Water-Soluble Tris(hydroxymethyl)phosphine Complexes with Nickel, Palladium, and Platinum. Crystal Structure of [Pd{P(CH₂OH)₃}₄]·CH₃OH

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The large-scale synthesis of the water-soluble phosphine P(CH₂OH)₃ (**1**) from either PH₃ or [P(CH₂OH)₄]Cl is described. Treatment of [MX₂(COD)] (M = Pt or Pd; X = Cl, Br, or I; COD = cycloocta-1,5-diene) with **1** gives the corresponding [MX₂{P(CH₂OH)₃}₂] (**2–7**) complexes which are soluble in water, methanol, or dmso but insoluble in most common organic solvents. Methanolic or dmso solutions of the organoplatinum complex [Pt(CH₃)₂{P(CH₂OH)₃}₂] (**8**) can be generated from **1** and [Pt(CH₃)₂(COD)], but **8** decomposes in concentrated solutions. Treatment of [PtCl(CH₃)(COD)] with **1** gives the stable, water-soluble mixture of organoplatinum complexes *cis*- and *trans*-[PtCl(CH₃){P(CH₂OH)₃}₂] (**9a,b**) which reacts with LiBr or LiI to give the corresponding [PtX(CH₃){P(CH₂OH)₃}₂] (**10** and **11**). The zerovalent complex [Ni{P(CH₂OH)₃}₄] (**12**) is made by adding **1** in methanol to a toluene solution of [Ni(COD)₂] whereas the best method for synthesizing the palladium analogue **13** is by addition of an aqueous solution of **1** to a CH₂Cl₂ solution of [Pd(PPh₃)₄] followed by isolation of the product from the aqueous layer. The crystal structure of [Pd{P(CH₂OH)₃}₄]·CH₃OH shows the Pd(0) center to be tetrahedrally coordinated by P(CH₂OH)₃ ligands (Pd–P 2.326 (3), 2.321 (1) Å). The hydroxyl groups are all involved in either intramolecular or intermolecular OH⋯O hydrogen bonding (O⋯O distances 2.68 (1)–2.76 (1) Å). Treatment of a suspension of [Pt(PPh₃)₄] or [Pt(COD)₂] in methanol with **1** gave a compound with composition [Pt{P(CH₂OH)₃}₄]·H₂O (**14**), which, from NMR and IR spectroscopy in solution, is shown to be an equilibrium mixture of [Pt{P(CH₂OH)₃}₄] (**14a**) and the five-coordinate hydridoplatinum(II) complex [PtH{P(CH₂OH)₃}₄]OH (**14b**). The chemical and spectroscopic properties of the complexes of **1** are compared with analogous PMe₃ and PEt₃ species, and it is concluded that, in many respects, **1** has coordination properties that would be expected of a small hydrophilic trialkylphosphine but, in addition, has some unique properties associated with the hydrogen bonding present among the coordinated P(CH₂OH)₃ ligands.

Introduction

There is increasing interest in organometallic chemistry in aqueous media[1–6] because of its applications in catalysis and organic sythesis,[2–5] its relevance to the Rhône-Poulenc hydroformylation process,[2] and its novelty.[6] The most common method employed to transfer organometallic chemistry from organic to

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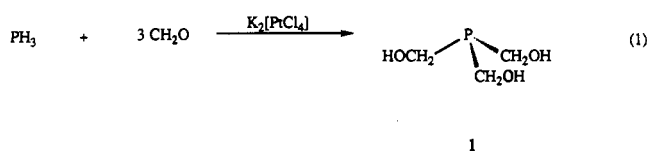
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aqueous media has been to use hydrophilic arylphosphine ligands (especially those containing SO₃Na substituents), and comparatively little work has been carried out on hydrophilic trialkylphosphines.[1]
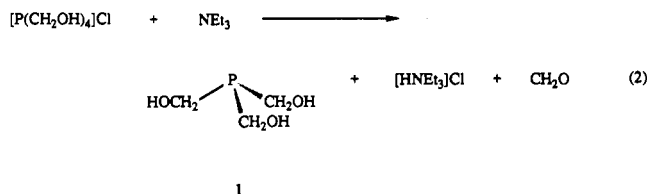
Tris(hydroxymethyl)phosphine (1) is an unusual trialkylphosphine in being a crystalline solid at room temperature (mp 58 °C), water soluble, and moderately air stable. In view of these favorable properties, it is surprising that its coordination chemistry has been little studied.[7,8] In this paper, we report that complexes of 1 with platinum(II) and palladium(II) are water soluble but in most other respects they are similar to analogous PMe₃ or PEt₃ complexes whereas complexes of 1 with nickel(0), palladium(0), and platinum(0) have exceptional properties in terms of stability and reactivity.

Results and Discussion

The addition of PH₃ to CH₂O in water in the presence of K₂[PtCl₄] (eq 1) is an efficient route[9] to P(CH₂OH)₃ (1) (see Experimental Section) but requires the handling of highly toxic PH₃ on a large scale which may have been a significant impediment

$$PH_3 \quad + \quad 3\ CH_2O \quad \xrightarrow{K_2[PtCl_4]} \quad HOCH_2 - \overset{P}{\underset{CH_2OH}{\overset{|}{\diagdown}}} CH_2OH \qquad (1)$$

1

to the development of the chemistry of 1. An alternative synthesis of 1, not requiring PH₃, is the reaction of the readily available phosphonium salt [P(CH₂OH)₄]Cl with base[10] (eq 2). Phosphine 1 can be readily made on a large scale (>50 g) using our modification of this route (see Experimental Section).

$$[P(CH_2OH)_4]Cl \quad + \quad NEt_3 \quad \longrightarrow$$
$$HOCH_2 - \overset{P}{\underset{CH_2OH}{\overset{|}{\diagdown}}} CH_2OH \quad + \quad [HNEt_3]Cl \quad + \quad CH_2O \qquad (2)$$

1

Platinum(II) and Palladium(II) Complexes of P(CH₂OH)₃. A reliable synthesis of the dihalo complexes [MX₂{P(CH₂OH)₃}₂] (2–7) is from the corresponding [MX₂(COD)] (COD = cycloocta-1,5-diene) and ligand 1. The dibromo and diiodo complexes can also be made by metathesis of the dichloro complexes using LiBr or LiI in water or methanol. Chatt et al.[7a] previously reported the synthesis of the dichloro complexes 2 and 5 from the appropriate [MCl₄]²⁻ salt, but in our hands this route gave poor yields of impure products. All the complexes 2–7 are soluble in water, though the diiodo complexes only sparingly so; 10⁻² M
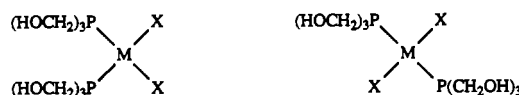
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	C	H	halogen
2	13.80 (14.00)	3.65 (3.55)	14.10 (13.80)
3	12.30 (11.95)	3.00 (3.00)	26.30 (26.50)
4	10.95 (10.35)	2.70 (2.60)	36.10 (36.40)
5	17.00 (16.95)	4.30 (4.25)	16.70 (16.65)
6	13.75 (14.00)	3.65 (3.55)	30.90 (31.10)
7	11.90 (11.85)	3.15 (3.00)	41.80 (41.75)
9	17.25 (17.05)	4.45 (4.30)	6.95 (7.20)
11	14.20 (14.40)	3.80 (3.65)	21.95 (21.65)
12	26.20 (26.00)	6.65 (6.55)	
13	24.60 (24.65)	6.55 (6.35)	
14	20.45 (20.30)	5.40 (5.40)	

[a] Calculated values in parentheses.

aqueous solutions of the dichloro complexes 2 and 5 have pH's in the range 3–4, indicating that coordination of P(CH₂OH)₃ has increased the acidity of the hydroxyl protons since the pH of 10⁻² M solutions of P(CH₂OH)₃ is ca. 6.5. None of the complexes is soluble in CH₂Cl₂, CHCl₃, or toluene, but they are freely soluble in MeOH or dmso.

|				
2a M = Pt X = Cl			**4b** M = Pt X = I	
3a M = Pt X = Br			**5b** M = Pd X = Cl	
4a M = Pt X = I			**6b** M = Pd X = Br	
5a M = Pd X = Cl			**7b** M = Pd X = I	
6a M = Pd X = Br				
7a M = Pd X = I				

Complexes 2–7 have been characterized by a combination of elemental analysis and IR and NMR spectroscopy; these characterizing data are collected in Tables I–III. The geometries of complexes 2–7 were established in solution by ³¹P{¹H}, ¹⁹⁵Pt{¹H}, ¹³C{¹H}, and ¹H NMR and in some cases by comparison of these data with known PMe₃ or PEt₃ analogues.[11] The tendency to form the trans isomer is in the order Pd > Pt and I > Br > Cl, as would be expected from many previous studies of [MX₂(PR₃)₂] complexes.[11] Hence in the platinum series 2–4, only in dmso solutions of the diiodo species were significant amounts of trans isomer **4b** detected (freshly generated solutions of 4 contained 66% trans isomer but after 14 h this proportion had reduced to 9%); in the palladium series 5–7 the dichloro complex is almost exclusively *cis*-**5a** while the dibromo complex 6 in aqueous solution exists as a 10:1 *cis*-**6a**:*trans*-**6b** mixture; similarly, the diiodo complex 7 is a 1:11 *cis*-**7a**:*trans*-**7b** mixture in dmso solution.

Treatment of [Pt(CH₃)₂(COD)] with P(CH₂OH)₃ in dmso or methanol gave [Pt(CH₃)₂{P(CH₂OH)₃}₂] (8) quantitatively. Although 8 has been fully characterized by NMR spectroscopy

8	**9a**	**9b** X = Cl
		10 X = Br
		11 X = I
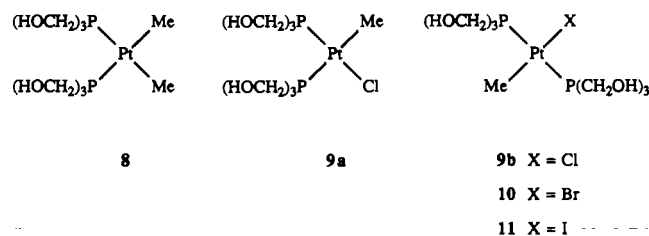
in solution (see Tables II and III), attempts to isolate this species from methanol were unsuccessful because of rapid decomposition

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Table II. $^{31}P\{^1H\}$ NMR Data[a] for $P(CH_2OH)_3$ Complexes and Analogous PMe_3 and PEt_3 Complexes

	P(CH$_2$OH)$_3$			PMe$_3$		PEt$_3$	
	δ(P)	^1J(PtP)	$\Delta\delta^b$	^1J(PtP)	$\Delta\delta^b$	^1J(PtP)	$\Delta\delta^b$
2	9.5	3431	33.5	3480	38.7^c	3516	29.1^d
3	10.1	3369	34.1	3426	38.9^c	3479	29.1^d
4a	9.7	3227	33.7	3306	36.7^c	3374	26.4^d
4b	−6.6^e	2162	17.4	2230	30.5^c	2273	20.4^d
5a	34.4^e		58.4		60.8^c		54.5^f
5b	14.8		38.8		50.8^c		38.2^d
6a	31.8		55.8		61.0^c		
6b	7.1		31.1		45.8^c		35.2^d
7a	29.4^e		53.4				
7b	1.3^e		25.3		34.8		28.8^d
8	8.8^e	1765	32.8			1846	29.6^d
9a	11.7^e	2817	35.7			2821	36.6^g
9b	13.3^{e,h}	1650	37.3			1719	35.0^g
	8.3^e	4032	32.3			4179	29.1^g
10	9.6^e	2810	33.6			2797	34.3^g
11	6.1^e	2764	30.1			2753	31.2^g
12	22.9		46.9		84.9		22.8^i
13	16.2		36.6		27.9^j		18.9^j
14	1.2^k	3227					
14b	−5.5^{k,l}	2653	18.5			2730^m	17.4
	−11.6	1824	12.4			2125	20.8

[a] Spectra (36.2 MHz) measured in D_2O at 28 °C unless otherwise stated. Chemical shifts (δ) in ppm (±0.1) to high frequency of 85% H_3PO_4. Coupling constants (J) in Hz (±3). [b] $\Delta\delta = \delta$(complex) − δ(phosphine). δ(P(CH$_2$OH)$_3$) = −24.0 (D$_2$O); δ(PMe$_3$) = −62.7 (from ref 17); δ(PEt$_3$) = −20.4 (from ref 17). [c] Data from ref 11a. [d] Spectra measured in CDCl$_3$. [e] Spectra measured in (CD$_3$)$_2$SO. [f] Data from ref 11b. [g] Data from ref 32. [h] P trans to CH$_3$; ^2J(PP) = 15 Hz. [i] Data from ref 33. [j] Data from ref 34; at 27 °C, $w_{1/2}$ = 100 Hz. [k] Spectra measured in CD$_3$OD containing 1 equiv of aqueous HCl. [l] At −78 °C; ^2J(PP) = 29 Hz. [m] Data from ref 15 measured in CHClF$_2$ at −137 °C; ^2J(PP) = 31 Hz.

to platinum metal upon concentration of the solutions. The instability of **8** may be due to the acidity of the coordinated $P(CH_2OH)_3$ ligands (see above) leading to loss of methane.

Stable organoplatinum species are formed upon treatment of $[PtCl(CH_3)(COD)]$ with $P(CH_2OH)_3$; both *cis*- and *trans*-$[PtCl(CH_3)\{P(CH_2OH)_3\}_2]$ (**9a,b**) have been characterized in solution. Metathesis of (**9a,b**) with LiBr or LiI gave the corresponding complexes *trans*-$[PtX(CH_3)\{P(CH_2OH)_3\}_2]$ [X = Br (**10**) and X = I (**11**)] (see Tables I–III for characterizing data).

Nickel(0) and Palladium(0) Complexes of $P(CH_2OH)_3$. The nickel complex $[Ni\{P(CH_2OH)_3\}_4]$ (**12**) is precipitated immediately and quantitatively upon addition of 4 equiv of $P(CH_2OH)_3$ in methanol to a toluene solution of $[Ni(COD)_2]$. The palladium

P(CH$_2$OH)$_3$
|
(HOCH$_2$)$_3$P—M—P(CH$_2$OH)$_3$
|
P(CH$_2$OH)$_3$
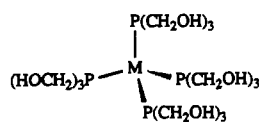
12 M = Ni

13 M = Pd

complex $[Pd\{P(CH_2OH)_3\}_4]$ (**13**) can be made in an analogous manner by treatment of $[Pd(dibenzylideneacetone)_2]$ in toluene with $P(CH_2OH)_3$ in methanol, but the most convenient synthesis of **13** uses a two phase aqueous/organic system. Aqueous $P(CH_2OH)_3$ is added to a CH_2Cl_2 solution of $[Pd(PPh_3)_4]$, and the layers are rapidly stirred; after 3 h the color completely transferred from the organic layer to the aqueous layer. The water-soluble product **13** is then readily freed from displaced PPh_3 simply by separating the layers. Both complexes **12** and **13** are soluble in water and very polar organic solvents (e.g. MeOH, dmso) but insoluble in common halocarbon or hydrocarbon solvents. They have been fully characterized by elemental analysis

Table III. ^1H,[a] $^{13}C\{^1H\}$,[b] and $^{195}Pt\{^1H\}$[c] Data

	δ(PCH$_2$O)	^3J(PtH)	δ(PCH$_2$O)	$|^1J$(PC) = ^3J(PC)$|$	δ(^{195}Pt)
2	4.32^d	21.6	56.2^e	44.6	−4
3	4.39	23.0	55.3	43.9	−306
4a	4.49	21.8	57.2	43.2	−793^g
4b	4.47	21.8	55.9	41.2	−1053^g
5a	4.33^f		55.4	35.9	
6a	4.40		56.5	34.6	
7b	4.44		57.6	33.9	
8			56.5^h	i	−192^g
9a					−88
9b	4.36^j	18.4	54.0^k		+42
10	4.41^l	17.5	54.4^m		−114
11	4.28^n	o	53.9^p		−353
12	3.69^q		60.3	11.5	
13	3.68		59.7	o	
14	3.65^r		60.8	o	

[a] Spectra (270 MHz) measured in (CD$_3$)$_2$SO at 18 °C unless otherwise stated; chemical shifts (δ) in ppm (±0.01) to high frequency of SiMe$_4$ and coupling constants (J) in Hz (±0.1). [b] Spectra (67.5 MHz) measured in (CD$_3$)$_2$SO at 20 °C unless otherwise stated; chemical shifts (δ) in ppm (±0.1) to high frequency of SiMe$_4$ and coupling constants (J) in Hz (±0.1). [c] Spectra (19.2 MHz) measured in D$_2$O at 28 °C unless otherwise stated; chemical shifts (δ) in ppm (±0.5) to high frequency of Ξ(Pt) = 21.4 MHz. [d] A δ value (in CD$_3$OD) of 4.50 ppm and ^3J(PtH) of 23.4 Hz have been previously reported.[7a] [e] In CD$_3$OD; ^2J(PtC) = 45.2 Hz. [f] A δ value (in CD$_3$OD) of 4.50 ppm has been previously reported.[7a] [g] In (CD$_3$)$_2$SO. [h] Data for the PtCH$_3$ resonance: δ 2.1 ppm, ^1J(PtC) = 584.3 Hz, $|^2J$(PC) = ^2J(P$'$C)$|$ = 104.9 Hz. [i] Multiplet observed. [j] Data for the PtCH$_3$ resonance: δ 0.60 ppm, ^2J(PtH) = 83.1 Hz, ^3J(PH) = 6.2 Hz. [k] Data for the PtCH$_3$ resonance: δ −26.8 ppm, ^1J(PtC) = 634.2 Hz, ^2J(PC) = 6.5 Hz. [l] Data for the PtCH$_3$ resonance: δ 0.64 ppm, ^2J(PtH) = 82.5 Hz, ^3J(PH) = 6.4 Hz. [m] Data for the PtCH$_3$ resonance: δ −23.7 ppm, ^1J(PtC) = 638.4 Hz, ^2J(PC) = 6.4 Hz. [n] Data for the PtCH$_3$ resonance: δ 0.73 ppm, ^2J(PtH) = 82.9 Hz, ^3J(PH) = 6.4 Hz. [o] Not resolved. [p] Data for the PtCH$_3$ resonance: δ −18.3 ppm, ^1J(PtC) = 634.1 Hz, ^2J(PC) = 6.5 Hz. [q] In CD$_3$OD. [r] See caption for Figure 3 for the data from the low-temperature spectra.
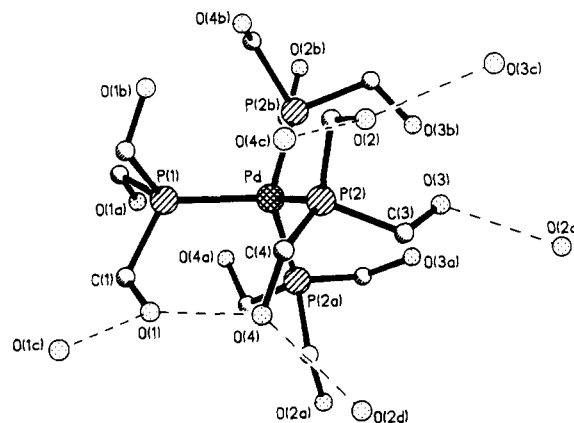

Figure 1. Molecular structure of $[Pd\{P(CH_2OH)_3\}_4]\cdot MeOH$ (**13**) showing atom-labeling scheme. The crystallographic 3-fold axis (parallel to the z axis of the unit cell) passes through the Pt and P(1) atoms. All hydrogen atoms have been omitted for clarity. The unique O···O hydrogen bond contacts involving the hydroxyl groups (O···O < 2.8 Å) are shown.

and NMR spectroscopy (see Tables I–III), and the X-ray crystal structure of the palladium complex **13** has been determined.

X-ray Crystal Structure of $[Pd\{P(CH_2OH)_3\}_4]\cdot MeOH$. Deep yellow crystals of **13**·MeOH were obtained from a methanol/ diethyl ether solution, and the crystal structure was determined. The complex crystallizes as discrete molecules which lie on C_3 axes in the trigonal space group $R\bar{3}c$ with one molecule of methanol cocrystallized per molecule of **13**. Bond lengths and angles (numbering scheme shown in Figure 1) are listed in Table IV. The molecular structure shows the expected tetrahedral coordination at the palladium(0) [P–Pd–P 108.5 (1), 110.4 (1)°] with Pd–P distances similar to those of other palladium(0) trialkylphosphine complexes [Pd–P 2.326 (3), 2.321 (1) Å in **13**; Pd–PMe$_3$ average 2.287 Å, Pd–PEt$_3$ average 2.315 Å].[12] The
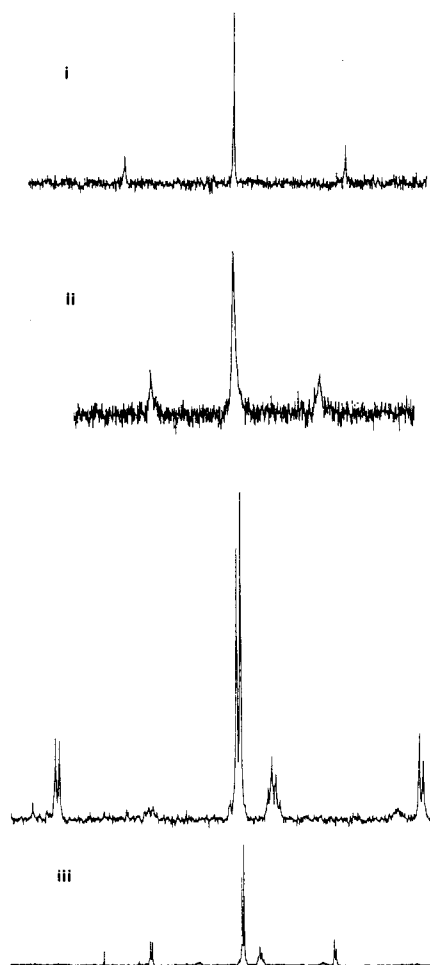
Figure 2. $^{31}P\{^1H\}$ NMR spectra of $[Pt\{P(CH_2OH)_3\}_4]$ in CD_3OD: (i) at +28 °C; (ii) at +28 °C in the presence of 1 equiv of aqueous HCl; (iii) at −78 °C in the presence of 1 equiv of aqueous HCl.

**Table IV.** Bond Lengths (Å) and Bond Angles (deg) for **13**-MeOH

Pd–P(1)	2.326 (3)	Pd–P(2)	2.321 (1)	P(1)–C(1)	1.858 (11)
C(1)–O(1)	1.364 (13)	C(1)–O(1')	1.222 (30)	P(2)–C(2)	1.845 (7)
P(2)–C(3)	1.849 (7)	P(2)–C(4)	1.848 (7)	C(2)–O(2)	1.437 (6)
C(3)–O(3)	1.410 (9)	C(4)–O(4)	1.428 (10)	C(9)–O(9)	1.302 (39)
P(1)–Pd–P(2)	108.5 (1)	P(2)–Pd–P(2A)	110.4 (1)
Pd–P(1)–C(1)	117.8 (3)	C(1)–P(1)–C(1A)	100.1 (3)
P(1)–C(1)–O(1)	113.1 (6)	P(1)–C(1)–O(1')	118.9 (20)
Pd–P(2)–C(2)	116.5 (2)	Pd–P(2)–C(3)	119.1 (2)
C(2)–P(2)–C(3)	100.7 (3)	Pd–P(2)–C(4)	119.3 (2)
C(2)–P(2)–C(4)	98.9 (3)	C(3)–P(2)–C(4)	98.5 (3)
P(2)–C(2)–O(2)	115.9 (5)	P(2)–C(3)–O(3)	111.4 (6)
P(2)–C(4)–O(4)	112.8 (4)		

water solubility of **13** is due to the palladium atom being sheathed by 12 alcohol groups and thereby presenting a highly hydrophilic surface to an approaching solvent. The most striking feature of the crystal structure is the extensive hydrogen-bonding pattern (see Figure 1). First, there is an intramolecular hydrogen bond between O(1) and O(4) (2.68 (1) Å). Secondly, there are two symmetry-related hydrogen bonds (O···O 2.73 (1) Å) that link molecules into a two-dimensional layer network perpendicular to the c axis of the unit cell. These are between O(2) and O(4c) and between O(4) and O(2d). Finally, there are intermolecular hydrogen bonds that link together these hydrogen-bonded layers of molecules. These are O(1)···O(1c) (2.76 (1) Å), O(2)···O(3c), and O(3)···O(2c) (2.69 (1) Å). O(2d) is generated from O(2) by the symmetry operation $-x + y$, $1 - x$, z, O(4c) is generated from O(4) by $1 - y$, $1 + x - y$, z, O(1c) is related to O(1) by

0.3333 − x + y, 0.6667 − y, 0.6667 − z, O(2c) is related to O(2) by 0.6667 + y, −0.6667 − x − y, 0.3333 − z, and O(3c) is related to O(3) by the 0.6667 + x − y, 0.3333 + x, 0.3333 − z operation. The methanol of crystallization does not form any strong (<2.8 Å) O···HO hydrogen bonds with molecules of **13**. Lickiss and co-workers[13] have observed a variety of intra- and intermolecular hydrogen-bonding patterns in topologically similar tetrahedral species with hydroxyl groups [e.g. $C(SiMe_2OH)_4$], but **13** differs from these in having 12 hydroxyl groups (rather than four) all of which are involved in hydrogen bonding.

Platinum Complex $[Pt\{P(CH_2OH)_3\}_4]\cdot H_2O$ (14). Treatment of $[Pt(COD)_2]$ or $[Pt(PPh_3)_4]$ with $P(CH_2OH)_3$ yielded a product which, from elemental analysis, had a composition corresponding to $[Pt\{P(CH_2OH)_3\}_4]\cdot H_2O$ (**14**), i.e. ostensibly the platinum(0) analogue of complexes **12** and **13**. Treatment of **14** with iodine in methanol gave **4**, the product that would be expected from oxidative addition of I_2 to platinum(0). However, unlike **12** and **13**, species **14** forms strongly alkaline aqueous solutions (10^{-2} M solutions have a pH of ca. 11) which we associate with the presence of an equilibrium mixture of the tetrahedral platinum(0) complex **14a** and the trigonal-bipyramidal hydridoplatinum(II) complex **14b** (eq 3). This assignment is supported by much spectroscopic evidence, as detailed below.

14a

14b
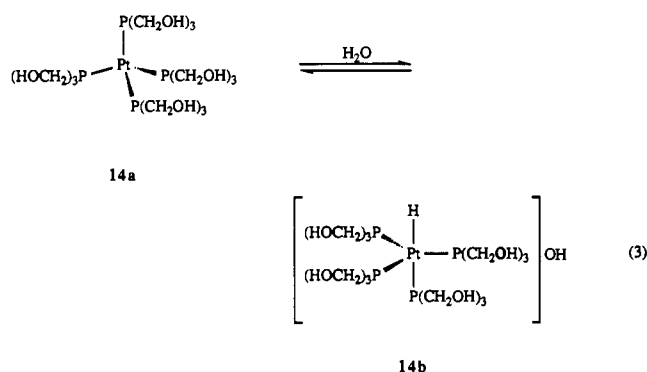
The IR spectrum of **14** in the solid state and in MeOH solution features a weak band at 2110 (CsI disk) or 2103 (MeOH) cm^{-1} assigned to ν(PtH).

The $^{31}P\{^1H\}$ NMR (36.2 MHz) signal for **14** in methanol at +28 °C is a broad singlet ($w_{1/2}$ = 28 Hz) with ^{195}Pt satellites which, upon addition of 1 equiv of aqueous HCl, broadens further ($w_{1/2}$ = 40 Hz) and shifts to lower frequency (from +1.2 to −7.3 ppm), and the ^1J(PtP) value falls nearly 800 Hz (from 3227 to 2437 Hz). At −78 °C, the broad signals of this acidified solution are resolved into a doublet and a quartet (see Figure 2), as expected for the trigonal-bipyramidal **14b**. Above −78 °C, these signals broaden and coalesce at ca. −40 °C, and then at −5 °C, a minimum line width is observed ($w_{1/2}$ = 8 Hz). At +28 °C, the values of δ(P) and ^1J(PtP) are the weighted averages of the values at −78 °C, which is consistent with **14b** being fluxional on the NMR time scale, as is observed in other five-coordinate platinum hydrides.[15,16] The low-temperature (−78 °C) $^{31}P\{^1H\}$ NMR spectrum of **14** is the same in the absence or the presence of added acid, which indicates that the equilibrium (eq 3) shifts to the right at low temperatures. Addition of $P(CH_2OH)_3$ (**1**) to nonacidified solutions of **14** results in further broadening of the signal for **14** and a broad signal for free phosphine **1**, indicating that phosphine exchange takes place at ambient temperature (see below).

(12) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1.

(13) Al-Juaid, S. S.; Eaborn, C.; Hitchcock, P. B.; Lickiss, P. D. *J. Organomet. Chem.* **1988**, *353*, 297.

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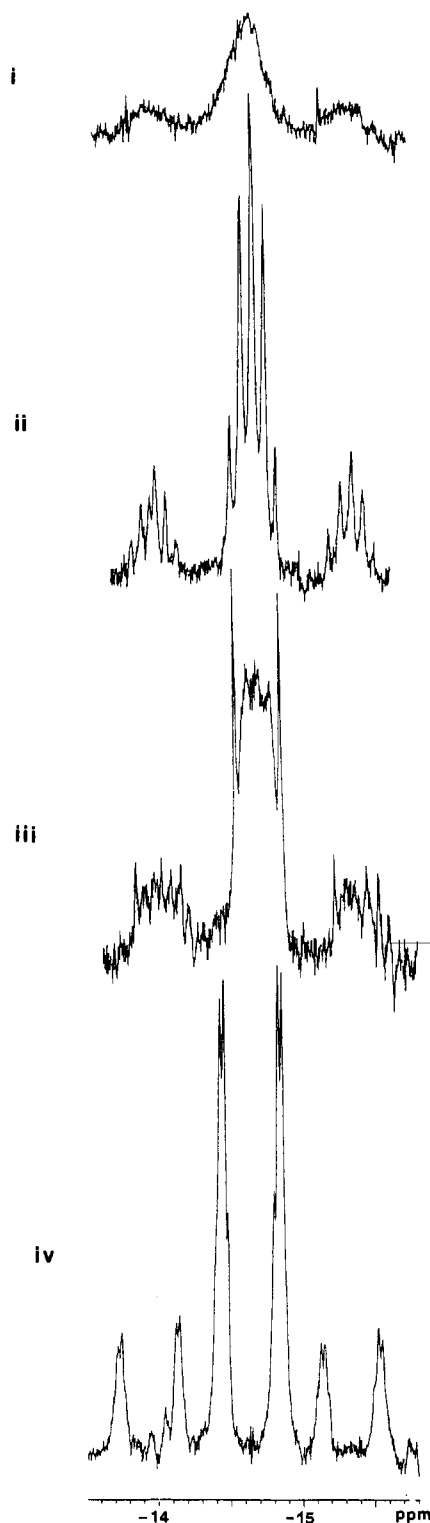
Figure 3. Hydride region of the ^{1}H NMR spectrum (400 MHz) of [Pt{P(CH$_2$OH)$_3$}$_4$] in the presence of 1 equiv aqueous HCl in CD$_3$OD: (i) +21 °C δ(H) –13.90, ^1J(PtH) = ca. 550 Hz; (ii) –10 °C δ(H) –14.06, ^1J(PtH) = 544 Hz, ^2J(PH) = 31 Hz; (iii) –30 °C; (iv) –65 °C δ(H) –14.60, ^1J(PtH) = 566 Hz, ^2J(PH) = 10 and 162 Hz.

The variable-temperature ^{1}H NMR spectra (Figure 3) of acidified methanolic solutions of **14** strongly support the above conclusions. At –65 °C, a doublet of quartets (not fully resolved) is observed at –14.60 ppm, as expected for the axial hydride ligand in the static trigonal-bipyramidal structure **14b**. Upon warming of the solution, this signal broadens and then sharpens into a quintet at –10 °C, showing unambiguously that the [PtH(PR$_3$)$_4$]$^+$ structure is maintained. Above –10 °C, the signal broadens and fine structure due to H–P coupling is lost, consistent

with **14b** undergoing phosphine exchange on the NMR time scale (presumably via the square-planar transient **15**). Interestingly,

15

16a R = Et

16b R = OMe
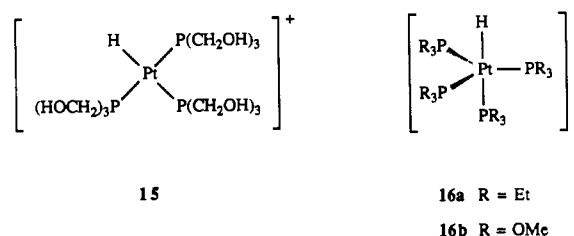
Pt–H coupling is retained, indicating that proton exchange from **14b**, in acidic media, is not rapid on the NMR time scale at ambient temperatures. However, proton exchange (eq 3) is rapid in alkaline solution, as evidenced by the absence of a hydride resonance in aqueous methanolic solutions of **14**.

Complex **14b** is a rare example of a five-coordinate platinum hydride that is stable at ambient temperatures.[14] The species [PtH(PEt$_3$)$_4$]$^+$ (**16a**) has been observed[15] at very low temperatures, but above –100 °C, it is completely dissociated into [PtH(PEt$_3$)$_3$]$^+$ (an analogue of **15**). The fluxional phosphite complex [PtH{P(OMe)$_3$}$_4$]$^+$ (**16b**)[16] (which, coincidentally, is an isomer of **14b**) is stable at +25 °C.

Comparison of P(CH$_2$OH)$_3$ with PMe$_3$ and PEt$_3$. In order to put the chemistry described above into context, it is instructive to compare it with analogous PMe$_3$ and PEt$_3$ chemistry. The pK_a values for P(CH$_2$OH)$_3$, PMe$_3$, and PEt$_3$ (5.5, 8.65, and 8.69, respectively)[17] show that P(CH$_2$OH)$_3$ is significantly less basic, presumably as a result of the presence of the three electron-withdrawing OH substituents. The cone angle[18] for P(CH$_2$OH)$_3$ should lie between that of PMe$_3$ (118°) and PEt$_3$ (132°), and one might anticipate that it would lie closer to that of PEt$_3$.

In Table II the ^{31}P coordination chemical shifts for all the metal(II) complexes are collected along with the values for analogous PMe$_3$ and PEt$_3$ complexes. The coordination shifts and ^1J(PtP) values for platinum(II) and palladium(II) complexes of P(CH$_2$OH)$_3$, PMe$_3$, and PEt$_3$ are similar and it is therefore clear from these data that, notwithstanding its lower Brønsted basicity, P(CH$_2$OH)$_3$ coordinates to these metal centers like other small, basic trialkylphosphines.

There are significant differences in the properties of the complexes formed by P(CH$_2$OH)$_3$ and other trialkylphosphines which may be associated with the hydrophilicity and hydrogen-bonding capacity of the OH groups. The most obvious is the water solubility of all the P(CH$_2$OH)$_3$ complexes reported here. More subtle differences emerge when the complexes [M{P(CH$_2$OH)$_3$}$_4$] [M = Ni (**12**) or Pd (**13**)] are compared with the analogous [M(PR$_3$)$_4$] (M = Ni or Pd; R = Me or Et) (**17a–d**). The P(CH$_2$OH)$_3$ complexes are essentially air-stable in the solid state and in solution whereas the analogous PMe$_3$ or PEt$_3$ complexes **17a–d** are extremely air sensitive, even pyrophoric.[19] The PMe$_3$ and PEt$_3$ complexes **17a–d** react readily with EtOH to form hydrides [MH(PR$_3$)$_4$]$^+$ (M = Ni, R = Me) or [MH(PR$_3$)$_3$]$^+$ (M = Ni or Pd, R = Me or Et)[20] whereas we observe no reaction between **12** or **13** and alcohols.

When P(CH$_2$OH)$_3$ is added to solutions of **12** or **13**, sharp ^{31}P NMR signals are observed for the complexes and free ligand, indicating that dissociative phosphine exchange (eq 4) is slow on the NMR time scale. In this respect **12** and **13** resemble the

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(20) Schunn, R. A. *Inorg. Chem.* **1976**, *15*, 208.

$$\text{(4)}$$
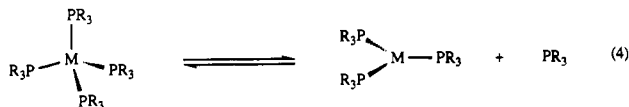
12 M = Ni R = CH$_2$OH

13 M = Pd R = CH$_2$OH

17a M = Ni R = Me

17b M = Ni R = Et

17c M = Pd R = Me

17d M = Pd R = Et

PMe$_3$ analogues **17a,c** rather than the PEt$_3$ analogues **17b,d** which are extensively dissociated in solution.[19] Since dissociative equilibria of this type (eq 4) are normally governed by steric rather than electronic effects, we might conclude that P(CH$_2$OH)$_3$ has an effective cone angle closer to PMe$_3$ than PEt$_3$. Another possible explanation is that dissociation of the phosphines from **12** and **13** is inhibited by intramolecular hydrogen bonding between the coordinated P(CH$_2$OH)$_3$ ligands; a similar explanation has been given for the high energy barrier to phosphine dissociation from [RhH(CO){P(*m*-C$_6$H$_4$SO$_3$Na)$_3$}$_3$].[2j]

The protonation of the platinum(0) complex **14a** by H$_2$O to give the five-coordinate hydride **14b** (eq 3) should be contrasted with the reaction[20] between [Pt(PEt$_3$)$_4$] (**18**) and EtOH which gives the four-coordinate hydride [PtH(PEt$_3$)$_3$]$^+$ (**19**) (eq 5).

$$\text{(5)}$$

18   19
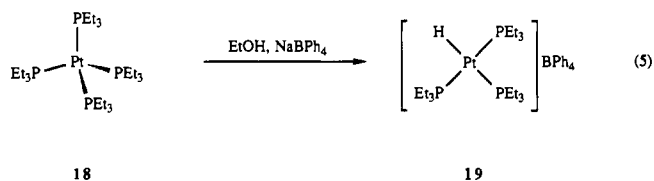
The intramolecular hydrogen bonding detected in the crystal structure of [Pd{P(CH$_2$OH)$_3$}$_4$] links the four ligands in such a way that the {P(CH$_2$OH)$_3$}$_4$ unit may be considered as a tetradentate ligand. Viewed in this way, the stability of the palladium(0) and nickel(0) complexes **12** and **13** can be rationalized in terms of the multiple-chelate effect of the linked P(CH$_2$OH)$_3$ ligands. The {P(CH$_2$OH)$_3$}$_4$ unit can also be thought of as analogous to the tripod tetradentate ligand P(CH$_2$CH$_2$PPh$_2$)$_3$ which has recently been shown[21] to be an excellent ligand for the stabilization of trigonal-bipyramidal geometry for platinum(II) (e.g. the hydridoplatinum(II) complex **20**). Hence the stabili-
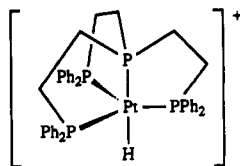
20

zation of the trigonal-bipyramidal hydridoplatinum(II) complex **14b** can be interpreted as a manifestation of the tripodal qualities of the hydrogen-bonded {P(CH$_2$OH)$_3$}$_4$ unit. Further study of this analogy is in progress.

Conclusion

The overall conclusion from our work with P(CH$_2$OH)$_3$ is that its coordination chemistry with nickel, palladium, and platinum,

in many respects, resembles PMe$_3$ or PEt$_3$ but the OH substituents not only confer water solubility on the complexes but also influence the chemistry in more subtle ways, such as stabilizing low oxidation states and high coordination numbers.

Experimental Section

All syntheses were carried out under a nitrogen atmosphere unless otherwise stated and solvents dried, when necessary, by refluxing over the appropriate drying reagents (calcium hydride for dichloromethane, sodium/benzophenone for diethyl ether, toluene, and *n*-hexane) and distilled under nitrogen prior to use. Commercial reagents were used as supplied unless otherwise stated; the phosphonium salt [P(CH$_2$OH)$_4$]Cl can be obtained from Albright and Wilson (see above address) as an 80% solution in water. The following starting materials were prepared according to literature methods: [PtX$_2$(COD)] (X = Cl, Br, I, CH$_3$),[22,23] [PtCl(CH$_3$)(COD)],[24] [Pt(COD)$_2$],[25] [Pt(PPh$_3$)$_4$],[26] [PdX$_2$(COD)] (X = Cl, Br),[23] [Pd(dba)$_2$],[27] [Pd(PPh$_3$)$_4$],[28] [Ni(COD)$_2$].[29]

Synthesis of Tris(hydroxymethyl)phosphine (1) from PH$_3$. (*CAUTION: Phosphine gas is extremely toxic and should only be handled in a well-ventilated fume cupboard*). A 250-cm^3, three-necked flask, equipped with gas inlet, mechanical stirrer, and a gas exhaust outlet, was charged with aqueous formaldehyde (37%, 100 cm^3, 0.88 mol). The solution was purged thoroughly with nitrogen for ca. 30 min, then the K$_2$[PtCl$_4$] catalyst (0.5 g, 1.04 mmol) added as a solid in one portion. Further purging with nitrogen was continued for ca. 10 min; then PH$_3$ was admitted at a slow rate to the vigorously stirred solution at room temperature. The reaction was complete when PH$_3$ adsorption had ceased (ca. 2.5 h). Removal of all volatiles on a vacuum line with a warm external water bath affords crystalline ligand **1** in essentially quantitative yields.

Synthesis of Tris(hydroxymethyl)phosphine from [P(CH$_2$OH)$_4$]Cl. For this preparation, it is important to have anhydrous [P(CH$_2$OH)$_4$]Cl which can be conveniently obtained as follows. The 80% aqueous solution of [P(CH$_2$OH)$_4$]Cl is evaporated to dryness on a rotary evaporator, and the resulting solid is then further dried by azeotropic distillation with toluene; finally, the solid is recrystallized from twice its weight of 2-propanol. Anhydrous [P(CH$_2$OH)$_4$]Cl is very hygroscopic and should therefore be stored under anhydrous conditions.

A 1-L three-necked flask was charged with anhydrous [P(CH$_2$OH)$_4$]Cl (95.25 g, 0.500 mol). Dry triethylamine (600 cm^3) was then added in one portion under nitrogen with stirring. The resulting mixture was then heated to 60 °C for 1 h and then allowed to cool to room temperature. The solid [NEt$_4$]Cl byproduct was filtered off and the filtrate collected. The triethylamine solvent was distilled out at atmospheric pressure to give the crude product (at this stage it is a mixture of **1** and its hemiacetal adducts) which was then heated at 90 °C for 5 h under reduced pressure (1 mmHg) using a nitrogen bleed. The product, a viscous oil or low-melting solid was obtained in quantitative yield and was 96% pure by ^{31}P{^{1}H} NMR spectroscopy. Recrystallization was achieved by dissolving 60 g of crude product in 44 g of MeOH and then cooling the solution to −20 °C for 16 h to yield 52 g (84%) of crystalline product (98.5% purity by ^{31}P{^{1}H} NMR analysis). Phosphine **1** is slowly oxidized by atmospheric oxygen, is hygroscopic, and has an unpleasant smell; it should therefore be stored under nitrogen. Purification of **1** by distillation has been reported[7b] but we do not recommend this method for large-scale preparations because above 130 °C, **1** decomposes exothermically, releasing PH$_3$ gas in the process.

Preparation of [PtCl$_2${P(CH$_2$OH)$_3$}$_2$] (2). A solution of P(CH$_2$OH)$_3$ (0.361 g, 2.91 mmol) in methanol (4 cm^3) was added to a suspension of [PtCl$_2$(COD)] (0.532 g, 1.42 mmol) in methanol (20 cm^3) and the mixture stirred until all the solid had dissolved (ca. 30 min). Evaporation of the solvent to ca. 1–2 cm^3 followed by addition of dichloromethane (30 cm^3) gave the white solid product **2** (0.658 g, 90%).

Preparation of [PtBr$_2${P(CH$_2$OH)$_3$}$_2$] (3). A solution of P(CH$_2$OH)$_3$ (0.192 g, 1.55 mmol) in methanol (2 cm^3) was added to a suspension of

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(29) Schunn, R. A. *Inorg. Synth.* **1974**, *15*, 5.

[PtBr$_2$(COD)] (0.350 g, 0.76 mmol) in methanol (15 cm^3) and the mixture stirred for 1 h. Evaporation of the resulting solution to ca. 2 cm^3, followed by addition of dichloromethane (30 cm^3), gave the white solid product **3** (0.409 g, 90%).

Preparation of [PtI$_2$\{P(CH$_2$OH)$_3$\}$_2$] (4). (i) A solution of P(CH$_2$OH)$_3$ (0.076 g, 0.61 mmol) in methanol (1 cm^3) was added to a suspension of [PtI$_2$(COD)] (0.166 g, 0.30 mmol) in methanol (10 cm^3). The suspension dissolves to give a yellow solution and then, after ca. 5 min, the yellow solid product **4** precipitates; it was filtered off and dried in vacuo (0.166 g, 80%).

(ii) A solution of lithium iodide (0.268 g, 2.00 mmol) in methanol (2 cm^3) was added to a solution of [PtCl$_2$\{P(CH$_2$OH)$_3$\}$_2$] (0.103 g, 0.20 mmol) in methanol (3 cm^3). The solution immediately turns deep yellow followed by precipitation of a yellow solid. After the mixture was stirred for an additional 3 h, the precipitated product **4** was filtered off and washed with water (5 cm^3). The product was then dried in vacuo (0.092 g, 66%).

(iii) A solution of iodine (0.217 g, 0.86 mmol) in methanol (2 cm^3) was added to a solution of [Pt\{P(CH$_2$OH)$_3$\}$_4$]·H$_2$O (0.202 g, 0.28 mmol) in methanol/water (15 cm^3/1 cm^3) and the mixture stirred for ca. 4 h. The yellow solid product **4** which had formed was filtered off and dried in vacuo (0.113 g, 58%).

Preparation of [PdCl$_2$\{P(CH$_2$OH)$_3$\}$_2$] (5). A solution of P(CH$_2$OH)$_3$ (0.285 g, 2.30 mmol) in methanol (3 cm^3) was added to a suspension of [PdCl$_2$(COD)] (0.320 g, 1.12 mmol) in methanol (20 cm^3) and the mixture stirred until all the solid had dissolved (ca. 10 min). Evaporation of the solvent to ca. 1–2 cm^3, followed by addition of dichloromethane (20 cm^3), gave the yellow solid product **5** (0.418 g, 88%).

Preparation of [PdBr$_2$\{P(CH$_2$OH)$_3$\}$_2$] (6). A solution of P(CH$_2$OH)$_3$ (0.119 g, 0.96 mmol) in methanol (3 cm^3) was added to a suspension of [PdBr$_2$(COD)] (0.174 g, 0.47 mmol) in methanol (5 cm^3) and the mixture stirred until all the solid had dissolved (ca. 5 min) to give an orange solution. Evaporation of the solvent to ca. 1–2 cm^3 followed by addition of dichloromethane (20 cm^3) gave the yellow solid product **6** (0.159 g, 68%).

Preparation of [PdI$_2$\{P(CH$_2$OH)$_3$\}$_2$] (7). A solution of lithium iodide (0.361 g, 2.70 mmol) in water (2 cm^3) was added to a solution of [PdCl$_2$\{P(CH$_2$OH)$_3$\}$_2$] (0.114 g, 0.27 mmol) in water (7 cm^3). Immediately, the dark orange product **7** precipitates. After ca. 5 min, this solid was filtered off and dried in vacuo (0.141 g, 87%).

In Situ Preparation of [Pt(CH$_3$)$_2$\{P(CH$_2$OH)$_3$\}$_2$]. A solution of [Pt(CH$_3$)$_2$(COD)] (0.045 g, 0.14 mmol) and P(CH$_2$OH)$_3$ (0.035 g, 0.28 mmol) in (CD$_3$)$_2$SO (0.5 cm^3) was examined by ^{31}P\{^{1}H\}, ^{13}C\{^{1}H\}, and ^{195}Pt\{^{1}H\} NMR spectroscopy. The spectroscopic data were conistent with the formation of complex **8**.

Preparation of cis- and trans-[PtCl(CH$_3$)\{P(CH$_2$OH)$_3$\}$_2$] (9a,b). A solution of P(CH$_2$OH)$_3$ (0.166 g, 1.30 mmol) in methanol (2 cm^3) was added to a suspension of [PtCl(CH$_3$)(COD)] (0.235 g, 0.67 mmol) in methanol (8 cm^3), and the mixture was stirred until all the solid had dissolved (ca. 15 min). Evaporation of the solvent to ca. 1 cm^3 and addition of dichloromethane (30 cm^3) afforded the solid product **9** which was filtered off and dried in vacuo (0.238 g, 73%).

Preparation of trans-[PtBr(CH$_3$)\{P(CH$_2$OH)$_3$\}$_2$] (10). [PtCl(CH$_3$)\{P(CH$_2$OH)$_3$\}$_2$] (0.020 g, 0.041 mmol) and lithium bromide (0.035 g, 0.041 mmol) were dissolved in dmso (0.5 cm^3), and the resulting solution was examined by ^{31}P\{^{1}H\} and ^{195}Pt\{^{1}H\} NMR spectroscopy. The only species observed was assigned to trans-[PtBr(CH$_3$)\{P(CH$_2$OH)$_3$\}$_2$] (10), but this was not isolated.

Preparation of trans-[PtI(CH$_3$)\{P(CH$_2$OH)$_3$\}$_2$] (11). A solution of lithium iodide (0.350 g, 2.30 mmol) in methanol (2 cm^3) was added to a solution of [PtCl(CH$_3$)\{P(CH$_2$OH)$_3$\}$_2$] (0.114 g, 0.23 mmol) in methanol (5 cm^3) to give a pale yellow solution. After ca. 5 min a white precipitate formed and the mixture was then stirred for a further 20 min. The product was filtered off, washed with small portions of water (2 × 5 cm^3), acetone (2 × 5 cm^3), and n-hexane (2 × 5 cm^3), and finally dried in vacuo (0.087 g, 65%).

Preparation of [Ni\{P(CH$_2$OH)$_3$\}$_4$] (12). A solution of P(CH$_2$OH)$_3$ (1.818 g, 14.66 mmol) in methanol (6 cm^3) was added to a solution of [Ni(COD)$_2$] (0.996 g, 3.62 mmol) in toluene (70 cm^3) to give a buff precipitate immediately. The mixture was stirred for ca. 15 min and then the product **12** filtered off under nitrogen. The solid was dried in vacuo (1.889 g, 94%).

Preparation of [Pd\{P(CH$_2$OH)$_3$\}$_4$] (13). (i) A solution of P(CH$_2$OH)$_3$ (1.20 g, 9.68 mmol) in water (60 cm^3) was added to a solution of [Pd(PPh$_3$)$_4$] (2.70 g, 2.34 mmol) in dichloromethane (80 cm^3). The two phases were stirred vigorously for 3 h, during which the orange/yellow

formula: C$_{13}$H$_{40}$O$_{13}$P$_4$Pd	fw: 634.8
$a = 10.202$ (3) Å	space group: $R\bar{3}c$ (No. 167)
$c = 86.937$ (25) Å	$T = 295$ °C
$V = 7837$ (4) Å^3	$\bar{\lambda} = 0.710\,69$ Å
$Z = 12$	μ(Mo Kα) = 9.9 cm^{-1}
$\rho_{calc} = 1.62$ g cm^{-3}	$F($ooo$) = 3924$
$R^a = 0.057$	$S = 2.05^a$
$R_w = 0.067$	

^{a} $R = \sum|\Delta|/\sum|F_o|$; $R_w = [\sum w\Delta^2/\sum wF_o^2]^{1/2}$; $S = [\sum w\Delta^2/($NO$-$NV$)]^{1/2}$; $\Delta = F_o = F_c$.

Table VI. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for **13·MeOH**

atom	x	y	z	$U_{eq}{}^a$
Pd	0	0	1258 (1)	33 (1)
P(1)	0	0	991 (1)	44 (1)
C(1)	−1071 (10)	782 (9)	891 (1)	74 (4)
O(1)	−704 (11)	2191 (10)	942 (1)	119 (6)
O(1')	−1113 (32)	766 (32)	751 (3)	80 (11)
P(2)	1737 (2)	2415 (2)	1343 (1)	38 (1)
C(2)	3730 (6)	2878 (6)	1354 (1)	51 (3)
O(2)	4797 (4)	4390 (5)	1403 (1)	59 (2)
C(3)	1490 (7)	3027 (8)	1536 (1)	55 (3)
O(3)	1246 (7)	1938 (7)	1649 (1)	86 (3)
C(4)	2002 (7)	4073 (7)	1232 (1)	57 (3)
O(4)	603 (6)	3964 (5)	1187 (1)	68 (2)
C(9)	6667	3333	617 (3)	150 (11)
O(9)	7163 (31)	2526 (30)	684 (4)	173 (19)

^{a} Equivalent isotropic U defined as one-third of the trace of the orthogonalized U$_{ij}$ tensor.

color transferred from the organic to the aqueous layer. The dichloromethane layer was syringed off and the aqueous layer washed with dichloromethane (2 × 50 cm^3). Evaporation of the water under reduced pressure and trituration of the residue with diethyl ether (50 cm^3) affords **13** as an orange solid (1.085 g, 77%).

(ii) A solution of P(CH$_2$OH)$_3$ (0.527 g, 4.25 mmol, 4.05 equiv) in methanol (4 cm^3) was added to a solution of [Pd(dba)$_2$] (0.600 g, 1.05 mmol) in toluene (60 cm^3). After ca. 5 min, the dark purple solution turned deep yellow and then an olive green solid precipitated. The solid product was filtered off under nitrogen and dried in vacuo (0.702 g, 89%). It was identical spectroscopically to the orange product obtained from [Pd(PPh$_3$)$_4$] and the green coloration is assumed to be due to the presence of a small amount of metallic palladium.

Preparation of [Pt\{P(CH$_2$OH)$_3$\}$_4$]·H$_2$O (14). (i) A solution of P(CH$_2$OH)$_3$ (0.860 g, 6.94 mmol, 4.16 equiv) in methanol (10 cm^3) was added to a suspension of [Pt(PPh$_3$)$_4$] (2.08 g, 1.67 mmol) in methanol (125 cm^3), and the resulting pale yellow solution was stirred for 4 h. The solvent was then evaporated under reduced pressure to ca. 5–10 cm^3, and diethyl ether (90 cm^3) was added to precipitate the off-white solid product **14** (0.98 g, 83%).

(ii) A solution of P(CH$_2$OH)$_3$ (0.185 g, 1.49 mmol) in methanol (2 cm^3) was added to a suspension of [Pt(COD)$_2$] (0.141 g, 0.34 mmol) in methanol (10 cm^3), and the resulting solution was stirred for 15 min and then concentrated to ca. 1–2 cm^3. The product **14** was precipitated by the addition of dichloromethane (18 cm^3) (0.108 g, 45%).

Crystal Structure of [Pd\{P(CH$_2$OH)$_3$\}$_4$]·MeOH, (13)·MeOH. Crystal data for **13·MeOH** are listed in Table V. A single crystal of **13·MeOH** (approximate dimensions 0.4 × 0.4 × 0.25 mm) was mounted in a thin-walled glass capillary under N$_2$. All diffraction measurements were made on a Nicolet P3m diffractometer at room temperature, using graphite-monochromated Mo Kα X-radiation. Unit cell dimensions were determined from 15 centered reflections in the range $16.0 < 2\theta < 25.0°$. Diffracted intensities were measured in a hemisphere of reciprocal space for $4.0 < 2\theta < 50.0°$ by $\omega/2\theta$ scans. Three check reflections were remeasured after every 100 ordinary data over the period of data collection, and a correction for long-term intensity fluctuation was applied on the basis of the variation in their intensities. Of the 4786 noncheck, nonabsence, intensity data collected, 1567 unique observations remained after averaging of duplicate and equivalent measurements, of these 1237 (=NO) with $I > 2\sigma(I)$ were retained for use in structure solution and refinement. No absorption correction was applied. Lorentz and polarization corrections were applied.

The structure was solved by heavy-atom (direct and Fourier) methods and refined by full-matrix least squares. The complex and solvent

molecules each lie on crystallographic 3-fold axes. In the case of the solvent, this leads to disorder, with the oxygen disordered between three off-axis sites and the carbon on-axis. The hydroxymethyl groups on P(1) suffer a 2-fold disorder, with the oxygens in two sites of refined occupancy 0.82 (1) (O(1)) and 0.18 (1) (O(1')). All non-hydrogen atoms other than O(1') were assigned anisotropic displacement parameters, and O(1') was assigned a refined isotropic displacement parameter. All hydrogen atoms were assigned fixed (at ca. 1.2 times that of their attached carbon) isotropic displacement parameters. All methylene hydrogen atoms were constrained to idealized geometries (C–H 0.96 Å) and other hydrogens omitted from the model. Refinement of this model (NV = 105 parameters) converged (average parameter shift/esd in final cycle of least-squares <0.01) to the final residual indices given in Table V. Weights, w, were set equal to $[\sigma_c{}^2(F_o) + gF_o{}^2]^{-1}$. Here $\sigma_c{}^2(F_o)$ is the variance in F_o due to counting statistics and $g = 0.0005$ was chosen to minimize the variation in S as a function of F_o. Final difference electron density maps showed no features outside the range $+0.5$ to -1 e Å^{-3}, the largest of these being close to the palladium atoms. Table VI lists the final atomic positional parameters for the non-hydrogen atoms, and Table IV the derived bond lengths and interbond angles. All calculations were carried out on a Nicolet R3m/V structure determination system using programs of the SHELXTL-PLUS package.[30] Complex neutral-atom scattering factors were taken from ref 31.

Supplementary Material Available: Tables of thermal parameters and positions of hydrogen atoms and a textual presentation of crystallographic details (4 pages); a listing of structure factors (6 pages). Ordering information is given on any current masthead page.

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