Transformation of $O_2S(C\equiv CCMe_3)_2$ to an Exoalkylidene Thiete 1,1-Dioxide Ligand by Pt–H Addition and Rearrangement Reactions

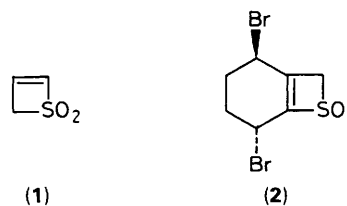**Charles M. Lukehart,*[a] Andrew T. McPhail,*[b] Donald R. McPhail,[b] and Margret D. Owen[a]**
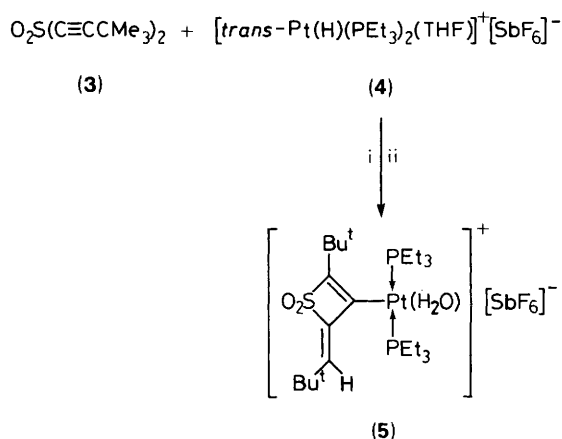[a] *Department of Chemistry, Vanderbilt University, Nashville, TN 37235, U.S.A.*
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Addition of a Pt–H bond to the C≡C bond of an alkynyl substituent of a dialkynylsulphone occurs regioselectively to give an exoalkylidene thiete 1,1-dioxide ligand following a subsequent insertion and rearrangement of the second alkynyl substituent; a proposed mechanism for the unusual formation of the heterocyclic ligand is presented.
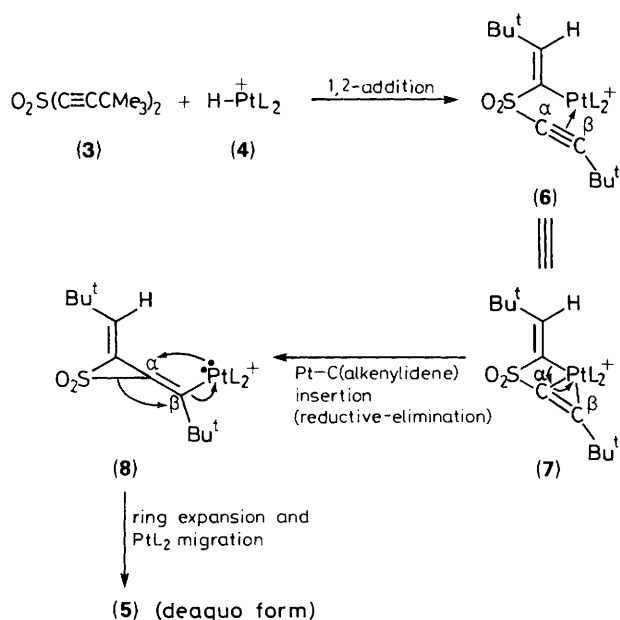
The chemistry of thiete 1,1-dioxides has been of interest because of the high reactivity of the strained, unsaturated four-membered ring in these molecules. For example, thiete 1,1-dioxides usually undergo ring opening reactions upon reduction with hydrides, treatment with hydroxide ion and other selected nucleophiles, or upon thermolysis or photolysis to produce vinyl sulphines which have been trapped chemically by subsequent reaction. Thiete 1,1-dioxides also undergo Michael additions to produce 3-substituted thietane 1,1-dioxides, Diels–Alder cycloadditions, or cycloaddition of 1,3-dipolar reagents. Unstable cycloaddition adducts frequently liberate SO_2 to give cyclic organic molecules.[1] In addition, certain 3-aminothiete 1,1-dioxides reportedly have antihypertensive or anti-inflammatory properties and may be useful in the preparation of cyanine dyes.[1] The structures of thiete 1,1-dioxide (**1**) and the bicyclic thiete sulphone (**2**) have

been determined by X-ray diffraction.[2,3] Thiete 1,1-dioxides have been prepared generally by overall multi-step procedures, such as oxidation of thietes or thiete 1-oxides, elimination reactions of thietane 1,1-dioxides, or by cycloadditions of sulphenes to ynamines.[1] Only two examples of thiete sulphones containing an exoalkylidene functional group

(1)   (2)

$O_2S(C\equiv CCMe_3)_2$ + $[trans\text{-}Pt(H)(PEt_3)_2(THF)]^+[SbF_6]^-$

(3)   **(4)**

(5)

Scheme 1. *Reagents and conditions:* i, THF, 25 °C, 3 h; ii, H_2O (moderate excess).

$O_2S(C\equiv CCMe_3)_2$ + $H\overset{+}{-}PtL_2$ $\xrightarrow{1,2\text{-addition}}$

(3)   **(4)**

(6)

(8)   **(7)**

Pt–C(alkenylidene) insertion (reductive-elimination)

ring expansion and PtL_2 migration

(5) (deaquo form)

Scheme 2. A proposed mechanism for the formation of complex **(5)**.
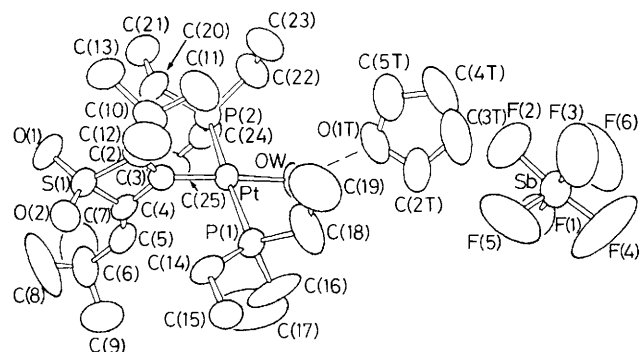

Figure 1. An ORTEP diagram of **(5)** · THF (thermal ellipsoids at the 40% probability level) showing the atomic numbering scheme. Hydrogen atoms have been omitted for clarity. Values of selected interatomic distances (Å) and angles (°) follow: Pt–P(1) 2.333(4), Pt–P(2) 2.332(4), Pt–O(W) 2.14(1), Pt–C(3) 1.99(1), S(1)–C(2) 1.75(1), S(1)–C(4) 1.78(1), S(1)–O(1) 1.44(1), S(1)–O(2) 1.45(1), C(2)–C(3) 1.36(2), C(2)–C(10) 1.52(2), C(3)–C(4) 1.44(2), C(4)–C(5) 1.35(2), C(5)–C(6) 1.47(2), P(1)–Pt–P(2) 175.7(2), C(3)–Pt–O(W) 176.0(5), C(2)–S(1)–C(4) 76.4(6), S(1)–C(2)–C(3) 93(1), S(1)–C(2)–C(10) 128(1), C(3)–C(2)–C(10) 139(1), C(2)–C(3)–C(4) 102(1), S(1)–C(4)–C(3) 89(1), S(1)–C(4)–C(5) 137(1), C(3)–C(4)–C(5) 134(1), C(4)–C(5)–C(6) 132(2).

formation of the aquo complex. The spectroscopic data for **(5)** are consistent with the molecular structure shown above. The S–O stretching bands of the SO_2 group appear in the IR spectrum (solid state) at 1260, 1245 and 1120, 1104 cm^{-1}. The corresponding SO_2 stretching bands reported for 2-methylene-4-phenyl-2*H*-thiete 1,1-dioxide appear at 1305, 1190 and 1153, 1124 cm^{-1}.[6] The ^{1}H and ^{31}P NMR data for **(5)** are also consistent with the molecular symmetry shown above. For example, the proton resonances of the two t-butyl substituents are nonequivalent (where $\Delta\delta$ 0.16 p.p.m.), and the ^{31}P resonances for the two PEt_3 ligands are equivalent (δ 13.5 p.p.m.) and reveal a $^1J_{PtP}$ coupling constant of 2534 Hz. A broad resonance for the proton nuclei of the aquo ligand appears at δ 4.60.

The constitution of **(5)** was confirmed by an *X*-ray diffraction study.§ An ORTEP diagram showing the atomic numbering scheme of the asymmetric crystal unit is presented in Figure 1. The *trans*-$Pt(PEt_3)_2(H_2O)^+$ moiety has the expected structural features and is bonded to the thiete ring through a Pt–C(3) alkenyl single bond of length 1.99(1) Å.¶ The

as a substituent on the four-membered ring have been reported.[1]

We now report a facile, low-temperature synthesis of an exoalkylidene thiete 1,1-dioxide ring system utilizing transition metal, organometallic addition and rearrangement reactions, as shown in Scheme 1. When the dialkynylsulphone **(3)**[4]† is treated with the cationic platinum hydride complex **(4)**,[5] the product **(5)** is isolated in 67% yield as pale yellow needles by crystallization from a tetrahydrofuran (THF)/pentane solution at −15 °C.‡ A drop of water is added to the reaction solution following the reaction to ensure complete

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† The dialkynylsulphone **(3)** is conveniently prepared from thionyl chloride using a procedure similar to that reported by Brandsma and coworkers.[4]

‡ Complex **(5)**: m.p. (decomp.) 200—201 °C.; IR (KBr) $\nu(SO_2)$ 1260, 1245, 1120, 1104 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.13—1.41 (m, 18, PCH$_2$C*H$_3$), 1.25 (s, 9, CMe$_3$), 1.41 (s, 9, CMe$_3$), 1.80—1.95 (m, 12, PC*H$_2$CH$_3$), 4.60 (br. s, 2, H$_2$O), 5.71 (s, 1, CH,$^4J_{PtH}$ < 1.5 Hz); ^{31}P{H} NMR (CDCl$_3$) δ 13.5 (s, PEt$_3$,$^1J_{PtP}$ 2, 534 Hz).

exoalkylidene thiete 1,1-dioxide ring system is characterized by an endocyclic C(2)–C(3) double-bond distance of 1.36(2) Å, an exocyclic C(4)–C(5) double-bond distance of 1.35(2) Å, and a strained, intra-ring angle, C(2)–S(1)–C(4) 76.4(6)°, centred at the sulphur atom. The corresponding endocyclic C=C distances and C–S–C angles of (1) and (2) are respectively, 1.39(3), 80.5, and 1.32(2) Å, 79(1)°.[2,3] The S=O lengths for compounds (1), (2), and (5) all fall within the range of 1.41(1)—1.45(1) Å. A molecule of THF is associated with the cationic portion of complex (5) through O–H · · · O hydrogen bonding to one of the protons of the aquo ligand [O(W) · · · O(1T) 2.59(1) Å]. The second aquo proton is involved in hydrogen bonding to a sulphonyl oxygen atom of another cation related by the crystallographic b-glide plane [O(W) · · · O(2) 2.68(1) Å]. These O · · · O separations fall close to the normal range of 2.72 ± 0.04 Å for O · · · O distances in systems exhibiting O–H · · · O hydrogen bonding.[7] A normal range of O · · · O distances in related systems exhibiting O–H · · · O⁻ hydrogen bonding is 2.75 ± 0.13 Å.[7]

A proposed mechanism for the formation of complex (5) is shown in Scheme 2. Regioselective cis addition of the Pt–H bond of (4) across the C≡C bond of one of the alkynyl substituents of (3) would give a Pt, S μ-alkenylidene intermediate, like (6), in which the second alkynyl substituent of (3) co-ordinates to the cationic Pt^{II} centre. Reaction of (4) with the monoalkynyl phosphine oxide, Ph$_2$(PhC≡C)P=O, gives a complex of similar structure to (6) with the same regioselectivity for the Pt–H addition, [Ph$_2$P(μ-C=CPhH)(μ-O)PtL$_2$]$^+$.[8] Intermediate (6) can be represented formally as the oxidative-addition structure (7). Insertion of the alkynyl substituent into the Pt–C (alkenylidene) bond whereby the Pt atom adds to C(β) of the alkynyl substituent would give a

highly-strained, thiirane intermediate, such as (8). Ring expansion and migration of the PtL$_2$ moiety, as shown, would give (5) prior to co-ordination of the water molecule.

The general scope of this synthetic method and the chemical reactivity of compound (5) are under current investigation.

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