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ORGANOCHROMIUM π-COMPLEXES—VI.* THE PREPARATION OF $Cp'(\eta^3\text{-ALLYL})_2Cr$ COMPOUNDS AND THEIR REACTIONS WITH DONOR LIGANDS

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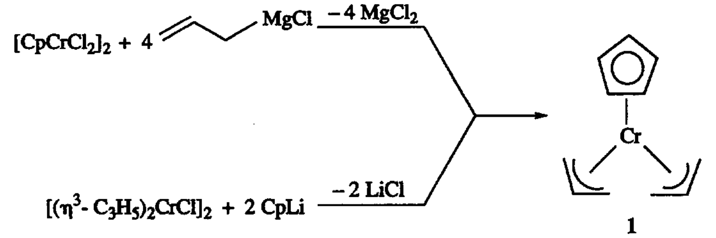
Abstract—The title compounds have been prepared by reacting a $Cp'CrCl_2$ or a $(\eta^3\text{-allyl})_2CrCl$ species with either an allylmagnesium halide or a substituted cyclopentadienyllithium derivative. The compounds react further at room temperature to give the dinuclear species $[Cp'(\mu\text{-}\eta^3\text{-allyl})Cr]_2$, and with P-donor ligands with reductive coupling of the allyl groups to give $Cp'(\eta^2,\eta^2\text{-1,5-hexadiene})CrPR_3$ species. Diene exchange is observed upon reacting the hexadiene compounds with butadiene or cyclohexadiene. The crystal structures of $[Cp(\mu\text{-}\eta^3\text{-}C_3H_5)Cr]_2$, $[(\eta^5\text{-indenyl})(\mu\text{-}\eta^3\text{-}C_3H_5)Cr]_2$, $(\eta^5\text{-indenyl})(\eta^2,\eta^2\text{-1,5-hexadiene})CrP(OMe)_3$ and three compounds containing a 1,3-diene, *viz.* $Cp(\eta^4\text{-1,3-}C_4H_6)CrPMe_3$, $(\eta^5\text{-}Me_5C_5)(\eta^4\text{-1,3-}C_4H_6)CrCO$ and $Cp(\eta^4\text{-1,3-cyclohexadiene})CrP(OMe)_3$ have been established by X-ray diffraction.

In this and the following two publications we describe the preparation of a series of paramagnetic $Cp'(\eta^3\text{-allyl})_2Cr$ complexes and discuss their reactions with donor ligands and unsaturated organic compounds. Some of the results have been mentioned in a short communication.[2]

RESULTS AND DISCUSSION

The simplest member of the series, $Cp(\eta^3\text{-}C_3H_5)_2Cr$ (**1**), may be prepared in high yield by reacting $[CpCrCl_2]_2$ with *ca* 10% excess of allylmagnesium chloride in ether at −60°C. The yields are lower if the reaction is carried out at higher temperatures, if allylmagnesium bromide is used or if the Grignard reagent is added too quickly. The compound can also be prepared in *ca* 70% yield by reacting $[(\eta^3\text{-}C_3H_5)_2CrCl]_2$ (prepared from $(\eta^3\text{-}C_3H_5)_3Cr$ and HCl; see experimental section) with cyclopentadienyllithium (eq. 1).



1

(1)

Compound **1** is an orange–red solid which is soluble in all common solvents. Solutions react further above *ca* −15°C (see below) whereas the solid can be handled briefly at room temperature in an inert atmosphere without noticeable decomposition. Samples should, however, be stored at −20°C. The allyl groups are readily displaced as 1,5-hexadiene upon reaction with HCl, CH_2Cl_2 or I_2 and $[CpCrX_2]_2$ (X = Cl, I) is formed. Protonation with acetylacetone results in the formation of $Cr(acac)_3$ and the liberation of propene and cyclopentadiene. Treatment with excess triphenylphosphine at 100°C

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* For part V see ref. 1.

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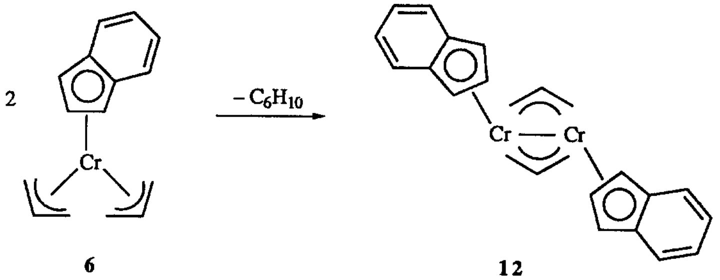
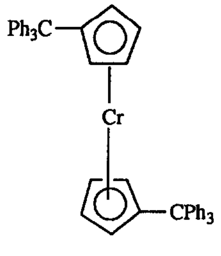
is accompanied by the release of a mixture of C_6-hydrocarbons. The magnetic moment (μ_B 1.9 B.M.) is consistent with the presence of one unpaired electron and the crystal structure has been confirmed by X-ray diffraction and reported in a preliminary communication.[2]

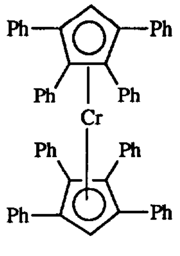


6 **12** (2)

The related compounds $(\eta^5\text{-}RC_5H_4)(\eta^3\text{-}C_3H_5)_2Cr$ (R = Me, **2**; R = t-C_4H_9, **3**; R = Me_2PhC, **4**), $(\eta^5\text{-}Me_5C_5)(\eta^3\text{-}C_3H_5)_2Cr$ (**5**) and (η^5-indenyl)$(\eta^3\text{-}C_3H_5)_2Cr$ (**6**) have been prepared by reacting $[(\eta^3\text{-}C_3H_5)_2CrCl]_2$ with the appropriate organolithium derivative. In addition, $Cp(\eta^3\text{-}2\text{-}MeC_3H_4)_2Cr$ (**7**) and (η^5-indenyl)$(\eta^3\text{-}2\text{-}MeC_3H_4)_2Cr$ (**8**) have been prepared from $[(\eta^3\text{-}2\text{-}MeC_3H_4)_2CrCl]_2$. Reaction between $[(\eta^3\text{-}C_3H_5)_2CrCl]_2$ and tritylcyclopentadienyllithium or tetraphenylcyclopentadienyllithium takes a different course: the allyl groups are displaced and the chromocene derivatives **9** (MS: *m/z* 666, M^+) and **10** (MS: *m/z* 792, M^+) are formed in *ca* 20% yield. Both of these compounds are more conveniently prepared directly from $CrCl_2$.[3]



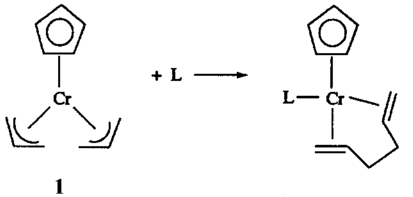
9



10

$Cp(\eta^3\text{-}C_3H_5)_2Cr$ (**1**) reacts further in solution above *ca* -15°C to give a brown, paramagnetic (μ_B 4.1) species which had previously been isolated from the reaction between $[CpCrCl_2]_2$ and allylmagnesium chloride in THF at room temperature and identified as the dinuclear species $[Cp(\mu\text{-}\eta^3\text{-}C_3H_5)Cr]_2$ (**11**).[4] The corresponding indenyl derivative **6** reacts similarly to give the dark brown dinuclear compound **12**. The presence of bridging allyl groups in both **11** and **12** has been confirmed by X-ray diffraction (see below).

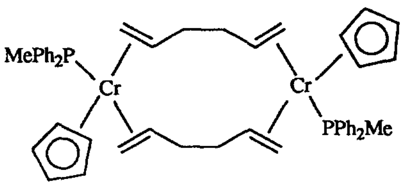
$Cp(\eta^3\text{-}C_3H_5)_2Cr$ (**1**) reacts with a variety of donor ligands with reductive coupling of the allyl groups to give compounds containing metal-bonded 1,5-hexadiene (eq. 3). The products of the reaction with the monodentate ligands CO, PMe_3, $P(OMe)_3$ and $P(OPh)_3$ are the dark green compounds **13**–**16** in which the hexadiene is bonded as an η^2,η^2-organic ligand. These compounds, which can also be prepared in a one-pot procedure by reacting $[CpCrCl_2]_2$ consecutively with allylmagnesium chloride and the donor ligand, are stable at room temperature and are relatively insensitive towards oxygen. The crystal structures of **14** and **15** have been determined by X-ray diffraction and have been reported earlier.[2] The reaction of **1** with CO or PMe_3 is accompanied by the formation in low yield of species having the composition $Cp_2Cr_2L_5$ (L = CO, PMe_3).



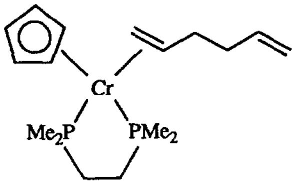
1 (3)

13 L = CO; **14** L = PMe_3;
15 L = $P(OMe)_3$; **16** L = $P(OPh)_3$

In contrast to the examples described above, the adducts formed by reacting **1** with PPh_2Me or PPh_3 are bright yellow and a cryoscopic molecular weight determination of the species containing diphenylmethylphosphine shows it to be dimeric. This, combined with the magnetic moment (two unpaired electrons), suggests a structure (**17**) in which two hexadiene molecules bridge two $CpCr(PPh_2Me)$-fragments. The presence of an uncomplexed double bond (ν 1635 cm^{-1}) in the IR-spectrum of the adduct formed by reacting **1** with the bidentate ligand bis(dimethylphosphino)ethane, suggests that this has a structure (**18**) in which the hexadiene molecule is acting as an η^2-organic ligand. Steri-



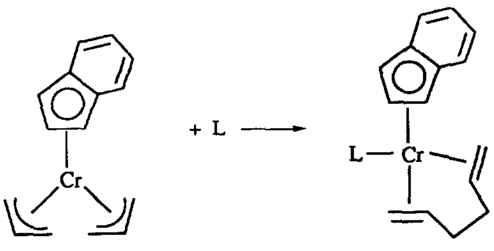
17



18

cally demanding phosphines such as $P(C_3H_7\text{-i})_3$, $P(C_4H_9\text{-t})_3$ and PCy_3 react with **1** much less readily and well defined products could not be isolated.

(η^5-Indenyl)(η^3-C_3H_5)$_2$Cr (**6**) reacts with donor ligands in an analogous manner and the adducts **19** and **20** have been isolated from the reaction with trimethylphosphite or trimethylphosphine (eq. 4). The structure of **19** has been confirmed by X-ray diffraction (see below).

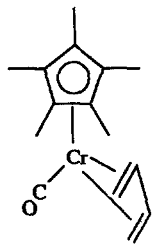


(4)

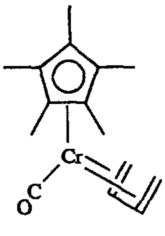
6

19 L = P(OMe)$_3$;
20 L = PMe$_3$

The hexadiene molecule in compounds **14**, **15** and **20** can be readily displaced by 1,3-butadiene and Cp(η^4-1,3-C_4H_6)CrPR$_3$ (**21**, R = Me; **22**, R = OMe) and (η^5-indenyl)(η^4-1,3-C_4H_6)CrPMe$_3$ (**23**) have been isolated. Compounds **21** and **22** can also be prepared by reacting $[CpCrCl_2]_2$ with magnesium-butadiene in the presence of the donor ligand and the same procedure has been used to prepare (η^5-Me$_5$C$_5$)(η^4-1,3-C_4H_6)CrPR$_3$ (**24**, R = Me; **25**, R = OMe). The reaction of **24** (R = Me) with CO is accompanied by donor-ligand exchange and (η^5-Me$_5$C$_5$)(η^4-1,3-C_4H_6)CrCO (**26**) is formed. The *prone* arrangement of the butadiene molecule in **21** and **26** has been established by the crystal structure determinations discussed below and extended-Hückel MO calculations for **26** indicate that this arrangement (**a**) is *ca* 9 kcal mol^{-1} more stable than the *supine* arrangement (**b**).[12] This result is in contrast to that obtained for related compounds containing early transition metals such as Cp(η^4-1,3-C_4H_6)TaCl$_2$ for which it has been calculated that the *supine* arrangement is *ca* 16 kcal mol^{-1} more stable than the *prone* arrangement.[13]

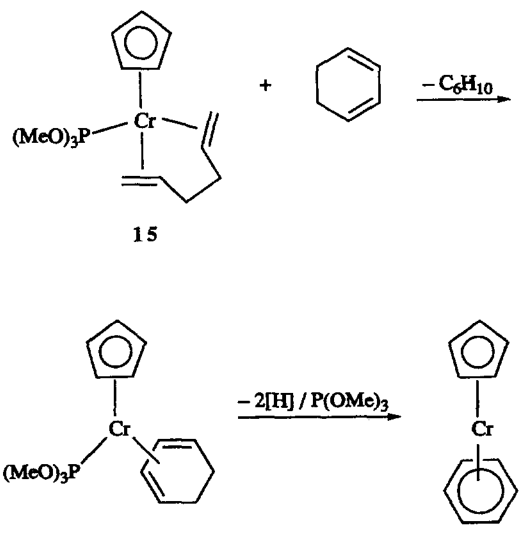


26a



26b

The reaction of **15** with 1,3-cyclohexadiene also results in diene exchange and the η^4-1,3-cyclohexadiene compound **27** is formed as a red, crystalline solid (eq. 5). This reaction is accompanied by the formation of lesser amounts of Cp(η^6-C_6H_6)Cr (**28**) which is the product of the further reaction of **27** in solution at room temperature. This last reaction presumably proceeds by phosphite dissociation followed by Cr-induced dehydrogenation of the cyclohexadiene molecule. A related reaction leading to the formation of **28** has been observed upon reacting Cp(η^3-C_3H_5)$_2$Cr (**1**) with 1,3-cyclohexadiene and has been suggested to involve H-transfer from the diene to the metal followed by homolytic cleavage of the resulting Cr—H bond and the indiscriminant reaction of the H-radical with the reaction media.[5]



15

27

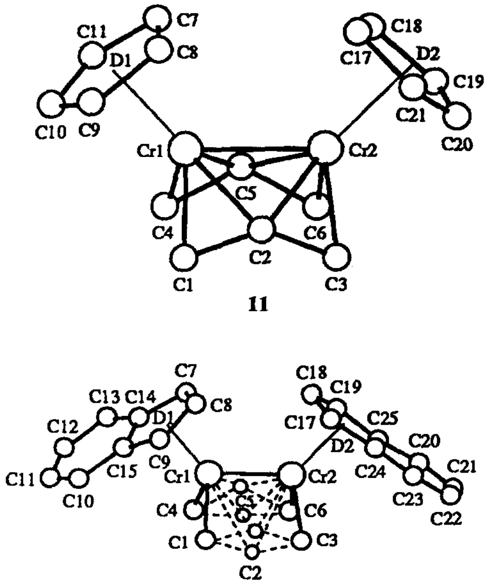
28

(5)

CRYSTAL STRUCTURE DETERMINATIONS

We have already discussed in an earlier publication the crystal structure of Cp(η^2,η^2-1,5-hexadiene)CrPMe$_3$ (**14**)[2] and here we report that of the related complex (η^5-indenyl)(η^2,η^2-1,5-hexadiene)CrP(OMe)$_3$ (**19**) the analysis of which was undertaken mainly to determine the hapticity of the indenyl fragment. The molecular structure is shown in Fig. 1 and selected structural parameters are listed in Table 1. The structure is similar to that of **14** with the indenyl group acting as an η^5-organic ligand, i.e. the indenyl group is essentially planar: the fold angle between the five- and six-membered rings is only 1.8°.

The crystal structure of both [Cp(μ-η^3-C$_3$H$_5$)Cr]$_2$ (**11**) and [(η^5-indenyl)(μ-η^3-C$_3$H$_5$)Cr]$_2$ (**12**) have been determined by X-ray diffraction. **12** contains two independent molecules in the unit cell which differ slightly in the coordination of the indenyl-group to the metal atom. The molecular structure of **11** and **12a** (molecule 1) is shown in Fig. 2 while selected bond distances and angles for **11** and both molecules of **12** are listed in Table 2.

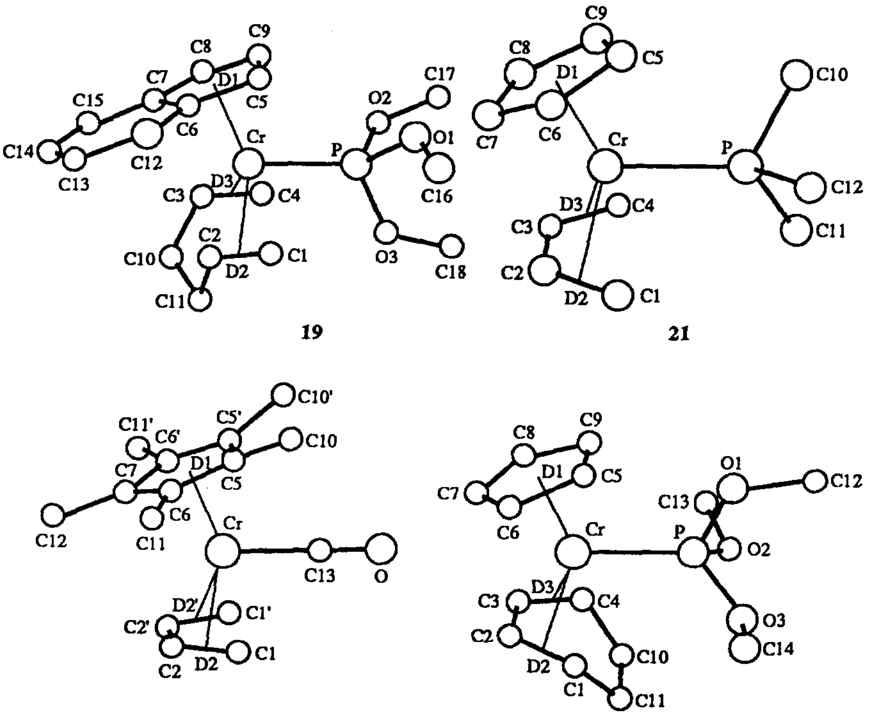


11

12

Fig. 2. The molecular structure of [Cp(μ-η^3-C$_3$H$_5$)Cr]$_2$ (**11**) and [(η^5-indenyl)(μ-η^3-C$_3$H$_5$)Cr]$_2$ (**12**, molecule 1).

In both compounds, two Cr-atoms are bridged by two μ-η^3-allyl groups. In **11**, the two allyl groups adopt a *cis*-configuration with the two meso-C atoms pointing towards the Cr—Cr bond and with a dihedral angle of 54.9° between the two allyl planes (C1/C2/C3 and C4/C5/C6). Three of the four allyl groups in the two independent molecules of **12** are disordered and have been treated accordingly.



19 **21**

26 **27**

Fig. 1. The molecular structures of (η^5-indenyl)(η^2,η^2-1,5-hexadiene)CrP(OMe)$_3$ (**19**), Cp(η^4-1,3-C$_4$H$_6$)CrPMe$_3$ (**21**), (η^5-Me$_5$C$_5$)(η^4-1,3-C$_4$H$_6$)CrCO (**26**) and Cp(η^4-1,3-cyclohexadiene)Cr P(OMe)$_3$ (**27**).

Table 1. Selected structural parameters for (η^5-indenyl)(η^2,η^2-1,5-hexadiene)CrP(OMe)$_3$ (**19**), Cp(η^4-1,3-C_4H_6)CrPMe$_3$ (**21**), (η^5-Me$_5$C$_5$)(η^4-1,3-C_4H_6)CrCO (**26**) and Cp(η^4-1,3-cyclohexadiene)CrP(OMe)$_3$ (**27**)

Distance/ angle (ESD)	**19**[b]	**21**	**26**[c]	**27**[e]
Cr—P	2.243(1)	2.326(1)	1.837(4)[d]	2.265(1)
Cr—C1	2.207(5)	2.156(3)	2.183(3)	2.220(1)
Cr—C2	2.162(5)	2.073(3)	2.095(2)	2.104(1)
Cr—C3	2.190(6)	2.075(2)	—	2.099(1)
Cr—C4	2.172(6)	2.155(2)	—	2.207(1)
Cr—C5	2.245(4)	2.208(2)	2.171(2)	2.177(1)
Cr—C6	2.345(4)	2.219(3)	2.196(2)	2.200(1)
Cr—C7	2.324(4)	2.186(2)	2.218(3)	2.228(1)
Cr—C8	2.226(5)	2.165(2)	—	2.227(1)
Cr—C9	2.213(5)	2.193(3)	—	2.184(1)
Cr—D1[a]	1.926(5)	1.843(3)	1.827(3)	1.841(1)
Cr—D2[a]	2.072(5)	1.994(3)	2.023(3)	2.043(1)
Cr—D3[a]	2.065(6)	1.997(2)	—	2.033(1)
C1—C2	1.387(7)	1.408(4)	1.394(4)	1.422(2)
C2—C3	—	1.402(5)	1.423(4)[d]	1.425(2)
C3—C4	1.407(8)	1.393(4)	—	1.423(2)
C5—C6	1.415(6)	1.388(4)	1.409(3)	1.419(2)
C6—C7	1.424(6)	1.399(3)	1.424(2)	1.418(2)
C7—C8	1.430(7)	1.393(4)	—	1.417(2)
C8—C9	1.394(7)	1.409(3)	—	1.424(2)
C5—C9	1.412(8)	1.410(4)	1.440(3)[d]	1.442(2)
D1—Cr—D2	120.5(1)	131.7(1)	132.3(1)	128.6(1)
D1—Cr—D3	124.0(1)	130.9(1)	—	131.7(1)
D2—Cr—D3	99.2(1)	63.6(1)	63.1(1)[d]	59.7(1)
D3—Cr—P	96.1(1)	105.3(1)	—	105.1(1)
D2—Cr—P	96.9(1)	102.0(1)	101.1(1)[d]	108.1(1)
D1—Cr—P	114.4(1)	112.9(1)	114.8(1)[d]	112.8(1)
C1—C2—C3	—	120.2(3)	119.9(2)	115.0(1)
C2—C3—C4	—	119.8(2)	—	115.3(1)
C1—Cr—C2	37.0(2)	38.8(1)	38.0(1)	38.3(1)
C3—Cr—C4	37.6(2)	38.4(1)	—	38.5(1)
C1—Cr—C4	108.5(2)	81.1(1)	80.2(1)	73.0(1)

[a] Midpoints of C5-ring, C1—C2 and C3—C4, respectively.

[b] C2—C11 1.514(8), C11—C10 1.50(1), C10—C3 1.496(8), C6—C12 1.425(7), C12—C13 1.348(7), C13—C14 1.398(8), C14—C15 1.346(8), C7—C15 1.425(7), C1—C2—C11 123.0(5), C4—C3—C10 121.6(5), C2—C11—C10 108.5(5), C3—C10—C11 110.3(5).

[c] C13—O 1.151(5), C5/6/7—C10/11/12 1.491(5)—1.507(4), Cr—C13—O 178.8(4).

[d] Cr—P ≡ Cr—CO, C2—C2* ≡ C2—C3, C5—C5* ≡ C5—C9, D2—Cr—D2* ≡ D2—Cr—D3, D$_n$—Cr—P ≡ D$_n$—Cr—C13.

[e] C1—C11 1.523(2), C4—C10 1.522(2), C10—C11 1.546(2), C2—C1—C11 117.1(1), C3—C4—C10 118.1(1), C1—C11—C10 110.8(1), C4—C10—C11 111.0(1).

Table 2. Selected structural parameters for [Cp(μ-η^3-C_3H_5)Cr]$_2$ (**11**) and [(η^5-indenyl)(μ-η^3-C_3H_5)Cr]$_2$ (**12**)

Distance/angle (ESD)	**11**	**12a** (Mol. 1)	**12b** (Mol. 2)
Cr1—Cr2	2.299(1)	2.171(1)	2.198(1)
Cr1—C1	2.098(3)	2.108(6)	2.095(5)
Cr1—C2	2.303(3)	2.425(8)	2.335(5)
Cr1—C4	2.091(3)	2.089(5)	2.103(6)
Cr1—C5	2.309(3)	2.329(7)	2.426(7)
Cr2—C2	2.308(3)	2.439(8)	2.342(5)
Cr2—C3	2.083(3)	2.106(5)	2.098(5)
Cr2—C5	2.316(3)	2.359(7)	2.442(7)
Cr2—C6	2.081(3)	2.102(5)	2.111(5)
Cr1—C7	2.251(4)	2.281(5)	2.301(7)
Cr1—C8	2.239(3)	2.256(5)	2.255(7)
Cr1—C9	2.285(3)	2.299(5)	2.277(5)
Cr1—C10	2.308(3)	2.450(5)[b]	2.411(5)[b]
Cr1—C11	2.269(3)	2.452(5)[c]	2.441(5)[c]
Cr—D1	1.940(4)[a]	2.021(5)[d]	2.008(7)[d]
Cr—D2	1.938(6)[a]	2.030(6)[d]	2.012(9)[d]
C1—C2	1.405(5)	1.35(1)	1.429(9)
C2—C3	1.428(5)	1.38(1)	1.426(8)
C4—C5	1.419(4)	1.40(1)	1.349(9)
C5—C6	1.427(4)	1.443(9)	1.411(9)
C7—C8	1.407(6)	1.393(8)	1.35(1)
C8—C9	1.399(6)	1.394(8)	1.411(9)
C9—C10	1.359(6)	1.427(7)[e]	1.428(8)[e]
C10—C11	1.380(6)	1.418(7)[f]	1.437(7)[f]
C11—C7	1.388(6)	1.416(7)[g]	1.416(8)[g]
C10—C15	—	1.393(8)	1.412(7)
C10—C11	—	1.33(1)	1.32(1)
C11—C12	—	1.41(1)	1.40(1)
C12—C13	—	1.383(9)	1.39(1)
C13—C14	—	1.433(8)	1.401(8)
D1—Cr1—Cr2	131.2(1)	132.4(1)	132.9(1)
D2—Cr2—Cr1	132.4(1)	132.8(1)	133.3(1)
C1—C2—C3	126.3(3)	133.6(7), 145(1)[h]	125.3(5)
C4—C5—C6	125.5(3)	125.7(6), 165(2)[h]	129.9(6), 151(2)[h]

[a] Midpoints of planes defined by C7—C11 and C17—C21.

[b] Cr1—C15

[c] Cr1—C14

[d] Midpoints of planes defined by C7—C9, C14, C15 and C17—C19, C24, C25.

[e] C9—C15.

[f] C14—C15.

[g] C7—C14.

[h] Disordered at C2 and C5.

No significance should therefore be attached to the associated bonding parameters. The main interest in **12** centres on the hapticity of the indenyl—Cr bond: the indenyl group in both molecules is essentially planar (the fold angle between the five- and six-membered rings are 2.2°/4.7° for molecule 1 and 2.4°/2.4° for molecule 2) while all of the C-atoms of the five-membered ring are within a bonding distance to the metal so that the indenyl group is best regarded as being bonded in an η^5-manner to the metal atom and not in an η^3-manner. In contrast, in (η^3-indenyl)Ir($PMe_2Ph)_3$ for example, the two C-atoms shared by both the five- and six-membered rings are much further away [3.036/3.014(8) Å] from the metal atom than the other three [2.047(8)–2.236(13) Å] and there is a 20° angle between the planes of the allyl group and the six-membered ring.[6] The slight differences in the indenyl—Cr bond lengths for the two independent molecules of **12** suggest that **12b** has more η^5-character than **12a** and this may well be the result of packing effects within the crystal. **12** is diamagnetic (NMR; see experimental) and this combined with the much shorter Cr—Cr distance observed in the structurally related $[(\eta^3\text{-}C_3H_5)(\mu\text{-}\eta^3\text{-}C_3H_5)Cr]_2$ [1.97(6) Å] for which a quadruple metal–metal bond has been suggested,[7,8] could be taken as an indication that **12** contains a metal–metal double bond. One ambiguity, however, remains unresolved: $[Cp(\mu\text{-}\eta^3\text{-}C_3H_5)Cr]_2$ (**11**) is paramagnetic and it remains unclear whether this is an artefact (due to impurities in the bulk sample) or is the result of a difference in the multiplicity of the metal–metal bond.

The crystal structures of two donor-ligand stabilized Cp′(η^4-1,3-C_4H_6)-species (**21** and **26**) have been determined by X-ray diffraction. The molecular structures are shown in Fig. 1 and selected structural parameters are compared in Table 1. In both cases the butadiene molecule has a single-*cis* geometry and is bonded in an η^4-manner to the metal atom. The pentamethylcyclopentadienyl group in **26** is essentially planar with the methyl groups bent by an average of only 1.8° out of the ring-plane away from the metal atom. The Cr—C—O fragment is practically linear [Cr—C13—O 178.8(4)°] with the oxygen atom bent slightly towards the ring.

The crystal structure of Cp(η^4-1,3-cyclohexadiene)CrP(OMe)$_3$ (**27**) has also been determined (Fig. 1) and selected structural parameters are listed in Table 1. The 1,3-cyclohexadiene molecule is bonded as an η^4-organic ligand, the methylenic C-atoms are directed away from the metal atom. Complexation to the metal leads to a delocalization of the electrons within the 1,3-diene fragment (for free 1,3-cyclohexadiene C1—C2 = 1.348 and C2—C3 = 1.465 Å).[14] The cyclopentadienyl ring is planar.

EXPERIMENTAL

All experiments were carried out under an atmosphere of argon. Solvents (diethylether, pentane) were dried and freed from dissolved oxygen by distillation from diethylmagnesium. Chromocene,[9] $(\eta^3\text{-}C_3H_5)_3Cr$ and $(\eta^3\text{-}2\text{-}MeC_3H_4)_3Cr$[10] were prepared by published procedures. The alkali metal salts of cyclopentadiene, substituted cyclopentadiene and indene were prepared by standard methods either by reaction with n-butyllithium or the alkali metal.

Infrared spectra were recorded with a Nicolet-FT-IR-spectrometer and the magnetic susceptibility was measured using a magnetic balance constructed in the Institute mainly from Varian parts (field strength 9000 G).

$[CpCrCl_2]_2$

The following synthesis is a modification of the published procedure.[11] Cp_2Cr (20 g, 110 mmol) was dissolved in pentane (1 l) at 0°C. The resulting red solution was stirred vigorously and treated with dry, gaseous HCl. The product was formed immediately as a green precipitate and the reaction was continued until the pentane became colourless. The compound, a green powder (dec. > 250°C) which is relatively insensitive to air but extremely moisture sensitive, was isolated and washed with pentane (3 × 100 cm^3) at room temperature. Yield 18.6 g (90% theory).

$[(\eta^3\text{-}C_3H_5)_2CrCl]_2$

The following synthesis is a modification of the published procedure.[11] $(\eta^3\text{-}C_3H_5)_3Cr$[10] (6.1 g, 34.9 mmol) was dissolved in diethylether (200 cm^3) and an ethereal solution of HCl (66 cm^3 of a 0.5 N solution, 33 mmol) was added dropwise at −78°C with vigorous stirring to give the product as a red–brown precipitate. Solvent was removed at −25°C under high vacuum and the residue washed with 50 cm^3 aliquots of pentane [to remove unreacted $(\eta^3\text{-}C_3H_5)_3Cr$] until the washings were colourless. The compound, which decomposes above −20°C, was dried at −40°C. Yield 5.33 g (90% theory). Found: C, 42.4; H, 5.9; Cl, 21.0; Cr, 30.7. Calc. for $C_{12}H_{20}Cl_2Cr_2$: C, 42.5; H, 5.9; Cl, 20.9; Cr, 30.7%. MS: *m*/*z* 296 (M^+-C_3H_6), 221, 210, 185, 175, 134, 93.

$[(\eta^3\text{-}2\text{-MeC}_3H_4)_2CrCl]_2$

$(\eta^3\text{-}2\text{-MeC}_3H_4)_3Cr$ [prepared in an analogous manner to $(\eta^3\text{-}C_3H_5)_3Cr$[10]] (7.6 g, 34.9 mmol) was dissolved in diethylether (200 cm^3) at −78°C and treated with ethereal-HCl (66 cm^3 of a 0.5 N solution, 33 mmol) as described above. The compound was isolated as a red–brown powder which decomposed above −20°C and which inflamed spontaneously in air. Yield 6.23 g (90% theory). Found: C, 48.2; H, 7.6; Cl, 18.0; Cr, 25.8. Calc. for $C_{16}H_{28}Cl_2Cr_2$: C, 48.6; H, 7.1; Cl, 17.9; Cr, 26.3%. MS: *m/z* 394 (M^+), 339 (M^+-C_4H_7), 284, 229, 217, 162, 107.

$Cp(\eta^3\text{-}C_3H_5)_2Cr$ (**1**)

Allylmagnesium chloride (1.06 l of a 0.308 mol l^{-1} ethereal solution, 325.6 mmol) was added dropwise to a suspension of $[CpCrCl_2]_2$ (27.86 g, 74.1 mmol) in diethylether (300 cm^3) at −60°C over 12 h. The reaction mixture was stirred at −60°C for a further 14 h and the solvent removed under high vacuum at −50°C. The residue was dried under high vacuum and then extracted with aliquots of carefully dried pentane at −30°C until the extract was colourless. The combined extract (*ca* 5 l) was cooled to −78°C to give the compound as orange–red crystals. Yield 24.78 g (83.9% theory). The compound can also be prepared (yield *ca* 70%) by reacting $[(\eta^3\text{-}C_3H_5)_2CrCl]_2$ with cyclopentadienyllithium in ether at −35°C. The compound reacts further above −20°C. Found: C, 66.2; H, 7.6; Cr, 26.0. Calc. for $C_{11}H_{15}Cr$: C, 66.3; H, 7.6; Cr, 26.1%. MS (70 eV, 40°): *m/z* 199 (M^+), 171, 158 (M^+-C_3H_5), 117. Magn. moment: μ_{eff} 1.8 BM. IR (KBr, −45°C): ν 3100, 3000, 1495, 1435, 1370, 1210, 1125, 1060, 1005, 910, 825, 750, 580. Crystal structure: see ref. 2.

Reaction of **1** *with* HCl

$Cp(\eta^3\text{-}C_3H_5)_2Cr$ (1.31 g, 6.57 mmol) was suspended in pentane (40 cm^3) at −50°C and treated with gaseous HCl (306.7 cm^3, 13.69 mmol) from a gas burette. Propene was liberated and determined by GC (98.6% theory) and a turquoise-coloured suspension of $(CpCrCl_2)_2$ was formed. Yield 1.08 g (87.9% theory). The same compound is also formed upon treatment of **1** with CH_2Cl_2 and is accompanied by the liberation of 1,5-hexadiene.

Reaction of **1** *with* I_2

$Cp(\eta^3\text{-}C_3H_5)_2Cr$ (0.95 g, 4.77 mmol) was suspended in pentane (60 cm^3) at −78°C and iodine (1.82 g, 7.17 mmol) in diethylether (5 cm^3) was added. The reaction mixture was allowed to warm to 0°C and stirred overnight. 1,5-Hexadiene (33% theory, GC) was liberated with formation of green $(CpCrI_2)_2$. Yield 1.26 g (71.3% theory). Found: Cr, 13.9; I, 68.6. Calc. for $C_{10}H_{10}Cr_2I_4$: Cr, 14.0; I, 68.4%. MS (CI, 230°): *m/z* 742 (M^+), 615 (M^+—I).

Reaction of **1** *with acetylacetone*

$Cp(\eta^3\text{-}C_3H_5)_2Cr$ (1.69 g, 8.9 mmol) was dissolved in diethylether (100 cm^3) at −78°C and treated with excess acetylacetone (3 cm^3) at −20°C. The reaction mixture became dark red. The solvent was distilled off and shown by GC to contain propane (61.6% theory) and cyclopentadiene (100.4% theory) and the solid identified as $Cr(acac)_3$. Yield 1.98 g (66.8% theory).

Reaction of **1** *with excess* PPh_3

Excess PPh_3 (5.2 g) was added to solid $Cp(\eta^3\text{-}C_3H_5)_2Cr$ (1.23 g, 6.17 mmol) at −78°C and the reaction vessel connected by a glass bridge to a trap. The apparatus was evacuated and closed and the reaction vessel lowered into a bath at 100°C while the trap was cooled in liquid N_2. 0.53 g (103.9% theory) of condensate was liberated and shown to consist of 1,5-hexadiene (60.9% theory) and other C_6-hydrocarbons (33.4% theory).

$(\eta^5\text{-MeC}_5H_4)(\eta^3\text{-}C_3H_5)_2Cr$ (**2**)

Methylcyclopentadienyllithium (1.17 g, 13.6 mmol) was added to a stirred suspension of $[(\eta^3\text{-}C_3H_5)_2CrCl]_2$ (2.1 g, 6.2 mmol) in diethylether (200 cm^3) at −78°C. The reaction mixture was stirred at −35°C for 16 h, evaporated to dryness and the residue extracted with pentane (3 × 100 cm^3). The extract was filtered and cooled to −78°C to give the compound as red, cubic crystals which decomposed at −20°C. Yield 1.85 g (70% theory). Found: C, 67.4; H, 8.1; Cr, 24.4. Calc. for $C_{12}H_{17}Cr$: C, 67.6; H, 8.0; Cr, 24.4%. MS: *m/z* (M^+), 172 (M^+-C_3H_5), 131. Magn. moment: μ_B 1.6 BM. IR (KBr, −45°C): ν 3080, 2990, 2920, 1495, 1455, 1375, 1210, 1050, 1000, 830, 745, 580.

$(\eta^5\text{-t-}C_4H_9C_5H_4)(\eta^3\text{-}C_3H_5)_2Cr$ (**3**)

Prepared as above from t-butylcyclopentadienyllithium as yellow crystals which decompose above −20°C. Yield 65% theory. Found: C, 70.1; H, 9.2; Cr, 20.9. Calc. for $C_{15}H_{23}Cr$: C, 70.6; H, 9.1; Cr, 20.4%. MS: the compound decomposed. IR (KBr,

$-45°C$): ν 3100, 3000, 2930, 1490, 1380, 1360, 1215, 1045, 1005, 920, 830, 745, 580.

(η^5-$Me_2PhCC_5H_4$)(η^3-C_3H_5)$_2$Cr (**4**)

Prepared as above from 2-phenylisopropylcyclopentadienyllithium as red needles which decompose above $-20°C$. Yield 65% theory. Found: C, 75.6; H, 7.8; Cr, 16.5. Calc. for $C_{20}H_{25}Cr$: C, 75.7; H, 7.9; Cr, 16.4%. MS: the compound decomposed. IR (KBr, $-45°C$): ν 3100, 3060–3040, 2980, 1620, 1590, 1490, 1380, 1205, 1040, 1000, 775, 705, 580.

(η^5-Me_5C_5)(η^3-C_3H_5)$_2$Cr (**5**)

Prepared as above from pentamethylcyclopentadienyllithium as red needles which decompose above $-20°C$. Yield 65% theory. Found: C, 71.0; H, 9.4; Cr, 19.7. Calc. for $C_{16}H_{25}Cr$: C, 71.3; H, 9.4; Cr, 19.3%. MS. *m*/*z* 269 (M^+), 187 (M^+-C_6H_{10}), 131. Magn. moment: μ_B 2.0 BM. IR (KBr, $-45°C$): ν 3060, 2990, 2920, 1490, 1435, 1375, 1210, 995, 590.

(η^5-*Indenyl*)(η^3-C_3H_5)$_2$Cr (**6**)

[(η^3-C_3H_5)$_2$CrCl]$_2$ (5.1 g, 15 mmol) was suspended in diethylether (400 cm^3) at $-78°C$ and treated with indenyllithium (3.78 g, 31 mmol). The reaction mixture was warmed to $-40°C$ and stirred for 14 h to give an intensive red–brown solution. The solvent was removed at $-35°C$ and the residue extracted with pentane (3 × 100 cm^3). The resulting solution was cooled to $-78°C$ to give the compound as dark brown needles which decompose above $-20°C$. Yield 5.16 g (69% theory). Found: C, 72.1; H, 7.1; Cr, 20.7. Calc. for $C_{15}H_{17}Cr$: C, 72.3; H, 6.9; Cr, 20.9%. MS (70 eV, 30°C): *m*/*z* 249 (M^+), 208 (M^+-C_3H_5), 167. Magn. moment: μ_B 1.6/1.8. IR (KBr, $-45°$): ν 3090–3040, 1630, 1610, 1490, 1450, 1380, 1350, 1210, 995, 745, 580.

Cp(η^3-2-MeC_3H_4)$_2$Cr (**7**)

[(η^3-2-MeC_3H_4)$_2$CrCl]$_2$ (2.1 g, 5.3 mmol) was suspended in diethylether (200 cm^3) at $-78°C$ and treated with cyclopentadienyllithium (0.79 g, 11 mmol). The reaction mixture was stirred for 16 h at $-35°C$ to give a red–violet solution. The solvent was evaporated at $-35°C$ and the residue extracted with pentane (3 × 100 cm^3). Cooling to $-78°C$ failed to cause precipitation of the compound which was isolated as a red–violet oil (which decomposed at $-20°C$) by evaporation to dryness. Yield 0.72 g (30% theory). Satisfactory elemental analysis of this thermolabile oil could not be obtained. MS: *m*/*z* 227 (M^+), 117 (M^+-C_8H_{14}). IR (film): ν 3080, 2940, 2860, 2810, 1480, 1375, 1095, 1010, 790, 580.

(η^5-*Indenyl*)(η^3-2-MeC_3H_4)$_2$Cr (**8**)

[(η^3-2-MeC_3H_4)$_2$CrCl]$_2$ (2.1 g, 5.3 mmol) was suspended in diethylether (200 cm^3) at $-78°C$ and treated with indenyllithium (1.34 g, 11 mmol). The reaction mixture was stirred for 16 h at $-35°C$. The solvent was removed and the residue extracted with pentane (3 × 100 cm^3). Removal of the solvent at $-40°C$ gave the product as a violet oil which decomposed above $-20°C$. Yield 0.88 g (30% theory). Satisfactory analytical data could not be obtained for this thermolabile oil. MS: the compound decomposed. IR (film): ν 3060, 2960–2860, 1480, 1440, 1375, 1210, 740.

[Cp(μ-η^3-C_3H_5)Cr]$_2$ (**11**)[4]

Cp(η^3-C_3H_5)$_2$Cr (**1**) (1.83 g, 9.19 mmol) was suspended in pentane (50 cm^3) at $-78°C$ and toluene (30 cm^3) was added. The reaction mixture was allowed to slowly warm to $-15°C$ and stirred for 24 h. A brown solid precipitated. Yield 1.01 g (69.8% theory; the yield in the absence of toluene was only *ca* 25%). Found: C, 60.9; H, 6.3; Cr, 32.8. Calc. for $C_{16}H_{20}Cr_2$: C, 60.8; H, 6.4; Cr, 32.9%. Magn. moment: μ_{eff} 4.1 BM. Crystal structure: see Fig. 2.

[(η^5-*Indenyl*)(μ-η^3-C_3H_5)Cr]$_2$ (**12**)

(η^5-Indenyl)(η^3-C_3H_5)$_2$Cr (**6**) (0.60 g, 2.4 mmol) was dissolved in diethylether (50 cm^3) at $-30°C$ in an atmosphere of ethylene and the solution allowed to reach room temperature over 24 h. The solvent was removed and the residue separated from polyethylene (0.6 g) by extraction. The resulting brown solid was treated with Avicel and cooled to $-78°C$ to give the compound as dark brown crystals. Yield 0.21 g (40% theory). The same compound is formed in the absence of ethylene. Found: C, 69.1; H, 5.9; Cr, 25.1. Calc. for $C_{24}H_{24}Cr_2$: C, 69.2; H, 5.8; Cr, 25.0%. MS: *m*/*z* 374 (M^+-C_3H_6), 334 (M^+-C_6H_{12}), 282, 208, 167. IR (KBr, room temperature): ν 2040, 1605, 1480, 1335, 1215, 995, 820, 745. ^1H NMR (d_8-THF, 30°C): δ 7.01, 6.75 (indenyl); 6.26, 5.91 (indenyl); 4.79, 3.27, 2.28, 1.50 (allyl). Crystal structure: see Fig. 2.

Cp(η^2,η^2-1,5-*hexadiene*)CrCO (**13**)[2]

Cp(η^3-C_3H_5)$_2$Cr (**1**) (2.18 g, 10.94 mmol) was suspended in pentane (40 cm^3) at $-78°C$ and the reaction vessel connected to a glass burette filled with CO. The reaction mixture was stirred vigorously and warmed to 0°C. CO (12.83 mmol) was absorbed and the solution became dark green. A small amount of a green–grey solid (yield *ca* 4%; presumably $Cp_2Cr_2(CO)_5$, ν(CO) 1945, 1845, 1780, 1730) was filtered off and the solution evaporated to dryness to give the compound as green needles. Yield 2.12 g (85.3% theory). Found: C, 65.1; H, 7.1; Cr, 22.8. Calc. for $C_{12}H_{15}CrO$: C, 63.4; H, 6.7; Cr, 22.8%. MS (70 eV, 30°C): *m*/*z* 227 (M^+), 144 (M^+-CO), 171, 117. Magn. moment: μ_{eff} 1.61/1.58 BM. IR (KBr, −40°C): ν(CO) 1870vs, 1830sh, 1012, 1002, 820, 803, 590, 556, 546, 487.

$Cp(\eta^2,\eta^2$-1,5-*hexadiene*)$CrPMe_3$ (**14**)[2]

$Cp(\eta^3\text{-}C_3H_5)_2Cr$ (**1**) (6.33 g, 31.8 mmol) was suspended in pentane (100 cm^3) at −78°C and PMe_3 (2.42 g, 3.3 cm^3, 31.8 mmol) added slowly with a pipette. The reaction mixture was allowed to warm to 0°C during which the colour changed to dark green. The solution was stirred overnight, filtered to remove a small amount of a grey–green solid [approx. composition $Cp_2Cr_2(PMe_3)_5$] and cooled to −78°C to give the compound as a dark green, crystalline solid which decomposed at 80°C. Yield 7.18 g (82% theory). Found: C; 61.1; H, 8.7; Cr, 18.8; P, 11.3. Calc. for $C_{14}H_{24}CrP$: C, 61.1; H, 8.8; Cr, 18.9; P, 11.3%. MS (70 eV, 50°C): *m*/*z* 275 (M^+), 193 (M^+-C_6H_{10}), 117. Magn. moment: μ_B 1.9 BM. IR (KBr, room temperature): ν 3100, 3020, 2920, 1470, 1465, 1420, 1120, 950, 800. Crystal structure: see ref. 2.

$Cp(\eta^2,\eta^2$-1,5-*hexadiene*)$CrP(OMe)_3$ (**15**)[2]

Prepared as above as dark green needles in 89% yield. Found: C, 52.1; H, 7.6; Cr, 16.1; P, 9.5. Calc. for $C_{14}H_{24}CrO_3P$: C, 52.0; H, 7.5; Cr, 16.1; P, 9.6%. MS (70 eV, 50°C): *m*/*z* 323 (M^+), 241 (M^+-C_6H_{10}), 182, 117. Magn. moment: μ_{eff} 1.9/2.0 BM. IR (KBr, room temperature): ν 3100, 3040, 2940, 2840, 1480, 1450, 1440, 1120, 1040, 805, 760, 700. Crystal structure: the structure has been confirmed by an X-ray diffraction study but disorder prevented refinement of the data.

$Cp(\eta^2,\eta^2$-1,5-*hexadiene*)$CrP(OPh)_3$ (**16**)

Prepared as above as a dark green, relatively insoluble compound in 85% yield. Found: Cr, 10.1; P, 6.0. Calc. for $C_{29}H_{30}CrO_3P$: Cr, 10.2; P, 6.1%. MS (70 eV, 110°C): *m*/*z* 509 (M^+), 428, 427 (M^+-C_6H_{10}), 326, 311, 182, 117. Magn. moment: μ_{eff} 2.2 BM.

$[Cp(\eta^2,\eta^2$-1,5-*hexadiene*)$CrPPh_2Me]_2$ (**17**)

$Cp(\eta^3\text{-}C_3H_5)_2Cr$ (**1**) (1.50 g, 7.5 mmol) and PPh_2 Me (1.60 g, 8 mmol) were dissolved in diethylether (80 cm^3) at −30°C and the mixture warmed to 0°C and stirred overnight. The resulting yellow solution was evaporated, the residue extracted with pentane and the extract cooled to −78°C to give the compound as lemon-yellow crystals which decompose at 80°C. Yield 2.41 g (80% theory). Found: C, 72.1; H, 7.0; Cr, 13.0; P, 7.9. Calc. for $C_{48}H_{56}Cr_2P_2$: C, 72.2; H, 7.1; Cr, 13.0; P, 7.8%. Mol. wt (cryoscopic, C_6H_6): 782 (calc. 799). MS (70 eV, 90°C): *m*/*z* 317 ($[CpCrPPh_2Me]^+$). Magn. moment: μ_{eff} 2.7/2.6 BM. IR (KBr, room temperature): ν 3080, 3000, 2920, 2820, 1540, 1480, 1435, 1270, 815.

$Cp(\eta^2$-1,5-*hexadiene*)$Cr(Me_2PC_2H_4PMe_2)$ (**18**)

$Cp(\eta^3\text{-}C_3H_5)_2Cr$ (**1**) (1.50 g, 7.5 mmol) and 1,2-bis(dimethylphosphino)ethane (1.20 g, 8 mmol) were dissolved in diethylether (100 cm^3) at −30°C and the solution allowed to reach 0°C over 16 h. The reaction mixture was evaporated to dryness and the residue extracted with pentane. Filtration and cooling to −78°C gave the compound as a brown, crystalline solid which decomposed at 80°C. Yield 2.36 g (90% theory). Found: C, 58.6; H, 8.6; Cr, 14.7; P, 17.9. Calc. for $C_{17}H_{31}CrP_2$: C, 58.4, H, 8.9; Cr, 14.9; P, 17.7%. MS: *m*/*z* 349 (M^+), 267 (M^+-C_6H_{10}). Magn. moment: μ_{eff} 1.8 BM. IR (KBr, room temperature): ν 3100, 3060, 2960, 2840, 1635, 1535, 1005, 990, 905.

(η^5-*Indenyl*)(η^2,η^2-1,5-*hexadiene*)$CrP(OMe)_3$ (**19**)

Trimethylphosphite (0.57 g, 4.6 mmol) was added to an ethereal solution of (η^5-indenyl)$(\eta^3\text{-}C_3H_5)_2Cr$ (**6**) at −30°C and the solution stirred at −10°C for 12 h. The solution was evaporated to dryness at room temperature in a high vacuum and the residue dissolved in hexane, filtered and the solution cooled to −78°C to give the compound as red, needle-shaped crystals which were dried under high vacuum and which decompose above 70°. Yield 1.16 g (80% theory). Found: C, 57.9; H, 7.0; Cr, 13.9; P, 8.3. Calc. for $C_{18}H_{26}CrO_3P$: C, 58.2; H, 6.9; Cr, 14.2; P, 8.3%. IR (KBr, room temperature): ν 3080, 2940, 2820, 1600, 1480, 1460, 1040. MS: *m*/*z* 373 (M^+), 291 (M^+-C_6H_{10}), 249 [M^+-$P(OMe)_3$]. Crystal structure: see Fig. 1.

(η^5-*Indenyl*)(η^2,η^2-1,5-*hexadiene*)CrPMe$_3$ (**20**)

Prepared as above by reacting trimethylphosphine with (η^5-indenyl)(η^3-C_3H_5)$_2$Cr (**6**) in diethylether at -10°C. The compound decomposes above 70°C. Yield 80%. Found: C, 66.5; H, 8.1; Cr, 16.0; P, 9.5. Calc. for $C_{18}H_{26}CrP$: C, 66.3; H, 7.9; Cr, 16.2; P, 9.3%. IR (KBr, room temperature): ν 3070, 3030, 2950, 2800, 1600, 1470, 1420, 1340, 1270, 940. MS. *m*/*z* 325 (M^+), 249 (M^+-PMe$_3$), 243 (M^+-C_6H_{10}).

Cp(η^4-1,3-C_4H_6)CrPMe$_3$ (**21**)

Cp(η^2,η^2-1,5-hexadiene)CrPMe$_3$ (**14**) (1.79 g, 6.5 mmol) was dissolved in diethylether (100 cm^3) and treated with a 10-fold excess of 1,3-butadiene at 0°C and stirred for 48 h. The colour of the reaction mixture changed from dark green to orange–red. The solvent was removed under high vacuum and the residue extracted with pentane. The extract was cooled to -78°C to give the compound as ruby red needles which melt at 94°C and decompose above 130°C. Yield 1.45 g (90% theory). The compound can also be prepared in a manner analogous to that described below (yield 61% theory) by reacting [CpCrCl$_2$]$_2$ consecutively with PMe$_3$ and magnesium-butadiene in THF. Found: C, 57.9; H, 8.0; Cr, 21.2; P, 12.4. Calc. for $C_{12}H_{20}CrP$: C, 58.3; H, 8.2; Cr, 21.0; P, 12.5%. MS: *m*/*z* 247 (M^+), 193, 171, 117, 76, 52. IR (KBr): ν 3110, 3040, 2960, 2910, 1445, 1420, 1280, 1210, 1105, 1000, 950, 800. Crystal structure: see Fig. 1.

Cp(η^4-1,3-C_4H_6)CrP(OMe)$_3$ (**22**)

[CpCrCl]$_2$ (1.88 g, 5 mmol) was suspended in THF (300 cm^3) and P(OMe)$_3$ (1.36 g, 11 mmol) was added. The resulting deep blue solution was cooled to -78°C and C_4H_6Mg(THF)$_2$ (2.33 g, 10.5 mmol) was added. The reaction mixture was stirred and allowed to warm to room temperature over 16 h during which time it became red. Solvent was removed under high vacuum and the residue extracted with pentane (3 × 100 cm^3) at room temperature. The resulting red extract was concentrated and cooled to -78°C to give the compound as orange red crystals (m.p. 120°C) which were recrystallized from hexane. Yield 1.77 g (60% theory). The compound can also be prepared as described above (yield 90% theory) by reacting Cp(η^2,η^2-1,5-hexadiene)CrP(OMe)$_3$ (**15**) with excess butadiene in ether. Found: C, 48.7; H, 7.0; Cr, 17.9; P, 10.3. Calc. for $C_{12}H_{20}CrO_3P$: C, 48.8; H, 6.8; Cr, 17.6; P, 10.5%. MS: *m*/*z* 295 (M^+), 241, 171, 117, 52. IR (KBr): ν 3105, 3040, 2940, 2830, 1455, 1430, 1110, 1020, 805, 770, 725.

(η^5-*Indenyl*)(η^4-1,3-C_4H_6)CrPMe$_3$ (**23**)

Prepared as described for **21** by reacting (η^5-indenyl)(η^2,η^2-1,5-hexadiene)CrPMe$_3$ with excess butadiene at 0°C. The compound was isolated as dark green needles (m.p. 50°C dec.) in 79% yield. Found: C, 64.7; H, 7.4; Cr, 17.6; P, 10.2. Calc. for $C_{16}H_{22}CrP$: C, 64.6; H, 7.5; Cr, 17.5; P, 10.4%. MS: *m*/*z* 243 (M^+-C_4H_6), 221, 167. IR (KBr): ν 3080, 3030, 2960, 2910, 1605, 1470, 1420, 1330, 945.

(η^5-Me$_5$C$_5$)(η^4-1,3-C_4H_6)CrPMe$_3$ (**24**)

Cp*Cr(THF)Cl$_2$ (100 cm^3 of a 0.081 molar solution, 8.1 mmol) was treated with PMe$_3$ (1 cm^3, 9.6 mmol) in THF at room temperature. The solution was cooled to -78°C and a suspension of (C_4H_6)Mg(THF)$_2$ (2 g, 9 mmol) in THF (100 cm^3) was added. The reaction mixture was stirred at -20°C for 7 h, evaporated to dryness and the residue extracted with pentane (210 cm^3) at -10°C. The extract was filtered, concentrated and cooled to -78°C to give the compound as dark red platelets. Yield: 1.85 g (72% theory). Found: C, 63.9; H, 10.2; Cr, 16.2; P, 9.7. Calc. for $C_{17}H_{30}CrP$: C, 64.3; H; 9.5; Cr, 16.4; P, 9.8%. MS (70 eV): *m*/*z* 241 (M^+-PMe$_3$, 60%), 187 (M^+-PMe$_3$/C_4H_6, 100%). IR (KBr): ν(Cp*) 1460m, 1370s, 1070m, 1020s; (C_4H_6) 1490m, 1230m, 880m, 830m; (PMe$_3$) 1300m, 1280s, 950s, 720m.

(η^5-Me$_5$C$_5$)(η^4-1,3-C_4H_6)CrP(OMe)$_3$ (**25**)

Prepared as above in the presence of P(OMe)$_3$ as a red crystalline compound in 75% yield. Found: C, 55.8; H, 8.7; Cr, 14.2; P, 8.4. Calc. for $C_{17}H_{30}CrO_3P$: C, 55.9; H, 8.3; Cr, 14.2; P, 8.5%. MS (70 eV): *m*/*z* 365 (M^+, 10%), 334 (3%), 311 (M^+-C_4H_6, 8%), 241 (M^+-P(OMe)$_3$, 89%), 218 (64%), 187 (M^+-C_4H_6/P(OMe)$_3$, 100%). IR (KBr): ν(Cp*) 1440m, 1370m, 1080m; (C_4H_6) 1490msh, 1230m, 880m; (PR$_3$) 1470m, 1180m, 1020s, 760m, 720s, 545m.

(η^5-Me$_5$C$_5$)(η^4-1,3-C_4H_6)CrCO (**26**)

(η^5-Me$_5$C$_5$)(η^4-1,3-C_4H_6)CrPMe$_3$ (**24**) (0.5 g, 1.58 mmol) was dissolved in pentane (50 cm^3), cooled to -70°C and the apparatus connected to a gas-burette filled with CO. The reaction mixture was stirred and allowed to warm to room temperature. The resulting green solution was cooled to -78°C to give the compound as red crystals.

Table 3. Crystal structure data for **19**, **21**, **26** and **27**[a]

	19	**21**	**26**	**27**
Formula	$C_{18}H_{26}CrO_3P$	$C_{12}H_{20}CrP$	$C_{15}H_{21}CrO$	$C_{14}H_{22}CrO_3P$
Molecular weight	373.4	247.3	269.3	321.3
Crystal size [mm]	0.07 × 0.40 × 0.40	0.32 × 0.50 × 0.43	0.25 × 0.47 × 0.40	0.40 × 0.43 × 0.54
Crystal system	orthorhombic	monoclinic	monoclinic	monoclinic
Space group [No.]	*Pbca* [61]	$P2_1/n$ [14]	$P2_1/m$ [11]	$P2_1/a$ [14]
a [Å]	8.657(1)	7.602(1)	7.097(1)	14.474(2)
b [Å]	16.887(2)	15.024(2)	11.664(1)	7.629(1)
c [Å]	24.642(4)	11.724(1)	8.567(1)	14.838(2)
β [°]	—	107.19(1)	96.69(1)	114.48(1)
V [Å^3]	3602(1)	1279(1)	704(1)	1491(1)
Z	8	4	2	4
Calculated density [g cm^{-3}]	1.38	1.28	1.27	1.43
μ [cm^{-1}]	7.17	9.60	7.75	8.54
Mo-K_α radiation [Å]	0.71069	0.71069	0.71069	0.71069
$F(000)$ [e]	1576	524	286	676
Temperature [K]	293	293	293	113
Diffractometer	Enraf–Nonius CAD4	Enraf–Nonius CAD4	Enraf–Nonius CAD4	Enraf–Nonius CAD4
Scan mode	ω–2θ	ω–2θ	ω–2θ	ω–2θ
$[\sin\theta/\lambda]_{max}$ [Å^{-1}]	0.65	0.70	0.70	0.74
Total number of reflections	6053 $(+h, +k, +l)$	3991 $(\pm h, +k, +l)$	2266 $(\pm h, +k, +l)$	10,907 $(\pm h, \pm k, +l)$
Independent reflections	4051	3695	2134	5129
Observed reflections [$I > 2\sigma(I)$]	2250	2820	1858	4505
Refined parameters	208	207	85	260
R, R_w [$w = 1/\sigma^2(F_o)$]	0.055, 0.047	0.030, 0.036	0.045, 0.058	0.025, 0.036
Error of fit	1.8	1.9	2.7	1.9
Residual electron density [e Å^{-3}]	0.39	0.28	0.51	0.38
Method of structure solution (SHELX86)	heavy atom	heavy atom	heavy atom	heavy atom

[a] Further details of the crystal structure investigations and lists of final atomic coordinates, thermal parameters, distances, angles, and structure factors may be obtained from the Cambridge Crystallographic Data Centre (CCDC).

Yield 0.35 g (81% theory). Found: C, 66.7; H, 8.0; Cr, 19.2. Calc. for $C_{15}H_{21}CrO$: C, 66.9; H, 7.8; Cr, 19.3%. MS: m/z 269 (M^+), 241, 187, 52. IR (KBr): ν 3060, 3040, 2980–2920, 2880, 1900 (CrCO), 1480, 1380, 1220, 1180, 880, 860. Crystal structure: see Fig. 1.

Cp(η^4-1,3-*cyclohexadiene*)CrP(OMe)$_3$ (**27**)

Cp(η^2,η^2-1,5-hexadiene)CrP(OMe)$_3$ (**15**) (1.62 g, 5 mmol) in diethylether was treated with a 10-fold excess of 1,3-cyclohexadiene and stirred at room temperature for 4 days. The resulting orange–brown solution was evaporated to dryness and the residue extracted with pentane. Diethylether was added to the extract (ether : pentane 1 : 5) and the compound isolated by fractional crystallization. Yellow crystals of Cp(η^6-C_6H_6)Cr (**28**) (0.25 g, 28% yield[5]) were deposited initially followed by **27** as dark red crystals which decomposed in solution above 25°C. Yield 0.92 g (57% theory). Found: C, 52.4; H, 7.0; Cr, 16.3; P, 9.5. Calc. for $C_{14}H_{22}CrO_3P$: C, 52.3; H, 6.9; Cr, 16.2; P, 9.6%. MS: m/z 321 (M^+), 197, 195, 124, 117, 52. IR (KBr): ν 3080, 2940, 2820, 1460, 1430, 1110, 1020, 800, 755, 710. Crystal structure: see Fig. 1.

Crystal structure determination

Crystal data for **19**, **21**, **26**, and **27** are summarized in Table 3 and those for **11** and **12** in Table 4.

Table 4. Crystal structure data for **11** and **12**[a]

	11	**12**
Formula	$C_{16}H_{20}Cr_2$	$C_{24}H_{24}Cr_2$
Molecular weight	316.3	416.5
Crystal size [mm]	0.21 × 0.49 × 0.39	0.18 × 0.29 × 0.32
Crystal system	orthorhombic	monoclinic
Space group [No.]	$Pna2_1$ [33]	$P2_1/a$ [14]
a [Å]	21.618(1)	21.140(5)
b [Å]	8.674(1)	6.972(1)
c [Å]	7.502(1)	27.856(7)
β [°]	—	110.46(2)
V [Å^3]	1407(1)	3847(1)
Z	4	8
Calculated density [g cm^{-3}]	1.49	1.44
μ [cm^{-1}]	14.88	11.07
Mo-K_α radiation [Å]	0.71069	0.71069
F(000) [e]	656	1728
Temperature [K]	293	293
Diffractometer	Enraf–Nonius CAD4	Enraf–Nonius CAD4
Scan mode	ω–2θ	ω–2θ
$[\sin\theta/\lambda]_{max}$ [Å^{-1}]	0.77	0.65
Total number of reflections	5715 ($\pm h$, $\pm k$, $+l$) transformed	9370 ($\pm h$, $+k$, $+l$)
Independent reflections	3976	8652
Observed reflections [$I > 2\sigma(I)$]	3529	5060
Refined parameters	231	466
R, R_w [$w = 1/\sigma^2(F_o)$]	0.033, 0.037	0.051,0.051
Error of fit	1.5	2.3
Residual electron density [e Å^{-3}]	0.71	0.61
Method of structure solution (SHELX86)	heavy atom abs. conf. determined	heavy atom disordered π-allyl-groups

[a] Further details of the crystal structure investigations and lists of final atomic coordinates, thermal parameters, distances, angles, and structure factors may be obtained from the Cambridge Crystallographic Data Centre (CCDC).

REFERENCES

1. P. W. Jolly and U. Zakrzewski, *Polyhedron* 1991, **10**, 1427.
2. K. Angermund, A. Döhring, P. W. Jolly, C. Krüger and C. C. Romão, *Organometallics* 1986, **5**, 1268.
3. M. P. Castellani, S. J. Geib, A. L. Rheingold and W. C. Trogler, *Organometallics* 1987, **6**, 1703.
4. J. Nieman, J. W. Pattiasina and J. H. Teuben, *J. Organomet. Chem.* 1984, **262**, 157.
5. K. Angermund, P. Betz, A. Döhring, P. W. Jolly, C. Krüger and K. U. Schönfelder, *Polyhedron* 1993, **12**, 2663.
6. J. S. Merola, R. T. Kacmarcik and D. V. Engen, *J. Am. Chem. Soc.* 1986, **108**, 329.
7. T. Aoki, A. Furusaki, Y. Tomiie, K. Ono and F. Tanaka, *Bull. Chem. Soc. Jpn* 1969, **42**, 545.
8. F. A. Cotton and R. A. Walton, in *Multiple bonds between metal atoms*, Wiley-Interscience, New York (1982).
9. F. A. Cotton and G. Wilkinson, *Z. Naturforsch.* 1954, **9B**, 417.
10. W. Oberkirch, Dissertation, Techn. Hochschule Aachen, 1963.
11. H. J. Klocke, Dissertation, Ruhr-Universität, Bochum, 1984.
12. R. Emrich, Dissertation Ruhr-Universität, Bochum 1991.
13. H. Yasuda, K. Tatsumi, T. Okamoto, K. Mashima, K. Lee, A. Nakamura, Y. Kai, N. Kanehisa and N. Kasai, *J. Am. Chem. Soc.* 1985, **107**, 2410.
14. H. Oberhammer and S. H. Bauer, *J. Am. Chem. Soc.* 1969, **91**, 10.