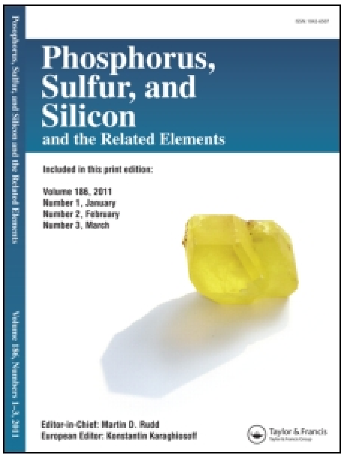

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Late Transition Metal Complexes of a Coumarin-Functionalized Ditertiary Phosphine

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Late Transition Metal Complexes of a Coumarin-Functionalized Ditertiary Phosphine

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The synthesis of a new coumarin-modified ditertiary phosphine is reported along with three square-planar Pd^{II} and Pt^{II} complexes. All compounds have been characterised by $^{31}P\{^{1}H\}$ and ^{1}H NMR spectroscopy, FT–IR spectroscopy and microanalysis. Furthermore a single crystal X-ray structure determination of one of these complexes has been undertaken.

Keywords Tertiary phosphine; coumarin; platinum; palladium; X-ray crystallography

INTRODUCTION

Coumarin-containing compounds have found important uses as ligands for the synthesis of coordination complexes based on Mo,[1] Ru,[2] Os,[3] Ir,[4] Pd,[5] and Pt.[6] In these complexes, the coumarin group can participate in monodentate, didentate or η^6-arene binding modes to a metal centre based upon the coumarin/donor atoms present. Coumarins and/or their metal complexes have been shown to display interesting biological,[5] cation/anion sensor,[7,8] phosgene detection,[9] and luminescent properties.[4] As part of ongoing studies[10] investigating new phosphine ligands, accessible through simple condensation reactions, we describe here the preparation of a new coumarin based ditertiary phosphine and a preliminary study of its coordination chemistry to some d^8 square planar metal centers.

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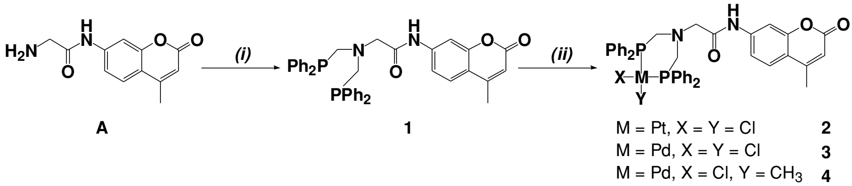
RESULTS AND DISCUSSION

The ditertiary phosphine ligand **1** containing an aminocoumarin modified group was prepared according to Scheme 1. The precursor **A** was prepared from 7-amino-4-methylcoumarin using a procedure similar to one previously reported.[11] In the $^{31}P\{^1H\}$ NMR spectrum of **1**, a phosphorus resonance at $\delta(P)$ −26.2 ppm ($CDCl_3$) was observed in a region typical for this kind of ditertiary phosphine.[10]

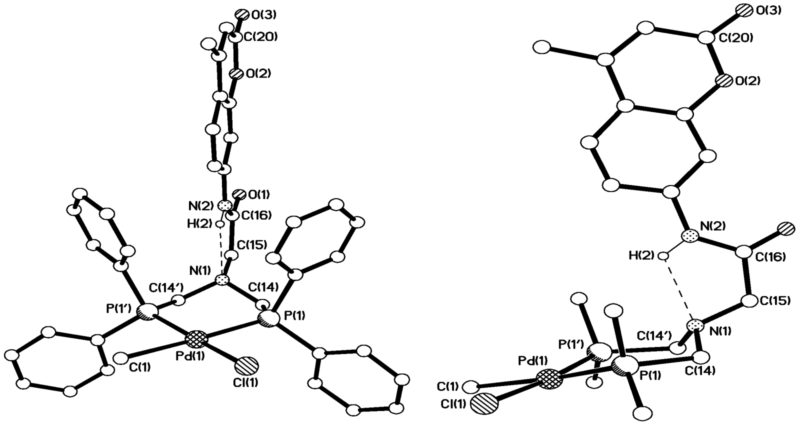


SCHEME 1 (*i*) Ph_2PCH_2OH, CH_3OH *(ii)* $MCl_2(COD)$ or $Pd(CH_3)Cl(COD)$, CH_2Cl_2.

Reaction of **1** with either $MCl_2(COD)$ (M = Pt, Pd; COD = cycloocta-1,5-diene) or $Pd(CH_3)Cl(COD)$ in CH_2Cl_2 gave the corresponding complexes **2–4** in good yields. The $^{31}P\{^1H\}$ NMR data fully support *P*, *P*-chelation as indicated by the downfield shift in the phosphorus signals. Furthermore, a $^1J(PtP)$ coupling constant of 3419 Hz was observed for **2** and in accord with a *cis* arrangement of the ditertiary phosphine. All complexes were also characterized by FT–IR spectroscopy and microanalysis (see Experimental Section for details).

Suitable crystals of **4** were obtained by vapour diffusion of diethyl ether into a CH_2Cl_2 solution over the course of several days. The single crystal X-ray structure[12] of **4** has been determined (Figure 1) with selected bond lengths and angles given in Table I. The coordination environment around the palladium center comprises a chelating ditertiary phosphine **1**, one chloride and a methyl group. The molecule lies on a crystallographic mirror plane which runs through Pd(1), the chain from N(1) to N(2) and through the coumarin fused rings. This results in 50:50 positional disorder in the metal-coordinated chloride and methyl groups. Within the Pd−P−C−N−C−P six-membered ring the nitrogen atom lies 0.799 Å above the plane of the P_2C_2 substituents and the palladium(II) atom 0.467 Å below this plane. There is also an intramolecular N(2)−H(2)· · ·N(1) hydrogen bond [N(2)· · ·N(1) 2.756(9) Å, H(2)· · ·N(1) 2.27 Å; N(2)−H(2)· · ·N(1) 114°].

In summary, we have shown that a new coumarin functionalised ditertiary phosphine can be prepared and complexed to Pd^{II} and Pt^{II}



(a) (b)

FIGURE 1 a) Molecular structure of **4**; and (b) PdP_2C_2N ring conformation in **4**. All hydrogen atoms except H(2) and solvent molecules have been omitted for clarity. Symmetry operator ′= x, 1−y, z.

metal centres. Further studies are currently underway looking at other coumarin based ligands, their complexes and electronic properties.

EXPERIMENTAL

The phosphine ligand **1** was prepared by a standard procedure.[10] $^{31}P\{^{1}H\}$ NMR [$CDCl_3$]: δ(P) −26.2 ppm. ^{1}H NMR: 8.32–6.44 (arom. *H*), 6.18 (COC*H*), 4.10 (N*H*), 3.71 (NCH_2CO), 3.67 (PCH_2N), 2.39 (CH_3) ppm. The following method is a general procedure used for the synthesis of complexes **2–4**. For **2**: To a CH_2Cl_2 (5 mL) solution of $PtCl_2$(COD) (0.044 g, 0.118 mmol) was added ligand **1** (0.103 g, 0.164 mmol) in CH_2Cl_2 (5 mL). The solution was stirred for 45 min, and the volume reduced to *ca.* 2 mL under reduced pressure. Addition of diethyl ether

TABLE I Selected Bond Lengths (Å) and Angles (°) for 4. Symmetry Operator ′ = x, 1−y, z

Pd(1)–P(1)	2.2963(13)	P(1)–Pd(1)–P(1′)	95.02(7)
Pd(1)–Cl(1)	2.3579(19)	P(1)–Pd(1)–C(1)	173.99(6)
Pd(1)–C(1)	2.3579(19)	P(1)–Pd(1)–Cl(1)	88.06(6)
O(2)–C(20)	1.380(10)	Cl(1)–Pd(1)–C(1)	88.43(9)
O(3)–C(20)	1.254(12)	C(14)–N(1)–C(14‘)	111.6(6)

(5 mL) gave a solid **2**, which was collected by filtration and dried in vacuo. Yield: Quantitative. Compounds **3** and **4** were prepared in a similar manner. Selected data for **2**: $^{31}P\{^1H\}$ NMR [$(CD_3)_2SO$]: δ(P) −9.7 ppm, ^1J(PtP) 3419 Hz. ^1H NMR: 10.18 (N*H*), 7.95–7.36 (arom *H*), 6.34 (COC*H*), 4.28 (PCH_2N), 3.59 (NCH_2CO), 2.45 (CH_3) ppm. FT—IR (KBr): ν_{NH} 3324, ν_{CO} 1718, 1701, ν_{PtCl} 314, 293 cm^{-1}. FAB-MS: *m/z* 859 [M–Cl]. Calcd. for $C_{38}H_{34}N_2O_3P_2PtCl_2\cdot 0.1CH_2Cl_2$: C, 50.67; H, 3.82; N, 3.10. Found: C, 50.80; H, 4.11; N, 3.70. Selected data for **3**: $^{31}P\{^1H\}$ NMR [$(CD_3)_2SO$]: δ(P) 6.0 ppm. ^1H NMR: 10.15 (N*H*), 7.88–7.29 (arom. *H*), 6.25 (COC*H*), 4.16 (PCH_2N), 3.54 (NCH_2CO), 2.38 (CH_3) ppm. FT—IR (KBr): ν_{NH} 3316, 3263, ν_{CO} 1719, 1702, ν_{PdCl} 304, 298 cm^{-1}. FAB-MS: *m/z* 771 [M–Cl]. Calcd. for $C_{38}H_{34}N_2O_3P_2PdCl_2\cdot 0.5CH_2Cl_2$: C, 54.50; H, 4.16; N, 3.30. Found: C, 54.58; H, 4.17; N, 3.64. Selected data for **4**: $^{31}P\{^1H\}$ NMR [$(CD_3)_2SO$]: δ(P) 22.6, −11.0 ppm, ^2J(PP) 48 Hz. ^1H NMR: 9.73 (N*H*), 7.58–7.00 (arom. *H*), 6.04 (COC*H*), 3.94 and 3.80 (both PCH_2N), 3.24 (NCH_2CO), 2.17 (CH_3), 0.12 ($PdCH_3$) ppm. FT–IR (KBr): ν_{NH} 3317, ν_{CO} 1724, 1702 cm^{-1}. FAB-MS: *m/z* 771 [M–CH_3]. Calcd. for $C_{39}H_{37}N_2O_3P_2PdCl\cdot 0.5CH_2Cl_2$: C, 57.30; H, 4.63; N, 3.38. Found: C, 57.48; H, 4.65; N, 3.62.

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[12] Crystal data for **4**: $C_{40}H_{36}Cl_3N_2O_3P_2Pd$, $M = 867.40$; orthorhombic, *Pnma*, $a = 28.571(3)$, $b = 17.5634(18)$, $c = 8.2536(8)$ Å, $V = 4141.6(7)$ Å^3; $Z = 4$, ρ_{cal} 1.391 g cm^{-3}; μ(Mo-Kα) = 0.757 mm^{-1}; λ = 0.71073 Å, $T = 150(2)$ K; 32496 reflections were collected on a Bruker SMART 1000 CCD diffractometer[13] using narrow ω-scans, 4871 of which were independent ($R_{\text{int}} = 0.0611$). The structure was solved by Patterson synthesis and refined on F^2 values to give a final $R = 0.0628$ for 4871 data with $F^2 > 2\sigma$ (F^2); $wR_2 = 0.1612$ for all data.[14] The chloride/methyl ligands exhibit 50:50 positional disorder across the crystallographic mirror plane. **4** was found to contain disordered molecules of CH_2Cl_2; these were modelled by the Platon Squeeze procedure.[15] A complete set of X-ray crystallographic structural data for compound **4** (CCDC no. 642380) is available at the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.ac.uk) on request, quoting the deposition number.

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