Samples of $3 \cdot 0.167C_6H_6$ were dissolved in CH_2Cl_2 and kept at −25 °C for several days. Orange irregular crystals of unsolvated **3** precipitated, which were collected by filtration and dried in vacuo (78 °C); mp 152–171 °C dec. Anal. Calcd for $C_{30}H_{25}Cl_5NOP_2Re$: C, 42.85; H, 3.00; Cl, 21.08. Found: C, 43.06, 42.89; H, 3.13, 3.05; Cl, 20.63, 21.47.

Crystal Structure of 3. Unit cell determination and data collection were performed on a Syntex P$\bar{1}$ diffractometer as outlined in Table II (see also supplementary material). The unit cell was determined using 15 centered reflections with $16° < 2\theta < 29°$. A structure was solved with standard heavy-atom techniques, using the UCLA crystallographic package.[39] Empirical absorption corrections were made, and hydrogen atoms were placed in calculated positions. Non-hydrogen atoms were refined with anisotropic thermal parameters. No extinction corrections were made.

Reactions of 2, 9, and 10 with Potential Halide-Abstracting Reagents and Related Compounds. Full details of these experiments are described elsewhere.[9] Representative reactions are as follows.

Experiment A. A 5-mm NMR tube was charged with **9** (0.030 g, 0.045 mmol) and $Ph_3C^+PF_6^-$ (0.018 g, 0.046 mmol) and was capped with a septum, connected to a vacuum line, and evacuated. The tube was cooled to −196 °C and CH_2Cl_2 (0.400 mL) was added. The mixture was freeze–thaw (ca. −90 °C) degassed and placed under N_2. The sample was transferred to a −91 °C NMR probe. $^{31}P\{^1H\}$ NMR: 126.65 (br s), 107.04 (br s), 7.78 ppm (d, J_{PP} = 14.0 Hz); no $^1J_{PH}$ coupling was observed in the ^{1}H-coupled spectrum. The 126.65 and 107.04 resonances showed reversible coalescence (T_c ca. −60 °C) to a broad singlet at 118.38 ppm (−30 °C); the 7.78 ppm resonance did not exhibit temperature dependence (−91 to −30 °C). The sample was kept at room temperature for 10 min and then returned to the −30 °C NMR probe. The $^{31}P\{^1H\}$ NMR spectrum showed the disappearance of the resonances noted above and a new major product [132.57 (d, J_{PP} = 23.0 Hz), 10.87 ppm (d, J_{PP} = 23.0 Hz)] and minor product resonances; no $^1J_{PH}$ coupling was observed in the ^{1}H-coupled spectrum.

Experiment B. A Schlenk tube was charged with **9** (0.283 g, 0.424 mmol), $Ph_3C^+PF_6^-$ (0.165 g, 0.425 mmol), and a stir bar and was cooled to −78 °C. Then THF (5 mL) was added by syringe, and the mixture was stirred. The resulting red slurry was transferred to a −23 °C bath. Within 30 min a yellow precipitate formed. The cold bath was removed, and when the mixture reached room temperature, the solid was collected by filtration, washed with THF (1 mL), washed with hexane (2 × 5 mL), and dried in vacuo (56 °C). This gave a yellow solid in low yield (0.047 g); mp 155–161 °C dec. Data: IR (cm^{-1}, KBr) 3125–2868 w, ν_{NO} 1710 vs, 1483 m, 1464 m, 1436 m, 1420 m, 1400 w, 1369 w, 1162 w, 1151 w, 1090 m, 1063 m, 1027 w, 1014 w, 1000 w, ν_{PF} 840 vs vbr, 773 m, 746 m, 699 s, 649 w, 632 w, 624 w; $^{31}P\{^1H\}$ NMR (ppm, CD_2Cl_2, −41 °C) 132.36 (d, J_{PP} = 23.0 Hz), 10.95 (d, J_{PP} = 23.0 Hz); ^{1}H NMR (δ, CD_2Cl_2, −15 °C) 7.58–7.33 (m, 20 H), 7.13–7.09 (m, 5 H), 6.83–6.76 (m, 1 H), 6.33–6.26 (m, 1 H), 6.02–5.93 (m, 1 H), 5.75 (s, 5 H, C_5H_5), 5.01 (br d, J_{HP} = ca. 36 Hz, 1 H), 4.90–4.82 (m, 1 H), 3.71–3.67 (m, 1.0 × 4 H, THF solvate), 1.85–1.80 (m, 1.0 × 4 H, THF solvate), 1.52 (d, J_{HP} = 17.7 Hz, 9 H, *t*-Bu); $^{13}C\{^1H\}$ NMR (ppm, CD_2Cl_2, −15 °C) phenyl/vinyl carbons and 92.28 (s, C_5H_5), 68.15 (s, THF), 48.17 (d, J_{CP} = 20.7 Hz, *C*Me$_3$), 28.08 (br s, CH_3).

Experiment C. A 5-mm NMR tube was charged with **10** (0.065 g, 0.086 mmol) and CH_2Cl_2 (0.100 mL) and was capped with a septum, connected to a vacuum line, cooled to −196 °C, and evacuated. Then a solution of $Ph_3C^+PF_6^-$ (0.037 g, 0.095 mmol) in CH_2Cl_2 (0.300 mL) was added by syringe and the mixture was freeze–thaw (ca. −90 °C) degassed and placed under N_2. The sample was transferred to a −90 °C NMR probe and gradually warmed. The $^{31}P\{^1H\}$ NMR spectrum showed a product that persisted up to room temperature. No decomposition was observed after 10 min at room temperature, but attempted recrystallization from CH_2Cl_2/ether was unsuccessful. Spectral data: $^{31}P\{^1H\}$ NMR (ppm, CH_2Cl_2, −30 °C) 133.58 (d, J_{PP} = 21.8 Hz), 11.29 (d, J_{PP} = 21.8 Hz); no $^1J_{PH}$ coupling was observed in the ^{1}H-coupled spectrum.

Experiment D. A 5-mm NMR tube was charged with **10** (0.35 g, 0.046 mmol) and $AlCl_3$ (0.012 g, 0.092 mmol) and was capped with a septum, connected to a vacuum line, and evacuated. The tube was cooled to −196 °C, and CH_2Cl_2 (0.400 mL) was added. The mixture was freeze–thaw (ca. −90 °C) degassed and placed under N_2. The sample was transferred to a −90 °C NMR probe. $^{31}P\{^1H\}$ NMR (ppm, −90 °C): 143.2 (br s), 13.2 (br s), and minor resonances. The 143 ppm resonance showed $^1J_{PH}$ = 489 Hz in a ^{1}H-coupled spectrum. Extensive deterioration of the sample began upon warming to −50 °C.

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Supplementary Material Available: Full versions of Tables II, IV, and V and a table of anisotropic thermal parameters (4 pages); a table of calculated and observed structure factors for **3** (22 pages). Ordering information is given on any current masthead page.

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[39] Programs employed included CARESS (R. W. Broach, Argonne National Laboratory; CARESS incorporates features of PROFILE: Blessing, R. G.; Coppend, P.; Becker, P. *J. Appl. Cryst.* **1972**, *7*, 488), NORMAL, EXFFT, and SEARCH (all from the MULTAN 80 package, Peter Main, Department of Physics, University of York, York, England) and ORFLS (ORNL-TM-305), ORFE (ORNL-TM-306), and ORTEP (ORNL-TM-5138).

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The Reaction of Cobaltocene with Secondary Phosphine Oxides Revisited. Trapping of an Intermediate Cobalt(I) Complex

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The secondary phosphine oxides $HP(O)R_2$ (R = *n*-butyl (**1a**), isobutyl (**1b**), cyclohexyl (**1c**)) and 9*H*-9-phosphabicyclononane 9-oxide (**1d**) have been prepared. They react at room temperature with bis(cyclopentadienyl)cobalt to yield dihydrogen and cobalt(I) compounds of the type $[(C_5H_5)Co(1\text{-}exo\text{-}R'\text{-}C_5H_5)]$ (R′ = P(O)R_2 (**2a–d**)). The complexes **2a,b** have also been prepared from cobaltocenium iodide and in situ prepared solutions of KP(O)(*n*-butyl)$_2$ and KP(O)(isobutyl)$_2$, respectively. Bis(cyclopentadienyl)cobalt, **2a**, and $[(C_5H_5)Co(1\text{-}exo\text{-}Ph\text{-}C_5H_5)]$ have been shown to react with **1a,b** (but not with the more bulky phosphine oxides **1c,d**) above 100 °C to give the trinuclear cobalt(III, II) complexes $[Co((C_5H_5)Co(P(O)R_2)_3)_2]$ (**3a,b**). **3a** is cleaved by sodium cyanide in the presence of air to yield $Na[(C_5H_5)Co(P(O)R_2)_3]$ (**4a**) and $Na_3[Co(CN)_6]$.

1. Introduction

The chemistry of cobaltocene (bis(cyclopentadienyl)cobalt) is dominated by its tendency to act as an electron-rich radical that can undergo one-electron-oxidation, ring-addition, and ring-substitution reactions. Secondary phosphites react with cobaltocene in a complex manner that includes both oxidation and ring substitution to produce the trinuclear complexes $[Co((C_5H_5)Co(P(O)R_2)_3)_2]$ (R = alkoxy, **3**) in good yields. This reaction is of high synthetic value since it gives ready access to the anionic complexes $[(C_5H_5)Co(P(O)R_2)_3]^-$ (R = alkoxy, **4**), an interesting class of tris-chelating oxygen ligands. An important feature of these ligands is their rich and unusual organometallic chemistry.[1] Recently we have found that the steric as well as the electronic

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[1] See e.g.: (a) Kläui, W.; Müller, A.; Eberspach, W.; Boese, R.; Goldberg, I. *J. Am. Chem. Soc.* **1987**, *109*, 164 and references cited therein. (b) Kläui, W.; Müller, A.; Herbst, R.; Egert, E. *Organometallics* **1987**, *6*, 1824. (c) Kläui, W.; Hamers, H. *J. Organomet. Chem.* **1988**, *345*, 287.

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Table I. P-H Stretching Frequencies of the Compounds HPR_2 and $HP(O)R_2$ (**1a-d**; in Tetrachloroethylene, cm^{-1})

PR_2	HPR_2	$HP(O)R_2$
$P(CH_2CH_2CH_2CH_3)_2$ (**a**)	2285	2300
$P(CH_2CH(CH_3)_2)_2$ (**b**)	2280	2315
$P(CHCH_2CH_2CH_2CH_2CH_2)_2$ (**c**)	2260	2285
$PCHCH_2CH_2CH_2CHCH_2CH_2CH_2$, $PCHCH_2CH_2CHCH_2CH_2CH_2CH_2$ (**d**)	2260	2305

properties can be controlled by the substituents on the phosphorus atoms.[2] We have therefore tried to prepare the series of analogue ligands $[(C_5H_5)Co(P(O)R_2)_3]^-$ (**4**) where the six *alkoxy* groups have been replaced by various *alkyl* groups.

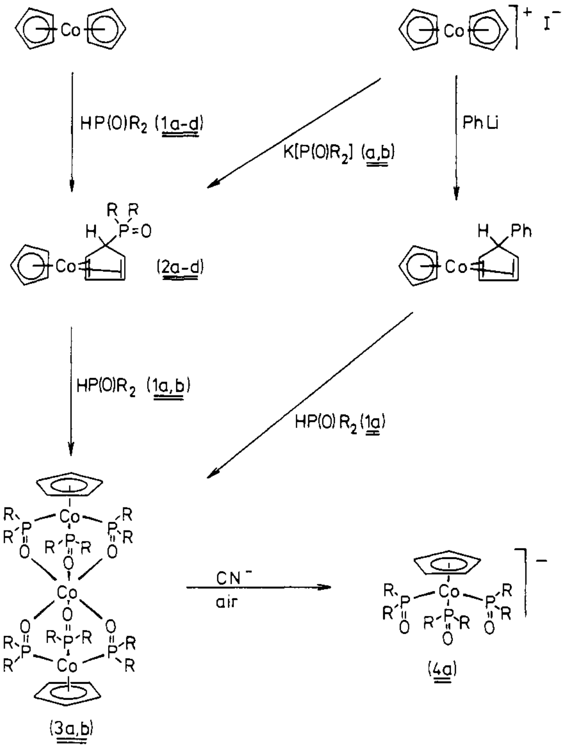
2. Results

2.1. Secondary Phosphine Oxides $HP(O)R_2$ (1a-d). We have synthesized the secondary phosphine oxides by oxidation of the secondary phosphines with dry air in anhydrous isopropyl alcohol according to the general procedure given by Rauhut.[3] The products **1a-c** were isolated as deliquescent colorless crystals, whereas the bicyclic phosphine oxide **1d**, a mixture of the [3.3.1] and [4.2.1] isomers, could not be crystallized. To prevent further oxidation of the phosphine oxides to phosphinic acids, the reaction was monitored by IR spectroscopy (ν(P-H) vibrations of the phosphines HPR_2 and the phosphine oxides $HP(O)R_2$; Table I).

2.2. Reaction of Cobaltocene with Secondary Phosphine Oxides.[4] When a 1:2 mixture of cobaltocene and secondary phosphites $HP(O)(OR)_2$ is heated without solvent to 100-140 °C, a black viscous slurry results, from which after a few hours air-stable orange crystals of $[Co((C_5H_5)Co(P(O)(OR)_2)_3)_2]$ separate. With $OR = OC_2H_5$ the yield of this reaction is 90%.[5] Cobaltocene and the secondary phosphine oxides $HP(O)R_2$ (**1a,b**) under the same reaction conditions give the trinuclear compounds **3a** and **3b** in 42 and 8% yield, respectively. However, no formation of **3c,d** was observed from the reaction of **1c** and **1d** with cobaltocene. At lower temperatures (20-70 °C) the compounds **3** could not be synthesized at all. Instead quantitative formation of the cobalt(I) cyclopentadiene complexes $[(C_5H_5)Co(1\text{-}exo\text{-}P(O)R_2\text{-}C_5H_5)]$ (**2a-d**) was observed. The compounds **2a-d** (see Scheme I) could all be isolated as red-black crystals. They are very sensitive to air and moisture in solution as well as in the solid state. Their composition and structure follow from the elemental analyses and the IR and NMR data. The ^1H NMR[6,7] as well as the ^{13}C NMR spectra[8] and the IR spectra[9] show the characteristic pattern of cobalt(I) complexes of the type $[(C_5H_5)Co(1\text{-}exo\text{-}R\text{-}C_5H_5)]$ (see below). **2a,b** are also accessible from cobaltocenium iodide and the potassium salts $KP(O)R_2$ ($R = n\text{-}C_4H_9$, $i\text{-}C_4H_9$). The complex **2a** reacts with **1a** to give the trinuclear complex **3a** (see Discussion).

In an attempt to purify the compound **2b** by chromatography on silica, we observed a clean and fast hydrolysis of the ring-phosphorus bond. The red-brown band that was eluted proved to contain $[(C_5H_5)Co(C_5H_6)]$,[6] not the starting compund $[(C_5H_5)Co(1\text{-}exo\text{-}(P(O)(CH_2CH(CH_3)_2)_2)\text{-}C_5H_5)]$. Solvolysis of the ring-phosphorus bond also occurs in $CDCl_3$ at room temperature after several hours.[10]

Scheme I. Reaction Sequence for the Preparation of the Cobalt Complexes **2-4**



3. Discussion

The Cobalt(I) Complexes $[(C_5H_5)Co(1\text{-}exo\text{-}P(O)R_2\text{-}C_5H_5)]$ (2a-d): Are They Intermediates in the Synthesis of the Trinuclear Complexes 3? The unexpected isolation of the compounds **2a-d** from the reaction of cobaltocene with the secondary phosphine oxides $HP(O)R_2$ has led to the questions (a) How are they formed? (b) Are they intermediates on the way to the trinuclear complexes **3**? There are two important pathways to synthesize cobalt(I) complexes of the general composition $[(C_5H_5)Co(1\text{-}exo\text{-}R\text{-}C_5H_5)]$ from cobaltocene:

$$[Co(C_5H_5)_2] + RX \rightarrow [Co(C_5H_5)_2]^+X^- + R^\bullet$$
$$[Co(C_5H_5)_2] + R^\bullet \rightarrow [(C_5H_5)Co(1\text{-}exo\text{-}R\text{-}C_5H_5)] \quad (1)$$
$$[Co(C_5H_5)_2] + RH \xrightarrow{O_2 \text{ or } H_2O_2} [(C_5H_5)Co(1\text{-}exo\text{-}R\text{-}C_5H_5)] \quad (2)$$

There is convincing evidence that organic halides react with cobaltocene according to a two-step radical mechanism (eq 1).[7,9,11] The reaction of cobaltocene with the C-H acids RH = acetonitrile, acetone, phenylacetylene, etc.[12] proceeds only in the presence of oxygen. Recently it has been reported that cobaltocene can also react with RH = cyclopentadiene and indene in the presence of hydrogen peroxide as oxidizing agent.[8] Very probably these synthetic routes (eq 2) also involve radical mechanisms. We have observed that the reaction of cobaltocene with the secondary phosphine oxides **1a-d** occurs under an inert atmosphere with evolution of molecular hydrogen.[13] We are not aware of any other example of this type of reaction. The mechanistic details are unclear. Protonation of cobaltocene by the secondary phosphine oxide followed by formation of a cobaltocenium ion and elimination of dihydrogen, an a priori plausible pathway (eq 3 and 4),

$$[Co(C_5H_5)_2] + HP(O)R_2 \xrightarrow{-H_2} [Co(C_5H_5)_2]^+ + P(O)R_2^- \quad (3)$$
$$[Co(C_5H_5)_2]^+ + P(O)R_2^- \rightarrow \mathbf{2a\text{-}d} \quad (4)$$

seems unlikely in view of the most recent results on the kinetics

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(10) From the ^1H NMR spectrum we conclude that the product is $[(C_5H_5)Co(1\text{-}exo\text{-}CDCl_2\text{-}C_5H_5)]$. Cobaltocene reacts with chloroform to give the analogous complex $[(C_5H_5)Co(1\text{-}exo\text{-}CHCl_2\text{-}C_5H_5)]$.[7]

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(13) Hydrogen was identified by GC.

Table II. ^1H NMR Spectral Data (Chemical Shifts (δ) and Coupling Constants (J, Hz)) for **2a–d**[a]

compd[d]	H_a	H_b	H_c	H_d	$^3J(H_bH_c)$	$^3J(H_bP)$	$^2J(H_cP)$
2a	5.15 vt	2.48 p[b]	3.30 dt	4.50 s	2.4	2.4	7.4
2b	5.15 vt	2.50 p[b]	3.33 dt	4.51 s	2.4	1.4	8.0
2c	5.26 vt	2.54 p[b]	3.40 q[c]	4.52 s	2.3	1.7	2.3
2d	5.43 vt 5.19 vt	2.5 m	3.51 p[c] 3.23 p[c]	4.55 s 4.52 s	2.2	2.1	4.4

[a] Measured in C_6D_6 at 80.1 MHz; v is the abbreviation for virtual. [b] Pseudopentet, see text. [c] From overlapping dt. [d] Signals of the groups R: **2a**, 0.7–0.9 (m, 6 H, CH_3), 1.0–1.7 (br m, 12 H, CH_2); **2b**, 0.7–1.3 (d and m, 16 H, CH_2 and CH_3), 1.9–2.2 (m, 2 H, CH); **2c**, 1.0–1.9 (br m, 22 H, C_6H_{11}); **2d**, 1.0–1.9 (br m, 28 H, CH, CH_2).

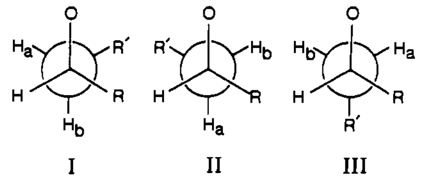


Figure 1. Newman projections along the P–C bonds of the three staggered conformations of secondary phosphine oxides.

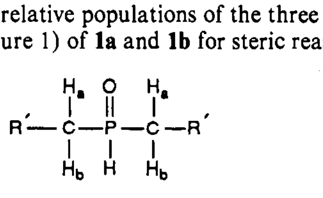
of the reduction of protons by cobaltocene.[14] Nevertheless, this idea has led us to try the reaction of cobaltocenium iodide with the potassium salts $K[P(O)R_2]$ (R = n-C_4H_9, i-C_4H_9). Indeed, the cobalt(I) compounds **2a,b** are formed in high yields. From a preparative point of view this is an interesting alternative since it avoids the air-sensitive cobaltocene.

To answer the question whether the complexes **2** are intermediates in the synthesis of the trinuclear complexes **3**, we heated a mixture of pure **2a** and the secondary phosphine oxide **1a** to about 110 °C and obtained **3a** in good yield. Instead of **2a** we could equally well use the cobalt(I) complex $[(C_5H_5)Co(1\text{-}exo\text{-}Ph\text{-}C_5H_5)]$ as starting compound (see Scheme I). The yield of **3a** is even slightly better (83%). Bönnemann has prepared a series of similar (cyclopentadienyl)cobalt(I) complexes, e.g. compounds of the type $[(C_5H_5)Co(1\text{-exo-R-}C_5H_5)]$ and $[(C_5H_4R)Co(COD)]$ (COD = cyclooctadiene). They are useful catalyst precursors for the formation of pyridines from acetylene and nitriles.[15] He has given clear evidence that the first step leading into the catalytic cycle is the thermal decomposition of the catalyst precursors to produce a (cyclopentadienyl)cobalt fragment. The cyclooctadiene ligand starts to split off readily at ca. 80–120 °C. This is the temperature at which we observe formation of **3a**. It seems therefore reasonable to assume that the formation of **3a** from either **2a** or $[(C_5H_5)Co(1\text{-}exo\text{-}Ph\text{-}C_5H_5)]$ also starts with the formation of a (cyclopentadienyl)cobalt fragment.

4. Spectra

4.1. ^1H NMR Spectra of the Secondary Phosphine Oxides 1a,b.

The ^1H NMR spectra of the phosphine oxides **1a,b** show an interesting difference. The signal of the proton directly bonded to phosphorus occurs as a doublet with a large coupling constant ($^1J(PH)$ = 437 and 438 Hz) with further coupling due to the two diastereotopic vicinal CH_2 protons. This gives rise to pentets for the P–H proton of **1a** but triplets of triplets for the P–H proton of **1b**. The coupling constants $^3J(HPCH_a)$ and $^3J(HPCH_b)$ obviously are very similar in the phosphine oxide **1a** (~3.5 Hz) but very different in **1b** (1.8 and 6.0 Hz). This can be explained if one assumes unequal relative populations of the three staggered conformers I–III (Figure 1) of **1a** and **1b** for steric reasons. The conformer II with its antiperiplanar arrangement of the substituents R and R′ will be favored energetically over I and III, much more so in **1b** than in **1a**. The variation in vicinal coupling constants $^3J(HPCH)$ that we observe is in very good agreement with the calculated Karplus-type angular correlation described by Samitov et al.[16]



$$\begin{array}{ccccccccc} & & H_a & & O & & H_a & & \\ & & | & & \| & & | & & \\ R' & - & C & - & P & - & C & - & R' \\ & & | & & | & & | & & \\ & & H_b & & H & & H_b & & \end{array}$$

1a: $R' = CH_2CH_2CH_3$, $R = CH_2CH_2CH_2CH_3$

1b: $R' = CH(CH_3)_2$, $R = CH_2CH(CH_3)_2$

Table III. Selected ^{13}C NMR Data for the Compounds **2a,b**[a]

compd	C_a	C_b	C_c	C_d	$^2J(C_bP)$	$^1J(C_cP)$
2a	76.65	36.40	54.82	79.59	6.5	34.3
2b	76.62	36.72	56.02	79.59	6.9	33.8

[a] Chemical shifts (δ) and coupling constants (J, Hz) measured in C_6D_6 at 67.9 MHz.

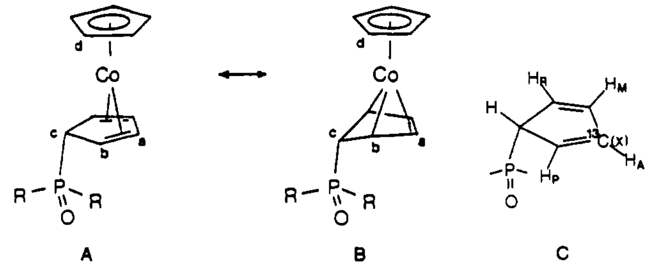


Figure 2. Proposed structure of the cobalt(I) complexes **2a–d** and the numbering scheme for the ring atoms used in the description of the NMR spectra.

4.2. ^1H and ^{13}C NMR Spectra of the Cobalt(I) Compounds $[(C_5H_5)Co(1\text{-}exo\text{-}P(O)R_2\text{-}C_5H_5)]$ (2a–d).

The characteristic ^1H and ^{13}C NMR data for compounds **2a–d** are summarized in Tables II and III. The olefinic protons H_a and H_b of the cyclopentadiene ring form an AA′XX′ spin system. The signal of H_a is a virtual triplet with $|^3J(H_aH_b) + {^4J}(H_aH_{b'})| = 4.0$ Hz. The signal of H_b is a pseudopentet because of additional coupling with H_c and P, with $|^3J(H_aH_b) + {^4J}(H_{a'}H_b)| \approx 2|^3J(H_bH_c)| \approx 2|^3J(H_bP)|$. The cycloaliphatic proton H_c occurs as a doublet of triplets with $^2J(H_cP) \approx 2$–8 Hz and $^3J(H_cH_b) \approx 2$ Hz. The coupling $^4J(H_cH_a)$ is not observed (≤ 0.3 Hz). The values of the coupling constants $^2J(H_cP)$ and $^3J(H_bP)$ indicate the direct link P–C_c. Additional proof comes from the coupling constant $^1J(C_cP) \approx 34$ Hz, which is typical for an aliphatic carbon atom bonded to a $P(O)R_2$ unit.[17] The coupling constants $^3J(H_aH_b)$, $^3J(H_aH_{a'})$, $^4J(H_aH_{b'})$, and $J(H_bH_{b'})$ are not available from the AA′XX′ spectrum because of the virtual appearance of the multiplets. They could, however, be obtained from the ^{13}C satellites[18] of the H_a signal, for example. The ^{13}C satellites of the H_a signal are not the AA′ part of an AA′XX′ spectrum but the A part of an AMPR type spectrum (see Figure 2C). To have a complete set of coupling constants, at least for one of the compounds, we have analyzed the ^{13}C satellite spectrum in the 300-MHz ^1H NMR spectrum of **2b**. We obtained the following values: $^3J(H_aH_b) = 2.5$ Hz, $^3J(H_aH_{a'}) = 2.0$ Hz, $^4J(H_aH_{b'}) = 1.5$ Hz, and $^5J(H_bH_{b'}) = 1.7$ Hz.

We have not been able to grow crystals suitable for an X-ray structure determination. The conformation of the cyclopentadiene ligand is therefore not known. However, the rather high-field

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chemical shifts of H_b ($\delta \approx 2.5$ ppm) and C_b ($\delta \approx 36$ ppm) are in accord with a distinct contribution of the enediyl resonance form compared to the diene form (see Figure 2A,B). The concomitant pronounced nonplanarity of the cyclopentadiene ligand has been verified by crystal structure determinations of the complexes $[(C_5H_5)Co(1\text{-}exo\text{-}R\text{-}C_5H_5)]$ (R = Ph, C(O)Ph).[19,20]

4.3. IR Spectra of the Cobalt(I) Compounds $[(C_5H_5)Co(1\text{-}exo\text{-}P(O)R_2\text{-}C_5H_5)]$ (2a–d). The IR spectra support the proposed constitution of the cobalt(I) compounds **2a–d**. The frequencies and relative intensities of the absorptions due to the PR_2 part are unchanged relative to those of $HP(O)R_2$. In addition we observe a typical pattern of five to six absorption bands in the region 750–1110 cm^{-1} (1108–1110 m, 1066–1070 m, 1005–1009 m, 993–995 w, 792–812 m–s cm^{-1}), which is regarded as diagnostic of (1-*exo*-organylcyclopentadiene)cobalt(I) complexes.[7,9] The absence of the $C\text{–}H_{exo}$ stretching vibration, a strong band around 2700–2800 cm^{-1},[21] confirms the exo position of the $P(O)R_2$ substituents. Finally, the P=O stretching frequencies in the range 1140–1152 cm^{-1} (see Experimental Section) indicate that the $P(O)R_2$ fragment in **2a–d** is bonded through phosphorus to the cyclopentadiene ring, not through oxygen.

5. Concluding Remarks

In this paper we have described two alternative routes to the new cobalt(I) complexes of the general composition $[(C_5H_5)Co(1\text{-}exo\text{-}P(O)R_2\text{-}C_5H_5)]$ (**2a–d**). The complexes **2** are the first isolable intermediates in the synthesis of the trinuclear complexes **3a**,**b** from the reaction of cobaltocene and the secondary phosphine oxides **1a**,**b**. The reaction of cobaltocene with the sterically demanding phosphine oxides **1c**,**d**, however, ends with the formation of **2c**,**d**. It is very probably the bulk of these phosphine oxides that completely prevents the formation of the trinuclear complexes **3c**,**d**.

The $P(O)R_2$ units are the first phosphorus nucleophiles that have been reported to add to cobaltocenium. The only other nucleophiles are carbanions and hydride.[22] The use of a cobaltocenium salt[23] instead of cobaltocene for the preparation of the oxygen tripod ligands **4** is an effective alternative that gives access to an interesting class of tris-chelating oxygen ligands from readily available starting materials.

6. Experimental Section

6.1. General Details. All reactions were performed under dry nitrogen in conventional Schlenk glassware unless otherwise quoted. The secondary phosphines were obtained from Hoechst AG, Knapsack, FRG, and were used without further purification. Phosphabicyclononane is a mixture of the [3.3.1] and the [4.2.1] isomers.[24] Cobaltocene was freshly sublimed prior to use. Infrared spectra were recorded on a Perkin-Elmer PE 580 spectrometer. ^1H, ^{13}C, and ^{31}P NMR spectra were obtained on Bruker WP 80 (80-MHz) and WH 270 (270-MHz) and Varian VXR 300 (300-MHz) instruments. Chemical shifts are given in ppm (positive downfield) relative to TMS (^1H, ^{13}C) and external 85% H_3PO_4 (^{31}P). Elemental analyses were performed by Analytical Laboratories, D-5250 Engelskirchen, FRG. The complexes $[Co(C_5H_5)_2]$,[25] $[Co(C_5H_5)_2]I$,[26] and $[(C_5H_5)Co(1\text{-}exo\text{-}Ph\text{-}C_5H_5)]$[27] were prepared according to the published procedures.

6.2. Secondary Phosphine Oxides (1a–d). General Procedure.[3] A 500-mL three-necked flask equipped with a reflux condenser, gas inlet tube, and thermometer was charged with 0.4 mol of the dialkylphosphine, HPR_2, and 200 mL of isopropyl alcohol. The rapidly stirred mixture was cooled in an ice bath and treated with dry air. The internal temperature was kept below 45 °C. The reaction was followed by IR spectroscopy (P–H stretching vibrations of HPR_2 and $HP(O)R_2$) to prevent further oxidation to give phosphinic acids, $R_2P(O)OH$. A typical reaction time is 2 h. The solvent was distilled off in vacuo, and from the residue the secondary phosphine oxides **1a–c** were obtained as hygroscopic white crystals by recrystallization from hexane at −30 °C (**1a**,**c**) or −70 °C (**1b**). **1d** was isolated as a colorless viscous oil. The yields were ca. 50%.

Di-*n*-butylphosphine oxide, $HP(O)(C_4H_9)_2$ (1a): IR (C_2Cl_4, cm^{-1}) 2300 (s, ν(P—H)), 1180 (vs, ν(P=O)); ^1H NMR (80 MHz, C_6D_6) δ 0.77 (t, 6 H, ^3J(HCCH) = 6.6 Hz, CH_3), 0.91–1.36 (m, 12 H, CH_2), 6.60 (dm, br, 1 H, ^1J(PH) = 437 Hz, PH; dp, ^3J(HPCH) = 3.5 Hz in $CDCl_3$).

Diisobutylphosphine oxide, $HP(O)(CH_2CH(CH_3)_2)_2$ (1b): IR (C_2Cl_4, cm^{-1}) 2315 (s, ν(P—H)), 1190 (vs, ν(P=O)); ^1H NMR (80 MHz, C_6D_6) δ 0.89 (d, 12 H, ^3J(HCCH) = 6.5 Hz, CH_3), 1.00–1.67 (m, 4 H, CH_2), 1.99 (m, 2 H, CH), 6.79 (dtt, 1 H, ^1J(PH) = 438 Hz, ^3J(HPCH) = 6.0 Hz, ^3J(HPCH) = 1.8 Hz, PH).

Dicyclohexylphosphine oxide, $HP(O)(C_6H_{11})_2$ (1c): IR (C_2Cl_4, cm^{-1}) 2285 (s, ν(P—H)), 1177 (vs, ν(P=O)); ^1H NMR (80 MHz, C_6D_6) δ 0.7–2.0 (m, 22 H, C_6H_{11}), 6.17 (d, 1 H, ^1J(PH) = 427 Hz, PH).

9*H*-9-Phosphabicyclo[3.3.1]nonane 9-oxide, $H(O)PCHCH_2CH_2CH_2CHCH_2CH_2CH_2$, and 9*H*-9-phosphabicyclo[4.2.1]nonane 9-oxide, $H(O)PCHCH_2CH_2CHCH_2CH_2CH_2CH_2$ (1d, mixture of isomers): IR (C_2Cl_4, cm^{-1}) 2305 (s, ν(P—H)), 1174 (vs, ν(P=O)); ^1H NMR (80 MHz, C_6D_6) δ 0.83–2.63 (m, 14 H, CH, CH_2), 6.6 (d, 1 H, ^1J(PH) = 451 Hz, PH).

6.3. Preparation of the Cobalt(I) Compounds 2a–d. $[(C_5H_5)Co(1\text{-}exo\text{-}(P(O)(C_4H_9)_2)\text{-}C_5H_5)]$ (2a). Method 1. Cobaltocene (945 mg, 5.0 mmol) and di-*n*-butylphosphine oxide (**1a**; 1.62 g, 10.0 mmol) were stirred in 5 mL of toluene for 2 days. The solvent was distilled off in vacuo, and the black residue was extracted with hexane. Excess phosphine oxide crystallized from the dark red hexane solution after 1–2 h at −20 °C. The hexane solution was decanted and set aside at −20 °C to crystallize more phosphine oxide. This was repeated several times. The cobalt complex **2a** crystallizes only when the hexane solution is essentially free from phosphine oxide. The yield was 735 mg (42%) of very air sensitive, red-brown, fine crystals: IR (KBr, cm^{-1}) 1145 (vs, ν(P=O)); ^{31}P NMR (109 MHz, C_6D_6) δ 29.0 (s). Anal. Calcd for $C_{18}H_{28}CoOP$: C, 61.71; H, 8.05. Found: C, 62.42, 8.21.

Method 2. To a solution of $K[P(O)(C_4H_9)_2]$, prepared in situ from di-*n*-butylphosphine oxide (**1a**; 1.62 g, 10.0 mmol) and potassium hydride in ether, was added with rapid stirring cobaltocenium iodide ($[Co(C_5H_5)_2]^+I^-$; 948 mg, 3.0 mmol). The solution, which immediately turned dark red, was stirred for 30 min at 0 °C (stirring at room temperature leads to the formation of the trinuclear complex **3a**). The solvent was removed in vacuo, and the residue was extracted with hexane. The red hexane solution was filtered through Celite and then cooled to −20 °C to precipitate excess $K[P(O)(C_4H_9)_2]$. The solution was decanted and concentrated until the cobalt compound **2a** started to crystallize; yield 395 mg (38%).

$[(C_5H_5)Co(1\text{-}exo\text{-}(P(O)(CH_2CH(CH_3)_2)_2)\text{-}C_5H_5)]$ (2b). Method 1. Cobaltocene (945 mg, 5.0 mmol) and diisobutylphosphine oxide (**1b**; 1.62 g, 10.0 mmol) were stirred in 5 mL of toluene for 6 h at 60 °C. Slow cooling of the reaction mixture to 20 °C yielded black needlelike crystals that were 1–2 cm long. These black needles contain paramagnetic impurites. They were filtered off and dissolved again in toluene. The solution was filtered through Celite and taken to dryness. Excess phosphine oxide sublimed under high vacuum at 40–50 °C. Recrystallization from hexane/toluene (80/20) yielded 1.33 g (76%) of large, air-sensitive, black crystals: IR (KBr, cm^{-1}) 1159 (vs, ν(P=O)). Anal. Calcd for $C_{18}H_{28}CoOP$: C, 61.71; H, 8.05. Found: C, 61.64; H, 7.93.

Method 2. **2b** was obtained from diisobutylphosphine oxide (**1b**; 1.62 g, 10.0 mmol), potassium hydride, and cobaltocenium iodide ($[Co(C_5H_5)_2]^+I^-$; 948 mg, 3.0 mmol) as described for **2a**, method 2. The dark red reaction mixture was stirred for 1 h at 20 °C. The solution was brought to dryness, the residue was extracted with hexane, and the resulting solution was filtered through Celite. The red product that crystallized upon concentration was impure. It was carefully dried under high vacuum at 40–50 °C and finally recrystallized from hexane/toluene; yield 840 mg (80%).

$[(C_5H_5)Co(1\text{-}exo\text{-}(P(O)(C_6H_{11})_2)\text{-}C_5H_5)]$ (2c). **2c** was obtained from cobaltocene (945 mg, 5.0 mmol) and dicyclohexylphosphine oxide (**1c**; 2.14 g, 10.0 mmol) as described for the preparation of **2a**, method 1. The yield was 0.85 g (42%) of air-sensitive red-black crystals: IR (KBr, cm^{-1}) 1152 (vs, ν(P=O)); ^{31}P NMR (109 MHz, C_6D_6) δ 30.5 (s).

$[(C_5H_5)Co(1\text{-}exo\text{-}((O)PCHCH_2CH_2CH_2CHCH_2CH_2CH_2)\text{-}C_5H_5)]$ and $[(C_5H_5)Co(1\text{-}exo\text{-}((O)PCHCH_2CH_2CHCH_2CH_2CH_2CH_2)\text{-}C_5H_5)]$

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(2d). **2d** was obtained from cobaltocene (945 mg, 5.0 mmol) and 9*H*-9-phosphabicyclononane 9-oxide (**1d**; 1.58 g, 10.0 mmol) as described for the preparation of **2a**, method 1. The yield was 1.12 g (65%) of air-sensitive red-black crystals: IR (KBr, cm^{-1}) 1140 (vs, $\nu(P{=}O)$); ^{31}P NMR (109 MHz, C_6D_6) δ 28.9 (s).

6.4. Preparation of the Oxygen Tripod Compounds 3a,b and 4a. $[Co((C_5H_5)Co(P(O)R_2)_3)_2]$ (R = *n*-C_4H_9, 3a). Synthesis from Cobaltocene. A mixture of di-*n*-butylphosphine oxide (**1a**; 10.4 g, 64.1 mmol) and cobaltocene (6.0 g, 31.7 mmol) was heated slowly without solvent to 110 °C. After 4–6 h the highly viscous dark brown solution was cooled to 10 °C and stirred with a minimum amount of cold methanol or acetone. The air-stable product that separates as fine yellow crystals was filtered off, washed with a small amount of cold methanol, and dried under high vacuum. Recrystallization from hexane yielded 5.65 g (4.43 mmol, 42%) of air-stable paramagnetic orange crystals: IR (KBr, cm^{-1}) 1080 (vs, $\nu(P{=}O)$), 510 s, $\delta(P{=}O)$). Anal. Calcd for $C_{58}H_{118}Co_3O_6P_6$: C, 54.67; H, 9.33. Found: C, 54.53; H, 9.45.

Synthesis from 2a. A solution of **2a** (700 mg, 2.0 mmol) and di-*n*-butylphosphine oxide (**1a**; 974 mg, 6.0 mmol) was heated slowly to 110 °C for 4 h to give a brown-yellow solution. Further workup was as described above for the direct preparation of **3a** from cobaltocene. The yield was 550 mg (0.43 mmol, 65%).

Synthesis from $[(C_5H_5)Co(1\text{-}exo\text{-}Ph\text{-}C_5H_5)]$. A solution of $[(C_5H_5)Co(1\text{-}exo\text{-}Ph\text{-}C_5H_5)]$ (532 mg, 2.0 mmol) and di-*n*-butylphosphine oxide (**1a**; 974 mg, 6.0 mmol) was heated slowly to 120 °C. The red reaction mixture slowly turned yellow. After ca. 4–5 h the solution became dark yellow. Further workup was as described above for the preparation of **3a** from cobaltocene; yield 700 mg (0.55 mmol, 83%).

Synthesis from $[Co(C_5H_5)_2]^+I^-$. A reaction mixture of $K[P(O)(C_4H_9)_2]$ and $[Co(C_5H_5)_2]^+I^-$ was prepared as described for the synthesis of **2a**, method 2, and stirred for 1.5 h. The ether was removed in vacuo, and the reddish residue was heated slowly to 110 °C. After ca. 4 h the mixture had turned yellow. The product was extracted with ether, and the solution was filtered and brought to dryness. The solid, which contains a very air-sensitive impurity, was stirred with a small amount of methanol to precipitate the yellow microcrystalline product yield 700 mg (0.55 mmol, 55%).

$[Co((C_5H_5)Co(P(O)R_2)_3)_2]$ (R = *i*-C_4H_9, 3b). A mixture of diisobutylphosphine oxide (**1b**; 10.4 g, 64.1 mmol) and cobaltocene (6.0 g, 31.7 mmol) was heated without solvent for 12 h to 120 °C. The cooled reaction mixture was dissolved in hexane and filtered. The solution was concentrated and chromatographed on a silica column. A yellow band was eluted with hexane/ether (90/10). Slow evaporation of the solvent yielded 1.1 g (0.86 mmol, 8.2%) of paramagnetic air-stable orange crystals: IR (KBr, cm^{-1}) 1080 (vs, $\nu(P{=}O)$), 510 (s, $\delta(P{=}O)$). Anal. Calcd for $C_{58}H_{118}Co_3O_6P_6$: C, 54.67; H, 9.33. Found: C, 54.25; H, 9.36.

$Na[(C_5H_5)Co(P(O)R_2)_3]$ (R = *n*-C_4H_9, 4a). A suspension of **3a** (3.0 g, 2.4 mmol) and sodium cyanide (1.0 g, 20.0 mmol) in 50 mL of methanol was stirred in air. After about 2 days a clear solution was formed. The solvent was removed, and the residue was dried under high vacuum. The sodium salt **4a** was separated from sodium hexacyanocobaltate and the excess sodium cyanide by extraction with dry ether. The orange-yellow oily product was recrystallized from methanol/water to give 2.1 g (3.3 mmol, 69%) of air-stable yellow crystals: IR (KBr, cm^{-1}) 1090 (vs, $\nu(P{=}O)$), 510 (s, $\delta(P{=}O)$); ^1H NMR (80 MHz, $CDCl_3$) δ 0.94–2.04 (m, 54 H, CH_2, CH_3), 4.84 (s, 5 H, C_5H_5). Anal. Calcd for $C_{29}H_{59}CoNaO_3P_3\cdot{}^2/_3H_2O$: C, 54.20; H, 9.46. Found: C, 54.19; H, 9.47.

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Registry No. **1a**, 4559-70-0; **1b**, 15924-55-7; **1c**, 14717-29-4; **1d** (isomer 1), 113985-74-3; **1d** (isomer 2), 113985-75-4; **2a**, 122293-60-1; **2b**, 122293-61-2; **2c**, 122293-62-3; **2d** (isomer 1), 122293-63-4; **2d** (isomer 2), 122293-64-5; **3a**, 122312-94-1; **3b**, 122293-65-6; **4a**, 113779-91-2; $K[P(O)(C_4H_9)_2]$, 19114-97-7; $(C_5H_5)Co(1\text{-}exo\text{-}Ph\text{-}C_5H_5)$, 64681-94-3; $[Co(C_5H_5)_2]^+I^-$, 11087-17-5; di-*n*-butylphosphine, 1732-72-5; diisobutylphosphine, 4006-38-6; dicyclohexylphosphine, 829-84-5; 9*H*-9-phosphabicyclo[3.3.1]nonane, 13887-02-0; 9*H*-9-phosphabicyclo[4.2.1]nonane, 13396-80-0; cobaltocene, 1277-43-6; sodium hexacyanocobaltate, 14039-23-7.

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Electronic Structure of 42- and 44-Electron $Cp_2M_2(CO)_4E_2$ Butterfly Complexes (M = Cr, Mo, W; E = S, Se, SR, PR...): Rationalization of Their Structures and Isomerization Processes

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The structures of 42- and 44-electron $Cp_2M_2(CO)_4(\mu\text{-}E)_2$ complexes (M = Cr, Mo, W; E = S, Se, SR, PR) and related compounds have been rationalized on the basis of EH-MO calculations. In particular, the possibility of the existence of cis/trans conformations of the Cp and CO ligands has been analyzed, together with the M–M versus E–E bonding in the 42-electron species. The possibility of interconversion between isomers has been envisaged. The electrochemical behavior of the $[Cp_2Mo_2(\mu\text{-}SR)_2]^{0/2+}$ complexes has been investigated, and a rationalization of the electrochemical activation of these compounds toward CO substitution is proposed.

Introduction

Among the large family of dinuclear transition-metal compounds, one of the most extensively investigated categories is the group of complexes in which the two metal atoms are bridged by one or several main-group atoms or ligands. In these compounds, the two metal atoms and their bridges can be considered as forming the core of a mixed organometallic cluster. For example, dimers of the general formula $(L_nM)_2E_2$, having two bridging main-group fragments or bare atoms E, constitute four-vertex clusters, the structures of which are strongly correlated with their electron count.

The most compact structure is the tetrahedron 1. Within the framework of the polyhedral skeletal electron pair (PSEP) theory[1]

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