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Template Synthesis of the Coordinated Triphosphorus Ligands $(Ph_2PCH_2CRR'O)_2PPh$, R or R′ = H or CH_3

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Abstract

The new tridentate ligands $(Ph_2PCH_2CRR'_2O)_2PPh$ (R or R′ = H or CH_3) can be made using Ni(II), Pd(II) or Pt(II) as a template. Hence treatment of $[MX_2(Ph_2PCH_2CRR'_2OH)_2]$ (R or R′ = H or CH_3; X = Cl, M = Pt or Pd; X = CN, M = Ni) with $PhPCl_2$ gives complexes of the type $[MCl(Ph_2PCH_2CRR'OP(Ph)OCRR'CH_2PPh_2)]Cl$ (M = Pt or Pd) or $[Ni(CN)_2(Ph_2PCH_2CRR'OP(Ph)OCRR'CH_2PPh_2)]$. The nickel complexes are fluxional on the NMR timescale.

Introduction

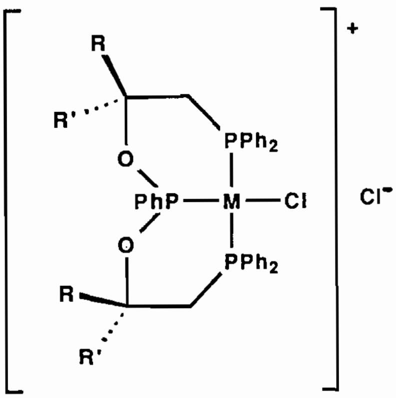
The coordination chemistry of multidentate phosphines has been well studied [1] but the chemistry of multidentate phosphinite, phosphonite, phosphite [2] or mixed P-donor ligands remains largely unexplored. This paper describes the synthesis of one class of diphosphine–phosphonite ligand within the coordination sphere of Pt(II), Pd(II) or Ni(II).

Results and Discussion

Our attempts to make ligands of the type $(Ph_2PCH_2CR_2O)_2PPh$ by the method shown in eqn. (1) were unsuccessful, giving many uncharacterised products. However treatment of either *cis* or *trans*-platinum complexes **1a** [3] with $PhPCl_2$ gave, after spontaneous elimination of HCl, the desired salt **2a** in good yield. This reaction (eqn. (2)) has been extended to the related platinum complexes **1b**, **c** [4] and the palladium complexes **1d**–**f** [5]. The products **2a**–**f** have been characterised by a combination of elemental analysis, solution conductivity measurements, IR and particularly $^{31}P\{^1H\}$ NMR spectroscopy (see Tables 1 and 2). For example, complex **1a** has a conductivity typical of a 1:1 electrolyte and a single ν(Pt–Cl) band at 315 cm^{-1}. The $^{31}P\{^1H\}$ NMR spectrum of **2a** consists of a doublet in the normal

$$PhPCl_2 + 2Ph_2PCH_2CMe_2OH \longrightarrow PhP(OCMe_2CH_2PPh_2)_2 \qquad (1)$$

$$[MCl_2(Ph_2PCH_2CRR'OH)_2] \xrightarrow{PhPCl_2}$$



(2)

1a	M = Pt	R = R′ = Me	**2a**	M = Pt	R = R′ = Me
1a	M = Pt	R = R′ = Me	**2a**	M = Pt	R = R′ = Me
1c	M = Pt	R = R′ = H	**2c**	M = Pt	R = R′ = H
1d	M = Pd	R = R′ = Me	**2d**	M = Pd	R = R′ = Me
1e	M = Pd	R = Me, R′ = H	**2e**	M = Pd	R = Me, R′ = H
1f	M = Pd	R = R′ = H	**2f**	M = Pd	R = R′ = H

TABLE 1. Elemental analysis[a] and conductivity data[b]

	C	H	Cl	Λ[b]
2a	49.35 (49.35)	4.45 (4.90)	7.55 (7.65)	80
2b	48.25 (48.25)	4.25 (4.60)		115
2c	47.45 (47.05)	3.90 (4.30)	8.25 (8.15)	51
2d	54.20 (54.60)	5.15 (5.40)	8.50 (7.70)	92
2e	53.65 (53.55)	4.75 (5.10)		
2f	51.95 (52.30)	4.35 (4.75)		

[a] All the compounds are dihydrates. Calculated values in parentheses. [b] Measured in acetone as 10^{-3} M solutions; units of cm^2 Ω^{-1} mol^{-1}.

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TABLE 2. $^{31}P\{^1H\}$ NMR[a] and IR[b] data

	$\delta(P_A)$	$^1J(PtP_A)$	$\delta(P_X)$	$^1J(PtP_X)$	$^2J(P_AP_X)$	IR bands
2a	1.7	2260	77.2	3861	26	315
2b	3.8	2243	92.4	4036	25	315
2b′	10.9	2340	88.7	4001	24	
2b″	9.5[c, d]	2247	94.9	4031	28	
	4.8	2285			28	
2c	4.2	2271	145.7	4016	26	320
2d	−0.9		110.1		25	320
2e	12.9		119.6		18	305
2e′	2.0		129.6		20	
2e″	12.4[c, e]		124.0		22	
	2.8				17	
2f	6.1		121.7		18	315
5	−17.5[f]		147.9		79	2315[g]

[a] All spectra measured in $CDCl_3$ at 28 °C and 40.25 MHz unless stated otherwise. Chemical shifts are in ppm (±0.1) to high frequency of external 85% H_3PO_4 and coupling constants are in Hz (± 3). P_A are the phosphines and P_X is the phosphonite within a complex. [b] CsCl discs. The bands are ν(MCl) unless stated otherwise. [c] Contains inequivalent phosphine groups (see structures 2b and 2c) and hence an ABX pattern observed. [d] $^2J(P_AP_B)$ 360 Hz. [e] $^2J(P_AP_B)$ 394 Hz. [f] At −40 °C. [g] ν(CN).

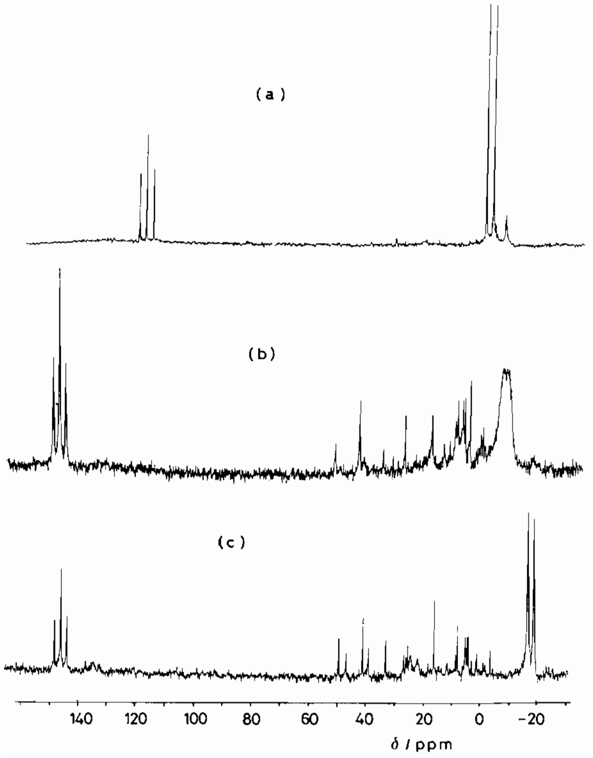
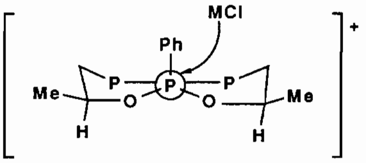
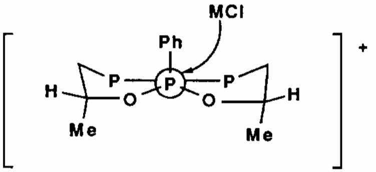


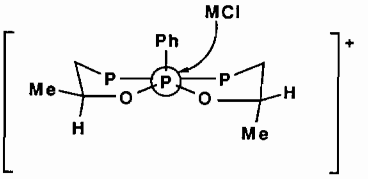
Fig. 1. $^{31}P\{^1H\}$ NMR spectra of: (a) the product of 3 + $PhPCl_2$ and assigned structure 4; (b) the product of 4 + NEt_3 and assigned structure 5 at +28 °C; (c) 5 at −60 °C; the signals in the range 0 to +50 ppm are unidentified impurities.



(i) meso



(ii) meso



(iii) d,l-

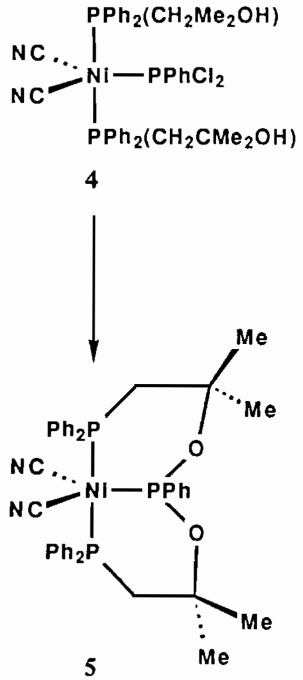
The three diastereoisomers (i) - (iii) of 2b (M = Pt) and 2e (M = Pd)

phosphine region and a triplet at high frequency assigned to the phosphonite phosphorus; the small ^2J(PP) is consistent with the coupled phosphorus nuclei being mutually *cis* and the ^1J(PtP) values are consistent with the phosphine phosphorus nuclei being *trans* to each other (see Table 1). The $^{31}P\{^1H\}$ NMR spectra of the complexes **2b** and **2e** show the presence of three species which are assigned to the diastereoisomeric structures shown.

The nickel cyanide complex **3** reacts with $PhPCl_2$ to give a deep red solution, the $^{31}P\{^1H\}$ NMR spectrum (at +28 °C) of which shows a sharp doublet at 3.3 and a sharp triplet at 123.9 ppm with ^2J(PP) 93 Hz; this species is tentatively assigned the five-coordinate structure **4** (eqn. (3)). Treatment of **4**

$[Ni(CN)_2(Ph_2PCH_2CMe_2OH)_2] + PhPCl_2 \longrightarrow$

3



4

5

(3)

with triethylamine gives a yellow solution containing a complex whose $^{31}P\{^1H\}$ NMR spectrum at +28 ℃ is broad but at −40 ℃ is clearly a sharp doublet and triplet (Fig. 1). This yellow species has been isolated and is assigned structure **5** on the basis of its non-conductivity in acetone solution, infrared and $^{31}P\{^1H\}$ NMR spectroscopy (see Tables 1 and 2). The fluxionality of **5** may be due to interconversion of four- and five-coordinate species e.g. by reversible dissociation of one of the P atoms from the nickel (see Scheme 1).

Experimental

All operations were carried out under a dry nitrogen atmosphere although the products were not air sensitive once isolated. Compounds **1a**–**e** were made as previously described [3–5].

Preparation of *$[Cl\overset{|}{P}t(Ph_2\overset{|}{P}CH_2CMe_2OP(Ph)OCMe_2CH_2\overset{|}{P}Ph_2)]Cl$ (2a)*

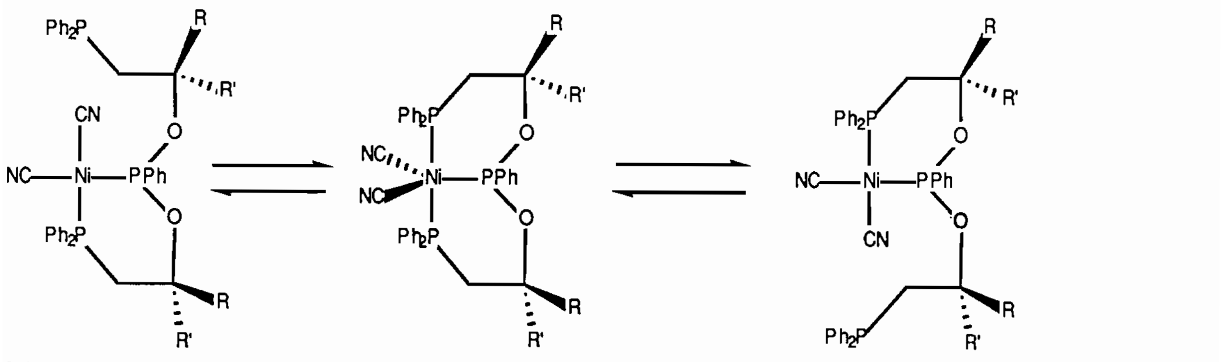
A solution of $PhPCl_2$ (28 mg, 0.16 mmol) in $CDCl_3$ (0.5 cm^3) was added dropwise to a solution of *trans*-$[PtCl_2(Ph_2PCH_2CMe_2OH)_2]$ (**1a**) (205 mg, 0.25 mmol) in $CDCl_3$ (1.0 cm^3) over 5 min. The reaction was complete upon mixing, as shown by $^{31}P\{^1H\}$ NMR spectroscopy. The solvent was removed at reduced pressure and the crude product recrystallised from acetone/diethyl ether to give the white solid product (150 mg, 60%). The following were made similarly in the yields indicated: **2b** (62%), **2c** (55%), **2d** (92%), **2e** (51%), **2f** (55%).

Preparation of trans-$[Ni(CN)_2(Ph_2PCH_2CMe_2OH)_2] \cdot H_2O$ (3)

A suspension of $Ni(CN)_2 \cdot 4H_2O$ (155 mg, 0.85 mmol) and $Ph_2PCH_2CMe_2OH$ (790 mg, 3.1 mmol) in ethanol (25 cm^3) was heated to reflux for 16 h. The mixture was then filtered and the filtrate reduced to dryness to give a yellow oil. This oil was dissolved in $CHCl_3$ (5 cm^3), cooled to 0 ℃ and then diethyl ether was added to precipitate the product as a yellow powder (340 mg, 62%). *Anal.* Found: C, 63.05; H, 6.20; N, 4.45. Calc. for $C_{34}H_{40}N_2NiO_3$: C, 63.25; H, 6.15; N, 4.31%. Molecular weight (in $CHCl_3$): 618 (calc. 627).

Preparation of *$[(NC)_2\overset{|}{N}i(Ph_2PCH_2CMe_2O\overset{|}{P}(Ph)OCMe_2CH_2\overset{|}{P}Ph_2)]$ (5)*

A solution of **3** (103 mg, 0.16 mmol) in $CDCl_3$ (1.0 cm^3) was treated with a solution of $PhPCl_2$ (31 mg, 0.17 mmol) in $CDCl_3$ (0.5 cm^3) to give a red solution. Triethylamine (0.1 cm^3) was then added; an exothermic reaction took place and the solution lightened to yellow. The solvent was then removed *in vacuo* and the residue extracted with $CHCl_3$ (2 X 5 cm^3); the resulting solution was then concentrated to 2 cm^3 and the yellow product precipitated by the



Scheme 1. A possible mechanism for the fluxionality of complex 5.

addition of light petroleum (boiling point 60–80 °C). Satisfactory elemental analysis results were not obtained: C, 62.6 (65.5); H, 6.0 (5.65); N, 3.55 (3.85).

Acknowledgements

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