Tetrakis(methylthio)ethene as a Bidentate Chelating and Quadridentate Bridging Thioether

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In the complex $[PtClMe\{(MeS)_2C{=}C(SMe)_2\}]$ the thioether functions as a bidentate chelate, and in $[(PtBrMe_3)_2(MeS)_2C{=}C(SMe)_2]$ as a bridging quadridentate ligand. In both compounds sulphur inversion is fast at room temperature.

Our recent studies on complexes of bis(methylthio)ethers $R(SMe)_2$ with transition metals have shown [1] that the ligand functions either as a bidentate chelate or as a bridging ligand depending on the organic backbone R, and in no case were we able to isolate complexes in which the ligand showed both types of behaviour. In particular the ligand MeSCH=CHSMe always prefers a chelating role.[2] We now report that the fully substituted ethene $(MeS)_2C{=}C(SMe)_2$ acts as a bridging ligand to trimethylplatinum(IV) and as a bidentate chelate to platinum(II), in contrast to the results of Lappert and co-workers who found a bidentate S,S″ chelate thioether in $[Cr(CO)_4\{C_2(SMe)_4\}]$,[3] and a product resulting from cleavage of two of the S–Me bonds in the reaction of $C_2(SMe)_4$ with $[\{PtCl_2(PEt_3)\}_2]$.[4]

Experimental

The compounds [PtClMe(cod)] (cod = cyclo-octa-1,5-diene),[5] $[(PtBrMe_3)_4]$,[6] and $C_2(SMe)_4$ [7] were prepared by literature methods.

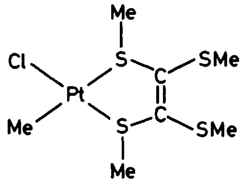
$[PtClMe\{C_2(SMe)_4\}]$.—A solution of [PtClMe(cod)] (483 mg, 1.37 mmol) and excess of $C_2(SMe)_4$ (310 mg, 1.46 mmol) in chloroform (10 cm^3) was refluxed for 3 h. Removal of solvent and crystallisation from chloroform–light petroleum (b.p. 60—80 °C) gave pale yellow needles of *product* (520 mg, 83%). M.p. 158—159 °C (Found: C, 18.25; H, 3.15. Calc. for $C_7H_{15}ClPtS_4$: C, 18.35; H, 3.30%).

$[(PtBrMe_3)_2C_2(SMe)_4]$.—This white compound was prepared in an analogous manner from $[(PtBrMe_3)_4]$ (222 mg, 0.695 mmol) and $C_2(SMe)_4$ (84.4 mg, 0.398 mmol). Yield 206 mg, 70%. M.p. 194 °C (decomp.) (Found: C, 17.1; H, 3.60. Calc. for $C_{12}H_{30}Br_2Pt_2S_4$: C, 16.9; H, 3.50%).

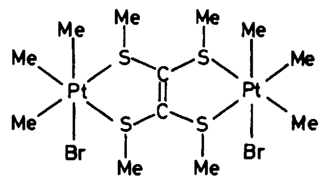
100-MHz ^1H n.m.r. spectra were obtained using either a JEOL MH-100 spectrometer operating in the continuous-wave mode under internal field-frequency lock conditions, or a JEOL PS/PFT-100 spectrometer operating in the Fourier-transform mode. A JES-VT-3 variable-temperature unit was used to control the probe temperature.

Results and Discussion

Microanalytical data and n.m.r. spectra for the two complexes are consistent with the structures shown. Attempts to make a binuclear platinum(II) species analogous to (2) using a 2 : 1 molar ratio of [PtClMe(cod)] to ligand gave only the mononuclear species (1) and unreacted platinum precursor. There was no evidence for S–Me bond cleavage in either reaction.



(1)



(2)

At temperatures down to −100 °C the simplicity of the ^1H n.m.r. spectrum of complex (1) in CS_2–CD_2Cl_2 (1 : 1 v/v) shows that sulphur inversion is fast on the n.m.r. time-scale. All four ligand methyl groups give distinct signals. Those from the two sulphur methyl groups bound to platinum are at lowest frequency (δ 2.77 and 2.85 at −66.9 °C) and show coupling to ^{195}Pt. The ^3J coupling constants, 70.3 Hz for SMe *trans* to chloride and 16.8 Hz for SMe *trans* to methyl, are as expected from the values for corresponding platinum(II) complexes with bidentate thioethers,[2] and clearly reflect the striking difference in *trans* influence between the methyl and chloride ligands. Confirmatory support for this assignment was derived from the n.m.r. spectrum of the very unstable complex $[PtMe_2\{C_2(SMe)_4\}]$, for which a ^3J value for the SMe protons of *ca.* 17 Hz was found. The two non-co-ordinated SMe groups in complex (1) give singlets at δ 2.52 and 2.47, with no $^5J(Pt–H)$ coupling observable. At lower frequency a single Pt–Me signal (δ 0.69) with ^{195}Pt satellites ($^2J = 71.8$ Hz) is present. If sulphur inversion were slow in this temperature range two isomers with *syn* and *anti* co-ordinated sulphur methyls would have been expected, and a correspondingly more complex spectrum, except in the unlikely event of one isomer being very much more stable. It is not possible on the basis of spectroscopic data alone to discriminate between the S,S′ and S,S″ bonding alternatives.

On cooling a solution of complex (1) to −114 °C some broadening of the spectral lines was seen. This is without doubt due to a slowing of the rate of pyramidal inversion at the sulphur atom *trans* to methyl, the spectra being sensitive to only the lower of the two sulphur inversion barriers. This extremely low barrier to sulphur inversion in a platinum(II) complex may be attributed to the high *trans* influence of the platinum methyl group and the presence of the olefinic backbone which stabilises the transition state by $(3p–2p)\pi$ conjugation.[2] While it was impossible to slow down the inversion process sufficiently to enable an accurate calculation of inversion barrier energies to be made, it is possible to estimate the barrier height. Comparing the values [2] of ΔG/kJ mol^{-1} for the related complexes $[PtCl_2(MeSCH{=}CHSMe)]$ (68.6), $[PtClMe\{MeS(CH_2)_2SMe\}]$ (59.8), and $[PtCl_2\{MeS(CH_2)_2$-

SMe}] (80.0) shows that replacing Cl by Me lowers the barrier by about 20 kJ mol^{-1}, and replacing the aliphatic backbone by the olefin lowers it by about 11 kJ mol^{-1}. The incorporation of both in compound (1) should result in an inversion energy barrier of *ca.* 50 kJ mol^{-1}.

The binuclear trimethylplatinum(IV) compound (2) is the first such halide complex in which the halides are not the bridge atoms. Inversion at all four sulphur atoms is fast in CD_2Cl_2 at room temperature, and a single SMe proton signal (intensity 12 H) is seen at δ 2.82 with clear $^3J(^{195}Pt-^1H)$ coupling (12.1 Hz). Two platinum methyl signals (intensity 18 H) at high field in the ratio 2 : 1 correspond to methyls *trans* to bridging sulphur (δ 1.52, ^2J 71.6 Hz) and terminal halide (δ 1.04, ^2J 71.0 Hz) respectively. The simplicity of the spectrum indicates that only one geometric isomer is present, with the terminal halides either *cis* or *trans*. The presence of two such isomers would be readily detected.[8]

On cooling the sample to −70 °C a much more complicated spectrum results due to the slowing of the rate of inversion at sulphur. Since in structure (2) each sulphur methyl can take up two conformations with respect to the bridging plane, a total of 16 isomers are possible. A 400-MHz spectrum in CD_2Cl_2 at −70 °C shows two groups of well separated lines centred at δ 3.0 and 2.6 corresponding to these two conformations. In the complicated platinum methyl region it is possible to pick out four main signals assignable to methyl *trans* to sulphur (δ 1.34, 1.33, 1.30, and 1.26 with ^2J 71.0, 72.0, 71.3, and 70.3 Hz respectively) and two for methyls *trans* to halide (δ 1.05 and 1.02, both with ^2J 71.7 Hz) among several less intense signals. This would suggest that only two or three isomers are present in any abundance.

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