

## Reductive dehalogenation of chloro(alkynyl)phosphines by octacarbonyldicobalt

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### Abstract

Reductive dehalogenation of the (chloro)(phenylethynyl)phosphine (2,4,6-<sup>t</sup>Bu<sub>3</sub>C<sub>6</sub>H<sub>2</sub>O)(PhC≡C)PCl, I, by Co<sub>2</sub>(CO)<sub>8</sub>, II, yields the neutral phosphonium ion complex [(R)(R')P=Co(CO)<sub>3</sub>], III, (R = 2,4,6-<sup>t</sup>Bu<sub>3</sub>C<sub>6</sub>H<sub>2</sub>O; R' = (η<sup>2</sup>-C≡CPh)Co<sub>2</sub>(CO)<sub>6</sub>), which contains a trigonally planar coordinated phosphorus atom. When NaCo(CO)<sub>4</sub>, V, is used instead of II a dinuclear complex, Co<sub>2</sub>(CO)<sub>8</sub>[μ<sup>2</sup>-P(R)(R')]<sub>2</sub>, VI, (R = 2,4,6-<sup>t</sup>Bu<sub>3</sub>C<sub>6</sub>H<sub>2</sub>O; R' = C≡CPh) is formed in which the phosphido ligands P(R)(R'), bridge in a μ<sub>2</sub> fashion two Co(CO)<sub>3</sub> units. The mechanism of formation of VI, involving a formal dimerization of two [(2,4,6-<sup>t</sup>Bu<sub>3</sub>C<sub>6</sub>H<sub>2</sub>O)(PhC≡C)]P=Co(CO)<sub>3</sub> fragments, is discussed. However, (<sup>t</sup>Bu)(PhC≡C)PCl, VII, reacts with II, to yield the cluster compound VIII, containing the two μ<sub>2</sub>-bridging units (<sup>t</sup>Bu)[(η<sup>2</sup>-C≡CPh)Co<sub>2</sub>(CO)<sub>5</sub>]P and (<sup>t</sup>Bu)(PhC≡C)P.

Compounds III and VI–VIII were identified from their analytical and spectroscopic (IR, <sup>1</sup>H-, <sup>13</sup>C- and <sup>31</sup>P-NMR) data. The molecular structure of the cluster compound VIII was determined by an X-ray diffraction study.

### Introduction

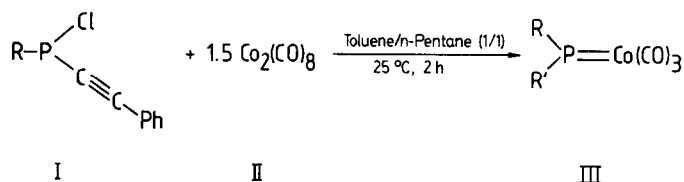
In contrast to the well studied reactions of alkynyl-substituted phosphines R<sub>n</sub>P(C≡CR')<sub>3-n</sub> (*n* = 0–2; R, R' = organic ligand) with octacarbonyldicobalt [1,2], little is known about the reactions of chloro-substituted alkynyl phosphines with metal carbonyl compounds [3]. We have previously reported that metal carbonyl anions induce heterolytic cleavage of phosphorus-halogen bonds in phenylethynyl-chloro-phosphines with formation of multiply functionalized neutral phosphonium ion compounds of the type [(R)(PhC≡C)]P=MoCp'(CO)<sub>2</sub> (R = 2,4,6-<sup>t</sup>Bu<sub>3</sub>C<sub>6</sub>H<sub>2</sub>O, 2,6-<sup>t</sup>Bu<sub>2</sub>-4-MeC<sub>6</sub>H<sub>2</sub>O; Cp' = η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>, η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>) [3d,3e]; the bifunctional reactivity of these complexes (involving metal-phosphorus and carbon-carbon multiple bonds) gives rise to a wide range of reactions [3].

We report here the reaction of (2,4,6-<sup>t</sup>Bu<sub>3</sub>C<sub>6</sub>H<sub>2</sub>O)(PhC≡C)PCl, I, [3b], and (<sup>t</sup>Bu)(PhC≡C)PCl, VII, with Co<sub>2</sub>(CO)<sub>8</sub>, II, and NaCo(CO)<sub>4</sub>, V, respectively. The influence of the steric demands of 2,4,6-<sup>t</sup>Bu<sub>3</sub>C<sub>6</sub>H<sub>2</sub>O compared with those of <sup>t</sup>Bu and the difference in the reactivity of Co<sub>2</sub>(CO)<sub>8</sub> and NaCo(CO)<sub>4</sub> are discussed.

## Results and discussion

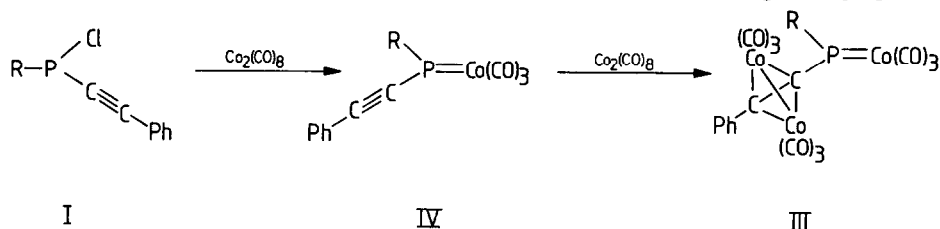
*Reaction of (2,4,6-<sup>t</sup>Bu<sub>3</sub>C<sub>6</sub>H<sub>2</sub>O)(PhC≡C)PCl, I, with Co<sub>2</sub>(CO)<sub>8</sub>, II, and NaCo(CO)<sub>4</sub>, V*

The reaction of (2,4,6-<sup>t</sup>Bu<sub>3</sub>C<sub>6</sub>H<sub>2</sub>O)(PhC≡C)PCl, I, [3a,3e] and 1.5 equivalents of Co<sub>2</sub>(CO)<sub>8</sub>, II, in a 1/1 mixture of toluene and n-pentane at 25 °C (2 h) resulted in slow elimination of CO. The solution gradually turned purple and then dark green. The yield of isolated {(2,4,6-<sup>t</sup>Bu<sub>3</sub>C<sub>6</sub>H<sub>2</sub>O)[(η<sup>2</sup>-C≡CPh)Co<sub>2</sub>(CO)<sub>6</sub>]}P=Co(CO)<sub>3</sub>, III, was 73%. The crystals of III are air-stable for short periods and the crystalline solid shows a metallic lustre, whereas the solutions of III are bright green.



R = 2,4,6-<sup>t</sup>Bu<sub>3</sub>C<sub>6</sub>H<sub>2</sub>O; R' = (η<sup>2</sup>-C≡C-Ph)Co<sub>2</sub>(CO)<sub>6</sub>

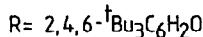
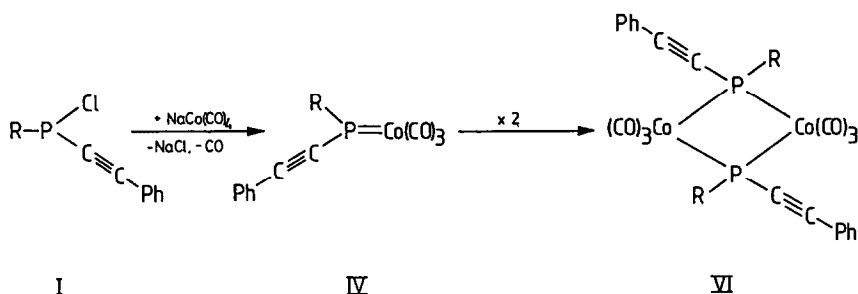
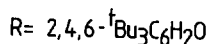
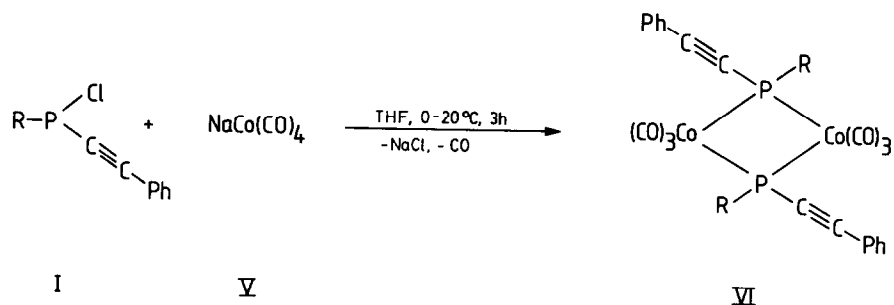
The color change during the reaction of I with II from purple to green led us to postulate the participation of the intermediate IV, implying that initially reductive dehalogenation takes place to give IV as the reactive species. η<sup>2</sup>-Coordination of the PhC≡C-ligand in IV then gives in the second step the kinetically stabilized phosphonium ion compound {(2,4,6-<sup>t</sup>Bu<sub>3</sub>C<sub>6</sub>H<sub>2</sub>O)[(η<sup>2</sup>-C≡CPh)Co<sub>2</sub>(CO)<sub>6</sub>]}P=Co(CO)<sub>3</sub>, III, which contains a sterically hindered dicobalt-tetrahedrane fragment [3a].



R = 2,4,6-<sup>t</sup>Bu<sub>3</sub>C<sub>6</sub>H<sub>2</sub>O

The possibility that an intermediate such as IV might be formed during the reaction of I with II was demonstrated using sodium tetracarbonylcobaltate, V, instead of octacarbonyldicobalt, II. Thus reaction of NaCo(CO)<sub>4</sub>, V, with (2,4,6-<sup>t</sup>Bu<sub>3</sub>C<sub>6</sub>H<sub>2</sub>O)(PhC≡C)PCl, I, in THF at 25 °C (3 h) gave a purple solution which slowly turned yellow-brown on continued stirring. After the THF had been removed *in vacuo*, the residue was extracted with n-pentane and purified by column chromatography on silica gel. With n-pentane/CH<sub>2</sub>Cl<sub>2</sub> (20/1) as eluent a yellow-brown zone was obtained. Recrystallization of the recovered dark solid from n-pentane gave VI as a brownish powder.

Spectroscopic data and the similarity between the synthetic methods we used and those used in earlier work, e.g. by Hayter [4] or Dahl [5], led us to formulate VI as a symmetrically μ<sub>2</sub>-phosphido bridged bimetallic compound, in which (2,4,6-<sup>t</sup>Bu<sub>3</sub>C<sub>6</sub>H<sub>2</sub>O)(PhC≡C)P units bridge two Co(CO)<sub>3</sub> fragments (see below). However, compound VI could not be satisfactorily crystallized due to the bent structure of the Co<sub>2</sub>P<sub>2</sub> framework, which gives rise to the presence of three isomers (see Experimental section).



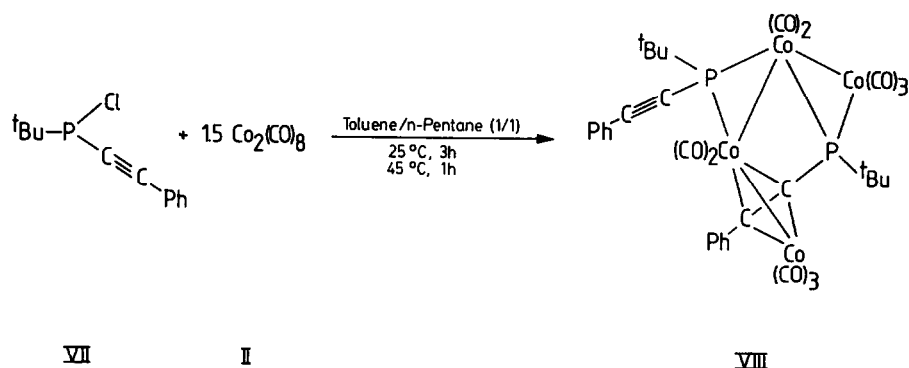
The formation of compound VI can be attributed to simple dimerization of intermediate IV, as shown above.

#### *Reaction of (<sup>t</sup>Bu)(PhC≡C)PCl, VII, with Co<sub>2</sub>(CO)<sub>8</sub>, II*

To study the influence of the steric demand between a kinetically stabilizing group such as 2,4,6-<sup>t</sup>Bu<sub>3</sub>C<sub>6</sub>H<sub>2</sub>O and a less steric ligand like <sup>t</sup>Bu, we carried out the above described reaction with (<sup>t</sup>Bu)(PhC≡C)PCl, VII, instead of (2,4,6-<sup>t</sup>Bu<sub>3</sub>C<sub>6</sub>H<sub>2</sub>O)(PhC≡C)PCl, I.

In a similar experiment Co<sub>2</sub>(CO)<sub>8</sub>, II, was treated with (<sup>t</sup>Bu)(PhC≡C)PCl, VII, prepared in 52% yield by reaction of <sup>t</sup>BuPCl<sub>2</sub> [6] with an equimolar amount of BrMgC≡CPh at -90°C in a n-pentane/THF mixture. The chloro-substituted compound VII always contained some of the corresponding bromo phosphine (<sup>t</sup>Bu)(PhC≡C)PBr formed by metathetical exchange with MgBr<sub>2</sub>; this by-product was identified by <sup>1</sup>H-, <sup>13</sup>C- and <sup>31</sup>P-NMR spectroscopy. After 3 h stirring at room temperature and 1 h at 45°C and appropriate work-up, the cluster VIII was isolated as shiny black crystals. Analytically pure samples of VIII were obtained by recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/n-pentane at -30°C.

Characterization of compounds III, VI-VIII was based on analytical and spectroscopic data.



The infrared spectra of III, VI and VIII in the  $\nu(\text{CO})$  region show five strong bands for III and three for VIII, whereas VI shows seven absorption bands due to the presence of isomers (see above). The non-coordinated phenylethynyl units in VI give a band at  $2152 \text{ cm}^{-1}$  and that in VIII at  $2155 \text{ cm}^{-1}$ , whereas for the starting compounds I and VII the  $\nu(\text{C}\equiv\text{C})$  absorption band was found at  $2159$  (I) and  $2157$  (VII)  $\text{cm}^{-1}$  respectively.

The  $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum of III shows a singlet at 339.8 ppm. The large downfield shift of the signal compared with that from the starting compound  $(2,4,6\text{-}^t\text{Bu}_3\text{C}_6\text{H}_2\text{O})(\text{PhC}\equiv\text{C})\text{PCl}$ , I, (139.0 ppm [3b]) is observed for most phosphonium ion complexes [7].

The  $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum for VI shows, in addition to two doublets centered at  $\delta = 168.5$  and  $226.0$  ( $J(\text{PP}) = 30 \text{ Hz}$ ) from the isomer in which the axial positions are alternately occupied by the  $2,4,6\text{-}^t\text{Bu}_3\text{C}_6\text{H}_2\text{O}$  or  $\text{C}\equiv\text{CPh}$  groups, two singlets ( $\delta = 210.7$  and  $227.0$ ) which can best be accounted for in terms of the occupation of the axial or equatorial positions either by the  $2,4,6\text{-}^t\text{Bu}_3\text{C}_6\text{H}_2\text{O}$  or the  $\text{C}\equiv\text{CPh}$  groups. Similar behaviour was observed for compounds of the type  $\text{Fe}_2(\text{CO})_6[\mu_2\text{-P(R)(R')}]_2$  [8].

For VIII two signals are found at 200.1 ppm  $[(\text{PhC}\equiv\text{C})(^t\text{Bu})\text{P}]$  and 251.8 ppm  $\{[(\eta^2\text{-C}\equiv\text{CPh})\text{Co}_2(\text{CO})_5](^t\text{Bu})\text{P}\}$ , which is consistent with the different chemical environments of the two bridged phosphorus atoms in VIII. Similar downfield shifts were observed for compounds such as  $(\text{R})_n\text{P}(\text{C}\equiv\text{CR}')_{3-n}/(\text{R})_n\text{P}[(\eta^2\text{-C}\equiv\text{C-R}')\text{Co}_2(\text{CO})_6]_{3-n}$  ( $\text{R}, \text{R}' = \text{organic ligand}; n = 0\text{--}2$ ) [1,9].

The  $^{13}\text{C}$ -NMR spectrum assigned for III is consistent with its proposed formulation as a terminal neutral phosphonium ion complex [3]. The acetylenic carbon atoms of III give rise to a doublet at 87.6 ppm ( $J(\text{PC}) = 54 \text{ Hz}$ ) and a singlet at 102.2 ppm.

The signals of the carbonyl ligands appear at 197.3 ( $\text{Co}_2(\text{CO})_6$  unit) and at 206.1 ppm ( $\text{Co}(\text{CO})_3$  fragment).

An X-ray structure determination confirmed the proposed structure of VIII. A view of the molecular structure is shown in Fig. 1. The atomic coordinates are listed in Table 1; Table 2 shows selected bond distances and angles. Details of the data collection are summarized in [10\*].

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

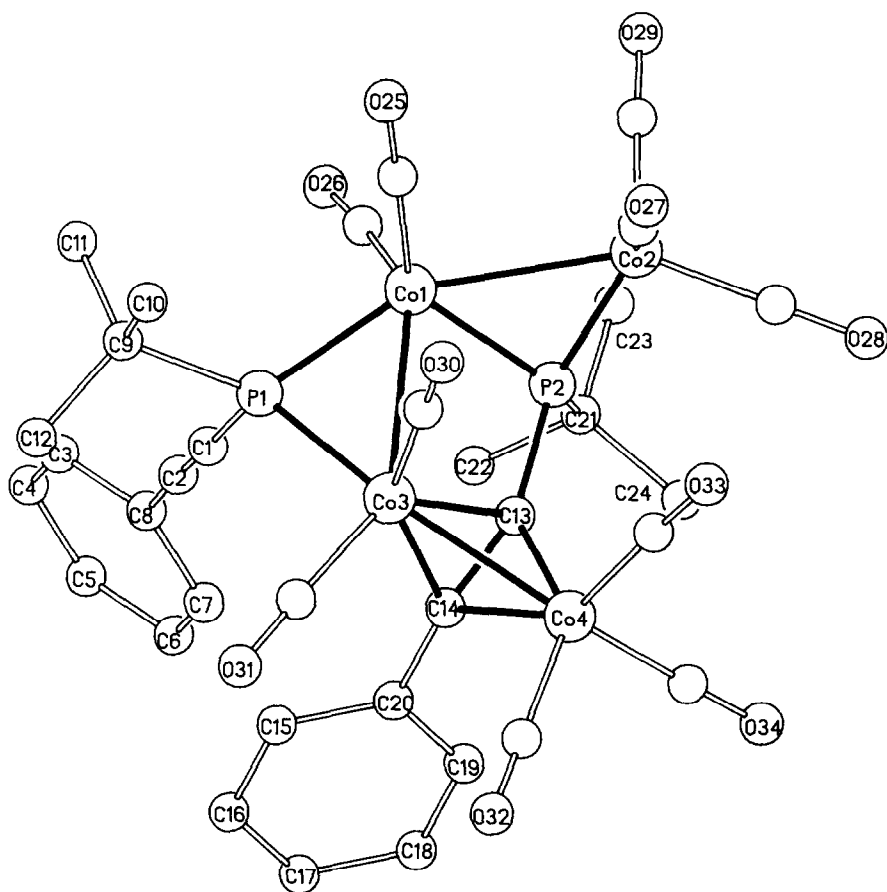


Fig. 1. Molecular geometry and atom labelling scheme for VIII [10\*].

The most notable feature of VIII is the presence of two phosphorus-containing entities ( $\text{PhC}\equiv\text{C}\text{P}(\text{tBu})$ ) and  $[(\eta^2\text{-C}\equiv\text{CPh})\text{Co}_2(\text{CO})_5]\text{P}(\text{tBu})$ , each of which is bonded in a  $\mu_2$ -fashion. The  $\text{P}(1)\text{-Co}(1)/\text{Co}(3)$  and  $\text{P}(2)\text{-Co}(1)/\text{Co}(2)$  distances of 212–220 pm (Fig. 1) fall in the range observed for a series of Co–P cluster compounds [3b,12]. The  $\text{Co}(3)\text{-Co}(4)$  distance of 249.1 pm in the tetrahedrane fragment and the acetylene bond length  $\text{C}(13)\text{-C}(14)$  of 133.5 pm are comparable with distances in other cobalt-containing tetrahedrane fragments of the type  $(\eta^2\text{-RC}\equiv\text{CR}')\text{Co}_2(\text{CO})_6$  [3,12]. The  $\text{Co}(1)\text{-Co}(2)$  and  $\text{Co}(1)\text{-Co}(3)$  distances of 266 and 276 pm are longer than Co–Co distances in many cobalt cluster compounds [3,11–13].

Complex VIII may be formed by the formal dimerization of two “ $[(\text{tBu})(\text{PhC}\equiv\text{C})]\text{P}=\text{Co}(\text{CO})_3$ ” fragments or of “ $[(\text{tBu})(\text{PhC}\equiv\text{C})]\text{P}=\text{Co}(\text{CO})_3$ ” and “ $\{(\text{tBu})[(\eta^2\text{-C}\equiv\text{CPh})\text{Co}_2(\text{CO})_6]\text{P}=\text{Co}(\text{CO})_3\}$ ” with decarbonylation (see above). As discussed earlier, there is evidence that the first step involves reductive dehalogenation of VII by octacarbonyldicobalt, which is followed by the  $\eta^2$ -coordination of the acetylenic unit to “ $\text{Co}_2(\text{CO})_6$ ”.

Table 1

Atomic coordinates and equivalent isotropic displacement parameters for VIII

| Atom | <i>x</i>   | <i>y</i>   | <i>z</i>   | <i>U</i> <sup>a</sup> |
|------|------------|------------|------------|-----------------------|
| Co1  | 0.07162(5) | 0.14202(2) | 0.25584(5) | 0.0408(2)             |
| Co2  | 0.01212(6) | 0.18766(2) | 0.06731(5) | 0.0456(2)             |
| Co3  | 0.32045(5) | 0.16553(2) | 0.29614(5) | 0.0364(2)             |
| Co4  | 0.40431(6) | 0.19159(2) | 0.12547(5) | 0.0428(2)             |
| P1   | 0.2169(1)  | 0.11701(4) | 0.3848(1)  | 0.0410(4)             |
| P2   | 0.1219(1)  | 0.13483(4) | 0.8814(9)  | 0.0350(4)             |
| C1   | 0.2508(5)  | 0.0594(2)  | 0.3686(4)  | 0.048(2)              |
| C2   | 0.2647(5)  | 0.0202(2)  | 0.3520(4)  | 0.049(2)              |
| C3   | 0.2254(3)  | −0.0595(1) | 0.3873(3)  | 0.077(3)              |
| C4   | 0.2383(3)  | −0.1053(1) | 0.3631(3)  | 0.093(3)              |
| C5   | 0.3069(3)  | −0.1183(1) | 0.2797(3)  | 0.083(2)              |
| C6   | 0.3626(3)  | −0.0855(1) | 0.2205(3)  | 0.076(2)              |
| C7   | 0.3497(3)  | −0.0397(1) | 0.2447(3)  | 0.064(2)              |
| C8   | 0.2811(3)  | −0.0267(1) | 0.3281(3)  | 0.052(2)              |
| C9   | 0.2078(5)  | 0.1200(2)  | 0.5398(4)  | 0.057(2)              |
| C10  | 0.1926(6)  | 0.1691(2)  | 0.5743(4)  | 0.080(3)              |
| C11  | 0.0972(6)  | 0.0915(2)  | 0.5605(5)  | 0.093(3)              |
| C12  | 0.3285(6)  | 0.1016(2)  | 0.6069(4)  | 0.083(3)              |
| C13  | 0.2828(4)  | 0.1443(1)  | 0.1331(3)  | 0.034(1)              |
| C14  | 0.3923(4)  | 0.1284(1)  | 0.1846(4)  | 0.037(1)              |
| C15  | 0.5351(3)  | 0.0720(1)  | 0.2940(2)  | 0.057(2)              |
| C16  | 0.6197(3)  | 0.0363(1)  | 0.2976(2)  | 0.074(2)              |
| C17  | 0.6518(3)  | 0.0194(1)  | 0.1975(2)  | 0.074(2)              |
| C18  | 0.5993(3)  | 0.0382(1)  | 0.0937(2)  | 0.073(2)              |
| C19  | 0.5147(3)  | 0.0739(1)  | 0.0901(2)  | 0.061(2)              |
| C20  | 0.4826(3)  | 0.0908(1)  | 0.1903(2)  | 0.043(2)              |
| C21  | 0.1087(4)  | 0.0837(1)  | −0.0060(4) | 0.043(2)              |
| C22  | 0.1712(5)  | 0.0429(1)  | 0.0581(4)  | 0.057(2)              |
| C23  | −0.0285(5) | 0.0740(2)  | −0.0488(5) | 0.072(2)              |
| C24  | 0.1756(6)  | 0.0955(2)  | −0.1059(4) | 0.066(2)              |
| C25  | −0.0156(5) | 0.1828(2)  | 0.3250(4)  | 0.061(2)              |
| O25  | −0.0753(4) | 0.2060(2)  | 0.3688(4)  | 0.097(2)              |
| C26  | −0.0152(5) | 0.0921(2)  | 0.2508(4)  | 0.066(2)              |
| O26  | −0.0673(4) | 0.0587(2)  | 0.2532(4)  | 0.108(2)              |
| C27  | −0.0008(5) | 0.2423(2)  | 0.1323(5)  | 0.062(2)              |
| O27  | −0.0007(5) | 0.2783(1)  | 0.1679(4)  | 0.093(2)              |
| C28  | 0.0072(6)  | 0.2008(2)  | −0.0707(5) | 0.079(3)              |
| O28  | 0.0177(6)  | 0.2080(2)  | −0.1622(4) | 0.133(3)              |
| C29  | −0.1684(5) | 0.1663(2)  | 0.0483(5)  | 0.065(2)              |
| O29  | −0.2681(4) | 0.1534(2)  | 0.0328(4)  | 0.103(2)              |
| C30  | 0.2504(5)  | 0.2184(2)  | 0.3282(4)  | 0.051(2)              |
| O30  | 0.2173(4)  | 0.2529(1)  | 0.3516(3)  | 0.073(2)              |
| C31  | 0.4611(5)  | 0.1682(2)  | 0.3955(4)  | 0.057(2)              |
| O31  | 0.5529(4)  | 0.1702(1)  | 0.4560(4)  | 0.088(2)              |
| C32  | 0.5624(5)  | 0.2076(2)  | 0.1902(5)  | 0.068(2)              |
| O32  | 0.6595(4)  | 0.2163(2)  | 0.2289(5)  | 0.121(2)              |
| C33  | 0.3259(5)  | 0.2461(2)  | 0.1042(5)  | 0.062(2)              |
| O33  | 0.2804(4)  | 0.2805(1)  | 0.0907(4)  | 0.098(2)              |
| C34  | 0.4304(5)  | 0.1822(2)  | −0.0181(5) | 0.064(2)              |
| O34  | 0.4441(5)  | 0.1755(2)  | −0.1081(4) | 0.108(2)              |

<sup>a</sup> Equivalent isotropic *U* defined as one third of the orthogonalized *U*<sub>*ij*</sub> tensor.

Table 2

Bond distances (pm) and angles (°) for VIII

|                           |          |                                |                   |
|---------------------------|----------|--------------------------------|-------------------|
| <i>Distances</i>          |          |                                |                   |
| Co(1)–Co(2)               | 265.9(1) | P(1)–Co(1)                     | 215.3(1)          |
| Co(1)–Co(3)               | 276.3(1) | P(1)–Co(3)                     | 220.0(2)          |
|                           |          | P(1)–C(1)                      | 176.0(5)          |
| Co(3)–Co(4)               | 249.1(1) | P(1)–C(9)                      | 187.7(5)          |
| Co(3)–C(13)               | 202.9(4) |                                |                   |
| Co(3)–C(14)               | 198.5(4) | P(2)–Co(1)                     | 217.6(1)          |
|                           |          | P(2)–Co(2)                     | 212.2(1)          |
| Co(4)–C(13)               | 193.9(4) | P(2)–C(13)                     | 176.9(4)          |
| Co(4)–C(14)               | 200.8(4) | P(2)–C(21)                     | 187.7(4)          |
| C(1)–C(2)                 | 119.0(7) | C <sub>Ph</sub> [C(3)–C(8)]    | 139.5(0)          |
| C(2)–C(8)                 | 143.1(6) | C <sub>Ph</sub> [C(15)]–C(20)] | 139.5(0)          |
| C(13)–C(14)               | 133.5(5) | C(9)–C(10)–C(12)               | 152.1(9)–152.7(8) |
| C(14)–C(20)               | 147.7(5) | C(21)–C(22)–C(24)              | 152.6(7)–153.8(7) |
| Co(1)–C(25), C(26)        |          | 181.6(6), 174.7(6)             |                   |
| Co(2)–C(27), C(28), C(29) |          | 178.8(5), 174.3(7), 179.6(6)   |                   |
| Co(3)–C(30), C(31)        |          | 180.7(5), 178.2(5)             |                   |
| Co(4)–C(32), C(33), C(34) |          | 183.2(6), 182.1(5), 180.9(6)   |                   |
| <i>Angles</i>             |          |                                |                   |
| Co(3)–P(1)–Co(1)          | 78.8(0)  | Co(1)–P(2)–Co(2)               | 76.4(0)           |
| C(1)–P(1)–Co(1)           | 113.2(2) | C(13)–P(2)–Co(1)               | 95.1(1)           |
| C(1)–P(1)–Co(3)           | 116.4(2) | C(13)–P(2)–Co(2)               | 123.2(1)          |
| C(1)–P(1)–C(9)            | 101.5(2) | C(21)–P(2)–Co(1)               | 128.8(2)          |
| C(9)–P(1)–Co(1)           | 122.8(2) | C(21)–P(2)–Co(2)               | 122.5(1)          |
| C(9)–P(1)–Co(3)           | 124.1(2) | C(21)–P(2)–C(13)               | 106.6(2)          |
| Co(2)–Co(1)–Co(3)         | 102.2(0) | Co(4)–Co(3)–Co(1)              | 114.5(0)          |
| P(1)–Co(1)–Co(2)          | 153.2(0) | P(1)–Co(3)–Co(1)               | 49.8(0)           |
| P(1)–Co(1)–Co(3)          | 51.3(0)  | P(1)–Co(3)–Co(4)               | 151.8(0)          |
| P(2)–Co(1)–Co(2)          | 50.9(0)  | C(13)–Co(3)–Co(1)              | 73.4(1)           |
| P(2)–Co(1)–Co(3)          | 78.4(0)  | C(13)–Co(3)–Co(4)              | 49.5(1)           |
| P(2)–Co(1)–P(1)           | 111.2(1) | C(13)–Co(3)–P(1)               | 102.8(1)          |
|                           |          | C(14)–Co(3)–Co(1)              | 103.0(1)          |
| C(2)–Co(2)–Co(1)          | 52.7(0)  | C(14)–Co(3)–Co(4)              | 51.8(0)           |
|                           |          | C(14)–Co(3)–P(1)               | 104.6(1)          |
| C(13)–Co(4)–Co(3)         | 52.7(1)  | C(14)–Co(3)–C(13)              | 38.8(2)           |
| C(14)–Co(4)–Co(3)         | 51.0(1)  |                                |                   |
| C(14)–Co(4)–C(13)         | 39.5(2)  | C(2)–C(1)–P(1)                 | 174.7(4)          |
|                           |          | C(1)–C(2)–C(8)                 | 178.2(5)          |
| Co(4)–C(13)–Co(3)         | 77.8(1)  |                                |                   |
| P(2)–C(13)–Co(3)          | 112.2(2) | Co(4)–C(14)–Co(3)              | 77.2(1)           |
| P(2)–C(13)–Co(4)          | 138.6(2) | C(13)–C(14)–Co(3)              | 72.4(3)           |
| C(14)–C(13)–Co(3)         | 68.8(2)  | C(13)–C(14)–Co(4)              | 67.4(2)           |
| C(14)–C(13)–Co(4)         | 73.1(2)  | C(20)–C(14)–C(13)              | 145.3(4)          |
| C(14)–C(13)–P(2)          | 148.3(3) | C(20)–C(14)–Co(3)              | 135.8(3)          |
|                           |          | C(20)–C(14)–Co(4)              | 129.3(3)          |

## Experimental

All reactions were carried out under nitrogen by Schlenk techniques. The solvents were purified by distillation (toluene: sodium; n-pentane: calcium hydride; methyl-

ene chloride: phosphorus pentoxide; THF: sodium/benzophenone). The reagents (2,4,6-<sup>1</sup>Bu<sub>3</sub>C<sub>6</sub>H<sub>2</sub>O)(PhC≡C)PCl [3b], <sup>1</sup>BuPCl<sub>2</sub> [6] and BrMgC≡CPh [14] were prepared by published procedures.

#### (A) Synthesis of III

A solution of 1.7 g (4.0 mmol) of (2,4,6-<sup>1</sup>Bu<sub>3</sub>C<sub>6</sub>H<sub>2</sub>O)(PhC≡C)PCl, I, [3b] in 150 ml of toluene/n-pentane (1/1) was cooled to 0°C and treated dropwise with a solution of 2.05 g (6.0 mmol) of Co<sub>2</sub>(CO)<sub>8</sub> in 100 ml of toluene/n-pentane (1/1). The mixture was allowed to warm to 20°C and then stirred for 2 h at that temperature. Evolution of CO occurred and the colour changed from yellow to purple and then to green. The volatile materials were removed under high vacuum and the residue was purified by column chromatography (column size: 25 × 2.5 cm; -20°C; n-pentane; silica gel). Elution with n-pentane/methylene chloride (10/1-5/1) gave a dark green zone. Removal of the solvents and recrystallization of the residue from toluene/n-pentane at -30°C gave deep green crystals of III (2.4 g, 73% based on I).

Found: C, 51.39; H, 4.33. C<sub>35</sub>H<sub>34</sub>Co<sub>3</sub>O<sub>10</sub>P (822.42) calc.: C, 51.11; H, 4.17%. M.p. 125-127°C (dec.). IR (n-pentane, CaF<sub>2</sub>-cells): ν(CO): 2099s, 2068vs, 2044vs, 1986vs, 1978s cm<sup>-1</sup>. <sup>1</sup>H-NMR (CDCl<sub>3</sub>): 1.35 (s, 9H, *p*-<sup>1</sup>Bu); 1.47 (s, 18H, *o*-<sup>1</sup>Bu); 7.39 (s, 2H, C<sub>6</sub>H<sub>2</sub>); 7.3-7.9 (m, 5H, Ph). <sup>31</sup>P{<sup>1</sup>H}-NMR (CDCl<sub>3</sub>): 339.8 (s, 1P). <sup>13</sup>C-NMR (CDCl<sub>3</sub>): 31.5 (q, *J*(CH) = 125 Hz, 3C, *p*-<sup>1</sup>Bu); 33.3 (q, *J*(CH) = 125 Hz, 6C, *o*-<sup>1</sup>Bu); 34.8 (s, 1C, <sup>1</sup>C/*p*-<sup>1</sup>Bu); 36.4 (s, 2C, <sup>1</sup>C/*o*-<sup>1</sup>Bu); 87.6 (d, *J*(PC) = 54 Hz, 1C, C≡C); 102.2 (s, 1C, C≡C); 124.5 (d, *J*(CH) = 155 Hz, 2C, C<sub>6</sub>H<sub>2</sub>/Ph); 129.0 (d, *J*(CH) = 162 Hz, 3C, C<sub>6</sub>H<sub>2</sub>/Ph); 129.7 (d, *J*(CH) = 160 Hz, 2C, C<sub>6</sub>H<sub>2</sub>/Ph); 136.9 (s, 1C, C<sub>6</sub>H<sub>2</sub>/Ph); 140.9 (s, 2C, C<sub>6</sub>H<sub>2</sub>/Ph); 147.6 (s, 1C, C<sub>6</sub>H<sub>2</sub>/Ph); 148.8 (s, 1C, C<sub>6</sub>H<sub>2</sub>/Ph); 197.3 (s, 6C, CO); 206.1 (s, 3C, CO). MS [*m/e* (rel. int.)]: *M*<sup>+</sup> 822(5), *M*<sup>+</sup> - 3CO 738(10), *M*<sup>+</sup> - 7CO 626(12), *M*<sup>+</sup> - 8CO 598(10), *M*<sup>+</sup> - 9CO - 2Co - Ph 375 (48), *M*<sup>+</sup> - 9CO - 2Co - Bu 318 (28), Bu<sub>3</sub>C<sub>6</sub>H<sub>2</sub>OH<sup>+</sup> 262 (58), Bu<sub>3</sub>C<sub>6</sub>H<sub>2</sub>OH<sup>+</sup> - Me 247 (100), Bu<sup>+</sup> 57 (80).

#### (B) Synthesis of VI

A THF solution of 1.2 g (2.8 mmol) of (2,4,6-<sup>1</sup>Bu<sub>3</sub>C<sub>6</sub>H<sub>2</sub>O)(PhC≡C)PCl, I, (actually a 2/1 Cl/Br mixture) [3b] was cooled to 0°C and treated dropwise with an equimolar amount of NaCo(CO)<sub>4</sub> [15] in THF. The mixture was stirred for an additional 3 h at 25°C during which CO evolved and the colour changed from pale yellow to orange-brown. The volatile materials were removed *in vacuo* and the dark residual material was then purified by column chromatography (column size: 40 × 1.5 cm; -20°C; n-pentane). Elution with n-pentane/CH<sub>2</sub>Cl<sub>2</sub> (20/1) gave a yellow-brown zone containing VI, and removal of the solvents and recrystallization of the residue from n-pentane at -20°C gave VI (800 mg, 53% based on I) as a brownish powder.

Found: C, 65.08; H, 7.02. C<sub>58</sub>H<sub>68</sub>Co<sub>2</sub>O<sub>8</sub>P<sub>2</sub> (1072.99) calc.: C, 64.93; H, 6.39%. M.p. 194°C (dec.). IR (n-pentane, CaF<sub>2</sub>-cells): ν(C≡C): 2152 br. w cm<sup>-1</sup>; ν(CO): 2098w, 2068m, 2051s, 2026vs, 2005vs, 1989s, 1967w cm<sup>-1</sup>. <sup>1</sup>H-NMR (CDCl<sub>3</sub>): 1.40 (s, 9H, *p*-<sup>1</sup>Bu); 1.42 (s, 9H, *p*-<sup>1</sup>Bu); 1.70 (s, 18H, *o*-<sup>1</sup>Bu); 1.73 (s, 18H, *o*-<sup>1</sup>Bu); 6.8-7.8 (m, 14H, C<sub>6</sub>H<sub>2</sub>/Ph). <sup>31</sup>P{<sup>1</sup>H}-NMR (CDCl<sub>3</sub>): 168.5 (d, *J*(PP) = 30 Hz); 210.7 (s); 226.0 (d, *J*(PP) = 30 Hz); 227.0 (s). MS-EI [*m/e* (rel. int.)]: *M*<sup>+</sup> - 3CO

988(2),  $M^+ - 4\text{CO}$  960 (4),  $M^+ - 6\text{CO}$  904 (14),  $M^+ - 6\text{CO} - \text{C}_4\text{H}_8$  848 (5),  $M^+ - 6\text{CO} - \text{OR}$  643 (100).

### (C) Synthesis of VII

A solution of 10.0 g (62.9 mmol) of  $(^i\text{Bu})\text{PCl}_2$  [6] in 200 ml of n-pentane was cooled to  $-90^\circ\text{C}$  and treated slowly with a solution of (phenylethynyl)magnesium bromide [14] in THF, prepared from 6.6 g (64.6 mmol) of  $\text{PhC}\equiv\text{CH}$  and 8.5 g (63.8 mmol) of  $\text{EtMgBr}$ . The mixture was allowed to warm to room temperature and then stirred for 4 h at  $25^\circ\text{C}$ . After evaporation of the volatile materials *in vacuo* the residue was extracted three times with a 200 ml portion of n-pentane and the combined extracts were filtered through Celite. Removal of the solvent and distillation (0.38 mbar) of the resulting oily product at  $104^\circ\text{C}$  gave 8.0 g (56% yield based on  $(^i\text{Bu})\text{PCl}_2$  used) of VII.

Compound VII,  $(^i\text{Bu})(\text{PhC}\equiv\text{C})\text{PCl}$ , was always obtained mixed in varying proportions with the corresponding bromophosphine  $(^i\text{Bu})(\text{PhC}\equiv\text{C})\text{PBr}$  (1/1–4/1 Cl/Br ratio) (formed by metathetical exchange with  $\text{MgBr}_2$ ) as revealed by  $^1\text{H}$ -,  $^{31}\text{P}$ - and  $^{13}\text{C}$ -NMR respectively. The analysis for VII was calculated for a 1/1 mixture of chloro/bromo derivative: Found: C, 58.16; H, 5.75. Calc.: C, 58.8; H, 5.76%.

$(^i\text{Bu})(\text{PhC}\equiv\text{C})\text{PCl}$ , VII:  $\text{C}_{12}\text{H}_{14}\text{ClP}$  (224.67). IR (n-pentane, NaCl):  $\nu(\text{C}\equiv\text{C})$ :  $2157\text{ cm}^{-1}$ .  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ ): 1.36 (d,  $J(\text{PH}) = 15\text{ Hz}$ , 9H,  $^i\text{Bu}$ ); 7.3–7.6 (m, 5H, Ph).  $^{31}\text{P}\{^1\text{H}\}$ -NMR ( $\text{CDCl}_3$ ): 71.9 (s, 1P).  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ ): 25.9 (q,  $J(\text{CH}) = 128\text{ Hz}$ , 3C, Me/ $^i\text{Bu}$ ); 34.2 (d,  $J(\text{PC}) = 26\text{ Hz}$ ,  $i$ - $^i\text{Bu}$ ); 85.5 (d,  $J(\text{PC}) = 18\text{ Hz}$ , 1C,  $\text{C}\equiv\text{C}$ ); 111.2 (s, 1C,  $\text{C}\equiv\text{C}$ ); 121.7 (s, 1C,  $^i\text{C}/\text{Ph}$ ); 128.4 (d,  $J(\text{CH}) = 163\text{ Hz}$ , Ph); 129.6 (d,  $J(\text{CH}) = 160\text{ Hz}$ , Ph); 132.0 (d,  $J(\text{CH}) = 162\text{ Hz}$ , Ph).

$(^i\text{Bu})(\text{PhC}\equiv\text{C})\text{PBr}$ :  $\text{C}_{12}\text{H}_{14}\text{BrP}$  (269.12). IR (n-pentane, NaCl):  $\nu(\text{C}\equiv\text{C})$ :  $2157\text{ cm}^{-1}$ .  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ ): 1.32 (d,  $J(\text{PH}) = 15\text{ Hz}$ , 9H,  $^i\text{Bu}$ ); 7.3–7.5 (m, 5H, Ph).  $^{31}\text{P}\{^1\text{H}\}$ -NMR ( $\text{CDCl}_3$ ): 82.5 (s, 1P).  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ ): 25.7 (q,  $J(\text{CH}) = 123\text{ Hz}$ , Me/ $^i\text{Bu}$ ); 35.4 (d,  $J(\text{PC}) = 23\text{ Hz}$ , 1C,  $i$ - $^i\text{Bu}$ ); 84.4 (d,  $J(\text{PC}) = 16\text{ Hz}$ , 1C,  $\text{C}\equiv\text{C}$ ); 110.5 (s, 1C,  $\text{C}\equiv\text{C}$ ); 121.8 (s, 1C,  $^i\text{C}/\text{Ph}$ ); 128.8 (d,  $J(\text{CH}) = 163\text{ Hz}$ , Ph); 129.6 (d,  $J(\text{CH}) = 160\text{ Hz}$ , Ph); 131.7 (d,  $J(\text{CH}) = 160\text{ Hz}$ , Ph).

### (D) Synthesis of VIII

In a procedure analogous to that used for the reaction of  $(2,4,6\text{-}^i\text{Bu}_3\text{C}_6\text{H}_2\text{O})\text{-(PhC}\equiv\text{C)PCl}$ , I, [3b] with  $\text{Co}_2(\text{CO})_8$ , II, 2.0 g (8.9 mmol) of  $(^i\text{Bu})(\text{PhC}\equiv\text{C})\text{PCl}$ , VII, was treated with 1.5 equivalents of  $\text{Co}_2(\text{CO})_8$ , II, (4.6 g (13.4 mmol)) in 150 ml of n-pentane/toluene (1/1) at  $25^\circ\text{C}$ . After 3 h stirring at  $25^\circ\text{C}$  and 1 h at  $45^\circ\text{C}$  the volatile materials were removed on a high vacuum line and the residue purified by column chromatography (column size:  $25 \times 2.5\text{ cm}$ ; n-pentane; silica gel;  $-20^\circ\text{C}$ ). Elution with n-pentane/ $\text{CH}_2\text{Cl}_2$  (10/1–6/1) gave a deep-brown zone, and recrystallization from n-pentane at  $-20^\circ\text{C}$  gave analytically pure VIII (1.3 g, 33% based on VII).

Found: C, 45.86; H, 3.31.  $\text{C}_{34}\text{H}_{28}\text{Co}_4\text{O}_{10}\text{P}_2$  (894.28) calc: C, 45.67; H, 3.16%. M.p.  $148\text{--}152^\circ\text{C}$  (dec.). IR (n-pentane, NaCl):  $\nu(\text{C}\equiv\text{C})$ :  $2154\text{w cm}^{-1}$ ;  $\nu(\text{CO})$ : 2081s, 2043vs, 2028s, 2001m, 1983m, 1973w,  $1963\text{w cm}^{-1}$ .  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ ): 1.43 (d,  $J(\text{PH}) = 17\text{ Hz}$ , 9H,  $^i\text{Bu}$ ); 1.70 (d,  $J(\text{PH}) = 18\text{ Hz}$ , 9H,  $^i\text{Bu}$ ); 6.6–7.4 (m, 10H, Ph).  $^{31}\text{P}\{^1\text{H}\}$ -NMR ( $\text{CDCl}_3$ ): 200.1 (s, 1P); 251.8 (s, 1P).

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Diffraction data were collected on a Siemens (Nicolet) R3 diffractometer by the  $\theta-2\theta$  technique ( $2\theta$  limits  $2-50^{\circ}$ , scan range  $0.75^{\circ}$ , scan speed  $2.5 \leq \dot{\omega} \leq 29.3$  deg min<sup>-1</sup> (in  $2\theta$ ) and Mo-K $\alpha$  radiation ( $\lambda=71.069$  pm) at 293 K. The structure was solved by direct methods (SHELXTL-PLUS [16] for 5181 unique reflections with  $F \geq 4\sigma(F)$  (total number of reflections measured: 6744). An empirical absorption correction was applied. The structure was refined anisotropically for all non-hydrogen atoms (isotropic on hydrogen atoms). The hydrogen atoms were placed in calculated positions (C-H distance, 0.96 Å). The functional discrepancy indices were  $R_F=0.042$  and  $R_{wF}=0.036$ . Number of variables refined: 430. Weighting scheme:  $w(hkl)=1/\sigma^2(F)$ .  
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