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The reactions of η^1 and η^3 cobalt(I) allyl complexes with bis(phosphine) ligands: a synthetic and spectroscopic study. The crystal structure of $\{(\eta^3\text{-}C_3H_5)Co(CO)_2\}_2(\mu\text{-dppe-PP})$

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Abstract

The reactions of $(\eta^3\text{-}RC_3H_4)Co(CO)_3$ (R = H, CH_3) with the bis(tertiary phosphines) bis(diphenylphosphino)methane (dppm) and bis(diphenylphosphino)ethane (dppe) have been investigated. Reactions involving dppe give dimers, with a single dppe unit bridging two cobalt centres; those involving dppm generate monomers with "dangling" dppm ligands. ^{31}P NMR, $^{13}C\{^1H\}$ and ^1H studies of these η^3-allyl products, $[Co_2(\eta^3\text{-}C_3H_4R)_2(CO)_4(\mu\text{-dppe-PP})]$ and $[Co(\eta^3\text{-}C_3H_4R)(CO)_2(dppm)]$ (R = H, CH_3) afford further proof of the bonding mode of the bis(phosphine) ligands. Resonances are readily assigned, and spin patterns explained in terms of two magnetically inequivalent ^{31}P nuclei and the magnitude of $^nJ(PP)$. The η^3-allyl compounds were alternatively prepared by first synthesizing the η^1-allyl phosphine precursors and then converting them into the η^3-allyls. $^{31}P\{^1H\}$ NMR spectroscopy again showed the ratio of bridged product to monodentate product to be large for dppe and very small for dppm. An X-ray crystal structure determination on the novel complex $[Co_2(\eta^3\text{-}C_3H_5)_2(CO)_4(\mu\text{-dppe-PP})]$ (4c) revealed both the η^3-allyl and dppe groups to be severely strained. The cobalt atom is at the centre of a distorted square pyramid.

Introduction

The reaction of compounds of the general type $(\eta^3\text{-allyl})Co(CO)_3$ with phosphines result in the replacement of one carbonyl ligand according to equation 1 [1]. The use of various phosphines and substituted allyl groups have led to a variety of

$$(\eta^3\text{-allyl})Co(CO)_3 + PR_3 \rightarrow (\eta^3\text{-allyl})Co(CO)_2(PR_3) + CO \qquad (1)$$

products with the general formula $(\eta^3\text{-allyl})Co(CO)_2(PR_3)$—of these few, amongst which R = PPh_3 and R = n-Bu, have been isolated and characterized fully [2,3]. A crystal structure determination of the former has been published [2]. Dimeric η^3-allyl complexes $\{(CO)_3Co((CH_2)_2\text{-}CCH_2)\}_2$ and $\{((CH_3O)_3\text{-}P)(CO)_2Co((CH_2)_2\text{-}CCH_2)\}_2CO$ have been prepared by reaction of (chloromethyl)allylchloride and $Na[Co(CO)_4]$ in refluxing THF followed by treatment with the phosphite and their structures determined by single-crystal X-ray diffraction techniques [4]. The reactions of $(\eta^3\text{-allyl})Co(CO)_3$ with bis(tertiary phosphines) have not yet received attention.

In this paper the reactions of (η^3-RC_3H_4)$Co(CO)_3$ (R = H, CH_3) with dppm (dppm = bis(diphenylphosphino)methane) and dppe (dppe = bis(diphenylphosphino)ethane) are described. Inasmuch as it is not easy to substitute two carbonyl ligands in complexes of the type (η^3-allyl)$Co(CO)_3$ (according to eqn. 1), it was provided that the reaction of (η^3-allyl)$Co(CO)_3$ with bidentate phosphine ligands would not only be interesting from a synthetic point of view, but also regarding the nature of the products formed. It was therefore anticipated that the reaction of (η^3-RC_3H_4)$Co(CO)_3$ with dppe would upon chelation either enforce ring opening of the η^3-allyl ligand or substitute a second carbonyl. In contrast, dppm may prefer forming dimers with bridged phosphine ligands.

The major products of the reactions of $Ph_2P(CH_2)_nPPh_2$ ($n = 1, 2$) with (η^3-allyl)$Co(CO)_3$, (η^3-RC_3H_4)$Co(CO)_2$(dppm) and [{(η^3-RC_3H_4)$Co(CO)_2$}$_2$(μ-dppe-PP)] (R = H, CH_3) were isolated and studied spectroscopically. ^1H, $^{31}P\{^1H\}$, $^{13}C\{^1H\}$ and ^{13}C spectra, as well as infrared and mass spectra were recorded for these compounds and found to be readily interpreted. The unexpectedness of the dppm remaining monodentate and dppe not chelating but forming bridged dimers was thought to be a consequence of structural factors. This prompted a detailed structural analysis together with a careful comparison thereof with similar five-coordinate structures.

A number of structures of five-coordinated carbonyl complexes of the type $Co(CO)_{5-n}L_n$ have been solved. For $n = 1$ or 2 these structures are more or less ideal trigonal bipyramids with the remaining three carbonyls occupying the equatorial sites. Some typical examples are [$Co(PPh_3)(CO)_3R$] (R = $COCH_2Cl$, CH_2Cl), [$Co(CO)_3(XPh_3)(SnMe_3)$] (X = As, P) [5,6]. When an additional carbonyl is substituted (i.e. $n = 3$), again trigonal bipyramidal structures are predominantly found, but examples of square pyramidal structures do occur. The compound [Co(dppe-PP)$(CO)_2$\{C(O)CH(OEt)CH(OEt)CH_3\}] is an almost ideal trigonal bipyramid with two carbonyl ligands and one of the phosphorus atoms of dppe in the equatorial plane [7]. As opposed to this, the complex [Co(η^3-C_3H_5)$(CO)_2(PPh_3)$] (where n also is 3) is best described as a distorted square pyramid [2].

In order to achieve a better understanding of the course of these reactions, some of the η^3-allyl products were alternatively prepared by first synthesizing the η^1-allyl phosphine precursors and then allowing them to convert to the η^3-allyl compounds.

Results and discussion

Syntheses. A reaction scheme was compiled with the aid of $^{31}P\{^1H\}$ and ^1H spectra (Scheme 1).

Reactions i and ii: Treatment of the η^1-allyl compounds (η^1-RC_3H_4)$Co(CO)_4$ (R = H, CH_3) with P–P (P–P = dppm, dppe) in THF at −10°C resulted in a colour change from pale yellow to dark yellow. The products (Table 1) were recovered (as mixtures of **1** and **2**) by removal of the solvent followed by extraction with ether. The compounds are yellow solids soluble in diethyl ether and acetone and insoluble in non-polar solvents. They can be handled below −50°C. Above this temperature, gradual conversion to the η^3-allyl compound (in solution) or to some insoluble brown compound(s) (in the solid state) takes place.

(η^1-RC_3H_4)$Co(CO)_4$, upon treatment with dppe, mainly formed **2c**, regardless of whether one or half an equivalent of the ligand was added. The formation of **2c**

$$\begin{tikzcd}
(\eta^1\text{-RC}_3\text{H}_4)\text{Co(CO)}_4 + \text{P—P} \arrow[r, "(i)"] & \underset{\mathbf{1}}{(\eta^1\text{-RC}_3\text{H}_4)\text{Co(CO)}_3(\text{P—P})} \arrow[rr, "(ii)"] \arrow[d, "(iii)"] & & \underset{\mathbf{2}}{(\eta^1\text{-RC}_3\text{H}_4)\text{Co(CO)}_3(\text{P—P})(\text{CO})_3\text{Co}(\eta^1\text{-RC}_3\text{H}_4)} \arrow[d, "(iii)"] \\
(\eta^3\text{-RC}_3\text{H}_4)\text{Co(CO)}_3 + \text{P—P} \arrow[r, "(iv)"] & \underset{\mathbf{3}}{(\eta^3\text{-RC}_3\text{H}_4)\text{Co(CO)}_2(\text{P—P})} & + & \underset{\mathbf{4}}{(\eta^3\text{-RC}_3\text{H}_4)\text{Co(CO)}_2(\text{P—P})(\text{CO})_2\text{Co}(\eta^3\text{-RC}_3\text{H}_4)}
\end{tikzcd}$$

Product	P–P	R
a	dppm	H
b	dppm	CH_3
c	dppe	H
d	dppe	CH_3

Scheme 1

Table 1

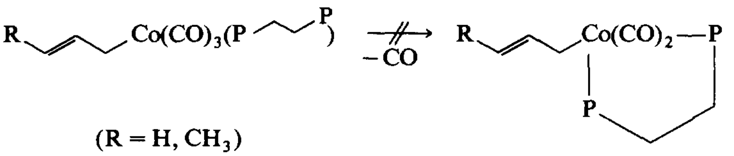
Yields of products **1**, **2**, **3** and **4** [a]

Product	Reaction	Yield (P–P) (%)	
		dppm	dppe
1	i	> 70	< 5
2	ii	< 5	> 80
3	iii	> 80	< 5
4	iii	< 5	> 80
3	iv	> 95	< 1
4	iv	< 5	> 95

[a] Determined with the aid of $^{31}P\{^1H\}$ NMR spectra.

therefore does not seem to occur via **1c**, although it is possible that the latter is converted almost instantaneously. The opposite is observed for the reaction of $(\eta^1\text{-}RC_3H_4)Co(CO)_4$ ($R = H, CH_3$) with dppm, where only small amounts of **2b** formed, judging from the amount of **4b** that was eventually measured.

Interestingly, although it was anticipated that dppe would perhaps replace a second carbonyl from the η^1-allyl compound,



(R = H, CH$_3$)

this chelated compound was not detected in solution. (Chelated dppm is rare in five-coordinate environments.)

Reaction iii: $(\eta^1\text{-allyl})Co(CO)_4$ compounds have been shown to convert spontaneously and quantitatively to their η^3-allyl counterparts with loss of CO [8]. This also occurs in the case of the η^1-allyl bis(phosphine) complexes, with **1b** converting mostly to **3b** and **2c** mostly to **4c**. The $^{31}P\{^1H\}$ NMR spectrum of **1b** is shown in Fig. 1.

Reaction iv: Products **3** and **4** were prepared in high yield by reacting $(\eta^3\text{-allyl})Co(CO)_3$ with the bis(phosphine) at room temperature. The reactions proved to be solvent dependent. With THF as solvent, evolution of CO was rapid and reactions were complete within 30 minutes. In a less polar solvent such as benzene, CO evolution was extremely slow. In the latter case only small quantities of **3** and **4** could be recovered. Attempts to run the reaction at an increased temperature or for a prolonged period of time invariably led to decomposition.

Reactions were again performed, first with half and then with one equivalent of the bis(phosphine) and produced similar results to those obtained for the η^1-allyls (reactions i and ii).

The η^3-allyl products, $(\eta^3\text{-}RC_3H_4)Co(CO)_2(dppm)$ ($R = H$ **3a**, $R = CH_3$ **3b**) and $\{(\eta^3\text{-}RC_3H_4)Co(CO)_2\}_2(\mu\text{-dppe-}PP)$ ($R = H$ **4c**, $R = CH_3$ **4d**)—in colour ranging from yellow to orange—are soluble in benzene, toluene and dichloromethane and insoluble in petroleum ethers or highly polar solvents.

The stabilities of the new compounds differ vastly, with **4c** being air-stable and **3b** only stable at −80°C under inert atmosphere. The relative stabilities vary in the order **4c** > **4d** > **3a** $\gg$ **3b**.

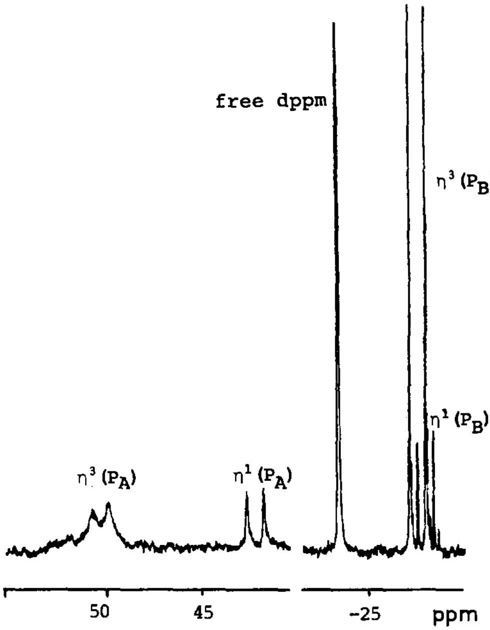


Fig. 1. $^{31}P\{^1H\}$ NMR spectrum of [(η^1-C_4H_7)Co(CO)$_3$(dppm)] (**1b**), partially converted to (η^3-C_4H_7)Co(CO)$_2$(dppm) (**3b**) at room temperature. (P_A is the coordinated phosphorus atom; P_B is the uncoordinated phosphorus atom.)

The result of the dppm reaction is somewhat surprising considering the relatively few monodentate dppm complexes that have been isolated so far [9–11]. A study by Brill and coworkers of the solution chemistry of CpCo(CO)I_2 when treated with dppm, revealed the existence of an intermediary product thought to be [CpCo(dppm)I_2] which contains a monodentate dppm ligand [12]. This product could unfortunately not be studied spectroscopically as it was short-lived and was converted to the chelated product in solution. The two dppm compounds prepared in this work, are to our knowledge the first examples of monodentate cobalt dppm compounds which could be isolated and studied extensively.

The coordination of dppe in a bridged fashion is not altogether unexpected—amongst others the bridged dimer {Co(NO)(CO)$_2$}$_2$(μ-dppe-PP) has been characterized [13]. Moreover, in view of the known inability of phosphines to replace more than one carbonyl ligand from (η^3-allyl)Co(CO)$_3$, it was not anticipated that dppe would coordinate in a chelated fashion [1]. Finally, the rarity of monodentate dppe ligands effectively ruled out this possibility.

The question of dppm remaining monodentate was at this stage still unanswered. Attempts to obtain a suitable crystal of (η^3-C_3H_5)Co(CO)$_2$(dppm) for an X-ray structure determination were unsuccessful. However, it was hoped that a structural analysis of one of the bridged dppe compounds would clarify the matter. The crystal structure of {(η^3-C_3H_5)Co(CO)$_2$}$_2$(μ-dppe-PP) (**4c**) showed the allyl group to be strained. The inability of the "dangling" dppm ligand to attach itself to a second cobalt centre therefore appeared to be a consequence of the even more limited space available for movement of the phenyl groups. This is discussed in more detail in the section on the crystal structure.

Table 2

Carbonyl stretching frequencies for the η^3-allyl compounds [a]

Complex	ν(CO) (cm^{-1}) [b]	ν(CO) (cm^{-1}) [c]
3a	1977, 1920	1984, 1926
3b	1978, 1908	1984, 1925
4c	1971, 1912	1979, 1919
4d	1970, 1919	1978, 1919

[a] Bands are of equal intensity. [b] KBr pellet. [c] CH_2Cl_2 solution.

Infrared spectroscopy. The carbonyl stretching bands for the new complexes are given in Table 2. Two bands of equal intensities were found as is expected for two *cis* carbonyl ligands. The frequencies correspond with those recorded for (η^3-RC_3H_4)Co(CO)$_2$(PPh$_3$) (R = H, CH_3) [14,3]. A more complete study of the vibrational spectra of (η^3-RC_3H_4)Co(CO)$_3$ has also been reported [15].

No spectra were obtained for the η^1-allyl compounds due to their instability in solution at room temperature.

^1H NMR spectroscopy. Values of the chemical shifts of the ^1H resonances for the new η^3-allyl complexes are given in Table 3. Assignments were made on the basis of the allyl ligand being fluxional and were compared with those of the analogous triphenylphosphine complex (η^3-C_4H_7)Co(CO)$_2$(PPh$_3$) [3]. The presence (or absence) of coupling between any two protons was confirmed by recording a ^1H–^1H correlated spectrum (COSY) for **4d**—any additional splitting of the resonances was then ascribed to coupling with the two phosphorus atoms.

In contrast to the dppm complexes (**3a** and **4c**) which have simple first-order spectra, those of the μ-dppe compounds exhibit second-order phenomena preventing the extraction of all the coupling constants. For instance, the resonance of the *syn*-protons, H_A and H_E, of **3a** is a simple doublet of doublets. For **4c** it is observed as a broad triplet. On closer inspection, it seems that, as a result of the involvement of both phosphorus nuclei, these *syn* protons form part of an AA′XY ($A = {}^{31}P$, $X = Y = {}^1H$) spin system involving H_C. Such a spin system would give rise to a deceptively simple spectrum under conditions which require $J(AA')$ and $J(XY)$ to be large compared to $\delta(AA')$ amongst other things (δ here being the difference in chemical shift). A mathematical analysis of this spin system has been carried out [16]. The resonance of the *anti* protons of **4c** (H_B and H_D), which can also be said to form part of an AA′XY system (involving H_C as $^2J(H_{anti}H_{syn}) = 0$), has a slightly different appearance (broadened quintet) as a consequence of $J(AX)$ being larger for the *syn* than for the *anti* protons. Unlike the methyl resonance of **3b** which is a doublet of doublets, that of **4d** occurs as a doublet of non-1 : 2 : 1 triplets [17*]. This phenomenon also stems from the involvement of two other spin-$\frac{1}{2}$ nuclei—these protons can thus be regarded as the X-part of an AA′X$_3$Y system ($Y = H_D$) which only allows calculation of the average coupling constant $\frac{1}{2}[J(AX) + J(AX')]$.

The two methylene protons of **3a** and **3b** respectively, are magnetically equivalent and result in a doublet of doublets due to $J(PP)$ being large. The broad singlet

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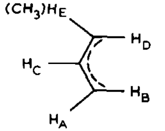
* Reference number with asterisk indicates a note in the list of references.

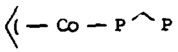
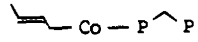
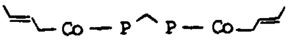
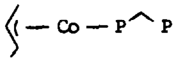
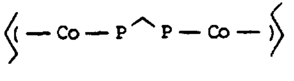
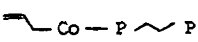
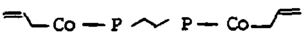
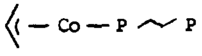
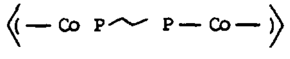
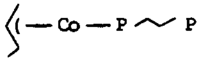
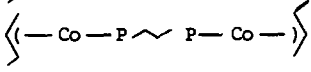
Table 3. ^1H NMR spectral data for **3a**, **3b**, **4c** and **4d** [a]

Compound	Allyl protons 					Methylene protons		Phenyl protons	
	H_A, H_E [c] *syn*	H_B, H_D *anti*	H_C			$\delta(H)$	$J(PH)$	H_{ortho}	$H_{meta} + H_{para}$
3a	2.51 (dd, 2H) $^2J(H_AH_B)$ 0.0	1.85 (d, 2H) $^3J(H_BH_C)$ 10.4	4.30 (sp, 1H) $^3J(H_AH_C)$ 5.9			3.15 (dd, 2H)	8.4 P_A 2.1 P_B	7.48 P_A (m, 4H) 7.29 P_B (m, 4H)	6.94 (m, 12H)
3b	2.49 (dt, 2H) $^2J(H_AH_B)$ 0.0	1.88 (d, 2H) $^3J(H_BH_C)$ 10.4	4.31 (sp, 1H) $^3J(H_AH_C)$ 5.9			2.63 (s br, 4H)	[b]	7.48 P_A (m, 8H)	6.94 (m, 12H)
	H_A [d] *syn*	H_B *anti*	H_C	H_D *anti*	CH_3	$\delta(H)$	$J(PH)$	H_{ortho}	$H_{meta} + H_{para}$
4c	2.28 (dd, 1H) $^2J(H_AH_B)$ 0.0 $^3J(P_AH_A)$ 9.6	1.55 (dd, 1H) $^3JH_BH_C)$ 10.2 $^3J(P_AH_B)$ 4.5	4.21 (dt, 1H) $^3J(H_AH_C)$ 6.1 $^3J(P_AH_C)$ 0.0	2.65 (qn, 1H) $^3J(H_CH_D)$ 9.9 $^3J(P_AH_D)$ [b]	1.46 (dd, 3H) $^3J(H_DH_{CH_3})$ 6.2 $^3J(P_AH_{CH_3})$ 4.5	3.16 (dd, 2H)	8.5 P_A 1.5 P_B	7.50 P_A (m, 4H) 7.30 P_B (m, 4H)	6.94 (m, 12H)
4d	2.20 (qn, 2H) $^2J(H_AH_B)$ 0.0 $^3J(P_AH_A)$ [b]	1.59 (t, 2H) $^3J(H_BH_C)$ 10.3 $^3J(P_AH_B)$ [b]	4.24 (qn, 2H) $^3J(H_AH_C)$ [b] $^3J(P_AH_C)$ 0.0	2.69 (m, 2H) $^3J(H_CH_D)$ [b] $^3J(P_AH_D)$ [b]	1.46 (dt, 6H) $^3J(H_DH_{CH_3})$ 10.3 [e] 2.1	2.64 (s br, 4H)	[b]	7.50 (m, 8H)	6.97 (m, 12H)

[a] Measured at 300 MHz; chemical shift values in ppm relative to benzene-d_6 ($\delta = 7.15$ ppm); coupling constants in Hz; abbreviations: dt = doublet of triplets, dd = doublet of doublets, qn = quintet, sp = septet, m = multiplet, br = broad; P_A is the coordinated phosphorus, P_B is the "dangling" phosphorus. [b] Coupling constants not directly obtainable due to second-order effects (see text). [c] $^3J(P_AH_A) = {}^3J(P_AH_E) = 4.0$ Hz. [d] $^3J(P_AH_A) = {}^3J(P_AH_E) = 2$ Hz. [e] Average value: $\frac{1}{2}[J(H_{CH_3}P_{A_1}) + J(H_{CH_3}P_{A_2})]$.

Table 4

$^{31}P\{^1H\}$ NMR spectral data [a]

	Product [d]	P_A [c]	P_B	$J(P_AP_B)$
3a		46.8	−32.3	96
4a		46.3		
1b		42.1	−27.1	98
2b		[d]		
3b		45.6	−32.4	96
4b		45.2		
1c		[d]		
2c		68.7		
3c		52	−18.8	38.5
4c		51.1		
3d		51.5	−18.7	38.6
4d		50.3		

[a] Products **1** and **2** measured in acetone-d_6; products **3** and **4** measured in benzene-d_6; referenced against external 85% H_3PO_4. [b] Carbonyls omitted for clarity. [c] P_A is the coordinated phosphorus; P_B is the free phosphorus. [d] Products were thermally too unstable or yields to low to be detected.

observed for the methylene protons of **4c** and **4d** seems to be the result of the coincidence of chemical shift and a relatively small J(PP), not an unknown problem with coordinated dppe [16]. The observance of three distinct multiplets (in the ratio 4 : 4 : 12) in the aromatic region is consistent with the different environments in which the two phosphorus nuclei of **3a** and **3b** find themselves. The resonance with the largest downfield shift is assigned to the four *ortho* protons of the two phenyl rings on the coordinated phosphorus atom, the higher field multiplet to the other four *ortho* protons and the large multiplet to the remaining, least shielded phenyl protons. In contrast, the spectra of **4c** and **4d** only contain two multiplets (ratio 8 : 12) in this region as all eight *ortho* protons are equivalent.

$^{31}P\{^1H\}$ NMR spectroscopy. Chemical shifts and coupling constants for the ^{31}P resonances for some of the new compounds are given in Table 4.

Not only was ^{31}P NMR useful for recognizing compounds in a crude product mixture, but it was used for characterisation purposes together with ^{1}H NMR. ^{31}P NMR instantly revealed whether a bis(phosphine) was coordinated in a bridged or monodentate fashion. Bridged ligands give rise to a broad singlet, while a high-field doublet (unattached phosphorus) together with a broad low-field doublet are observed for monodentate bis(phosphines) (see e.g. Fig. 1). The observed broadening of the low-field resonances is thought to be a consequence of the large quadrupole moment ($I = \frac{7}{2}$) of the cobalt nucleus.

Attempts to make a meaningful comparison of the observed magnitude of ^2J(PP) (96–98 Hz) with that of existing compounds, were made difficult by the failure (for various reasons) of authors to supply these values [9,12]. Values of a comparable magnitude were, however, recorded for $[(C_7H_7)Mo(CO)_2(dppm)][PF_6]$ and $[C_5H_5Fe(CO)_2(dppm)][PF_6]$ (^2J(PP) = 97.7 and 90.0 Hz respectively) [18].

^{13}C NMR spectroscopy. ^{13}C resonances were readily assigned and confirmed by recording proton coupled ^{13}C spectra. Chemical shifts and coupling constants are given in Table 5.

Allyl carbons. The resonances of the three allyl carbons occur in the expected ranges [19]. Substitution of one of the protons on a terminal allyl carbon by a methyl group, causes this allyl carbon to shift downfield by about 16 ppm whereupon its ^{1}H coupled resonance changes from a triplet ($^1J(C_CH)$ = 159 Hz) to a doublet ($^1J(C_CH)$ = 169 Hz). The other two allyl carbons are not shifted to any significant extent.

The two-bond coupling with phosphorus ($^2J(P_AC_A)$ and $^2J(P_AC_C)$) can unfortunately not be quantified, partly because of the broadening effect of the ^{59}Co on the carbon resonances and partly because of these P–Co–C angles deviating from 180°—causing J(PC) to be extremely small. Rinze, in contrast, managed to extract a coupling for ^2J(PC) of 2.9 Hz [2].

Methylene carbons. The single methylene carbon of each of the dppm compounds **3a** and **3b** forms the X-part of a simple AMX system (A = M = ^{31}P) and as such is observed as a doublet of doublets. The stronger coupling is thought to be the result of coupling with the uncoordinated phosphorus, as the movement of electron density from the coordinated phosphorus towards the cobalt centre would lead to weaker coupling between P_A and C compared to that in free dppm where ^1J(PC) is 24 Hz. The proton coupled spectrum of **3b** shows the methylene carbon as a triplet of doublets of doublets with a ^1J(CH) of 136 Hz.

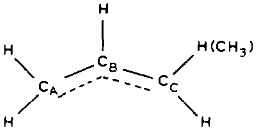
In the bridged dppe compounds, **4c** and **4d**, the two phosphorus nuclei are chemically equivalent, but magnetically non-equivalent. This implies that the PCCP arrangement forms an AA′X (A = ^{31}P, X = ^{13}C) spin pattern. On the ^{13}C{^{1}H} spectrum of **3b**, the ^{13}C methylene carbon appears as a 1 : 2 : 1 triplet. This is a second order phenomenon resulting from the presence of two or more spin-$\frac{1}{2}$ nuclei other than ^{13}C or ^{1}H, which are strongly coupled. From this triplet it is thus not possible to obtain anything other than an average coupling constant.

The two methylene carbons in **4d** seem to be slightly inequivalent (a possible consequence of the anisotropy introduced by the methyl group), giving rise to two overlapping triplets instead of the single one mentioned above.

Phenyl carbons. The carbon atoms of the phenyl rings resonate in the region 140–128 ppm. Four distinct groups of resonances (representing C_{ipso}, C_{ortho}, C_{para}, C_{meta} in that order) can be distinguished on each of the spectra of the η^3-allyl compounds.

Table 5

^{13}C and $^{13}C\{^1H\}$ NMR data [a]



Compound	Allyl carbons							Methylene carbons	
	C_C	C_B	C_A	CH_3	$^2J(PC)$	and	$^1J(CH)$	$\delta(C)$	J
3a [f]	47.3(s)	80.8(s)	47.3(s)	-		[b,c]		34.30(dd)	$^1J(P_AC) = 20.4$ $^1J(P_BC) = 31.8$
3b [g]	47.3(s)	81.0(s)	47.3(s)	-		[b,c]		27.64(t)	$^{1+2}J(P_AC) = 14.1$
4c [h]	62.7(s)	83.7(s)	46.4(s)	20.4(s)	$^2J(P_AC_C)$: b $^1J(C_CH) = 169$ $^1J(C_AH) = 159$	; ; ;	$^2J(P_AC_A)$: b $^1J(C_BH) = 162$ $^1J(CH_3H) = 126$	34.18(dd)	$^1J(P_AC) = 19.4$ $^1J(P_BC) = 31.2$ $^1J(CH) = 136.1$
4d [f]	63.0(s)	83.8(s)	46.4(s)	20.5(s)	$^2J(P_AC_C)$: b $^1J(C_CH) = 164$ $^1J(C_AH) = 151$	; ; ;	$^2J(P_AC_A)$: b $^1J(C_BH) = 166$ $^1J(CH_3H) = 127$	27.64(t) 27.57(t)	$^{1+2}J(P_AC) = 13.7$ $^1J(CH) = 132.2$

[a] Obtained at 75 MHz; chemical shifts in ppm relative to the solvent (benzene-d_6: $\delta = 128.0$ ppm); coupling constants in Hz; P_A is the coordinated phosphorus, P_B is the free phosphorus. Abbreviations: dd = doublet of doublets, t = apparent triplet, add = apparent doublet of doublets; br = broad. [b] Resonances of carbons bonded to C_o do not permit calculation of $^2J(CP)$ (see text). [c] ^1H coupled spectra of **1c**

Spectra are not only complicated by the two magnetically inequivalent (from a ^{13}C point of view) ^{31}P nuclei, but by an increasing degree of inequivalence of the phenyl rings in the order **4c** (all four rings equivalent) < **4d**, **3a** (two + two rings equivalent) < **3h** (all four rings inequivalent). Being the least complicated, the spectrum of **4c** was used as a starting point in the analysis. The C_{ipso}, C_{ortho} and C_{meta} resonances of **4c** are apparent triplets, as each forms the X-part of an AA′X spin set from which it is possible to calculate $\frac{1}{2}[^nJ(AX) + {}^{n+3}J(A'X)]$.

The magnitudes of $^nJ(AX)$ and $^nJ(A'X)$ (and therefore that of $^nJ(AX) + {}^{n+3}J(A'X)$) have been shown to depend on the magnitude of $^nJ(AA')$ [20,21]. This is elegantly illustrated by making a comparison between the phenyl spectral region of free dppe with that of bridged dppe, the latter in effect being a dppe unit with a small magnet attached to each end. In Fig. 2, the decrease in $^3J(AA')$ ($A = {}^{31}P$) upon going from free dppe to bridged dppe is clearly shown by the changes in the patterns of the C_{ipso} and C_{ortho} resonances when compared with the simulated patterns [20,21].

The *ipso* carbons of **4d** and **3a**, on the other hand, occur as two sets of doublets of doublets respectively (each set therefore representing two carbon atoms). Whereas the *ipso* carbons of **3a** are without doubt the X-part of a simple AMX system, the pattern observed for those of **4d** appears to be the result of an AA′X system ($X = {}^{13}C$) but this time with $^3J(AA')$ very small compared to $J(AX) + J(A'X)$. The *ortho* carbon atoms of **4d** occur as apparent triplets (non-1 : 2 : 1) with the distance between the outer lines $^{2+5}J(P_AC)$ being 5 Hz. The expected doublet of doublets for C_{ortho} of **3a** is observed as a broad doublet probably as a consequence of $^4J(P_BC)$ being small.

Phenyl carbons				Carbonyl carbons	
C_i	C_o	C_m [e]	C_p	$(CO)_2$	$(CO)_2$
139.32(dd) $^1J(P_AC_i) = 16.6$ $^3J(P_BC_i) = 7.8$ 137.22(dd) $^1J(P_AC_i) = 37.7$ $^3J(P_BC_i) = 4.0$	133.40(d,br)	128,6(s,br)	129.61(s)	207.10(br)	
136.57(t) $^{1+4}J(P_AC_i) = 19$	132.05(t) $^{2+5}J(P_AC_o) = 5$	128.72(t) $^{3+6}J(P_AC_m) = 4$	129.9(br)	207.02(br)	
140.0–136.6	133.51–132.7	128.7–128.2	131.6–129.4	207.29	208.72
137.25(add) $^{1+4}J(P_AC_i) = 37.0$	132.27(t) $^{2+5}J(P_AC_o) = 5$	128.69(br)	129.85(s)	207.44	208.44
136.40(add)	132.00(t) $^{2+5}J(P_AC_o) = 5$		129.70(s)		

and **2c** were not recorded. [d] C_i refers to the four *ipso* carbons; C_o and C_m to the eight *ortho* and *meta* carbons, respectively, and C_p to the four *para* carbons of the phenyl groups. [e] Occasionally partially obscured by strong solvent signal. [f] 2+2 phenyl groups equivalent (see text). [g] All 4 phenyl groups equivalent (see text). [h] All 4 phenyl groups inequivalent (see text).

Due to the inequivalence of all four phenyl groups of compound **4c** extensive overlapping of peaks prevents the extraction of any coupling constants. However, each of the four distinct groups of peaks were (by way of comparison with the spectra of the other compounds) assigned to either the *ipso, ortho, meta* or *para* carbon atoms.

Carbonyl carbons. Notwithstanding the obvious inequivalence of the two carbonyl ligands, only one slightly broadened signal is observed on the $^{13}C\{^1H\}$ NMR spectrum. This was also the case with $(\eta^3\text{-}C_3H_5)Co(CO)_2(PPh_3)$ where, even after cooling to 183 K, only one signal emerged [2]. In contrast, two resonances are observed for each of the methylallyl compounds **3b** and **4d**.

The observed equivalence of the carbonyl groups cannot only be explained in terms of limited rotation of the η^3-allyl group [2]. Provision also has to be made for an extent of rotation of the entire $(\eta^3\text{-allyl})Co(CO)_2$-unit at the Co–P bond in order to vindicate this apparent equivalence, as one CO clearly extends towards the two phenyl groups while the other extends away from them. Such rotation would also justify the earlier described observation regarding similarity/dissimilarity of the phenyl groups.

Mass spectroscopy. The η^3-allyl compounds are observed to fragment by way of the consecutive loss of ligands in the order (i) CO (ii) allyl (iii) phosphine, which is the expected order [22].

The molecular ion peak is not observed for any of the compounds. The peak of highest *m/e*-value is invariably $M^+ - 2CO$ except for the least stable compound, **3b**, for which it is $[Co(dppm)]^+$. If peak intensities are considered, it appears that the

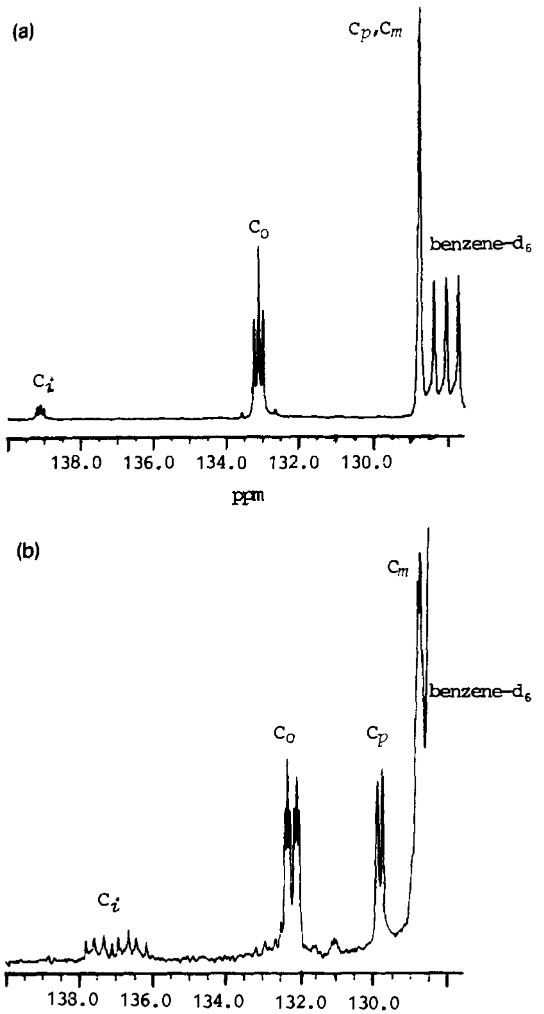
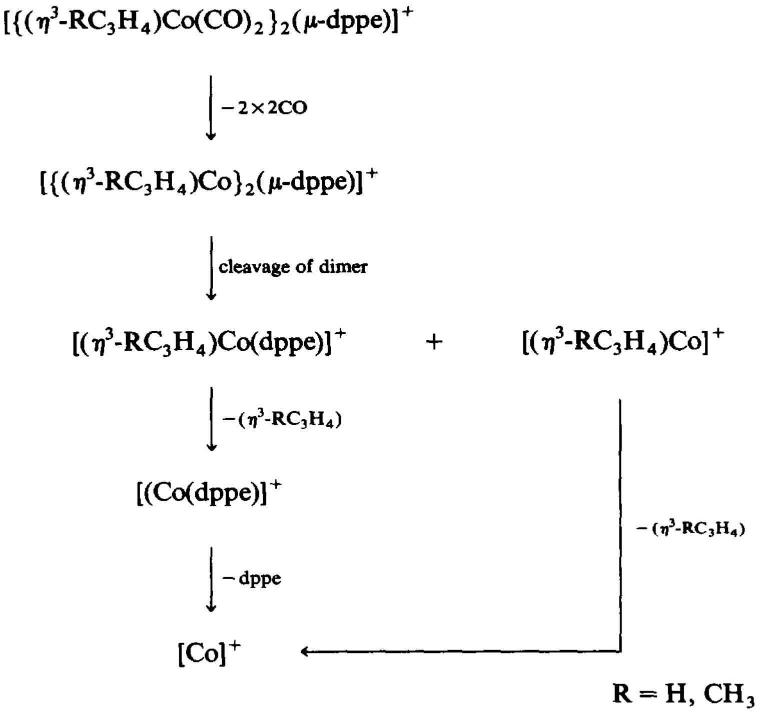


Fig. 2. $^{13}C\{^1H\}$ NMR spectra (phenyl regions) of a) free dppe, b) bridged dppe, showing the dependence of the spin pattern on ^3J(PP).

μ-dppe complexes are cleaved initially (after losing the CO) to give the fragments $[(\eta^3\text{-}RC_3H_4)Co(dppe)]^+$ and $[(\eta^3\text{-}RC_3H_4)Co]^+$ ($R = H, CH_3$) which subsequently fragment further. The fragmentation pattern for **4c** and **4d** is shown in Scheme 2.

*Crystal structure of **4c**.* The reluctance of dppm to coordinate at both ends was thought to be a consequence of structural restrictedness, which could only be verified with a complete structural analysis. Fortunately, although no suitable crystals could be grown of $(\eta^3\text{-}C_3H_5)Co(CO)_2(dppm)$, valuable indirect information was derived from the structure of **4c**, which in itself proved unusual.

Orange, air stable, single crystals of **4c** suitable for diffraction studies were grown from dichloromethane/hexane mixtures. The asymmetric unit consisted of one half of the molecule and is shown in Fig. 3 with the atomic numbering scheme used. Fig.



Scheme 2

4 offers a stereoview of **4c** and selected interatomic distances and angles are listed in Table 6.

The molecular environment of which cobalt forms the centre can be described as either pseudo tetrahedral with the allyl ligand occupying one coordination site or as

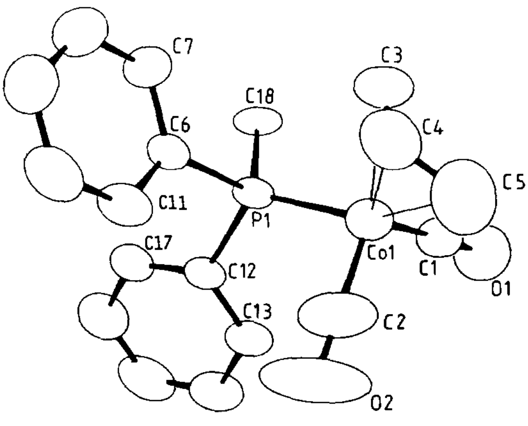


Fig. 3. Perspective view (ORTEP) [23] of $\{(\eta^3\text{-C}_3\text{H}_5)\text{Co(CO)}_2\}_2(\mu\text{-dppe-PP})$ (**4c**) showing the numbering of the atoms.

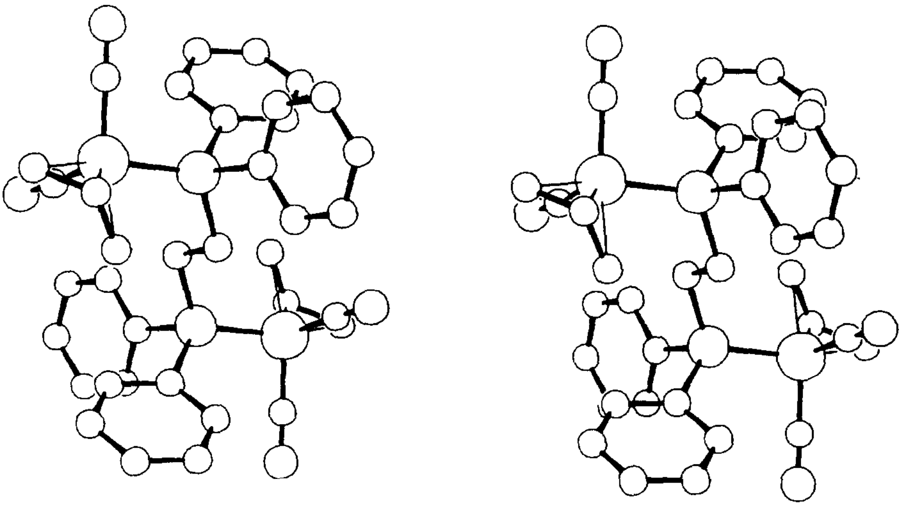


Fig. 4. Stereoscopic view of $\{(\eta^3\text{-C}_3\text{H}_5)\text{Co(CO)}_2\}_2(\mu\text{-dppe-PP})$ (**4c**).

a square pyramid. The first description is often used for the isoelectronic complexes $\text{Mn}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3$, $\text{Fe}(\eta^4\text{-C}_4\text{H}_6)(\text{CO})_3$ and $\text{Co}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_3$, the dppe complex **4c** is a derivative of the latter, with the organic ligand occupying a single coordina-

Table 6

Selected bond lengths (Å) and valence angles (°) for $\{(\eta^3\text{-C}_3\text{H}_5)\text{Co(CO)}_2\}_2(\mu\text{-dppe-PP})$ (**4c**)

Co(1)-P(1)	2.158(2)	Co(1)-C(1)	1.756(6)
Co(1)-C(2)	1.747(7)	Co(1)-C(3)	2.151(6)
Co(1)-C(4)	2.012(6)	Co(1)-C(5)	2.093(6)
P(1)-C(6)	1.822(5)	P(1)-C(12)	1.864(5)
P(1)-C(18)	1.828(5)	O(1)-C(1)	1.152(6)
O(2)-C(2)	1.130(7)	C(3)-C(4)	1.452(9)
C(4)-C(5)	1.388(9)	C(18)-C′(18)	1.601(9)
P(1)-Co(1)-C(1)	105.3(2)	P(1)-Co(1)-C(2)	96.2(3)
C(1)-Co(1)-C(2)	109.2(3)	P(1)-Co(1)-C(3)	88.7(2)
C(1)-Co(1)-C(3)	104.2(3)	C(2)-Co(1)-C(3)	143.5(3)
P(1)-Co(1)-C(4)	111.6(2)	C(1)-Co(1)-C(4)	125.3(3)
C(2)-Co(1)-C(4)	105.4(3)	C(3)-Co(1)-C(4)	40.6(2)
P(1)-Co(1)-C(5)	151.0(2)	C(1)-Co(1)-C(5)	98.0(3)
C(2)-Co(1)-C(5)	92.1(3)	C(3)-Co(1)-C(5)	68.7(3)
C(4)-Co(1)-C(5)	39.5(3)	Co(1)-P(1)-C(6)	113.4(2)
Co(1)-P(1)-C(12)	118.5(2)	C(6)-P(1)-C(12)	103.0(2)
Co(1)-P(1)-C(18)	117.9(2)	C(6)-P(1)-C(18)	102.0(2)
C(12)-P(1)-C(18)	99.4(2)	Co(1)-C(1)-O(1)	176.2(6)
Co(1)-C(2)-O(2)	177.6(6)	Co(1)-C(3)-C(4)	64.5(3)
Co(1)-C(4)-C(3)	74.8(3)	Co(1)-C(4)-C(5)	73.4(4)
C(3)-C(4)-C(5)	115.0(7)	Co(1)-C(5)-C(4)	67.1(4)
P(1)-C(6)-C(7)	122.3(4)	P(1)-C(6)-C(11)	119.1(4)
C(7)-C(6)-C(11)	118.3(5)	C(13)-C(12)-C(17)	121.1(5)

tion site [8,24*,25]. The greatest deviations from an ideal tetrahedron in **4c** are found in the large C(4)–Co–C(1) and small C(2)–Co–P(1) angles of 125.3(3) and 96.2(3)°, respectively. We find a distorted square pyramid to be a better description for the geometry around the cobalt in **4c**. A carbonyl ligand, which is the strongest π-acceptor ligand, occupies the apical position, the bulkier phosphine, allyl and the second carbonyl ligand form the base. The basal ligands are bent away from the apical one. Correlation is found with the structures of (η^4-diene)Fe(CO)$_3$ complexes where the metal adopts approximately square-pyramidal geometry [26]. Five coordinated cobalt(I) complexes with square pyramidal structures may be the result of electronic requirements as is the case with allyl ligands, or steric considerations as was demonstrated for [Co(PPh$_3$)$_2$(SiMe$_3$)(CO)$_2$] [27].

The overall picture emerging from a comparison of the structure of **4c** with those of [Co(η^3-C$_3$H$_5$)(PPh$_3$)(CO)$_2$], [{Co(CO)$_3${η^3-(CH$_2$)$_2$CCH$_2$}}$_2$], [{Co(P(OMe)$_3$)(CO)$_2${η^3-(CH$_2$)$_2$CCH$_2$}}$_2$CO] and [Co(CO)$_3${η^3-(CPh)$_3$CO}] is that the structure of **4c** is severely distorted [2,4,28]. In addition to the expected asymmetry due to cobalt–η^3-allyl bonding (Co–C(terminal) distance > Co–C(central) distance), C(3) in particular is pushed and twisted away from the adjacent bulky dppe ligand [4,29–31]. As shown in Fig. 4, C(5) which is approximately *trans* to P(1) (C(5)–Co–P = 151°) is apparently bonded more strongly to Co than C(3) (Co–C(3) = 2.151(6) Å vs. Co–C(5) = 2.093(6) Å). Moreover, C(3)–C(4) (1.452(9) Å) is significantly longer than C(4)–C(5) (1.388(9) Å) which suggests Co–allyl backbonding in the C(4)–C(5) portion of the allyl ligand to be less important. The fact that the longer C–C(allyl) bond distance occurred *trans* to the phosphite ligand in [{Co(P(OMe)$_3$)(CO)$_2${η^3-(CH$_2$)$_2$CCH$_2$}}$_2$CO], was attributed to electronic effects by Pettit [4]. A further indication as to the strained condition of the allyl group is the smaller C(3)–C(4)–C(5) angle (115°) measured for **4c** compared to 119° for (η^3-C$_3$H$_5$)Co(CO)$_2$(PPh$_3$) and 123° for the unsubstituted (η^3-C$_3$H$_5$)Co(CO)$_3$ (electron diffraction) [2,25]. Additionally, the dppe ligand has had to adjust itself in the available space in order to accommodate the cobalt moiety on each end. The distance between the phosphorus atom and the phenyl group closest in space to the allyl group (i.e. the P(1)–C(6) bond) is shorter than the distance to the other phenyl group (P(1)–C(12)). This need for space in which to extend and orientate its phenyl groups explains why dppm did not form the bridged compound.

Apart from the abovementioned structural deviations, a further structural comparison could not be realised due to the lack of comparable structures in the literature. Notable was the substantial variation of the Co–P bond length of 2.158(2) Å for **4c** which is shorter than for instance the values of 2.233(2) Å and 2.240(2) Å for the trigonal bipyramidal structure of [Co(dppe-PP)(CO){C(O)CH(OEt)CH(OEt)CH$_3$}] and 2.185(1) Å for the square pyramidal structure of [Co(η^3-C$_3$H$_5$)(CO)$_2$(PPh$_3$)], although the environment around the phosphorus compares poorly with that of **4c** [7,2]. Co–C(carbonyl) bond lengths, however, are less sensitive to changes from trigonal bipyramidal to square pyramidal geometries (range 1.72–1.78 Å) [27,32].

Experimental

General procedures. All reactions were carried out under strict inert conditions. Solvents were distilled under nitrogen after having been pre-dried. Commercial

$Co_2(CO)_8$ and dppm (Strem Chemicals) were used without further purification. Dppe (Fluka) was recrystallised from dichloromethane/hexane before use.

Melting points were determined on a Gallenkamp hot-stage melting point apparatus and are uncorrected.

Elemental analyses were determined at the PCMT division, Council for Scientific and Industrial Research, Pretoria.

Infrared spectra were recorded with a Bomem Michelson - 100 FTIR spectrometer. Spectra were obtained from solutions as well as solids. Spectroscopic grade solvents were degassed by three freeze–thaw cycles prior to preparation of the sample solutions under N_2. Cells were purged with N_2 before use.

NMR spectra were recorded on a Bruker AC 300 instrument at 303 K. Deuterated solvents were degassed using liquid N_2 (as above). Samples were prepared under N_2 and lids of sample tubes secured with PTFE ribbon to prevent air from

Table 7

Structural, acquisition and refinement details of the X-ray crystallographic studies of $\{(\eta^3\text{-}C_3H_5)Co(CO)_2\}_2(\mu\text{-dppe-}PP)$ (**4c**)

Empirical formula	$C_{36}H_{34}Co_2O_4P_2$
Molecular weight	710
Crystal dimension, mm	0.18×0.55×0.20
Space group	$P\bar{1}$
Cell dimensions	
a, Å	8.825 (8)
b, Å	9.557 (4)
c, Å	11.828 (5)
α, °	105.39 (4)
β, °	101.88 (6)
γ, °	111.30 (5)
Z	1
Volume, Å^3	843.9
D(calc), g·cm^{-3}	1.397
μ, cm^{-1}	10.49
Radiation (λ, Å)	Mo-K_α ($\lambda = 0.7107$)
T, °C	25
$F(000)$	366
Scan type ($\omega:2\theta$)	1:1
Scan range (θ °)	$3 \leqslant \theta \leqslant 30$
hkl-indices	
h	0:12
k	−13:13
l	−16:16
Scan speed (variable, deg.min^{-1})	max 5.49
Scan angle ($\omega + 0.34 \tan\theta$)°	0.55
Aperture size (mm)	1.3×4.0
Reflections collected	4928
R_{int}	0.064
Unique reflections used ($> 4\sigma I$)	3193
Parameters refined	200
R_w	0.056
R	0.071

Table 8

Fractional coordinates ($\times 10^4$) and equivalent thermal factors ($\times 10^3$ Å^2) for $\{(\eta^3\text{-}C_3H_5)Co(CO)_2\}_2(\mu\text{-dppe-}PP)$ [a]

Atom	x	y	z	U_{eq}
Co(1)	1257(1)	2499(1)	2952(1)	50(1)
P(1)	−921(2)	2906(2)	3211(1)	36(1)
O(1)	4191(6)	5683(5)	4043(5)	93(2)
O(2)	157(10)	1652(6)	299(5)	142(3)
C(1)	3037(8)	4418(8)	3650(6)	58(2)
C(2)	584(11)	1952(7)	1338(7)	82(2)
C(3)	1260(10)	1543(9)	4406(8)	84(2)
C(4)	1186(11)	495(8)	3235(8)	80(3)
C(5)	2616(11)	1101(9)	2876(8)	95(3)
C(6)	−2859(7)	1046(6)	2808(5)	39(1)
C(7)	−3399(8)	509(6)	3710(6)	53(2)
C(8)	−4821(8)	−972(7)	3369(7)	65(2)
C(9)	−5702(8)	−1921(7)	2139(7)	70(2)
C(10)	−5170(9)	−1427(7)	1226(6)	71(2)
C(11)	−3737(8)	52(6)	1573(6)	60(2)
C(12)	−1713(7)	4004(6)	2335(5)	39(1)
C(13)	−630(8)	4872(6)	1811(5)	52(2)
C(14)	−1126(10)	5821(7)	1254(6)	69(2)
C(15)	−2636(11)	5894(8)	1256(6)	76(2)
C(16)	−3712(9)	5035(8)	1768(6)	72(2)
C(17)	−3232(8)	4088(7)	2324(5)	54(2)
C(18)	−710(7)	4084(5)	4780(5)	46(1)

[a] $U_{eq} = \frac{1}{3}\Sigma_i \Sigma_j U_{ij} a_i^{\star} a_j^{\star} (\mathbf{a}_i \cdot \mathbf{a}_j)$.

entering. Spectra were obtained at the following frequencies: 300.13 MHz (^{1}H), 75.47 MHz (^{13}C) and 121.49 MHz (^{31}P). For ^{13}C spectra, approximately 20 mg sample was dissolved in 0.5 mL solvent. Data accumulation was done using a 45° pulse delayed for 2–4 seconds. Although 2000 scans were usually sufficient to obtain an acceptable S/N ratio, carbonyl ligands required several thousand more scans in order to be detected.

Mass spectra were recorded on a Varian MAT-212 double focussing direct inlet spectrometer operating at 70 eV at the PCMT division, CSIR, Pretoria.

X-ray analysis. All diffraction measurements were performed at room temperature and data collected with an Enraf–Nonius CAD4 diffractometer using monochromated Mo-K_α radiation. Diffraction quality prismatic single crystals of **4c** were obtained after recrystallization from dichloromethane and hexane. The lattice constants were obtained from a least squares fit of 25 centered reflections ($6° < \theta < 18°$) and are listed with other relevant crystal data in Table 7. The data were corrected for Lorentz and polarization effects, and for absorption using an empirical method involving ψ-scans. Intensity checks were carried out every hour and an orientation control every 200 reflections. The maximum and minimum transmission factors were 0.9984 and 0.9067 (0.9415 average). Three standard reflections were used to check orientation and crystal stability at regular intervals, and the decay during data collection was less than 1%. The structure was solved by Patterson and subsequent Fourier methods and refined anisotropically with a full-matrix method ($1/\sigma^2F$-weights) using SHELX [33]. All hydrogen atoms were placed in calculated positions and refined with a common isotropic temperature factor that converged to $U = 0.117(6)$ Å^2. Scattering factors for cobalt(I) were taken from the literature [34]. The final difference electron density map revealed one peak with $\rho > 1$ e$^-$/Å^3 approximately 1 Å from the cobalt atom. Fractional coordinates and equivalent thermal factors for **4c** are listed in Table 8.

Supplementary material. Tables of anisotropic temperature factors, bond lengths and bond angles, and observed and calculated structure factors are available from the authors.

Synthesis. $Na[Co(CO)_4]$ was synthesized by essentially the same method as that of Edgell and (η^3-RC_3H_4)$Co(CO)_3$ according to a modified version of that of Heck [35,14].

$Na[Co(CO)_4]$. 0.342 g (1 mmol) $Co_2(CO)_8$ together with 0.08 g (2 mmol) NaOH in 20 mL THF was commonly used. This salt was prepared immediately prior to further use; the THF-solution of $Na[Co(CO)_4]$ was merely filtered into the flask to be used for the next reaction.

*(η^1-C_4H_7)$Co(CO)_3$(dppm) (**1b**).* To a cooled (−10°C) solution of $Na[Co(CO)_4]$ (2 mmol) in THF, a solution of dppm (0.768 g, 2 mmol) in 2 mL dichloromethane/5 mL THF was added slowly. A solution of crotyl chloride (0.19 mL, 2 mmol) was added dropwise, followed by stirring for an hour. The solvent was removed under reduced pressure. The residue was washed twice with cold pentane (−30°C), whereafter the product was dissolved in cold diethyl ether and filtered to remove excess dppm. The clear yellow solution was reduced to dryness to reveal a pale yellow powder which was dried further in vacuo. The product can be stored on dry ice for a few days. Because of its immense instability, the product was only characterized by its ^1H spectrum: δ(acetone-d_6) = 1.27 ppm (br, 3H, CH_3), δ 1.62 ppm (d, 2H, $-CH_2-$), δ 3.44 ppm (dd, 2H, PCH_2P), δ 3.64 ppm (br d, 1H, $CH_3-CH=$), δ 5.48 ppm (m, ^1H, $=CH-CH_2-Co$).

(η^3-RC_3H_4)$Co(CO)_3$ ($R = H$, CH_3). A solution of $Na[Co(CO)_4]$ (2 mmol) in THF was chilled to −10°C. To this, 2 mmol of the particular allylchloride was added dropwise. The solution was stirred overnight (12–14 h) at 0°C, whereafter the temperature was raised to 30°C. Continued stirring for 3–4 (for R = H) or 6–8 hours (for $R = CH_3$) resulted in a dark orange solution consisting of 80–90% of the η^3-allyl product according to ^1H NMR. After filtration to remove NaCl, these oily solutions were used without further purification.

*$[(\eta^3\text{-}RC_3H_4)Co(CO)_2]_n(Ph_2P(CH_2)_nPPh_2)$. [$R = H$, $n = 1$ (**3a**); $R = H$, $n = 2$ (**4c**); $R = CH_3$, $n = 1$ (**3b**); $R = CH_3$, $n = 2$ (**4d**)].* A solution of (η^3-RC_3H_4)$Co(CO)_3$ ($R = H$, CH_3) (2 mmol) in THF was treated with the bis(phosphine) (2 mmol). The solution was stirred for 30 min at room temperature or until evolution of CO ceased. The volume of the solution was reduced by half and an equal volume of hexane added. This process was repeated until an orange solid precipitated from the cold hexane. The solution was not reduced to dryness, but the last 10 mL of orange solution removed with a pipette. The product was repeatedly washed with pentane (−20°C for **3a** and **3b**) until the solvent remained clear, followed by in vacuo drying. **4c** and **4d** were purified further by recrystallization from dichloromethane/hexane. **3a** was purified on a short column (silica gel, 0.063–0.2 mm, packed in hexane under N_2). **3b** was not purified any further.

1c: Yield 65–70%, Mp 129–130°C (dec); Anal. Calc. $C_{30}H_{27}CoO_2P_2$: C 66.6, H 5.0; Found: C 68.6, H 4.8%.
3d: Yield 90–95%; orange; Mp 145–147°C; Anal. Calc. $C_{36}H_{34}Co_2O_4P_2$: C 60.8, H 4.8; Found (%): C 60.1, H 4.7%.
2c: Yield 50–70%; pale orange; decomposes without melting.
4d: Yield 85–95%; orange; Mp 159–160°C; Anal. Calc. $C_{38}H_{38}Co_2O_4P_2$: C 61.8, H 5.1; Found: C 61.9, H 4.9%.

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