Preparation of Metallacyclosulphones of Nickel, Palladium, and Platinum and the *X*-Ray Crystal Structure of *trans*-2,4-Diphenyl-1,1-bis(triphenylarsine)platinathietane-3,3-dioxide

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A variety of metallathietane-3,3-dioxides of platinum(II), palladium(II), and nickel(II), $[\overline{\text{M}\{\text{CHPhS(O)}_2\text{C}}\text{HPh}\}\text{L}_2]$ are formed in high yield by the action of the dianion $[\text{PhCHS(O)}_2\text{CHPh}]^{2-}$ upon either *cis*- or *trans*-$[\text{MCl}_2\text{L}_2]$; the *X*-ray structure of the title compound (**1a**) establishes the presence of a puckered platinathietane-3,3-dioxide ring with no substantial Pt · · · S transannular bonding.

We have recently described a variety of highly puckered metallacyclobutanone $\overline{\text{M–C–C(O)–C}}$ rings of platinum(II) and palladium(II) which contain an important transannular Pt · · · C(O) bonding contribution in the four-membered ring system.[1] In view of the importance of cross-ring interactions in carbon skeletal rearrangements of metallacyclobutanes we are investigating the chemistry and structures of four-membered metallacycles and herein report some metallacycles which contain the $\overline{\text{M–C–S(O)}_2\text{–C}}$ (M = Ni, Pd, or Pt) ring system.

Metallathietane-3,3-dioxides have not been previously described but we find that a variety of platinum, palladium, and nickel thietane-3,3-dioxide complexes (**1a**—**h**) are obtained in high yield by treating the complexes *cis*- or *trans*-$[\text{MCl}_2\text{L}_2]$ (M = Pt, L = AsPh_3, PPh_3, or SEt_2; M = Pd, L = PPh_3, PMe_3, or PEt_3; M = Ni, L = PMe_3, L_2 = $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$) with either $\text{K}_2[\text{PhCHS(O)}_2\text{CHPh}]^2$ or $\text{Li}_2[\text{PhCHS(O)}_2\text{CHPh}]$.[3] Thus in a typical experiment treatment of *cis*-$[\text{PtCl}_2(\text{AsPh}_3)_2]$ with $\text{K}_2[\text{PhCHS(O)}_2\text{CHPh}]$ in tetrahydrofuran affords (94%) a white microcrystalline air-stable compound (**1a**) [m.p. 245—248 °C (decomp.)]. The i.r. spectrum of (**1a**) exhibits a strong S=O stretching frequency at 1118 cm^{-1} and the ^1H n.m.r. spectrum shows signals at δ 7.3—6.9 (m, 40H, Ph) and 4.24 [s, 2H, ring CH, $^2J(\text{PtH})$ 84.9 Hz]. In order to establish the geometry of (**1a**) a single crystal *X*-ray diffraction study was carried out.†

The principal feature of interest in the structure of (**1a**) concerns the geometry of the platinacyclosulphone ring (Figure 1). The ring is folded about the line C(1)–C(2) by 24.5°, the angle of pucker being within the range of 9—31° found for thietane-1,1-dioxide, $\overline{\text{C–C–C–S}}\text{(O)}_2$ rings.[4] The thietane-1,1-dioxides $\text{CCl}_2\text{SCCl}_2\text{S(O)}_2{}^5$ and

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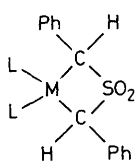
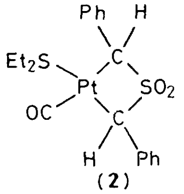
† *Crystal data* for (**1a**): $\text{C}_{50}\text{H}_{42}\text{As}_2\text{O}_2\text{PtS}$, M = 1051.9, orthorhombic, space group *Pbca*, a = 18.29(2), b = 24.65(2), c = 22.07(5) Å, U = 9951.3 Å^3, Z = 8, D_c = 1.404 g cm^{-3}, Mo-K_α *X*-radiation, $\bar{\lambda}$ = 0.71069 Å, $\mu(\text{Mo-}K_\alpha)$ = 42.4 cm^{-1}; current R 0.0725 (R_w 0.0725) for 3734 independent reflections [$I \geqslant 2.5\sigma(I)$] collected at 293 K on a Stoe STADI-2 Weissenberg diffractometer in the range $7 < 2\theta < 54°$. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

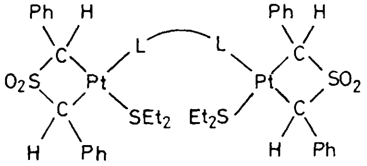


(1)



(2)

a; M = Pt, L = $AsPh_3$
b; M = Pt, L = PPh_3
c; M = Pt, L = SEt_2
d; M = Pd, L = PPh_3
e; M = Pd, L = PMe_3
f; M = Pd, L = PEt_3
g; M = Ni, L = PMe_3
h; M = Ni, $L_2 = Ph_2PCH_2CH_2PPh_2$



(3)

a; L–L = bipy
b; L–L = cod

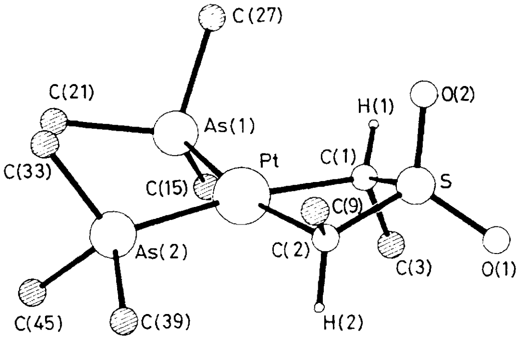


Figure 1. Molecular structure of (**1a**). The attached carbon atom of a phenyl ring is represented by a shaded circle. Interatomic distances: Pt–As(1) 2.421(2), Pt–As(2) 2.403(2), Pt–S 2.792(5), Pt–C(1) 2.09(2), Pt–C(2) 2.07(2), C(1)–S 1.76(2), C(2)–S 1.73(2), S–O(1) 1.45(2), S–O(2) 1.44(2) Å; angles: As(2)–Pt–As(1) 98.1(1), C(1)–Pt–As(1) 91.8(6), C(2)–Pt–As(2) 95.5(5), C(1)–Pt–C(2) 75.0(8), C(1)–S–C(2) 92.9(9)°.

$\overline{CX_2S(O)_2CX_2S}(O)_2$ (X = H, F, Cl, or Br)[5,6] have been shown to contain planar rings. The Pt · · · S distance is 2.792(5) Å, but since the S–O distances in (**1a**) are normal (S–O distance in thietane-1,1-dioxides are commonly in the range 1.42—1.46 Å)[4] it seems unlikely that there is any substantial bonding between the platinum and the sulphur in (**1a**). The Pt–C bond lengths are normal but the C–S bonds are shorter than the range of 1.79—1.88 Å found in six other thietane-1,1-dioxides.[4] It is interesting that (**1a**) is the *trans*-isomer with one of the phenyl groups in a pseudo-axial position. Recent calculations on the metallacyclic species $[\overline{M(CHR^1CHR^2CHR^3})Cl_4]$ indicate that a diequatorial substitution is the favoured conformation for a 2,4-substituted (octahedrally co-ordinated) metallacycle.[7] In the four co-ordinate system (**1a**) it seems likely that torsional effects between equatorial substituents and the *cis*-arsine ligands will destabilise the diequatorial isomer causing the observed equatorial–axial isomer to be favoured [the torsion angles As(2)–Pt–C(2)–C(9) and As(1)–Pt–C(1)–C(3) are 46.29 and 81.10° respectively]. This isomer also appears to be the favoured conformation for puckered four-co-ordinate metallacyclobutan-3-ones.[1]

Preliminary studies indicate that the diethyl sulphide complex (**1c**) provides an access to a wide range of platinacyclosulphones. Thus treatment of (**1c**) with carbon monoxide (1 atm) affords the monocarbonyl derivative (**2**) [ν(CO) 2070 cm^{-1}] with no indication of insertion into a Pt–C bond as has been observed with the platinacyclobutane derivative $[\overline{Pt(CH_2CH_2CH_2})(bipy)]$ (bipy = 2,2′-bipyridyl).[8] Interestingly the reaction of an excess of bipy with (**1c**) in refluxing dichloromethane also results in displacement of one diethyl sulphide ligand per platinum to afford the binuclear complex (**3a**).‡ An analogous cyclo-octa-1,5-diene (cod) binuclear complex (**3b**)‡ can similarly be obtained.

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‡ *Selected spectroscopic data* (*J* in Hz): (**3a**), i.r. (KBr disc): ν_{SO_2} 1109 cm^{-1}; n.m.r. (CD_2Cl_2): ^1H (400 MHz), δ 8.46—7.18 (m, 28H, aromatic CH), 4.94 [s, 2H, ring CH, *J*(PtH) 104.0], 4.36 [s, 2H, ring CH, *J*(PtH) 98.0], 2.49 [m, 4H $(CH_3CH_2)_2S$], 2.29 [m, 4H, $(CH_3CH_2)_2S$], and 1.20 [t, 12H, $(CH_3CH_2)_2S$, ^3J(HH) 7.4]; $^{13}C\{^1H\}$ (100 MHz), δ 150.99—122.72 (m, aromatic C), 48.27 [s, ring CH, *J*(PtC) 624.0], 40.71 [s, ring CH, *J*(PtC) 614.0], 30.02 [s, $(CH_3CH_2)_2S$], and 13.29 [s, $(CH_3CH_2)_2S$]; (**3b**), i.r. (KBr disc): ν_{SO_2} 1113 cm^{-1}; n.m.r. ($CDCl_3$): ^1H (400 MHz), δ 7.56—6.96 (m, 20 H, Ph), 5.21 [m, 4H, C=CH, *J*(PtH) 19.1], 4.50 [s, 2H, ring CH, ^2J(PtH) 104.0], 4.40 [s, 2H, ring CH, ^2J(PtH) 100.0], 2.44 [m, 4H, $(CH_3CH_2)_2S$], 2.21 (m, 8H, CH_2, cod), 2.11 [m, 4H, $(CH_3CH_2)_2S$], and 1.16 [t, 12H, $(CH_3CH_2)_2S$, ^3J(HH) 7.4]; $^{13}C\{^1H\}$(100 MHz), δ 138.92—125.77 (m, Ph), 103.39 [s, C=C, *J*(PtC) 84.76], 101.38 [s, C=C, *J*(PtC) 70.51], 57.28 [s, ring CH, *J*(PtC) 586.1], 47.81 [s, ring CH, *J*(PtC) 604.3], 30.28 (s, CH_2, cod), 29.57 [s, $(CH_3CH_2)_2S$], 28.12 (s, CH_2, cod), and 13.07 [s, $(CH_3CH_2)_2S$].