REARRANGEMENTS OF THE UNSATURATED LIGAND 1,1-BIS(DIPHENYLPHOSPHINOMETHYL)ETHENE AND ITS CHALCOGENIDES AND GROUP VI METAL CARBONYL COMPLEXES

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Abstract—In contrast to the behaviour of other unsaturated organophosphines, treatment of the new ligand $(Ph_2PCH_2)_2C=:CH_2$ with Ph_2PH in the presence of KOBu' does not result in addition to the double bond; instead, an allylic rearrangement occurs to give *cis* and *trans* $Ph_2PCH=:C(CH_3)CH_2PPh_2$ in a 3:7 ratio. In the case of $(Ph_2P(E)CH_2)_2C=:CH_2$ [E = S, Se] only the *trans* isomer is obtained from this reaction, while under similar conditions $(CO)_4M(Ph_2PCH_2)_2C=:CH_2$ [M = Cr, Mo, W] yields only a *cis* product in which the two phosphorus atoms remain chelated. The products of these and related reactions are characterized by elemental analysis and ¹³C and ³¹P NMR spectroscopy.

The base-catalysed addition of primary and secondary phosphines to activated carbon-carbon multiple bonds is an established route to secondary and tertiary phosphines respectively.¹⁻⁵ Activation by one⁶ or two (geminally related)⁷ Ph₂P groups is of especial interest because the products are then polyphosphines that are important as polydentate ligands, a simple example being (Ph₂P)₂CHCH₂ PPh₂ which can be formed by the addition of Ph₂PH to (Ph₂P)₂C=CH₂ as in eq. (1). phorus is coordinated to a metal atom or is in a higher oxidation state, as in the $Ph_2P(E)$ [E = O, S, Se] moiety.⁸

It is unclear whether any activating ability is retained when a CH_2 group is inserted between Ph_2P and the multiple bond since there is now also the possibility of an allylic rearrangement (double bond migration) which is normally the favoured pathway, and which would probably proceed via a carbanion intermediate as in eq. (2).





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However, when the two phosphorus atoms of the starting olefin are coordinated to the same metal atom, two products are obtained in this reaction the rearranged olefin with the two coordinated Ph_2P groups mutually *cis* at the double bond, and also the expected triphosphine Ph_2PCH_2CH $(PPh_2)CH_2PPh_2$ with two of its phosphorus atoms coordinated and one free.⁹ It is clear then that in this case the double bond is still activated towards addition, but this may be due to the presence of the remaining adjacent Ph_2P group, and in order to test this possibility we have studied the corresponding behaviour of 1,1-bis(diphenyl-

Table 1. Melting points and analytical data for new compounds

Compound	M.p.	%C	%C	%H Found	%H
Compound		round	Calc.	round	Calc.
1	85	78.5	79.2	6.3	6.2
2	129	68.6	68.8	5.5	5.4
3	135	58.0	57.7	4.5	4.5
4 a	209	65.3	65.3	4.6	4.4
4b	207	60.7	60.8	4.0	4.1
4c	215	53.3	53.4	3.6	3.6
10	161	68.6	68.8	5.5	5.4
11	146	57.4	57.7	4.3	4.5
7a	234	65.1	65.3	4.5	4.4
7b	226	60.6	60.8	4.2	4.1
7c	242	53.5	53.4	3.7	3.6

phosphinomethyl)ethene (1) and its metal complexes and dichalcogenides. For this system the simple addition reaction would lead to the new ligand $(Ph_2PCH_2)_3CH$.

RESULTS AND DISCUSSION

1 was prepared in ca 70% yield by the reaction between the readily available 3-chloro-2-chloromethylprop-1-ene and NaPPh₂ in refluxing liquid ammonia. It was isolated as white crystals which can be handled in air but which may be oxidized on prolonged exposure. Microanalytical data and melting points are given in Table 1.

The molecular structure of 1 is confirmed by its ³¹P and ¹³C NMR spectra which are summarized in Tables 2–7. The equivalent phosphorus(III) atoms have $\delta(^{31}P) = -18.3$ ppm which may be compared with a value of -16 ppm calculated from group contributions.¹⁰ The carbons of the chemically equivalent CH₂ groups are each part of an AA'X [A,A' = ³¹P, X = ¹³C] spin system, but since the coupling ⁴J(³¹P³¹P) is very small their ¹³C resonances appear as a doublet of doublets at $\delta = 38$ ppm with splittings of 7.3 and 15.3 Hz that correspond very closely to the actual AX and A'X couplings and which are assigned to ³J(³¹P—¹³C) and ¹J(³¹P—¹³C) respectively on the basis of com-

Table 2. ³¹P, ⁷⁷Se, ⁹⁵Mo and ¹⁸³W NMR data for the new species

Compound ^a	$\frac{\delta(^{31}\mathbf{P}_{\mathbf{A}})^{b}}{(\text{ppm})}$	$\delta({}^{3}{}^{1}P_{X})^{b}$ (ppm)	J(P _A P _X) (Hz)	δ(M) (ppm)	¹ J(P _A M) (Hz)	ⁱ J(P _x M) (Hz)
1	-18.3		_			
2	+ 39.0		_			
3	+31.2		-	-321.1°	731.2 ^d	
4 a	+46.2		_	158 ^e	134 ^f	
4b	+21.4		_		_	
4c	+7.7		-	+3149	227.1 [*]	
5	-13.8	-31.6	3.1			
6	-17.4	-28.4	5.5			
7a	+62.4	+35.6	41.5			
7b	+47.0	+17.4	30.5	$+126^{e}$	134 ^{<i>f</i>}	134 ^{<i>f</i>}
7c	+31.5	-1.5	24.4	$+268^{g}$	244.1 ^h	222.2 ^h
8	+38.3	+28.1	5.5			
9	+27.7	+16.7	6.1	j	745.8 ^d	717.8 ^d
10	+40.0	+28.3	9.8			
11	+ 32.9	+18.5	9.7	j	738.5 ^d	714.3 ^d

^a As ca 10% solutions in CDCl₃.

^b To high frequency of 85% H₃PO₄.

 $^{c}\delta(^{77}\text{Se})$ relative to SeMe₂ = 0.0 ppm.

 $^{d}M = {}^{77}Se.$

^e To high frequency of Mo(CO)₆.

 $f \pm 3$ Hz, M = 95Mo.

^g To high frequency of $W(CO)_6$.

 $^{h}M = {}^{\overline{183}}W.$

Compound	$\delta(^{13}C_1)^a$ (ppm)	$\begin{array}{c} N(C_1P) \\ (Hz) \end{array}$	$\delta(^{13}C_2)^a$ (ppm)	² <i>J</i> (C ₂ P) (Hz)	$\delta(^{13}C_3)^a$ (ppm)	³ <i>J</i> (C ₃ P) (Hz)
1	38.0	8.0	141.0	8.2	115.5	10.1
2	40.8	53.4	130.8	9.2	122.5	10.5
3	40.5	45.8	130.8	8.5	123.2	10.6
4a	42.4	19.8	137.9	0.0	118.6	8.1
4 b	42.6	19.8	138.0	0.0	119.4	8.8
4 c	42.9	23.4	138.0	0.0	119.9	8.8

Table 3. ¹³C NMR data for the ligands in the symmetrical species 1, 2, 3 and 4a-4c

^a To high frequency of Me₄Si.

^b As ca 10% solutions in CDCl₃.

 $^{c}N = {}^{1}J({}^{31}P - {}^{13}C) + {}^{3}J({}^{31}P - {}^{13}C).$

parison with similar molecules. The olefinic CH₂ and C groups are symmetrically related to two phosphorus atoms and their ¹³C spectra are simple triplets which were assigned by ¹³C-{¹H} gated decoupling experiments.

1 reacted with elemental sulphur or selenium in refluxing benzene to give the corresponding dichalcogenides (2) and (3) [see Scheme 1] as air-stable white solids. These have ³¹P and ¹³C NMR spectra with the same basic structure as those of 1, but with changes in the chemical shifts and coupling constants of the magnitudes and in the directions expected¹¹ to accompany the P^{III} \rightarrow P^V transformation, and with 77 Se satellites in the 31 P spectrum of 3.

With the group VI metal hexacarbonyls in refluxing diglyme (2,5,8-trioxanonane) 1 gave the corresponding metal tetracarbonyl chelate complexes (4a-c) are pale yellow air-stable crystals whose melting points and analytical data are in Table 1. Their ³¹P chemical shifts correspond well with those calculated using established¹² values of coordination chemical shifts for chromium, molybdenum and tungsten tetracarbonyl complexes with six-membered chelate rings. The values of $\delta({}^{95}Mo)$, ${}^{1}J({}^{95}Mo{}^{31}P)$, $\delta({}^{183}W)$ and ${}^{1}J({}^{183}W{}^{31}P)$



			Table 4. ¹³ C	NMR data	for the liganc	ls in the uns	ymmetrical	species, 5–11 [,]	-			
Compound	$\delta^{(13}C_1)^b$ (ppm)	$^{2}J(C_{1}P_{A})$ (Hz)	$^{2}J(C_{1}P_{X})$ (Hz)	$\delta^{(13}C_2)^b$ (ppm)	${}^{3}J(C_{2}P_{A})$ (Hz)	$^{1}J(C_{2}P_{X})$ (Hz)	$\delta^{(13}C_3)^b$ (ppm)	$^{1}J(C_{3}P_{A})$ (Hz)	${}^{3}J(C_{3}P_{X})$ (Hz)	$\delta^{(1^3C_4)^b}$	³ J(C ₄ P _A) (Hz)	³ <i>J</i> (C ₄ P _X) (Hz)
v	152.2	9.7	26.2	125.2	6.1	6.1	36.5	15.9	24.4	27.3	10.4	6.5
9	150.6	7.3	26.9	125.7	8.1	8.1	42.7	16.5	6.1	21.6	7.9	24.4
7a	151.4	0.9	11.0	121.3	11.7	33.3	35.8	15.4	13.2	31.0	3.3	11.3
ዲ	151.0	1.0	10.7	121.4	11.0	33.7	36.7	14.7	12.8	30.7	2.7	11.0
7c	151.6	2.2	9.5	121.2	10.3	38.8	36.9	19.0	11.7	31.0	2.9	11.7
œ	154.2	0.0	7.3	120.9	9.8	86.6	38.3	51.9	8.5	28.9	3.1	15.9
6	150.9	2.4	8.5	124.8	9.8	86.6	46.3	49.4	16.5	23.9	1.2	8.5
10	154.1	0.0	6.1	121.0	10.4	78.1	38.1	46.4	9.1	28.6	3.6	15.9
11	150.5	3.3	6.0	124.2	10.4	78.7	46.2	42.1	17.1	23.9	1.8	9.2
⁶ As ca 10% solution ^b To high frequency	ns in CDCl ₃ . of Me₄Si.	Tab	le 5. ¹³ C NM	IR data for th	he carbonyl _i	groups of th	e complexes	4a-4c and 7a	-7c ^a			
	δ(¹³ CO	$M_2 q(1)$	(CPA)	$^{2}J(CP_{x})$	δ(¹³ CO,	$f^{(1)} = f^{(2)}$	CP)	² J(CP)	δ(¹³ CO ₄)	^b ² J(C	CP) ²	J(CP)
Compound	udd)	•	(ZH)	(Hz)	(mqq)	. E)	Hz)	(Hz)	(mdd)	(H)	Hz)	(Hz)
48	221.5	7 1	3.6		226.7		c	c				
4	210.5	8	8.8		215.5		đ	đ	I	Ι	1	
4	203.1	1	7.0	1	206.3		9	v			1	
7a	221.2	2 1	3.7	13.7	227.7	13	9.9	4.4	227.2	11.	Γ.	5.9
4	210.3	3	8.4	8.4	216.6	6	9.5	27.1	216.1	7	2	23.1
7c	202.(9	6.6	9.9	207.1	Ŷ	5.6	24.9	206.5	Ś	Г	22.7

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^a As ca 10% solutions in CDCl₃. ^b To high frequency of Me₄Si. ^c $N({}^{13}C^{31}P) = {}^{2}J(CP)_{cis} + {}^{2}J(CP)_{trans} = 18.3 \text{ Hz}.$ ^d $N({}^{13}C^{31}P) = {}^{2}J(CP)_{cis} + {}^{2}J(CP)_{trans} = 15.3 \text{ Hz}.$ ^e $N({}^{13}C^{31}P) = {}^{2}J(CP)_{cis} + {}^{2}J(CP)_{trans} = 16.1 \text{ Hz}.$

Compound	$\frac{\delta({}^{13}\mathrm{C}_i)^b}{(\mathrm{ppm})}$	$N(C_i P)^c$ (Hz)	$\delta(^{13}C_o)^b$ (ppm)	N(C _o P) ^c (Hz)	$\frac{\delta({}^{13}C_m)^b}{(ppm)}$	$\frac{N(\mathbf{C}_m\mathbf{P})^c}{(\mathbf{Hz})}$	$\delta({}^{13}C_p)^b$ (ppm)	<i>N</i> (C _p P) ^c (Hz)
1	138.9	14.6	133.2	18.9	128.7	7.3	128.9	< 1.0
2	132.7	79.7°	131.7	10.4	128.9	12.2	131.8	3.1
3	131.5	71.4 ¹	132.3	10.2	128.9	11.9	132.0	2.4
4 a	138.5	36.6	132.6	10.3	128.8	8.8	130.2	< 1.0
4b	138.5	34.4	132.7	11.7	128.9	8.8	130.2	< 1.0
4c	138.0	41.0	132.8	11.7	128.9	9.5	130.4	< 1.0

Table 6. ¹³C NMR data for the phenyl groups of the symmetrical species 1-4c^a

^{*a*} As *ca* 10% solutions in CDCl₃.

^b i = ipso, o = ortho, m = meta, p = para.

 ${}^{c}N(\mathbf{C}_{i}\mathbf{P}) = {}^{n}J(\mathbf{C}_{i}\mathbf{P}) + {}^{m}J(\mathbf{C}_{i}\mathbf{P}').$

^dTo high frequency of TMS.

 ${}^{e}{}^{1}J(C_{i}P) = 81.2 \text{ Hz}, {}^{5}J(C_{i}P) = -1.5 \text{ Hz}.$

 $f^{-1}J(C_iP) = 73.2 \text{ Hz}, \, {}^{5}J(C_iP) = -1.8 \text{ Hz}.$

also accord with those expected¹³ for this type of complex, and the ¹³C spectra show the presence of axial and equatorial carbonyl groups in a 2:2 ratio.

In its reaction with Ph₂PH in the presence of KOBu^t 1 has the potential to undergo either an addition reaction to yield the known triphosphine (Ph₂PCH₂)₃CH or a double bond migration (an allylic rearrangement). In fact, under a range of conditions the result was invariably a mixture of the cis and trans rearrangement products (5 and 6) (see Scheme 1) in a ca 3:7 ratio. This mixture was a viscous oil from which 5 and 6 could not be obtained in analytically pure forms. However, it was possible to purify them sufficiently to record their individual NMR spectra. The ¹³P spectrum (see Table 2) of each of these shows an AX spin system with values of $\delta({}^{31}P_A)$ and $\delta({}^{31}P_X)$ near -15 and -30 ppm as expected¹⁴ for Ph₂PCH₂—R and Ph₂PCH₂=CR₂ fragments respectively, and small values of $J({}^{31}P{}^{31}P)$ as expected for a four-bond coupling. In the ¹³C spectra (Table 4) the multiplicities were assigned by gated ¹³C-{¹H} decoupling experiments, and selective ${}^{13}C-{}^{31}P$ decoupling experiments were used to assign the various ³¹P—¹³C coupling constants. The couplings ${}^{2}J({}^{31}P_{A}{}^{13}C_{1}), {}^{2}J({}^{31}P_{X}{}^{13}C_{1}), {}^{3}J({}^{31}P_{A}{}^{13}C_{2}), {}^{1}J({}^{31}P_{X}{}^{13}C_{2}), {}^{1}J({}^{31}P_{A}{}^{13}C_{2}), {}^{3}J({}^{31}P_{A}{}^{13}C_{4}) {}^{2}can$ be expected to be substantially independent of the geometry at the double bond and indeed are very similar in 5 and 6. In contrast ${}^{3}J({}^{3}PC:C{}^{1}C)$ is known¹⁵ to be characteristically large when the coupled nuclei are cis and small when they are trans; the values of 24.4 and 6.5 Hz for this coupling in 5 and 6 respectively therefore lead us confidently to assign to these isomers cis and trans geometries respectively. This conclusion is supported by the

ability of 5 but not 6 to form chelate metal complexes (vide infra).

The 3:7 mixture of 5 and 6 reacted with elemental sulphur or selenium to yield respectively the disulphides 8 and 10 and the diselenides 9 and 11, the 3:7 isomer ratio being retained in the products in each case. In each case the major [i.e. 10 or 11] isomer was isolated by fractional crystallization as a white air-stable solid (analytical data and melting points in Table 1) and had NMR spectra that confirmed its structure. In particular, the values of $\delta(^{31}P)$ are in the expected regions, and the values of $J({}^{31}P-{}^{13}C)$ are ca 50 Hz for P^V bound to sp^3 hybridized carbon and ca 80 Hz for P^V bound to sp^2 -hybridized carbon. It was also possible to obtain most of the NMR parameters of 8 and 9 and these too confirmed the proposed structures. Insufficient is known about the stereochemical dependence of ${}^{3}J({}^{31}P^{V}C:C{}^{13}C)$ to use this coupling to establish the geometry at the double bond, but the nature of the reaction of P^{III} with chalcogen and the retention of the 3:7 isomer ratio indicate that no isomerization will have occurred, and that 8 and 9 have the *cis* geometry and 10 and 11 the *trans*.

It was also found that the disulphide 2 reacted with Ph₂PH in the presence of KOBu' to yield *exclusively* the *trans* isomer 10. Furthermore, in this reaction no replacement of Ph₂P(S) by Ph₂P occurred, thus confirming that these isomerizations are true allylic rearrangements. Quantitative rearrangement behaviour was also observed when the complexes 4a-4c were treated with Ph₂PH/ KOBu^t, the *cis* products 7a-7c being isolated as air-stable pale yellow crystals (melting points and elemental analyses in Table 1). This is in contrast to the situation found for the *cis* M(CO)₄ [M = Cr,

Compound		$\delta^{(13}C_i)^c$	¹ J(C,P) (Hz)	³ J(C,P) (Hz)	$\delta({}^{13}C_o)^c$	${}^{2}J(C_{o}P)^{d}$ (Hz)	$\delta^{(13}C_{m})^{c}$	${}^{3}J(C_{m}P)^{d}$ (Hz)	$\delta(^{13}C_p)^c$ (ppm)	${}^{4}J(C_{p}P)^{d}$ (Hz)
7а	A	137.6	31.9	1.9	132.2	11.0	128.9	8.8	130.0	1_8
7a	x	138.3	38.1	2.6	132.3	10.6	129.0	9.2	130.3	8
£	¥	137.4	30.4	0.9	132.4	11.7	129.0	8.8	130.1	1.5
10	×	138.1	36.3	1.8	132.5	12.8	129.1	9.5	130.4	1.5
Tc	A	137.3	35.9	1.5	132.6	11.0	129.1	8.8	130.4	2.2
7c	X	138.0	41.8	2.9	132.7	12.5	129.2	9.5	130.7	2.2

c i = ipso, o = ortho, m = meta, p = para.

^dLonger range couplings all < 0.5 Hz.

Mo, W] complexes of $Ph_2PC(CH_2PPh_2)=CH_2$ where either addition of a Ph_2P group or rearrangement can occur. The complexes **7a**-**7c** can also be prepared by the reaction in refluxing diglyme of the 3:7 mixture of **5** and **6** with a 30% equivalent of $M(CO)_6$. This process leaves **6** essentially unaltered and further confirms the assignment of a *cis* geometry to **5**. The use of a larger amount of $M(CO)_6$ again yields **7a**-**7c**, but in addition di- and polymeric species are formed as a result of coordination by **6** which is unable to form monometallic chelates.

The structures of 7a-7c are fully confirmed by their NMR spectra (Table 2-6). These show three ¹³CO resonances with 2:1:1 intensity ratios, arising from two equivalent axial and two inequivalent equatorial carbonyl groups. The ligand backbone ¹³C resonances are at chemical shift positions close to those found in the corresponding *cis* species 5, 8 and 9, and the apparently unaltered values of ¹J(³¹P¹³C) upon coordination in reality conceal an algebraic increase of *ca* 32 Hz because of a change of sign from -16 Hz in 5 to *ca* + 16 Hz in 7a-7c.

The values of ${}^{2}J({}^{31}P_{A}{}^{31}P_{X})$ of 41.5, 30.5, and 24.4 Hz for **7a**, **7b** and **7c** respectively are close to those found by Grim¹⁶ as the metal-mediated contributions in unstrained chelate rings for Cr, Mo and W, and thus confirm that any four-bond backbone component can be disregarded.

The overall pattern of these reactions is summarized in Scheme 1 and it is clear that for (Ph₂P $(E)CH_2_2C = CH_2 [E = \text{lone pair, S, Se, } M(CO)_4/2]$ treatment with Ph₂PH in the presence of KOBu^t leads exclusively to a rearrangement reaction with the double bond migrating to a position closer to one of the Ph₂P groups, and that addition does not occur at room temperature. The stereochemistry of such rearrangements depends upon the relative thermodynamic stability of the products since the cis and trans isomers share a common intermediate. For E = lone pair the rearrangement is 70% selective for the *trans* product; for E = S, Se it is 100% selective for the *trans* product; and for $E = M(CO)_4/2$ the *cis* product is formed exclusively. This pattern therefore represents the relative stabilities of the (feasible) products and is probably sterically determined—in the last case by necessity, and in the first and second by the moderate and somewhat greater sizes of the Ph_2P and $Ph_2P(E)$ groups respectively.

Finally, it should be noted that all of the products of these rearrangement reactions have a double bond with a single adjacent (and therefore potentially activating) Ph_2P group and yet Ph_2PH does not add to them under our conditions. This we attribute to the presence of relatively bulky substituents on the olefinic carbon atoms which make attack difficult. In the case of $(Ph_2P)_2C$: CHR the addition of Ph₂PH becomes substantially slower when R is changed from H to CH₃.¹⁵

EXPERIMENTAL

NMR spectra were measured on a JEOL FX90 Q multinuclear spectrometer at 2.1 T in CH_2Cl_2 or CDCl₃ solutions in 10-mm o.d. spinning tubes. Solvents were dried and deaerated by standard procedures and all manipulations were conducted under an atmosphere of dry dinitrogen or ammonia. For the complexes the procedure used for the chromium congener is given in each case; identical methods were used with molybdenum and tungsten and their proton NMR data are given in that order following the corresponding chromium parameter.

1,1-Bis(diphenylphosphinomethyl)ethene (1)

Triphenylphosphine (65.5 g, 0.25 mol) in tetrahydrofuran (thf) (200 cm³) was added over 0.5 h to a stirred solution of sodium (11.5 g, 0.5 mol) in refluxing anhydrous ammonia (1000 cm³). Solid ammonium bromide (24.5 g, 0.25 mol) was then added over 0.5 h to a give a bright red solution to which 3-chloro-2-chloromethylprop-1-ene (15.6 g, 0.125 mol) in thf (50 cm³) was added dropwise over 0.75 h. The solution became cream-coloured and after removal of ammonia and thf by evaporation the residue was extracted with diethylether (2×200 cm³). The combined extracts were dried over anhydrous sodium sulphate and the solvent was removed under vacuum to give a viscous oil. On addition of ethanol (200 cm³) and storage at -20° C for 24 h a white solid crystallized. Recrystallization of this from methanol (150 cm³)/dichloromethane (50 cm³) at -20° C gave the product as colourless crystals in 68% yield. ¹H NMR : (CDCl₃) δ (--CH₂--) 3.01 ppm, complex multiplet, 4H; δ (=-CH₂) 4.74 ppm, complex multiplet, 2H; $\delta(C_6H_5)$ 7.0–7.5 ppm, complex overlapping multiplets, 20H.

Cis and trans-1,3-bis(diphenylphosphino)-2-methylpropene (5, 6)

To a solution of 1 (10.0 g, 24 mmol) and diphenylphosphine (0.2 g, 1 mmol) in dry thf (50 cm³) was added potassium tert-butoxide (0.05 g, catalytic amount). The solution was stirred until ³¹P NMR indicated quantitative conversion into a 3:7 mixture of **5** and **6** (*ca* 2 h) and the solvent was then removed under vacuum. Methanol (50 cm³) was added to the residue which then yielded a colourless oil upon standing at -20° C for 24 h. After the methanolic mother liquor had been decanted the crude product was dissolved in dichloromethane (20 cm^3) and methanol (80 cm^3) was added to the resulting solution. After standing at -20° C for 24 h the mother liquor was decanted and the oily product was washed with cold methanol $(2 \times 200 \text{ cm}^3)$ and vacuum dried to give an air-sensitive viscous oil containing the isomers **5** and **6** in a 3:7 ratio. Yield: 88%. Attempts to separate the isomers by fractional distillation were unsuccessful.

¹H NMR : (CDCl₃) : (**5**); δ (CH₃) 1.92 ppm, broad singlet, 3H; δ (CH₂) 3.39 ppm, multiplet, 2H; δ (CH) 5.84 ppm, multiplet, 1H; δ (C₆H₅) 6.9–7.5 ppm, complex overlapping multiplets, 20H. (**6**); δ (CH₃) 2.05 ppm, broad singlet, 3H; δ (CH₂) 2.96 ppm, broad singlet, 2H; δ (CH) 5.64, broad singlet, 1H; δ (C₆H₅) 6.9–7.5 ppm, complex overlapping multiplets, 20H.

1,1-Bis(diphenylphosphinomethyl(ethene-P,P'disulphide (2)

A solution of 1 (4.2 g, 10 mmol) in benzene (30 cm³) containing elemental sulphur (1 g; excess) was stirred at room temperature for 2 h and then refluxed for 0.1 h. After filtration of the cooled solution, methanol (30 cm³) was added to the filtrate to give a white solid which was recrystallized from methanol (30 cm³)/dichloromethane (50 cm³) to give the product as air-stable colourless crystals in 90% yield.

¹H NMR : (CDCl₃) : δ (—CH₂—) 3.53 ppm, complex multiplet, 4H ; δ (=CH₂) 4.64 ppm, complex multiplet, 2H ; δ (C₆H₅) 7.3–7.8 ppm, complex overlapping multiplets, 20H.

1,1-Bis(diphenylphosphinomethyl(ethene-P,P'diselenide (3)

This compound was prepared in a similar manner to the disulphide 2 using elemental selenium and a reflux period of 2 h. The product was isolated as airstable colourless crystals in 86% yield.

¹H NMR : (CDCl₃) : δ (—CH₂—) 3.80 ppm, complex multiplet, 4H; δ (—CH₂) 4.59 ppm, complex multiplet, 2H; δ (C₆H₅) 6.9–7.9 ppm, complex overlapping multiplets, 20H.

Cis[1,1-bis(diphenylphosphinomethyl)ethene-P,P']tetracarbonylchromium(0) (4a)

A mixture of hexacarbonylchromium (4.4 g, 20 mmol) and 1 (8.4 g, 20 mmol) in diglyme (50 cm³) was heated under reflux for 2 h. Methanol (50 cm³) was added to the cooled and filtered solution to yield a yellow solid which was recrystallized from

methanol (50 cm³)/dichloromethane (30 cm³) to give the product as air-stable yellow crystals in 75% yield.

¹H NMR : (CDCl₃) : δ (CH₃) 1.36, 1.28, 1.30 ppm, ⁴*J*(H_{methyl}H_{olefinic}) 1.2, 1.6, 1.7 Hz, ⁴*J*(H_{methyl}³¹P_A) 0, 0, 0 Hz, ⁴*J*(H_{methyl}³¹P_X) 1.2, 1.6, 1.7 Hz, ⁴*J*(H_{methyl}H_{aliphatic}) 0, 0, 0 Hz; δ (CH₂) 2.60, 2.65, 2.87 ppm, ²*J*(H³¹P_A) 8.3, 7.8, 8.5 Hz. ⁴*J*(H³¹P_X) 0, 0, 0 Hz, 2H; δ (CH) 5.98, 5.89, 5.83 ppm, ⁴*J*(H³¹P_A) 2.9, 4.4, 4.0 Hz, ²*J*(H³¹P_X) 2.9, 4.4, 5.4 Hz, 1H; δ (C₆H₅) 7.0–7.7, 7.0–7.7, 7.0–7.7 ppm, complex overlapping multiplets, 20H.

Trans-1,3-bis(diphenylphosphino)-2-methylprop-1ene-P,P'-disulphide (10)

Potassium tert-butoxide (0.05 g, catalytic amount) was added to a solution of **2** (4.9 g, 10 mmol) and diphenylphosphine (0.5 g, catalytic amount) in thf (50 cm³). The mixture was stirred for 24 h, its volume was reduced to 25 cm³ at the pump and methanol (50 cm³) was then added to give a white crude solid which was recrystallized from methanol (30 cm³)/dichloromethane (15 cm³) to give the product as air-stable pale yellow crystals in 74% yield.

¹H NMR : (CDCl₃) : δ (CH₃) 1.83 ppm, ⁴*J*(H_{methyl} H_{olefinic}) 0.9 Hz, ⁴*J*(H_{methyl}³¹P_A) 2.9 Hz, ⁴*J*(H_{methyl}³¹P_X) 2.9 Hz, 3H; δ (CH₂) 2.93 ppm, ²*J*(H³¹P_A) 14.4 Hz, 2H; δ (CH) 6.01 ppm, ²*J*(H³¹P_X) 21.5 Hz, ⁴*J*(H³¹P_A) 5.4 Hz, 1H; δ (C₆H₅) 6.0–8.0 ppm, complex overlapping multiplets, 20H.

Trans-1,3-bis(diphenylphosphino)-2-methylprop-1ene-P,P'-diselenide (11)

This compound was prepared using an identical method to that for the disulphide 10 starting from the corresponding diselenide 3. The product was isolated as air-stable colourless crystals in 78% yield.

¹H NMR : (CDCl₃) : δ (CH₃) 1.76 ppm, ⁴J(H_{methyl}

H_{olefinic}) 1.4 Hz, ${}^{4}J(H_{methyl}{}^{31}P_{A})$ 3.0 Hz, ${}^{4}J(H_{methyl}{}^{31}P_{X})$ 3.0 Hz, 3H; $\delta(CH_{2})$ 3.09 ppm, ${}^{2}J(H^{31}P_{A})$ 14.4 Hz, 2H; $\delta(CH)$ 6.04 ppm, ${}^{2}J(H^{31}P_{X})$ 21.0 Hz, ${}^{4}J(H^{31}P_{A})$ 5.4 Hz, 1H; $\delta(C_{6}H_{5})$ 6.9–8.1 ppm, complex overlapping multiplets, 20H.

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