Reactions of Sulphoxide–Thioether Bidentate Ligands with Platinum(II). Determination of the Mode of Binding by Cyclic Voltammetry

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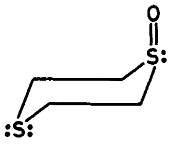
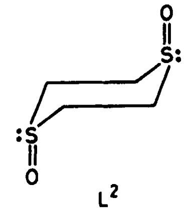
Cyclic voltammetry has been employed to study the mode of binding of 1,4-dithiacyclohexane 1-oxide (L^1) to platinum(II). Use of model compounds of the type $[PtCl_2(PPh_3)L]$ (L = unidentate thioether or sulphoxide) shows that thioether complexes require more negative potentials for reduction than analogous sulphoxide complexes. Preferential binding of L^1 to platinum(II) *via* the thioether functionality was established in the reaction with $[Pt_2(\mu\text{-}Cl)_2Cl_2(PPh_3)_2]$ using the magnitude of the peak potential for the platinum(II)→platinum(0) reduction as a structural diagnostic.

The reaction of halide-bridged dimeric complexes of platinum(II) of the type $[Pt_2(\mu\text{-}Cl)_2Cl_2(PR_3)_2]$ (R = aryl or alkyl) with nucleophiles allows easy access to the mixed-ligand complexes *cis*- or *trans*-$[PtCl_2(PR_3)L]$ (L = CO, amine, thioether, *etc.*).[1–3] Such complexes have been widely utilized to study steric and electronic ligand effects on homogeneous catalytic processes, since both PR_3 and L may be varied independently.[4–6]

During a recent study[7,8] of the reactivity of $[Pt_2(\mu\text{-}Cl)_2Cl_2(PR_3)_2]$ complexes with potentially bidentate *S*-functional ligands, such as L^1 and L^2, we encountered problems in characterization because of the extremely limited solubility of the resulting complexes in a wide variety of organic solvents. In particular, since a mixed sulphoxide–thioether ligand, such as L^1, has the potential to bind preferentially to platinum(II) *via* either one of the two functionalities it was of interest to find a suitable analytical technique to probe the mode of co-ordination. Previously we have successfully employed[9,10] cyclic voltammetry to monitor the chemistry of low-concentration electroactive platinum(II) complexes, and so it seemed possible that the extreme sensitivity of this technique would allow very dilute solutions of the complexes to be examined electrochemically. Since the peak potentials for platinum(II)→platinum(0) reductions are extremely sensitive to variations in the ligand set,[9,10] the question of preferential binding of thioethers and sulphoxides was examined.



L^1



L^2

Experimental

$[Pt_2(\mu\text{-}Cl)_2Cl_2(PPh_3)_2]$,[11] L^1 (ref.7), and L^2 (ref. 12) were prepared and characterized as previously described. Acetonitrile (Fischer, high-performance liquid chromatography grade) was purified and dried by the literature method[13] and stored over activated 4A molecular sieve. Tetra-n-butylammonium perchlorate (Aldrich, 98%) was recrystallized twice from ethanol and dried *in vacuo* at 50 °C prior to use as a background electrolyte (concentration 0.1 mol dm^{-3}). Cyclic voltammograms were obtained by use of a model CV-1A Bioanalytical Systems control unit equipped with a Houston 100 XY recorder. A single-compartment cell, thermostatted to 25.0 ± 0.1 °C was employed with an Ag–AgCl reference electrode [−35 mV *vs.* saturated calomel electrode (s.c.e.)], a platinum wire counter electrode, and a gold amalgam working electrode of 1.77 mm^2 surface area. Voltammograms were typically obtained for 10^{-3} mol dm^{-3} solutions of the complexes in a benzene–acetonitrile solvent system (3:7).

$^{31}P\text{-}\{^1H\}$ N.m.r. spectra of model compounds were obtained for $CDCl_3$ solutions at 36.2 MHz on a JEOL FX 90Q n.m.r. spectrometer operating in the Fourier-transform mode. Chemical shifts are relative to 85% H_3PO_4 with more positive values of the chemical shift representing deshielding. I.r. spectra were obtained as solid solutions in KBr over the range 4 600—400 cm^{-1} using a Nicolet 5DX Fourier-transform i.r. spectrometer. Elemental analyses were performed by Micanal, Arizona.

All reactions of $[Pt_2(\mu\text{-}Cl)_2Cl_2(PPh_3)_2]$ were performed similarly, using the following general method. The complex $[Pt_2(\mu\text{-}Cl)_2Cl_2(PPh_3)_2]$ (0.19 mmol) and the ligand L (0.38 mmol) in dichloromethane solution (4 cm^3) were refluxed with stirring for 1 h. The product was precipitated with hexane, filtered off, washed with hexane, and air dried. Spectroscopic, voltammetric, and analytical data are presented in the Table.

Results and Discussion

In order to provide suitable comparative electrochemical data, a series of model compounds, *cis*-$[PtCl_2(PPh_3)L]$, was prepared employing simple monodentate sulphoxide and thioether ligands (L). The complexes were characterized by standard methods, including $^{31}P\text{-}\{^1H\}$ n.m.r. spectroscopy to determine geometry and Fourier-transform i.r. spectroscopy to determine the mode of co-ordination (*i.e.*, *S*- or *O*-bonded) for the sulphoxide complexes. In the case of dibenzyl sulphide, both *cis* and *trans* isomers could be separately isolated and characterized. Spectroscopic and analytical data are presented in the Table.

Single-sweep cyclic voltammograms were obtained for each complex as a deoxygenated 10^{-3} mol dm^{-3} solution in benzene–acetonitrile (3:7) containing 0.1 mol dm^{-3} tetra-n-butylammonium perchlorate as the background electrolyte. Voltammograms were measured at a sweep rate of 200 mV s^{-1} at a gold amalgam electrode over the potential range +0.50 to −2.00 V *vs.* Ag–AgCl and each complex exhibited a single reductive peak corresponding to the diffusive, irreversible

Table. Spectroscopic, cyclic voltammetric, and analytical data of *cis*-[$PtCl_2(PPh_3)L$] complexes

L	$^1J(^{195}Pt^{31}P)$/ Hz	δ(P)/p.p.m.	ν(S=O)/cm^{-1}	E_p/V *vs.* Ag–AgCl	Analysis[a] (%)		
					C	H	Cl
$C_6H_5CH_2SCH_3$	3 671	11.7		−1.625	46.70 (46.85)	3.60 (3.80)	
$C_6H_5CH_2SC_2H_5$	3 684	11.9		−1.675	45.35 (47.65)	3.90 (4.00)	
$(C_6H_5CH_2)_2S$[b]	3 678	11.7		−1.650	51.75 (51.75)	3.90 (3.95)	
$\overline{SCH_2CH_2S(O)CH_2CH_2}$ (L^1)	*c*	*c*	1 053	−1.550	39.30 (39.75)	3.45 (3.50)	11.05 (10.65)
$C_6H_5CH_2S(O)CH_3$[d]	3 732	16.4	1 130, 1 165	−1.425	45.30 (45.75)	3.50 (3.80)	
$C_6H_5CH_2S(O)C_2H_5$[d]	3 740	15.9	1 125, 1 162, 1 175w	−1.425	46.30 (46.55)	3.90 (3.90)	
$(C_6H_5CH_2)_2SO$[d]	3 742	15.8	1 121, 1 171	−1.425	50.45 (50.65)	3.75 (3.85)	
$\overline{S(O)CH_2CH_2S(O)CH_2CH_2}$ (L^2)[d]	*c*	*c*	1 016, 1 045, 1 136, 1 153[e]	−1.375	37.85 (38.85)	3.30 (3.40)	9.90 (10.40)
$(CH_3)_2SO$[d]	3 719	16.8	1 150	−1.450	39.80 (39.60)	3.50 (3.50)	
$(C_6H_5)_2SO$[d]	3 661	16.1	1 075, 1 135	−1.300	49.60 (49.30)	3.50 (3.45)	

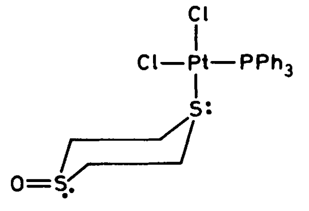
[a] Calculated values in parentheses. [b] Structure confirmed by *X*-ray cystallography, R. A. Jones and T. C. Wright, personal communication, 1984. [c] Too insoluble for routine measurement. [d] *S*-bonded. [e] See text for assignments.

platinum(II)→platinum(0) reduction. Peak potentials were measured *versus* an Ag–AgCl reference electrode (−35 mV *vs.* s.c.e.) and are reported in the Table.

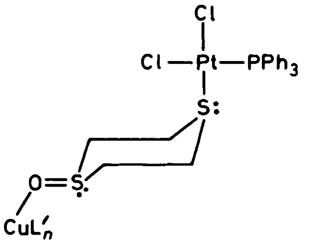
The peak potentials for the three pairs of *cis* sulphoxide and thioether complexes, [$PtCl_2(PPh_3)L$] [L = $C_6H_5CH_2SR$ or $C_6H_5CH_2S(O)R$; R = CH_3, C_2H_5, or $C_6H_5CH_2$], clearly indicate that more negative potentials are required for the platinum(II)→platinum(0) reduction of the thioether complexes than for the sulphoxide complexes (*i.e.*, *ca.* −1.650 *vs.* −1.425 V). The peak potentials measured by cyclic voltammetry depend on both the kinetics and thermodynamics of the electron-transfer process[14] and this limits rationalization of such trends to qualitative observations only. Detailed comparisons of structural and spectroscopic data of transition-metal thioether[15] and sulphoxide[16] complexes indicate that thioethers are poorer σ-donors and poorer π-acceptors than sulphoxides. Since the sulphoxide complexes are reduced at less negative potentials, the enhanced π-acceptor ability of sulphoxides would appear to be dominant in reducing the electron density at the metal centre. This argument gains support from the observation that the *trans* isomer of [$PtCl_2(PPh_3)$-{$(C_6H_5CH_2)_2S$}] is reduced at a more negative potential (−1.750 V) than the *cis* isomer since in the *trans* isomer the poor π-acceptor $(C_6H_5CH_2)_2S$ is in competition with the *trans* PPh_3 group for electron density. Clearly this will result in a higher electron density at the metal centre than in the *cis* isomer where competition between the $(C_6H_5CH_2)_2S$ and PPh_3 groups for metal π-electron density is much reduced. No complexes with *trans* PR_3 and R_2SO groups have yet been isolated and examined to compare this situation for sulphoxides.

The reaction of [$Pt_2(\mu-Cl)_2Cl_2(PPh_3)_2$] with two equivalents of the ligand 1,4-dithiacyclohexane 1,4-dioxide (L^2) (*i.e.* Pt:L^2 = 1:1) leads to the isolation of a product with the stoicheiometry [$PtCl_2(PPh_3)L^2$]. The i.r. spectrum is complex in the ν(S=O) region, but suggests that both *S*-bonded [ν(S=O) = 1 153 and 1 136 cm^{-1}] and uncomplexed [ν(S=O) = 1 045 and 1 016 cm^{-1}] sulphoxide moieties are present, indicating that a mononuclear complex is formed where L^2 acts as a unidentate ligand. The cyclic voltammogram of this complex, obtained under identical conditions to those described above, exhibits a single peak at −1.375 V, as expected from the Table for a *cis-S*-bonded sulphoxide complex. The reaction of [$Pt_2(\mu-Cl)_2Cl_2(PPh_3)_2$] with two equivalents of 1,4-dithiacyclohexane 1-oxide (L^1) similarly leads to the isolation of a complex of stoicheiometry [$PtCl_2(PPh_3)L^1$]. The i.r. spectrum is not definitive in determining whether L^1 co-ordinates *via* the thioether or the sulphoxide functional groups, since the ν(S=O) mode in the free ligand at 1 018 cm^{-1} shifts to 1 053 cm^{-1} in the complex. A value of Δν(S=O) of only +35 cm^{-1} could be attributable to complexation *via* the sulphur of the sulphoxide group,[16] or to conformational perturbations caused by complexation of the distant thioether group. For example, ν(S=O) of an equatorial S=O group is commonly *ca.* 20 cm^{-1} higher than that of an axial S=O group.[17,18] The cyclic voltammogram of this complex exhibited a single, irreversible reductive peak at −1.550 V. Examination of the data in the Table allows the mode of co-ordination of L^1 to be determined. Thus, the differences in peak potentials for the Pt^{II}→Pt^0 reduction of the complexes of $C_6H_5CH_2SR$ and $C_6H_5CH_2S(O)R$ are 0.200, 0.250, and 0.225 V (R = CH_3, C_2H_5, or $C_6H_5CH_2$) respectively. The difference in peak potentials for the complexes of L^1 and L^2 is 0.175 V, with the value for the complex of L^1 being the more negative. The ligand L^1 thus exhibits a preference for co-ordination *via* the thioether functionality in cleavage reactions of [$Pt_2(\mu-Cl)_2Cl_2(PPh_3)_2$], yielding the *cis* complex (**1**). Further evidence that the S=O group of (**1**) remains uncomplexed is obtained by the solid-state reaction of (**1**) with copper(II) chloride. The i.r. spectrum after reaction shows a decrease in intensity of the band at 1 053 cm^{-1} and a new band at 966 cm^{-1} due to complexation of the S=O group *via* oxygen to copper(II), yielding (**2**) (L′ = neutral ligand, *e.g.* H_2O).

In conclusion, the sensitivity of the peak potentials for the platinum(II)→platinum(0) reduction of simple platinum(II) complexes to structural variations in the ligand set and the ability of cyclic voltammetry to examine low-concentration samples of electroactive species in a routine manner allows



(1)



(2)

structural problems, such as the preferential mode of binding of L^1 *via* the thioether functionality, to be probed. Choice of the model systems for comparative data is critical since irreversible peaks are subject to kinetic shifts and the validity of the comparison requires that the kinetics be directly comparable. For example, the *cis*-$[PtCl_2(PPh_3)L]$ complexes of $C_6H_5CH_2S(O)R$ ($R = CH_3, C_2H_5$, or $C_6H_5CH_2$) all give peaks at −1.425 V and the analogous complex of $(CH_3)_2SO$ exhibits only a slightly shifted peak (−1.450 V). However, the shift becomes very pronounced with the diaryl sulphoxide $(C_6H_5)_2SO$ (−1.300 V). Comparisons can only be valid with directly comparable model systems. Related applications, such as the study of the binding of platinum(II) to biologically significant macromolecules, may be anticipated.

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