Addition Reactions and Rearrangements of 2,3-Bis(diphenylphosphino)propene and its Complexes with Group 6 Metal Carbonyls: Routes to Complexes of 1,2,3-Tris(diphenylphosphino)propane

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The preparation of 2,3-bis(diphenylphosphino)propene (1) and its Group 6 metal tetracarbonyl complexes are described. The attempted base-catalysed addition of PR_2H to (1) results in rearrangement to *trans*-1,2-bis(diphenylphosphino)propene (2) instead of the expected triphosphine. Under the same conditions the Group 6 metal carbonyl complexes of (1) can rearrange to complexes of the *cis* isomer of (2), but may also undergo the addition reaction to yield $M(CO)_4$ complexes of the new ligand 1,2,3-tris(diphenylphosphino)propane by adjustment of the reaction conditions. These on heating yield the corresponding $M(CO)_3$ complexes. Proton, ^{13}C, and ^{31}P n.m.r. spectral parameters of the new compounds are presented and are discussed in terms of metal- and backbone-mediated contributions and co-ordination chemical shifts.

The base-catalysed addition of primary and secondary phosphines to activated carbon–carbon multiple bonds provides a convenient route to a range of tri- and poly-organophosphines with versatile ligating capabilities.[1–5] In this regard the diphenylphosphino group is an effective activating moiety, and for example both free and co-ordinated diphenylvinylphosphine have been used in this way as substrates for the addition of diphenylphosphine to give a range of derivatives.[1,6] The presence of a pair of geminal diphenylphosphino substituents is especially effective, and additions of a range of species with one or more phosphorus–hydrogen bonds to free[3] or co-ordinated[5,7] 1,1-bis(diphenylphosphino)ethene offers an important route to many new polyorganophosphines and their complexes, including 1,1,2-tris(diphenylphosphino)ethane and bis[2,2-bis(diphenylphosphino)ethyl]phenylphosphine.[3] By contrast the symmetrical species *cis*- and *trans*-1,2-bis(diphenylphosphino)-ethene do not undergo such additions under normal conditions.[8]

In order to explore further the scope of this type of addition we have synthesised the new diphosphine 2,3-bis(diphenylphosphino)propene (1) in which *one* of the diphenylphosphino groups should be able to activate the double bond, and have examined the reaction of diphenylphosphine with it and with some of its Group 6 metal carbonyl complexes.

Results and Discussion

Compound (1) was prepared in 51% yield by the reaction between 2,3-dichloropropene and $Na(PPh_2)$ in liquid ammonia as white air-stable crystals, soluble in most common organic solvents other than alcohols. Microanalytical data are in Table 1. The structure of (1) is confirmed by its n.m.r. spectra which show a pair of inequivalent ^{31}P nuclei in the phosphorus(III) region, and an ABX_2 pattern in the non-aromatic part of the ^{31}P-decoupled proton spectrum with inequivalent [$J(AB) = 1.2$ Hz] olefinic protons and equivalent methylene protons. The ^{13}C n.m.r. spectrum (Table 3) is also consistent with the proposed structure.

Compound (1) reacted with Group 6 metal carbonyls in

refluxing diglyme (2,5,8-trioxanonane) to give the corresponding tetracarbonyl derivatives (4a)—(4c) as pale yellow air-stable crystals (melting points and microanalytical data in Table 1). Their proton, ^{13}C, and ^{31}P n.m.r. spectra again confirm their structures, and in particular the ^{13}C spectra show that the equatorial carbonyl groups are inequivalent owing to the asymmetry of the ligand. It was also possible with the assistance of selective ^{31}P decoupling fully to assign the ^{13}C spectra (see the Figure for an example) and to demonstrate the presence of two types of phenyl group as expected. Thus for the backbone irradiation at $^{31}P_X$ collapses the double doublet due to C_β to a doublet with a splitting of 33.7 Hz [*i.e.* $^1J(^{31}P_A{}^{13}C_\beta)$], and irradiation at $^{31}P_A$ results in collapse to a doublet with a splitting of 11.3 Hz [*i.e.* $^2J(^{31}P_X{}^{13}C_\beta)$]. These experiments also showed that the only *resolved* coupling to $^{13}C_\alpha$ is that from $^{31}P_X$.

It was hoped that the reaction of compound (1) with diphenylphosphine in the presence of potassium t-butoxide would yield the new triphosphine (3) by addition across the double bond, but in practice the only product was (2) (see Scheme) which arises from rearrangement of (1). Note that small amounts of (2) were also formed in the preparation of (1). Compound (2) was isolated in 70% yield as white air-stable needles and is assigned a *trans* configuration on the basis of $^3J(^{31}P^{31}P) = 6.7$ Hz [*cf.* values of 13.4 and 105.5 Hz for the *trans* and *cis* isomers respectively of 1,2-bis(diphenylphosphino)ethene[9], of $^3J(^{31}PH_{olefinic}) = 12.9$ Hz [*cf.* values of 10.7 and 25.3 Hz for the corresponding *cis* and *trans* couplings respectively of $Ph_2P(CMe=CH_2)^{10}$], and of its inability to form chelate complexes by reaction with metal carbonyl substrates. Compound (1) also underwent rearrangement to (2) on treatment with other secondary phosphines including ethylphenylphosphine, n-butylphenylphosphine, and bis(2,4,6-trimethylphenyl)phosphine in the presence of potassium t-butoxide, thus showing the reaction to be a true allylic isomerisation whose steric course is determined by the *trans* isomer being the thermodynamically more stable product.

Clearly, this reaction route would not be possible if the two diphenylphosphino groups of (1) were locked in a mutually *cis* configuration, as in the complexes (4a)—(4c), and we have confirmed this experimentally. Treatment of the latter with a small (catalytic) amount of diphenylphosphine in the presence of potassium t-butoxide led only to the corresponding species (5a)—(5c) which are complexes of the unknown ligand (6).

Table 1. Elemental analyses and melting points

		Found		Calc.		
Compound	Metal	C	H	C	H	M.p. (°C)
(1)	—	79.0	5.9	79.0	5.9	90
(2)	—	79.0	5.9	79.0	5.9	78
(4a)	Cr	64.8	4.1	64.8	4.2	168
(4b)	Mo	60.2	3.9	60.2	3.9	175
(4c)	W	52.7	3.3	52.7	3.4	185
(5a)	Cr	64.6	4.2	64.8	4.2	218
(5b)	Mo	60.0	3.9	60.2	3.9	186
(5c)	W	52.5	3.5	52.7	3.4	206
(7a)	Cr	67.3	4.7	67.9	4.6	179
(7b)	Mo	63.9	4.4	64.2	4.4	183
(7c)	W	56.9	3.8	57.9	3.9	191
(8a)	Cr	68.8	4.8	68.9	4.8	255 (decomp.)
(8b)	Mo	64.0	4.5	65.0	4.5	275 (decomp.)
(8c)	W	57.2	4.0	58.3	4.1	285 (decomp.)

Analysis/% spans Found and Calc.

Table 2. ^{31}P N.m.r. parameters of compounds (1)—(8)[a,b]

Compound	M	$\delta(^{31}P_A)$	$\delta(^{31}P_M)$	$\delta(^{31}P_X)$	$J(P_AP_M)$	$J(P_AP_X)$	$J(P_MP_X)$
(1)	—	−0.8	—	−17.7	—	+33.7[c]	—
(2)	—	+6.9	—	−26.4	—	+6.7[c]	—
(4a)	Cr	+76.3	—	+60.6	—	(−)15.9[d]	—
(4b)	Mo[e]	+53.8[f]	—	+36.8[f]	—	(−)7.3[d]	—
(4c)	W	+38.7[g]	—	+19.5[h]	—	0[d]	—
(5a)	Cr	+94.5	—	+76.2	—	(−)4.9[d]	—
(5b)	Mo	+70.4	—	+52.1	—	(+)7.3[d]	—
(5c)	W	+55.0[i]	—	+37.0[i]	—	(+)18.3[d]	—
(7a)	Cr	+91.0	−17.9	+71.0	8.5[c]	(−)14.6[d]	0[j]
(7b)	Mo	+68.4	−18.4	+49.0	9.8[c]	(−)4.9[d]	0[j]
(7c)	W	+53.7[k]	−17.8	+34.0[l]	11.3[c]	(+)4.9[d]	0[j]
(8a)	Cr	+98.3	—	+62.9	m	(−)7.3[d]	n
(8b)	Mo	+77.0	—	+41.1	m	(+)2.1[d]	n
(8c)	W	+66.0[o]	—	+24.9[p]	m	(+)11.0[d]	n

[a] Chemical shifts in p.p.m. ± 0.1 p.p.m. to high frequency of external 85% H_3PO_4. [b] Coupling constants in Hz ± 0.1 Hz. Signs in parentheses are suggested on the basis of the arguments in the main text. Signs without parentheses have been determined by selective multiple resonance experiments. [c] ^3J. [d] ^2J. [e] $\delta(^{95}Mo) = +119.7$ p.p.m. relative to [Mo(CO)$_6$]. [f] $^1J(^{95}Mo^{31}P) = 122 \pm 5$ Hz. [g] $^1J(^{183}W^{31}P) = 228.0 \pm 0.2$ Hz. [h] $^1J(^{183}W^{31}P) = 230.5 \pm 0.2$ Hz. [i] $^1J(^{183}W^{31}P) = 231.9 \pm 0.2$ Hz. [j] ^4J. [k] $^1J(^{183}W^{31}P) = 230.4 \pm 0.2$ Hz. [l] $^1J(^{183}W^{31}P) = 230.1 \pm 0.2$ Hz. [m] Equivalent to $J(P_AP_X)$. [n] Equivalent to $J(P_XP_X)$ and therefore not measurable directly. The components were insufficiently soluble for indirect ^{13}C-{^{31}P, ^{1}H} experiments to be used to determine this coupling constant. [o] $^1J(^{183}W^{31}P) = 211.2 \pm 0.2$ Hz. [p] $^1J(^{183}W^{31}P) = 207.5 \pm 0.2$ Hz.

Table 3. ^{13}C N.m.r. parameters of backbone carbon atoms[a]

		$\delta(^{13}C)$			$J(^{31}P_A{}^{13}C)$			$J(^{31}P_M{}^{13}C)$			$J(^{31}P_X{}^{13}C)$		
Compound	Metal	α	β	γ	α	β	γ	α	β	γ	α	β	γ
(1)	—	125.3	144.2	35.8	+10.0	−17.3	+23.4	—	—	—	+13.9	+8.0	−16.9
(2)	—	20.2	151.5	137.5	+20.6	−21.0	+17.5	—	—	—	+22.9	+20.0	−16.6
(4a)	Cr	125.6	144.8	39.7	0	28.5	34.4	—	—	—	13.9	16.1	22.7
(4b)	Mo	126.9	144.4	40.2	0	28.6	31.9	—	—	—	12.8	12.8	22.7
(4c)	W	126.1	145.8	40.2	0	33.7	30.4	—	—	—	12.8	11.3	26.4
(5a)	Cr	20.9	159.8	146.1	0	23.0	42.5	—	—	—	16.6	33.2	36.6
(5b)	Mo	21.1	157.9	145.5	1.0	23.9	39.5	—	—	—	15.8	30.3	36.8
(5c)	W	20.4	159.4	146.6	2.1	28.0	41.5	—	—	—	15.3	28.0	37.2
(7a)	Cr[b]	29.8	36.0	32.4	2.6	18.4	21.4	17.1	13.7	10.3	11.1	18.4	21.4
(7b)	Mo[b]	29.5	35.2	32.2	1.7	17.9	18.8	16.3	14.5	10.3	10.3	17.9	23.1
(7c)	W[b]	29.1	36.7	33.3	2.2	22.7	17.6	16.1	14.7	11.0	9.4	14.7	27.1

[a] Chemical shifts in p.p.m. ± 0.1 p.p.m. relative to $SiMe_4$, coupling constants in Hz ± 0.2 Hz, one-bond couplings are represented by bold type, two-bond couplings by italic type, and three-bond by roman type. [b] The assignment of C_α and C_γ is based on the observation that in complexes of dppe $\delta(^{13}C)$ for the methylene carbons is several p.p.m. higher than for the free ligand.[11]

These complexes are pale yellow air-stable solids (analytical data and melting points in Table 1) whose structures were confirmed by their n.m.r. spectra (Tables 2—4 and the Experi-mental section). Thus in this case the allylic isomerisation proceeds to give the *cis* isomer as this is now favoured thermodynamically.
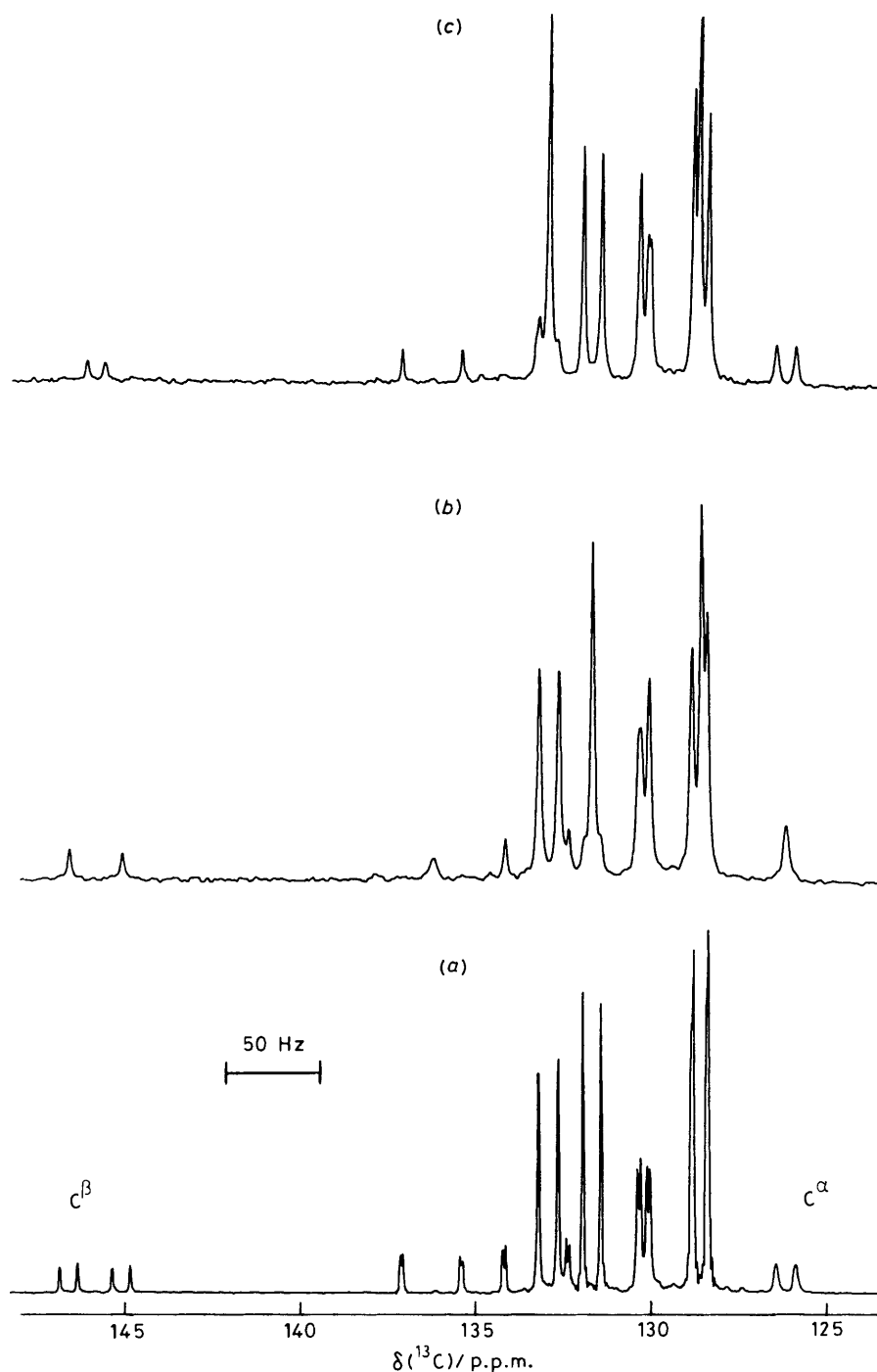
Figure. ^{13}C N.m.r. spectra at 22.5 MHz of the olefinic and aromatic regions of the tungsten complex (**4c**): (a) normal spectrum, (b) with $^{31}P_X$ decoupled, and (c) with $^{31}P_A$ decoupled

(3)

(6)
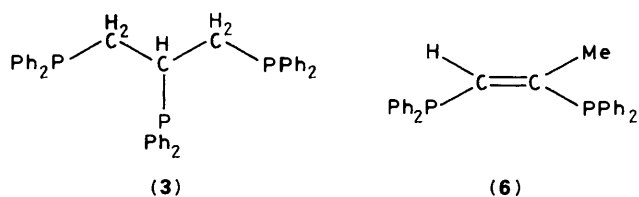
However, when a complex (**4a**)—(**4c**) was added to an *excess* of diphenylphosphine in the presence of potassium t-butoxide the main (>95%) product was a complex (**7a**)—(**7c**) resulting

from the *addition* reaction as originally expected. These complexes were isolated in 80% yield as pale yellow air-stable solids (see Table 1 for analytical and other data) whose structures were again confirmed by their n.m.r. spectra. In particular, they have AMX ^{31}P spectra and their ^{13}C and proton spectra show the presence of a methyl group. These complexes have a pendant diphenylphosphino group with the potential to co-ordinate to a metal atom and accordingly when they were heated in refluxing (162 °C) diglyme they lost one molecule of carbon monoxide to yield (**8a**)—(**8c**) which were also isolated as pale yellow crystals (analytical data, *etc.* in Table 1). Phosphorus-31 n.m.r. data are in Table 2, but the complexes were too insoluble to give satisfactory
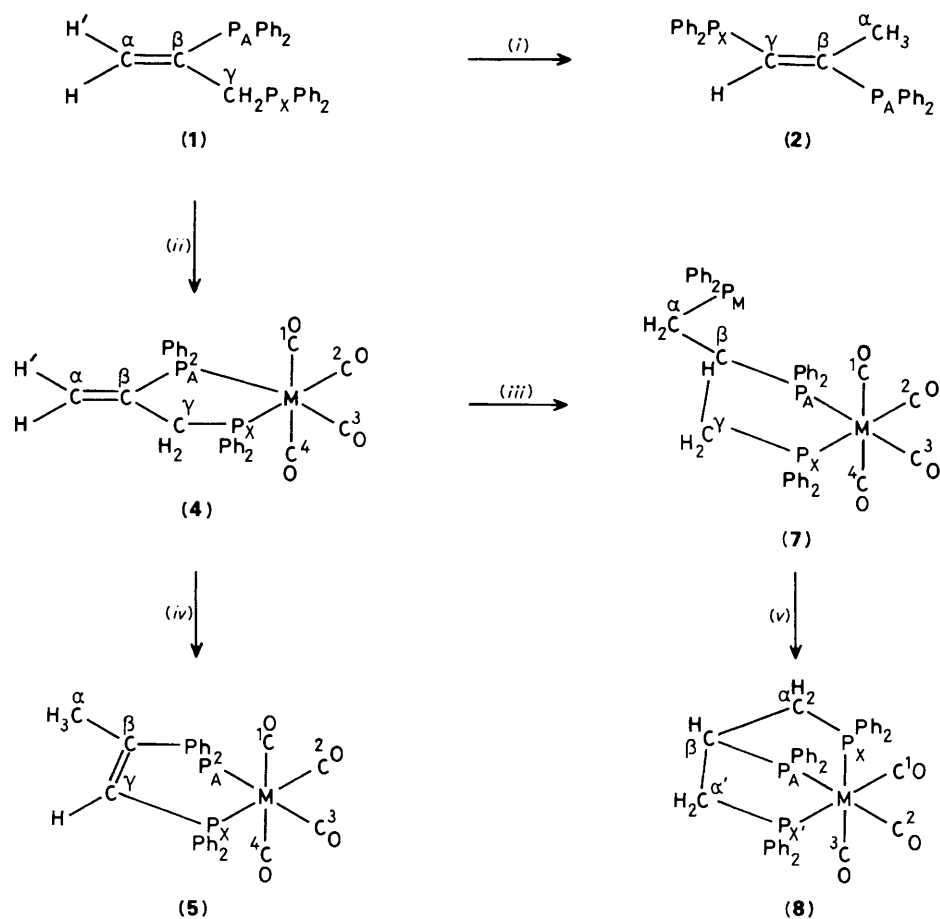
Scheme. (*i*) PR_2H, $KOBu^t$; (*ii*) $[M(CO)_6]$; (*iii*) PPh_2H (excess), $KOBu^t$; (*iv*) PR_2H (catalyst), $KOBu^t$; (*v*) heat

Table 4. ^{13}C N.m.r. parameters for the carbonyl groups of complexes (4), (5), and (7)[a]

Complex	M	$\delta(C^{1,4})$[b]	$\delta(C^2)$	$\delta(C^3)$	$^2J(P_AC^{1,4})$[b]	$^2J(P_AC^2)$	$^2J(P_AC^3)$	$^2J(P_XC^{1,4})$	$^2J(P_XC^2)$	$^2J(P_XC^3)$
(4a)	Cr	220.5	228.4	228.6	13.0	13.5	4.7	13.0	4.7	12.5
(4b)	Mo	210.4	216.9	217.2	8.8	8.8	24.9	8.8	24.9	8.8
(4c)	W[c]	201.8	207.8	208.0	7.0	6.6	23.4	7.0	23.4	6.6
(5a)	Cr	220.6	228.8	229.7	12.7	12.7	3.9	12.7	3.9	12.7
(5b)	Mo	209.7	217.4	218.6	8.6	8.6	21.0	8.6	21.1	8.6
(5c)	W	201.8	208.7	209.3	6.6	6.0	24.4	6.6	23.5	6.4
(7a)[d]	Cr	218.8, 222.5	228.0	228.7	12.0, 13.3	12.6	3.9	12.0, 13.3	4.5	13.6
(7b)	Mo	208.1, 211.5	216.7	217.3	8.1, 8.9	8.5	25.6	8.1, 8.9	24.8	8.5
(7c)	W	200.2, 203.4	207.6	208.1	5.9, 7.3	6.6	24.9	5.9, 7.3	24.4	6.6

[a] Chemical shifts in p.p.m. $\pm$ 0.1 p.p.m. to high frequency of $SiMe_4$. Coupling constants in Hz $\pm$ 0.1 Hz. [b] For complex (5) the relative assignments of C^1 and C^4 are not established, but there is a correspondence in the table of the entries for $\delta(C^{1,4})$, $^2J(P_AC^{1,4})$, and $^2J(P_XC^{1,4})$. [c] $^1J(^{183}WC^{1,4}) = 125.3$, $^1J(^{183}WC^3) = 148.4$ Hz. [d] $^5J(P_MC) < 0.5$ Hz.

^{13}C spectra. They are assigned a *fac* configuration because (*a*) molecular models indicate that the *mer* isomers would be very highly strained, and (*b*) for (8c) the coupling $^1J(^{183}W^{31}P_A)$ is 207.5 Hz which indicates that P_A is *trans* to CO.[11]

The mass spectra of the two isolated ligands (1) and (2) and of all but two of the complexes showed the molecular ion. In the cases of (7a) and (7b) the highest observed mass corresponded to the loss of one CO. Generally, it was also possible to observe the sequential loss of CO in the mass spectra of all the complexes.

The pattern of reactions is thus represented by the Scheme, in which it will be noticed that complexed (1) [*i.e.* (4)] can be converted into complexed (3) [*i.e.* (7)] or complexed (6) [*i.e.* (5)] simply by controlling the reaction conditions. Attempts to make

diphenylphosphine add to (2) or (5) failed, as did similar experiments on co-ordinated *cis*- and *trans*-1,2-bis(diphenyl-phosphino)ethene. Thus although the new ligand (3) has not been isolated, several of its complexes have been prepared in two of its five possible monometallic modes of co-ordination. This versatile behaviour apparently stems from the relative acidity of the methylene protons of compound (1) (arising from their proximity to two diphenylphosphino groups[12,13]) leading to the formation of a carbanion (9) which subsequently gives (2) by proton attack on C_α. In this case the *trans* isomer (2) is more stable than the *cis* (6), but when the formation of (2) is prevented by co-ordination of the two phosphorus atoms to the same metal atom [*i.e.* as in (4)] the *cis* product (5) [*i.e.* a complex of

(9)
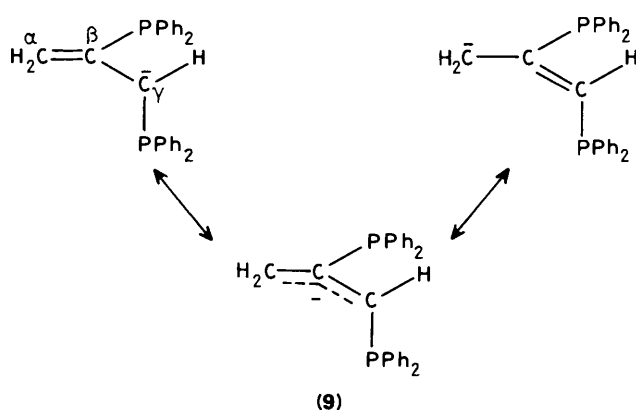
(6)] results. It also appears that the carbanion intermediate in the complexed case is somewhat less stable, as attack to give the expected[1] anti-Markownikov addition product (7) can also occur.

Phosphorus chemical shifts in metal complexes can be derived[14] from those of the free ligands by the use of 'co-ordination chemical shifts'.* These in turn depend upon the particular metal atom and, for chelate complexes, upon the size and nature of the chelate ring.[15] In the case of compound (1) the co-ordination chemical shifts for chelated chromium, molybdenum, and tungsten respectively are found to be 77.1, 54.6, and 39.5 p.p.m. for P_A and 78.3, 53.5, and 37.2 p.p.m. for P_X. These figures are in excellent self-agreement and are some 15 p.p.m. less than found for chelating dppe ($Ph_2PCH_2CH_2PPh_2$).[11] This is presumably due to the exocyclic double bond which apparently has similar effects upon P_A and P_X despite its different relationship to them. Comparison of the complexes of (6) with those of cis-1,2-bis(diphenylphosphino)ethane shows differences in phosphorus chemical shifts that can be attributed to changes in the numbers and stereochemistry of hydrogen atoms α and β to phosphorus,[16] as can similar differences between dppe and tppe [1,1,2-tris(diphenylphosphino)ethane],[5] and also between their bidentate (five-membered ring) complexes.[5] That is, the co-ordination chemical shifts are essentially unaffected by substitution at a backbone carbon atom, and should be approximately the same for (6) and cis-1,2-bis(diphenylphosphino)ethene, viz. 111, 87, and 73 p.p.m. for chromium, molybdenum, and tungsten respectively.[11] Hence, we conclude that for the at present unknown free ligand (6) itself δ(P_A) = −17 ± 1 and δ(P_X) = −35 ± 1 p.p.m. Similar reasoning can be applied to the complexes (7) and leads to the conclusion that for (3) δ(P_A) = 0 ± 1 and δ(P_X) = −19.5 ± 1.5 p.p.m. As expected, the latter figure is close to δ(P_M) for (7) which is unlikely to be much affected by co-ordination of the other two phosphorus atoms. For the complexes (8) there is likely to be some ring strain, and the calculated co-ordination chemical shifts for chromium, molybdenum, and tungsten respectively are 98.3, 77.0, and 66.0 p.p.m. for P_A, and 82.4, 60.6, and 44.4 p.p.m. for P_X.

The ^{13}C n.m.r. chemical shifts of the carbonyl groups in the complexes are unexceptional and very close to those found for complexes of dppe.[11] In particular, the mean of δ(^{13}C) for the two kinds of axial carbonyl in (7) is very close to the single values found for the equivalent axial carbonyl groups of (4) and (5).

In Group 6 metal carbonyl complexes of tertiary phosphines ^2J(PMP) is known to increase algebraically as the atomic

number of the metal increases.[17] This approach is known[11] to be usually satisfactory for determining the sign of the coupling in complexes with five-membered chelate rings although it can have pitfalls; it was used here to give the signs of the couplings in Table 2. There is now substantial evidence that observed values of ^2J(PMP) are the algebraic sum of metal- and backbone-mediated contributions, and this is supported by the present results for the complexes (4), (5), and (7). Thus, by using values of −41, −30, and −23 Hz for the metal-mediated contributions of chromium, molybdenum, and tungsten respectively[5] the backbone contributions for the corresponding ligands (1), (6), and (7) are +24, +41, and +28 Hz respectively. Note that these figures refer to the ligands in the normally adopted conformation when co-ordinated and should not be compared directly with the values of $J(^{31}P^{31}P)$ for the free ligands since both the average conformation and phosphorus hybridisation will be different. This is not a serious problem in the present study since two of the ligands themselves are unknown.

The backbone contribution for compound (3) is virtually identical with that found earlier for dppe,[11] and differs only slightly from that for (1) despite the presence of an sp^2-hybridised carbon in the backbone of the last. However, there is probably little strain in the five-membered chelate rings of any of the complexes, whereas a comparison of dppm (Ph_2PCH_2-PPh_2) (backbone contribution +55 Hz) and 1,1-bis(diphenyl-phosphino)ethene (ca. +100 Hz) shows a marked difference which can be attributed to differing abilities to relieve the strain in these four-membered chelate rings. For (6) the backbone contribution is the same as for cis-1,2-bis(diphenylphosphino)-ethene and its increased size compared with that for dppe probably reflects the availability of a π-coupling path. In complex (8) there is a third (metal + backbone) coupling path available, but as this involves five bonds it is probably unimportant. The 'normal' backbone contribution can then be calculated as +33 Hz and the difference from the value for (7) can be attributed to ring strain, although it should be noted that this may also lead to deformation of the interbond angles at the metal atom which in turn might affect the metal-mediated contribution.

The ^{31}P to ^{13}C carbonyl couplings in (4), (5), and (7) are very close to those for complexes of dppe and of cis-1,2-bis(diphenyl-phosphino)ethene, as expected in view of the similarity of the relevant geometrical relationships. Thus, for chromium the cis coupling is ca. 13 Hz and the trans ca. 4 Hz, while for both molybdenum and tungsten the corresponding values are ca. 8 and 24 Hz, irrespective of whether P_A or P_X is involved.

For the ligands (1) and (2) the ^{31}P-^{13}C couplings show the expected pattern, ^1J negative, ^2J and ^3J positive; $^1J(^{31}P^{13}C)$ normally becomes positive on increase of co-ordination number of phosphorus from three to four[9] and on this basis we conclude that for (4)—(6) the values of $^1J(^{31}P_A{}^{13}C_β)$ and $^1J(^{31}P_XC_γ)$ are all positive. Co-ordination of phosphorus also results in an algebraic decrease in $^2J(^{31}P$-$^{13}C)$, and this is consistent with values close to zero for $^2J(P_A{}^{13}C_α)$ for (4). This coupling has similar values for (5) and (7) also, suggesting that for the ligands (6) and (3) it would be similar to that for (1). The other nominally two-bond phosphorus-carbon couplings of the backbone could also involve a metal-mediated three-bond pathway, although the absence of a strong dependence upon the particular metal atom suggests that this may not be an important factor.

Experimental

Solvents were dried and deaerated by standard procedures and all manipulations were conducted under an atmosphere of dry nitrogen or ammonia. For the complexes the procedure used for the chromium congener is given in each case; identical methods

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* A co-ordination chemical shift Δδ is defined by Δδ = δ(complex) − δ(free ligand).

were used with molybdenum and tungsten, and their proton n.m.r. data are given in that order following the corresponding chromium parameter.

2,3-Bis(*diphenylphosphino*)*propene* (**1**).—Triphenylphosphine (65.5 g, 0.25 mol) in tetrahydrofuran (thf) (200 cm^3) was added over 0.5 h to a stirred solution of sodium (11.5 g, 0.5 mol) in refluxing anhydrous ammonia (1 000 cm^3). Solid ammonium bromide (24.5 g, 0.25 mol) was then added over 0.5 h to give a bright red solution to which 2,3-dichloropropene (13.9 g, 0.125 mol) in thf (50 cm^3) was added dropwise over 0.75 h. The solution became cream coloured and after removal of ammonia and thf by evaporation the residue was extracted with diethyl ether (2 × 200 cm^3). The combined extracts were dried over anhydrous sodium sulphate and the solvent was removed under vacuum to give an oil which crystallised on addition of ethanol (200 cm^3). The white solid was recrystallised from methanol (150 cm^3)–dichloromethane (50 cm^3) to give the product as air-stable white crystals, in 51% yield. $\delta(H_a)$ 5.70, $^2J(H_aH_{a'})$ 1.2, $^4J(H_aH_y)$ 1.3, $^3J(^{31}P_AH_a)$ + 18.7, $^4J(^{31}P_XH_a)$ 3.4 Hz; $\delta(H_{a'})$ 5.05, $^4J(H_{a'}H_y)$ 0.5, $^3J(^{31}P_AH_{a'})$ 8.5, $^4J(^{31}P_XH_{a'})$ 0.7 Hz; $\delta(H_y)$ 3.07, $^2J(^{31}P_XH_y)$ 1.2, $^3J(^{31}P_AH_y)$ 9.1 Hz; $\delta(H_{phenyl})$ 7.2—7.4. On standing the ethanol solution deposited crystals of compound (**2**) in *ca.* 10% yield.

trans-1,2-*Bis*(*diphenylphosphino*)*propene* (**2**).—To a solution of compound (**1**) (4.1 g, 10 mmol) and diphenylphosphine (0.186 g, 1 mmol) in dry thf (30 cm^3) was added potassium t-butoxide (0.05 g, catalytic amount). The solution immediately turned bright yellow and after it had been stirred for 0.5 h the volume was reduced to 10 cm^3 at the pump. Addition of methanol (30 cm^3) then gave a white solid which was recrystallised from methanol (30 cm^3)–dichloromethane (10 cm^3) to give the product as air-stable white crystals in 70% yield. $\delta(H_a)$ 2.13, $^3J(^{31}P_AH_a)$ 9.3, $^4J(^{31}P_XH_a)$ 0, $^4J(H_aH_y)$ 1.2 Hz; $\delta(H_y)$ 6.57, $^2J(^{31}P_XH_y)$ 1.2, $^3J(^{31}P_AH_y)$ 12.9 Hz; $\delta(H_{phenyl})$ 7.2—7.5.

cis-[2,3-*Bis*(*diphenylphosphino*)*propene*-PP′]*tetracarbonyl-chromium*(0) (**4a**).—A mixture of hexacarbonylchromium (4.4 g, 20 mmol) and compound (**1**) (8.2 g, 20 mmol) in diglyme (50 cm^3) was heated under reflux for 2 h. Light petroleum (b.p. 40—60 °C, 50 cm^3) was added to the cooled and filtered yellow solution to yield a yellow solid which was recrystallised from methanol (50 cm^3)–dichloromethane (25 cm^3) to give the product as yellow crystals in 82% yield. $\delta(H_a)$ 6.13, 6.07, 6.09; $^2J(H_aH_{a'})$ 0, 0, 0, $^4J(H_aH_y)$ 0, 0, 0, $^3J(^{31}P_AH_a)$ 24.2, 23.7, 24.9, $^4J(^{31}P_XH_a)$ 3.7, 4.4, 3.9 Hz; $\delta(H_{a'})$ 5.31, 5.28, 5.26; $^4J(H_{a'}H_y)$ 0, 0, 0, $^3J(^{31}P_AH_{a'})$ 11.2, 11.7, 12.2, $^4J(^{31}P_XH_{a'})$ 2.7, 3.4, 2.9 Hz; $\delta(H_y)$ 3.39, 3.49, 3.40; $^2J(^{31}P_XH_y)$ 11.0, 10.5, 10.7, $^3J(^{31}P_AH_y)$ 18.6, 18.6, 18.0 Hz; $\delta(H_{phenyl})$ 7.3—7.8, 7.3—7.7, 7.1—7.6.

cis-[*cis*-1,2-*Bis*(*diphenylphosphino*)*propene*-PP′]*tetracarbon-ylchromium*(0) (**5a**).—Potassium t-butoxide (0.05 g, catalytic amount) was added to a solution of complex (**4a**) (2.87 g, 5 mmol) and diphenylphosphine (0.1 g, 0.5 mmol) in thf (20 cm^3). The mixture was stirred for 0.2 h, its volume was reduced to 5 cm^3 at the pump, and methanol (25 cm^3) was then added to yield a solid which was recrystallised from methanol (20 cm^3)–dichloromethane (10 cm^3) to give the product as air-stable yellow crystals in 73% yield. $\delta(H_a)$ 2.16, 2.14, 2.17; $^4J(H_aH_y)$ 1.5, 1.5, 1.5, $^3J(^{31}P_AH_a)$ 6.1, 6.1, 6.3, $^4J(^{31}P_XH_a)$ 1.5, 1.5, 1.5 Hz; $\delta(H_{phenyl})$ 7.4—7.7, 7.4—7.6, 7.4—7.6; $\delta(H_y)$ 7.51, 7.40, 7.44; $^2J(^{31}P_XH_y)$ 5.4, 4.4, 5.4, $^3J(^{31}P_AH_y)$ 50.5, 48.6, 47.6 Hz.

cis-*Tetracarbonyl*[1,2,3-*tris*(*diphenylphosphino*)*propane*-PP′]*chromium*(0) (**7a**).—Potassium t-butoxide (0.05 g, catalytic amount) was added to a solution of complex (**4a**) (2.87 g, 5

mmol) and diphenylphosphine (1.86 g, 10 mmol) in thf (30 cm^3) and the mixture was stirred for 0.5 h. The solvent was removed under vacuum and addition of methanol (30 cm^3) yielded a yellow powder which was recrystallised from methanol (20 cm^3)–dichloromethane (10 cm^3) to give the product as air-stable yellow crystals in 79% yield. Very complex proton spectra showing aliphatic and aromatic but no olefinic resonances.

fac-*Tricarbonyl*[1,2,3-*tris*(*diphenylphosphino*)*propane*-PP′P″]*chromium*(0) (**8a**).—A solution of compound (**7a**) (1.5 g, 2 mmol) in diglyme (35 cm^3) was refluxed for 15 h. The solution was then cooled to room temperature and filtered. Addition of methanol (50 cm^3) to the filtrate precipitated a pale yellow solid which was recrystallised from methanol (25 cm^3)–dichloro-methane (50 cm^3) to give the product as pale yellow needles in 83% yield. Very complex proton n.m.r. spectra were observed showing aliphatic and aromatic but no olefinic resonances.

Proton, ^{13}C, ^{31}P, and ^{95}Mo n.m.r. spectra were obtained by standard multinuclear techniques at frequencies of 89.56, 22.50, 36.20, and 5.85 MHz respectively using a JEOL FX90Q spectrometer. Samples were dissolved in deuteriochloroform and were measured in spinning tubes (outside diameter 10 mm). ^1H-$\{^{31}P\}$ Double- and ^{13}C-$\{^{31}P,H\}$ triple-resonance experiments were conducted on the same instrument with, in the latter case, time sharing of the ^{31}P irradiation and the ^{13}C receiver to reduce electronic interference. Mass spectra were obtained on a JEOL DMX300 spectrometer using electron-impact ionization at 70 eV (*ca.* 112 × 10^{-19} J).

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