$[Cr(CO)_5PCl_3]$ – A Starting Material for Phosphorus-Rich P_x Ligand Complexes☆

Manfred Scheer*[a], Kay Schuster[a], André Krug[b], and Helmut Hartung[b]

Institut für Anorganische Chemie der Universität Karlsruhe[a],
Engesserstraße, D-76128 Karlsruhe, Germany
Fax: (internat.) +49(0)721/661921
E-mail: mascheer@achibm6.chemie.uni-karlsruhe.de

Institut für Physikalische Chemie der Universität Halle[b],
Mühlpforte 1, D-06108 Halle/S., Germany
Fax: (internat.) +49(0)345/5527156
E-mail: hartung@chemie.uni-halle.de

Received April 7, 1997

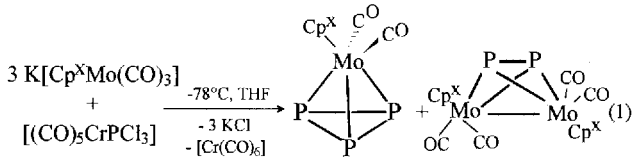
Keywords: P ligands / P–P bond formation reaction / Molybdenum / Chromium / Nickel / Carbonyl complexes / Main group elements

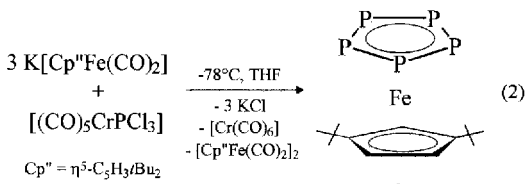
$[Cr(CO)_5PCl_3]$ reacts with different metallates $K[Cp^xMo(CO)_3]$ [Cp^x = η^5-C_5H_4tBu (Cp'), η^5-$C_5H_3tBu_2$-1,3 (Cp")], $K[Cp"Fe(CO)_2]$, $K[Cp'Cr(CO)_3]$, $K[Cp^*Ni(CO)]$ and $Na_2[Cr_2(CO)_{10}]$ at −78 °C in THF to yield various P_2, *cyclo*-P_3 and *cyclo*-P_5 ligand complexes of the formulae $[Cp'Mo(CO)_2(\eta^3\text{-}P_3)]$ (**1a**), $[Cp"Mo(CO)_2(\eta^3\text{-}P_3)]$ (**1b**), $[\{Cp'Mo(CO)_2\}_2(\mu,\eta^2\text{-}P_2)]$ (**2a**), $[\{Cp"Mo(CO)_2\}_2(\mu,\eta^2\text{-}P_2)]$ (**2b**), $[Cp"Fe(\eta^5\text{-}P_5)]$ (**3**), $[(Cp'Cr)_2(\mu,\eta^5\text{-}P_5)]$ (**4**), $[\{Cp'Cr(CO)_2\}_2(\mu,\eta^2\text{-}P_2)]$ (**5**), $[(Cp^*Ni)_2(\mu,\eta^2\text{-}P_2)\{Cr(CO)_5\}_2]$ (**6**), $[\{(CO)_5Cr\}Cl_2PPCl_2\{Cr(CO)_5\}]$ (**7**) and $[\{Cr(CO)_5\}_2PCl]$ (**8**). Comprehensive studies of the reaction pathway leading to formation of the *cyclo*-P_3 product **1a** give strong indications that a sequence involving metal-halogen exchange and stepwise P–P bond formation takes place, proceeding via $[\{(CO)_5Cr\}Cl_2PPCl_2\{Cr(CO)_5\}]$ (**7**) and the *cyclo*-P_3 precursor compound $[\{Cp'Mo(CO)_3\}\{Cp'Mo(CO)_2\}_2\{Cr(CO)_5\}(\mu,\eta^{3:1:1}\text{-}P_3)]$ (**9**). The latter two complexes have been isolated and structurally characterized.

P_x ligand complexes are usually synthesized using P_4 phosphorus as the starting material.[1] There have been only two literature reports of P–P bond-forming reactions starting from PX_3 (X = Cl, Br), leading to the P_2 ligand complexes $[Co_2(CO)_6(\mu,\eta^2\text{-}P_2)]$[2] and $[Co_2(CO)_6(\mu,\eta^2\text{-}P_2)(ML_n)_2]$ [ML_n = $M(CO)_5$, $CpMn(CO)_2$; M = Cr, W].[3]

In contrast, we found that $[Cr(CO)_5PCl_3]$ acts as a P_1 building block in the formation of complexes with *cyclo*-P_x ligands. Thus, in the reactions with Cp^x-containing carbonyl metallates of molybdenum and iron, the *cyclo*-P_3 and *cyclo*-P_5 ligand complexes **1** and **3** are formed as the main products [eq. 1 and 2].[4] This represents a novel approach for P-rich ligand complexes.

We report herein on an extension of this synthetic concept, involving the reaction of $[Cr(CO)_5PCl_3]$ with various metallates, as well as on the results of a mechanistic study of the reaction.

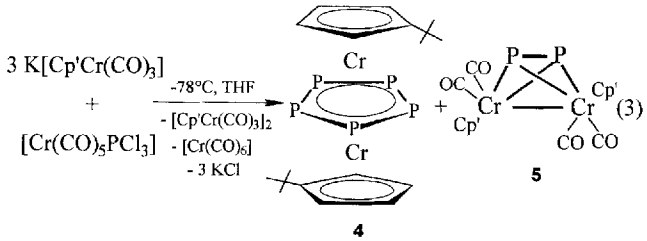


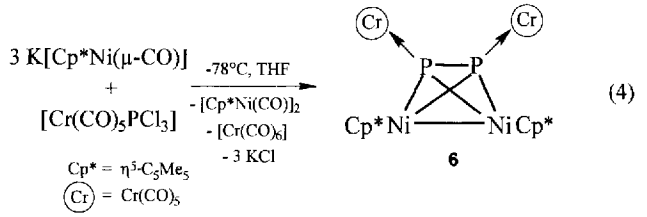


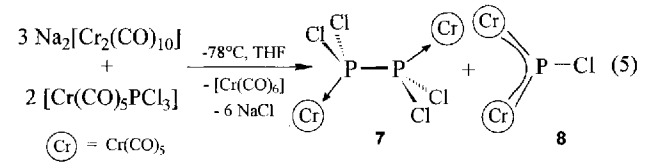
Results and Discussion

The reaction of $[Cr(CO)_5PCl_3]$ with $K[Cp'Cr(CO)_3]$ at −78 °C in THF affords three distinct phosphorus-containing products, as indicated by a ^{31}P-NMR spectrum of the crude reaction mixture [eq. 3]. Only the major product $[(Cp'Cr)_2(\mu,\eta^5\text{-}P_5)]$ (**4**) could be isolated by column chromatography; both of the other products decomposed on the column. By comparison with known complexes formed during the cothermolysis of P_4 with $[CpCr(CO)_3]_2$,[5] the weakest signal at δ = 102.6 can be assigned to $[\{Cp'Cr(CO)_2\}_2(\mu,\eta^2\text{-}P_2)]$ (**5**). The singlet at δ = −102.3 (about 35 mol % P) does not correspond to any previously reported analogous compound.

Complex **4** was obtained as a brownish-black powder, and was found to be sparingly soluble in pentane, but readily soluble in CH_2Cl_2 and THF. The ^{31}P-NMR resonance of **4** appears as a broad signal ($w_{1/2}$ = 70 Hz) at δ = −290 owing to the paramagnetism of this 27 VE complex. In the







mass spectrum, the molecular peak was observed. All data obtained for **4** (Table 1) correspond to those of the structurally and spectroscopically characterized compounds $[(Cp^xCr)_2(\mu,\eta^5\text{-}P_5)]$ ($Cp^x = \eta^5\text{-}C_5H_4R$, R = H, Me, *t*Bu). [6].

The reaction of $[Cr(CO)_5PCl_3]$ with K[Cp*Ni(CO)] leads to the tetrahedral complex $[(Cp^*Ni)_2\langle(\mu,\eta^2\text{-}P_2)\{Cr(CO)_5\}_2\rangle]$ (**6**) [eq. 4]. All chemical and spectroscopic properties of this brown, crystalline product (Table 1) correspond to those of the structurally characterized complex **6**, which we recently obtained by reacting $[\{Cr(CO)_5\}_2PCl]$ with K[Cp*Ni(CO)] in THF at −78°C. [7].

$Na_2[Cr_2(CO)_{10}]$ reacts with $[Cr(CO)_5PCl_3]$ at −78°C in THF to form $[\{(CO)_5Cr\}Cl_2PPCl_2\{Cr(CO)_5\}]$ (**7**) and $[\{Cr(CO)_5\}_2PCl]$ (**8**) [eq. 5] as the only compounds detectable by ^{31}P-NMR spectroscopy (**7**: δ = 207.9; **8**: δ = 186.4). The main product **7** was isolated in about 30% yield, while **8** decomposed upon attempted column chromatography. The latter was first obtained and characterized by Huttner et al. [8].

7 is a yellow, crystalline complex that is sparingly soluble in *n*-pentane, but readily soluble in toluene, CH_2Cl_2 and THF. The solid is stable in air for a short time, but is sensitive to light, so it is recommended that it is stored in the dark under an inert gas atmosphere. The IR and mass spectroscopic data (Table 1) are in a good agreement with those described by Fritz et al., who obtained **7** by electrochemical reduction of $[Cr(CO)_5PCl_3]$. [9] An X-ray structure analysis of **7** has not previously been reported.

7 crystallizes in the monoclinic space group $P2_1/c$ with two molecules in the unit cell (Figure 1). It represents a tetrachlorodiphosphane, in which the lone pairs of each of

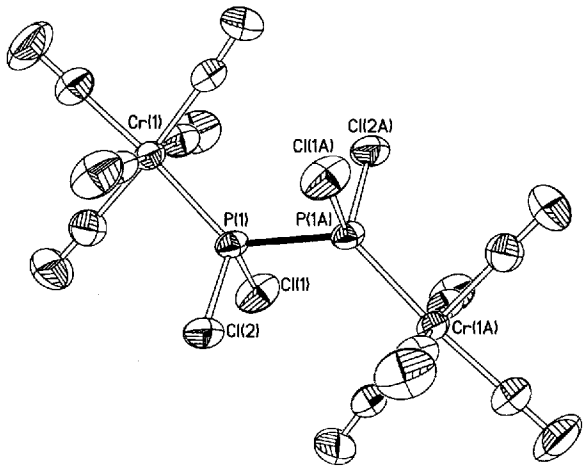
Table 1. NMR and IR data of the complexes **4**–**7** and **9**; δ in ppm, *J* in Hz, $\tilde{\nu}$ in cm^{-1}

		4	**5**	**6**	**7**	**9**
^1H[a]	CH_3	0.73 (s, 9 H)	[b]	1.6 (s)		0.99 (s, 9 H)
	CH (A)	20.1 (s, br, 2 H)				5.66 (t, 2 H)
	CH (B)	17.1 (s, br, 2 H)				5.74 (t, 2 H)
						J_{HH} = 2,4
	CH_3					1.09 (s, 18 H)
	CH (A)					5.85 (t, 4 H)
	CH (B)					6.08 (m, 4 H)
						J_{HH} = 2,3
^{31}P[a]		−290.0 (s)	102.6 (s)	240.4 (s)	207.9 (s)	A: −18.8 (d)
						M: −57.4 (dd)
						X: −170.0 (d)
						$^1J_{AM}$ = 370
						$^1J_{MX}$ = 385[c]
$\tilde{\nu}$(CO)[d]			[b]	2042 (s)	2077 (m)	2067 (m)[e]
				2030 (s)	2013 (m, sh)	1993 (sh)
				1983 (s)	1967 (vs, br)	1979 (s)
				1962 (sh)		1968 (sh)
				1947 (vs)		1940 (vs, br)
				1937 (sh)		1900 (sh)
EI-MS[f]:		501 (11) [M^+],	[b]	833 (1.6) [M^+],	588 (28) [M^+],	524 (28) [{Cp'Mo(CO)P}$_2^+$],
m/z (%)		439 (9) [$M^+ - P_2$],		641(1.7) [M^+],	560 (5) [$M^+ - CO$],	496 (87) [{Cp'MoP}$_2^+$],
		173 (15) [$M^+ - P_2$]		501 (10) [$M^+ - Cr(CO)_{10}$],	553 (8) [$M^+ - Cl$],	368 (19) [Cp'Mo(CO)P_3^+],
				220 (26) [$Cr(CO)_6^+$],	448 (15) [$M^+ - Cl$]	310 (71) [Cp'MoP_3^+],
				136 (43) [$Cr(CO)_3^+$],		108 (49) [$(CO)_2Cr^+$],
				52 (56) [Cr^+],		52 (100) [Cr^+],
				28 (100) [CO^+]		28 (45) [CO^+]

[a] In C_6D_6. – [b] Product decomposes on the column material (for structural analogue of **5** cf. ref.[6]). – [c] $^2J_{AX}$ not observed, $w_{1/2}$ = 70 Hz. – [d] In hexane. – [e] In Nujol. – [f] 70 eV, 270°C.

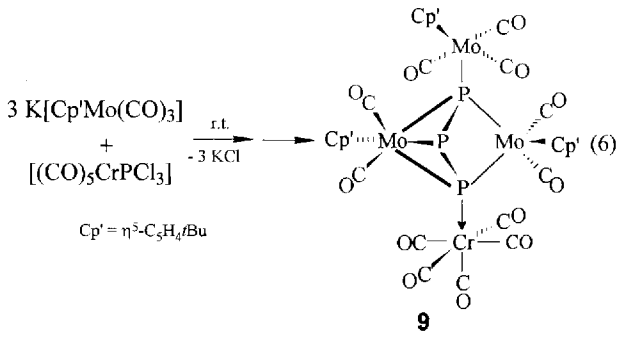
the P atoms are coordinated to $Cr(CO)_5$ units. The chromium pentacarbonyls are *trans*-oriented. The P–P bond length is 2.268(3) Å, and is therefore somewhat longer than the single bond distance of 2.21 Å[10]. It is comparable with that found in the complexed diphosphane $[(CO)_3Ni(PPh_2)_2Ni(CO)_3]$ [2.277(4) Å]. [11] However, the diphosphane complexes $[\{(CO)_5Cr\}(Cl)PhPPPh(Cl)\{Cr(CO)_5\}]$[12a] and $[\{Cp(CO)_2Mn\}(MeP\mathit{t}Bu)_2\{Mn(CO)_2Cp\}]$[12b] exhibit much longer P–P bonds (2.290, 2.327 and 2.350 Å), clearly due to the steric influence of the organic groups.

Figure 1. Molecular structure of $[\{(CO)_5Cr\}Cl_2PPCl_2\{Cr(CO)_5\}]$ (**7**); selected bond distances [Å] and angles [°]: Cr(1)–P(1) 2.268(3), P(1)–Cl(1) 2.039(2), P(1)–Cl(2) 2.048(3), P(1)–P(1A) 2.268(3); Cl(1)–P(1)–Cr(1) 117.46(9), Cl(1)–P(1)–Cl(2) 100.63(11), Cl(2)–P(1)–Cr(1) 115.36(9), Cl(1)–P(1)–P(1A) 95.14(11), Cl(2)–P(1)–P(1A) 95.20(10), Cr(1)–P(1)–P(1A) 127.73(10)



Study of the Reaction Pathway: The pathway of reaction (1) starting from $K[Cp'Mo(CO)_3]$ was extensively studied by varying the reaction conditions (temperature and stoichiometry). In principle, there are two possibilities: (i) a stepwise P–P bond formation, and (ii) the formation of reactive intermediates of the type $[Cp'(CO)_2Mo{\equiv}P]$ (for evidence of the existence of such species see ref.[13]). Recently, we found that chlorophosphinidenes of the type $[\{M'(CO)_5\}_2PCl]$ (M' = Cr, W) react with different transition metallates to yield P_2M_2 tetrahedral complexes.[7] Studies of the reaction pathway in such cases provided strong evidence for phosphido (P^{3-}) ligand complexes being intermediates in these reactions. In contrast, starting with $[Cr(CO)_5PCl_3]$ there are no indications for such intermediates. Thus, for example, if reaction (1) is carried out at different temperatures (−78°C, −40°C, 25°C) in the presence of 2,4-dimethylbutadiene or phosphaalkyne, the same product distribution is found as in reactions conducted in the absence of these compounds. As shown in the following, there is strong evidence for a stepwise P–P bond formation reaction.

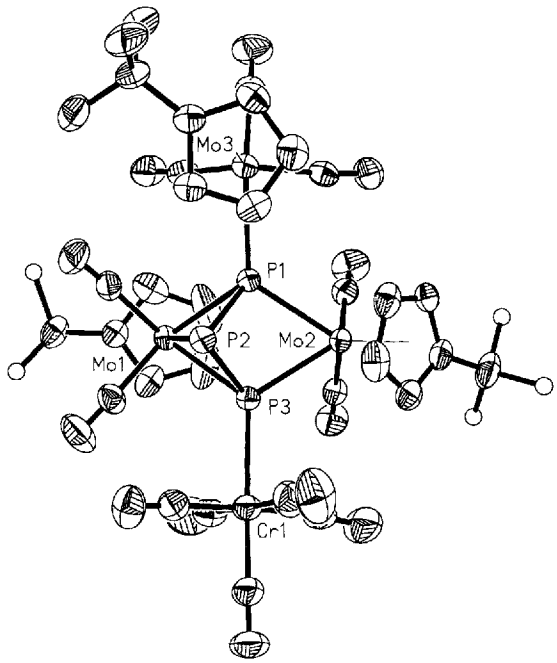
Stoichiometric amounts of $K[Cp'Mo(CO)_3]$ were reacted with $[Cr(CO)_5PCl_3]$ in THF at ambient temperature [eq. 6]. The reactions were terminated immediately after addition of the metallate by completely removing the solvent in vacuo. Besides **1b** and **2b**, $[\{Cp'Mo(CO)_3\}\{Cp'Mo(CO)_2\}_2\{Cr(CO)_5\}(\mu,\eta^{3:1:1}\text{-}P_3)]$ (**9**) was isolated as a brown, crystalline compound after column chromatographic work-up and was characterized by NMR, IR and mass spectroscopy (Table 1). In the ^{31}P-NMR spectrum, an AMX spin system is observed with large $^1J(^{31}P,^{31}P)$ couplings of 370 and 385 Hz. A $^2J(^{31}P, ^{31}P)$ coupling could not be determined due to the broad signals (about 70 Hz). In the ^1H-NMR spectra at 301 K and 203 K, only two distinct Cp' groups in the ratio 1:2 could be detected, indicating a fast exchange of the P_3 unit between the Mo(1) and Mo(2) atoms (Table 1).



Complex **9** crystallizes in the triclinic space group $P\bar{1}$ with two molecules in the unit cell; its molecular structure is shown in Figure 2. The allylic-like P_3 structural entity is attached to each of the three Mo atoms in a different manner: it is capped by the first and bridged by the second $[Cp'Mo(CO)_2]$ moiety, while the $[Cp'Mo(CO)_3]$ unit is bonded in a terminal position at P1. A $[Cr(CO)_5]$ moiety is additionally coordinated at P3. The two *t*Bu groups attached to the Cp' ligands of Mo(1) and Mo(2), respectively, show disorder in the sense that they can occupy two alternative positions, each with a site occupation of about 0.5. The allylic-like description of the P_3 unit is supported by the bond lengths P(1)–P(2) = 2.160(1) Å and P(2)–P(3) = 2.149(1) Å, which are almost equal, while the P(1)···P(3) distance of 2.700(1) Å indicates a non-bonding situation between the terminal atoms. The two P–P bonding distances are distinctly shorter than the best approximation for the P–P single bond distance of 2.228 Å,[14] but are quite similar to those found in the allylic P_3-subunit of $[\{(CH_3CN)_2(CO)_2WCl\}\{\eta^3\text{-}P_3\{W(CO)_5\}_2P\{(OH)W(CO)_5\}\}]$ [2.172(5) and 2.158(4) Å].[15] The two P–P distances observed in the allylic P_3Et ligand complex $[L_3Co(\eta^3\text{-}P_3Et)CoL_3][BF_4]_2$ [L_3 = triphos = $CH_3C(CH_2PPh_2)_3$] [2.211(1) and 2.110(1) Å][16] differ markedly but, on average, are almost the same as those observed in **9**. In the *cyclo*-P_3-complex $[CpMo(CO)_2(\eta^3\text{-}P_3)]$, a slightly shorter P–P distance (average 2.131 Å) was found.[17] The preference for the open geometry of a bifacial coordinated P_3 ligand like that in **9** to a *cyclo*-P_3 structure has been discussed in the literature.[16].

Complex **9** acts as the source for the final *cyclo*-P_3 product formed, $[Cp'Mo(CO)_2(\eta^3\text{-}P_3)]$ (**1a**), which can be experimentally verified. Stirring a solution of **9** for 1 h at room temperature results in the formation of $[Cr(CO)_6]$, $[Cp'Mo(CO)_2]_2$ and **1a**. Thus, the bond formation between P(1) and P(3) occurs by elimination of $[Cr(CO)_6]$ and $[Cp'Mo(CO)_2]_2$.

Figure 2. Molecular structure of [{Cp'Mo(CO)$_3$}{Cp'Mo(CO)$_2$}$_2${Cr(CO)$_5$}{$\mu,\eta^{3:1:1}$-P$_3$}] (**9**); H atoms omitted; selected bond distances [Å] and angles [°]: Mo(1)–P(1) 2.572(1), Mo(1)–P(2) 2.577(1), Mo(1)–P(3) 2.594(1), Mo(2)–P(1) 2.545(1), Mo(2)–P(3) 2.540(1), Mo(3)–P(1) 2.635(1), Cr(1)–P(3) 2.463(1), P(1)–P(2) 2.160(1), P(2)–P(3) 2.149(1); P(1)–Mo(1)–P(2) 49.60(3), P(1)–Mo(1)–P(3) 63.02(3), P(2)–Mo(1)–P(3) 49.10(3), P(1)–Mo(2)–P(3) 64.15(3), Mo(1)–P(1)–Mo(2) 106.10(3), Mo(1)–P(1)–Mo(3) 126.65(3), Mo(1)–P(1)–P(2) 65.31(4), Mo(2)–P(1)–Mo(3) 126.07(3), Mo(2)–P(1)–P(2) 98.99(4), Mo(3)–P(1)–P(2) 111.47(4), Mo(1)–P(2)–P(1) 65.09(4), Mo(1)–P(2)–P(3) 65.87(4), P(1)–P(2)–P(3) 77.62(5), Mo(1)–P(3)–Mo(2) 105.62(3), Mo(1)–P(3)–Cr(1) 127.01(3), Mo(1)–P(3)–P(2) 65.03(4), Mo(2)–P(3)–Cr(1) 123.95(3), Mo(2)–P(3)–P(2) 99.46(4), Cr(1)–P(3)–P(2) 117.87(4)



In the course of our mechanistic studies, the stoichiometry of the reaction was verified in order to check all possible side reactions that might accompany formation of the *cyclo*-P$_3$ complex **1a**. If [Cr(CO)$_5$PCl$_3$] is reacted with only one equivalent of K[Cp'Mo(CO)$_3$], the final product [Cp'Mo(CO)$_2$(η^3-P$_3$)] (**1b**) is formed, but the tetrachlorodiphosphane [{(CO)$_5$Cr}Cl$_2$PPCl$_2${Cr(CO)$_5$}] (**7**) and the substitution product [{Cp'Mo(CO)$_3$}PCl$_2$] can also be detected by ^{31}P NMR (δ = 349.4) [18]. The latter compound is a possible source of the P$_2$ complex **2a**. Clearly, the formation of **7** requires a good reducing agent such as, e.g., Na$_2$[Cr$_2$(CO)$_{10}$] in reaction (5). Consistent with this observation is the fact that the use of Na$_2$[W$_2$(CO)$_{10}$] instead of Na$_2$[Cr$_2$(CO)$_{10}$] in reaction (5) leads to an almost analogous product distribution. **7** is shown to be an important intermediate of the reaction (1).

Reaction of **7** with four equivalents of K[Cp'Mo(CO)$_3$] at −78 °C in THF leads in 85 mol % P [19] to the unknown complex **10**, indicated in the ^{31}P-NMR spectrum by a sharp singlet at δ = −148.0. Isolation of **10** failed due to decomposition on the column material. Since the P$_2$ complex **7** was used, it may be possible that **10** is a P$_2$ compound in which two or all four Cl atoms are substituted by Mo-containing moieties. This assumption is supported by the ^{1}H-NMR spectrum of **10**, which features only very broad singlets for the *t*Bu groups and for the ring H atoms [^{1}H NMR: δ = 1.76 (s, br, 9 H), 5.28 (s, br, 4 H)]. Furthermore, the ^{31}P-NMR chemical shift in **10** falls in the range of the values found in *cis*-[{Cp*(CO)Mo}$_2$(μ,η^2-P$_2$)$_2$] [20] [AA'BB' spin system: δ = −101.9 (dd), −131.4 (dd); $^1J(^{31}P,^{31}P)$ = 499.6 Hz, $^2J(^{31}P,^{31}P)$ = 15.7 and 24.1 Hz].

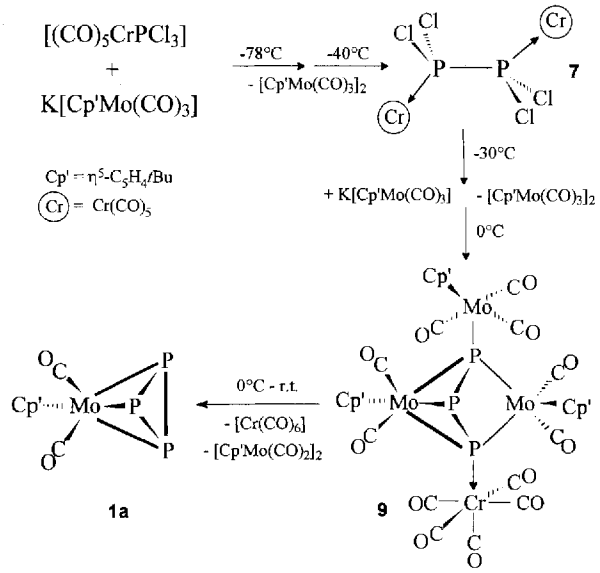
Addition of five equivalents of K[Cp'Mo(CO)$_3$] to a mixture of [{(CO)$_5$Cr}Cl$_2$PPCl$_2${Cr(CO)$_5$}] (**7**) and [{Cr(CO)$_5$}$_2$PCl] at −78 °C in THF gives only the *cyclo*-P$_3$ complex **1a** and **10** is no longer observed. Clearly, for the synthesis of the *cyclo*-P$_3$ complex **1a** starting from the diphosphane derivative **7**, an additional P$_1$-building unit is needed.

Finally, ^{31}P-NMR spectroscopy was used to monitor the reaction. The reagents of reaction (1) were combined at −100 °C in an NMR tube. At this temperature, the formation of the tetrachlorodiphosphane **7** is observed. At the same time, in addition to signals of the starting material [Cr(CO)$_5$PCl$_3$], two doublets at δ = 273 and 260 with a large ^{31}P,^{31}P coupling constant of 462 Hz are observed, indicating the formation of an unsymmetrically substituted P$_2$ ligand complex with P–P double bond character. Complex **7** and [Cr(CO)$_5$PCl$_3$] are detectable up to −40 °C, whereas the above mentioned doublets disappear at −60 °C. In this temperature range, a new pair of doublets appears at δ = 226 and −58, with a ^{31}P,^{31}P coupling constant of 375 Hz. At a temperature of about −30 °C, the formation of the P$_3$-precursor [{Cp'Mo(CO)$_3$}{Cp'Mo(CO)$_2$}$_2${Cr(CO)$_5$}($\mu,\eta^{3:1:1}$-P$_3$)] (**9**), as well as that of the final product [Cp'Mo(CO)$_2$(η^3-P$_3$)] (**1a**), is observed. The P$_2$ product [{Cp'Mo(CO)$_2$}$_2$(μ,η^2-P$_2$)] (**2a**) is also detected in trace amounts. The spectrum at room temperature shows only **1a** and **2a** in a ratio of 4:1, accounting for about 90% of all the phosphorus-containing products.

In summary, our investigations show that the reaction pathway proceeds via stepwise P–P bond formation, induced by a relatively fast metal-halogen exchange reaction at low temperature (Scheme 1). The tetrachlorodiphosphane **7** is formed below −40 °C, representing an important intermediate along the reaction pathway. Thus, both **7** and the P$_1$-unit [Cr(CO)$_5$PCl$_3$], are components of the crude reaction mixture and, by further metal-halogen exchange reactions, P–P bond formation, and substitution reactions, the P$_3$-complexes are formed. The metal-halogen exchange reactions explain the appearance of the oxidation product [Cp'Mo(CO)$_3$]$_2$. Also possible are substitution reactions of [Cr(CO)$_5$PCl$_3$] or **7** by [Cp'Mo(CO)$_3$]$^-$, which is observed at −60 °C, giving rise to unsymmetrically substituted P$_2$ complexes. The formation of the *cyclo*-P$_3$-precursor compound [{Cp'Mo(CO)$_3$}{Cp'Mo(CO)$_2$}$_2${Cr(CO)$_5$}($\mu,\eta^{3:1:1}$-P$_3$)] (**9**) is observed at −30 °C, which gives after elimination of [Cp'Mo(CO)$_2$]$_2$ and [Cr(CO)$_6$], the final product **1a**.

The influence of [Cr(CO)$_5$] complex fragments on the reactions (1)–(3) is of critical importance. If these reactions are carried out with simple PCl$_3$, the percentage of formed P$_2$ derivatives increases considerably. In the case of the reaction of PCl$_3$ with K[Cp"Mo(CO)$_3$], complex **2b** is formed as the main product. In a corresponding reaction (2) without [Cr(CO)$_5$THF], the *cyclo*-P$_3$ complex **3** is no longer formed. Therefore, the pentacarbonylchromium(0) complex fragments promote the loss of CO via the formation of [Cr(CO)$_6$], which

Scheme 1. Proposed reaction pathway for the formation of $[Cp'Mo(CO)_2(\eta^3\text{-}P_3)]$ (**1a**) via the reaction of $[Cr(CO)_5PCl_3]$ with $K[Cp'Mo(CO)_3]$



can be obtained almost quantitatively, and generate $[Cp^xMo(CO)_2]$, [Cp''Fe] as well as [Cp'Cr] units.

We are grateful to the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie* for comprehensive financial support of our work.

Experimental Section

All experiments were performed under argon in anhydrous solvents. – NMR: Bruker AC 250 (^{1}H: 250.13 MHz; ^{31}P: 101.256 MHz) with standards Me_4Si (^{1}H), 85% H_3PO_4 (^{31}P). – MS: Finnigan MAT 311 ADF at 70 eV. – IR: Perkin-Elmer PE 883.

Crystal Structure Analyses of **7** *and* **9**: General notes: Stoe STADI IV; ω/θ-scan mode; Mo-K_α radiation (λ = 0.71073 Å); empirical absorption corrections (Psi scans); structure solution by direct methods using SHELXS-86,[21] full-matrix least-squares refinement on F^2 (for **7**) and F (for **9**) in SHELXL-93[21] (**7**) and SHELX-76[21] (**9**), respectively, with anisotropic displacement for non-H atoms; hydrogen atoms located in idealized positions and refined isotropically according to a riding model. Crystal data and some details of the refinement are shown in Table 2. Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen on quoting the depository numbers CSD-406803 (**7**) and CSD-406652 (**9**), respectively.

Complex **4**: A solution of 1.12 g (3.4 mmol) $[Cr(CO)_5PCl_3]$[22] in 15 ml THF was treated at −78°C with 3.03 g (10.2 mmol) of solid $K[Cp'Cr(CO)_3]$ and the mixture was stirred for 1 h at this temperature. The mixture was then slowly allowed to warm to room temperature. After complete removal of the solvent, the residue was redissolved in 20 ml toluene and the KCl was filtered off. The filtrate was concentrated to dryness in vacuo and the residue was applied to the top of a column (30 × 2.5 cm) of silica gel (Merck 230–400 mesh). Elution with *n*-hexane afforded a green fraction containing **4** (330 mg, 12%); subsequent elution with *n*-hexane/CH_2Cl_2 (1:3) yielded a dark-brown fraction containing $[Cp'Cr(CO)_3]_2$ (52 mg, 20%). – **4**: $C_{18}H_{26}Cr_2P_5$ (501.27): calcd. C 43.13, H 5.23; found C 42.60, H 4.80.

Complex **6**: To a solution of 0.21 g (0.63 mmol) $[Cr(CO)_5PCl_3]$ in 15 ml THF at −78°C, a slurry of 0.57 g (1.88 mmol) $K[Cp^*Ni(CO)]$[23], obtained from C_8K and $[Cp^*Ni(CO)]_2$[24] in THF at −78°C, was added by means of a cannula. An immediate color change to dark-red was observed. The mixture was stirred for a further 1 h at this temperature and was then allowed to warm to room temperature. The graphite was filtered off and the filtrate was concentrated to dryness. As described above, the residue was separated by column chromatography on silica gel. Elution with *n*-hexane gave a red fraction containing $[Cp^*Ni(CO)]_2$ (150 mg, 36%); further elution with *n*-hexane/toluene (10:1) yielded a brown fraction. From the latter 60 mg (21%) of $[(Cp^*Ni)_2\langle(\mu,\eta^2\text{-}P_2)\{Cr(CO)_5\}_2\rangle]$ (**6**) was isolated. – **6**: $C_{30}H_{30}Cr_2Ni_2O_{10}P_2$ (833.88): calcd. C 43.21, H 3.63; found C 42.91, H 3.47.

Complexes **7** *and* **8**: A solution of 1.98 g (6 mmol) $[Cr(CO)_5PCl_3]$ in 15 ml THF was treated at −78°C with 1.70 g (4 mmol) of solid $Na_2[Cr_2(CO)_{10}]$.[25] The yellow color of the mixture darkened. Upon slowly warming to room temperature, the color changed to red-brown. The NaCl produced was removed as described above. Extraction of the dry residue with *n*-pentane followed by crystallization at −20°C gave 175 mg (30%) of $[\{(CO)_5Cr\}Cl_2PPCl_2\{Cr(CO)_5\}]$ (**7**), whereas separation by column chromatography resulted in a yield of just 11%, obtained from a yellow fraction eluted with *n*-hexane. Complex **8** was found to be stable only in solution. – **7**: $C_{10}Cl_4P_2Cr_2O_{10}$ (587.84): calcd. C 20.43; found C 20.18.

Complex **9**: A stirred solution of 0.41 g (1.25 mmol) $[Cr(CO)_5PCl_3]$ in 15 ml THF was treated at ambient temperature with 1.48 g (3.75 mmol) of solid $K[Cp'Mo(CO)_3]$. The solvent was immediately removed in vacuo. Chromatography of the residue on silica gel with hexane/toluene (50:1) as the eluent gave 43 mg (22%)

Table 2. Crystal structure data of **7** and **9**

		7	**9**
Empirical formula		$C_{10}Cl_4Cr_2O_{10}P_2$	$C_{39}H_{39}CrMo_3O_{12}P_3$
Molecular mass [g mol^{-1}]		587.84	1132.47
Crystal dimensions [mm]		0.5 × 0.5 × 0.3	0.35 × 0.33 × 0.16
Crystal system		monoclinic	triclinic
Space group		$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
Lattice constants	a [Å]	11.216(14)	12.255(3)
	b [Å]	7.269(9)	13.543(3)
	c [Å]	13.367(14)	15.084(3)
	α [°]		115.073(9)
	β [°]	104.42(8)	97.95(1)
	γ [°]		96.02(1)
V [Å^3]		1056(2)	2208.2(9)
Z		2	2
$F(000)$		572	1128
$d_{calc.}$ [g cm^{-3}]		1.850	1.703
μ (Mo-K_α) [cm^{-1}]		17.3	12.1
Diffractometer		Stoe STADI 4	Stoe STADI 4
Temperature [K]		200	293
2θ range [°]		3–50	3–51
Scan mode		ω/θ	ω/θ
Measured reflections		2882	8240
Independent reflections		1691	7694
Observed reflections [$\|F_o\| > 4.0\sigma(\|F_o\|)$]		1436	6285
Refined parameters		127	520
Min./max. Δρ [e Å^{-3}]		−0.65/0.64	−0.40/0.54
$R(F_o)$ / $wR(F_o)$	[a]	0.052/–	0.029/0.030
$wR(F_o^2)$	[b]	0.155	–

[a] $F_o > 4.0\sigma(F_o)$. – [b] All data.

$[Cp'Mo(CO)_2(\eta^3\text{-}P_3)]$ (**1a**), and subsequent elution with hexane/toluene (2:1) gave 530 mg of a mixture of $[\{Cp'Mo(CO)_2\}_2(\mu,\eta^2\text{-}P_2)]$ (**2a**), $[Cp'Mo(CO)_3]_2$ and $[Cp'Mo(CO)_2]_2$[26]. Elution with hexane/CH_2Cl_2 (2:1) resulted in a red-brown fraction containing $[\{Cp'Mo(CO)_3\}\{Cp'Mo(CO)_2\}_2\{Cr(CO)_5\}(\mu,\eta^{3:1:1}\text{-}P_3)]$ (**9**) (80 mg, 17%). – **9**: $C_{39}H_{39}CrMo_3O_{12}P_3$ (1132.47): calcd. C 41.36, H 3.47; found C 40.94, H 3.62.

[☆] Dedicated to Prof. Dr. *Joachim Strähle* on the occasion of his 60th birthday.

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