Chelate-stabilised Alcohol- and Alkoxo-palladium(II) Complexes derived from the Ligands $Ph_2PCH_2CR_2OH$ (R = Me or H)

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The ligands $Ph_2PCH_2CRR'OH$ [R = R' = Me (**1a**), R = Me, R' = H (**1b**); R = R' = H (**1c**)] form complexes of stoicheiometry $PdCl_2(Ph_2PCH_2CRR'OH)_2$ which are in the neutral form *trans*-$[PdCl_2(Ph_2PCH_2CRR'OH)_2]$ where R,R' = Me or H(**2a**)—(**2c**) in $CDCl_3$ solution, and the ionic form *cis*-$[PdCl(Ph_2PCH_2CRR'OH)(Ph_2PCH_2CRR'OH)]Cl$, where R = R' = Me (**4a**) or R = Me, R' = H (**4b**) in CD_3OD solution. The complex $[PdCl_2(Ph_2PCH_2CH_2OH)_2]$ dissolves in D_2O to give an acidic solution of pH 3.9. Treatment of *trans*-$[PdCl_2(Ph_2PCH_2CRR'OH)_2]$ (**2a**) or (**2b**) with $AgClO_4$ in acetone gives *cis*-$[Pd(Ph_2PCH_2CRR'OH)_2][ClO_4]_2$ (**6a**) or (**6b**). Deprotonation of (**6a**) or (**6b**) with Et_3N in $CDCl_3$ or deprotonation of $[PdCl_2(Ph_2PCH_2CRR'OH)_2]$ (**2a**)—(**2c**) with NaOH in ethanol gave the bis(alkoxo) complexes $[Pd(Ph_2PCH_2CRR'O)_2]$ (**7a**)—(**7c**). Deprotonation of $[PdCl_2(Ph_2PCH_2CH_2OH)_2]$ (**2c**) with Et_3N in $CDCl_3$ gave a mixture of three Pd species, including the binuclear complex $[Pd_2(\mu\text{-}Ph_2PCH_2CH_2O)_2(Ph_2PCH_2CH_2OH)_2]Cl_2$ (**9**). All products have been characterised by a combination of elemental analysis, i.r., ^1H, and ^{31}P n.m.r. spectroscopy.

The chemistry of alcohol- or alkoxo-palladium(II) complexes is largely unexplored because isolable complexes are rare[1] and often unstable with respect to formation of hydrides or palladium(0). However such complexes are postulated to be intermediates in stoicheiometric or catalytic reactions of palladium complexes in alcoholic solvents.[2,3]

We have recently shown[4–6] that kinetically very stable alcohol- and alkoxo-platinum(II) complexes can be synthesised by incorporating the O donor into the chelating ligands (**1a**)—(**1c**). We now report the extension of this principle to the synthesis of stable alcohol- and alkoxo-palladium(II) complexes.

Results and Discussion

The ligands (**1a**)—(**1c**) react with $[PdCl_2(NCPh)_2]$ in dichloromethane to give pale yellow complexes of stoicheiometry $[PdCl_2(Ph_2PCH_2CRR'OH)_2]$. The number and position of the ν(Pd–Cl) bands in the i.r. spectra (Table 1) of these solids indicate that *trans* complexes (**2a**)—(**2c**) are present; only for the complex of the least bulky ligand (**1c**) is there i.r. evidence of the presence of a *cis* isomer (**3c**).

The *trans* geometry of (**2a**) persists in $CDCl_3$, as shown by the virtual triplet observed for the ^1H n.m.r. signal of the PCH_2 protons. The similarity of δ(P) for the three complexes (**2a**)—(**2c**) in $CDCl_3$ suggests they all have the same geometry in this solvent. Their $^{31}P\text{-}\{^1H\}$ n.m.r. spectra remained sharp singlets over the temperature range −60 to +25 °C.

Complex (**2a**) dissolves in methanol to give a conducting solution (Table 1), the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of which consists of a single resonance at +37.1 p.p.m., some 26 p.p.m. to high frequency of δ(P) for (**2a**) in $CDCl_3$. The signal broadens as the temperature is lowered and splits into two broad signals at −75 °C which become two sharp, equally intense, singlets at −100 °C (δ +47.6 and +29.5 p.p.m.). These spectral changes are interpreted in terms of the interconversions shown in the Scheme. At −100 °C structure (**4a**) is static on the n.m.r. timescale and hence two ^{31}P n.m.r. signals are seen for the inequivalent P_A and P_B with P_A at high frequency, as expected for a phosphorus that is part of a five-membered ring.[7] The coupling $^2J(P_AP_B)$ was not resolved and must therefore be less than 3 Hz (the linewidth) which is consistent with the *cis* geometry of (**4a**). At ambient temperatures, rapid interconversion of the tautomers (**4a**) and (**4a'**) takes place, equilibrating the signals for P_A and P_B, giving a time-averaged single peak. The observed conductivity of methanol solutions of (**4a**) is typical of a 1:1 electrolyte but it is possible that the interconversion of (**4a**) and (**4a'**) takes place *via* the transient formation of the neutral isomer (**3a**).

Table 1. Elemental analysis, i.r. spectral, and conductivity data

Complex	Analysis[a]/% C	H	ν(Pt–Cl)[b]/ cm⁻¹	Λ[c]/ Ω^{-1} cm² mol⁻¹
(**2a**)	55.40 (55.40)	5.50 (5.50)	350	78
(**2b**)	54.75 (54.10)	5.25 (5.15)		—
(**2c**)/(**3c**)	51.75 (52.75)	4.75 (4.75)	350, 330	166[d]
(**6a**)	46.15 (46.75)	4.50 (4.65)		170
(**6b**)	45.15 (45.40)	4.25 (4.30)		202
(**7a**)·3.5H_2O	55.95 (56.20)	6.25 (6.35)		—

[a] Calculated values in parentheses. [b] Nujol mulls. [c] In acetone (10^{-3} dm⁻³). [d] In water (10^{-3} mol dm⁻³).

Complex (**2b**) also dissolves in methanol to give solutions showing variable-temperature n.m.r. behaviour similar to (**4a**) and is therefore assigned the analogous structure (**4b**); *meso* and D, L diastereoisomers of (**4b**) were detected (see Table 2).

Complex (**2c**)/(**3c**) is insoluble in methanol but, remarkably, is slightly soluble in water giving a conducting solution with pH 3.9 (10^{-3} mol dm⁻³). The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum in D_2O is a broad singlet ($w_{\frac{1}{2}}$ 60 Hz) at 49.6 p.p.m. Low-temperature n.m.r. studies were precluded by the small liquid range of D_2O but it can be deduced from the high-frequency chemical shift that chelates are present and from the solution conductivity that salts are present; we tentatively assign structure (**4c**) to this aqueous species. It is likely that (**4c**) is fluxional in the same way that (**4a**) and (**4b**) are (Scheme). The pH of the solution shows that (**4c**) is significantly ionised, presumably to give alkoxo species such as (**5**).

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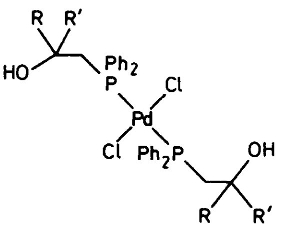
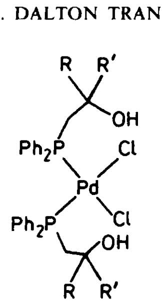
$Ph_2PCH_2CMe_2OH$ (**1a**)
$Ph_2PCH_2CMeHOH$ (**1b**)
$Ph_2PCH_2CH_2OH$ (**1c**)





(**2a**) R = R' = Me (**3a**)
(**2b**) R = Me, R' = H (**3b**)
(**2c**) R = R' = H (**3c**)

Table 2. Phosphorus-31 n.m.r. data[a]

Complex	Solvent	$\delta(P_A)$ p.p.m.	$\delta(P_B)$ p.p.m.	$^2J(P_AP_B)$/Hz
(**2a**)	$CDCl_3$	+9.1		
(**2b**)	$CDCl_3$	+11.9		
(**2c**)	$CDCl_3$	+12.3		
(**4a**)[b]	CD_3OD	+47.6	+29.5	<3
(**4b**)[b]	CD_3OD	+51.3	+33.7	<3
		+50.2	+36.1	<3
(**4c**)	D_2O	+49.6		
(**6a**)	$(CD_3)_2CO$	+47.0		
(**6b**)	$(CD_3)_2CO$	+62.0		
		+60.9		
(**7a**)	$CDCl_3$	+44.6		
(**7b**)	$CDCl_3$	+52.5		
		+51.7		
(**7c**)	$CDCl_3$	+56.4		
(**8a**)[b]	$CDCl_3$	+39.3	+ 8.5	479
(**8b**)[b]	$CDCl_3$	+44.8	+15.5	473
		+45.9	+16.6	474
(**9**)	$CDCl_3$	+68.9	+20.8	15
		+64.2	+20.4	10

[a] At 36.4 MHz and +25 °C unless stated otherwise. Chemical shifts are in p.p.m. to high frequency of 85% H_3PO_4 ($\pm$0.2 p.p.m.), coupling constants in Hz ($\pm$5 Hz). Where there are two P resonances, P_A is in the chelate ring. [b] At −60 °C.

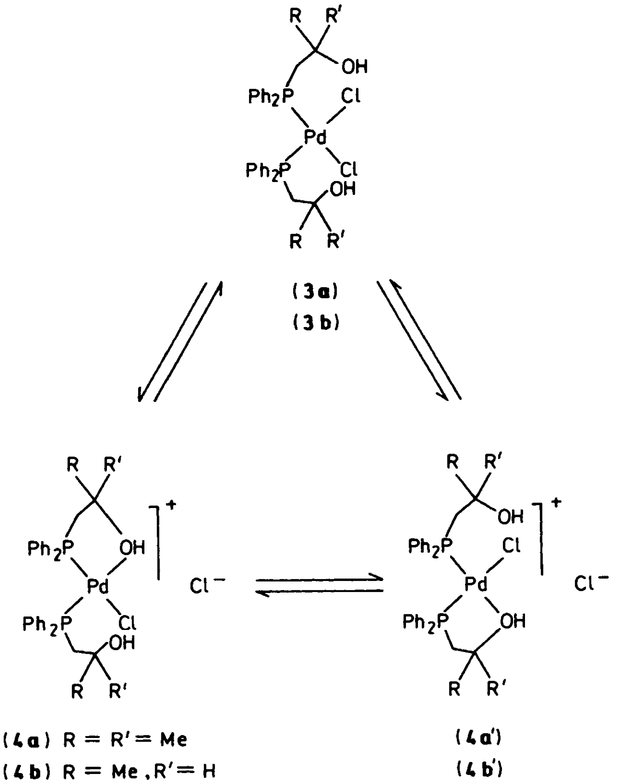
Table 3. Proton n.m.r. data[a]

Complex	Solvent	$\delta(PCH_2)$[b]	δ(HOCH)	δ(Me)	δ(OH)
(**2a**)[c]	$CDCl_3$	2.90(t)	—	1.04	3.75
(**2b**)[d]	$CDCl_3$	3.13	3.90	1.23	
(**6a**)[c]	$(CD_3)_2CO$	3.45(d)	—	1.45	8.75
(**6b**)[d]	$(CD_3)_2CO$	3.50, 2.85	4.01	1.53	
		3.25—3.16	4.39	1.35	
(**7a**)[c]	$CDCl_3$	2.80(d)	—	1.35	3.68[e]

[a] In $CDCl_3$; chemical shifts ($\pm$0.01) to high frequency of $SiMe_4$. [b] t = Virtual triplet, d = filled-in doublet. [c] At 90 MHz. [d] At 400 MHz. [e] Includes the signal for 3.5 H_2O of crystallisation.

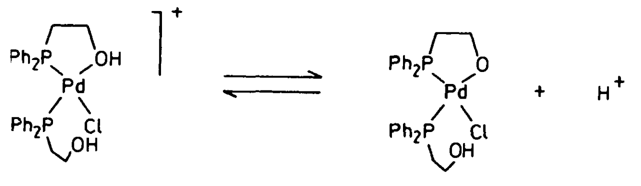
Treatment of acetone suspensions of $[PdCl_2(Ph_2PCH_2CRR'OH)_2]$ (**2a**) or (**2b**) with $AgClO_4$ gave dicationic bis(chelate) complexes (**6a**) and (**6b**) (see Tables 1—3 for characterising data). The filled-in doublet appearance of the PCH_2 ^1H n.m.r. signal of (**6a**) is consistent with the *cis* geometry and the high-frequency ^{31}P chemical shifts are expected for the bis(chelate) structures (**6a**) and (**6b**). These salts dissolve in water to give acidic solutions [for 10^{-3} mol dm^{-3} solutions pH 4.4 (**6a**) and 4.2 (**6b**)].

The deprotonation of (**6a**) with Et_3N in $CDCl_3$ gave the bis(alkoxo)palladium(II) complex (**7a**) quantitatively. Complex (**7a**) was characterised by (*i*) elemental analysis (Table 1), (*ii*) the high-frequency δ(P) as expected for the chelate, and (*iii*) the filled-in doublet appearance of the PCH_2 ^1H n.m.r. signal confirming the *cis* geometry of (**7a**). Complex (**6b**) was similarly deprotonated to give (**7b**) as a mixture of diastereoisomers and characterised in solution (Table 2).

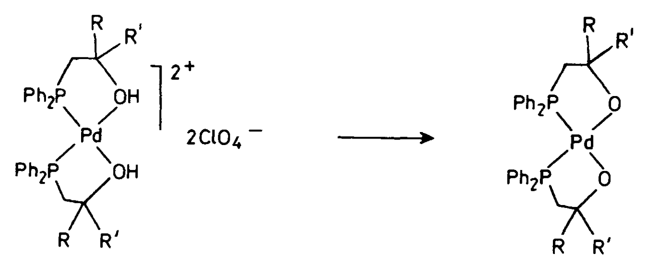


Scheme.

The complexes $[PdCl_2(Ph_2PCH_2CRR'OH)_2]$ (**2a**)—(**2c**) can also be deprotonated but the products depend on the base and the complex. In alcohols the complexes $[PdCl_2(Ph_2PCH_2CRR'OH)_2]$ have *cis*, ionic structures (**4a**)—(**4c**) (see above) and treatment of such solutions with NaOH gave the *cis*-alkoxo complexes (**7a**)—(**7c**). However, in $CDCl_3$, $[PdCl_2(Ph_2PCH_2CRR'OH)_2]$ have the *trans*, neutral structures (**2a**) and (**2b**) (see above) and treatment of these solutions with Et_3N gave predominantly the *trans*, mono(alkoxo) complexes (**8a**) and (**8b**), identified from their ^{31}P-{^1H} n.m.r. spectra (Table 2): inequivalent ^{31}P nuclei, one at high frequency (P_A in the chelate ring) and a large $^2J(P_AP_B)$ showing P_A and P_B are *trans*. Solutions of (**8a**) or (**8b**) generated as above were contaminated

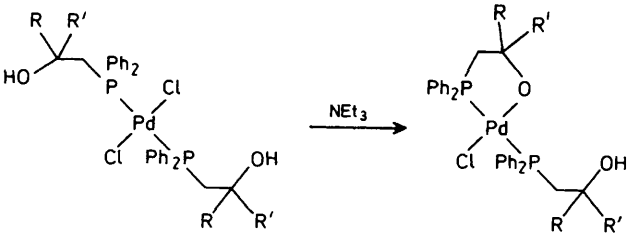


(4c) (5)



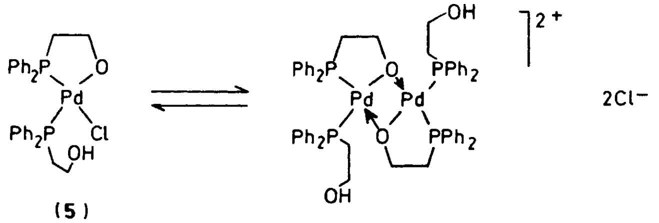
(6a) R = R′ = Me
(6b) R = Me, R′ = H

(7a) R = R′ = Me
(7b) R = Me, R′ = H
(7c) R = R′ = H



(2a)
(2b)

(8a) R = R′ = Me
(8b) R = Me, R′ = H



(5) (9)

with up to 15% of the bis(alkoxo) complex (**7a**) or (**7b**). The signals for (**8a**) and (**8b**) were sharp.

A suspension of complex (**2c**) in $CDCl_3$ dissolves upon addition of Et_3N to give a yellow solution which gave a single broad ^{31}P resonance at ambient temperatures. It is clear that three species are present from the $^{31}P-\{^1H\}$ n.m.r. spectrum at -50 °C. A singlet at $+56.4$ p.p.m. (15%) is most likely due to the bis(alkoxo) complex (**7c**) discussed above. The ^{31}P n.m.r. spectra of the other two species (70 and 15%) are AB patterns, the data for which (Table 2) are consistent with the presence of one chelate and one non-chelate phosphine *cis* to each other. The possible structures for these species are (**5**), the species postulated to be present in aqueous solutions of (**4c**) (see above) and the dimer (**9**), the platinum analogue of which we have recently identified.[6]

All the alcohol- and alkoxo-palladium(II) complexes described above are remarkably air, water, and thermally stable. It is therefore clear that, like alkoxoplatinum(II) complexes, [5,8] the observed instability of alkoxopalladium(II) complexes is due to kinetic factors rather than inherently weak Pd–O bonds.

Experimental

The ligands (**1a**)—(**1c**) were prepared by literature methods.[5,6] General experimental procedures were as previously described.[5]

Preparation of $[PdCl_2(Ph_2PCH_2CMe_2OH)_2]$.—A solution of $Ph_2PCH_2CMe_2OH$ (0.48 g, 1.86 mmol) in dichloromethane (5 cm^3) was added to $[PdCl_2(NCPh)_2]$ (0.34 g, 0.89 mmol) in dichloromethane (5 cm^3) to give a pale yellow solution. The solution was stirred for 16 h, reduced in volume to 1 cm^3, and then diethyl ether (5 cm^3) and light petroleum (b.p. 60—80 °C, 5 cm^3) were added to give the yellow solid product (0.55 g, 89%). The complexes $[PdCl_2(Ph_2PCH_2CMeHOH)_2]$ and $[PdCl_2(Ph_2PCH_2CH_2OH)_2]$ were made similarly in 89 and 86% yields respectively. The latter compound was difficult to purify because of its lack of solubility in common organic solvents (see Table 1 for microanalytical data).

Preparation of $[Pd(Ph_2PCH_2CMe_2OH)_2][ClO_4]_2$ (**6a**).—A solution of $AgClO_4$ (0.22 g, 1.06 mmol) in toluene (5 cm^3) was added to a solution of $[PdCl_2(Ph_2PCH_2CMe_2OH)_2]$ (0.167 g, 0.24 mmol) in toluene (15 cm^3) to give a yellow precipitate immediately. The mixture was rapidly stirred for 1 h to coagulate the solid. The toluene was then removed under reduced pressure and the residue stirred with dichloromethane (75 cm^3). The resulting yellow solution was filtered to remove silver salts and then reduced in volume to 10 cm^3. Diethyl ether (10 cm^3) was added and the mixture cooled to 0 °C to give the pale yellow product (0.175 g, 88%). The complex $[Pd(Ph_2PCH_2CMeHOH)_2][ClO_4]_2$ (**6b**) was made similarly in 79% yield.

Preparation of $[Pd(Ph_2PCH_2CMe_2O)_2]$ (**7a**).—A solution of $[PdCl_2(Ph_2PCH_2CMe_2OH)_2]$ (0.10 g, 0.15 mmol) in ethanol (5 cm^3) was stirred with NaOH (0.10 g, 2.50 mmol) to give a clear solution which gradually became turbid over a period of 15 min. A few drops of water were added to give a clear yellow solution. After 1 h the ethanol was removed under reduced pressure and the residue triturated with water (5 cm^3) and the tan product filtered off (0.07 g, 71%). The complex $[Pd(Ph_2PCH_2CH_2O)_2]$ (**7c**) was obtained in a similar fashion in low (21%) yield. This material decomposes slowly in solution to give palladium metal. Complexes (**7a**) and (**7b**) were obtained quantitatively (as shown by $^{31}P-\{^1H\}$ n.m.r. spectroscopy) by treatment of (**6a**) with Et_3N in $CDCl_3$.

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References

1 C. D. Montgomery, N. C. Payne, and C. J. Willis, *Inorg. Chim. Acta*, 1986, **117**, 103.
2 H. E. Bryndza, S. A. Kretchmar, and T. H. Tulip, *J. Chem. Soc., Chem. Commun.*, 1985, 977 and refs. therein.
3 H. Alper, B. Despeyroux, and J. Woell, *Tetrahedron Lett.*, 1983, **24**, 5691.
4 N. W. Alcock, A. W. G. Platt, and P. G. Pringle, *Inorg. Chim. Acta*, 1987, **128**, 215.

5 N. W. Alcock, A. W. G. Platt, and P. G. Pringle, *J. Chem. Soc., Dalton Trans.*, 1987, 2273.

6 N. W. Alcock, A. W. G. Platt, and P. G. Pringle, *J. Chem. Soc., Dalton Trans.*, 1989, 139.

7 P. E. Garrou, *Inorg. Chem.*, 1975, **14**, 1435.

8 H. E. Bryndza, L. K. Fong, R. A. Paciello, W. Tam, and J. E. Bercaw, *J. Am. Chem. Soc.*, 1987, **109**, 1444.

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