Tris-Chelating Oxygen Ligands: New Synthetic Routes to Sterically Demanding Ligands

Wolfgang Kläui*[a], Hark-Oluf Asbahr[b], Georg Schramm[a], and Ulli Englert[b]

Institut für Anorganische Chemie und Strukturchemie I, Heinrich-Heine-Universität Düsseldorf[a],
Universitätsstraße 1, D-40225 Düsseldorf, Germany
Fax (internat.): +49(0)211/811-2287
E-mail: klaeui@uni-duesseldorf.de

Institut für Anorganische Chemie, RWTH Aachen[b],
Templergraben 55, D-52056 Aachen, Germany
E-mail: ullrich.englert@ac.rwth-aachen.de

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The lithium and sodium compounds $A[P(O)R_2]$ (A^+ = Li^+, Na^+; R = OPh, O*i*Pr) have been prepared in situ from $HP(O)R_2$ and butyllithium or sodium hydride. They react with the cyclopentadienyl complexes $[(C_5H_5)MI_2(CO)]$ (M = Co, Rh), $[(C_5Me_5)CoCl_2]_2$, and $[(C_5H_5)CoI_2]_n$ to yield alkali metal salts AL of tridentate oxygen ligands (A^+ = Li^+, Na^+; L^- = $[(C_5R'_5)M\{P(O)R_2\}_3]^-$, R' = H, Me; M = Co, Rh; R = OPh, O*i*Pr) (**2**). For the ligand $L_{Co,OPh}$ = $[(C_5H_5)Co\{P(O)(OPh)_2\}_3]^-$, an alternative synthesis has been developed, starting from $[(C_5H_5)_2Co]PF_6$. The structure of the sodium salt $NaL_{Co,OPh}$ (**2d**) has been determined by X-ray diffraction. The ligand $L_{Co,OPh}{}^-$, with a cone angle Θ of about 200°, completely blocks one half of the coordination sphere around the sodium centre. The ligand profile has been calculated to allow appraisal of the angular encumbrance of the ligand.

Introduction

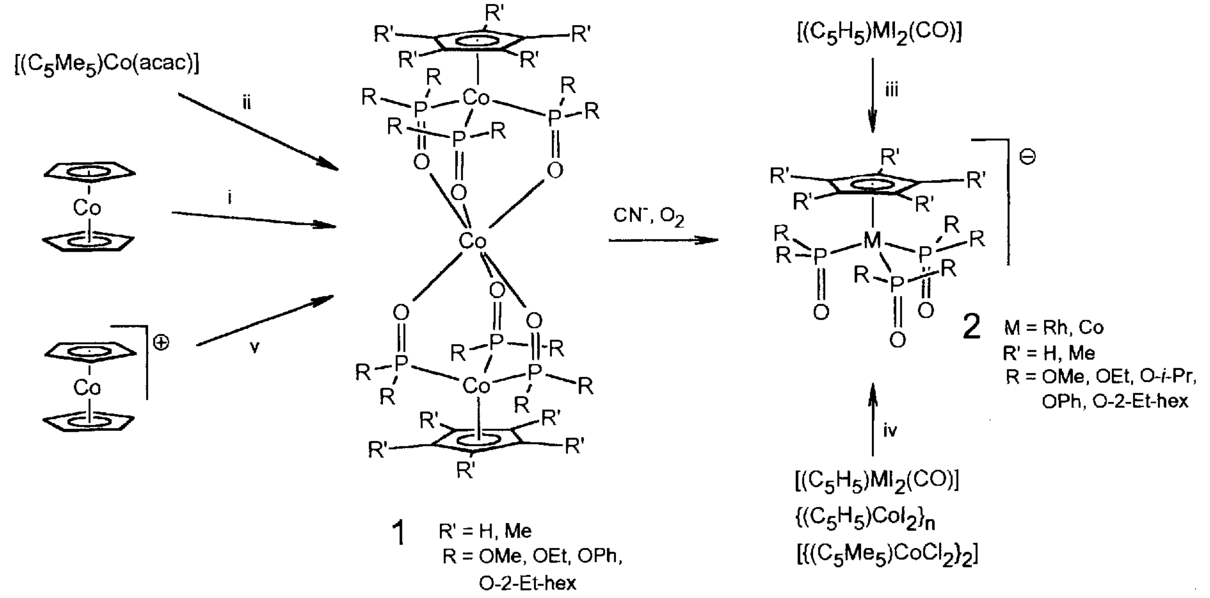
In recent years we have developed syntheses for a variety of tris-chelating oxygen ligands of the general composition $[(C_5R'_5)M\{P(O)R_2\}_3]^-$ (R' = H, CH_3, R = alkyl, aryl, alkoxy, M = Co, Rh). Their pronounced tendency to form complexes with ions of both main-group and transition metals in virtually all oxidation states, together with their thermal and hydrolytic stability, makes these ligands potentially useful for a broad spectrum of applications. They have been shown to be of interest in organometallic chemistry, as catalyst components, and as ionophores for the transport of alkali metal ions through membranes, to name just a few applications[1–3]. An overview of the chemistry of these ligands has been published[4]. Nearly all of the ligands, abbreviated in the following as L^-, have been prepared from cobaltocene and secondary phosphane oxides or diesters of phosphorous acid (route **i** in Scheme 1).

The primary products are the cobalt complexes $[CoL_2]$, from which the free ligands L^- are released by cleaving with cyanide in the presence of atmospheric oxygen. In this way, we have prepared more than a dozen different ligands, some of them on a 50–100 g scale. The principal limitations and drawbacks of this method are as follows: Thermally labile phosphorus compounds $HP(O)R_2$ cannot be used since the reaction with cobaltocene proceeds only at temperatures exceeding 90–140°C. Acidic phosphorus compounds $HP(O)R_2$ cannot be used either since oxidation of cobaltocene to cobalticenium is the prevailing reaction under such conditions. In some cases the cobalt compounds $[CoL_2]$ were found to be highly insoluble such that they proved impossible to cleave with cyanide[5,6]. Furthermore, the permethylated ligands L^-, (M = Co, R' = Me) are not available via the cobaltocene route. The reason for this is that decamethylcobaltocene has such a negative reduction potential (E_0 = -1.48 V vs. SCE) that it invariably reacts with oxidation to decamethylcobalticenium[7]. However, the permethylated ligands L^- (M = Co, R' = Me) are accessible via an alternative route. Those with R = OMe and OEt are available in good yields from $[(C_5Me_5)Co(acac)]$ (route **ii** in Scheme 1)[8–10]. The ligand with R = O*i*Pr has only been synthesized in 1% yield. It seems that sterically demanding substituents R cannot be introduced easily via route **ii**. A third method uses an organometallic version of the Michaelis-Arbuzov reaction, i.e. the demethylation of coordinated phosphites, phosphonites, and phosphinites $PR_2(OMe)$ with sodium iodide, for the preparation of the ligands L^- (route **iii** in Scheme 1). The ligands prepared in this manner normally contain sodium iodide, which is difficult to remove. In the following, we describe two alternative methods. The first one employs the sodium or lithium salts $A[P(O)R_2]$, which are often easier to prepare than the methyl esters $PR_2(OMe)$. This method yields the alkali metal salts of the ligands L^- directly (route **iv** in Scheme 1). The second method leads to the cobalt complexes $[CoL_2]$, starting from cobalticenium salts and $HP(O)R_2$ and proceeding via a Co^I intermediate (route **v**).

Results and Discussion

Alkali metal salts of phosphorus acid diesters and phosphinous acids can be prepared from the corresponding

Scheme 1. Syntheses and schematic structure of the ligands L^-. – **i**: $+HP(O)(O{-}Et{-}Hex)_2$; **ii**: $+HP(O)(OEt)_2$ or $HP(O)(OMe)_2$; **iii**: $+P(OMe)_3 + NaI$, M = Rh; **iv**: + *n*BuLi + $HP(O)(OPh)_2$ or $HP(O)(O\textit{i}Pr)_2$; +NaH + $HP(O)(OPh)_2$; **v**: +*n*BuLi + $HP(O)(OPh)_2$



compounds of the type $HP(O)R_2$ and alkali metals, alkali metal hydrides, amides, or phenyllithium[11–13]. The anions $[P(O)R_2]^-$ are good nucleophiles and have been widely used in organic synthesis. Their use in transition metal chemistry is not so widespread and simple ligand substitution reactions seem uncommon. The reaction of $Na[P(O)(OR)_2]$ (R = Me, Et, Ph) with $[(C_6H_6)Mn(CO)_3]PF_6$ has been described[14,15]. The nucleophile adds to the benzene ring, yielding $[(exo\text{-}(RO)_2(O)P{-}\eta^5\text{-}C_6H_6)Mn(CO)_3]$. We have observed a similar reaction of $K[P(O)Bu_2]$ with cobalticenium salts, which yields the ring addition product $[(exo\text{-}Bu_2(O)P{-}\eta^4\text{-}C_5H_5)Co(C_5H_5)]$[16]. Interestingly, the phosphorus nucleophiles $[P(O)R_2]^-$ do not add to the cyclopentadienyl ring in the cobalt and rhodium complexes $[(C_5H_5)MI_2(CO)]$. Instead, they displace the carbon monoxide and iodide ligands and form the anionic complexes $[(C_5H_5)M\{P(O)R_2\}_3]^-$ (= $L_{M,R}{}^-$, where necessary the indices M and R are used to further specify the nature of the ligand) (route **iv** in Scheme 1). The polymeric compound $[(C_5H_5)CoI_2]_n$ and the pentamethylcyclopentadienyl complex $[(C_5Me_5)CoCl_2]_2$ can be used equally effectively for such reactions.

For example, solutions of $Li[P(O)R_2]$ (R = O*i*Pr, OPh), prepared from butyllithium and the appropriate secondary phosphorous acid esters, react instantly with $[(C_5H_5)CoI_2(CO)]$ in THF at −78°C. Evolution of gas and the absence of a CO stretching vibration in the IR spectrum indicate that the carbon monoxide ligand is easily displaced. The dark-violet colour due to the iodo–cobalt charge-transfer bands also disappears within seconds. The same reaction is observed when the complexes $[(C_5Me_5)CoCl_2]_2$, $[(C_5H_5)CoI_2]_n$, and $[(C_5H_5)RhI_2(CO)]$ are used. The sodium salt $Na[P(O)(OPh)_2]$ reacts with $[(C_5H_5)CoI_2(CO)]$ in THF at room temperature in an analogous manner.

In spite of the rapid displacement of the iodo and carbonyl ligands, it is necessary to reflux the reaction mixtures for many hours to obtain high yields. For example, the yield of $LiL_{O\textit{i}Pr}$ is only 29% when the reaction mixture is stirred for 2 hours at room temperature, but it increases to 79% if the mixture is refluxed for 22 hours. It would seem that an intermediate is formed first, which slowly reacts upon heating to give the final product. However, we have not been able to identify any intermediate. In the case of $LiL_{Co,OPh}$, an appreciable amount of $[Co(L_{Co,OPh})_2]$ is formed as a paramagnetic by-product.

The second new synthetic route leads to the bisligand cobalt complex **1** as the main product. When $[(C_5H_5)_2Co]PF_6$ is reacted with *n*-butyllithium in diethyl ether at −78°C, it yields the ring addition product $[(exo\text{-}Bu\text{-}\eta^4\text{-}C_5H_5)Co(C_5H_5)]$[17]. In this Co^I intermediate, the η^4- and η^5-bound ligands are sufficiently labile to be displaced by $HP(O)(OPh)_2$ as a nucleophile. The mechanistic details of this new synthetic route are still vague. The reaction mixture has to be heated to 80°C for several hours to drive the redox reaction to completion. The free ligand can be obtained by cleavage of **1** with cyanide in the usual way.

To examine the expected high steric demand of the phenoxy-substituted ligand $[(C_5H_5)Co\{P(O)(OPh)_2\}_3]^-$ (= $L_{Co,OPh}{}^-$) in detail, the crystal structure of its sodium salt was determined. A number of selected interatomic distances and angles are collected in Table 1.

A PLATON[18] drawing of the molecular structure of the ligand is shown in Figure 1. The unit cell contains two dimeric units $[(NaL)_2]$ with the sodium ions coordinated by four P=O oxygen donor atoms. The polyhedron around each sodium can be described as being octahedral, with two *cis* positions blocked by a phenyl ring. The distance from the centre of the phenyl ring to the sodium is 3.09 Å, while

Table 1. Selected distances and angles of **2d**

Angles [°]		Distances [Å]	
P1–Co–P2	91.70(3)	Co–P1	2.172(1)
P1–Co–P3	93.63(4)	Co–P2	2.183(1)
P2–Co–P3	92.72(4)	Co–P3	2.192(1)
Co–P1–O11	123.46(9)	P1–O11	1.482(2)
Co–P2–O21	122.40(9)	P2–O21	1.473(2)
Co–P3–O31	123.7(1)	P3–O31	1.469(2)
Cp[b]–Co–Na	178.04(3)	Cp[b]–Co	1.7057(5)
Na–O11–P1	125.0(1)	Na–O11	2.350(2)
Na–O21–P2	128.7(2)	Na–O21	2.247(2)
Na–O31–P3	127.1(2)	Na–O31	2.256(3)
O11–Na–O21	88.53(8)	Na–O11′	2.306(2)
O11–Na–O31	85.12(9)	Na–CR[a]	3.093(1)
O21–Na–O31	88.56(9)	Na···Na′	3.320(2)
O11–Na–O11′	89.01(8)		
O11′–Na–O21	160.2(1)		
O11′–Na–O31	110.8(1)		
Na–O11–Na′	90.99(8)		

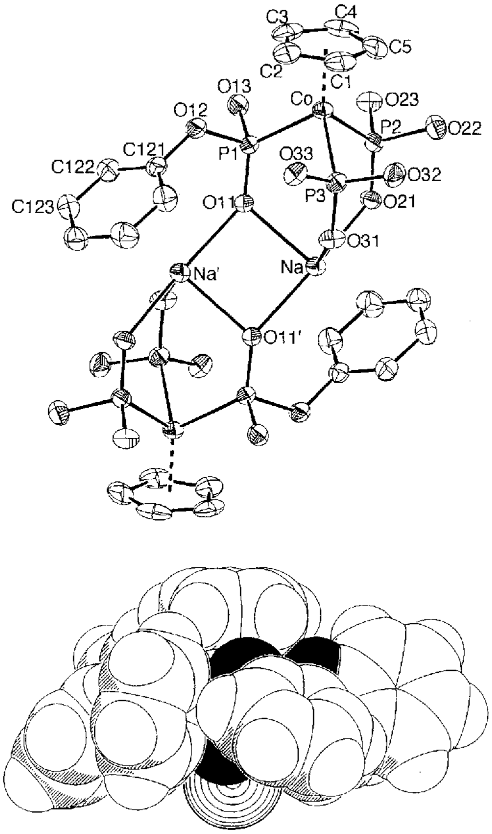
[a] CR: centre of the phenyl ring closest to the sodium atom. – [b] Cp: Cobalt projection onto the cyclopentadienyl ring plane; primed atoms are related to unprimed ones by the symmetry operation $-x$, $1-y$, $-z$.

the phenyl carbon to sodium distances are in the range 3.13–3.63 Å. This indicates that there is no strong interaction between the aromatic ring and the sodium ion. The "bite" of the tridentate oxygen ligand, as given by the nonbonding O···O distances between the P=O oxygen atoms, is in the range 3.12–3.21 Å, which is similar to the bite of other tridentate ligands of this type[19,20]. From the space-filling model, it is apparent that the six OPh groups effectively block one half of the coordination sphere of a metal coordinated by this ligand. To quantify the steric requirements of the ligand, we have calculated the cone angle Θ = 200°. Alternatives to the cone angle concept of Tolman[21] are the solid cone angle Ω proposed by Immirzi and Musco[22] and the ligand profile of Ferguson et al.[23,24]. The latter is a very informative way of visualizing the spatial arrangement of ligands in complexes[25,26]. In Figure 2, the ligand profile of **2d** is shown using the circular diagram of Oliver[27].

To what extent the bulkiness of the ligand influences its coordination chemistry remains to be seen. So far, we have prepared the rhodium dicarbonyl complex $[L_{OPh}Rh(CO)_2]$[28]. Of all the analogous complexes that we have synthesized, this is the first one that does not undergo decarbonylation under 1 atm. of CO (see eq. 1). It does form the dirhodium complex $[LRh(\mu\text{-}CO)_3RhL]$[29], but only when carbon monoxide is removed from the equilibrium.

We take this as a first indication that the steric demand of this ligand does indeed control its coordination chemistry.

Figure 1. Molecular structure of $Na[(C_5H_5)Co\{P(O)(OPh)_2\}_3]$ (= $NaL_{Co,OPh}$, **2d**) as PLATON[18] plot (top) and space-filling model (Corey-Pauling-Koltum) (bottom); in the upper part of the figure, ellipsoids enclose 30% probability; hydrogen atoms and five of the six phenyl rings are omitted; primed atoms are related to unprimed ones by the symmetry operation $-x$, $1-y$, $-z$; in the CPK model below, oxygen atoms are drawn as filled circles and the sodium atom with contour lines



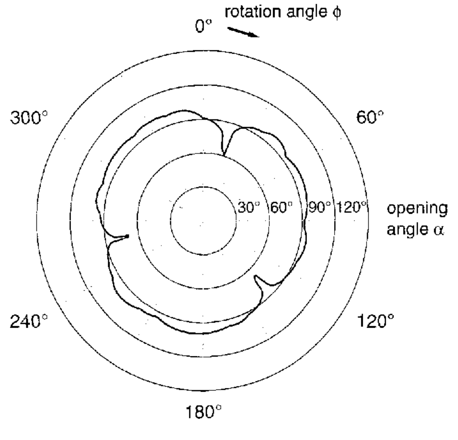


Figure 2. Ligand profile of $L_{Co,OPh}^-$

$$[L_{OPh}Rh(CO)_2] \underset{+\,1\ \text{atm CO}}{\overset{-\,CO}{\rightleftharpoons}} [L_{OPh}Rh(\mu\text{-}CO)_3RhL_{OPh}] \qquad (1)$$

To summarize, the tris-chelating oxygen ligands L_R^- are monoanionic six-electron ligands, formally equivalent to cyclopentadienyl ligands. Their electronic properties, however, bear much more resemblance to those of oxide ions[4]. The novel access routes to ligands L_R^- (routes **iv** and **v** in Scheme 1) that we have described herein, appear to be simple ligand substitution reactions but are, in fact, complicated redox reactions, the intermediates of which are as yet unidentified. Nevertheless, they are elegant ways of preparing pentamethylcyclopentadienyl-substituted ligands, ligands with a high steric demand, and they allow the use of phosphorus compounds $HP(O)R_2$ that are too acidic for the cobaltocene route. Route **v** is especially attractive as it starts from air-stable cobalticenium. Preliminary experiments have shown that the cobalticenium route is not limited to the preparation of **1d**, but provides a general access to this class of tridentate oxygen ligands.

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Experimental Section

All reactions were performed under dry nitrogen in conventional Schlenk glassware unless otherwise stated. The complexes $\{Co(C_5H_5)_2]$[30], $[(C_5H_5)CoI_2(CO)]$[31], $[(C_5H_5)RhI_2(CO)]$[31], $[(C_5H_5)CoI_2]_n$[32], $[(C_5Me_5)CoCl_2]_2$[33], and $[(C_5Me_5)Co(acac)]$[8] were prepared according to the published procedures. LiC_5Me_5 was synthesized by reaction of HC_5Me_5 with a 1.3-fold excess of *n*-butyllithium in hexane. The lithium salt precipitated, was filtered off, washed with pentane, and dried in vacuo. The white pyrophoric powder was used without further purification. Cobaltocene was freshly sublimed prior to use. Di(2-ethylhexyl)phosphite was a gift from Hoechst AG, Knapsack. The lithium and sodium salts $Li[P(O)R_2]$ and $Na[P(O)R_2]$ were synthesized by reaction of the secondary phosphites with *n*-butyllithium and sodium hydride, respectively. They were used without further purification. – Infrared spectra were recorded on a Perkin-Elmer 1720 X and a Bruker IFS 66 FT-IR spectrometer. – ^{1}H-, ^{13}C-, and ^{31}P-NMR spectra were recorded on Bruker WP 80 (80 MHz), Bruker AM 200 SY (200 MHz), and Bruker WH 270 (270 MHz) instruments. Chemical shifts are given in ppm (positive downfield) relative to TMS (^{1}H, ^{13}C) and external 85% H_3PO_4 (^{31}P). – Elemental analyses were performed on a Carlo-Erba Elemental Analyzer Model 1106. – Osmometric molecular weight determinations were performed at the Mikroanalytisches Labor Pascher, D-53424 Remagen.

Bis[tris(dimethyl phosphito-P)(pentamethylcyclopentadienyl)cobalt-O,O′,O″]cobalt(II), $[Co(L^{*}_{Co,OMe})_2]$ (**1a**): The acetylacetonate complex $[\{C_5Me_5\}Co(acac)]$ was prepared from 3.55 g (25.0 mmol) of LiC_5Me_5 and 6.10 g (23.7 mmol) of $[Co(acac)_2]$ in THF at −78°C[8]. The brown reaction mixture was concentrated to dryness and heated at 120°C overnight with a threefold excess of dimethyl phosphite. The resulting mixture, which consisted of a yellow solid and a green solution, was then stirred in air with 100 ml of water. The solid was filtered off, washed twice with methanol and pentane, and purified by Soxhlet extraction with diethyl ether (yield: 5.34 g yellow crystals, 4.85 mmol, 61%). – IR (KBr): $\tilde{\nu}$ = 1121 cm^{-1} [vs, ν(P=O)], 598 [vs, δ(P=O)]. – $C_{32}H_{66}Co_3O_{18}P_6$ (1101.51): calcd. C 34.89, H 6.04; found C 34.55, H 6.07.

Sodium Tris(dimethyl phosphito-P)(pentamethylcyclopentadienyl)cobaltate(1−), $Na[L^{*}_{Co,OMe}]$ (**2a**): 5.34 g (4.85 mmol) of **1a** was suspended in 200 ml of methanol and air was bubbled through the mixture. Over a period of 30 min, 1.66 g (33.9 mmol) of sodium cyanide was added in small portions. The clear solution was then concentrated to dryness, the residue was dissolved in dichloromethane, and the resulting solution was filtered. Evaporation of the solvent gave yellow crystals (yield: 5.10 g, 9.07 mmol, 94%). – IR (KBr): $\tilde{\nu}$ = 1157 cm^{-1} [vs, ν(P=O)], 576 [s, δ(P=O)]. – ^{1}H NMR (80.1 MHz, $CDCl_3$): δ = 3.9 (br. s, H_2O), 3.5 (pseudo q, $^3J_{POCH}$ = 10 Hz, 18H, OCH_3), 1.6 (q, $^4J_{PCoCCH}$ = 2 Hz, 15H, C_5Me_5). – $C_{16}H_{33}CoNaO_9P_3 \cdot H_2O$ (562.29): calcd. C 34.18, H 6.27; found C 33.66, H 6.11.

Bis[tris(diethyl phosphito-P)(pentamethylcyclopentadienyl)cobalt-O,O′,O″]cobalt(II), $[Co(L^{*}_{Co,OEt})_2]$ (**1b**): $[\{C_5Me_5\}$-$Co(acac)]$ was prepared as described above from 4.02 g (28.3 mmol) of LiC_5Me_5 and 6.90 g (26.8 mmol) of $[Co(acac)_2]$, and then heated with a threefold excess of diethyl phosphite at 120°C overnight. The resulting suspension was worked-up as described above (yield: 9.01 g, 7.10 mmol, 79% of an orange powder). – IR (KBr): $\tilde{\nu}$ = 1124 cm^{-1} [vs, ν(P=O)], 594 [vs, δ(P=O)]. – $C_{44}H_{90}Co_3O_{18}P_6$ (1269.83): calcd. C 41.62, H 7.14; found C 41.62, H 7.24.

Sodium Tris(diethyl phosphito-P)(pentamethylcyclopentadienyl)cobaltate(1−), $Na[L^{*}_{Co,OEt}]$ (**2b**): The cleavage of **1b** (9.01 g, 7.10 mmol) with sodium cyanide (2.43 g, 49.6 mmol) in 150 ml of methanol was performed as described above. The reaction mixture was concentrated to dryness, stirred with 100 ml of diethyl ether, and filtered. Removal of the solvent and drying in vacuo gave a yellow crystalline product (yield: 8.80 g, 13.6 mmol, 96%). – IR (KBr): $\tilde{\nu}$ = 1158 cm^{-1} [vs, ν(P=O)], 575 [s, δ(P=O)]. – ^{1}H NMR (80.1 MHz, $CDCl_3$): δ = 3.5 (br. s, H_2O), 3.9 (q/pseudo q, $^3J_{HCCH}$ = 7 Hz, $^3J_{POCH}$ = 7 Hz, 12H, OCH_2), 1.6 (q, $^4J_{PCoCCH}$ = 2 Hz, 15H, C_5Me_5), 1.2 (t, $^3J_{HCCH}$ = 7 Hz, 18H, CH_3). – $C_{22}H_{45}CoNaO_9P_3 \cdot H_2O$ (646.46): calcd. C 40.88, H 7.33; found C 40.76, H 7.34.

Bis[cyclopentadienyltris{bis(2-ethylhexyl) phosphito-P}cobalt-O,O′,O″]cobalt(II), $[Co(L_{Co,O-2-Et-Hex})_2]$ (**1c**): 1.13 g (5.97 mmol) of cobaltocene and 5.37 ml (18.0 mmol) of di(2-ethylhexyl) phosphite were heated without solvent to 140°C for 40 h. Cyclopentadiene was then distilled off and the yellow-brown slurry was stirred with 25 ml of methanol. A bright-yellow solid precipitated, which was filtered off, dried under reduced pressure, and chromatographed on a silica gel column (15 cm). Excess phosphite was eluted with hexane, and then the product was eluted with methanol. After evaporation of the solvent, the orange, highly viscous residue was dissolved in hexane, the resulting solution was filtered through a membrane, and the filtrate was concentrated to dryness (yield: 3.55 g, 1.66 mmol, 83%). – IR (KBr): $\tilde{\nu}$ = 1128 cm^{-1} [s, ν(P=O)], 596 [s, δ(P=O)].

Sodium Cyclopentadienyltris{bis(2-ethylhexyl) phosphito-P}cobaltate(1−), $Na[L_{Co,O-2-Et-hex}]$ (**2c**): A suspension of 2.08 g (0.970 mmol) of **1c** and 290 mg (5.90 mmol) of sodium cyanide in 50 ml of methanol was refluxed for three days. The yellow reaction mixture was then concentrated and the residue was subjected to a Soxhlet extraction with hexane, with exposure to air. The Soxhlet extraction was repeated with dichloromethane to yield an orange, highly viscous oil (yield: 0.79 g, 0.74 mmol, 38%). – IR (KBr): $\tilde{\nu}$ = 1141 cm^{-1} [s, ν(P=O)], 586 [s, δ(P=O)]. – ^{1}H NMR (80.1 MHz, $CDCl_3$): δ = 5.03 (s, 5H, C_5H_5), 3.9–3.7 (m, 12H, OCH_2), 1.6–1.2 (m, 54H, CH, CH_2), 1.1–0.8 (m, 36H, CH_3). – $^{13}C\{^1H\}$ NMR (67.9 MHz, C_6D_6): δ = 89.6 (s, C_5H_5), 66.3 (br. s, OC^aH_2), 41.3 (s, C^bH), 31.0 (s, C^cH_2), 29.6 (s,C^dH_2), 24.2 (s, C^gH_2), 23.7 (s, C^eH_2), 14.4 (s, C^fH_3), 11.6 (s, C^hH_3) with $OC^aH_2C^bH(C^gH_2C^hH_3)$-$C^cH_2C^dH_2C^eH_2C^fH_3$. – $^{31}P\{^1H\}$ NMR (32.4 MHz, $CDCl_3$, −40°C): δ = 104.1 (s). – $C_{53}H_{107}CoNaO_9P_3 \cdot H_2O$ (1081.29): calcd. C 58.87, H 10.16; found C 58.70, H 10.16.

Bis[cyclopentadienyltris{diphenyl phosphito-P}cobalt-O,O′,O″]-cobalt(II), $[Co(L_{Co,OPh})_2]$ (**1d**): To a suspension of 10.0 g (29.9 mmol) of cobalticenium hexafluorophosphate in 50 ml of diethyl ether at −78°C, 18.7 ml (29.9 mmol) of 1.6 M *n*-butyllithium in hexane was slowly added. After 30 min, the dark-red solution was allowed to warm to room temperature and the solvent was evaporated. Then, 23.0 ml (120 mmol) of diphenyl phosphite was added and the reddish-brown reaction mixture was heated to 80°C for 10

h. The resulting yellow-brown suspension was washed with two 50-ml portions of hexane and then with several 20-ml portions of methanol. The beige-coloured precipitate was filtered off, redissolved in dichloromethane, and this solution was filtered through Celite. After evaporation of the solvent, the product was obtained as yellow crystals by recrystallization from dichloromethane/hexane (yield: 9.52 g, 5.58 mmol, 56%). – IR (KBr): $\tilde{\nu}$ = 3063 and 3037 cm^{-1} [w, ν(C−H)], 1591 (s), 1489 (vs) and 1453 (w) [ν(C=C)], 1215 and 1193 [vs, ν(P−OAryl)], 1161 (s), 1138 [vs, ν(P=O)], 887 [vs, δ(P=O)], 756 and 688 [s, γ(C−H)]. – ^1H NMR (200.1 MHz, $CDCl_3$): δ = 36.5 (br. s, 10H, C_5H_5), −1.02 (br. s, 12H, 3-H of C_6H_5), −5.04 (br. s, 24H, 2-H of C_6H_5), −21.42 (br. s, 24H, 1-H of C_6H_5). – $C_{82}H_{70}Co_3O_{18}P_6$ (1706.09): calcd. C 57.73, H 4.14; found C 58.04, H 4.09.

Sodium Cyclopentadienyltris(diphenyl phosphito-P)cobaltate-(1−), Na[$L_{Co,OPh}$] (**2d**). – *Method A:* 180 mg (6.00 mmol) of sodium hydride (80% in paraffin oil) was added to a solution of 1.53 ml (7.99 mmol) of diphenyl phosphite in 20 ml of THF. Evolution of gas occurred; after about 30 min the reaction was complete. To the clear, yellowish solution, 15 ml of THF and 406 mg (1.00 mmol) of [$(C_5H_5)CoI_2(CO)$] were added. The reaction mixture was stirred for 1 h at room temperature and then heated to reflux for 22 h. The cooled suspension was subsequently hydrolysed with a small amount of water and the solvent was removed in vacuo. The residue was stirred with two 20 ml portions of hexane and then washed with a large volume of water and a small amount of methanol. Filtration with diethyl ether through Celite and evaporation of the solvent gave a yellow powder, which was crystallized by slow diffusion of hexane into a dichloromethane solution (yield: 0.38 g, 0.45 mmol, 45%).

Method B: 8.51 g (5.00 mmol) of **1d** was suspended in 50 ml of toluene and 10 ml of methanol. Over a period of 30 min, 1.87 g (35.0 mmol) of NaCN was added in small portions while air was bubbled through the suspension. After stirring for 4 h, the solvent was removed from the yellow solution in vacuo. The off-yellow residue was extracted with 40 ml of dichloromethane, the resulting yellow solution was filtered through Celite and the filtrate was concentrated in vacuo. The yellow powder was recrystallized from dichloromethane/hexane (yield: 7.13 g, 8.42 mmol, 84%). – IR (KBr): $\tilde{\nu}$ = 3064 cm^{-1} [w, ν(C−H)], 1591 (s) and 1490 (vs) [ν(C=C)], 1213, 1192 [vs, ν(P−OAryl)], 1159 [s, ν(P=O)], 873 [vs, δ(P=O)], 764 and 690 [s, γ(C−H)]. – ^1H NMR (80.1 MHz, $CDCl_3$): δ = 6.9–6.8 (m, 30H, C_6H_5), 5.67 (s, 5H, C_5H_5). – $^{31}P\{^1H\}$ NMR (81.0 MHz, $CDCl_3$): δ = 103.8 (br. s). – $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$): δ = 153.2 (pseudo q, $^2J_{POC}$ = 10.0 Hz, C-1 of C_6H_5), 129.4 (s, C-3 of C_6H_5), 123.8 (s, C-4 of C_6H_5), 122.5 (s, C-2 of C_6H_5), 91.5 (s, C_5H_5). – $C_{41}H_{35}CoNaO_9P_3$ (846.57): calcd. C 58.17, H 4.17; found C 58.16, H 4.23.

Lithium Cyclopentadienyltris(diphenyl phosphito-P)cobaltate(1−), Li[$L_{Co,OPh}$] (**2e**): To a solution of 1.72 ml (9.00 mmol) of diphenyl phosphite in 15 ml of THF at −78°C, 3.50 ml (5.60 mmol) of 1.6 M *n*-butyllithium in hexane was slowly added. After stirring for 2 h, 10 ml of THF and 450 mg (1.11 mmol) of the cobalt complex [$(C_5H_5)CoI_2(CO)$] were added. The reaction mixture turned red at first and then a dark-brown suspension formed. This was stirred for 1 h at −78°C, then for 1 h at room temperature, and finally heated to reflux for 22 h. After cooling to room temperature, several ml of water were added, with exposure to air. On evaporation of the solvents, an ochre oil formed, which was washed several times with a minimum volume of methanol so as to remove most of the phosphite. The pure product was obtained by chromatography on silica and recrystallization from dichloromethane/pentane (yield: 0.58 g, 0.70 mmol, 64%). – IR (KBr): $\tilde{\nu}$ = 3063 and 3037 cm^{-1} [w, ν(C−H)], 1591 (s), 1489 (s) and 1453 (w) [ν(C=C)], 1210 and 1193 [vs, ν(P−OAryl)], 1161 [s, ν(P=O)], 767 and 692 [s, γ(C−H)]. – ^1H NMR (80.1 MHz, CD_2Cl_2): δ = 7.0–6.7 (m, 30H, C_6H_5), 5.67 (s, 5H, C_5H_5). – $^{13}C\{^1H\}$ NMR (67.9 MHz, $CDCl_3$): δ = 152.7 (pseudo. q, $^2J_{POC}$ = 13.6 Hz, C-1 of C_6H_5), 128.9 (s, C-3 of C_6H_5), 123.0 (s, C-4 of C_6H_5), 121.6 (s, C-2 of C_6H_5), 90.8 (s, C_5H_5). – ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 152.8–152.4 (m, C-1 of C_6H_5), 128.8 (d/m, $^1J_{HC}$ = 158.7 Hz, C-3 of C_6H_5), 123.0 (d/t, $^1J_{HC}$ = 160.4 Hz, $^3J_{HCCC}$ = 7.5 Hz, C-4 of C_6H_5), 121.6 (br. d, $^1J_{HC}$ = 162.8 Hz, C-2 of C_6H_5), 90.8 (d/t, $^1J_{HC}$ = 182.1 Hz, $^2J_{HCC}$ = 6.4 Hz, C_5H_5). – $^{31}P\{^1H\}$ NMR (32.4 MHz, $CDCl_3$, −60°C): δ = 103.4 (s). – $C_{41}H_{35}CoLiO_9P_3$ (830.52): calcd. C 59.29, H 4.25; found C 59.47, H 4.25. – Mol. mass 1610 (osmometry in CH_2Cl_2).

Lithium Cyclopentadienyltris(diisopropyl phosphito-P)cobaltate(1−), Li[$L_{Co,OiPr}$] (**2f**): 1.75 ml (2.80 mmol) of a 1.6 M solution of *n*-butyllithium in hexane was slowly added to a solution of 0.75 ml (4.5 mmol) of diisopropyl phosphite in 8 ml of THF at −78°C. After stirring for 2 h, 20 ml of THF and 225 mg (0.560 mmol) of [$(C_5H_5)CoI_2(CO)$] were added. The mixture was kept at −78°C for 1 h, then left for 1 h at room temperature, and was finally heated to reflux for 22 h. The colour changed from dark-violet to yellow-brown. After cooling to room temperature, a small amount of water was added to hydrolyse the excess lithium phosphite. The solution was concentrated in vacuo, and the ochre precipitate was centrifuged in air, washed several times with water and then with small portions of methanol. The crude product was dried in vacuo and crystallized by slow diffusion of pentane into a dichloromethane solution. Pale-yellow air-stable needles were obtained (yield: 0.28 g, 0.44 mmol, 79%). The product could be prepared in similar yields from the polymeric iodide complex [$(C_5H_5)CoI_2]_n$. – IR (KBr) $\tilde{\nu}$ = 1158–1106 cm^{-1} [s, ν(P=O)], 578 [s, δ(P=O)]. – ^1H NMR (80.1 MHz, $CDCl_3$): δ = 4.80 (s, 5H, C_5H_5), 4.9–4.5 (m, 6H, OCH), 1.23 (d, $^3J_{HCCH}$ = 6.2 Hz, 18H, CH_3), 1.20 (d, $^3J_{HCCH}$ = 6.1 Hz, 18H, CH_3). – $C_{23}H_{47}CoLiO_9P_3$ (626.42): calcd. C 44.10, H 7.56; found C 44.08, H 7.56. – Mol. mass 1442 (osmometry in CH_2Cl_2).

Lithium Tris(diisopropyl phosphito-P)(pentamethylcyclopentadienyl)cobaltate(1−), Li[$L^*_{Co,OiPr}$] (**2g**): A solution of Li[P(O){$OCH(CH_3)_2\}_2$] in 50 ml of THF at −78°C was prepared from 1.33 ml (7.98 mmol) of diisopropyl phosphite and 3.75 ml (6.00 mmol) of 1.6 M *n*-butyllithium in hexane, as described above. 530 mg (1.00 mmol) of the cobalt complex [$(C_5Me_5)CoCl_2]_2$[34−37] was then added and the mixture was stirred for 1 h at −78°C, for 1 h at room temperature, and finally heated to reflux for 22 h. Excess lithium phosphite was hydrolysed with a small amount of water. The solvent was removed in vacuo, and the residue was washed with water, with exposure to air. After removing the phosphite in high vacuum at about 50°C, a yellow powder was obtained, which was washed twice with a large volume of water and a small amount of methanol. The pale-yellow product was dried in vacuo and crystallized from pentane (yield: 1.03 g, 1.48 mmol, 74%). – IR (KBr): $\tilde{\nu}$ = 1155–1108 cm^{-1} [s, ν(P=O)], 585 [s, δ(P=O)]. – ^1H NMR (80.1 MHz, $CDCl_3$): δ = 4.8–4.7 (m, 6H, OCH), 1.58 (q, $^4J_{PCoCCH}$ = 1.8 Hz, 15H, C_5Me_5), 1.24 (d, $^3J_{HCCH}$ = 6.2 Hz, 18H, CH_3), 1.20 (d, $^3J_{HCCH}$ = 6.1 Hz, 18H, CH_3). – $^{13}C\{^1H\}$ NMR (67.9 MHz, $CDCl_3$): δ = 98.8 (s, C_5Me_5), 66.3 (s, OCH), 25.1 (s, CH_3), 24.7 (s, CH_3), 10.8 (s, C_5Me_5). – ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 98.8 (s, C_5Me_5), 66.4 (d, $^1J_{HC}$ = 145.0 Hz, OCH), 25.2 (q, $^1J_{HC}$ = 124.4 Hz, CH_3), 24.7 (q, $^1J_{HC}$ = 124.4 Hz, CH_3), 10.8 (q, $^1J_{HC}$ = 128.1 Hz, C_5Me_5). – $^{31}P\{^1H\}$ NMR (32.4 MHz, $CDCl_3$, −50°C): δ = 106.5 (br. s). – $C_{28}H_{57}CoLiO_9P_3$ (696.55): calcd. C 48.28, H 8.25; found C 48.11, H 8.40.

Lithium Cyclopentadienyltris(diisopropyl phosphito-P)rhodate(1−), $Li[L_{Rh,OiPr}]$ (**2h**): $Li[P(O)\{OCH(CH_3)_2\}_2]$ was prepared as described above from 1.33 ml (7.98 mmol) of diisopropyl phosphite in 15 ml of THF and 3.75 ml (6.00 mmol) of 1.6 M *n*-butyllithium in hexane at −78°C. To the solution was added 25 ml of THF and 450 mg (1.00 mmol) of the rhodium complex $[(C_5H_5)RhI_2(CO)]$. The suspension was stirred for 1 h at −78°C, and then for 1 h at room temperature, whereupon a clear, red-brown solution was obtained. Heating to reflux for 22 h yielded an orange solution. After cooling to room temperature, a small amount of water was added to hydrolyse the excess lithium phosphite. The solvent was removed in vacuo and the residue was washed with water, with exposure to air. The excess phosphite was distilled off in vacuo at about 50°C. The slightly sticky powder was alternately washed with large volumes of water and small volumes of methanol. The pale, sand-coloured powder was dried in vacuo (yield: 0.29 g, 0.43 mmol, 43%). An additional crop of 108 mg (16%) of crude product could be obtained from the combined methanol solutions. − IR (KBr): $\tilde{\nu} = 1167-1107\ cm^{-1}$ [s, $\nu(P=O)$], 583 [s, $\delta(P=O)$]. − ^1H NMR (80.1 MHz, $CDCl_3$): $\delta = 5.19$ (q/d, $^3J_{PRhCH} = 2.4$ Hz, $^2J_{RhCH} = 0.5$ Hz, 5H, C_5H_5), 4.8−4.7 (m, 6H, OCH), 1.20 (d, $^3J_{HCCH} = 6.2$ Hz, 18H, CH_3), 1.17 (d, $^3J_{HCCH} = 6.1$ Hz, 18H, CH_3). − $^{13}C\{^1H\}$ NMR (67.9 MHz, $CDCl_3$): $\delta = 93.2$ (s, C_5H_5), 66.6 (s, OCH), 24.6 (s, CH_3). − ^{13}C NMR (67.9 MHz, $CDCl_3$): $\delta = 93.2$ (d/m, $^1J_{HC} = 182.2$ Hz, C_5H_5), 66.6 (d, $^1J_{HC} = 145.2$ Hz, OCH), 24.5 (q, $^1J_{HC} = 124.1$ Hz, CH_3). − $^{31}P\{^1H\}$ NMR (32.4 MHz, $CDCl_3$): $\delta = 82.7$ (d, $^1J_{RhP} = 187.8$ Hz).

Sodium Cyclopentadienyltris(dimethyl phosphito-P)rhodate(1−), $Na[L_{Rh,OMe}]$ (**2i**): A solution of 5.00 ml (42.4 mmol) of trimethylphosphite in 40 ml of acetone was slowly added to a stirred suspension of 4.34 g (9.70 mmol) of $[(C_5H_5)RhI_2(CO)]$ in 400 ml of acetone. Evolution of gas occurred and within 24 h the colour changed from dark-violet to yellow. A small amount of a white solid precipitated, which was filtered off. Subsequently, a solution of 11.0 g (73.4 mmol) of NaI in 40 ml of acetone was added dropwise to the reaction mixture. After about 15 minutes, a white precipitate started to form. The mixture was stirred for 24 h. The yellow-to-greenish solution was decanted from the product, which was washed with small amounts of acetone and subsequently dried in vacuo. The product could be recrystallized from methanol at −78°C or by slow diffusion of diethyl ether into a methanolic solution at room temperature. In either case, it was contaminated with sodium iodide[38]. − IR (KBr): $\tilde{\nu} = 1150\ cm^{-1}$ [vs, $\nu(P=O)$], 570 [vs, $\delta(P=O)$]. − ^1H NMR (80.1 MHz, CD_3OD): $\delta = 5.51$ (q, $^1J_{PRhCH} = 2.7$ Hz, 5H, C_5H_5), 3.58 (pseudo q, $^3J_{POCH} = 11.6$ Hz, 18H, OCH_3). − $^{31}P\{^1H\}$ NMR (32.4 MHz, D_2O): $\delta = 91.9$ (d, $^1J_{RhP} = 190.8$ Hz).

Crystal-Structure Determination: Suitable crystals of $NaL_{Co,OPh}$ (**2d**) were obtained by slow diffusion of hexane into a dichloromethane solution of the sodium salt. An orange, translucent parallelepiped of approximate dimensions 0.4 × 0.4 × 0.3 mm was used for geometry and intensity data collection at room temperature with Mo-K_α radiation ($\lambda = 0.71073$ Å) on an Enraf-Nonius CAD4 diffractometer equipped with a graphite monochromator. Crystal data: $C_{41}H_{35}CoNaO_9P_3$, formula weight 846.58 g · mol^{-1}, monoclinic space group $P2_1/n$ (no. 14), $a = 14.238(3)$, $b = 20.705(7)$, $c = 14.864(6)$ Å, $\beta = 116.23(3)°$, $V = 3931(5)$ Å^3, $Z = 4$, $D_{calcd.} = 1.430$ g · cm^3, μ(Mo-K_α) = 6.18 cm^{-1}, $F(000) = 1744$. 5883 reflections with ω-scan in the range $3.0 < \Theta < 23.0$ in the $hk \pm l$ quadrant of the diffraction sphere, empirical absorption correction on the basis of azimuthal scans[43] with relative min. transmission 0.93, max. trans. 1.00, 4239 unique observations with $I > 1.0\ \sigma(I)$. Structure solution by direct methods[44], refinement on F with the SDP program system[45]. Convergence for 497 variables (anisotropic displacement parameters for non-hydrogen atoms, hydrogen atoms in calculated positions with C−H = 0.98 Å, $U_{iso}(H) = 1.3 \cdot U_{eq}(C)$) at $R = 0.044$, $R_w = 0.047$ [$w^{-1} = (\sigma_{F_{obs}})^2$]. Further details of the crystal structure investigation are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-406976, the names of the authors, and the journal citation.

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