

# Unexpected substitution reactions of bis(phosphine)platinum ethene complexes

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Reaction of  $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PR}_3)_2]$  ( $\text{R} = \text{Ph}$  or  $\text{C}_6\text{H}_4\text{Me-4}$ ) with moderately bulky phosphines at low temperatures did not give the expected tris- or tetrakis-phosphine complexes. Instead, mixed-phosphine complexes of the type  $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PR}_3)(\text{PR}'_3)]$  ( $\text{R}' = \text{C}_6\text{H}_{11}$ ,  $\text{C}_6\text{H}_4\text{OMe-4}$ ,  $\text{C}_6\text{H}_4\text{OMe-2}$ ,  $\text{C}_6\text{H}_4\text{Me-4}$  or  $\text{CH}_2\text{Ph}$ ) were formed. With less bulky phosphines, chelating diphosphines or phosphites, mixed tetrakis complexes, many of them prone to disproportionation, were formed. The complexes were characterised by  $^{31}\text{P}$  and  $^{195}\text{Pt}$  NMR spectroscopy in solution.

The complex  $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2]$  has been widely used as a precursor for the preparation of organometallic complexes,<sup>1</sup> co-ordination complexes<sup>2</sup> and oxidative-addition products.<sup>3</sup> It has always been assumed that the ethene ligand is easily displaced. We now report reactions of this type of complex with a wide range of added phosphines, diphosphines and phosphites; with moderately bulky monodentate phosphines, surprisingly, it is the triarylphosphine rather than the ethene which is most readily displaced. A preliminary account of some of this work has been published.<sup>4</sup>

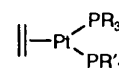
## Results and Discussion

### Reactions of $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PR}_3)_2]$ ( $\text{R} = \text{Ph}$ or $\text{C}_6\text{H}_4\text{Me-4}$ ) with bulky tertiary phosphines

The complexes  $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PR}_3)_2]$  ( $\text{R} = \text{Ph}$  or  $\text{C}_6\text{H}_4\text{Me-4}$ ) were prepared as previously described<sup>5</sup> and were then treated at low temperature with solid samples of a range of phosphines under a positive pressure of argon. The sample was allowed to warm slowly to room temperature and  $^{31}\text{P}$  and  $^{195}\text{Pt}$  NMR spectra were recorded as a function of time and of temperature.

The reaction of  $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2]$ , **1**, with tricyclohexylphosphine was typical. When the  $^{31}\text{P}$  NMR spectrum was recorded at 223 K the major species present gave rise to an AB quartet corresponding to  $[\text{Pt}(\text{C}_2\text{H}_4)\{\text{P}(\text{C}_6\text{H}_{11})_3\}(\text{PPh}_3)]$ , **2** (Table 1). In the  $^{195}\text{Pt}$  NMR spectrum (Table 2) the signal was a doublet of doublets, since  $^1J_{\text{PPt}}$  is significantly different for the two phosphine ligands. Proton NMR spectroscopy revealed a signal for bound ethene at  $\delta$  2.64 (as compared with  $\delta$  2.60 for the starting material) without platinum satellites. Admission of ethene to the sample resulted in a broadened signal at  $\delta$  2.85, indicating that free and bound ethene were undergoing exchange under the conditions of the experiment. This exchange results in transfer of ethene between platinum isotopes, so that coupling information is lost. On warming, the  $^{31}\text{P}$  NMR spectrum became increasingly complex; the optimum concentration (ca. 80% of the material in solution) of the mixed-ligand complex, **2**, was observed at 253 K. At this temperature there is also a small amount of  $[\text{Pt}(\text{PPh}_3)_3]$  ( $\delta$  52.0,  $^1J_{\text{PPt}} = 4400$  Hz) and  $[\text{Pt}(\text{PPh}_3)_4]$  ( $\delta$  11.0).<sup>6</sup> At 298 K we could also identify  $[\text{Pt}(\text{C}_2\text{H}_4)\{\text{P}(\text{C}_6\text{H}_{11})_3\}_2]$ ,<sup>†</sup> ( $\delta$  42.0,  $^1J_{\text{PPt}} = 3658$  Hz),

† It should be noted that it is rare to obtain an exact match for the literature data. Both chemical shifts and coupling constants depend quite strongly on both solvent and temperature. Early reports use a different sign convention.



	R	R'		R	R'
<b>1</b>	Ph	Ph	<b>9</b>	Ph	$\text{CH}_2\text{Ph}$
<b>2</b>	Ph	Cyclohexyl	<b>10</b>	4-MeC <sub>6</sub> H <sub>4</sub>	$\text{CH}_2\text{Ph}$
<b>3</b>	Cyclohexyl	Cyclohexyl	<b>11</b>	4-MeOC <sub>6</sub> H <sub>4</sub>	4-MeOC <sub>6</sub> H <sub>4</sub>
<b>4</b>	Ph	4-MeOC <sub>6</sub> H <sub>4</sub>	<b>12</b>	4-MeC <sub>6</sub> H <sub>4</sub>	4-MeC <sub>6</sub> H <sub>4</sub>
<b>5</b>	Ph	2-MeOC <sub>6</sub> H <sub>4</sub>	<b>13</b>	2-MeOC <sub>6</sub> H <sub>4</sub>	2-MeOC <sub>6</sub> H <sub>4</sub>
<b>6</b>	4-MeC <sub>6</sub> H <sub>4</sub>	2-MeOC <sub>6</sub> H <sub>4</sub>	<b>14</b>	$\text{CH}_2\text{Ph}$	$\text{CH}_2\text{Ph}$
<b>7</b>	Ph	4-MeC <sub>6</sub> H <sub>4</sub>	<b>15</b>	Ph	$\text{R}'_3 = \text{PPhBu}^t_2$
<b>8</b>	4-MeC <sub>6</sub> H <sub>4</sub>	Cyclohexyl			

$[\text{Pt}\{\text{P}(\text{C}_6\text{H}_{11})_3\}_3]$  ( $\delta$  56.0,  $^1J_{\text{PPt}} = 4380$  Hz)<sup>8</sup> and free  $\text{P}(\text{C}_6\text{H}_{11})_3$  ( $\delta$  -7.0).

Although the mixed-ligand complex clearly disproportionated over time it was more stable than we had expected. Neither bubbling nitrogen through the solution nor evacuation had any significant effect. Addition of the sterically undemanding phosphite,  $\text{P}(\text{OPh})_3$ , to **2** did not result in the simple displacement of ethene. The main species produced in this case were  $[\text{Pt}\{\text{P}(\text{OPh})_3\}_2(\text{PPh}_3)_2]$  and  $[\text{Pt}\{\text{P}(\text{OPh})_3\}_3(\text{PPh}_3)]$ , which were identified by comparison with the spectra of these species produced independently (*vide infra*).

Additions of other bulky phosphines to  $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PR}_3)_2]$  proceeded similarly, though the products were formed less cleanly and were in general less stable and more prone to dynamic exchange processes. The  $^{31}\text{P}$  NMR spectroscopic data are given in Table 1; assignment of the phosphine chemical shifts was assisted by using data from the complexes  $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PR}_3)_2]$ , synthesised independently. The  $^{195}\text{Pt}$  NMR spectroscopic data are given in Table 2. Some of the spectra appear as doublets of doublets, and some as triplets, depending on the relative values of  $^1J(\text{Pt}-\text{PPh}_3)$  and  $^1J(\text{Pt}-\text{PR}_3)$ .

One reaction was particularly unusual, that of 1 mol of  $\text{PPhBu}^t_2$  with  $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2]$ ; at 193 K the  $^{31}\text{P}$  NMR spectrum showed that several products had been formed. Starting material was evident, as was the mixed-phosphine complex  $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)(\text{PPhBu}^t_2)]$ . The other species were identified only after warming the solution, when they became more abundant. At 233 K the  $^{31}\text{P}$  NMR spectrum showed a sharp doublet at  $\delta$  -18.5 ( $^1J_{\text{PPt}} = 3765$  Hz) and a quartet at  $\delta$  11.5 ( $^1J_{\text{PPt}} = 3662$  Hz). These were assigned to  $[\text{Pt}(\text{PPh}_3)_3(\text{PPhBu}^t_2)]$  since it was assumed that it would not be possible to make the tetrakis complex in which there were three of the more bulky phosphine ligands, although the shifts are unusual. At 203 K a small amount of the surprisingly sterically hindered species

**Table 1** The  $^{31}\text{P}\{-^1\text{H}\}$  NMR spectroscopic data (thf solution) for complexes 1–15

Complex	<i>T</i> /K	$\delta(\text{PR}_3)$	$^1J(\text{Pt}-\text{PR}_3)/\text{Hz}$	$\delta(\text{PR}'_3)$	$^1J(\text{Pt}-\text{PR}'_3)/\text{Hz}$	$^2J(\text{P}-\text{P})/\text{Hz}$
1	193	35.0	3702			
2	223	33.0	3680	40.6	3620	56
3	298	42.0	3658			
4	193	34.5	3685	29.8	3722	59
5	203	37.3	3916	19.5	3668	54
6	203	34.8	3930	19.5	3684	51
7	190	34.8	3698	31.2	3698	54
8	253	31.0	3680	41.0	3615	56
9	188	39.5	3670	21.0	3570	61
10	193	32.0	3664	16.0	3562	58
11	193	30.6	3692			
12	190	33.0	3701			
13	273	13.0	3452			
14	223	17.0	3589			
15	203	34.0	3647	18.5	3582	59

**Table 2** The  $^{195}\text{Pt}\{-^1\text{H}\}$  NMR spectroscopic data (thf solution) for bis(phosphine)platinum ethene complexes

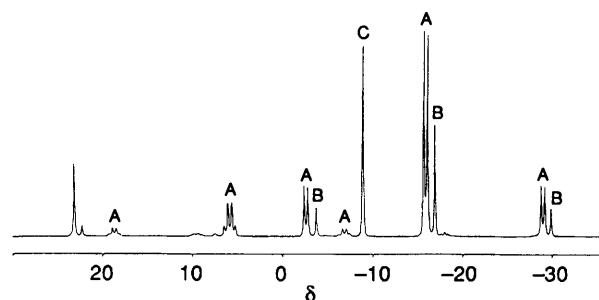
Complex	<i>T</i> /K	$\delta$	$^1J(\text{Pt}-\text{PR}_3)/\text{Hz}$	$^1J(\text{Pt}-\text{PR}'_3)/\text{Hz}$
1	203	-626	3704	
2	253	-645	3680	3620
4	193	-633	3685	3723
7	190	-630	3701	3701
8	253	-627	3690	3619
9	193	-598	3670	3570
11	293	-652	3693	
12	293	-635	3701	

$[\text{Pt}(\text{PPh}_3)_2(\text{PPhBu}'_2)_2]$  could be identified ( $\delta$  11.2,  $^1J_{\text{PPt}} = 3784$ ,  $\delta -23.0$ ,  $^1J_{\text{PPt}} = 3764$ ,  $^2J_{\text{PP}} = 54$  Hz). When the sample was warmed to room temperature and recooled,  $[\text{Pt}(\text{PPh}_3)_3(\text{PPhBu}'_2)]$  was the only platinum-containing species. Reaction of  $\text{PPhBu}'_2$  with  $[\text{Pt}(\text{C}_2\text{H}_4)\{\text{P}(\text{C}_6\text{H}_4\text{Me}-4)_3\}_2]$  gave only  $[\text{Pt}(\text{PPhBu}'_2)\{\text{P}(\text{C}_6\text{H}_4\text{Me}-4)_3\}_2]$ .

Addition of  $\text{PBU}'_3$  to  $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2]$  at low temperature gave no reaction. On warming, the known complex  $[\text{Pt}(\text{PBU}'_3)_2]$  was formed.<sup>9</sup> A number of tris- and tetrakis-phosphine platinum complexes were formed in these reactions after allowing them to equilibrate at room temperature. These were not further investigated, but  $^{31}\text{P}$  NMR spectroscopic data are collected in Table 3 for comparison with the complexes produced in reactions with less bulky phosphines.

#### Reactions of $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PR}_3)_2]$ ( $\text{R} = \text{Ph}$ or $\text{C}_6\text{H}_4\text{Me}-4$ ) with sterically undemanding phosphines

Addition of 1 molar equivalent of  $\text{PPh}_2\text{H}$  to  $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2]$  at 203 K gave a bright yellow solution of  $[\text{Pt}(\text{PPh}_3)_2(\text{PPh}_2\text{H})_2]$  which showed an  $\text{A}_2\text{B}_2\text{X}$  system in its  $^{31}\text{P}$  NMR spectrum (Table 4). Small amounts of  $[\text{Pt}(\text{PPh}_3)(\text{PPh}_2\text{H})_3]$  and  $[\text{Pt}(\text{PPh}_2\text{H})_4]$  were also produced. Warming the solution to 223 K resulted in an essentially complete conversion into  $[\text{Pt}(\text{PPh}_3)(\text{PPh}_2\text{H})_3]$ . When the substrate was  $[\text{Pt}(\text{C}_2\text{H}_4)\{\text{P}(\text{C}_6\text{H}_4\text{Me}-4)_3\}_2]$  the reaction was slower, but the same  $\text{A}_2\text{B}_2\text{X}$  and  $\text{AB}_3\text{X}$  complexes were obtained. Similar results were obtained with  $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2]$  and  $\text{PPh}_2\text{Me}$ ,  $\text{PPh}_2\text{Et}$  or  $\text{PMe}_3$ . All yielded complexes of the type  $\text{A}_2\text{B}_2\text{X}$ ,  $\text{AB}_3\text{X}$  and  $\text{B}_4\text{X}$ , with the proportions depending on the amount of phosphine added. Attempts to isolate the complexes were almost uniformly unsuccessful. Large orange needles were deposited from a solution containing  $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2]$  and an excess of  $\text{PMe}_3$ . However, these proved to be  $[\text{Pt}(\text{PMe}_3)(\text{PPh}_3)_2]\cdot\text{C}_6\text{H}_5\text{Me}$  which was not observed spectroscopically in solution. A preliminary X-ray diffraction study gave the gross formulation (Found: C, 59.1; H, 4.5. Calc. for  $\text{C}_{46}\text{H}_{47}\text{P}_3\text{Pt}$ : C, 58.9; H, 4.9%) but the structural data were of poor quality as the crystal lost solvent

**Fig. 1** The  $^{31}\text{P}\{-^1\text{H}\}$  NMR spectrum [tetrahydrofuran (thf), 243 K] of  $[\text{Pt}(\text{PPh}_3)(\text{PPh}_2\text{Me})_3]$  (A),  $[\text{Pt}(\text{PPh}_2\text{Me})_4]$  (B) and  $\text{PPh}_3$  (C)

very easily. The FAB mass spectrum showed a peak at  $m/z = 719$  corresponding to  $[\text{Pt}(\text{PPh}_3)_2]^+$ . This is reminiscent of our earlier isolation of  $[\text{Pt}(\text{PPh}_3)_3]$  from a sample containing  $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2]$  and  $\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2$ .<sup>10</sup> It is evident that isolation of crystalline material is related to solubility, and does not necessarily reflect the solution equilibria.

#### Reactions of $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PR}_3)_2]$ ( $\text{R} = \text{Ph}$ or $\text{C}_6\text{H}_4\text{Me}-4$ ) with chelating diphosphines

Reaction of 1 mol of  $\text{dppe}$  [1,2-bis(diphenylphosphino)ethane] with  $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2]$  at room temperature gave only starting material and  $[\text{Pt}(\text{dppe})_2]$ . When the reaction was repeated at 203 K the  $^{31}\text{P}$  NMR spectrum showed a complex pattern, accompanied by platinum satellites. These were assigned to  $[\text{Pt}(\text{dppe})(\text{PPh}_3)_2]$ , **16**. These and related spectra were simulated using PANIC<sup>11</sup> (Fig. 2) and the data are given in Table 5. Spectroscopic data for complexes of the type bis(chelating diphosphine)platinum, which were usually formed, at least as a small component of the reaction mixture, are given in Table 6. The  $^{195}\text{Pt}$  NMR spectrum of **16** shows a platinum signal at  $\delta$  507 as a triplet of triplets ( $^1J_{\text{PPt}} = 4070$ ,  $3525$  Hz) (Fig. 3). On warming to 283 K the  $\text{A}_2\text{B}_2\text{X}$  pattern decreased in intensity and the proportion of  $[\text{Pt}(\text{dppe})_2]$  increased. Similar results were obtained with  $[\text{Pt}(\text{C}_2\text{H}_4)\{\text{P}(\text{C}_6\text{H}_4\text{Me}-4)_3\}_2]$  and  $\text{dppe}$ . Reaction of  $\text{dcpe}$  [1,2-bis(dicyclohexylphosphino)ethane] with  $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2]$  at 203 K gave only  $[\text{Pt}(\text{dcpe})_2]$ . Addition of 1 mol of  $\text{dmpe}$  [1,2-bis(dimethylphosphino)ethane] to  $[\text{Pt}(\text{C}_2\text{H}_4)\{\text{P}(\text{C}_6\text{H}_4\text{Me}-4)_3\}_2]$  gave  $[\text{Pt}(\text{dmpe})\{\text{P}(\text{C}_6\text{H}_4\text{Me}-4)_3\}_2]$ .

Reaction of  $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2]$  with  $\text{dppp}$  [1,3-bis(diphenylphosphino)propane] gave the expected complex **18**. For the disproportionation product,  $[\text{Pt}(\text{dppp})_2]$ , two sets of phosphorus nuclei were inequivalent at low temperature, as previously reported.<sup>12</sup> Some formation of  $[\text{Pt}(\text{PPh}_3)_4]$  was also noted. At higher temperatures further disproportionation

**Table 3** The  $^{31}\text{P}\{-^1\text{H}\}$  NMR spectroscopic data (thf solution) for other complexes produced in the reactions of  $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PR}_3)_2]$  with bulky phosphines

Complex	<i>T</i> /K	$\delta(\text{PR}_3)$	$^1J(\text{Pt}-\text{PR}_3)/\text{Hz}$	$\delta(\text{PR}'_3)$	$^1J(\text{Pt}-\text{PR}'_3)/\text{Hz}$	$^2J(\text{P}-\text{P})/\text{Hz}$
$[\text{Pt}(\text{PPh}_3)_2\{\text{P}(\text{C}_6\text{H}_4\text{OMe-4})_3\}_2]$	243	22.1	3518	17.2	4082	46
$[\text{Pt}(\text{PPh}_3)_3(\text{PPhBu}'_2)]$	183	10.4	3770	-19.2	3644	54
$[\text{Pt}(\text{PPh}_3)_2(\text{PPhBu}'_2)_2]$	183	11.2	3784	-23.0	3764	54
$[\text{Pt}\{\text{P}(\text{C}_6\text{H}_4\text{Me-4})_3\}_3(\text{PPhBu}'_2)]$	203	-19.0 <sup>a</sup>	3772	8.5 <sup>a</sup>	3655	<i>b</i>
$[\text{Pt}(\text{PBu}'_3)_2]$	203			98.0	4492	

<sup>a</sup> Assignments uncertain. <sup>b</sup> Not determined.

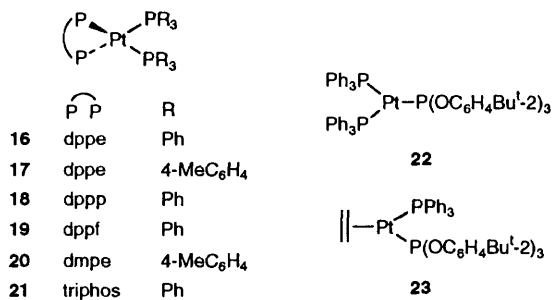
**Table 4** The  $^{31}\text{P}$  NMR spectroscopic data (thf solution) for tetrakis(phosphine)platinum(0) complexes

Phosphine added, $\text{PR}'_3$	Complex	<i>T</i> /K	$\delta(\text{PR}_3)$	$^1J(\text{Pt}-\text{PR}_3)/\text{Hz}$	$\delta(\text{PR}'_3)$	$^1J(\text{Pt}-\text{PR}'_3)/\text{Hz}$	$^2J(\text{P}-\text{P})/\text{Hz}$
PPh <sub>2</sub> H	$[\text{Pt}(\text{PPh}_3)_2(\text{PPh}_2\text{H})_2]$	203	15.2	3924	-15.0	3646	49
	$[\text{Pt}(\text{PPh}_3)(\text{PPh}_2\text{H})_3]$	243	15.2	3742	-13.7	3799	49
	$[\text{Pt}(\text{PPh}_2\text{H})_4]$	243			-16.5	3786	
	$[\text{Pt}\{\text{P}(\text{C}_6\text{H}_4\text{Me-4})_3\}_2(\text{PPh}_2\text{H})_2]$	203	13.0	3914	-13.8	3660	49
PPh <sub>2</sub> Me	$[\text{Pt}\{\text{P}(\text{C}_6\text{H}_4\text{Me-4})_3\}_2(\text{PPh}_2\text{H})_2]$	273	13.3	3773	-14.0	3792	49
	$[\text{Pt}(\text{PPh}_3)_2(\text{PPh}_2\text{Me})_2]$	203	11.6	3824	-15.6	3820	56
	$[\text{Pt}(\text{PPh}_3)(\text{PPh}_2\text{Me})_3]$	203	7.3	3706	-13.0	3843	59
	$[\text{Pt}(\text{PPh}_2\text{Me})_4]$	203			-14.5	3806	
PPh <sub>2</sub> Et*	$[\text{Pt}(\text{PPh}_3)(\text{PPh}_2\text{Et})_3]$	213	9.6	3730	1.3	3828	58
	$[\text{Pt}(\text{PPh}_2\text{Et})_4]$	213			1.3	3780	
PPhMe <sub>2</sub>	$[\text{Pt}(\text{PPh}_3)_2(\text{PPhMe}_2)_2]$	203	15.1	3779	-38.3	3900	51
	$[\text{Pt}(\text{PPh}_3)(\text{PPhMe}_2)_3]$	203	18.2	3770	-37.0	3798	56
	$[\text{Pt}(\text{PPhMe}_2)_4]$	203			-33.4	3806	
PMe <sub>3</sub>	$[\text{Pt}(\text{PMe}_3)_2(\text{PPh}_3)_2]$	273	17.0	3784	-52.0	3860	52
	$[\text{Pt}(\text{PMe}_3)_3(\text{PPh}_3)]$	273	19.4	3762	-51.7	3837	48
	$[\text{Pt}(\text{PMe}_3)_4]$	273			-52.7	3836	

\* Unusually in this case, no  $[\text{Pt}(\text{PPh}_3)_2(\text{PPh}_2\text{Et})_2]$  was observed.

**Table 5** The  $^{31}\text{P}\{-^1\text{H}\}$  NMR spectroscopic data (thf solution) for the complexes  $[\text{Pt}(\text{chelating diphosphine})(\text{PR}_3)_2]$

Complex	<i>T</i> /K	$\delta(\text{diphosphine})$	$^1J(\text{Pt}-\text{PP})$	$\delta(\text{PR}_3)$	$^1J(\text{Pt}-\text{PR}_3)$	$^2J(\text{P}-\text{P})$
<b>16</b>	203	27.2	3513	22.5	4082	53
<b>17</b>	253	14.3	4092	21.8	3530	54
<b>18</b>	203	13.0	3916	-15.0	3562	49
<b>19</b>	180	12.4	3759	6.0	4058	62
<b>20</b>	233	20.4	4140	-12.0	3476	57
<b>21</b>	203	26.0	5288	-14.0	3093	50



occurred, but the mixed-ligand complex was stable to 263 K, and was reformed on cooling the solution.

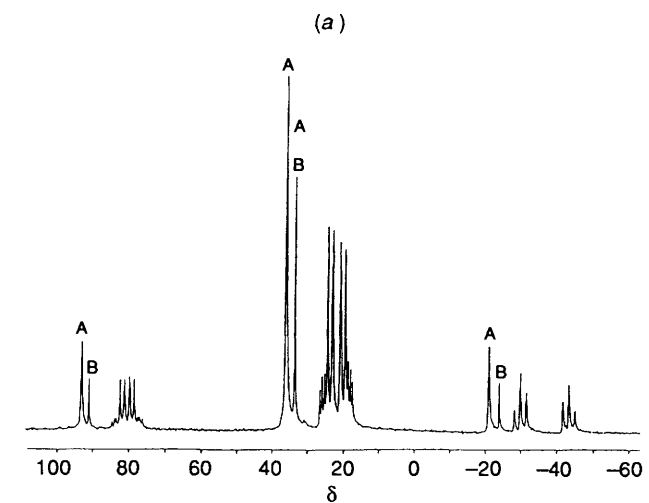
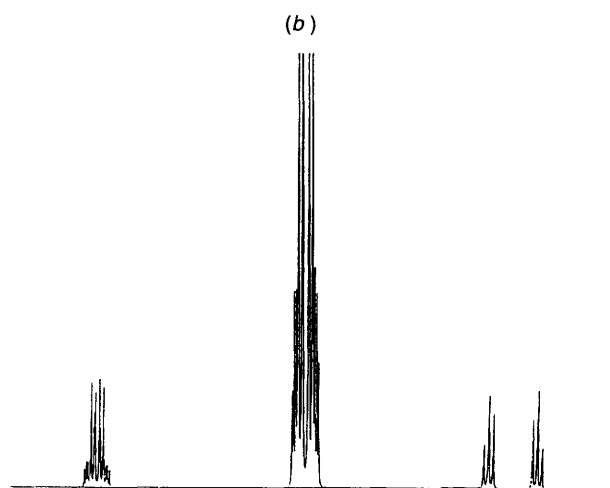
When 1 equivalent of dmpp [ $\text{Me}_2\text{P}(\text{CH}_2)_3\text{PPh}_2$ ] was added to  $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2]$  at 203 K the  $^{31}\text{P}$  NMR spectrum indicated that the major product was  $[\text{Pt}(\text{dmpp})_2]$ . The spectrum showed triplets at  $\delta -8.7$  ( $J_{\text{Pt}} = 3618$  Hz) and  $-49.7$  ( $J_{\text{Pt}} = 3667$ ,  $J_{\text{PP}} = 46$  Hz). The signal at  $\delta -8.7$  was assigned to the PPh<sub>2</sub> group by analogy with the free diphosphine. Of interest are the related data for  $[\text{Pd}(\text{dmpp})_2]$  which shows greater co-ordination shifts ( $\delta$  23.0, 10.0,  $J_{\text{PP}} = 27$  Hz). This was, however, formed only as a minor component of the reaction mixture, when  $[\text{Pd}(\text{C}_2\text{H}_4)(\text{dppe})]$  was treated with dmpp.<sup>13</sup> The mixed-phosphine complex  $[\text{Pt}(\text{dmpp})(\text{PPh}_3)_2]$  is also present in the reaction mixture. The expected doublet of doublets for the PPh<sub>3</sub> nuclei appears as a triplet at  $\delta$  18.0 ( $J_{\text{PPt}}$

= 3920 Hz). The doublets of triplets expected for the PPh<sub>2</sub> and PMe<sub>2</sub> phosphorus nuclei are present at  $\delta$  12.0 ( $J_{\text{PPt}} = 3632$ ,  $J_{\text{PP}} = 44$  Hz) and  $-50.0$  ( $J_{\text{PPt}} \approx 3490$ ,  $J_{\text{PP}} \approx 44$  Hz).

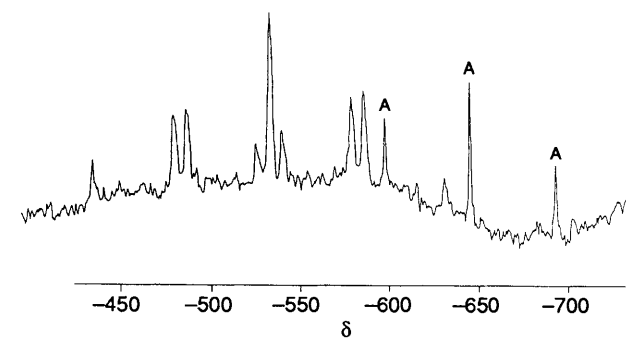
When  $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2]$  was treated with 1 mol of dpfp [1,1'-bis(diphenylphosphino)ferrocene] at 183 K  $[\text{Pt}(\text{dpfp})(\text{PPh}_3)_2]$  was obtained. Above this temperature the signals were broadened and  $[\text{Pt}(\text{dpfp})_2]$  became the major product. Reaction with triphos [ $\text{PhP}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2$ ] in toluene gave  $[\text{Pt}(\text{PPh}_3)(\text{triphos})]$ , for which the spectroscopic data were in good agreement with those previously reported.<sup>14</sup>

#### Reactions of $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PR}_3)_2]$ (R = Ph or C<sub>6</sub>H<sub>4</sub>Me-4) with phosphites

Phosphites are generally sterically undemanding, and low in basicity; thus formation of four co-ordinate platinum(0) complexes should be easy. This indeed proved to be the case. Addition of 1 molar equivalent of triphenyl phosphite to  $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2]$  at 203 K gave  $[\text{Pt}\{\text{P}(\text{OPh})_3\}_2(\text{PPh}_3)_2]$  and  $[\text{Pt}\{\text{P}(\text{OPh})_3\}_3(\text{PPh}_3)]$ , as well as free PPh<sub>3</sub>, as the major species observable in solution. These could be readily identified by comparison of their spectroscopic data with those reported by Pregosin and Sze.<sup>15</sup> Interestingly, when our sample was warmed to 263 K the singlet due to free phosphine was dramatically broadened, suggesting an exchange phenomenon. At 283 K the signals due to  $[\text{Pt}\{\text{P}(\text{OPh})_3\}_2(\text{PPh}_3)_2]$  were broadened, but those due to  $[\text{Pt}\{\text{P}(\text{OPh})_3\}_3(\text{PPh}_3)]$  were sharp.



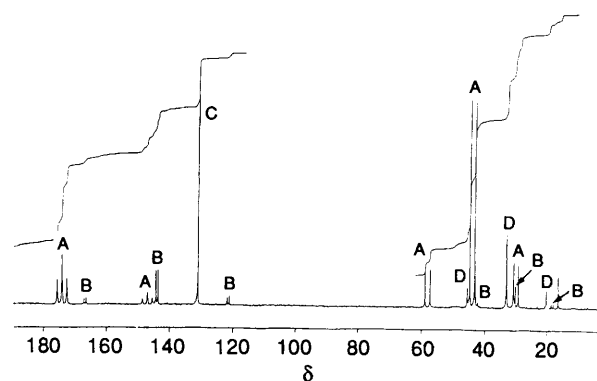
**Fig. 2** Experimental (a) and computer-simulated (b)  $^{31}\text{P}\{-^1\text{H}\}$  NMR spectra (thf, 203 K) of  $[\text{Pt}(\text{dppe})(\text{PPh}_3)_2]$ ; the sample also contains  $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2]$  (A) and  $[\text{Pt}(\text{dppe})_2]$  (B)



**Fig. 3** The  $^{195}\text{Pt}\{-^1\text{H}\}$  NMR spectrum (thf, 203 K) of  $[\text{Pt}(\text{dppe})(\text{PPh}_3)_2]$ ; the sample also contains  $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2]$  (A)

We postulate that dissociative exchange of  $\text{PPh}_3$  occurs more readily in the complex  $[\text{Pt}\{\text{P}(\text{O}^i\text{Pr})_3\}_2(\text{PPh}_3)_2]$ , since loss of  $\text{PPh}_3$  reduces steric crowding. With an excess of  $\text{P}(\text{O}^i\text{Pr})_3$  the main species present were  $[\text{Pt}\{\text{P}(\text{O}^i\text{Pr})_3\}_3(\text{PPh}_3)]$  and  $[\text{Pt}\{\text{P}(\text{O}^i\text{Pr})_3\}_4]$ . Similar results were obtained using  $\text{P}(\text{O}^i\text{Pr})_3$  and  $[\text{Pt}(\text{C}_2\text{H}_4)\{\text{P}(\text{C}_6\text{H}_4\text{Me}-4)_3\}_2]$  and with  $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2]$  with  $\text{P}(\text{OMe})_3$  or  $\text{P}(\text{OPr}^i)_3$ . Spectroscopic data are given in Table 7.

Reaction of the bulky phosphite  $\text{P}(\text{OC}_6\text{H}_4\text{Bu}^i-2)_3$  (cone angle  $175^\circ$ ) with  $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2]$  proceeded differently. Mixing at 203 K gave a colourless solution showing  $^{31}\text{P}$  NMR spectroscopic signals for starting material, free phosphite and two platinum complexes,  $[\text{Pt}(\text{PPh}_3)_2\{\text{P}(\text{OC}_6\text{H}_4\text{Bu}^i-2)_3\}]$ , **22**, and  $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2\{\text{P}(\text{OC}_6\text{H}_4\text{Bu}^i-2)_3\}]$ , **23**, in the ratio of



**Fig. 4** The  $^{31}\text{P}\{-^1\text{H}\}$  NMR spectra (thf, 243 K) of  $[\text{Pt}(\text{PPh}_3)_2\{\text{P}(\text{OC}_6\text{H}_4\text{Bu}^i-2)_3\}]$  (A),  $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2\{\text{P}(\text{OC}_6\text{H}_4\text{Bu}^i-2)_3\}]$  (B),  $\text{P}(\text{OC}_6\text{H}_4\text{Bu}^i-2)_3$  (C) and  $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2]$  (D)

**Table 6** The  $^{31}\text{P}\{-^1\text{H}\}$  NMR spectroscopic data (thf solution) for complexes  $[\text{Pt}(\text{diphosphine})_2]$

Complex	T/K	$\delta$	$^1J(\text{Pt}-\text{P})$
$[\text{Pt}(\text{dppe})_2]$	203	32.0	3735
$[\text{Pt}(\text{dmpe})_2]$	203	32.0	3708
$[\text{Pt}(\text{dcpe})_2]$	203	73.0	3135
$[\text{Pt}(\text{dppp})_2]$	203	-11.0	3647
$[\text{Pt}(\text{dppb})_2]$	223	-1.0	3765
$[\text{Pt}(\text{dppf})_2]$	183	23.0	4033

approximately 2:1 (Fig. 4). The assignments of the structures of **22** and **23** were confirmed by their  $^{195}\text{Pt}$  NMR spectra: **22** gave rise to a doublet of triplets ( $\delta -224$ ,  $J_{\text{Pt}} = 4123, 7811$  Hz) whilst **23** gave a doublet of doublets ( $\delta -651$ ,  $J = 3553, 6589$  Hz). The possibility of two-co-ordinate complexes was considered, but precedent<sup>16</sup> suggests that this would cause a substantial change (to  $\delta \approx -2000$ ) in the  $^{195}\text{Pt}$  chemical shift. The coupling constant,  $^2J_{\text{PP}}$ , for **22** is worthy of comment as at first sight it looks most unusual. Very few trigonal complexes of the type  $[\text{Pt}(\text{P}_a)_2\text{P}_b]$  have been reported with good spectroscopic characterisation. The complex  $[\text{Pt}(\text{dcpe})\{\text{P}(\text{C}_6\text{H}_{11})_3\}]$  was reported<sup>17</sup> to have  $^2J_{\text{PP}} = 161$  Hz (although the compound, most surprisingly, is reported to be magenta) and  $[\text{Pt}(\text{PR}_3)_2\{\text{P}[\text{NSiMe}_3\text{Bu}^i](=\text{NBu}^i)\}]$  has  $^2J_{\text{PP}} = 177$  (R = Ph) or 244 Hz (R = OPh).<sup>18</sup> This suggests that the coupling in our complex is less unusual than it might at first appear.

Reaction of  $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2]$  with  $\text{PPh}(\text{OMe})_2$  gave mainly the mixed-phosphine/phosphite complex  $[\text{Pt}\{\text{PPh}(\text{OMe})_2\}_2(\text{PPh}_3)_2]$  at low temperature. On warming to 273 K  $[\text{Pt}\{\text{PPh}(\text{OMe})_2\}_3(\text{PPh}_3)]$  was formed, but the original spectrum was regenerated on cooling.

## Conclusion

Reactions of  $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2]$  with bulky phosphines yield initially  $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)(\text{PR}_3)]$ . We suggest that association of  $\text{PR}_3$  first gives an unobserved, crowded four-co-ordinate 18-electron complex which loses  $\text{PPh}_3$  (to give product) or  $\text{PR}_3$  (to regenerate starting material) rather than ethene. The accessibility of this process is limited by the cone angle of  $\text{PR}_3$ . Phosphines with cone angles less than  $140^\circ$  seem to give tetrakis complexes so readily that no intermediate stage is observed, whilst those with cone angles greater than  $180^\circ$  are too large to add to give the four-co-ordinate complex. Since in no case we have observed a complex of the composition  $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PR}_3)_3]$ , we must assume that these species are not stable.

Reactions with sterically undemanding phosphines, chelating diphosphines and phosphites yield species of the types  $[\text{Pt}(\text{P}_a)_2(\text{P}_b)_2]$ ,  $[\text{Pt}(\text{P}_a)(\text{P}_b)_3]$  and  $[\text{Pt}(\text{P}_b)_4]$  where  $\text{P}_b$  is the added species. These are generally in dynamic equilibrium, and

**Table 7** The  $^{31}\text{P}\{-^1\text{H}\}$  NMR spectroscopic data (thf solution) for complexes formed on reaction of  $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PR}_3)_2]$  with phosphites

R	Phosphite	T/K	Complex	$\delta$ (Phosphine)	$^1J(\text{Pt-P})$ / Hz	$\delta$ (Phosphite)	$^1J(\text{Pt-P})$ / Hz	$^2J(\text{P-P})$ / Hz
Ph	$\text{P}(\text{OPh})_3$	223	$[\text{Pt}(\text{PPh}_3)_2\{\text{P}(\text{OPh})_3\}_2]$	14.0	3433	99.3	6477	74
		223	$[\text{Pt}(\text{PPh}_3)\{\text{P}(\text{OPh})_3\}_3]$	12.7	3345	99.0	6023	64
		203	$[\text{Pt}\{\text{P}(\text{OPh})_3\}_4]$			98.2	5783	
$\text{C}_6\text{H}_4\text{Me-4}$		213	$[\text{Pt}\{\text{P}(\text{C}_6\text{H}_4\text{Me-4})_3\}_2\{\text{P}(\text{OPh})_3\}_2]$	11.0	3440	100.0	6468	76
		273	$[\text{Pt}\{\text{P}(\text{C}_6\text{H}_4\text{Me-4})_3\}\{\text{P}(\text{OPh})_3\}_3]$	10.3	3404	100.0	6060	63
Ph	$\text{P}(\text{OMe})_3$	203	$[\text{Pt}(\text{PPh}_3)_2\{\text{P}(\text{OMe})_3\}_2]$	10.0	3290	136.0	6114	65
		213	$[\text{Pt}(\text{PPh}_3)\{\text{P}(\text{OMe})_3\}_3]$	5.5	*	135.5	5766	40
		203	$[\text{Pt}\{\text{P}(\text{OMe})_3\}_4]$			133.5	5376	
Ph	$\text{P}(\text{OPr}^i)_3$	203	$[\text{Pt}(\text{PPh}_3)_2\{\text{P}(\text{OPr}^i)_3\}_2]$	9.0	3398	131.0	6054	68
		203	$[\text{Pt}(\text{PPh}_3)\{\text{P}(\text{OPr}^i)_3\}_3]$	10.0	3382	129.0	5664	58
		203	$[\text{Pt}\{\text{P}(\text{OPr}^i)_3\}_4]$			128.0	5386	
Ph	$\text{P}(\text{OC}_6\text{H}_4\text{Bu}^i\text{-2})_3$	243	$[\text{Pt}(\text{PPh}_3)_2\{\text{P}(\text{OC}_6\text{H}_4\text{Bu}^i\text{-2})_3\}]$	45.0	4123	174.8	7822	225
		203	$[\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)\{\text{P}(\text{OC}_6\text{H}_4\text{Bu}^i\text{-2})_3\}]$	31.0	3553	145.0	6584	97
Ph	$\text{PPh}(\text{OMe})_2$	193	$[\text{Pt}(\text{PPh}_3)_2\{\text{PPh}(\text{OMe})_2\}_2]$	11.5	3430	140.3	5200	58
		273	$[\text{Pt}(\text{PPh}_3)\{\text{PPh}(\text{OMe})_2\}_3]$	11.0	3430	140.7	4984	60

\* Not determined.

fluxional on the NMR spectroscopic time-scale. There is some preference for the more crowded species  $[\text{Pt}(\text{P}_a)_2(\text{P}_b)_2]$  at low temperature. Isolation is difficult and does not always lead to the expected species, only to the least-soluble one. A three-coordinate species  $[\text{Pt}(\text{P}_a)_2\text{P}_b]$  was formed only with the crowded phosphite  $\text{P}(\text{OC}_6\text{H}_4\text{Bu}^i\text{-2})_3$ .

## Experimental

All procedures were carried out under an atmosphere of dry nitrogen using Schlenk techniques. Tetrahydrofuran was distilled from sodium-benzophenone and toluene from sodium metal before use. The  $^{31}\text{P}\{-^1\text{H}\}$  NMR spectra were recorded on a Bruker WP80SY (32.4 MHz) or WM360 spectrometer (145.8 MHz), shifts being expressed relative to external 85%  $\text{H}_3\text{PO}_4$ , and  $^{195}\text{Pt}\{-^1\text{H}\}$  spectra using the same spectrometers with shifts relative to  $\Xi$  21.4 MHz.

### Preparation of $[\text{Pt}(\text{C}_2\text{H}_4)\{\text{P}(\text{C}_6\text{H}_{11})_3\}(\text{PPh}_3)]$

The complex  $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2]$  (0.2 g, 0.26 mmol) was added to a NMR tube (8 mm), which was evacuated and filled with argon. Distilled degassed thf (0.5  $\text{cm}^3$ ) was transferred to the tube *via* cannula and this was then cooled to  $-78^\circ\text{C}$ . Tricyclohexylphosphine (0.07 g, 0.26 mmol) was added, as a solid, under a gentle pressure of argon, and the tube warmed slightly to allow dissolution. The tube was then recooled to  $-80^\circ\text{C}$  and the variable-temperature  $^{31}\text{P}$  and  $^{195}\text{Pt}$  NMR spectra recorded.

The procedures for the synthesis of the other mixed-phosphine platinum complexes were similar. Most liquid phosphines were added by microsyringe under argon. The most volatile phosphines were converted into standard solutions in thf before addition.

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