

## Nucleophilic (Michael) Additions to $(\text{Ph}_2\text{P})_2\text{C}=\text{CH}_2$ when Chelated to Dimethylplatinum(II), Di(*o*-tolyl)platinum(II), or Iodo(trimethyl)platinum(IV). Crystal Structure of $[\text{PtMe}_3\{\text{P}(\text{Ph}_2)\text{CH}(\text{P}(\text{Ph}_2)\text{CH}_2\text{NHCH}_2\text{Ph})\}]^\dagger$

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Treatment of  $[\text{PtMe}_2(\text{cod})]$  (cod = cyclo-octa-1,5-diene) with  $(\text{Ph}_2\text{P})_2\text{C}=\text{CH}_2$  (vdpp) gave  $[\text{PtMe}_2(\text{vdpp-PP}')]$  (**1a**). Treatment of  $[\text{Pt}(\text{C}_6\text{H}_4\text{Me-}o)_2(\text{cod})]$  with vdpp, or better,  $[\text{PtCl}_2(\text{vdpp-PP}')]$  with *o*-tolylmagnesium bromide gave  $[\text{Pt}(\text{C}_6\text{H}_4\text{Me-}o)_2(\text{vdpp-PP}')]$  (**1b**). The vinylidene double bond in (**1a**) or (**1b**) was highly activated towards nucleophilic attack (Michael addition) by a variety of amines and hydrazines, yielding adducts of the type  $[\text{PtMe}_2\{\text{P}(\text{Ph}_2)_2\text{CHCH}_2\text{R}\}]$  with R =  $\text{NHNH}_2$  (**2**),  $\text{NHNHMe}$  (**3a**),  $\text{NHCH}_2\text{C}\equiv\text{CH}$  (**4**),  $\text{NMeCH}_2\text{C}\equiv\text{CH}$  (**5**),  $\text{NHCH}_2\text{CH}=\text{CH}_2$  (**6a**),  $\text{NMeCH}_2\text{CH}=\text{CH}_2$  (**7**), *L*- $\text{NHCHMePh}$  (**8a**), *D*- $\text{NHCHMePh}$  (**8b**),  $\text{NHCH}_2\text{Ph}$  (**9**),  $\text{NHCH}_2\text{C}_6\text{H}_4\text{OMe-}4$  (**10**),  $\text{NHCH}_2\text{CH}_2\text{Me}$  (**11**), and  $\text{NHCH}_2\text{CH}_2\text{NH}_2$  (**12**), or of the type  $[\text{Pt}(\text{C}_6\text{H}_4\text{Me-}o)_2\{\text{P}(\text{Ph}_2)_2\text{CHCH}_2\text{R}\}]$  with R =  $\text{NHNHMe}$  (**3b**) or  $\text{NHCH}_2\text{CH}=\text{CH}_2$  (**6b**). Some of the additions were reversible and the adducts of (**1b**) were not isolated pure. The platinum(II) complex (**1a**) reacted with MeI to give *fac*- $[\text{PtMe}_3\text{I}(\text{vdpp-PP}')]$  (**13**) which reacted with  $\text{PhCH}_2\text{NH}_2$  to give  $[\text{PtMe}_3\{\text{P}(\text{Ph}_2)_2\text{CHCH}_2\text{NHCH}_2\text{Ph}\}]$  (**14**) which isomerised in solution to give a mixture of  $[\text{PtMe}_3\{\text{P}(\text{Ph}_2)\text{CH}(\text{P}(\text{Ph}_2)\text{CH}_2\text{NHCH}_2\text{Ph})\}]$  [the title compound, (**15a**)] and (**15b**) in which the H and  $\text{CH}_2\text{Ph}$  on N are interchanged. Eventually, (**15b**) isomerised completely to (**15a**). N.m.r. and i.r. data are given. Crystals of the compound (**15a**) are orthorhombic, space group *Pca*<sub>2</sub>, with *a* = 2 713.1(5), *b* = 1 177.9(2), *c* = 2 139.6(4) pm; final *R* factor 0.0475 for 3 927 observed reflections.

Although tertiary phosphines are important ligands in coordination and organometallic chemistry and are an essential component in many catalytic systems, relatively little has been reported with functionalised phosphines. This is partly due to the multi-stage synthesis often required, particularly in the case of bidentate ligands. We have reported that, although the vinylidene double bond in unco-ordinated 1,1-bis(diphenylphosphino)ethene (vdpp) is not susceptible to nucleophilic attack, complexation to the fragment  $\text{M}(\text{CO})_4$  (*M* = Cr, Mo, or W) activates the double bond such that a variety of nucleophiles (amines, hydrazines, acetylides, other carbanions) can undergo conjugate or Michael addition to it under mild conditions.<sup>1,2</sup> One might anticipate that complexation of vdpp to a metal which is more polarising than  $\text{M}(\text{CO})_4$  would activate the vinylidene double bond towards nucleophilic addition even more. We now report on conjugate additions to vdpp, when complexed to platinum(II) or platinum(IV). A preliminary account of some of this work has been published.<sup>3</sup>

### Results and Discussion

Treatment of  $[\text{PtMe}_2(\text{cod})]$  (cod = cyclo-octa-1,5-diene) with vdpp in dichloromethane gave  $[\text{PtMe}_2(\text{vdpp-PP}')]$  (**1a**), characterized by elemental analysis and i.r. spectroscopy (Table 1) and by  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r.,  $^1\text{H}$ , and  $^1\text{H}\{-^{31}\text{P}\}$  n.m.r. spectroscopy (Table 2). Similar treatment of  $[\text{Pt}(\text{C}_6\text{H}_4\text{Me-}o)_2(\text{cod})]$ <sup>4</sup> with vdpp in dichloromethane gave  $[\text{Pt}(\text{C}_6\text{H}_4\text{Me-}o)_2(\text{vdpp-PP}')]$  (**1b**), although a better yield was obtained by

treating  $[\text{PtCl}_2(\text{vdpp-PP}')]$  with a large excess of *o*-tolylmagnesium bromide (see Experimental section).

Treatment of  $[\text{PtMe}_2(\text{vdpp-PP}')]$  (**1a**) with hydrazine gave the required Michael addition product  $[\text{PtMe}_2\{\text{P}(\text{Ph}_2)_2\text{CHCH}_2\text{-NHNH}_2\}]$  (**2**). Similar treatment of  $[\text{PtMe}_2(\text{vdpp-PP}')]$  (**1a**) with a large excess (*ca.* 50 fold) of methylhydrazine in benzene gave  $[\text{PtMe}_2\{\text{P}(\text{Ph}_2)_2\text{CHCH}_2\text{NHNHMe}\}]$  (**3a**) in a few minutes. This formulation is based on (i) microanalytical data (Table 1); (ii) the i.r. spectrum, which showed a sharp band at 3 300  $\text{cm}^{-1}$  assigned to  $\nu(\text{N-H})$  (Table 1); (iii) the  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. spectrum, which showed a singlet with satellites at  $\delta(\text{P}) = -23.6$  p.p.m.,  $^1J(\text{PtP}) = 1 485$  Hz (Table 2); and (iv) the  $^1\text{H}\{-^{31}\text{P}\}$  n.m.r. and  $^1\text{H}$  n.m.r. spectra, which showed a  $\text{CHCH}_2$  moiety, with both types of proton coupled to phosphorus and to each other, a singlet due to NMe protons, and a broad singlet due to NH protons (data in Table 2). The  $^1\text{H}\{-^{31}\text{P}\}$  n.m.r. pattern of the  $\text{Me}_2\text{Pt}$  protons showed a singlet at  $\delta(\text{H}) = 0.93$  p.p.m., flanked by satellites [ $^2J(\text{PtH}) = 73$  Hz] and in the  $^1\text{H}$  n.m.r. pattern these methyls showed a second order triplet pattern with  $|^3J(\text{PMe})(\text{cis}) + ^3J(\text{PMe})(\text{trans})| = 8$  Hz (data in Table 2). The adduct of methylhydrazine and the *o*-tolyl complex  $[\text{Pt}(\text{C}_6\text{H}_4\text{Me-}o)_2(\text{vdpp-PP}')]$ , *viz.* (**3b**), was made similarly but not isolated pure, showing some tendency to revert back to (**1b**) and was characterized only by n.m.r. (see Table 2).

A wide range of other adducts of  $[\text{PtMe}_2(\text{vdpp-PP}')]$  (**1a**) or of  $[\text{Pt}(\text{C}_6\text{H}_4\text{Me-}o)_2(\text{vdpp-PP}')]$  (**1b**) with hydrazines or amines were prepared and characterized (see Experimental section and Tables 1 and 2 for details). Thus the adducts shown in parentheses were prepared from the following:  $\text{H}_2\text{NCH}_2\text{C}\equiv\text{CH}$  [(**4**)];  $\text{NHMeCH}_2\text{C}\equiv\text{CH}$  [(**5**)];  $\text{H}_2\text{NCH}_2\text{CH}=\text{CH}_2$  [(**6a**) and (**6b**) (identified by n.m.r. and not isolated)];  $\text{HNMeCH}_2\text{CH}=\text{CH}_2$  [(**7**)]; *L*- $\text{H}_2\text{NCHMePh}$  [(**8a**)] and *D*- $\text{H}_2\text{NCHMePh}$  [(**8b**)];  $\text{H}_2\text{NCH}_2\text{Ph}$  [(**9**)];  $\text{H}_2\text{NCH}_2\text{C}_6\text{H}_4\text{OMe-}p$  [(**10**)];  $\text{H}_2\text{NCH}_2\text{CH}_2\text{Me}$  [(**11**)]; and  $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$  [(**12**)]. The NH of olefinic and acetylenic amines added readily to the

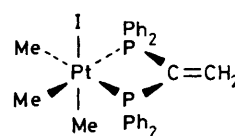
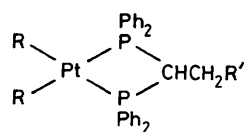
<sup>†</sup>  $[\text{1-Benzylamino-2,2-bis(diphenylphosphino)ethane-N}(\text{Pt}),\text{P}(\text{Pt})\text{-iodotrimethylplatinum(IV)}]$ .

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

**Table 1.** Infrared and analytical data

Complex	Analysis <sup>a</sup> (%)				I.r. data <sup>b</sup> (cm <sup>-1</sup> )
	C	H	N	I	
(1a)	54.1 (54.1)	4.5 (4.5)			1 608w ν(C=C)
(1b)	62.2 (62.0)	4.7 (4.7)			
(2)	51.2 (51.5)	5.0 (5.0)	4.2 (4.3)		3 300m
(3a)	52.5 (52.2)	5.3 (5.2)	4.2 (4.2)		3 300m
(4)	55.4 (55.0)	4.9 (4.9)	2.4 (2.0)		
(5)	55.3 (55.7)	4.9 (5.1)	2.3 (2.0)		
(6a)	54.7 (54.9)	5.1 (5.0)	2.2 (2.1)		3 250m
(7)	55.2 (55.5)	5.6 (5.4)	2.2 (2.0)		
(8a) <sup>c</sup> -0.25CH <sub>2</sub> Cl <sub>2</sub>	56.9 (56.9)	5.1 (5.0)	1.9 (2.0)		3 300w
(8b) <sup>d</sup>	58.9 (58.3)	5.3 (5.3)	2.0 (1.9)		
(9)-0.2CH <sub>2</sub> Cl <sub>2</sub>	57.7 (57.3)	5.3 (5.3)	2.0 (1.9)		3 300m
(10)	56.7 (57.0)	5.1 (5.0)	2.0 (1.9)		
(11)-0.3CH <sub>2</sub> Cl <sub>2</sub>	53.8 (53.7)	5.6 (5.6)	2.1 (2.0)		
(12)	52.9 (52.9)	5.4 (5.4)	3.9 (4.0)		
(13)	45.9 (45.7)	4.0 (4.0)		16.6 (16.7)	
(14)	50.6 (50.5)	4.8 (4.8)	2.1 (2.0)	13.8 (14.0)	3 400m
(15a)-0.3PhCH <sub>2</sub> NH <sub>2</sub>	52.6 (52.9)	5.1 (5.0)	2.9 (2.9)	12.7 (12.9)	3 400w

<sup>a</sup> Calculated values in parentheses. The presence of solvent or free amine was confirmed by <sup>1</sup>H n.m.r. spectroscopy. <sup>b</sup> Nujol mulls. Bands are due to ν(NH) except where otherwise stated. <sup>c</sup> [α]<sup>26</sup> = -9.3° in chloroform. <sup>d</sup> [α]<sup>26</sup> = +9.3° in chloroform.



	R	R'		R	R'
(2)	Me	NHNH <sub>2</sub>	(7)	Me	NMeCH <sub>2</sub> CH=CH <sub>2</sub>
(3a)	Me	NHNHMe	(8a)	Me	L-NHCHMePh
(3b)	C <sub>6</sub> H <sub>4</sub> Me-o	NHNHMe	(8b)	Me	D-NHCHMePh
(4)	Me	NHCH <sub>2</sub> C≡CH	(9)	Me	NHCH <sub>2</sub> Ph
(5)	Me	NMeCH <sub>2</sub> C≡CH	(10)	Me	NHCH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> OMe-4
(6a)	Me	NHCH <sub>2</sub> CH=CH <sub>2</sub>	(11)	Me	NHCH <sub>2</sub> CH <sub>2</sub> Me
(6b)	C <sub>6</sub> H <sub>4</sub> Me-o	NHCH <sub>2</sub> CH=CH <sub>2</sub>	(12)	Me	NHCH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub>

double bond of the vdpp complex (1a). Thus H<sub>2</sub>NCH<sub>2</sub>C≡CH and NHMeCH<sub>2</sub>C≡CH gave the adducts (4) and (5), respectively, NH<sub>2</sub>CH<sub>2</sub>CH=CH<sub>2</sub> gave (6a) and (6b), and HNMeCH<sub>2</sub>CH=CH<sub>2</sub> gave (7). There was no evidence of further interaction of C≡C or C=C bonds with the platinum.

When the vdpp complex (1a) was treated with an excess of 1,2-diaminoethane, only one of the NH<sub>2</sub> groups added and the adduct (12) was obtained in good yield. Of particular interest are the adducts (8a) and (8b) of the optically active amines L- and D-(methylbenzyl)amine. The <sup>31</sup>P-{<sup>1</sup>H} n.m.r. spectra were identical and showed that the two P nuclei were no longer chemically identical with δ(P) = -23.9 and -24.7 p.p.m., <sup>1</sup>J(PtP) = 1 480 Hz in each case, but <sup>1</sup>J(PP) ca. 0 Hz; geminal coupling constants are often very small. The specific rotations of (8a) and (8b) were -9.3 and +9.3°, respectively.

Although [Pt(C<sub>6</sub>H<sub>4</sub>Me-o)<sub>2</sub>(vdpp-PP')] (1b) reacted readily with an excess of methylhydrazine to give the adduct (3b), to the extent of 100% in solution as shown by the <sup>31</sup>P-{<sup>1</sup>H} n.m.r. spectrum, this adduct could not be isolated free from (1b) (<sup>1</sup>H-{<sup>31</sup>P} n.m.r. evidence). Similarly, <sup>31</sup>P-{<sup>1</sup>H} n.m.r. monitoring suggested that allylamine reacted with (1b) to give (6b) to the extent of 100% but this could not be isolated pure. Clearly therefore the additions are reversible and the adducts of (1b) are

less stable than those of (1a), requiring an excess of the nucleophile in solution to drive the reaction to completion. In an attempt to induce the ethynyl group of (4) to react further with the platinum centre, a solution of (4) was heated in boiling toluene for 18 h but the only reaction we could detect was the partial re-formation of the vdpp complex (1a) by reversal of the Michael addition.

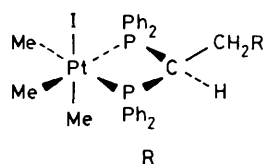
We anticipated that, on co-ordination to platinum(IV), the vinylidene double bond of vdpp would be activated towards Michael addition even more than on co-ordination to platinum(II) because of the additional polarising effect of the platinum(IV) centre. We have therefore investigated the activating effect of a PtMe<sub>3</sub>I moiety co-ordinated to vdpp. Treatment of (1a) with methyl iodide in dichloromethane or toluene gave the oxidative addition product (13) in high yield (further details are given in the Experimental section and characterising data are in the Tables).

On treating [PtMe<sub>3</sub>I(vdpp-PP')] (13) with benzylamine in deuteriochloroform, the adduct [PtMe<sub>3</sub>I{(PPh<sub>2</sub>)<sub>2</sub>CHCH<sub>2</sub>NHCH<sub>2</sub>Ph}] was formed in < 5 min at room temperature. This complex was isolated and fully characterised (data in Tables). In particular only one stereoisomer was formed, to which we assign the structure (14) with the CH hydrogen and the iodide ligand on opposite sides of the PtP<sub>2</sub> plane, because of the subsequent reactions described below. In time, in CDCl<sub>3</sub> solution, the benzylamine adduct (14) changed to two new species, as shown by <sup>31</sup>P-{<sup>1</sup>H} n.m.r. spectroscopy. Both these species showed AX patterns, with satellites due to coupling with platinum-195. Their presence became apparent after 30 min and after 16 h the signals due to the adduct (14) had almost disappeared and the two new patterns were well resolved. The major product had δ(P) = 15.8 p.p.m., J(PtP) = 1 155 Hz and δ(P) = -16.2 p.p.m., J(PtP) = 15 Hz, while the minor product

**Table 2.**  $^{31}\text{P}\{-^1\text{H}\}^a$  and selected  $^1\text{H}^b$  and  $^1\text{H}\{-^{31}\text{P}\}^b$  n.m.r. spectroscopic data

Complex	$^{31}\text{P}\{-^1\text{H}\}$ n.m.r.	$^1\text{H}$ and $^1\text{H}\{-^{31}\text{P}\}$ n.m.r.	Complex	$^{31}\text{P}\{-^1\text{H}\}$ n.m.r.	$^1\text{H}$ and $^1\text{H}\{-^{31}\text{P}\}$ n.m.r.
(1a)	-7.2 (1 475)	5.79 [2 H, C=CH <sub>2</sub> , <i>J</i> (PH) 5.9] <sup>c</sup>	(9)	-24.6 (1 482)	4.45 [CHCH <sub>2</sub> , <i>J</i> (HH) 8]
(1b)	-13.1 (1 450)	6.05 [2 H, C=CH <sub>2</sub> , <i>J</i> (PH) 5.3] 2.34, 2.59 [MeC <sub>6</sub> H <sub>4</sub> , <i>J</i> (PtH) 3.3] <sup>c,d</sup>	(10)	-24.1 (1 482)	3.43 [NHCH <sub>2</sub> Ph] 2.48 [CHCH <sub>2</sub> , <i>J</i> (HH) 8]
(2)	-24.3 (1 477)	4.71 [CHCH <sub>2</sub> , <i>J</i> (HH) 8] 2.94 [NH] 2.48 [CHCH <sub>2</sub> , <i>J</i> (HH) 8] <sup>c</sup>	(11)	-24.4 (1 482)	4.42 [CHCH <sub>2</sub> , <i>J</i> (HH) 8] 3.80 [OMe] 3.36 [NHCH <sub>2</sub> ] 2.46 [CHCH <sub>2</sub> , <i>J</i> (HH) 8] <sup>c</sup>
(3a)	-23.6 (1 485)	5.03 [CHCH <sub>2</sub> , <i>J</i> (HH) 7] 2.85 [NH] 2.00 [CHCH <sub>2</sub> , <i>J</i> (HH) 7] 1.58 [NHMe] <sup>c</sup>	(12)	-24.1 (1 482)	4.44 [CHCH <sub>2</sub> , <i>J</i> (HH) 7.1] 2.41 [CHCH <sub>2</sub> , br] 2.18 [NHCH <sub>2</sub> CH <sub>2</sub> , <i>J</i> (HH) 5.4, <i>J</i> (HNH) 6.6] 1.26 [CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ] 0.77 [CH <sub>2</sub> CH <sub>3</sub> , <i>J</i> (HH) 7.4]
(3b)	-24.1 (1 426)	4.79 [CHCH <sub>2</sub> , <i>J</i> (HH) 8] 2.68 [CHCH <sub>2</sub> , <i>J</i> (HH) 8] 2.48 [NH] 2.26 [MeC <sub>6</sub> H <sub>4</sub> , <i>J</i> (PtH) 3] 1.89 [NHMe]	(13)	-36.5 (893)	4.46 [CHCH <sub>2</sub> , <i>J</i> (HH) 7.9] 2.44 [CHCH <sub>2</sub> , <i>J</i> (HH) 7.9] 2.55 [NHCH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub> , <i>J</i> (HH) 5.6] 2.28 [NHCH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub> , <i>J</i> (HH) 5.6] 1.26 [NH] 6.36 [P <sub>2</sub> C=CH <sub>2</sub> ] 1.69 [ <i>cis</i> -PtMe <sub>2</sub> , <i>J</i> (PtH) 63] 0.72 [PtMe( <i>trans</i> -I), <i>J</i> (PtH) 7.7]
(4)	-23.8 (1 490)	4.38 [CHCH <sub>2</sub> , <i>J</i> (HH) 8] 3.11 [NMeCH <sub>2</sub> C] 2.52 [CHCH <sub>2</sub> , <i>J</i> (HH) 8] 2.11 [C≡CH, <i>J</i> (HH) 2]	(14)	-37.3 (930)	5.30 [P <sub>2</sub> CHCH <sub>2</sub> , <i>J</i> (HH) 7.4, <i>J</i> (PH) 14.0] 3.70 [NHCH <sub>2</sub> ] 3.20 [P <sub>2</sub> CHCH <sub>2</sub> , <i>J</i> (HH) 7.4, <i>J</i> (PH) 10] 4.37 [dd, H <sup>5</sup> , <i>J</i> (H <sup>5</sup> H <sup>6</sup> ) 12.5, <i>J</i> (H <sup>5</sup> H <sup>4</sup> ) 4.3] 3.20 [P <sub>2</sub> CHCH <sub>2</sub> , <i>J</i> (HH) 7.4, <i>J</i> (PH) 10]
(5)	-23.6 (1 482)	5.65, 4.95, 4.93 [H <sup>1</sup> , H <sup>2</sup> , H <sup>3</sup> respectively, <i>J</i> (H <sup>1</sup> H <sup>2</sup> ) 10.3, <i>J</i> (H <sup>1</sup> H <sup>3</sup> ) 17.2, <i>J</i> (H <sup>2</sup> H <sup>3</sup> ) 1.5, CH <sub>2</sub> CH <sup>1</sup> =CH <sup>2</sup> H <sup>3</sup> , H <sup>3</sup> <i>trans</i> H <sup>1</sup> ] 2.86 [NHCH <sub>2</sub> C, <i>J</i> (HH <sup>1</sup> ) 6.0] 2.41 [CHCH <sub>2</sub> , <i>J</i> (HH) 8.1] 1.50 [NH]	(15a) <sup>e</sup>	15.8 [ <i>J</i> (PtP)] 1 155, [ <i>J</i> (PP) 15] -16.2 [ <i>J</i> (PtP)] 15]	4.29 [dd, H <sup>9</sup> , <i>J</i> (HH) <sup>f</sup> 14, <i>J</i> (PtH <sup>9</sup> ) 9.4] 3.91 [br, m, NH] 3.19 [dd, H <sup>8</sup> , <i>J</i> (HH) <sup>f</sup> 14, <i>J</i> (PtH <sup>8</sup> ) 8.8] 2.95 [m, H <sup>4</sup> , <i>J</i> (H <sup>4</sup> H <sup>5</sup> ) 4.1 or 4.3, <i>J</i> (H <sup>4</sup> H <sup>6</sup> ) 4.3 or 4.1, <i>J</i> (P <sup>1</sup> H <sup>4</sup> ) 13, <i>J</i> (P <sup>2</sup> H <sup>4</sup> ) <i>ca.</i> 0] 2.37 [m, H <sup>6</sup> , <i>J</i> (P <sup>1</sup> H <sup>6</sup> ) 12, <i>J</i> (P <sup>2</sup> H <sup>6</sup> ) <i>ca.</i> 0] 1.47 [d, PtMe <sup>1</sup> , <i>J</i> (PtH) 72, <i>J</i> (P <sup>1</sup> H) 6.8] <sup>g</sup> 1.32 [d, PtMe <sup>2</sup> , <i>J</i> (PtH) 50, <i>J</i> (P <sup>1</sup> H) 7.6] <sup>g</sup> 0.79 [d, PtMe <sup>3</sup> , <i>J</i> (PtH) 76, <i>J</i> (P <sup>1</sup> H) 7.3] <sup>g</sup>
(6a)	-24.5 (1 477)	5.65, 4.95, 4.93 [H <sup>1</sup> , H <sup>2</sup> , H <sup>3</sup> respectively, <i>J</i> (H <sup>1</sup> H <sup>2</sup> ) 10.3, <i>J</i> (H <sup>1</sup> H <sup>3</sup> ) 17.0, <i>J</i> (H <sup>2</sup> H <sup>3</sup> ) 1.7, CH <sub>2</sub> CH <sup>1</sup> =CH <sup>2</sup> H <sup>3</sup> , H <sup>3</sup> <i>trans</i> H <sup>1</sup> ] 4.38 [CHCH <sub>2</sub> , <i>J</i> (HH) 6.4] 2.71 [N(Me)CH <sub>2</sub> , <i>J</i> (HH <sup>1</sup> ) 6.4] 2.10 [CHCH <sub>2</sub> , <i>J</i> (HH) 6.4] 2.02 [N(Me)CH <sub>2</sub> ]	(15b)	16.5 [ <i>J</i> (PtP)] 1 133, [ <i>J</i> (PP) 51] -23.8 [ <i>J</i> (PtP)] 15, [ <i>J</i> (PP) 51]	
(6b)	-24.8 (1 415)	5.63, 5.08, 5.05 [H <sup>1</sup> , H <sup>2</sup> , H <sup>3</sup> respectively, <i>J</i> (H <sup>1</sup> H <sup>2</sup> ) 10.3, <i>J</i> (H <sup>1</sup> H <sup>3</sup> ) 17.0, <i>J</i> (H <sup>2</sup> H <sup>3</sup> ) 1.7, CH <sub>2</sub> CH <sup>1</sup> =CH <sup>2</sup> H <sup>3</sup> , H <sup>3</sup> <i>trans</i> H <sup>1</sup> ] 4.38 [CHCH <sub>2</sub> , <i>J</i> (HH) 6.4] 2.71 [N(Me)CH <sub>2</sub> , <i>J</i> (HH <sup>1</sup> ) 6.4] 2.10 [CHCH <sub>2</sub> , <i>J</i> (HH) 6.4] 2.02 [N(Me)CH <sub>2</sub> ]	(16)	-38.8 (928)	
(7)	-22.6 (1 487)	4.35 [CHCH <sub>2</sub> , <i>J</i> (HH) 7.9] 3.27 [NHCHMePh, <i>J</i> (HH) 6.6] 2.29 [CHCH <sub>2</sub> , <i>J</i> (HH) 7.9] 1.06 [NHCHMePh, <i>J</i> (HH) 6.6]	(17)	-45.0 (908)	
(8a) <sup>h</sup>	23.9, -24.7 [ <i>J</i> (PtP) 1 480, <i>J</i> (PP) <i>ca.</i> 0]	Identical to (8a)	(18)	-39.5 (941)	
(8b) <sup>h</sup>	-23.9, -24.7 [ <i>J</i> (PtP) 1 480, <i>J</i> (PP) <i>ca.</i> 0]		(19)	-38.7 (928)	

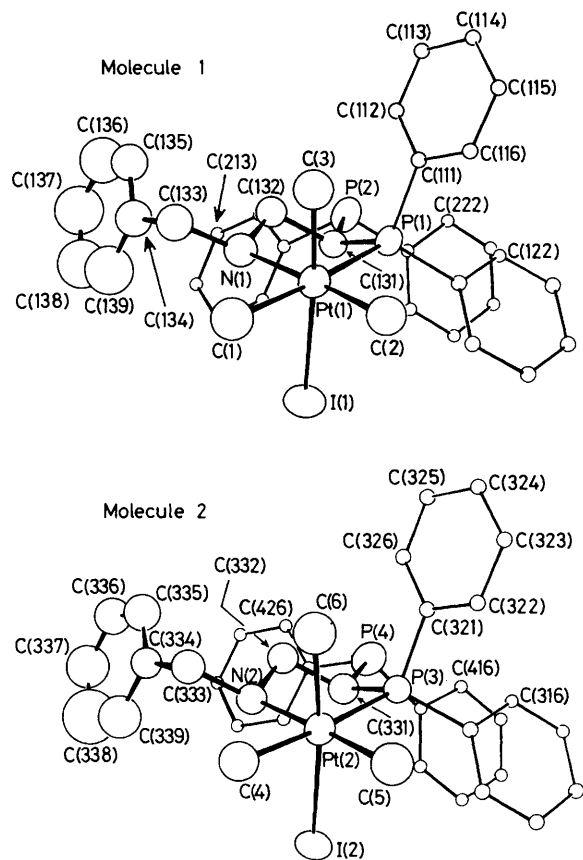
<sup>a</sup> Measured at 40.3 MHz in CDCl<sub>3</sub> solution, unless otherwise indicated. Chemical shifts in p.p.m., *J* in Hz. <sup>b</sup> Measured at 400 MHz in CDCl<sub>3</sub> solution, unless otherwise indicated. The PtMe<sub>2</sub> moiety, common to many of the complexes, is not included. Typically,  $\delta = 0.92$  p.p.m., *J*(PtH) 73 Hz,  $|J(\text{P}_A\text{H}) + J(\text{P}_B\text{H})| = 8$  Hz. In the  $^1\text{H}$  n.m.r. spectra, additional coupling to phosphorus occurs in all P<sub>2</sub>CHCH<sub>2</sub> units as outlined in the text for (3a). <sup>c</sup> Measured at 99.5 MHz in CDCl<sub>3</sub>. <sup>d</sup> Two resonances due to *syn* and *anti* rotameric forms in solution. <sup>e</sup> For proton and phosphorus numbering scheme, see Figure. Multiplicities refer to the  $^1\text{H}\{-^{31}\text{P}\}$  n.m.r. spectrum. <sup>f</sup> *J*(H<sup>8</sup>H<sup>9</sup>) or *J*(H<sup>9</sup>NH). <sup>g</sup> Tentative assignments. <sup>h</sup> Measured at 161.9 MHz in CDCl<sub>3</sub>.



- (14) NHCH<sub>2</sub>Ph  
(16) NHCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>OMe - 4  
(17) NHCH<sub>2</sub>C≡CH  
(18) NMeCH<sub>2</sub>CH=CH<sub>2</sub>  
(19) NHCH<sub>2</sub>CH=CH<sub>2</sub>

showed  $\delta(\text{P}) = 16.5$  p.p.m., *J*(PtP) = 1 133 Hz and  $\delta(\text{P}) = -23.8$  p.p.m., *J*(PtP) = 15 Hz. Clearly, from the magnitude of the coupling to  $^{195}\text{Pt}$ , the second phosphorus was

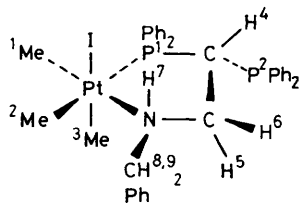
no longer co-ordinated to platinum in either product. After 72 h both (14) and the minor product had disappeared and the only phosphorus-containing product was the major isomer. This was isolated and characterised fully. The microanalytical data (Table 1) and the  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. data (Table 2) suggested that a rearrangement of (14) had occurred in which a phosphorus donor atom had been displaced by the secondary amine function. In order to determine the stereochemistry of the new complex its crystal structure was determined by X-ray diffraction and shown to be (15a), see below and also the Figure. The intermediate and minor isomer discussed above is assigned structure (15b) and differs only from (15a) in that pyramidal inversion at nitrogen has occurred. The  $^1\text{H}$  and  $^1\text{H}\{-^{31}\text{P}\}$  n.m.r. spectra (Table 2) are fully consistent with the structure and are quite complex, with all the CH protons rendered inequivalent by the chelate ring and all three Pt-Me groups inequivalent. The assignments shown in Table 2 were con-



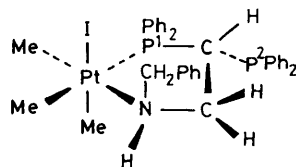
**Figure.** ORTEP drawings of the two crystallographically distinct molecules of  $[\text{PtMe}_3\text{I}\{(\text{PPh}_2)\text{CH}(\text{PPh}_2)\text{CH}_2\text{NHCH}_2\text{Ph}\}]$  (**15a**). The two molecules differ by a slight rotation of the unco-ordinated  $\text{PPh}_2$  group [cf. dihedral angle  $\text{C}(132)\text{--C}(131)\text{--P}(2)\text{--C}(211) = -66.4^\circ$  in molecule 1 and  $\text{C}(332)\text{--C}(331)\text{--P}(4)\text{--C}(421) = -53.6^\circ$  in molecule 2]

firmed by selective  $^1\text{H}\text{--}\{^1\text{H}\}$  and  $^1\text{H}\text{--}\{^31\text{P}\}\{^1\text{H}\}$  decoupling experiments.

The isomerisation of (**14**) to (**15a**) is presumably promoted by the relief of steric strain on expansion from a four- to a five-membered ring and by the co-ordination of the hard  $N$ -donor to the  $\text{Pt}^{\text{IV}}$  centre in place of the softer  $P$ -donor: the dissociation of phosphines from  $\text{fac}\text{--}[\text{PtMe}_3\text{X}(\text{PR}_3)_2]$  has been proposed



(**15a**)



(**15b**)

**Table 3.** Selected interatomic distances (pm) and angles ( $^\circ$ ) for complex (**15a**) with estimated standard deviations (e.s.d.s) in parentheses

Molecule 1		Molecule 2	
I(1)–Pt(1)	285.3(6)	I(2)–Pt(2)	282.5(6)
P(1)–Pt(1)	240.6(9)	P(3)–Pt(2)	235.9(9)
C(1)–Pt(1)	213(3)	C(4)–Pt(2)	211(3)
C(2)–Pt(1)	201(3)	C(5)–Pt(2)	211(3)
C(3)–Pt(1)	207(3)	C(6)–Pt(2)	215(3)
N(1)–Pt(1)	225(2)	N(2)–Pt(2)	222(2)
C(131)–P(1)	186(3)	C(331)–P(3)	185(3)
C(131)–P(2)	184(3)	C(331)–P(4)	190(3)
C(132)–C(131)	158(3)	C(332)–C(331)	153(3)
N(1)–C(132)	147(3)	N(2)–C(332)	151(3)
C(133)–N(1)	152(3)	C(333)–N(2)	153(3)
P(1)–Pt(1)–I(1)	91.7(3)	P(3)–Pt(2)–I(2)	92.3(3)
N(1)–Pt(1)–I(1)	83.0(5)	N(2)–Pt(2)–I(2)	83.0(5)
N(1)–Pt(1)–C(2)	178.6(8)	N(2)–Pt(2)–C(5)	178.0(8)
N(1)–C(132)–C(131)	110(2)	N(2)–C(332)–C(331)	105(2)
C(132)–N(1)–Pt(1)	112(1)	C(332)–N(2)–Pt(2)	113(1)

as the first step in the reductive elimination of ethane and exchange of  $\text{PMe}_2\text{Ph}$  for  $\text{AsMe}_2\text{Ph}$  has been observed on mixing solutions of  $\text{fac}\text{--}[\text{PtMe}_3\text{X}(\text{AsMe}_2\text{Ph})_2]$  ( $X = \text{halide}$ ) and  $\text{PMe}_2\text{Ph}$ .<sup>5</sup>

**Crystal Structure of  $[\text{PtMe}_3\text{I}\{(\text{PPh}_2)\text{CH}(\text{PPh}_2)\text{CH}_2\text{NHCH}_2\text{Ph}\}]$  (**15a**).**—The complex was crystallised from dichloromethane–ethanol. There are two crystallographically independent molecules in the asymmetric part of the unit cell and these are shown in the Figure. The large values of the e.s.d.s, particularly for the Pt–C and Pt–N distances, preclude any detailed comparison but there appear to be no greatly significant differences in bond lengths and angles between the two molecules (see Table 3). They differ most in the twist of the unco-ordinated  $\text{PPh}_2$  group (see caption to Figure). The stereochemistry of the chelate ring confirms the assignment of structure (**14**) to the initial adduct, *i.e.* stereospecific addition of the amine such that the iodine and CH proton are on opposite sides of the  $\text{PtP}_2$  plane. This presumably occurs because of the steric effect of the large iodide ligand.

## Experimental

The general methods used were the same as in other recent papers from this laboratory.<sup>6</sup>

**Preparation of  $[\text{PtMe}_2(\text{vdpp}\text{--}PP')]$  (**1a**).**—1,1-Bis(diphenylphosphino)ethene (vdpp) (0.4 g, 1.0 mmol) was added to a solution of  $[\text{PtMe}_2(\text{cod})]$  (0.33 g, 1.0 mmol) in toluene (20  $\text{cm}^3$ ). The mixture was then stirred for 40 min at  $20^\circ\text{C}$ , after which the solvent was removed *in vacuo* and the residue triturated with hexane, then diethyl ether (10  $\text{cm}^3$ ), to give the required product as white microcrystals. Yield 0.54 g, 87%.

**Preparation of  $[\text{Pt}(\text{C}_6\text{H}_4\text{Me-}o)_2(\text{vdpp}\text{--}PP')]$  (**1b**).**—(i) A mixture of  $[\text{Pt}(\text{C}_6\text{H}_4\text{Me-}o)_2(\text{cod})]$  (0.10 g, 0.21 mmol) and vdpp (0.084 g, 0.21 mmol) in dichloromethane (3  $\text{cm}^3$ ) was heated under reflux for 18 h and then evaporated to dryness. This gave the required product as yellow microcrystals, which were triturated with methanol, filtered off, *etc.* Yield 0.061 g, 38%.

(ii)  $[\text{PtCl}_2(\text{vdpp}\text{--}PP')]$  (0.22 g, 0.33 mmol) and then benzene (5  $\text{cm}^3$ ) were added to a solution of *o*-tolylmagnesium bromide, prepared from magnesium (0.185 g, 7.6 mmol) and *o*-bromotoluene (1.3 g, 7.6 mmol) in dry tetrahydrofuran (thf) (10  $\text{cm}^3$ ). The resultant mixture was stirred for 2 h and then

methanol (5 cm<sup>3</sup>) was added at 0 °C. The solvent was removed *in vacuo* and the residue washed with methanol. This gave the required product. Yield 0.125 g, 49%.

*Preparation of the Michael Addition Products.*—A similar general method was used for all addition products.

[PtMe<sub>2</sub>{(PPh<sub>2</sub>)<sub>2</sub>CHCH<sub>2</sub>NHNH<sub>2</sub>}] (2). Hydrazine hydrate (0.5 cm<sup>3</sup>) was added to a solution of (1a) (0.050 g, 0.08 mmol) in toluene (1 cm<sup>3</sup>). The resultant mixture was then heated under reflux for 30 min, after which it was evaporated under reduced pressure and ethanol added. The required product separated as a white microcrystalline solid. Yield 0.04 g, 77%.

[PtMe<sub>2</sub>{(PPh<sub>2</sub>)<sub>2</sub>CHCH<sub>2</sub>NHNHMe}] (3a). Methylhydrazine (0.1 cm<sup>3</sup>) was added to a solution of (1a) (0.030 g, 0.048 mmol) in benzene (1 cm<sup>3</sup>). The resulting mixture was put aside for 10 min, during which the required product separated out as white needles. These were filtered off, washed with diethyl ether, and dried. Yield 0.029 g, 77%.

[PtMe<sub>2</sub>{(PPh<sub>2</sub>)<sub>2</sub>CHCH<sub>2</sub>NHCH<sub>2</sub>C≡CH}] (4). This was prepared similarly, except that a reaction time of 1 h was used and the product was isolated as pale yellow microcrystals by

evaporation of the reaction mixture and recrystallisation of the residue from dichloromethane–n-hexane. Yield 74%.

[PtMe<sub>2</sub>{(PPh<sub>2</sub>)<sub>2</sub>CHCH<sub>2</sub>NMeCH<sub>2</sub>C≡CH}] (5). This was prepared in a similar manner to (4) and formed pale yellow microcrystals from dichloromethane–n-hexane. Yield 68%.

[PtMe<sub>2</sub>{(PPh<sub>2</sub>)<sub>2</sub>CHCH<sub>2</sub>NHCH<sub>2</sub>CH=CH<sub>2</sub>}] (6a). This was prepared by dissolving [PtMe<sub>2</sub>(vdpp-PP')] (0.030 g, 0.048 mmol) in neat allylamine (0.5 cm<sup>3</sup>). The required product separated out as white needles and was filtered off *etc.* after 30 min. Yield 60%.

[PtMe<sub>2</sub>{(PPh<sub>2</sub>)<sub>2</sub>CHCH<sub>2</sub>NMeCH<sub>2</sub>CH=CH<sub>2</sub>}] (7). This was prepared in a similar manner and scale to (3a) using toluene (1 cm<sup>3</sup>) as solvent. It separated out as white needles. Yield 90%.

[PtMe<sub>2</sub>{(PPh<sub>2</sub>)<sub>2</sub>CHCH<sub>2</sub>NHCHMePh-L}] (8a). This was prepared in a similar manner to (7) and separated from the reaction mixture as white microcrystals. Yield 84%.

[PtMe<sub>2</sub>{(PPh<sub>2</sub>)<sub>2</sub>CHCH<sub>2</sub>NHCHMePh-D}] (8b). This was prepared in a similar manner to (8a). Yield 61%.

[PtMe<sub>2</sub>{(PPh<sub>2</sub>)<sub>2</sub>CHCH<sub>2</sub>NHCH<sub>2</sub>Ph}] (9). This was prepared in a similar manner to (7). White needles were formed. Yield 51%.

[PtMe<sub>2</sub>{(PPh<sub>2</sub>)<sub>2</sub>CHCH<sub>2</sub>NHCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>OMe-4}] (10). This

Table 4. Atomic co-ordinates ( $\times 10^4$ ) for compound (15a)

Atom	x	y	z	Atom	x	y	z
Pt(1)	5 493.4(3)	4 192.9(7)	-772*	C(216)	5 703	3 860	1 828
Pt(2)	3 037.3(3)	835.7(7)	4 070.4(4)	C(221)	4 569(5)	5 415(14)	1 649(8)
I(1)	5 330(1)	2 158(1)	-79(1)	C(222)	4 238	6 238	1 860
I(2)	2 881(1)	2 924(1)	3 452(1)	C(223)	3 776	5 916	2 084
P(1)	4 945(2)	5 246(5)	-105(4)	C(224)	3 644	4 771	2 097
P(2)	5 184(2)	5 811(5)	1 383(3)	C(225)	3 975	3 949	1 887
P(3)	2 474(2)	-120(4)	3 416(4)	C(226)	4 437	4 271	1 663
P(4)	2 626(2)	-713(5)	1 946(3)	C(311)	1 836(4)	336(12)	3 308(7)
C(1)	6 036(10)	3 294(21)	-1 296(12)	C(312)	1 686	1 393	3 531
C(2)	5 016(9)	3 834(20)	-1 462(12)	C(313)	1 205	1 766	3 426
C(3)	5 673(9)	5 612(20)	-1 293(12)	C(314)	875	1 081	3 097
C(4)	3 580(9)	1 602(20)	4 636(12)	C(315)	1 025	24	2 874
C(5)	2 537(9)	1 174(20)	4 802(13)	C(316)	1 506	-349	2 980
C(6)	3 234(9)	-705(21)	4 552(13)	C(321)	2 381(6)	-1 631(9)	3 595(8)
C(111)	4 864(6)	6 730(9)	-305(7)	C(322)	2 072	-1 826	4 105
C(112)	5 079	7 638	14	C(323)	1 993	-2 931	4 317
C(113)	4 994	8 748	-186	C(324)	2 224	-3 841	4 019
C(114)	4 694	8 950	-705	C(325)	2 533	-3 646	3 510
C(115)	4 480	8 042	-1 023	C(326)	2 612	-2 541	3 298
C(116)	4 565	6 932	-823	C(331)	2 842(9)	21(16)	2 690(14)
C(121)	4 318(4)	4 775(12)	48(8)	C(332)	3 375(8)	-326(19)	2 830(11)
C(122)	3 986	5 485	355	N(2)	3 559(6)	544(13)	3 290(8)
C(123)	3 495	5 155	424	C(333)	4 087(9)	207(20)	3 462(14)
C(124)	3 337	4 114	186	C(334)	4 426(6)	268(16)	2 898(7)
C(125)	3 670	3 403	-120	C(335)	4 558	-685	2 549
C(126)	4 161	3 734	-189	C(336)	4 827	-557	1 998
C(131)	5 303(8)	5 104(15)	633(12)	C(337)	4 963	524	1 795
C(132)	5 848(7)	5 407(18)	438(10)	C(338)	4 831	1 477	2 144
N(1)	6 036(6)	4 551(14)	1(9)	C(339)	4 563	1 349	2 696
C(133)	6 569(9)	4 765(20)	-189(13)	C(411)	2 083(4)	76(10)	1 696(7)
C(134)	6 891(6)	4 767(17)	412(8)	C(412)	1 999	1 224	1 818
C(135)	7 027	5 812	666	C(413)	1 561	1 734	1 625
C(136)	7 276	5 854	1 236	C(414)	1 206	1 097	1 309
C(137)	7 389	4 851	1 552	C(415)	1 290	-50	1 187
C(138)	7 253	3 807	1 298	C(416)	1 728	-561	1 380
C(139)	7 004	3 764	728	C(421)	3 100(6)	-332(16)	1 380(8)
C(211)	5 616(5)	5 023(11)	1 887(7)	C(422)	3 226	812	1 329
C(212)	5 860	5 646	2 347	C(423)	3 610	1 143	937
C(213)	6 192	5 107	2 747	C(424)	3 869	330	595
C(214)	6 278	3 944	2 688	C(425)	3 743	-815	645
C(215)	6 034	3 321	2 228	C(426)	3 358	-1 146	1 038

\* Co-ordinate fixed.

was prepared in a similar manner to (7) except that ethanol (5 cm<sup>3</sup>) was added to complete precipitation of the product. White prisms were formed. Yield 56%.

[PtMe<sub>2</sub>{(PPh<sub>2</sub>)<sub>2</sub>CHCH<sub>2</sub>NHCH<sub>2</sub>CH<sub>2</sub>Me}] (11). This was prepared as for (7) except that n-hexane (3 cm<sup>3</sup>) was added to complete the precipitation of the product, white microcrystals. Yield 51%.

[PtMe<sub>2</sub>{(PPh<sub>2</sub>)<sub>2</sub>CHCH<sub>2</sub>NHCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>}] (12). The diamine (H<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>) (0.05 g, 0.82 mmol) was added to a solution of (1a) (0.10 g, 0.16 mmol) in toluene (1 cm<sup>3</sup>). The mixture was put aside for 30 min at room temperature, after which the solvent was removed *in vacuo* and the residue triturated with n-hexane and filtered off. The product was obtained as white microcrystals. Yield 0.065 g, 56%.

[PtMe<sub>3</sub>I(vdpp-PP')] (13). Methyl iodide (0.05 cm<sup>3</sup>) was added to a solution of (1a) (0.020 g, 0.32 mmol) in dichloromethane (2 cm<sup>3</sup>). After 30 min the resultant solution was evaporated to a small volume and diethyl ether added, to give the required product as a pale yellow solid. Yield 0.17 g, 71%.

[PtMe<sub>3</sub>I{(PPh<sub>2</sub>)<sub>2</sub>CHCH<sub>2</sub>NHCH<sub>2</sub>Ph}] (14). Benzylamine (0.1 cm<sup>3</sup>) was added to a solution of (13) (0.05 g, 0.065 mmol) in CDCl<sub>3</sub> (0.5 cm<sup>3</sup>). When the <sup>31</sup>P-{<sup>1</sup>H} n.m.r. spectrum revealed complete conversion to (14) (<5 min), the colourless solution was evaporated *in vacuo* and ethanol added. This gave the required product as white needles. Yield 0.025 g, 43%.

[PtMe<sub>3</sub>I{(PPh<sub>2</sub>)CH(PPh<sub>2</sub>)CH<sub>2</sub>NHCH<sub>2</sub>Ph}] (15a). Benzylamine (0.05 g, 0.47 mmol) was added to a solution of (13) (0.10 g, 0.13 mmol) in CDCl<sub>3</sub> (0.5 cm<sup>3</sup>). After 72 h, <sup>31</sup>P-{<sup>1</sup>H} n.m.r. spectroscopy indicated only (15a) to be present. The solvent was then removed under reduced pressure and the resultant residue was triturated with ethanol. This gave the required product as white needles which were filtered off *etc.* Yield 0.070 g, 55%.

The following four adducts were shown to be formed in solution by <sup>31</sup>P-{<sup>1</sup>H} n.m.r. spectroscopy (data in Table 2), on adding the appropriate amine to [PtMe<sub>3</sub>I(vdpp-PP')], but were not isolated.

Three adducts of the type [PtMe<sub>3</sub>I{(PPh<sub>2</sub>)<sub>2</sub>CHCH<sub>2</sub>NHR}] with R = CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>OMe-4 (16), CH<sub>2</sub>C≡CH (17), CH<sub>2</sub>CH=CH<sub>2</sub> (19), and also [PtMe<sub>3</sub>I{(PPh<sub>2</sub>)<sub>2</sub>CHCH<sub>2</sub>NMeCH<sub>2</sub>CH=CH<sub>2</sub>}] (18).

Two adducts of the type [Pt(C<sub>6</sub>H<sub>4</sub>Me-*o*)<sub>2</sub>{(Ph<sub>2</sub>P)<sub>2</sub>CHCH<sub>2</sub>-NHR}] with R = NHMe (3b) or CH<sub>2</sub>CH=CH<sub>2</sub> (6b) were shown to be formed in solution by <sup>31</sup>P-{<sup>1</sup>H} n.m.r. spectroscopy (data in Table 2) but were not isolated in a pure state because, on attempted isolation, some reversion to (1b) occurred. The reaction conditions were the same as for (3a) or (6a), respectively.

*Demonstration of the Reverse of Michael Addition with (4).*—A solution of [PtMe<sub>2</sub>{(PPh<sub>2</sub>)<sub>2</sub>CHCH<sub>2</sub>NHCH<sub>2</sub>C≡CH}] (4) (0.018 g) in toluene (3 cm<sup>3</sup>) was heated under reflux for 18 h. <sup>31</sup>P-{<sup>1</sup>H} n.m.r. spectroscopy showed an *ca.* 40% reversion to (1a).

*X-Ray Crystallography.*—A sample of compound (15a) suitable for single-crystal diffraction analysis was crystallised from a dichloromethane-ethanol mixture.

*Crystal data for compound (15a).* C<sub>36</sub>H<sub>40</sub>INP<sub>2</sub>Pt *M* = 856.65, orthorhombic, *a* = 2 713.1(5), *b* = 1 177.9(2), *c* = 2 139.6(4) pm, *U* = 6.838 nm<sup>3</sup>, *Z* = 8, space group *Pca*2<sub>1</sub>, *D*<sub>c</sub> = 1.66 g cm<sup>-3</sup>, *μ* = 48.86 cm<sup>-1</sup>, *F*(000) = 3 392.

*Data collection.* Scans running from 0.9° below *K*<sub>α1</sub> to 0.9° above *K*<sub>α2</sub>, scan speeds 2.0–29.3° min<sup>-1</sup>, 4.0 < 2θ < 45.0°. 5 136 Data collected, 3 927 observed [*I* > 2.0σ(*I*)], *T* = 290 K.

*Structure refinement.* Number of parameters = 248, weighting parameter *g* = 0.0005, *R* = 0.0475, *R'* = 0.0495.

All crystallographic measurements were made on a Nicolet P3/F diffractometer operating in the ω/2θ scan mode using graphite-monochromatised Mo-*K*<sub>α</sub> radiation (λ = 71.069 pm) following a standard procedure described in detail elsewhere.<sup>7</sup> The data set was corrected for absorption empirically once the structure had been solved.<sup>8</sup> The compound was solved by direct methods using the SHELX 86 program<sup>9</sup> and refined by full-matrix least squares using the SHELX 76 program.<sup>10</sup> The solution gave two molecules in the asymmetric unit which differed only by the slight rotation of the unco-ordinated PPh<sub>2</sub> group (for comparison see the Figure). Only the Pt, I, and P atoms were assigned anisotropic thermal parameters, all other atoms were assigned individual isotropic thermal parameters. All phenyl groups were treated as rigid bodies and were refined with idealised hexagonal symmetry (C–C = 139.5 pm). No hydrogen atoms were located. The weighting scheme *w* = [σ<sup>2</sup>(*F*<sub>o</sub>) + *g*(*F*<sub>o</sub>)<sup>2</sup>]<sup>-1</sup> was used at the end of refinement with the parameter *g* included in refinement so as to give a flat analysis of variance with increasing sinθ and [*F*/*F*<sub>max</sub>]<sup>1/2</sup>. Refinement of the structure which had been inverted through a centre of symmetry led to slightly higher *R* values. Final atomic co-ordinates are given in Table 4.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

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