$[(C_5H_5)Co\{P(O)(OH)_2\}_3H]$: A Novel Organometallic Tris-phosphonic Acid That Dissolves Glass to Form a Six-Coordinate Silicon Complex

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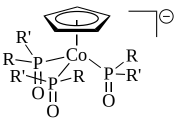
Dedicated to Professor Gottfried Huttner on the occasion of his 65th birthday

Abstract: The sodium salt of the tripodal oxygen ligand $Na[(C_5H_5)Co\{P(O)(OMe)_2\}_3]$ (**1**) reacts with gaseous hydrogen chloride in dichloromethane to give sodium chloride and $[(C_5H_5)Co\{P(O)(OMe)_2\}_3H_2]Cl$ (**2**). Addition of an equimolar amount of **1** leads to precipitation of sodium chloride again to yield the acid form of the ligand $[(C_5H_5)Co\{P(O)(OMe)_2\}_3H]$ (**3**). Its solid-state structure contains a very short intramolecular OH···O hydrogen bond. The compound hydrolyses in boiling water to give methanol and the title complex $[(C_5H_5)Co\{P(O)(OH)_2\}_3H]$ (**4**). This complex is a rather strong tris-phosphonic acid (pK_{a_1} 2.0, pK_{a_2} 4.0, pK_{a_3} 6.3, and pK_{a_4} 9.6). Attempts to grow single crystals of this highly water-soluble yellow crystalline compound lead to the silicon complex $[\{(C_5H_5)Co[P(O)(OH)_2]_2[P(O)_2(OH)]\}_2Si]\cdot 8H_2O$ (**5**). The crystal structure determination shows that it is a molecular complex of two tris-phosphonic acids that each act as a tris-chelating ligand. Additional water molecules form a complex net of hydrogen bonds between the complexes of **5**. The SiO_6 octahedron is only insignificantly distorted with Si−O bond lengths of 1.78 Å. Complex **4** reacts with stoichiometric amounts of potassium carbonate to yield the potassium salt $K[(C_5H_5)Co\{P(O)(OH)_2\}_3]$ (**6**). The crystal structure of **6** has also been determined. In the solid state it is a two-dimensional coordination polymer with each potassium ion being coordinated by twelve oxygen atoms of six tris-phosphonic acids.

Keywords: O ligands · phosphonic acids · silicon · tripodal ligands

Introduction

Complexes of the type $[(C_5H_5)Co\{P(O)RR'\}_3]^-$, R, R′ = alkyl, O-alkyl, aryl, O-aryl, (Figure 1) have become known as tripodal oxygen ligands,[1, 2] that form complexes with a large variety of metal ions and organometallic fragments.[3, 4] Ligands of this type have been used in various areas of transition metal chemistry, for example in homogeneous organometallic catalysis[4] or to transport lithium selectively across membranes[5, 6] or to extract alkali metal ions, magnesium and calcium ions.[7] The attachment of such ligands to solid supports would allow the preparation of novel ion exchange materials and would be a method to heterogenize catalytically active complexes. To this end we decided to develop syntheses of ligands with functional groups at the cyclopentadienyl ring, which can be linked covalently to macromolecular structures such as polyesters and polystyrenes. So far we have succeeded in introducing the vinyl functional group and the carboxylic acid function.[8] We have tried to esterify the complex $[(C_5H_4COOH)Co\{P(O)(OMe)_2\}_3]H$ but we obtained a complicated mixture of products. Once we had discovered that this is due to partial hydrolysis and transesterification of the six methyl phosphite groups we could develop a procedure for the straightforward preparation of the title complex $[(C_5H_5)Co\{P(O)(OH)_2\}_3H]$.



R, R' = alkyl, O-alkyl, aryl, O-aryl

Figure 1. Structure of the tripodal oxygen ligands $[(C_5H_5)Co\{P(O)RR'\}_3]^-$.

Results and Discussion

Syntheses of $[(C_5H_5)Co\{P(O)(OMe)_2\}_3H]$ (3) and $[(C_5H_5)Co\{P(O)(OH)_2\}_3H]$ (4): The sodium salt of the

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tripodal oxygen ligand Na[$(C_5H_5)Co\{P(O)(OMe)_2\}_3$] (**1**) is readily accessible in a two-step reaction starting from cobaltocene and dimethylphosphite.[9] Protonation with dry hydrogen chloride gas in dichloromethane leads to a compound of the composition [$(C_5H_5)Co\{P(O)(OMe)_2\}_3H_2$]Cl (**2**). Deprotonation with one equivalent of **1** gives the acid form of ligand [$(C_5H_5)Co\{P(O)(OMe)_2\}_3H$] (**3**), a yellow crystalline solid that is soluble in water and most organic solvents. The ^{1}H and $^{31}P\{^1H\}$ NMR spectra are very similar to those of the starting compound **1** (see Experimental Section). Single crystals suitable for X-ray structure determination have been obtained from diethyl ether solutions (Figure 2, see below). [$(C_5H_5)Co\{P(O)(OMe)_2\}_3H$] (**3**) hydrolyses in boiling water to give methanol and the title complex, the tris-phosphonic acid [$(C_5H_5)Co\{P(O)(OH)_2\}_3H$] (**4**). The hydrolysis of the sodium salt Na[$(C_5H_5)Co\{P(O)(OMe)_2\}_3$] (**1**) is orders of magnitudes slower, even in the presence of dilute sulfuric acid the hydrolysis is still several times slower. The reason for this is not completely clear. It would be interesting to see whether the addition of excess sodium ions further slows down the acid catalyzed hydrolysis. We are currently measuring the sodium complex stability constants of [$(C_5H_5)Co\{P(O)(OMe)_2\}_3$]$^-$. The complex stability constant of the homologous complex Na[$(C_5H_5)Co\{P(O)(OEt)_2\}_3$] has been determined. It is rather high, higher than those of sodium/crown ether complexes.[10] Aqueous alkaline solutions of **1** and **3** are stable. The methyl ester functions are not hydrolysed and the cobalt complexes do not decompose. Alkaline solutions of the tris-phosphonic acid **4**, however, turn green after a few days and finally yield cobalt(II) hydroxide.

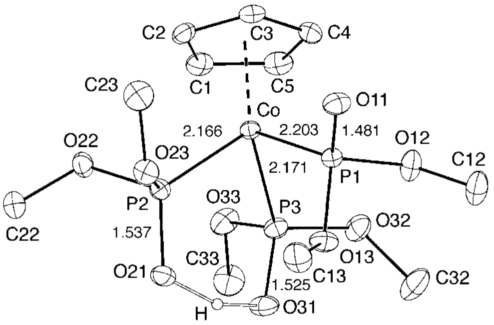

Figure 2. The crystal structure of **3** with displacement parameters of 25 % probability. Co–P and main P–O bond lengths are displayed. Estimated standard deviations are 0.001 to 0.002 Å. For clarity only the OH hydrogen atom is shown.

The tris-phosphonic acid **4** is isolated as a yellow powder that analyses as [$(C_5H_5)Co\{P(O)(OH)_2\}_3H$]$\cdot H_2O$. It is extremely well soluble in water (≈270 g **4** in 100 g water), soluble in DMSO and DMF and hardly soluble in methanol and acetone. It is a rather strong acid; titration with 1M sodium hydroxide (see Experimental Section) gives pK_{a_1} 2.0, pK_{a_2} 4.0, pK_{a_3} 6.3 and pK_{a_4} 9.6. The NMR chemical shifts (cyclopentadienyl ring and the phosphorus signal) are very similar to those of **1** and **3**. The IR spectrum is dominated by the broad bands typical[11] of phosphonic acids (see Experimental Section).

The organic parent compound methane tris-phosphonic acid[12] has been prepared by Gross and co-workers. Blackburn et al. have prepared the analogous chloro- and fluoromethyl tris-phosphonic acids and have determined the values pK_{a_4} and pK_{a_5} under physiological conditions (sodium chloride solution). These compounds are of interest in biochemistry as "supercharged" analogues of pyrophosphoric acid.[13]

We have not been able to grow single crystals of the tris-phosphonic acid **4**. However, upon addition of potassium carbonate to an aqueous solution of **4** we could isolate the potassium salt K[$(C_5H_5)Co\{P(O)(OH)_2\}_3$] (**6**) as large orange crystals that were suitable for X-ray structure determination (Figure 4, see below). When we tried to isolate the tris-phosphonic acid **4** from a 1:1 water/acetone solution we could collect crystals, which were growing slowly on the wall of the glass vessel. The compound turned out not to be **4** but a silicon complex of the tris-phosphonic acid. The silicon is six-coordinate, two tris-phosphonic acids each act as a tris-chelating ligand (Figure 3, see below). This was a completely unexpected but still an important observation since it is known from analytical chemistry that pH glass electrodes tend to deteriorate when they remain in contact with phosphonic acids for longer periods of time![14] The formation of the silicon complex **5** is probably the first example of this type of reaction on a preparative scale.

Crystal structure of [$(C_5H_5)Co\{P(O)(OMe)_2\}_3H$] (3): Preliminary results have been reported elsewhere.[15] Yellow crystals of complex **3** were obtained from diethyl ether solutions. The structure determination shows that **3** crystallizes in the form of monomeric molecules. Selected geometric parameters for the molecule are given in Table 1. The acidic proton forms a short intramolecular hydrogen bond with a distance O···O of 2.468(2) Å between two P–O groups. This short distance and two similar P–OH as well as O–H distances suggest the interpretation as a centered hydrogen bond. Figure 2 shows the crystal structure of **3**.

By mesomerism the distances Co–P2 and Co–P3 of 2.166(1) and 2.171(1) Å, respectively, are shortened to partial double bonds in comparison to the single bond Co–P1 of 2.203(1) Å. These values are in a reciprocal correlation in good agreement with the distances P–OH of 1.537(2) and 1.525(2) Å and the double bond P=O of 1.481(2) Å, respectively. The six bond lengths P–OMe vary only within 3σ from their average of 1.600(2) Å.

Table 1. Selected bond lengths [Å] and angles [°] of **3** with estimated standard deviations in parentheses.

Co–P1	2.203(1)	P2–O22	1.560(2)
Co–P2	2.166(1)	P2–O23	1.597(2)
Co–P3	2.171(1)	P3–O31	1.525(2)
Co–C1	2.077(2)	P3–O32	1.594(2)
Co–C2	2.093(2)	P3–O33	1.599(2)
Co–C3	2.105(2)	O21···O31	2.468(2)
Co–C4	2.082(2)	O21–H	1.28(5)
Co–C5	2.072(2)	O31–H	1.25(5)
P1–O11	1.481(2)		
P1–O12	1.608(2)	P2-Co-P1	92.52(2)
P1–O13	1.603(2)	P2-Co-P3	91.19(2)
P2–O21	1.537(2)	P3-Co-P1	94.60(2)

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Crystal structure of $[\{(C_5H_5)Co[P(O)(OH)_2]_2[P(O)_2(OH)]\}_2Si]\cdot 8H_2O$ (5): The silicon complex **5** forms yellow plates from acetone/water solution (1:1). It contains eight molecules of water per formula unit. Figure 3 shows the complex part of **5** without the surrounding water in the solid state. Selected bond lengths and bond angles are given in Table 2. The crystal structure is that of a molecular complex of two tris-phosphonates that each act as a tris-chelating ligand. The SiO_6 octahedron with the Si atom on the symmetry centre of the space group is only slightly distorted (deviations of the O-Si-O angles from 90° are about 2° and the three independent Si–O bond lengths are rather similar). The geometry is very similar to the one in the related complex $[\{(C_5Me_4Et)Ru[P(O)(OMe)_2]_3\}_2Si]$[16] and in other molecular SiO_6 arrangements.[17–19] The Co–C distances are not significantly different from those of **3**. All hydrogen atoms of the complex part have been localized by difference Fourier syntheses. As shown in Figure 3 the oxygen atom O11, not bonding to the Si atom is deprotonated. In accordance with this it forms the shortest P–O bond and it is the only oxygen atom of the molecule that accepts three hydrogen bonds. The other five P–OH oxygen atoms form only one hydrogen bond each and always act as donors of the respective protons. O11 accepts two hydrogen bonds from water molecules and one hydrogen bond from an oxygen atom O32 of a neighbouring molecule, which leads to a one-dimensional chain along the *b* axis of hydrogen-bonded complex molecules of **5**. Because of some disorder of the co-crystallized eight water molecules, not all of their hydrogen atoms could be localised by difference Fourier syntheses. Analysing the occurring O–O distances and assuming that water molecules typically form four hydrogen bonds (two donor and two acceptor functions), the positions of the missing hydrogen atoms were calculated. Thus, a rather complicated H-bonded framework of water and complex molecules is formed.

Table 2. Selected bond lengths [Å] and angles [°] of **5** with estimated standard deviations in parentheses.

Co1–P1	2.1658(6)	P1-Co1-P2	89.96(2)
Co1–P2	2.1396(7)	P1-Co1-P3	88.85(2)
Co1–P3	2.1427(6)	P2-Co1-P3	91.02(2)
P1–O11	1.5297(14)	P1-O13-Si1	134.54(9)
P1–O12	1.5883(16)	P2-O23-Si1	131.58(8)
P1–O13	1.5663(14)	P3-O33-Si1	132.84(8)
P2–O21	1.5887(19)	O13-Si1-O23	91.65(6)
P2–O22	1.5684(18)	O13-Si1-O33	92.11(7)
P2–O23	1.5499(14)	O23-Si1-O33	92.06(6)
P3–O31	1.5807(18)	O13-Si1-O23[a]	88.35(6)
P3–O32	1.5652(15)	O13-Si1-O33[a]	87.89(7)
P3–O33	1.5554(13)	O23-Si1-O33[a]	87.94(6)
Si1–O13	1.7759(13)		
Si1–O23	1.7914(13)		
Si1–O33	1.7748(13)		

[a] Symmetry code: $1-x, 1-y, -z$.

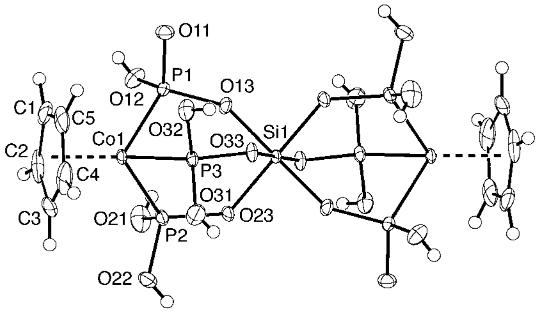

Figure 3. The crystal structure of the complex part of **5** with displacement parameters representing a probability of 40%. Surrounding water molecules and all intermolecular hydrogen bonds have been omitted for clarity.

Crystal structure of $K[(C_5H_5)Co\{P(O)(OH)_2\}_3]$ (6): The potassium salt **6** crystallizes from water as orange plates. Selected interatomic distances and angles are given in Table 3. Compound **6** has a two-dimensional polymeric structure, reminiscent of a sandwich construction with the inorganic components embedded between two layers of CpCo fragments. Figure 4 shows the structure of the anion of **6** with its environment of six potassium cations in the crystal. The anion is involved in a complex O-H···O hydrogen-bonding network. In addition to two "intramolecular" O-H···O bridges of moderate strengths accepted by O4 there are eight "intermolecular" ones, four of which are symmetry-independent. In contrast to **3** the shortest hydrogen bonds in **6** occur between the anions. Within the anion all bond lengths are as to be expected. The most interesting geometric feature is the great variance of the O-P-O angles (99.31(13)–108.69(14)°) indicating the deforming force of the solid-state interaction. Twelve oxygen atoms belonging to six anions form the coordination sphere of the potassium ion with K–O distances in the range 2.894(2)–3.290(3) Å.

Table 3. Selected bond lengths [Å] and angles [°] of **6** with estimated standard deviations in parentheses.[a]

Co1–P1	2.1748(9)	K1–O7	3.059(3)
Co1–P2	2.1756(8)	K1–O4^{VI}	3.068(2)
Co1–P3	2.1821(9)	K1–O2^{VII}	3.141(2)
Co1–C1	2.072(3)	K1–O3^{VI}	3.167(3)
Co1–C2	2.072(3)	K1–O9	3.206(3)
Co1–C3	2.082(3)	K1–O5^{VI}	3.290(3)
Co1–C4	2.088(3)	O2···O7^{I}	2.562(3)
Co1–C5	2.084(3)	O3···O4	2.659(3)
P1–O1	1.526(2)	O5···O1^{II}	2.471(3)
P1–O2	1.585(2)	O6···O7^{II}	2.592(3)
P1–O3	1.589(2)	O8···O5^{VII}	2.677(3)
P2–O4	1.537(2)	O4···O9	2.748(3)
P2–O5	1.574(2)		
P2–O6	1.585(2)	O1-P1-O2	108.69(14)
P3–O7	1.524(2)	O1-P1-O3	101.55(13)
P3–O8	1.594(2)	O2-P1-O3	99.31(13)
P3–O9	1.596(2)	O4-P2-O5	106.98(12)
K1–O4^{VIII}	2.894(2)	O4-P2-O6	108.56(13)
K1–O3	2.894(3)	O5-P2-O6	105.78(13)
K1–O9^{III}	2.919(2)	O7-P3-O8	108.16(13)
K1–O1	2.973(3)	O7-P3-O9	101.98(13)
K1–O2^{VI}	3.001(3)	O8-P3-O9	103.32(13)
K1–O1^{V}	3.029(2)		

[a] Symmetry codes: I: $x, y, z-1$; II: $x+1, y, z$; III: $x-0.5, -y+0.5, z-0.5$; V: $x+0.5, -y+0.5, z+0.5$; VI: $x-0.5, -y+0.5, z+0.5$; VII: $x, y, z+1$; VIII: $x-1, y, z$.

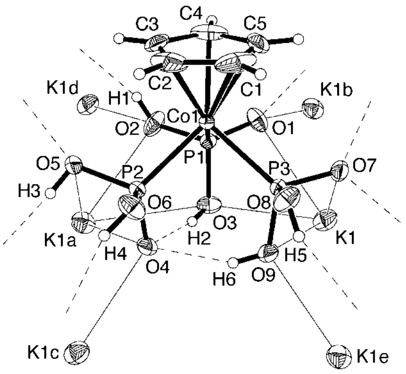

Figure 4. Diagram of the anion of **6** with its environment of potassium cations. Displacement ellipsoids are drawn at the 50% probability level, radii of hydrogen atoms are chosen arbitrarily, and the labels of hydrogen atoms of the cyclopentadienyl ligand are omitted. Dashes indicate intramolecular as well as the direction of intermolecular O-H···O hydrogen bonding.

Conclusion

The sodium, silver, and thallium salts of the tripodal oxygen ligand $[(C_5H_5)Co\{P(O)(OMe)_2\}_3]^-$ are useful starting materials for the preparation of organometallic derivatives mainly when they can be reacted with organometallic halide complexes to eliminate insoluble sodium, silver, or thallium halides. The acid form of this ligand, $[(C_5H_5)Co\{P(O)(OMe)_2\}_3H]$ (**3**), which we have described here, is an important alternative synthon. It can be reacted with metal carbon bonds M-R to eliminate R-H, a reaction that provides a very high driving force. We hope that this strategy allows us to enter the field of catalytically active early transition metal alkyl derivatives with tripodal oxygen ligands instead of cyclopentadienyl ligands.

Metal–hydride complexes of tripodal oxygen ligands are probably accessible via oxidative addition reaction of the O-H bond of **3** to low-valent transition metal centres. This type of reaction is not very common but has been observed with similar ligands.[20]

It will be worthwhile to compare the tris-phosphonic acid **4** with methane tris-phosphonic acid. As mentioned above this acid has been used as an analogue of pyrophosphate. Blackburn et al. have shown that methane tris-phosphonic acid is a strong inhibitor of some hydrolases.[21] The condensation of methane tris-phosphonic acid with adenosine monophosphate has given "supercharged" analogues of ATP[22] and diadenosine tetraphosphate. Tripodal "supercharged" analogues of adenosine nucleotides provide powerful inhibitors of hydrolases suc as the tumour suppressing Fhit-protein.[21]

Preliminary experiments have shown that the methylphosphonito compounds $Na[(C_5H_5)Co\{P(O)(OMe)R\}_3]$, R = Et, Ph, can be hydrolysed such as the dimethylphosphito compound $Na[(C_5H_5)Co\{P(O)(OMe)_2\}_3]$ (**1**) to give the acids $[(C_5H_5)Co\{P(O)(OH)Et\}_3H]$ (**7**) and $[(C_5H_5)Co\{P(O)(OH)Ph\}_3H]$ (**8**). Their solubility in protic solvents is as expected between that of **3** and **4** (see Experimental Section). They are chiral acids with its usefulness yet to be explored.

Our initial aim, the development of syntheses of tripodal oxygen ligands that can be covalently attached to solid supports is still in its infancy. Instead we have discovered a series of interesting compounds that seem to open up completely different areas of chemistry.

Experimental Section

General remarks: The starting compounds $Na[(C_5H_5)Co\{P(O)(OMe)_2\}_3]$, $Na[(C_5H_5)Co\{P(O)(OMe)Et\}_3]$, and $Na[(C_5H_5)Co\{P(O)(OMe)Ph\}_3]$ were prepared according to the published procedures.[9] NMR spectra were recorded with Bruker 200 SY and DRX 500 spectrometers. The ^1H and $^{13}C\{^1H\}$ NMR spectra were calibrated against the residual proton signals of the solvents as internal references ($CDCl_3$: $\delta_H = 7.3$ and $\delta_C = 77.0$; $[D_6]DMSO$: $\delta_H = 2.6$ and $\delta_C = 39.4$), while the $^{31}P\{^1H\}$ NMR spectra were referenced to external 85% H_3PO_4. Infrared spectra were recorded with a Bruker IFS 66 FT-IR spectrometer. FAB mass spectra were recorded with a Finnigan MAT 8200 mass spectrometer. Elemental analyses were performed by the Institut für Pharmazeutische Chemie at the Heinrich-Heine-Universität Düsseldorf using a Perkin–Elmer 2400 elemental analyzer. The dissociation constants pK_a were determined according to standard procedures.[23–25] PC-guided high precision titrations were performed using tools described in refs. [26–28]. Calibration of glass electrode (Blue Line, SCHOTT) by blank titration using 1M HCl vs. 1M NaOH. Data generation and registration: computer titrator MINI_T.[26] Data evaluation: AUTOBLANK.[26] pK_W 13.80. Potentiometric titration of **4**: Titrand: 2.00 mmol **4**, 2.01 mmol HCl, and 2.92 g NaCl to a total of 50.0 mL by H_2O bidest.; titrator: max. 20 mL in 400 equidistant steps, 1.00M NaOH; 25 ± 0.1 °C. Data evaluation using 221 data points in the range $1.2 < pH < 11.5$ by WINSCORE.[28] Details of further analytical studies will be published in a forthcoming paper.[29]

$[(C_5H_5)Co\{P(O)(OMe)_2\}_3H]$ (3): This preparation was carried out under dinitrogen, using standard Schlenk techniques. $Na[(C_5H_5)Co\{P(O)(OMe)_2\}_3]$ (**1**) (0.40 g, 0.84 mmol) was dissolved in dry dichloromethane (35 mL). HCl gas was bubbled through the solution until the precipitation of NaCl was complete. The solid was filtered off through Celite and to the filtrate was added an equimolar amount of **1** (0.40 g, 0.84 mmol). The mixture was stirred for 1 h and the precipitate (NaCl) was again filtered off. The solvent was removed in vacuo and the product **3** was obtained as orange oil that slowly solidifies to give a microcrystalline powder (0.71 g, 93%). ^1H NMR (80 MHz, $CDCl_3$): $\delta = 13.3$ (s, 1H, H^+), 5.2 (s, 5H, C_5H_5), 3.7 (q, $[A[X_3]_2]_3$, $^3J(H,P) = 11.1$ Hz, 18H, OCH_3); $^{31}P\{^1H\}$ NMR (32 MHz, $CDCl_3$, −50 °C): $\delta = 116$ (s); IR (Nujol): $\tilde{\nu} = 1145$ (P=O), 563 cm^{-1} (PO_2); elemental analysis calcd (%) for $C_{11}H_{24}CoO_9P_3$ (252.2): C 29.2, H 5.4; found C 29.0, H 5.4.

$[(C_5H_5)Co\{P(O)(OH)_2\}_3H]$ (4): $[(C_5H_5)Co\{P(O)(OMe)_2\}_3H]$ (**3**) (0.50 g, 1.11 mmol) was dissolved in water (50 mL) and refluxed for 1 h. After cooling to ambient temperature the solution was extracted with dichloromethane (2 × 30 mL). The aqueous phase was collected and evaporated to dryness. Compound **4** was obtained as monohydrate in the form of a yellow powder. The product (0.40 g, 98%) is extremely well soluble in water, and soluble in DMSO and DMF. ^1H NMR (500 MHz, $[D_6]DMSO$): $\delta = 5.1$ (s, 5H, C_5H_5), 10 (br s, 10H, OH, H_2O); $^{31}P\{^1H\}$ NMR (200 MHz, $[D_6]DMSO$): $\delta = 113$ (s, $\tilde{\nu}_{1/2} = 48$ Hz); IR (KBr): $\tilde{\nu} = 3400–2000$ (HO···H), 3122 (C-H(Cp)), 1428 (Cp ring), 1100–800 (P=O), 500 cm^{-1} (PO_2); MS (FAB$^-$): m/z (%): 367 (14) $[M-H]^-$; elemental analysis calcd (%) for $C_5H_{14}CoO_{10}P_3$ (386.0): C 15.6, H 3.7; found C 15.6, H 3.3.

$K[(C_5H_5)Co\{P(O)(OH)_2\}_3]$ (6): $[(C_5H_5)Co\{P(O)(OH)_2\}_3H]$ (**4**) (0.15 g, 0.40 mmol) was dissolved in water (3 mL). The addition of K_2CO_3 (55.3 mg, 0.400 mmol) dissolved in water (2 mL) leads to the precipitation of small orange crystals of **6**, which were filtered off, washed with small amounts of cold water and dried (0.65 g, 39%). $^{31}P\{^1H\}$ NMR (200 MHz, D_2O): $\delta = 109$ (s, $\tilde{\nu}_{1/2} = 96$ Hz); IR (KBr): $\tilde{\nu} = 3400–2000$ (HO···H), 3131 (C-H(Cp)), 1426 (Cp ring), 1100–700 (P=O); elemental analysis calcd (%) for $C_5H_{11}CoKO_9P_3$ (406.1): C 14.8, H 2.7; found C 14.8, H 2.6.

$[(C_5H_5)Co\{P(O)(OH)Et\}_3H]$ (7): $Na[(C_5H_5)Co\{P(O)(OMe)Et\}_3]$ (0.51 g, 1.09 mmol) was dissolved in water (ca. 70 mL) containing concentrated hydrochloric acid (ca. 0.2 mL). The mixture was refluxed for 5 h. The solution was concentrated to ca. 10 mL. Yellow crystals of **7** grew over night, which were filtered off, washed with a small amount of cold water and dried in vacuo (0.30 g, 68 %). The product is soluble in DMSO, DMF, water, and acetone. ^{1}H NMR (500 MHz, [D$_6$]DMSO): $\delta = 0.9$ (m, 9H, CH_3), 1.9–1.6 (m, 6H, CH_2), 5.1 (s, 5H, C$_5$$H_5$), 6.0–7.0 (br s, O$H$, H_2O); ^{31}P{^{1}H} NMR (200 MHz, [D$_6$]DMSO): $\delta = 143$ (s, $\tilde{\nu}_{1/2} = 40$ Hz); ^{13}C{^{1}H} NMR (500 MHz, [D$_6$]DMSO): $\delta = 6.8$ (CH$_3$), 34.7 (CH$_2$), 89.3 (C_5H$_5$); MS (FAB$^+$): m/z (%): 405 (9) [M+H]$^+$; IR (KBr): $\tilde{N} = 3400-2000$ (HO$\cdots$H), 3104 (C-H(Cp)), 2965 (CH$_3$), 2934 (CH$_2$), 1426 (Cp ring); elemental analysis calcd (%) for $C_{11}H_{24}CoO_6P_3$ (404.2): C 32.7, H 6.0; found C 32.3, H 6.0.

[(C$_5$H$_5$)Co{P(O)(OH)Ph}$_3$H] (8): Na[(C$_5$H$_5$)Co{P(O)(OMe)Ph}$_3$] (0.50 g, 0.82 mmol) was dissolved in water/dioxane (1:1) (70 mL) containing concentrated hydrochloric acid (ca. 0.2 mL). The solution was refluxed 10 h. The solution was reduced to ca. 10 mL and the product **8** was extracted with dichloromethane (2 × 30 mL). The organic layer was cooled over night to precipitate yellow crystals of **8** which were filtered off and dried in vacuo (0.32 g, 71 %). The product is soluble in DMSO, DMF, THF dioxane, water, and acetone. ^{1}H NMR (500 MHz, [D$_6$]DMSO): $\delta = 4.1$ (br s, OH, H_2O), 4.4 (s, 5H, C$_5$$H_5$), 7.4–7.5 (m, 15H, Ph-$H$); ^{31}P{^{1}H} NMR (200 MHz, [D$_6$]DMSO): $\delta = 119$ (s, $\tilde{\nu}_{1/2} = 37$ Hz); ^{13}C{^{1}H} NMR (500 MHz, [D$_6$]DMSO): $\delta = 90.5$ (C_5H$_5$), 128.3 (d, ^1J(PC) = 71 Hz, C^{1}_{Ph}), 130.0 (d, ^2J(PC) = 46 Hz, $C^{2,6}_{\mathrm{Ph}}$), 144.7 (s, $C^{3,4,5}_{\mathrm{Ph}}$); MS (FAB$^+$): m/z (%): 549 (48) [M+H]$^+$; IR (KBr): $\tilde{\nu} = 3400-2000$ (HO$\cdots$H), 3104 (C-H(Cp)), 3060 (C-H(Ph)), 1587, 1573, 1482 (Ph ring), 1457, 1425 (Cp ring), 1181 (P=O), 539 (PO$_2$); elemental analysis calcd (%) for $C_{23}H_{26}CoO_7P_3$ (566.3): C 48.8, H 4.6; found C 48.7, H 4.7.

Crystal structure determinations of compounds 3, 5, and 6: Crystal data and details of the structure determinations are summarised in Table 4. Crystals suitable for X-ray study were selected by means of a polarisation microscope and investigated on 4-circle diffractometers using graphite monochromatized Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). Unit cell parameters were determined by least-squares refinements on the positions of 24, 40 and 50 centered reflections in the range of $10° < \theta < 17.5°$, $18° < \theta < 20°$ and $12° < \theta < 17°$, respectively. Space group No. 14 was uniquely determined in all cases. The structures were solved by direct methods[30] and the positions of all hydrogen atoms were found for **3** and **6**. In the case of **5** some positions needed to be calculated. Refinements[31] by full-matrix least-squares calculations on F^2 converged to the indicators given in Table 4 (**3**: $S = 0.84$, $(\Delta/\sigma)_{\max} = 0.001$; **5**: $S = 1.08$ $(\Delta/\sigma)_{\max} = 0.001$; **6**: $S = 1.13$, $(\Delta/\sigma)_{\max} = 0.001$). Anisotropic displacement parameters were refined for all non-hydrogen atoms. All atom coordinates and isotropic displacement parameters were refined for the hydrogen atoms of **3** and of the complex unit of **5**. The water molecules of **5** were treated as rigid groups with idealized bond lengths and angles. For **6** the hydrogen atoms of the cyclopentadienyl ligand were treated in idealized positions applying the riding model. The O−H bond lengths were restrained to 0.82 Å within a standard deviation of 0.02. For **3** in addition an empirical extinction parameter was refined. Scattering factors, dispersion corrections and absorption coefficients were taken from International Tables for Crystallography (*Vol. C*, Tables 6.114, 4.268, 4.2.4.2, **1992**).

Table 4. Summary of crystal data and details of intensity measurements, and structure refinements of **3**, **5**, and **6**.

	3	**5**	**6**
formula	$C_{11}H_{24}CoO_9P_3$	$C_{10}H_{36}Co_2O_{26}P_6Si$	$C_5H_{11}CoKO_9P_3$
M_W	452.14	904.16	406.08
crystal system	monoclinic	monoclinic	monoclinic
space group; no.	$P2_1/c$; 14	$P2_1/n$; 14	$P2_1/n$; 14
a [Å]	9.583(1)	11.316(2)	6.9927(13)
b [Å]	9.164(1)	9.970(2)	26.020(6)
c [Å]	20.952(3)	14.197(3)	7.1678(18)
β [°]	94.76(1)	109.710(10)	114.293(16)
V [Å^3]	1833.6(4)	1507.9(5)	1188.7(5)
Z	4	2	4
$F(000)$	936	924	816
ρ_{calcd} [Mg m^{-3}]	1.638	1.991	2.269
μ (Mo$_{K\alpha}$) [mm^{-1}]	1.24	1.56	2.24
crystal size [mm]	0.5 × 0.3 × 0.2	0.5 × 0.45 × 0.4	0.58 × 0.21 × 0.17
diffractometer	Bruker P3	Bruker P3	Siemens-Stoe AED2
monochromator	graphite	graphite	graphite
T [K]	295	295	295
data collecting mode	$\omega:2\theta$	$\omega:2\theta$	$\omega:\theta$
θ range [°]	$2 < \theta < 32.5$	$2.5 < \theta < 30$	$3 < \theta < 27.5$
hkl ranges	$0 \leq h \leq 14$	$0 \leq h \leq 15$	$-9 \leq h \leq 8$
	$0 \leq k \leq 13$	$0 \leq k \leq 14$	$0 \leq k \leq 33$
	$-31 \leq l \leq 31$	$-20 \leq l \leq 18$	$-9 \leq l \leq 9$
reflns. measd.	7374	4578	5428
unique reflns.	6657	4391	2717
reflns. obsd. $I > 2\sigma(I)$	3908	3915	2467
no. param./restraints	314/0	264/0	201/6
$R1$ [$I > 2\sigma(I)$][a]	0.0351	0.0380	0.0322
weight[a]	0.0335; 0	0.0764; 0.2367	0.0250; 2.5
$wR2$[a]	0.0789	0.1035	0.0790
Max./min. $\Delta\rho$ [e Å^{-3}]	0.33/ – 0.38	1.134/ – 1.150	0.55/ – 0.46
extinction parameter	0.0026(2)	–	–

[a] As defined in SHELXL 97-2.

CCDC-171 692 (**3**), -171 270 (**5**), and -171 271 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; (fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk).

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