Cyclodimerisation and addition reactions of $Bu^tC{\equiv}P$ at a cobalt(I) centre

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(Received December 16, 1993)

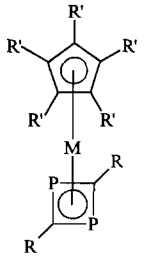
Abstract

Syntheses and characterisation of $[Co(\eta^5\text{-}C_5Me_4CH_2CH_2CH{=}CH_2)(\eta^4\text{-}C_2Bu^t{}_2P_2)]$ and $[Co_2(\eta^5\text{-}C_5Me_4CH_2CH_2CH{=}CH_2)_2(CO)(COPCBu^t)]$ are reported. The former has been prepared by four different routes, resulting from cyclodimerisation of $Bu^tC{\equiv}P$ within the coordination sphere of cobalt(I) and the mechanistic pathway for its formation is discussed. The latter results from addition of $Bu^tC{\equiv}P$ to the Co=Co double bond of $[Co_2(\eta^5\text{-}C_5Me_4CH_2CH_2CH{=}CH_2)_2(CO)_2]$. Both complexes have been characterised by $^{31}P\{^1H\}$, $^{13}C\{^1H\}$, ^1H NMR and mass spectroscopic studies.

Key words: Cobalt complexes; Phosphaalkyne complexes

Introduction

Earlier work by Nixon and co-workers [1] and Binger *et al.* [2–4] show that phosphaalkynes cyclodimerise within the coordination sphere of rhodium(I), cobalt(I) or iron(0) to form complexes of type **1**, **2** (M = Co, Rh) or **3**.



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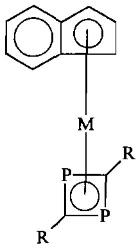
R = Ad, Bu^t, Pr^i
R' = H or Me



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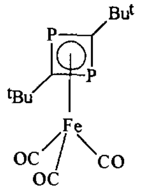
R = Ad or Bu^t



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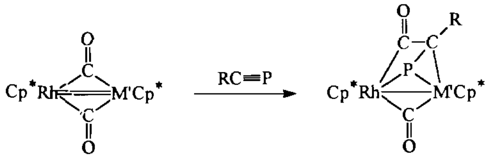
Phosphaalkynes are also known to add across M=M′ double bonds to give complexes **4–6** [5–7].



4 M′ = Rh, R = Ad
5 M′ = Rh, R = Bu^t
6 M′ = Co, R = Bu^t

Now we report further development in the cyclodimerisation and addition reactions of $Bu^tC{\equiv}P$ with cobalt(I) complexes.

Results and discussion

Okuda *et al.* [8] have shown that treatment of $[Co(\eta^5{:}\eta^2\text{-}C_5Me_4CH_2CH_2CH{=}CH_2)(\eta^2\text{-}C_2H_4)]$ (**7**) with $RC{\equiv}CR$ ($R = CO_2Me$ or Ph) leads to ethylene displacement followed by intra-molecular co-cyclotrimerisation of two alkynes with the coordinated C=C double bond of **7** to afford **8** and **9**, respectively.

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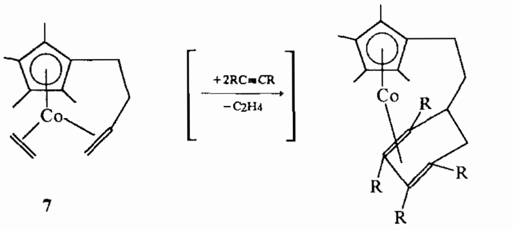
0020-1693/94/$07.00
SSDI 0020-1693(94)03888-U

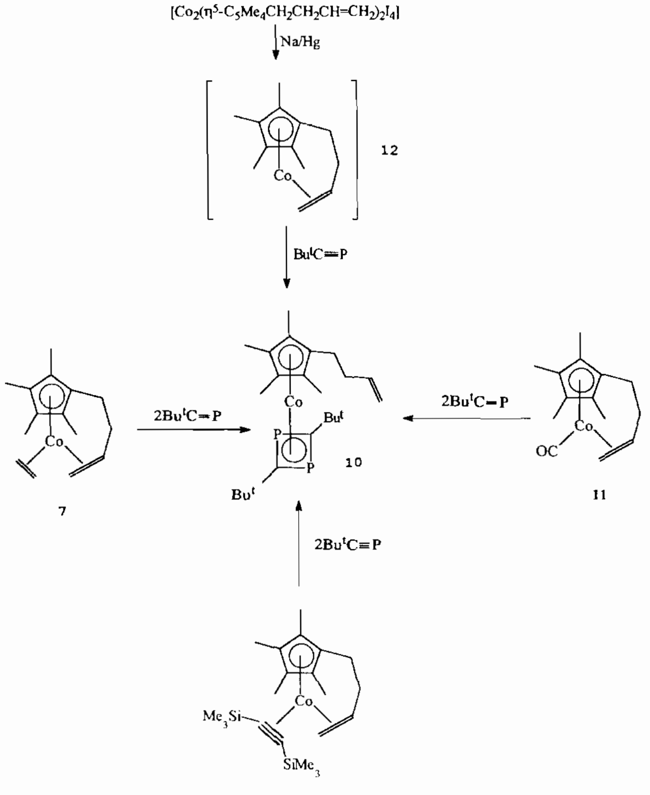


7

8 R = CO_2Me
9 R = Ph

Despite the similarities between phosphaalkynes and alkynes, co-cyclotrimerisation of $Bu^tC{\equiv}P$ with the η^2-bonded alkene of **7** does not take place. Treatment of **7** with two equivalents of $Bu^tC{\equiv}P$ leads to the cyclodimerisation product **10** (Scheme 1). Likewise, complex **10** is obtained by treatment of the carbonyl complex **11** with $Bu^tC{\equiv}P$ or by trapping of the $16e^-$ fragment **12** with the phosphaalkyne (Scheme 1).

Surprisingly, reaction of $Bu^tC{\equiv}P$ with **13** (Scheme 1) leads to complex **10**, unlike earlier reports by Binger *et al.* [9] showing that treatment of $[Rh(\eta^5\text{-}C_5H_5)(\eta^2\text{-}C_2Ph_2)PPr^i{}_3]$ with $Bu^tC{\equiv}P$ affords an η^4-bonded 2,3-phenyl-4-tert-butyl-1-phosphacyclobutadiene complex, viz. $[Rh(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_3Ph_2Bu^tP)]$. These results emphasise the high stability of the η^4-1,3-diphosphacyclobutadiene complex compared with its related η^4-cyclobutadiene metal compound.



Scheme 1.

Characterisation of **10** was based on ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$ NMR and mass spectroscopy studies. The mass spectrum of **10** shows a peak corresponding to the molecular ion ($m/z = 434$) and a peak attributed to the loss of the $[C_2Bu^t{}_2P_2]$ fragment ($m/z = 234$), in accordance with the proposed formulation. The $^{31}P\{^1H\}$ NMR spectrum of **10** consists of a singlet at 30.7 ppm, which lies in the range of ^{31}P chemical shifts found for related η^4-bonded $C_2Bu^t{}_2P_2$ complexes [1–4, 10]. No change was observed in the $^{31}P\{^1H\}$ NMR spectra at low temperatures (25 to 80 °C), which suggests either a rapid rotation of at least one of the rings or a rigid conformation in which the 'dangling' alkene is in a symmetrical position between the two phosphorus atoms.

Confirmation of the 'dangling' alkene in **10** arises from its ^1H and $^{13}C\{^1H\}$ NMR spectra. The ^1H NMR spectrum of **10** exhibits a singlet corresponding to two equivalents Bu^t groups, and two further singlets from the two different types of methyl groups. The low field resonances corresponding to the $=CH$ and $=CH_2$ protons (av. δ 5.74(m) and 4.98(m), respectively) are indicative of a non-coordinated alkene [11]. Other multiplets corresponding to $-CH_2$ protons occur at δ 2.0 and 2.71 (av.), and data are in accordance with those found for $[CoI_2(\eta^5\text{-}C_5Me_4CH_2CH_2CH{=}CH_2)CO]$ [11]. The $^{13}C\{^1H\}$ NMR spectrum of **10** (Fig. 1) confirms the presence of a non-coordinated alkene, since the singlets at 138.8 and 115.2 ppm can be attributed to C^1 and C^2, respectively. One would expect the ^{13}C chemical shifts of C^1 and C^2 in the case of a coordinated alkene to be similar to those found for $[CoI_2(\eta^5\text{-}C_5Me_4CH_2CH_2CH{=}CH_2)CO]$, i.e. 62.3 ($C^1$) and 40 ($C^2$) ppm [11]. The resonance for C^{12} was not observed, but signals for C^{10} and C^{11} offer no doubt than the η^4-bonded $C_2Bu^t{}_2P_2$ ring system is present. The resonances for C^{10} and C^{11} consist of triplets at 35.2 and 30.9 ppm, respectively, and the $^2J(CP)$ (7.3 Hz) and $^3J(CP)$ (5.1 Hz) are the same as those found for $[Co(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_2Bu^t{}_2P_2)]$ (7.1 and 4.1 Hz, respectively) [10].

The results from the interaction of the $16e^-$ fragment $[Co(\eta^5{:}\eta^2\text{-}C_5Me_4CH_2CH_2CH{=}CH_2)]$ (**12**) with $Bu^tC{\equiv}P$ are important, since they provide helpful information on the mechanism of the co-cyclotrimerisation to form the η^4-cyclohexadiene complexes **8** and **9**, described by Okuda *et al.* [8]. Two mechanistic pathways have been suggested [12] (Scheme 2). The first step in both mechanistic pathways is the displacement of ethylene by the alkyne to give **13** or **14**. In route (i), the approach of a second alkyne displaces the intra-molecular bonded alkene, to form the bis(alkyne)complex **15** or **16**, which undergoes a coupling reaction to give rise to the cobaltacyclopentadiene intermediate **17** or **18**. Formation of the intermediate **20** is supported by the isolation of $[Co(\eta^5\text{-}C_5Me_4CH_2CH_2CH{=}CH_2)(\eta^4\text{-}C_4Ph_4)]$, in very

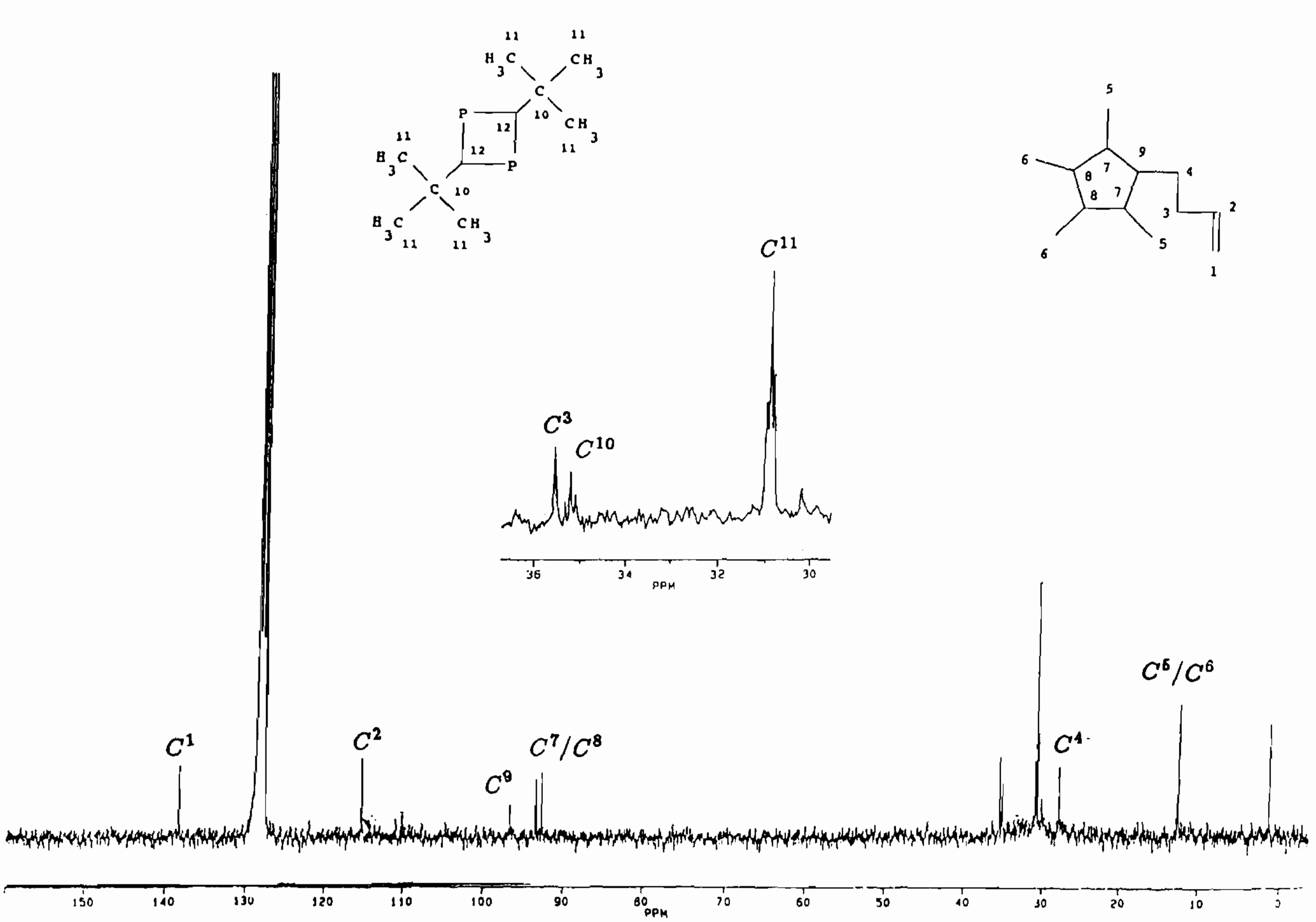
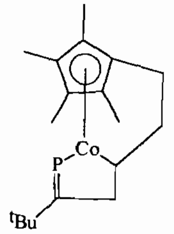


Fig. 1. $^{13}C\{^1H\}$ NMR spectrum of $[Co(\eta^5\text{-}C_5Me_4CH_2CH_2CH{=}CH_2)(\eta^4\text{-}C_2Bu^t{}_2P_2)]$ (**10**).

low yields [8, 12]. The metalacyclic complex **17** or **18** is converted to **8** or **9**, but the mechanism for this step is still poorly understood.

On the other hand, complex **13** or **14** could form **17** or **18** by route (ii), which involves co-cyclodimerisation of the alkyne with the intra-molecular bonded alkene. Insertion of another alkyne into the cobalta-cyclopentene ring in **17** or **18** affords the cobalta-cycloheptadiene complexe **21** or **22**, which rearranges to form **8** or **9** [12].

In the present work, no evidence has been found for a cyclotrimerisation reaction between two phosphaalkynes and the intra-molecular bonded alkene of **7**. This might suggest that the formation of **8** or **9** occurs via pathway (i), ruling out the formation of the cobalta-phosphacyclopentene intermediate **23** analogous to **17** and **18**.



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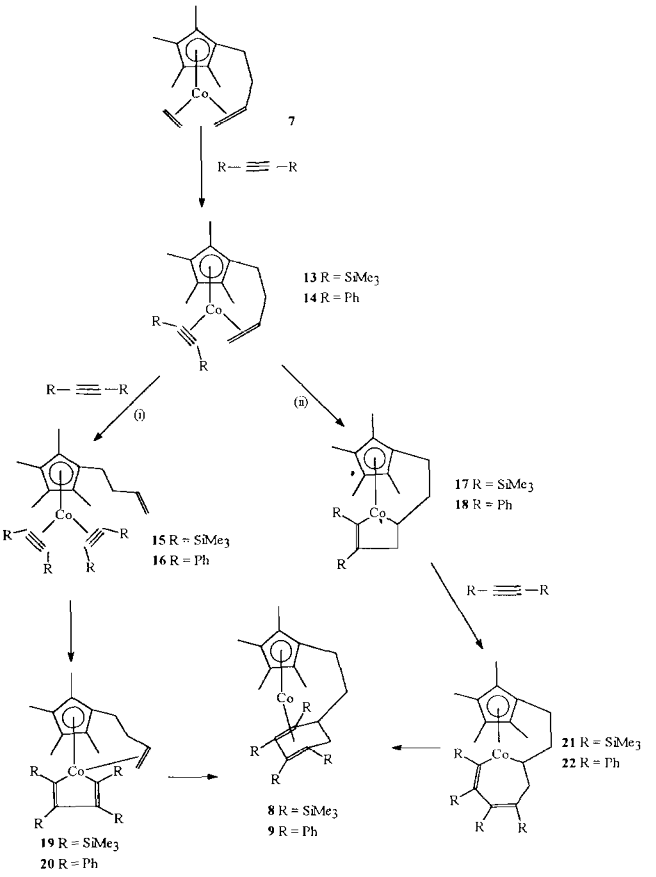
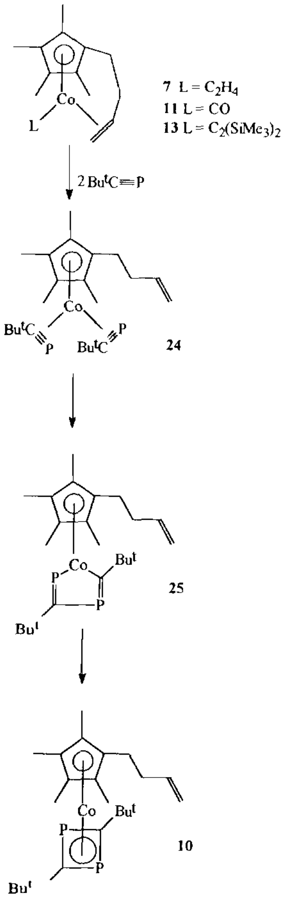
Therefore, the mechanism for the formation of **10** can tentatively be proposed as depicted in Scheme 3. This mechanism has previously been proposed to explain the formation of $[M(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_2Bu^t{}_2P_2)]$ (M = Co (**26**) or Rh (**27**)) [3] and later confirmed in a similar system by Binger *et al.* [13]. They showed that treatment of $[Rh_2Cl_2(C_2H_4)_4]$ with $Bu^tC{\equiv}P$, in the presence of PMe_3, affords complex **28** containing a rhodadiphosphacyclopentadiene ring. The structure of **28** has been confirmed by single crystal X-ray diffraction study, but interestingly, it slowly rearranges to give **29**. The molecular structure of the latter reveals that the η^4-bonded $C_2Bu^t{}_2P_2$ ring system is not planar. The Rh–P (ring) bonds are similar, whereas the Rh–C bond, approximately *trans* to chlorine is shorter than the other Rh–C bond [13]. However, displacement of chloride with lithium indenyl gives the known complex **30**, in which the η^4-$C_2Bu^t{}_2P_2$ ring system has been shown to be planar [3] (Scheme 4).



Scheme 2.

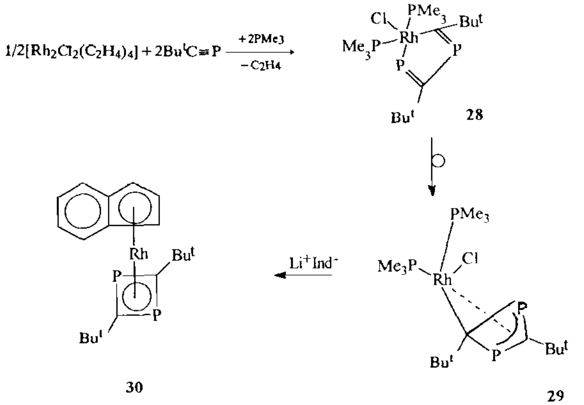


Scheme 3.

The interaction between the metal and the 'diphosphabutadiene' ligand in **25** might be stronger than with the 'butadiene' and the metal in **19** (or **20**). Therefore, an attack of the 'dangling' alkene on the cobalta-cyclopentadiene ring in **19** (or **20**) to form the η^4-hexadiene complex **8** or **9** is easier than on the analogous cobalta-diphosphacyclopentadiene complex **25**.

Very recently, Gleiter *et al.* [14] have published photoelectron spectroscopic studies and molecular orbital calculations of $[Fe(CO)_3(\eta^4\text{-}C_2Bu^t{}_2P_2)]$ (**3**) and $[Co(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_2Bu^t{}_2P_2)]$ (**26**) and their related organic complexes. These results revealed that the interaction between the 1,3-diphosphacyclobutadiene ring and the metal fragment is stronger than with the cyclobutadiene and the metal. This observation is supportive evidence for the non-formation of complexes resulting from a co-cyclotrimerisation of two $Bu^tC{\equiv}P$ molecules with the alkene in **7**.

Concerning addition reactions of Co=Co bonds, Okuda and Zimmermann [15] have reported that the bridging dicarbonyl complex $[Co_2(\eta^5\text{-}C_5Me_4CH_2\text{-}CH{=}CH_2)_2(CO)_2]$ (**33**) can be obtained either by photolysis of **31** in hexane, under forcing conditions,

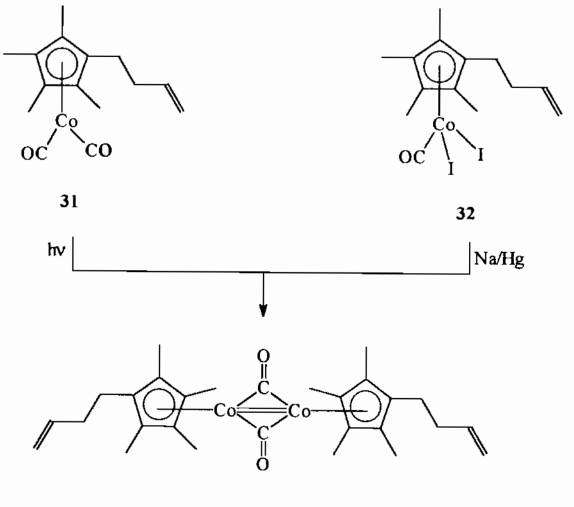


Scheme 4.

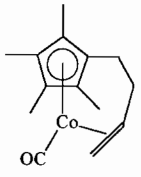
or by reduction of **32** with a large excess of sodium amalgam.

Complex **11** is also formed in both preparations, but **33** can easily be separated by chromatography. Complex **33** offers the opportunity to study addition reactions of phosphaalkynes across the Co=Co double bond. In the present work, it was found that treatment of **33**, in toluene, with an excess of $Bu^tC{\equiv}P$ exclusively affords complex **34**.

Nixon and co-workers [6] reported that formation of the analogous rhodium complex **4** depends on the stoichiometry of the reaction mixture. Treatment of **35** with AdC≡P in an 1:1 ratio affords only **4**, whereas use of an excess of the phosphaalkyne affords both **4** and **36**; the latter has been fully characterised by a single crystal X-ray diffraction study [6].



31 **32** **33**



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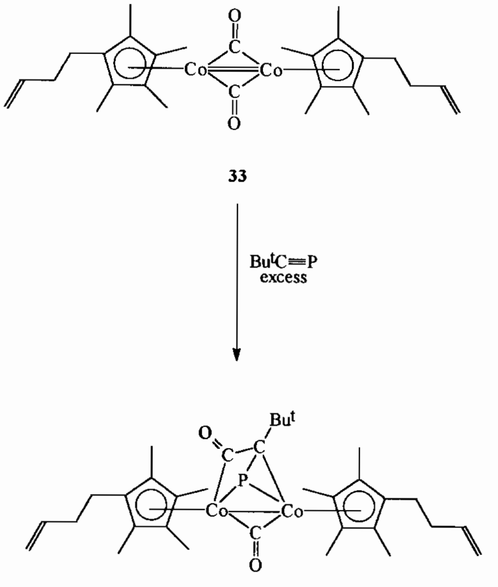
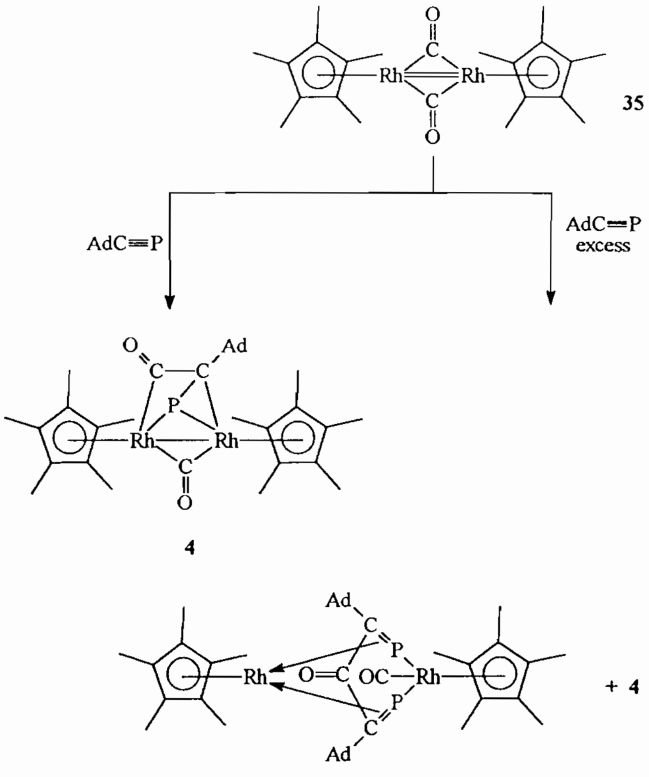


33 **34**



35 **4** **36**

Complex **34** was characterised by $^{31}P\{^1H\}$, ^1H, $^{13}C\{^1H\}$ NMR, IR and mass spectroscopic studies. Two intense carbonyl stretching bands are observed in the IR spectrum of **34**, ν(CO): 1780(s), (Co_2CO) and 1651(br) (CoCOCBu^{t}P) cm^{-1}, which are similar to those found for complexes **4**–**6** [5–7, 16].

Further confirmation on the formulation of **34** is obtained from its mass spectrum (Fig. 2), which exhibits a weak parent ion (M^+) (Fig. 2(b)), and peaks corresponding to the stepwise loss of CO, i.e. $m/z = 596$ ($M^+ - CO$) and $m/z = 568$ ($M^+ - 2CO$), thus supporting the proposed formulation.

The presence of an uncoordinated alkene in **34** is confirmed by its ^1H NMR spectrum, which shows low-field resonances for the CH (δ 5.71) and CH_2 protons (δ 4.91–4.97) [11].

$^{13}C\{^1H\}$ NMR spectroscopic studies of **34** suggest the presence of two non-equivalent $C_5Me_4CH_2CH_2CH{=}CH_2$ ring systems. Unfortunately, the region of the spectrum corresponding to the sp^2 carbon within the Cp* rings and the methyl groups attached to them could not be resolved. However, the $^{13}C\{^1H\}$ NMR of **34** (Fig. 3) exhibits the expected pattern of lines, which have been fully assigned. The $^1J(C^3P)$ coupling constant (76.9 Hz) is the only J(CP) observed. All the others $^2J(C^2P)$, $^2J(C^4P)$, $^3J(C^5P)$ are presumably too small (~ 0 Hz) to be observed.

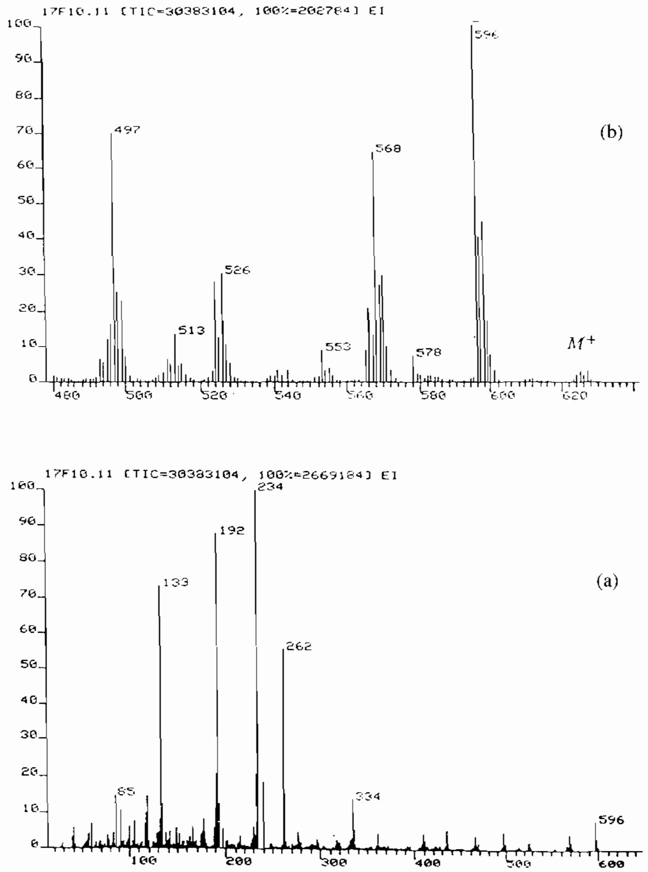


Fig. 2. Mass spectrum (EI) of $[Co_2(\eta^5\text{-}C_5Me_4CH_2CH_2CH{=}CH_2)_2(CO)(Bu^tCPCO)]$ (**34**).

Experimental

All the reactions herein described were carried out employing standard procedures for manipulation of air-sensitive materials, either under an atmosphere of dry dinitrogen using standard Schlenk tubes, syringe or high vacuum line techniques. All the glassware employed had been flame-dried *in vacuo*, and solvents were dried, freshly distilled under a blanket of dinitrogen and degassed prior to use. IR spectra were recorded as Nujol mulls using a Perkin-Elmer model 1720FT-IR spectrometer, calibrated relative to polystyrene. Mass spectra were recorded at the University of Sussex, using Kratos MS25 or MS80RF double-focusing mass spectrometers. The NMR spectra were recorded using a Bruker AC-P250, WM-360 or AMX500, at the operating frequencies shown in Table 1. Unless otherwise indicated, chemical shifts were measured at ambient probe temperatures, and are quoted in ppm with positive values to low field of the indicated reference material and are corrected with respect to the appropriate deuterium frequency. Coupling constants are quoted in Hertz.

The following compounds were synthesized according to literature methods. $Bu^tC{\equiv}P$: from $(Me_3Si)P{=}C(OSiMe_3)(Bu^t)$ and NaOH [17]; $[Co(\eta^5{:}\eta^2\text{-}C_5Me_4CH_2CH_2CH{=}CH_2)(\eta^2\text{-}C_2H_4)]$: from Na/Hg, C_2H_4 and $[Co_2I_4(\eta^5\text{-}C_5Me_4CH_2CH_2CH{=}CH_2)_2]$ [8, 11]; $[Co(\eta^5{:}\eta^2\text{-}C_5Me_4CH_2CH_2CH{=}CH_2)(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)]$: from Na/Hg, $Me_3SiC{\equiv}CSiMe_3$ and $[Co_2I_4(\eta^5\text{-}C_5Me_4CH_2CH_2CH{=}CH_2)_2]$ [8, 11]; $[Co(\eta^5{:}\eta^2\text{-}C_5Me_4CH_2CH_2CH{=}CH_2)CO]$: from Na/Hg, CO and $[Co_2I_4(\eta^5\text{-}C_5Me_4CH_2CH_2CH{=}CH_2)_2]$ [8, 11]; $[Co_2(\eta^5\text{-}C_5Me_4CH_2CH_2CH{=}CH_2)_2(CO)_2]$: from Na/Hg (excess), CO and $[Co_2I_4(\eta^5\text{-}C_5Me_4CH_2CH_2CH{=}CH_2)_2]$ [8, 11].

Synthesis of $[Co(\eta^5\text{-}C_5Me_4CH_2CH_2CH{=}CH_2)(\eta^4\text{-}C_2Bu^t_2P_2)]$ *(10)*

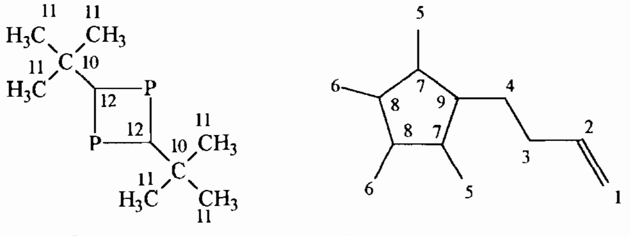
Complex **10** was obtained in several different ways, as described below.

Method A: Phosphaalkyne $Bu^tC{\equiv}P$ (600 mg, 0.9 ml, 6 mmol) was condensed into a solution of $[Co(\eta^5{:}\eta^2\text{-}C_5Me_4CH_2CH_2CH{=}CH_2)(\eta^2\text{-}C_2H_4)]$ (**7**) (520 mg, 2 mmol) in THF (5 ml) and the mixture stirred for 24 h. The excess of $Bu^tC{\equiv}P$ was recovered and the solvent removed, to give an oil which was extracted with toluene and purified by column chromatography (alumina/toluene) to yield **10** as a yellow oil (640 mg, 74%), identified on the basis of $^{31}P\{^1H\}$, ^1H, $^{13}C\{^1H\}$ NMR and mass spectroscopy.

$^{31}P\{^1H\}$ NMR data (101.3 MHz; toluene-d_8; 25 °C): $\delta_P = 30.7$ ppm.

^1H NMR data (250.1 MHz; C_6D_6; 25 °C): δ 5.67–5.80 (m, 1H, $-CH{=}$); 4.92–5.04 (m, 2H, $-CH_2{=}$); 2.68–2.74 (m, 2H, $-CH_2-$); 1.90–2.10 (m, 2H, $-CH_2-$); 2.00 (s, 6H, CH_3); 1.95 (s, 6H, CH_3); 1.06 (s, 18H, Bu^t).

$^{13}C\{^1H\}$ NMR data (62.9 MHz; C_6D_6; 25 °C) (ppm): δ 138.8 (s, C^1); 115.2 (s, C^2); 96.5 (s, C^9); 93.4 (s, C^7 or C^8); 92.6 (s, C^8 or C^7); 35.6 (s, C^3); 35.2 (t, $^2J(CP) = 7.3$ Hz, C^{10}); 30.9 (t, $^3J(CP) = 5.1$ Hz, C^{11}); 27.9 (s, C^4); 12.7 (s, C^5 or C^6); 12.6 (s, C^6 or C^5).



Method B. Phosphaalkyne (600 mg, 0.9 ml, 6 mmol) was condensed into a solution of $[Co_2I_4(\eta^5\text{-}C_5Me_4CH_2CH_2CH{=}CH_2)_2]$ (500 mg, 1 mmol), in diethyl ether (10 ml), kept at −50 °C and treated with sodium amalgam (1.5%, 26 g). The reaction mixture was left to warm to room temperature, under stirring, over a period of 1 h. The excess of $Bu^tC{\equiv}P$ was recovered and the product purified as outlined in Method A to yield **10** (200 mg, 22%).

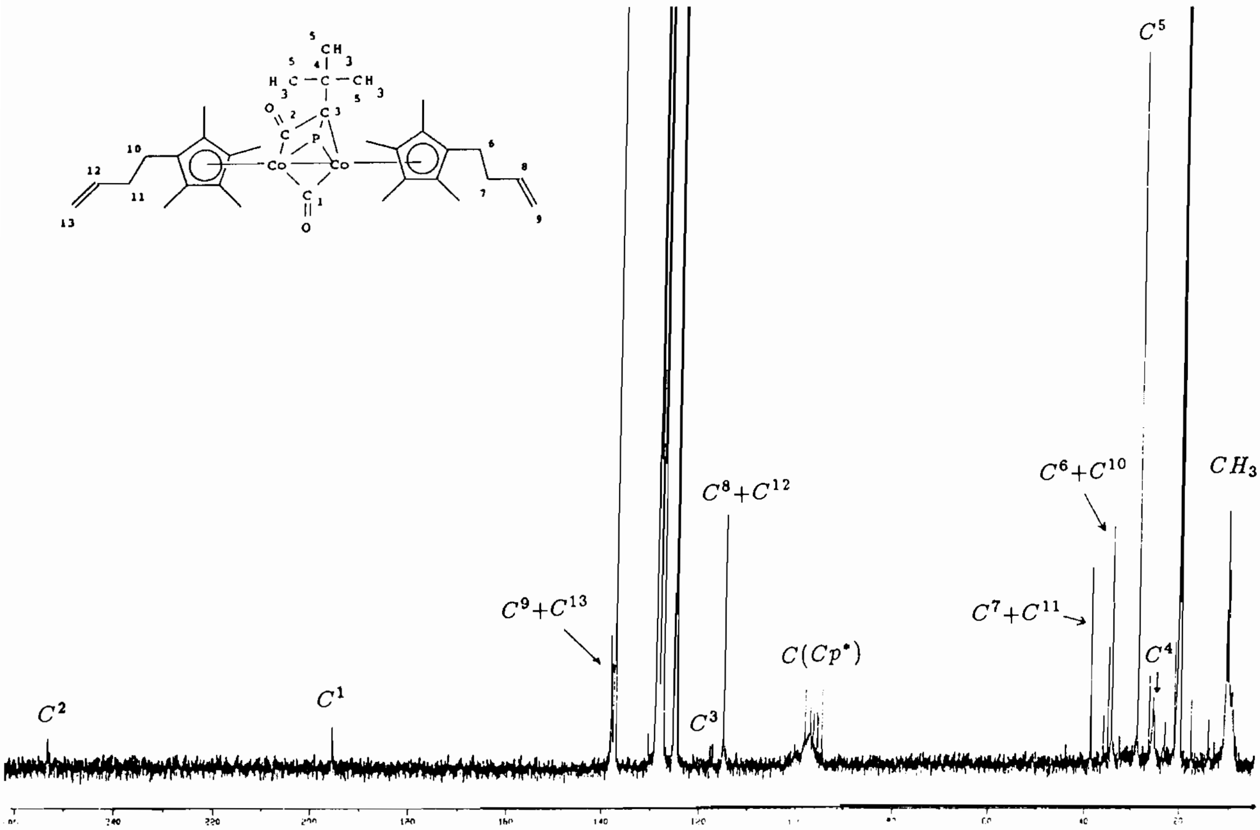
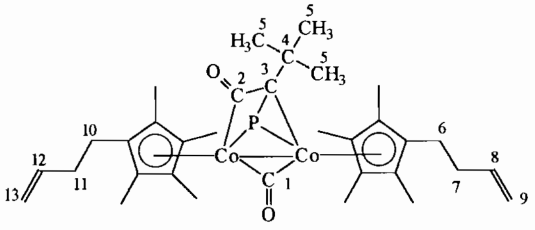


Fig. 3. $^{13}C\{^1H\}$ NMR spectrum of $[Co_2(\eta^5\text{-}C_5Me_4CH_2CH_2CH{=}CH_2)_2(CO)(Bu^tCPCO)]$ (**34**).

TABLE 1. Operating frequencies and standard references used to record the NMR spectra

Nucleus	AC-P250	WM-360	AMX500	Reference
^1H	250.1	360.1	500.1	TMS
^{13}C	62.9	90.6	125.8	TMS
^{31}P	101.3	145.8	202.5	85% H_3PO_4



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Method C. Treatment of $[Co(\eta^5{:}\eta^2\text{-}C_5Me_4CH_2CH_2\text{-}CH{=}CH_2)(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)]$ (**13**) (800 mg, 2 mmol), in THF, with $Bu^tC{\equiv}P$ (600 mg, 0.9 ml, 6 mmol), following the procedure outlined in Method A, afforded **10** (520 mg, 61%).

Method D. The same procedure described in Methods A and C was employed in the reaction of the phosphaalkyne $Bu^tC{\equiv}P$ (200 mg, 0.3 ml, 2 mmol) with $[Co(\eta^5{:}\eta^2\text{-}C_5Me_4CH_2CH_2CH{\equiv}CH_2)CO]$ (**11**) (60 mg, 0.23 mmol), in toluene (3 ml) to yield complex **10** (87 mg, 87%).

Synthesis of $[Co_2(\eta^5\text{-}C_5Me_4CH_2CH_2CH{=}CH_2)_2\text{-}(CO)(Bu^tCPCO)]$ (34)

Phosphaalkyne $Bu^tC{\equiv}P$ (400 mg, 0.6 ml, 4 mmol) was condensed into a solution of $[Co_2(\eta^5\text{-}C_5Me_4\text{-}CH_2CH_2CH{=}CH_2)_2(CO)_2]$ (**33**) (200 mg, 0.4 mmol), in toluene (2 ml) and the resulting mixture stirred for 24 h. The excess of $Bu^tC{\equiv}P$ was recovered and the toluene solution purified by column chromatography (alumina/toluene) to yield a green oil, **34** (130 mg, 54%).

$^{31}P\{^1H\}$ NMR data (101.3 MHz; C_6D_6; 25 °C): $\delta_P = 409$ ppm.

^1H NMR data (360.1 MHz; C_6D_6; 25 °C): δ 5.71 (bm, 2H, $-CH{=}$); 4.91–4.97 (m, 4H, $=CH_2$); 2.42 (bm, 4H, $-CH_2-$); 2.11 (bm, 4H, $-CH_2-$); 1.75, 1.72, 1.65 (s, 24H, CH_3); 1.05 (s, 9H, Bu^t).

$^{13}C\{^1H\}$ NMR data (125.8 MHz; toluene-d_8; 25 °C) (ppm): δ 253.3 (s, C^1); 196.1 (s, C^2); 138.3 (s, C^8 or C^{12}); 138.0 (s, C^{12} or C^8); 117.8 (d, $^1J(CP) = 76.9$ Hz, C^3); 115.0 (s, C^9 or C^{13}); 114.8 (s, C^{13} or C^9); 97.5 (bm, C–Cp); 39.9 (s, C^7 or C^{11}); 35.9 (s, C^6 or C^{10}); 35.4 (s, C^{10} or C^6); 25.6 (bs, C^4); 23.9 (s, C^5); 10.7 (bm, CH_3(Cp)).

Acknowledgement

R.M.M. thanks CNPq (Brazil) for a fellowship. J.O. thanks the Volkswagen Foundation for financial support.

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