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Organochromium π-complexes

IV *. The preparation and reactions of (η^5-pentadienyl)Cr^{II} complexes. Crystal structure of (η^5-2,4-$Me_2C_5H_5$)(η^3-C_3H_5)$CrPMe_3$

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Abstract

(η^5-2,4-Dimethylpentadienyl)$Cr(PMe_3)_2Cl$ (prepared from $Cr(PMe_3)_2Cl_2$ and K-2,4-$Me_2C_5H_5$) reacts with allylmagnesium chloride to give initially (η^3-2,4-$Me_2C_5H_5$)(η^3-C_3H_5)$Cr(PMe_3)_2$, which above −30 °C undergoes phosphine elimination to give (η^5-2,4-$Me_2C_5H_5$)(η^3-C_3H_5)$CrPMe_3$, the structure of which has been determined by X-ray diffraction. In contrast, systems containing either the bidentate ligand bis(dimethylphosphino)ethane or the cyclopentadienyl ligand react with allylmagnesium chloride to give the diamagnetic compounds (η^5-2,4-$Me_2C_5H_5$)(η^3-C_3H_5)$Cr(Me_2PC_2H_4PMe_2)$ and Cp(η^3-C_3H_5)$Cr(PMe_3)_2$.

Introduction

Although the first η^5-pentadienyl complex of chromium, (η^5-C_5H_7)$_2$Cr (**1**), was isolated in 1968 and the open-chromocene nature confirmed by a crystal structure determination of the related derivative (η^5-2,4-$Me_2C_5H_5$)$_2$Cr (**2**), the subsequent development in this area has been slow and is apparently limited to the observations that **2** reacts with donor ligands such as CO, CNC_4H_9-t and $Me_2PC_2H_4PMe_2$ with displacement of both organic ligands and with (i-C_3H_7)$_3$NHCl-$Me_2PC_2H_4PMe_2$ to give (η^5-2,4-$Me_2C_5H_5$)$Cr(Me_2PC_2H_4PMe_2)Cl$ (**3**), which can also be prepared directly from $Cr(Me_2PC_2H_4PMe_2)_2Cl_2$ and K-2,4-$Me_2C_5H_5$ [1–3]. In addition, Cp(η^5-2,4-$Me_2C_5H_5$)Cr was prepared by treating $[CpCrCl_2]_2$ or $[CpCrOC_4H_9\text{-t}]_2$ with K-2,4-$Me_2C_5H_5$ or treating $CrCl_2$ with NaCp/K-2,4-$Me_2C_5H_5$. This compound and **2** have been studied as supported catalysts for the polymerization of ethylene [4–6].

As part of a study of the organometallic chemistry of divalent chromium we

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* For Part III see ref. 8.

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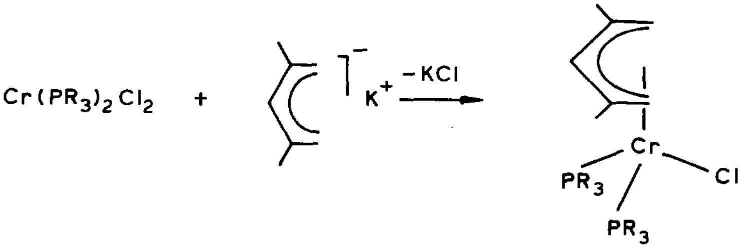
turned our attention to the η^5-pentadienyl group, and report here the preparation and reaction of complexes containing this group and P-donor ligands.

Results and discussion

Our initial efforts to prepare mono(η^5-pentadienyl)Cr-complexes were unsuccessful: (η^5-C_5H_7)$_2$Cr (**1**) was found to react with HCl or allyl chloride even at −78 °C with displacement of both pentadienyl groups to give $CrCl_2$, and attempts to prepare (η^5-2,4-$Me_2C_5H_5$)(η^3-C_3H_5)$_2$Cr by treating K-2,4-dimethylpentadienyl with either Cr(THF)$_3$Cl$_3$ and allylmagnesium chloride or with [(η^3-C_3H_5)$_2$CrCl]$_2$ led instead to reduction of the chromium and formation of a mixture of (η^3-C_3H_5)$_3$Cr and (η^3-C_3H_5)$_2$(μ-η^3-C_3H_5)$_2$Cr$_2$. However, by using a procedure analogous to that developed by Ernst et al. for the preparation of **3** [3], we were able to make the red-brown (η^5-2,4-$Me_2C_5H_5$)Cr-compounds **4** and **5** from the appropriate Cr(PR$_3$)$_2$Cl$_2$ species and K-2,4-dimethylpentadienyl in THF at −30 °C (eq. 1).

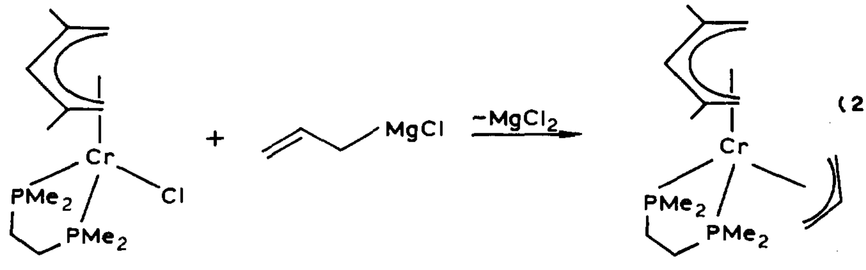


(1)

4, $PR_3 = PMe_3$; **5**, $PR_3 = PMe_2Ph$

Red solutions, which presumably contain related compounds, are also formed upon treatment either of Cr(PR$_3$)$_2$Cl$_2$ with K-C_5H_7 or of [Cr(^{i}Pr$_2$PC$_2$H$_4$P^{i}Pr$_2$)Cl$_2$]$_2$ with K-2,4-$Me_2C_5H_5$ but in both cases the products decompose above −65 °C and could not be obtained analytically pure. **4** and **5** are thermolabile, and break down above −30 °C to give (η^5-2,4-$Me_2C_5H_5$)$_2$Cr (**2**).

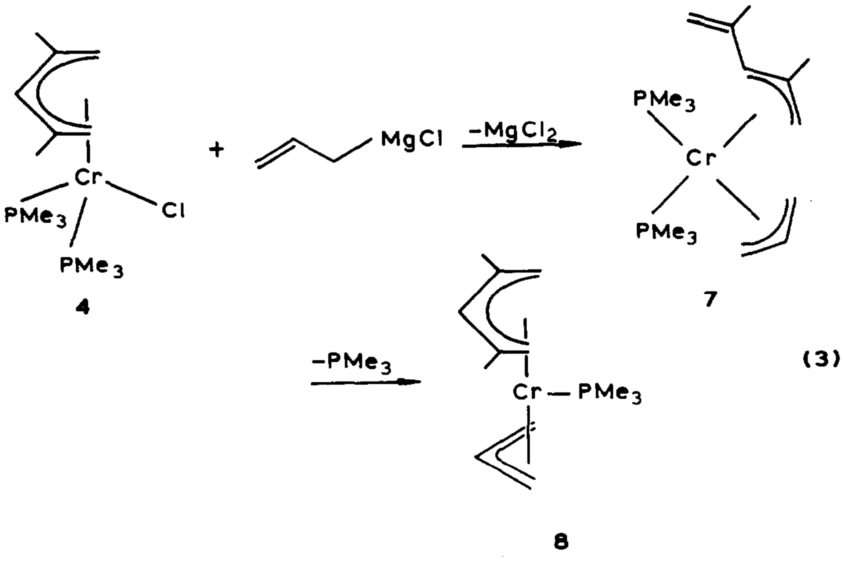
The bis(dimethylphosphino)ethane-stabilized derivative **3** reacts with allylmagnesium chloride to give the diamagnetic compound **6** (eq. 2) the structure of which has been deduced from the ^{1}H NMR spectroscopic data (see Experimental section).



(2)

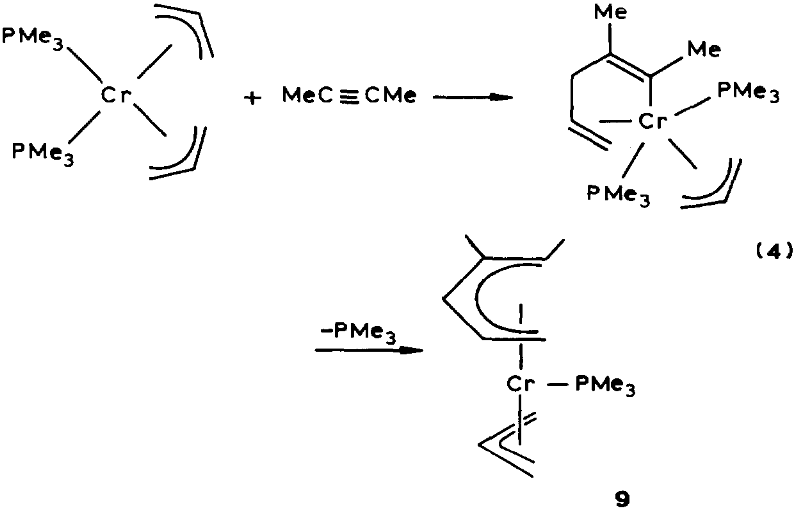
3 **6**

The analogous reaction between allylmagnesium chloride and **4** or **5**, however, was found to take a different course. The initial product of the reaction involving **4** is a paramagnetic compound whose elemental analysis and the presence of a band



(3)

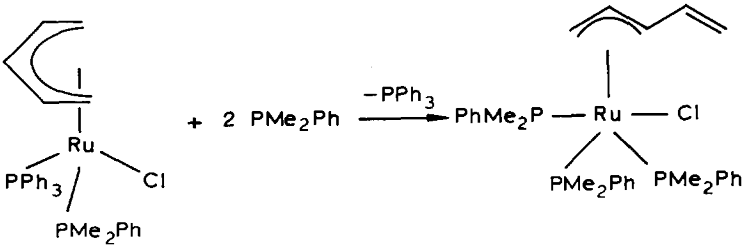
at 1640 cm^{-1} in the IR spectrum supported its formulation as the (η^3-allyl)$_2$Cr(PMe$_3$)$_2$ species **7**, in which the hapticity of the 2,4-dimethylpentadienyl group has been reduced. (A rearrangement involving a change in the hapticity of the η^3-allyl group is less likely on energetic grounds; the loss of resonance energy in going from an η^5- to an η^3-pentadienyl group is less than that on going from an η^3- to an η^1-allyl group [7].) Compound **7** is unstable, and reacts further above −30 °C with loss of a donor ligand to give the compound **8** (eq. 3), whose crystal structure has been established by an X-ray diffraction study (see below). An analogous



(4)

reaction of the PMe_2Ph-stabilized compound **5** with allylmagnesium chloride led directly to $(\eta^5\text{-}2,4\text{-}Me_2C_5H_5)(\eta^3\text{-}C_3H_5)CrPMe_2Ph$ (**9**) even at −60 °C.

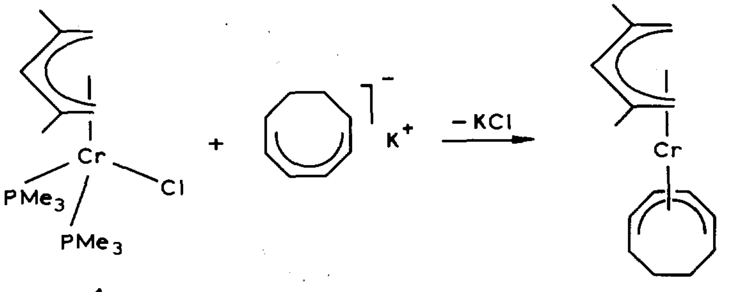
We described in an earlier publication the syntheses of $(\eta^3\text{-allyl})_2Cr(PR_3)_2$ species related to **7** [8] and a compound having a structure similar to **8**, viz. $(\eta^5\text{-}1,2\text{-}Me_2C_5H_5)(\eta^3\text{-}C_3H_5)Cr$ (**9**), is believed to be the final product of the reaction between $(\eta^3\text{-}C_3H_5)_2Cr(PMe_3)_2$ and 2-butyne (eq. 4). Furthermore, phosphine-induced hapticity changes similar to that shown in equation 3 have been described in the literature, and an example involving the $(\eta^5$-pentadienyl)Ru-species **10** is shown below (eq. 5). [9].



(5)

10

Compound **4** was found to react with potassium cyclooctadienyl with displacement of both P-donor ligands to give **11** (MS: m/z 254, M^+) in which two different η^5-organic ligands are bonded to the metal atom (eq. 6). The compound was, however, contaminated with $(\eta^5\text{-}2,4\text{-}Me_2C_5H_5)_2Cr$ (**2**) and $(\eta^5$-cyclooctadienyl$)_2Cr$ and could not be obtained analytically pure.

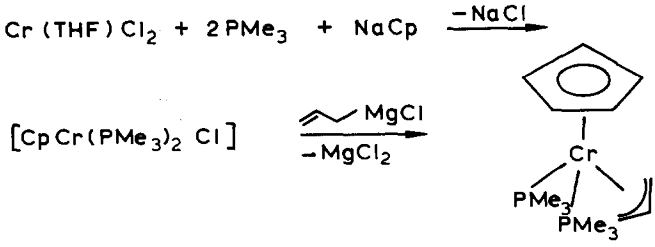


(6)

4

11

That **4** reacts with allylmagnesium chloride to give **8** instead of the expected diamagnetic species $(\eta^5\text{-}2,4\text{-}Me_2C_5H_5)(\eta^3\text{-}C_3H_5)Cr(PMe_3)_2$, analogous to **6**, must in part be the result of steric crowding in the target molecule. Bearing in mind that a cyclopentadienyl ligand is sterically less demanding than a 2,4-dimethylpentadienyl ligand (the cone angles for the two have been estimated to be ca 136 and ca 180°, respectively, at an M–C-distance of ca 2.36 Å [10]), we decided to attempt to isolate $Cp(\eta^3\text{-}C_3H_5)Cr(PMe_3)_2$ (**12**). Although we were unable to prepare the required starting material $(CpCr(PMe_3)_2Cl)$, we were able to synthesize **12** in a one-flask reaction from Cr(THF)Cl_2, PMe_3, NaCp and allylmagnesium chloride at −30° (eq. 7).



(7)

12

As expected, **12** is diamagnetic and relatively stable (decomposing above −20 °C), showing no tendency either to rearrange with a change in the hapticity of the ring or to lose a phosphine ligand.

The crystal structure of (η^5-2,4-$Me_2C_5H_5$)(η^3-C_3H_5)$CrPMe_3$ (**8**) was determined by an X-ray diffraction study. The molecular structure is shown in Fig. 1, and selected structural parameters and atomic fractional coordinates are listed in Tables 1 and 2. The chromium atom lies in a pseudo-trigonal planar environment defined by the P-atom and the mid-points of the allyl and pentadienyl planes (D1, D2). The two organic groups are arranged essentially parallel to each other (interplanar angle 5.6°) and are almost eclipsed. The chromium atom is situated equidistant from the C-atoms of both organic groups. The central C-atom of the allyl group is unusually close to the metal atom while the pentadienyl fragment exhibits torsion angles of 8.5° (C7–C8–C9–C10) and 6.9° (C11–C10–C9–C8).

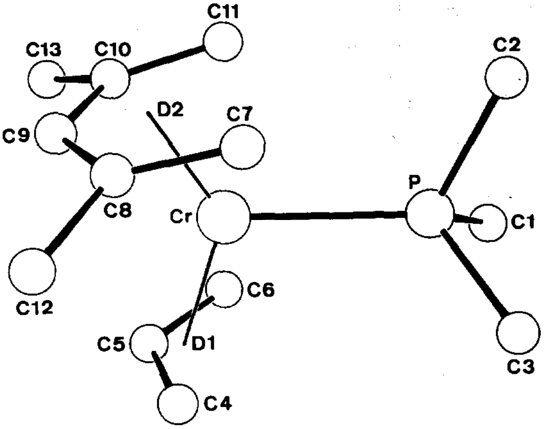


Fig. 1. The molecular structure of (η^5-2,4-$Me_2C_5H_5$)(η^3-C_3H_5)$CrPMe_3$ (**8**). D1 and D2 denote the mid-points of the allyl and cyclopentadienyl planes, respectively.

Table 1

Selected structural parameters for (η^5-2,4-dimethylpentadienyl)(η^3-C_3H_5)$CrPMe_3$ (8) with esd's in parentheses

Bond lengths (Å)		Bond angles (°)	
Cr–D1	1.958	D1–Cr–D2	133.1
Cr–D2	1.569	D1–Cr–P	104.8
Cr–P	2.367(1)	D2–Cr–P	121.6
Cr–C4	2.220(3)	C4–C5–C6	122.3(3)
Cr–C5	2.175(3)	C7–C8–C9	124.1(3)
Cr–C6	2.259(3)	C8–C9–C10	128.0(3)
Cr–C7	2.153(3)	C9–C10–C11	124.0(3)
Cr–C8	2.136(3)		
Cr–C9	2.171(3)	C7–C8–C12	118.8(3)
Cr–C10	2.174(3)	C11–C10–C13	118.0(3)
Cr–C11	2.166(3)	C9–C8–C12	116.9(3)
C4–C5	1.391(5)	C9–C10–C13	117.3(3)
C5–C6	1.388(5)	Cr–P–C1	119.6(1)
C7–C8	1.416(4)	Cr–P–C2	115.4(1)
C8–C9	1.427(4)	Cr–P–C3	117.1(1)
C9–C10	1.421(4)	C1–P–C3	99.8(2)
C10–C11	1.406(4)	C1–P–C2	100.1(2)
C8–C12	1.516(4)	C2–P–C3	101.8(2)
C10–C13	1.511(4)		
P–C1/2/3	1.822(4)		

Experimental

All reactions were carried out under argon in anhydrous and oxygen-free solvents. K-2,4-dimethylpentadienyl and K-pentadienyl were prepared by treating the appropriate diene with potassium sand [10]. $Cr(PMe_3)_2Cl_2$, $Cr(PMe_2Ph)_2Cl_2$ and $Cr(Me_2PC_2H_4PMe_2)_2Cl_2$ were prepared from $Cr(THF)Cl_2$ and the appropriate P-donor ligand [8]. (η^5-2,4-$Me_2C_5H_5$)$Cr(Me_2PC_2H_4PMe_2)Cl$ (3) was prepared by treating $Cr(Me_2PC_2H_4PMe_2)_2Cl_2$ with K-2,4-$Me_2C_5H_5$. [3] ^1H NMR-, ^{31}P NMR- and IR-spectra were recorded on Bruker WM 400, Bruker AC 200 and Nicolet FT-7199 instruments respectively. Microanalysis were carried out by Dornis and Kolbe, Microanalytical Laboratory, Mülheim a.d. Ruhr.

(η^5-2,4-$Me_2C_5H_5$)$Cr(PMe_3)_2Cl$ (4)

A solution of K-2,4-dimethylpentadienyl in THF (25 ml) was added during 2 h to a suspension of $Cr(PMe_3)_2Cl_2$, prepared from $Cr(THF)Cl_2$ (1.74 g, 8.9 mmol) and PMe_3 (1.9 ml, 18 mmol) in diethyl ether (50 ml) and cooled to −78 °C. The colour of the mixture changed from blue to red. The mixture was stirred at −30 °C for 12 h and then filtered and the filtrate evaporated to dryness at −30 °C. The red-brown residue was washed with pentane (3 × 10 ml) at −78 °C and dried at this temperature under high vacuum. Yield 2.1 g (70% theory). Found: C, 47.3, H, 8.3; Cl, 10.3;, Cr, 15.3; P, 18.2. $C_{13}H_{29}ClCrP_2$ calc.: C, 46.6; H, 8.7; Cl, 10.6; Cr, 15.5; P, 18.5%. IR (KBr, −60 °C): ν 3060, 3040, 1490, 1420, 1380, 1280, 960 cm^{-1}.

Table 2

Atomic fractional coordinates with standard deviations in parentheses and equivalent isotropic thermal parameters (Å^2) for **8**

Atom	x	y	z	U_{eq} [a]
Cr	0.1553(1)	0.1602(1)	0.2725(1)	0.014
P	0.2944(1)	0.1923(1)	0.1369(1)	0.018
C(1)	0.4691(4)	0.2625(3)	0.1804(3)	0.030
C(2)	0.3580(5)	0.0805(3)	0.0749(4)	0.040
C(3)	0.2016(5)	0.2637(4)	0.0092(4)	0.047
C(4)	0.0197(4)	0.2988(2)	0.2709(3)	0.027
C(5)	0.1251(4)	0.2894(2)	0.3758(3)	0.023
C(6)	0.2774(4)	0.2862(2)	0.3846(3)	0.026
C(7)	0.0390(3)	0.0511(2)	0.1489(3)	0.019
C(8)	−0.0314(3)	0.0595(2)	0.2396(2)	0.018
C(9)	0.0451(3)	0.0516(2)	0.3581(3)	0.017
C(10)	0.2017(3)	0.0471(2)	0.4078(2)	0.019
C(11)	0.3089(3)	0.0394(2)	0.3443(3)	0.021
C(12)	−0.1954(3)	0.0876(3)	0.2116(3)	0.026
C(13)	0.2561(4)	0.0672(3)	0.5350(3)	0.025
H(1a)	0.530(4)	0.232(3)	0.249(3)	0.039
H(1b)	0.527(4)	0.250(2)	0.121(3)	0.031
H(1c)	0.463(5)	0.324(3)	0.204(4)	0.067
H(2a)	0.420(4)	0.042(3)	0.139(4)	0.058
H(2b)	0.415(4)	0.093(3)	0.026(3)	0.043
H(2c)	0.273(5)	0.045(3)	0.033(4)	0.063
H(3a)	0.270(4)	0.268(3)	−0.039(3)	0.046
H(3b)	0.156(6)	0.325(4)	0.030(4)	0.092
H(3c)	0.124(5)	0.232(3)	−0.028(4)	0.051
H(4a)	0.044(3)	0.325(2)	0.213(3)	0.020
H(4b)	−0.082(4)	0.294(3)	0.269(3)	0.027
H(5)	0.089(3)	0.272(2)	0.440(3)	0.016
H(6a)	0.310(3)	0.322(2)	0.334(3)	0.014
H(6b)	0.346(4)	0.270(3)	0.448(3)	0.045
H(7a)	0.106(3)	0.006(3)	0.151(3)	0.029
H(7b)	−0.017(4)	0.067(2)	0.075(3)	0.025
H(9)	−0.009(3)	0.060(2)	0.407(2)	0.004
H(11a)	0.409(3)	0.047(2)	0.381(3)	0.018
H(11b)	0.303(3)	0.002(3)	0.285(3)	0.026
H(12a)	−0.221(4)	0.124(3)	0.272(3)	0.031
H(12b)	−0.261(3)	0.029(3)	0.199(3)	0.025
H(12c)	−0.221(4)	0.129(3)	0.144(3)	0.032
H(13a)	0.339(4)	0.112(3)	0.554(3)	0.046
H(13b)	0.286(3)	0.001(3)	0.574(3)	0.032
H(13c)	0.183(4)	0.091(3)	0.565(3)	0.033

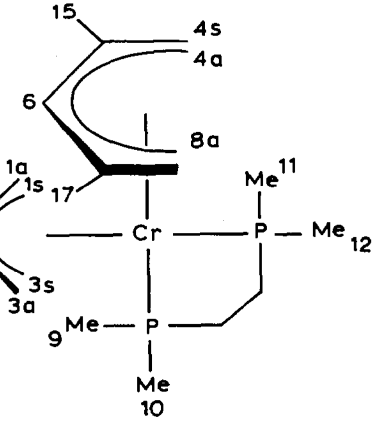
[a] $U_{eq} = 1/3\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* (\mathbf{a}_i \cdot \mathbf{a}_j)$.

(η^5-2,4-$Me_2C_5H_5$)Cr(PMe_2Ph)$_2$Cl (5)

Prepared, as a red-brown solid in 65% yield, by the procedure used for **4** but from Cr(PMe_2Ph)$_2$$Cl_2$ and K-2,4-dimethylpentadienyl in THF. Found: C, 62.0, H, 8.3; Cl, 7.2; Cr, 10.3; P, 12.3. $C_{23}H_{33}ClCrP_2$ calc.: C, 60.2; H, 7.3; Cl, 7.7; Cr, 11.3; P, 13.5%; contamination with traces of an oil (which could not be removed by repeated recrystallization) leads to some inaccuracy in the analytical data, which nevertheless indicate a 1/1/2 Cl : Cr : P molar ratio.

(η^5-2,4-$Me_2C_5H_5$)(η^3-C_3H_5)Cr($Me_2PC_2H_4PMe_2$) (**6**)

To a solution of (η^5-2,4-$Me_2C_5H_5$)Cr($Me_2PC_2H_4PMe_2$)Cl (**3**) (0.65 g, 1.95 mmol) in diethyl ether (50 ml) at −30 °C was added dropwise an ethereal solution of allylmagnesium chloride (12 ml of a 0.33 *M* solution, 3.9 mmol). The mixture was stirred for 24 h, then filtered at −30 °C, and the filtrate evaporated to dryness under high vacuum. The residue was dissolved in precooled pentane at −30 °C (30 ml) and the solution was filtered and cooled to −78 °C to give the product as red crystals, which were isolated and dried at −30 °C. Yield 0.54 g (82% theory). Found: C, 56.7, H, 9.6; Cr, 15.4; P, 18.2. $C_{16}H_{32}CrP_2$ calc.: C, 56.8; H, 9.5; Cr, 15.4; P, 18.3%. MS (70 eV, 120 °C): m/z 338 (M^+), 297, 243, 202. IR (KBr): ν 3060, 1490, 1420, 1280, 1210, 940 cm^{-1}. ^1H NMR (THF-d_8, −30 °C): δ 4.68 (s, 6-H); 2.52 (m, 2-H); 2.14 (s, 15-H); 1.81 (m, 4s-H); 1.76 (m, 3s-H); 1.64 (d, 9-H); 1.34 (d, 10-H); 1.22 (s, 17-H); 1.11 (m, 1s-H); 1.05 (d, 11-H); 0.81 (d, 12-H); 0.21 (m, 1a-H); −0.40 (m, 3a-H); −0.52 (m, 4a-H); −1.05 (m, 8a-H); ^3J(1s,2) ca 6, ^3J(1a,2) 8.6, ^3J(2,3s) ca 6, ^3J(2,3a) 9.2, ^3J(4a,4s) 0, ^3J(8a,8s) ca 1, J(1s,P) 10.3, J(1a,P) 5.8, ΣJ(2,P) 13.4, ΣJ(3s,P) ca 4.5, J(3a,P) 1, J(4a,P) 13.1, J(4s,P) 6.6, ΣJ(8a,P) 19.4, J(9,P) 7.1, J(10,P) 7.6, J(11,P) 5.7, J(12,P) 6.1—numbering scheme shown below. ^{31}P NMR (THF-d_8, −30 °C): δ 70.1; 79.3; J(P,P) 38.5.



(η^5-2,4-$Me_2C_5H_5$)(η^3-C_3H_5)CrPMe_3 (**8**)

To a solution of (η^5-2,4-$Me_2C_5H_5$)Cr$(PMe_3)_2$Cl (**4**) (3.1 g, 9.3 mmol) in diethyl ether (50 ml) at −78 °C was slowly added an ethereal solution of allylmagnesium chloride (25 ml of a 0.38 *M* solution, 9.4 mmol). The mixture was stirred at −30 °C for 12 h then filtered, and the solvent removed under high vacuum. The residue was dissolved in pentane (30 ml) and the solution was filtered and cooled to −78 °C to give the product as red crystals, which were dried and sublimed in high vacuum at 40 °C. M.p. 45–50 °C. Yield 1.9 g (77% theory). Found: Cr, 19.4; P, 11.3. $C_{13}H_{25}CrP$ calc.: Cr, 19.7; P, 11.7%. MS (70 eV, 50 °C): m/z 204 (M^+), 223, 188, 96. Magn. moment: μ_{eff} 2.7 BM. IR (KBr): ν 3060, 3040, 1495, 1420, 1380, 1280, 950 cm^{-1}. Crystal structure: see text.

(η^5-2,4-$Me_2C_5H_5$)(η^3-C_3H_5)CrPMe_2Ph (**9**)

This was prepared, as described for **8**, as red crystals in 72% yield from (η^5-2,4-dimethylpentadienyl)Cr$(PMe_2Ph)_2$Cl (**5**) and allylmagnesium chloride in diethyl ether, and isolated by crystallization from pentane at −78 °C. Found: C, 66.0; H, 8.6; Cr, 15.8; P, 9.4. $C_{18}H_{27}CrP$ calc.: C, 66.2; H, 8.3; Cr, 15.9; P, 9.5%.

$(\eta^3\text{-}1\text{-}CH_2{=}CMe,2\text{-}MeC_3H_3)(\eta^3\text{-}C_3H_5)Cr(PMe_3)_2$ (7)

To a suspension of $(\eta^5\text{-}2,4\text{-}Me_2C_5H_5)Cr(PMe_3)_2Cl$ (4) in ether (100 ml) at −78 °C was slowly added an ethereal solution of allylmagnesium chloride (20 ml of a 0.38 *M* solution, 7.5 mmol). The mixture was stirred at −78 °C for 12 h then filtered at −60 °C, and the filtrate was evaporated to dryness at this temperature. The residue was dissolved in precooled pentane at −60 °C and the solution filtered. Cooling the filtrate to −78 °C gave the compound as red crystals. Yield 1.4 g (59% theory). Found: C, 55.8; H, 9.4; Cr, 15.5; P, 18.5. $C_{16}H_{34}CrP_2$ calc.: C, 56.5; H, 10.1; Cr, 15.3; P, 18.2%. IR (KBr, −60 °C): ν 3060, 3040, 1640(C=C), 1490, 1420, 1380, 1280, 960 cm^{-1}.

Table 3

Crystal structure data for **8** [a]

Formula	$C_{13}H_{25}CrP$
Molecular weight	264.3
Crystal size (mm)	0.29 × 0.54 × 0.14
Crystal colour	dark red
Crystal system	monoclinic
Space group	$P2_1/n$ (No.14)
a (Å)	9.258(2)
b (Å)	13.218(3)
c (Å)	12.066(2)
β (°)	104.90(2)
V ($Å^3$)	1426.9
Z	4
Calculated density ($g \cdot cm^{-3}$)	1.23
μ (cm^{-1})	8.65
Mo-K_α-radiation (Å)	0.71069
F(000) (e)	568
Temperature (K)	100
Diffractometer	Enraf–Nonius CAD4
Scan mode	$\omega - 2\theta$
$[(\sin\theta)/\lambda]_{max}$ ($Å^{-1}$)	0.65
Total number of reflections ($\pm h$, $\pm k$, $+l$)	6776
Independent reflections	3233
Observed reflections [$I > 2\sigma(I)$]	2641
Refined parameters	236
R	0.040
R_w ($w = 1/\sigma^2(F_o)$)	0.046
Error of fit	2.1
Residual electron density ($eÅ^{-3}$)	0.91
Method of structure solution	heavy atom
H-atom positions located and refined isotropically	

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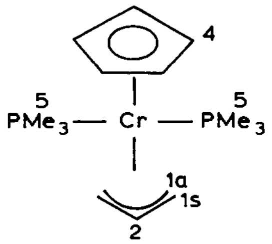
[a] Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, W-7514 Eggenstein-Leopoldshafen 2, Germany, on quoting the depository number CSD-55193, the names of the authors, and the journal citation.

$Cp(\eta^3\text{-}C_3H_5)Cr(PMe_3)_2$ (12)

A solution of $Cr(PMe_3)_2Cl_2$, prepared from $Cr(THF)Cl_2$ (1.17 g, 6.0 mmol) and PMe_3 (1.25 ml, 12.0 mmol) in THF (70 ml), was cooled to −78°C and a THF solution of NaCp · THF (20 ml, 5.9 mmol) was added slowly. The mixture was stirred for 3 h then warmed to −30°C and an ethereal solution of allylmagnesium chloride (16 ml of a 0.38 *M* solution, 6.0 mmol) was added during 1 h. The mixture was stirred at −30°C for a further 12 h then filtered and the filtrate was evaporated to dryness under high vacuum. The residue was extracted at −30°C with precooled pentane and the extract cooled to −78°C to give the product as red crystals, which were washed at −78°C with pentane and dried under high vacuum at this temperature. Yield 0.8 g (43% theory). Found: C, 54.1; H, 9.1; Cr, 16.8; P, 19.9. $C_{14}H_{28}CrP_2$ calc.: C, 54.2; H, 9.1; Cr, 16.8; P, 20.0%. IR (KBr): ν 3110, 3065, 1455, 1420, 1180, 1110, 1000, 940 cm^{-1}. ^1H NMR (THF-d_8, −30°C): ν 3.68 (t, 4-H); 2.27 (m, 2-H); 1.62 (m, 1s-H); 1.12 (t, 5-H); 0.96 (m, 1a-H); ^3J(1a,2) 8.7, ^3J(1s,2) ca 5.5, ^4J(4,P) 2.0, ΣJ(5,P) 6.2, ΣJ(1s,P) ca 14, ΣJ(1a,P) 5.6, J(2,P) ca 5.5 —numbering scheme shown below. ^{31}P NMR (THF-d_8, −30°C): δ 49.39.



Crystal structure determination

Atomic fractional coordinates for **8** are listed in Table 2 and crystal structure data are given in Table 3.

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