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Preliminary communication

Unexpected substitution reactions of bis(phosphine)platinum ethene complexes

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Abstract

Reaction of [Pt(PPh$_3$)$_2$(C$_2$H$_4$)] with moderately bulky phosphines at low temperatures did not give the expected tris(phosphine)platinum complexes. Instead mixed phosphine-alkene complexes [Pt(PPh$_3$)(PR$_3$)(C$_2$H$_4$)] were formed, and were characterised by ^{31}P and ^{195}Pt NMR spectroscopy in solution.

The complex [Pt(PPh$_3$)$_2$(C$_2$H$_4$)] has been widely used as a precursor for other organometallic complexes [1], coordination complexes [2] and oxidative addition products [3], since the ethene ligand is generally easily displaced. We now describe the reactions of the complex with moderately bulky phosphines at low temperatures, in which one of the triphenylphosphine ligands, rather than the ethene, is displaced.

[Pt(PPh$_3$)$_2$(C$_2$H$_4$)] was prepared as previously described [4]. A solution in thf was degassed and cooled, and solid PCy$_3$ was added under a positive pressure of argon. The tube was sealed and the solution was allowed to warm slowly in an NMR spectrometer probe until reaction occurred. At 243 K the principal species observed was [Pt(PPh$_3$)(PCy$_3$)(C$_2$H$_4$)], characterised by ^{31}P and ^{195}Pt NMR spectroscopy in solution (Fig. 1, Tables 1 and 2). Two strongly coupled phosphine resonances were observed in the ^{31}P spectrum, assigned to the PPh$_3$ and PCy$_3$ ligands. In the ^{195}Pt spectrum the signal was observed as a doublet of doublets, since ^1J(PPt) is significantly different for the two ligands. ^{1}H NMR spectroscopy revealed a signal for bound ethene at δ 2.64 (bound ethene in the starting material shows a signal at δ 2.60), without platinum satellites. Admission of free ethene to the sample resulted in a broadened signal at δ 2.85, indicating that free and bound ethene were undergoing fast exchange under the conditions of the experiment. This exchange results in the rapid transfer of ethene between platinum isotopes, so that coupling information is lost. The warming of the solution to room temperature resulted in the formation of a range of bis- and tris-(phosphine)-platinum complexes, but the mixed phosphine-ethene complex was still a significant component of the mixture under these conditions.

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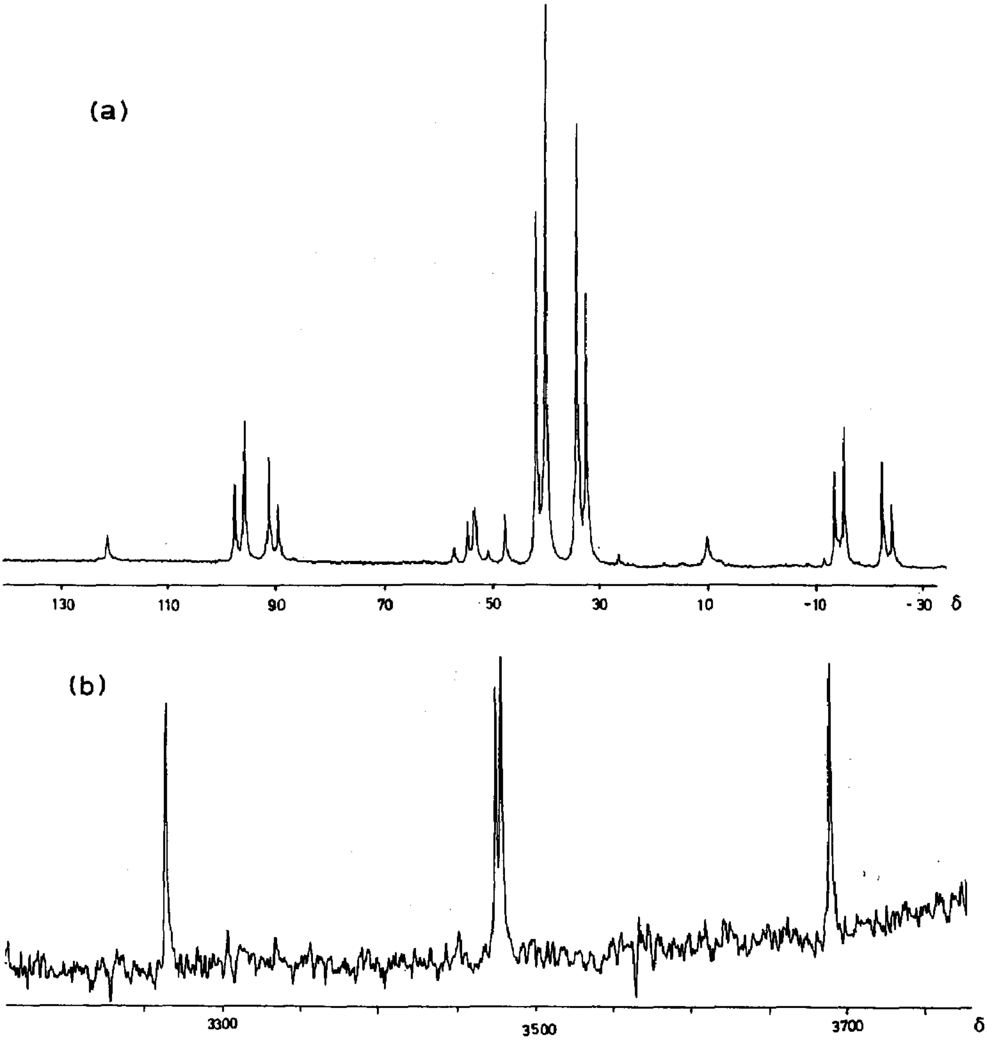

Fig. 1. (a) ^{31}P NMR spectrum of [Pt(PPh$_3$)(PCy$_3$)(C$_2$H$_4$)]; (b) ^{195}Pt NMR spectrum of [Pt(PPh$_3$)(PCy$_3$)(C$_2$H$_4$)].

Table 1

^{31}P NMR spectroscopic data for (bis)phosphine platinum ethene complexes

Major product [a]	Temperature (K)	$\delta(P_A)$ [b]	$\delta(P_B)$	$^1J(P_APt)$	$^1J(P_BPt)$	$^2J(P_AP_B)$
[Pt(PPh$_3$)(PCy$_3$)(C$_2$H$_4$)] [c]	243	39.0	31.0	3680	3620	56
[Pt(PPh$_3$)(PBz$_3$)(C$_2$H$_4$)] [d]	183	38.0	19.0	3670	3570	61
[Pt(PPh$_3$)(Ptol$_3$)(C$_2$H$_4$)] [e]	183	29.2	32.0	3698	3698	51
[Pt(PPh$_3$)(PAn$_3$)(C$_2$H$_4$)] [f]	193	29.2	34.5	3722	3685	59
[Pt(PPh$_3$)$_2$(C$_2$H$_4$)]	[g]	33.0		3747		
[Pt(PCy$_3$)$_2$(C$_2$H$_4$)] [h]		42.0		3614		

[a] Product concentration was optimised at the temperature indicated. [b] Chemical shifts are quoted in ppm downfield from 85% H$_3$PO$_4$. In each case P$_A$ is nominally the added phosphine and P$_B$ is PPh$_3$, but several of the assignments could be reversed. For [Pt(PPh$_3$)(PCy$_3$)(C$_2$H$_4$)] the assignment was made by comparison with [Pt(PCy$_3$)$_2$(C$_2$H$_4$)] [6]. [c] Cone angle [5] of PCy$_3$ = 170 °. [d] Bz = CH$_2$Ph, cone angle of PBz$_3$ = 165 °. [e] tol = 4-MeC$_6$H$_4$, cone angle of Ptol$_3$ = 145 °. [f] An = 4-MeOC$_6$H$_4$. [g] The spectrum is temperature invariant. [h] Data from ref. 6.

Table 2

^{195}Pt NMR spectroscopic data for bis(phosphine) platinum ethene complexes

Complex	δ(Pt) [a]	Signal	$^1J(P_APt)$ [b]	$^1J(P_BPt)$
$[Pt(PPh_3)(PCy_3)(C_2H_4)]$	−3476	d of d	3680	3620
$[Pt(PPh_3)(PBz_3)(C_2H_4)]$	−3429	d of d	3670	3570
$[Pt(PPh_3)(Ptol_3)(C_2H_4)]$	−3461	t	3701	3701
$[Pt(PPh_3)(PAn_3)(C_2H_4)]$	−3464	d of d	3719	3681
$[Pt(PPh_3)_2(C_2H_4)]$	−3450	t	3701	

[a] δ is quoted in ppm downfield from $K_2[PtCl_6]$. [b] P_A is the added phosphine and P_B is PPh_3.

Reactions with a range of other moderately bulky phosphines were also carried out (Tables 1 and 2). The temperatures given are those at which the concentration of the mixed complex was optimised. At higher temperatures the spectra were generally much more complex. It appears that the mixed complexes are the products of kinetic control in all these cases, and are significant products under conditions of thermodynamic control. The very bulky phosphine $(Me_3C)_3P$ (cone angle 182°) did not react with $[Pt(PPh_3)_2(C_2H_4)]$, even at room temperature. It is noteworthy that all the phosphines from which the complexes could be prepared in this way had cone angles of > 142°. In the reactions with smaller phosphines and phosphites, tris(phosphine) complexes were formed (for example $[Pt(PPh_3)\{P(OPh)_3\}_2]$, $\delta(P(OPh)_3)$ 97.5 ppm, $J(PPt)$ 6017 Hz, $\delta(PPh_3)$ 12.3 ppm $J(PPt)$ 3433 Hz, $J(PP)$ 73 Hz), whereas in the presence of an excess of the phosphine ligand the predominent species were mixed tetrakisphosphineplatinum complexes. A range of related species were prepared, and their properties will be reported elsewhere.

It is clear that the reactions of $[Pt(PPh_3)_2(C_2H_4)]$ with phosphine ligands are appreciably more complex than had hitherto been suspected. These observations have considerable implications for the in situ preparations of platinum phosphine complexes for homogeneous catalysis, and, more generally, open a route to the facile preparation of a range of mixed-phosphine derivatives.

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