Transition-metal Complexes of Di- and Tri-phosphines derived from 1,1-Bis(diphenylphosphinomethyl)ethene†

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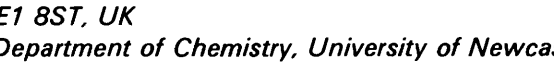
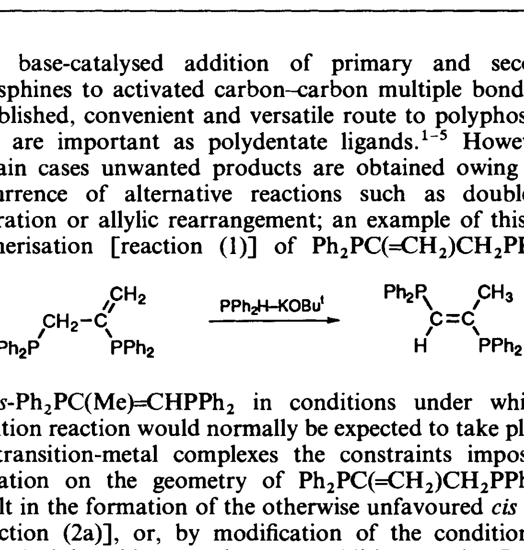
Base-catalysed rearrangements of and/or additions of PPh_2H to [M(CO)$_4${($Ph_2PCH_2)_2C$=CH_2}] (M = Cr **1a**, Mo **1b** or W **1c**) lead to *cis*-[M(CO)$_4${*cis*-Ph_2PCH=C(Me)CH_2PPh_2}] **2a–2c** and to *fac*-[M(CO)$_3${($Ph_2PCH_2)_2$C(Me)PPh_2}] **3b**, **3c**. The structures of **1b**, **2b** and **3b** have been determined by single-crystal X-ray diffraction. Marked differences are seen in the chelate-ring conformations of **1b** with an exocyclic C=C bond, **2b** with an endocyclic C=C bond, and *cis*-[Mo(CO)$_4${$Ph_2P(CH_2)_3PPh_2$}] with no C=C bond. Proton, ^{13}C and ^{31}P NMR data for **3b** and **3c** were obtained and a two-dimensional rotating frame nuclear Overhauser experiment was used to identify anisochronous methylene resonances in the proton NMR spectrum of **3b** thus confirming a dependence of ^3J(PH) on dihedral angle in these rigid polycyclic systems.

The base-catalysed addition of primary and secondary phosphines to activated carbon–carbon multiple bonds is an established, convenient and versatile route to polyphosphines that are important as polydentate ligands.[1–5] However, in certain cases unwanted products are obtained owing to the occurrence of alternative reactions such as double-bond migration or allylic rearrangement; an example of this is the isomerisation [reaction (1)] of $Ph_2PC(=CH_2)CH_2PPh_2$ to

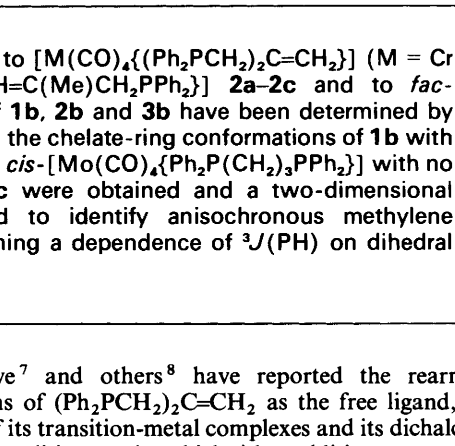

(1)

trans-$Ph_2PC(Me)$=$CHPPh_2$ in conditions under which an addition reaction would normally be expected to take place. In its transition-metal complexes the constraints imposed by chelation on the geometry of $Ph_2PC(=CH_2)CH_2PPh_2$ can result in the formation of the otherwise unfavoured *cis* isomer [reaction (2a)], or, by modification of the conditions, the desired triphosphine complex *via* an addition reaction [reaction (2b), thf = tetrahydrofuran].[6]

Previously, as part of extensive studies into reactions of this


(2a)
(2b)

type, we[7] and others[8] have reported the rearrangement reactions of $(Ph_2PCH_2)_2C$=CH_2 as the free ligand, and also those of its transition-metal complexes and its dichalcogenides. Under conditions under which either addition or rearrangement might be expected this ligand was found in fact to undergo normal allylic rearrangements with the geometry of the product being crucially dependent on the original form of the ligand. Thus rearrangement of $(Ph_2PCH_2)_2C$=CH_2 itself yielded a 30:70 mixture of its *cis* and *trans* isomers [reaction (3)] whereas when co-ordinated to a Group 6 metal carbonyl moiety the ligand is constrained by chelation and gave only a complex of its *cis* isomer [reaction (4)]. We now report that under more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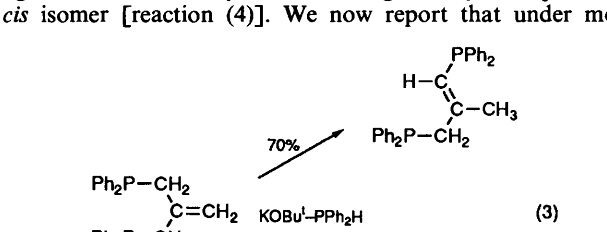
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M		M
1a Cr		**2a** Cr
1b Mo		**2b** Mo
1c W		**2c** W

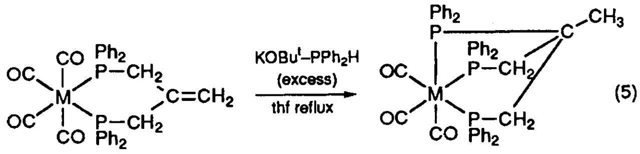
forcing conditions addition reactions can take place in complexes of this ligand to yield the desired new triphosphine complexes **3b** and **3c**. These have been isolated and characterised by elemental analysis and NMR spectroscopy. We also report the structures of the two molybdenum tetracarbonyl diphosphine complexes and the molybdenum tricarbonyl triphosphine complex as determined by single-crystal X-ray diffraction.

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Results and Discussion

Compound **3b** was prepared in 67% yield by the base-catalysed reaction of diphenylphosphine (*ca.* 50% excess) with **1b** in refluxing tetrahydrofuran. It was isolated after recrystallisation from dichloromethane–methanol as air-stable pale yellow crystals of the 1:1.5 dichloromethane solvate which has low solubility in common organic solvents. Compound **3c** was prepared in a similar manner from **1c**. These products were also obtained by treatment of **2b** and **2c** respectively with diphenylphosphine under similar conditions. Neither of the above procedures yielded the analogous chromium complex **3a** from **1a** or from **2a**. The mass spectra of **3b** and **3c** showed the molecular ions as well as ions corresponding to the loss of one CO, of two CO, and of three CO groups.

The mechanism of reaction (5) probably involves an initial ligand isomerisation **1b**/**1c** ⟶ **2b**/**2c** since this is known to be



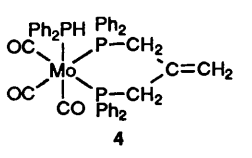
(5)

1b **1c** M **3b** Mo **3c** W

fast under these conditions.[6–9] Furthermore, identical products are obtained in this reaction from **1b**/**1c** and from **2b**/**2c**. However, it is less clear whether the subsequent addition reaction occurs before or after carbonyl displacement. Previously, we have shown that in similar compounds it is possible to prepare species with pendant PPh_2 moieties using addition reactions at room temperature and then to co-ordinate the pendant donor atom by displacement of CO at a higher temperature.[6,10] In this instance it is not possible to study the analogous stepwise reaction owing to the higher temperature required for the addition reaction.

An attempt was made to prepare *fac*-[Mo(CO)$_3$(PPh$_2$H){(Ph$_2$PCH$_2$)$_2$C=CH$_2$}] **4** by the direct 1:1 reaction of **1b** with PPh$_2$H in refluxing thf (2 h) in the absence of KOBu^t to determine whether this would then yield **3b** on addition of KOBu^t. However, the direct reaction yielded the *mer* isomer **5** (together with a range of by-products) in *ca.* 50% yield as indicated by ^{31}P NMR spectroscopy and this species was not isolated in analytically pure form. Subsequent addition of KOBu^t to this crude mixture and reflux (0.1 h) yielded only isomers **6** and **7** as the products readily identifiable in the reaction mixture. The most likely mechanism of the reaction of **1** to give **3** therefore appears to be isomerisation followed by addition and finally chelation.

Single-crystal X-Ray Analysis of Compounds **1b**, **2b** *and* **3b**.—Crystals of all three compounds suitable for single-crystal X-ray analysis were grown by diffusion of methanol into their solutions in dichloromethane. Crystals of **3b** were obtained as a 1:1.5 dichloromethane solvate. There are no unusually short intermolecular contacts in any of the structures. The structure of



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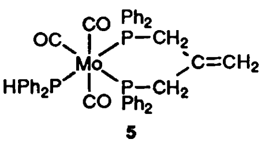

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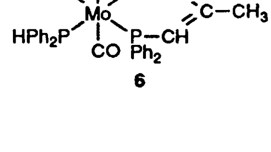

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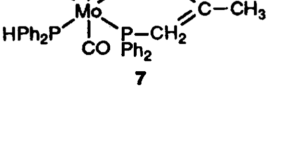

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3b contains both ordered and disordered (across an inversion centre) molecules of dichloromethane solvent.

The molecular structures of **1b**, **2b** and **3b** are shown in Figs. 1, 2 and 3 respectively whilst selected bond lengths and angles are given in Tables 1–4 together with those of [Mo(CO)$_4$(dppp)]. [dppp = 1,3-bis(diphenylphosphino)propane].[11]

Molybdenum–phosphorus bond lengths in the three complexes lie within the range 2.505–2.535 Å and are similar to those found in analogous complexes of 1,2-bis(diphenylphosphino)ethane (dppe)[12] and dppp.[11] Molybdenum–carbon bond lengths fall within the range 2.016–2.032 Å for Mo–C bonds *trans* to carbon, and within the range 1.973–1.999 Å for Mo–C bonds *trans* to phosphorus. In the two molybdenum diphosphine complexes **1b** and **2b** the P–Mo–P interbond

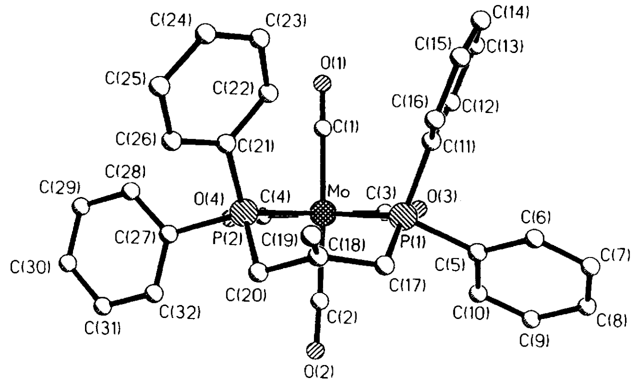

Fig. 1 Molecular structure of compound **1b**. The view is in the MoP$_2$C$_2$ co-ordination plane. Hydrogen atoms are omitted for clarity

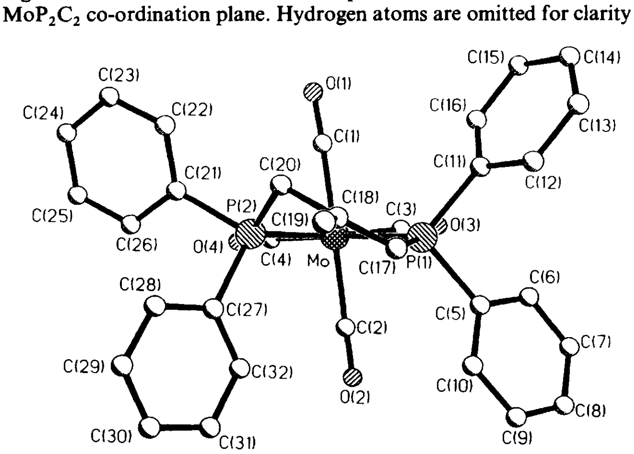

Fig. 2 Molecular structure of compound **2b**. The view is equivalent to that of Fig. 1. Hydrogen atoms are omitted for clarity

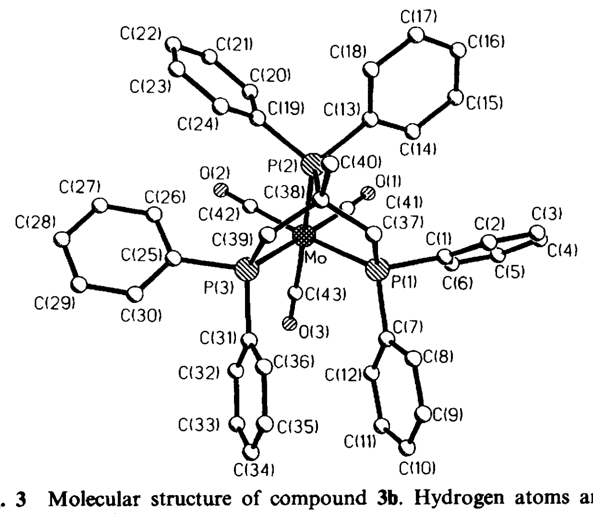

Fig. 3 Molecular structure of compound **3b**. Hydrogen atoms are omitted for clarity

Table 1 Selected bond lengths (Å) for compounds **1b**, **2b** and [Mo(CO)$_4$(dppp)]

	1b	**2b**	[Mo(CO)$_4$(dppp)][a]
P(1)–Mo	2.5199(11)	2.5164(11)	2.538(1)
P(2)–Mo	2.5094(13)	2.5050(11)	2.538(1)
C(1)–Mo	2.016(4)	2.032(5)	2.035(7)
C(2)–Mo	2.030(4)	2.030(5)	2.023(7)
C(3)–Mo	1.999(4)	1.993(5)	1.968(5)
C(4)–Mo	1.986(4)	1.987(5)	1.968(5)
C(17)–P(1)	1.846(4)	1.801(5)	1.833[b]
C(20)–P(2)	1.849(4)	1.830(5)	1.833[b]
C(17)–C(18)	1.503(5)	1.359(7)	1.524[b]
C(18)–C(19)	1.320(6)	1.488(8)	—
C(18)–C(20)	1.509(5)	1.454(7)	1.524[b]

[a] Atom numbering as for **1b** and **2b**. [b] Calculated from the atomic coordinates given in ref. 11.

Table 2 Selected bond lengths (Å) for **3b**

Mo–P(1)	2.5342(12)	P(1)–C(37)	1.864(4)
Mo–P(2)	2.5159(13)	P(2)–C(38)	1.891(4)
Mo–P(3)	2.5254(12)	P(3)–C(39)	1.865(3)
Mo–C(41)	1.973(4)	C(37)–C(38)	1.545(5)
Mo–C(42)	1.973(4)	C(38)–C(39)	1.537(5)
Mo–C(43)	1.976(4)	C(38)–C(40)	1.544(5)

Table 3 Selected bond angles (°) for compounds **1b** and **2b**

	1b	**2b**
P(1)–Mo–P(2)	85.14(4)	85.36(4)
P(1)–Mo–C(1)	98.29(11)	96.2(2)
P(1)–Mo–C(2)	89.84(12)	88.39(13)
P(1)–Mo–C(3)	90.52(11)	89.7(2)
P(1)–Mo–C(4)	174.92(13)	176.64(14)
P(2)–Mo–C(1)	95.90(11)	84.32(14)
P(2)–Mo–C(2)	88.52(13)	98.79(12)
P(2)–Mo–C(3)	175.57(11)	172.8(2)
P(2)–Mo–C(4)	91.33(12)	93.06(13)
C(1)–Mo–C(2)	171.0(2)	174.7(2)
C(1)–Mo–C(3)	83.8(2)	91.0(2)
C(1)–Mo–C(4)	85.7(2)	86.6(2)
C(2)–Mo–C(3)	92.4(2)	86.3(2)
C(2)–Mo–C(4)	86.4(2)	88.9(2)
C(3)–Mo–C(4)	93.1(2)	92.1(2)
Mo–P(1)–C(5)	117.95(12)	112.3(2)
Mo–P(1)–C(11)	115.74(11)	119.3(2)
Mo–P(1)–C(17)	115.65(11)	117.6(2)
Mo–P(2)–C(20)	112.83(13)	110.7(2)
Mo–P(2)–C(21)	122.78(12)	113.40(14)
Mo–P(2)–C(27)	112.16(13)	124.35(14)
P(1)–C(17)–C(18)	119.2(2)	124.9(4)
C(17)–C(18)–C(19)	121.7(3)	118.4(5)
C(17)–C(18)–C(20)	118.2(3)	126.5(5)
C(19)–C(18)–C(20)	120.1(4)	114.9(5)
C(18)–C(20)–P(2)	112.2(2)	115.4(3)

angles are 85.1 and 85.4° respectively and these values are approximately midway between the corresponding angles in [Mo(CO)$_4$(dppe)] (80.2°) and [Mo(CO)$_4$(dppp)] (89.7°).

For the present discussion of the structures of **1b**, **2b** and [Mo(CO)$_4$(dppp)] it is convenient to define an orthogonal coordinate system with Mo at the origin, the *z* axis perpendicular to the mean plane of the atoms P(1), P(2), Mo, C(3) and C(4) {none of these atoms deviates from this plane by more than 0.09 Å; root-mean-square deviations are 0.038 Å for **1b**, 0.065 Å for **2b** and 0.028 Å for [Mo(CO)$_4$(dppp)]}, and the *x* axis bisecting the P–Mo–P interbond angle. The chelate rings of **1b** and [Mo(CO)$_4$(dppp)] each adopt a chair conformation, but that in the former has much greater distortions from planarity. Thus in **1b** C(17), C(18) and C(20) are 1.055, 0.850 and 1.210 Å respectively below the *xy* plane, whereas in [Mo(CO)$_4$(dppp)] the corresponding deviations are −0.367, +0.286 and −0.367 Å. This difference must arise primarily from the larger interbond angle of 118.2° at the sp^2 hybridised C(18) in **1b**.

In **2b** *two* of the carbon atoms of the chelate ring are sp^2 hybridised, and in addition P(2), C(20), C(18) and C(17) are constrained to be approximately coplanar by the carbon–carbon double bond. This has a dramatic effect upon the ring-puckering [deviations from the *xy* plane are −0.251, +0.355 and +1.018 Å for C(17), C(18) and C(20) respectively] as can be seen from Figs. 1 and 2. Particularly noteworthy is the effect that the asymmetry of the chelate ring has upon the carbonyl groups. In **1b** and in [Mo(CO)$_4$(dppp)] the axial carbonyl groups are very close to the *xz* plane but are bent away from the chelate ring: C–Mo–C angles are 171 and 174.7° respectively. In **2b** however, the axial carbonyls are again bent away from the chelate ring (174.7°) but their bonds are also skewed by *ca.* 6° about the *y* axis. The sense of this rotation is such as to reduce their potential interactions with the P-phenyl groups.

In **3b** the P–Mo–P interbond angles are 81.3° for the two P atoms within the six-membered chelate ring and 77.8 and 78.5° for those within the five-membered rings. These reduced angles when compared to analogous angles in complexes of dppp and dppe reflect the increased ring strain(s) associated with a facially co-ordinated tridentate ligand with this 'bite capacity'. In addition, P–Mo–C$_{cis}$ bond angles are all similar and lie within the range 95.3–98.7°. Taken with the C–Mo–C$_{cis}$ angles of 84.8–88.7° this reveals an elongation of the molecule to reduce both the interphosphorus and intercarbonyl distances and angles.

Table 4 Selected bond angles (°) for **3b**

P(1)–Mo–P(2)	77.82(4)	C(41)–Mo–C(42)	84.8(2)
P(1)–Mo–P(3)	81.31(4)	C(41)–Mo–C(43)	88.7(2)
P(2)–Mo–P(3)	78.46(4)	C(42)–Mo–C(43)	87.2(2)
P(1)–Mo–C(41)	97.08(11)	Mo–P(1)–C(37)	106.35(12)
P(1)–Mo–C(42)	173.81(11)	Mo–P(2)–C(38)	101.52(11)
P(1)–Mo–C(43)	98.67(12)	Mo–P(3)–C(39)	107.17(12)
P(2)–Mo–C(41)	97.51(12)	P(1)–C(37)–C(38)	116.2(2)
P(2)–Mo–C(42)	96.10(12)	P(2)–C(38)–C(37)	104.9(2)
P(2)–Mo–C(43)	173.22(11)	P(2)–C(38)–C(39)	107.6(2)
P(3)–Mo–C(41)	175.88(11)	P(3)–C(39)–C(38)	115.5(2)
P(3)–Mo–C(42)	96.43(11)	C(37)–C(38)–C(40)	106.2(3)
P(3)–Mo–C(43)	95.34(12)	C(39)–C(38)–C(40)	109.1(3)

NMR Spectroscopy.—The NMR parameters of **1a**–**1c** and **2a**–**2c** have been presented and discussed previously;[7] proton and phosphorus-31 data for **3b** and **3c** are in Table 5 and their carbon-13 data are given in the Experimental section. NMR labelling for **3b** and **3c** is shown in Fig. 4. Although the parent triphosphine $Ph_2P_AC(CH_3)(CH_2P_BPh_2)_2$ is not yet available the ^{31}P chemical shifts of P$_A$ and P$_B$ can be estimated as δ +17 and −21 respectively by the use of group contribution theory.[13] In the absence of significant conformational imbalances these estimates can be expected to be correct to within ±3 ppm. Together with the observed chemical shifts in the complexes these values then give co-ordination chemical shifts[14,15] of *ca.* +69 and +55 ppm for P$_A$ and P$_B$ in **3b** and of +56 and +38 ppm in **3c**. The values of co-ordination chemical shifts for P$_A$ (which is included only in five-membered chelate rings) are close to those found for the tetracarbonyl molybdenum and tungsten complexes of dppe (+67.2 and +52.6 ppm respectively). The chemical shift values for P$_B$ lie approximately midway between the values found in the same molybdenum and tungsten complexes of dppe and their dppp analogues (δ +38.3 and +17.3).[16–18] They are therefore consistent with the inclusion of P$_B$ in both five-membered and six-membered chelate rings.

The proton spectra of **3b** and **3c** were assigned with the aid of ^{1}H-{^{31}P} decoupling experiments, although these did not permit the relative assignment of the inequivalent protons A

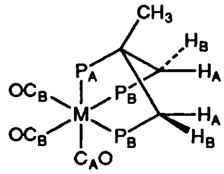

Fig. 4 Atomic labelling for NMR spectroscopy for compounds **3b** and **3c**. Phenyl groups are omitted for clarity

Table 5 Proton and ^{31}P NMR data for **3b** and **3c**[a]

	3b[b] (Mo)	**3c**[c] (W)
$\delta(CH_3)$	1.72	1.78
$\delta(CH_A)(CH_2)$	2.71	2.76
$\delta(CH_B)(CH_2)$	2.61	2.64
$\delta(C_6H_5)$	6.8–7.5	6.8–7.5
$^3J(P_ACH_3)$	2.2	2.1
$^4J(P_BCH_3)$	6.6	7.0
$^2J(P_BH_A)$	6.0	6.0
$^2J(P_BH_B)$	6.0	6.3
$^3J(P_AH_A)$	33.6	33.1
$^3J(P_AH_B)$	< 1	< 1
$^2J(H_AH_B)$	15.3	14.9

[a] Proton chemical shifts in ppm, ±0.02 ppm relative to $Si(CH_3)_4$ (δ = 0.00); ^{31}P chemical shifts in ppm, ±0.1 ppm relative to external 85% H_3PO_4 (δ = 0.0); coupling constants in Hz ±0.2 Hz. [b] $\delta(^{31}P_A)$ +86.1, $\delta(^{31}P_B)$ +33.7; $J(P_AP_B)$ 1.5 Hz. [c] $\delta(^{31}P_A)$ +73.2, $\delta(^{31}P_B)$ +16.8, $J(P_AP_B)$ 4.2 Hz; $^1J(^{183}W^{31}P_A)$ 211.2 Hz, $^1J(^{183}W^{31}P_B)$ 210.0 Hz.

and B of the CH_2 groups. In view of the striking difference in the coupling of P_A to each of these protons this assignment is important however and was accomplished using the two-dimensional rotating frame nuclear Overhauser (ROESY) experiment[19] illustrated in Fig. 5 for **3b**. This was obtained using the pulse sequence 90°–t_1–spin lock–acquire with a spin locking time of 400 ms and a radio frequency field $\gamma B_1/2\pi$ of 6000 Hz and was used in preference to a NOESY experiment[20] in order to avoid dependence upon molecular tumbling rate. By comparing the intensity of the off-diagonal peak at δ 1.71/2.61 with the combined intensities of the pair centred on δ 1.71/2.71 it can be seen that the NOE interaction of the methylene proton at δ 2.61 with the methyl protons is 1.5 times as great as that of those at δ 2.71. This reflects a smaller average internuclear distance in the former case. The magnitude of the NOE depends upon r^{-6} where r is the distance between the interacting nuclei; when there is internal motion it is necessary to calculate a suitably weighted average of r^{-6}. In general this is not easy because relative populations of conformations will not be known, but in the present case the only important relevant internal motion will be rotation of the methyl group which is reasonable to assume will be essentially unrestricted. On this assumption and that of idealised geometry at the methyl and methylene carbons [*i.e.* taking r_{CH} = 1.09 Å, H_ACH_B = 109° and the bisector of this angle to lie in the P(1)–C(37)–C(38) plane] numerical integration gives a ratio of the average values of $\langle r_{BCH_3}{}^{-6}\rangle/\langle r_{ACH_3}{}^{-6}\rangle$ of 1.6 thus showing that H_A gives the resonance at δ 2.71 and H_B that at δ 2.61. The same result was obtained for the protons of C(39).

The mean dihedral angles about the C(37)–C(38) and the C(38)–C(39) bonds relating P_A to H_A and H_B are 193 and 77° respectively, and thus correlate well with the observed $^3J(^{31}PH)$ couplings of 33.6 and *ca.* 0 Hz. Previous work on the angular dependence of such couplings[21] has suggested a Karplus ($\cos^2\theta$) type of relationship with large values of the coupling for $\theta \approx 180°$ and small ones for $\theta \approx 60$–$90°$. This is in conformity with the present result. By contrast, H_A and H_B have very similar stereochemical relationships to the neighbouring P_B and their two values of $^2J(^{31}PH)$ are almost identical.

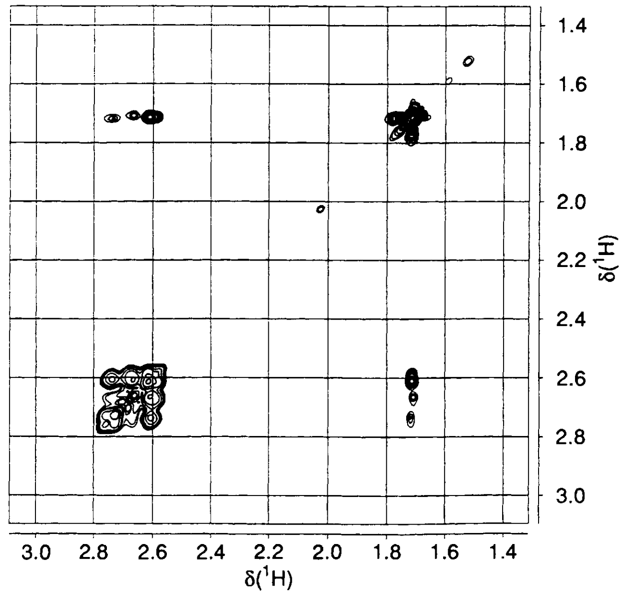

Fig. 5 Part of the phase-sensitive two-dimensional proton ROESY spectrum of compound **3b** measured at 500 MHz. 512 Free induction decays of 512 points each were transformed into a 1024 × 1024 matrix using a sine-bell weighting function in each dimension. Peaks on the main diagonal are positive and those off it are negative. Relative intensities quoted in the text were obtained by volume integration

Experimental

Solvents were dried and deaerated by standard procedures immediately prior to use and all manipulations were conducted under an atmosphere of dry nitrogen. Diphenylphosphine was purchased from Strem Chemicals and used without further purification. Compounds **1a**–**1c** and **2a**–**2c** were prepared using methods published previously.[7]

NMR spectra were recorded using $CDCl_3$ solutions contained in 5 mm outside diameter tubes on a Bruker AMX 500 spectrometer at measuring frequencies of 500.14, 125.76 and 202.46 MHz for ^1H, ^{13}C and ^{31}P respectively.

fac-*Tricarbonyl*[1,2,3-*tris*(*diphenylphosphino*)-2-*methylpropane*-P,P′,P″]*molybdenum*(0) **3b**.—A mixture of *cis*-[1,1-bis(diphenylphosphinomethyl)ethene-*P*,*P*′]tetracarbonylmolybdenum(0) **1b** (4.0 g, 6.3 mmol), diphenylphosphine (2.0 g, excess) and a catalytic amount of potassium *tert*-butoxide in thf (40 cm^3) was heated under reflux for 6 h. Methanol (40 cm^3) was added to the cooled and filtered solution to yield pale yellow crystals. Recrystallisation from dichloromethane (200 cm^3)–methanol (30 cm^3) gave the product as air-stable pale yellow crystals, yield 3.9 g, 67%. M.p. 285 °C (decomp.) (Found: C, 58.5; H, 4.4. $C_{43}H_{37}MoO_3P_3\cdot1.5CH_2Cl_2$ requires C, 58.2; H, 4.4%). ^{13}C NMR: δ 24.2 [dt, $^2J(P_AC)$ 3.7, $^3J(P_BC)$ 11.5, CH_3], 40.7 [m, $^2J(P_AC)$ 8.4, $^1J(P_BC)$ + $^3J(P_BC)$ 25.5, CH_2], 47.1 [dt, $^1J(P_AC)$ 18.9, $^2J(P_BC)$ 15.3, CCH_3], 134.0 [d, $^2J(P_AC)$ 11.5, *ortho*-P_APh], 131.4 [m, $^2J(P_BC)$ + $^4J(P_BC)$ 13.8, *ortho*-P_BPh], 130.7 [m, $^2J(P_BC)$ + $^4J(P_BC)$ 12.8, *ortho*-P_BPh′], 127.4 [d, $^3J(P_BC)$ 9.1, *meta*-P_APh], 128.0 [m, $^3J(P_BC)$ + $^5J(P_BC)$ 9.2, *meta*-P_BPh], 128.0 [m, $^3J(P_BC)$ + $^5J(P_BC)$ 9.6, *meta*-P_BPh′], 129.2 (s), 128.7 (s), 128.3 (s), *para*-PPh, 137.0 (complex m, *ipso*-P_APh), 137.0 (complex m, *ipso*-P_BPh), 139.5 [m, $^1J(P_BC)$ + $^3J(P_BC)$ 37.1, $^3J(P_AC)$ < 1, *ipso*-P_BPh′], 222.1 [m, $^2J(P_BC)_{cis}$ + $^2J(P_BC)_{trans}$ 16.6, $^2J(P_AC)_{cis}$ 7.9, C_BO] and 223.2 [dt, $^2J(P_AC)_{trans}$ 28.0, $^2J(P_BC)_{cis}$ 9.5 Hz, C_AO].

The analogous tungsten complex was prepared in a manner similar to that for the molybdenum complex described above starting from *cis*-[1,1-bis(diphenylphosphinomethyl)ethene-*P*,*P*′]tetracarbonyltungsten(0) **1c** and yielded air-stable pale yellow crystals in 70% yield. M.p. 310 °C (decomp.) (Found: C, 53.8; H, 3.7. $C_{43}H_{37}O_3P_3W\cdot1.5CH_2Cl_2$ requires C, 53.1; H,

Table 6 Crystallographic data

Compound	**1b**	**2b**	**3b**
Formula	$C_{32}H_{26}MoO_4P_2$	$C_{32}H_{26}MoO_4P_2$	$C_{43}H_{37}MoO_3P_3{\cdot}1.5CH_2Cl_2$
M	632.41	632.41	917.96
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1/n$	$P\bar{1}$
a/Å	9.030(3)	11.0726(12)	8.878(3)
b/Å	21.882(8)	16.933(2)	12.906(5)
c/Å	15.381(6)	16.385(2)	19.265(7)
α/°	90	90	79.43(3)
β/°	105.47(4)	103.687(11)	77.73(2)
γ/°	90	90	76.72(2)
U/Å^3	2929(2)	2984.9(6)	2078.1(13)
Z	4	4	2
D_c/g cm^{-3}	1.434	1.407	1.467
Radiation, λ/Å	Cu-Kα, 1.541 84	Cu-Kα, 1.541 84	Mo-Kα, 0.710 73
μ/mm^{-1}	4.98	4.89	0.66
F(000)	1288	1288	938
T/K	295	240	240
Crystal size/mm	0.30 × 0.20 × 0.15	0.40 × 0.25 × 0.25	0.58 × 0.24 × 0.20
Maximum 2θ/°	130	130	50
Maximum indices *hkl*	10, 25, 18	12, 19, 19	10, 15, 22
Transmission	0.257–0.406	0.083–0.240	
Reflections measured	5295	5060	11 370
Unique reflections	4873	5060	7338
R_{int}	0.018		0.025
Weighting parameters, *a*, *b*	0.0560, 1.6800	0.0985, 29901	0.0423, 3.4448
Extinction coefficient *x*	0.000 99(9)	0.000 44(11)	0
No. of refined parameters	353	354	497
R' (all data)	0.104	0.157	0.113
R (observed data)	0.034 (4008)	0.053 (4590)	0.043 (6319)
Goodness of fit	1.047	1.109	1.048
Max. shift/e.s.d.	0.003	0.001	< 0.0005
Max., min. electron density/e Å^{-3}	0.44, −0.76	1.40, −1.80	1.15, −1.14

Table 7 Atomic coordinates (× 10^4) for compound **1b**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Mo	2656.1(3)	6041.69(11)	6425.1(2)	C(14)	1088(5)	8582(2)	4760(3)
P(1)	2924.2(10)	6605.7(4)	5046.8(5)	C(15)	2562(6)	8479(2)	4734(4)
P(2)	5294.2(10)	6444.7(4)	7162.1(5)	C(16)	3169(5)	7890(2)	4826(3)
C(1)	1513(4)	6690(2)	6916(2)	C(17)	4864(4)	6601(2)	4865(2)
O(1)	749(4)	7000(2)	7213(2)	C(18)	6220(4)	6772(2)	5632(2)
C(2)	3652(5)	5295(2)	6037(3)	C(19)	7071(5)	7255(2)	5592(3)
O(2)	4192(5)	4856(2)	5864(3)	C(20)	6633(4)	6359(2)	6447(2)
C(3)	549(5)	5765(2)	5759(2)	C(21)	5659(4)	7244(2)	7496(2)
O(3)	−695(4)	5638(2)	5390(2)	C(22)	4534(5)	7681(2)	7197(3)
C(4)	2632(5)	5569(2)	7524(3)	C(23)	4852(6)	8299(2)	7355(3)
O(4)	2637(5)	5293(2)	8158(2)	C(24)	6299(6)	8482(2)	7815(3)
C(5)	1865(4)	6312(2)	3934(2)	C(25)	7434(6)	8053(2)	8131(3)
C(6)	1493(5)	6684(2)	3189(2)	C(26)	7119(5)	7440(2)	7967(3)
C(7)	721(6)	6464(2)	2350(3)	C(27)	6239(4)	6018(2)	8183(2)
C(8)	280(6)	5861(3)	2254(3)	C(28)	6085(5)	6207(2)	9012(3)
C(9)	669(6)	5483(2)	2989(3)	C(29)	6629(6)	5855(2)	9778(3)
C(10)	1446(6)	5700(2)	3825(3)	C(30)	7316(6)	5309(2)	9723(3)
C(11)	2278(4)	7402(2)	4950(2)	C(31)	7476(8)	5115(3)	8920(4)
C(12)	795(4)	7517(2)	4998(2)	C(32)	6933(7)	5463(2)	8141(3)
C(13)	199(5)	8102(2)	4897(3)				

4.0%). ^{13}C NMR: δ 23.1 [dt, $^2J(P_AC)$ 3.5, $^3J(P_BC)$ 11.4, CH_3], 41.5 [m, $^2J(P_AC)$ 8.6, $^1J(P_BC)$ + $^3J(P_BC)$ 31.2, CH_2], 50.6 [dt, $^1J(P_AC)$ 22.5, $^2J(P_BC)$ 13.8, CCH_3], 133.9 [d, $^2J(P_AC)$ 12.0, *ortho*-P_APh], 131.4 [m, $^2J(P_BC)$ + $^4J(P_BC)$ 13.8, *ortho*-P_BPh], 130.7 [m, $^2J(P_BC)$ + $^4J(P_BC)$ 12.0, *ortho*-P_BPh′], 127.5 [d, $^3J(P_BC)$ 10.0, *meta*-P_APh], 128.0 [m, $^3J(P_BC)$ + $^5J(P_BC)$ 10.0, *meta*-P_BPh], 128.0 [m, $^3J(P_BC)$ + $^5J(P_BC)$ 10.0, *meta*-P_BPh′], 129.4 (s), 128.7 (s), 128.6 (s), *para*-PPh, 133.6 [dt, $^1J(P_AC)$ 31.5, $^3J(P_AC)$ 2.5, *ipso*-P_APh], 136.6 [m, $^1J(P_BC)$ + $^3J(P_BC)$ 35.2, $^3J(P_AC)$ 6.3, *ipso*-P_BPh], 139.2 [m, $^1J(P_BC)$ + $^3J(P_BC)$ 44.0, $^3J(P_AC)$ 0, *ipso*-P_BPh′], 213.8 [m, $^2J(P_BC)_{cis}$ + $^2J(P_BC)_{trans}$ 17.6, $^2J(P_AC)_{cis}$ 7.4, C_BO] and 215.1 [dt, $^2J(P_AC)_{trans}$ 27.6, $^2J(P_BC)_{cis}$ 6.3 Hz, C_AO].

Attempts to prepare the analogous chromium complex using this procedure were unsuccessful.

X-Ray Crystallography.—Crystals of complexes **1b**, **2b** and **3b** were examined on a Stoe–Siemens four-circle diffractometer with graphite-monochromated radiation, and with a Cryostream cooler[22] for **2b** and **3b**. Crystallographic data are in Table 6. Cell parameters were refined from 2θ values of 32 reflections in each case, measured at ± ω to minimise systematic errors. Intensities were measured by ω–θ scans and on-line profile fitting.[23] A partial set of equivalent reflections was collected for **1b** and **3b**. No significant variation was observed in the intensities of three standard reflections monitored at regular

Table 8 Atomic coordinates ($\times 10^4$) for compound **2b**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Mo	2 232.0(3)	3 701.5(2)	7 461.7(2)	C(14)	7 701(5)	3 499(5)	7 059(4)
P(1)	3 743.7(10)	2 703.6(7)	7 146.7(6)	C(15)	6 835(5)	4 055(4)	7 149(3)
P(2)	2 372.1(10)	2 929.5(7)	8 785.0(6)	C(16)	5 640(5)	3 814(3)	7 158(3)
C(1)	3 527(5)	4 408(3)	8 201(3)	C(17)	4 096(6)	1 858(3)	7 829(3)
O(1)	4 198(4)	4 832(3)	8 617(3)	C(18)	4 260(4)	1 878(3)	8 677(3)
C(2)	842(4)	3 087(3)	6 692(3)	C(19)	4 735(10)	1 156(5)	9 167(5)
O(2)	45(3)	2 780(3)	6 234(2)	C(20)	3 936(5)	2 524(3)	9 169(3)
C(3)	2 353(5)	4 309(3)	6 442(3)	C(21)	2 161(4)	3 536(3)	9 668(3)
O(3)	2 441(5)	4 646(3)	5 841(3)	C(22)	3 150(4)	3 872(3)	10 252(3)
C(4)	968(5)	4 438(3)	7 709(3)	C(23)	2 922(5)	4 341(3)	10 886(3)
O(4)	237(4)	4 869(2)	7 839(3)	C(24)	1 733(5)	4 478(3)	10 957(3)
C(5)	3 178(4)	2 236(3)	6 118(3)	C(25)	742(5)	4 148(3)	10 386(3)
C(6)	3 353(5)	2 623(3)	5 405(3)	C(26)	961(4)	3 682(3)	9 744(3)
C(7)	2 865(6)	2 298(4)	4 615(3)	C(27)	1 389(5)	2 080(3)	8 876(3)
C(8)	2 228(6)	1 602(4)	4 537(4)	C(28)	1 438(6)	1 736(4)	9 649(3)
C(9)	2 044(6)	1 217(4)	5 233(5)	C(29)	693(7)	1 113(3)	9 727(4)
C(10)	2 520(5)	1 541(3)	6 030(4)	C(30)	−105(8)	816(4)	9 057(4)
C(11)	5 310(4)	3 025(3)	7 102(3)	C(31)	−135(11)	1 131(5)	8 278(5)
C(12)	6 195(5)	2 474(4)	6 995(4)	C(32)	615(8)	1 765(4)	8 193(4)
C(13)	7 385(6)	2 722(5)	6 986(5)				

Table 9 Atomic coordinates ($\times 10^4$) for compound **3b**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Mo	4 324.9(3)	7 002.2(2)	2 360.2(2)	C(25)	2 646(4)	9 230(3)	959(2)
P(1)	2 284.6(10)	5 827.5(7)	2 778.5(5)	C(26)	3 392(5)	9 934(3)	1 164(2)
P(2)	2 262.1(10)	8 099.0(7)	3 193.9(5)	C(27)	3 562(5)	10 901(3)	734(3)
P(3)	2 398.6(10)	7 961.9(7)	1 545.4(5)	C(28)	3 021(6)	11 176(4)	95(3)
C(1)	2 568(4)	4 761(3)	3 548(2)	C(29)	2 272(6)	10 489(4)	−115(2)
C(2)	1 358(5)	4 517(3)	4 097(2)	C(30)	2 088(5)	9 525(3)	314(2)
C(3)	1 681(7)	3 716(4)	4 663(2)	C(31)	2 011(4)	7 197(3)	910(2)
C(4)	3 166(7)	3 140(4)	4 675(3)	C(32)	3 295(4)	6 791(3)	409(2)
C(5)	4 362(6)	3 337(4)	4 116(3)	C(33)	3 104(5)	6 205(3)	−87(2)
C(6)	4 074(5)	4 148(3)	3 552(3)	C(34)	1 641(5)	6 016(3)	−100(2)
C(7)	1 768(4)	5 016(3)	2 203(2)	C(35)	374(5)	6 407(3)	391(2)
C(8)	268(5)	4 778(3)	2 306(2)	C(36)	551(4)	6 992(3)	892(2)
C(9)	−37(5)	4 113(3)	1 888(2)	C(37)	398(4)	6 734(3)	3 097(2)
C(10)	1 136(6)	3 650(3)	1 381(2)	C(38)	392(4)	7 952(3)	2 934(2)
C(11)	2 617(6)	3 867(4)	1 280(2)	C(39)	470(4)	8 384(3)	2 131(2)
C(12)	2 934(5)	4 555(3)	1 687(2)	C(40)	−1 171(4)	8 510(3)	3 357(2)
C(13)	1 929(4)	7 744(3)	4 176(2)	C(41)	5 714(4)	6 288(3)	3 055(2)
C(14)	2 664(5)	6 752(3)	4 489(2)	C(42)	5 743(4)	8 040(3)	2 083(2)
C(15)	2 379(6)	6 470(4)	5 232(2)	C(43)	5 748(4)	6 153(3)	1 639(2)
C(16)	1 394(6)	7 175(4)	5 660(2)	O(1)	6 603(4)	5 901(3)	3 440(2)
C(17)	667(6)	8 171(4)	5 359(2)	O(2)	6 640(3)	8 607(3)	1 932(2)
C(18)	934(5)	8 457(3)	4 619(2)	O(3)	6 621(4)	5 680(3)	1 219(2)
C(19)	2 318(5)	9 529(3)	3 111(2)	C(44)	7 059(9)	1 525(8)	1 680(5)
C(20)	3 662(6)	9 737(4)	3 280(2)	C(45)	4 632(29)	519(18)	5 054(13)
C(21)	3 859(8)	10 788(5)	3 228(3)	Cl(1)	8 966(2)	1 252.7(13)	1 293.3(8)
C(22)	2 763(8)	11 634(4)	3 001(3)	Cl(2)	6 869(4)	2 308(2)	2 405(2)
C(23)	1 448(7)	11 444(4)	2 822(2)	Cl(3)	6 452(4)	278(3)	4 667(2)
C(24)	1 219(5)	10 398(3)	2 883(2)				

intervals. Semiempirical absorption corrections were applied, except in the case of **3b**, based on sets of equivalent reflections measured at a range of azimuthal angles.[24]

The structures were solved by heavy-atom (**1b**) or direct (**2b**, **3b**) methods. Full-matrix least-squares refinement was carried out on F^2 values, with a weighting scheme $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = (2F_c^2 + F_o^2)/3$. Anisotropic thermal parameters were refined, and isotropic hydrogen atoms were constrained. An isotropic extinction correction multiplies F_c by the factor $(1 + 0.001F_c^2x\lambda^3/\sin 2\theta)^{-\frac{1}{4}}$, where x is the refined extinction coefficient. Residual indicators are defined as $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for 'observed' reflections with $F_o^2 > 2\sigma(F_o^2)$, $R' = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$ for all measured data. Atomic scattering factors were inbuilt in the refinement program.[24] Atomic coordinates are given in Tables 7–9.

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

Acknowledgements

We thank the SERC, Royal Society and Leverhulme Trust for financial support and Mr. J. Creighton for discussions.

References

1 R. B. King and P. N. Kapoor, *J. Am. Chem. Soc.*, 1969, **91**, 5191.
2 R. B. King, J. C. Cloyd jun. and P. N. Kapoor, *J. Chem. Soc., Perkin Trans.*, 1973, **1**, 2226.
3 R. B. King and J. C. Cloyd jun., *J. Am. Chem. Soc.*, 1975, **97**, 46.

4 J. L. Bookham, W. McFarlane and I. J. Colquhoun, *J. Chem. Soc., Chem. Commun.*, 1986, 1041.
5 J. L. Bookham, W. McFarlane, M. Thornton-Pett and S. Jones, *J. Chem. Soc., Dalton Trans.*, 1990, 3621.
6 J. L. Bookham and W. McFarlane, *J. Chem. Soc., Dalton Trans.*, 1990, 489.
7 J. L. Bookham and W. McFarlane, *Polyhedron*, 1991, **10**, 2381.
8 B. L. Shaw and J. D. Vessey, *J. Chem. Soc., Dalton Trans.*, 1991, 3303.
9 H. Schmidbauer, C. Paschalidis, O. Steigelmann and G. Müller, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1700.
10 J. L. Bookham, W. McFarlane and I. J. Colquhoun, *J. Chem. Soc., Dalton Trans.*, 1988, 503.
11 C.-H. Ueng and G.-Y. Hwang, *Acta Crystallogr., Sect. A*, 1991, **47**, 522.
12 I. Bernal, G. M. Reisner, G. R. Dobson and C. B. Dobson, *Inorg. Chim. Acta*, 1986, **121**, 199.
13 S. O. Grim, W. McFarlane and E. F. Davidoff, *J. Org. Chem.*, 1967, **32**, 781.
14 L. S. Merriwether and J. R. Leto, *J. Am. Chem. Soc.*, 1961, **83**, 1113.
15 B. E. Mann, C. Masters and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1972, 704.
16 S. O. Grim, W. L. Briggs, R. C. Barth, C. A. Tolman and J. P. Jesson, *Inorg. Chem.*, 1974, **13**, 1095.
17 G. T. Andrews, I. J. Colquhoun and W. McFarlane, *Polyhedron*, 1983, **2**, 783.
18 P. E. Garrou, *Chem. Rev.*, 1981, **81**, 229.
19 A. Bax and D. G. Davis, *J. Magn. Reson.*, 1985, **63**, 207.
20 A. Kumar, R. R. Ernst and K. Wüthrich, *Biochem. Biophys. Res. Commun.*, 1980, **95**, 1.
21 C. Benezra, *J. Am. Chem. Soc.*, 1973, **95**, 6890.
22 J. Cosier and A. M. Glazer, *J. Appl. Crystallogr.*, 1986, **19**, 105.
23 W. Clegg, *Acta Crystallogr., Sect. A*, 1981, **37**, 22.
24 G. M. Sheldrick, SHELXTL/PC manual, Siemens Analytical X-ray Instruments, Inc., Madison, USA, 1990; SHELXL-93, program for refinement of crystal structures, beta-test version, University of Göttingen, 1992.

Received 23rd *June* 1993; *Paper* 3/03616B