Use of Michael Additions to $(Ph_2P)_2C{=}CH_2$ Complexes to prepare Thiophene- and Pyrrole-functionalised Metal–Phosphine Complexes†

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The complex $[Pd(O_2CMe)_2(vdpp)]$ **1a** [vdpp = $(Ph_2P)_2C{=}CH_2$] undergoes nucleophilic addition at the double bond with primary alcohols to afford $[Pd(O_2CMe)_2\{(Ph_2P)_2CHCH_2OR\}]$ **2** [R = Me, Et, $CH_2CH_2C_4H_3S$-3 or $CH_2C_6H_3(OMe)_2$-3,4]. These were not isolated pure, but metathesis with NaI gave the corresponding diiodides **3**, which were isolated, and have been fully characterised by microanalysis and infrared and NMR (^1H and ^{31}P-$\{^1H\}$) spectroscopies. By using 2-(3-thienyl)ethanol as the nucleophile, the complex $[PdI_2\{(Ph_2P)_2CHCH_2OCH_2CH_2C_4H_3S\text{-}3\}]$ **3c** was obtained, and its electrochemistry examined. The reactivity of the double bond in **1a** towards other potential weak nucleophiles has been examined. In particular, pyrrole underwent electrophilic addition with **1a** to give, after work-up with NaI, $[PdI_2\{(Ph_2P)_2CHCH_2C_4H_3NH\}]$ **4b**. Proton NMR spectroscopy established that **4b** was a mixture of 2- and 3-pyrrole isomers (*ca.* 3:1). The complexes $[MCl_2(vdpp)]$ (M = Pd **1c** or Pt **1d**) were less reactive, but underwent addition with alcohols in the presence of NEt_3 as catalyst to afford $[MCl_2\{(Ph_2P)_2CHCH_2OR\}]$ (M = Pd **5** or Pt **6**, R = Et or $CH_2CH_2C_4H_3S$-3). The complex $[Pt(vdpp)_2][PF_6]_2$ **7** has been prepared from $[PtCl_2(PhCN)_2]$, vdpp and $AgPF_6$ in dichloromethane–acetonitrile. Details of the reaction of **7** with 2-(3-thienyl)ethanol are given. The crystal structure of **3c** has been determined.

Much effort is currently being expended on devising new methods for modifying electrode surfaces, stimulated by the potential for applications in, for example, analysis.[1] We are interested in the modification of electrodes with metal complexes having potential electrocatalytic or catalytic properties.[2] An elegant method of electrode modification is the electropolymerisation of a suitable monomer,[2–4] since precise control of the amount of metal complex deposited per unit area is then possible, *via* control of the charge passed in the electropolymerisation. The anodic polymerisation of a metal complex incorporating thiophene- or pyrrole-functionalised ligands affords a poly(heterocycle) coating on the electrode.[2,5–8] For the metal complex to be incorporated into the polymer film intact, it must be stable at the anodic potential required to oxidise the heterocycle to its radical cation, the key intermediate in the subsequent polymerisation.

Although tertiary phosphines have been widely employed in co-ordination and organometallic chemistry, and their platinum metal complexes display wide-ranging catalytic activity, we are not aware of any reports of polymer-modified electrodes involving such ligands. This may in part be due to the fact that suitable functionalised phosphines, particularly bidentate examples, would be both difficult and tedious to synthesise.

Shaw and co-workers have shown that, although the double bond in unco-ordinated 1,1-bis(diphenylphosphino)ethene (vdpp) is not normally susceptible to nucleophilic attack, complexation to a variety of metal centres {*e.g.* $M(CO)_4$ (M = Cr, Mo or W),[9,10] PtX_2 (X = Me, Cl or I),[11,12] or $[PtMe_3I(vdpp)]^{12}$} activates the double bond such that various nucleophiles (particularly hydrazines, amines and carbanions) can undergo conjugate or Michael addition to it under mild conditions. We wished to see whether this reaction could be used to synthesise heterocycle-functionalised diphosphine complexes, for possible electropolymerisation.

It has been shown that the electrooxidation of pyrroles functionalised with pendant amines,[13] or of thiophenes in the presence of added amines,[14] does not afford conducting polymers. This is probably due to rapid deprotonation of the electrogenerated heterocycle radical cation. Therefore we required a non-basic (and electroinactive) link between the diphosphine and the heterocycle moiety. For this reason, we wished to avoid amine groups, and identified alcohols as suitable nucleophiles. Alcohols are very weak nucleophiles, but a preliminary communication has appeared indicating that Pd^{II} [$PdCl_2$, and particularly $Pd(O_2CMe)_2$] activates vdpp very greatly, to such an extent that addition of alcohols to $[Pd(O_2CMe)_2(vdpp)]$ to afford (after metathesis) $[PdI_2\{(Ph_2P)_2CHCH_2OR\}]$ occurs readily.[15] We have used this reaction to isolate and characterise fully complexes of formula $[PdI_2\{(Ph_2P)_2CHCH_2OR\}]$, including an example with a pendant 3-thiophene moiety (R = $CH_2CH_2C_4H_3S$-3) which has been characterised crystallographically. A preliminary electrochemical investigation of some of these complexes has been undertaken. We have also found that the addition of alcohols to $[MCl_2(vdpp)]$ (M = Pd or Pt) is catalysed by excess of NEt_3.

Since the NH group in pyrrole has a pK_a similar to the OH group in alcohols, we also wished to see whether pyrrole would react with palladium(II) complexes of vdpp to give complexes of the $(Ph_2P)_2CHCH_2NC_4H_4$ moiety, which might also serve as monomers for electropolymerisation reactions. We report the results of these studies here, together with preliminary details of the synthesis and reactivity of a novel cationic complex, $[Pt(vdpp)_2]^{2+}$.

Results and Discussion

Additions to $[Pd(O_2CMe)_2(vdpp)]$.—Treatment of $Pd(O_2CMe)_2$ in dichloromethane with 1 equivalent of vdpp gave

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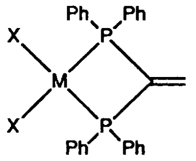
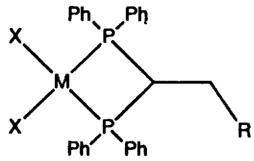
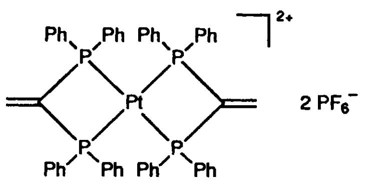
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Non-S.I. unit employed: mmHg ≈ 133 Pa.





	M	X		M	X	R
1a	Pd	O_2CMe	**2a**	Pd	O_2CMe	OMe
1b	Pd	I	**2b**	Pd	O_2CMe	OEt
1c	Pd	Cl	**2c**	Pd	O_2CMe	$OCH_2CH_2C_4H_3S$-3
1d	Pt	Cl	**2d**	Pd	O_2CMe	$OCH_2C_6H_3(OMe)_2$-3,4
			3a	Pd	I	OMe
			3b	Pd	I	OEt
			3c	Pd	I	$OCH_2CH_2C_4H_3S$-3
			3d	Pd	I	$OCH_2C_6H_3(OMe)_2$-3,4
			4a	Pd	O_2CMe	C_4H_3NH(mix of 2- and 3- isomers)
			4b	Pd	I	C_4H_3NH(mix of 2- and 3- isomers)
			5a	Pd	Cl	OEt
			5b	Pd	Cl	$OCH_2CH_2C_4H_3S$-3
			6a	Pt	Cl	OEt
			6b	Pt	Cl	$OCH_2CH_2C_4H_3S$



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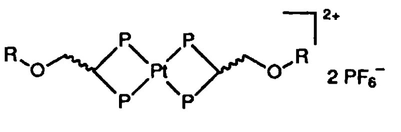

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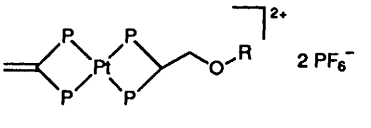

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R = $CH_2CH_2C_4H_3S$-3
(phenyl rings omitted for clarity)

$[Pd(O_2CMe)_2(vdpp)]$[15] **1a**. Preliminary attempts to add 2-(3-thienyl)ethanol to **1a** using a very large excess of alcohol[15] were unsatisfactory; work-up proved difficult. However, $^{31}P-\{^1H\}$ NMR spectroscopy established that when methanol or ethanol (3 mol equivalents) was added to a solution of **1a**, prepared *in situ* in dichloromethane, $>85\%$ conversion into $[Pd(O_2CMe)_2\{(Ph_2P)_2CHCH_2OR\}]$[15] (R = Me **2a** or Et **2b**) occurred over 5–10 h, and these were isolated satisfactorily as the diiodides **3a** and **3b** respectively, after metathesis with NaI. Analytical and spectroscopic data for **2a**, **2b**, **3a** and **3b** were in agreement with those reported.[15] Similarly $[PdI_2\{(Ph_2P)_2CHCH_2OCH_2CH_2C_4H_3S\text{-}3\}]$ **3c** was therefore prepared from **1a** and a three-fold excess of 2-(3-thienyl)ethanol. It was characterised by (*i*) microanalytical data (Table 1), (*ii*) the $^{31}P-\{^1H\}$ NMR spectrum, which showed a singlet at δ(P) −49.22, upfield from that of $[PdI_2(vdpp)]$ **1b** as expected,[12] and in the same region as **3a** and **3b**, (*iii*) X-ray crystallography (see later) and (*iv*) the ^1H NMR spectrum. The latter showed a $CHCH_2$ moiety with both types of proton coupled to phosphorus and to each other, resonances at δ(H) 7.12 and 6.69 due to two of the three thiophene-ring protons (the third is at lower field and obscured by resonances due to phenyl-ring protons) and a pair of triplets at δ(H) 3.12 and 2.64 due to the OCH_2CH_2 moiety. In common with most of the adducts described below, the complexes **3** showed a tendency to crystallise with non-stoichiometric amounts of solvent strongly occluded. Proton NMR spectroscopy was useful in characterising this. Attempts to obtain solvent-free complexes by drying *in vacuo* with heating invariably resulted in partial reversal of the addition reaction.

Benzyl alcohols added readily to complex **1a**. For example, 3,4-dimethoxybenzyl alcohol added to give $[PdI_2\{(Ph_2P)_2CHCH_2OCH_2C_6H_3(OMe)_2\text{-}3,4\}]$ **3d**. However these benzyl ethers were labile and could not be obtained pure.

The NH group of pyrrole has a pK_a similar to that of alcohols. There has been much interest in metal complex-functionalised heterocyclic polymers derived from *N*-functionalised pyrroles[5,6] and we wished to see whether addition of pyrrole to complex **1a** would occur at nitrogen, thus affording a potential monomer for electropolymerisation. When excess of pyrrole and **1a** were mixed in dichloromethane an adduct **4a** formed. This was isolated as the diiodide **4b** and characterised by (*i*) microanalytical data (Table 1) and (*ii*) the $^{31}P-\{^1H\}$ NMR spectrum, which showed a rather broad singlet at δ(P) −45.33. However, the ^1H NMR spectrum (Table 2) revealed that **4b** was a mixture of isomers (*ca.* 3:1). The major isomer had resonances due to pyrrole CH groups at δ(H) 6.42, 5.90 and 5.41 (all multiplets), the minor isomer at δ(H) 6.60, 5.74 and 5.71 (all multiplets). The resonances due to the P_2CH moieties for the isomers are distinct, but those due to the P_2CHCH_2 protons apparently overlap. The data clearly indicate that the isomers are due to addition of pyrrole *via* C(2) and C(3) (presumably major and minor isomers respectively, given the known reactivity of pyrrole towards electrophiles). This is further supported by the IR spectrum of **4b** which showed a weak, sharp band at 3330 cm^{-1}, assigned to ν(N–H). *N*-Methylpyrrole also appears to undergo addition ($^{31}P-\{^1H\}$ NMR evidence) but a pure product could not be isolated.

There is precedent for this reaction. Pyrroles, with or without N-substituents, will react with electron-deficient alkenes and alkynes at both 2 and 3 positions to afford either maleic or fumaric acid derivatives (Michael addition), or (2 + 4) cycloaddition products (Diels–Alder reaction), depending on the reaction conditions and on the pyrrole-substitution pattern.[16]

We tried adding other aromatic molecules activated towards electrophilic substitution to complex **1a**. 1,2-Dimethoxybenzene, thiophene and 4-fluoro-1,2-dimethoxybenzene did not react. We have also examined a wide range of weak nucleophiles to see which were capable of adding to **1a**. That secondary alcohols and phenols (*via* oxygen) added was established by $^{31}P-\{^1H\}$ NMR spectroscopy, but the adducts could not be obtained pure and showed a tendency to decompose rapidly in solution upon attempted work-up, to $[PdI_2(vdpp)]$ and dark, uncharacterised products. When added to a solution of **1a**, Bu^tOH caused decomposition. No signal in the correct region for an addition product was observed in the $^{31}P-\{^1H\}$ NMR spectrum of the mixture. Amides did not react with **1a** and terminal acetylenes caused rapid decomposition to dark, uncharacterised products.

Electrochemistry of Complexes **3a**–**3c**.—Cyclic voltammetry studies of complex **3c** (5 mmol dm^{-3} in 0.2 mol dm^{-3} tetraethylammonium tetrafluoroborate–acetonitrile electrolyte) showed a broad irreversible anodic process centred at +0.9 V *vs.* saturated calomel electrode (SCE). A related cathodic process centred at +0.6 V was observed on the reverse sweep. A second irreversible process was seen at > +1.70 V. Since the electrochemistry of **3a** and **3b** was similar except for this second

Table 1 Analytical, FAB-mass and selected IR spectral data

Compound	Analysis[a] (%) C	H	N	IR[b]/cm^{-1}	FAB,[c] m/z
1a	57.3 (58.0)	4.40 (4.55)		1610, 1595s [ν(C=O)]	
3c	43.35 (43.45)	3.45 (3.40)			758 [M − I]$^+$
4b	44.90 (44.95)[d]	3.65 (3.45)[d]	1.65 (1.60)[d]	3330m (sharp) [ν(NH)] 1710m [ν(C=O)][d]	697 [M − I]$^+$
5a	54.30 (54.25)	4.55 (4.55)			
5b	54.60 (54.75)	4.30 (4.30)			
6a	47.35 (47.45)	3.95 (4.00)			
6b	48.20 (48.50)	4.40 (4.40)	≈0.2 (0.00)[e]		755 [M − Cl]$^+$
7	48.75 (48.90)	3.50 (3.45)			
8 and **9**[f]	49.70 (50.10)	3.90 (3.95)			1389, 1243, 1414, 1260[g]

[a] Calculated values in parentheses. [b] As Nujol mulls. [c] Recorded in 3-nitrobenzyl alcohol; see Experimental section. [d] Figures calculated for acetone solvate on the basis of IR and ^{1}H NMR data. [e] Due to $\mathrm{NEt_3}$ (^{1}H NMR evidence). [f] Calculated values apply to complex **8**. [g] See text for assignments.

Table 2 ^{31}P-{^{1}H}[a] and selected ^{1}H[b] NMR spectroscopic data

Complex	^{31}P-{^{1}H} NMR	^{1}H NMR
1a	−16.4	
2c	−34.6	
2d	−33.0	
3c	−49.2	7.12 (m), 6.69 (m) (thiophene CH) 5.00 [$\mathrm{C}H\mathrm{CH_2}$, J(HH) 8, J(HP) 11.4] 3.12 ($\mathrm{OC}H_2\mathrm{CH_2}$) 3.02 [$\mathrm{CHC}H_2$, J(HP) 12.4] 2.64 ($\mathrm{OCH_2C}H_2$)
3d	−49.3	4.48 [$\mathrm{(CH_3O)_2C_6H_3C}H_2\mathrm{O}$] 3.83, 3.70 [$\mathrm{(C}H_3\mathrm{O)_2C_6H_3CH_2O}$] 3.15 [$\mathrm{CHC}H_2$, J(HP) 12]
4a	−30.3	
4b	−45.3	6.42, 5.90, 5.41 (pyrrole CH)[c] 6.60, 5.74, 5.71 (pyrrole CH)[d] 5.07 [$\mathrm{C}H\mathrm{CH_2}$, J(HH) 8.2, J(HP) 11.7][c] 4.96 ($\mathrm{C}H\mathrm{CH_2}$, m)[d] 2.65 [$\mathrm{CHC}H_2$, J(HP) 14][e]
5a	−41.6	4.68 [$\mathrm{C}H\mathrm{CH_2}$, J(HH) 8, J(HP) 12.0] 3.11 [$\mathrm{CHC}H_2$, J(HP) 12.7] 2.99 (q), 1.03 (t) ($\mathrm{OCH_2CH_3}$)
5b	−41.4	7.16, 6.90 (each 1 H, m, thiophene CH) 4.76 [$\mathrm{C}H\mathrm{CH_2}$, J(HH) 7, J(HP) 11.0] 3.25 [$\mathrm{OC}H_2\mathrm{CH_2}$, J(HH) 6] 3.20 [$\mathrm{CHC}H_2$, J(PH) 13.0] 2.81 ($\mathrm{OCH_2C}H_2$)
6a	−51.5 [J(PPt) 3105]	4.71 [$\mathrm{C}H\mathrm{CH_2}$, J(HH) 8.2, J(HP) 11.3][f] 3.06 [$\mathrm{CHC}H_2$, J(HP) 12.8] 2.95, 1.04 [$\mathrm{OCH_2CH_3}$, J(HH) 7]
6b	−51.6 [J(PPt) 3095]	7.17, 6.80 (both ^{1}H, m, thiophene CH) 4.57 [$\mathrm{C}H\mathrm{CH_2}$, J(HH) 8.1] 3.09 [$\mathrm{OC}H_2\mathrm{CH_2}$, J(HH) 6.4] 3.00 [$\mathrm{CHC}H_2$, J(HP) 13.0] 2.69 ($\mathrm{OCH_2C}H_2$)
7	−12.1 [J(PPt) 2083]	6.79 [$\mathrm{C}H\mathrm{CH_2}$, complex m, J(HPt) 11][g]
8	27.1[h] [J(PPt) 2028]	5.86 [$\mathrm{C}H\mathrm{CH_2}$, J(HH) 7.8, J(HP) 13.1, J(HPt) 11.4][g] 3.42 [$\mathrm{OC}H_2\mathrm{CH_2}$, J(HH) 5.6] 3.38 ($\mathrm{CHC}H_2$, complex m) 2.70 ($\mathrm{OCH_2C}H_2$)
9	−9.4, −25.1 (AA′XX′)[h] [$J(\mathrm{P_APt})$ 2094, $J(\mathrm{P_XPt})$, 2055, $J(\mathrm{P_AP_X})$, *ca.* 10, $J(\mathrm{P_AP_{A'}})$ *ca.* 40, $J(\mathrm{P_AP_{X'}})$ 390][i]	6.62 (complex m, $\mathrm{CH_2}$)[g] 5.79 (complex m, $\mathrm{C}H\mathrm{CH_2}$) 3.37 (t, $\mathrm{OC}H_2\mathrm{CH_2}$) 3.32 (complex m, $\mathrm{CHC}H_2$) 2.64 [$\mathrm{OCH_2C}H_2$, J(HH) 6]

[a] Recorded in $\mathrm{CDCl_3}$ at 101.2 MHz unless otherwise noted, chemical shifts in δ, J in Hz. [b] Measured at 250.1 MHz in $\mathrm{CDCl_3}$ unless otherwise noted. [c] Major isomer (2-pyrrole substitution). [d] Minor isomer (3-pyrrole substitution). [e] Resonances for both isomers overlap. [f] Broad lines due to further unresolved coupling to ^{195}Pt. [g] Spectra recorded at 400.1 MHz in $\mathrm{CD_3CN}$. [h] Spectra recorded at 161.9 MHz in $\mathrm{CD_3CN}$. [i] Coupling constants obtained using PANIC.

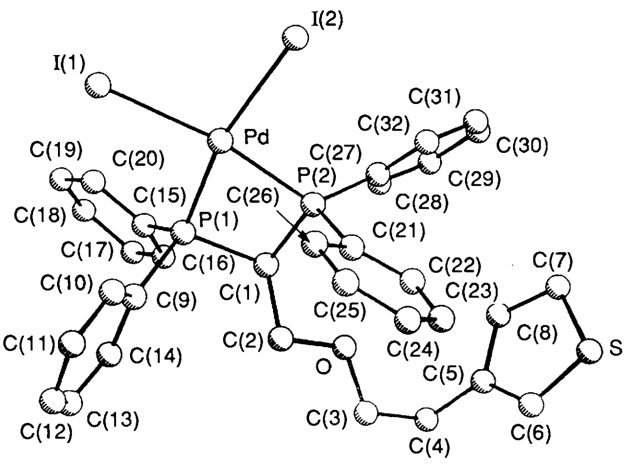

Fig. 1 Molecular structure of $[PdI_2\{(Ph_2P)_2CHCH_2OCH_2CH_2C_4H_3S\text{-}3\}]$ **3c** showing the principal atom numbering scheme. Plot obtained with PLUTO[17]

Table 3 Selected bond lengths (Å) and angles (°) for $[PdI_2\{(Ph_2P)_2CHCH_2OCH_2CH_2C_4H_3S\text{-}3\}]$ **3c**

I(1)–Pd	2.672(3)	C(4)–C(5)	1.55(3)
I(2)–Pd	2.651(3)	C(5)–C(6)	1.43(4)
P(1)–Pd	2.262(6)	C(5)–C(8)	1.44(4)
P(2)–Pd	2.269(6)	C(6)–S(1)	1.64(3)
P(1)–C(1)	1.85(2)	C(7)–S(1)	1.70(2)
P(2)–C(1)	1.84(2)	P(1)–C(9)	1.83(2)
C(1)–C(2)	1.52(3)	P(1)–C(15)	1.81(2)
C(2)–O(1)	1.38(2)	P(2)–C(21)	1.83(2)
O(1)–C(3)	1.44(3)	P(2)–C(27)	1.85(2)
C(3)–C(4)	1.51(3)		
I(1)–Pd–I(2)	95.07(9)	Pd–P(1)–C(1)	94.8(7)
I(1)–Pd–P(1)	98.2(2)	Pd–P(2)–C(1)	94.9(7)
I(1)–Pd–P(2)	169.5(2)	P(1)–C(1)–P(2)	95(1)
I(2)–Pd–P(1)	166.5(2)	P(1)–C(1)–C(2)	120(1)
I(2)–Pd–P(2)	93.0(2)	P(2)–C(1)–C(2)	118(2)
P(1)–Pd–P(2)	74.1(2)	C(1)–C(2)–O(1)	108(2)

Table 4 Atomic coordinates with e.s.d.s in parentheses for complex **3c**

Atom	*x*	*y*	*z*
I(2)	0.514 8(1)	0.823 3(2)	0.358 57(8)
I(2)	0.480 7(1)	0.679 6(3)	0.186 20(8)
Pd	0.398 7(1)	0.704 3(2)	0.267 33(8)
S	0.073 7(6)	0.146(1)	0.015 1(5)
P(1)	0.305 0(3)	0.710 9(7)	0.316 8(3)
P(2)	0.295 4(3)	0.580 5(7)	0.204 4(3)
O	0.124(1)	0.466(2)	0.207 8(7)
N*	0.523(3)	0.292(6)	0.383(3)
C(1)	0.229(1)	0.626(2)	0.251(1)
C(2)	0.178(1)	0.504(3)	0.264 4(9)
C(3)	0.075(2)	0.348(4)	0.215(1)
C(4)	0.010(1)	0.326(4)	0.154(1)
C(5)	0.036(1)	0.295(4)	0.095(1)
C(6)	0.043(2)	0.158(4)	0.077(1)
C(7)	0.085(1)	0.325(2)	0.002 5(8)
C(8)	0.064(2)	0.388(2)	0.054(2)
C(9)	0.318(1)	0.602(2)	0.388(1)
C(10)	0.387(1)	0.522(3)	0.414(1)
C(11)	0.397(2)	0.442(3)	0.469(1)
C(12)	0.340(1)	0.446(3)	0.498(1)
C(13)	0.275(2)	0.521(3)	0.477(1)
C(14)	0.262(1)	0.602(3)	0.421(1)
C(15)	0.264(1)	0.881(3)	0.333(1)
C(16)	0.186(1)	0.907(3)	0.316(1)
C(17)	0.156(2)	1.038(3)	0.333(1)
C(18)	0.209(2)	1.143(3)	0.360(1)
C(19)	0.284(2)	1.121(3)	0.376(1)
C(20)	0.318(1)	0.989(3)	0.362(1)
C(21)	0.310(1)	0.384(2)	0.204(1)
C(22)	0.255(1)	0.300(3)	0.165(1)
C(23)	0.267(1)	0.151(3)	0.168(1)
C(24)	0.333(2)	0.094(3)	0.214(1)
C(25)	0.385(2)	0.182(3)	0.251(1)
C(26)	0.375(1)	0.330(3)	0.247(1)
C(27)	0.246(1)	0.638(2)	0.123(1)
C(28)	0.184(1)	0.725(3)	0.107(1)
C(29)	0.147(2)	0.760(3)	0.040(1)
C(30)	0.176(2)	0.705(3)	−0.003(1)
C(31)	0.238(2)	0.618(3)	0.014(1)
C(32)	0.276(1)	0.578(3)	0.078(1)
C(33)*	0.543(3)	0.215(7)	0.427(3)
C(34)*	0.579(3)	0.142(6)	0.482(3)

* Occupancy 0.5.

wave, we tentatively suggest that the first wave is due to oxidation to Pd^{IV}, which is likely to be an electrochemical process followed by a chemical process (EC) [equation (1)]. Further work, including coulometry, is in progress to characterise this more fully.

$$[PdI_2(P\text{–}P)] \xrightarrow{-2e^-} \{[PdI_2(P\text{–}P)]^{2+}\} \xrightarrow{+2MeCN} [PdI_2(P\text{–}P)(MeCN)_2]^{2+} \quad (1)$$

Crystal Structure of $[PdI_2\{(Ph_2P)_2CHCH_2OCH_2CH_2C_4H_3S\text{-}3\}]$ **3c**.—Air-stable orange block crystals formed when the electrolyte solution of complex **3c** (above) was set aside overnight. Proton NMR spectroscopy confirmed that the crystals were indeed **3c** and showed the presence of acetonitrile of solvation. The molecular structure is shown in Fig. 1 and selected bond lengths and angles are given in Table 3. It confirms that addition of the alcohol to co-ordinated vdpp has occurred, as deduced from the ^1H NMR spectrum. The rather high *R* factor and estimated standard deviations (e.s.d.s) are due to a combination of the presence of disordered acetonitrile solvate molecules in partial occupancy (fixed at 50% during refinement) and the unusually large thermal parameters found for the thiophene moiety. The co-ordination environment about palladium may be compared with that of the closely related complexes $[PdI_2\{(Ph_2P)_2CH_2\}]$[18] and $[PdCl_2\{(Ph_2P)_2CH_2\}]$.[19] Substitution at the ligand methylene carbon has some effect on the geometry of the PdP_2C unit; the Pd–P bond lengths in **3c** are somewhat longer [average 2.266(6) Å] than those of $[PdI_2\{(Ph_2P)_2CH_2\}]$ [average 2.247(1) Å],[18] although the P–M–P bond angles are little different {**3c** 74.1(2); $[PdI_2\{(Ph_2P)_2CH_2\}]$, 72.68(5)°}. In both $[PdI_2\{(Ph_2P)_2CH_2\}]$ [2.241(1), 2.2525(9) Å] and $[PdCl_2\{(Ph_2P)_2CH_2\}]$[19] [2.234(1), 2.250(1) Å] there are significant differences in the Pd–P bond lengths, and this is reflected in the Pd–X bond lengths. The Pd–X bonds *trans* to the shorter Pd–P bonds are themselves longer, and this was rationalised as being due to competition for π-electron density from Pd. However, in **3c** the difference in the Pd–P bond lengths is of the same order as the e.s.d.s and certainly much smaller than the differences seen for $[PdI_2\{(Ph_2P)_2CH_2\}]$ and $[PdCl_2\{(Ph_2P)_2CH_2\}]$. Interestingly, the differences in Pd–I bond lengths in **3c** are, however, much bigger than in $[PdI_2\{(Ph_2P)_2CH_2\}]$ {**3c**, 2.672(3) and 2.651(3); $[PdI_2\{(Ph_2P)_2CH_2\}]$, 2.6514(4) and 2.6519(4) Å}. This illustrates the difficulty inherent in using arguments concerning π bonding to rationalise relatively small bond-length differences.

NEt_3-*Catalysed Addition of Alcohols to* $[MCl_2(vdpp)]$ (M = Pt *or* Pd).—We wished to extend these studies to chloro-complexes, which might be more robust towards electrochemical oxidation to Pd^{IV}. Although alcohols will add to $[PdCl_2(vdpp)]$

1c the reaction is rather slow and requires a large excess of alcohol.[15] Michael additions are generally base-catalysed, and additions to co-ordinated vdpp are no exception.[10–12] We have found that NEt_3 catalyses the addition of alcohols to **1c** markedly. Thus, $[PdCl_2\{(Ph_2P)_2CHCH_2OEt\}]$ **5a** and $[PdCl_2\{(Ph_2P)_2CHCH_2OCH_2CH_2C_4H_3S\text{-}3\}]$ **5b** were isolated in high yield by reaction of a five-fold molar excess of the alcohol with **1c** in dichloromethane in the presence of an excess of amine. It is important to purify the NEt_3 carefully; commercial NEt_3 contains significant amounts of primary and secondary amines which readily add to **1**.

Electrochemically generated platinum(IV) complexes should be more stable than those of Pd^{IV}. However, alcohols did not undergo nucleophilic addition to $[PtCl_2(vdpp)]$ **1d**.[12] We have since found that addition does occur in the presence of NEt_3. Thus a dichloromethane solution of **1d** reacted with ethanol (five-fold excess) over 16 h to afford $[PtCl_2\{(Ph_2P)_2CHCH_2OEt\}]$ **6a** and with 2-(3-thienyl)ethanol to afford $[PtCl_2\{(Ph_2P)_2CHCH_2OCH_2CH_2C_4H_3S\text{-}3\}]$ **6b**. These were characterised by (*i*) microanalytical data (Table 1), (*ii*) fast atom bombardment (FAB) mass spectroscopy (Table 1) which showed peaks due to the parent ions, with isotope patterns close to those calculated, and (*iii*) $^{31}P\text{-}\{^1H\}$ NMR spectroscopy which showed single lines upfield from $[PtCl_2(vdpp)]$ with satellites due to coupling with ^{195}Pt [$^1J(Pt\text{-}P)$ *ca.* 3100 Hz]. Again, the ^1H NMR spectra were particularly informative (Table 2), with that of **6b** showing the distinctive $CHCH_2$ moiety, two of the three thiophene ring protons at δ(H) 7.17 and 6.80 and triplets at δ(H) 2.69 and 3.09 due to the OCH_2CH_2 moiety.

Presumably NEt_3 acts by simple base catalysis, since $^{31}P\text{-}\{^1H\}$ NMR spectra of reaction mixtures always showed exclusively complex **1c** or **1d** and the addition product. No intermediates (involving, for example, substitution of NEt_3 for Cl at the metal centre) were detected. We are investigating the electrochemistry of these complexes; details will be reported elsewhere.

Synthesis and Reactivity of $[Pt(vdpp)_2]^{2+}$.—We reasoned that a cationic metal complex might be even more reactive towards nucleophilic additions than **1a**. However, attempts to prepare $[Pd(vdpp)_2]^{2+}$ by a variety of routes $\{Na_2[PdCl_4]$ + 2 vdpp in ethanol; $PdCl_2$ or $[PdCl_2(PhCN)_2]$ + 2 vdpp in ethanol; $[PdCl_2(PhCN)_2]$, 2 vdpp and 2 $AgPF_6$ in MeCN$\}$ were unsuccessful. A mixture of products was always obtained. $^{31}P\text{-}\{^1H\}$ NMR spectroscopy showed resonances downfield of free vdpp, suggesting that bi- or poly-nuclear diphosphine-bridged species were formed in these reactions.

Attempts to make $[Pt(vdpp)_2]^{2+}$ were more successful. Treatment of $K_2[PtCl_4]$ with 2 mol equivalents of vdpp in ethanol–water afforded an impure and intractable product. However $^{31}P\text{-}\{^1H\}$ NMR evidence suggested that this was largely $[Pt(vdpp)_2]Cl_2$. Pure $[Pt(vdpp)_2][PF_6]_2$ **7** was readily made by treating $[PtCl_2(PhCN)_2]$ in $MeCN\text{-}CH_2Cl_2$ with 2 mol equivalents of vdpp, followed immediately by 2 mol equivalents of $AgPF_6$. Characterising data for **7** are in Tables 1 and 2. In particular, the $^{31}P\text{-}\{^1H\}$ NMR spectrum (acetone–CD_3CN solution) showed a single resonance at δ(P) −12.36 with satellites due to coupling with ^{195}Pt [$^1J(Pt\text{-}P) = 2084$ Hz]. The ^1H NMR spectrum showed a complex second-order multiplet at δ(H) 7.0–6.5, due to the vinylidene $C{=}CH_2$ protons, coupled to all four phosphorus atoms (virtual coupling) and with satellites due to coupling to ^{195}Pt.

The addition of alcohols to complex **7** occurs readily, but the products are labile. When a solution of **7** in acetonitrile was treated with an excess of 2-(3-thienyl)ethanol $^{31}P\text{-}\{^1H\}$ NMR spectroscopy after 24 h showed signals due to $[Pt\{(Ph_2P)_2CHCH_2OCH_2CH_2C_4H_3S\text{-}3\}_2][PF_6]_2$ **8** [δ −26.09; $^1J(Pt\text{-}P) = 2030$ Hz] and $[Pt(vdpp)\{(Ph_2P)_2CHCH_2OCH_2CH_2C_4H_3S\text{-}3\}][PF_6]_2$ **9** (δ −10.20 and −25.08, AA′XX′), together with a small amount (<5%) of starting material. The relative amounts of **7**–**9** were little changed by addition of either more 2-(3-thienyl)ethanol or NEt_3. Work-up yielded a mixture of **8** and **9**. Characterising data are in Tables 1 and 2. Of particular interest is the FAB mass spectrometric data which showed that on dissolution in the matrix compound 3-nitrobenzyl alcohol either alkoxy exchange, or addition of matrix to **9**, or a combination of these processes occurs. Thus, in addition to ions due to $[\mathbf{8} - PF_6]^+$ (*m*/*z* 1389, 20%) (Table 1) and $[\mathbf{8} - HPF_6 - PF_6]^+$ (*m*/*z* 1243, 30%), more intense peaks, with the correct isotope pattern, were evident at 1414 (98%) $[\mathbf{9} + 3\text{-}O_2NC_6H_4CH_2OH - PF_6]^+$ and 1260 (100%) $[\mathbf{9} + 3\text{-}O_2NC_6H_4CH_2OH - HPF_6 - PF_6]^+$. Further studies of the reactivity of **7** with a variety of other nucleophiles are in progress.

Experimental

Infrared spectra were measured as Nujol mulls using a Perkin Elmer 1720X FT spectrometer from 400 to 4500 cm^{-1}, ^1H and $^{31}P\text{-}\{^1H\}$ spectra using a Bruker WM 250 MHz FT spectrometer at 250 and 101 MHz respectively. Selected ^1H NMR spectra were recorded at 400 MHz on a Bruker AMX spectrometer. Samples were dissolved in $CDCl_3$ except for complexes **7**–**9** which were dissolved in CD_3CN. Internal tetramethylsilane (^1H) and external 85% H_3PO_4 ($^{31}P\text{-}\{^1H\}$) were used as references. The FAB mass spectra were recorded using a VG 7070E instrument in positive-ion mode with 3-nitrobenzyl alcohol as solvent and xenon as bombardment gas. Cyclic voltammetry experiments were performed using a laboratory-built potentiostat and a conventional three-electrode cell configuration. Working electrodes were polished platinum discs, counter electrodes were platinum gauzes and the reference electrode was a commercial saturated calomel electrode separated from the working compartment by a glass frit and Luggin capillary. All potentials quoted are referred to the SCE. The ferrocene–ferrocenium couple was examined routinely to check the stability of the reference electrode and junction potentials. Acetonitrile (BDH HPLC grade) was dried by reflux over and distillation from CaH_2. The electrolyte, tetraethylammonium tetrafluoroborate, was prepared from the bromide (Lancaster Synthesis) and 50% HBF_4 (Fluka) in water, and recrystallised three times from hot ethanol. It was dried for 48 h at 10^{-1} mmHg. The ligand vdpp was prepared by a modification of the published method,[20] as were complexes **1c**[15] and **1d**.[12] 2-(3-Thienyl)ethanol was purchased from Aldrich Chemical Co. and stored over 4 Å molecular sieve. Triethylamine was refluxed over and distilled from toluene-*p*-sulfonyl chloride, then redistilled from 4 Å molecular sieves. Pyrrole (Aldrich) was distilled under nitrogen. All other chemicals were used as received.

Preparation of the Alcohol Addition Products.—A similar method was used for all alcohol addition products.

$[PdI_2\{(Ph_2P)_2CHCH_2OMe\}]$ **3a**. To a solution of $Pd(O_2CMe)_2$ (0.30 g, 1.34 mmol) in dichloromethane (5 cm^3) was added vdpp (0.53 g, 1.34 mmol), then methanol (1.0 cm^3, 25 mmol). The formation of $[Pd(O_2CMe)_2\{(Ph_2P)_2CHCH_2OMe\}]$ **2a** was monitored by $^{31}P\text{-}\{^1H\}$ NMR spectroscopy. After 16 h, only **2a** could be detected. The solution was treated with NaI (0.60 g, 4 mmol) in methanol (15 cm^3) with stirring. The product **3a** separated, and was filtered off, washed with methanol and dried *in vacuo* (10^{-1} mmHg) at room temperature for 48 h. Yield 0.87 g, 79%. The complex $[PdI_2\{(Ph_2P)_2CHCH_2OEt\}]$ **3b** was made similarly, on the same scale. Yield 0.98 g, 91%.

$[PdI_2\{(Ph_2P)_2CHCH_2OCH_2CH_2C_4H_3S\text{-}3\}]$ **3c**. To a solution of $Pd(O_2CMe)_2$ (0.20 g, 0.89 mmol) in dichloromethane (5 cm^3) was added vdpp (0.37 g, 0.94 mmol), then 2-(3-thienyl)ethanol (0.38 g, 3.0 mmol). The formation of $[Pd(O_2CMe)_2\{(Ph_2P)_2CHCH_2OCH_2CH_2C_4H_3S\text{-}3\}]$ **2c** was monitored by $^{31}P\text{-}\{^1H\}$ NMR spectroscopy. After 16 h, >95% conversion into **2c** had occurred. The solution was treated with NaI (0.45 g, 3 mmol) in acetone (10 cm^3). Solvent was removed *in vacuo* and the residue extracted with dichloromethane. The product **3c** separated as orange microcrystals on addition of light petroleum (b.p. 40–60 °C). It was filtered off and dried *in vacuo* for 24 h, then recrystallised from acetonitrile as orange prisms. Yield 0.480 g, 61%.

$[PdI_2\{(Ph_2P)_2CHCH_2C_4H_3NH\}]$ **4b** (*mixture of* 2 *and* 3 *isomers*). To a solution of $Pd(O_2CMe)_2$ (0.20 g, 0.89 mmol) in deoxygenated dichloromethane (5 cm^3) was added vdpp (0.37 g, 0.94 mmol), then pyrrole (1.5 cm^3, 22 mmol) under nitrogen. The mixture was put aside in the dark for 16 h. The formation of $[Pd(O_2CMe)_2\{(Ph_2P)_2CHCH_2C_4H_3NH\}]$ **4a** was monitored by $^{31}P\text{-}\{^1H\}$ NMR spectroscopy. After 16 h, >95% conversion into **4a** had occurred. A solution of NaI (0.45 g, 3 mmol) in methanol (8 cm^3) was added. The product **4b** separated as an orange-brown solid. This was filtered off, washed briefly with methanol and dried, *etc.* Yield 0.477 g, 65%.

NEt_3-*Catalysed Additions to* $[MCl_2(vdpp)]$ (M = Pd *or* Pt).—These reactions were all performed using the same general method.

$[PtCl_2\{(Ph_2P)_2CHCH_2OCH_2CH_2C_4H_3S\text{-}3\}]$ **6b**. To a solution of complex **1d** (0.55 g, 0.83 mmol) in dichloromethane (40 cm^3) was added 2-(3-thienyl)ethanol (0.4 cm^3, 2.8 mmol) and triethylamine (0.3 cm^3, 2.0 mmol). The solution was set aside at room temperature, and the progress of the reaction monitored by $^{31}P\text{-}\{^1H\}$ NMR spectroscopy. After 7 d, *ca.* 90% conversion into **6b** had occurred. Solvent was removed under reduced pressure and the residue was triturated with diethyl ether and filtered off. The product was recrystallised from acetone–diethyl ether as cream microcrystals and was dried *in vacuo*. Yield 0.47 g, 75%. It retained occluded NEt_3, diethyl ether and acetone (^1H NMR evidence) which could not be removed at room temperature even on prolonged pumping at 10^{-1} mmHg. Reversion to **1d** occurred on heating *in vacuo*. The complex $[PdCl_2\{(Ph_2P)_2CHCH_2OEt\}]$ **5a** was similarly prepared, but using a larger excess of ethanol (65-fold). Conversion was complete in <4 h.

$[PdCl_2\{(Ph_2P)_2CHCH_2OCH_2CH_2C_4H_3S\text{-}3\}]$ **5b**. This complex was prepared in the same way as **6b**. On recrystallisation from acetone–diethyl ether a small amount of the starting material precipitated initially. This was filtered off and the mother-liquor stored overnight at 5 °C. The product crystallised and was filtered off and dried *etc.* Yield 48%.

$[PtCl_2\{(Ph_2P)_2CHCH_2OEt\}]$ **6a**. This was prepared as for complex **5a**. Conversion as monitored by $^{31}P\text{-}\{^1H\}$ NMR spectroscopy was essentially complete after 7 d. Yield 90%.

$[Pt(vdpp)_2]^{2+}$ *and Adducts*.—$[Pt(vdpp)_2][PF_6]_2$. The complex $[PtCl_2(PhCN)_2]$ (0.25 g, 0.53 mmol) in acetonitrile–dichloromethane (1:1; 50 cm^3) was treated with $AgPF_6$ (0.276 g, 1.09 mmol) in acetonitrile (10 cm^3). The ligand (0.432 g, 1.09 mmol) was added with stirring and AgCl precipitated. The mixture was stirred for 30 min, then filtered through a pad of Kieselguhr. The solvent was removed under reduced pressure. The residue was taken up in a little acetonitrile and the yellow solution filtered again under gravity. The product **7** precipitated upon addition of diethyl ether, as an off-white solid. It was filtered off and dried *in vacuo* for 48 h. Yield 0.54 g, 67%.

Addition of 2-(3-*thienyl*)*ethanol to complex* **7**. To complex **7** (0.24 g, 0.16 mmol) in acetonitrile (10 cm^3) was added 2-(3-thienyl)ethanol (0.2 cm^3). The reaction was monitored by $^{31}P\text{-}\{^1H\}$ NMR spectroscopy. A mixture of **8** and **9** formed (see Results and Discussion). Addition of more 2-(3-thienyl)ethanol (0.4 cm^3) failed to drive the reaction to completion. After 7 d the solvent was removed *in vacuo*, and the residue was taken up in acetone. A pale yellow solid precipitated upon the addition of diethyl ether. This was filtered off, *etc.*

X-Ray Crystallography.—A sample of complex **3c** suitable for single-crystal diffraction analysis was crystallised from acetonitrile–0.2 mol dm^{-3} tetraethylammonium tetrafluoroborate solution.

Crystal data. $C_{33}H_{31.5}I_2OP_2PdN_{0.5}S$, $M = 905.33$, monoclinic, space group $P2_1/a$, $a = 17.90(2)$, $b = 9.202(6)$, $c = 22.23(1)$ Å, $\beta = 107.19(6)°$, $U = 3498(4)$ Å^3, λ (Mo-Kα) = 0.710 69 Å, $Z = 4$, $D_c = 1.719$ g cm^{-3}, $F(000) = 1756$, orange block 0.25 × 0.25 × 0.15 mm, $\mu = 24.42$ cm^{-1}.

Data collection and processing. Rigaku AFC6S diffractometer, ω–2θ mode with maximum 2θ 50.1°, ω scan width = $(1.47 + 0.30 \tan\theta)°$, ω scan speed 8° min^{-1}. Graphite-monochromated Mo-Kα radiation; 7777 reflections measured, 6589 unique [$R_{int} = 0.040$ after empirical absorption correction (minimum, maximum transmission factors = 0.93, 1.00)], giving 1932 with $I > 4.00\sigma(I)$. The intensities of three representative reflections, measured after every 150, remained constant indicating that the crystal did not decompose during data collection.

Structure analysis and refinement. The structure was solved by direct methods.[21] All non-hydrogen atoms except phenyl carbons and the acetonitrile atoms were refined anisotropically. Phenyl carbons were refined isotropically. All H atoms were included in calculated positions and were not refined. The weighting scheme was based on counting statistics and included a factor ($p = 0.03$) to downweight the most intense reflections. The final cycle of full-matrix least-squares refinement,[22] based on 249 variable parameters, converged with unweighted and weighted agreement factors $\{R = \Sigma||F_o| - |F_c||/\Sigma|F_o|, R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2)]^{\frac{1}{2}}\}$ of 0.055 and 0.061 respectively. Neutral atom scattering factors were from Cromer and Waber.[23] Anomalous dispersion effects were included in F_c; the values for $\Delta f'$ and $\Delta f''$ were those of Cromer and Waber.[23] All calculations were performed using the TEXSAN[24] crystallographic software package. The figure was produced using PLUTO.[17]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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