Complexation Behaviour of a Morpholino-phosphine Containing 'Hard' and 'Soft' Donor Sites

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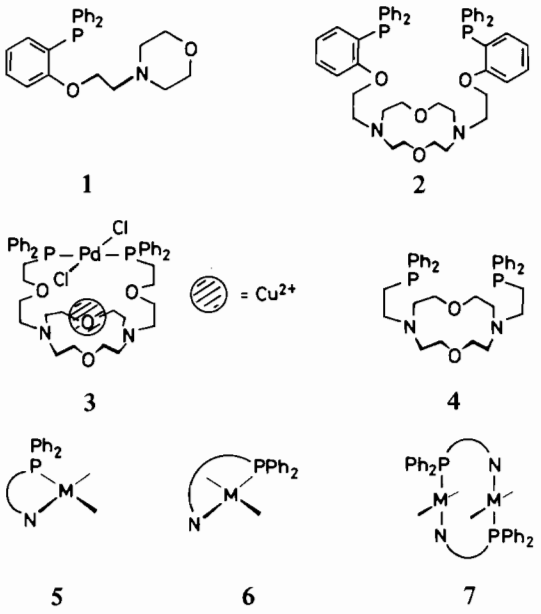
There is considerable interest in phosphines functionalized with additional 'hard' donor groups, which may form complexes containing two dissimilar metals [1]. The functionalization of macrocyclic systems (which are typically composed of nitrogen and oxygen donor atoms) with phosphine containing 'side arms', gives ligands which are capable of binding both 'hard' and 'soft' metal atoms simultaneously, for example **1**. It has been found that in phosphine functionalized macrocyclic systems [2], such as **2**, chelation of the 'soft' metals to the PN binding sites occurred to give five-membered P–M–N rings, rather than formation of a P–M–P moiety.



The functionalized phosphine (**3**), has been studied in order to probe the general coordination chemistry of the related functionalized macrocycle (**4**). Models suggest that coordination of the phosphine to a d^8-metal centre (e.g. Rh(I), Pd(II), Pt(II)) generates square-planar complexes which may possess a *cis* (**5**) or *trans* (**6**) arrangement about the metal. Dimerization may also occur to give species of type **7**.

Results and Discussion

The ligand **3** was prepared by reaction of chlorodiphenylphosphine with the Grignard reagent derived from N-(*o*-ethoxybromophenyl)morpholine in tetrahydrofuran.

Treatment of a CH_2Cl_2 solution of $[RhCl(CO)_2]_2$ with one (or two) equivalents of phosphine **3**, per metal atom, gave the yellow complex *trans*-$[RhCl(CO)(3)]_2$*. The infrared spectra revealed one carbonyl band, $\nu(CO)$ = 1965 cm^{-1}, and the positive ion Fast Atom Bombardment (FAB) mass spectrum [3] of the complex in a thioglycerol matrix revealed the presence of the $[RhCO)(3)]^+$ fragment ion, (m/e 522). A molecular weight determination in $CHCl_3$ suggests that the species is dimeric in solution {M_r = 1063 (calc. 558 (monomer) 1116 (dimer))}.

The ^1H NMR spectra at 298 K in CD_2Cl_2 contained four sets of triplets due to the methylene protons; two sets due to the morpholino protons and the other two sets due to the ethoxy methylene protons. With the nitrogen atom coordinated to the metal centre, and hence preventing intramolecular inversion, the two protons on each methylene group of the morpholino ring system would be expected to be inequivalent, thus four sets of signals due to the morpholino ring would be observed. As only two signals are observed there must be a rapid process which equivalences the two protons on the methylene groups. Rupture of the nitrogen–metal bond, inversion about the nitrogen atom, followed by nitrogen–metal bond reformation would be such a process. Indeed, at 223 K the two sets of morpholino triplets split into four broad signals, indicating inequivalence of the methylene protons, presumably due to rate limiting nitrogen–metal bond rupture. Further support for such a dissociative mechanism comes from the observed solvent dependence of the inversion process. The variable temperature ^1H NMR spectra in C_7D_8 and $(CD_3)_2CO$ were similar in form to those obtained in CD_2Cl_2 but showed a coalescence phenomenon occurring at higher temperatures. An intramolecular inversion mechanism would not be expected to be solvent dependent.

Treatment of a CH_2Cl_2 solution of $PdCl_2(PhCN)_2$ with one equivalent of the phosphine **3** gave the pale-brown complex *trans*-$[PdCl_2(3)]$.* Infrared and

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*All new compounds gave satisfactory analytical and spectroscopic data (^1H, ^{31}P $\{^1H\}$ NMR; infrared; m/e consistent with their structures. NMR data may be found in Table 1.

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TABLE I. ^{1}H[a] and ^{31}P[b] NMR Data for $Ph_2P(o\text{-}C_6H_4)OC(H_a)_2C(H_b)N(C(H_c)_2C(H_d)_2)_2O$ (3) and its Complexes

Compound	Solvent	T (°C)	δ H_a (J)	δ H_b (J)	δ H_c (J)	δ H_d (J)	δ ^{31}P	^{1}J (MP)
(3)[c]	$CDCl_3$	25	4.06(5.3)	2.53(5.3)	2.36(4.7)	3.51(4.7)	−14.2	
[RhCl(CO)(3)]	CD_2Cl_2	25	3.97(5.8)	2.44(5.8)	2.21(4.6)	3.47(4.6)	23.4	131
		−50	3.94(br)	2.41(br)	2.31(br)	3.49(br)	21.9	127
					1.91(br)	3.31(br)		
$[PdCl_2(3)]$[d]	$CDCl_3$	25	4.88 (N = 16.6)	3.05(br)	H_{c1} 2.01	H_{d1} 3.85	23.8	
				^{4}J(PH) = 3.5	H_{c2} 4.00	H_{d2} 4.37		
					^{2}J(HH) = 11.1	^{2}J(HH) = 12.3		
					$^{4}J(PH_{c1})$ = 10.5	$^{3}J(H_{c1}H_{d2})$ = 10.7		
		−50	4.79(vbr)	3.14(vbr)	H_{c1} 2.04	H_{d1} 3.89	24.6	
					H_{c2} 4.00	H_{d2} 4.36		
$[PdCl_2(3)_2]$	$CDCl_3$	25	4.15(br)	2.64(br)	2.25(br)	3.49(4.3)	15.9	
		−50	4.16(br)	2.64(br)	2.36(br)	3.52(br)	15.9	
					2.00(br)	3.42(br)		
$[PtCl_2(3)]$	$CDCl_3$	25	4.15(br)	2.65(br)	2.30(br)	3.50(4.5)	13.4	2696
		−50	4.10(br)	2.36(br)	2.06(br)	3.54(br)	n.d.	
					1.82(br)	3.42(br)		
$[PtCl_2(3)_2]$	$CDCl_3$	25	4.03(5.8)	2.52(5.8)	2.22(4.6)	3.51(4.6)	14.2	2702
		−50	4.05(br)	2.54(br)	2.34(br)	3.56(br)	n.d.	
					1.95(br)	3.39(br)		

[a]Measured at 360 MHz. Chemical shifts (δ) in ppm (±0.01 ppm) to high frequency of $SiMe_4$; coupling constants (J) in Hz (±0.1) br = broad, vbr = very broad. [b]Measured at 146 MHz. Chemical shifts (δ) in ppm (±0.1 ppm) to high frequency of 85% H_3PO_4; coupling constants (J) in Hz (±2). [c] ^{13}C NMR data. Measured at 22.6 MHz in CD_2Cl_2 at 25 °C. Chemical shifts (δ) in ppm (±0.1 ppm) to high frequency $SiMe_4$. δ C_a 68.7, C_b 58.8, C_c 55.6, C_d 68.3 ppm. [d]See text for details of decoupling experiments. Methylene protons H_a and H_b form an AA'XX' spin system with H_b further coupled to phosphorus. $N = \frac{1}{2}|J_{AX} + J_{AX'}|$. Methylene protons H_{c1}, H_{c2}, H_{d1} and H_{d2} form an AHMX spin system with H_{c1} further coupled to phosphorus.

Raman spectroscopy showed only one Pd–Cl stretching frequency (ν = 359 cm^{-1}) implying a *trans* geometry (**6**). The positive ion FAB mass spectra of the complex in a thioglycerol/glycerol matrix gave an isotope pattern centred at m/e 497 corresponding to the molecular ion $[Pd(3)]^{+\cdot}$.

The ^{31}P $\{^{1}H\}$ NMR spectra in $CDCl_3$ at 298 K consisted of one signal at δ +23.8 ppm. The ^{1}H NMR spectra in $CDCl_3$ at 298 K consisted of six sets of signals corresponding to the methylene protons, see Fig. 1. Homonuclear decoupling experiments showed that the signals at δ = 4.86 and δ = 3.05 ppm were mutually coupled, with the signal at δ = 3.05 ppm further coupled to phosphorus. These signals are due to the methylene protons of the ethoxy group forming an AA'XX' spin system, (the separation of the outer lines of the signal at δ = 4.86 ppm being $N = \frac{1}{2}|J_{AX} + J_{AX'}|$). The chemical shifts of δ = 4.86 and δ = 3.05 ppm are to higher frequency than normally observed (typically δ = 4.00 and δ = 2.50 ppm, respectively), probably because these protons are close to the metal. A similar effect has been observed in the complex $[Pd\{PPh(t\text{-}Bu)_2\}_2]$ [4a] (for further examples of this effect with other ligands see ref. 4b), where the proton resonance for the *ortho*-aromatic ring proton is strongly deshielded, resonating at δ = 9.33 ppm.

The other four sets of signals are due to four pairs of inequivalent protons in the morpholino ring. Homonuclear decoupling experiments showed which protons were mutually coupled, and also that the signal at δ = 2.01 ppm was further coupled to phosphorus. These results are consistent with the stereochemical arrangement depicted in Fig. 2. Again the chemical shift of H_{c2} and H_{d2} protons was moved to higher frequency, presumably due to the close proximity of these protons to the metal centre.

When a CH_2Cl_2 solution of $PdCl_2(PhCN)_2$ was treated with two equivalents of the phosphine **3** the complex *trans*-$[PdCl_2(3)_2]$* was formed in which **3** acts as a monodentate ligand binding through

*All new compounds gave satisfactory analytical and spectroscopic data (^{1}H, ^{31}P $\{^{1}H\}$ NMR; infrared; m/e consistent with their structures. NMR data may be found in Table I.

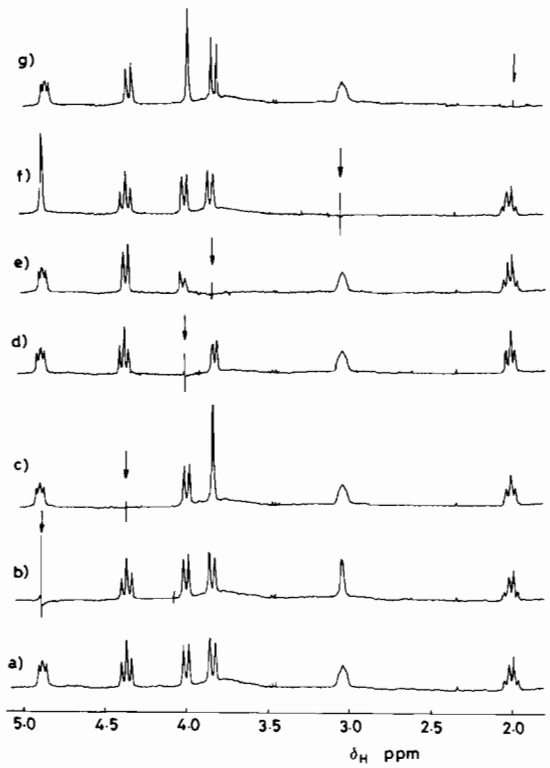

Fig. 1. (a) ^{1}H NMR spectra of the methylene proton region of $[PdCl_2(3)]$ in $CDCl_3$; with homonuclear decoupling at, (b) δ = 4.88, (c) δ = 4.37, (d) δ = 4.00, (e) δ = 3.85, (f) δ = 3.05, and (g) δ = 2.01 ppm.

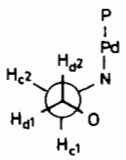

Fig. 2. Stereochemical arrangement of morpholino protons in $[PdCl_2(3)]$.

the phosphorus atom. The infrared and Raman spectra showed only one Pd–Cl stretching frequency (ν = 360 cm^{-1}) indicative of a *trans* geometry. The complex is non-conducting in acetone solution. The FAB mass spectra of the complex in a thioglycerol/glycerol matrix gave isotope patterns centred at m/e 497 and 888 corresponding to $[Pd(3)]^{+\bullet}$ and $[Pd(3)_2]^{+\bullet}$, respectively. A molecular weight determination in $CHCl_3$ indicates the species to be monomeric [M_r = 967 (calc. 960)].

The ^{1}H NMR spectra in $CDCl_3$ at 298 K consisted of four sets of broad signals due to the methylene protons. On cooling to 223 K the two signals of the morpholino ring separate into four. These results suggest that the morpholino ring may be undergoing a rapid chair-boat interconversion at 298 K via inversion about the nitrogen and oxygen atoms; at 223 K this process is slow enough on the NMR time scale to cause inequivalence of each methylene group.

Treatment of a MeCN solution of *cis*-$[PtCl_2(MeCN)_2]$ with one equivalent of the phosphine **3** gave the complex *trans*-$[PtCl_2(3)]$*. The infrared spectrum showed only one stretching frequency (ν = 350 cm^{-1}) ndicative of a *trans* geometry (**6**). The positive ion FAB mass spectra of the complex in a thioglycerol matrix gave an isotope pattern centred at m/e 586 corresponding to the fragment ion $[Pt(3)]^{+\bullet}$.

The ^{31}P {^{1}H} NMR spectra in $CDCl_3$ at 298 K consisted of a singlet (δ_P = 13.4 ppm) flanked by ^{195}Pt satellites [giving a 1:4:1 triplet (^{195}Pt I = ½, 33% natural abundance)] ^1J(PtP) = 2696 Hz.

The ^{1}H NMR spectra in $CDCl_3$ at 298 K consisted of four sets of triplets due to the methylene protons. Cooling to 223 K caused the methylene resonances of the morpholino ring to split. Again a nitrogen–metal bond cleavage/reformation process may be occurring.

Treatment of a MeCN solution of *cis*-$[PtCl_2(MeCN)_2]$ with two equivalents of the phosphine **3** gave the complex *trans*-$[PtCl_2(3)_2]$.* The ^{1}H NMR spectra in $CDCl_3$ at 298 K and 223 K were similar to the Pd analogue. A molecular weight determination in $CHCl_3$ indicated that species was monomeric (M_r = 1109 (calc. 1049)). The positive ion FAB spectra of the complex in a thioglycerol matrix consisted of an isotope pattern due to the molecular ion $[PtCl_2(3)_2]^{+\bullet}$, (m/e 1048). The ^{31}P {^{1}H} NMR spectra in $CDCl_3$ at 298 K consisted of a 1:4:1 triplet, δ = 14.2 ppm, ^1J(PtP) = 2702 Hz, consistent with *trans*-$[PtCl_2(3)_2]$ [5].

In conclusion it appears that the monophosphine d^8-metal complexes may either form 8-membered chelate ring complexes with a *trans* geometry (**6**) or may dimerize to give 16-membered rings (**7**). In solution, dynamic behaviour is observed and a rapid nitrogen–metal bond rupture/reformation process may be occurring. Complexes containing two phosphines per metal atom are only formed with Pd(II) and Pt(II). These complexes prefer a *trans* geometry with the ligand binding through the phosphorus atom.

Experimental

All operations were carried out under an atmosphere of argon.

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Preparation of N-(o-ethoxyphenyldiphenylphosphino)morpholine (3)

To a solution of N-(*o*-ethoxybromophenyl)morpholine (4.00 g, 14.0 mmol) in dry tetrahydrofuran (200 cm^3), was added magnesium turnings (0.342 g, 14.0 mmol) and a small crystal of iodine. After stirring for 3 h, a solution of chlorodiphenylphosphine (3.08 g, 14.0 mmol) in tetrahydrofuran (10 cm^3) was added and the mixture stirred (1 h). The mixture was filtered and the filtrate evaporated to yield a pale-yellow oil which was redissolved in toluene (10 cm^3) and passed down a short column of alumina. Removal of the solvent *in vacuo* at 293 K gave a colourless oil (5.05 g, 92%). *Anal.* Found: C, 73.5; H, 6.91; N, 3.40; P, 7.60. $C_{24}H_{26}NO_2P$ requires: C, 73.3; H, 6.65; N, 3.58; P, 7.93%. m/e = 392 (M^+ +1), 391 (M^+), 303, 279, 276, 199, 185.

Preparation of trans-[RhCl(CO)(3)]·0.7C_6H_6

To a solution of **3**, (0.100 g, 0.256 mmol) in CH_2Cl_2 (2 cm^3), was added a solution of $[RhCl(CO)_2]_2$ (0.048 g, 0.2 mmol) in CH_2Cl_2 (2 cm^3). The solvents were removed under reduced pressure to leave an oily residue. This was dissolved in C_6H_6 (3 cm^3) and the product precipitated by the slow addition of petroleum ether (b.p. 40–60 °C) (~10 cm^3). The cream product was collected and dried *in vacuo* over P_2O_5. The same product was obtained if two equivalents of the phosphine **3**, per metal atom, was used. *Anal.* Found: C, 57.1; H, 4.93; N, 2.28. $C_{25}H_{26}NO_3PRh \cdot 0.7C_6H_6$ requires: C, 57.7; H, 5.01; N, 2.32%.

Preparation of trans-[PdCl$_2$(3)]

To a solution of **3** (0.125 g, 0.32 mmol) in benzene (3 cm^3) was added a solution of $PdCl_2(RhCN)_2$ (0.12 g, 0.313 mmol) in dichloromethane (3 cm^3). After removal of solvents under reduced pressure, the residue was triturated with ether to yield a pale brown solid which was filtered and dried *in vacuo* over P_2O_5 (517 mg, 91%). *Anal.* Found: C, 50.4; H, 4.71; N, 2.20. $C_{24}H_{26}Cl_2NO_2PPd$ requires: C, 50.7; H, 4.58; N, 2.46%.

Preparation of trans-[PdCl$_2$(3)$_2$]

This was prepared as described above for $[PdCl_2(3)]$, but using (0.114 g, 0.29 mmol) of **3**, and (0.055 g, 0.143 mmol) of $PdCl_2(PhCN)_2$, to yield a brown solid (110 mg, 80%). *Anal.* Found: C, 59.8; H, 5.73; N, 2.61; Pd, 10.8. $C_{48}H_{52}Cl_2N_2O_4P_2Pd$ requires: C, 60;1; H, 5.42; N, 2.92. Pd, 11.1%.

Preparation of trans-[PtCl$_2$(3)]·0.5CH_2Cl_2

To a solution of **3** (0.05 g, 0.128 mmol) in acetonitrile (1 cm^3) was added a solution of *cis*-$[PtCl_2(MeCN)_2]$ (44 mg, 0.126 mmol) in acetonitrile (2 cm^3). After removal of solvent under reduced pressure, the residue was triturated with ether and a yellow solid collected, and dried *in vacuo* over P_2O_5. The product was recrystallised from CH_2Cl_2/EtOH (1:3) to give a yellow solid (61 mg, 68%). *Anal.* Found: C, 42.4; H, 4.16; N, 1.61. $C_{24}H_{26}Cl_2NO_2PPt \cdot 0.5CH_2Cl_2$ requires: C, 42.2; H, 3.94; N, 1.97%.

Preparation of trans-[PtCl$_2$(3)$_2$]

To a solution of **3** (0.1 g, 0.256 mmol), in acetonitrile (2 cm^3) was added a solution of *cis*-$PtCl_2(MeCN)_2$ (0.044 g, 0.126 mmol) in acetonitrile (2 cm^3). After stirring for two hours, the solvent was removed under reduced pressure, and the residue dissolved in dichloromethane (2 cm^3). Upon slow addition of methanol (3 cm^3), a yellow solid formed which was filtered off and dried *in vacuo* (92 mg, 70%). *Anal.* Found: C, 54.6; H, 5.21; N, 1.55. $C_{48}H_{52}Cl_2N_2O_4P_2Pt$ requires: C, 54.9; H, 4.96; N, 1.33%.

Acknowledgements

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