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Stereoselective addition reactions of diphenylphosphine to pyridyl and pyrimidylalkynes: chiral 1,2-diheteroaryl-1,2-bis(diphenylphosphino)ethanes and their Group 6 metal carbonyl complexes

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Abstract

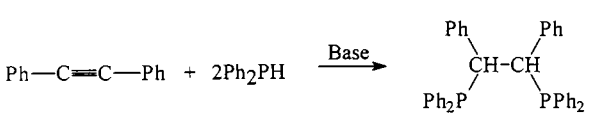
The base-catalysed addition of diphenylphosphine to the diarylethynes RC≡CR′ (R = R′ = 2-pyridyl **1**; R = R′ = 3-pyridyl **2**; R = 2-pyridyl, R′ = 3-pyridyl **3**; R = phenyl, R′ = 2-pyridyl **4**, 3-pyridyl **5**, 2-pyrimidyl **6**) yield diphosphines of general formula $Ph_2PCH(R)CH(R')PPh_2$ together with alkene by-products $Ph_2PC(R)=CHR'$ and $HC(R)=C(R')PPh_2$ in all cases except **1**. Selected *P*,*P*′-coordinated $M(CO)_4$ complexes (M = Mo, W) of the diphosphines have been prepared and their ^1H-, ^{13}C- and ^{31}P-NMR data are presented. The pattern of ^{13}CO-NMR signals for the tetracarbonyl complexes was used unambiguously to determine the stereochemistry of the parent diphosphine. At moderately elevated temperatures, nitrogen coordination of 2-pyridyl and 2-pyrimidyl groups occurred for tetracarbonyl complexes of *meso*- or *erythro*-stereochemistry, but not for complexes of *rac*- or *threo*-form, to yield corresponding *fac*-tricarbonyl complexes. At 162°C the complex *cis*-*rac*-$(CO)_4W\{P,P'$-$Ph_2PCH(R)CH(R)PPh_2\}$ (R = R′ = 2-pyridyl) is converted quantitatively into *fac*-*erythro*-$(CO)_3W\{P,P',N$-$Ph_2PCH(R)CH(R)PPh_2\}$ via an inversion/*N*-coordination pathway. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Stereoselective addition; Diphenylphosphine; Group 6 metals; Carbonyl complexes

1. Introduction

The addition of primary and secondary phosphines to activated C=C double bonds is now an established method for the preparation of polyphosphines that are valuable as chelating ligands [1–5]. With appropriate modifications this sort of addition reaction is also capable of yielding ambidentate phosphorus ligands containing, for example, pendant arms with N or S donor atoms by addition of N–H or S–H bonded species to a C=C double bond bearing a phosphine residue [6–8], or by addition of P–H bonded species to C=C double bonds bearing heteroatomic atoms or groups [9,10]. Less use has been made of additions to triple bonds but we have shown recently that these are also viable, as shown in Scheme 1 [11,12], and give potentially valuable products with structures related to that of 'chiraphos' [2,3-bis(diphenylphosphino)butane].

As part of a continuing study into the addition reactions of phosphines to multiple bonds we have now extended Scheme 1 to include bis-heterocyclic alkynes in order to prepare potentially important chiral phosphine ligands with additional donor atoms such as oxygen, sulfur, and in this paper, nitrogen. Phosphorus/



Scheme 1.

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nitrogen donor ligands have been the subject of renewed and refocused studies in recent years; an excellent review of pyridyl phosphines and related species by Newkome [13] describes the variety and versatility of these ligands in their coordination chemistry. More specifically, Brown and co-workers [14] have demonstrated effective asymmetric hydroboration using a rhodium complex of 1-(2-diphenylphosphino-1-naphthyl)isoquinoline, a ligand related structurally to the more familiar 'binap' [2,2′-bis(diphenylphosphino)-1,1′-binaphthyl] system. Their study is just one example of recent interest in chiral P–N ligands for asymmetric synthesis [15].

In a recent communication we have reported a preliminary account of the unusual inversion behaviour of *rac*-$Ph_2PCH(R)CH(R)PPh_2$ (R = 2-pyridyl) [16]. In this paper we report a broad range of reactions of diphenylphosphine with diarylethynes containing combinations of 2-pyridyl, 3-pyridyl, 2-pyrimidyl, and phenyl substituents to yield symmetrical and unsymmetrical chiral diphosphines of the type $Ph_2PCH(R)CH(R')PPh_2$. The preparation and reactions of octahedral complexes of general formula $M(CO)_4L$ and $M(CO)_3L$ [M = Mo, W; L = diphosphine ligand] are also reported as well as multielement NMR characterisation of all products.

2. Results and discussion

2.1. Alkyne synthesis

Di(2-pyridyl)ethyne **1** was prepared using a modification of Rossi's method [17] via a Pd(0) catalysed coupling reaction of 2-methyl-3-butyn-2-ol with two equivalents of 2-bromopyridine under phase transfer conditions. Similar reactions yielded di(3-pyridyl)ethyne **2** from 3-bromopyridine, and the unsymmetrical alkyne (2-pyridyl)(3-pyridyl)ethyne **3** from the appropriate stepwise reaction. Each of these reactions afforded yellow or pale yellow solids in good yield following distillation under reduced pressure. The products were found to be essentially pure by GC/MS and NMR and entirely suitable for subsequent reactions and were therefore used as obtained. Phenyl(2-pyridyl)ethyne **4**, phenyl(3-pyridyl)ethyne **5** and phenyl(2-pyrimidyl)ethyne **6** were prepared from phenylethyne and the appropriate aryl bromide using a modification of the method of Sonogashira [18]. Analytically pure specimens of all alkynes were obtained following a further vacuum sublimation/distillation and/or column chromatography and showed no significant differences in their subsequent reactions to those compounds obtained directly from the reaction mixtures.

2.2. Hydrophosphination reactions

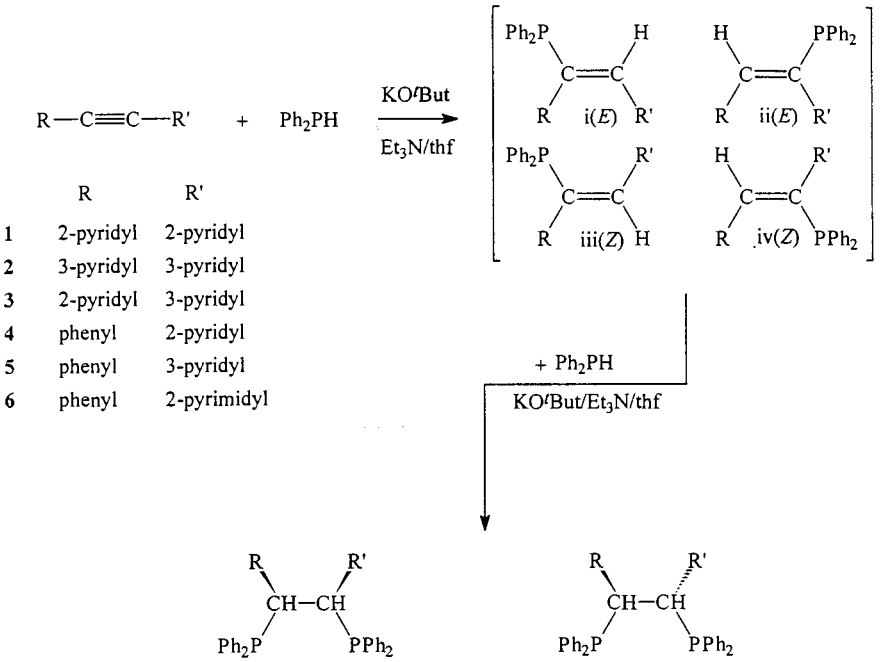
In THF/triethylamine, and in the presence of catalytic amounts of potassium *tert*-butoxide, di(2-pyridyl)ethyne **1** reacted rapidly with two equivalents of diphenylphosphine at room temperature (r.t.) to afford *meso*-1,2-di(2-pyridyl)-1,2-bis(diphenylphosphino)ethane **7** and *rac*-1,2-di(2-pyridyl)-1,2-bis(diphenylphosphino)ethane **8** each in ca. 40% isolated yield.

Corresponding reactions of diphenylphosphine with **2–6** occur as summarised in Scheme 2. Specific outcomes and isolated yields are in shown in Table 1.

The isolated compounds of *meso*-stereochemistry **7** and **9** are essentially insoluble in all common organic solvents including dichloromethane, chloroform, methanol, ethanol, and importantly, the reaction solvent THF, from which crude products precipitate as they form. Compounds of the *rac*-form and the less symmetrical *erythro*-, or *threo*-isomers are more soluble in dichloromethane, chloroform and THF but not also insoluble in methanol or ethanol. Separation of **7** and **8** was therefore readily achieved by fractional crystallisation but in the majority of other cases the comparable solubilities of diastereomer pairs combined with the formation of appreciable quantities of the corresponding phosphinoalkene intermediates (i–iv) precluded the separation and isolation of analytically pure products although their NMR parameters could be obtained satisfactorily from crude products. Elemental analyses for the diphosphine ligands are therefore reported for their metal carbonyl derivatives for which purification was straightforward (Table 2).

All phosphines reported here are moderately sensitive to aerial oxidation in the solid state, and rather more so in solution. Their isomeric identities were deduced from the ^{13}CO-NMR spectra of their metal carbonyl derivatives (see later).

In two previous studies [11,12], we have shown that additions of diphenylphosphine to diphenyl- and ditolylethynes proceed via *Z*-alkene intermediates which react further under the experimental conditions to give *meso*- (or *erythro*-)diphosphines. The corresponding *E*-isomers are inert to further addition and can occasionally be isolated from the reaction mixture. Similarly here, the addition of diphenylphosphine to **1–6** is likely to initially yield one or more of the corresponding isomeric alkene intermediates (i–iv), and any subsequent addition yields one or both diphosphine isomers. Alkenes of *E* stereochemistry (i or ii) were identified in the reaction mixtures from all ethynes except **1** using ^{31}P-NMR spectroscopy (see Table 1) but were not isolated pure. In the case of **5** both *E*-isomers were detected. In contrast to our previous studies, *rac*- or *threo*-diphosphines are formed directly in the majority



	R	R'
1	2-pyridyl	2-pyridyl
2	3-pyridyl	3-pyridyl
3	2-pyridyl	3-pyridyl
4	phenyl	2-pyridyl
5	phenyl	3-pyridyl
6	phenyl	2-pyrimidyl

stereochem.	cpd	R	R'	cpd	*stereochem.*
meso	7	2-pyridyl	2-pyridyl	8	*rac*
meso	9	3-pyridyl	3-pyridyl	10	*rac*
erythro	11	2-pyridyl	3-pyridyl	12	*threo*
erythro	13	phenyl	2-pyridyl	14	*threo*
erythro	15	phenyl	3-pyridyl	16	*threo*
erythro	17	phenyl	2-pyrimidyl	18	*threo*

Scheme 2.

of cases reported herein. In both previous studies referred to earlier only *meso*- or the geometrically related *erythro*-isomers were obtained.

General aspects of the stereochemistry of addition of phosphines to alkynes have been described or discussed in a number of published papers [19–23]. Previously, we proposed that the formation a *meso*- (or *erythro*-)diphosphine via a *Z*-alkene intermediate can only result effectively from successive *anti*- and *syn*-additions to the C≡C and C=C multiple bonds, respectively [12]. The formation of *rac*- and *threo*-isomers in several instances reported here, presumably also via their *Z*-alkene precursors, reveals that *anti*-/*anti*-addition is also a viable pathway for the alkynes in this study. The formation of tetraphenyl diphosphane in similar reactions has also been observed previously [12].

2.3. Complexation reactions

Compound **7** reacted smoothly with $Mo(CO)_4(pip)_2$ (pip = piperidine) in dichloromethane at r.t. to give **19,** similar reactions with **8**, **9**, **11**, **13**, **14**, **17**, and **18** afforded **21**, **23–27**, and **29,** respectively. In each of these cases the diphosphine ligand adopts a *P*,*P*′-coordination mode (Scheme 3). Occasionally, crystallisation from the reaction mixture yielded an analytically pure sample directly, in other cases these were obtained by recrystallisation from methanol/chloroform. Similar reactions with $W(CO)_4(pip)_2$ in refluxing chloroform yielded **20**, **22**, **28**, and **30** from their corresponding free ligands **7**, **8**, **17**, and **18**, respectively. All preceding complexes were isolated in good yield as air-stable pale yellow crystalline solids which are soluble in dichloromethane and chloroform but insoluble in alcohols.

On refluxing a solution in chloroform of the *cis-meso*-{*P*,*P*′}molybdenum tetracarbonyl derivative **19** virtually quantitative conversion to its *fac-erythro*-{*P*,*P*′,*N*}tricarbonyl counterpart **31** occurred via displacement of a CO ligand by a pyridyl nitrogen. Compounds **33–35** were prepared similarly from **24**, **25**, and **27**, respectively. Reaction of the free ligands **7**, **11**, **13**, and **17** with $Mo(CO)_4(pip)_2$ in refluxing chloroform yielded **31** and **33–35,** directly. The formation of

Table 1
Yields of products from the reactions of diphenylphosphine with various alkynes[a]

Alkyne	Major products[b]			
1	**7** [40%] *38%*	**8** [60%] *39%*	–	–
2	**9** [38%] *34%*	**10** [0%]	i (≡ii) [29%]	Ph_2PPPh_2 [31%]
3	**11** [40%] *26%*	**12** [15%]	i or ii [12%]	Ph_2PPPh_2 [18%]
4	**13** [32%] *25%*	**14** [6%] *5%*	i or ii [55%]	Ph_2PPPh_2 [7%]
5	**15** [36%]	**16** [0%]	i and ii [50%]	Ph_2PPPh_2 [14%]
6	**17** [39%] *22%*	**18** [11%] *8%*	i or ii [33%]	Ph_2PPPh_2 [17%]

[a] Approximate molar proportions are calculated from ^{31}P-NMR integrals obtained directly from the reaction mixtures and are shown in square brackets. Approximate isolated yields, where relevant, are shown in italics.

[b] Compound labelling is shown in Scheme 2. Intermediate alkenes are identified as of type (i)–(iv) for the relevant alkyne/reaction.

these complexes demonstrates the ability of 2-pyridyl and 2-pyrimidyl groups on the ligand backbone to undergo facile *N*-coordination. Attempts to force similar *N*-coordination of a 3-pyridyl group in **23** were unsuccessful using these or more forcing conditions.

Analogous *N*-coordination reactions of the tungsten complexes **20** and **28** were achieved by refluxing their solutions in toluene at 110°C for 12 h and gave **32** and **36**, respectively. The higher temperature required for carbonyl substitution in tungsten derivatives in comparison to their molybdenum counterparts is well-documented [24]. Surprisingly, similar treatment of the *rac*-{*P*,*P*′}tungsten complex **22** also yielded **32**. This conversion is essentially quantitative after 24 h at 110°C and must involve an inversion at one of the chiral sp^3 hybridised backbone carbon atoms. At 162°C (diglyme [2,5,8-trioxanonane] at reflux) the same conversions, **20** to **32** and **22** to **32,** are more rapid and are essentially complete in 4 and 12 h, respectively. No other complex of the *rac* or *threo* forms reported herein (**21**, **26**, **29**, and **30**) undergo inversion analogous to that of **22** under similar experimental conditions. Prolonged reflux in diglyme of the molybdenum complexes **21**, **26**, **29** results in a very slow formation of insoluble brown products, possibly polymeric in nature. Prolonged reflux of a solution of **30** in diglyme effects no change.

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

Compound	C	H	N
19[a]	59.0 (58.3)	3.7 (3.8)	3.3 (3.3)
20	56.7 (56.6)	3.6 (3.6)	3.3 (3.3)
21	62.8 (63.2)	3.8 (4.0)	3.5 (3.7)
22	56.6 (56.6)	3.5 (3.6)	3.3 (3.3)
23	63.0 (63.2)	3.8 (4.0)	3.6 (3.7)
24[b]	56.6 (56.0)	3.4 (3.5)	3.2 (3.2)
25[c]	62.2 (62.2)	3.7 (4.0)	1.7 (1.7)
26	64.5 (64.8)	4.0 (4.1)	1.8 (1.8)
27	62.8 (63.2)	3.7 (4.0)	3.5 (3.7)
28	56.0 (56.6)	3.3 (3.5)	3.2 (3.3)
29	63.5 (63.2)	3.8 (4.0)	3.5 (3.7)
31[d]	63.4 (63.2)	4.1 (4.3)	3.7 (3.7)
32	57.1 (57.1)	3.6 (3.7)	3.4 (3.4)
33	63.7 (63.9)	4.1 (4.1)	3.7 (3.8)
34	65.6 (65.7)	4.3 (4.3)	1.8 (1.9)
35	66.9 (67.0)	4.5 (4.6)	3.3 (3.4)

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

[b] Isolated as a 1:1 chloroform solvate to which these figures apply.

[c] Isolated as a 1:0.5 dichloromethane solvate to which these figures apply.

[d] Isolated as a 1:0.5 methanol solvate to which these figures apply.

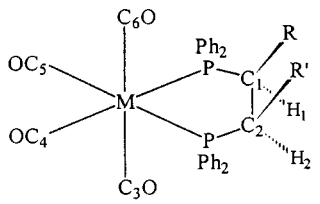
All facially *P*,*P*′,*N*-coordinated tricarbonyl complexes were obtained in high yield as air-stable orange or red crystalline solids with significantly lower solubility than their tetracarbonyl precursors in all common organic solvents.

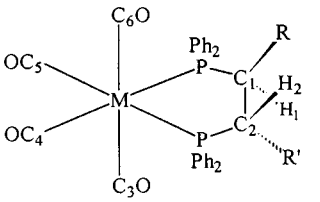
The inability of the complexes of *rac*- or *threo*-stereochemistry **21**, **22**, **26**, **29**, **30** to undergo simple *N*-coordination with retention of stereochemistry can be explained on steric grounds. In a previous study on their C-phenyl analogues we have shown that in the crystalline state the two C-phenyl groups adopt exclusively equatorial positions with respect to the chelate ring (Fig. 1(iii)) rather than the alternative arrangement where they are both axial (Fig. 1(iv)) [11]. The former arrangement minimises steric interactions between C-phenyl and P-phenyl groups which would be significant in the latter conformation. If the complexes reported here predominantly adopt analogous conformations in solution then *N*-coordination of a C-pyridyl or C-pyrimidyl group in an available axial position forces the other C-aryl substituent into an axial position with the result that both groups then experience severe steric interactions with the P-phenyl groups.

Conversely, in the case of *meso* stereochemistry, the two substituents between them necessarily adopt one axial and one equatorial position (Fig. 1(i/ii)). Therefore, coordination of a C-(2-pyridyl) or C-(2-pyrimidyl) group in a complex of *meso* or *erythro* stereochemistry is likely to cause little additional steric disruption over that already present in the tetracarbonyl derivative itself. Support for this postulation is provided by scrutiny of the NMR parameters (see later).

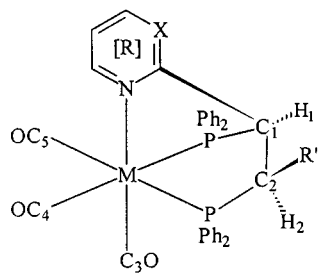
2.4. Deuterium exchange studies

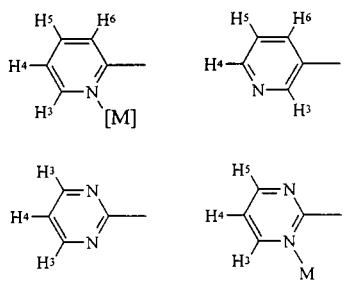
In a refluxing mixture of diglyme/D_2O (100:1 v/v, b.p. ca. 135°C, 24 h) the conversion of **22** to **32** as described results in ca. 70% deuterium incorporation at each of the two ligand backbone positions (H^1 and H^2) as determined from the ^{1}H-NMR spectrum. Experiments involving a shorter reflux period (ca. 6 h) allowed the recovery of unreacted starting material which NMR spectroscopy showed to be ca. 55% deuterated at the H^1

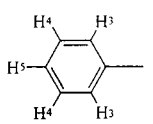




Stereochem.	M: Mo	M: W	R	R'	M: Mo	M: W	Stereochem.
meso	**19**	**20**	2-pyridyl	2-pyridyl	**21**	**22**	*rac*
meso	**23**	-	3-pyridyl	3-pyridyl	-	-	-
erythro	**24**	-	2-pyridyl	3-pyridyl	-	-	-
erythro	**25**	-	2-pyridyl	phenyl	**26**	-	*threo*
erythro	**27**	**28**	2-pyrimidyl	phenyl	**29**	**30**	*threo*







Stereochem.	M: Mo	M: W	X	[R]	R'
erythro	**31**	**32**	CH	[2-pyridyl]	2-pyridyl
erythro	**33**	-	CH	[2-pyridyl]	3-pyridyl
erythro	**34**	-	CH	[2-pyridyl]	phenyl
erythro	**35**	**36**	N	[2-pyrimidyl]	phenyl

Scheme 3.

and H^2 positions. Surprisingly also, the conversion of **20** to **32** shows 30% deuterium exchange under similar conditions (24 h reflux) although no inversion is actually necessary for this transformation. Relevant ^{1}H-NMR spectra from these experiments have been published in a preliminary communication [16].

The formation of **32** from **22** clearly involves inversion at one of the backbone carbon atoms and the results of the H/D exchange experiments suggest strongly a mechanism involving deprotonation at a backbone carbon atom to give a carbanion followed by reprotonation. Inversion of carbon via a carbanion intermediate during a chemical transformation has many literature precedents [25] although this case is an unusual example. In this instance inversion, in the absence of added base, implies that the pyridyl groups in **22** are themselves strong enough bases at the reaction temperature to deprotonate a backbone CH group. This process is probably also facilitated by a relatively high acidity of the CH protons (in accord with the known acidities of methyl protons in 2-methylpyridine [26] and methylphosphine derivatives [27]) and enhanced further by the coordination of the phosphorus. The inability of **21**, **29**, and **30** to undergo inversion under similar conditions also suggests that both the number and exact locations of the pyridyl nitrogens are crucial to the deprotonation step, a requirement with close parallels to that of certain proton-sponges [28] and that the deprotonation step may be an intramolecular rather than an intermolecular process. The recovery of partially deuterated **22** combined with the formation of deuterated **32** and the absence of **20** from reaction mixtures show that (i) the deprotonation step is reversible, (ii) the reprotonation step is non-diastereoselective, and (iii) that the *N*-coordination step is rapid at the reaction temperature for the *meso*-form.

2.5. NMR parameters

Selected ^{31}P-, ^{1}H- and ^{13}C-NMR parameters for all isolated species are given in Tables 3 and 4.

2.5.1. Free ligands

^{31}P chemical shifts for the the *meso* and *erythro* free ligands are typically 10–12 ppm higher than for their *rac* and *threo* counterparts, this feature parallels that found for their bis(C-phenyl) analogues previously reported. Magnitudes of $^{3}J(^{31}P^{31}P)$ for the unsymmetrical species range from 11.0 to 30.0 Hz, although no obvious pattern is evident. The spectra of **7** and **8** showed significant broadening of the ^{31}P resonance which is possibly indicative of restricted rotation within the molecule. The unsymmetrical diphosphines **11**, **13**–**15**, **17** and **18** each show broadening of only one of the two resonances. The ^{1}H and ^{13}C spectra for the free ligands are highly complex and only parameters for the backbone CH groups were deducible. No clear distinction between the various stereochemistries is apparent from the available ^{1}H- and ^{13}C-NMR data for these species and this is as expected based on the known difficulty in rationalising values of $J(^{31}P^{1}H)$ and $J(^{31}P^{13}C)$ in molecules containing P^{III}.

2.5.2. Tetracarbonyl complexes

δ^{31}P for the complexes **19**–**30** are in conformity with those expected from considerations of size of chelate-rings incorporating phosphorus for the relevant metal [29]. In contrast to the ^{1}H- and ^{13}C-NMR data for the free ligands, corresponding data for their tetracarbonyl complexes reveal extensive information on stereochemistry and also, importantly, on chelate ring conformations.

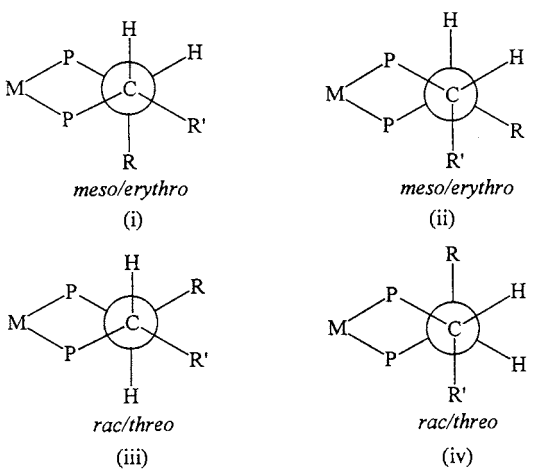


Fig. 1. Newman projections down the C^2–C^1 bond showing idealised staggered conformations of *meso*-(R = R′), *erythro*-(R ≠ R′), *rac*-(R = R′), and *threo*-(R ≠ R′) diphosphine complexes of formula $M(CO)_4L$. Carbonyl ligands and P-phenyl groups have been omitted for clarity.

Patterns of resonances in the ^{13}C spectra in the carbonyl region for the tetracarbonyl complexes **19**–**30** serve unequivocally to identify the stereochemistry of the parent ligands. The spectrum of **19** shows one equatorial and two axial resonances consistent only with *meso* stereochemistry. The spectrum of its isomer **21** shows one equatorial and one axial resonance consistent with the *rac* form. Moreover the chemical shift of the two equivalent axial carbonyl carbons (210.7 ppm) in **21** lies approximately at the mean position of the two inequivalent axial signals in **19** which are separated by 6.6 ppm (206.9 and 213.5 ppm). Corresponding patterns are seen in other *meso* or *rac* complexes **20**, **22** and **23**. The less symmetrical tetracarbonyl complexes **24**–**30** each have two equatorial and two axial carbonyl signals in their ^{13}C-NMR spectra irrespective of ligand stereochemistry but close inspection of the patterns allows a deduction of the stereochemistry. As an example, **25** exhibits signals separated by 5.4 ppm (213.3 and 207.9 ppm) which from chemical shift and coupling data are clearly from two chemically inequivalent axial carbonyls. In its isomer **26** these resonances are at separated by 0.2 ppm (211.0 and 211.2 ppm) and this reflects very similar but not identical chemical environments. Comparison with the chemical shift separations for the unambiguous *meso* and *rac* patterns of **19** and **21** mentioned earlier (6.6 and 0 ppm, respectively) leads to the clear assignment of **25** and **26** as *erythro* and *threo*, respectively. Corresponding patterns of axial resonances also identify the stereochemistry in the other tetracarbonyl derivatives **27**–**30**, the general pattern being separations of 5.4–6.3 ppm for the *erythro* complexes and 0.2–1.1 ppm for the *threo* ones. Small chemical shift separations between the inequivalent equatorial carbonyls are also observed in **24**–**30**. These are in the mutually exclusive ranges 1.2–1.6 ppm and 0.4–0.6 ppm for *erythro*- and *threo*-stereochemistries, respectively but these are too close to each other to be used diagnostically with any certainty. Representative ^{13}CO spectra for the four possible stereochemical forms are shown in Fig. 2(a)–(d).

The symmetrical tetracarbonyl derivatives **19**–**23** have resonances for H^1 and H^2 which can be analysed as arising from the A portion of an AA′XX′ spin system [30] (A = H^1/ H^2, X = P^1/P^2). In this system no single coupling constant can be determined from analysis of the spectrum without making assumptions concerning the magnitudes and signs of the other coupling constants defining the spin system. In contrast, the lower symmetry of complexes **24**–**30** permits a full analysis and the diagnostically important parameter $^{3}J(H^1H^2)$ can be determined. The magnitudes of $^{3}J(H^1H^2)$ in complexes of *erythro*- and *threo*-stereochemistry (4.0–4.6 and 13.7–14.1 Hz, respectively) indicate H^1–C^1–C^2–H^2 dihedral angles of ca. 50 and

Table 3
Selected ^{31}P- and ^{1}H-NMR data for the new diphosphine ligands and their complexes[a]

Compound	$\delta(^{31}P)$[b,c]	$\delta(H^1)$[j,k]	$\delta(H^2)$[j,k]	$\delta(H^R)$[l]	$\delta(H^{R'})$[l]
7	+3.1	4.95	4.95	[m]	[m]
8	−9.5	4.37	4.37	[m]	[m]
9	−4.5	4.86	4.86	[m]	[m]
11	−1.3, +0.5 (15.7)	4.74 (9.7, 6.0, 3.7)	4.49 (9.7, 7.9, 3.5)	[m]	[m]
13	−1.6, −0.1 (15.9)	4.65 (9.2, 6.1, 4.9)	4.54 (9.2, 9.2, 3.4 b)	[m]	[m]
14	−10.9, −12.0 (11.0)	4.30 (7.9, 5.9, 3.0)	3.90 (7.9, 5.9, 3.0)	[m]	[m]
15	−4.7, −5.0 (20.7)	4.20 ([m])	4.20 ([m])	[m]	[m]
17	+1.1, +2.8 (14.6)	4.87 (11.4, 7.5, 2.7)	4.79 (11.4, 4.7, 4.1)	[m]	[m]
18	−7.7, −10.8 (30.0)	4.53 (7.6, 5.3, 5.3)	4.11 (7.6, 5.0, 5.0)	[m]	[m]
19	+68.2	4.82 [11.1]	4.82 [11.1]	8.38, 6.91, 6.87, 5.66	8.38, 6.91, 6.87, 5.66
20	+52.9[d]	4.82 [9.5]	4.82 [9.5]	8.37, 6.93, 6.89, 5.69	8.37, 6.93, 6.89, 5.69
21	+63.8	4.82 [0]	4.82 [0]	8.02, 6.64, 6.92, 6.24	8.02, 6.64, 6.92, 6.24
22	+47.1[e]	4.84 [0]	4.84 [0]	8.03, 6.66, 6.94, 6.27	8.03, 6.66, 6.94, 6.27
23	+69.6	4.56 [9.2]	4.56 [9.2]	8.03, 8.26, 6.75, 6.93	8.03, 8.26, 6.75, 6.93
24	+67.3, +70.3 (11.0)	4.62 (4.0, 36.6, 11.3)	4.45 (4.0, 8.9, 4.6)	8.14, 6.94, 6.87, 6.04	8.09, 8.30, 6.68, 6.14
25	+65.9, +68.9 (11.0)	4.66 (4.3, 37.2, 11.6)	4.47 (4.3, 9.1, 5.2)	8.09, 6.93, 6.85, 6.06	6.44, 6.90, 7.06
26	+63.4, +65.0 (17.1)	4.52 ([m])	4.52 ([m])	8.06, [m], [m], 6.07	6.48, [m], [m]
27	+66.2, +69.0 (11.0)	5.06 (4.4, 37.8, 11.0)	4.46 (4.4, 9.5, 4.8)	8.10, 6.81	6.26, 6.90, 7.06
28	+51.4, +54.5 (<1)[f]	5.09 (4.6, 37.2, 11.6)	4.49 (4.6, 10.4, 4.6)	8.09, 6.83	6.28, 6.90, 7.06
29	+63.9, +64.9 (15.9)	4.79 (14.1, 5.0, 4.3)	4.75 (14.1, 6.9, 4.9)	8.01, 6.55	6.52, 6.73, 6.78
30	+47.1, +48.4 (6.1)[g]	4.80 (13.7, 4.6, 3.5)	4.76 (13.7, 6.4, 4.0)	8.02, 6.57	6.54, 6.73, 6.80
31	+52.2, +65.5 (4.9)	4.80 (3.0, 32.5, 8.6)	4.33 (3.0, 8.8, 6.6)	9.18, 7.03, 7.50, 7.29	8.28, 6.85, 6.85, 5.27
32	+41.5, +58.3 (3.0)[h]	4.98 (3.0, 32.0, 8.5)	4.37 (3.0, 9.5, 6.4)	9.30, 6.99, 7.53, 7.29	8.27, 6.81, 6.84, 5.38
33	+50.5, +63.9 (3.6)	4.43 (3.0, 32.0, 8.0)	4.11 (3.0, 8.9, 5.5)	9.36, 7.16, 7.50, 6.86	7.64, 8.20, 6.58, 5.65
34	+49.2, +63.1 (4.9)	4.46 (3.0, 32.6, 8.5)	4.08 (3.0, 9.2, 6.1)	9.33, 7.13, 7.46, 6.89	5.86, 6.81, 6.95
35	+50.0, +60.3 (7.3)	4.82 (3.0, 33.0, 8.2)	4.11 (3.0, 9.8, 6.6)	9.27, 7.05, 8.51	5.90, 6.83, 6.95
36	+ 40.9, +52.9 (<1)[i]	5.05 (3.0, 33.0, 8.2)	4.09 (3.0, 9.8, 7.0)	9.50, 7.01, 8.55	5.93, 6.84, 6.97

[a] NMR labelling as in Scheme 3.

[b] In ppm (±0.2ppm) to high frequency of external 85% H_3PO_4 (0.0 ppm), numbers in brackets are magnitudes of $^3J(^{31}P^{31}P)$ where measurable from the spectrum directly.

[c] Data for the free ligands (**7**–**18**) are from reaction mixtures in THF, data for the complexes (**19**–**36**) are from pure materials in $CDCl_3$.

[d] $^1J(^{183}W^{31}P) = 239.5$ Hz.

[e] $^1J(^{183}W^{31}P) = 230.9$ Hz.

[f] $^1J(^{183}W^{31}P) = 238.1$, 241.5 Hz.

[g] $^1J(^{183}W^{31}P) = 232.0$, 231.4 Hz.

[h] $^1J(^{183}W^{31}P) = 212.4$, 218.5 Hz.

[i] $^1J(^{183}W^{31}P) = 216.1$, 216.1 Hz.

[j] In ppm (±0.01) relative to internal TMS = 0.0 ppm, entries in parentheses are coupling constants, values of $J(^1H^1H)$ are underlined, values of $J(^{31}P^1H)$ follow in order of decreasing magnitude, entries in square brackets are values of $|^2J(^{31}P^1H)+^3J(^{31}P^1H)|$ in cases where the individual components can not be determined by inspection due to molecular symmetry.

[k] Relative assignment of H^1 and H^2 is arbitrary and may be reversed.

[l] Quoted in order $\delta(H^3)$, $\delta(H^4)$, $\delta(H^5)$, etc., for each aromatic group.

[m] Not determined due to unfavourable signal overlap.

180°, respectively, on the basis of a Karplus relationship [31] and this confirms the dominance in solution of conformation (iii) of Fig. 1 for the *rac* and *threo* isomers. Proton chemical shift separations between H^1 and H^2 in *erythro* isomers are significantly larger than for the *threo* isomers and this reflects the spatially and hence chemically dissimilar (axial and equatorial) environments of H^1 and H^2 in the former case and the similar (axial and axial) positions in the latter. Further corroboration is evident in the striking differences between coupling parameters for H^1 and H^2 in *erythro* complexes in comparison to their similarity in each *threo* case. ^{13}C parameters for C^1 and C^2 show similar but less pronounced features.

In molecules of *rac*- or *meso*-stereochemistry the aromatic groups fall into three chemically inequivalent types whereas in complexes of *erythro*- or *threo*-stereochemistry all six aromatic groups are inequivalent. As a result the aromatic regions of the spectra are complex. However in all species the C-aromatic substituents give remarkably disperse signals which allows a near complete analysis for these groups. Particularly striking are the peculiarly low chemical shifts for protons *ortho* to the carbon bonded to the ligand backbone. In **19** these

Table 4
Selected ^{13}C-NMR data for the new diphosphine ligands and their complexes[a]

Compound	$\delta(C^1)$[b]	$\delta(C^2)$[b]	$\delta(C^3)$[b]	$\delta(C^4)$[b]	$\delta(C^5)$[b]	$\delta(C^6)$[b]
7	[c]	[c]	–	–	–	–
8	48.2 [2.7]	48.2 [2.7]	–	–	–	–
9	[c]	[c]	–	–	–	–
11	45.8 (22.9, 20.2)	51.4 (23.8, 18.3)	–	–	–	–
13	48.5 (22.9, 18.3)	51.6 ([d])	–	–	–	–
14	45.7 (15.6, 15.6)	47.7 ([d])	–	–	–	–
15	47.1 (16.1, 16.1)	49.3 (18.4, 15.6)	–	–	–	–
17	48.8 (24.8, 20.2)	52.8 (12.0, 12.0)	–	–	–	–
18	46.9 (18.3, 18.3)	49.4 (16.5, 12.8)	–	–	–	–
19	53.7 [30.1]	53.7 [30.1]	213.5 (10.0, 10.0)	217.4 [18.9]	217.4 [18.9]	206.9 (7.6, 7.6)
20	54.8 [32.9]	54.8 [32.9]	205.7 (9.1, 9.1)	208.2 [19.5]	208.2 [19.5]	199.3 (4.3, 4.3)
21	53.3 [36.6]	53.3 [36.6]	210.7 (8.0, 8.0)	216.7 [17.1]	216.7 [17.1]	210.7 (8.0, 8.0)
22	54.7 [39.0]	54.7 [39.0]	203.1 (6.4, 6.4)	207.9 [18.3]	207.9 [18.3]	203.1 (6.4, 6.4)
23	50.6 [31.7]	50.6 [31.7]	214.4 (8.5, 8.5)	215.8 [17.1]	215.8 [17.1]	206.3 (6.7, 6.7)
24	54.4 (12.7, 12.7)	48.8 (20.8, 9.8)	213.2 (9.8, 9.8)	217.6 (26.9, 8.6)	216.1 (28.5, 8.6)	207.5 (6.3, 6.3)
25	54.1 (14.8, 14.8)	51.8, (20.1, 11.0)	213.3 (9.8, 9.8)	218.0 (26.5, 8.5)	216.4 (27.5, 8.5)	207.9, (6.7, 6.7)
26	53.2 (23.2, 13.4)	51.8 (22.6, 15.3)	211.2 (8.6, 8.6)	216.9 (24.4, 8.6)	216.5 (25.7, 8.6)	211.0 (8.0, 8.0)
27	55.4 (15.0, 15.0)	52.3 (19.5, 9.8)	213.9 (9.8, 9.8)	217.8 (26.9, 8.5)	216.2 (27.5, 8.5)	207.6 (7.0, 7.0)
28	55.7 (18.3, 13.4)	54.0 (17.1, 15.9)	205.9 (8.6, 8.6)	208.4 (25.7, 6.1)	207.2 (26.8, 6.1)	200.2 (4.3, 4.3)
29	53.1 ([e])	53.1 ([e])	211.5 (8.5, 8.5)	217.0 (24.4, 8.5)	216.4 (25.7, 8.5)	210.4 (8.0, 8.0)
30	54.6 (20.7, 20.7)	53.7 (23.2, 15.9)	203.7 (7.3, 7.3)	208.1 (23.2, 6.1)	207.5 (23.4, 6.1)	202.8 (7.3, 4.9)
31	55.3 (17.2, 17.0)	45.9 (17.6, 7.4)	228.0 (8.1, 8.1)	222.1 (36.5, 10.0)	220.8 (36.5, 10.0)	–
32	58.6 (17.7, 17.7)	46.3 (17.1, 11.0)	220.2 (4.9, 4.9)	218.3 (35.4, 7.4)	215.5 (36.7, 7.4)	–
33	58.5 (19.5, 14.7)	40.9 (18.3, 8.5)	227.9 (7.4, 7.4)	223.0 (36.6, 9.8)	221.0 (36.6, 9.8)	–
34	58.7 (19.2, 15.2)	43.8 (17.1, 8.5)	228.3 (7.3, 7.3)	223.4 (36.6, 9.8)	221.3 (36.6, 9.8)	–
35	58.5 (17.6, 17.6)	44.4 (16.5, 8.5)	228.0 (7.6, 7.6)	220.7 (36.0, 9.8)	222.9 (35.4, 9.8)	–
36	60.5 (17.7, 17.7)	44.0 (15.9, 12.8)	219.8 (4.9, 4.9)	217.8 (34.8, 7.4)	215.0 (35.4, 7.4)	–

[a] NMR labelling as in Scheme 3, relative assignments of C^1 and C^2, of C^3 and C^6, and of C^4 and C^5 are arbitrary and each may be reversed.
[b] In ppm (± 0.1 ppm) relative to internal TMS = 0.0 ppm, entries in parentheses are $^nJ(^{31}P^{13}C)$ placed in order of decreasing magnitude, entries in square brackets are values of $|^1J(^{31}P^{13}C)+^2J(^{31}P^{13}C)|$ for cases where the individual components can not be determined by inspection due to molecular symmetry.
[c] Not determined due to insolubility of the compound.
[d] Not resolved due to a broad signal.
[e] Not determined due to unfavourable signal overlap and/or molecular symmetry.

protons (H^6) give a signal at 5.66 ppm which is ca. 1.5 ppm lower than would normally be anticipated. The most likely cause of this low chemical shift is probably anistropic ('ring-current') effects from the nearby aromatic groups. This feature is repeated in all tetracarbonyl derivatives reported herein (with the exception of **23**). In the unsymmetrical species each C-aromatic group exhibits this feature to some extent and the effect is generally greater in complexes of *meso* or *erythro* geometry than their *rac* or *threo* counterparts.

2.5.3. Tricarbonyl derivatives

The ^{31}P, ^{13}C and ^{1}H parameters of the tricarbonyl complexes **31**–**36** are consistent with the structures shown in Scheme 3 but in no case is the ligand stereochemistry itself simply apparent. However, consideration of the NMR data supports that proposed in Scheme 3, in particular the close parallel between ^{1}H-NMR parameters for the *erythro*-tricarbonyl complexes and their *erythro*-tetracarbonyl precursors. A simple *N*-coordination step for a tetracarbonyl complex results in relatively small changes in the magnitudes of all five couplings involving H^1 and/or H^2. These small changes support the earlier proposal that in the *erythro*-tetracarbonyl derivatives an aromatic substituent occupies a position close to that required for axial coordination and hence causes little conformational perturbation on doing so. Fig. 3 shows relevant portions of selected ^{1}H spectra to illustrate this proposal.

N-Coordination of one of the aromatic groups causes ca. 1 and 0.5 ppm increases, respectively, in δ for the protons *ortho* and *para* to the coordinating nitrogen, the effects on the *meta* protons being less pronounced. Interproton coupling constants involving aromatic protons are unremarkable and are not reported here.

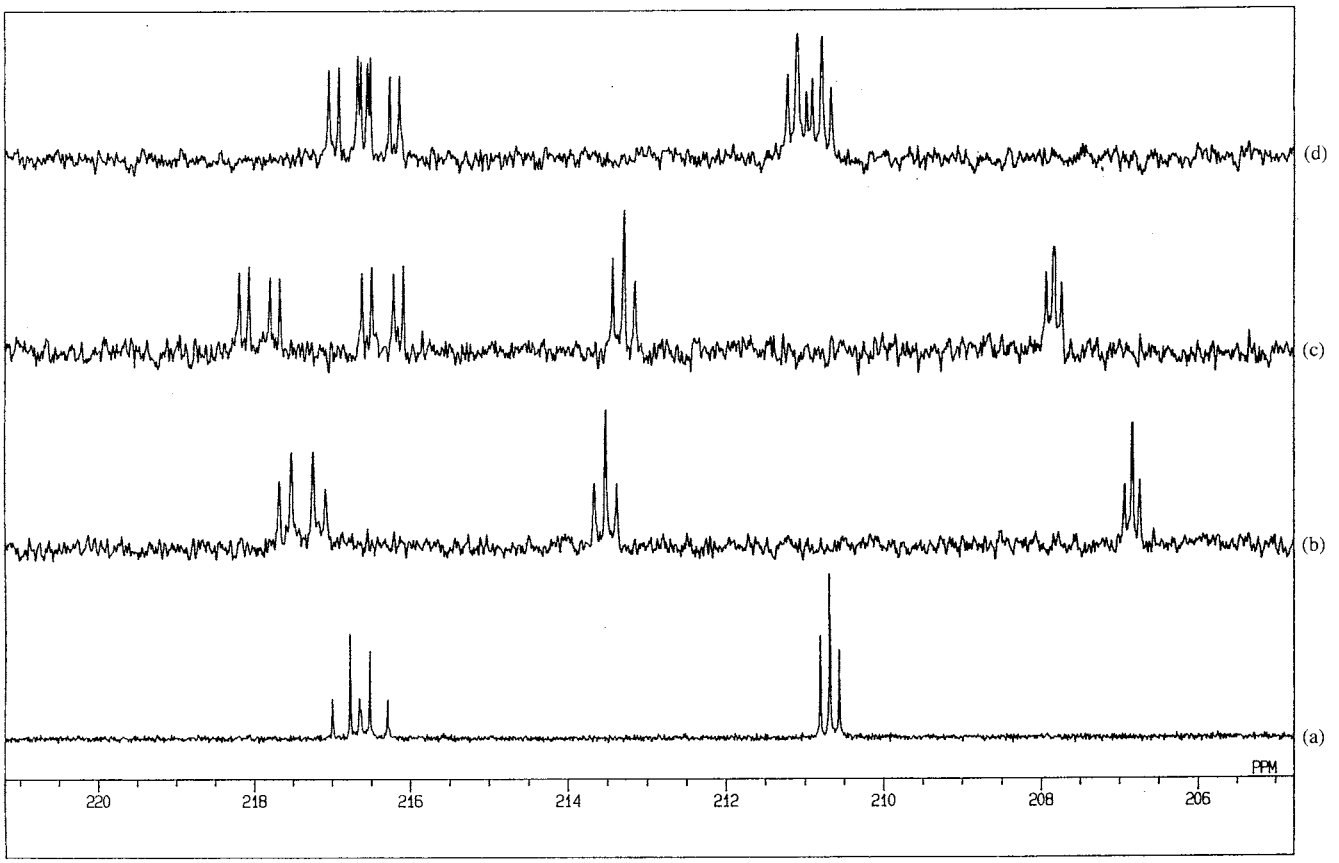


Fig. 2. (a)–(d) ^{13}C-NMR spectra at 67.8 MHz of the carbonyl regions for **21**, **19**, **25**, and **26** illustrating the diagnostic patterns for *rac*-, *meso*-, *erythro*-, and *threo*-stereochemistries, respectively.

3. Experimental

Solvents were dried and deaerated by standard procedures prior to use and all manipulations were performed under an atmosphere of dry N_2. Diphenylphosphine and benzyltriethylammonium chloride were purchased from Strem Chemicals Inc. and Lancaster Synthesis, respectively, and used without further purification. $Mo(CO)_4(piperidine)_2$ and $W(CO)_4(piperidine)_2$ [24] and $Pd(PPh_3)_4$ [32] were prepared immediately before use by previously published methods.

3.1. Alkyne synthesis

3.1.1. Di(2-pyridyl)ethyne **1**

2-Bromopyridine (40 g, 0.25 mol) and 2-methyl-3-butyn-2-ol (10.5 g, 0.125 mol) were dissolved in toluene (100 cm^3) and added to a suspension of $Pd(PPh_3)_4$ (2 g, catalytic amount), (2 g, catalytic amount), and benzyltriethylammonium chloride (2 g, catalytic amount), in 5.5 N aqueous sodium hydroxide (100 cm^3). The two phase mixture was stirred under nitrogen at 60–70°C until the reaction, as monitored by GC/MS analysis of the toluene layer, was complete (ca. 168 h). The cooled mixture was then filtered through a course filter and the product extracted with diethylether/water. After drying and evaporation of the solvent under reduced pressure the product was distilled at reduced pressure (240°C, 1 mmHg) to give the product as yellow oil (17.4 g, 77%) which crystallised slowly on standing.

3.1.2. Di(3-pyridyl)ethyne **2**

This was prepared and isolated using a procedure analogous to that above using 3-bromopyridine in place of 2-bromopyridine and gave a product of similar appearance and in a similar yield to that described above.

3.1.3. (2-Pyridyl)(3-pyridyl)ethyne **3**

Again, this was prepared and isolated similarly to the above using a one-pot stepwise 1:1 reaction of 2-bromopyridine with 2-methyl-3-butyn-2-ol at 40°C for 48 h followed by addition of 3-bromopyridine and stirring at 60–70°C for a further 96 h. The first step of the reaction was monitored by GC/MS to ensure the complete conversion of 2-bromopyridine to 4-(2-pyridyl)-2-methyl-3-butyn-2-ol before introduction of the second reagent.

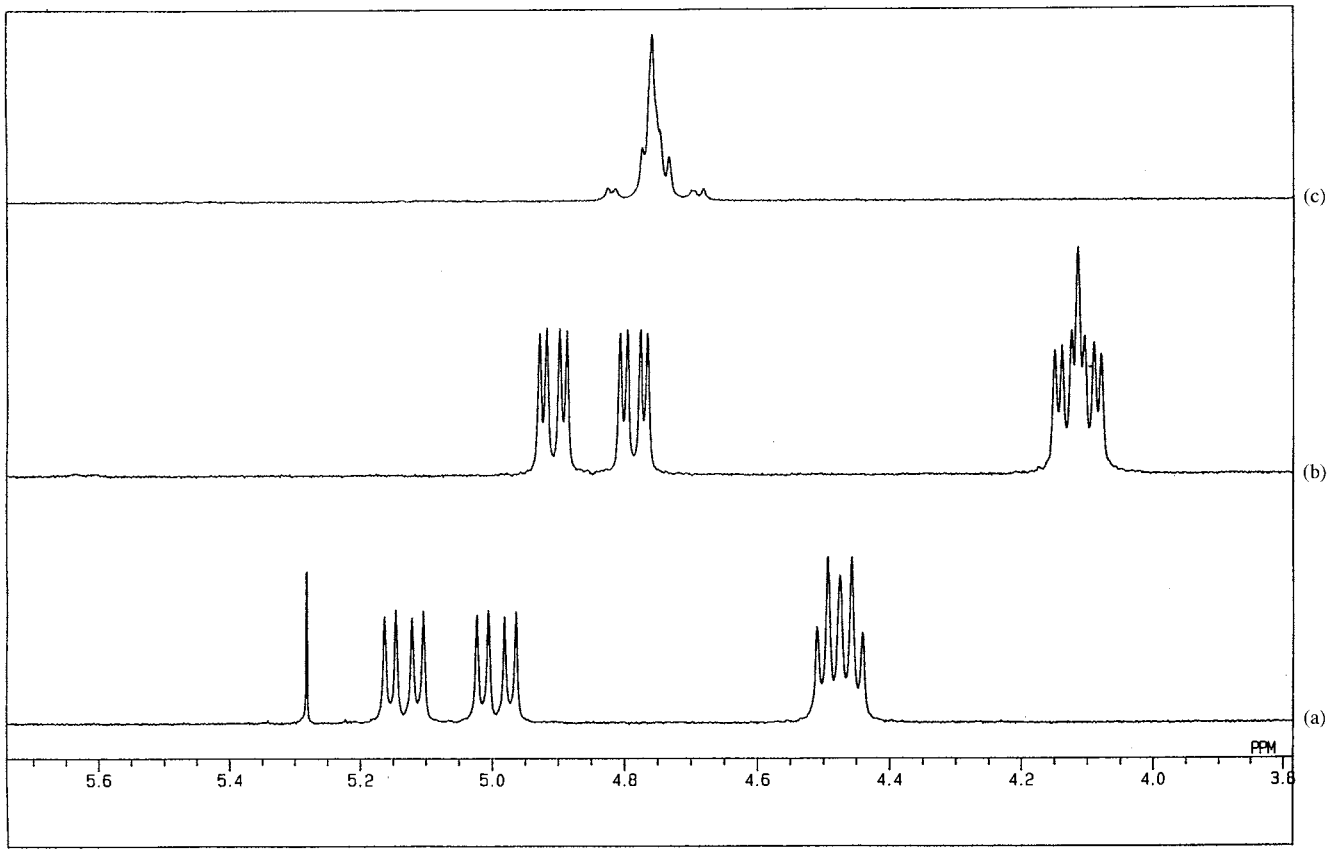


Fig. 3. Portions of the ^{1}H-NMR spectra at 270 MHz of the H^1 and H^2 regions for **27**, **35**, and **29** [(a)–(c), respectively] showing the similar patterns for a *cis-erythro*-tetracarbonyl complex **27** and its *fac-erythro*-tricarbonyl derivative **35**; this is consistent in each case with chemically dissimilar (axial and equatorial) protons H^1 and H^2. In contrast, the corresponding *threo*-isomer **29** gives a highly second order pattern consistent with chemically similar H^1 and H^2 environments. The signal at δ 5.27 ppm in (a) is due to dichloromethane as an impurity.

3.1.4. Phenyl(2-pyridyl)ethyne **4**

A mixture of phenylacetylene (10 g, 0.1 mol), 2-bromopyridine (16 g, 0.1 mol), $PdCl_2(PPh_3)_2$ (1 g, catalytic amount), and CuI (1 g, catalytic amount) in diisopropylamine (100 cm^3) was stirred under an inert atmosphere for 24 h. After the addition of diethylether (100 cm^3) the solution was filtered and the solvent was removed at the pump to give a crude brown oil. The product was obtained as a pale yellow liquid (17 g, 90%) after distillation of the crude residue under reduced pressure (ca. 200°C, 1 mmHg). Phenyl(3-pyridyl)ethyne **5** and phenyl(2-pyrimidyl)ethyne **6** were obtained similarly using 3-bromopyridine and 2-bromopyrimidine in place of 2-bromopyridine.

3.2. Hydrophosphination reactions

3.2.1. Typical procedure

A solution of the ethyne (20 mmol), diphenylphosphine (40 mmol) and potassium *tert*-butoxide (0.5 g, catalytic amount) in a mixture of dry THF (50 cm^3) and triethylamine (25 cm^3) was stirred under an atmosphere of dry nitrogen for 2 h. Methanol (25 cm^3) was then added to the mixture which was subsequently left to stand until crystallisation was complete. The resultant solid was filtered, washed with methanol (50 cm^3) and dried in vacuo. The mother liquor and the methanol washings were combined and refrigerated for 48 h to give a further crystalline product which was isolated as before. Concentration of the mother liquor followed by extended refrigeration yielded further crystalline products in some cases. In all instances the first product to crystallise was the diphosphine with *meso*- or *erythro*-stereochemistry. Commonly, the second product was the diphosphine of *rac*- or *threo*-stereochemistry (when formed—see Table 1) and this was often contaminated with one or both of the corresponding phosphinoalkenes of *E*-stereochemistry (see Scheme 2 and Table 1). Later crystallising fractions contained greater proportions of these alkenes.

3.3. Diphosphine complexation reactions

3.3.1. Tetracarbonyl molybdenum derivatives

In a typical procedure mixture of the diphosphine (4 mmol) and $Mo(CO)_4(piperidine)_2$ (1.5 g, 4 mmol) in dichloromethane (40 cm^3) was stirred under nitrogen at ambient temperature for 2 h. The resulting solution was

filtered and methanol (40 cm^3) was added to the filtrate. The solution was refrigerated until crystallisation appeared complete at which point the product was filtered, washed with methanol (20 cm^3) and dried under vacuum. Recrystallisation from dichloromethane/methanol when necessary yielded the product as air stable pale-yellow crystals. Typical yields 80–90%.

3.3.2. Tetracarbonyl tungsten complexes

In a typical procedure a mixture of the diphosphine (4 mmol) and $W(CO)_4(piperidine)_2$ (1.8 g, 4 mmol) in chloroform (40 cm^3) was refluxed under nitrogen for 6 h. After cooling to r.t. and filtration the products were isolated from the filtrate as pale yellow crystals in exactly the same manner as described for the molybdenum derivatives above. Typical yields 80–90%.

3.3.3. Tricarbonyl molybdenum derivatives

In a typical procedure a solution of the appropriate tetracarbonyl precursor (2 mmol) in chloroform (25 cm^3) was refluxed under nitrogen for 2 h. The cooled solution was filtered and methanol (25 cm^3) was added to the filtrate. On standing orange/red crystals were deposited which were collected by filtration, washed with methanol, and dried in vacuo. Typical yields 80–90%.

3.3.4. Tricarbonyl tungsten derivatives

These were prepared in a similar manner to the tricarbonyl molybdenum derivatives above using a 4 h reflux in toluene in place of the 2 h reflux in chloroform. The isolation procedure was the same and yielded orange/red crystalline products in similarly high yields

None of the metal carbonyl complexes **19**–**36** exhibited clean melting behaviour; typically, decomposition without melting occurred on heating to temperatures of 250°C or above.

NMR spectra of pure products were recorded using $CDCl_3$ solutions contained in 5 mm outside diameter tubes on a JEOL EX270 spectrometer operating at 270.1, 67.8 and 109.4 MHz for ^1H, ^{13}C and ^{31}P, respectively. ^{31}P-NMR spectra of reaction mixtures were obtained following the addition of ca. 5% C_6D_6 to provide an internal locking signal.

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