SYNTHESIS AND CHARACTERIZATION OF NEW HETEROMETALLIC COMPLEXES CONTAINING TWO PYRAZOLIDE BRIDGES

Claudio Pettinari

Dip. Scienze chimiche, Università degli Studi di Camerino,
Via S. Agostino 1, I - 62032 Camerino, Italy

Abstract

The platinum(II) derivative $(\text{DPE})\text{Pt}(\text{pz})_2$ (**L**) where DPE stands for 1,2-bis(diphenylphosphino)ethane, and pzH for pyrazole, gives 1:1 adducts with CdX_2 ($\text{X} = \text{Cl}, \text{I}$), HgX_2 ($\text{X} = \text{I}, \text{Br}$), AuCl and PdCl_2 and 1:2 adducts with HgX_2 ($\text{X} = \text{Cl}, \text{Br}$). The compounds have been characterized by elemental analysis and spectroscopy (IR, ^1H , ^{13}C , ^{31}P NMR for the soluble compounds). The reactions of **L** with several $\text{R}_n\text{SnCl}_{4-n}$, ZnX_2 and CoX_2 ($\text{X} = \text{Cl}$ or Br) have been investigated: in all cases cleavage of platinum-nitrogen bonds was observed and the likely polynuclear $[\text{R}_n\text{SnCl}_{4-n-2}(\text{pz})_2]_n$, $[\text{Zn}(\text{pz})_2]_n$ and $[\text{Co}(\text{pz})_2]_n$ are respectively obtained.

Introduction

We have recently reported on the synthesis, reactivity and spectroscopic characterization of complexes of main groups and transition elements with poly(azol-1-yl)alkanes¹, a family of stable and flexible nitrogen-donor polidentate ligands, discovered by Trofimenko², which have been shown to afford several type of complexes, depending on the nature of the acceptor and on the steric and electronic properties of the donor.

Several platinum bis(pyrazolide)complexes (Fig. 1), homologues of poly(azol-1-yl)alkanes, able to act as bidentate chelating ligands affording both 1:1 and 2:1 adducts, have been described in 1977 by Minghetti *et al*³. These molecules are of interest for their potential role in homogeneous catalysis⁴ and for the unusual electronic and magnetic properties due to possible strong metal-metal interaction⁵.

It thus seemed of interest to extend our research to study of interaction between these molecules and several transition and main groups metal ions and we report here the initial results on the chelating ability of $[(\text{DPE})\text{Pt}(\text{pz})_2]$.

Material and methods

The samples for microanalysis were dried *in vacuo* to constant weight (20°C, *ca* 0.1 Torr). Elemental analyses (CHN) were carried out in the house with a Carlo Erba model 1106 instrument. IR spectra were recorded from 4000 to 100 cm^{-1} and from 4000 to 600 cm^{-1} with a Perkin-Elmer instrument System 2000 FT-IR and a 1600 Series FT-IR instrument, respectively. ^1H - ^{31}P - and ^{13}C NMR spectra were recorded on a VX-300 Varian spectrometer operating at room temperature (300 MHz for ^1H , 121.4 MHz for ^{31}P and 75 MHz for ^{13}C). Melting points were taken on an IA 8100 Electrothermal instrument. The electric resistance of solutions was measured with a Crison CDTM 522 conductimeter at room temperature.

The ligand $(\text{DPE})\text{Pt}(\text{pz})_2$ (**L**) was prepared according to the literature method⁶. The other chemicals were analytical reagent grade.

Fig. 1. Structure of the bis(pyrazolide)platinum(II) ligands.

Synthesis of the adducts 1-8

A diethyl ether solution (10 cm³) of mercury(II) bromide (180 mg, 0.5 mmol) was added dropwise to a stirred suspension (20 cm³) of the ligand (DPE)Pt(pz)₂ (L) (364 mg, 0.5 mmol) in the same solvent. A white crystalline precipitate separated out, which was filtered 2 days later and washed with diethyl ether to afford compound 3 (245 mg, 0.45 mmol); it was purified by dissolving in methylene chloride (10 cm³) and precipitating with diethyl ether (15 cm³) to give the analytical sample (218 mg, 0.40 mmol). Compounds 1, 2, 4, 5 and 7 were prepared similarly, while compound 6 was obtained from a methanol solution. Compound 8 was obtained by adding a diethyl ether suspension (20 cm³) of the donor L (365 mg, 0.5 mmol) to a stirred suspension of (CH₃)₂SAuCl (147 mg, 0.5 mmol) in the same solvent (15 cm³). The reaction mixture was stirred for two days and then evaporated to dryness. The residue was extracted with dichloromethane and the extract concentrated to 3 cm³; addition of diethyl ether (10 cm³) gave a white crystalline precipitate which was filtered and washed with hot methanol (20 cm³) (432 mg, 0.45 mmol).

Reaction of (DPE)Pt(pz)₂ with R_nSnX_{4-n}, ZnX₂ and CoX₂ (X = Cl or Br)

A diethyl ether solution (10 cm³) of CH₃SnCl₃ (120 mg, 0.5 mmol) was added dropwise to a stirred suspension (20 cm³) of the ligand (DPE)Pt(pz)₂ (L) (363 mg, 0.5 mmol) in the same solvent. A white crystalline precipitate separated out. After 1 day the suspension was filtered and the precipitate washed with diethyl ether (10 cm³) and shown to be (DPE)PtCl₂ by analytical and spectral data which are in accordance with those reported in literature⁷. The solution was evaporated to dryness and the residue washed with dichloromethane to afford compound [(CH₃)(pz)₂SnCl]_n (0.23 mol, 45%), m.p. >250°C; IR (nujol mull): 3110w, 571m, 339m, 320s, 249m. Found: C, 27.9; H, 3.1; N, 18.6; calcd for C₇H₉ClN₄Sn: C, 27.7; H, 3.0, N, 18.5.; ¹H NMR (DMSO, δ): 7.60s br, 6.30s br, 1.0 br.

Results and Discussion

The interaction between [(DPE)Pt(pz)₂] and several anhydrous cadmium and mercury(II) halide acceptors in diethyl ether and/or methanol afforded the corresponding adducts 1-4 (Table 1) according to the following general equation 1:

The 1:1 adduct [(DPE)Pt(pz)₂]HgCl₂ previously synthesized by Bandini *et al*⁸ was also obtained when the reaction was carried out in methanol whereas in diethyl ether with HgCl₂ and HgBr₂ the sparingly soluble 1:2 adducts 5 and 6 were respectively isolated: the obtainment of this type of compounds also when the reaction was carried out in a strong excess of the (DPE)Pt(pz)₂ donor can appear surprising but could be explainable with the strong and well-known tendency⁹ of mercury(II) derivatives to afford chlorine-bridged structures involving tetrahedrally coordinated Hg(II) species of the type shown in Fig. 2.

Fig. 2. Structure proposed for compounds 5 and 6.

No 1:2 adduct was synthesized when the reaction between [(DPE)Pt(pz)₂] and HgI₂ was carried out in ether in a strong excess of acceptor. Attempts to obtain 1:2 adducts by reaction of 3 and 4 with HgBr₂ and HgI₂ respectively, were also unsuccessful.

The complexes [(DPE)Pt(pz)₂(PdCl₂)], 7 and [(DPE)Pt(pz)₂(AuCl)] 8, were instead obtained by displacement by (DPE)Pt(pz)₂ of a labile or volatile ligand such as acetonitrile or dimethylsulphoxide from (CH₃CN)₂PdCl₂ and (CH₃)₂SAuCl respectively.

The reactions of (DPE)Pt(pz)₂ with several tin(IV) and organotin(IV) derivatives, namely (CH₃)₂SnCl₂, Ph₂SnCl₂, CH₃SnCl₃ and SnCl₄ were carried out under a variety of conditions (in diethyl ether and under N₂ stream, at room temperature or in refluxing ethanol, petroleum ether, CH₂Cl₂ or acetonitrile) but in any case DPEPtCl₂ was obtained: this implies a cleavage of the Pt-N bond and scrambling of the ligands, in accordance with eqn. 2:

For example when the reaction between (DPE)Pt(pz)₂ and CH₃SnCl₃ in diethyl ether was carried out, the formation of a precipitate by empirical composition C₇H₉ClN₄Sn, has been observed. Poor solubility in most of the usual solvents prevented its full characterization. It's also impossible to record ¹¹⁹Sn Mössbauer spectrum because of the extreme instability of the precipitate towards moisture. We tentatively postulate a polynuclear structure of the type [(CH₃)(pz)₂SnCl]_n with bridging azolato groups between two tin(IV) atoms on the basis of previous reports on imidazolate and pyrazolate derivatives of trialkyltin(IV) acceptors¹⁰.

Table 1

Physical, Analytical and conductivity data of derivatives 1-8

Compound and formula ^a	No.	Yield %	M.p. (°C)	El. Analyses (%); Found(Calc.)			Conductivities ^b		
				C	H	N	solv.	conc.	Λ
(DPE)Pt(pz) ₂ CdCl ₂ C ₃₂ H ₃₀ CdCl ₂ N ₄ P ₂ Pt	(1)	45	246-8	42.0 (42.2)	3.2 (3.3)	6.3 (6.2)	CH ₂ Cl ₂	1.0	0.8
(DPE)Pt(pz) ₂ CdI ₂ C ₃₂ H ₃₀ CdI ₂ N ₄ P ₂ Pt	(2)	92	184d	35.2 (35.1)	3.1 (2.8)	4.9 (5.1)	CH ₂ Cl ₂	1.1	0.9
(DPE)Pt(pz) ₂ HgBr ₂ C ₃₂ H ₃₀ Br ₂ HgN ₄ P ₂ Pt	(3)	80	269-70	35.3 (35.3)	2.8 (2.8)	5.3 (5.2)	CH ₂ Cl ₂	0.8	0.7
(DPE)Pt(pz) ₂ HgI ₂ C ₃₂ H ₃₀ HgI ₂ N ₄ P ₂ Pt	(4)	90	197-8	32.3 (32.5)	2.5 (2.6)	4.4 (4.7)	CH ₂ Cl ₂	1.2	1.3
[(DPE)Pt(pz) ₂ (HgBr ₂) ₂] C ₃₂ H ₃₀ Br ₄ Hg ₂ N ₄ P ₂ Pt	(5)	85	295-8	26.6 (26.5)	2.1 (2.1)	3.5 (3.9)	insoluble		
[(DPE)Pt(pz) ₂ (HgCl ₂) ₂] C ₃₂ H ₃₀ Cl ₄ Hg ₂ N ₄ P ₂ Pt	(6)	60	266-8	30.0 (30.3)	2.4 (2.4)	4.3 (4.4)	insoluble		
(DPE)Pt(pz) ₂ PdCl ₂ C ₃₂ H ₃₀ Cl ₂ N ₄ P ₂ PdPt	(7)	45	280d	42.2 (42.5)	3.5 (3.3)	5.9 (6.2)	CH ₂ Cl ₂	1.2	0.6
(DPE)Pt(pz) ₂ AuCl C ₃₂ H ₃₀ AuClN ₄ P ₂ Pt	(8)	90	180d	40.2 (40.0)	3.2 (3.2)	5.4 (5.8)	CH ₂ Cl ₂	1.2	1.6

^a DPE = 1,2-bis(diphenylphosphino)ethane, pzH = pyrazole.^b At room temperature and at the molar concentration $\times 10^{-3}$.

Scrambling of the ligand occurred also when (DPE)Pt(pz)₂ reacts in ethanol and/or diethyl ether with ZnCl₂, ZnI₂ and CoCl₂, the well-known polymeric [Zn(pz)₂]_n and [Co(pz)₂]_n¹¹ respectively being formed.

The different behaviour of (DPE)Pt(pz)₂ with respect to (DPE)Pt(pz')₂ previously investigated by Bandini *et al*⁸ is likely due to presence in the latter of electron-releasing groups as the methyl, which makes L' better donor than L and shields Pt(II) atom from chloride attack.

All the compounds 1-8 were identified through analytical data (Table 1) infrared (Table 2) and when possible also with magnetic resonance spectra (Tables 3, 4 and 5 for ¹H, ¹³C and ³¹P NMR respectively). They are colourless (with exception of 7, which is pale-yellow), air stable, sparingly soluble in chlorinated solvents (with exception of 5 and 6) and in DMSO whereas they are generally insoluble in alcohol, acetone, and hydrocarbons. The molar conductivities in dichloromethane showed the complexes 1-4, 7 and 8 to be non-electrolytes, ruling out ionic formulae such as [(DPE)Pt(μ-pz)₂M(μ-pz)₂Pt(DPE)]²⁺ [MX₄]²⁻ or ionic dissociation such as 3.

The infrared spectra (Table 2) are in agreement with the formulae given. In all the compounds the bands typical of the azolato ligand are easily detected: weak and medium vibrations at *ca* 3100 cm⁻¹ due to C-H stretching of the heterocyclic ring, and other more intense ones between 1600 and 1500 cm⁻¹ typical of ring breathing¹². No significative change was observed

upon complexation, because we noted that in the 4000-600 cm^{-1} region the IR spectra of the adducts **1-8** resemble strictly that of the $(\text{DPE})\text{Pt}(\text{pz})_2$.

Table 2**Selected IR data (cm^{-1})^a**

Compound	No.	>3000	1600-1500	< 500	other data
$(\text{DPE})\text{Pt}(\text{pz})_2$		3118w 3070w	1585w 1570w	540m, 490m, 475w 360m, 270w	
$(\text{DPE})\text{Pt}(\text{pz})_2\text{CdCl}_2$	(1)	3140w 3070w	1590w	545m, 495m, 480w 450w, 405w	$\mu(\text{Cd-Cl})$: 280m
$(\text{DPE})\text{Pt}(\text{pz})_2\text{CdI}_2$	(2)	3110w 3040sh	1585w	540m, 490w, 480w	
$(\text{DPE})\text{Pt}(\text{pz})_2\text{HgBr}_2$	(3)	3105vw 3060w	1590w 1575w	540s, 490m, 480m 450w, 400vw	
$(\text{DPE})\text{Pt}(\text{pz})_2\text{HgI}_2$	(4)	3110w 3070w	1590w	540m, 490m, 480m 460w br	
$[(\text{DPE})\text{Pt}(\text{pz})_2(\text{HgBr}_2)_2]$	(5)	3100w	1589w 1570w	535s, 495s, 480m	
$[(\text{DPE})\text{Pt}(\text{pz})_2(\text{HgCl}_2)_2]$	(6)	3108w 3060w	1590w 1576w	540s, 493m, 485m 441w, 425w	$\mu(\text{Hg-Cl})$: 305m
$(\text{DPE})\text{Pt}(\text{pz})_2\text{PdCl}_2$	(7)	3140w, 3060w	1585w 1570w	530m, 488 m br 483w, 409w	$\mu(\text{Pd-Cl})$: 285m
$(\text{DPE})\text{Pt}(\text{pz})_2\text{AuCl}$	(8)	3140w 3120w 3040w	1587w	538s, 490m, 480w 450w, 361m	$\mu(\text{AuCl})$: 310br 300br

^a Nujol mull

In the low-frequency region of compounds **1** and **6-8** bands due to metal-chloride stretching frequencies are also observed, whereas we find no evidence of M-N stretching vibrations because they are likely hidden under some $\text{DPEPt}(\text{pz})_2$ absorptions.

The ^1H and ^{13}C NMR spectra (Tables 3 and 4), recorded for the sufficiently soluble derivatives, showed always bands due to bidentate P-donor ligand and two pyrazolato moieties, suggesting that the organic ligands have not undergone any structural change or rearrangement upon coordination.

All the signals assignable to proton of pyrazolate ring are generally shifted downfield upon complexation, whereas no conclusion could to be reached on the bis(diphenylphosphino)ethane protons because of the broadening of the absorption.

The ^{13}C NMR data of compounds **5-8** were not reported: in fact the expected signals are not detected because the poor solubility of compounds (*ca* 1.5×10^5 cycles acquired). In the spectra of derivatives **1-4** the complex patterns and/or the broadening of carbon signals is explainable with the non-equivalence of the phenyl rings due to restricted rotations of the phenyls around the P-C bonds and with the poor solubility also.

The ^{31}P NMR spectra of complexes **1-4** and **7** show a single resonance in the region 32-35 ppm (external reference 85% H_3PO_4) generally flanked by ^{195}Pt satellites with $^1J_{\text{Pt-P}}$ of *ca* 3.1 kHz. The two phosphorus nuclei are therefore magnetically equivalent also in these adducts, where the signals appear to be slightly deshielded with respect to that of the free donor.

In the ^{31}P spectrum of compound **8** two sharp resonances are observed, different from that of the starting L donor and indicative of magnetical non-equivalence of the two phosphorus atoms. Gold(I) compounds¹³ generally prefer bi-coordination and also in this compound likely only one pyrazolato group is coordinated to gold(I) atom, as proposed in Fig. 3.

Fig. 3. Structure proposed for compound 8.

Table 3

 ^1H NMR data^a for derivatives 1-8

Compound	No	Solvent	CH ₂	3-CH	4-CH	5-CH	Aromatics
(DPE)Pt(pz) ₂		CD ₂ Cl ₂	2.2-2.4m br	6.7d	5.9pt	7.3d	7.4-7.6m, 7.7-7.9m
		CDCl ₃	2.2-2.5m br	6.8d	5.9pt	7.3d	7.4-7.6m, 7.7-7.9m
(DPE)Pt(pz) ₂ CdCl ₂	(1)	CD ₂ Cl ₂	2.2-2.8br	6.9d	6.0pt	^b	7.4-7.9m br
(DPE)Pt(pz) ₂ CdI ₂	(2)	CD ₂ Cl ₂	2.0-3.0br	7.0br	6.0br	^b	7.3-8.0br
		CDCl ₃	2.1-2.9br	7.0d	6.0pt	^b	7.3-7.7m br, 7.8-8.0m br
		C ₅ D ₅ N	2.5-3.0br	7.1br	6.0br	^b	7.1-8.2br
		C ₆ D ₄ NO ₂	2.5-3.0br	7.3d	6.0pt	7.8d	7.5m, 7.7m, 8.1m
(DPE)Pt(pz) ₂ HgBr ₂	(3)	CDCl ₃	2.2-2.6br	6.9d	5.9pt	^b	7.4-8.0br
(DPE)Pt(pz) ₂ HgI ₂	(4)	CDCl ₃	2.4-2.7br	7.0d	6.0pt	^b	7.3-7.9m br
(DPE)Pt(pz) ₂ PdCl ₂	(7)	CDCl ₃	2.0-2.9br	7.0br	6.0br	^b	7.2-8.0 br
(DPE)Pt(pz) ₂ AuCl	(8)	CDCl ₃	2.2-2.9br	7.0br	6.0br	^b	7.1-8.0 br

^a δ in ppm from internal TMS, m = multiplet, d = doublet, pt = pseudotriplet, br = broad.^b The doublet due to 5-CH could not be assigned because is hidden under the aromatic signals.

Table 4

 ^{13}C NMR data^a of derivatives 1-4

Compound	No	Solvent	CH ₂	C-3	C-4	C-5	Aromatics
(DPE)Pt(pz) ₂		CD ₂ Cl ₂	29.34dd	139.4s	102.8s	138.8s	127.9s, 129.0br
			$J_{\text{PC}} = 7.5$	$^4J_{\text{PC}} = 3.0$		$^3J_{\text{PC}} = 2.1$	131.9s, 134.1d
		CDCl ₃	29.60dd	139.7s	103.0s	137.3s	127.8s, 129.1br
			$J_{\text{PC}} = 7.5$	$^4J_{\text{PC}} = 3.8$		$^3J_{\text{PC}} = 2.5$	131.9s, 134.0d
(DPE)Pt(pz) ₂ CdCl ₂	(1)	CD ₂ Cl ₂	29.73dd br	141.0br	105.6s	139.4br	130.0m, 133.0s br
(DPE)Pt(pz) ₂ CdI ₂	(2)	CDCl ₃	29.0br	140.4br	104.9s	138.4br	133.7s, 134.4br
(DPE)Pt(pz) ₂ HgBr ₂	(3)	CDCl ₃	30.3dd	140.0br	104.6s	137.7br	129.2m, 132.0s
(DPE)Pt(pz) ₂ HgI ₂	(4)	CDCl ₃	$J_{\text{PC}} = 8.0$				132.3s, 133.7m br
			30.0br	n.o.	n.o.	n.o.	129.4br, 132.5s
							133.5m
							128.9m, 133.0s
							133.9m

^a δ in ppm from internal TMS, m = multiplet, d = doublet, t = triplet, br = broad; J in Hz.

Table 5
³¹P NMR data

Compound	No.	Solvent	³¹ P δ	¹ J(Pt-P)
(DPE)PtCl ₂		CDCl ₃	41.6	3636
(DPE)Pt(pz) ₂		CDCl ₃	33.4	3123
(DPE)Pt(pz) ₂ CdCl ₂	(1)	CD ₂ Cl ₂	35.8	3160
(DPE)Pt(pz) ₂ CdI ₂	(2)	CD ₂ Cl ₂	34.3	3131
(DPE)Pt(pz) ₂ HgBr ₂	(3)	CDCl ₃	35.0	3161
(DPE)Pt(pz) ₂ HgI ₂	(4)	CDCl ₃	33.9	3120
(DPE)Pt(pz) ₂ PdCl ₂	(7)	CDCl ₃	37.0br	n.o.
(DPE)Pt(pz) ₂ AuCl	(8)	CDCl ₃	35.2	n.o.
			38.6	n.o.

Acknowledgements

We would like to thank the Consiglio Nazionale delle Ricerche (CNR, Roma) and Ministero dell'Università e della Ricerca Scientifica e Tecnologica (M.U.R.S.T.) for financial support.

References

- (a) F. Bonati, A. Cingolani, G. Gioia Lobbia, D. Leonesi, A. Lorenzotti and C. Pettinari, *Gazz. Chim. Ital.*, 1990, **120**, 341; (b) C. Pettinari, C. Santini, D. Leonesi, P. Cecchi, *Polyhedron*, 1994, **13**, 1553; (c) C. Pettinari, A. Lorenzotti, A. Cingolani, D. Leonesi, M. Marra and F. Marchetti, *Gazz. Chim. Ital.*, 1993, **123**, 481.
- S. Trofimenko, *J. Am. Chem. Soc.*, 1970, **92**, 5118.
- G. Minghetti, G. Banditelli and F. Bonati, *Chem. Ind. (London)* 1977, 123.
- (a) B. C. Hui and G. L. Rempel, *Chem. Commun.*, 1970, 1195; (b) W. R. Cullen, T.-J. Kim, N. F. Han and J. Trotter, *Inorg. Chem.*, 1987, **26**, 514.
- M. Inoue and M. Kubo, *Coord. Chem. Rev.*, 1976, **21**, 1.
- (a) G. Banditelli, A. L. Bandini, F. Bonati and G. Minghetti, *Inorg. Chim. Acta*, 1982, **60**, 93; (b) G. Minghetti, G. Banditelli and F. Bonati, *J. Chem. Soc. Dalton Trans.*, 1979, 1851.
- D. H. Farrar and G. Ferguson, *J. Cryst. Spectrosc. Res.*, 1982, **12**, 465 and references therein.
- A. L. Bandini, G. Banditelli, G. Minghetti and F. Bonati, *Can. J. Chem.*, 1979, **57**, 3237.
- W. Levason and C. A. McAuliffe, "The coordination Chemistry of Mercury" in *The Chemistry of Mercury*, C. A. McAuliffe ed., McMillan Press, London (1977).
- J. G. A. Luijten and G. J. M. Van der Kerk, *Rec. Trav. Chim.*, 1963, **82**, 1181; J. G. A. Luijten, M. J. Janssen and G. J. M. Van der Kerk, *Rec. Trav. Chim.*, 1962, **81**, 202; R. Gassend, J. C. Maire, J. C. Pommier, *J. Organomet. Chem.*, 1977, **132**, 69.
- J. G. Vos and W. L. Groeneveld, *Inorg. Chim. Acta*, 1977, **24**, 123.
- K. Nakamoto, in *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th edn, Wiley Interscience, New York (1986).
- F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 4th edn, Wiley Interscience, New York (1980), p. 975.

Received: January 3, 1995 - Accepted: January 25, 1995 - Received in camera-ready format: February 12, 1995