocycle and this possibility is being investigated.

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References

- 1 S. R. Cooper, *Acc. Chem. Res.*, 1988, **21**, 141.
- 2 M. Schröder, *Pure Appl. Chem.*, 1988, **60**, 517.
- 3 A. J. Blake and M. Schröder, *Adv. Inorg. Chem.*, 1990, **35**, 1.
- 4 S. R. Cooper and S. C. Rawle, *Struct. Bonding*, 1990, **72**, 1.
- 5 J. Buter, R. M. Kellogg and F. van Bollhuis, *J. Chem. Soc., Chem. Commun.*, 1990, 282.
- 6 W. N. Setzer, E. L. Cacioppo, Q. Guo, G. J. Grant, D. D. Kim, J. L. Hubbard and D. G. VanDerveer, *Inorg. Chem.*, 1990, **29**, 2672.
- 7 B. de Groot, G. R. Giesbrecht, S. J. Loeb and G. K. H. Shimizu, *Inorg. Chem.*, 1991, **30**, 177; J. Buter and R. M. Kellogg, *Org. Synth.*, 1987, **65**, 150, and reference cited therein.
- 8 G. van Koten, J. Terheijden, J. A. M. van Beek, I. C. M. Wehman-Ooyevaar, F. Muller and C. H. Stam, *Organometallics*, 1990, **9**, 903, and references cited therein.
- 9 J. Dupont and M. Pfeffer, *J. Chem. Soc., Dalton Trans.*, 1990, 3193, and references cited therein.
- 10 C. J. Moulton and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1976, 1020, and references cited therein.
- 11 J. P. Collman, L. S. Hegedus, J. R. Norton and R. J. Finke, *Principles and Applications of Organotransition Metal Chemistry*, University Science Books, Mill Valley, USA, 1987.