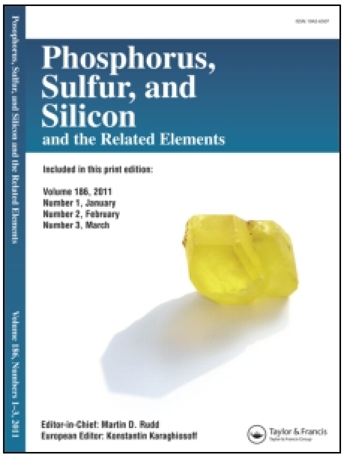

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# $P_x$ - Hückel Systems as Complex Ligands

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# $P_x$ - HÜCKEL SYSTEMS AS COMPLEX LIGANDS

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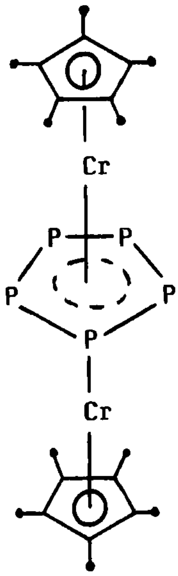
Abstract Recent developments in the chemistry of $[Cp^*Mo(\mu,\eta^6-P_6)MoCp^*]$, $[Cp^*Cr(\mu,\eta^5-P_5)CrCp^*]$ and $[Cp^*_2Co_2(P_4)]$ are discussed.

The interaction of $[Cp^*(CO)_2M]_2(M{\equiv}M)$, M=Cr, Mo, $Cp^* = \eta^5-C_5Me_5$, and white phosphorus affords beside $[Cp^*(CO)_2M(\eta^3-P_3)]$ (1), $[\{Cp^*(CO)_2Mo\}_2(\mu,\eta^2-P_2)]$ (2), $[Cp^*(CO)Mo(\mu,\eta^2-P_2)]_2$ (3) the triple-decker sandwich complexes 4a [1] and 5 [2].

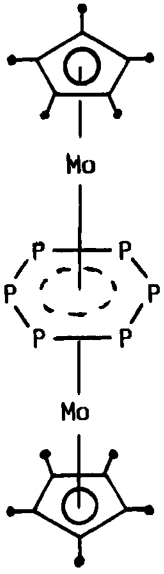
In 2 (Cp instead of $Cp^*$) the $P_2$ unit of the $Mo_2P_2$ tetrahedrane can further coordinate as 4-electron donor to the $Re_2(CO)_6(\mu-Br)_2$ fragment [3].

ESR and magnetic susceptibility ($\mu = 2.07\mu B$) [4] studies confirm the paramagnetism of 4a, which is a delocalized mixed-valence complex ($d^4|d^5$ system) with a cyclo-$P_5^-$ ($P_5^- \triangleq C_5H_5^-$) bridge between two equivalent chromium centres. Suitable educts for $[\{(\eta^5-C_5H_4R)Cr\}_2(\mu,\eta^5-P_5)]$, R = H (4b, $^{31}P\{^1H\}$: -285(s)), $CH_3$ (4c, -283(s)), $CH_2C_6H_5$ (4d, -280(s)), are the dinuclear compounds $[(\eta^5-C_5H_4R)(CO)_3Cr]_2(Cr-Cr)$.

3, a dinuclear complex, for which a structure consisting of two $P_2Mo_2$ tetrahedra (cf. 6) with a common Mo-Mo edge and cis arrangement of the $Cp^*$ and CO ligands was proposed [2], has been characterized as its derivative 6.



—• = $CH_3$

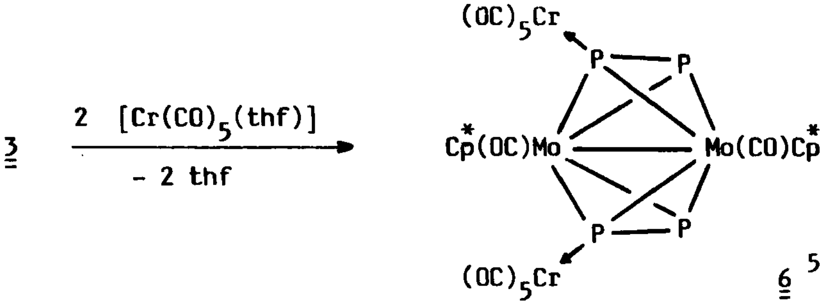


**4a** [1]

**5** [2]

27 VE; $^{31}P\{^1H\}$: -290.5(s)
P-P = 2.15-2.21(2) Å
Cr-Cr = 2.727(5) Å
$E_{ox}$ = 0.07; $E_{red}$ = -0.97 V

28 VE; $^{31}P\{^1H\}$: -315.6(s)
P-P = 2.167-2.175(3) Å
Mo-Mo = 2.647(1) Å



**6** [5]

The X-ray structure determination of **6** [5] shows the $(P_2)_2$ unit to be coplanar in a trapezoidal arrangement. While the bonding P-P distances (2.063(5) and 2.071(5) Å) lie in the expected range, the P...P distances are quite different. 2.849(5) Å was found for the "short" side and 3.959(5) Å for the "long" side (P-atoms coordinated to $Cr(CO)_5$) of the $P_4$ trapezoid. These results are in good agreement with recent ab initio calculations [6] for the transition state ($D_{3h}$) of the cyclo-$P_6$ formation.

If $P_2$ can be considered as an acetylene analogue (P is isoelectronic with CH), then a cyclo-$P_6$ (hexaphosphabenzene) synthesis is possibly an analogue of the Reppe benzene synthesis ($3\ P_2 \rightarrow P_6$, cf. also ref. 6). Evidence for this hypothesis comes from the finding that the triple-decker 5 can directly be formed by the cothermolysis of 3 (cf. compound 6) and white phosphorus (replacement of the two CO ligands by the third $P_2$ unit).

A still unsolved problem is the structure of 7 which has been synthesized according to the equation:

$$[Cp^*Co(CO)_2] \xrightarrow[\text{ca. 110°C, ca. 24 h}]{P_4,\ \text{toluene}} [Cp^*_2Co_2(P_4)]$$

$Cp^* = \eta^5\text{-}C_5Me_5$

7

Elemental analysis and mass spectrum [(EI-MS|70 eV, 25°C): m/z 512 ($M^+$, 100 %)] confirm the composition of 7, that can be isolated in ca. 30 % yield as black microcrystalline powder, readily soluble in pentane and toluene, moderately soluble in ether and acetonitrile. The $^{31}P\{^1H\}$-NMR spectrum affords (even at ca. -80°C) a sharp singlet ($\delta$ = -17 ppm, 25°C, $CD_2Cl_2$, 85 % $H_3PO_4$ ext.). $^1H$-NMR (200 MHz, $C_6D_6$, TMS int.): quintet at 1.65 ppm ($^4J(PH)$ = 0.6 Hz). Cyclic voltammetry measurements (in $CH_2Cl_2$ or DMF) gave an irreversible one-electron oxidation step ($E_{ox}$ = + 0.3 V) [7]. ESR spectroscopically no evidence for paramagnetism was found [7].

The most probable structure alternatives for 7 are:

a) The 32 VE (valence electrons) triple-decker $[Cp^*Co(\mu,\eta^4\text{-}P_4)\text{-}CoCp^*]$ with cyclo-$P_4$ ($Co^+$, $d^8$), the all-phosphorus analogue of cyclobutadiene, or cyclo-$P_4^{2-}$ ($Co^{2+}$, $d^7$) as the "middle deck" (cf. the MO studies of complexes containing the $M_2(CO)_6$ or $M_2Cp_2$ binuclear transition-metal fragment bonded to cyclobutadiene or other ligands [8]).

b) $[Cp^*Co(\mu,\eta^2\text{-}P_2)_2CoCp^*]$ with two 4-electron donor $P_2$-bridges between the cobalt atoms (18 VE for each Co).

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