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The preparation and reactions of alkynylphosphonate hexacarbonyldicobalt complexes

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Abstract

The preparation of a series of hexacarbonyldicobalt alkynylphosphonate complexes, $Co_2(CO)_6[R^1C{\equiv}CP(O)(OR^2)_2]$ is reported. They are found to be unreactive under a range of conditions and this is ascribed to a combination of electron deficiency and alkyne π to phosphorus π-acceptor orbital interactions. Complexes of alkynyl carboxylates are more reactive. Reaction of diethyl 1-propynylphosphonate with dicarbonylcyclopentadienylcobalt results in the formation of (η^5-cyclopentadienyl) (η^4-2,4-dimethylcyclopentadienone-3,5-diphosphonate tetraethyl ester)cobalt (I), the X-ray crystal structure of which has been determined. This is a rare example of an unsymmetrically substituted cyclopentadienone complex. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Cobalt carbonyl; Alkynylphosphonate; Cyclopentadienone

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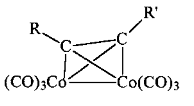
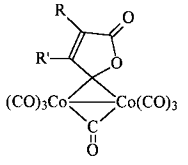
1. Introduction

The reaction of dicobalt octacarbonyl with 1 mol of alkyne results in the formation of complexes having the formula $Co_2(CO)_6(RC{\equiv}CR')$ which have the well-established dicobaltatetrahedrane structure **1** [1]. Such complexes are known with a wide range of alkynes. In the course of our studies we became interested in the reactions of alkynes having phosphonate ester functional groups. While various alkynes of this type are known, their cobalt carbonyl complexes have not previously been reported.



1a R = R' = $P(O)(OMe)_2$
b R = $P(O)(OMe)_2$, R' = Cl
c R = $P(O)(OEt)_2$, R' = Ph
d R = $P(O)(OEt)_2$, R' = Me
e R = $P(O)(OEt)_2$, R' = tBu
f R = $P(O)(OEt)_2$, R' = C_5H_{11}
g R = $P(O)(OEt)_2$, R' = CO_2Me



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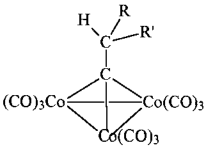

3a R = CO_2Me, R' = H
b R = R' = CO_2Me

Phosphonate groups are strongly electron withdrawing in nature and thus, alkynyl phosphonates are markedly electron deficient. The majority of the reported reactions of complexes $Co_2(CO)_6(RC{\equiv}CR')$ are with alkynes having electron donating through to weakly electron withdrawing groups. However, two particular examples of well-established reaction types with more electron deficient alkynes have revealed unusual reactivities, which suggested that further investigation was warranted. Carbonylation reactions carried out at elevated temperatures and under pressure of CO typically give rise to the lactone complexes **2** [2] but when R = R' = CO_2Me, the products of the reaction were assigned as the trinuclear clusters **3a** and **3b** [3]. The second example was in the Khand reactions [4] between $Co_2(CO)_6(HC{\equiv}CR)$ and norbornene. Whereas with electron-rich alkynes, the R group was found exclusively in the position α to the carbonyl group (structure **4a**), when R = CO_2Me or C(O)Me, the selectivity was reversed, the R group occupying the β position (structure **4b**) [5]. The result was ascribed primarily to electronic rather than steric effects.

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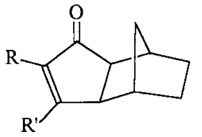


4a R = alkyl or Ph, R' = H
b R = H, R' = CO_2Me or C(O)Me
c R = R' = CO_2Me

This anomalous behaviour was intriguing and gave us hope that some unusual chemistry might be uncovered in the chemistry of $Co_2(CO)_8$ with the highly electron deficient alkynyl phosphonates. Thus, a study of the preparation and reactivity of the cobalt carbonyl complexes of these alkynes was initiated. We also undertook comparative studies with some broadly analogous available alkynyl carboxylates and their complexes [6–8].

2. Results and discussion

2.1. Preparation of alkynylphosphonate cobalt complexes

A series of alkynyl phosphonates, RC≡CP(O)(OR′)$_2$, was prepared by literature methods or adaptations thereof. Their cobalt carbonyl complexes, **1**, were readily obtained by reaction at room temperature of equimolar quantities of the alkyne and $Co_2(CO)_8$ in THF. Purification by column chromatography resulted in the formation of red oils, some of which solidified on storage at −18°C. Few simple cobalt carbonyl complexes of phosphorus containing alkynes are known, since when the alkyne carries tertiary phosphine groups, the lone pair on the phosphorus is able to interact with neighbouring molecules, substituting CO and giving rise to dimeric or polymeric materials [9]. In the present case, the alkyne substituent has no lone pair available on phosphorus (V) for such an interaction. The complexes can be stored for long periods at low temperature, but decompose slowly in solution. Their infrared spectra in the carbonyl stretching region are characteristic of $Co_2(CO)_6$(alkyne) complexes. The stretching frequencies are shifted towards the higher end of the observed frequency range for $Co_2(CO)_6$(alkyne) complexes, consistent with the strongly electron-withdrawing nature of the substituents, and the thus greater π-acceptor ability of the alkyne. Absorptions arising from the P=O stretches are also prominent at ca. 1200–1300 cm^{-1}. Mass spectrometry further confirms the formulation, with parent ions observed in some cases, and ions corresponding to $[Co_2(CO)_5(\text{alkyne})]^+$ being observed in others.

Attempts to prepare the complexes $Co_4(CO)_{10}$(RC≡CR′) by reaction of the alkynyl phosphonates with $Co_4(CO)_{12}$ were unsuccessful, resulting only in the formation of the dicobalt complexes $Co_2(CO)_6$(RC≡CR′). It has been noted previously [10] that the tetracobalt complexes are less stable than the dicobalt complexes, and apparently the complexes with the alkynyl phosphonates, if formed, are so unstable that they decompose, either in solution or on the silica column.

2.2. Reactions of [RC≡CP(O)(OR′)$_2$]$Co_2(CO)_6$ complexes

In the light of the remarkable transformation [3] of the dimethyl acetylenedicarboxylate (DMAD) complex to the trinuclear species **3a**,**b** which we have confirmed [6], our first attempted reaction was to treat the bisphosphonate complex **1a** under CO under the same conditions. However, only unreacted complex (60%) was recovered. Similar lack of reactivity was observed when we tried to obtain a cyclopentenone derivative from the same complex + norbornene (Khand reaction [4]) either in hot toluene or at room temperature with *N*-oxide promotion, conditions that succeed with the DMAD complex yielding the cyclopentenone derivative **4c** [6]. This failure was repeated with two monophosphonate complexes **1b** and **1c**, with a lot of starting material being recovered, even after extended reaction times.

One of our major objectives was to link an alkynylphosphonate as its $Co_2(CO)_6$ complex to a second molecule of the same or a different alkyne on the route towards arenes from three such species. We had successfully used a variety of alkynyl carboxylates or their complexes in the formation of cobaltacyclopentadienes [7] and of ‘flyovers’ (alkyne)$_3$$Co_2(CO)_4$ and arenes [8], but again the complexes **1a** and **1c** failed to react similarly. The inertness of the hexacarbonyldicobalt alkynylphosphonate complexes to a range of reaction types is intriguing. It is possible to ascribe this in part to the electron withdrawing effect of the phosphonates. As noted (vide supra) the ν(CO) stretching frequencies are at the high energy end of the observed range for complexes of this type, which implies that the metal is relatively electron poor. This in turn can be taken as indicative of an increased metal–alkyne π-back-bonding interaction at the expense of the metal–CO back-bonding consistent with a markedly electron deficient alkyne. A similar lack of reactivity has been noted for the complex $Co_2(CO)_6(F_5SC{\equiv}CSF_5)$ [11], which also has a markedly electron deficient alkyne, with highly electronegative pentafluorosulfanyl groups. It has previously been suggested that ^{13}C-NMR spectroscopy is a potentially useful tool for predicting the propensity of $Co_2(CO)_6$(alkyne) to undergo C–C coupling reactions, such as carbonylation, the Khand reaction and cyclotrimerisation [12]. The activation of the alkyne on complexation is best quantified in terms of

Table 1
Coordination shifts in ^{13}C-NMR data of $(RO)_2(O)P–C(1)≡C(2)–X$ and their dicobalthexacarbonyl complexes

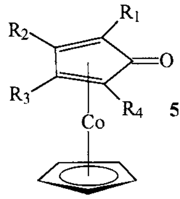
Alkyne	R	δ, Free alkyne				δ, Coordinated alkyne			Δδ, Coordination shifts		
X		$\delta_{C(1)}$	$\delta_{C(2)}$	$\delta_{C(2)}-\delta_{C(1)}$		$\delta_{C(1)}$	$\delta_{C(2)}$	$\delta_{C(2)}-\delta_{C(1)}$	$\Delta(\delta_{C(2)}-\delta_{C(1)})$ [a]	$\Delta\delta_{C(1)}$ [b]	$\Delta\delta_{C(2)}$ [c]
Me	Et	69.6	98.7	29.1	**1d**	68.7	100.3	31.6	+2.5	−0.9	+1.6
^{t}Bu	Et	68.5	110.0	41.5	**1e**	67.9	118.9	51.0	+9.5	−0.6	+8.9
$^nC_5H_{11}$	Et	70.3	103.0	32.7	**1f**	68.3	106.6	38.4	+5.7	−2.0	+3.6
Ph	Et	78.3	98.9	20.6	**1c**	69.7	98.0	28.3	+7.7	−0.9	−8.6
EtO_2C	Et	74.4	86.4	12.0	**1g**	68.6	83.7	15.1	+3.1	−2.71	−5.8
Cl	Me				**1b**	61.7	107.2	45.5			
$(MeO)_2(O)P$	Me	87.6	87.6	0	**1a**	78.7	78.7	0	0	−8.9	−8.9

[a] $\Delta(\delta_{C(2)}-\delta_{C(1)}) = \{(\delta_{C(2)}-\delta_{C(1)})_{coord}-(\delta_{C(2)}-\delta_{C(1)})_{free}\}$.
[b] $\Delta\delta_{C(1)} = \{\delta_{C(1)coord}-\delta_{C(1)free}\}$.
[c] $\Delta\delta_{C(2)} = \{\delta_{C(2)coord}-\delta_{C(2)free}\}$.

the coordination shifts of the alkynyl carbon atoms, Δδ ($=\delta_{coord}-\delta_{free}$). It was decided, therefore, to analyse our alkynes and their complexes in this way. For the alkynyl phosphonates, $(RO)_2(O)P–C(1)≡C(2)–X$, (see Table 1) the coordination shift of C(1), $\Delta\delta_{C(1)}$, is negative (upfield) in each case, while shifts for C(2), $\Delta\delta_{C(2)}$, are positive (downfield) for X = alkyl, but negative (upfield) for X = Ph, CO_2Et and $P(O)(OMe)_2$. This parallels the results of Happ et al. [12] who found that SiR_3 groups also gave substantial upfield shifts, and ascribe this to the expected strong π–d interactions between the carbon and silicon, which neutralise the deshielding effect normally seen on complexation. A similar interaction is possible with phosphorus[1] in our compounds and with sulfur in the pentafluorosulfanyl derivative [11]. Happ also noted that compounds that had one of the $\delta(^{13}C)$ values ≤ 80 ppm in the free alkyne and ≤ 90 ppm in the complexed alkyne underwent carbonylation reactions. By these criteria all the alkynylphosphonate complexes, except **1a**, should also be carbonylated. It seems, therefore, that the electron withdrawing nature of the phosphonate group, in addition to the interaction with the phosphorus π-acceptor orbitals, results in a rather inert Co_2C_2 core, which prevents C–C coupling reactions. This should be ameliorated by the incorporation of electron donating groups (e.g. alkyl) on the other alkynyl carbon atom.

2.3. Reaction of $MeC≡CP(O)(OEt)_2$ with $CpCo(CO)_2$

In view of the lack of reactivity of the alkynyl phosphonate complexes (**1a**–**c**) under the forcing carbonylation conditions and under Khand reaction conditions, even in the presence of TMANO, it was decided to attempt the reaction of the alkynyl phosphonates with the complex $CpCo(CO)_2$, which shows considerable activity in a range of reactions with alkynes [13]. When diethyl 1-propynylphosphonate was reacted with $CpCo(CO)_2$ in toluene, a red crystalline solid was obtained after chromatographic purification. Microanalysis and mass spectrometry showed the complex to have an empirical formula corresponding to $CpCo[MeC≡CP(O)(OEt)_2]_2(CO)$. The infrared spectrum had no vibration in the metal carbonyl region, but did have a strong band at ca. 1700 cm^{-1}, indicative of carbonyl insertion and the formation of a cyclopentadienone. NMR spectroscopy revealed the presence of two methyl environments and two phosphorus environments, suggesting an unsymmetrical arrangement of the alkyne ligands. Thus, the complex obtained was formulated as **5a**. Single crystal X-ray diffraction confirmed this assignment and hence the fact that in this system combination of two alkynyl phosphonates and carbonylation does occur.



5a $R_1 = R_3 = P(O)(OEt)_2$, $R_2 = R_4 = Me$
b $R_1 = R_3 =$ mesityl, $R_2 = R_4 = Ph$
c $R_1 = R_4 = Si(CH_3)_3$, $R_2 = R_3 = H$

A thermal ellipsoid plot is shown in Fig. 1 and selected bond lengths and angles are in Table 2. The compound crystallises as a monohydrate, the water presumably diffusing into the solution from the atmosphere during crystal growth. The structure confirms the cyclopentadienone to be unsymmetrically substituted, with the methyl groups in the 2 and 4 positions and the phosphonate groups in the 3 and 5 positions. This is only the second structurally characterised example of an unsymmetrical cyclopentadienone formed in this manner, the only previous structure being of (η^5-cyclopentadienyl)-

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[1] In the case of phosphine ligands, the π-acceptor orbitals are widely accepted to be a combination of d- and σ* antibonding orbitals [32].

(η^4-2,4-dimesityl-3,5-diphenylcyclopentadienone)cobalt (**5b**) [14]. The majority of cyclopentadienone complexes formed from unsymmetrical alkynes have a cyclopentadienone, which is substituted symmetrically, with the most bulky substituents in the 2 and 5 positions, for instance, the trimethylsilylacetylene derived complex **5c** [15]. The structural features largely mirror those found in other mononuclear cobalt cyclopentadienone complexes. The cyclopentadienone is coordinated in an η^4 fashion through the diene moiety, while the carbonyl group is tilted out of the diene plane. Thus, the maximum deviation of the diene carbon atoms from the least-squares plane is 0.003(2) Å, while the carbonyl carbon C(20) sits some 0.248 Å above the plane. This results in a fold along the C(7)–C(15) axis of 13.0°. This is comparable with the respective dihedral angles of 9° and 10.2° in the tetramethyl- [16] and 2,5-bis(trimethylsilyl)- [15] cyclopentadienone analogues, and rather less than the 21.3° in the tetrakis(trifluoromethyl)-cyclopentadienone complex [17]. As previously observed, the bond lengths in the diene moiety, 1.437(3), 1.453(3) and 1.436(3) Å are shorter than the C–C(=O) bond lengths of 1.474(3) and 1.487(3) Å, indicative that complete delocalisation of the π-electron density around the ring does not occur. The diene is not symmetrically bonded to cobalt, with C(8) and C(14) at distances of 1.992(2) and 1.991(2) Å and C(7) and C(15) at 2.053(2) and 2.050(3) Å. The Co–C(20) (the carbonyl carbon) distance is substantially longer at 2.309(3) Å, confirming the η^4-bonding of the cyclopentadienone. The cyclopentadienyl ring and diene planes are parallel with one another (dihedral angle = 0.1°).

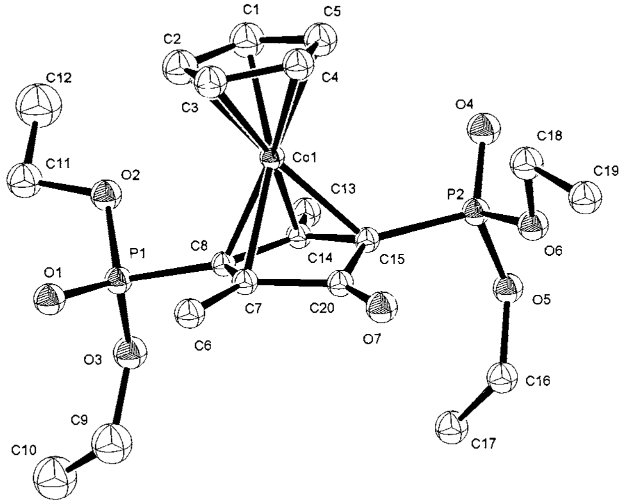

Fig. 1. Thermal ellipsoid plot of **5a** showing the atom numbering scheme and the thermal ellipsoids at the 50% level. Hydrogen atoms are omitted for clarity.

Table 2
Selected bond lengths (Å) and angles (°) for **5a**

Bond lengths			
Co(1)–C(1)	2.052(3)	C(8)–C(14)	1.453(3)
Co(1)–C(2)	2.044(3)	C(13)–C(14)	1.502(3)
Co(1)–C(3)	2.045(3)	C(14)–C(15)	1.436(3)
Co(1)–C(4)	2.057(3)	C(7)–C(20)	1.474(3)
Co(1)–C(5)	2.037(3)	C(15)–C(20)	1.487(3)
Co(1)–C(7)	2.050(3)	C(20)–O(7)	1.236(3)
Co(1)–C(8)	1.992(2)	P(1)–O(1)	1.473(2)
Co(1)–C(14)	1.991(2)	P(1)–O(2)	1.566(2)
Co(1)–C(15)	2.053(2)	P(1)–O(3)	1.576(2)
Co(1)–C(20)	2.309(3)	P(2)–O(4)	1.469(2)
C(6)–C(7)	1.500(3)	P(2)–O(5)	1.574(2)
C(7)–C(8)	1.437(3)	P(2)–O(6)	1.569(2)
C(8)–P(1)	1.786(3)		
Bond angles			
C(6)–C(7)–C(8)	128.2(2)	C(13)–C(14)–C(15)	125.8(2)
C(6)–C(7)–C(20)	121.4(2)	C(14)–C(15)–P(2)	122.6(2)
C(8)–C(7)–C(20)	109.0(2)	C(14)–C(15)–C(20)	109.4(2)
C(7)–C(8)–P(1)	125.7(2)	C(20)–C(15)–P(2)	127.1(2)
C(7)–C(8)–C(14)	108.2(2)	C(7)–C(20)–O(7)	126.9(2)
C(14)–C(8)–P(1)	125.9(2)	C(15)–C(20)–O(7)	129.2(2)
C(8)–C(14)–C(13)	127.0(2)	C(7)–C(20)–C(15)	103.6(2)
C(8)–C(14)–C(15)	107.2(2)		

3. Experimental

3.1. General remarks

All reactions were carried out under a dry nitrogen atmosphere and solvents were purified and dried under nitrogen before use. Anhydrous trimethylamine-*N*-oxide was obtained by recrystallisation from hot DMF [18]. $Co_2(CO)_8$ was obtained from Strem Chemicals and used as purchased. Chromatography was carried out using either silica gel (230–400 mesh) or ungraded alumina, neutralised with ethyl acetate, washed with ethanol and water and oven dried. Melting points were obtained in open capillaries and are uncorrected. ^{1}H-NMR and ^{13}C-NMR spectra were recorded at frequencies of 400.134 and 100.614 MHz, respectively, both being referenced to an internal solvent standard. ^{31}P-NMR spectra were recorded at a frequency of 161.977 MHz and referenced to external H_3PO_4.

The following were prepared by literature methods: dimethyl (chloroethynyl)phosphonate [19], tetramethyl ethynyl-1,2-diphosphonate [19], ethyl 3-(diethoxyphosphinyl) propynoate [20] and (η^5-C_5H_5)Co(CO)$_2$ [21], and had satisfactory spectroscopic and analytical data.

The remaining alkynyl phosphonates, MeC≡CP(O)(OEt)$_2$, ^{t}BuC≡CP(O)(OEt)$_2$, C_5H_{11}C≡CP-(O)-(OEt)$_2$ and PhC≡CP(O)(OEt)$_2$ were prepared by an essentially identical procedure, an adaptation of the method of Aguiar [22], replacing the Grignard reagent with an alkynyllithium generated in situ from $RC\equiv CH$ and BuLi (except 1-propynyl lithium, which was prepared from 1-bromopropene and BuLi [23]). A typical procedure is given below.

3.2. Preparation of diethyl 1-heptynylphosphonate

To a cooled solution (−65°C) of 1-heptyne (1.2 g, 12.5 mmol) in dry THF (20 ml), a solution of ^{n}BuLi (2.5 M in hexanes, 5.0 ml, 12.5 mmol) was added via syringe. The pale brown homogeneous mixture was allowed to warm to room temperature and then transferred via cannula into a cooled solution (−70°C) of diethyl chlorophosphate (2.2 g, 12.5 mmol) in dry THF (30 ml). The mixture was allowed to warm slowly to room temperature and after stirring for 16 h the THF was removed in vacuo. The residues were partitioned between CH_2Cl_2 (100 ml) and 20% aqueous K_2CO_3 solution, and after a further CH_2Cl_2 extraction of the aqueous phase, the combined organic portions were dried, filtered and evaporated to dryness. The product was purified by distillation under reduced pressure (1 mmHg, 250°C) in a Kugelrohr apparatus. Yield, 2.4 g, 85%.

3.3. Preparation of hexacarbonyldicobalt alkyne complexes, general procedure

Octacarbonyldicobalt (1–4 mmol) was dissolved in THF (15 ml) and an equimolar quantity of the alkyne in THF (5 ml) was slowly added via syringe over 10 min with vigorous evolution of carbon monoxide. After stirring for 4 h at room temperature the reaction mixture was filtered through kieselguhr and the solvent removed under reduced pressure. The residue was chromatographed on silica gel [1:1 light petroleum:ethyl acetate] to yield a red oil.

All $Co_2(CO)_6(RC\equiv CR')$ complexes were prepared in this way and analytical data for the new complexes are presented below. Microanalyses are only presented for those complexes which crystallised. The oils obtained, which contained occluded solvent and thus did not analyse satisfactorily, were characterised on the basis of IR, MS and NMR data.

*3.3.1. $Co_2(CO)_6[(MeO)_2(O)PC\equiv CP(O)(OMe)_2]$ (**1a**)*

Yield, 73%. Analysis. Found: C, 27.32; H, 2.34%. Calc. for $C_{12}H_{12}Co_2O_{12}P_2$: C, 27.29; H, 2.29%. MS. Found: $m/z = 499.8428$. $[M^+ - CO]$, $M_r = 499.8519$. IR (hexane), ν(CO) 2178, 2111, 2078, 2057 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 3.77 (d, $^3J\{^{31}P–^1H\} = 9.4$ Hz) ppm. ^{13}C-NMR ($CDCl_3$) δ 53.68 (d, $^2J\{^{31}P–^{13}C\} = 5.8$ Hz), 78.72 (dd, $^1J\{^{31}P–^{13}C\} = 224$ Hz, $^2J\{^{31}P–^{13}C\} = 4.8$ Hz), 202.86 (br) ppm. ^{31}P-NMR δ 26.0 (s) ppm.

*3.3.2. $Co_2(CO)_6[ClC\equiv CP(O)(OMe)_2]$ (**1b**)*

Yield, 68%. Analysis. Found: C, 26.48; H, 1.38%. Calc. for $C_{10}H_6ClCo_2O_9P$: C, 26.43; H, 1.33%. MS. Found: $m/z = 425.8216$. $[M^+ - CO]$, $M_r = 425.8153$. IR (hexane), ν(CO) 2110, 2078, 2049 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 3.89 (d, $^3J\{^{31}P–^1H\} = 11.3$ Hz) ppm. ^{13}C-NMR ($CDCl_3$) δ 53.47 (d, $^2J\{^{31}P–^{13}C\} = 5.7$ Hz), 61.70 (d, $^1J\{^{31}P–^{13}C\} = 220.1$ Hz), 107.21 (d, $^2J\{^{31}P–^{13}C\} = 4.6$ Hz), 196.82 (br) ppm. ^{31}P-NMR ($CDCl_3$) δ 27.5 (s) ppm.

*3.3.3. $Co_2(CO)_6[PhC\equiv CP(O)(OEt)_2]$ (**1c**)*

Yield, 78%. Analysis. Found: C, 41.33; H, 2.90%. Calc. for $C_{18}H_{15}Co_2O_9P$: C, 41.25; H, 2.88%. MS. Found: $m/z = 495.8988$. $[M^+ - CO]$, $M_r = 495.9168$. IR (hexane), ν(CO) 2107, 2068, 2043 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 1.35 (td, 6H, $^3J = 7.07$ Hz, $^4J\{^{31}P–^1H\} = 0.67$ Hz) 4.26 (qd, 4H, $^3J = 7.07$ Hz, $^3J\{^{31}P–^1H\} = 2.14$ Hz), 7.35–7.74 (m, 5H) ppm. ^{13}C-NMR ($CDCl_3$) δ 16.08 (d, $^3J\{^{31}P–^{13}C\} = 10.31$ Hz) 62.57 (d, $^2J\{^{31}P–^{13}C\} = 5.1$ Hz), 69.67 (d, $^1J\{^{31}P–^{13}C\} = 228$ Hz), 98.01 (d, $^2J\{^{31}P–^{13}C\} = 4.8$ Hz), 128.96, 129.36, 130.18, 137.39, 198.94 (br) ppm. ^{31}P-NMR ($CDCl_3$) δ 25.0 (s) ppm.

*3.3.4. $Co_2(CO)_6[MeC\equiv CP(O)(OEt)_2]$ (**1d**)*

Yield, 71%. MS. Found: $m/z = 433.8999$. $[M^+ - CO]$, $M_r = 433.9012$. IR ($CHCl_3$), ν(CO) 2101, 2066, 2037 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 1.35 (t, 6H), 2.75 (d, 3H, $^4J\{^{31}P–^1H\} = 2.3$ Hz), 4.20 (m, 4H) ppm. ^{13}C-NMR ($CDCl_3$) δ 16.23 (d, $^3J\{^{31}P–^{13}C\} = 7.0$ Hz), 20.91, 62.35 (d, $^2J\{^{31}P–^{13}C\} = 6.0$ Hz), 68.71 (d, $^1J\{^{31}P–^{13}C\} = 228$ Hz), 100.31, 198.22 (br) ppm.

*3.3.5. $Co_2(CO)_6[^tBuC\equiv CP(O)(OEt)_2]$ (**1e**)*

Yield, 75%. MS. Found: $m/z = 503.9371$ $[M^+]$, $M_r = 503.9431$. IR ($CHCl_3$), ν(CO) 2098, 2062, 2036 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 1.36 (m, 15H), 4.22 (m, 4H) ppm. ^{13}C-NMR ($CDCl_3$) δ 16.28 (d, $^3J\{^{31}P–^{13}C\} = 7.0$ Hz), 32.75, 62.54 (d, $^2J\{^{31}P–^{13}C\} = 6$ Hz) 69.89 (d, $^1J\{^{31}P–^{13}C\} = 117$ Hz), 118.86, 198.83 (br) ppm.

*3.3.6. $Co_2(CO)_6[C_5H_{11}C\equiv CP(O)(OEt)_2]$ (**1f**)*

Yield, 55%. MS. Found: $m/z = 489.9687$. $[M^+ - CO]$, $M_r = 489.9638$. IR ($CHCl_3$), ν(CO) 2099, 2064, 2036 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 0.92 (t, 3H), 1.35 (m, 8H), 1.43 (m, 2H), 1.70 (m, 2H), 2.88 (m, 2H), 4.19 (m, 4H) ppm. ^{13}C-NMR ($CDCl_3$) δ 13.77, 16.24 (d, $^3J\{^{31}P–^{13}C\} = 7$ Hz), 22.29, 31.47, 31.50, 34.23, 62.36 (d, $^2J\{^{31}P–^{13}C\} = 6$ Hz), 68.28 (d, $^1J\{^{31}P–^{13}C\} = 230$ Hz), 106.64 (d, $^2J\{^{31}P–^{13}C\} = 7$ Hz), 198.5 (br) ppm.

*3.3.7. $Co_2(CO)_6[EtO_2CC\equiv CP(O)(OEt)_2]$ (**1g**)*

Yield, 80%. MS. Found: $m/z = 491.9035$. $[M^+–CO]$, $M_r = 491.9067$. IR ($CHCl_3$), ν(CO) 2111, 2079, 2051 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 1.35 (br m, 9H), 4.24 (br m, 4H), 4.32 (br m, 2H) ppm. ^{13}C-NMR ($CDCl_3$) δ 13.98, 16.11 (d, $^3J\{^{31}P–^{13}C\} = 7$ Hz), 62.31, 62.65 (d, $^2J\{^{31}P–^{13}C\} = 6$ Hz), 68.47 (d, $^1J\{^{31}P–^{13}C\} = 224$ Hz), 83.67, 168.52, 196.80 (br) ppm.

3.4. Reactions of [RC≡CP(O)(OR′)$_2$Co$_2$(CO)$_6$]

3.4.1. Attempted carbonylation

Complex **1a** (582 mg, 1.1 mmol) in hexane (50 ml) was placed under 200 atm CO and heated in a rocking autoclave to 80°C for 40 h. Cooling and work-up (using chromatography on alumina) gave 60% recovery of **1a** together with an unidentified white solid and only traces of other products.

3.4.2. Attempted Khand reactions

Using the highly reactive alkene, norbornene, and the conditions that successfully convert dimethyl acetylenedicarboxylate to the expected cyclopentenone [6] gave mainly recovered complex and no ketonic product from **1a** (toluene/70°C/4 days or Me_3NO/CH_2Cl_2/r.t./30 h), **1b** (toluene/70°C/5 days) or **1c** (toluene/70°C/4 days or Me_3NO/CH_2Cl_2/r.t./24 h).

3.4.3. Attempted coupling of [RC≡CP(O)(OR′)$_2$Co$_2$(CO)$_6$] with alkynes

Again, conditions used successfully with alkynyl ester complexes [7,8] were chosen. Only trace amounts of unidentified products resulted from the following combinations: **1a** + $C_2[P(O)(OMe)_2]_2$ or C_2Me_2 or $C_2(COOMe)_2$ or PhC_2H/toluene/reflux; **1c** + $PhC_2P(O)(OEt)_2/Me_3NO/CH_2Cl_2$/r.t./3 days.

3.5. Reaction of (η^5-C_5H_5)Co(CO)$_2$ with CH_3C≡CP(O)(OEt)$_2$

Diethyl 1-propynylphosphonate (1.0 g, 5.7 mmol) and $CpCo(CO)_2$ (0.30 g, 1.7 mmol) were dissolved in toluene (20 ml). The mixture was heated to reflux for 2 h, after which time TLC showed all the $CpCo(CO)_2$ to have been consumed. The solvent was removed in vacuo and chromatography of the residue on silica (ethyl acetate) yielded an orange complex **5a** (0.30 g, 35%). Recrystallisation from CH_2Cl_2/hexane yielded a red–orange crystalline material.

5a: Analysis. Found: C, 45.92; H, 6.0. Calc. for $C_{20}H_{31}O_7P_2Co.H_2O$: C, 45.97; H, 6.3. MS. Found: $m/z = 504.0858$, [M^+] $M_r = 504.0877$. IR (CH_2Cl_2) ν(C=O) 1619, ν(P=O) 1249 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 1.30 (t, 3H, $^3J = 7.27$ Hz), 1.36 (t, 3H, $^3J = 7.08$ Hz), 1.37 (t, 3H, $^3J = 7.07$ Hz), 1.43 (t, 3H, $^3J = 6.98$ Hz), 1.85 (s, 3H), 2.41 (s, 3H), 4.17 (m, 6H), 4.38 (m, 2H), 5.03 (s, 5H). ^{13}C-NMR ($CDCl_3$) δ 10.87, 13.10, 16.28 (d, $^3J\{^{31}P–^{13}C\} = 6.8$ Hz), 16.34 (d, $^3J\{^{31}P–^{13}C\} = 6.8$ Hz), 16.50 (d, $^3J\{^{31}P–^{13}C\} = 6.8$ Hz), 62.18 (d, $^2J\{^{31}P–^{13}C\} = 6.2$ Hz), 62.30 (d, $^2J\{^{31}P–^{13}C\} = 6.1$ Hz), 62.47 (d, $^2J\{^{31}P–^{13}C\} = 5.9$ Hz), 62.62 (d, $^2J\{^{31}P–^{13}C\} = 6.4$ Hz), 64.91 (dd, $^1J\{^{31}P–^{13}C\} = 194$ Hz, $^3J\{^{31}P–^{13}C\} = 6.8$ Hz), 74.85 (dd, $^1J\{^{31}P–^{13}C\} = 101$ Hz, $^3J\{^{31}P–^{13}C\} = 13$ Hz), 81.64 (br dd or t, $^2J\{^{31}P–^{13}C\} = 13.4$ Hz), 84.61, 97.53 (dd, $^2J\{^{31}P–^{13}C\} = 13.2$ Hz, $^2J\{^{31}P–^{13}C\} = 15.4$ Hz), 161.69 (br) ppm. ^{31}P-NMR ($CDCl_3$) δ 19.7 (s, br, 1P), 20.6 (d, 1P, $J = 3$Hz) ppm.

Table 3
Crystallographic data for **5a**

Molecular formula	$C_{20}H_{31}CoO_7P_2 \cdot H_2O$
Molecular weight	522.36
Crystal colour, habit	Red, plate
Crystal size (mm)	0.6 × 0.4 × 0.1
Space group	$P2_1/c$ (#14)
a (Å)	14.868(3)
b (Å)	10.053(3)
c (Å)	16.077(2)
β (°)	94.57(1)
V (Å^3)	2395.4(7)
Z	4
$\rho_{calc.}$ (g cm^{-3})	1.448
μ(Mo–K$_\alpha$) (cm^{-1})	8.92
F(000)	1096.00
Diffractometer	Rigaku AFC7S
Radiation	Mo–K$_\alpha$
Wavelength (Å)	0.71069
Temperature (K)	123
Scan type	ω–2θ
Scan rate (° min^{-1})	16 (in ω)
Scan width	$1.15 = 0.35 \tan\theta$
θ Range	2.5–27.5
Index ranges	h, 0–19; k, 0–13; l, −20–20
Reflcns measured	6047
Unique reflcns	5830 ($R_{int} = 0.025$)
Observed reflections ($I = 2.00\sigma(I)$)	4069
No. of variables	281
GOF	1.44
R	0.035
R_w	0.042
Residual electron density (eÅ^3)	0.47 to −0.45

3.6. X-ray crystal structure determination

Red plates of complex **5a** were grown from dichloromethane/hexane. The complex crystallises in the monoclinic space group $P2_1/c$. A suitable crystal (0.6 mm × 0.4 mm × 0.1 mm) was coated in oil, mounted on a glass capillary and cooled to −150°C (at which temperature all data measurements were performed). Cell constants were obtained from 22 accurately centred reflections in the range $33.20 \leq 2\theta \leq 40.71°$ using graphite monochromated Mo–K$_\alpha$ radiation on a Rigaku AFC7S diffractometer [24]. A total of 6074 reflections were collected of which 5830 were unique ($R_{int} = 0.025$). An empirical absorption correction (ψ-scans, $T_{min} = 0.79$, $T_{max} = 1.00$) was applied. The structure was solved by direct methods [25] and expanded by Fourier techniques [26]. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms placed in calculated positions but not refined. Full-matrix least-squares refinement based on 4069 reflections ($I = 2\sigma(I)$) and 281 variables converged with $R = 0.035$, $R_w = 0.042$ and GOF = 1.44. The residual electron density was in the range -0.45–0.47 e Å^{-3}.

The crystallographic details are collected in Table 3. In each case the neutral atom scattering factors [27], $\Delta f'$ and $\Delta f''$ [28] and mass attenuation coefficients [29] were taken from the International Tables for Crystallography. Anomalous dispersion effects were included in F_{calc} [30]. All calculations were performed using the TeXsan crystallographic package [31].

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 111842 for compound **5a**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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References

[1] R.D.W. Kemmitt, D.R. Russell, in: G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, vol. 5, Pergamon Press, Oxford, 1982, p. 192.

[2] (a) H.W. Sternberg, J.G. Shukys, C. Delle-Donne, R. Markby, R.A. Friedel, I. Wender, J. Am. Chem. Soc. 81 (1959) 2339. (b) O.S. Mills, G. Robinson, Inorg. Chim. Acta 1 (1967) 61.

[3] G. Váradi, V. Galamb, J. Palágyi, G. Pályi, Inorg. Chim. Acta 53 (1981) L29.

[4] (a) P.L. Pauson, Tetrahedron 41 (1985) 5855. (b) N.E. Schore, in B.M. Trost (Ed.), Comprehensive Organic Synthesis, vol. 5, Pergamon Press, Oxford, 1991, p. 1037. (c) N.E. Schore, Organic Reactions 40 (1991) 1.

[5] (a) M.E. Krafft, R.H. Romero, I.L. Scott, J. Org. Chem. 57 (1992) 5277. (b) M.E. Krafft, R.H. Romero, I.L. Scott, Synlett (1995) 204.

[6] R.J. Baxter, G.R. Knox, P.L. Pauson, M.D. Spicer, J. Organomet. Chem. 579 (1999) 90.

[7] R.J. Baxter, G.R. Knox, P.L. Pauson, M.D. Spicer, Organometallics 18 (1999) 197.

[8] R.J. Baxter, G.R. Knox, J.H. Moir, P.L. Pauson, M.D. Spicer, Organometallics 18 (1999) 206.

[9] M. Went, Polyhedron 14 (1995) 465.

[10] W. Hübel, U. Krüerke, Chem. Ber. 94 (1961) 2829.

[11] T. Henkel, K. Klauck, K. Seppelt, J. Organomet. Chem. 501 (1995) 1.

[12] B. Happ, T. Bartik, C. Zucchi, M.C. Rossi, F. Ghelfi, G. Pályi, G. Váradi, G. Szalontai, I.T. Horváth, A. Chiesi-Villa, C. Guastini, Organometallics 14 (1995) 809.

[13] R.D.W. Kemmitt, D.R. Russell, in: G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, vol. 5, Pergamon Press, Oxford, 1982, p. 228.

[14] A. Clearfield, P. Rudolph, I. Bernal, M.D. Rausch, Inorg. Chim. Acta 42 (1980) 17.

[15] (a) R. Boese, D. Bläser, R.L. Halterman, K.P.C. Vollhardt, Angew. Chem. Int. Ed. Engl. 27 (1988) 553. (b) J.H. Bieri, A.S. Dreiding, T.C.C. Gartenmann, E.R.F. Gesing, R.W. Kunz, R. Prewo, J. Organomet. Chem. 306 (1986) 241.

[16] L.F. Dahl, D.L. Smith, J. Am. Chem. Soc. 83 (1961) 752.

[17] M. Gerloch, R. Mason, Proc. R. Soc. Lond. Ser. A 279 (1964) 170.

[18] J.A. Soderquist, C.L. Anderson, Tetrahedron Letts. 27 (1986) 3961.

[19] (a) D. Seyferth, J.D.H. Paetsch, J. Org. Chem. 34 (1969) 1483. (b) A.S. Kende, P. Fludzinski, Synthesis (1982) 455.

[20] R.G. Hall, S. Trippett, Tetrahedron Letts. 23 (1982) 2603.

[21] M.D. Rausch, R.A. Genetti, J. Org. Chem. 35 (1970) 3888.

[22] M.S. Chatta, A.M. Aguiar, J. Org. Chem. 36 (1971) 2719.

[23] J. Suffert, D. Toussaint, J. Org. Chem. 60 (1995) 3550.

[24] Molecular Structure Corporation, MSC/AFC Diffractometer Control Software. Revised Edition, 1992. MSC, 3200 Research Forest Drive, Woodlands, TX 77381, USA.

[25] A. Altomare, M.C. Burla, M. Camalli, M. Cascarano, C. Giacovazzo, A. Guagliardi, G. Polidori, J. Appl. Crystallogr. 27 (1994) 435.

[26] DIRDIF92: P.T. Beurskens, G. Admiraal, G. Beurskens, W.P. Bosman, S. Garcia-Granda, J.M.M. Smits, C. Smykalla, DIRDIF Programme System, 1992. Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.

[27] D.T. Cromer, J.T. Waber, International Tables for Crystallography, vol. 4, The Kynoch Press, Birmingham, UK, 1974.

[28] D.C. Creagh, W.J. McAuley, in: A.J.C. Wilson (Ed.), International Tables for Crystallography, vol. C, Kluwer Academic Publishers, Boston, 1992, p. 219.

[29] D.C. Creagh, J.H. Hubbell, in: A.J.C. Wilson (Ed.), International Tables for Crystallography, vol. C, Kluwer Academic Publishers, Boston, 1992, p. 200.

[30] J.A. Ibers, W.C. Hamilton, Acta Crystallogr. 17 (1964) 781.

[31] Molecular Structure Corporation, TeXsan. Texray Structure Analysis Package, 1985. MSC, 3200 Research Forest Drive, Woodlands, TX 77381, USA.

[32] A.G. Orpen, N.G. Connelly, J. Chem. Soc. Chem. Commun. (1985) 1310.