Stereoselective Addition Reactions of Diphenylphosphine: *meso*- and *rac*-1,2-Diphenyl-1,2-bis(diphenylphosphino)ethane and their Group 6 Metal Tetracarbonyl Complexes. Crystal Structures of the Molybdenum Derivatives[†]

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The addition of diphenylphosphine, PPh_2H, to diphenylethyne in the presence of $KOBu^t$ has been followed by ^{31}P n.m.r. spectroscopy, and according to the reaction conditions can yield *cis*, (**2**) or *trans*, (**3**), 1,2-diphenyl(diphenylphosphino)ethene and then *meso*, (**4**), or *rac*, (**5**), 1,2-diphenyl-1,2-bis(diphenylphosphino)ethane, all of which have been isolated and characterised by elemental analysis and ^1H, ^{13}C, and ^{31}P n.m.r. spectroscopy. The $M(CO)_4$ (M = Cr, Mo, or W) complexes of (**4**) and (**5**) have been prepared, and the structures of the molybdenum derivatives determined by single-crystal *X*-ray diffraction. In the solid state the chelate rings are puckered with one axial and one equatorial CPh group for the *meso* diastereomer, and two equatorial for the *rac*. Carbon-13 n.m.r. data suggest that the latter conformation is not fully maintained in solution.

The addition of primary and secondary phosphines to activated carbon–carbon double bonds provides an important route to a range of poly(organophosphines) that are valuable as chelating ligands.[1–5] Less use has been made of corresponding additions to carbon–carbon triple bonds although these are also capable of yielding many useful polyphosphines,[6–9] for example tris(diphenylphosphino)ethene.[10] In the light of more recent interest in polyphosphorus ligands we have now investigated the reaction of diphenylphosphine with diphenylethyne in the presence of potasssium t-butoxide and find that the main products are *cis*-1,2-diphenyl(diphenylphosphino)ethene (**2**) and the new diphosphine *meso*-1,2-diphenyl-1,2-bis(diphenylphosphino)ethane (**4**), see Scheme. We also find it possible to prepare the *rac* diastereomer (**5**) in good yield by isomerisation of the *meso*-diastereomer (**4**). It has been previously reported that this isomer results from the reaction between lithium diphenylphosphide and the ditosylate (**8**).[11] However, that product did not undergo co-ordination to rhodium on treatment with $[Rh(nbd)_2]BF_4$ (nbd = norbornadiene) and our present results indicate that the material produced was most probably diphenylphosphine oxide, PPh_2HO.

Both (**4**) and (**5**) are of particular interest as chelating ligands as they are analogues of 1,2-bis(diphenylphosphino)ethane (dppe or diphos) which can produce environments of altered or reduced symmetry at metals to which they are chelated, and hence can affect their catalytic behaviour and facilitate the measurement of additional n.m.r. parameters. We have therefore prepared the $M(CO)_4$ (M = Cr, Mo, or W) derivatives of (**4**) and (**5**) and have determined the structures of the two molybdenum complexes by single-crystal *X*-ray diffraction. We have also studied the reactions between lithium diphenylphosphide and *meso*- and *rac*-1,2-dibromo-1,2-diphenylethane but find that these lead to debromination to give stilbene and diphenylphosphine oxide. Previously it has been proposed that the addition of diphenylphosphine to compound (**1**) does not proceed beyond the first step, and that treatment of (**1**) with sodium or lithium diphenylphosphide can also yield (**2**) or (**3**).[9]

Results and Discussion

The course of the reaction in tetrahydrofuran (thf) between diphenylphosphine and diphenylethyne in the presence of potassium t-butoxide was followed by ^{31}P n.m.r. spectroscopy, and was found to depend upon the conditions as shown in the Scheme.

(*a*) At room temperature a 2:1 molar ratio of PPh_2H and diphenylethyne yields *cis*-1,2-diphenyl(diphenylphosphino)ethene (**2**) and *meso*-1,2-diphenyl-1,2-bis(diphenylphosphino)ethane (**4**) as the isolable products in a *ca.* 2:5 molar ratio together with unreacted PPh_2H. Compound (**2**) was identified as the *cis* isomer on the basis of $^3J(^{31}P–H)_{Olefinic} = 9.3$ Hz compared with a much larger value expected[12] and found for the *trans* isomer. Compound (**4**) was identified as the *meso* isomer on the basis of the ^{13}CO n.m.r. spectra of its Group 6 metal tetracarbonyl complexes (see below). This reaction provides a convenient route to (**2**) and (**4**) since they are readily separated by crystallisation, and each forms air-stable colourless crystals.

(*b*) Under the same conditions a 1:1 molar ratio of the reactants gives significant amounts of the *trans* olefin (**3**) in addition to (**2**) and (**4**); by substantially increasing the proportion of diphenylethyne it was found possible to isolate (**3**) in moderate yield. The latter has been previously reported[9] and is now identified as the *trans* isomer on the basis of $^3J(^{31}P–H)_{Olefinic} = 23.2$ Hz (measured from the ^{31}P n.m.r. spectrum since the olefinic proton resonance is hidden by the phenyl resonances).

(*c*) At room temperature compound (**3**) reacts with PPh_2H to give (**2**) and (**4**) in a *ca.* 1:6 molar ratio in 1 h, but (**2**) reacts only

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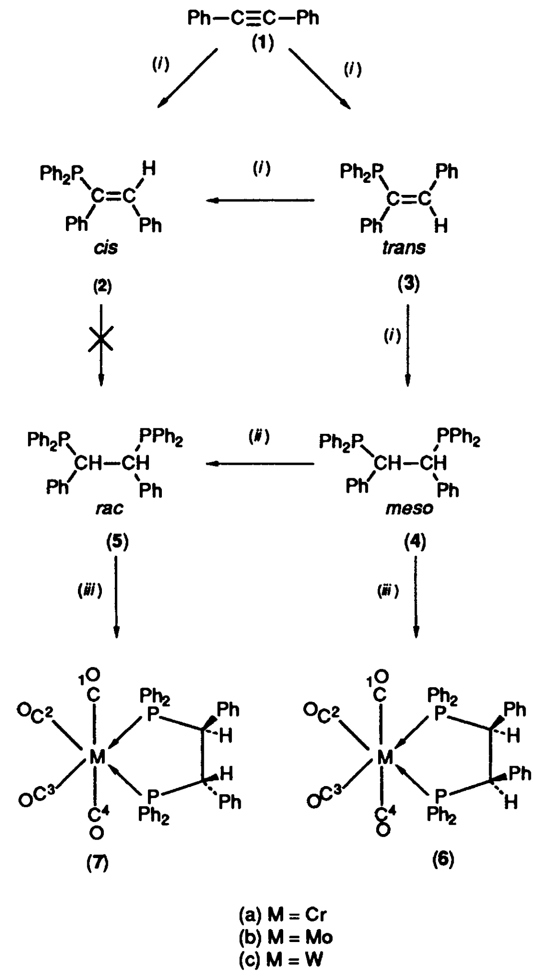
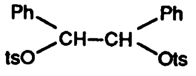
[†] *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.



Scheme. (*i*) PPh_2H, $KOBu^t$, room temperature; (*ii*) PPh_2H, $KOBu^t$, 142 °C; (*iii*) $[M(CO)_6]$, 162 °C



(8)

very slowly indeed under the same conditions to give (**4**) and (**5**) in a *ca.* 3:2 ratio, the reaction being *ca.* 5% complete in 24 h. However, at 142 °C in di-n-butyl ether the reaction is essentially complete in less than 1 h.

(*d*) The *meso* isomer (**4**) is stable to heat (up to 162 °C), but in the presence of PPh_2H and potassium t-butoxide it isomerises to (**5**) at 142 °C although no reaction occurs at room temperature.

(*e*) Figure 1 shows ^{31}P n.m.r. spectra of a 1:1 mixture of PPh_2H and diphenylethyne in thf in the presence of potassium t-butoxide recorded at room temperature over a period of 65 min. In the initial stages the predominant reaction product is (**3**) but the proportions of (**2**) and (**4**) increase during the reaction, and furthermore the *relative* proportions of these two components *change* during the reaction. Thus at t = 1 min the (**2**):(**3**) ratio is 1:5.7 whereas at t = 65 min it is 1:2.5; and the (**4**):(**3**) ratio changes from 1:5.6 to 1:0.68 over this time period. Compound (**4**) is formed *solely* from (**3**) [under (*c*) above it is pointed out that under these conditions no significant conversion of (**2**) into (**4**) occurs] and if this were also true for the formation of (**2**) then the *relative* proportions (**2**) and (**4**) would remain constant. Since this is not the case it follows that (**2**) must also be produced directly from diphenylethyne [note again that no loss of (**2**) or (**4**) occurs once either is formed].

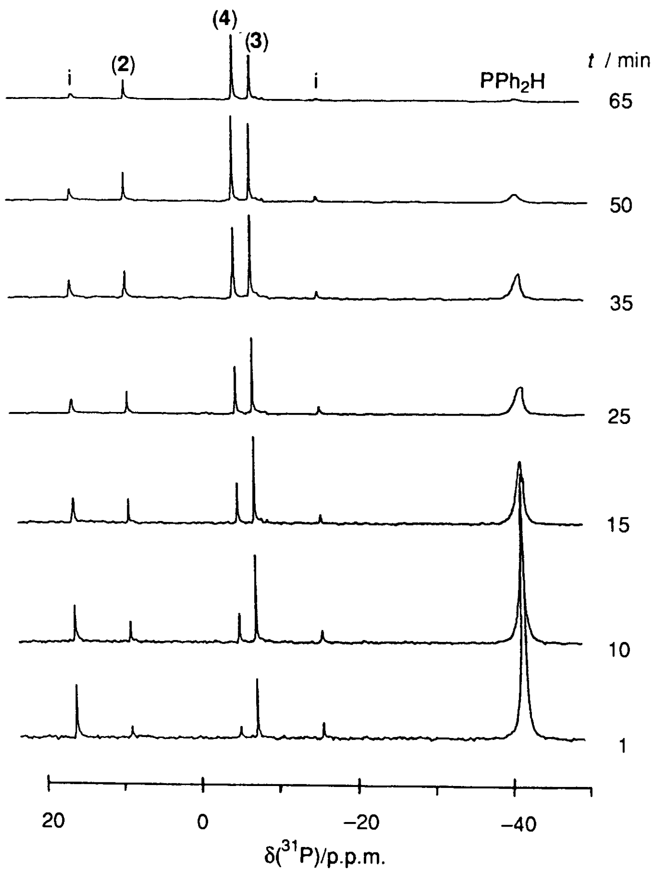


Figure 1. ^{31}P N.m.r. spectra at 36.2 MHz of the mixture resulting from the reaction between equimolar amounts of diphenylphosphine and diphenylethyne in the presence of $KOBu^t$ at room temperature. i = Impurity, t = time elapsed since mixing

Table 1. Analytical data for 1,2-diphenyl-1,2-bis(diphenylphosphino)-ethane (L) and its derivatives

Compound	M.p./°C	Analysis */% C	H
meso-L	197	82.50 (82.90)	5.80 (5.85)
rac-L	131	82.85 (82.90)	5.85 (5.85)
meso-$[Cr(CO)_4L]$	264	70.25 (70.60)	4.45 (4.50)
meso-$[Mo(CO)_4L]$	245 (decomp.)	66.30 (66.50)	4.15 (4.25)
meso-$[W(CO)_4L]$	255 (decomp.)	58.85 (59.60)	3.75 (3.80)
rac-$[Cr(CO)_4L]\cdot CH_2Cl_2$	249	63.75 (64.60)	4.10 (4.30)
rac-$[Mo(CO)_4L]\cdot CH_2Cl_2$	246	61.00 (61.25)	3.90 (4.05)
rac-$[W(CO)_4L]\cdot CH_2Cl_2$	262	54.95 (55.45)	3.60 (3.70)

* Calculated values in parentheses.

Overall, the *cis* olefin (**2**) and the *trans* olefin (**3**) arise initially in a *ca.* 1:6 ratio from the reaction between equimolar amounts of PPh_2H and diphenylethyne. The *trans* olefin (**3**) can then further react with PPh_2H to give more of its *cis* isomer (**2**) and

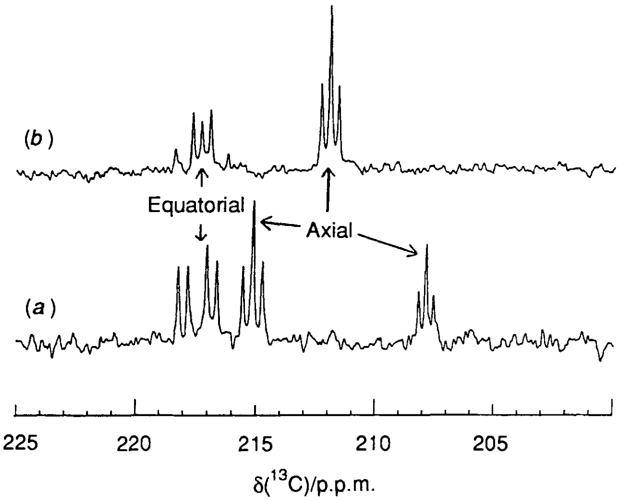


Figure 2. ^{13}C N.m.r. spectra at 22.5 MHz of the carbonyl regions of complexes (**6b**) (*a*) and (**7b**) (*b*). The conditions of measurement were not appropriate for accurate intensity determinations

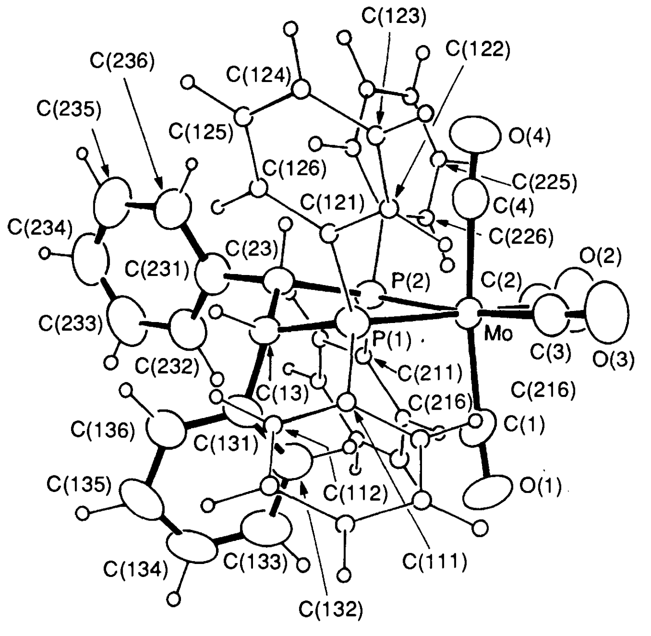


Figure 3. ORTEP drawing of complex (**6b**)

also (**4**) (again in a *ca.* 1:6 molar ratio), whilst (**2**) reacts no further. If excess of PPh_2H is present the *trans* olefin (**3**) reacts quantitatively and the only two products are the *cis* olefin (**2**) and the *meso* diastereomer (**4**). Addition of PPh_2H to (**2**) occurs to a significant extent only at elevated temperatures and yields both *meso* and *rac* isomers of 1,2-diphenyl-1,2-bis(diphenylphosphino)ethane [(**4**) and (**5**)] in a *ca.* 3:2 molar ratio although quantitative conversion of (**4**) into (**5**) is possible under certain conditions.

Thus, whilst the reaction of PPh_2H with diphenylethyne can yield any of the four conceivable products (**2**)—(**5**), it is possible by controlling the conditions to select chosen pathways and hence obtain any desired product in fair or good yield. All of these four products are of interest as ligands but in particular the *meso* and *rac* diastereoisomers (**4**) and (**5**) are important since they can also chelate.

Both compounds (**4**) and (**5**) react smoothly in refluxing $MeOCH_2CH_2OCH_2CH_2OMe$ with $[M(CO)_6]$ (M = Cr, Mo, or W) to yield the corresponding complexes $[M(CO)_4L]$ (**6a**)—(**6c**) and (**7a**)—(**7c**) as pale yellow air-stable crystals. Melting points and elemental analyses are in Table 1. N.m.r. data are in Tables 2 and 3 and some data on dppe complexes are included for comparison. The ^{13}C n.m.r. spectra in the carbonyl region of the complexes (**6a**)—(**6c**) show one equatorial and *two* axial resonances whereas the complexes (**7a**)—(**7c**) show one axial and one equatorial resonance (see Figure 2).

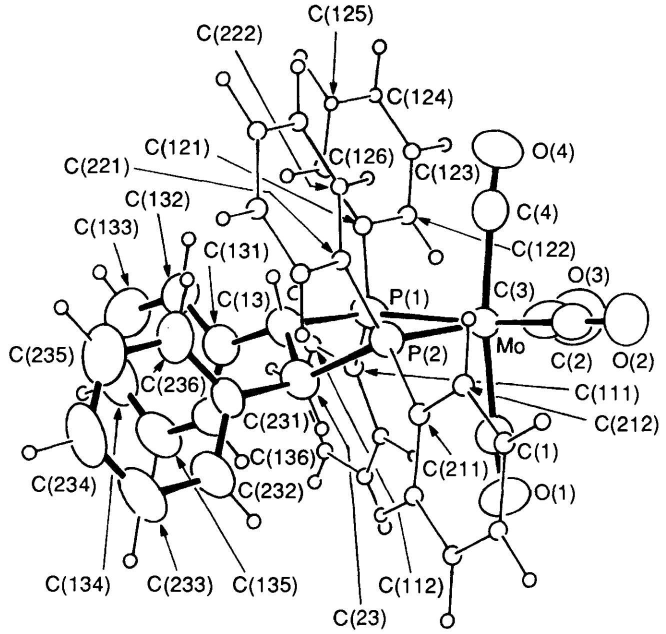


Figure 4. ORTEP drawing of complex (**7b**)

Table 2. ^{31}P Chemical shifts for *meso* and *rac* isomers of $Ph_2PCH(Ph)CH(Ph)PPh_2$ (L) and their tetracarbonyl complexes of Cr, Mo, and W

	meso		*rac*	
Compound[a]	$\delta(^{31}P)$[b]	$\Delta(^{31}P)$[b,c]	$\delta(^{31}P)$[b]	$\Delta(^{31}P)$[b,c]
L	−5.4		−11.4	
$[Cr(CO)_4L]$	+91.2	+96.6	+86.8	+98.2
$[Mo(CO)_4L]$	+68.7[d]	+74.1	+64.8[e]	+76.2
$[W(CO)_4L]$	+53.6[f]	+59.0	+48.0[g]	+59.4

[a] In $CDCl_3$. [b] In p.p.m. ±0.1 p.p.m. relative to external 85% H_3PO_4 (0.0 p.p.m.). [c] $\Delta(^{31}P) = \delta(^{31}P)_{\text{co-ord.}} - \delta(^{31}P)_{\text{free ligand}}$. [d] $\delta(^{95}Mo) = +139$ p.p.m. relative to $[Mo(CO)_6]$ (0.0 p.p.m.). [e] $\delta(^{95}Mo) = +149$ p.p.m. relative to $[Mo(CO)_6]$. [f] $^1J(^{183}W-^{31}P) = 236.8$ Hz, $\delta(^{183}W) = +277.2$ p.p.m. relative to $[W(CO)_6]$. [g] $^1J(^{183}W-^{31}P) = 229.5$ Hz, $\delta(^{183}W) = +312.6$ p.p.m. relative to $[W(CO)_6]$.

These patterns serve unequivocally to identify the complexes of (**4**) and (**5**) as *meso* and *rac* respectively and hence to define the symmetry of the ligands themselves since it is not reasonable to suppose that complex formation would be accompanied by inversion at a backbone carbon atom. The mass spectra of the complexes show the parent ion and also peaks due to loss of one, two, three, and four carbonyl groups.

Single-crystal X-*Ray Analysis of Compounds* (**6b**) *and* (**7b**).— Crystals of both compounds suitable for single-crystal *X*-ray analysis were grown by diffusion of methanol into the respective dichloromethane solutions. Crystals of (**7b**) were obtained as a 1:1 dichloromethane solvate.

ORTEP drawings of (**6b**) and (**7b**) are shown in Figures 3 and 4 respectively whilst comparative bond lengths and angles, along with those of the 'unsubstituted' complex

Table 3. ^{13}C N.m.r. data for complexes of $Ph_2PCH(Ph)CH(Ph)PPh_2$ (L) and of dppe[a]

	C^1O		$C^2O = C^3O$		C^4O		Backbone	
Complex	$\delta(^{13}C)$	$J(^{31}P^{13}C)^b$	$\delta(^{13}C)$	$N(^{31}P^{13}C)^c$	$\delta(^{13}C)$	$J(^{31}P^{13}C)^b$	$\delta(^{13}C)$	$N(^{31}P^{13}C)^c$
meso-$[Cr(CO)_4L]$	226.3	12.8	228.6	15.8	218.6	10.3	54.3	34.8
rac-$[Cr(CO)_4L]$	222.9	11.7	228.1	16.2	222.9	11.7	52.1	40.3
$[Cr(CO)_4(dppe)]$	221.5	13.4	230.4	−17.4	221.5	13.4	28.4	40.0
meso-$[Mo(CO)_4L]$	215.1	8.8	217.4	16.9	207.9	7.0	54.0	31.7
rac-$[Mo(CO)_4L]$	212.1	8.1	217.4	16.1	212.1	8.1	51.9	38.8
$[Mo(CO)_4(dppe)]$	209.9	8.9	218.0	+16.2	209.9	8.9	27.9	39.9
meso-$[W(CO)_4L]$	207.3	7.5	208.2	18.6	200.4	4.7	55.0	34.4
rac-$[W(CO)_4L]$	204.3	6.2	208.5	17.6	204.3	6.2	53.2	41.0
$[W(CO)_4(dppe)]$	201.9	6.8	208.8	+17.2	201.9	6.8	29.7	41.8

[a] Chemical shifts are in p.p.m. to high frequency of $SiMe_4$, ±0.1 p.p.m. Coupling constants are in Hz, ±0.1 Hz. [b] For the *rac* isomers $0.5[J(^{31}P^{13}C) + J(^{31}P'^{13}C)]$ is quoted. [c] $N(^{31}P^{13}C) = J(^{31}P^{13}C) + J(^{31}P'^{13}C)$.

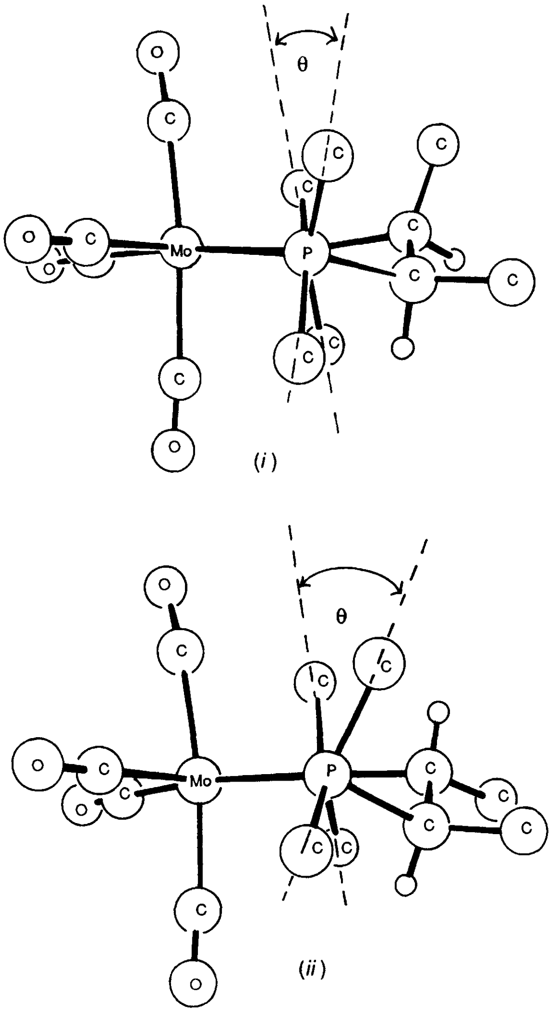


Figure 5. Comparative views of complexes (**6b**) (*i*) and (**7b**) (*ii*) viewed along the P(1)P(2) vector. All parts of phenyl groups other than the *ipso* carbon atoms have been omitted for clarity. The angle θ which defines the relative orientation of the two C_{ipso}–P–C_{ipso} planes is 18.0(1)° for (**6b**) and 31.2(1)° for (**7b**)

$[Mo(CO)_4(dppe)]$ [13] are given in Tables 5 and 6. Bond lengths about the molybdenum atom are very similar in all three complexes with the carbonyl groups *trans* to the phosphorus atoms having shorter Mo–C bond lengths than those *trans* to carbon. However, the two carbon-attached phenyl substituents of the MoP_2C_2 five-membered ring cause a slight lengthening of both the C–C and P–C bonds of this ring, presumably as a result of inductive effects.

Table 4. Crystallographic data for compounds (**6b**) and (**7b**) *

Compound	(**6b**)	(**7b**)
Formula	$C_{42}H_{32}MoO_4P_2$	$C_{42}H_{32}MoO_4P_2 \cdot CH_2Cl_2$
M	758.60	843.53
a/pm	1 207.9(1)	941.9(2)
b/pm	1 762.7(2)	1 106.3(2)
c/pm	1 764.0(2)	1 918.9(4)
α/°		84.22(2)
β/°	106.21(1)	86.28(2)
γ/°		76.88(2)
U/nm^3	3.606 3(7)	1.949 8(7)
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
D_c/g cm^{-3}	1.40	1.44
Z	4	2
F(000)	1 552	860
μ/cm^{-1}	4.28	5.26
No of data collected	6 757	7 047
No. observed	5 695 [$I > 2\sigma(I)$]	6 410 [$I > 2\sigma(I)$]
R	0.0330	0.0377
R'	0.0403	0.0439
Weighting factor g	0.0008	0.000 171
No of variables	377	404

* For both compounds: scan widths 2.0° + α-doublet splitting; scan speeds 2.0—29.3° min^{-1}; 4.0 < 2θ < 50.0°.

The *meso* complex (**6b**) has one CPh group in an axial position with the second equatorial. The apical carbonyl ligands are bent away from the diphosphine chelate [C_{apical}–Mo–C_{apical} 170.9(1)°]. This is in contrast to the dppe analogue where the bend of the apical carbonyl groups is less pronounced and slightly towards the chelate ring [C_{apical}–Mo–C_{apical} 176.6(3)°]. Surprisingly, these CPh groups appear to have little effect on the puckering of the five-membered MoP_2C_2 ring because, as in the complex of dppe itself, the two annular carbon atoms, C(13) and C(23), are displaced by approximately equal amounts on opposite sides of the MoP_2 plane [37.2(2) and 34.0(2) pm for (**6b**) 39.4(8) and 36.8(9) pm for the dppe complex].

In complex (**7b**) the extra-annular CPh groups can adopt one of two possible conformations with either both groups equatorial or both axial. It is the former of these which is observed in the crystal structure presumably because the latter would be more sterically strained. The non-linearity of the apical carbonyl metal system is almost identical to that in (**6b**)

[C_{apical}–Mo–C_{apical} 171.0(1)°]. However, even though the CPh groups are both equatorially situated, there still appears to be a significant amount of steric strain associated with the five-membered ring. In order to relieve this strain a clockwise rotation has occurred about one of the molybdenum–phosphorus bonds [Mo–P(2)] so that the angle between the planes defined by P(1),C(111),C(121) and P(2),C(211),C(221) (θ in Figure 5) changes from the value of 18.0(1)° observed in (**6b**) to 31.2(1)° in (**7b**). This has dramatically altered the puckering of the five-membered ring. One annular carbon atom, C(13), is now nearly in the MoP_2 plane [deviation from the plane = 4.9(3) pm] while the second has moved further away from this plane [deviation of C(23) from the plane = 82.2(3) pm]. This effect can be seen readily in Figure 5 which shows comparable views of both isomers along the phosphorus–phosphorus vector.

Table 5. Selected bond lengths (pm) for compounds (**6b**), (**7b**), and [$Mo(CO)_4$(dppe)] *

	(**6b**)	(**7b**)	[$Mo(CO)_4$(dppe)]
P(1)–Mo	251.4(4)	248.6(3)	249.5(2)
P(2)–Mo	250.9(4)	249.7(3)	250.0(2)
C(1)–Mo	203.5(5)	202.4(5)	205.4(8)
C(2)–Mo	198.0(5)	200.2(5)	199.9(9)
C(3)–Mo	198.6(5)	198.3(5)	197.5(9)
C(4)–Mo	202.5(5)	204.3(5)	203.0(8)
C(111)–P(1)	183.2(3)	183.1(3)	183.2(4)
C(121)–P(1)	184.6(3)	183.3(3)	182.7(5)
C(13)–P(1)	187.2(4)	189.9(5)	184.4(8)
C(211)–P(2)	183.2(3)	183.5(3)	184.5(5)
C(221)–P(2)	184.8(3)	182.6(3)	184.7(5)
C(23)–P(2)	188.6(4)	189.9(5)	184.6(8)
C(131)–C(13)	151.7(5)	152.4(5)	
C(23)–C(13)	156.4(5)	155.2(5)	152.6(12)
C(231)–C(23)	152.6(5)	151.5(5)	
C(13)–H(13)	88(4)	85(4)	
C(23)–H(23)	106(4)	94(4)	
O(1)–C(1)	113.8(5)	114.1(5)	111.9(11)
O(2)–C(2)	114.8(5)	114.0(5)	113.9(10)
O(3)–C(3)	114.2(4)	114.3(5)	116.4(11)
O(4)–C(4)	114.1(5)	114.7(5)	114.1(11)

* Values taken from ref. 13.

Table 6. Selected bond angles (°) for compounds (**6b**), (**7b**), and [$Mo(CO)_4$(dppe)]

	(**6b**)	(**7b**)	[$Mo(CO)_4$(dppe)]
P(2)–Mo–P(1)	80.5(2)	79.8(1)	80.2(1)
C(1)–Mo–P(1)	90.2(2)	96.4(2)	88.2(2)
C(1)–Mo–P(2)	100.2(2)	88.3(2)	86.5(2)
C(2)–Mo–P(1)	169.4(1)	170.2(1)	176.4(3)
C(2)–Mo–P(2)	88.9(2)	92.4(2)	96.4(3)
C(2)–Mo–C(1)	90.8(2)	89.3(2)	93.0(3)
C(3)–Mo–P(1)	99.6(2)	93.4(2)	93.1(2)
C(3)–Mo–P(2)	173.5(1)	171.2(1)	171.3(2)
C(3)–Mo–C(1)	86.3(2)	86.9(2)	87.8(3)
C(3)–Mo–C(2)	91.0(2)	94.9(2)	90.4(3)
C(4)–Mo–P(1)	90.4(2)	87.9(2)	88.4(2)
C(4)–Mo–P(2)	88.8(2)	100.3(2)	92.6(3)
C(4)–Mo–C(1)	170.9(1)	171.0(1)	176.6(3)
C(4)–Mo–C(2)	90.3(2)	87.7(2)	90.4(3)
C(4)–Mo–C(3)	84.7(2)	84.9(2)	92.7(3)
C(111)–P(1)–Mo	119.7(2)	123.1(2)	114.8(2)
C(121)–P(1)–Mo	115.0(2)	110.3(2)	121.9(2)
C(121)–P(1)–C(111)	100.5(2)	102.0(2)	100.2(2)
C(13)–P(1)–Mo	110.6(2)	110.2(2)	108.0(3)
C(13)–P(1)–C(111)	106.5(2)	103.2(2)	106.2(3)
C(13)–P(1)–C(121)	102.8(2)	106.6(2)	104.5(3)
C(211)–P(2)–Mo	121.1(2)	110.9(2)	119.9(2)
C(221)–P(2)–Mo	111.7(2)	124.9(2)	116.4(2)
C(221)–P(2)–C(211)	99.6(2)	103.4(2)	103.6(2)
C(23)–P(2)–Mo	107.8(2)	106.0(2)	107.6(3)
C(23)–P(2)–C(211)	111.7(2)	108.3(2)	102.6(3)
C(23)–P(2)–C(221)	103.5(2)	102.3(2)	105.0(3)
O(1)–C(1)–Mo	175.5(3)	174.9(3)	176.9(7)
O(2)–C(2)–Mo	177.9(3)	178.5(3)	178.3(6)
O(3)–C(3)–Mo	176.1(3)	177.8(3)	177.1(6)
O(4)–C(4)–Mo	174.7(3)	174.3(3)	179.1(7)
C(131)–C(13)–P(1)	116.4(3)	112.5(3)	
C(23)–C(13)–P(1)	108.0(3)	109.5(3)	110.0(5)
C(23)–C(13)–C(131)	115.0(3)	114.1(3)	
C(231)–C(23)–P(2)	120.4(2)	115.6(3)	
C(13)–C(23)–P(2)	113.3(3)	107.0(3)	110.0(5)
C(231)–C(23)–C(13)	112.3(3)	112.6(3)	

N.M.R. Parameters.—The theory of group contributors to ^{31}P chemical shifts[14] predicts that $\delta(^{31}P)$ for compounds (**4**) and (**5**) should be identical. However, this theory takes no account of long-range through-space interactions and the observed difference between (**4**) and (**5**) of 6.0 p.p.m. can therefore be attributed to significant differences in rotamer populations in the two diastereomers. In the complexes this chemical shift difference is somewhat reduced, but it is still the case that the remaining longer-range interactions are different for the two diastereomers. The ^{31}P co-ordination chemical shifts[15] with each of the metals are *ca.* 6 p.p.m. greater than for dppe.[16]

The equatorial ^{13}CO chemical shifts do not differ greatly between the *meso* and *rac* complexes, and are also close to those found for the corresponding complexes of dppe,[16] suggesting that electronic effects are unimportant. However, significant differences are found for the axial ^{13}CO resonances. In solution, chelate ring flipping to interchange axial and equatorial CPh groups will be rapid, and for the *meso* complexes the two conformers will be equally populated. Thus one axial CO group will always be exposed to a single relatively proximate phenyl group and the other will not be, and should be in an environment like that in a dppe complex; the ^{13}C chemical shifts suggest that this is C^4O, and that the presence of the proximate phenyl group increases $\delta(^{13}C)$ for C^1O by some 7—8 p.p.m. If the solution conformations of the *rac* complexes were the same as in the solid state than each axial carbonyl should have $\delta(^{13}C)$ similar to that for C^4O in the *meso* complexes. In fact $\delta(^{13}C)$ for the *rac* complexes is some 4 p.p.m. greater than this, suggesting a population of up to 50% of the other conformer with axial backbone phenyl groups.

The axial ^{13}CO to ^{31}P coupling constants suggest that there are permanent average distortions of the P–M–CO interbond angles since for the *meso* diastereomers $^2J(^{31}P^{13}C^1)$ is *ca.* 2—3 Hz greater than $^2J(^{31}P^{13}C^4)$, and for the *rac* diastereoisomers the measurable average couplings are close to the means for the *meso* diastereomers. For the equatorial carbonyl groups only $N(^{31}P^{13}C)$ was determined, but comparison with analogous complexes of dppe[16] suggests that for molybdenum and tungsten the *trans* couplings will be large and positive and the *cis* couplings moderate and negative, while for chromium both the *cis* and *trans* couplings are negative. This can then account for the fact that $N(^{31}P^{13}C)$ is greater for the *meso* than for the *rac* diastereomer for molybdenum and tungsten, but smaller for chromium.

Experimental

All manipulations were performed under an atmosphere of dry oxygen-free dinitrogen, and solvents were dried and deaerated by standard procedures before use.

Table 7. Non-hydrogen atom co-ordinates (× 10^4) for compound **(6b)**

Atom	*x*	*y*	*z*
Mo	550.2(2)	484.1(1)	2 187.0(1)
P(1)	1 849.6(5)	1 543.3(3)	2 009.2(4)
P(2)	−293.3(5)	1 553.3(3)	2 783.4(4)
C(1)	−382(3)	583(2)	1 036(2)
O(1)	−881(3)	591(2)	385(2)
C(2)	−628(3)	−200(2)	2 400(2)
O(2)	−1 324(3)	−580(2)	2 533(2)
O(3)	1 332(3)	−385(2)	1 838(2)
O(3)	1 757(3)	−911(1)	1 665(2)
C(4)	1 621(2)	258(2)	3 270(2)
O(4)	2 255(2)	85(1)	3 854(1)
C(111)	2 220(2)	1 636(1)	1 075(1)
C(112)	2 109(2)	992(1)	600(1)
C(113)	2 485(2)	1 007(1)	−79(1)
C(114)	2 971(2)	1 667(1)	−284(1)
C(115)	3 082(2)	2 311(1)	191(1)
C(116)	2 706(2)	2 296(1)	870(1)
C(121)	3 302(1)	1 540(1)	2 715(1)
C(122)	3 963(1)	894(1)	2 699(1)
C(123)	5 073(1)	836(1)	3 208(1)
C(124)	5 523(1)	1 422(1)	3 735(1)
C(125)	4 863(1)	2 068(1)	3 752(1)
C(126)	3 752(1)	2 127(1)	3 242(1)
C(13)	1 257(2)	2 484(1)	2 199(1)
C(131)	496(1)	2 891(1)	1 485(1)
C(132)	−496(1)	2 554(1)	1 002(1)
C(133)	−1 228(1)	2 968(1)	390(1)
C(134)	−967(1)	3 720(1)	262(1)
C(135)	25(1)	4 057(1)	745(1)
C(136)	757(1)	3 643(1)	1 357(1)
C(211)	−1 799(1)	1 842(1)	2 372(1)
C(212)	−2 300(1)	2 353(1)	2 782(1)
C(213)	−3 456(1)	2 554(1)	2 481(1)
C(214)	−4 113(1)	2 244(1)	1 769(1)
C(215)	−3 612(1)	1 733(1)	1 359(1)
C(216)	−2 455(1)	1 532(1)	1 660(1)
C(221)	−307(1)	1 336(1)	3 806(1)
C(222)	621(1)	1 504(1)	4 457(1)
C(223)	601(1)	1 276(1)	5 210(1)
C(224)	−348(1)	880(1)	5 312(1)
C(225)	−1 276(1)	712(1)	4 660(1)
C(226)	−1 256(1)	941(1)	3 907(1)
C(23)	720(2)	2 387(1)	2 904(1)
C(231)	408(1)	3 146(1)	3 205(1)
C(232)	−513(1)	3 588(1)	2 776(1)
C(233)	−723(1)	4 295(1)	3 063(1)
C(234)	−12(1)	4 561(1)	3 779(1)
C(235)	909(1)	4 119(1)	4 208(1)
C(236)	1 119(1)	3 412(1)	3 921(1)

Table 8. Non-hydrogen atom co-ordinates (× 10^4) for compound **(7b)**

Atom	*x*	*y*	*z*
Mo	2 012.2(2)	1 088.8(2)	3 724.3(1)
P(1)	381.3(8)	2 642.3(6)	2 969.3(4)
P(2)	953.5(8)	−309.4(6)	3 048.5(4)
C(111)	1 016(2)	2 861(2)	2 385(1)
C(112)	80(2)	4 966(2)	2 192(1)
C(113)	554(2)	5 848(2)	1 708(1)
C(114)	1 966(2)	5 624(2)	1 417(1)
C(115)	2 902(2)	4 518(2)	1 609(1)
C(116)	2 427(2)	3 636(2)	2 093(1)
C(121)	−1 045(2)	3 535(2)	3 508(1)
C(122)	−618(2)	4 438(2)	3 861(1)
C(123)	−1 557(2)	5 040(2)	4 363(1)
C(124)	−2 923(2)	4 739(2)	4 512(1)
C(125)	−3 350(2)	3 836(2)	4 159(1)
C(126)	−2 410(2)	3 234(2)	3 656(1)
C(13)	−567(3)	1 839(2)	2 360(1)
C(131)	−1 117(2)	2 685(2)	1 719(1)
C(132)	−2 492(2)	3 426(2)	1 762(1)
C(133)	−2 969(2)	4 288(2)	1 205(1)
C(134)	−2 071(2)	4 410(2)	605(1)
C(135)	−696(2)	3 669(2)	562(1)
C(136)	−220(2)	2 806(2)	1 118(1)
C(211)	2 303(2)	−1 687(1)	2 863(1)
C(212)	2 400(2)	−2 708(1)	3 359(1)
C(213)	3 528(2)	−3 720(1)	3 299(1)
C(214)	4 558(2)	−3 711(1)	2 744(1)
C(215)	4 461(2)	−2 690(1)	2 248(1)
C(216)	3 334(2)	−1 678(1)	2 307(1)
C(221)	−672(2)	−936(2)	3 324(1)
C(222)	−1 721(2)	−278(2)	3 760(1)
C(223)	−3 026(2)	−679(2)	3 930(1)
C(224)	−3 284(2)	−1 740(2)	3 662(1)
C(225)	−2 235(2)	−2 399(2)	3 226(1)
C(226)	−930(2)	−1 997(2)	3 056(1)
C(23)	430(3)	608(2)	2 183(1)
C(231)	−230(2)	−65(2)	1 674(1)
C(232)	643(2)	−561(2)	1 118(1)
C(233)	67(2)	−1 182(2)	639(1)
C(234)	−1 382(2)	−1 309(2)	717(1)
C(235)	−2 254(2)	−813(2)	1 274(1)
C(236)	−1 679(2)	−191(2)	1 752(1)
C(1)	3 744(4)	901(3)	3 035(2)
O(1)	4 773(3)	833(3)	2 681(2)
C(2)	3 054(3)	−330(3)	4 341(2)
O(2)	3 620(3)	−1 147(2)	4 695(1)
C(3)	2 860(4)	2 361(3)	4 123(2)
O(3)	3 317(3)	3 124(3)	4 341(2)
C(4)	471(3)	1 376(3)	4 521(2)
O(4)	−327(3)	1 602(2)	4 988(1)

Proton, ^{13}C, ^{31}P, and ^{95}Mo n.m.r. spectra were obtained by standard multinuclear techniques using a JEOL FX90Q spectrometer operating at frequencies of 89.56, 22.50, 36.20, and 5.85 MHz respectively; ^{183}W data were obtained at 2.48 MHz from ^{31}P-{^{183}W,H} spin-tickling experiments conducted on a modified JEOL FX60 spectrometer. Samples were dissolved in dichloromethane containing *ca.* 20% C_6D_6 to provide a field–frequency locking signal for the spectrometer and were examined at 296 K in spinning tubes (outside diameter 10 mm).

meso-1,2-*Diphenyl*-1,2-*bis*(*diphenylphosphino*)*ethane* (**4**).—A mixture of diphenylethyne (5 g, 28 mmol), diphenylphosphine (10.4 g, 56 mmol), and potassium t-butoxide (50 mg, catalytic amount) in thf (50 cm^3) was stirred at room temperature for 1 h. After filtration, methanol (100 cm^3) was added to the filtrate to precipitate the product as a white powder, which was filtered off and recrystallised from dichloromethane–methanol (200:50 cm^3) to give colourless air-stable needles, m.p. 197 °C, yield 11.0 g (71%). Proton n.m.r.: δ 7.5—7 (complex multiplets, 30 H) and 4.19 [m, 2 H, $^2J(^{31}PH) + {}^3J(^{31}PH)$ 5.4 Hz].

cis-1,2-*Diphenyl*(*diphenylphosphino*)*ethene* (**2**).—The mother-liquor from the preceding preparation was treated with methanol (100 cm^3) and allowed to stand at −20 °C for 15 h to give colourless needles of compound (**2**), 2.6 g (88% of remainder). Proton n.m.r.: δ 7.5—7 (complex multiplet, 30 H) and 6.5 [1 H, $^3J(^{31}PH)$ 9.3 Hz].

trans-1,2-*Diphenyl(diphenylphosphino)ethene* (**3**).—A solution of diphenylphosphine (2.5 g, 13.4 mmol) in thf (30 cm^3) was added dropwise over 1 h to a stirred solution of diphenylethyne (25 g, 140 mmol) and potassium t-butoxide (50 mg, catalytic amount) in thf (30 cm^3). The mixture was stirred for a further 15 h and then filtered. Methanol (500 cm^3) was added to the filtrate to give a white crystalline solid which was recrystallised twice from dichloromethane–methanol (10:20 cm^3) to give the product as fine white needles, yield 2.49 g (51%).

rac-1,2-*Diphenyl*-1,2-*bis(diphenylphosphino)ethane* (**5**).—A solution of compound (**4**) (5 g, 9.1 mmol), diphenylphosphine (5 g, 27 mmol), and potassium t-butoxide (50 mg, catalytic amount) in di-n-butyl ether (50 cm^3) was refluxed for 48 h. Methanol (100 cm^3) was added to the cooled solution to precipitate a small amount of (**4**) which was filtered off, and the filtrate was allowed to stand at −20 °C for 15 h when colourless needles of (**5**) were deposited. Recrystallisation from dichloromethane–methanol (50:100 cm^3) gave the product in 80% yield, m.p. 131 °C. Proton n.m.r.: δ 7.5—7 (complex multiplet, 30 H) and 3.89 [m, 2 H, $^2J(^{31}PH) + {}^3J(^{31}PH) = 1.0$ Hz].

cis-meso-*Tetracarbonyl*-1,2-*diphenyl*-1,2-*bis(diphenylphosphino)ethane*]*chromium*(0) (**6a**).—Chromium hexacarbonyl (2.2 g, 10 mmol) and compound (**4**) (5.5 g, 10 mmol) were refluxed in diglyme (50 cm^3) for 2 h. The cooled solution was filtered and methanol (50 cm^3) was added. The product crystallised overnight and was recrystallised from dichloromethane–methanol (25:50 cm^3) to give pale yellow crystals of (**6a**), yield 5.4 g, 75%. The molybdenum and tungsten analogues were prepared in the same manner and gave similar yields. Proton n.m.r.: Cr, δ 7.5—7 (30 H) and 4.50 [2 H, $^2J(^{31}PH) + {}^3J(^{31}PH) = 9.5$]; Mo, 7.5—7 (30 H) and 4.49 [2 H, $^2J(^{31}PH) + {}^3J(^{31}PH) = 8.8$]; W, 7.5—7 (30 H) and 4.51 [2 H, $^2J(^{31}PH) + {}^3J(^{31}PH) = 8.8$ Hz].

The tetracarbonyl-chromium, -molybdenum, and -tungsten complexes of compound (**5**) were also prepared in good yield as above. Proton n.m.r.: Cr, δ 7.5—7 (30 H) and 4.20 [2 H, $^2J(^{31}PH) = {}^3J(^{31}PH) = 1.2$]; Mo, 7.5—7 (30 H) and 4.22 [2 H, $^2J(^{31}PH) + {}^3J(^{31}PH) = 0.5$]; W, δ 7.5—7 (30 H) and 4.26 [2 H, $^2J(^{31}PH) + {}^3J(^{31}PH) = 0.7$ Hz].

Single-crystal X-*Ray Analysis*.—All crystallographic measurements were made on a Nicolet P3/F diffractometer operating in the ω—2θ scan mode using a standard procedure described elsewhere with graphite monochromated Mo-K_α radiation (λ = 71.069 pm).[17] Both sets of data were corrected for absorption empirically once the structures had been determined.[18]

The structures of both complexes were determined by standard heavy-atom methods and were refined by full-matrix least-squares using the SHELX program system.[19] Refinement was essentially the same for both compounds with all non-hydrogen atoms [including those of a CH_2Cl_2 solvate molecule in compound (**7b**)] being assigned anisotropic thermal parameters. The methine hydrogen atoms were located by a Fourier difference synthesis and together with the phenyl hydrogen atoms, which were included in calculated positions, were assigned an overall isotropic parameter. In both cases the weighting scheme $w = [\sigma^2 F_o + g(F_o)^2]^{-1}$ was used at the end of the refinement in order to obtain satisfactory agreement analyses. Crystal data, data-collection and structure-refinement parameters are given in Table 4 and atomic co-ordinates for compounds (**6b**) and (**7b**) are given in Tables 7 and 8 respectively.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

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