Hard Ligands as Donors to Soft Metals. Part 1. Formation of Oxygen-bonded Dimethyl Sulphoxide Complexes of Palladium(II) and Platinum(II) promoted by Steric Crowding

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Cationic oxygen-bonded dimethyl sulphoxide (dmso) complexes of the types $[M(Ph_2PCH_2CH_2PPh_2)(dmso)_2][X]_2$ and $[M(Ph_2PCH_2CH_2PPh_2)(dmso)Cl][X]$, where X is a non-co-ordinating anion, have been prepared with palladium(II) and platinum(II). The bis(sulphoxide) complexes are stable in solution and in the solid state, however the sulphoxide ligand in the mono(sulphoxide) complexes is very labile. In solution $[Pd(Ph_2PCH_2CH_2PPh_2)(dmso)Cl][X]$ readily forms the corresponding thioether (SMe_2) complex by loss of oxygen from the dimethyl sulphoxide.

PREVIOUSLY there has been little work done on mixed neutral-ligand complexes of soft metals including co-ordinated dimethyl sulphoxide (dmso).[1,2] As part of our study [3] on the role of solvento-complexes as active catalytic species involving hard ligands bound to soft metal ions we have included the ambidentate ligand dmso, which normally bonds through sulphur to soft metals and through oxygen to hard metals or when forced into a sterically crowded environment.[4-7] This latter point, brought to our attention by the work of Wayland and co-workers [6,7] who prepared the complexes $[M(dmso)_4]^{2+}$ [M = Pd(II) or Pt(II)], which contain two sulphur-bonded and two oxygen-bonded dmso ligands, suggested that other neutral ligands might stabilise the complex and at the same time cause steric hindrance at the other donor sites on the metal ion. Dimethyl sulphoxide complexes have also recently been shown to act as hydrogenation catalysts.[8] We have, therefore, studied the co-ordination chemistry of palladium(II) and platinum(II) complexes containing 1,2-bis(diphenylphosphino)ethane (dppe) and dimethyl sulphoxide (dmso).

RESULTS

In an effort to prepare complexes which have an active site we first attempted the preparation of species of the type $[M(dppe)(dmso)Cl]^+$. The complex $[Pd(dppe)Cl_2]$ (1) in dichloromethane–dmso (2 : 1 v/v) solution was treated with silver perchlorate or hexafluorophosphate in a 1 : 1 mol ratio. Silver chloride precipitated immediately and after 15 min the filtered solution was worked up to give complex (2) contaminated by a small amount of complex (3), a halide-bridged dimer {equation (1), a : X = $[ClO_4]^-$, b : X = $[PF_6]^-$}. The presence of a bridged dimer was not unexpected since attempts to prepare other complexes [M(dppe)(S)Cl][X] (S = hard ligand) gave the bridged dimer

$$\underset{(1)}{[Pd(dppe)Cl_2]} + AgX \xrightarrow[15\ min]{CH_2Cl_2-dmso} \underset{(2a),\ (2b)}{[Pd(dppe)(dmso)Cl][X]} + \underset{(3a),\ (3b)}{[\{Pd(dppe)Cl\}_2][X]_2} + AgCl \quad (1)$$

as the sole product.[9] The small amount of complex (3) could not be removed by recrystallisation suggesting the equilibrium shown in equation (2). The presence of the

$$2[Pd(dppe)(dmso)Cl][X] \rightleftharpoons [\{Pd(dppe)Cl\}_2][X]_2 + 2\ dmso \quad (2)$$

dimer was indicated by a band in the i.r. spectra (Table 1) at 273 cm^{-1} associated with the halide bridge. The terminal M–Cl vibration in complex (2) was also clearly seen at 310 cm^{-1}. If the isolated solids (2a) + (3a) and (2b) + (3b) were dissolved in dmso and then reprecipitated with diethyl ether, the absorption at 273 cm^{-1} virtually disappeared, again supporting the above equilibrium. The complexes (2a) and (2b) could not be isolated in a pure state, however the mode of co-ordination of the dmso ligand was studied.

The i.r. spectra of sulphoxide complexes can in most cases differentiate between oxygen- and sulphur-bonding.[5,6] The S=O stretching mode in free dmso is observed at 1 055 cm^{-1}; co-ordination *via* the sulphur atom is indicated by an increase in the value of ν(S=O), co-ordination *via* the oxygen atom by a decrease. The choice of non-co-ordinating counter ion X^- was thus important since it may obscure the ν(S=O) region; the perchlorate ion $[ClO_4]^-$ absorbs at *ca.* 1 080 cm^{-1}, the tetrafluoroborate ion $[BF_4]^-$

TABLE 1

Infrared data (cm^{-1})

Complex	ν(S=O)	Δ(S=O) [a]	δ(C–S–C)	ν(M–Cl)	δ[M(μ–Cl)$_2$M]	ν(X) [b]
(2a) $[Pd(dppe)(dmso)Cl][ClO_4]$	950s	105	985s	310m		1 100s, 620s
(2b) $[Pd(dppe)(dmso)Cl][PF_6]$	955s	100	985s	310m		830s, 560s
(4) $[Pt(dppe)(dmso)Cl][PF_6]$	920s	135	985m	315m		830s, 560s
(4′)	920s	135	985m	315m		830s, 560s
(3a) $[\{Pd(dppe)Cl\}_2][ClO_4]_2$					273m	1 100s, 620s
(5) $[Pd(dppe)(SMe_2)Cl][ClO_4]$			*c*	310m		1 100s, 620s
(6a) $[Pd(dppe)(dmso)_2][ClO_4]_2$	948s [d]	107	985s [d]			1 080s, 620s
(6b) $[Pd(dppe)(dmso)_2][PF_6]_2$	942s [d]	113	988s [d]			830s, 560s

[a] Δ(S=O) = [ν(S=O) (unco-ordinated) − ν(S=O) (co-ordinated)]. [b] X = $[ClO_4]^-$ or $[PF_6]^-$. [c] Cannot be unambiguously assigned. [d] Average position of slightly split absorptions, splitting due to *cis* configuration of the complexes.

TABLE 2

N.m.r. data

	Compound	δ(phenyl)/ p.p.m.[a]	δ(–CH$_2$–CH$_2$–)/ p.p.m.[a]	^2J(P–H)/ Hz	δ(CH$_3$)/ p.p.m.[a]	Ref.
	dmso				2.53	
	SMe$_2$				2.11	
(2a)	[Pd(dppe)(dmso)Cl][ClO$_4$] [b]	7.68(m)	2.92(d)	25	2.59(s)	
(2b)	[Pd(dppe)(dmso)Cl][PF$_6$] [b]	7.67(m)	2.94(d)	25	2.56(s)	
(4)	[Pt(dppe)(dmso)Cl][PF$_6$]	7.62(m) (10.0)	2.93(d) (2.0)	31	2.61(s) (3.0)	
(4′)		7.64(m) (10.0)	2.94(d) (2.0)	29	2.65(s) (3.0)	
	[Pt(dppe)(SMe$_2$)Cl][PF$_6$]	7.64(m) (5.0)	2.86(d) (1.0)	25	2.24(s) (0.9)	
(6a)	[Pd(dppe)(dmso)$_2$][ClO$_4$]$_2$	7.78(m) (5.1)	2.96(d) (1.0)	25	2.61(s) (2.9)	
(6b)	[Pd(dppe)(dmso)$_2$][PF$_6$]$_2$	7.76(m) (5.2)	2.94(d) (1.0)	25	2.54(s) (3.6)	
	[Pd(dmso)$_4$][ClO$_4$]$_2$				3.67, 3.06	7
	[Pt(dmso)$_2$Cl$_2$] [c]				3.55	5
	[Pd(dien)(dmso)Cl][ClO$_4$] [d]				3.3	2
	[Pd$_2$Cl$_2$(SMe$_2$)$_2$] [e]				2.28	15
	trans-[PdCl$_2$(SMe$_2$)$_2$] [e]				2.38	15

[a] Relative intensities are given in parentheses, s = singlet, d = doublet, m = multiplet. [b] Intensities not given due to small impurities of dimers (3a) [with (2a)] and (3b) [with (2b)]. [c] In CDCl$_3$. [d] In D$_2$O. [e] In CD$_2$Cl$_2$.

TABLE 3

Analytical, spectroscopic, and conductivity data

	Complex	Analysis (%) [a] C	Analysis (%) [a] H	B [b]	$\lambda_{max.}$/nm	ε/dm^3 mol^{-1} cm^{-1}
(3a)	[{Pd(dppe)Cl}$_2$][ClO$_4$]$_2$	48.3 (48.8)	3.7 (3.8)	386	350	2 100
(4)	[Pt(dppe)(dmso)Cl][PF$_6$]	38.6 (39.5)	3.4 (3.5)	243	315	1 000
(4′)		39.2 (39.5)	3.5 (3.5)	239	316	1 100
(5)	[Pd(dppe)(SMe$_2$)Cl][ClO$_4$]	47.7 (46.9)	4.0 (4.2)	*c*	*c*	*c*
(6a)	[Pd(dppe)(dmso)$_2$][ClO$_4$]$_2$	41.7 (41.9)	4.3 (4.2)	351	334	2 000
(6b)	[Pd(dppe)(dmso)$_2$][PF$_6$]$_2$	38.8 (37.9)	3.8 (3.8)	331	333	2 700

[a] Calculated values are given in parentheses [b] From $\Lambda_e = \Lambda_0 - Bc^{\frac{1}{2}}$ with linear regression >0.99, B Ω^{-1} l$^{\frac{1}{2}}$ equiv.$^{-\frac{1}{2}}$, determined in nitromethane solution(10^{-2}—10^{-5} equiv. l^{-1}) (ref. 24). [c] A 10^{-3} mol dm^{-3} solution in acetone had $\Lambda = 97$ Ω^{-1} cm^2 mol^{-1}, too unstable for dilution study or spectroscopic study.

at *ca.* 1 060 cm^{-1}, and the hexafluorophosphate ion [PF$_6$]$^-$ at *ca.* 830 cm^{-1}. After studying the initial 1 : 1 dmso complexes it was found that the [PF$_6$]$^-$ ion was transparent across the whole ν(S=O) region and was, thus, the preferred choice, although the [ClO$_4$]$^-$ ion was equally as good to study oxygen-bonded dmso complexes. Two strong absorptions were seen in the region 900—1 100 cm^{-1} due to the dmso (Table 1), one at 950 cm^{-1} (2a) [955 cm^{-1} (2b)] and one at 985 cm^{-1} (both complexes). By comparison with other studies [10] we assigned the lower of the bands to ν(S=O) and the higher to the deformation (C–S–C). This indicated that the dmso was oxygen-bonded and this was supported by the n.m.r. data (Table 2) which showed δ(CH$_3$) values of 2.59 p.p.m. (2a) and 2.56 p.p.m. (2b). Unco-ordinated dmso gives a singlet δ(CH$_3$) at 2.53 p.p.m. relative to SiMe$_4$ whereas sulphur-bonded dmso gives a downfield shift of *ca.* 1.0 p.p.m. and oxygen-bonded dmso a downfield shift of at most 0.5 p.p.m. Several literature values are included in Table 2 for comparison. Since dmso bonds *via* oxygen in these complexes the Pd–dmso linkage, being a soft–hard interaction, would be expected to be weak.[11] This is borne out by the apparent desire of these complexes to form the chloride-bridged dimer by loss of dmso, a phenomenon that we have found to be typical of complexes of the type [ML$_2$(S)Cl]$^+$ where S is a weak ligand.[3,9] It is perhaps surprising that the complex [Pt(en)(dmso)Cl]Cl (en = ethylenediamine) reverts to [Pt(en)Cl$_2$] on standing [12] or heating in vacuum,[2] a similar type of reaction to the dimerisation described above, since here the dmso is sulphur-bonded and as such the metal–ligand bond is the more favourable soft–soft interaction.[11]

Complex (2a) was heated at 78 °C under a vacuum of 10^{-3} Torr * for 7 d to give a pure sample of the chloro-bridged dimer [{Pd(dppe)Cl}$_2$][ClO$_4$]$_2$ (3a) (Table 3). The i.r. spectrum contained no absorptions attributable to dmso, the ν(M–Cl) seen with (2a) had completely disappeared, and only the band at 273 cm^{-1} due to the bridging chloride remained. The n.m.r. spectrum also supported the disappearance of the dmso ligand. Other chloro-complexes of palladium(II) with sulphoxide ligands have been shown to be unstable to dimerisation, for example [Pd(SEt$_2$O)$_2$Cl$_2$] is in equilibrium with [Pd$_2$(SEt$_2$O)$_2$Cl$_4$] in chloroform solution.[5]

The platinum(II) complex [Pt(dppe)(dmso)Cl][PF$_6$] (4) (Table 3) could be isolated as a pure species with no dimer impurity from a reaction similar to that used to prepare the palladium analogue. The ν(S=O) absorption at 920 cm^{-1} and the position of δ(CH$_3$) in the n.m.r. spectrum at 2.61 p.p.m. showed that again the dmso was oxygen-bonded. The absence of any of the bridged dimeric species indicated the relative stability of the platinum(II) complex compared to that of palladium(II). This stability was probably due to the kinetic inertness of platinum(II) over palladium(II).[13] However, it was also noted that stronger bonding of the dmso to platinum(II) was indicated by the substantially larger values of Δ(S=O) (Table 1) for platinum(II) compared with those for the palladium(II) complexes.

If the reaction of [Pd(dppe)Cl$_2$] with 1 equivalent of silver salt in CH$_2$Cl$_2$–dmso was allowed to continue in solution for 3 h, instead of 15 min as above, a further reaction occurred. After working up the reaction mixture a complex was isolated having a ν(M–Cl) absorption at 310 cm^{-1} in the i.r. spectrum but no evidence of the S=O bond (Table 1). The complex, isolated in >60% yield, analysed as [Pd(dppe)(SMe$_2$)Cl][ClO$_4$] (5) (Table 3) and gave a Λ value of 97 Ω^{-1} cm^2 mol^{-1} as a 10^{-3} mol dm^{-3} acetone solution (1 : 1 electrolytes in acetone fall in the range 80—150 Ω^{-1} cm^2 mol^{-1}).[14] This complex was also unstable to dimerisation giving the

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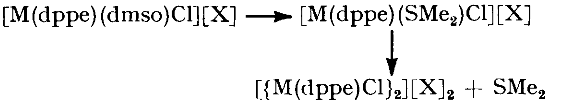
* Throughout this paper: 1 Torr = (101 325/760) Pa.

bridged dimeric species (3a) and free SMe_2 after either *ca.* 1 h in solution or several months in the solid state. This was indicated by a lack of a ν(M–Cl) mode, a band of medium intensity at 273 cm^{-1} (chloro-bridge) in the i.r. spectrum of the solid sample, and a resonance at 2.06 p.p.m. relative to $SiMe_4$ in the n.m.r. spectrum due to unco-ordinated SMe_2. The platinum(II) complex of structure (4) could be isolated as (4′) (Table 3), after reaction in solution for 3 h, again demonstrating the inherent stability of the platinum(II) complex compared to the palladium(II) analogue. However, when left in nitromethane solution for 1 month, the n.m.r. spectrum of the platinum(II) complex contained not only the singlet at 2.67 p.p.m. of (4) but also a singlet at 2.22 p.p.m. indicative of co-ordinated SMe_2 [15] (see comparative n.m.r. spectra in Table 2). It would therefore appear that the following reaction sequence (see Scheme) occurs, fairly readily with palladium(II), but very slowly with platinum(II) (X = unco-ordinated counter ion).



SCHEME

Several other deoxygenation reactions of co-ordinated sulphoxide ligands have been reported. These include organic halide solvents as part of the reaction sequence,[16,17] oxidation of the metal ion with concomitant reduction of the sulphoxide,[18] hydrogenation reactions,[19] and several others.[20–23]

The reaction of [Pd(dppe)Cl_2] (1) with 2 equivalents of silver ion was more straightforward. Both the perchlorate and hexafluorophosphate complexes were prepared to ascertain by an i.r.-spectroscopic study whether the dmso was oxygen- or sulphur-bonded. The complexes obtained were $[Pd(dppe)(dmso)_2][X]_2$, X = $[ClO_4]^-$ (6a) or $[PF_6]^-$ (6b) (Table 3). The i.r. spectra (Table 1) showed absorptions at 948 cm^{-1} (6a) and 942 cm^{-1} (6b) for the ν(S=O) bond indicative of oxygen bonding; the C–S–C deformation modes were at 985 cm^{-1} (6a) and 988 cm^{-1} (6b). This mode of co-ordination was supported by the n.m.r. spectra (Table 2) in CD_3NO_2 having resonances at 2.61 p.p.m. (6a) and 2.54 p.p.m. (6b) for the $\delta(CH_3)$ of dmso. These complexes were completely stable even in solution due, almost certainly, to the absence of any competing ligands. Dilution conductivity studies (Table 3) indicated that the complexes were 1 : 2 electrolytes in nitromethane solution having slope values (B) from a plot of $(\Lambda_0 - \Lambda_e)$ against $c^{\frac{1}{2}}$ of 351 and 331 Ω^{-1} $l^{\frac{1}{2}}$ $equiv.^{-\frac{1}{2}}$ for (6a) and (6b) respectively.[24]

The electronic spectra (Table 3) indicated that the complexes were square-planar palladium(II) and platinum(II) species.[25] All perchlorate complexes exhibited a strong broad band at *ca.* 1 100 cm^{-1} and a medium-strength sharp band at 620 cm^{-1} in their i.r. spectra due to ν_3 and ν_4 of $[ClO_4]^-$ respectively, which were unsplit indicating that the perchlorate ions did not interact with the cation.[26] Similarly, the hexafluorophosphates exhibited bands at 830 and 560 cm^{-1} in their spectra.

DISCUSSION

In general, sulphoxides bond *via* oxygen to hard metals such as main-group and first-row transition metals and *via* sulphur to soft metals such as the Group 8 metals.[4] It has been shown here however, that when steric factors are important sulphoxides can bond to a soft metal such as palladium(II) or platinum(II) *via* the hard donor, oxygen, and thus avoid the steric strain inherent in sulphur bonding [7] which would otherwise be the preferred soft–soft interaction.[11] Both [Pd(dien)(dmso)]$[ClO_4]_2$ [1,*] and $[Pt\{H_2N(CH_2)_nNH_2\}(dmso)Cl]Cl$ (n = 2—4),[2] in which there is no steric hindrance from the amine ligands, contain sulphur-bonded dmso even though symbiosis [27] might suggest the possibility of the dmso bonding through the hard oxygen donor site. Tolman [28] has shown that the effective cone angle for dppe is 125° and the present work indicates that this is incompatible with a sulphur-bonded dmso with its essentially tetrahedral environment around the sulphur atom.[29] Space-filling models support this, the methyl groups of the dmso interacting with the phenyl groups of the dppe. Bonding *via* the oxygen is shown by models to be sterically unrestricted.

In our search for complexes containing active sites we have shown that dmso in square-planar palladium(II)- and platinum(II)–dppe complexes co-ordinates *via* the hard oxygen-donor site and as such is a weakly bonded ligand. We are currently investigating the interaction of these complexes with small molecules.

EXPERIMENTAL

Dimethyl sulphoxide was distilled before use and stored over molecular sieves. Nitromethane and dichloromethane were purified by literature methods; [30] silver salts were dried at 56 °C under a vacuum of 10^{-3} Torr. Infrared spectra were recorded as Nujol and hexachlorobutadiene mulls between CsI plates on a Perkin-Elmer 577 spectrometer. N.m.r. spectra were obtained in CD_3NO_2 solutions (*ca.* 10%) using $SiMe_4$ as an internal standard on a Perkin-Elmer R 32 spectrometer. Conductivity studies were performed using a Universal Wayne–Kerr bridge with a glass cell containing platinum electrodes. Solution electronic spectra were recorded in 10-mm quartz cells using a Pye–Unicam SP 1700 spectrophotometer.

Preparations.—[M(dppe)Cl_2] (M = Pd^{II} or Pt^{II}). These complexes were prepared by dissolving the appropriate MCl_2 in refluxing acetonitrile, filtering while hot, then adding dppe in a 1 : 1 mol ratio with the metal ion. After stirring for another hour the volume of the solution was reduced, and the complex filtered off, recrystallised from dimethylformamide, and dried *in vacuo* at 78 °C for 24 h (Found: C, 46.7; H, 3.7. $C_{26}H_{24}Cl_2P_2Pt$ requires C, 47.0; H, 3.7. Found: C, 54.4; H, 4.2. $C_{26}H_{24}Cl_2P_2Pd$ requires C, 54.2; H, 4.2%).

[Pd(dppe)(dmso)Cl]$[ClO_4]$ (2a). Complex (1) [Pd(dppe)Cl_2] (0.575 g, 1 mmol) was dissolved in dichloromethane (20 cm^3). Silver perchlorate (0.207 g, 1 mmol) in dmso (10 cm^3) was added with stirring. After stirring for another 15 min the solution was filtered, the volume rapidly reduced *in vacuo*, and then an oil precipitated with diethyl ether. The oil, after separation, was dissolved in dichloromethane, filtered, and a yellow solid precipitated by careful addition of diethyl ether. The complex was filtered off, washed with ethanol and diethyl ether, and dried in air. Yield 0.56 g. The hexafluorophosphate salt (2b) was prepared similarly using $Ag[PF_6]$ (0.253 g, 1 mmol). Yield 0.53 g.

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* dien is $H_2N(CH_2)_2NH(CH_2)_2NH_2$.

[{Pd(dppe)Cl}$_2$][ClO$_4$]$_2$ (3a). This complex was prepared by heating (2a) at 78 °C under a vacuum of 10^{-3} Torr for 7 d to give 100% conversion.

[Pt(dppe)(dmso)Cl][PF$_6$] (4) *and* (4′). The complex [Pt(dppe)Cl$_2$] (0.664 g, 1 mmol) was dissolved in dichloromethane (20 cm^3). Silver hexafluorophosphate (0.253 g, 1 mmol) dissolved in dmso (10 cm^3) was added with stirring. Stirring was continued for 15 min (4) or 3 h (4′) and then the solution filtered, evaporated to an oil, dissolved in nitromethane and precipitated by careful addition of diethyl ether to give a white solid. The product was again dried in air. Yields: (4), 0.57 g (70%); (4′), 0.51 g (62%).

[Pd(dppe)(SMe$_2$)Cl][ClO$_4$] (5). The reaction described above in preparing (2a) was followed, except that the reaction mixture was stirred for 3 h before work up. Complex (5) was isolated. The complex was dried in air. Yield 0.50 g.

[Pd(dppe)(dmso)$_2$][ClO$_4$]$_2$ (6a). Complex (1) [Pd(dppe)Cl$_2$] (0.575 g, 1 mmol) was dissolved in dichloromethane (20 cm^3) and dmso (10 cm^3). Silver perchlorate (0.415 g, 2 mmol) dissolved in nitromethane (20 cm^3) was added with stirring and the solution stirred for another 3 h. The silver chloride precipitate was filtered off and the solution reduced to an oil on the rotary evaporator. The oil was dissolved in nitromethane (10 cm^3), filtered, and a pale yellow solid was precipitated with addition of diethyl ether. The solid was washed with ethanol then diethyl ether and dried *in vacuo* at room temperature for 24 h. Yield 0.58 g (68%).

The hexafluorophosphate salt (6b) was prepared similarly using Ag[PF$_6$] (0.506 g, 2 mmol). Yield 0.56 g (59%).

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