# 165. Metal $\pi$-Complexes of Benzene Derivatives

Part 38[1]

## Pentaphenyltriphosphane(5) as a Chelating $\eta^{12}$-Ligand. Unusual Formation of an Interannular $-(PPh)_3-$ Bridge at Bis(benzene)chromium

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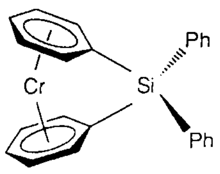
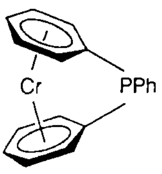
[(1–6):(1′–6′)-$\eta$-Pentaphenyltriphosphane(5)]chromium (**8**), which is formed from bis(lithio-$\eta^6$-benzene)-chromium and dichlorophenylphosphane, and which is prepared more rationally from bis(chloro-$\eta^6$-benzene)-chromium and $K_2P_3Ph_3$, is the first sandwich complex featuring an interannular oligophosphane bridge $-(PPh)_n-$, $n \geq 2$; $^{31}P\{^1H\}$- and $^1H$-NMR spectra suggest that the stereoisomer **8**-*meso*$_1$ is formed exclusively and that the $-(PPh)_3-$ link in this triphospha[3]chromocyclophane is non-fluxional in the range $193 < T < 348$ K.

**Introduction.** – The interest in metallocenophanes [2] results from the faculty of interannular bridges to confer kinetic stabilization to the sandwich unit, to interact by means of their $\sigma$-bonding orbitals with the $\pi$-electron system of the central unit and to effect compression, elongating or tilting distortion of the sandwich structure. Transferring these aspects to the bis($\eta^6$-arene)metal series, we have previously prepared a number of homo- and hetera-metallocyclophanes, the latter bearing heteroatoms in the interannular bridges [3].

Since very few tilted bis(arene)metal complexes are known, and the effect of bending on the chemical and spectroscopic properties is of some concern, we have tried to introduce the one atom interannular bridge $-PPh-$[2]. Due to the shorter bond distance $d(C-P)$, as compared to $d(C-Si)$, bending in the target molecule **2** should be more extensive than in ($\eta^{12}$-tetraphenylsilane)chromium (**1**; $\theta = 16.4°$ [3d]). We report here the unexpected outcome of our attempts to prepare ($\eta^{12}$-triphenylphosphane)chromium (**2**).



**1**



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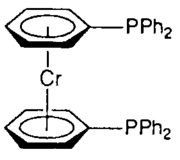

**3**

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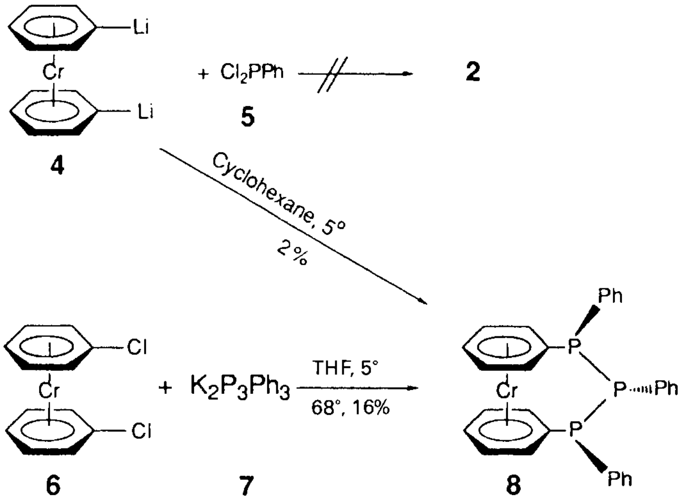
[1] Part 37: [1].

[2] The corresponding ferrocene derivative, $[C_6H_5-P(\eta^5-C_5H_5)_2]Fe$, had been prepared in the past [4].

**Results and Discussion.** – Since co-condensation techniques only afforded the bis(phosphano)derivative **3** we treated 1,1′-dilithiated bis(benzene)chromium **4** with dichlorophenylphosphane (**5**) (*Scheme*). Surprisingly, instead of the coupling product **2**, only [(1–6):(1′–6′)-$\eta$-pentaphenyltriphosphane(5)]chromium (**8**) was isolated from this reaction.

*Scheme*



Better yields of **8** are obtained, if bis($\eta^6$-chlorobenzene)chromium (**6**) prepared by means of metal-vapor synthesis [5] is treated with dipotassiumtriphenylcyclotriphosphane (**7**) [6]. The new triphospha[3]chromocyclophane **8** represents the first sandwich complex bearing an interannular oligophosphane link $-(\mathrm{PPh})_n-$ ($n \geqslant 2$). The thermal stability of **8** is demonstrated by the fact, that in its mass spectrum the molecular ion constitutes the base peak. Compared to parent bis(benzene)chromium ($E_{1/2}^{+/0} = -0.67$ V, DME/0.1M $\mathrm{Bu_4NClO_4}$ *vs.* SCE), the redox potential of **8** is shifted anodically ($E_{1/2}^{+/0} = -0.45$ V, CV reversible). Therefore, the $-(\mathrm{PPh})_3-$ bridge acts as an electron acceptor, increasing the partial positive charge on the central metal, which is the site of oxidation. Further oxidation $\mathbf{8}^{+/2+}$ as well as the reduction $\mathbf{8}^{0/-}$ occur irreversibly (*Fig. 1*). The EPR spectrum of the radical cation $\mathbf{8}^{+}$ in fluid solution displays hyperfine splitting from 10 protons which are equivalent within the resolution attained (*Fig. 1*). The proton hyperfine structure in the EPR spectra of bis(arene)metal($d^5$) complexes is known to respond sensitively to deviations from a parallel disposition of the two rings [7], the equivalence of the $\eta^6$-arene protons being raised upon tilting. Therefore, the observation of an undecet for $\mathbf{8}^{+}$ implies that the sandwich axis is virtually linear.

Since crystals suitable for X-ray structural analysis could not be obtained, the configuration of the $-(\mathrm{PPh})_3-$ link must be inferred from NMR data, bearing in mind the preferred conformations in similar units. The $^{31}\mathrm{P}\{^1\mathrm{H}\}$-NMR spectrum of **8** (*Fig. 2*) consists of a *doublet* and a *pseudotriplet* which are unequivocally assigned to the positions $\mathrm{P_A}$ and $\mathrm{P_B}$. This simple pattern which indicates the formation of only one isomer of $C_s$ symmetry is remarkable in view of the fact, that the $-(\mathrm{PPh})_3-$ link bears three centers of chirality so that 8 stereoisomers are conceivable. The closest analogy to the $-(\mathrm{PPh})_3-$ link

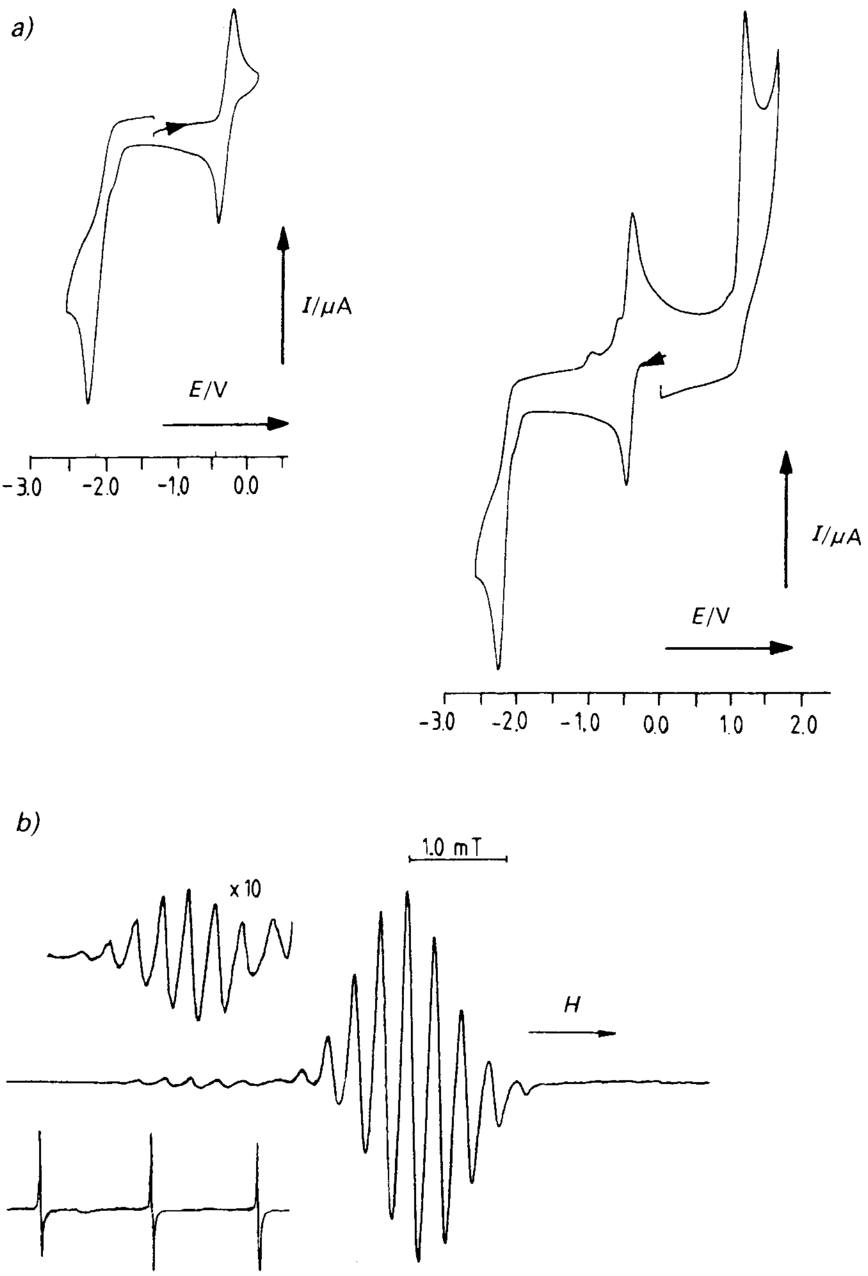


Fig. 1. a) *Cyclic voltammograms of* **8** *in DME/0.1* M *$Bu_4NClO_4$* vs. *SCE at glassy carbon.* $T = 25°$, $v = 0.05$ $Vs^{-1}$, $E_{pc} = -2.22$ V (irreversible), $E_{1/2}^{+/0} = -0.45$ V, $\Delta E_{1/2} = 78$ mV (reversible), $E_{pa} = 1.22$ V (irreversible). b) *EPR spectrum of* **8**$^+$ (air oxidation, $CHCl_3$/DMF 1:1, 25°). ‹g› = 1.9866, a(10 $^1$H) = 0.325 mT, a($^{53}$Cr) = 1.78 mT.

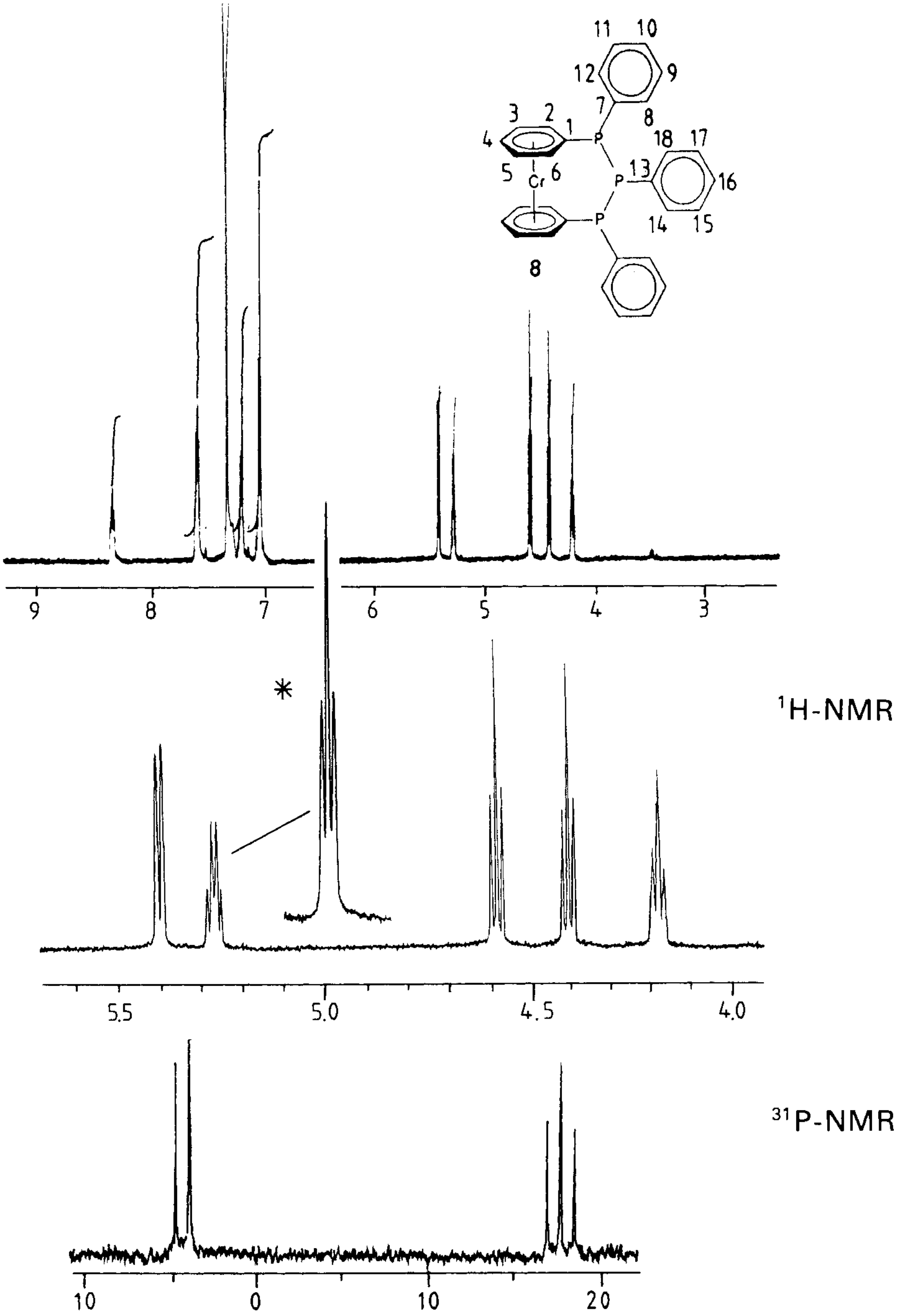
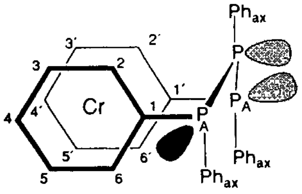
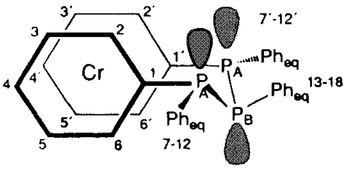


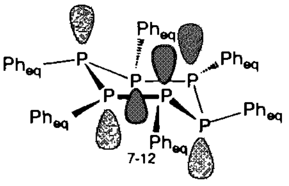
Fig. 2. *¹H- and ³¹P{¹H}-NMR spectra of* **8** *in $C_6D_6$.* * = Multiplet structure of H–C(2) upon homonuclear decoupling of H–C(3) displaying virtual coupling of H–C(2) to the $P_3$ chain.



**8**-*meso*$_2$



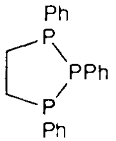
**8**-*meso*$_1$



**9**

in **8** exists in hexaphenylcyclohexaphosphane(6) **9** which adopts a chair form, the Ph groups all residing in equatorial positions and the lone pairs alternating around the ring in a *trans*-manner [8] [9]. The same configuration most likely is assumed by the $-(PPh)_3-$ bridge in **8**. Considering the pronounced dependence of the shifts $\delta(^{31}P)$ in cyclophosphanes on ring size and PPP angle [9], it is gratifying to note that $\delta(^{31}P_B) = -18.5$ ppm in **8** closely resembles the value $\delta(^{31}P) = -21.7$ ppm in **9** [10].

Possible dynamic processes of the $-(PPh)_3-$ interannular bridge include pyramidal atomic inversion at P and ring reversion caused by P—P bond rotation. Whereas inversion at three-coordinate P-atom is generally assumed to possess a high barrier such that organophosphanes are configurationally stable on the $^{31}$P-NMR time scale [11], the observation of ring reversion should be feasible. In this process, the two distinct forms **8**-*meso*$_1$ and **8**-*meso*$_2$ are interconverted. Therefore, in the slow-exchange limit, two pairs of *doublets* and *triplets*, respectively, should be detected, whereas in the fast-exchange limit one *doublet* and one *triplet* should arise, displaying temperature-dependent chemical shifts which are governed by the temperature dependence of the population ratio $K$ = [**8**-*meso*$_1$]/[**8**-*meso*$_2$]. The two conformations are expected to strongly differ in energy, because **8**-*meso*$_1$ features equatorial Ph groups and *trans*-oriented P lone pairs, whereas in **8**-*meso*$_2$ 1,3-diaxial interaction of Ph groups and lone pairs in synclinal disposition are encountered. Since only one *doublet* and one *triplet* is observed, both of which lacking temperature dependence of the shifts $\delta(^{31}P)$, it must be concluded that only the form **8**-*meso*$_1$ with a $-(PPh_{eq})_3-$ bridge is present in solution. The existence of a single (*meso*) form had also been established for the related triphosphanes **10** [12], **11** [13], and **12** [14].



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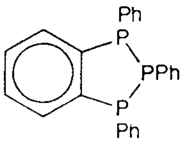

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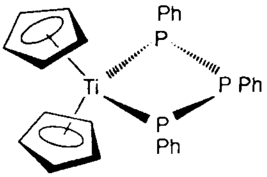


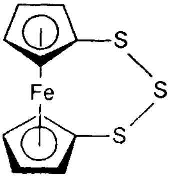
**12**

Additional evidence for the presence of a single conformer of **8** in solution is provided by the $^1$H-NMR spectrum (*Fig. 2*) which is temperature-independent in the range $193 < T < 348$ K. The assignments are based on COSY ($^1$H,$^1$H) and homonuclear decoupling experiments. To differentiate between H—C(2) and H—C(6), NOE-difference

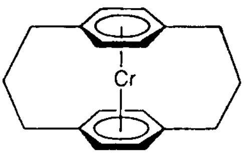
Table. *$^{13}C\{^{1}H\}$- and $^{31}P\{^{1}H\}$-NMR Data for [$\eta^{12}$-Pentaphenyltriphosphane(5)]chromium* (**8**) *in $C_6D_6$*
($\delta(P_A) = 3.9$, $\delta(P_B) = -18.5$, $^{2}J(P,P) = 134.0$ Hz)

| *i* | $\delta$(H–i) [ppm] | i,j | $^{3}J$(H–i, H–j) [Hz] | *J*(H–i, P) [Hz] | NOE % $f_i\{j,k\}$ | $\delta$(C(i)) [ppm] | Separation [Hz] |
|---|---|---|---|---|---|---|---|
| 1 | | | | | | 78.9 *m* | |
| 2 | 5.27 | 2, 3 | 5.2 | | $f_2\{8,12\} = 0.6$ | 84.7 '*d*' | 11.2 |
| 3 | 4.41 | 3, 4 | 5.4 | < 2 | | 75.9 '*t*' | 6.6 |
| 4 | 4.19 | 4, 5 | 5.3 | < 2 | | 75.4 *s* | |
| 5 | 4.58 | 5, 6 | 5.4 | < 2 | $f_6\{14,18\} = 0.9$ | 77.7 *s* | |
| 6 | 5.41 | 5, 6 | 5.4 | < 2 | $f_6\{8,12\} = 3.3$ | 85.7 '*t*' | 16.7 |
| 8, 12 | 7.47 | | | | $f_{8,12}\{6\} = 9.3$ | | |
| 9, 11 | 6.87 | | | | $f_{8,12}\{2\} = 3.5$ | | |
| 10 | 6.87 | | | | | | |
| 14, 18 | 8.20 | | | | $f_{14,18}\{6\} = 1.5$ | | |
| 15, 17 | 7.04 | | | | $f_2\{14,18\} = 0.8$ | | |
| 16 | 7.04 | | | | $f_{14,18}\{2\} = 1.3$ | | |

spectra were recorded. The relevant NOE enhancements $f_i\{j,k\}$ [%] are included in the *Table*. The fact that the $\eta^6$-arene protons (H–C(2)–H–C(6)) are anisochronous does not necessarily imply a static structure for **8** in solution, because reversion of the –(PPh)$_3$– bridge interconverts the forms **8**-*meso*$_1$ and **8**-*meso*$_2$ without effecting an exchange between sites H–C(2), H–C(6) and H–C(3), H–C(5), respectively. However, in the unlikely case that the fast exchange limit applies in the whole temperature range investigated, a pronounced temperature relation of the chemical shifts should be encountered, because the rotamers **8**-*meso*$_1$ and **8**-*meso*$_2$ prevail in a temperature-dependent equilibrium. As for $^{31}$P-NMR, the temperature invariance of the $^{1}$H-NMR spectrum suggests a slow-exchange situation and the virtually exclusive presence of a single rotamer in solution, which must be the form **8**-*meso*$_1$. The differentiation between **8**-*meso*$_1$ and **8**-*meso*$_2$ again rests on the NOE results. For **8**-*meso*$_2$, the group $Ph_{ax}$ at $P_B$ would assume a disposition relative to H–C(2) similar to that of $Ph_{ax}$ at $P_A$ relative to H–C(6). This should lead to comparable NOE enhancements $f_{8,12}\{6\}$ and $f_{14,18}\{2\}$, contrary to observation (*Table*). Rather, the at best marginal NOE enhancements $f_{14,18}\{2\}$ and $f_{14,18}\{6\}$ imply that the Ph ring at $P_B$ occupies an equatorial position as in the form **8**-*meso*$_1$. With regard to the rigidity of the –(PPh)$_3$– bridge in **8**, it is interesting to note that for the trithia[3]metallocenophane **13** even in the absence of bulky substituents at the third-row-element interannular bridge, a high energy barrier for the dynamic process was reported [15], whereas the trimethylene bridges in ($\eta^{12}$-[3.3]paracyclophane)chromium **14** [16] are highly fluxional.



**13**



**14**

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## Experimental Part

*General.* All reactions were performed under pure $N_2$. Solvents were thoroughly dried and saturated with $N_2$. NMR spectra: *Bruker AC-300* and *AM-400*. EPR spectra: *Varian EE12*. MS: *MAT CH7A* (EI-MS), *MAT 711* (FD-MS). Cyclic voltammetry: *Amel 552* (potentiostat), *566* (function generator), *563* (multipurpose unit); *Nicolet 2090-1* (storage oscilloscope); working electrode: glassy carbon, counter electrode: Pt, reference electrode: SCE.

*[(1–6):(1′–6′)-η-Pentaphenyltriphosphane(5)]chromium* (**8**). A mixture of $K_2[P(C_6H_5)]_3 \cdot$THF (**7**; 2.20 g, 4.46 mmol) and $(Cl{-}\eta^6{-}C_6H_5)_2Cr$ (**6**; 1.28 g, 4.46 mmol) in THF (100 ml) was refluxed for 6 h. The solvent was removed *in vacuo* and replaced by toluene (15 ml). This soln. was chromatographed on $Al_2O_3$ (1% $H_2O$) to form three zones (orange, red, and brown, respectively). From the first zone, 620 mg of a viscous oil is obtained which can be crystallized from toluene/pentane 1:4 to yield **8** (400 mg, 16% yield) as orange needles. Compound **8** partially decomposes during sublimation at 145°. MS: 530 ($M^+$, EI-MS, FD-MS). Anal. calc. for $C_{30}H_{25}P_3Cr$ (530.44): C 67.92; H 4.75; found: C 67.61, H 4.76.

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