

The Preparation and Structures of Metallathietane-3-oxides and -3,3-dioxides of Platinum and Palladium: the Crystal Structures of *trans*-2,4-Dibenzoyl-1,1-bis(triphenylphosphine)platinathietane-3-oxide and *trans*-2,4-Dibenzoyl-1,1-bis(triphenylphosphine)platinathietane-3,3-dioxide

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High yields of platinathietane-3-oxides and metallathietane-3,3-dioxides may be obtained by treatment of $[MCl_2L_2]$ with $[RCH_2S(O)_nCH_2R]$ ($n = 1$, $R = CPh$; $n = 2$, $R = CPh$ or CO_2Me) and silver(I) oxide; single crystal X-ray studies on the title complexes establish the presence of puckered metallacycles, the sulphanyl oxygen of the platinathietane-3-oxide adopting an equatorial environment.

The utility of silver(I) oxide in the synthesis of an η^3 -oxodimethylenemethane complex *via* the ketone (**1**)¹ led us to investigate reactions of related compounds, *e.g.* (**2**) and (**3**) in metallacyclic synthesis. Treatment of the sulphoxide (**2**) with *cis*- $[PtCl_2L_2]$ ($L = PPh_3$, $PMePh_2$, or PMe_2Ph) and silver(I) oxide in refluxing dichloromethane afforded the air-stable platinathietane-3-oxide complexes (**4a–c**) in quantitative yield.† A series of platina- and pallada-thietane-3,3-dioxides (**5a–l**) were also formed in quantitative yield *via* reactions of $[MCl_2L_2]$ ($M = Pt$ or Pd , $L = PPh_3$, $PMePh_2$, PMe_2Ph , PMe_3 , PEt_3 , or PBu^t_3) with the sulphone (**3a**) and silver(I) oxide. Similarly treatment of $[MCl_2(PPh_3)_2]$ ($M = Pt$ or Pd) with the dimethyl ester of sulphonyldiacetic acid, in the presence of silver(I) oxide, afforded the metallathietane-3,3-dioxide complexes (**5m**) and (**5n**).

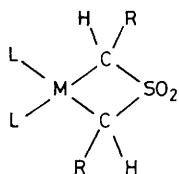
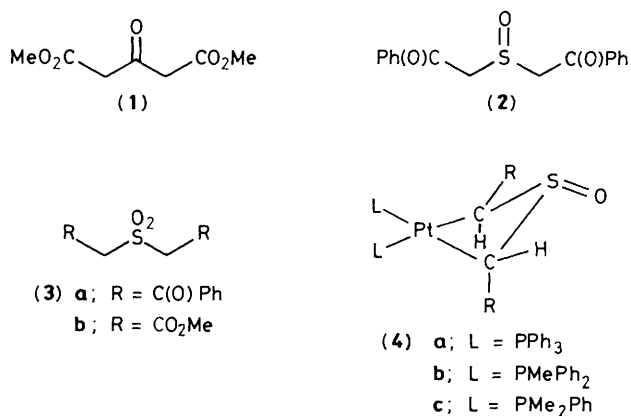
The synthesis of the metallathietane-3-oxide complexes (**4a–c**) provides a very convenient route to the first examples of the metallacyclic ring system $\overline{M-C-S(O)-C}$ and this is particularly noteworthy since our attempts to generate a source of the dianionic species $[PhCHS(O)CHPh]^{2-}$ *via* $(PhCH_2)_2SO$ and Bu^tLi and use this reagent in metallathietane-3-oxide synthesis have not been successful. In contrast

the sulphone dianion $[PhCHS(O)_2CHPh]^{2-}$ is available and can be used in metallacyclosulphone synthesis.²

In previous studies on metallacyclobutan-3-ones of Pt^{II} and Pd^{II} the presence of highly puckered metallacyclic rings and transannular $M \cdots CO$ interactions has been established.^{1,3,4} The availability of platinathietane-3-oxide complexes (**4**) afforded the opportunity to investigate the conformation of this ring system and in particular to determine the competing conformational requirements of an oxygen atom and a non-bonding sulphur electron pair in a metallacyclosulphoxide. Accordingly a single crystal X-ray structure determination of (**4a**) was carried out together with that of the metallacyclic sulphone (**5a**) for comparative purposes.‡

‡ *Crystal data:* Crystals of (**4a**) and (**5a**) were grown slowly from dichloromethane–light petroleum. Data were collected at 293 K using $Mo-K_{\alpha}$ X-radiation, $\lambda = 0.71069 \text{ \AA}$, on a Stöe STADI-2 Weissenberg diffractometer. (**4a**); $C_{52}H_{42}O_3P_2PtS \cdot 2CH_2Cl_2$, $M = 1173.8$, triclinic, space group $P\bar{1}$, $a = 13.819(3)$, $b = 12.940(4)$, $c = 19.24(1) \text{ \AA}$, $\alpha = 118.0(1)$, $\beta = 55.5(1)$, $\gamma = 113.48(5)^\circ$, $U = 2464.66 \text{ \AA}^3$, $Z = 2$, $D_c = 1.36 \text{ g cm}^{-3}$, $\mu(Mo-K_{\alpha}) = 30.60 \text{ cm}^{-1}$; final R 0.0487 (R_w 0.0512) for 7864 independent reflections [$I \geq 3\sigma(I)$] in the range $7 < 2\theta < 55^\circ$. (**5a**); $C_{52}H_{42}O_4P_2PtS \cdot 2CH_2Cl_2$, $M = 1189.8$, triclinic, space group $P\bar{1}$, $a = 20.835(2)$, $b = 10.628(2)$, $c = 12.577(4) \text{ \AA}$, $\alpha = 109.6(1)$, $\beta = 105.8(1)$, $\gamma = 91.4(1)^\circ$, $U = 2501.97 \text{ \AA}^3$, $Z = 2$, $D_c = 1.36 \text{ g cm}^{-3}$, $\mu(Mo-K_{\alpha}) = 30.16 \text{ cm}^{-1}$; final R 0.0595 (R_w 0.0580) for 5553 independent reflections [$I \geq 3\sigma(I)$] in the range $7 < 2\theta < 54^\circ$. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1986.

† *Selected n.m.r. spectroscopic data* (J in Hz); (**4a**): 1H (300 MHz, $CDCl_3$, room temp.), δ 7.52–6.79 (m, 40H, Ph), 5.05{d, 1H, H(1), $^3J[P(1)H(1)]$ 10.31, $^2J[PtH(1)]$ 77.3}, and 4.65{d,d, 1H, H(2), $^3J[P(1)H(2)]$ 10.05, $^3J[P(2)H(2)]$ 2.06, $^2J[PtH(2)]$ 48.8}; ^{31}P { 1H } (24 MHz, dichloromethane, relative to 85% H_3PO_4), second order AB spin system, δ 17.3{d, P(1), $^1J[PtP(1)]$ 2920, $^2J[P(2)P(1)]$ 19.5}, and 12.6 {d, P(2), $^1J[PtP(2)]$ 2783, $^2J[P(1)P(2)]$ 19.5}.



- (5) a; L = PPh₃
b; L = PMePh₂
c; L = PMe₂Ph
d; L = PMe₃
e; L = PEt₃
f; L = PBuⁿ₃
g; L = PPh₃
h; L = PMePh₂
i; L = PMe₂Ph
j; L = PMe₃
k; L = PEt₃
l; L = PBuⁿ₃
- M = Pt; R = C(O)Ph
- M = Pd; R = C(O)Ph
- m; L = PPh₃; M = Pt; R = CO₂Me
n; L = PPh₃; M = Pd; R = CO₂Me

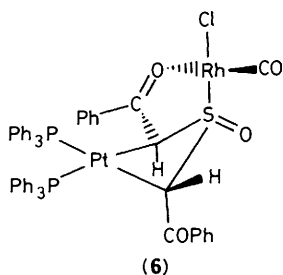


Figure 1 shows the geometry of the platinathietane-3-oxide ring, which is folded about the line C(1)–C(2) by 36.7°, and is considerably more puckered than the platinathietane-3,3-dioxide ring in (5a), Figure 2, (fold angle = 15.2°). The sulphanyl oxygen in (4a) occupies an equatorial environment as observed in C–C–C–S(O) rings, fold angles in these compounds lying in the range 27–41°. Thus the strong equatorial preference of sulphanyl oxygen in puckered thietane-1-oxides is not disturbed by substitution of a d⁸ square planar Pt^{II} fragment β to the sulphoxide group.

Interestingly, despite different fold angles in (4a) and (5a), the Pt ··· S distances are equal [2.840(5) Å]. The S–O

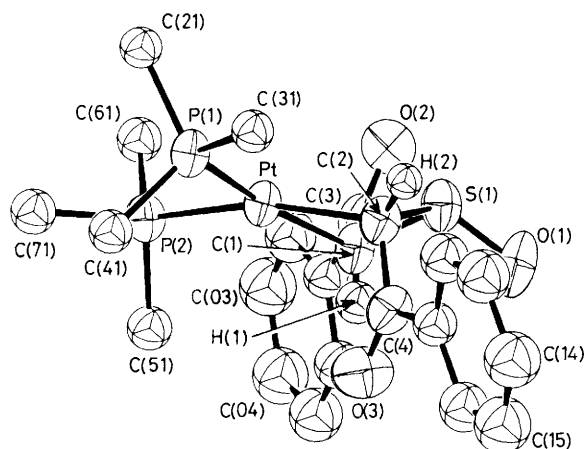


Figure 1. Molecular structure of [Pt{CH(COPh)S(O)CH(COPh)}(PPh₃)₂] (4a) with triphenylphosphine carbons other than those bonded to P, and H atoms of phenyl rings, being omitted. Atoms are shown as 50% thermal ellipsoids. Interatomic distances: Pt–P(1) 2.290(2), Pt–P(2) 2.319(2), Pt–C(1) 2.163(7), Pt–C(2) 2.123(6), Pt–S 2.840(5), C(1)–S 1.779(7), C(2)–S 1.797(7), S–O(1) 1.493(6) Å. Angles: P(2)–Pt–P(1) 97.7(1), C(1)–Pt–P(2) 95.1(2), C(2)–Pt–P(1) 94.8(2), C(1)–Pt–C(2) 72.6(2), C(1)–S–C(2) 90.4(3)°.

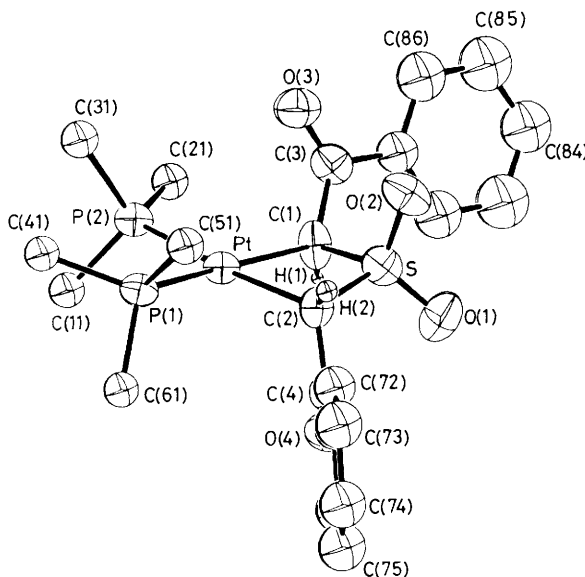


Figure 2. Molecular structure of [Pt{CH(COPh)S(O)₂CH(COPh)}(PPh₃)₂] (5a) with triphenylphosphine carbons other than those bonded to P, and H atoms of phenyl rings, being omitted. Atoms are shown as 50% thermal ellipsoids. Interatomic distances: Pt–P(1) 2.327(3), Pt–P(2) 2.285(3), Pt–C(1) 2.106(10), Pt–C(2) 2.125(11), Pt–S 2.840(5), C(1)–S 1.762(11), C(2)–S 1.755(11), S–O(1) 1.439(9), S–O(2) 1.445(8) Å. Angles: P(2)–Pt–P(1) 98.5(1), C(1)–Pt–P(2) 94.2(3), C(2)–Pt–P(1) 91.9(3), C(1)–Pt–C(2) 75.4(4), C(1)–S–C(2) 94.8(5)°.

distances, however, are normal for thietane-1-oxides (in the range 1.52–1.70 Å⁵) and thietane-1,1-dioxides (1.42–1.46 Å⁶) and there is thus no significant transannular Pt ··· S interaction in (4a) or (5a). The shorter Pt–C and C–C ring distances in (5a) compared with (4a) are presumably related to the more highly electronegative S^{VI} atom in (5a). The C–S ring bonds are shorter than expected (1.79–1.89 Å⁵) in (4a) and

also in $[\text{Pt}\{\overline{\text{C}}\text{HPhS}(\text{O})_2\overline{\text{C}}\text{HPh}\}(\text{AsPh}_3)_2]^2$ and **(5a)**; this appears to be characteristic of $\text{Pt}-\text{C}-\text{S}(\text{O})_n-\text{C}$ ($n = 1$ or 2) rings, and has also recently been observed in the organolithium compounds $[\{\text{LiPhCHS}(\text{O})_2\text{Ph}\}\cdot\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2]_2^7$ and $[\{\text{LiCH}_2\text{S}(\text{O})_2\text{Ph}\}\cdot\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2]_2^8$. In view of the interest in the conformation of puckered metallacyclobutane rings⁹ it is noteworthy that **(4a)** and **(5a)** are *trans* isomers with one of the benzoyl groups in a pseudo-axial environment, as found in $[\text{Pt}\{\overline{\text{C}}\text{HPhS}(\text{O})_2\overline{\text{C}}\text{HPh}\}(\text{AsPh}_3)_2]^2$ and several metallacyclobutan-3-ones of Pt^{II} and Pd^{II} .^{1,3,4}

The ^1H n.m.r. spectrum† of **(4a)** is consistent with the static structure shown. The magnitudes of the three bond couplings (*cis*-P-Pt-C-H) for the axial and equatorial ring protons of **(4a)** are under dihedral angle control as has been observed in highly puckered metallacyclobutan-3-one complexes.^{1,3,4} Thus, $\text{H}(2)_{\text{eq}}$ exhibits coupling to both the *cis*-P [*cis*-P-Pt-C-H(2) torsion angle $-42.4(6)^\circ$] and *trans*-P ligands, but $\text{H}(1)_{\text{ax}}$ shows no discernible coupling to its *cis*-P ligand [*cis*-P-Pt-C-H(1) torsion angle $-88.3(5)^\circ$], and appears as a doublet due to *trans*-P coupling only; furthermore, $^2J(\text{PtH}_{\text{ax}}) > ^2J(\text{PtH}_{\text{eq}})$. Similar features are observed for **(4b)** and **(4c)**. These observations are indicative of a puckered metallathietane-3-oxide ring which is not undergoing rapid ring inversion in solution. However, we cannot discount the possibility of a rapid equilibrium between the highly predominant isomer shown and a small amount of the conformer formed by inversion of the four-membered ring.

Preliminary studies show that the sulphur lone pair in the platinathietane-3-oxide **(4a)** has ligand properties and reacts with $[\text{Rh}_2\text{Cl}_2(\text{CO})_4]$ to afford the novel chelating complex **(6)**, characterised by an X-ray study, details of which will be published elsewhere. Finally, we note that recent work has shown that the reaction of thiirane-*S*-oxide with zerovalent platinum does not lead to platinathietane-3-oxides.¹⁰

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