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Stereoselective addition of diphenylphosphine to substituted diphenylethynes: synthetic, NMR and X-ray crystallographic studies

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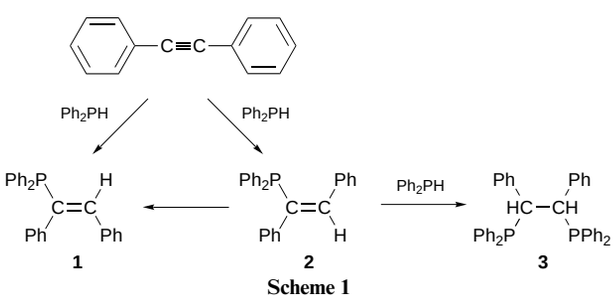
The base-catalysed addition of diphenylphosphine to the substituted diphenylethynes RC≡CR′ (R = Ph, R′ = Ph, *o*-tolyl, *m*-tolyl or 2-biphenyl; R = *m*-tolyl, R′ = *o*-tolyl or *m*-tolyl) yielded $Ph_2PC(R)=CHR'$ and/or $Ph_2PCH(R)CH(R')PPh_2$. Proton, ^{13}C, ^{13}P and two-dimensional rotating frame Overhauser enhancement ^1H NMR spectra have been used to determine the stereochemical pathways of the reactions and the stereochemistry of the products. In general the more hindered alkynes undergo monoaddition ultimately to yield phosphinoalkenes with the Ph_2P attached to the carbon bearing the least bulky substituent and *cis* to the olefinic proton, while for the less hindered alkynes the *trans* isomer is formed initially and this then reacts further to give *meso*/*erythro*-diphosphinoalkanes. Bis(*o*-tolyl)ethyne does not react with Ph_2PH under the same conditions. Crystal structures were determined for *E*- and *Z*-$Ph_2P(Ph)C=CHPh$ and show distortions of interbond angles consistent with the pattern of strain implied by the foregoing reactions. The sulfides of the phosphinoalkenes and the $Mo(CO)_4$ complexes of the diphosphinoalkanes were also prepared and their ^1H, ^{13}C and ^{31}P NMR spectra recorded. In several cases the pattern of ^{13}CO NMR signals for the complexes was used unambiguously to determine the stereochemistry of the parent diphosphines.

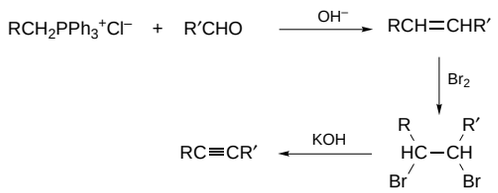
Base-catalysed anti-Markovnikov additions of diphenylphosphine to substrates with activated carbon–carbon multiple bonds are of interest because they can lead to a wide range of bi- and poly-dentate phosphines with versatile co-ordinative behaviour.[1–6] Recently we have shown that these reactions may provide a potential route to chiral 1,2-diphosphinoalkanes which find wide application in metal-mediated asymmetric synthesis. An example is the reaction of diphenylethyne with 2 equivalents of diphenylphosphine which affords the 1,2-diphosphine *meso*-$Ph_2PCH(Ph)CH(Ph)PPh_2$ **3** as the major and *E*-$Ph_2PC(Ph)=CHPh$ **1** as a minor product (Scheme 1).[7]

Conclusions from this study were that (i) the first step initially yields a mixture of the intermediate isomeric alkenes *E*- and *Z*-$Ph_2PC(Ph)=CHPh$ **1** and **2** (*i.e.* C-phenyl groups *cis* and *trans* respectively), (ii) only the *Z* isomer **2** reacts further and gives the diphosphine **3**, (iii) the *E* isomer **1** is formed both directly from the parent alkyne and also by isomerisation of its *Z* isomer under the reaction conditions used, and (iv) the *E* isomer **1** is inert to further addition under the reaction conditions (and also at elevated temperatures) and remains as a by-product of the reaction.

We have now prepared ranges of substituted and heterobis-(aromatic) diarylalkynes in order both to study further the efficiency and stereoselectivity of such addition reactions of phosphines and to provide a route to new and unusual chiral diphosphines and their derivatives. In this paper we report the synthesis of a series of symmetrical and unsymmetrical methyl- and phenyl-substituted diphenylalkynes and their subsequent base-catalysed addition reactions with diphenylphosphine. We also report the results of comprehensive one- and two-dimensional NMR studies on the products of these reactions and on their sulfide and $Mo(CO)_4$ derivatives, together with the molecular structures of **1** and **2** determined by single-crystal X-ray diffraction.



Scheme 1



Scheme 2 R, R′ = Aryl

Results and Discussion

(i) Alkyne synthesis

(2-Methylphenyl)phenylethyne [phenyl(*o*-tolyl)ethyne], (3-methylphenyl)phenylethyne [phenyl(*m*-tolyl)ethyne], bis(2-methylphenyl)ethyne [bis(*o*-tolyl)ethyne], (2-methylphenyl)(3-methylphenyl)ethyne [(*m*-tolyl)(*o*-tolyl)ethyne], and (2-biphenyl)-phenylethyne were prepared from appropriate starting reagents using the reaction sequence of Scheme 2. Bis(*m*-tolyl)ethyne was prepared from 3-bromotoluene and 2-methylbut-3-yn-2-ol using a modified palladium coupling method of Rossi and co-workers.[8] Bis(*o*-tolyl)ethyne could not be prepared by this latter method presumably due to steric hindrance. In all cases the final alkynes were obtained after work-up as colourless or

Table 1 Yields of product from the addition of diphenylphosphine to diarylethynes

Ethyne (RC≡CR′)				
R	R′	Product	Approx. molar proportion[a] (%)	Isolated yield (%)
Ph	Ph	**1**	27	26[b]
		3	73	71[b]
Ph	*o*-Tolyl	**4**	85	31
		9	15	9
m-Tolyl	*o*-Tolyl	**5**	>95	68
Ph	*m*-Tolyl	**10**	>95	75
m-Tolyl	*m*-Tolyl	**11**	>95	70
Ph	2-Biphenyl	**6**	40	57[c]
		7	60	57[c]
o-Tolyl	*o*-Tolyl	No reaction	—	—

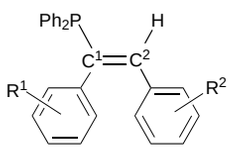
[a] Calculated from the integrals of the ^{31}P NMR signals in the reaction mixtures. [b] Taken from ref. 7. [c] Compounds **6** and **7** combined.

Table 2 Analytical data (%) for the new isolated species with calculated values in parentheses

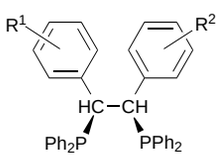
Compound	C	H
4	85.8 (85.7)	6.0 (6.1)
5	85.8 (85.7)	6.4 (6.4)
6	87.5 (87.3)	5.5 (5.7)
4s	78.2 (79.0)	5.5 (5.7)
5s	79.6 (79.2)	5.9 (5.9)
9	83.3 (83.0)	6.1 (6.1)
10	82.4 (83.0)	5.8 (6.1)
11	83.0 (83.0)	6.1 (6.3)
9m*	61.8 (61.6)	4.0 (4.2)
10m	67.0 (66.9)	4.4 (4.4)
11m	66.9 (67.2)	4.3 (4.6)

* Isolated as a 1:1 dichloromethane solvate to which these figures apply.

pale yellow viscous oils which were found to be essentially pure by gas chromatography–mass spectroscopy and used without further purification.

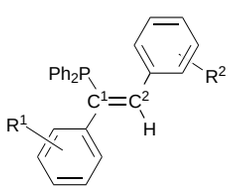


	R^1	R^2
1	H	H
4	H	*o*-Me
5	*m*-Me	*o*-Me
6	H	*o*-Ph
8	*o*-Me	*o*-Me



	R^1	R^2
3	H	H
9	H	*o*-Me
10	H	*m*-Me
11	*m*-Me	*m*-Me
12	*o*-Me	*o*-Me

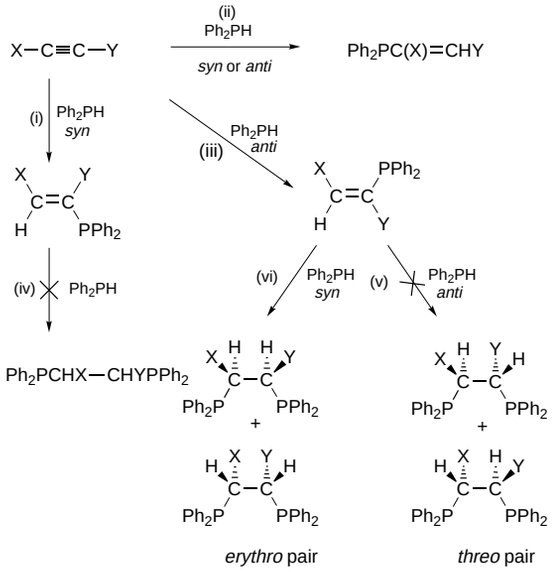
	R^1	R^2
2	H	H
7	H	*o*-Ph



(ii) Addition reactions with Ph_2PH

Table 1 summarises the outcomes of reactions of diphenylphosphine with the alkynes. Microanalytical data for all isolated species are shown in Table 2. Treatment of phenyl(*o*-tolyl)ethyne with 2 equivalents of diphenylphosphine in tetrahydrofuran (thf) at room temperature in the presence of potassium *tert*-butoxide led to the formation of two isolable products in an approximately 6:1 molar ratio. The major product was identified as *E*-1-diphenylphosphino-1-phenyl-2-(*o*-tolyl)ethene **4** and results from the addition of a single equivalent of Ph_2PH. The minor product was identified as the diphosphine **9** resulting from two successive additions. An analogous reaction starting from (*m*-tolyl)(*o*-tolyl)ethyne yielded solely the corresponding alkene intermediate *E*-1-diphenylphosphino-1-(*m*-tolyl)-2-(*o*-tolyl)ethene **5**. The isomeric identities of **4** and **5** (and all subsequent new compounds) were established by NMR spectroscopy (see below). In neither of the preceding reactions was there any *direct* evidence for the formation of significant amounts of the corresponding *Z* isomer although this can be inferred indirectly in the former case from the formation of the diphosphine **9**. The reaction of phenyl(*m*-tolyl)ethyne under the same conditions led to the formation of 1,2-bis(diphenylphosphino)-1-phenyl-2-(*m*-tolyl)ethane **10** as the sole isolable product. There was no direct evidence for the formation of significant amounts of either of the corresponding alkene intermediates. An analogous reaction starting from bis(*m*-tolyl)ethyne proceeded similarly to afford 1,2-bis(diphenylphosphino)-1,2-bis(*m*-tolyl)ethane **11**. The ^{31}P NMR spectrum of the reaction mixture showed, in addition to this main product, a very small peak (*ca.* 2% of total) at δ +8.8 which is tentatively attributed to a trace of the corresponding *E*-alkene on the basis of its chemical shift, although this compound was not isolated from the mixture. Compounds **9**, **10** and **11** were confirmed as being *erythro*, *erythro* and *meso* respectively on the basis of the ^{13}C NMR spectra of their octahedral $Mo(CO)_4$ derivatives (see below). From the reaction of (2-biphenyl)phenylethyne with 2 equivalents of diphenylphosphine a mixture of the expected *E*-alkene **6** with, unusually, its corresponding *Z* isomer **7** was isolated in an approximately 2:3 ratio, as indicated by ^{31}P NMR spectroscopy. There was no evidence for the formation of any diphosphine in this reaction. The reaction of bis(*o*-tolyl)ethyne with diphenylphosphine gave no isolable addition products under the same reaction conditions. A ^{31}P NMR spectrum of this reaction mixture showed essentially all phosphorus to be present either as unchanged diphenylphosphine at *ca.* δ −41 or tetraphenyldiphosphane at *ca.* δ −16 together with two new peaks at δ +6.5 and −5.8 (*ca.* 1 and 4% relative to Ph_2PH) which may be very tentatively assigned as arising from *E*-1-diphenylphosphino-1,2-bis(*o*-tolyl)ethene **8** and *meso*-1,2-bis(diphenylphosphino)-1,2-bis(*o*-tolyl)ethane **12** respectively on the basis of their ^{31}P chemical shifts (see discussion of NMR later). When the reaction conditions included a 6 h reflux period a ^{31}P NMR spectrum of the reaction mixture showed only slightly greater proportions of **8** and **12** (*ca.* 5% each relative to Ph_2PH). Increased reaction duration at either room or reflux temperature to as much as 168 h had little further effect on the relative proportions of these products and all attempts to separate them from the unchanged diphenylphosphine were unsuccessful.

In all the foregoing reactions ^{31}P NMR spectroscopy of the reaction mixtures showed a peak at approximately δ −16 arising from the by-product tetraphenyldiphosphane. We have



Scheme 3

found this behaviour previously in a wide range of addition and substitution reactions involving the Ph_2P^- anion, especially in cases where there is appreciable steric hindrance to the desired reaction.[9] This may account for the relatively low overall yields in some of the addition reactions reported herein; nevertheless, the relatively high solubility of tetraphenyldiphosphane allowed the products to be isolated in the majority of cases. None of the *E*-alkenes isolated from the reaction mixtures was found to undergo further addition reactions with diphenylphosphine under normal or more forcing reaction conditions nor was there any indication of isomerisation of the *Z* form.

Addition reactions of diphenylphosphine and other secondary phosphines to alkynes have had some attention but most recent studies centre on reactions carried out under free-radical conditions. Early reports of ionic additions[10] include the exclusive formation of compound **2** following hydrolysis of the products of the addition of $LiPPh_2$ to diphenylethyne in thf.[10a] In the presence of diethylamine the same reaction was reported to yield **1** but with butylamine the main product was **2**.[10b] The use of $NaPPh_2$ in place of $LiPPh_2$ was also reported to yield **2** for several amines. The relative instability of the *Z* isomer **2** with respect to isomerisation to the *E* isomer **1** is also documented.[10b] Recent reports of ionic additions concentrate on reactions of co-ordinated Ph_2PH with co-ordinated phosphinoalkynes[11] but the electronic and steric effects have little relevance to this study.

Under radical conditions the addition of Ph_2PH to PhC≡CR (R = H or Me) yields primarily but not exclusively *Z*-alkene derivatives with the *Z* isomer increasingly favoured after prolonged standing of the reaction mixture,[12] an apparent contrast to the previous case using ionic conditions. The same study also showed the formation of by-products of the type *Z*-$Ph_2PC(R)$=$CHPPh_2$ from the reaction of RC≡CH with Ph_2PH, presumably as a result effectively of *syn* addition of tetraphenyldiphosphane, from combination of two $Ph_2P^•$ radicals. None of the foregoing reports gives any evidence for the formation of diphosphines resulting from two successive addition reactions. but it is known that the alkynes with more electron-withdrawing substituents $MeO_2CC{\equiv}CCO_2Me$ and $F_3CC{\equiv}CCF_3$ can undergo double addition reactions of this sort, probably under radical conditions, to give diphosphines in each case.[13–16] The behaviour found here is summarised in Scheme 3 in which X is assumed to be bulkier than Y. Initial nucleophilic Michael-like attack by Ph_2P^- is on the ethynic carbon atom which carries the least bulky substituent as in (i) (*syn*) or (iii) (*anti*). In the case of (i) no further reaction occurs and the *E* isomer of the mono(diphenylphosphino)alkene can be isolated in the cases of **4**–**6**. Following (iii) a further attack by Ph_2P^- on the more hindered carbon of the olefin occurs with a *syn* orientation (vi) to yield the *erythro*-diphosphine. Reaction (ii) does not occur readily when X is of even moderate bulk, presumably for steric reasons. Note that the *erythro*-diphosphine can arise only from a *syn–anti* or an *anti–syn* mechanism and that in fact the latter can be excluded owing to the established unreactivity of the *E*-alkenes which would precede its second step.

It is apparent that relatively small steric effects have a strong influence on the outcome of these reactions. The failure of bis(*o*-tolyl)ethyne to react demonstrates the strong retarding impact of an *ortho*-methyl group, presumably a consequence of steric hindrance. This is confirmed by the behaviour of (*o*-tolyl)(*m*-tolyl)ethyne in which only 1 equivalent of diphenylphosphine adds to the triple bond under our reaction conditions and the sole product is the *E*-alkene in which the bulky diphenylphosphino group is bonded to C^1 rather than the more hindered C^2. The same stereochemical outcome was observed for the corresponding reaction of phenyl(*o*-tolyl)ethyne, although in this case the formation of a small amount of the diphosphine product was also observed. Conversely, the presence of a methyl group at the *meta* position on the parent alkyne has little apparent effect on the rate or steric course of the addition reaction as phenyl(*m*-tolyl)ethyne and bis(*m*-tolyl)-ethyne undergo successive addition reactions with diphenylphosphine to produce diphosphines analogous to that from the reaction with diphenylethyne. Steric effects also appear to influence the isomerisation of *Z*- to *E*-alkenes in the reaction mixture. It is reasonable to suggest that this involves deprotonation at C^2 (by Ph_2P^- and/or Bu^tO^-) followed by reprotonation. The extreme bulk of the biphenyl group on C^2 in **7** appears not only to prevent further addition but also retards the isomerisation sufficiently to permit the isolation of both isomeric alkenes resulting from a single addition.

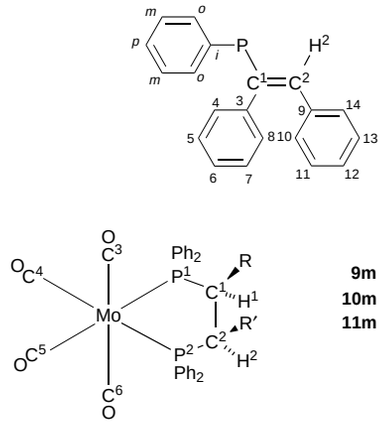
As discussed above it is evident that the mechanism of addition is complex, but it is clear that the extent and stereochemistry of addition are critically dependent on quite small variations in reaction conditions. The inertness of the *E*-alkenes to further addition compared to the reactivity of the *Z*-alkenes is difficult to explain in terms of variations in electronic effects and may be steric in origin. The crystal structures of compounds **1** and **2** (see later) indicate that the immediate environment of the C=C double bond of **2** is less crowded than its counterpart in **1** and, in apparent conformity, preliminary molecular modelling studies[9] based on optimised geometrical models derived from the crystal structures suggest that in **1** any close approach of Ph_2P^- (and indeed of Ph_2PH and $Ph_2P^•$) is prevented by steric hindrance from the phenyl groups, whereas this is not so in **2**. These effects may account for the very different reactivities of **1** and **2** towards phosphine addition under the conditions used here.

The isolated vinylphosphines **1**, **2**, **4**–**7** reacted smoothly with an atomic equivalent of elemental sulfur in various solvents to yield their corresponding phosphine sulfides **1s**, **2s**, **4s**–**7s** in virtually quantitative yields as indicated by ^{31}P NMR spectroscopy. The diphosphines **9**–**11** [L] reacted readily with *cis*-$[Mo(CO)_4(pip)_2]$ (pip = piperidine) in chloroform to give the corresponding *cis*-$[Mo(CO)_4L]$ derivatives **9m**–**11m** which were isolated as pale yellow air-stable crystals.

All new isolated phosphines, phosphine sulfides and carbonyl complexes were obtained as air-stable solids, soluble in chlorinated solvents such as dichloromethane or chloroform but insoluble in alcohols such as methanol or ethanol.

(iii) NMR spectroscopy

(a) Phosphinoalkenes. Proton, ^{13}C and ^{31}P NMR data for the phosphinoalkenes are in Tables 3–6 and the labelling scheme for ^1H and ^{13}C NMR assignments is in Scheme 4. The ^{31}P chemical shifts for the new methyl-substituted derivatives are close to



	R	R′
9m	*o*-tolyl	Ph
10m	*m*-tolyl	Ph
11m	*m*-tolyl	*m*-tolyl

Scheme 4 The NMR labelling schemes. Upper: for the phosphinoalkenes **1**, **2**, **4**–**7** and their corresponding sulfides (the system is the same for both *E* and *Z* stereochemistries). The substitution patterns are: **4**, **4s**, 14-methyl; **5**, **5s**, 7,14-dimethyl; **6**, **6s**, **7**, **7s**, 14-phenyl. Lower: for the metal complexes **9m**–**11m**

Table 3 Phosphorus-31 and proton NMR data for the methyl-substituted phosphinoalkenes

	Compound			
Parameter	**4**	**4s**	**5**	**5s**
$\delta(^{31}P)$ [a]	5.3	48.5	5.3	48.4
$\delta(H^2)$ [b]	6.40	7.58	6.41	7.62
$\delta(H^4)$	7.18	6.97	6.95	6.73
$\delta(H^5)$	7.06	7.09	6.94	6.94
$\delta(H^6)$	7.01	7.12	6.83	6.92
$\delta(H^7)$	7.06	7.09	2.13	2.07
$\delta(H^8)$	7.18	6.97	7.11	6.70
$\delta(H^{10})$	6.72	6.76	6.79	6.78
$\delta(H^{11})$	6.77	6.80	6.77	6.78
$\delta(H^{12})$	6.94	7.05	6.94	7.03
$\delta(H^{13})$	7.01	7.09	7.01	7.07
$\delta(H^{14})$	2.10	2.22	2.11	2.22
$\delta(H_o)$	7.46	7.87	7.48	7.83
$\delta(H_m)$	7.28	7.43	7.28	7.40
$\delta(H_p)$	7.28	7.49	7.26	7.46

[a] In ppm (±0.2 ppm) to high frequency of external 85% H_3PO_4 (δ 0.0). [b] $^3J(^{31}P^1H^2)$ = 8.4, 23.9, 7.3 and 21.2 Hz (±0.2 Hz) for **4**, **4s**, **5** and **5s** respectively.

Table 4 Phosphorus-31 and selected proton NMR data for the phosphinoalkenes without methyl substituents

Compound	$\delta(^{31}P)$ [a]	$\delta(H^2)$	$^3J(^{31}P^1H^2)$ [b]
1	8.7	6.50	9.3
1s	48.5	7.65	23.8
2	−7.8	7.45	24.1
2s	36.8	7.47	37.9
6	7.3	6.16	7.0
6s	48.4	7.01	23.2
7	−5.5	7.30	25.6
7s	36.4	7.35	39.0

[a] In ppm (±0.2 ppm) to high frequency of external 85% H_3PO_4 (δ 0.0). [b] In Hz (±0.2 Hz).

those of their unsubstituted homologues and are unremarkable. Stereochemistries were determined by detailed analyses of ^1H and ^{13}C spectra together with two-dimensional ROESY (rotating frame Overhauser enhancement spectroscopy) and COSY experiments.

For the *E*-phosphinoalkenes **1**, **4**–**6** $\delta(H^2)$ is in the range 6.16–6.50 with ^3J(PH) in the range 7.0–9.3 Hz. The NMR parameters determined for H^2 in **1** was the basis of the original identification of the P/H *cis* geometry [7] and this has now been confirmed by the additional NMR experiments and X-ray diffraction

Table 5 Carbon-13 NMR data for the phosphinoalkenes with methyl substituents

	Compound [b]			
Parameter [a]	**4**	**4s**	**5**	**5s**
$\delta(C^1)$	142.6, *17.8*	136.8, *74.7*	142.3, *17.6*	136.8, *74.1*
$\delta(C^2)$	137.7, *11.9*	143.5, *13.3*	137.4, *11.3*	143.4, *13.5*
$\delta(C^3)$	140.7, *19.8*	135.9, *9.7*	140.4, *22.6*	135.9, *9.3*
$\delta(C^4)$	130.3, *7.9*	131.0, *4.6*	127.3, *7.5*	128.2, *4.3*
$\delta(C^5)$	129.0, *0*	128.8, *0*	128.6, *0*	128.6, *0*
$\delta(C^6)$	127.7, *1.8*	128.3, *2.3*	128.4, *1.5*	129.0, *1.0*
$\delta(C^7)$	129.0, *0*	128.8, *0*	138.2, *0*	138.4, *0*
$\delta(C^{7'})$ [c]	—	—	22.1, *0*	22.2, *0*
$\delta(C^8)$	130.3, *7.9*	131.0, *4.6*	130.6, *8.8*	131.8, *3.5*
$\delta(C^9)$	137.5, *4.5*	134.9, *17.4*	137.3, *5.0*	135.1, *17.9*
$\delta(C^{10})$	130.0, *0*	129.7, *0*	129.7, *0*	129.7, *0*
$\delta(C^{11})$	126.2, *0*	126.0, *0*	125.9, *0*	126.0, *0*
$\delta(C^{12})$	127.9, *0*	128.3, *0*	127.6, *0*	129.0, *0*
$\delta(C^{13})$	130.7, *0*	130.7, *0*	130.5, *0*	130.7, *0*
$\delta(C^{14})$	137.4, *1.0*	138.2, *1.0*	137.1, *1.2*	138.4, *4.4*
$\delta(C^{14'})$ [c]	20.9, *0*	20.9, *0*	20.7, *0*	20.9, *0*
$\delta(C_i)$	136.5, *11.8*	132.2, *84.3*	136.3, *11.3*	132.2, *84.3*
$\delta(C_o)$	135.2, *20.2*	133.3, *10.1*	135.0, *20.1*	133.4, *10.2*
$\delta(C_m)$	129.4, *7.2*	129.0, *12.3*	129.1, *6.3*	128.9, *12.3*
$\delta(C_p)$	129.9, *0*	132.1, *3.2*	129.6, *0*	132.1, *2.7*

[a] Chemical shifts in ppm (±0.1 ppm) relative to $SiMe_4$ (δ 0.0). [b] Figures in italics are values of $^nJ(^{31}P^{13}C)$ in Hz (±0.2 Hz). [c] $C^{n'}$ refers to the methyl carbon attached to position *n*.

Table 6 Carbon-13 NMR data for the phosphinoalkenes without methyl substituents [a]

	Compound [c]			
Parameter [b]	**1**	**1s**	**2**	**2s**
$\delta(C^1)$	142.1, *19.2*	135.6, *73.8*	*c*	136.8, *75.2*
$\delta(C^2)$	138.6, *18.3*	144.4, *13.4*	145.6, *28.4*	146.5, *6.4*
$\delta(C^3)$	140.6, *16.5*	136.1, *8.5*	*c*	*d*
$\delta(C^4)/\delta(C^8)$	192.8, *6.4*	*f*	130.5, *8.3*	*d*
$\delta(C^5)/\delta(C^7)$	129.1, *0*	*f*	*c*	*d*
$\delta(C^6)$	127.6, *1.8*	*f*	126.9, *0*	*d*
$\delta(C^9)$	136.7, *6.4*	135.4, *18.9*	*c*	*d*
$\delta(C^{10})/\delta(C^{14})$	129.9, *0*	*f*	*c*	*d*
$\delta(C^{11})/\delta(C^{13})$	128.6, *0*	*f*	*c*	*d*
$\delta(C^{12})$	127.9, *0*	*f*	*c*	*d*
$\delta(C_i)$	136.0, *11.9*	131.7, *84.8*	*c*	132.5, *83.8*
$\delta(C_o)$	134.9, *19.2*	133.2, *10.4*	134.0, *18.3*	132.4, *10.1*
$\delta(C_m)$	129.1, *6.4*	128.8, *12.2*	*c*	128.3, *12.4*
$\delta(C_p)$	129.6, *0*	132.1, *3.0*	*c*	131.2, *2.8*

[a] Compounds **6**, **6s**, **7** and **7s**: $\delta(C^2)$ $[^2J(^{31}P^{13}C)]$ = 137.7[*10.1*], 143.1[*12.8*], 146.2[*33.0*] and 146.2[*6.5*] respectively; other signals were not assigned due to unfavourable signal overlaps. [b] Chemical shifts in ppm (±0.1 ppm) relative to $SiMe_4$ (δ 0.0). [c] Figures in italics are values of $^nJ(^{31}P^{13}C)$ in Hz (±0.2 Hz). [d] Assignment uncertain/overlapping signals [δ 143.6 (d, *3.4*), 139.9 (d, *27.8*), 137.4 (d, *4.3*), 136.9 (d, *11.6* Hz) and 128.9–127.9 (complex overlapping signals)]. Assignment uncertain [δ 141.7 (d, *10.5*), 135.8 (d, *5.0*), 130.6 (d, *1.4*), 129.3 (d, *4.6*), 128.7 (s), 128.5 (d, *1.0*), 128.8 (s) and 127.8 (d, *1.4* Hz)]. [f] Assignment uncertain [δ 130.8 (s), 130.7 (d, *1.2*), 129.5 (s), 129.1 (d, *1.8*), 128.7 (s) and 128.4 (d, *2.5* Hz)].

studies reported here. Sulfurisation of the phosphorus causes the H^2 signal to move approximately 1.0–1.2 ppm to high frequency and ^3J(PH) shows an expected [17] increase in magnitude in conformity with unaltered stereochemistry about the C=C double bond. Changes in the parameters for the P-phenyl protons are also in accord with those found in previous studies.[18]

In compound **4** the relative positions of the phenyl and *o*-tolyl groups on the C^1–C^2 backbone were established in two-dimensional ROESY experiments.[19] These showed a strong NOE interaction between the methyl proton resonance H^{14} at δ 2.10 and the olefinic proton resonance at δ 6.40 thus establishing that the *o*-tolyl group is attached to C^2.

In compound **5** phenyl proton H^8 showed an intense NOE

interaction with the methyl resonance at δ 2.13 and no discernible interaction with the methyl resonance at δ 2.11. This therefore establishes the signals at δ 2.13 and 2.11 as arising from the *meta*- and *ortho*-methyl substituents respectively. Furthermore, the olefinic proton resonance H^2 shows a strong NOE interaction with the *ortho*-methyl resonance at δ 2.11 and no detectable interaction with the *meta*-methyl resonance at δ 2.13 thus confirming that the *ortho*-tolyl group is on C^2 and the *meta*-tolyl group is on C^1.

The two-dimensional ROESY spectra of compounds **4s** and **5s** show analogous NOE interactions to those in **4** and **5** respectively confirming both the original alkene stereochemistry of their parent phosphorus(III) species and the retention of that stereochemistry on sulfurisation. Fig. 1 shows a relevant portion of the ROESY spectrum obtained for **5s**.

(b) Diphosphines. Selected NMR data for the diphosphine ligands **9**–**11** and their complexes **9m**–**11m** are given in Tables 7 and 8. The NMR labelling scheme for these species is in Scheme 4. The unsymmetrical diphosphine **9** has five chemically inequivalent phenyl groups and a single *ortho*-tolyl group; the aromatic region of its ^1H NMR spectrum was too complex to analyse. The two backbone protons H^1 and H^2 give multiplets at δ 4.51 and 4.38 with $^3J(HH)$ of 6.2 Hz. A slight broadening of these signals possibly arises from restricted conformational interchange. The somewhat lowered chemical shift of the methyl group protons (δ 1.70 compared with 2.0–2.2 for all its precursors and analogues in the synthetic pathway) may be attributable to their being sterically forced into a position above a neighbouring phenyl group where they experience the diamagnetic shielding effect of the ring current. This is consistent with the foregoing suggestion of restricted conformational mobility. In **10** the inequivalent backbone CH protons have such similar chemical shifts that they appear as a doublet at δ 4.16. The resonance of the methyl protons is at δ 2.01 suggesting that the steric effects proposed for **9** are negligible here, owing to their more remote location. The chemical shifts of the methyl and backbone

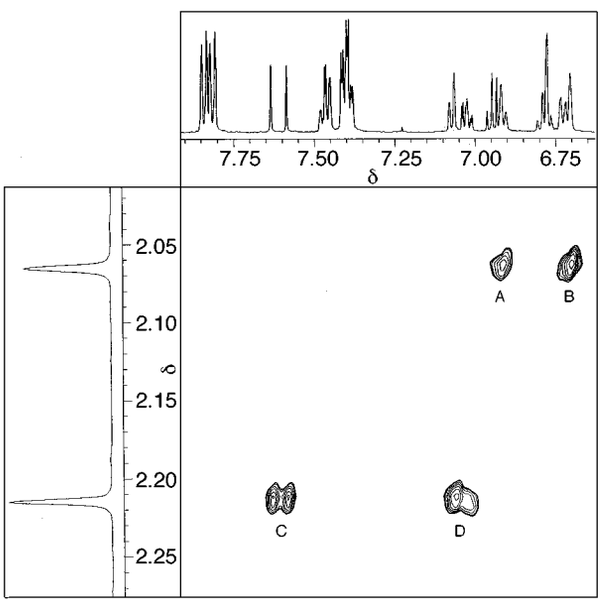


Fig. 1 Part of the two-dimensional phase-sensitive 500 MHz ROESY spectrum obtained for compound **5s**. The NOE correlations are as follows: **A**, H^7–H^6; **B**, H^7–H^8; **C**, H^{14}–H^2; **D**, H^{14}–H^{13}

Table 7 Selected phosphorus-31, carbon-13 and proton NMR data for the diphosphines. Data for compound **3** are from ref. 7

	Compound[b]			
Parameter[a]	**9**	**10**	**11**	**3**
$\delta^{31}P^1$	− 3.8	− 4.5	− 4.0	− 5.4
$\delta^{31}P^2$	− 3.8	− 4.5	− 4.0	− 5.4
$J(^{31}P^1–^{31}P^2)$	*c*	*c*	*c*	*c*
$\delta(H^1)$	4.51, *11.8*, *5.6*	4.16[c,d]	4.15, [*4.1*]	4.19, [*5.4*]
$\delta(H^2)$	4.38, *7.0*, *6.0*	4.16[c,d]	4.15, [*4.1*]	4.19, [*5.4*]
$^3J(H^1H^2)$	6.2	*c*	*c*	*c*
$\delta(CH_3)$	1.70	2.01	2.0	—
$\delta(C^1)$	44.2, *22.0*, *18.8*	50.0[c,d]	50.0 [<1.0]	50.0 [<1.0]
$\delta(C^2)$	50.0, *21.5, 18.8*	50.0[c,d]	50.0 [<1.0]	50.0 [<1.0]
$\delta(CH_3)$	20.0	21.1	21.0	—

[a] Phosphorus-31 chemical shifts in ppm (±0.2 ppm) to high frequency of external 85% H_3PO_4 (δ 0.0); carbon-13 and proton chemical shifts in ppm (±0.1 ppm) relative to $SiMe_4$ (δ 0.0). [b] Figures in italics are coupling constants to ^{31}P in Hz (±0.2 Hz) where observed, figures in square brackets are values of $N(^{31}P^{13}C) = |J(^{31}P^1–^{13}C) + J(^{31}P^2–^{13}C)|$. [c] Coupling constant data not determined due to unfavourable signal overlap and/or molecular symmetry. [d] Quoted as a mean value.

Table 8 Selected phosphorus-31, carbon-13 and proton NMR data for the tetracarbonylmolybdenum diphosphine derivatives. Data for compound **3m** are from ref. 7

	Compound[b]			
Parameter[a]	**9m**	**10m**	**11m**	**3m**
$\delta^{31}P^1$	68.9[c]	70.5[d]	68.5	68.7
$\delta^{31}P^2$	68.9[c]	68.0[d]	68.5	68.7
$J(^{31}P^1–^{31}P^2)$	*e*	*e*	*f*	*f*
$\delta(H^1)$	4.98, *37.3*, *12.4*	4.54, *15.9*, *11.7*	4.48, [*9.8*]	4.49, [*8.8*]
$\delta(H^2)$	4.44, *10.5*, *4.9*	4.50, *11.7*, *5.0*	4.48, [*9.8*]	4.49, [*8.8*]
$^3J(H^1H^2)$	6.2	5.8	*f*	*f*
$\delta(CH_3)$	1.58	1.91	1.91	—
$\delta(C^1)$	45.6, *16.8*, *16.8*	53.6, *18.9*, *13.4*	53.2, [*32.1*]	54.3, [*34.8*]
$\delta(C^2)$	54.6, *22.8*, *9.3*	54.1, *20.8*, *11.0*	53.2, [*32.1*]	54.3, [*34.8*]
$\delta(C^3)$	214.9, *8.5*, *8.5*	215.1, *9.2*, *9.2*	214.5, *9.2*, *9.2*	215.1, *8.8*, *8.8*
$\delta(C^4)$[g]	216.2, *26.2*, *7.9*	217.4, *26.2*, *8.5*	216.9, [*17.5*]	217.4, [*16.9*]
$\delta(C^5)$[g]	217.7, *26.2*, *8.5*	217.7, *26.3*, *8.6*	216.9, [*17.5*]	217.4, [*16.9*]
$\delta(C^6)$	206.9, *7.0*, *7.0*	207.9, *7.0*, *7.0*	207.3, *6.9*, *6.9*	207.9, *7.0*, *7.0*
$\delta(CH^3)$	19.9	21.5	20.9	—

[a] Phosphorus-31 chemical shifts in ppm (±0.2 ppm) to high frequency of external 85% H_3PO_4 (δ 0.0); carbon-13 and proton chemical shifts in ppm (±0.1 and ±0.01 ppm) relative to $SiMe_4$ (δ 0.0). [b] Figures in italics are coupling constants to ^{31}P in Hz (±0.2 Hz) where observed. Figures in square brackets are values of $N(^{31}P^1H) = |J(^{31}P^1–^1H) + J(^{31}P^2–^1H)|$ and $N(^{31}P^{13}C) = |J(^{31}P^1–^{13}C) + J(^{31}P^2–^{13}C)|$ for ^1H and ^{13}C resonances respectively. [c] Quoted as a mean value. [d] Assignment uncertain. [e] Not observed due to line broadening. [f] Not available by inspection due to chemical equivalence. [g] Assignment of C^4 and C^5 uncertain and may be interchanged.

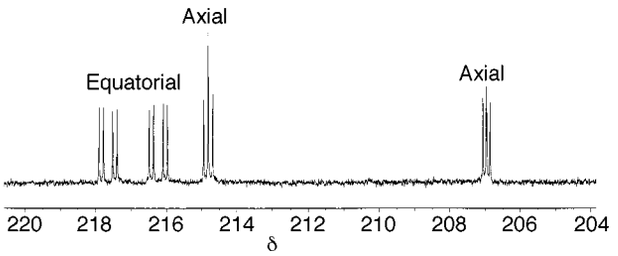


Fig. 2 The carbonyl region of the ^{13}C NMR spectrum at 67.8 MHz of complex **9m** showing the two axial and two equatorial CO resonances

protons in the symmetrical diphosphine **11** are almost exactly the same as those of **10** thus confirming the small steric demands of methyl groups in *meta* positions on the C-phenyl rings.

Co-ordination of compounds **9**, **10** and **11** to molybdenum decreases the shielding of H^1 and H^2 by about 0.3 ppm and in the case of **9** also increases their chemical shift separation. This is in addition to a significant divergence in $''J(^{31}P^1H)$ which reflects the sensitivity of these parameters to small changes in conformation and which is most dramatic in **9m**.

The ^{13}C NMR spectra of compounds **9**–**11** each show complex overlapping signals in the aromatic region from which little useful information can be obtained. For **9** the backbone carbons appear as two nearly identical double doublets at δ 44.2 and 50.0. For **10** the two corresponding signals are essentially isochronous at δ 50.0 and for **11** are truly equivalent also at δ 50.0. Upon co-ordination, changes in the NMR parameters of the backbone carbons C^1 and C^2 parallel those of H^1 and H^2 described previously.

The ^{13}C NMR spectra in the carbonyl region of complexes **9m**–**11m** serve unequivocally to identify the stereochemistry of the parent ligands **9**–**11** since it is unreasonable to suppose that co-ordination of phosphorus would be accompanied by inversion at C^1 or C^2. For **11m** the presence of one equatorial and *two* axial resonances can arise only from a *meso* stereochemistry of the co-ordinated ligand and hence of free **11**. The alternative (*rac* or DL) form for the co-ordinated ligand produces only *one* axial resonance and we have previously shown that for the complex of the *rac* or DL isomer of **3** this signal appears very close to the mean position of the two axial signals for the *meso* isomer.[7] The lower symmetry of **9** and **10** results in chemical inequivalence of the two equatorial carbonyl carbons. These signals are separated by 1.5 and 0.3 ppm for **9** and **10** respectively and this difference is consistent with the closer proximity of the methyl group in **9**. The signals for the two axial carbonyl carbons in **9m** and **10m** are separated by 8.0 and 7.2 ppm respectively and are essentially similar to those for **11m** where the separation is 7.2 ppm. The relevant region of the ^{13}C spectrum of **9m** is shown in Fig. 2. This pattern is consistent only with an *erythro* stereochemistry of the co-ordinated ligand. In analogy with the distinction of the *meso* and *rac* isomers above, the corresponding *threo* stereochemistry of **9** and **10** would be expected to give rise to nearly isochronous signals for the two axial carbonyls at a position close to the mean chemical shift position of the signals from the *erythro* isomer. For example, in a sequence of related $Mo(CO)_4$ derivatives of $Ph_2PCH(Ph)CH(R)PPh_2$ (R = pyridyl or pyrimidyl) the axial carbonyl resonances in each complex are separated by *ca.* 7 and *ca.* 1 ppm for the *erythro* and *threo* isomers respectively.[20]

(iv) Single-crystal X-ray analysis of compounds 1 and 2

Crystals of compounds **1** and **2** suitable for single-crystal X-ray analysis were obtained by diffusion of methanol into their respective dichloromethane solutions. The ORTEP-type[21] drawings of the molecular structures are shown in Figs. 3 and 4

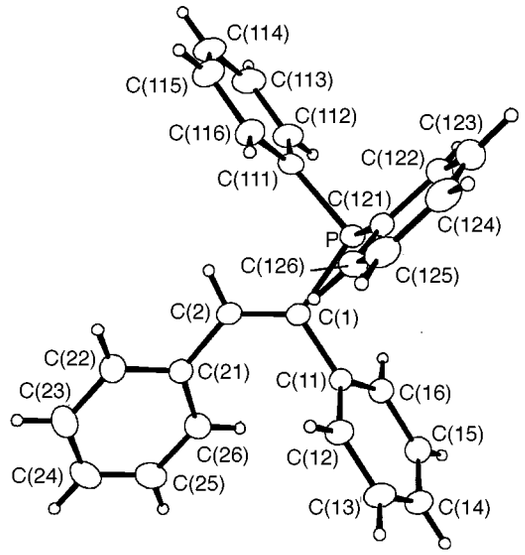


Fig. 3 An ORTEP-type[21] diagram of compound **1** viewed normal to the C(1)–C(2) bond vector. Ellipsoids are shown at the 40% probability level and, in the interests of clarity, hydrogen atoms have been drawn as circles with an arbitrary small radius

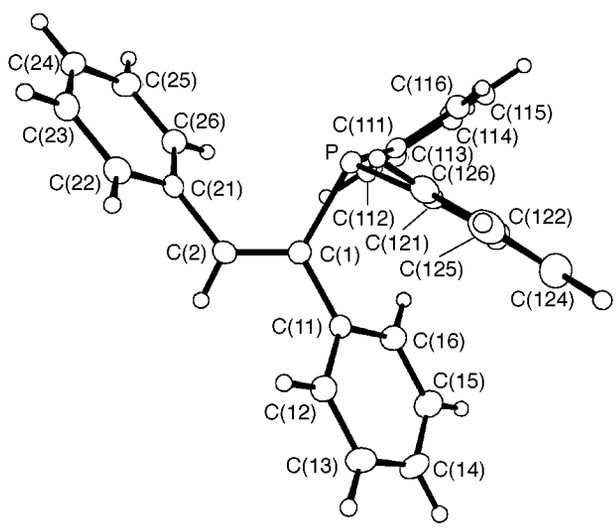


Fig. 4 ORTEP-type[21] diagram of **2** viewed normal to the C(1)–C(2) bond vector. Ellipsoids are shown at the 40% probability level and, in the interests of clarity, hydrogen atoms have been drawn as circles with an arbitrary small radius

whilst comparable bond lengths, bond angles and torsion angles are in Table 9. Bond lengths are comparable for the two structures with the exception of the P–C(1) distance which is some 0.014 Å longer in **2**. The most obvious difference in the structure of the two isomers is the orientation of the PPh_2 group relative to the ethylene bond vector.

In compound **1** the orientation of the Ph_2P group leads to a C(11)–C(1)–P–lp dihedral angle (lp being the phosphorus lone pair in an idealised tetrahedral position) of 45.2°. Thus the two P-phenyl groups are directed away from the phenyl group on C(1), that is towards the remainder of the molecule and close to the proton on C(2). In **2** a similar orientation of the PPh_2 group relative to the C=C double bond would create severe steric interaction with the phenyl group on C(2) which is in the corresponding position to the proton on C(2) in **1**. As a consequence the PPh_2 group in **2** adopts an orientation where the C(11)–C(1)–P–lp dihedral angle is −153.4°. Since this is in the opposite sense and approximately opposed to that of **1** the P-phenyl groups are directed away from the remainder of the molecule. One consequence of the difference

Table 9 Selected bond distances (Å), angles (°) and dihedral angles (°) for compounds **1** and **2** with estimated standard deviations (e.s.d.s) in parentheses

	1	**2**
P–C(1)	1.8366(14)	1.851(2)
P–C(111)	1.837(2)	1.834(2)
P–C(121)	1.833(2)	1.838(2)
C(1)–C(2)	1.335(2)	1.338(2)
C(1)–C(11)	1.501(2)	1.492(2)
C(2)–C(21)	1.475(2)	1.484(2)
C(111)–P–C(1)	105.08(6)	104.35(7)
C(121)–P–C(1)	102.09(7)	99.07(7)
C(111)–P–C(121)	100.39(6)	102.78(7)
P–C(1)–C(2)	123.84(10)	119.52(13)
P–C(1)–C(11)	112.26(10)	120.84(11)
C(11)–C(1)–C(2)	123.84(13)	119.19(14)
C(1)–C(2)–C(21)	129.32(13)	127.9(2)
lp*–P–C(1)–C(11)	45.2	−153.4
lp*–P–C(1)–C(2)	−132.3	16.8
C(12)–C(11)–C(1)–C(2)	−65.0(2)	−55.4(2)
C(22)–C(21)–C(2)–C(1)	149.7(2)	110.9(2)

* lp corresponds to the phosphorus lone pair placed in an idealised tetrahedral co-ordination position.

between the two orientations is greater exposure of the C=C bond and the proton on C(2) in **2**. The different relative dispositions of the two C-phenyl groups within each isomer, in conjunction with the contrasting PPh_2 group orientations, appear also to impose significantly different degrees of strain at C(1). In **2** all three interbond angles at C(1) are within 1° of the regular sp^2 angle of 120° whereas in the more crowded environment in **1** they are 123.8° for P–C(1)–C(2), 112.3° for P–C(1)–C(11), and 123.8° for C(11)–C(1)–C(2) respectively. Interestingly the angular distortions observed in free **1** are somewhat different to those in the reported $[Mn_2(CO)_9]$ complex,[22] presumably because the relative orientations of the PPh_2 group are different.

Experimental

General

Diphenylphosphine from the Strem Chemical Company was used without further purification. All reactions and manipulations involving diphenylphosphine were carried out under an atmosphere of dry dinitrogen. Tetrahydrofuran was dried over sodium wire, distilled, and deaerated immediately prior to use. Tetrakis(triphenylphosphine)palladium(0) was prepared immediately prior to use using Clouson's method.[23] Benzyltriphenylphosphonium chloride was prepared by standard literature methods involving treatment of benzyl chloride with triphenylphosphine in refluxing 1,2-dichlorobenzene. (2-Methylbenzyl)triphenylphosphonium chloride was prepared in a similar manner from 2-methylbenzyl chloride. Yields were typically over 90%. Biphenyl-2-carbaldehyde was prepared from commercially available 2-aminobiphenyl by modification of established procedures for (i) the conversion into 2-iodobiphenyl *via* a standard diazotisation procedure, and (ii) conversion of the iodide into the aldehyde using butyllithium and dimethylformamide.[24]

Proton, ^{13}C and ^{31}P NMR spectra were obtained from $CDCl_3$ solutions by standard techniques using JEOL EX270 and Lambda 500 and Bruker AMX500 spectrometers. Phase-sensitive (using the time-proportional phase incrementation method) ROESY spectra were acquired using the sequence 90°–t_1–spin lock–acquire(t_2) using a spin-locking field given by $\gamma B_1/2\pi \approx 5000$ Hz and a spin-locking (mixing) time of 100–250 ms. Typically 32 free induction decays were acquired into 1K data points for each of 512 values of t_1 and a shifted sine-bell window function was used in each dimension prior to Fourier transformation into a 1K × 1K data matrix.

Synthesis of phenyl(*o*-tolyl)ethyne

(i) 1-Phenyl-2-(*o*-tolyl)ethene. To a rapidly stirred suspension of benzyltriphenylphosphonium chloride (38.9 g, 0.1 mol) in dichloromethane (150 cm^3) was added *o*-tolualdehyde (11.0 g, 0.1 mol) and then immediately aqueous sodium hydroxide (100 cm^3, 18 M). After the vigorous reaction had subsided the mixture was stirred at room temperature for 0.5 h until the yellow coloration had completely disappeared. The resultant alkene mixture was poured into water (500 cm^3) and extracted with dichloromethane (3 × 75 cm^3). The combined extracts were washed liberally with water until free of base, dried over magnesium sulfate and the dichloromethane solvent was removed at low pressure. The crude residue was triturated with cold *n*-hexane (3 × 50 cm^3), the hexane extracts were filtered and the solvent was removed at the pump to give a viscous oil containing a crude mixture of *E*- and *Z*-2-methylstilbene (16 g, 83%).

(ii) Bromination. The crude mixture was dissolved in carbon tetrachloride (50 cm^3) and heated to approximately 70 °C. Bromine (15 g, 83 mmol) in carbon tetrachloride (50 cm^3) was then added slowly with stirring to the solution over a period of 0.5 h and the mixture was cooled to room temperature. Addition of methanol (100 cm^3) initiated crystallisation which was accelerated by cooling to 0 °C. Filtration of the white solid and drying under vacuum yielded a crude mixture of the stereoisomers of 1,2-dibromo-1-phenyl-2-(*o*-tolyl)ethane (20 g, 70%).

(iii) Dehydrobromination. A mixture of the crude dibromides (20 g, 58 mmol) and potassium hydroxide (20 g, 0.36 mmol) in dry ethanol (200 cm^3) was heated under reflux for 12 h at which point GC-MS analysis of the mixture showed almost quantitative dehydrobromination of the bromides. After cooling, the reaction mixture was poured into water (200 cm^3) and the organic components were extracted with dichloromethane (3 × 100 cm^3). The combined extracts were washed with water and dried with magnesium sulfate and the solvents were removed under reduced pressure to give the desired alkyne as an oil. The crude product was distilled rapidly at low pressure to give the product as a straw coloured viscous liquid (9 g, 80%). Gas chromatography–mass spectrometry and NMR spectroscopy showed the product to be essentially pure and it was therefore used for addition reactions without further purification.

Phenyl(*m*-tolyl)ethyne and (2-biphenyl)phenylethyne were prepared similarly from benzyltriphenylphosphonium chloride and the appropriate aldehyde. Bis(*o*-tolyl)ethyne and (*o*-tolyl)(*m*-tolyl)ethyne were also prepared in a similar manner from (2-methylbenzyl)triphenylphosphonium chloride and the appropriate aldehyde. Overall yields were similar in all cases to that described above. Bis(*m*-tolyl)ethyne was prepared from 3-bromotoluene and 2-methylbut-3-yn-2-ol by modification of Rossi's method.[8]

Addition reactions

Typical procedure. A catalytic amount of potassium *tert*-butoxide (*ca.* 1 mmol) was added to a solution of the alkyne (10 mmol) and diphenylphosphine (20 mmol) in thf (20 cm^3). The mixture was stirred until the potassium *tert*-butoxide had dissolved, and when a permanent orange-red coloration was apparent the solution was left to stand until ^{31}P NMR spectroscopy of the mixture indicated no further reaction was occurring (usually no more than 2 h). Addition of methanol (20 cm^3) and refrigeration induced the formation of a white solid which was filtered off, washed with methanol, and dried under vacuum to give the major product in each case (see Table 1 for yields). Further crops of products were obtained from the

Table 10 Crystal data for compounds **1** and **2**[a]

	1	**2**
Crystal dimensions/mm	0.42 × 0.28 × 0.20	0.52 × 0.37 × 0.28
Space group	$P2_1/c$	$C2/c$
a/Å	12.2602(6)	22.2502(10)
b/Å	6.0689(3)	11.8137(5)
c/Å	27.289(2)	18.7963(7)
β/°	100.484(5)	127.833(3)
U/Å^3	1996.2(2)	3902.2(3)
Z	4	8
D_c/g cm^{-3}	1.21	1.28
μ/mm^{-1}	1.248	1.277
F(000)	768	1536
Maximum, minimum transmission factors	0.788, 0.622	0.716, 0.556
θ Range/°	3.29–64.61	4.47–64.55
Index ranges	$-14 \leqslant h \leqslant 14$, $-6 \leqslant k \leqslant 6$, $-31 \leqslant l \leqslant 31$	$-26 \leqslant h \leqslant 26$, $-12 \leqslant k \leqslant 13$, $-21 \leqslant l \leqslant 19$
Reflections collected	6513	4874
Unique reflections, n (R_{int})	3297 (0.019)	3036 (0.034)
Reflections with $F_c^2 > 2.0\sigma(F_c^2)$	2800	2936
T/K	293	160
Goodness of fit on F^2, s[b]	1.028	1.067
Extinction coefficient, x[c]	0.0060(3)	0.001 44(6)
$R1$[d]	0.0308	0.0334
$wR2$[e]	0.0873	0.0822
Weighting parameters a,b[f]	0.0397, 0.4537	0.0269, 4.8144
Largest difference peak and hole/e Å^{-3}	0.162, −0.150	0.321, −0.306

[a] Common to both structures: empirical formula $C_{26}H_{21}P$; $M = 364.40$; monoclinic: absorption correction *via* ψ scans; $4.0 \leqslant 2\theta \leqslant 130°$: 245 parameters. [b] $s = [w(F_o^2 - F_c^2)^2/(n-p)]^{\frac{1}{2}}$. [c] $F_c^* = kF_c[1 + (0.001xF_c^2\lambda^3/\sin 2\theta)]^{-\frac{1}{4}}$. [d] $R1 = \Sigma ||F_o| - |F_c||/\Sigma|F_o|$. [e] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$. [f] $w = [\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$.

combined methanol washings and filtrate after refrigeration. Products were purified by recrystallisation from methanol–dichloromethane. In the case of the reaction of (2-biphenyl)-phenylethyne with diphenylphosphine the two isomeric phosphinoalkene products could not be separated by fractional crystallisation and therefore were analysed as a mixture.

Sulfurisation. Small-scale reactions were performed in $CDCl_3$ solution by weighing stoichiometric amounts of the phosphinoalkene and elemental sulfur directly into a 5 mm NMR tube. Virtually quantitative yields of the corresponding phosphine sulfides were indicated by NMR spectroscopy after agitation for 0.5 h and the products were unambiguously characterised in solution but not isolated. Gram-scale preparations of compounds **4s** and **5s** were achieved by stirring stoichiometric amounts of the phosphinoalkene and elemental sulfur (*ca.* 2.5 mmol) in chloroform (20 cm^3) for 1 h. Addition of methanol (20 cm^3) followed by refrigeration and filtration gave in each case analytically pure samples of the corresponding phosphine sulfide as air-stable colourless crystals in virtually quantitative yield. These products had identical NMR spectra to those prepared directly in NMR tubes by the previous method.

Complexation. In a typical procedure a solution in chloroform (20 cm^3) of the diphosphine ligand (2 mmol) and tetracarbonylbis(piperidine)molybdenum(0) (2 mmol) was refluxed for 0.25 h. Methanol (10 cm^3) was added to the cooled and filtered reaction mixture to induce crystallisation of a solid which was recrystallised from methanol–dichloromethane to give the product as pale yellow crystals (yield > 80% in each case).

Crystallography

Data were collected on a Stoe STAD14 diffractometer operating in the ω–θ scan mode using Cu-Kα radiation (λ = 1.541 84 Å) at 293 K for compound **1** and at 160 K for **2**. Full details of crystal data, data collection and structure refinement are given in Table 10. The structures of both compounds were solved by direct methods using SHELXS 86.[25] Refinement, by full-matrix least squares on F^2 using SHELXL 97,[26] was essentially the same for both compounds. Non-hydrogen atoms were refined with anisotropic displacement parameters. Restraints were applied to the phenyl rings so that they remained flat and of overall C_{2v} symmetry. Hydrogen atoms were constrained to idealised positions using a riding model.

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See http://www.rsc.org/suppdata/dt/1998/811/ for crystallographic files in .cif format.

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