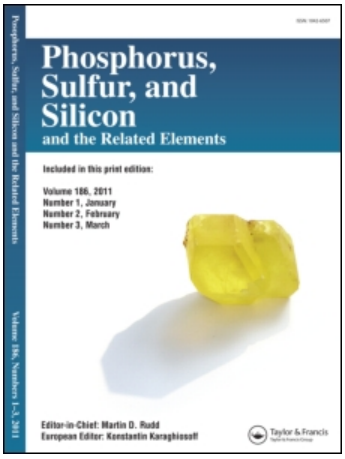

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P_8-, P_{10}- and P_{12}- Units as Increments in Cobalt Complexes

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P_8-, P_{10}- AND P_{12}- UNITS AS INCREMENTS IN COBALT COMPLEXES

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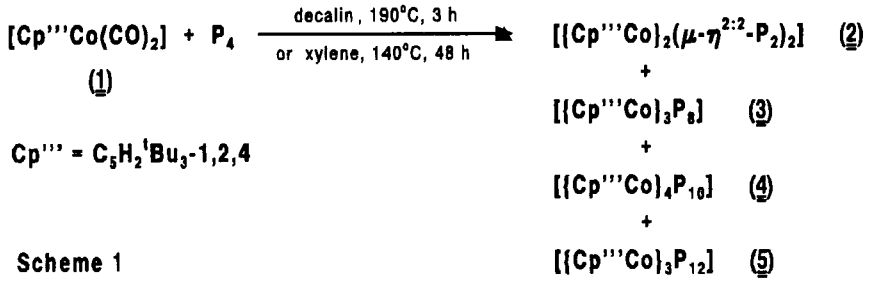
Abstract Within the coordination sphere of the metal complex fragment {Cp'''Co} the phosphorus increments P_8, P_{10} and P_{12} have been stabilized. Extended ^{31}P-NMR-spectroscopic investigations revealed detailed information about the structural properties of these species.

P_n-units which are stabilized by cyclopentadienyl-cobalt fragments have been known since 1972 [1]. By reaction of dicarbonyl-cyclopentadienylcobalt with white phosphorus the first complex of that kind, $[\{CpCo\}_4(\mu_3\text{-}P)_4]$ [1], is generated. Replacement of Cp by alkyl-substituted cyclopentadienyl perimeters leads to the formation of $[\{LCo\}_2(\mu\text{-}\eta^{2:2}\text{-}P_2)_2]$ [2], L= C_5Me_5, C_5Me_4Et, $C_5H_2{}^iPr_3$, $C_5H_3{}^tBu_2$, and $[\{LCo\}_4P_{10}]$ [3], L= C_5Me_4Et, $C_5H_3{}^tBu_2$, whereof the analogous rhodium compound $[\{Cp''Rh\}_4P_{10}]$, Cp''= $C_5H_3{}^tBu_2$, has been determined by X-ray analysis [4].

The variation of the cyclopentadienyl ligand to even higher substitution with more bulky groups seems to be the most effective way to stabilize new polyphosphorus increments.

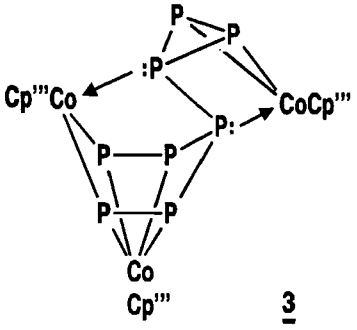
According to Scheme 1 the cothermolysis of $[Cp'''Co(CO)_2]$ (1) with white phosphorus forms the complexes 2-5.



Scheme 1

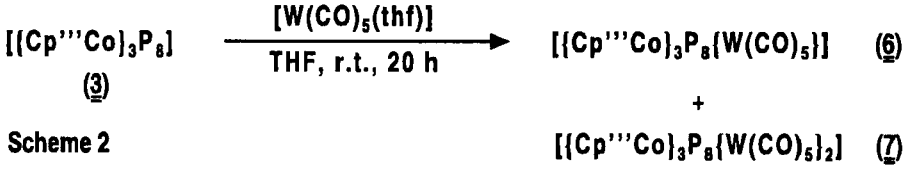
The structural characteristics of the compounds 3-5 are derived from ^{31}P-NMR-spectroscopy.

In case of [{Cp'''Co}$_3$P$_8$] (3), the ^{31}P-NMR-spectrum shows an ABMM'XX'Y$_2$-spinsystem [5]. Further examination with ^{31}P^{31}P-COSY45-NMR-spectroscopy reveals a phosphorus skeleton built of a three- and a five-membered ring joined by an exocyclic bonding. That P$_8$-framework - an all-phosphorus analogue of the postulated dihydrocalicene, (CH)$_8$ [6] - is coordinated by three {Cp'''Co}-fragments in the way known from [{Cp'Rh}$_4$P$_{10}$] [4] to form the trinuclear complex 3.



3

Addition of [W(CO)$_5$(thf)] to [{Cp'''Co}$_3$P$_8$] (3) leads to the mono- and disubstituted species 6 and 7, which are detected as ABCDEFGH-spinsystems in ^{31}P-NMR-spectroscopy [5] (Scheme 2).



Scheme 2

The P$_8$-core remains uninfluenced by addition of unsaturated fragments, which can clearly be derived from two-dimensional NMR-spectroscopy (Fig. 1).

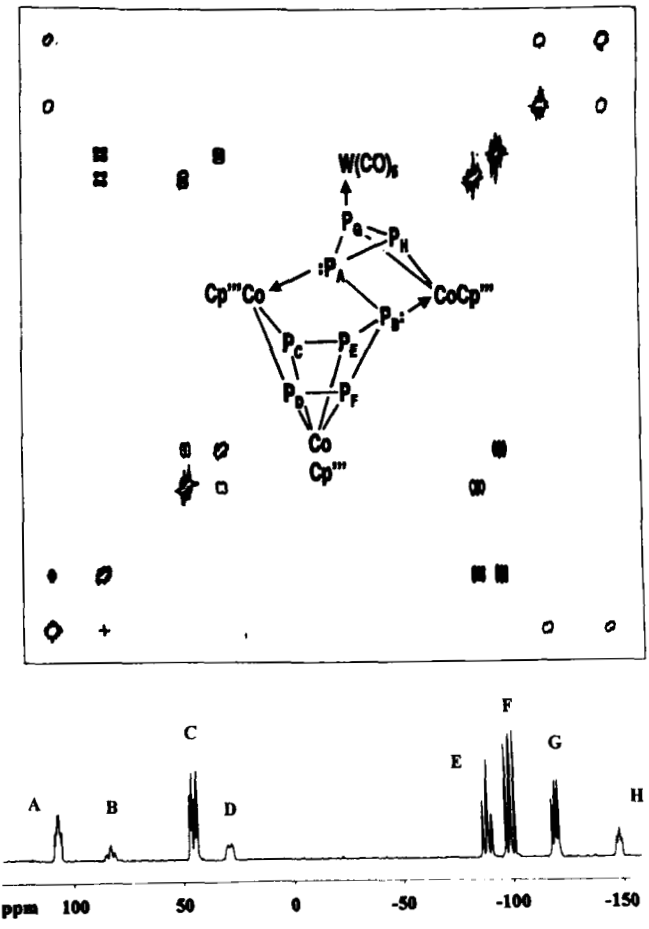
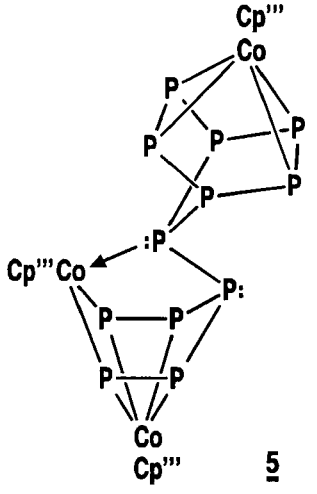


Fig. 1: $^{31}P^{31}P$-COSY45-NMR-spectrum of $[\{Cp'''Co\}_3P_8\{W(CO)_5\}]$ (6) ; 161.98 MHz, $CDCl_3$, r.t., 4096x256, d1=3.5s, gaussian.

Complex 4 encapsulates the same P_{10}-increment constructed of two five-membered rings linked by an exocyclic bond as the rhodium analogue $[\{Cp''Rh\}_4P_{10}]$ [4]. The more complex phosphorus NMR-spectrum of 4 - ABCDEFGHIJ in contrast to AA'BB'B''B'''CC'C''C''' - reveals a less symmetric geometry.

$[\{Cp'''Co\}_3P_{12}]$ (5), the compound with the most extended "naked" phosphorus skeleton in transition metal chemistry, gives rise to twelve different chemical shifts in phosphorus resonance experiments [5]. The constitution derived from two-dimensional NMR-spectroscopy shows a five-membered ring joined to a norbornane unit via an exocyclic bonding.



5

The coordination mode of the norbornane system in 5 is comparable to that one of the anions $[As_7Cr(CO)_3]^{3-}$ [7] and $[Sb_7Mo(CO)_3]^{3-}$ [8].
In analogy to P_{10} [4] the five-membered ring of 3 and 5 - 7 is probably open-edged.

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