Chemistry of Cobalt Complexes with 1,2-Bis(diethylphosphino)ethane: Hydrides, Carbon Disulfide Complexes, and C–H Cleavage in Activated Alk-1-ynes. Crystal Structure of $[CoH(C{\equiv}CCO_2Et)(Et_2PCH_2CH_2PEt_2)_2][BPh_4]$†

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The reaction of anhydrous $CoCl_2$ with depe [1,2-bis(diethylphosphino)ethane] yields $[CoCl_2(depe)_2]$ **1**, which reacts with $Na[BPh_4]$ in ethanol to give five-co-ordinate $[CoCl(depe)_2][BPh_4]$ **2**. Both complexes have been studied by EPR spectroscopy. Complex **1** reacts with $NaBH_4$ in ethanol yielding $[CoH_2(depe)_2]^+$, isolable as the tetraphenylborate salt **3**. This compound is stereochemically non-rigid in solution, having a *cis* configuration at low temperatures. The spin–lattice relaxation times (T_1) for the hydrides of **3** suggest a classical formulation for this complex. The monohydride $[CoH(depe)_2]$ **4** is obtained by deprotonation of **3** using $KOBu^t$. Complex **3** reacts with CO and CS_2 with reductive elimination of H_2, yielding $[Co(CO)(depe)_2][BPh_4]$ **5** and $[Co(\eta^2\text{-}CS_2)(depe)_2][BPh_4]$ **6**, respectively, both stereochemically non-rigid in solution. The reaction of **6** with alkyl halides leads to CS_2 elimination, and formation of $[CoX(depe)_2][BPh_4]$ derivatives (X = Br **7** or I **8**). Complex **6** reacts with activated alk-1-ynes eliminating CS_2 and undergoing an oxidative addition of the alkyne, yielding the hydridoalkynyl complexes $[CoH(C{\equiv}CR)(depe)_2][BPh_4]$ (R = Ph **9** or CO_2Et **10**). A mechanistic study of the reaction between **6** and $HC{\equiv}CCO_2Et$ has been carried out, and the X-ray crystal structure of **10** determined.

The activation of small molecules by metal complexes is relevant to homogeneous catalysis and the chemistry of biological processes such as nitrogen fixation. We have studied systems with iron and strong electron-releasing phosphines such as 1,2-bis(dimethylphosphino)ethane (dmpe) and 1,2-bis(diethylphosphino)ethane (depe) in relation to nitrogen fixation.[1] This led to the isolation of hydridodihydrogen, hydridodinitrogen, and other small molecule adducts of iron.[2] Furthermore, protonation of dinitrogen bound to iron(0) to yield ammonia was achieved, which is consistent with the existence of an iron-only based nitrogenase.[3] During our work with the iron–hydride system, we found many similarities between its chemical behaviour and that of hydrides of cobalt such as $[CoH_3(PPh_3)_3]$[4] and $[Co(H_2)(tdppep)]^+$ [tdppep = tris(2-diphenylphosphinoethyl)phosphine].[5] Despite the fact that cobalt has not yet been found in any nitrogenase, we have carried out a study on the cobalt–1,2-bis(diethylphosphino)ethane system, which parallels those made on iron, in order to compare chemical reactivity, and synthesise new hydrides and small molecule adducts of cobalt.

Results and Discussion

Synthesis and Characterisation of Chloro- and Hydrido-complexes.—It has been known for some time that depe reacts with cobalt halides yielding a series of complexes whose composition depends upon the reaction conditions.[6] Thus, air-oxidation of mixtures of cobalt(II) salts and depe gives cobalt(III) complexes $[CoX_2(depe)_2]X$ (X = Cl, Br or I), whereas in the absence of air, cobalt(II) complexes of empirical formulae $CoI_2(depe)_2$ and $CoBr_2(depe)$ were isolated. Tentative structural assignments were made using magnetic data. On this basis, an octahedral (or tetragonally distorted octahedral) structure was suggested for $[CoI_2(depe)_2]$ in the solid state, with a *trans* stereochemistry, although it behaves as a 1:1 electrolyte in nitromethane, suggesting iodide dissociation and, therefore, the existence of five-co-ordinate $[CoI(depe)_2]^+$ cations in solution. However, the complex of empirical formula $CoBr_2(depe)$ seems to be different, and to be better formulated as $[Co(depe)_2][CoBr_4]$. No data were available for cobalt(II) chloride complexes with depe.

We have found that anhydrous cobalt(II) chloride reacts with depe (molar ratio 1:2) in tetrahydrofuran (thf) yielding a dark green, crystalline solid, for which analytical data suggest a formula $[CoCl_2(depe)_2]$ **1**. This paramagnetic, air-sensitive compound exhibits the thf-solution EPR spectrum at 25 K consisting of one single signal centred at $g = 2.14$, with unresolved hyperfine coupling with ^{59}Co ($I = \frac{7}{2}$), suggesting a highly symmetrical co-ordination environment for Co^{II}, as expected in *trans*-$[CoCl_2(depe)_2]$. Conductivity measurements on green thf solutions indicate that this material is a non-electrolyte. However, from ethanol yellow $[CoCl(depe)_2][BPh_4]$ **2** was isolated upon addition of sodium tetraphenylborate, as inferred from analytical data. This suggests that dissociation of one chloride is appreciable in ethanolic solution, in contrast with what happens in thf. The behaviour of the cobalt system compares with that of $[FeCl_2(L\text{–}L)_2]$ (L–L = depe or dmpe), which gives green non-conducting solutions in solvents such as thf or toluene, but orange-to-red conducting solutions when dissolved in ethanol or methanol under an atmosphere of nitrogen.[7] From these solutions, monodinitro-

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

Non-SI unit employed: cal ≈ 4.184 J.

Table 1 The $^{31}P-\{^1H\}$ and ^1H NMR data for the complexes*

Compound	$^{31}P-\{^1H\}$	^1H (CoH)
3	P_A −56.6(br) P_B −71.4(br) (183 K)	−14.86(br) (298 K)
4	−67.8(s) (183 K) ($CD_3C_6D_5$)	−16.50(qnt) $^2J_{HP}$ = 27 (213 K)
5	−70.7(s) (213 K)	—
6	P_A −68.8, P_B −77.7, P_C −87.4, P_D −97.8 $^2J_{AB}$ = 214, $^2J_{AC}$ = 59 $^2J_{AD}$ = 25, $^2J_{BC}$ = 42 $^2J_{BD}$ = 42, $^2J_{CD}$ = 32 (183 K)	—
9	−57.4(s) (298 K)	−16.32(qnt) $^2J_{HP}$ = 45.5 (298 K)
10	−63.4(s) (298 K)	−16.02 (qnt) $^2J_{HP}$ = 46.1 (298 K)

* In [$^2H_6$]acetone unless otherwise stated. Chemical shifts in ppm from $SiMe_4$ (^1H) or $P(OMe)_3$ ($^{31}P-\{^1H\}$), *J* in Hz; s = singlet, qnt = quintet, br = broad.

gen complexes such as $[FeCl(N_2)(dmpe)_2][BPh_4]$ and $[\{FeCl(depe)_2\}_2(\mu-N_2)][BPh_4]_2$ have been isolated, although the true nature of the latter has not been satisfactorily established. No dinitrogen uptake was observed for our cobalt complex under the conditions in which the iron compounds react with dinitrogen.

The thf solution EPR spectrum of **2** at 25 K differs from that of **1**, showing two main features: one centred at $g = 2.26$, with a broad shoulder at an approximate g value of 2.43, suggesting overlapping of two g components; and another centred at $g = 1.96$ with an eight-line pattern, due possibly to hyperfine coupling with ^{59}Co [$A(^{59}Co) = 90$ G (9×10^{-3} T)]. This spectrum is quite similar to that observed for the compounds $[CoX(L-L)_2]Y$ [X = Cl, Br or I; L–L = 1,2-bis(diphenylphosphino)ethane (dppe) or bis(diphenylphosphino)methane (dppm); Y = BPh_4 or ClO_4], for which a square-pyramidal structure has been proposed.[8] The differences between the EPR spectra of **1** and **2** strongly suggest that the latter exists in thf as a five-co-ordinate species, presumably with a square-pyramidal structure, whereas **1** is a discrete six-co-ordinate molecule, most probably *trans*.

Complex **1** reacts with $NaBH_4$ in ethanol yielding yellow solutions containing the hydride complex *cis*-$[CoH_2(depe)_2]^+$ **3**, isolable as its tetraphenylborate salt. The same complex is obtained by reaction of anhydrous $CoCl_2$ with depe and $NaBH_4$ in ethanol, followed by addition of $Na[BPh_4]$. This product displays medium-strong bands at 1937 and 1918 cm^{-1}, assigned to ν(CoH). The ^1H NMR spectrum at room temperature displays a broad signal at δ −14.86 attributable to the hydridic protons. This broad signal shows some fine structure at −90 °C, which is only partially resolved, but it certainly resembles the XX′ part of a multiplet from an AA′BB′XX′ spin system rather than a quintet arising from coupling to four equivalent phosphorus atoms. We assume a *cis* stereochemistry for **3** on these bases. This is supported by the variable-temperature $^{31}P-\{^1H\}$ NMR spectrum. The spectrum consists of two very broad, almost flat, features at room temperature, suggesting fluxional behaviour. As the temperature is raised, these coalesce, whereas if the temperature is lowered, they sharpen. In Table 1 are given relevant $^{31}P-\{^1H\}$ and ^1H NMR data for this and other compounds prepared in this work. At −90 °C, the $^{31}P-\{^1H\}$ spectrum of **3** in [$^2H_6$]acetone consists of two signals, although still rather broad. This suggests the presence of two groups of non-equivalent phosphorus atoms, and it is consistent with an unresolved A_2B_2 pattern. This supports a non-rigid *cis* structure for **3**, as has been found for other hydrides such as $[FeH_2(L-L)_2]$ (L–L = dppe, dmpe or depe).[9] These are isoelectronic with our cobalt complex, if we consider it formally as Co^{III} (d^6). Indeed the analogous hydrido complex *cis*-$[CoH_2(dppe)_2]^+$ exhibits similar spectral properties, including the two CoH stretching bands in its IR spectrum.[10,11] Other cobalt complexes with the same set of donor atoms (CoH_2P_4) have been prepared, such as $[Co(H_2)(tdppep)]^+$ (ref. 5) and $[CoH_2\{PPh(OEt)_2\}_4]^+$.[12] All these complexes have in common that they were obtained by protonation of a cobalt(I) monohydride. However, it is known that alcohols are acids strong enough to protonate basic hydrido complexes to yield dihydrogen adducts.[13] For example, $[FeCl_2(L-L)_2]$ (L–L = dmpe or depe) reacts with $NaBH_4$ in ethanol yielding $[FeH_2(L-L)_2]$ first, and then $[FeH(H_2)(L-L)_2]^+$, the additional proton coming from the alcohol solvent.[2,12] The species $[FeH_2(L-L)_2]$ is obtained upon removal of the solvent, due to the equilibrium (1). However, the

$$[FeH_2(L-L)_2] \xrightleftharpoons{EtOH} [FeH(H_2)(L-L)_2]^+ + RO^- \quad (1)$$

equilibrium can be shifted to the right by precipitation of the dihydrogen complex using $Na[BPh_4]$, in almost quantitative yield. Something similar seems to happen here. Strong electron-releasing phosphines, such as dmpe and depe, provide very basic hydride complexes, able to react with weak acids such as alcohols. This is not the case for dppe or tdppep hydrido complexes, which require strong acids to achieve protonation.

In the reaction of **1** with $NaBH_4$, $[CoH(depe)_2]$ **4** must form first, but this must be very basic and readily protonated by the alcohol used as solvent, yielding **3**. Attempts to isolate **4** as a solid were unsuccessful due to its great solubility and tendency to react with traces of moisture. However, we have been able to isolate it as a pyrophoric oil, or maintain it in solution where it seems to be stable. Thus, a thf solution of **3** was allowed to react with 1 equivalent of $KOBu^t$, yielding a white precipitate of $K[BPh_4]$. From the supernatant liquor we obtained a yellow-green pyrophoric oil upon removal of the solvent. Its ^1H NMR spectrum at room temperature displays a broad hydride signal at δ −16.50, which resolves into a binomial quintet as the temperature is lowered, suggesting coupling to four equivalent phosphorus atoms. The $^{31}P-\{^1H\}$ NMR spectrum consists of a broad singlet at room temperature, which sharpens at low temperatures. These data are consistent with the presence of square-pyramidal $[CoH(depe)_2]$ in these solutions. If the oil **4** is dissolved in ethanol, **3** is isolated upon addition of $Na[BPh_4]$.

It has been shown in recent years that protonation of 'classical' hydrides is a method for the preparation of dihydrogen complexes.[14] Complex **3** may be either a *cis*-dihydride or a dihydrogen complex. The two CoH stretching bands near 1900 cm^{-1} are more consistent with a terminal hydride or classical formulation, as in $[CoH_2\{PPh(OEt)_2\}_4]^+$. In order to establish the true character of the hydrogen ligands in **3**, we applied the T_1 (spin–lattice or longitudinal relaxation time) criterion proposed by Crabtree and Hamilton,[15] taking into account all the corrections made to this criterion since it first appeared.[16] Values of T_1 for the hydrides in **3** range from 52 ms at −90 °C to 280 ms at room temperature. A minimum was not observed, and thus 52 ms is greater than or equal to $(T_1)_{min}$ ([$^2H_6$]acetone, 270 MHz). This is relatively short. In order to get a T_1 reference value, we also measured $(T_1)_{min}$ for **4** (generated by deprotonation of **3**). For this complex, in which there is no hydride–hydride interaction, a minimum value of 60 ms was obtained ([$^2H_8$]toluene, 270 MHz), of the same order of magnitude as that for **3**. It has been pointed out[11] that in addition to the H–H dipolar mechanism, a M–H dipolar mechanism is also operative in hydride complexes of metals having isotopes with $I \geqslant \frac{5}{2}$ in high natural abundance. Consequently, relatively small relaxation times are always expected, and the relaxation times tell us little about the nature of the H ligands. However, all our data taken together suggest that **3** is a true classical *cis*-dihydride. A similar conclusion has

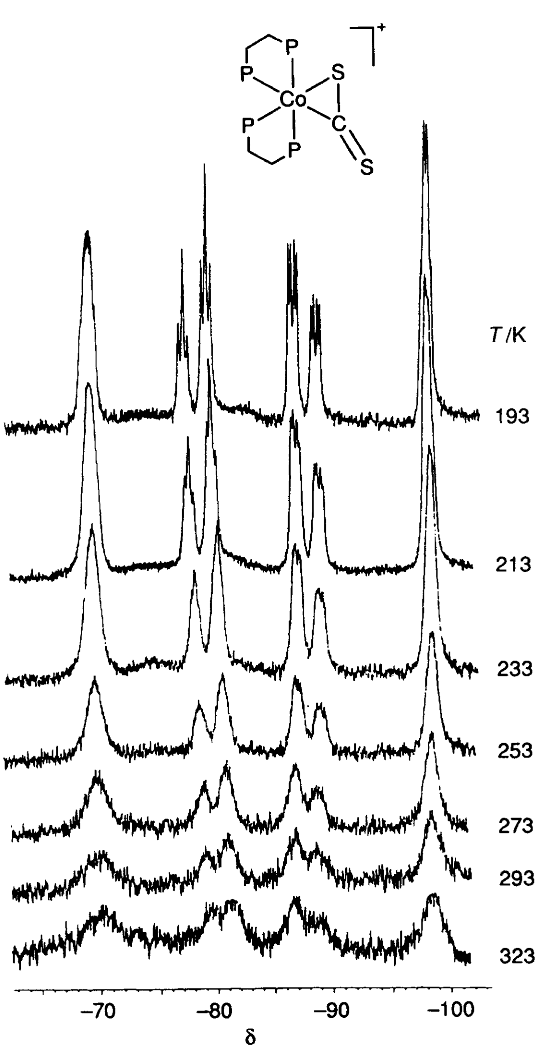

Fig. 1 Variable-temperature $^{31}P-\{^1H\}$ NMR spectrum of complex **6** in $[^2H_6]$acetone

been reached for $[CoH(dppe)_2]$ and $[CoH_2(dppe)_2]^+$, and for $[CoH\{PPh(OEt)_2\}_4]$ and $[CoH_2\{PPh(OEt)_2\}_4]^+$.[12]

Reactivity of $[CoH_2(depe)_2][BPh_4]$ *and Related Complexes.*—It has already been mentioned that **3** reacts with a strong base such as KOBu^t to yield the monohydride **4**. We have also studied the reactivity of **3** towards reductive elimination of dihydrogen. Complex **3** is unreactive towards ethylene, diphenylacetylene, carbon dioxide, acetonitrile or dinitrogen. However, it reacts with CO in thf yielding yellow-orange crystals of $[Co(CO)(depe)_2][BPh_4]$ **5**, which displays one ν(CO) band at 1917 cm^{-1} in its IR spectrum. This complex is non-rigid in solution. Its $^{31}P-\{^1H\}$ NMR spectrum consists of a very broad signal at room temperature, which becomes a singlet as the temperature is lowered. This suggests that the four phosphorus atoms are equivalent, consistent with a square-pyramidal structure with the CO ligand in the apical position.

The reaction of **3** with an excess of CS_2 in thf yields red-orange crystals of $[Co(CS_2)(depe)_2][BPh_4]$ **6**. One band at 1140 cm^{-1} on the IR spectrum has been assigned to ν(C=S) in a η^2-bound carbon disulfide ligand. This complex is also fluxional, and its $^{31}P-\{^1H\}$ NMR spectrum consists of very broad features at room temperature. However, at −90 °C it resolves into four doublets of doublets of doublets, corresponding to an ABCD spin system, as expected for the structure shown in Fig. 1, with mutually *cis*-phosphine ligands and one η^2-bound CS_2 ligand.

Carbon disulfide has an interesting reactivity when bound to a metal centre.[17,18] The reaction with alkyl halides or alkynes has been reported to yield dithiocarbene[19] or metallodithiolactones,[20] respectively. We carried out reactions of **6** with alkyl halides and alkynes. From the reaction of **6** with alkyl halides (MeI or $BrCH_2CH_2Br$) in thf at reflux temperature, paramagnetic, lemon-yellow crystals were obtained. The IR spectra of these compounds do not show any special features, apart from those due to depe and $[BPh_4]^-$ anion. Analytical data indicate a composition $[CoX(depe)_2][BPh_4]$ (X = Br **7** or I **8**), the absence of sulfur being confirmed by sulfur analysis. Thus, in the course of the reaction of **6** with alkyl halides, the CS_2 ligand is lost, and the cobalt(II) derivatives **7** and **8** are the ultimate metal-containing products.

The reaction of **6** with alkynes was studied in an attempt to obtain derivatives of cycloaddition of the alkyne to the bound CS_2 molecule but **6** does not react with diphenylacetylene or trimethylsilylacetylene. With bis(carboxymethyl)acetylene at the reflux temperature in thf, a mixture of a dark oil together with starting material was obtained. However, an interesting reaction was observed with activated alk-1-ynes. Complex **6** reacts with HC≡CR (R = Ph or CO_2Et) to yield crystalline materials, which exhibit one strong band near 2100 cm^{-1} in their IR spectra. For the product of the reaction with phenylacetylene, a weak band at 1888 cm^{-1} is also present, this being absent for the product of the reaction with ethyl propiolate. In this case, a strong band at 1658 cm^{-1} is assigned to ν(C=O) in the ester group. No sulfur was found in any of these derivatives, and the analytical data are consistent with a formula $[Co(HC{\equiv}CR)(depe)_2][BPh_4]$. The strong band near 2100 cm^{-1} is consistent with ν(C≡C) in an alkynyl complex. The $^{31}P-\{^1H\}$ NMR spectrum for each of the complexes consists of a sharp singlet at all temperatures studied, suggesting a *trans* phosphine arrangement. The ^1H NMR spectra display one quintet in the hydride region for both compounds, denoting the presence of one hydride ligand coupled to four equivalent phosphorus atoms, and accounting for the IR band at 1888 cm^{-1} for the phenylacetylene derivative, which can now be assigned to ν(CoH). Thus, these spectral data are consistent with the formation of hydridoalkynyl complexes of the type *trans*-$[CoH(C{\equiv}CR)(depe)_2][BPh_4]$ (R = Ph **9** or CO_2Et **10**). The *trans*-hydrido–alkynyl formulation has been unequivocally confirmed by an X-ray crystal structure analysis for compound **10**, and the results are discussed below.

In all reactions attempted, the η^2-CS_2 has been shown to be unreactive, presumably being lost and generating a 16-electron fragment, $[Co(depe)_2]^+$, which is electron-rich enough to cleave C–H bonds in activated alk-1-ynes. There are other examples in which electron-rich metal centres react with alk-1-ynes to give hydridoalkynyl complexes. The fragment $[Fe(dppe)_2]$, isoelectronic with $[Co(depe)_2]^+$, undergoes an oxidative addition reaction with phenylacetylene, yielding octahedral *trans*-$[FeH(C{\equiv}CPh)(dppe)_2]$.[21] The spectral properties of this complex match ours for **9** and **10**. We have not been able to isolate $[Co(depe)_2]^+$ as a solid salt, although the analogous complexes $[M(L-L)_2]^+$ (M = Rh or Ir, L–L = dmpe or depe)[22] are easily isolable. The intrinsic interest of C–H activation and the possible role of complex **6** in such processes prompted us to carry out a more detailed mechanistic study of the reaction with ethyl propiolate.

Kinetics of the Reaction of **6** *with Ethyl Propiolate.*—To confirm that the reactions of **6** proceed through initial loss of CS_2 and formation of a 16-electron intermediate, the kinetics of reaction with ethyl propiolate has been studied. The rate constants obtained at different temperatures and concentrations of alkyne are in Table 2. They indicate that the reaction is first order, with respect to the concentrations of both the cobalt complex and the alkyne. The values derived for the second-order rate constant are also in Table 2, and they lead to a value of $\Delta H^\ddagger = 23.2 \pm 0.7$ kcal mol^{-1}, and $\Delta S^\ddagger = 13 \pm 2$ cal K^{-1}

Table 2 Observed rate constants for the reaction of complex **6** with ethyl propiolate[a]

10^2[HC≡CR]/mol dm^{-3}	10^3k_{obs}/s^{-1}			
	T = 25	30	35	40 °C
1.86	—	—	3.01(0.01)	4.13(0.06)
2.08	0.79(0.01)	—	—	5.22(0.06)
2.41	—	1.96(0.01)	3.45(0.01)	5.96(0.04)
3.00	1.13(0.01)	2.58(0.01)	—	—
3.57	—	—	—	9.5(0.2)
4.03	1.53(0.02)	3.12(0.01)	6.28(0.06)	—
4.28	—	—	—	10.2(0.2)
5.16	—	4.50(0.04)	8.20(0.09)	—
5.35	1.91(0.01)	—	—	13.2(0.2)
5.62	—	4.54(0.02)	8.19(0.11)	—
6.42	2.46(0.01)	—	—	16.6(0.4)
10^2k_2/dm^3 mol^{-1} s^{-1} [b]	3.73(0.19)	8.33(0.74)	15.03(1.03)	26.0(1.1)

[a] Values in parentheses correspond to the standard deviations of the fit. [b] Value derived for the second-order rate constant.

Table 3 Observed rate constants for the reaction of complex **6** with ethyl propiolate in the presence of added carbon disulfide*

10^2[CS$_2$]/mol dm^{-3}	10^3k_{obs}/s^{-1}
0.00	2.46(0.01)
0.27	1.26(0.01)
0.54	1.075(0.004)
0.72	0.816(0.005)
1.00	0.533(0.003)
1.47	0.486(0.002)
2.00	0.313(0.003)

* T = 25 °C, [HC≡CCO$_2$Et] = 6.42 × 10^{-2} mol dm^{-3}. The values in parentheses correspond to the standard deviations of the fit.

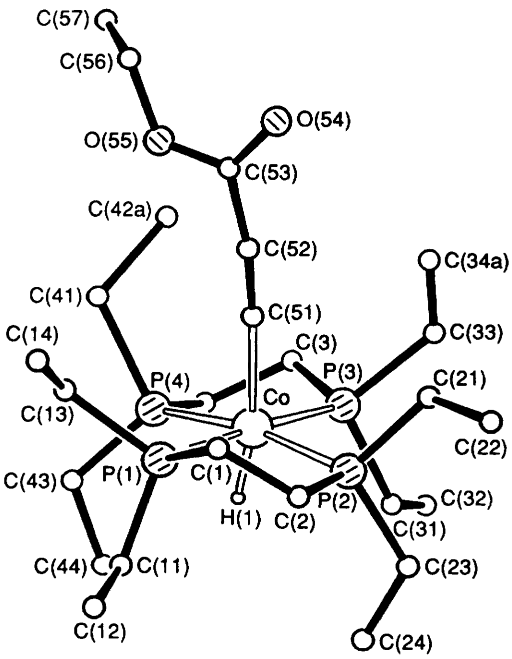

Fig. 2 View of the complex cation [CoH(C≡CCO$_2$Et)(depe)$_2$]$^+$, showing atom labelling. Of the disordered ethyl groups in the depe ligands only those of major occupation are shown

mol^{-1}. The reaction is slower in the presence of an excess of CS$_2$, as shown in Table 3. From these kinetic data, we infer the following mechanism [equations (2) and (3)]. The first step is a fast equilibrium of dissociation of CS$_2$. The rate equation for this mechanism is as in (4).

$$[\mathrm{Co(CS_2)(depe)_2}]^+ \xrightleftharpoons{K} [\mathrm{Co(depe)_2}]^+ + \mathrm{CS_2} \quad (2)$$

$$[\mathrm{Co(depe)_2}]^+ + \mathrm{HC{\equiv}CR} \xrightarrow{k_2} [\mathrm{CoH(C{\equiv}CR)(depe)_2}]^+ \quad (3)$$

$$k_{obs} = \frac{k_2K[\mathrm{HC{\equiv}CR}]}{[\mathrm{CS_2}] + K} \quad (4)$$

This equation reduces to $k_{obs} = k_2$[HC≡CR] in the absence of a CS$_2$ excess, consistent with data in Table 2. In the presence of an excess of CS$_2$ there is a linear correlation between $1/k_{obs}$ and [CS$_2$], which allows calculation of k_2[HC≡CR] and K from the fitting parameters. Using the data in Table 3 obtained with [HC≡CR] = 6.42 × 10^{-2} mol dm^{-3}, K was found to be (2.6 ± 0.5) × 10^{-3} mol dm^{-3}, and k_2[HC≡CR] (2.9 ± 0.5) × 10^{-3} s^{-1}, in good agreement with the value of k_{obs} in the absence of CS$_2$ (2.46 × 10^{-3} s^{-1}).

Thus, the kinetic study of this reaction is consistent with the suggestion that CS$_2$ is a labile ligand in complex **6**, but it does not provide definitive information about the mechanism of oxidative addition of the C–H bond to the 16-electron intermediate. Some authors[23] have presented evidence that the formation of hydridoalkynyl complexes involves initial formation of an alkyne complex, but there is also the possibility of nucleophilic attack on HC≡CR by the cobalt(I) intermediate, in a fashion similar to that inferred for oxidative addition of polar reagents to 16-electron species.[24] The formation of the *trans* isomer might also suggest this mechanism, but it could also result from an isomerisation following the oxidative addition.

X-Ray Crystal Structure of Complex **10**.—X-Ray crystal structure analysis yielded the structure shown in Fig. 2. Atomic coordinates and selected bond lengths and angles are presented in Tables 4 and 5, respectively. The asymmetric unit consists of one complex cation and one tetraphenylborate anion. The coordination around the cobalt atom is distorted octahedral, with hydrido and alkynyl ligands in mutually *trans* positions. The two depe ligands form a four-phosphorus-atom equatorial plane. The hydrido ligand is bent from the normal to this P$_4$ plane and forms a C(51)–Co–H(1) angle of 168(4)°. The Co–P and Co–C bond distances are as expected from previously reported structures, *e.g.* [CoH(CCPh)$_2$(PMe$_3$)$_3$].[25] The Co–H(1) distance appears slightly shorter than those found in hydrido complexes of cobalt(I),[26] but this is not unexpected since the cobalt atom has an oxidation state of +III in our complex. The chelating P–Co–P angles are normal for this ligand, at 85.3(1) and 85.6(1)°. The Co–C(51)–C(52) and C(51)–C(52)–C(53) angles confirm an almost linear alkynyl ligand. All the remaining bond dimensions in the ligands and in the tetraphenylborate anion are in the normal ranges and are satisfactory.

Interionic contacts are at normal van der Waals distances.

Experimental

All synthetic operations were performed under dry dinitrogen following standard Schlenk techniques. All the solvents were distilled under dinitrogen from the appropriate drying agents prior to use. 1,2-Bis(diethylphosphino)ethane was obtained according to literature methods.[27] Infrared spectra were recorded on a Perkin Elmer 882 instrument in Nujol mulls. NMR spectra were taken on a JEOL GSX-270 or a Varian Gemini 200 instrument, in the appropriate deuteriated solvents. Microanalyses were by Mr. Colin Macdonald, at the AFRC-IPSR Nitrogen Fixation Laboratory. EPR spectra were recorded by Dr. David J. Lowe on a Bruker ER-200D.

Table 4 Final atomic coordinates (fractional × 10^4) for *trans*-$[CoH(C{\equiv}CCO_2Et)(depe)_2]BPh_4$ **10** with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Co	1 528(1)	523.7(6)	9 165.5(5)	O(54)	5 046(14)	1 529(6)	10 530(5)
P(1)	3 057(2)	−8(1)	8 712(1)	O(55)	4 835(10)	479(5)	10 628(5)
C(11)	2 574(14)	−487(8)	8 119(7)	C(56)	5 774(16)	435(9)	11 052(8)
C(12)	3 470(15)	−580(9)	7 645(7)	C(57)	5 170(15)	152(10)	11 523(7)
C(13)	4 158(14)	−585(8)	9 115(12)	H(1)	888(76)	245(38)	8 829(30)
C(14)	5 354(19)	−591(10)	9 084(8)	B	6 319(11)	1 723(5)	6 828(4)
C(1)	4 072(9)	673(5)	8 460(4)	C(61)	4 772(8)	1 912(5)	6 820(3)
C(2)	3 241(9)	1 192(5)	8 174(4)	C(62)	3 805(9)	1 447(5)	6 745(4)
P(2)	1 885(2)	1 395(1)	8 606(1)	C(63)	2 525(10)	1 621(6)	6 694(4)
C(21)	2 331(14)	2 206(5)	8 919(5)	C(64)	2 172(12)	2 278(6)	6 737(5)
C(22)	2 753(17)	2 800(6)	8 536(7)	C(65)	3 075(13)	2 774(6)	6 823(5)
C(23)	714(13)	1 644(9)	8 098(6)	C(66)	4 376(11)	2 613(5)	6 868(4)
C(24)	172(13)	1 117(13)	7 767(6)	C(71)	7 026(9)	2 227(4)	7 256(4)
P(3)	−90(3)	1 029(1)	9 573(1)	C(72)	6 587(11)	2 311(5)	7 775(4)
C(31)	−1 525(14)	1 136(11)	9 113(6)	C(73)	7 203(13)	2 707(6)	8 190(5)
C(32)	−2 734(19)	1 206(16)	9 344(11)	C(74)	8 245(12)	3 023(6)	8 055(4)
C(33)	87(31)	1 883(8)	9 916(10)	C(75)	8 761(11)	2 963(5)	7 560(4)
C(34a)*	818(28)	2 010(14)	10 288(11)	C(76)	8 149(10)	2 570(5)	7 160(4)
C(34b)*	−151(49)	2 034(22)	10 442(18)	C(81)	6 876(9)	1 847(4)	6 191(3)
C(3)	−688(14)	499(8)	10 122(5)	C(82)	8 057(12)	1 600(6)	6 032(5)
C(4)	−605(12)	−253(7)	9 940(5)	C(83)	8 557(14)	1 668(6)	5 504(5)
P(4)	932(3)	−417(2)	9 605(2)	C(84)	7 917(14)	1 997(6)	5 138(5)
C(41)	2 012(22)	−639(10)	10 264(10)	C(85)	6 753(13)	2 276(6)	5 253(5)
C(42a)*	1 790(32)	−43(18)	10 788(13)	C(86)	6 227(10)	2 195(5)	5 782(4)
C(42b)*	2 001(54)	−1 083(27)	10 405(20)	C(91)	6 489(8)	907(4)	6 978(3)
C(43)	708(20)	−1 195(7)	9 266(15)	C(92)	6 918(9)	667(5)	7 483(4)
C(44)	−291(23)	−1 158(11)	8 839(12)	C(93)	7 021(10)	−37(5)	7 597(4)
C(51)	2 783(9)	811(5)	9 681(4)	C(94)	6 688(10)	−518(5)	7 222(4)
C(52)	3 610(11)	961(5)	9 991(4)	C(95)	6 288(11)	−315(5)	6 727(4)
C(53)	4 585(13)	1 012(7)	10 373(5)	C(96)	6 216(9)	386(5)	6 605(4)

* Site occupancy of 0.5.

The kinetics of reaction between **6** and ethyl propiolate in thf was studied following the decrease in absorbance at 366 nm of solutions resulting from mixing appropriate volumes of pre-thermostatted stock solutions of both reagents. The absorbance measurements were made with a Varian 2290 UV/VIS spectrophotometer interfaced to a Multitech P500 microcomputer, which was also used for treatment of data. The experiments were carried out under pseudo-first-order conditions, and the observed rate constants were obtained from a conventional linear fit of $\ln(A_t - A_\infty)$ *vs.* time data (A_t = absorbance at time t, A_∞ = final absorbance). The reported estimation of errors corresponds to the standard deviations of the fit.

Preparations.—*Bis*[1,2-*bis*(*diethylphosphino*)*ethane*]*dichlorocobalt*(II) **1**. Anhydrous cobalt(II) chloride (5 g, 38 mmol) was suspended in thf (100 cm^3), and treated with depe (18 g, 87 mmol). The resulting mixture was stirred at room temperature for 3 d. A dark green, crystalline precipitate was obtained, which was filtered off, washed with hexane, and dried *in vacuo*. Yield: 18 g, 90%. This product is pure enough for synthetic purposes. An analytically pure sample was obtained by recrystallisation from thf (Found: C, 44.7; H, 8.90. $C_{20}H_{48}Cl_2CoP_4$ requires C, 44.3; H, 8.85%).

Bis[1,2-*bis*(*diethylphosphino*)*ethane*]*chlorocobalt*(II) *tetraphenylborate* **2**. Complex **1** (0.5 g, *ca.* 1 mmol) was dissolved in ethanol yielding a dark green solution. Solid $Na[BPh_4]$ (0.35 g, 1 mmol) was added, and a yellow solid precipitated immediately. This was filtered off, washed with light petroleum (b.p. 36–60 °C) and dried *in vacuo*. The product was recrystallised by concentration of a thf–ethanol mixture and cooling to −20 °C. Yield: 0.53 g, 64% (Found: C, 63.8; H, 8.15. $C_{44}H_{68}BClCoP_4$ requires C, 63.9; H, 8.25%).

cis-*Bis*[1,2-*bis*(*diethylphosphino*)*ethane*]*dihydridocobalt*(III) *tetraphenylborate* **3**. To a suspension of $CoCl_2$ (0.35 g, 2.7 mmol) in absolute ethanol (100 cm^3), depe (1.4 cm^3, *ca.* 6 mmol) was added. A green colour developed immediately. After stirring for 10 min, $NaBH_4$ (0.11 g, 2.9 mmol) dissolved in EtOH (10 cm^3) was added *via* syringe. The colour gradually lightened and a yellow, cloudy solution was obtained. The mixture was stirred for 15 min. Then $Na[BPh_4]$ (1.15 g, *ca.* 3 mmol) in EtOH (10 cm^3) was added, producing a yellow solid precipitate. The mixture was stirred for another hour. The solid was then filtered off, washed with ethanol and hexane, and dried *in vacuo*. The light yellow product was dissolved in thf (40 cm^3). The solution was filtered through Celite and EtOH (40 cm^3) then added. Concentration of the resulting yellow solution and cooling to −20 °C afforded pale yellow crystals. Yield: 1.65 g, 77% (Found: C, 66.2; H, 8.9. $C_{44}H_{70}BCoP_4$ requires C, 66.6; H, 8.8%). IR: ν(CoH) 1937 and 1918 cm^{-1}. This complex was also obtained from **1** following a similar procedure.

Bis[1,2-*bis*(*diethylphosphino*)*ethane*]*hydridocobalt*(I) **4**. Complex **3** (0.7 g, 0.88 mmol) was dissolved in thf (30 cm^3). Solid $KOBu^t$ (0.96 g, 0.88 mmol) was added, and the mixture stirred for 30 min. A yellow-green suspension was obtained. This was filtered through Celite, and the Celite washed with thf. The resulting yellow-green solution was taken to dryness, leaving a pyrophoric oil. This oil was used for NMR studies.

Bis[1,2-*bis*(*diethylphosphino*)*ethane*]*carbonylcobalt*(I) *tetraphenylborate* **5**. A thf solution of **3** (0.35 g, 0.44 mmol) was stirred under CO (1 atm, 101 325 Pa). After several minutes, the solution turned orange. It was stirred for 1 h. Ethanol was then added. On concentration, yellow-orange crystals deposited, which were collected by filtration, washed with hexane and dried *in vacuo*. Yield: 0.3 g, 84% (Found: C, 65.9; H, 8.1. $C_{45}H_{68}BCoOP_4$ requires C, 65.9; H, 8.3%). IR: ν(CO) 1917 cm^{-1}.

Bis[1,2-*bis*(*diethylphosphino*)*ethane*](*carbon disulfide*)*cobalt*(I) *tetraphenylborate* **6**. Carbon disulfide (0.5 cm^3, an excess) was added to a thf solution of **3** (0.35 g, 0.44 mmol). The solution became orange and then red. It was stirred for 1 h. Then ethanol (40 cm^3) was added, and the mixture con-

Table 5 Selected bond lengths (Å) and angles (°) in *trans*-$[CoH(C{\equiv}CCO_2Et)(depe)_2]BPh_4$ **10** with e.s.d.s in parentheses

(*a*) About the Co atom			
Co–P(1)	2.211(2)	Co–P(4)	2.204(4)
Co–P(2)	2.202(3)	Co–C(51)	1.911(10)
Co–P(3)	2.205(3)	Co–H(1)	1.19(8)
P(1)–Co–P(2)	85.3(1)	P(3)–Co–C(51)	96.3(3)
P(1)–Co–P(3)	176.0(1)	P(4)–Co–C(51)	96.7(3)
P(1)–Co–P(4)	94.0(1)	H(1)–Co–P(1)	82(4)
P(1)–Co–C(51)	87.7(3)	H(1)–Co–P(2)	91(4)
P(2)–Co–P(3)	94.3(1)	H(1)–Co–P(3)	94(4)
P(2)–Co–P(4)	169.3(1)	H(1)–Co–P(4)	79(4)
P(2)–Co–C(51)	93.0(3)	H(1)–Co–C(51)	168(4)
P(3)–Co–P(4)	85.6(1)		
(*b*) In the depe ligands			
P(1)–C(11)	1.794(17)	C(2)–P(2)	1.822(10)
P(1)–C(13)	1.888(20)	P(2)–C(21)	1.807(11)
P(1)–C(1)	1.806(10)	P(2)–C(23)	1.817(15)
P(3)–C(31)	1.898(15)	C(4)–P(4)	1.845(13)
P(3)–C(33)	1.861(18)	P(4)–C(41)	2.020(24)
P(3)–C(3)	1.803(14)	P(4)–C(43)	1.733(22)
Co–P(1)–C(1)	105.4(3)	Co–P(2)–C(2)	109.3(3)
Co–P(1)–C(11)	116.0(5)	Co–P(2)–C(21)	116.4(4)
Co–P(1)–C(13)	117.5(8)	Co–P(2)–C(23)	120.7(5)
C(11)–P(1)–C(13)	107.0(9)	C(2)–P(2)–C(21)	103.2(6)
C(11)–P(1)–C(1)	105.6(6)	C(2)–P(2)–C(23)	101.2(6)
C(13)–P(1)–C(1)	104.1(6)	C(21)–P(2)–C(23)	103.7(7)
Co–P(3)–C(3)	110.9(5)	Co–P(4)–C(4)	109.0(5)
Co–P(3)–C(31)	113.5(5)	Co–P(4)–C(41)	113.8(6)
Co–P(3)–C(32)	121.3(10)	Co–P(4)–C(43)	121.4(11)
C(31)–P(3)–C(33)	104.5(11)	C(4)–P(4)–C(41)	100.3(8)
C(31)–P(3)–C(3)	102.9(7)	C(4)–P(4)–C(43)	104.0(9)
C(33)–P(3)–C(3)	101.8(9)	C(41)–P(4)–C(43)	105.9(11)
(*c*) In the alkynyl ligand			
C(51)–C(52)	1.192(15)	C(53)–O(55)	1.233(17)
C(52)–C(53)	1.393(17)	O(55)–C(56)	1.437(22)
C(53)–O(54)	1.176(18)	C(56)–C(57)	1.426(26)
Co–C(51)–C(52)	176.2(9)	O(54)–C(53)–O(55)	117.2(13)
C(51)–C(52)–C(53)	169.9(11)	C(53)–O(55)–C(56)	124.2(12)
C(52)–C(53)–O(54)	125.8(13)	O(55)–C(56)–C(57)	107.3(14)
C(52)–C(53)–O(55)	116.0(12)		
(*d*) Torsion angles in the depe ligands			
P(1)–C(1)–C(2)–P(2)	47.7(8)	P(3)–C(3)–C(4)–P(4)	43.8(11)

centrated. A red-orange crystalline precipitate was obtained. This was filtered off, washed with diethyl ether and dried *in vacuo*. Yield: 0.3 g, 79% (Found: C, 62.3; H, 8.0. $C_{45}H_{68}BCoP_4S_2$ requires C, 62.3; H, 7.8%). IR: ν(C=S) 1140 cm^{-1}.

Bis[1,2-*bis*(*diethylphosphino*)*ethane*]*bromocobalt*(II) *tetraphenylborate* **7**. Complex **6** (0.37 g, 0.43 mmol) was dissolved in thf (20 cm^3). 1,2-Dibromoethane (0.5 cm^3, an excess) was added. The mixture was heated under reflux for 5 min to give a green-brown solution which was stirred for 30 min at room temperature. It was concentrated under reduced pressure, and ethanol added. A yellow-green crystalline product was formed upon cooling to −20 °C. The crystals were filtered off, washed with diethyl ether and dried *in vacuo*. Yield: 0.25 g, 65% (Found: C, 60.5; H, 7.95. $C_{44}H_{68}BBrCoP_4$ requires C, 60.7; H, 7.80%).

Bis[1,2-*bis*(*diethylphosphino*)*ethane*]*iodocobalt*(II) *tetraphenylborate* **8**. This was obtained in a fashion analogous to that used for **7**, but using methyl iodide instead of 1,2-dibromoethane. Yield: 73% (Found: C, 57.9; H, 7.50. $C_{44}H_{68}CoIP_4$ requires C, 57.6; H, 7.40%).

trans-*Bis*[1,2-*bis*(*diethylphosphino*)*ethane*]*hydrido*(*phenylethynyl*)*cobalt*(III) *tetraphenylborate* **9**. Complex **6** (0.35 g, 0.4 mmol) was dissolved in thf (20 cm^3). Neat phenylacetylene (0.5 cm^3, an excess) was added. The mixture was heated under reflux for 5 min, and then stirred overnight at room temperature. Ethanol was added, the mixture concentrated under reduced pressure and then cooled to −20 °C. Yellow-orange crystals were obtained, which were filtered off, washed with diethyl ether and dried *in vacuo*. Yield: 0.31 g, 84% (Found: C, 70.0; H, 8.40. $C_{52}H_{74}BCoP_4$ requires C, 69.95; H, 8.30%). IR: ν(C≡C) 2096, ν(CoH) 1888 cm^{-1}.

trans-*Bis*[1,2-*bis*(*diethylphosphino*)*ethane*](*ethoxycarbonylethynyl*)*hydridocobalt*(III) *tetraphenylborate* **10**. This was obtained following the procedure used for **9**. It was recrystallised in the same way, but diethyl ether was added to the concentrated thf–EtOH mixture. Well formed pale yellow crystals were obtained. They were filtered off, washed with diethyl ether and dried *in vacuo*. Yield: 66% (Found: C, 65.8; H, 8.50. $C_{49}H_{74}BCoO_2P_4$ requires C, 66.2; H, 8.35%). IR: ν(C≡C) 2076; ν(C=O) 1658 cm^{-1}. No band assignable to ν(CoH) was observed.

Crystal Structure Determination of Complex **10**.—*Crystal data*. $C_{49}H_{74}BCoO_2P_4$, M = 888.8, orthorhombic, space group $P2_12_12_1$ (no. 19), a = 10.554(1), b = 19.328(1), c = 24.452(3) Å, U = 4987.9 Å^3, Z = 4, D_c = 1.183 g cm^{-3}, $F(000)$ = 1904, μ(Mo-Kα) = 5.0 cm^{-1}, λ(Mo-Kᾱ) = 0.710 69 Å.

A fine, pale yellow prismatic crystal with dimensions *ca*. 0.67 × 0.42 × 0.23 mm was mounted, in air, on a glass fibre. After preliminary photographic examination, it was transferred to an Enraf-Nonius CAD4 diffractometer (with monochromated radiation) where accurate cell parameters were refined from the settings of 25 reflections (θ *ca*. 10.5°), each centred in four orientations, and intensity data were measured for the reflections having $1.5 < \theta < 22°$. During processing, corrections were applied for Lorentz and polarisation effects, slight crystal deterioration (4% overall) and absorption (a minimal correction, analytically determined in SHELX[28]).

3435 Independent reflections were entered into the TEXSAN system[29] for structure determination by the heavy-atom method (for the Co atom) and phase-expansion and -refinement for the remainder of the structure. The asymmetric unit comprises a cationic cobalt complex and a tetraphenylborate anion. Refinement of the structural model was by full-matrix least-squares methods. In the cation, the non-hydrogen atoms (except for the disordered methyl C atoms of two depe ligands) were refined anisotropically, and, in the anion, all non-hydrogen atoms were refined isotropically. The hydride ligand was located in a difference map and was refined independently and satisfactorily. Other hydrogen atoms (except in the disordered ethyl groups) were included in idealised positions, with methyl groups staggered. The refined thermal parameters suggest that there is considerable vibration in several of the other ethyl groups and that there may be further examples of site disorder.

The refinement was terminated with R = 0.065 and R' = 0.069 for the 3044 reflections with $I > \sigma_I$ weighted $w = \sigma_F^{-2}$. Both enantiomers were refined, and the one reported in Table 4 had the marginally lower R factor. The final difference map showed no features outside the range of −0.4 to 0.4 e Å^{-3}.

Scattering curves for neutral atoms were taken from those included in the TEXSAN system which was running on a DEC VAX 3520 computer at the Servicios Centralizados de Ciencia y Tecnologia de la Universidad de Cadiz. The diffraction intensities were processed on a DEC MicroVAX II computer in the Nitrogen Fixation Laboratory, using programs listed in Table 4 of ref. 30.

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

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