Supplementary Material Available: Computer-generated drawings of the two crystallographically independent anions of **1** showing the closest interatomic contacts and water molecules (Figures S1 and S2), a complete list of crystal data (Table I continued), and tables of bond distances and bond angles (Tables S1 and S2), anisotropic displacement coefficients (Table S3), and H atom coordinates (Table S4) for **1** (9 pages); a table of observed and calculated structure factors for **1** (10 pages). Ordering information is given on any current masthead page.

Contribution from the Inorganic Chemistry Section,
School of Chemistry, University of Melbourne,
Parkville 3052, Australia

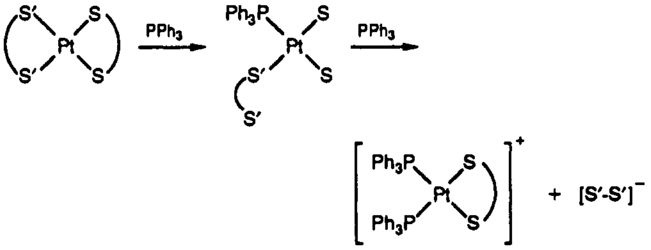
Ordering of Ligand Strengths for a Series of Dithiolate Ligands Attached to Platinum(II)

Ray Colton* and Vanda Tedesco

Received November 27, 1990

Pioneering work on the reactions of the bis(dithiolate)platinum(II) complexes $Pt(S\text{-}S)_2$ with monodentate group 15 donor ligands was done by Stephenson[1] and Fackler[2] and their coworkers. However, this work did not discriminate between the ligating powers of either the various dithiolates or the various group 15 ligands because the reaction sequences were very similar in all cases. More recently, we have established a consistent order of coordinating power for a series of group 15 and mixed group 15/group 16 donor bidentate ligands by investigating their reactions with $Pt(S_2P\{OEt\}_2)_2$[3] ($Pt(dtp)_2$), $Pt(S_2CNEt_2)_2$[4] ($Pt(dtc)_2$), and $Pt(S_2CO^nPr)_2$[5] ($Pt(xan)_2$). Evidence was also obtained from these studies that dithiocarbamate is a stronger ligand than dithiophosphate and xanthate.

In this note, we establish an order of relative ligating strengths for a number of dithiolates at platinum(II). The method is based upon the discovery that mixing two different dithiolates gives the mixed platinum dithiolate. With use of the work of Stephenson and Fackler, these were then reacted with PPh_3, and multinuclear magnetic resonance studies clearly reveal which dithiolate is displaced in the competitive situation



to give the $[(PPh_3)_2Pt(S\text{-}S)]^+$ complexes, which can be identified by their known NMR spectra.[6]

All NMR data are given in Table I.[7] Figure 1a is the platinum-195 NMR spectrum at −30 °C observed 1 week after mixing equimolar quantities of $Pt(dtp)_2$ and $Pt(xan)_2$ in dichloromethane. The triplet and the singlet are due to the starting materials, and the doublet is due to Pt(dtp)(xan). The relative proportions of the species are very close to 1:4:1, which shows that the mixed species is favored. Figure 1b is the platinum-195 NMR spectrum after the addition of an equimolar quantity of PPh_3 (i.e. PPh_3:total Pt = 1:1) to the solution at −30 °C. The spectrum is observed at low temperature to prevent intramolecular exchange between the bidentate and monodentate dithiolate ligands.[1] The spectrum consists of a weak doublet assigned to $(PPh_3)Pt(\eta^1\text{-xan})(\eta^2\text{-xan})$,[6] arising from the $Pt(xan)_2$ in the solution, and a doublet of doublets, which is clearly assignable to a species containing the phosphine and a coordinated dtp ligand. The coupling constant to the phosphorus of the dtp ligand is markedly reduced from the value in the starting materials and is consistent with monodentate coordination of the dtp ligand.[3,6] The complex in solution is therefore identified as $(PPh_3)Pt(\eta^1\text{-dtp})(\eta^2\text{-xan})$. Addition of a second equimolar quantity of PPh_3 produces the spectrum shown in Figure 1c. The main signal is a triplet, which is identified[6] as being due to $[(PPh_3)_2Pt(\eta^2\text{-xan})]^+$, and the weak triplet is assigned to $(PPh_3)_2Pt(S_2CO)$ formed by dealkylation of the coordinated xanthate ligand.[1] Confirmation of this reaction scheme is obtained from the phosphorus-31 NMR spectra, particularly with the appearance of a signal due to free $[dtp]^-$ after the reaction with 2 molar equiv of PPh_3. Thus these reactions show that in an even competition, *n*-propyl xanthate has a stronger coordinating power than diethyl dithiophosphate.

We have carried out similar studies with other pairs of dithiolates and have established the following order of ligating strengths:

$$[S_2CNEt_2]^- > [S_2CO^nPr]^- > [S_2P(OEt)_2]^- > [S_2PPh_2]^-$$

Another series of experiments was performed to substantiate this sequence. We have previously established[3-5] that $Ph_2PCH_2CH_2PPh_2$ (dpe) is the most strongly bound of all the group 15 bidentate ligands so that it effectively blocks two coordination sites at Pt(II) and allows a different type of competition reaction between different dithiolates. Reaction of $[Pt(dpe)_2]^{2+}$ with $Pt(S\text{-}S)_2$ gives $[(dpe)Pt(S\text{-}S)]^+$ quantitatively. These species were then reacted in dichloromethane solution at room temperature for a week with a different free dithiolate ion in the form of the salt $[PPh_3Bz][S\text{-}S]$,[8] and the results confirmed the order of ligand strengths given above. For example, addition of $[PPh_3Bz][xan]$ to $[(dpe)Pt(dtc)]^+$ gave no reaction, but $[PPh_3Bz][dtc]$ reacted with $[(dpe)Pt(xan)]^+$ to give $[(dpe)Pt(dtc)]^+$.

This second set of experiments allows the series of dithiolates studied to be extended. If reactions between dpe and $Pt(dtp)_2$ and $Pt(xan)_2$ are carried out at room temperature, the first formed products are $[(dpe)Pt(S\text{-}S)]^+$ and free $[S\text{-}S]^-$, which interact to give $(dpe)Pt(S_2P\{O\}\{OEt\})$ and $(dpe)Pt(S_2CO)$ and the appropriate dithiolate ester.[3,5] These dealkylated dithiolates are very strongly

Table I Phosphorus-31 and Platinum-195 NMR Data in Dichloromethane Solution[a]

compd	$\delta(^{31}P)$	$\delta(^{195}Pt)$	$^1J_{Pt,P}$, Hz	$^2J_{Pt,P}$, Hz	temp, °C
$Pt(xan)_2$		−4210 (s)			25
$Pt(dtp)_2$	99.9 (s)	−3985 (t)		445	25
$Pt(dtc)_2$		−3835 (s)			25
$Pt(S_2PPh_2)_2$	96.8 (s)	−3055 (t)		360	25
Pt(xan)(dtp)	102.8 (s)	−4110 (d)		415	25
Pt(xan)(dtc)		−4030 (s)			25
$Pt(xan)(S_2PPh_2)$	102.0 (s)	−3655 (d)		325	25
Pt(dtp)(dtc)	103.3 (s)	−3925 (d)		380	25
$Pt(dtp)(S_2PPh_2)$	99.2 (s), 97.5 (s)	−3520 (dd)		455, 365	25
$Pt(dtc)(S_2PPh_2)$	97.3 (s)	−3445 (d)		294	25
$(PPh_3)Pt(\eta^1\text{-dtp})(\eta^2\text{-xan})$	94.0 (s), 13.0 (s)	−4510 (dd)	3615	125	−30
$(PPh_3)Pt(\eta^1\text{-}S_2PPh_2)(\eta^2\text{-xan})$	86.0 (s), 12.0 (s)	−4515 (dd)	3650	88	−30
$(PPh_3)Pt(\eta^1\text{-}S_2PPh_2)(\eta^2\text{-dtp})$	97.3 (s), 85.7 (s), 13.5 (s)	−4485 (ddd)	3765	335, 120	−30
$(PPh_3)Pt(\eta^1\text{-xan})(\eta^2\text{-dtc})$	13.8 (s)	−4315 (d)	3580		−30
$(PPh_3)Pt(\eta^1\text{-dtp})(\eta^2\text{-dtc})$	97.2 (s), 14.0 (s)	−4325 (dd)	3505	117	−30
$(PPh_3)Pt(\eta^1\text{-}S_2PPh_2)(\eta^2\text{-dtc})$	85.1 (s), 13.4 (s)	−4345 (dd)	3530	99	−30

[a] Key: s = singlet; d = doublet; dd = doublet of doublets; ddd = doublet of doublet of doublets; t = triplet.

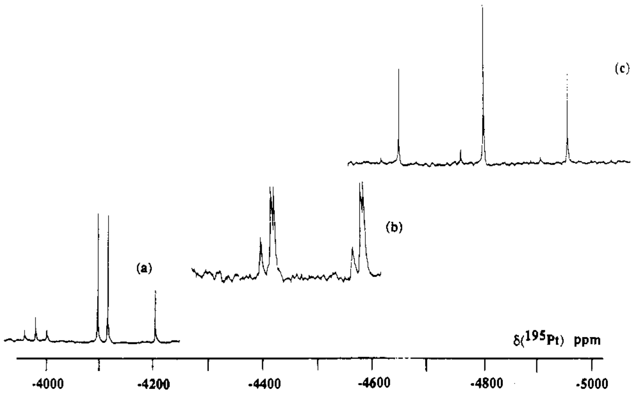


Figure 1. Platinum-195 NMR spectra at −30 °C in dichloromethane of (a) a solution containing initially equimolar proportions of $Pt(xan)_2$ and $Pt(dtp)_2$, (b) the solution after addition of equimolar quantity of PPh_3, and (c) the solution after addition of a second equimolar quantity of PPh_3.

bound to platinum, and neither $(dpe)Pt(S_2P\{O\}\{OEt\})$ nor $(dpe)Pt(S_2CO)$ react with $[dtc]^-$, showing that both are stronger ligands than dithiocarbamate. We have not yet devised a satisfactory method to discriminate between the ligating properties of these two anions.

Thus the complete sequence of ligating powers is found to be

$$[S_2P\{O\}\{OEt\}]^{2-} \cong [S_2CO]^{2-} > [S_2CNEt_2]^- > [S_2CO^nPr]^- > [S_2P(OEt)_2]^- > [S_2PPh_2]^-$$

Presumably, the double charges on the first two species are largely responsible for their ligating powers. The order among the singly charged species is consistent with the reducing contribution of cannonical forms involving delocalization within the ligands. An ordering of dithiolate ligand strengths on Ni(II) based upon spectral measurements has been reported by Fackler and Coucouvanis.[9]

Acknowledgment. V.T. thanks the Australian Government for a Postgraduate Research Award.

---

(1) (a) Alison, J. M. C.; Stephenson, T. A.; Gould, R. O. *J. Chem. Soc. A* **1971**, 3690. (b) Alison, J. M. C.; Stephenson, T. A. *J. Chem. Soc., Dalton Trans.* **1973**, 254. (c) Steele, D. F.; Stephenson, T. A. *J. Chem. Soc., Dalton Trans.* **1973**, 2124. (d) Cornock, M. C.; Stephenson, T. A. *J. Chem. Soc., Dalton Trans.* **1977**, 501.

(2) (a) Lin, I. J. B.; Chen, H. W.; Fackler, J. P., Jr. *Inorg. Chem.* **1978**, *17*, 394. (b) Fackler, J. P., Jr.; Thompson, L. D.; Lin, I. J. B.; Stephenson, T. A.; Gould, R. O.; Alison, J. M. C.; Fraser, A. J. F. *Inorg. Chem.* **1982**, *21*, 2397.

(3) Colton, R.; Ebner, J.; Hoskins, B. F. *Inorg. Chem.* **1988**, *27*, 1993.

(4) Colton, R.; Ebner, J. *Inorg. Chem.* **1989**, *28*, 1559.

(5) Colton, R.; Tedesco, V. *Inorg. Chim. Acta*, in press.

(6) Colton, R.; Stephenson, T. A. *Polyhedron* **1984**, *3*, 231.

(7) NMR spectra were observed by using a JEOL FX 100 spectrometer, phosphorus-31 at 40.32 MHz and platinum-195 at 21.32 MHz. References were external 85% H_3PO_4 and 1 M H_2PtCl_6 in concentrated HCl solution; the high frequency positive sign convention is used for chemical shifts.

(8) Triphenylbenzylphosphonium salts of the dithiolates were prepared by interaction of $[PPh_3Bz]Cl$ and the sodium dithiolate in acetone. The solution was evaporated to dryness and extracted with dichloromethane. After filtering, the solution was evaporated to dryness and the product recrystallized from dichloromethane/*n*-hexane.

(9) Fackler, J. P., Jr.; Coucouvanis, D. *J. Am. Chem. Soc.* **1966**, *88*, 3913.