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SYNTHESIS AND REACTIONS OF A NUCLEOPHILIC BIS(μ-DIMETHYLPHOSPHIDO)DICOBALT COMPLEX.
THE CRYSTAL AND MOLECULAR STRUCTURE OF $[C_5H_5Co(\mu\text{-}PMe_2)]_2$ AND $[(C_5H_5Co)_2(\mu\text{-}H)(\mu\text{-}PMe_2)_2]BPh_4$

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Summary

The bis(μ-dimethylphosphido)dicobalt complex $[C_5H_5Co(\mu\text{-}PMe_2)]_2$ (II) has been prepared from $Co(C_5H_5)_2$ and PMe_2H in almost quantitative yield. It has also been made by reduction of $[C_5H_5Co(PMe_2H)_3]I_2$ (IV) with NaH and from the reaction of $[C_5H_5(PMe_3)Co(\mu\text{-}CO)_2Mn(CO)C_5H_4Me]$ with PMe_2H. Protonation of II with CF_3CO_2H in the presence of NH_4PF_6 produces the PF_6^- salt of the (μ-hydrido)dicobalt cation $[(C_5H_5Co)_2(\mu\text{-}H)(\mu\text{-}PMe_2)_2]^+$ (V) which reacts with aqueous NaOH to give II. Similar treatment of $[C_5H_5Co(\mu\text{-}SMe)]_2$ with CF_3CO_2H/NH_4PF_6 leads to the formation of $[(C_5H_5Co)_2(\mu\text{-}SMe)_3]PF_6$ (VI). The nucleophilic character of complex II has also been demonstrated in the reaction with SO_2, which gives $[(C_5H_5Co)_2(\mu\text{-}PMe_2)_2(\mu\text{-}SO_2)]$ (VII). The crystal and molecular structures of II, the corresponding bis(μ-diphenylphosphido) compound $[C_5H_5Co(\mu\text{-}PPh_2)]_2$ (III) and the BPh_4^- salt of V have been determined. In both neutral complexes the Co_2P_2 cores are similarly puckered, as reflected in the dihedral angle between the CoP_2 and P_2Co' planes of 108.1 and 105.0° for R = Me and Ph, respectively. The Co–Co bond length and the P–P interatomic separations are essentially identical for both dimers. The Co–Co bond length in V, 2.517(1) Å, is lower than that in II, 2.542(2) Å. The only obvious structural variation between the unprotonated and the protonated species is the large difference in the degree of canting of the C_5H_5 rings with respect to each other. The angles between the C_5(ring)-centroid and the Co–Co line are ca. 150 and 167° in II and V, respectively, which reflects the influence of the bridging hydride ligand in the cationic complex.

Introduction

Cyclopentadienylcobalt and -rhodium compounds of the general type $C_5H_5ML_2$ (M = Co, Rh) behave as metal bases and react with a variety of electrophilic

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substrates EX to form products containing a new cobalt- or rhodium-to-element bond [1,2]. The order of metal basicity of $C_5H_5ML_2$ parallels the order of donor strength of the ligands L, and thus the bis(trialkylphosphine) complexes $C_5H_5M(PR_3)_2$ are more nucleophilic than their bis(trialkylphosphite) or dicarbonyl counterparts [3].

The type of product formed in the reactions of $C_5H_5M(PR_3)_2$ (R = alkyl) with electrophiles also depends, however, at least in the cobalt series, on steric effects. We found, for example, that whereas the bis(trimethylphosphine) compound $C_5H_5Co(PMe_3)_2$ (I) [4] reacts with methyl and ethyl iodide to yield cations $[C_5H_5CoE(PMe_3)_2]^+$ (E = Me, Et), in the reactions with iso-propyl or t-butyl halides the ring-substituted derivatives $[(C_5H_4E)CoH(PMe_3)_2]^+$ (E = i-Pr, t-Bu) are obtained [5]. When $C_5H_5Co(PEt_3)_2$ (i.e., a bis(trialkylphosphine)cobalt compound having a more bulky phosphine ligand than I), is used as starting material only methyl iodide gives a stable alkylcobalt cation $[C_5H_5CoCH_3(PEt_3)_2]^+$ [5b].

We concluded from these results that attempts to synthesise complexes $[C_5H_5CoE(PR_3)_2]^+$ with E = i-Pr, t-Bu, $SiMe_3$ etc. would probably only succeed if they started from a compound $C_5H_5Co(PR_3)_2$ possessing smaller phosphine ligands than PMe_3. For this dimethylphosphine would be a good candidate. The original aim of the present work was thus to prepare $C_5H_5Co(PMe_2H)_2$ and investigate its reactivity towards electrophiles. In fact, however, the binuclear dimethylphosphido-bridged compound $[C_5H_5Co(\mu\text{-}PMe_2)]_2$ (II) was obtained. The preparation, the chemical behaviour and the crystal structure of this molecule are described below. For comparison, the structure of the related compound $[C_5H_5Co(\mu\text{-}PPh_2)]_2$ (III) was redetermined [6]. A short communication presenting some preliminary results of the work has already appeared [7].

Results

The preparation of $[C_5H_5Co(\mu\text{-}PMe_2)]_2$ (II)

The bis(trialkylphosphine)cobalt complexes I and $C_5H_5Co(PEt_3)_2$ have both been prepared from $CoCl(PR_3)_3$ (R = Me, Et) and TlC_5H_5 [4,5b]. This method did not seem appropriate for the synthesis of the compound $C_5H_5Co(PMe_2H)_2$ because the preparation of the required unknown starting material $CoCl(PMe_2H)_3$ would involve the use of a reducing agent such as Na, Na/Hg or activated Zn, which would probably attack PMe_2H and so prevent formation of the tris(dimethylphosphine)cobalt(I) complex. We therefore decided to use an alternative route, namely the reaction of cobaltocene with L, which had already been used for the synthesis of $C_5H_5CoL_2$ with L = CO, PF_3 and $P(OR)_3$, respectively [8].

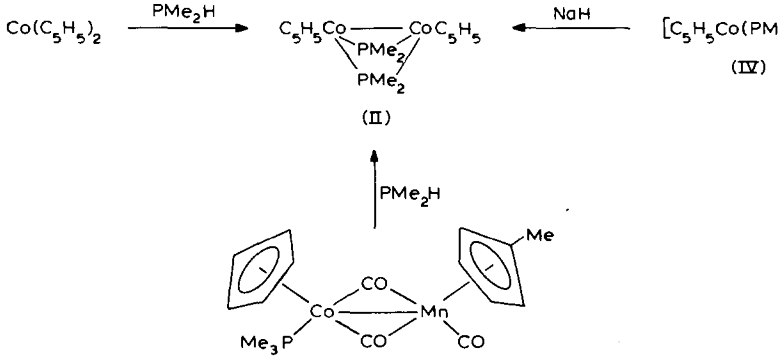
The attempted synthesis of $C_5H_5Co(PMe_2H)_2$ led, however, to an unexpected result. After a benzene solution of $Co(C_5H_5)_2$ and PMe_2H had been stirred for 24 h at room temperature, the binuclear complex $[C_5H_5Co(\mu\text{-}PMe_2)]_2$ (II) was obtained in almost quantitative yield. The corresponding bis(diphenylphosphido) compound $[C_5H_5Co(\mu\text{-}PPh_2)]_2$ (III) had previously been prepared by Hayter and Williams from $C_5H_5Co(CO)_2$ and P_2Ph_4 [9]; the reaction of $C_5H_5Co(CO)_2$ and P_2Me_4 follows a different course, leading to $C_5H_5(CO)Co(\mu\text{-}P_2Me_4)Co(CO)C_5H_5$ [9].

Another route which we thought might be useful for the synthesis of $C_5H_5Co(PMe_2H)_2$ again led to the formation of II. The cobalt(III) compound $C_5H_5Co(CO)I_2$, which on treatment with an excess of trimethylphosphine gives a salt of the dication $[C_5H_5Co(PMe_3)_3]^{2+}$ [10], also reacted with dimethylphosphine to give $[C_5H_5Co(PMe_2H)_3]I_2$ (IV).

Reaction of IV with NaH in THF mainly yields II; in addition, some insoluble paramagnetic material is obtained. The ^1H NMR spectrum of IV at 60 MHz shows a highly unsymmetrical signal for the PCH_3 protons. At 100 MHz there is a doublet (|^3J(HH)| 5.7 Hz) of virtual multiplets (|^2J(PH) + 2^4J(PH)| 12.3 Hz, with ^4J(PH) probably very small) at δ 1.82. As the central parts of the virtual multiplets (one would expect virtual quartets) show only an unresolved broad feature, only four lines are prominent in this part of the spectrum. The asymmetry in the 60 MHz spectrum due to strong ^3J(HH) coupling might seem surprising in view of the difference in chemical shift of 3.52 ppm between the PH and PCH_3 signals, but it is the effective chemical shift [11] which determines the degree of higher order interaction due to ^3J(HH) coupling. At 100 MHz we have a value of 408 Hz for the separation |^1J(PH) + 2^3J(PH)| of the outer septets of the PH signal (δ 5.34, |^3J(HH)| 5.7, |^1J(PH) + 2^3J(PH)| 408 Hz, with the central part of the virtual multiplet being broad and hardly discernible). This renders the effective chemical shift of the upfield septet very close to that of the methyl group signal at 60 MHz. For the C_5H_5 group a quartet at δ 6.00 (J(PH) 1.0 Hz) is observed.

Attempts to prepare the mono(dimethylphosphine) cobalt(I) compound $C_5H_5Co(PMe_3)PMe_2H$ failed. The binuclear (Co–Mn) complex $[C_5H_5(PMe_3)Co(\mu\text{-}CO)_2Mn(CO)C_5H_4Me]$, which proved to be an excellent starting material for making mixed-ligand cobalt(I) compounds of the general type $C_5H_5Co(PMe_3)L$ (L = PPh_3, $P(OMe)_3$ CS_2, C_2Ph_2, maleic anhydride, etc. [2a,12]), also reacts with PMe_2H to give II (and $(C_5H_4Me)Mn(CO)_3$); the expected intermediate, $C_5H_5Co(PMe_3)PMe_2H$, in this reaction could not be observed even at lower temperatures. The assumed lability of this species is in contrast to the stability of the analogous carbonyl complex $C_5H_5Co(CO)PMe_2H$, which was made by Keller and Vahrenkamp from $C_5H_5Co(CO)_2$ and PMe_2H [13].

Complex II forms air-stable, dark brownish-black crystals which are soluble in most organic solvents. The ^1H NMR spectrum in C_6H_6 indicates the presence of the cyclopentadienyl ligand (δ 4.60(t), J(PH) 0.8 Hz) and of the non-equivalent protons of the *endo*- and *exo*-PCH_3 groups (δ 1.70 and 1.20(vt), N 12.9 Hz).



Reactions of the bridged complexes $[C_5H_5Co(\mu\text{-}X)]_2$ (X = PMe_2, PPh_2, SMe) with electrophiles

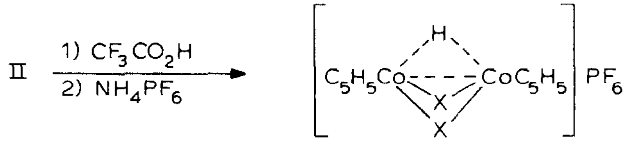
It has been shown by parameter-free MO calculations on complexes such as

$[(CO)_3Fe(\mu\text{-}PR_2)]_2$ that the electron-pair of the metal-to-metal bond occupies the a_1 HOMO in these species [14]. Thus it can be expected that the phosphido-bridged dimers will behave like Lewis bases and react with Lewis acids by electrophilic addition to the Fe–Fe bond. Evidence for such behaviour has already been obtained by Poilblanc et al. [15], who found that the phosphine-substituted diiron complexes $[(CO)_2PR'_3Fe(\mu\text{-}PR_2)]_2$ (R = Me, Ph; $PR'_3 = PMe_nPh_{3-n}$ with $n = 0$–3) are protonated by 60% aqueous $HClO_4$ to form the corresponding $Fe(\mu\text{-}H)Fe$ cations. Because of the formal isoelectronic (or isolobal [16]) relationship between the $(CO)_3Fe$ and C_5H_5Co fragments, a similar reactivity could be expected for the dicobalt complex II.

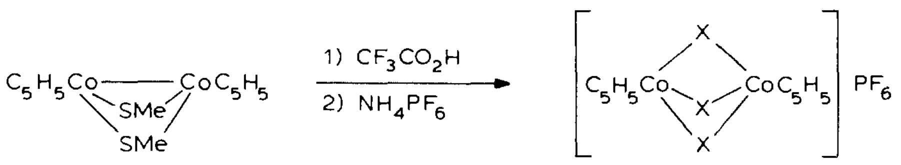
Protonation of II with CF_3CO_2H in toluene takes place readily, to yield, after metathetical reaction with NH_4PF_6, black crystalline $[(C_5H_5Co)_2(\mu\text{-}H)(\mu\text{-}PMe_2)_2]PF_6$ (= V[PF_6]). Compound V[PF_6] is significantly more stable than the related $Fe(\mu\text{-}H)Fe$ complexes, only a few derivatives of which could be isolated [15]. The addition of H^+ to the Co–Co bond is reversible, II being formed on treatment of V[PF_6] with aqeous sodium hydroxide.

The ^1H NMR spectrum of V[PF_6] (in DMSO-d_6) is consistent with the proposed bridged-structure, the signals of the cyclopentadienyl (δ 5.23 (t), J(PH) 0.4 Hz) and methyl protons (δ 1.73 and 1.54 (vt), N 16.4 Hz) being shifted to lower fields relative to the neutral compound II. The signal of the CoHCo proton appears as a broad triplet at δ −21.00 (J(PH) 60 Hz), the broadening probably being due to the fact that it is bound to two cobalt nuclei which have quadrupole moments.

Further experiments with the diphenylphosphido-bridged complex III and CF_3CO_2H (involving in situ monitoring of reactions in an NMR tube) indicated that in this case also a binuclear hydrido cation is probably formed. We failed, however, to isolate the corresponding hexafluorophosphate. Treatment of a benzene solution of $[C_5H_5Co(\mu\text{-}SMe)]_2$ with an equimolar amount of CF_3CO_2H gave, after addition of NH_4PF_6, the complex $[(C_5H_5Co)_2(\mu\text{-}SMe)_3]PF_6$ (VI) in 55% yield. The ^1H NMR spectrum of this black air-stable compound (in CD_3NO_2) shows only two singlets for the C_5H_5 (δ 5.09) and SMe protons (δ 1.85) in the expected intensity ratio of 10/9. The rhodium analogue of VI, $[(C_5H_5Rh)_2(\mu\text{-}SR)_3]PF_6$ (R = p-C_6H_4Me), has been prepared similarly by attack of the electrophile NO^+ on the Rh–Rh bond of $[C_5H_5Rh(\mu\text{-}SR)]_2$ [17].

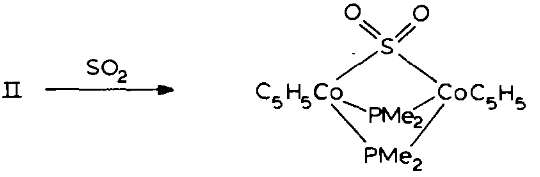


V[PF_6](X = PMe_2)



VI (X = SMe)

The nucleophilic behaviour of complex II was also demonstrated by its reaction with SO_2. Bubbling of gaseous SO_2 into a benzene solution of II at room temperature gave dark air-stable crystals of $[(C_5H_5Co)_2(\mu\text{-}PMe_2)_2(\mu\text{-}SO_2)]$ (VII), which was characterized by elemental analysis, ^{31}P NMR (δ −99.8(s); in acetone-d_6) and ^1H NMR data (δ 4.39 (s), C_5H_5; 2.50 and 1.85(vt), $N = 14.0$ and 12.0 Hz, PCH_3; in CD_3NO_2). The addition of SO_2 to the metal–metal bond of II has precedent in the reactions of the (M–M) bonded complexes $[ClM(\mu\text{-}dppm)]_2$ (M = Pd, Pt) [18], $[(PR_3)_2Pd_2(\mu\text{-}C_5H_5)(\mu\text{-}X)]$ (X = Cl, Br) [19] and of $[C_5Me_5Rh(\mu\text{-}CO)]_2$ [20].



(VII)

Description of the structures

The stereochemical consequence of the protonation of the Co–Co bond in II was determined by a structural comparison of the parent dimer with the protonated species as the tetraphenyloborate salt (which formed more suitable single crystals than the PF_6^- salt of V). The structural data for the related neutral compounds II and III were also compared. Since the structure of complex III had been determined from film-collected data [6], it was thought worthwhile to obtain a more precise structure with diffractometer data; no large differences were found between the results of the two diffraction studies.

Comparison of $[C_5H_5Co(\mu\text{-}PMe_2)]_2$ and $[C_5H_5Co(\mu\text{-}PPh_2)]_2$

The crystal structures of both phosphido-bridged compounds, II and III, consist of discrete molecules in which in each case two $Co(\eta^5\text{-}C_5H_5)$ fragments are linked to each other by two PR_2 ligands. The molecules are depicted in Figs. 1 and 2, and Table 1 lists the mean geometrical parameters for these two electronically equivalent and structurally similar molecules along with those for other related diphosphido-bridged dimers.

The PPh_2-bridged dimer possesses C_s-2 site symmetry such that only one-half of the molecule is independent, whereas the PMe_2-bridged dimer possesses C_1-1 site symmetry such that one dimer comprises the independent unit. There are no unusual intermolecular contacts in either structure. Both Co_2P_2 cores are similarly puckered, as reflected in the dihedral angle between the CoP_2 and P_2Co' planes of 108.1 and 105.0° for R = Me and R = Ph, respectively. The formal substitution of two diphenylphosphido ligands for two dimethylphosphido ligands gives rise to the following small structural changes: (1) an increase in the Co–Co bond length by only 0.008 Å from 2.542(2) to 2.550(2) Å; (2) an increase in the mean Co–P bond length by 0.029 Å from 2.123(av) to 2.152(av) Å; and (3) a decrease in the mean Co–P–Co bond angle by 0.9° (from 73.6 to 72.7°) and a decrease in the mean P–Co–P′ bond angle by 1.2° (from 84.5 to 83.3°). The P–P interatomic separations (2.854(3) and 2.861(6) Å) are essentially identical for the two dimers. The cyclopentadienyl rings show

TABLE 1

COMPARISON OF THE MEAN GEOMETRICAL PARAMETERS FOR SEVERAL DIPHOSPHIDO-BRIDGED DIMERS WITH AND WITHOUT ELECTRON PAIR METAL–METAL BONDS

Dimer	Idealized M_2P_2 geometry	M_2P_2 Dihedral angle [a]	M–M Bond order [b]	M–M (Å)	M–P (Å)	P···P (Å)	M–P–M (deg.)	P–M–P (deg.)
$[(CO)_3Fe(\mu\text{-}P(CF_3)_2)]_2$ [c]	C_{2v}(bent)	118.9	1.0	2.82	2.19	–	80.0	83.5
$[C_5H_5Co(\mu\text{-}PMe_2)]_2$ (II)	C_{2v}(bent)	108.1	1.0	2.54	2.12	2.85	73.6	84.5
$[C_5H_5Co(\mu\text{-}PPh_2)]_2$ (III)	C_{2v}(bent)	105.0	1.0	2.55	2.15	2.86	72.7	83.3
$[C_5H_5Co(\mu\text{-}PPh_2)]_2^{+}$ [d]	C_{2v}	–	0.5	2.65	2.22	–	–	–
$[(C_5H_5Co)_2(\mu\text{-}H)(\mu\text{-}PMe_2)_2]^{+}$ (V)	C_{2v}(bent)	107.8		2.52	2.14	2.94	72.0	86.6
$[(C_5H_5Co)_2(\mu\text{-}OH)(\mu\text{-}PPh_2)_2]^{+}$ [d]	C_{2v}(bent)	–	0	2.90	2.21	2.80	81.9	78.4
$[C_5H_5(CO)Fe(\mu\text{-}PPh_2)]_2$ [e]	C_{2v}(bent)	168.0	0	3.50	2.26	2.84	101.4	77.8

[a] Dihedral angle between the planes in the M_2P_2 core each formed by the bridging P atoms and one metal. [b] Calculated in accord with the EAN rule. [c] Ref. 21. [d] Ref. 22. [e] Ref. 23.

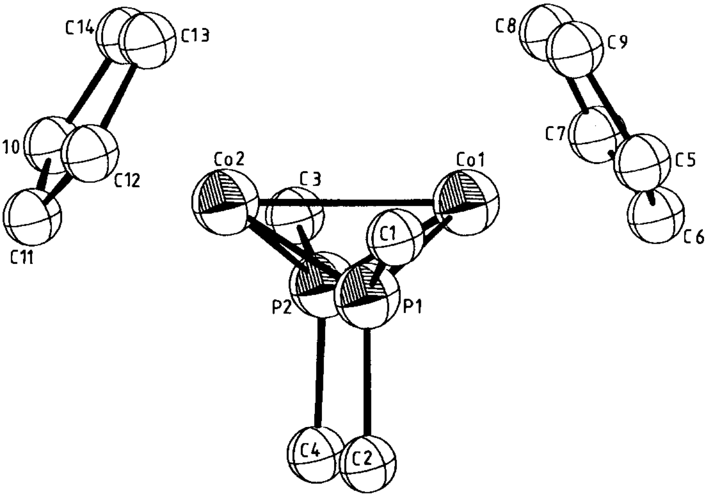


Fig. 1. ORTEP diagram of $[C_5H_5Co(\mu\text{-}PMe_2)]_2$ (II).

some distortion from localized fivefold symmetry, and the angles between the normal to each C_5 ring are 120.0 and 121.3° for the dimethylphosphido- and diphenylphosphido-bridged dimers, respectively.

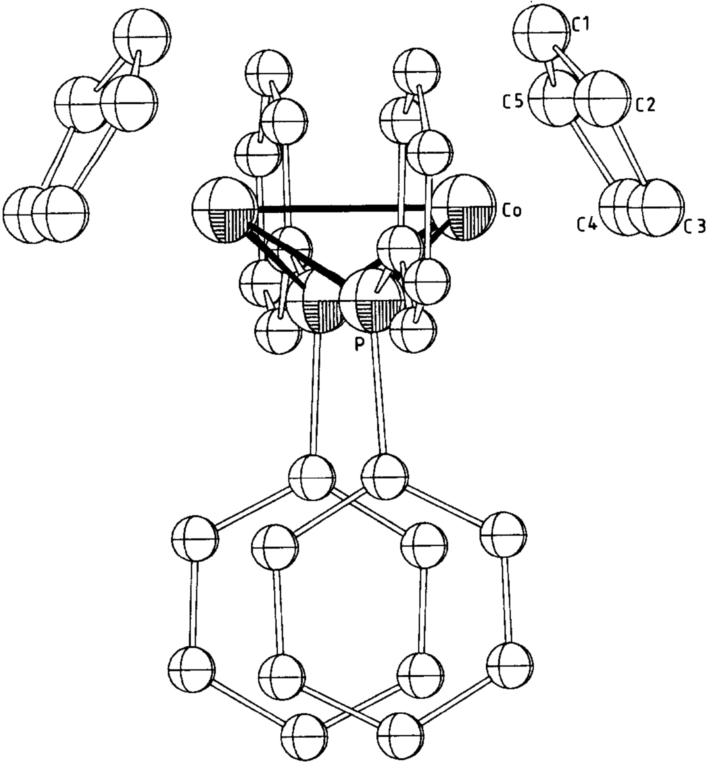


Fig. 2. ORTEP diagram of $[C_5H_5Co(\mu\text{-}PPh_2)]_2$ (III).

Comparison of $[C_5H_5Co(\mu\text{-}PMe_2)]_2$ and $[(C_5H_5Co)_2(\mu\text{-}H)(\mu\text{-}PMe_2)_2]BPh_4$

The monocation formed on protonation of II possesses C_1-1 site symmetry and is quite similar in appearance to the neutral species. There are, however, small but significant stereochemical changes in the configuration of the Co_2P_2 core. The Co–Co bond length decreases from 2.542(2) to 2.517(1) Å, while the mean Co–P and P · · · P distances increase from 2.123(av) to 2.141(av) Å and from 2.854(3) Å to 2.937(3) Å. Close examination of Fig. 3 reveals that the only obvious structural variation between the unprotonated and the protonated species is the large difference in the degree of canting of the C_5H_5 rings with respect to each other. The angle between the lines normal to each ring increases, markedly, by 34.2 from 120.0 to 154.2°, upon protonation. Other geometrical changes are much smaller in magnitude, although still significant. The dihedral angle between the CoP_2 and P_2Co' planes decreases from 108.1 to 107.8°, while upon protonation the mean Co–P–Co′ bond angle decreases from 73.6 to 72.0°, with a subsequent increase in the P–Co–P′ bond angle from 84.5 to 86.6°. The cyclopentadienyl rings in the $[(C_5H_5Co)_2(\mu\text{-}H)(\mu\text{-}PMe_2)_2]^+$ cation are distorted somewhat from idealized fivefold symmetry.

The position of the hydrogen atom in the monocation could not be determined from the X-ray analysis, but the observed geometrical changes in the structure of the parent dimer and the monocation together with the ^1H NMR spectroscopic evidence leave no doubt that the hydrogen atom is located in a dicobalt-bridged coordination site equidistant from both metal and both phosphorus atoms. The resulting steric effect of the bridging hydrogen atom is apparent from the tilting of each cyclopentadienyl ring from its normal orientation in the unprotonated neutral dimer so that the ring centroids are more nearly aligned with the Co–Co line. These angles between the C_5(ring)-centroid and the Co–Co line are ca. 150 and 167° in the neutral and protonated species, respectively, and this provides the necessary space for the proton to coordinate to the two cobalt atoms probably via a three-center two-electron Co–H–Co bond. The tetraphenyloborate counterion displays no unusual bond distances or bond angles.

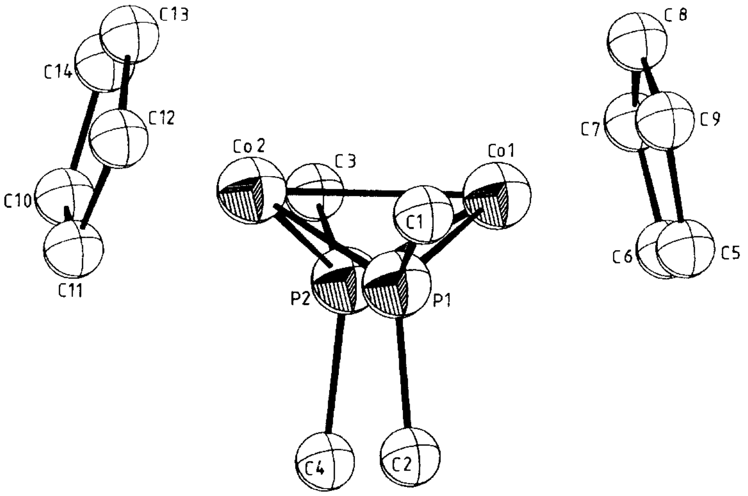


Fig. 3. ORTEP diagram of $[(C_5H_5Co)_2(\mu\text{-}H)(\mu\text{-}PMe_2)_2]^+$ (V). The position of the bridging hydrogen atom could not be determined from the X-ray data.

Experimental section

NMR spectra were recorded on Varian T 60 and XL 100 (^1H) and a Bruker WH 90-FT (^{31}P), IR spectra on a Perkin–Elmer 457 and mass spectra on a Varian MAT CH 7. The starting materials $Co(C_5H_5)_2$ [24], $C_5H_5Co(CO)I_2$ [25], $[C_5H_5(PMe_3)Co(\mu\text{-}CO)_2Mn(CO)C_5H_4Me]$ [12], $[C_5H_5Co(\mu\text{-}SMe)]_2$ [26], PMe_2H [27] and also the complex III [9] were prepared by published methods.

Preparation of $[C_5H_5Co(\mu\text{-}PMe_2)]_2$ (II)

A solution of 18.9 g (0.10 mol) $Co(C_5H_5)_2$ in 40 ml toluene was treated with 10.0 ml (0.11 mol) PMe_2H at room temperature and stirred for 24 h. The solvent was removed in vacuo and the dark residue extracted with 50 ml pentane. Concentration of the pentane solution to about half of its volume and cooling to −78°C gave dark-brown crystals. Yield 17.3 g (93%). M.p. 153–154°C. MS (70 eV): m/e (I_r) 370 (99%; M^+), 189 (100; $Co(C_5H_5)_2^+$), 185 (11; $C_5H_5CoPMe_2^+$), 124 (28; $CoC_5H_5^+$). Found: C, 45.50; H, 5.90; Co, 31.52. $C_{14}H_{22}Co_2P_2$ calcd.: C, 45.43; H, 5.99; Co, 31.84%.

Complex II was also obtained on reaction of $[C_5H_5(PMe_3)Co(\mu\text{-}CO)_2Mn(CO)C_5H_4Me]$ (140 mg, 0.33 mmol) with PMe_2H (0.1 ml, 1.10 mmol) in 5 ml toluene. The solution was stirred for 2 h at 50°C, filtered, and worked up as described above. Yield 40 mg (66%).

Preparation of $[C_5H_5Co(PMe_2H)_3]I_2$ (IV)

A solution of 406 mg (1.0 mmol) $C_5H_5Co(CO)I_2$ in 10 ml methanol was treated with 0.45 ml (5.0 mmol) PMe_2H and stirred for 30 min at room temperature. During this time gas evolution (CO) occurred and a yellow solid precipitated. The solvent was removed in vacuo and the residue washed repeatedly with hexane. Yield 502 mg (89%). Conductivity (CH_3NO_2): Λ 147.5 $cm^2\ \Omega^{-1}\ mol^{-1}$. Found: C, 23.22; H, 4.56; Co, 10.34. $C_{11}H_{26}CoI_2P_3$ calcd.: C, 23.43; H, 4.65; Co, 10.45%.

Reaction of IV with NaH

A solution of 225 mg (0.4 mmol) IV in 5 ml THF was treated with an excess of NaH (100 mg, 4.2 mmol) and stirred for 30 min at room temperature. The solution was then filtered and concentrated in vacuo. The residue was extracted with 2 × 5 ml pentane. Cooling of the pentane solution to −78°C gave complex II. Yield 35 mg (47%).

Preparation of $[(C_5H_5Co)_2(\mu\text{-}H)(\mu\text{-}PMe_2)_2]PF_6$ (= $V[PF_6]$)

A solution of 370 mg (1.0 mmol) II in 10 ml toluene was treated with 0.23 ml (3.0 mmol) CF_3CO_2H. A dark oily precipitate was immediately formed. The solvent and excess of CF_3CO_2H were removed in vacuo and a solution of 163 mg (1.0 mmol) NH_4PF_6 in 10 ml methanol was added. The dark solid was filtered and washed successively with water, methanol, acetone and hexane. Yield 465 mg (90%). Conductivity (CH_3NO_2): Λ 94.0 $cm^2\ \Omega^{-1}\ mol^{-1}$. Found: C, 31.84; H, 4.30; Co, 22.90. $C_{14}H_{23}Co_2F_6P_3$ calcd.: C, 32.58; H, 4.49; Co, 22.84%.

The corresponding BPh_4^- salt was prepared by treatment of $V[PF_6]$ with $NaBPh_4$ in acetone.

Preparation of $[(C_5H_5Co)_2(\mu\text{-}SMe)_3]PF_6$ *(VI)*

A solution of 342 mg (1.0 mmol) $[C_5H_5Co(\mu\text{-}SMe)]_2$ in 5 ml benzene was treated with 74 μl (1.0 mmol) CF_3CO_2H and stirred for 15 min at room temperature. The solvent was removed in vacuo, and a solution of 163 mg (1.0 mmol) NH_4PF_6 in 5 ml methanol was added to the oily residue. A dark crystalline solid was formed, and this was washed with a small amount of methanol and then repeatedly with benzene. Yield 293 mg (55%). Found: C, 29.12; H, 3.40; Co, 22.21. $C_{13}H_{19}Co_2F_6PS_3$ calcd.: C, 29.22; H, 3.58; Co, 22.06%.

Preparation of $[(C_5H_5Co)_2(\mu\text{-}PMe_2)_2(\mu\text{-}SO_2)]$ *(VII)*

A slow stream of SO_2 was bubbled through a solution of 432 mg (1.17 mmol) II in 5 ml benzene for 10 min at room temperature. The solvent was removed in vacuo and the residue recrystallized from THF/hexane. Dark-brown crystals were obtained. Yield 380 mg (75%). M.p. 176–178°C. IR (KBr): ν(SO) 1070, 960 cm^{-1}. Found: C, 39.68; H, 5.64; Co, 26.60. $C_{14}H_{22}Co_2O_2P_2S$ calcd.: C, 38.73; H, 5.11; Co, 27.15%.

X-Ray data collection for compounds II, III and V[BPh₄]

Suitable single crystals of II and III were grown by slow diffusion of hexane into a nearly saturated solution of THF (for II) or toluene (for III). Single crystals of V[BPh$_4$] were obtained similarly from acetone/ether. Each crystal was mounted inside a thin-walled Lindemann glass capillary which was evacuated, filled with argon, and flame-sealed. The crystals were optically aligned on a Synthex P$\bar{1}$ diffractometer equipped with a Nova on-line computer, a scintillation counter, a

TABLE 2

CRYSTAL DATA AND DATA COLLECTION PARAMETERS FOR II, III AND V[BPh$_4$] (T 22°C; Take off angle: 4°; Scan mode: θ–2θ; Scan speed: 2.0–24.0°; Scan range: 1.0° above K_{α_1}, 1.0° below K_{α_2}).

	II	III	V[BPh$_4$]
Crystal description	black parallelopiped 0.45×0.4×0.35 mm	red parallelopiped 0.5×0.4×0.3 mm	dark brown parallelopiped 0.6×0.8×0.8 mm
Formula	$C_{14}H_{22}Co_2P_2$	$C_{34}H_{30}Co_2P_2$	$C_{38}H_{43}BCo_2P_2$
Formula weight	370.1	618.4	690.4
F(000)	760	636	1440
Crystal system	orthorhombic	monoclinic	orthorhombic
Space group	$P2_12_12_1$ (No. 19)	$P2/c$ (No. 13)	$Pn2_1a$ (No. 33)
Z	4	2	4
a (Å)	13.290(4)	8.637(3)	17.160(4)
b (Å)	13.807(3)	10.312(3)	21.334(5)
c (Å)	8.936(2)	15.737(3)	9.478(2)
β (°)		90.69(2)	
V (Å^3)	1640(1)	1401(1)	3470(2)
Calcd. density (g/cm^3)	1.50	1.47	1.32
2θ-limits	3–60°	3–50°	3–60°
Total independent data	2130	2480	5022
Independent data ($I > 2\sigma(I)$)	1934	1417	4046
μ (cm^{-1})	22.7	13.7	11.1
$R_1(F)/R_2(F)$ (%)	5.70/5.08	9.68/9.17	5.29/5.15

pulse height analyzer adjusted to admit 90% of the Mo-K_α peak ($\lambda\alpha_1$ 0.7096, $\lambda\alpha_2$ 0.7154 Å), and a crystal-graphite monochromator set at a Bragg 2θ angle of 12.2°. For each crystal examined, fifteen reflections were used to determine lattice constants and an orientation matrix from which the angle settings for all data were generated. All intensity data collected were corrected for background counts and Lorentz-polarization effects and were subsequently reduced to structure factor amplitudes [28a]. There were no significant changes in the intensities of the standard reflections monitored during each data collection. All diffraction data with $3.0° \leqq 2\theta \leqq 40.0°$ were collected, while only statistically observed reflections (determined via a fast prescan) were measured for $2\theta > 40°$. The upper limits of the 2θ range for each crystal structure determination, as well as other data collection parameters are listed in Table 2. After a sorting and merging [28b] of the intensity data, only independent reflections with $I > 2\sigma(I)$ were used in the structural refinements.

$[C_5H_5Co(\mu\text{-}PPh_2)]_2$. The observed systematic absences of $[h0l]$ for $l = 2n + 1$ are consistent with the results of the previous X-ray structural study which was carried out with film-collected data. The same centrosymmetric monoclinic space group $P2/c$ (No. 13) was chosen instead of the non-centrosymmetric Pc (No. 7) and confirmed by the successful structural analysis and refinement.

$[C_5H_5Co(\mu\text{-}PMe_2)]_2$. An empirical absorption correction [28c] was applied to all intensity data; subsequent sorting and merging yielded 1934 reflections with $I > 2\sigma(I)$. Systematic absences of $[h00]$ for $h = 2n + 1$, $[0k0]$ for $k = 2n + 1$, and $[00l]$ for $l = 2n + 1$ unambiguously reveal the orthorhombic space group to be $P2_12_12_1$ (No. 19).

$[(C_5H_5Co)_2(\mu\text{-}H)(\mu\text{-}PMe_2)_2]BPh_4$. Systematic absences of $[0kl]$ for $k + l = 2n + 1$ and $[hk0]$ for $h = 2n + 1$ indicated that the orthorhombic space group was

TABLE 3

POSITIONAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS FOR $[C_5H_5Co(\mu\text{-}PPh_2)]_2$ (III) [a]

Atom	x	y	z
Co	0.1142(2)	0.7551(2)	0.3021(1)
P	0.1050(5)	0.8500(4)	0.1804(3)
C(1)	0.192(3)	0.576(2)	0.337(1)
C(2)	0.310(2)	0.644(3)	0.301(1)
C(3)	0.336(2)	0.758(2)	0.349(1)
C(4)	0.231(2)	0.757(2)	0.416(1)
C(5)	0.143(2)	0.643(2)	0.407(1)
C(6)	0.127	1.031	0.172
C(7)	0.015	1.103	0.129
C(8)	0.028	1.237	0.123
C(9)	0.154	1.300	0.161
C(10)	0.267	1.228	0.203
C(11)	0.254	1.093	0.209
C(12)	−0.230	0.797	0.406
C(13)	−0.245	0.664	0.416
C(14)	−0.331	0.614	0.483
C(15)	−0.402	0.698	0.539
C(16)	−0.387	0.831	0.529
C(17)	−0.301	0.881	0.462

[a] Carbon atoms C(6)–C(11) and C(12)–C(17) are those of the P-bonded phenyl groups.

TABLE 4

SELECTED INTERATOMIC DISTANCES (Å) AND BOND ANGLES (deg.) FOR $[C_5H_5Co(\mu\text{-}PPh_2)]_2$ (III)

Co–Co′	2.550(2)	C(1)–C(2)	1.37(3)	Co–P–Co′	72.7(2)
Co–P	2.151(5)	C(2)–C(3)	1.41(3)	P–Co–P′	83.3(2)
P–P′	2.861(6)	C(3)–C(4)	1.40(2)	C(1)–C(2)–C(3)	108.7(19)
Co–C(1)	2.04(2)	C(4)–C(5)	1.41(3)	C(2)–C(3)–C(4)	107.2(17)
Co–C(2)	2.04(2)	C(5)–C(1)	1.37(3)	C(3)–C(4)–C(5)	106.5(16)
Co–C(3)	2.05(2)			C(4)–C(5)–C(1)	109.3(17)
Co–C(4)	2.05(2)			C(5)–C(1)–C(2)	108.3(19)
Co–C(5)	2.03(2)				

TABLE 5

POSITIONAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS FOR $[C_5H_5Co(\mu\text{-}PMe_2)]_2$ (II)

Atom	*x*	*y*	*z*
Co(1)	−0.0955(1)	0.1648(1)	0.7026(1)
Co(2)	0.0658(1)	0.1118(1)	0.5734(1)
P(1)	0.0544(2)	0.1875(2)	0.7785(2)
P(2)	−0.0401(2)	0.2160(2)	0.4951(3)
C(1)	0.0936(8)	0.1238(9)	0.9498(10)
C(2)	0.1117(7)	0.3027(7)	0.8145(14)
C(3)	−0.1097(8)	0.1868(10)	0.3269(10)
C(4)	−0.0119(7)	0.3438(8)	0.4534(14)
C(5)	−0.1792(8)	0.1574(11)	0.8935(11)
C(6)	−0.2260(7)	0.2173(7)	0.7938(15)
C(7)	−0.2475(6)	0.1622(10)	0.6733(13)
C(8)	−0.2155(10)	0.0687(10)	0.6965(18)
C(9)	−0.1721(9)	0.0649(10)	0.8337(18)
C(10)	0.1205(9)	0.0506(8)	0.3791(10)
C(11)	0.2000(7)	0.0794(7)	0.4713(11)
C(12)	0.1927(8)	0.0287(8)	0.6016(12)
C(13)	0.1089(9)	−0.0338(7)	0.5956(14)
C(14)	0.0651(9)	−0.0203(8)	0.4593(14)

TABLE 6

SELECTED INTERATOMIC DISTANCES (Å) AND BOND ANGLES (deg.) FOR $[C_5H_5Co(\mu\text{-}PMe_2)]_2$ (II)

Co(1)–Co(2)	2.542(2)	Co(1)–C(5)	2.039(10)	C(1)–P(1)–Co(2)	73.6(1)
Co(1)–P(1)	2.128(3)	Co(1)–C(6)	2.049(10)	Co(1)–P(2)–Co(2)	73.5(1)
Co(1)–P(2)	2.117(3)	Co(1)–C(7)	2.037(8)	P(1)–Co(1)–P(2)	84.5(1)
Co(2)–P(1)	2.115(2)	Co(1)–C(8)	2.075(14)	P(1)–Co(2)–P(2)	84.5(1)
Co(2)–P(2)	2.131(3)	Co(1)–C(9)	2.076(14)	C(1)–P(1)–C(2)	98.9(5)
P(1)–P(2)	2.854(3)	Co(2)–C(10)	2.063(10)	C(3)–P(2)–C(4)	98.6(5)
P(1)–C(1)	1.841(10)	Co(2)–C(11)	2.053(10)	C(1)–P(1)–Co(1)	117.4(4)
P(1)–C(2)	1.793(10)	Co(2)–C(12)	2.055(11)	C(1)–P(1)–Co(2)	117.7(4)
P(2)–C(3)	1.810(10)	Co(2)–C(13)	2.100(10)	C(3)–P(2)–Co(1)	118.4(4)
P(2)–C(4)	1.842(11)	Co(2)–C(14)	2.090(11)	C(3)–P(2)–Co(2)	117.4(4)
				C(2)–P(1)–Co(1)	125.9(4)
				C(2)–P(1)–Co(2)	124.3(4)
				C(4)–P(2)–Co(1)	124.6(4)
				C(4)–P(2)–Co(2)	125.4(4)

either $Pn2_1a$ (alternative of $Pna2_1$ (No. 33)) or $Pnma$ (No. 62). The crystal structure was solved and successfully refined using the former (non-centrosymmetric) space group. The equivalent positions for $Pn2_1a$ are: x, y, z; $1/2-x$, $1/2+y$, $1/2+z$; $\bar{x}$, $1/2+y$, $\bar{z}$; $1/2+x$, y, $1/2-z$. Sorting and merging of the data gave 4046 independent reflections with $I>2\sigma(I)$.

TABLE 7

POSITIONAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS FOR V[BPh$_4$]

Atom	*x*	*y*	*z*
Co(1)	0.2309(1)	0.2318(1)	0.4958(1)
Co(2)	0.2555(1)	0.2410(1)	0.7568(1)
P(1)	0.1607(1)	0.1925(1)	0.6598(2)
P(2)	0.2298(1)	0.3170(1)	0.6171(2)
C(1)	0.1605(6)	0.1075(4)	0.6791(10)
C(2)	0.0593(5)	0.2127(5)	0.6741(10)
C(3)	0.3171(6)	0.3729(5)	0.5847(10)
C(4)	0.1415(7)	0.3692(5)	0.6457(10)
C(5)	0.1699(5)	0.2031(5)	0.3244(8)
C(6)	0.2008(5)	0.2623(4)	0.3000(7)
C(7)	0.2821(5)	0.2571(4)	0.3062(8)
C(8)	0.3009(5)	0.1944(5)	0.3313(8)
C(9)	0.2322(6)	0.1615(4)	0.3469(8)
C(10)	0.2883(13)	0.2908(5)	0.9251(13)
C(11)	0.2308(7)	0.2451(8)	0.9651(8)
C(12)	0.2662(7)	0.1894(5)	0.9372(10)
C(13)	0.3405(6)	0.1977(5)	0.8849(10)
C(14)	0.3548(8)	0.2582(8)	0.8772(14)
B	0.0969(4)	0.4756(3)	0.1892(8)
C(15)	0.1829(4)	0.4688(3)	0.1179(6)
C(16)	0.2024(4)	0.4901(3)	−0.0145(8)
C(17)	0.2753(5)	0.4821(3)	−0.0756(9)
C(18)	0.3334(4)	0.4524(3)	−0.0041(10)
C(19)	0.3164(4)	0.4294(4)	0.1307(9)
C(20)	0.2433(4)	0.4366(3)	0.1845(7)
C(21)	0.0604(3)	0.4040(3)	0.1966(7)
C(22)	0.0612(5)	0.3674(4)	0.0734(9)
C(23)	0.0288(5)	0.3072(4)	0.0747(10)
C(24)	−0.0046(5)	0.2832(4)	0.1893(12)
C(25)	−0.0048(4)	0.3173(4)	0.3118(10)
C(26)	0.0270(4)	0.3767(3)	0.3135(8)
C(27)	0.1006(4)	0.5065(3)	0.3496(6)
C(28)	0.1666(4)	0.5209(3)	0.4268(7)
C(29)	0.1636(5)	0.5454(4)	0.5645(9)
C(30)	0.0925(6)	0.5575(4)	0.6270(8)
C(31)	0.0264(5)	0.5453(4)	0.5526(9)
C(32)	0.0311(4)	0.5209(4)	0.4169(7)
C(33)	0.0406(4)	0.5215(3)	0.0960(6)
C(34)	−0.0287(5)	0.5046(4)	0.0342(9)
C(35)	−0.0778(6)	0.5455(5)	−0.0406(10)
C(36)	−0.0544(7)	0.6070(7)	−0.0514(11)
C(37)	0.0129(7)	0.6265(4)	0.0079(10)
C(38)	0.0634(5)	0.5852(5)	0.0820(8)

Structural determinations and refinements

Positional parameters of the independent cobalt and phosphorus atoms of III were taken from the previous structural determination [6]. Subsequent Fourier syntheses [28d] revealed all remaining nonhydrogen positions. The other crystal structures were solved by direct methods [28e], which in each case provided initial cobalt and phosphorus coordinates. Fourier and difference Fourier syntheses [28d] were then used to determine coordinates for all non-hydrogen atoms. Idealized positions for all hydrogen atoms except that bridging in V[BPh$_4$] were calculated from the positions of their respective carbon atoms.

Refinement of each structure was generally handled by initial block-diagonal least squares [28f] followed by full-matrix refinement with ORFLS [28g]. Anomalous dispersion [29] corrections were made for the cobalt and the phosphorus atoms.

$[C_5H_5Co(\mu\text{-}PPh_2)]_2$. For this molecule each phenyl ring was constrained as a rigid group of D_{6h} symmetry with fixed C–C bond lengths of 1.39 Å. Structural refinement converged at $R_1(F)$ 9.68% and $R_2(F)$ 9.17% [30] with no (parameter shift)-to-error ratio greater than 0.05. The data-to-parameter ratio was 15.7/1; a final Fourier difference map exhibited no unusual features. The atomic parameters for $[C_5H_5Co(\mu\text{-}PPh_2)]_2$ are presented in Table 3, interatomic distances and bond angles are listed in Table 4.

$[C_5H_5Co(\mu\text{-}PMe_2)]_2$. The final least-squares cycle converged at $R_1(F)$ 5.70% and $R_2(F)$ 5.08% with no (parameter shift)-to-error ratio greater than 0.02. The data-to-parameter ratio was 11.8/1. There were no anomalous features exhibited in the final Fourier difference map. The atomic parameters from the output of the final least-squares cycle are listed in Table 5, and interatomic distances and bond angles in Table 6.

$[(C_5H_5Co)_2(\mu\text{-}H)(\mu\text{-}PMe_2)_2]BPh_4$. Refinement converged at $R_1(F)$ 5.29% and $R_2(F)$ 5.15% with no (parameter shift)-to-error ratio greater than 0.06. The data-to-parameter ratio was 10.4/1, a final Fourier difference map revealed no unusual features. The atomic parameters from the output of the final least-squares cycle are listed in Table 7, and interatomic distances and bond angles in Table 8.

TABLE 8

SELECTED INTERATOMIC DISTANCES (Å) AND BOND ANGLES (deg.) FOR V[BPh$_4$]

Co(1)–Co(2)	2.517(1)	Co(1)–C(5)	2.027(8)	Co(1)–P(1)–Co(2)	72.2(1)
Co(1)–P(1)	2.138(2)	Co(1)–C(6)	2.033(7)	Co(1)–P(2)–Co(2)	71.9(1)
Co(1)–P(2)	2.151(3)	Co(1)–C(7)	2.072(8)	P(1)–Co(1)–P(2)	86.4(1)
Co(2)–P(1)	2.136(3)	Co(1)–C(8)	2.124(9)	P(1)–Co(2)–P(2)	86.8(1)
Co(2)–P(2)	2.139(3)	Co(1)–C(9)	2.059(8)	C(1)–P(1)–C(2)	103.3(4)
P(1)–P(2)	2.937(3)	Co(2)–C(10)	1.998(13)	C(3)–P(2)–C(4)	106.2(5)
P(1)–C(1)	1.823(9)	Co(2)–C(11)	2.021(8)	C(1)–P(1)–Co(1)	117.7(3)
P(1)–C(2)	1.798(9)	Co(2)–C(12)	2.042(10)	C(1)–P(1)–Co(2)	116.1(3)
P(2)–C(3)	1.939(11)	Co(2)–C(13)	2.111(10)	C(2)–P(1)–Co(1)	120.4(3)
P(2)–C(4)	1.900(12)	Co(2)–C(14)	2.083(14)	C(2)–P(1)–Co(2)	126.1(3)
				C(3)–P(2)–Co(1)	115.4(3)
				C(3)–P(2)–Co(2)	113.9(3)
				C(4)–P(2)–Co(1)	125.4(3)
				C(4)–P(2)–Co(2)	121.4(3)

Supplementary Material Available: Tables of thermal parameters and structure factors are available from the authors on request.

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