THE DISECONDARY PHOSPHINES [PhHP(CH₂),PHPh] (n = 2-4, 6): IMPROVED SYNTHESES, NMR SPECTRA AND COMPLEXATION BEHAVIOUR WITH GROUP VI TRANSITION METAL HEXACARBONYLS

BRYAN R. KIMPTON, WILLIAM McFARLANE,* ALAN S. MUIR and PALLAVI G. PATEL

Department of Chemistry, University of Newcastle upon Tyne, Newcastle upon Tyne NE1 7RU, U.K.

and

JONATHAN L. BOOKHAM

Department of Chemical and Life Sciences, University of Northumbria, Newcastle upon Tyne NE1 8ST, U.K.

(Received 20 April 1993; accepted 3 June 1993)

Abstract—Improved preparations of the disecondary phosphines PhHP(CH₂)_nPHPh (n = 2, mppe; n = 3, mppp; n = 4, mppb; n = 6, mpph) by the lithium cleavage of the corresponding ditertiary phosphine Ph₂P(CH₂)_nPPh₂ are described and various NMR parameters are reported; $a^{12/13}C$ isotope effect upon $\delta(^{31}P)$ is observed in the case of mppe. Reactions of mppe and mppp with [M(CO)₆] (M = Cr, Mo, W) yield 1:1 complexes; both the *meso* and the *rac* isomers are produced, are separated and are unequivocally characterized by elemental analysis, vibrational spectroscopy and ¹H, ¹³C and ³¹P NMR spectroscopy.

The ditertiary phosphines $Ph_2P(CH_2)_nPPh_2$ [e.g. dppm (n = 1) and dppe (n = 2)] have been used for many years as bidentate chelating ligands for a wide range of metal substrates,^{1,2} but the relatively high symmetry of these ligands and their complexes limits the data readily available from their ³¹P, ¹³C and ¹H NMR spectra. Ligands of lower symmetry are therefore of considerable interest and, hitherto, $RR'P(CH_2)_n PR'R$ and $R_2P(CH_2)_n PR'R$ $[\mathbf{R}, \mathbf{R}' = \mathbf{H}, \text{ alkyl, aryl}]$ have been studied with this in mind.³⁻²² Of particular potential value in this regard are the disecondary phosphines PhHP(CH₂), PHPh, both in view of the small size of the hydrogen substituent on phosphorus and the opportunities offered for further reactions, e.g. with BuLi or various unsaturated species. One published synthesis of mppe, $[PhHP(CH_2)_2PHPh]$ (1), involves the preparation of Ph(PrⁱO)P(O)CH₂ $CH_2(O)P(Pr^iO)Ph$ followed by its reduction

although another route via the hydrolysis of [(Li(thf)₂)₂(PhPCH₂CH₂PPh)] yielded 58% of the desired product.²⁴ A different procedure involving the reaction of either NaPPhH or KPPhH with the appropriate n-dihaloalkane has been used to prepare 1^7 as well as mppp, [PhHP(CH₂)₃PHPh]⁴ (2), mppb, $[PhHP(CH_2)_4PHPh]^4$ (3), and mpph, $[PhHP(CH_2)_6PHPh]^5$ (4), but is somewhat cumbersome. An attractive alternative is the lithium cleavage of ditertiary phosphines, $Ph_2P(CH_2)_n$ PPh_2 , to give $PhLiP(CH_2)_nPLiPh$, which can then be hydrolysed to the desired disecondary phosphine. Unfortunately, this reaction often yields substantial amounts of alternative products owing to cleavage of a P-CH₂ bond,²⁵⁻³⁰ but we find that under suitable conditions the formation of these and the consequent Ph₂PH can be minimized. Thus, the reaction offers a convenient, high-yielding route to 1 and also to 2, 3 and 4.

with LiAlH₄ and is somewhat inconvenient.^{10,11}

^{*} Author to whom correspondence should be addressed.

Although all of these ligands should form complexes with metal substrates, relatively little work has been reported in this area : the main results are for reactions of 1 with chalcogens, ^{7,10,31,32} methyl iodide, ^{7,10} nickel and cobalt halides¹¹ and the organoelement halides R_2ECl_2 and $RECl_2$.^{14,33} Similar reactions of 2 have been studied^{4,14,31–33} as well as its reactions with Ni(CO)₄, C₇H₈Mo(CO)₄ and Mo(CO)₆.¹⁹

We report here the improved syntheses of 1, 2, 3 and 4 and present their ³¹P, ¹³C and ¹H NMR parameters. Preparative, NMR and vibrational spectroscopic studies of the reactions between 1 and 2 and group VI transition metal hexacarbonyls are also reported and individual diastereomers (arising from the presence of the phosphorus chiral centres) of the complexes have been isolated as air-stable, microcrystalline solids.

RESULTS AND DISCUSSION

General

The reaction between a thf solution of dppe and metallic lithium was complete within ca 24 h at 300 K, but significant cleavage of P-CH₂ bonds occurred so that after hydrolysis substantial amounts (50%) of Ph₂PH were produced and the subsequent yield of the desired product [mppe, (1)] was low.²⁸ However, at 273 K the P-C bond cleavage was more selective and favoured the formation of PhLiPCH₂CH₂PLiPh so that crude yields (³¹P NMR evidence) of mppe in excess of 95% were achieved, although the reaction now took ca 200 h to complete.²⁸ With other α, ω -bis(diphenylphosphino)alkanes satisfactory yields of the desired disecondary phosphines [mppp, (2); mppb (3); mpph, (4)] were obtained when the cleavage reaction was conducted at 300 K or above and they were therefore complete more rapidly. For 1 and 2 ³¹P NMR showed that 1:1 mixtures of diastereomeric products were obtained, but these were not separated; presumably 3 and 4 were also diastereomeric mixtures.

The 1:1 diastereomeric mixtures of mppe (1) and mppp (2) each reacted smoothly in refluxing MeOCH₂CH₂OCH₂CH₂OMe with M(CO)₆ [M = Cr, Mo, W] to yield solutions containing the corresponding complexes $M(CO)_4L$ (5–16) in each case as diastereomeric pairs in the proportions shown in Table 1. For the mppe complexes it was possible to separate the individual *meso* and *rac* isomers in each case by fractional crystallization, and their melting points and analytical data are in Table 1. With mppp each of the diastereomers of the chromium complex was isolated, but only the *meso* forms were obtained pure for molybdenum and tungsten. Attempts to isolate the *rac* forms were thwarted by polymerization; this is consistent with a previous study of the mppp/Mo(CO)₆ system.¹⁹

Unequivocal identification of the *rac* and *meso* diastereomers was obtained from their ¹³CO NMR spectra since the former yields a triplet (from the two equivalent axial CO groups) and an ABX multiplet (from the equatorial CO groups), whilst the latter gives *two* triplets (from the inequivalent axial CO groups) and an ABX multiplet.^{34,35} Representative spectra are shown in Fig. 1. The formation of unequal proportions of the *rac* and *meso* diastereomers from a 1:1 mixture of the two diastereomers of the ligand indicates that inversion of phosphorus must occur at the reaction temperature (435 K).

NMR spectra

Tables 2 and 3 give ${}^{13}C$, ${}^{31}P$ and selected ${}^{1}H$ data for the disecondaryphosphines 1–4. For 3 and 4 the



Fig. 1. ¹³C NMR spectra at 50.3 MHz of carbonyl regions of complexes 11 and 12.

		Ĩ									
		s M	10	°C	%	H			Dafiuv		Isolated
ů	. Complex	(°C)	Calc.	Found	Calc.	Found	Colour	R.M.M.ª	time ^b	»%)/0/4
ŝ	Meso-Cr(CO) ₄ [PhHP(CH ₂) ₂ PHPh]	130-132	52.7	52.5	3.9	3.9	Pale yellow	410	90	52	14.5
9	Rac-Cr(CO)4[PhHP(CH ₂) ₂ PHPh]	149–151	52.7	52.8	3.9	3.9	Pale yellow	410	06	48	13.0
~	Meso-Mo(CO)4[PhHP(CH ₂)2PHPh]	146-149	47.6	47.4	3.5	3.4	Ochre	456	15	60	9.4
90	Rac-Mo(CO)4[PhHP(CH2)2PHPh]	157-159	47.6	47.4	3.5	3.4	Ochre	456	CI	40	12.7
9	Meso-W(CO)4[PhHP(CH2)2PHPh]	137-140	39.9	39.3	2.9	2.9	Brown	542	000	50	10.5
10	$Rac-W(CO)_{4}[PhHP(CH_{2})_{2}PHPh]$	165-168	39.9	39.8	2.9	2.9	Brown	542	060	50	22.9
11	Meso-Cr(CO)4[PhHP(CH2)3PHPh]	108-111	53.8	53.2	4.3	4.1	Bright yellow	424	00	53	11.3
12	Rac-Cr(CO)4[PhHP(CH2)3PHPh]	179–182	53.8	53.5	4.3	4.2	Pale yellow	424	90	47	18.9
13	Meso-Mo(CO)4[PhHP(CH ₂)3PHPh]	184-187	48.7	48.2	3.9	3.9	Golden brown	468	105	55°	27.1
15	Meso-W(CO) ₄ [PhHP(CH ₂) ₃ PHPh]	d > 168	41.0	40.3	3.3	3.1	Reddy brown	556	240	60 [¢]	16.5
D ^{<i>p</i>}	etermined mass spectrometrically.										
${}^{h}\mathbf{R}$	eflux time (in min) for the reaction of PhI	HP(CH ₂),PHPh	and M(C	O), in digl	yme.						
31 _p	o of particular isomer in unseparated react omeric murity >95% by ³¹ D NMR	tion mixture as	determine	ed by ³¹ P N	MR.						

Table 1. Analytical and other data for the complexes *cis*-[PhHP(CH₂)_nPHPh]M(CO)₄ [n = 2, 3; M = Cr, Mo, W]

"Isomeric purity >95% by "'P NMR. Although both isomers were observed in the reaction mixture, only the *meso* form proved isolable.

2527

	Table 2.	NMR paramet	ters for the dise	condary phosph	iines PhHP(CH ₂)"PHPh ($n = 2^{-1}$	$4, 6)^{a}$		
					δ(¹³ C), J(³¹ P ¹³ C	(T iteratives
No. Phosphine	$\delta^{(31}\mathbf{P})$	$(J_{1}^{31}D_{$	C _{b-bone}	Cortho	C _{meta}	C_{para}	C_{ipso}	<i>q</i> (H ₁) <i>φ</i>	ref.
1 PhHP(CH ₂) ₂ PHPh (mppe)	-45.6 -45.9	11.5±0.2	23.0 $J = \pm 15.7$ $J = \mp 8.8$ $v_0 \delta = 4^d$	$134.3(0.08)^{c}$ $^{2}J = 15.4$ $^{5}J < 1$	$128.4(0.006)^{c}$ ${}^{3}J = 5.6$ ${}^{6}J \sim 0$	$\frac{128.0(0.04)^{c}}{J \sim 0}$	$136.0(0.01)^{c}$ ${}^{1}J = 12.5$ ${}^{4}J \sim 0$ $v_{0}\delta = 3.4^{d}$	1.99 (CH ₂) 4.29 (PH)	7, 9, 30
			25.3 (α) 77 8 (β)	134.3	129.2	128.8	136.4	4.21 (Ph)	
2 PhHP(CH ₂) ₃ PHPh (mppp)	- 51.9 - 52.0	≪1	J = 12.2 J = 12.2 J = 7.4	$^{2}J = 15.8$	${}^{3}J = 5.5$	$0 \sim f$	¹ <i>J</i> = 12.2	³ J(HH) = 6.7	4
			$23.8 (\alpha)$	134.4	129.2	128.8	136.7	4.16 (PH)	
3 PhHP(CH ₂) ₄ PHPh (mppb)	-52.5	$\overline{\mathbf{v}}$	${}^{1}J = 12.2$ ${}^{2}J = 7.9$ ${}^{3}J = 7.9$	$^{2}J = 14.7$	$^{3}J = 6.1$	$0 \sim f$	J = 13.4	6·9 = (HH)/ε	4
			23.5 (α) 28.3 (γ) 30.6 (B)	133.7	128.6	128.2	136.0	4.21 (PH)	
4 PhHP(CH ₂) ₆ PHPh (mpph)	- 51.9	v	${}^{1}J = 10.8$ ${}^{2}J = 7.5$ ${}^{3}J = 9.1$	$^{2}J = 15.0$	${}^{3}J = 5.6$	$0 \sim f$	J = 11.0	$9.9 = (\mathrm{HH}) \ell^{\mathrm{e}}$	S
^a Chemical shifts are in ppm : for ³	¹ P to high fr	equency of exte	rnal 85% H ₃ PC	1_4 , for 13 C and	¹ H to high frequ	ency of SiMe4.	Coupling consta	ints are in Hz.	

^b Selected data shown as phenyl proton resonances were not well resolved.

^c Chemical shift difference between the two diastereomers indicated in parenthesis. ${}^{d}v_{0}\delta$ is the ${}^{12/13}$ C isotope effect in Hz upon $\delta({}^{31}$ P) of the corresponding carbon atom at 11.8 T.

No.	Complex	$\delta(^{31}\mathbf{P})$	$\Delta\delta(^{3})^{b}$	¹ J(³¹ P— ¹ H) ^c	${}^{2}J({}^{3}P-{}^{3}P)^{d}$
5	Meso-Cr(CO)₄mppe	48.9	94.6	331	21.9
6	Rac-Cr(CO) ₄ mppe	51.5	97.2	322 ^e	23.4
7	Meso-Mo(CO) ₄ mppe	17.6	63.3	321	16.2
8	Rac-Mo(CO) ₄ mppe	20.4	66.1	315 ^e	17.6
9	Meso-W(CO)₄mppe	1.1 ^f	46.8	337	12.6
10	Rac-W(CO)₄mppe	3.7 ^f	49.4	335 ^e	14.9
11	Meso-Cr(CO) ₄ mppp	17.6	69.5	329	15.0
12	Rac-Cr(CO)₄mppp	21.8	73.7	319	13.7
13	Meso-Mo(CO) ₄ mppp	-7.8^{g}	44.1	317	14.2
14	Rac-Mo(CO)₄mppp	$-9.8^{g,h}$	42.1	N.R .	N.R.
15	Meso-W(CO)₄mppp	-32.2^{f}	19.7	328	14.5
16	Rac-W(CO) ₄ mppp	-37.3 ^h	14.6	N.R .	N.R .

Table 3. ³ P parameters for the complexes *cis*-[PhHP(CH₂)_nPHPh]M(CO)₄ [n = 2, 3; M = Cr, Mo, W]^a

^aChemical shifts are in ppm to high frequency of external 85% H_3PO_4 . Coupling constants are in Hz.

 ${}^{b}\Delta\delta({}^{31}\mathrm{P}) = \delta({}^{31}\mathrm{P}) \text{ complex } -\delta({}^{31}\mathrm{P}) \text{ ligand.}^{36}$

^c Determined from ¹H spectrum.

^d Determined from ¹³C spectrum.

^{e 3}J(³¹P—¹H): 38 Hz for 6, 35 Hz for 8 and 38 Hz for 10.

 $f^{1}J(^{31}P-^{183}W)$ values all within 220–222 Hz.

^g Compared with values of -8.3 and -11.7 ppm.¹⁹

^h Values taken from reaction mixture (diglyme). Products not isolated.

N.R. = not recorded.

centres of chirality are sufficiently far apart for no differences between pairs of diastereomers to be apparent; and for 2 $\delta({}^{31}P)$ is the only parameter to show any differences. In the case of 1 there are small differences in the chemical shifts, but not in the coupling constants, and this presumably indicates that any conformational imbalances are relatively small as these molecules have no bulky substituents. Under conditions of broad-band proton decoupling the natural abundance ¹³C spectra of these species are from ABX spin systems [A, $B = {}^{31}P$, $X = {}^{13}C$] and their appearance is therefore dependent upon J(AB), J(AX) and J(BX), as well as $v_0\delta(AB)$, which arises from the ^{12/13}C isotope effect upon $\delta(^{31}P)$. In the absence of this effect the spin system is AA'X and would yield a symmetrical five-line pattern for the X sub-spectrum; most such spectra have previously been analysed on this basis. However, for higher values of $B_0 V_0 \delta_{AB}$ becomes appreciable and this leads to a splitting of the central X resonance so that a six-line pattern is obtained. This is illustrated in Fig. 2 and provides a convenient and precise indirect method of measuring ^{12/13}C isotope effects upon ³¹P shieldings, although it does not yield their signs. There appear to be very few *direct* observations of this effect. For the ipso-phenyl carbons of 1 the effect is 0.017 ppm and is 0.02 ppm for the directly bonded backbone carbons.

Although the differences in $\delta({}^{31}\text{P})$ for the two diastereomers of 1 and 2 are of undoubted diagnostic value, it is not appropriate to comment in detail upon their origin. However, it is noteworthy that in the complexes of these two ligands (vide infra), where the two chiral centres are separated by only two chemical bonds, the differences are much larger (ca 3 ppm) and are of similar magnitude for both phosphines. Presumably these differences



Fig. 2. ¹³C NMR spectrum of the backbone region of the disecondary phosphine 1 at 50.3 MHz. Equal proportions of the two diastereomers were present, but this had no observable effect upon the spectra, the splitting of the central line being due to the ^{12/13}C isotope effect upon $\delta(^{31}P)$.

would be retained in similar complexes of PhHP(CH_2)_nPHPh no matter how large the value of *n* owing to the availability of the two-bond route via the metal atom.

The analysis of the ¹³C spectra of the ligand parts of the complexes 5-16 proceeded as above and the results are summarized in Table 4. An important feature of this analysis is that it yields ${}^{2}J({}^{31}P{}^{31}P)$ [ideally from the ${}^{13}C_{meta}$ resonances of the phenyl groups for which ${}^{5}J({}^{31}P{}^{13}C)$ can be realistically taken as zero] and this then provides the key to the analysis of the carbonyl resonances. For axial carbonyls there are triplets resulting from coupling to the two ³¹P nuclei and for the equatorial characteristic ABX patterns are obtained. Only in those cases for which the signal-to-noise ratio was sufficient to observe all lines of the X spectrum was it possible to obtain separate values of ${}^{2}J({}^{31}P^{13}C_{cis})$ and ${}^{2}J({}^{31}P^{13}C_{trans})$. Although we have previously observed ^{12/13}C isotope effects upon $\delta(^{31}P)$ in the carbonyl spectra of metal phosphine complexes³⁶ the dispersion in the present study was insufficient for this. In a combined NMR and X-ray diffraction study³⁴ of meso-Ph₂PCHPhCHPhPPh₂Mo(CO)₄, which has the same local symmetry at molybdenum as 7, it was possible to make a reasonable assignment of the ¹³C resonances of the two types of axial carbonyl group on the basis of their large (7.2 ppm) chemical shift difference and a comparison with [Ph₂P(CH₂)₂PPh₂]Mo(CO)₄.³⁵ In the present series the corresponding chemical shift differences are much smaller (ca 3 ppm or less) so that no comparable conclusions can be drawn, and the two types of carbonyl are simply styled ax and ax', with ax being arbitrarily assigned the higher value of $\delta(^{13}C).$

This study brings out the clear effects of relatively small changes in interbond and dihedral angles upon chemical shifts and particularly coupling constants, since differences in electronic effects should be insignificant between the pairs of diastereomers. In the diphosphines themselves the observed effects are small, presumably because the absence of bulky substituents leads to a high degree of conformational mobility and because the different conformers have approximately equal populations.

The coordination chemical shifts $\Delta \delta({}^{31}\text{P}){}^{37}$ for the complexes of mppe are less than for dppe³⁵ with both molybdenum and tungsten, but are more with chromium, whilst those for mppp complexes are greater than for dppp except in the case of the *rac*-W(CO)₄ derivative. Coordination chemical shifts in chelate complexes have significant components arising from "ring strain" and the extent to which this can be relieved by ring puckering. This in turn will be affected by the bulk of substituents and should be an easy process in complexes of mppe and mppp; that is the extent of ring strain should be least in these. In conformity with this the differences in various ¹³C parameters [viz. δ (¹³C) and $J({}^{31}P{}^{13}C)$] between diastereometric pairs are quite small for these complexes and the parameters themselves follow patterns similar to those found for complexes of dppe and dppp.³⁵ There are, however, interesting differences in certain proton parameters for the members of diastereomeric pairs of the mppe complexes. Specifically, there is a chemical shift difference of ca 1.4 ppm in $\delta({}^{1}H)$ for the two types of CH₂ proton in the rac isomers, but of only ca 0.3 ppm for the meso isomers and these are paralleled by values of ${}^{3}J({}^{3}PCC{}^{1}H)$ of ca 38 Hz for one type of proton in the rac isomers. These observations can be understood if account is taken of a high degree of chelate ring puckering, as has been determined for complexes of dppe³⁸ and Ph₂ PCHPhCHPhPPh₂.³⁴ Figure 3 shows four idealized conformers for a PhHP(CH₂)₂PHPhM(CO)₄ complex: the two pairs (a) and (b), and (c) and (d)represent extremes of the rac and meso diastereomers, respectively. In the rac diastereomer the two conformers have either both Ph groups axial or both equatorial and will therefore differ in energy so that one form may predominate. Hence, protons A and A' will be mainly equatorial and B and B' mainly axial or vice versa. In the meso diastereomer the two conformers are of equal energy (each has one Ph group axial and one equatorial) and are thus equally populated; hence, the A,A' and B,B'protons will spend equal amounts of time in axial and equatorial positions; thus, the environments are partially averaged and the chemical shift difference is reduced. Also, in the latter diastereomer there will be a greater degree of averaging of dihedral angles relating P and CH₂ and hence smaller values of ${}^{3}J({}^{31}P^{1}H)$. Interestingly, this behaviour is also found in the complexes of mppp, despite the presumably greater flexibility of the sixmembered chelate ring.

Vibrational spectra

The vibrational characteristics of the dppe derivatives of group VI transition metal hexacarbonyls have previously been reported, ^{39,40} but no data appear to be available for the mppe homologues. In general, local C_{2v} symmetry in the *cis*- $L_2M[CO]_4$ species leads to four carbonyl stretching modes [2A₁, B₁, B₂], each being IR and Raman active. Selected vibrational frequencies for the mppe complexes (5–10) are presented in Table 5; the IR solution spectra (in CH₂Cl₂) were all similar with hardly any differences between the cor-

W] ^a
Mo,
Ъ,
= V
3; N
= ,
= u] 1
ĵ.
M
[H]
PF.
CH_2
HP(
-[Ph
s cis
lexe
omp
the c
for t
lata
AR o
Z
Ч, р
Can
, ¹³
lecte
. Sel
ble 4
Tai

No.	Complex	$\delta(^{13}C_{ax})$	$\delta^{(13)}C_{eq}$	$\delta^{(13)}C_{ax}$	$J(^{31}\mathrm{P}^{13}\mathrm{C}_{\mathrm{ax}})$	$J({}^{31}\mathrm{P}{}^{13}\mathrm{C}_{\mathrm{ax}'})$	$J({}^{31}\mathrm{P}{}^{13}\mathrm{C}_{\mathrm{eq}})$ $\pm J({}^{31}\mathrm{P}{}^{13}\mathrm{C}_{\mathrm{eq}})$	$\delta^{(13}\mathrm{C}_\mathrm{bb})^{\phi}$	$J({}^{31}\mathrm{P}{}^{13}\mathrm{C}{}^{\mathrm{bb}})^b$	$\delta({}^{ m dd}{ m H}^{ m 1})\delta$
S	Meso-Cr(CO)4mppe	220.8	227.7	219.3	14.9	12.7	16.7	24.7	$N = 44.1^c$	2.04, 2.22
9	Rac-Cr(CO) 4mppe	220.6	227.7	220.6	14.2	14.2	16.4	25.2	$N = 42.1^{c}$	$1.32, 2.79^d$
2	Meso-Mo(CO)4mppe	211.6	216.3	208.7	7.8	N.A.	17.1,° 8.3'	25.1	$N = 42.6^{\circ}$	2.00, 2.31
œ	Rac-Mo(CO)4mppe	209.2	216.0	209.2	9.4	9.4	25.9, ^e 9.2 ^f	25.1	34.3, ^g 6.5 ^h	$1.35, 2.83^{i}$
6	Meso-W(CO)4mppe	201.7	206.9	198.9	7.7	5.8	26.0, ^e 7.4 ^f	26.0	35.5, ⁹ 8.4 ^h	2.06, 2.38
10	Rac-W(CO)4mppe	200.2	206.6	200.2	7.1	7.1	25.4, 7.1	26.6	$32.8,^{g} 10.3^{h}$	1.40, 2.90'
11	Meso-Cr(CO)4mppe	222.8	225.6	220.1	15.6	14.2	19.9	26.7, 23.7	$24.4.^{\prime}2\pm0.5^{k}$	m
12	Rac-Cr(CO)4mppe	220.9	225.6	220.9	6.6	6.6	28.2	26.1, 21.5	$25.6,^{\prime}1.8\pm0.5^{\prime}$	ш
13	Meso-Mo(CO),mppe	211.6	214.3	208.1	10.1	9.2	13.0	27.9, 23.8	$24.0, 5\pm 1^{k}$	æ
15	Rac-Mo(CO)4mppe	203.3	204.8	199.2	8.5	7.0	14.3	27.7, 23.9	27.4, ⁷ N.A. ^k	E
	Chemical shifts in ppm ± 0.1 ob = backbone. $e N = {}^{1}J({}^{31}P$ $J({}^{31}P{}^{13}C_{max}).{}^{2}J({}^{31}P{}^{13}C_{cis}).$ $J.{}^{2}J({}^{31}P{}^{14}H) = 37.8$ Hz. Behaviour similar to that of A. = not available.	ppm to high fre ${}^{13}C) + {}^{2}X({}^{31}P^{13}C)$ ${}^{g1}J, h^{2}J, {}^{13}J({}^{31}p^{13}C)$ the mppe compl	quency of M $J_{a}^{a}J_{a}^{a}P^{1}P^{1}$ $P^{1}H = 35.0$ P ¹ H = 35.0 lexes, but alij	e ₄ Si. Couplir) = 37.6 Hz. Hz. ¹¹ J+ ³ J.	ng constants in al regions are n	$Hz \pm 0.1$. nore complex.				

The disecondary phosphines [PhHP(CH₂),PHPh]



A = H_A etc.

Fig. 3. Four idealized conformers of a [PhHP(CH₂)₂PHPh]M(CO₄) complex : (a) and (b) represent two extremes of the *rac* diastereomer whilst (c) and (d) represent two extremes of the *meso* diastereomer.

responding *rac/meso* pairs. In all cases a higher frequency carbonyl band at *ca* 2010–2020 cm⁻¹ was observed, together with a group of three overlapping lower frequency carbonyl bands in the 1850–1950 cm⁻¹ region. However, the solid-state spectra show marked differences between corresponding *rac* and *meso* pairs in both the v(CO)and v(P—H) spectral regions. The carbonyl region spectra were still essentially four-band, but various splittings and shoulders were observed, presumably indicative of differing environments in the crystal. For the chromium complexes 5 (*meso*) and 6 (*rac*), a higher frequency carbonyl mode occurs at 2011 and 2009 cm⁻¹, respectively, in the Raman spectra. The *meso* isomer also has strong bands at 1903, 1899 and 1865 cm⁻¹; the first two of these overlap and are therefore not totally resolved. By contrast, the *rac* isomer (6) displays a strong, broad band at 1904 cm⁻¹ with a higher frequency shoulder at 1921 cm⁻¹. Additional bands are present at 1881 and

No.	Complex	v(CO)	ν(PH)
5	Meso-Cr(CO)₄mppe	2011, 1919, 1896, 1875 (IR)° 2008, 1910, 1903, 1870, 1842, (IR)× 2009, 1903, 1897, 1865 (R)	2317, 2327 (IR) [×] 2319, 2326 (R)
6	Rac-Cr(CO)₄mppe	2011, 1922, 1896, 1877, (IR)° 2006, 1918, 1903, 1875, 1864, 1841, (IR)× 2009, 1921, 1904, 1881, 1865 (R)	2327, 2350 (IR)× 2329, 2355 (R)
7	Meso-Mo(CO)₄mppe	2023, 1927, 1908, 1893 (IR)° 2020, 1917, 1903, 1881, 1870, 1846 (IR)× 2023, 1913, 1906, 1867 (R)	2321, 2333 (IR)× 2320, 2332 (R)
8	Rac-Mo(CO)₄mppe	2023, 1928, 1908, 1892 (IR)° 2017, 1923, 1910, 1883, 1868, 1844 (IR)× 2018, 1920, 1912, 1887, 1869 (R)	2320, 2334, 2346 (IR)* 2334, 2347 (R)
9	Meso-W(CO)₄mppe	2018, 1914, 1896, 1873, 1847 (IR)×	2326, 2357 (IR)
10	Rac-W(CO)₄mppe	2019, 1919, 1899, 1884 (IR)° 2014, 1915, 1901, 1876, 1861, 1846 (IR)× 2016, 1911, 1904, 1881, 1863 (R)	2322, 2336 (IR)

Table 5. Selected vibrational spectroscopic data (cm⁻¹) for the *cis*-[PhHP(CH₂)PHPh]M(CO)₄ [M = Cr, Mo, W] complexes

(R) = Raman. \times Indicates KBr discs; $^{\circ}$ indicates CH₂Cl₂ solution.

1865 cm^{-1} ; of these the latter is much less intense than the corresponding one in the spectrum of the meso complex. The KBr disc IR spectra of 5 and 6 display similar characteristics, although with much reduced resolution. The molybdenum and tungsten congeners behave similarly and show the same band patterns in both the solid-state IR and Raman spectra. Overall these data indicate that in the solidstate there is undoubtedly some distortion from idealized pseudo-octahedral geometry and there are probably interactions between the phenyl moieties and the equatorial carbonyl groups; such effects have been crystallographically determined for Ph₂P(CH₂)₂PPh₂Mo(CO)₄.³⁸ However, in solution such interactions are presumably much reduced; this would account for the striking similarities between the spectra of corresponding meso/rac pairs in CH₂Cl₂ solution.

EXPERIMENTAL

¹H, ¹³C and ³¹P NMR spectra were recorded at room temperature in CH_2Cl_2 solutions contained in either 5 or 10 mm o.d. spinning tubes at field strengths of 2.1 (Jeol FX 90Q), 4.7 (Bruker AC 200F), 7.1 (Bruker WF 300) and 11.8 (Bruker AMX 500) T.

IR spectra were recorded as solutions in CH_2Cl_2 or as KBr discs using either a Perkin–Elmer 1600 or a Nicolet 20 PC FTIR spectrometer. Raman spectra were recorded on solid samples sealed in glass capillaries using a Coderg PHO spectrometer with excitation provided at 514.5 nm by a Coherent Radiation Argon Ion Laser.

All solutions were deaerated prior to use and manipulations were performed under an atmosphere of dry dinitrogen.

1,2-Bis(diphenylphosphino)ethane (dppe) and 1,3bis(diphenylphosphino)propane (dppp)

These were prepared by established procedures^{3,35,41} involving the reaction of sodium diphenylphosphide and the appropriate dichloroalkane in liquid ammonia. Other α, ω -bis(diphenylphosphino)alkanes were synthesized similarly [yields > 70%).

1,2-Bis(phenylphosphino)ethane [mppe, (1)]

Dppe (70.3 g, 0.176 mol) and thinly cut lithium metal strips (4.9 g, 0.704 mol) were reacted in dry thf (700 cm³); the mixture was stirred for *ca* 200 h at 273 K when ³¹P NMR indicated total reaction of the starting diphosphine. To the deep red solution degassed water (250 cm³) was added

(cautiously at first) to hydrolyse the lithiated disecondary phosphine and to remove any dissolved salts. Diethyl ether was added and the organic layer was separated and dried over Na₂SO₄; after filtration, the solvent was removed by distillation. The resulting straw-coloured viscous liquid was distilled [140°C/0.2 mm Hg: literature 161°C/ 0.8 mm Hg^{3.10}] to give a clear product (yield 85%) in which ³¹P NMR indicated the presence of two diastereomers in a 1:1 ratio, although no separation was attempted.

1,3-Bis(phenylphosphino)propane [mppe, (2)], 1,4bis(phenylphosphino)butane [mppe, (3)] and 1,6bis(phenylphosphino)hexane [mppe, (4)]

These disecondary phosphines were prepared in a similar way to mppe (1) using the appropriate bis(diphenylphosphino)alkane; reactions were monitored to completion by ³¹P NMR. For mppp (2), lithiation of dppp was completed within 24 h at room temperature and the product (77% yield) was isolated by distillation [190°C/4.0 mm Hg: literature 196°C/5 mm Hg^{3,4}]. The two diastereomers observed by ³¹P NMR were not separated. The lithiation of dppb to yield mppb (3) was effected by stirring at room temperature for 8 h followed by refluxing for 2 h to ensure complete reaction; the product was isolated in ca 75% yield by distillation [147°C/0.09 mm Hg; literature 208°C/4.0 mm $Hg^{3,4}$]. Mpph (4) was prepared from lithiated dpph (reaction was complete within 8 h at room temperature) and isolated in 80% yield by distillation [165°C/0.05 mm Hg: literature 178°C/0.2 mm $Hg^{3,5}$].

Reactions of mppe (1) and mppe (2) with $M(CO)_6$ [M = Cr, Mo, W]

The reactions of either mppe (1) or mppe (2) with $M(CO)_6$ were conducted in refluxing diglyme. Experimental details are presented in Table 1. After complete reaction (as monitored by ³¹P NMR) the solvent was removed *in vacuo* and addition of MeOH followed by refrigeration yielded a first crop of crystals (*rac* isomer). Repeated evaporation and refrigeration yielded further crystals (*meso* isomer). Products were recrystallized from CH₂Cl₂/MeOH. From the reactions of mppp (2) with molybdenum and tungsten hexacarbonyls only one product—the *meso* isomer—could be isolated.

Acknowledgements—We thank the NAB, the Royal Society, the Leverhulme Trust and the SERC for financial support, the former City of London Polytechnic for facilities, Mr S. Richards and Dr P. N. Gates (Royal Holloway and Bedford New College) for assistance with vibrational spectroscopy and Dr J. H. Carpenter for help-ful comments.

REFERENCES

- 1. R. J. Puddephat, Chem. Soc. Rev. 1983, 12, 99.
- 2. C A. McAuliffe and W. Levason, *Phosphine, Arsine* and Stibine Complexes of the Transition Elements. Elsevier, Amsterdam (1979).
- G. M. Kosolapoff and L. Maier, Organic Phosphorus Compounds, Vol. 1. Wiley–Interscience, New York (1972).
- 4. K. Issleib and D. Jacob, Chem. Ber. 1961, 94, 107.
- 5. K. Issleib and F. Krech, Chem. Ber. 1961, 94, 2656.
- 6. K. Issleib and G. Döll, Chem. Ber. 1961, 94, 2664.
- 7. K. Issleib and K. Staudtke, Chem. Ber. 1963, 96, 279.
- K. Issleib and G. Döll, Z. Anorg. Allg. Chem. 1963, 324, 259.
- K. Issleib, K. Krech and K. Gruber, *Chem. Ber.* 1963, 96, 2186.
- K. Issleib and H. Weichmann, Chem. Ber. 1968, 101, 2197.
- 11. K. Issleib and H. Weichmann, Z. Anorg. Allg. Chem. 1968, **362**, 33.
- 12. S. O. Grim, R. P. Molenda and R. L. Keiter, *Chem. Ind.* 1970, 1378.
- S. O. Grim, J. Del Gaudio, R. P. Molenda, C. A. Tolman and J. P. Jesson, J. Am. Chem. Soc. 1974, 96, 3416.
- K. Issleib and W. Böttcher, Z. Anorg. Allg. Chem. 1974, 406, 178.
- S. O. Grim and R. C. Barth, J. Organomet. Chem. 1975, 94, 327.
- S. O. Grim and J. D. Mitchell, *Inorg. Chem.* 1977, 16, 1762.
- 17. S. O. Grim and J. D. Mitchell, *Inorg. Chem.* 1977, **16**, 1770.
- S. O. Grim and J. D. Mitchell, *Inorg. Chem.* 1977, 16, 1776.
- 19. M. Baacke, S. Morton, O. Stelzer and W. S. Sheldrick, *Chem. Ber.* 1980, **113**, 1343.

- O. Stelzer, S. Hietkamp and H. Sommer, *Phosphorus Sulphur* 1983, 18, 279.
- 21. S. Heitkamp, H. Sommer and O. Stelzer, *Chem. Ber.* 1984, **117**, 3400.
- 22. H. Schmidbaur and S. Schnatterer, *Chem. Ber.* 1986, 119, 2832.
- K. P. Langhaus and O. Stelzer, Chem. Ber. 1987, 120, 1707.
- 24. D. M. Anderson, P. B. Hitchcock, M. F. Lappert and I. Moss, *Inorg. Chem. Acta* 1988, 141, 157.
- P. A. Brooks, M. J. Gallagher and A. Sarroff, Aust. J. Chem. 1987, 40, 1341.
- P. A. Brooks, D. C. Craig, M. J. Gallagher, A. D. Rae and A. Sarroff, J. Organomet. Chem. 1987, 323, C1.
- 27. I. J. Colquhoun, H. C. E. McFarlane and W. McFarlane, J. Chem. Soc., Chem. Commun. 1982, 220.
- P. G. Patel, PhD Thesis, City of London Polytechnic (1989).
- 29. W. Hewertson and H. R. Watson, J. Chem. Soc. 1962, 1490.
- 30. K. Sommer, Z. Anorg. Allg. Chem. 1970, 376, 37.
- B. Walther, R. Schöps and W. Kolbe, Z. Chem. 1979, 19, 417.
- 32. G. Grossman, B. Walther and U. Gastrock-Mey, *Phosphorus Sulphur* 1981, 11, 259.
- 33. K. Issleib and W. Böttcher, Synth. React. Inorg. Met. Org. Chem. 1976, 6, 179.
- J. L. Bookham, W. McFarlane, M. Thornton-Pett and S. Jones, J. Chem. Soc., Dalton Trans. 1990, 3621.
- 35. G. T. Andrews, I. J. Colquhoun and W. McFarlane, Polyhedron 1983, 2, 783.
- P. Groves and W. McFarlane, unpublished observations.
- 37. L. S. Merriweather and J. R. Leto, J. Am. Chem. Soc. 1961, 83, 1113.
- I. Bernal, G. M. Reisner, G. R. Dobson and C. B. Dobson, *Inorg. Chim. Acta* 1986, 121, 199.
- J. Chatt and H. R. Watson, J. Chem. Soc. 1961, 4980.
- 40. F. A. Cotton and C. S. Kraihanzel, J. Am. Chem. Soc. 1962, 84, 4432.
- 41. I. J. Colquhoun and W. McFarlane, J. Chem. Soc., Dalton Trans. 1982, 1915.