2-Methoxyphenyl Phosphite Complexes of Platinum(0) and Nickel(0)†

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The compounds $P(OC_6H_4OMe\text{-}2)_3$ and $P(OC_6H_4OMe\text{-}2)(OC_6H_4Me\text{-}4)_2$ have been prepared. The platinum(0) complex $[Pt\{P(OC_6H_4OMe\text{-}2)_3\}_3]$ **1** can be made by the reduction of $[PtCl_2\{P(OC_6H_4OMe\text{-}2)_3\}_2]$ in the presence of the phosphite or by addition of the latter to tris(η^2-norbornene)platinum, and $[Pt(\eta^2\text{-}C_2H_4)\{P(OC_6H_4OMe\text{-}2)_3\}_2]$ **2** by the reduction of $[PtCl_2\{P(OC_6H_4OMe\text{-}2)_3\}_2]$ in the presence of ethene or by adding of the phosphite to $[Pt(\eta^2\text{-}C_2H_4)_3]$. The crystal structures of the ligand $P(OC_6H_4OMe\text{-}2)_3$ and complex **2** have been determined and the effect of co-ordination on the conformation of the phosphite substituents is discussed. The ethene ligand in **2** is readily substituted by other alkenes and alkynes to give complexes **3**–**9** of the general type $[Pt(\eta^2\text{-alkene})\{P(OC_6H_4OMe\text{-}2)_3\}_2]$ or $[Pt(\eta^2\text{-alkyne})\{P(OC_6H_4OMe\text{-}2)_3\}_2]$. Reduction of $[Ni(acac)_2]$ (acac = acetylacetonate) with $AlMe_3$ in the presence of ethene gives $[Ni(\eta^2\text{-}C_2H_4)\{P(OC_6H_4OMe\text{-}2)_3\}_2]$ **10**. The air-sensitive complex $[Ni\{P(OC_6H_4OMe\text{-}2)_3\}_3]$ **11** can be generated in solution by treatment of $[Ni(cod)_2]$ (cod = cycloocta-1,5-diene) or **10** with the phosphite ligand. The tetrahedral complex $[Ni\{P(OC_6H_4OMe\text{-}2)(OC_6H_4Me\text{-}4)_2\}_4]$ **12** is readily made from $[Ni(cod)_2]$ and the phosphite. The catalytic activity of **11** and **12** for the monohydrocyanation of buta-1,3-diene is discussed in relation to similar well known catalysts and it is concluded that the methoxy groups inhibit the catalysis probably by a combination of steric hindrance and weak co-ordination of the ether oxygen.

The great utility of tertiary phosphine complexes in homogeneous catalysis[1] has prompted fundamental, systematic studies of phosphine ligands since the 1950s.[2] Detailed investigations of the steric and electronic effects of phosphorus substituents on the structure and bonding,[3] spectroscopic,[4] chemical[2] and catalytic[1] properties of the complexes has been facilitated by the ease with which the phosphine can be varied. Furthermore, the compatability of phosphines with many other functional groups has allowed the development of elaborate functionalised phosphines.[2] By comparison, phosphite ligands and their complexes have received little systematic study other than the outstanding article by Tolman[5] on the steric and electronic properties of substituted phosphites. For example, until recently there were no reports of metal complexes of phosphites that are bidentate, chiral, or functionalised.[6,7] It is surprising that metal phosphite chemistry has been neglected in view of the ready synthesis of phosphite ligands[8] and the importance of their complexes as catalysts for hydrocyanation,[9] alkene oligomerisation[10] and isomerisation,[11] C–C bond-forming reactions[12] and hydroformylation.[13] The lack of attention given to triaryl phosphite complexes compared with triarylphosphine complexes is amply illustrated by the number of accurate crystal structures of triphenyl phosphite and triphenylphosphine complexes in the Cambridge Crystallographic Database in a recent review: 15 and 720 respectively.[14]

We have begun a wide ranging study of phosphites which are multidentate, chiral, or are functionalised.[6] The presence of an ether substituent on phosphine ligands has been shown to influence markedly the chemistry of the complexes,[15] *e.g.* co-ordination of the ether donor, increased rate of oxidative addition, superior catalytic properties. In this paper we report the nickel(0) and platinum(0) co-ordination chemistry of the ether-functionalised phosphites $P(OC_6H_4OMe\text{-}2)_3$ or $P(OC_6H_4OMe\text{-}2)(OC_6H_4Me\text{-}4)_2$ and the effect the ether group has on the properties of these complexes.

Table 1 Elemental analyses (%) (calculated values in parentheses)

Compound	C	H
$P(OC_6H_4OMe\text{-}2)_3$	61.1 (62.0)	5.5 (5.3)
$P(OC_6H_4OMe\text{-}2)(OC_6H_4Me\text{-}4)_2$	65.0 (65.8)	5.3 (5.5)
1	53.7 (54.2)	4.6 (4.5)
2	51.1 (51.6)	4.6 (4.5)
3	53.4 (53.0)	5.0 (4.8)
4	57.3 (57.2)	4.6 (4.6)
10	58.5 (59.6)	5.3 (5.5)
12	65.0 (65.8)	5.3 (5.5)

Results and Discussion

Tris(2-methoxyphenyl)phosphite can readily be made on a 50 g scale by treatment of PCl_3 with lithium 2-methoxyphenoxide. The related ligand containing one 2-methoxyphenyl group can be made by a similar route (see Tables 1 and 2 for characterising data). The phosphite $P(OC_6H_4OMe\text{-}2)_3$ has been previously reported,[16] but its co-ordination chemistry has not been investigated. It is a rare example of a triaryl phosphite which is solid at ambient temperatures.

Crystal Structure of $P(OC_6H_4OMe\text{-}2)_3$.—Crystals suitable for X-ray crystallography were readily grown from toluene. Bond lengths and angles (with numbering scheme shown in Fig. 1) are listed in Table 3. The molecule lies on a C_3 axis in the cubic, non-centrosymmetric space group $P2_13$; the molecular structure thus does not deviate from exact C_3

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

Table 2 The $^{31}P^{a}$ and $^{195}Pt^{b}$ NMR data

Compound	δ(P_a)	J(PtP_a)	δ(P_b)	J(PtP_b)	J(P_aP_b)	δ(Pt)
$P(OC_6H_4OMe\text{-}2)_3$	134.3					
$P(OC_6H_4OMe\text{-}2)(OC_6H_4Me\text{-}4)_2$	130.5					
1	169.0	7022				−347.2 (q)
2	149.1	6099				−718.6 (t)
3	148.3	5814				−651.1 (t)
4	142.6	6128	142.2	5867	113	−667.1 (m)
5	136.9	5918				−634.9 (t)
6	133.4	6266	131.6	5830	50	−475.1 (d,d)
7	140.9	5746	138.2	6577	56	−727.2 (d,d)
8	142.0	5135	136.3	5730	71	−753.0 (d,d)
9	134.9	5646	132.2	5436	50	−403.4 (d,d)
10	142.8					
11	130.7					
12	131.0					

[a] Spectra (36.2 MHz) measured in $CDCl_3$ at 28 °C; chemical shifts (δ) in ppm (±0.1) to high frequency of 85% H_3PO_4 and coupling constants (J) in Hz (±3). [b] Spectra (19.2 MHz) measured in $CDCl_3$ at 28 °C; chemical shifts (δ) in ppm (±0.5) to high frequency of Ξ(Pt) = 21.4 MHz.

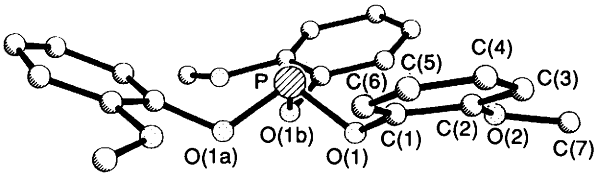
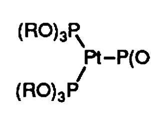


Fig. 1 Molecular structure of $P(OC_6H_4OMe\text{-}2)_3$ showing atom labelling scheme

Table 3 Bond lengths (Å) and angles (°) for $P(OC_6H_4OMe\text{-}2)_3$

P–O(1)	1.624(4)	C(1)–C(6)	1.334(13)
O(1)–C(1)	1.387(9)	C(2)–C(3)	1.332(15)
O(2)–C(2)	1.441(12)	C(3)–C(4)	1.467(17)
O(2)–C(7)	1.400(15)	C(4)–C(5)	1.274(18)
C(1)–C(2)	1.370(11)	C(5)–C(6)	1.365(15)
O(1)–P–O(1a)	96.6(2)	O(2)–C(2)–C(3)	122.7(8)
P–O(1)–C(1)	119.1(4)	C(1)–C(2)–C(3)	124.5(9)
C(2)–O(2)–C(7)	118.0(9)	C(2)–C(3)–C(4)	114.4(10)
O(1)–C(1)–C(2)	119.6(7)	C(3)–C(4)–C(5)	121.6(11)
O(1)–C(1)–C(6)	123.6(7)	C(4)–C(5)–C(6)	119.8(11)
C(2)–C(1)–C(6)	116.7(8)	C(1)–C(6)–C(5)	122.8(10)
O(2)–C(2)–C(1)	112.8(8)		



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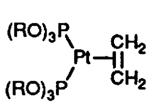
R = $C_6H_4OMe\text{-}2$



2

symmetry. The crystal structure consists of discrete $P(OC_6H_4OMe\text{-}2)_3$ molecules linked by a network of weak CH ··· O contacts (length 2.56 Å). While the compound is of course a racemic mixture as prepared, the crystal studied contains a single enantiomeric conformer, of the *R* form, assigned because the methoxy groups are oriented in a clockwise fashion.

Crystal structures of no other simple $P(OR)_3$ (R = aryl) compounds have been reported but the present P–O bond length [1.624(4) Å] is similar to those reported for two more-elaborate aryl phosphites.[17] These P–O bond lengths are greater than the average for co-ordinated aryl phosphite ligands, which is 1.600(11) Å.[14] See below for discussion of other aspects of the molecular geometry.

Platinum(0) *Chemistry*.—The 16-electron platinum(0) complex $[Pt\{OC_6H_4OMe\text{-}2)_3\}_3]$ **1** is conveniently made by the reduction of $[PtCl_2\{P(OC_6H_4OMe\text{-}2)_3\}_2]$ with $NaBH_4$ in MeCN in the presence of an excess of $P(OC_6H_4OMe\text{-}2)_3$. The same product can be made by displacement of alkene from $[Pt(C_2H_4)_3]$ or tris(norbornene)platinum. Its identity was established by a combination of elemental analysis and NMR spectroscopy (see Tables 1 and 2). The presence of the PtP_3 core is confirmed by its 1:3:3:1 quartet $^{195}Pt\text{-}\{^1H\}$ NMR spectrum. Like the related co-ordinatively unsaturated species $[Pt\{P(OC_6H_4Me\text{-}2)_3\}_3]$,[18] complex **1** does not react witl. further phosphite ligand to give a PtP_4 species. The bulkiness of the ligand undoubtedly contributes to the stability of **1** bu a weak platinum(0)–ether interaction may also be involved (see below).

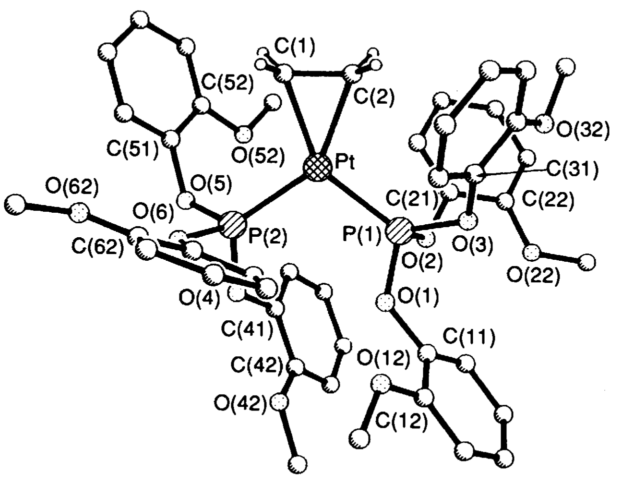


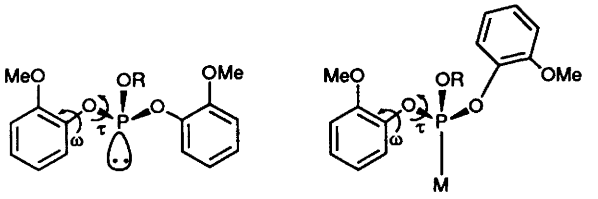
Fig. 2 Molecular structure of complex **2** showing labelling scheme

The complex $[Pt(\eta^2\text{-}C_2H_4)\{P(OC_6H_4OMe\text{-}2)_3\}_2]$ **2** can be synthesised by reduction of $[PtCl_2\{P(OC_6H_4OMe\text{-}2)_3\}_2]$ with $NaBH_4$ in the presence of ethene; it is also formed upon addition of 2 equivalents of the phosphite to $[Pt(C_2H_4)_3]$ (see Tables 1 and 2 for characterising data). Crystals were grown from CH_2Cl_2–pentane and its structure determined by X-ray crystallography to determine the nature of the co-ordination of the ligand to platinum and the effects of co-ordination on the bonding and conformation of the ligand.

Crystal Structure of $[Pt(\eta^2\text{-}C_2H_4)\{P(OC_6H_4OMe\text{-}2)\}_2]$ **2**.—Pale yellow crystals were obtained from a CH_2Cl_2–pentane solution; the complex crystallised as discrete molecules in the monoclinic space group *C*2/*c*. Bond lengths and angles (with the numbering scheme shown in Fig. 2) are listed in Table 4. The ethene, platinum and two phosphorus atoms of the phosphite

Table 4 Bond lengths (Å) and angles for complex **2**

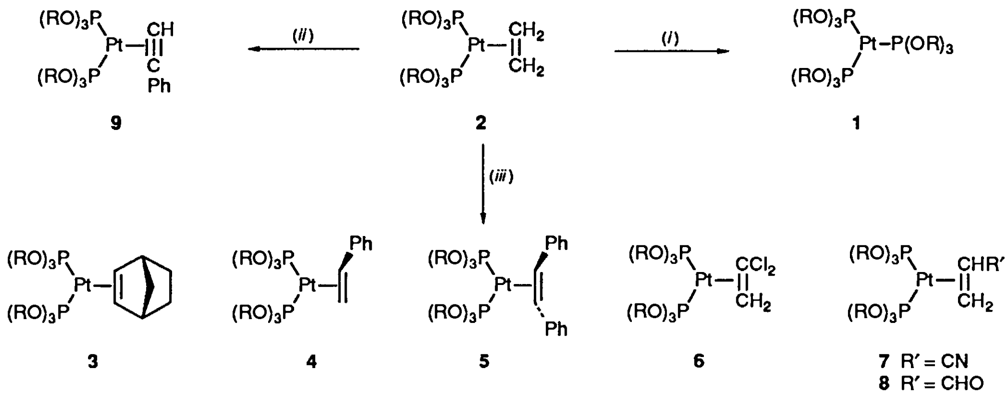
Pt–C(1)	2.128(5)	Pt–C(2)	2.131(4)	O(32)–C(37)	1.406(6)	P(2)–O(4)	1.613(3)
Pt–P(1)	2.228(2)	Pt–P(2)	2.227(2)	P(2)–O(5)	1.625(3)	P(2)–O(6)	1.621(3)
C(1)–C(2)	1.417(7)	P(1)–O(1)	1.602(3)	O(4)–C(41)	1.391(5)	C(41)–C(42)	1.400(6)
P(1)–O(2)	1.612(3)	P(1)–O(3)	1.631(3)	C(41)–C(46)	1.365(6)	C(42)–C(43)	1.409(7)
O(1)–C(11)	1.404(5)	C(11)–C(12)	1.387(6)	C(42)–O(42)	1.345(5)	C(43)–C(44)	1.388(7)
C(11)–C(16)	1.388(7)	C(12)–C(13)	1.385(7)	C(44)–C(45)	1.369(8)	C(45)–C(46)	1.393(7)
C(12)–O(12)	1.353(6)	C(13)–C(14)	1.389(8)	O(42)–C(47)	1.435(5)	O(5)–C(51)	1.395(5)
C(14)–C(15)	1.373(8)	C(15)–C(16)	1.386(7)	C(51)–C(52)	1.391(6)	C(51)–C(56)	1.371(6)
O(12)–C(17)	1.428(6)	O(2)–C(21)	1.399(5)	C(52)–C(53)	1.388(6)	C(52)–O(52)	1.367(6)
C(21)–C(22)	1.395(7)	C(21)–C(26)	1.380(7)	C(53)–C(54)	1.386(7)	C(54)–C(55)	1.374(7)
C(22)–C(23)	1.389(7)	C(22)–O(22)	1.364(6)	C(55)–C(56)	1.377(6)	O(52)–C(57)	1.417(6)
C(23)–C(24)	1.385(9)	C(24)–C(25)	1.364(9)	O(6)–C(61)	1.397(4)	C(61)–C(62)	1.391(6)
C(25)–C(26)	1.384(8)	O(22)–C(27)	1.428(7)	C(61)–C(66)	1.369(6)	C(62)–C(63)	1.403(6)
O(3)–C(31)	1.408(5)	C(31)–C(32)	1.387(6)	C(62)–O(62)	1.369(5)	C(63)–C(64)	1.388(7)
C(31)–C(36)	1.365(7)	C(32)–C(33)	1.382(7)	C(64)–C(65)	1.374(7)	C(65)–C(66)	1.399(6)
C(32)–O(32)	1.360(6)	C(33)–C(34)	1.377(8)	O(62)–C(67)	1.429(6)		
C(34)–C(35)	1.371(8)	C(35)–C(36)	1.388(7)				
C(1)–Pt–C(2)	38.9(2)	C(1)–Pt–P(1)	147.8(2)	C(33)–C(34)–C(35)	121.0(5)	C(34)–C(35)–C(36)	119.1(5)
C(2)–Pt–P(1)	108.9(1)	C(1)–Pt–P(2)	106.4(2)	C(31)–C(36)–C(35)	119.7(4)	C(32)–O(32)–C(37)	117.8(4)
C(2)–Pt–P(2)	145.2(1)	P(1)–Pt–P(2)	105.8(1)	Pt–P(2)–O(4)	122.9(1)	Pt–P(2)–O(5)	118.2(1)
Pt–C(1)–C(2)	70.7(3)	Pt–C(2)–C(1)	70.4(3)	O(4)–P(2)–O(5)	96.2(1)	Pt–P(2)–O(6)	119.8(1)
Pt–P(1)–O(1)	114.1(1)	Pt–P(1)–O(2)	120.2(1)	O(4)–P(2)–O(6)	96.2(2)	O(5)–P(2)–O(6)	98.0(2)
O(1)–P(1)–O(2)	99.2(2)	Pt–P(1)–O(3)	120.1(1)	P(2)–O(4)–C(41)	124.5(2)	O(4)–C(41)–C(42)	114.3(3)
O(1)–P(1)–O(3)	100.9(2)	O(2)–P(1)–O(3)	98.8(2)	O(4)–C(41)–C(46)	123.4(4)	C(42)–C(41)–C(46)	122.2(4)
P(1)–O(1)–C(11)	129.5(3)	O(1)–C(11)–C(12)	116.6(4)	C(41)–C(42)–C(43)	117.4(4)	C(41)–C(42)–O(42)	116.5(4)
O(1)–C(11)–C(16)	122.3(3)	C(12)–C(11)–C(16)	121.0(4)	C(43)–C(42)–O(42)	126.2(4)	C(42)–C(43)–C(44)	120.1(5)
C(11)–C(12)–C(13)	118.4(4)	C(11)–C(12)–O(12)	116.3(4)	C(43)–C(44)–C(45)	121.0(5)	C(44)–C(45)–C(46)	119.8(5)
C(13)–C(12)–O(12)	125.3(4)	C(12)–C(13)–C(14)	120.9(5)	C(41)–C(46)–C(45)	119.7(4)	C(42)–O(42)–C(47)	118.9(4)
C(13)–C(14)–C(15)	120.1(5)	C(14)–C(15)–C(16)	119.9(5)	P(2)–O(5)–C(51)	119.7(2)	O(5)–C(51)–C(52)	118.6(4)
C(11)–C(16)–C(15)	119.7(4)	C(12)–O(12)–C(17)	116.9(4)	O(5)–C(51)–C(56)	120.5(3)	C(52)–C(51)–C(56)	120.9(4)
P(1)–O(2)–C(21)	122.8(3)	O(2)–C(21)–C(22)	116.7(4)	C(51)–C(52)–C(53)	118.3(4)	C(51)–C(52)–O(52)	115.9(4)
O(2)–C(21)–C(26)	121.3(4)	C(22)–C(21)–C(26)	121.8(4)	C(53)–C(52)–O(52)	125.7(4)	C(52)–C(53)–C(54)	120.1(4)
C(21)–C(22)–C(23)	118.0(4)	C(21)–C(22)–O(22)	115.7(4)	C(53)–C(54)–C(55)	121.1(4)	C(54)–C(55)–C(56)	118.8(5)
C(23)–C(22)–O(22)	126.2(5)	C(22)–C(23)–C(24)	119.7(5)	C(51)–C(56)–C(55)	120.9(4)	C(52)–O(52)–C(57)	117.2(3)
C(23)–C(24)–C(25)	121.6(5)	C(24)–C(25)–C(26)	119.8(5)	P(2)–O(6)–C(61)	124.1(3)	O(6)–C(61)–C(62)	115.4(3)
C(21)–C(26)–C(25)	119.0(5)	C(22)–O(22)–C(27)	117.4(4)	O(6)–C(61)–C(66)	123.2(4)	C(62)–C(61)–C(66)	121.3(4)
P(1)–O(3)–C(31)	120.6(3)	O(3)–C(31)–C(32)	117.2(4)	C(61)–C(62)–C(63)	118.7(4)	C(61)–C(62)–O(62)	116.9(3)
O(3)–C(31)–C(36)	121.1(4)	C(32)–C(31)–C(36)	121.6(4)	C(63)–C(62)–O(62)	124.4(4)	C(62)–C(63)–C(64)	119.7(4)
C(3)–C(32)–C(33)	118.2(4)	C(31)–C(32)–O(32)	116.4(4)	C(63)–C(64)–C(65)	120.8(4)	C(64)–C(65)–C(66)	119.7(4)
C(33)–C(32)–O(32)	125.4(4)	C(32)–C(33)–C(34)	120.3(5)	C(61)–C(66)–C(65)	119.7(4)	C(62)–O(62)–C(67)	117.9(3)



Scheme 1 Definition of torsion angles ω and τ in (*i*) $P(OC_6H_4OMe\text{-}2)_3$ and (*ii*) complex **2** ($R = C_6H_4OMe\text{-}2$)

ligands lie nearly in the same plane (0.012 Å deviation from mean plane) and the dihedral angle between the P–Pt–P and platinum–olefin plane is 2.5(2)°. The crystal structures of a large number of metal–olefin complexes have been determined[14] and the Pt–C and C=C bond lengths in **2** [2.128(5), 2.131(4) and 1.417(7) Å respectively] are consistent with strong Pt(d)→π* bonding since the Pt–C distances are smaller than the average for co-ordinated ethene [2.172(42) Å] and the C=C bond length is longer than the average co-ordinated ethene bond length [1.392(44) Å]. No other crystal structures of triaryl phosphite platinum(0) complexes have been reported for comparison. A long-range interaction between one of the methoxy groups on the phosphite and the platinum centre is observed (see Fig. 2). The Pt ··· O(52) distance (3.79 Å) is considerably longer than those observed in structures where the methoxy group of a phosphine directly binds an unsaturated metal centre.[19]

The effect of co-ordination on the bond lengths and angles within the ligand is small. Thus the average P–O distance in complex **2** is 1.617(4) Å [*cf.* 1.624(4) Å in the phosphite] and the average O–P–O angle is 98.3(7)° [*cf.* 96.6(2)°]. As shown in Scheme 1, the conformational behaviour of the three aryloxy groups of the ligand may be described in terms of two torsion angles ω and τ about the $O\text{–}C_{ipso}$ and P–O bonds respectively. Thus τ describes whether the aryl group is *gauche* ($\tau = \pm 60°$) or *anti* (τ *ca.* 180°) to the metal attached to the phosphorus (or to the lone pair on P, as illustrated in Scheme 1), and ω describes the conformation of the methoxy group relative to the phosphorus atom. In order for the methoxy group to be interacting with the metal one would expect both ω and τ to take values fairly close to 0° (±60 say) and certainly to avoid *anti* conformations. The conformation of the molecules of the phosphite in the crystal has each of the aryloxy groups tipped towards the region of the lone pair (τ = 40.5°) and methoxy groups twisted away from the phosphorus (ω = −123.7°). In **2** one of the $P(OR)_3$ ligands [that incorporating P(2)] adopts the same general conformation as in the phosphite albeit the opposite enantiomer (τ = −45.9, −41.2, −35.4°; ω = 148.9, 99.5, 154.5° for the three aryloxy groups). As noted above, for a close approach of a methoxy oxygen to platinum, both ω and τ need to be close to 0°, and it is notable that the oxygen closest to platinum, O(52), is that with the smallest ω value (and a *gauche* conformation at the P–O bond). In contrast the $P(OR)_3$ ligand incorporating P(1) shows a different conformation with τ = −172.3, 61.1, 7.0° and ω = 133.2, 128.0, −115.7° for the three aryloxy groups. Thus one OR group [attached through O(1)] is in an *anti* conformation and for a second [O(3)] the



Scheme 2 Some substitution reactions of complex **2**: (*i*) $P(OR)_3$; (*ii*) PhC≡CH; (*iii*) the appropriate substituted alkene ($R = C_6H_4OMe$-2)

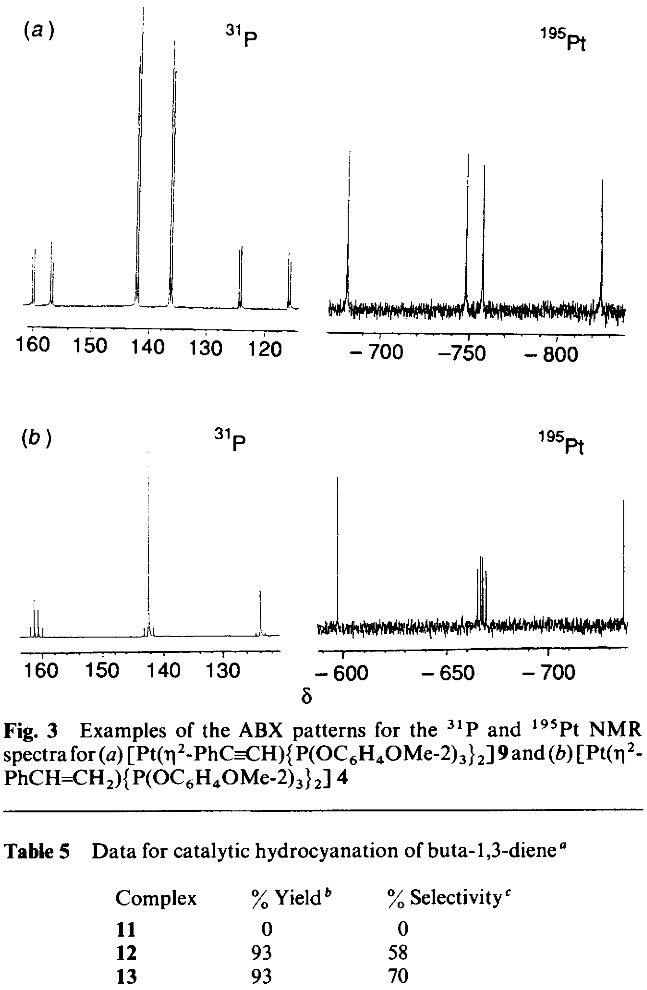


Fig. 3 Examples of the ABX patterns for the ^{31}P and ^{195}Pt NMR spectra for (*a*) [Pt(η^2-PhC≡CH){$P(OC_6H_4OMe\text{-}2)_3$}$_2$] **9** and (*b*) [Pt(η^2-PhCH=CH$_2$){$P(OC_6H_4OMe\text{-}2)_3$}$_2$] **4**

Table 5 Data for catalytic hydrocyanation of buta-1,3-diene[a]

Complex	% Yield[b]	% Selectivity[c]
11	0	0
12	93	58
13	93	70
14	82	63

[a] Reaction conditions given in Experimental section. [b] Yield of nitriles calculated from GC analysis; other products are mainly oligomers of butadiene. [c] Proportion of nitrile product that is the linear isomer (pent-3-enenitrile).

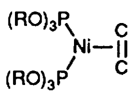
O–C_{ipso} bond nearly eclipses the Pt–P bond. Presumably these variations in conformational behaviour arise from the relative crowding in the region near the metal atom (or P lone pair) compared with the region behind the phosphorus (*i.e.* on the opposite side of the P atom to the metal or lone pair). In the absence of a metal atom and associated ligands a *gauche-gauche-gauche* (ggg) conformer with respect to the P–O bonds (as in the crystal structure of the phosphite ligand) is observed; in a more crowded situation (as in **2**) the *anti-gauche-gauche* (agg) conformer is also possible. The ggg conformation seen in the phosphite allows us to calculate a cone angle for this ligand of 181°, rather than that estimated by Tolman's method[5] (145°) on the basis of an assumed aaa conformation. As for the conformation about the O–C_{ipso} bonds the magnitudes of the ω values observed for the phosphite and complex **2** range from 99.5 to 154.5, *i.e.* rather far from the values required for co-ordination of the ether function. Therefore the ligand seems not to be well preorganised to chelate metals.

The ethene ligand in complex **2** is readily displaced by other alkenes, alkynes, or phosphites as summarised in Scheme 2. The products **3**–**9** have been characterised in solution by ^{31}P-{^1H} and ^{195}Pt-{^1H} NMR spectroscopy (see Table 2) and representative examples (**4** and **5**) have been isolated and completely characterised (see Tables 1 and 2); the spectra of the unsymmetrical alkene complexes are all examples of ABX spin systems and the observed splitting patterns vary from deceptively simple to very complex (see Fig. 3). To our knowledge complexes **2**–**9** are the first examples of complexes of the type [Pt(η^2-alkene){$P(OR)_3$}$_2$] or [Pt(η^2-alkyne){$P(OR)_3$}$_2$].

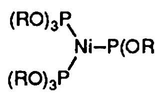
Nickel(0) *Chemistry.*—We were particularly interested in nickel(0) complexes of the phosphite ligands because of their potential use as hydrocyanation catalysts. The nickel analogue of the platinum complex **2**, [Ni(η^2-C_2H_4){$P(OC_6H_4OMe\text{-}2)_3$}$_2$] **10**, is readily made by reduction of [Ni(acac)$_2$] (acac = acetylacetonate) with $AlEt_3$ in the presence of ethene and $P(OC_6H_4OMe\text{-}2)_3$ (see Experimental section for details). When complex **10** is treated with 1 equivalent of the same phosphite a new species, assigned the structure [Ni{$P(OC_6H_4OMe\text{-}2)_3$}$_3$] **11** analogous to the platinum complex **1** above, was detected by ^{31}P-{^1H} NMR spectroscopy. The same species **11** was observed upon treatment of [Ni(cod)$_2$] (cod = cycloocta-1,5-diene) with the phosphite or upon reduction of [Ni(acac)$_2$] in the presence of the phosphite; it is very air sensitive and we were unable to isolate it in pure form. Both **10** and **11** are co-ordinatively unsaturated nickel(0) complexes, stabilised by the bulkiness of the phosphite ligand; similar species are known with $P(OC_6H_4Me\text{-}2)_3$ ligands.[20]

The less bulky phosphite $P(OC_6H_4OMe\text{-}2)(OC_6H_4Me\text{-}4)_2$ forms the four-co-ordinate nickel(0) complex [Ni{$P(OC_6H_4OMe\text{-}2)(OC_6H_4Me\text{-}4)_2$}$_4$] **12** upon treatment of [Ni(cod)$_2$] (see Tables 1 and 2 for characterising data).

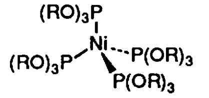
Hydrocyanation Catalysis.—The catalytic activity of our nickel(0) complexes **11** and **12** for the hydrocyanation of buta-1,3-diene has been investigated. The precise conditions used are given in the Experimental section and the results obtained presented in Table 5. Because of the air sensitivity of **11**, the complex was generated *in situ* from the ethene complex **10** and an excess of $P(OC_6H_4OMe\text{-}2)_3$. In order to evaluate the effect that the methoxy substituent has on the catalytic activity of the 2-methoxyphenyl phosphite complexes it was necessary to



10 R = C_6H_4OMe-2



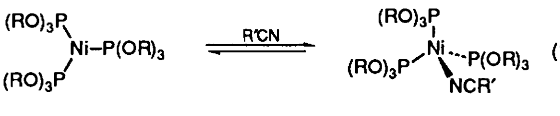
11 R = C_6H_4OMe-2
14 R = C_6H_4Me-2



12 $P(OR)_3 = P(OC_6H_4OMe\text{-}2)(OC_6H_4Me\text{-}4)_2$
13 R = C_6H_4Me-4
15 R = C_6H_4OMe-4

obtain comparable data for the related complexes $[Ni\{P(OC_6H_4Me\text{-}4)_3\}_4]$ **13** and $[Ni\{P(OC_6H_4Me\text{-}2)_3\}_3]$ **14** under similar conditions; these data are also presented in Table 5.

Complex **11** is not a catalyst for the hydrocyanation of buta-1,3-diene under the same conditions that **12**–**14** showed high activity and good regioselectivity. The lack of activity of **11** is not an electronic effect of the methoxy groups since it is known[9a] that $[Ni\{P(OC_6H_4OMe\text{-}4)_3\}_4]$ **15**, in which electronic effects will be similar, is an efficient catalyst. Bulky ligands are known[20] to reduce the rate of hydrocyanation and therefore the lack of activity of **11** may be due in part to steric effects since $P(OC_6H_4OMe\text{-}2)_3$ is larger than $P(OC_6H_4Me\text{-}2)_3$. Tolman[20] has explained the effect of bulky ligands on the catalysis in terms of the stability of the adduct formed between the nitrile product and the nickel(0) [equation (1)]. We have found that upon addition of 1 equivalent of MeCN or PhCN to solutions of **11** the ^{31}P NMR signal shifts *ca.* 4 ppm to high frequency, indicating that nitrile adducts [equation (1)] are readily formed.



(1)

11 or **14**

It is also possible that the low reactivity of **11** is due to co-ordination sites being occupied by the methoxy groups, though the high activity of **12**, where methoxy co-ordination is also possible, suggests that this effect alone is not a complete explanation.

In conclusion we have shown that 2-methoxyphenyl phosphites form zerovalent complexes with platinum and nickel and weak platinum(0)–ether interactions have been detected. A combination of steric effects and nickel(0)–ether interactions may explain the lack of catalytic activity of nickel(0) complexes of tris(2-methoxyphenyl) phosphite.

Experimental

All preparations were carried out in a dry nitrogen atmosphere using Schlenk techniques. After purification the ligands were stored under nitrogen in a freezer. Unless otherwise stated most metal complexes were found to be air stable in the solid state, so once prepared were stored in air. All reaction solvents were dried by refluxing over appropriate drying reagents (calcium hydride for dichloromethane and acetonitrile, sodium–benzophenone for diethyl ether, tetrahydrofuran, toluene, benzene, pentane and hexane, and anhydrous magnesium sulfate for acetone) and distilled under nitrogen prior to use. Commercial reagents were used as supplied unless otherwise stated and other reagents were prepared by literature methods: $[Pt(cod)_2]$,[21] $[Pt(\eta^2\text{-}C_2H_4)_3]$,[21] $[Ni(cod)_2]$.[22] The complex $[PtCl_2\{P(OC_6H_4OMe\text{-}2)_3\}_2]$ was made by the addition of the phosphite to $[PtCl_2(cod)]$ in CH_2Cl_2.[23] Microanalyses were carried out in the Microanalytical Laboratory of the School of Chemistry, Bristol University. Infrared spectra were recorded on a Perkin Elmer 1710 FT machine as solutions in dichloromethane, ^1H, ^{31}P, ^{13}C and ^{195}Pt NMR spectra on a JEOL FX90Q (90 MHz) or GX400 (400 MHz) instrument with chemical shifts to high frequency of the references given in the appropriate tables. Gas chromatography was performed on a Varian 800 gas chromatograph with autosampler.

CAUTION: Hydrogen cyanide is extremely toxic and should be handled only in a well ventilated fume cupboard with the operator wearing gloves and preferably breathing apparatus.

Preparations.—Tris(2-methoxyphenyl)phosphite. n-Butyllithium (48 cm^3, 0.5 mol, 10.4 mol dm^{-3} solution in hexane) was added dropwise to a cooled (0 °C) solution of 2-methoxyphenol (62.0 cm^3, 0.50 mol) in toluene (100 cm^3) over *ca.* 30 min and then a solution of PCl_3 (14.4 cm^3, 0.165 mol) in toluene (40 cm^3) was added dropwise over *ca.* 30 min. The solution was stirred for 18 h at room temperature to give a white suspension, to which water (600 cm^3) was then added. The organic layer was separated and dried over anhydrous magnesium sulfate (10 g), filtered, and then concentrated to give a clear oil, which upon trituration with pentane gave the pure white solid product. This solid (57.8 g, 89%) was filtered off and dried *in vacuo.*

Dichloro(2-methoxyphenoxy)phosphine. 2-Methoxyphenol (70 g, 0.56 mol) was added dropwise over *ca.* 15 min to PCl_3 (50 cm^3, 0.5 mol). The mixture was stirred for 1 h and then refluxed for 2 h. Unreacted PCl_3 and the solvent were evaporated under reduced pressure and then the residual oil was fractionally distilled to give the product (73.1 g, 70%) as a colourless oil, b.p. 90–120 °C (0.01 mmHg, *ca.* 1.33 Pa) [Found (Calc.): C, 38.4 (37.4); H, 3.3 (3.1)%]; δ(P) 189.5 ($CDCl_3$).

Bis(4-methylphenyl)(2-methoxyphenyl)phosphite. A solution of $PCl_2(OC_6H_4OMe\text{-}2)$ (see above) (5.0 g, 0.022 mol) in tetrahydrofuran (20 cm^3) was treated with NEt_3 (6.06 cm^3, 0.044 mol) to give a cloudy white suspension. The solution was cooled to −7 °C and then 4-methylphenol (4.76 g, 0.044 mol) was slowly added over *ca.* 2 min to give a colourless solution and a white precipitate. The mixture was stirred for 2 h and then the solid $[NEt_3H]Cl$ was filtered off and the solvent stripped off the filtrate to give the product (7.9 g, 97%) as a clear oil.

$[Pt\{P(OC_6H_4OMe\text{-}2)_3\}_3]$ **1**. (*a*) *From* $[PtCl_2\{P(OC_6H_4OMe\text{-}2)_3\}_2]$. The complex $[PtCl_2\{P(OC_6H_4OMe\text{-}2)_3\}_2]$ (1.0 g, 0.9 mmol) and $P(OC_6H_4OMe\text{-}2)_3$ (0.37 g, 0.9 mmol) were dissolved in acetonitrile (50 cm^3). Treatment of this solution with $NaBH_4$ (0.16 g, 4.3 mmol) caused immediate effervescence and a colour change from clear to yellow. After 1.5 h, the solvent was removed under reduced pressure. Addition of methanol (30 cm^3) to the residue gave a pale yellow suspension of the product (0.78 g, 59%) which was filtered off and dried *in vacuo.* The analogous complexes $[Pt\{P(OC_6H_4Me\text{-}2)_3\}_3]$ and $[Pt\{P(OPh)_3\}_3]$ were made by a similar method in 75 and 44% yield respectively.

(*b*) *From* $[Pt(cod)_2]$. The complex $[Pt(cod)_2]$ (0.04 g, 0.10 mmol) and $P(OC_6H_4OMe\text{-}2)_3$ (0.12 g, 0.30 mmol) were dissolved in toluene (4 cm^3) and the resulting solution stirred for 1 h. The solvent was then removed under reduced pressure to leave a pale yellow solid which was recrystallised by dissolving in the minimum of toluene (*ca.* 1 cm^3) and then crystallising by the dropwise addition of pentane. The product (0.13 g, 93%) was filtered off and dried *in vacuo.*

$[Pt(\eta^2\text{-}C_2H_4)\{P(OC_6H_4OMe\text{-}2)_3\}_2]$ **2** *from* $[PtCl_2\{P(OC_6H_4OMe\text{-}2)_3\}_2]$. The complex $[PtCl_2\{P(OC_6H_4OMe\text{-}2)_3\}_2]$ (1.07 g, 1.0 mmol) was dissolved in ethene-saturated acetonitrile (150 cm^3). Treatment of the resulting solution with $NaBH_4$ (0.13 g, 3.0 mmol) led to a change of colour from colourless to yellow. After 30 min ethene-saturated water (50 cm^3) was added dropwise, to give a precipitate which was filtered off and redissolved in dichloromethane (10 cm^3). This solution was dried over anhydrous magnesium sulfate, filtered and then the solvent reduced to *ca.* 1 cm^3 under reduced pressure. Dropwise

Table 6 Crystal structure analyses

Compound	$P(OC_6H_4OMe\text{-}2)_3$	**2**
Crystal data		
Formula	$C_{21}H_{21}O_6P$	$C_{44}H_{46}O_{12}P_2Pt$
M	400.4	1024.0
Crystal system	Cubic	Monoclinic
Space group	$P2_13$ (no. 198)	$C2/c$ (no. 15)
a/Å	12.681(2)	13.879(4)
b/Å	12.681(2)	17.070(3)
c/Å	12.681(2)	36.101(10)
β/°	90	98.12(2)
U/Å^3	2039(1)	8467(4)
T/K	200	295
Z	4	8
D_c/g cm^{-3}	1.30	1.60
$F(000)$	840	4112
μ(Mo-Kα)/cm^{-1}	1.6	34.8
Data collection and reduction		
Crystal dimensions (mm)	0.3 × 0.25 × 0.2	0.35 × 0.45 × 0.23
2θ range/°	4–50	4–50
Scan width, ω/°	$1.2 + \Delta\alpha_1\alpha_2$	$0.9 + \Delta\alpha_1\alpha_2$
Total data	1289	6633
Unique data	690	6114
'Observed' data [$F^2 > 1.5\sigma(F^2)$], N_o	599	5251
Minimum, maximum transmission coefficient	—	0.059, 0.104
Refinement		
Least-squares variables, N_v	86	532
R*	0.075	0.026
R'*	0.106	0.034
S*	2.15	1.10
g	0.0015	0.0005
Final difference map features/e Å^{-3}	+0.63, −0.31	+0.42, −0.61

* $R = \Sigma|\Delta|/\Sigma|F_o|$; $R' = (\Sigma w\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}}$; $S = [\Sigma w\Delta^2/(N_o - N_v)]^{\frac{1}{2}}$; $\Delta = F_o - F_c$; $w = [\sigma_c^2(F_o) + gF_o^2]^{-1}$, $\sigma_c^2(F_o)$ = variance in F_o due to counting statistics.

Table 7 Atomic coordinates (× 10^4) for $P(OC_6H_4OMe\text{-}2)_3$

Atom	x	y	z
P	7 606(1)	7 606(1)	7 606(1)
O(1)	7 782(4)	7 318(3)	8 841(3)
O(2)	6 394(6)	6 802(7)	10 280(5)
C(1)	7 756(7)	6 269(6)	9 152(6)
C(2)	7 062(6)	5 956(7)	9 918(6)
C(3)	7 007(9)	4 982(9)	10 309(8)
C(4)	7 734(11)	4 228(9)	9 817(11)
C(5)	8 404(10)	4 516(9)	9 125(10)
C(6)	8 409(8)	5 535(7)	8 777(8)
C(7)	5 818(10)	6 646(13)	11 209(11)

addition of pentane (5 cm^3) gave the yellow solid product (0.91 g, 88%) which was filtered off and dried *in vacuo*. The analogous complexes $[Pt(\eta^2\text{-}C_2H_4)\{P(OC_6H_4Me\text{-}2)_3\}_2]$ and $[Pt(\eta^2\text{-}C_2H_4)\{P(OPh)_3\}_2]$ were made similarly in 73 and 85% yield respectively.

$[Pt(\eta^2\text{-}L)\{P(OC_6H_4OMe\text{-}2)_3\}_2]$ **3–9** *from* $[Pt(\eta^2\text{-}C_2H_4)\{P(OC_6H_4OMe\text{-}2)_3\}_2]$. To a solution of $[Pt(\eta^2\text{-}C_2H_4)\{P(OC_6H_4OMe\text{-}2)_3\}_2]$ (0.05 g, 0.05 mmol) in toluene (10 cm^3) was added L (*ca.* 0.5 mmol) and the mixture then stirred for 1 h. Concentration of the solution to *ca.* 2 cm^3 followed by the dropwise addition of pentane (10 cm^3) precipitated the pale yellow product which was then filtered off, washed with pentane (10 cm^3) and dried *in vacuo*. This procedure was used for L = norbornene, *trans*-stilbene, phenylacetylene, styrene, vinylidene dichloride, acrylaldehyde and acrylonitrile.

$[Ni(\eta^2\text{-}C_2H_4)\{P(OC_6H_4OMe\text{-}2)_3\}_2]$ **10**. The complex $[Ni(acac)_2]$ (1.6 g, 6.3 mmol) and $P(OC_6H_4OMe\text{-}2)_3$ (5.0 g, 12.6 mmol) were dissolved in toluene (50 cm^3) at 0 °C. The solution was saturated with ethene and then triethylaluminium (9.86 cm^3, 1.9 mol dm^{-3} solution in toluene, 19.0 mmol) added rapidly with stirring. The solution was allowed to warm to room temperature, stirred for 3 h, and then concentrated to *ca.* 15 cm^3. Methanol (50 cm^3), saturated with ethene, was slowly added to give a yellow precipitate. The solid product (4.0 g, 51%) was filtered off and dried *in vacuo*.

$[Ni\{P(OC_6H_4OMe\text{-}2)_3\}_3]$ **11**. (*a*) *From* $[Ni(acac)_2]$. This preparation was carried out in a similar manner to that of complex **10** except that the reduction was performed in the presence of 3 equivalents of $P(OC_6H_4OMe\text{-}2)_3$ and without ethene. The complex is extremely air-sensitive and was characterised by $^{31}P\text{-}\{^1H\}$ NMR spectroscopy only.

(*b*) *From* $[Ni(cod)_2]$. A flask was charged with $[Ni(cod)_2]$ (0.34 g, 1.3 mmol) and $P(OC_6H_4OMe\text{-}2)_3$ (2.0 g, 5.0 mmol). After cooling to 0 °C, pentane (100 cm^3) was added dropwise to the stirred mixture. The suspension was then warmed to room temperature and stirred for 30 min. The product (1.8 g) was collected by filtration and dried *in vacuo*; $^{31}P\text{-}\{^1H\}$ NMR spectroscopy revealed this product was impure **11**.

$[Ni\{P(OC_6H_4OMe\text{-}2)(OC_6H_4Me\text{-}4)_2\}_4]$ **12**. A solution of $P(OC_6H_4OMe\text{-}2)(OC_6H_4Me\text{-}4)_2$ (4.01 g, 10.9 mmol) in toluene (50 cm^3) was added to a solution of $[Ni(cod)_2]$ (0.75 g, 2.7 mmol) and then the mixture stirred for 15 min. The solvent was removed under vacuum and the resulting oil triturated with pentane (30 cm^3) to give the white solid product which was then filtered off, washed with pentane (2 × 20 cm^3) and dried *in vacuo* (3.8 g, 92%).

Hydrocyanation of Buta-1,3-*diene with the* (*Triaryl phosphite*) *nickel*(0) *Complexes*.—The general procedure is exemplified for the catalyst $[Ni\{P(OC_6H_4Me\text{-}4)_3\}_4]$. A stainless-steel

Table 8 Atomic coordinates (× 10^4) for complex **2**

Atom	*x*	*y*	*z*
Pt	1716(1)	−23(1)	1224
C(1)	212(3)	271(3)	1160(2)
C(2)	595(3)	472(3)	829(1)
P(1)	3102(1)	−24(1)	978(1)
O(1)	4060(2)	32(2)	1282(1)
C(11)	5035(3)	131(2)	1229(1)
C(12)	5566(3)	689(3)	1450(1)
C(13)	6539(3)	788(3)	1414(2)
C(14)	6979(4)	328(4)	1168(2)
C(15)	6448(4)	−231(3)	955(2)
C(16)	5473(3)	−337(3)	986(1)
O(12)	5073(2)	1109(2)	1679(1)
C(17)	5638(4)	1505(3)	1984(2)
O(2)	3394(2)	−771(2)	745(1)
C(21)	2826(3)	−1033(3)	417(1)
C(22)	3302(3)	−1137(3)	105(1)
C(23)	2761(4)	−1411(4)	−222(1)
C(24)	1785(4)	−1585(4)	−229(2)
C(25)	1338(4)	−1506(4)	82(2)
C(26)	1860(3)	−1232(3)	412(2)
O(22)	4266(2)	−947(2)	154(1)
C(27)	4778(4)	−1044(4)	−159(2)
O(3)	3316(2)	666(2)	688(1)
C(31)	2683(3)	1311(2)	621(1)
C(32)	2187(3)	1395(3)	262(1)
C(33)	1561(4)	2024(3)	189(2)
C(34)	1418(4)	2534(3)	472(2)
C(35)	1902(4)	2439(3)	827(2)
C(36)	2547(3)	1818(3)	901(1)
O(32)	2352(2)	837(2)	9(1)
C(37)	1651(4)	741(4)	−309(2)
P(2)	2068(1)	−568(1)	1787(1)
O(4)	3108(2)	−965(2)	1932(1)
C(41)	3593(3)	−1477(2)	1722(1)
C(42)	4609(3)	−1441(3)	1801(1)
C(43)	5146(4)	−1964(3)	1609(2)
C(44)	4668(4)	−2485(3)	1351(2)
C(45)	3672(4)	−2504(3)	1280(2)
C(46)	3128(4)	−1996(3)	1470(1)
O(42)	4979(2)	−893(2)	2049(1)
C(47)	6015(3)	−845(3)	2150(2)
O(5)	1409(2)	−1303(1)	1889(1)
C(51)	403(3)	−1288(2)	1783(1)
C(52)	12(3)	−1696(2)	1463(1)
C(53)	−990(3)	−1681(2)	1359(1)
C(54)	−1575(3)	−1275(3)	1574(1)
C(55)	−1180(3)	−876(3)	1890(1)
C(56)	−185(3)	−884(3)	1991(1)
O(52)	666(2)	−2066(2)	1273(1)
C(57)	289(4)	−2478(3)	944(1)
O(6)	2010(2)	−48(1)	2159(1)
C(61)	2259(3)	744(2)	2192(1)
C(62)	1807(3)	1166(2)	2449(1)
C(63)	2039(3)	1961(2)	2505(1)
C(64)	2696(3)	2312(3)	2300(1)
C(65)	3140(3)	1885(3)	2049(1)
C(66)	2929(3)	1087(2)	1999(1)
O(62)	1160(2)	767(2)	2632(1)
C(67)	776(4)	1159(3)	2929(1)

cylinder (capacity 10 cm^3) containing a magnetic stirrer bar was charged with $[Ni\{P(OC_6H_4Me\text{-}4)_3\}_4]$ (0.124 g, 0.09 mmol) and $P(OC_6H_4Me\text{-}4)_3$ (0.17 cm^3, 0.55 mmol). Freshly distilled butadiene (4.0 cm^3, 0.05 mol) and HCN (1.0 cm^3, 0.03 mol) were then added to the cooled (−30 °C) cylinder which was sealed and the mixture heated at 120 °C in an oil-bath with stirring for 2 h. The internal temperature was monitored using a thermocouple. After 2 h the autoclave was recooled to −30 °C, opened carefully, and the product solution poured into a preweighed glass vial. After unreacted butadiene and HCN had evaporated, a sample was taken and analysed by gas chromatography. The remaining product was poured into an aqueous hypochlorite solution to destroy any unreacted HCN. The yield was 3.12 g and the ratio of products, vinylcyclohexane:2-methylbut-3-enenitrile:pent-3-enenitrile:tris(4-methylphenyl) phosphite was 0.04:0.17:0.41:0.9.

Crystal Structure Determinations.—Many of the details of the structure analyses carried out on $P(OC_6H_4OMe\text{-}2)_3$ and complex **2** are listed in Table 6. X-Ray diffraction measurements were made using Nicolet four-circle P3m diffractometers with Mo-Kα radiation (λ = 0.710 69 Å) on single crystals mounted in thin-walled glass capillaries. In the case of the phosphite all measurements were made at 200 K. Cell dimensions for each analysis were determined from the setting-angle values of 28 and 15 centred reflections respectively.

Intensity data were collected by ω–2θ scans for unique portions of reciprocal space and corrected for Lorentz, polarisation, and crystal decay (of 2 and 0% respectively) where appropriate, and, in the case of **2**, for absorption effects, the latter on the basis of azimuthal scan data. A total of 66 reflections were deleted from the dataset for the phosphite due to temporary failure of the cooling apparatus. The structures were solved by direct (for the phosphite) and heavy-atom (Patterson and Fourier difference) methods (for **2**), and refined by least-squares against F with a weighting scheme chosen to give minimum variation of the goodness-of-fit with F_o. All non-hydrogen atoms were assigned anisotropic displacement parameters. All hydrogen atoms were assigned fixed isotropic displacement parameters and were constrained to ideal geometries with C–H 0.96 Å. The chirality of the phosphite crystal was assigned on the basis of an η refinement [η = 2.4(1.4)].[24] The high standard deviation for η is consistent with the small f'' values for the elements present and renders this assignment tentative. The rather high values of the residual indices for the phosphite may be attributed at least in part to the difficulties in temperature control.

Final difference syntheses showed no chemically significant features, the largest being close to O(1) in the phosphite and to the metal atom in **2**. Refinements converged smoothly to residuals given in Table 6. Tables 7 and 8 report the positional parameters for these structure determinations. All calculations were made with Nicolet proprietary software.[25] Complex neutral-atom scattering factors were taken from ref. 26.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates and thermal parameters.

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