Transition Metal Complexes of Thiiren 1,1-Dioxides

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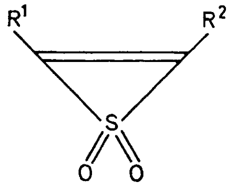
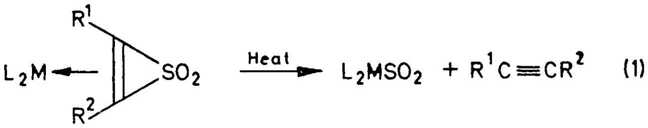
Summary The preparation and properties of platinum, palladium, and iridium complexes of thiiren 1,1-dioxides are described.

In the course of an investigation of the reactivity of thiiren 1,1-dioxides we studied the reaction of the dioxides (I)—(IV)[1] with palladium, platinum, and iridium complexes. These thiiren 1,1-dioxides did not react with *trans*-$(C_2H_4)(C_5H_5N)PtCl_2$, *trans*-$[(C_2H_4)PtCl_2]_2$, K_2PtCl_4, or $(PhCN)_2PdCl_2$. However, complexation occurred readily with L_2PtX ($L = PPh_3$; $X = C_2H_4$, CS_2, or L) and PdL_4. *trans*-$Ir(CO)ClL_2$ co-ordinated only with (I).

Crystalline complexes were obtained with (I) and (II) and with (III) and (IV) spectroscopic examination revealed co-ordination. The thiiren 1,1-dioxide complexes have very similar i.r. and n.m.r. spectra which are independent of the metal, indicating structures of the same type. The n.m.r. spectra are indicative of complexation at the C=C bond. The chemical shifts[†] and heteroatom–hydrogen spin–spin couplings[‡] were similar to those of the cyclopropene–platinum(0) complexes, the structure of which has been determined[2] unambiguously. Additional structural evidence is the absence of an allylic H–Me coupling in the complexes of (I), and the absence of an absorption in the C=C stretching frequency region of complexes of (I) [this absorption is present at 1614 cm^{-1} in unco-ordinated (I)]. Also, complexation affects the SO_2 absorption frequencies in the i.r. spectra,[1] several characteristic bands being present: 1225—1230, 1118—1130 and 1040—1050 cm^{-1} for palladium and platinum complexes. The iridium complex of (I) has similar absorptions (1250, 1140, and 1048 cm^{-1}).



(I) R^1=H R^2=Me
(II) R^1=R^2= Me
(III) R^1=Ph R^2=Me
(IV) R^1=R^2= Ph



Not all the complexes were sufficiently stable to be isolated. The thermal decomposition proceeds according to equation (1).[§] This reaction might also form part of a catalytic reaction sequence, by which thiiren 1,1-dioxides decompose into SO_2 and the corresponding acetylenes in the presence of the complexes.[3]

Thiiren 1,1-dioxides are very strong bonding ligands to zero-valent metals. The co-ordinating ability of 3-methylthiiren 1,1-dioxide is much larger than that of carbon disulphide owing to the partial release of ring strain upon complexation, as well as by the electron deficiency of the double bond.

(*Received, November 15th,* 1971; *Com.* 1968.)

[†] In the complexes the absorptions of the vinyl protons (δ_H 3·3 — 4·2 p.p.m.) and of the methyl protons (δ_{Me} 1·1 — 1·7 p.p.m.) are shifted upfield compared with compounds (I)—(III) by approximately 5 and 1 p.p.m., respectively.

[‡] Heteroatom-hydrogen coupling constants are: J_{P-H} 5—10, $J_{P'-H}$ 1, $|J_{P-Me}| + |J_{P'-Me}|$ 7, J_{Pt-H} 25, and J_{Pt-Me} 27—31 Hz.

[§] Attempted isolation of L_2MSO_2 always yielded L_2MSO_4.

[1] L. A. Carpino, L. V. McAdam iii, R. H. Rynbrandt, and J. W. Sprewak, *J. Amer. Chem. Soc.*, 1971, 93, 476.
[2] J. P. Visser, A. J. Schipperijn, J. H. Lukas, D. Bright, and J. J. de Boer, *Chem. Comm.*, 1971, 1266.
[3] D. N. Reinhoudt, C. G. Leliveld, and J. P. Visser, to be published.