

PLATINUM(0) COMPLEXES OF 3-ARYLTHIETE 1,1-DIOXIDES

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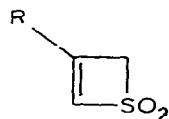
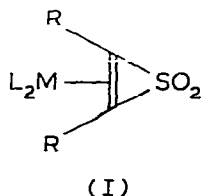
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Summary

3-Phenyl- and 3-*p*-bromophenyl-thiете 1,1-dioxides react with $[\text{Pt}(\textit{trans}\text{-stilbene})(\text{PPh}_3)_2]$ and $[\text{Pt}(\text{AsPh}_3)_4]$ to give the complexes $[\text{Pt}(\text{CH}=\text{CRCH}_2\text{SO}_2)(\text{MPh}_3)_2]$ ($\text{R} = \text{Ph}, p\text{-BrC}_6\text{H}_4$; $\text{M} = \text{P}, \text{As}$).

Introduction

Visser [1] has shown that thieten 1,1-dioxides form the olefin complexes I with palladium(0) and platinum(0), which on thermolysis yield an acetylene and



(IIa, $\text{R} = \text{Ph}$;

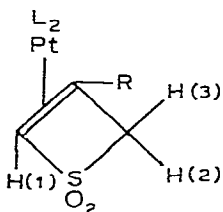
IIb, $\text{R} = p\text{-BrC}_6\text{H}_4$)

sulphur dioxide. In view of our interest [2] in the ability of zerovalent platinum to ring-open certain cyclobutenedione compounds we have investigated the interactions of thiете 1,1-dioxides (II) with palladium(0) and platinum(0) complexes. Dittmer has shown that thiете 1,1-dioxide forms an olefin complex with iron(0) [3] and there is a brief report on a platinum(0) complex of thiете 1,1-dioxide [1].

Results and discussion

3-Phenylthiете 1,1-dioxide (IIa) reacts with *trans*-stilbenebis(triphenylphosphine)platinum(0) in diethyl ether to give a white crystalline product (IIIa).

The ^1H NMR spectrum of IIIa reveals that the olefinic proton H(1) undergoes a large upfield shift (ca. 2.5 ppm), this large shielding being good evidence for



- (IIIa, R = Ph, L = PPh₃ ;
 IIIb, R = Ph, L = AsPh₃ ;
 IIIc, R = *p*-BrC₆H₄, L = PPh₃ ;
 IIId, R = *p*-BrC₆H₄, L = AsPh₃)

formation of a π -complex. Further, the proton H(1) exhibits coupling to both of the non-equivalent phosphorus ligands and to the ^{195}Pt nucleus. The methylene protons H(2) and H(3) exhibit very little shielding (ca. 0.3–0.5 ppm) upon coordination. The methylene protons should be non-equivalent (i.e. *cis* or *trans* with respect to the platinum). However, they appear as equivalent protons in the ^1H NMR spectrum and exhibit coupling to both ^{195}Pt and one of the phosphorus ligands, presumably the *trans*-phosphorus atom.

The IR spectrum of IIIa exhibits strong bands at 1276, 1196, 1130 and 1110 cm^{-1} , which can be assigned to the asymmetrical and symmetrical sulphur–oxygen stretching frequencies. The free ligand exhibits sulphur–oxygen stretching frequencies at 1320 and 1130 cm^{-1} . Much larger shifts in these values would be expected if the platinum was directly bound to sulphur. Further evidence for the formation of IIIa as a π -complex is provided by the reaction of IIIa with tetracyanoethylene which gives a quantitative yield of the thiete sulphone and $[\text{Pt}\{\text{C}_2(\text{CN})_4\}(\text{PPh}_3)_2]$. However, it should be noted that treatment of the thiirene complexes of platinum(0), with tetracyanoethylene does not result in displacement of the thiirene [1]. It would thus appear that the thiirenes coordinate more strongly to platinum(0) than the thiete sulphone IIa.

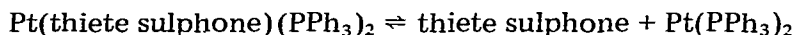
Treatment of IIa with $[\text{Pt}(\text{AsPh}_3)_4]$ in refluxing chloroform gives a cream coloured complex (IIIb) which appears to have a similar structure to IIIa. However, the ^1H NMR spectrum of IIIb reveals that the methylene protons H(2) and H(3) are no longer equivalent and an AB pattern is observed at τ 5.46. In addition the high field arms of the AB pattern show an additional small coupling of about 2 Hz. This small coupling can also be seen in the signal due to H(1) and the coupling can be ascribed to long-range proton coupling between H(1) and one of the methylene protons. A single crystal X-ray structural study has shown that the vinylic groups of the 1-methyl-2-phenylcyclobut-1-ene-3,4-dioneplatinum(0) complex are bent out of the plane away from the platinum [4]. The same situation probably exists in complex IIIb, thereby giving rise to a W-formation between H(1) and H(2) through the sulphone group. Protons which are present in this W-arrangement are known to exhibit this long range H–H coupling [5].

3-*p*-Bromophenylthiete 1,1-dioxide reacts with $[\text{Pt}(\textit{trans}\text{-stilbene})(\text{PPh}_3)_2]$ and $[\text{Pt}(\text{AsPh}_3)_4]$ to give the analogous complexes IIIc and IIId, respectively. As in the complex IIIa methylene protons of IIIc appear to be equivalent, but in contrast to IIIa they exhibit coupling to both of the phosphorus atoms.

The ^1H NMR spectrum of IIId, like that of IIIb, shows that the methylene protons are non-equivalent. The reported ^1H NMR spectrum of the thiete 1,1-dioxide complex of platinum(0) shows that the methylene protons in this complex are also non-equivalent [1].

We have found that the complex $[Pt(\textit{trans}\text{-stilbene})(PPh_3)_2]$ does not react with 3-tertiarybutylthiete 1,1-dioxide, cyclopent-3-ene-1-sulphone and 3-methyl cyclopent-3-ene-1-sulphone. Similarly, no complexes could be isolated from the reaction of IIIa with $[Pd(PPh_3)_4]$.

It was anticipated that on thermolysis the π -complexes III and IV would behave in a similar manner to the uncoordinated ligands [12], and that the initially formed vinyl sulphene might form a stable complex with the platinum. Unfortunately, none of the complexes is sufficiently volatile for flash vacuum thermolysis experiments to be undertaken, and heating them under nitrogen at 300°C for 1–2 h led to an uncharacterised black tar. Irradiation of a solution of IIIb in dichloromethane at 253 nm gave the thiete sulphone I Ib, which crystallised out of solution. Recovery of I Ib is surprising since it is known to rearrange upon photolysis [6]. However, if the photolysis involves the equilibrium



then this equilibrium will be driven to the right by crystallisation of the thiete sulphone from solution. It is probable that the small amount of thiete sulphone that remains in solution is not photolysed because the phenyl groups of the triphenylphosphine ligands effectively absorb all the incident light.

Experimental

¹H NMR spectra were recorded on a JEOL PS100 spectrometer using deuteriochloroform as solvent. Infrared spectra were obtained as Nujol mulls on a Perkin-Elmer 225 spectrophotometer between polythene plates.

The complexes $[Pt(\textit{trans}\text{-stilbene})(PPh_3)_2]$ [7], $[Pt(AsPh_3)_4]$ [8], $[Pd(PPh_3)_4]$ [9] and the compounds 3-phenyl- and 3-*p*-bromophenyl-thiete 1,1-dioxide [10,11] were prepared as described in the literature. The light petroleum used had a boiling range 40–60°C.

Reactions of $[Pt(\textit{trans}\text{-stilbene})(PPh_3)_2]$

(a) *With 3-phenylthiete 1,1-dioxide.* A mixture of *trans*-stilbenebis(triphenylphosphine)platinum(0) (0.45 g, 0.5 mmol) and 3-phenylthiete 1,1-dioxide (0.09 g, 0.5 mmol) was stirred in dry ether (25 ml). The reactants slowly dissolved to give a yellow solution. After 10 min a white solid crystallised and the solution became clear. Filtration gave 3-phenylthiete 1,1-dioxidebis(triphenylphosphine)platinum(0) (0.35 g, 78%), m.p. 172°C (from chloroform light petroleum), IR: $\nu(SO_2)$ 1276vs, 1196vs, 1130vs and 1110vs cm^{-1} . The ¹H NMR spectrum exhibited resonances at τ 3.10 (30 H, m), 4.18 (5 H, m), 5.82 (2 H, doublet with ¹⁹⁵Pt satellites, $J(PH)$ 9.8 Hz, $J(PtH)$ 79.6 Hz), and 5.68 (1 H, two doublets with ¹⁹⁵Pt satellites, $J(P\text{-}trans\text{-}H)$ 9.8 Hz, $J(P\text{ cis}\text{-}H)$ 4 Hz, $J(PtH)$ 58.2 Hz) Found: C, 60.3; H, 4.3. $C_{25}H_{28}O_2PtS$ calcd.: C, 60.1; H, 4.3%. M , found 883, calcd. 899.

(b) *With 3-*p*-bromophenylthiete 1,1-dioxide.* An identical procedure using 3-*p*-bromophenylthiete 1,1-dioxide gave 3-*p*-bromophenylthiete 1,1-dioxidebis(triphenylphosphine)platinum(0) (75%), m.p. 196–197°C (from chloroform-light petroleum), IR: $\nu(SO_2)$ 1286vs, 1196vs, 1130vs and 1110vs cm^{-1} . The ¹H NMR spectrum exhibited resonances at τ 3.16 (32 H, m), 3.93 (2 H, m), 5.69 (1 H, two doublets with ¹⁹⁵Pt satellites $J(PH)$ 8.5 and 4.5 Hz, $J(PtH)$ 58 Hz), and

5.83 (2 H, two doublets with ^{195}Pt satellites, $J(\text{PH})$ 9.5 and 3 Hz, $J(\text{PtH})$ 82 Hz). (Found: C, 55.0; H, 3.8. $\text{C}_{45}\text{H}_{37}\text{BrO}_2\text{P}_2\text{PtS}$ calcd.: C, 55.2; H, 3.8%).

Reactions of $[\text{Pt}(\text{AsPh}_3)_4]$

(a) *With 3-phenylthiote 1,1-dioxide.* A mixture of tetrakis(triphenylarsine)platinum(0) (0.66 g, 0.46 mmol) and 3-phenylthiote 1,1-dioxide (0.087 g, 0.48 mmol) was stirred in refluxing chloroform (30 ml) for 5 h. The solution was cooled, filtered and the solvent was removed under reduced pressure. The residual oil was crystallised from chloroform/light petroleum to give 3-phenylthiote 1,1-dioxidebis(triphenylarsine)platinum(0) (0.185 g, 40%), m.p. 185–186°C (decomp.), IR: $\nu(\text{SO}_2)$ 1281vs, 1197vs, 1126vs and 1109vs cm^{-1} . The ^1H NMR spectrum exhibited resonances at τ 2.22–2.88 (35 H, m), 5.04 (1 H, doublet with ^{195}Pt satellites $J(\text{HH})$ 2 Hz, $J(\text{PtH})$ 71 Hz), 5.36 (1 H, d, $J(\text{HH})$ 11.8 Hz), and 5.56 (1 H, dd, $J(\text{HH})$ 11.8 and 2 Hz). (Found: C, 54.7; H, 4.0. $\text{C}_{45}\text{H}_{38}\text{As}_2\text{O}_2\text{-PtS}$ calcd.: C, 54.7; H, 3.9%. M found 970, calcd. 988).

(b) *With 3-p-bromophenylthiote 1,1-dioxide.* An identical procedure using 3-p-bromophenylthiote 1,1-dioxide gave 3-p-bromophenylthiote 1,1-dioxidebis(triphenylarsine)platinum(0) (55%), m.p. 184–187°C (decomposition) (from chloroform/light petroleum), IR: $\nu(\text{SO}_2)$ 1289vs, 1201vs, 1135vs and 1115vs cm^{-1} . The ^1H NMR spectrum exhibited resonances at τ 2.60–3.20 (32 H, m), 3.62–3.80 (2 H, m), 5.27 (1 H, doublet with ^{195}Pt satellites, $J(\text{HH})$ 2 Hz, $J(\text{PtH})$ 66.5 Hz), 5.56 (1 H, d, $J(\text{HH})$ 11.3 Hz), and 5.79 (1, dd, $J(\text{HH})$ 11.3 and 2 Hz). (Found: C, 51.0, H, 3.6. $\text{C}_{45}\text{H}_{37}\text{As}_2\text{BrO}_2\text{PtS}$ calcd.: C, 50.7; H, 3.5%. M found 1040, calcd. 1067).

Reaction of 3-phenylthiote 1,1-dioxidebis(triphenylphosphine)platinum(0) with tetracyanoethylene

A solution of tetracyanoethylene (0.026 g, 0.20 mmol) in chloroform (10 ml) was slowly added to a solution of the complex IIIa (0.20 g, 0.20 mmol) in chloroform (10 ml). The solution turns dark green. After 20 min the solution was filtered and reduced in volume to 5 ml. Treatment with light petroleum gave 3-phenylthiote 1,1-dioxide (0.029 g, 80%).

Photolysis of 3-p-Bromophenylthiote 1,1-dioxidebis(triphenylphosphine)platinum(0)

A solution of the complex (0.15 g, 0.15 mmol) in dichloromethane (10 ml) was irradiated with light of wavelength 253 nm for 2 h. A white solid crystallised from solution. Filtration gave 3-p-bromophenylthiote 1,1-dioxide (0.036 g, 90%).

The original complex exhibits a very broad band in the ultraviolet, with a maximum at 265 nm.

Acknowledgements

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