P_8 and P_{12} as Complex Ligands☆

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The thermal and/or photochemical reaction of $[Cp'''Co(CO)_2]$ (**1**), $Cp''' = 1,2,4\text{-}t\text{Bu}_3C_5H_2$, with white phosphorus, P_4, gives besides $[(Cp'''Co)_2(P_2)_2]$ (**2**) the trinuclear complexes $[(Cp'''Co)_3P_8]$ (**3**) and $[(Cp'''Co)_3P_{12}]$ (**4**), the P_n ligands of which form P_5-P_3 and P_5-P_7 skeletons, structural motifs, which formally can be derived from Hittorf's phosphorus. The X-ray crystal structure analysis of **3** confirmed its P_5-P_3 framework.

During the past 20 to 30 years, particularly in recent years, interdisciplinary aspects of the chemistry of phosphorus have become more and more important. Thus, low-coordinated molecules containing one or several phosphorus multiple bonds[1] have stimulated considerable interest of many research groups. A comparison of polyphosphides[2] with mono- and polycyclic phosphanes[3] as well as with unsubstituted P_n ligands[4] reveals numerous structural similarities. These findings were supplemented by many remarkable theoretical contributions devoted to P_n molecules[5].

Synthesis of $[(Cp'''Co)_2(P_2)_2]$ (2), $[(Cp'''Co)_3P_8]$ (3), and $[(Cp'''Co)_3P_{12}]$ (4)

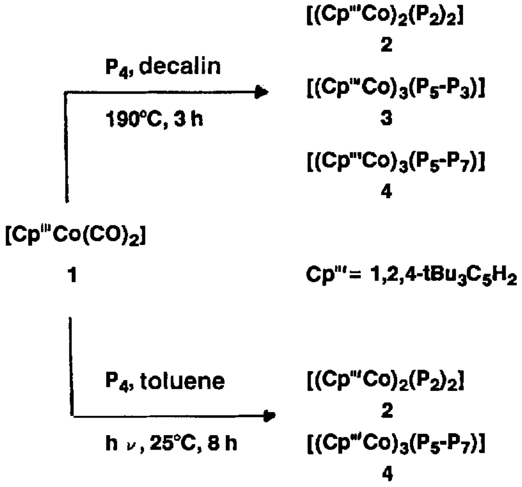
The preparation of Cp metal complexes bearing P_n ligands revealed that the substituents attached to the Cp ring are very important with respect to n[4]. When $[Cp'''Co(CO)_2]$ (**1**) was used as starting compound the polynuclear cobalt complexes **2**–**4** were obtained (Scheme 1). Photochemically the P_{12} complex **4** was prepared more selectively and in considerably higher yield.

The moderately air-sensitive, black-violet (**2**), brown (**3**) and olive-green (**4**) complexes are sparingly soluble in n-hexane (**3** is well soluble) and dissolve well in toluene and dichloromethane.

^1H- and ^{31}P-NMR-Spectroscopic and Mass-Spectrometric Data of Complexes 3 and 4

The NMR data of the dinuclear cobalt complex **2** were already reported in ref.[6] in connection with the ligand-controlled coupling of two P_2 units to an acyclic P_4 ligand. $[(Cp'''Co)_4(P_5-P_5)]$ (**5**), formed in traces by this thermolysis reaction, was characterized by NMR spectroscopy; it reveals a structure analogous to that of **6** the structure of which was determined by X-ray crystallography[7].

Scheme 1. Synthesis of the polynuclear cobalt complexes **2**–**4**



5: $[(Cp'''Co)_4(P_5-P_5)]$

6: $[(Cp''Rh)_2(P_5-P_5)(RhCp'')_2]$[7] $Cp'' = 1,3\text{-}t\text{Bu}_2C_5H_3$

P_8 Complex 3

In the ^1H-NMR spectrum of the P_8 complex **3** three different sets of signals (cf. Figure 1) are observed for the $1,2,4\text{-}t\text{Bu}_3C_5H_2$ ligands each in the expected ratio of 2:9:18 (Table 1). The ^{31}P-NMR spectrum consists of a complex spin system with five signal groups (Figure 1, $ABMM'XX'Y_2$ spin system) of the intensity ratio 1:1:2:2:2. The coupling constants were determined from the one-dimensional ^{31}P-NMR spectrum by using the results of a two-dimensional $^{31}P^{31}P$-COSY45-NMR experiment. The simulation was verified with the program PERCH. For the eight atoms of the phosphorus framework the connectivities given in **A** were derived.

Saturating formally the valences and taking into account the relatively small $^1J(P_AP_B)$ coupling constant of -95 Hz, which points to an antiperiplanar arrangement of the lone pairs at the P_2 bridge (P_AP_B) (cf. e.g. ref.[23]), additional evaluation of the cross peaks in the COSY-NMR spectrum

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[+] X-ray analysis.

[++] Short communication (conference report) in: G. Berg, O. J. Scherer, *Phosphorus, Sulfur, Silicon* **1994**, p. 93–94, 261–264.

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(long-range interaction of P_A with P_M, P_B with P_M and P_Y as well as P_X with P_Y) allows the construction of the conformation of the P_8 skeleton as denoted in **B**; as a 12e$^-$ donor it coordinates to three Cp‴Co fragments in **3**.

A

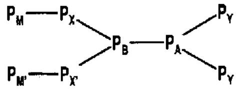


Table 1. ^{1}H- and ^{31}P-NMR data of the complexes **3** and **4**

	[(Cp‴Co)$_3$P$_8$] (**3**)	[(Cp‴Co)$_3$P$_{12}$] (**4**)
		370 K [b]
^{1}H NMR [a] δ	4.99 (s, 2 H), 4.81 (s, 2 H), 4.58 (s, 2 H), 1.64 (s, 9 H), 1.61 (s, 18 H), 1.58 (s, 18 H), 1.50 (s, 9 H), 1.49 (s, 18 H), 1.27 (s, 9 H)	5.40 (br. s, 2 H), 5.11 (s, 2 H), 4.60 (s, 2 H), 1.87 (s, 18 H), 1.70 (s, 9 H), 1.67 (s, 18 H), 1.49 (s, 18 H), 1.39 (s, 9 H), 1.38 (s, 9 H)
4 (258 K)[b]	5.64 (s, 1 H), 5.14 (s, 1 H), 5.06 (s, 1 H), 4.90 (s, 1 H), 4.32 (s, 2 H), 1.74 (s, 18 H), 1.60 (s, 9 H), 1.57 (s,9 H), 1.45 (s, 9 H), 1.25 (s, 18 H), 1.23 (s, 9 H), 1.17 (s, 9 H)	
Spin system	ABMM'XX'Y$_2$ (298 K)	ABCDEFGHIJKL (235 K)
^{31}P NMR[c] δ	76.6 (pdt, 1 P, P_A) 65.4 (pdt, 1 P, P_B) 42.2 (pdd, 2 P, $P_{MM'}$) -82.0 (pdt, 2 P, $P_{XX'}$) -128.4 (d, 2 P, P_Y)	397.0 (dt, 1 P, P_A), 54.5 (dd, 1 P, P_B) 48.1 (dd, 1 P, P_C), 31.5 (pq, 1 P, P_D) -28.6 (pq, 1 P, P_E), -44.9 (pq, 1 P, P_F) -78.4 (pt, 1 P, P_G), -92.9 (pt, 1 P, P_H) -108.9 (pt, 1 P, P_I), -118.1 (pt, 1 P, P_J) -147.4 (dd, 1 P, P_K), -149.4 (dd, 1 P, P_L)
	$^1J(P_AP_B) = -95$, $^1J(P_AP_Y) = -211$ $^1J(P_BP_X) = {}^1J(P_BP_{X'}) = -310$ $^1J(P_MP_X) = {}^1J(P_{M'X'}) = -361$ $^2J(P_MP_{M'}) = 143$ $^2J(P_AP_M) = {}^2J(P_AP_{M'}) = 25$ $^2J(P_BP_M) = {}^2J(P_BP_{M'}) = 17$ $^2J(P_MP_{X'}) = {}^2J(P_{M'}P_X) = 20$	$^1J(P_AP_D) = -226$, $^1J(P_AP_E) = {}^1J(P_AP_F) =$ -328, $^1J(P_{B,C}P_K) = {}^1J(P_{B,C}P_L) =$ -325, $^1J(P_DP_K) = {}^1J(P_DP_L) = -185$, $^1J(P_EP_G) = {}^1J(P_FP_H) = -286$, $^1J(P_EP_I) =$ $^1J(P_FP_J) = -288$, $^1J(P_GP_H) = -342$ $^1J(P_IP_J) = -331$, $^2J(P_BP_C) = 164$ $^3J(P_DP_I) = \pm 50$, $^3J(P_DP_J) = \pm 21$

[a] 400.14 MHz, C_6D_6, 298 K. – [b] 400.14 MHz, C_7D_8. – [c] 161.98 MHz, **3**: C_6D_6, **4**: $CDCl_3/CD_2Cl_2$ (2:1).

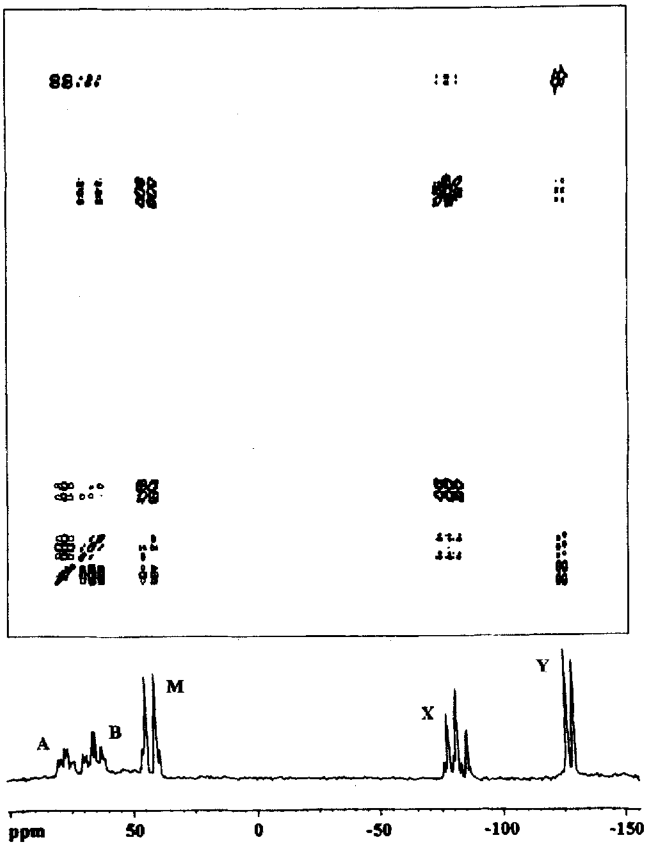
The large $J(P_MP_{M'})$ coupling of +143 Hz, recognized as a ^2J(PP) coupling, suggests that there is no bonding between P_M and $P_{M'}$ (cf. e.g. the molecular structure of the P_{10} complex **6**)[7].

P_{12} Complex 4

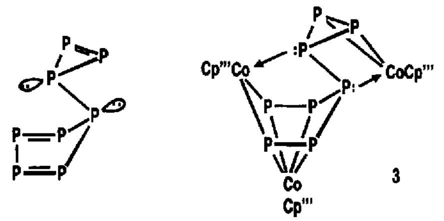
The ^{1}H-NMR spectrum recorded at 370 K (high-temperature spectrum) reveals free rotation of the three Cp‴ ligands around the Co–Cp‴ (centr.) axis, arranged in different chemical environment. In contrast, the ^{1}H-NMR spectrum recorded at 258 K (low-temperature spectrum) points to hindered rotation for two of the three Cp‴ ligands (Table 1). These are supposed to be the Cp‴Co fragments coordinated to the P_5 part of the P_{12} ligand (b in Scheme 3).

At room temperature the ^{31}P-NMR spectrum of the P_{12} complex **4** consists of eleven signal groups in the ratio of 1:1:1:1:1:1:1:1:1:1:2 in the shift range from δ ca. 400 to −150 (Figure 2). At 235 K (Table 1) the accidental equivalence of two nuclei disappears and the habit of an ABCDEFGHIJKL spin system (C_1-symmetrical molecule) is realized. The spectrum calculated by use of the given coupling constants (simulation and iteration with PERCH) is in very good agreement with the experimental data (Figure 2). The simulation had however to be carried out in two steps since the program does not allow to study more than ten different resonances. The habit of the spin system is invariant to the sign of the coupling constants P_DP_I and P_DP_J. Therefore, an unambiguous determination of these signs was not possible.

Figure 1. $^{31}P^{31}P$-COSY 45 NMR spectrum of [(Cp‴Co)$_3$P$_8$] (**3**): 81.01 MHz, C_6D_6, 298 K, 1024 × 256, d1 = 1.50, Gaussian multiplication



Scheme 2. P_8 skeleton and coordination mode of complex **3**

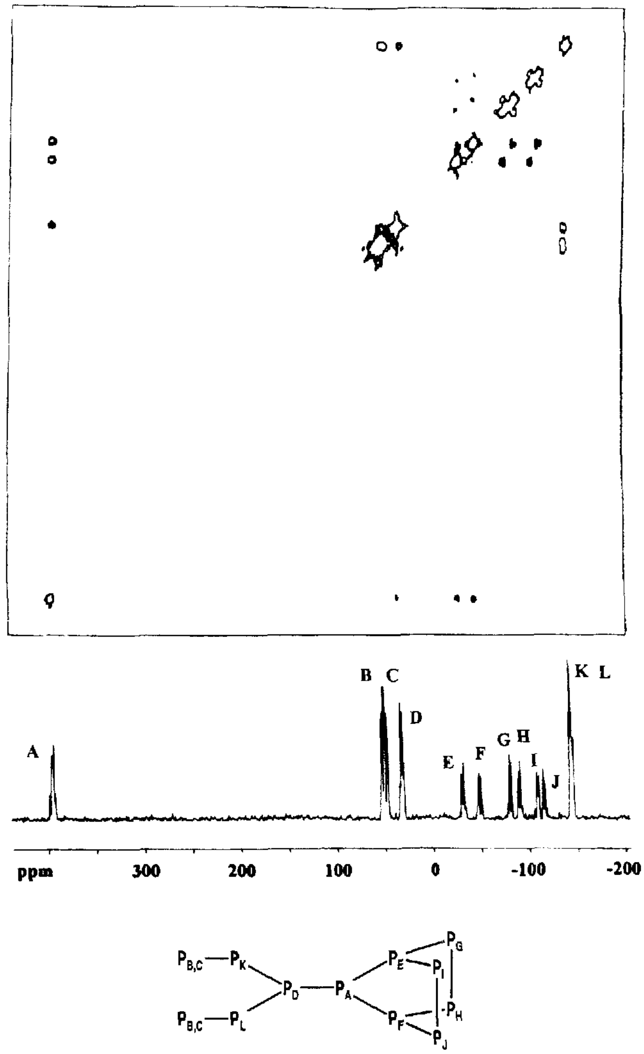


B **3**

The unsymmetrical P_{12} skeleton of complex **4** was derived by means of a two-dimensional $^{31}P^{31}P$-COSY45-NMR room-temperature spectrum in which only the ^1J(PP) couplings are resolved. The spectrum shows eleven cross peaks which are in accordance with the P_n skeleton given in **C**.

The signal P_A at lowest field shows cross peaks with the phosphorus atoms P_D, P_E, and P_F. In addition to P_A, P_D is also adjacent to P_K and P_L which, in turn, interact with P_B and P_C. On the basis of the accidental isochronism of P_K and P_L it could not be decided whether there is a bonding between $P_{B,C}$ and P_K and P_L, respectively. The pseudoquartet of P_E couples with the triplet-like signals of P_G and P_I. The "quartet" of P_F, lying at higher field, reveals binding

Figure 2. ^{31}P^{31}P-COSY 45 NMR spectrum of [(Cp‴Co)$_3$P$_{12}$] (4); 161.98 MHz, CH_2Cl_2/C_6D_6, 298 K, 2048 × 256, d1 = 4.0 s, Gaussian multiplication

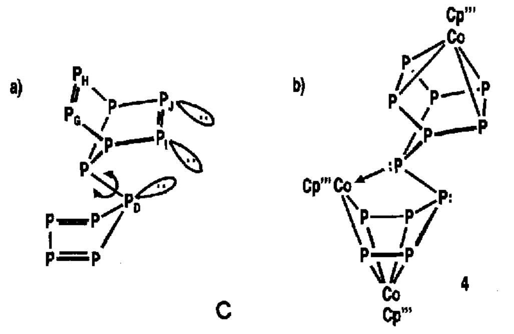


relations to P_H and P_J. Within the four triplet-shaped signals (Figure 2) P_G, P_H, P_I and P_J, P_G and P_H as well as P_I and P_J interact with each other by ^{1}J(PP) couplings. The very broad diagonal peak of the closely adjacent resonances of P_B and P_C does not reveal a coupling between these nuclei, unambiguously. As already in the case of the COSY spectra of [(Cp‴Co)$_3$(P_5−P_3)] (3) and [(Cp″Rh)$_4$(P_5−P_5)] (6)[7] the question of the cleavage of a P_5 ring edge is still unanswered. The positive sign of $J(P_BP_C)$, resulting from the simulation of 4, and a P···P′ distance of 2.62 Å in 6 point to an an open-edged P_5 ring which binds through a P−P bond to a P_7 norbornadiene (a in Scheme 3). At 275 K the ^{31}P-NMR spectrum shows a further splitting of the signals of P_I, P_J, and P_D attributed to ^{3}J(PP) or "through-space" couplings via lone pairs. The relative orientation of the "five-membered ring" relative to the P_7 bicycle can be determined by means of these "through-space" interactions requiring a spatial vicinity of the nuclei involved[8]. Consequently, the phosphorus atoms P_I and P_J lie above the lone pair of P_D (a in Scheme 3) so that P_G and P_H are automatically above the puckered "five-membered ring" (envelope conformation).

The detected long-range couplings with different values, $^{3}J(P_DP_I) = \pm 50$ and $^{3}J(P_DP_J) = \pm 21$ Hz as well as the existence of 12 different resonances point to an unsymmetrical P_{12} framework. Taking into account the dependence of the coupling constants from the torsion angle (e.g. ref.[23]) and the deviation of the lone pairs from antiperiplanarity, the relatively large coupling [$^{1}J(P_AP_D) = -226$ Hz] via the bridge is in agreement with this result.

Temperature-dependent ^{31}P-NMR measurements reveal that in the temperature range from 335 to 355 K, with the exception of the bridge atoms P_A and P_D, the original 12 signals (C_1 symmetry) coalesce in pairs to an AB_2DE_2-$G_2I_2K_2$ spin system (C_s symmetry on the NMR time scale). This fluxional behavior in the case of the P_{12} complex **4** may best be accounted for by a hindered "rotation" (pendulum motion) of the two building blocks P_5−P_7 around the exocyclic P−P bond (a in Scheme 3). The coordination of the P_{12} ligand (12e$^-$ donor) to three 14e$^-$ Cp‴Co fragments is described in Scheme 3. In the P_5 part this coordination corresponds both to that of the P_8 complex **3** (formulas **B**) and that of the P_{10} complex **6**.

Scheme 3. P_{12} skeleton and coordination mode of complex 4



Mass-Spectrometric Results

Table 2 compiles selected fragments of compounds **3** and **4**. The most remarkable result is the formation of the series

[(Cp‴Co)$_2$P$_n$]$^+$, n = 5−3 with **3** and 6−3 with **4**

[(Cp‴Co)P$_n$]$^+$, n = 5−3 with **3** and 4−3 with **4**,

which may be assigned to triple decker cations (30−33 valence electrons) in the case of dinuclear complexes and to sandwich complex cations in the case of mononuclear complexes. Worthwhile mentioning is the high intensity (86%) of P_4^+ for complex **4**, a naked P_n fragment which was not detected for the P_8 complex.

Molecular Structure of the P_8 Complex 3 in the Crystal

Due to the poor quality of the crystal structure analysis, which however unambiguously indicates the P_8 skeleton

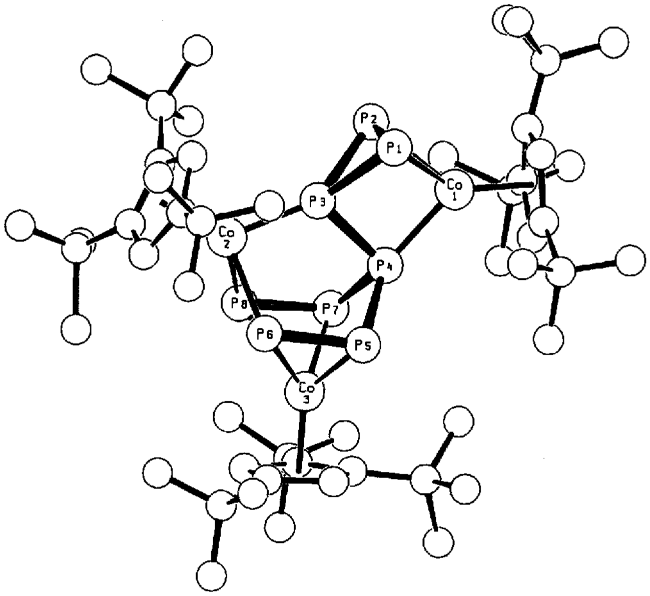
Table 2. Selected mass-spectrometric data of the complexes **3** and **4**

$[(Cp'''Co)_3P_8]$ (**3**)[a]		$[(Cp'''Co)_3P_{12}]$ (**4**)[b]	
$[Fragment]^+$	*m/z* (Intensity, %)	$[Fragment]^+$	*m/z* (Intensity, %)
$[(Cp'''Co)_3P_8]$, M^+	1124.2 (9)	$[(Cp'''Co)_3P_{12}]$, M^+	1248.5 (0.1)
$[(Cp'''Co)_2P_5]$	739.3 (100)	$[(Cp'''Co)_2P_6]$	770.5 (4)
$[(Cp'''Co)_2P_4]$	708.2 (95)	$[(Cp'''Co)_2P_5]$	739.6 (75)
$[(Cp'''Co)_2P_3]$	677.3 (80)	$[(Cp'''Co)_2P_4]$	708.7 (48)
$[(Cp'''Co)P_5]$	447.1 (3)	$[(Cp'''Co)_2P_3]$	677.6 (12)
$[(Cp'''Co)P_4]$	416.2 (21)	$[(Cp'''Co)P_4]$	416.3 (43)
$[(Cp'''Co)P_3]$	385.2 (16)	$[(Cp'''Co)P_3]$	385.4 (5)
$[(Cp'''Co)P_2]$	354.4 (11)	$[(Cp'''Co)P_2]$	354.4 (83)
[*t*Bu]	57.2 (52)	$[P_4]$	124.1 (86)
		[*t*Bu]	57.3 (100)

[a] EI, 70 eV, 220 °C. – [b] EI, 70 eV, 300 °C.

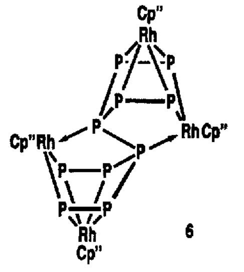
(Figure 3), it is not meaningful to tabulate bond lengths and bond angles.

Figure 3. SCHAKAL plot of complex **3**



Comparing the P_8 framework with that of the P_{10} complex $[(Cp''Rh)_2(P_5{-}P_5)(RhCp'')_2]$ (**6**)[7], characterized by crystal structure analysis, the following parallels can easily be recognized:

Scheme 4. Structure of $[(Cp''Rh)_2P_5{-}P_5(RhCp'')_2]$ (**6**)



6

The formal elimination of a "terminal" P_2 unit in one of the P_5 fragments of **6** gives with subsequent formation of a P–P bond (P1–P2 in **3**) the P_8 skeleton of **3** which approximately displays mirror symmetry.

The three Cp'''Co fragments show different coordination modes to the P_8 ligand. Co1: μ-$\eta^{2:1}$, Co2: μ-$\eta^{1:1:1}$, Co3: $\eta^{2:2}$. At Co1 and Co2 two of the for electrons are of a dative bond type (P lone pair as a $2e^-$ donor).

P_8 and P_{12} Building Blocks in Phosphorus Chemistry

The greatest structural variety occurs with polycyclic phosphanes[3] and polyphosphides[2], the P_n structural motifs of which frequently correspond to fragments of Hittorf's phosphorus[9], one of the most fascinating molecular structures in the chemistry of phosphorus.

Theoretical studies[5a–c,e,f,h,i,m,n] revealed that the energetically most favorable form of P_8 is the P_8 cunean which, in turn, occurs in the open-edged form as partial skeletal part in Hittorf's phosphorus as well as in the tetranuclear complexes **7**[10] and the polyphosphanes α-P_8R_4 (**8**)[11].

P_8R_4

7[10]: R = ML_n = $(C_5H_4Me)Fe(CO)_n$

8[11]: R = e. g. Et

Interestingly, P_8 dihydrocalicene [for $(CH)_8$ dihydrocalicene and its derivatives, see refs.[12,13]), a ligand wich in complex **3** probably exists in an open-edged form (P_5 ring, see **B**), represents the second-stable P_8 valence isomer as revealed by recent calculations[5o].

From solid-state chemistry of polyphosphides[2] we know: $MNiP_8$, M = Mo, W[14] with a threefold open-edged P_8^{6-} cubane building block, MNi_4P_{16}, M = V, Nb, W[15] the P_8^{8-} skeleton of which is composed of a P_6 chair with an exocyclic P_2 unit and Ca_5P_8[16] with isolated P_8^{10-} ions that show staggered conformation known from ethane.

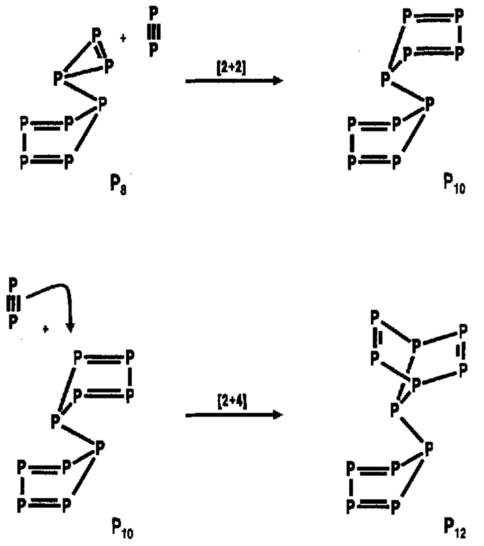
The question of the most stable P_{12} structure is more difficult to answer because the differences of several isomers are relatively small[5a]. $P_6(CtBu)_6$, a hexamer of $tBuC{\equiv}P$, which has a structure analogous to the D_{3d} symmetrical P_{12} polycycle (calculation see ref.[5a]), is composed of six polycondensed five-membered rings ($4 \times P_3C_2$, $2 \times P_2C_3$) and two PC_2 three-membered rings[17]. P_{12} building blocks with remarkable structures were found for MP_5, (M = La, Nd[18a]) and GdP_5[18b], composed of a layer structure of strongly puckered P_{12} rings and also for $Cu_2P_3I_2$[19], composed of a $^1_\infty[P_8]P_4$ structural motif (P_8 cunean/P_4 ring). The P_7 norbornadiene part of the P_{12} ligand in complex **4** may well be compared with $[P_7M(CO)_3]^{3-}$, M = Cr, Mo, W[20], an intensively studied class of compounds.

Interconversion Reactions

Regarding the formation of the P_8, P_{10}, and P_{12} skeletons of the complexes **3**, **4**, and **5** the question arose whether these P_n building blocks are generated formally by stepwise [2 + 2] and [2 + 4] cycloadditions (Scheme 5). Going from P_8 to P_{10} the [2 + 2] cycloaddition should be followed by an electrocyclic ring opening reaction with formation of the second P_5 cycle.

Thermolysis of $[(Cp'''Co)_2(\mu$-$\eta^{2:2}$-$P_2)_2]$ (**2**) in decalin at 190 °C for ten days afforded in ca. 13% yield the tetranuclear compound $[(Cp'''Co)_2(P_5{-}P_5)(CoCp''')_2]$ (**5**) as the only isolable P_n complex (besides mainly decomposition products). Heating of the P_8 complex **3** in decalin at 190 °C for 20 hours afforded the P_{10} complexes **5** and **2** in ca. 30% yield each. This result might be attributed to a formal [2 + 2] cycloaddition reaction of P_2 with the P_8 complex **3** (Scheme 5). Attempts to generate the P_{12} ligand of **4** thermally from **5** and P_4 or photochemically from the P_{10} complex **5** failed.

Scheme 5. Possible [2 + 2] and [2 + 4] cycloaddition reactions



Formal Derivation of the Polyphosphorus Skeletons P_8, P_{10}, and P_{12} from Hittorf's Phosphorus

Cutting out the building blocks P_8, P_{10} (P_8 + P_2), and P_{12} (P_8 + P_2 + P_2) from a structural sequence of Hittorf's phosphorus (Scheme 6) the ligands P_8, P_{10}, and P_{12} of the cobalt polynuclear complexes **3**, **5**, and **4** are obtained by formal ring opening reactions as well as by saturation of the P valences by double bonds and additional rotation around a P−P bond (Scheme 6).

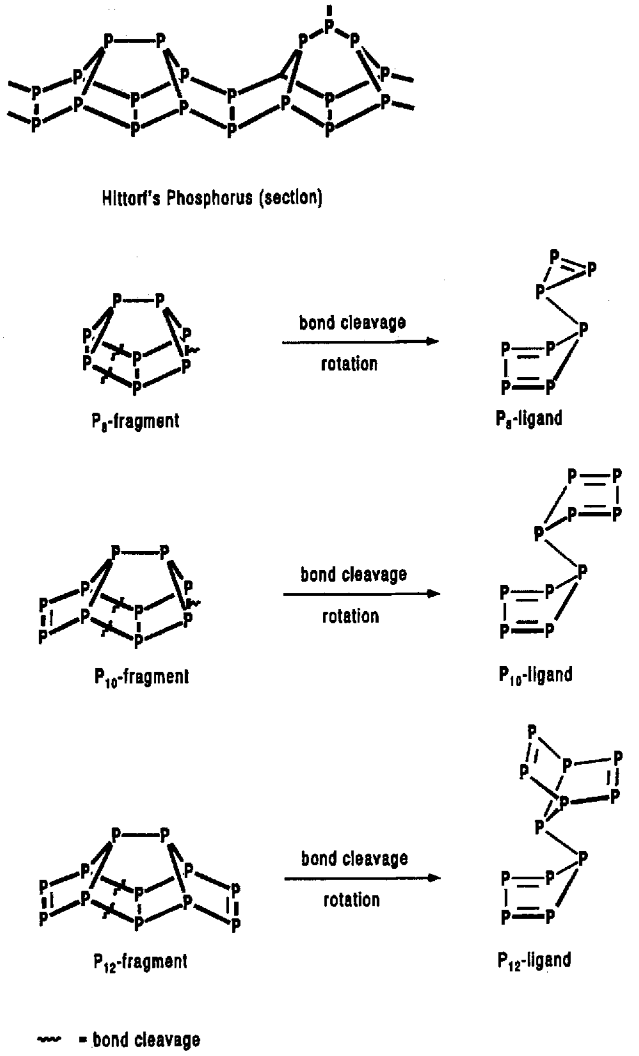
Besides $[P_4]^+$ as parent ion and $[P_1]^+$ to $[P_3]^+$ fragments small amounts of $[P_8]^+$[21a] as well as traces of $[P_{12}]^+$[21b] were detected in the vapor of red phosphorus.

We are indebted to *Fonds der Chemischen Industrie* for financial support of our work. G. B. was granted a scholarship from the Graduiertenkolleg "Phosphorchemie als Bindeglied verschiedener chemischer Disziplinen" and a "Landesgraduierten scholarship". We especially thank Prof. *J. Hahn*, Cologne, for recording the COSY-NMR spectrum of **3** and for his generous support.

Experimental

All experiments were carried out under argon in anhydrous solvents. – ^1H, ^{31}P NMR: Bruker AC 200 (200.13 MHz) and AMX 400 (400.14 MHz), ^{31}P NMR (81.01 and 161.98 MHz); pt = pseudotriplet, pq = pseudoquartet. Simulation and iteration of the experimentally determined spectra (32 k data points) were performed with the program PERCH: R. Laatikainen, M. Niemitz, University of Kuopio, Finland, **1994**. – MS: Finnigan MAT 90. – 1,2,4-$tBu_3C_5H_3$(Cp'''H): see ref.[22].

Scheme 6. Derivation of the P_8, P_{10}, and P_{12} building blocks from Hittorf's phosphorus (with formal saturation of the valences)



[Cp'''Co(CO)₂] (**1**): To a solution of 10.0 g (29.25 mmol) of $[Co_2(CO)_8]$ and 10.16 g (43.38 mmol) of Cp'''H in 50 ml of dichloromethane was added 2.5 ml of cyclohexadiene, and the mixture was heated to reflux with stirring for 90 min. Subsequently, further 5.11 g (21.76 mmol) of Cp'''H was added, and the reaction mixture was stirred under the same conditions for ca. 10 h (relative maximum of the CO bands of **1**). The solvent was evaporated under oil pump vacuum, the oily residue was placed on top of a darkened column (20 × 2.5 cm) filled with basic Al_2O_3-II, and the orange-brown zone of the light-sensitive **1** was eluted with petroleum ether. After evaporation of the solvent from the eluate under oil pump vacuum 18.61 g [91% based on $Co_2(Co)_8$] was obtained. – ^1H NMR (400 MHz, C_6D_6): δ = 4.85 (s, 2H), 1.30 (s, 18H), 1.14 (s, 9H). – IR: ν(CO) [cm^{-1}]: 2004 (vs), 1939 (s). – $C_{19}H_{29}CoO_2$ (348.7): calcd. C 65.51, H 8.39; found C 65.72, H 8.24.

Complexes **2**, **3**, **4**, *and* **5**: A mixture of 1.50 g (4.31 mmol) of **1** and 1.52 g (12.27 mmol) of P_4 in 50 ml of decalin was stirred at 190 °C for 3 h. After cooling to room temp. the black-violet solution was evaporated to dryness under oil pump vacuum. To a solution of the reaction product in ca. 10 ml of dichloromethane was added ca. 2 g of Al_2O_3, and the solvent was evaporated from the mixture in vacuum until it was free-flowing. Chromatography (column: 25 × 1 cm, basic Al_2O_3-II) with petroleum ether afforded a violet fraction (332.8 mg, 22%) $[(Cp'''Co)_2(P_2)_2]$ (**2**) followed by a brown zone of the same polarity containing 153.0 mg (9.5%) of $[(Cp'''Co)_3P_8]$ (**3**). The green tetranuclear complex $[(Cp'''Co)_4P_{10}]$ (**5**) could only be isolated in a mixture with **3** by elution with petroleum ether/diethyl ether gradient up to 50:1. The amount of **5** of the product mixture was determined by ^{31}P-NMR spectroscopy to be 1%. Elution of a narrow green zone with petroleum ether/diethyl ether (10:1) yielded a fraction from which 50.2 mg (3%) of $[Cp'''(Co)_3P_{12}]$ (**4**) was isolated. – $C_{51}H_{87}Co_3P_8$ (1124.8): calcd. C 54.46, H 7.80; found C 53.96, H 7.73. – $C_{51}H_{87}Co_3P_{12}$ (1248.8): calcd. C 49.05, H 7.02; found C 48.91, H 7.21.

Cophotolysis of $[Cp'''Co(CO)_2]$ (**1**) *and P_4:* A solution of 950.1 mg (2.73 mmol) of **1** and 869.4 mg (7.02 mmol) of P_4 in 110 ml of toluene was irradiated (150-W Hg high-pressure lamp, TQ 155, Heraeus Quarzlampen GmbH, Hanau) for 8 h (IR monitoring) by passing continuously a nitrogen stream through the solution. With advancing reaction time the color of the solution changed from pale orange to dark green. After evaporation of the solvent under oil pump vacuum the residue was dissolved in ca. 10 ml of dichloromethane, ca. 1.5 g of basic Al_2O_3-II was added, and the mixture was concentrated until it was free-flowing. Column chromatography (column 25 × 1 cm, basic Al_2O_3-II, elution with petroleum ether) afforded a narrow pale violet zone containing 39.7 mg (4%) of $[(Cp'''Co)_2(P_2)_2]$ (**2**). Petroleum ether/diethyl ether (10:1) eluted a deep green zone. From the eluate 265.2 mg (23% based on **1**) of $[(Cp'''Co)_3P_{12}]$ (**4**) was isolated.

Thermolysis of $[(Cp'''Co)_2(P_2)_2]$ (**2**): Thermolysis of 310.0 mg (0.44 mmol) of **2** in 20 ml of boiling decalin (predominant decomposition of **2** by ligand elimination, ^1H-NMR monitoring) for 10 d led to a black green solution of **5** which was worked up as described above. Column chromatographic forerun: 21.6 mg of starting compound **2**. Petroleum ether/diethyl ether (50:1) eluted a green zone. From the eluate 152.7 mg of **5** (13%, based on **2**) was isolated. – $C_{68}H_{116}Co_4P_{10}$ (1479.2): calcd. C 55.22, H 7.90; found C 55.81, H 7.93. – ^1H NMR (C_7D_8, 370 K): $\delta = 5.25$ (s, 2H), 4.91 (s, 2H), 4.77 (s, 2H), 4.48 (s, 2H), 1.79 (s, 9H), 1.67 (s, 18H), 1.57 (s, 18H), 1.55 (s, 18H), 1.46 (s, 36H), 1.24 (s, 9H); at 270 K the integral ratio of 2:18:9 is split into a ratio of 1:1:9:9:9, in agreement with a hindrance to rotation at the Cp'''–Co (centr.). – ^{31}P NMR ($CDCl_3/CD_2Cl_2$, 1:2, 230 K): ABCDEFGHIJ spin system: 260.6 (pdt, 1 P, P_A), 255.2 (pdt, 1 P, P_B), 58.2 (m, 1 P, P_C), 56.4 (m, 1 P, P_D), 54.6 (m, 1 P, P_E), 52.4 (m, 1 P, P_F), −138.6 (dd, 1 P, P_G), −142.9 (dd, 1 P_H), −154.2 (dd, 1 P, P_I), −160.5 (dd, 1 P, P_J). The coupling constants are not given since the quality of the available data set is insufficient for an optimal iteration (lacking information on coupling relations within the signal groups between 50 to 60 ppm). Determination of connectivities: $^{31}P^{31}P$-COSY45-NMR. – The complete unsymmetry of the P_{10} skeleton (**6** contains an inversion center), revealed by the ^{31}P-NMR data, may be attributed to a twisting of the P_5 building blocks about the P_A–P_B bridge. – MS (EI, 70 eV, 300 °C), *m/z* (%): $[(Cp'''Co)_4P_{10}]$ 1477.9 (100) $[M^+]$, $[(Cp'''Co)_3P_6]$ 1062 (45), $[(Cp'''Co)_3P_5]$ 1031 (3), $[(Cp'''Co)_2P_6]$ 770 (8), $[(Cp'''Co)_2P_5]$ 739.1 (25) $[M^+/2]$, $[(Cp'''Co)_2P_4]$ 708.1 (55), $[(Cp'''Co)_2P_3]$ 677.1 (71) and [*t*Bu] 57.3 (66).

☆ Dedicated to Prof. *Henri Brunner* on the occasion of his 60th birthday.

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