Synthesis and Properties of Novel Metal-Linked P_n Ligand Complexes

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Dedicated to Professor Herbert Schumann on the occasion of his 65th birthday

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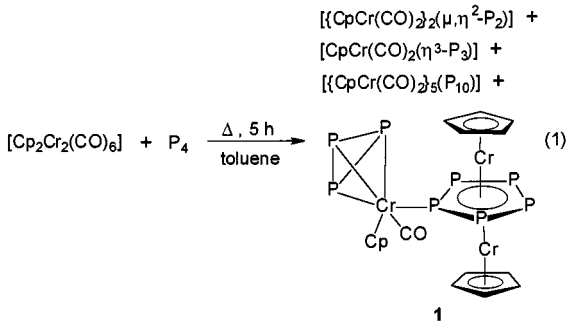
The reaction of $[CpCr(CO)_3]_2$ with P_4 in toluene at 90 °C for 5 h affords the triple-decker sandwich complex $[CpCr(CO)(\eta^3\text{-}P_3)(CpCr)_2(\mu,\eta^1{:}\eta^5{:}\eta^5\text{-}P_5)]$ (**1**) as a new product, along with the previously described products with P_2, P_3, and P_{10} units. The structure of the paramagnetic complex **1** has been established by single-crystal X-ray diffraction methods. A novel complex $[\{CpCr(CO)_2\}_2(\mu,\eta^1{:}\eta^1{:}\eta^2\text{-}P_2)\{Mo(CO)_4\}_2\{(\mu,\eta^1{:}\eta^1{:}\eta^5{:}\eta^5\text{-}P_5)(CpCr)_2\}]$ (**2**) has been obtained from the reaction of $[\{CpCr(CO)_2\}_2(\mu,\eta^2\text{-}P_2)]$ with $[Mo(CO)_4(NBD)]$ (NBD = norbornadiene). The X-ray structure of **2** reveals a six-membered Mo_2P_4 ring combining a Cr_2P_2 tetrahedral core and a triple-decker sandwich Cr_2P_5 moiety. The EPR spectra of the paramagnetic ($S' = 1/2$) complexes **1** and **2** are reported. A noticeable hyperfine interaction with two ^{31}P nuclei is observed for **2**.

Introduction

Research in the area of complexes with "naked" Group-15 elements as ligands has recently undergone a dynamic and exciting development.[1] The majority of publications in this field deal with the synthesis and structural features of E_n (E = P, As, Sb, Bi) containing complexes. However, during the last decade, various groups[2–5] have started to investigate the reactivities of such species, especially those of P_n ligand complexes. In continuation of our activities aimed at exploring unusual reactivity features of E_n-containing complexes, we have focussed our interest on studying the reactivity pattern of $[\{CpCr(CO)_2\}_2(\mu,\eta^2\text{-}P_2)]$, which was first obtained by Goh et al.[6] In one of our projects in this field, our interest lies in the synthesis of oligomers of such P_2 ligand complexes linked by transition metal moieties. In this context, we tried to obtain an Mo-bridged dimer of $[\{CpCr(CO)_2\}_2(\mu,\eta^2\text{-}P_2)]$ tetrahedral units by using the lone pairs of the phosphorus atoms. The surprising results are reported herein.

Results and Discussion

Goh et al. have described the isolation of $[\{CpCr(CO)_2\}_2(\mu,\eta^2\text{-}P_2)]$, $[CpCr(CO)_2(\eta^3\text{-}P_3)]$, $[(CpCr)_2(\mu,\eta^5{:}\eta^5\text{-}P_5)]$, and $[\{CpCr(CO)_2\}_5(P_{10})]$ from the thermolysis of $[CpCr(CO)_3]_2$ with P_4.[6] Additionally, from the same reaction we have obtained $[CpCr(CO)(\eta^3\text{-}P_3)(CpCr)_2(\mu,\eta^1{:}\eta^5{:}\eta^5\text{-}P_5)]$ (**1**) as a new product in good yields by stirring the reaction mixture for 5 h at 90 °C [Equation (1)].



Complex **1** was isolated along with $[\{CpCr(CO)_2\}_2(\mu,\eta^2\text{-}P_2)]$, $[CpCr(CO)_2(\eta^3\text{-}P_3)]$, and $[\{CpCr(CO)_2\}_5(P_{10})]$ after column chromatographic work-up. The ^{31}P NMR spectrum of the crude reaction mixture showed no signal attributable to the complex $[(CpCr)_2(\mu,\eta^5{:}\eta^5\text{-}P_5)]$. On the basis of this observation, one may speculate that **1** is formed by the subsequent reaction of $[CpCr(CO)_2(\eta^3\text{-}P_3)]$ with $[(CpCr)_2(\mu,\eta^5{:}\eta^5\text{-}P_5)]$, which are initially formed in the reaction of $[CpCr(CO)_3]_2$ with P_4. Complex **1** is insoluble in *n*-hexane but moderately soluble in toluene, CH_2Cl_2, and THF. Its infrared spectrum shows a broad absorption at 1897 cm^{-1} attributable to a terminal CO group. Due to the paramagnetic nature of **1**, no signal could be detected in its ^{31}P NMR spectrum. The mass spectrum of **1** shows peaks due to the parent ions $[CpCr(CO)(\eta^3\text{-}P_3)]$ and $[(CpCr)_2(\mu,\eta^5{:}\eta^5\text{-}P_5)]$ and fragmentation products thereof.

The molecular structure of **1** is shown in Figure 1. It consists of a triple-decker sandwich with a *cyclo*-P_5 middle deck, of which one of the P atoms coordinates to the Cr atom of the distorted $[CpCr(CO)(\eta^3\text{-}P_3)]$ tetrahedral moiety. The P–P distances in the P_5 middle deck fall into long [2.331(2) and 2.437(2) Å] and short [2.180(3) and 2.198(3) Å] categories, reflecting a lengthening of the P–P bonds around the atom P(4) due to its additional coordination to the Cr atom of the CrP_3 unit. This also leads to a slight

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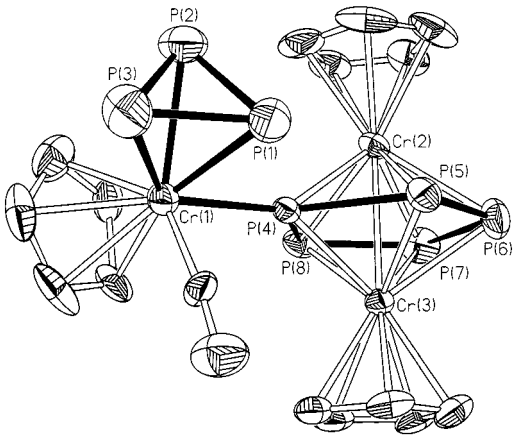
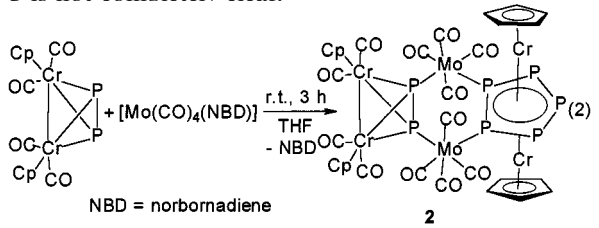


Figure 1. Molecular structure of **1** (ellipsoids drawn at a 50% probability level, H atoms of the Cp ligands are omitted for clarity); selected bond lengths [Å] and angles [°]: Cr(1)−P(1) 2.483(2), Cr(1)−P(2) 2.420(2), Cr(1)−P(3) 2.431(2), Cr(1)−P(4) 2.309(2), Cr(2)−Cr(3) 2.727(13), P(1)−P(2) 2.138(3), P(2)−P(3) 2.169(3), P(3)−P(1) 2.132(3), P(4)−P(5) 2.331(2), P(5)−P(6) 2.180(3), P(6)−P(7) 2.197(3), P(7)−P(8) 2.198(3), P(8)−P(4) 2.437(2); Cr(1)−P(4)−Cr(2) 141.18(8), P(4)−Cr(1)−P(1) 77.82(7), P(4)−Cr(2)−Cr(3) 53.54(5), P(1)−P(2)−P(3) 59.63(10)

shortening of the other P−P bonds within the *cyclo*-P_5 ring as compared to those in the *cyclo*-P_5 unit in $[(CpCr)_2(\mu,\eta^5{:}\eta^5\text{-}P_5)]$ [*d*(P−P) = 2.276(2)−2.206(3) Å],[6b] which is not additionally coordinated. In contrast, the P−P bond lengths in the *cyclo*-P_3 unit in **1** are slightly longer [2.132(3)−2.169(3) Å] than those in the *cyclo*-P_3 unit in $[CpCr(CO)_2(\eta^3\text{-}P_3)]$[6a] [2.118(3)−2.127(3) Å]. Due to this effect, a shortening of the Cr−P bond lengths in the tetrahedral CrP_3 unit of **1** is observed. These Cr−P bond lengths are in the range 2.420(2)−2.483(2) Å, thus making them slightly shorter than the corresponding distances observed in the complex $[CpCr(CO)_2(\eta^3\text{-}P_3)]$ [2.432(2)−2.494(1) Å]. The Cr−Cr distance in **1** [2.727(3) Å] is very similar to those in other triple-decker complexes reported in the literature, e.g. $[(CpCr)_2(\mu,\eta^5{:}\eta^5\text{-}P_5)]$ [2.738(1) Å] and $[(Cp^*Cr)_2(\mu,\eta^5{:}\eta^5\text{-}P_5)]$ [2.727(5) Å].[7]

Reactivity of $[\{CpCr(CO)_2\}_2(\mu,\eta^2\text{-}P_2)]$

Reaction of $[\{CpCr(CO)_2\}_2(\mu,\eta^2\text{-}P_2)]$ with one equivalent of $[Mo(CO)_4(NBD)]$ in THF at room temperature and subsequent column chromatographic work-up led to the isolation of $[\{CpCr(CO)_2\}_2(\mu,\eta^1{:}\eta^1{:}\eta^2\text{-}P_2)\{Mo(CO)_4\}_2\text{-}\{(\mu,\eta^1{:}\eta^1{:}\eta^5{:}\eta^5\text{-}P_5)(CpCr)_2\}]$ (**2**). In a further fraction, a paramagnetic complex − referred as **3** − was isolated as a minor product. In the mass spectrum of **3**, a small peak attributable to $[\{CpCr(CO)_2\}(\mu,\eta^1{:}\eta^1{:}\eta^3\text{-}P_3)\{Mo(CO)_4\}_2\text{-}\{(\mu,\eta^1{:}\eta^1{:}\eta^5{:}\eta^5\text{-}P_5)(CpCr)_2\}]$ was detected. All attempts to isolate suitable crystals for X-ray structure analysis failed, thus with only the mass spectral data available the nature of **3** is not completely clear.



The reddish-brown complex **2** was found to be insoluble in *n*-hexane but soluble in CH_2Cl_2. Its ^{31}P NMR spectrum features only a singlet at δ = 61.7, which can be assigned to the Cr_2P_2 part of the molecule.

The molecular structure of **2** is shown in Figure 2. It consists of a triple-decker sandwich and a tetrahedral Cr_2P_2 core bridged by two $[Mo(CO)_4]$ moieties, which results in a planar, six-membered Mo_2P_4 ring. Each Mo atom resides in a sixfold coordination environment made up of two P atoms, one from each of the $[\{CpCr(CO)_2\}_2(\mu,\eta^2\text{-}P_2)]$ and $[(CpCr)_2(\mu,\eta^5{:}\eta^5\text{-}P_5)]$ fragments, along with four carbonyl groups. This molecule represents the first example of a complex containing a tetrahedron as well as both five- and six-membered rings. The P_4Mo_2 and *cyclo*-P_5 moieties are coplanar and are connected by a shared P_2 edge. Scherer et al. have reported the complex $[\{[CpMo(CO)_2]_2(\mu,\eta^2{:}\eta^1{:}\eta^1\text{-}P_2)\}_2\{Re(CO)_3Br\}_2]$,[8] in which the two Re atoms and the P_2 units of two tetrahedral $[\{CpMo(CO)_2\}_2(\mu,\eta^2\text{-}P_2)]$ fragments form a planar six-membered ring. Due to the coordination to the $[Mo(CO)_4]$ moieties in **2**, the P(2)−P(2A) distance [2.438(5) Å] in the P_5 ring is lengthened as compared to those in $[(CpCr)_2(\mu,\eta^5{:}\eta^5\text{-}P_5)]$ [*d*(P−P) = 2.276(2)−2.206(3) Å]. The bond lengths and angles in the coordinated Cr_2P_2 tetrahedron in **2** differ very little from those in the uncoordinated molecule. The Mo−P bond lengths in **2** [2.517(2) and 2.541(2) Å] are slightly longer than that in $[\{CpCr(CO)_2\}_2(\mu,\eta^2{:}\eta^1{:}\eta^1\text{-}P_2)\{Mo(CO)_5\}_2]$ (2.506 Å).[9]

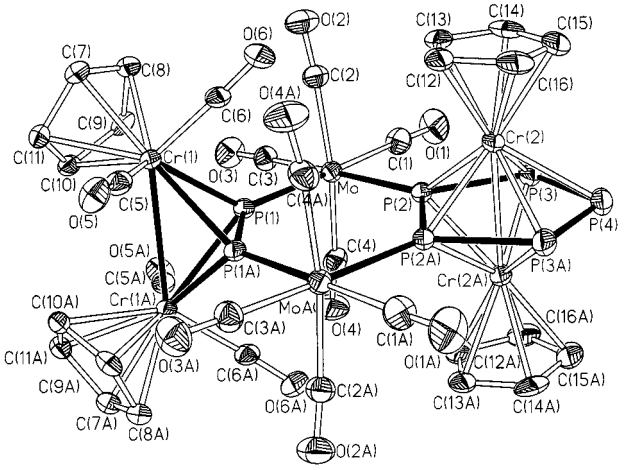


Figure 2. Molecular structure of **2** (ellipsoids drawn at a 30% probability level, H atoms of the Cp ligands are omitted for clarity); selected bond lengths [Å] and angles [°]: Mo−P(1) 2.517(2), Mo−P(2) 2.541(2), Cr(1)−Cr(1A) 3.019(1), Cr(2)−Cr(2A) 2.728(3), Cr(1)−P(1) 2.329(2), Cr(1)−P(1A) 2.514(2), Cr(1A)−P(1) 2.514(2), Cr(1A)−P(1A) 2.329(2), P(1)−P(1A) 2.087(4), P(2)−P(2A) 2.438(5), P(2)−P(3) 2.276(3), P(3)−P(4) 2.206(3), P(4)−P(3A) 2.206(3), P(4)−P(2A) 2.276(3); P(1)−Mo−P(2) 88.39(7), Cr(1)−P(1)−Mo 137.54(9), Cr(2)−P(2)−Mo 144.33(9), P(1A)−P(1)−Mo 138.87(5), P(2A)−P(2)−Mo 132.66(5)

EPR Investigations

The room-temperature X-band EPR spectrum of a CH_2Cl_2 solution of **1** consists of one line with a linewidth of $\Delta B_{pp} \approx 5$ mT and shows no hyperfine interactions. At low temperatures (T = 130 K), an EPR spectrum character-

ized by an axially symmetric $\boldsymbol{g}$ tensor is observed. Again, no hyperfine interactions can be detected. This spectrum is reproduced in Figure 3. The g values detected are given in Table 1.

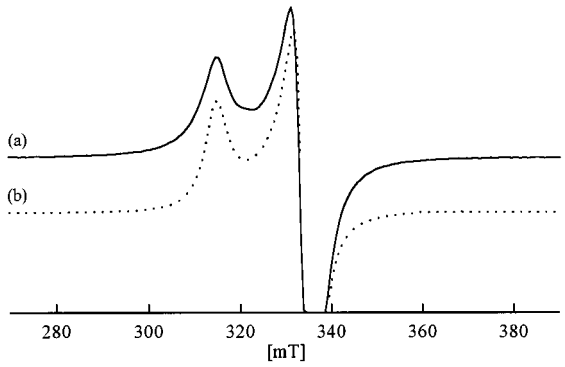


Figure 3. Experimental (a) and simulated (b) X-band EPR spectrum of **1** in CH_2Cl_2 at $T = 130$ K

Table 1. EPR parameters of **1** and **2**; hyperfine coupling constants are given in [10^{-4} cm^{-1}]

	1[a]		**2**[a]
$g_\perp$	2.018	g_1	1.991
$g_\parallel$	2.145	g_2	2.021
g_{av}[b]	2.060	g_3	2.048
g_0	2.073	g_{av}[c]	2.020
A^P_1	[d]	A^P_1	17.2
A^P_2	[d]	A^P_2	16.0
A^P_3	[d]	A^P_3	24.6
$A^P{}_{av}$[c]	–	$A^P{}_{av}$[c]	19.3

[a] Experimental error: $g_i \pm 0.003$; $A^P{}_i \pm 1.0$. – [b] $g_{av} = (2g_\perp + g_\parallel)/3$. – [c] $g_{av} = (g_1 + g_2 + g_3)/3$; $A^P{}_{av} = (A^P{}_1 + A^P{}_2 + A^P{}_3)/3$. – [d] Not resolved.

For compound **2**, the EPR spectrum recorded in THF at room temperature shows a 1:2:1 triplet of lines (the linewidth of $\Delta B_{pp} \approx 0.5$ mT is considerably smaller than that observed in the case of **1**), as expected for the interaction of one unpaired electron with two $I = 1/2$ nuclei (^{31}P). The derived isotropic parameters are: $g_0 = 2.022 \pm 0.002$ and $a^P_0 = (18.0 \pm 1.0) \times 10^{-4}$ cm^{-1}. The frozen-solution EPR spectrum of **2** is given in Figure 4 together with its simulation. For the simulation, the aforementioned isotropic parameters were taken into account. The main features of the spectrum can be rationalized by assuming a spin system consisting of one unpaired electron and its interaction with two equivalent ^{31}P nuclei. The derived parameters are listed in Table 1. However, the spectrum also shows some smaller splittings, possibly due to hyperfine interactions with neighbouring protons or phosphorus nuclei. Since no other signals could be detected in the accessible spectral range (neither for **1** nor for **2**), the spectra as described above were interpreted with the following "effective" spin Hamiltonian [Equation (3)].

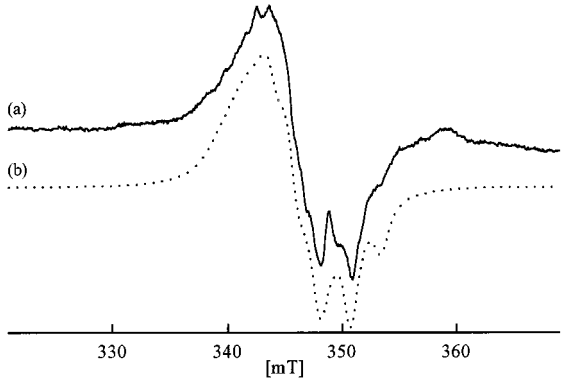


Figure 4. Experimental (a) and simulated (b) X-band EPR spectrum of **2** in THF at $T = 130$ K

$$\boldsymbol{H}_{sp} = \mu_B \cdot \boldsymbol{g} \cdot \boldsymbol{B}_0 \cdot \boldsymbol{S}' + \boldsymbol{S}' \cdot \boldsymbol{A}^P \cdot \boldsymbol{I}^P \quad (3)$$

In Equation (3), S' denotes $S = 1/2$; for compound **2**, two equivalent ^{31}P nuclei were taken into account. It should be noted that in spite of the aforementioned ^{31}P hyperfine interactions, no other hyperfine interactions (e.g. ^{53}Cr, $^{95,97}Mo$) could be detected.

The ^{31}P hyperfine parameters derived for **2** can be used to estimate the spin density on these nuclei. For this, the isotropic component A^P_{av} and the dipolar component b^P ($b^P = A^P_\perp - A^P_{av}$) of the ^{31}P coupling are needed. According to the nearly axially symmetric ^{31}P hyperfine tensor, A^P_1 and A^P_2 can be averaged to $A^P_\perp = 16.6 \cdot 10^{-4}$ cm^{-1}. Using the previously reported procedure[2c,10,11] and the atomic parameters calculated by Morton and Preston,[10] 0.5% and 2.2% of the spin density was calculated to reside in the 3s and 3p orbitals of P, respectively. Thus, 5.4% of the overall spin density is located on the two P atoms observed in the spectra. Since no other hyperfine interactions (e.g. $^{95,97}Mo$) could be successfully analysed for the $Cr_4Mo_2P_7$ unit of **2**, the bulk of the electron spin density seems to be localized in a $Cp_2Cr_2P_2$ unit, thereby accounting for the observed ^{31}P hyperfine interactions with the bridging P atoms of the P_5 ring.

Conclusions

Although the initial goal of the synthesis of a metal-linked dimer of tetrahedral Cr_2P_2 complexes has not been achieved, the interesting reactivity of [{$CpCr(CO)_2$}$_2$(μ,η^2-P_2)] has led to the generation of the unexpected product **2**. The formation of **1** and **2** under mild conditions is suggestive of preferential transformation to a triple-decker sandwich complex [$(CpCr)_2(\mu,\eta^5{:}\eta^5\text{-}P_5)$], even when this forms a part of more complex molecules, giving rise to novel structural features. This characteristic has previously been observed in the reaction of [{$CpCr(CO)_2$}$_2$(μ,η^2-P_2)] with $LiBEt_3H$, where the complex [{[$CpCr(CO)_2$]$_2$(μ-PH)}{$(CpCr)_2(\mu,\eta^1{:}\eta^1{:}\eta^5{:}\eta^5\text{-}P_5)$}] [2c] was formed as a side-product. In contrast to the situation in the analogous tetrahedral M_2P_2 ligand complexes of molybdenum and tungsten, the weaker Cr–Cr bond in [{$CpCr(CO)_2$}$_2$(μ,η^2-P_2)]

has been shown to be largely responsible for the unusual reactivity behaviour of this species. The formation of a triple-decker sandwich complex in **2** is one of its consequences. This effect is also observed in the reactions of $[\{CpCr(CO)_2\}_2(\mu,\eta^2\text{-}P_2)]$ with ECl_3 (E = P, As, Sb), which furnish the corresponding mixed *cyclo*-P_2E ligand complexes under elimination of $[CpCrCl_2]_2$.[2d] Further investigation of this interesting behaviour of $[\{CpCr(CO)_2\}_2(\mu,\eta^2\text{-}P_2)]$ is part of our ongoing research.

Experimental Section

General Techniques: All reactions and manipulations were performed under dry argon using standard Schlenk techniques. Solvents were dried and distilled under argon prior to use, toluene and THF with Na/benzophenone, hexane with $LiAlH_4$, dichloromethane with P_2O_5. – IR spectra were recorded with a Bruker IFS 28 FT-IR spectrometer, mass spectra with a Finnigan MAT 711 spectrometer at 70 eV. Satisfactory elemental analyses were obtained with an Elementar Vario EL at the Institute of Inorganic Chemistry, University of Karlsruhe.

Reaction of $[\{CpCr(CO)_3\}_2]$ with P_4: Dry P_4 (0.92 g, 7.45 mmol) was added to a deep-green solution of $[\{CpCr(CO)_3\}_2]$ (3.0 g, 7.45 mmol) in toluene (75 mL) and the resulting mixture was stirred at 90 °C for 5 h. The reddish-brown solution was then filtered through silica gel and the filtrate was concentrated to dryness in vacuo. The unchanged P_4 was removed by sublimation prior to chromatography. Chromatographic workup on a silica gel column (40 × 3.0 cm) eluting with *n*-hexane yielded a trace amount of unchanged P_4 followed by a yellowish-brown fraction containing $[CpCr(CO)_2(\eta^3\text{-}P_3)]$ (0.3 g, 1.13 mmol, 7.5%). Elution with *n*-hexane/toluene (2:1) gave a yellow fraction that turned brown, from which black crystals of $[CpCr(CO)(\eta^3\text{-}P_3)(CpCr)_2(\mu,\eta^1{:}\eta^5{:}\eta^5\text{-}P_5)]$ (**1**) (1.0 g, 1.59 mmol, 33% yield) crystallized. Using *n*-hexane/toluene (1:1) as eluent, a magenta-coloured fraction containing $[\{CpCr(CO)_2\}_2(\mu,\eta^2\text{-}P_2)]$ (1.1 g, 2.69 mmol, 36%) followed by a golden-brown fraction containing $[\{CpCr(CO)_2\}_5P_{10}]$ (1.2 g, 1.02 mmol, 7%) were obtained (yields are calculated on the basis of $[\{CpCr(CO)_3\}_2]$).

1: IR [KBr, ν(CO)/cm^{-1}]: 1897 (s, br). – ^{1}H NMR (250.13 MHz, CD_2Cl_2, TMS, 301 K): δ = 4.21 (br. s, $CpCrP_3$), 19.48 [br. s, $(CpCr)_2P_5$]. – EI-MS (70 eV, 150 °C): *m*/*z* (%) = 389 (100) $[Cp_2Cr_2P_5]$, 327 (86) $[Cp_2Cr_2P_3]$, 262 (6) $[CpCr_2P_3]$, 238 (24) $[CpCr(CO)P_3]$, 210 (59) $[CpCrP_3]$, 200 (12) $[CpCr_2P]$, 182 (74) $[CrCp_2]$, 135 (6) $[Cp_2Cr]$, 124 (33) $[P_4]$, 117 (60) [CrCp]. – $C_{16}H_{15}Cr_3OP_8$ (627.1): calcd. C 30.65, H 2.41; found C 30.05, H 2.61.

Reaction of $[\{CpCr(CO)_2\}_2(\mu,\eta^2\text{-}P_2)]$ with $[Mo(CO)_4(NBD)]$: $[\{CpCr(CO)_2\}_2(\mu,\eta^2\text{-}P_2)]$ (100 mg, 0.245 mmol) and $[Mo(CO)_4(NBD)]$ (74 mg, 0.245 mmol) were dissolved in THF (40 mL) and the resulting mixture was stirred at room temperature for 3 h. The solvent was then removed in vacuo. Chromatographic workup on a silica gel column (35 × 2.5 cm) eluting with *n*-hexane/CH_2Cl_2 (1:1) gave a magenta-coloured solution of unchanged $[\{CpCr(CO)_2\}_2(\mu,\eta^2\text{-}P_2)]$ (25 mg, 25%), a trace amount of $[Mo(CO)_4(NBD)]$, followed by a reddish-brown fraction containing $[\{CpCr(CO)_2\}_2(\mu,\eta^1{:}\eta^1{:}\eta^2\text{-}P_2)\{Mo(CO)_4\}_2\{(\mu,\eta^1{:}\eta^1{:}\eta^5{:}\eta^5\text{-}P_5)(CpCr)_2\}]$ (**2**) (50 mg, 34%). Elution with *n*-hexane/CH_2Cl_2 (1:3) yielded a dark-brown fraction containing **3** (20 mg).

2: IR [CH_2Cl_2, ν(CO)/cm^{-1}]: 2070 (w), 2023 (w), 1942 (s, br). – ^{31}P NMR (101.256 MHz, C_6D_6, 85% H_3PO_4): δ = 61.7 (s). – ^{1}H NMR (250.13 MHz, CD_2Cl_2, TMS, 301 K): δ = 3.38 (br. s, Cr_2P_2). – EI-MS (70 eV, 350 °C): *m*/*z* (%) = 989 (1) $[M^+ - 8CO]$, 840 (5) $[M^+ - Cp - 11CO]$, 676 (2) $[Cp_3Cr_4P_7(CO)_2]$. – **3**: IR [CH_2Cl_2, ν(CO)/cm^{-1}]: 2072 (w), 2020 (s), 1977 (s), 1940 (vs, br). – ^{31}P NMR (101.256 MHz, C_6D_6, 85% H_3PO_4): δ = −58.9 (s). – EI-MS (70 eV, 370 °C): *m*/*z* (%) = 1071 (0.02) $[Cp_3Cr_3P_8Mo_2(CO)_8]$,

Table 2. Crystallographic data for **1** and **2**

	1	**2** · 5 CH_2Cl_2
Empirical formula	$C_{16}H_{15}Cr_3OP_8$	$C_{37}H_{30}Cl_{10}Cr_4Mo_2O_{12}P_7$
M_w	627.04	1637.78
Crystal size [mm]	0.30 × 0.08 × 0.01	0.22 × 0.19 × 0.04
T [K]	200(1)	200(1)
Space group	monoclinic	monoclinic
Crystal system	$P2_1/n$	$C2/c$
a [Å]	15.995(3)	25.086(5)
b [Å]	7.2200(14)	19.073(4)
c [Å]	20.321(4)	15.341(3)
β [°]	112.38(3)	127.70(3)
V [Å^3]	1490.7(5)	5808(2)
Z	4	4
d_c [g/cm^3]	1.919	1.873
μ_c [mm^{-1}]	2.073	1.846
F(000)	1244	3212
diffractometer	STOE IPDS	STOE IPDS
2Θ range [°]	4.34 ≤ 2Θ ≤ 47.92	2.96 ≤ 2Θ ≤ 47.92
hkl range	−18 ≤ *h* ≤ 18	−28≤ *h* ≤ 27
	−7 ≤ *k* ≤ 8	−20 ≤ *k* ≤ 21
	−23 ≤ *l* ≤ 23	−17 ≤ *l* ≤ 17
Data/restraints/parameters	3150/0/253	4406/18/339
Independent reflections [$I > 2\sigma(I)$]	2283 (R_{int} = 0.0689)	2567 (R_{int} = 0.1052)
Goodness-of-fit on F^2	0.972	0.900
R_1,[a] wR_2 [b] [$I > 2\sigma(I)$]	0.0493, 0.1180	0.0630, 0.1447
R_1,[a] wR_2 [b] [all data]	0.0715, 0.1261	0.1042, 0.1627
largest diff. peak/hole [e Å^{-3}]	1.012, −0.524	1.291, −0.802

[a] $R = |F_o| - |F_c||/|F_o|$. – [b] $wR_2 = [\omega(F_o^2 - F_c^2)^2]/[(F_o^2)^2]^{1/2}$

857 (29) [$Cp_2Cr_3P_5Mo_2(CO)_8$], 844 (24) [$Cp_3Cr_3Mo_2P_7(CO)_3$], 502 (13) [$Cr_3P_5Mo_2$].

X-ray Structure Determination and Details of the Refinement: Data were collected with a STOE IPDS area detector diffractometer using Mo-K_α (λ = 0.71069 Å) radiation. Machine parameters, crystal data, and data collection parameters are summarized in Table 2. The structures were solved by direct methods using SHELXS-86[12a] and refined by full-matrix least-squares methods on F^2 using SHELXL-93[12b] with anisotropic displacement factors for non-H atoms; hydrogen atoms were placed in idealized positions and refined isotropically according to the riding model. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-142655 and -142656. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk.

EPR Measurements: EPR spectra were recorded in the X-band ($\nu \approx 9.5$ GHz) with a Bruker ESP 300E spectrometer in the temperature range 295−130 K using ca. 10^{-2}−10^{-3} M solutions of **1** (CH_2Cl_2) and **2** (THF). After cooling the samples, the formation of a good "glass" was proven. The EPR parameters were obtained using a modified version of the computer program written by White and Belford.[13,14]

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