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### Phosphanylalkylcyclopentadienyl ligands: synthesis, molecular structures and catalytic properties of [{ $(\eta^5-C_5H_4)CMe_2PHR$ }CrCl<sub>2</sub>(PMe<sub>2</sub>Ph)] (R = Ph, <sup>t</sup>Bu)

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#### Abstract

Li[ $(C_5H_4)CMe_2PHPh$ ] reacted with [CrCl<sub>3</sub>(THF)<sub>3</sub>] with formation of a mixture of products, among which only [{ $(\eta^5-C_5H_4)CMe_2PHP$ }] CrCl<sub>2</sub> (1) could be isolated. However, when [CrCl<sub>3</sub>(PMe<sub>2</sub>Ph)<sub>3</sub>] was treated with Li[(C<sub>5</sub>H<sub>4</sub>)CMe<sub>2</sub>PHR], the complexes [{ $(\eta^5-C_5H_4)CMe_2PHR$ }CrCl<sub>2</sub>(PMe<sub>2</sub>Ph)] (R = Ph (2), 'Bu (3)) were obtained in moderate yield. Complexes 1 and 2 were characterised by X-ray crystallography, 1–3 by IR spectroscopy. In the solid state, a phosphanido-bridged dimer is observed for 1, while 2 and 3 are monomeric complexes without coordination of the phosphanyl group of the cyclopentadienyl ring. 2 and 3 were also characterised by mass spectrometry and NMR and UV–Vis spectroscopy, and their magnetic moments were determined. 2 and 3 were studied in the catalytic polymerisation of ethylene with methylalumoxane (MAO) as cocatalyst. © 2004 Elsevier Ltd. All rights reserved.

Keywords: Phosphanylalkylcyclopentadienyl ligands; Chromium complexes; Polymerisation studies

#### 1. Introduction

After the discovery of  $\alpha$ -olefin polymerisation [1], numerous metallocene and monocyclopentadienyl derivatives with different steric and electronic properties were synthesised and employed as catalysts in polymerisation reactions. *Ansa*-metallocene dichlorides of Ti, Zr, and Hf (especially chiral ones) are important catalysts for the methylalumoxane-promoted isotactic polymerisation of olefins. Therefore, intensive research is being carried out towards the synthesis of improved catalysts [2–5]. Recently, monocyclopentadienyl derivatives in which the cyclopentadienyl ring has a heteroatom-functionalised side chain were prepared and employed in the polymerisation and copolymerisation of olefins [6]. These studies were also extended to phospholyl ligands [7].

While numerous cyclopentadienyl ligands with Oand N-functionalised side chains are known, the number of cyclopentadienes with a P-functionalised alkyl or silyl side chain is still small [8], and it was only in 1994 that Heidemann and Jutzi [9] reported the first compound in which the P atom bears a reactive P-H bond. We extended this class of compounds to other derivatives in 1999 [10,11]. The lithium salts [Li(TMEDA)]<sub>2</sub>[(C<sub>5</sub>H<sub>4</sub>)-CMe<sub>2</sub>PPh] [12] and [Li(TMEDA)][(C<sub>5</sub>H<sub>4</sub>)CMe<sub>2</sub>PR<sub>2</sub>] (R = Ph, Me) [13], 1-SiMe<sub>2</sub>PHMes\*C<sub>5</sub>Me<sub>4</sub>H and its dimeric dipotassium salt [K(THF)2]2[(C5Me4)SiMe2-PMes\*] (Mes\* =  $2,4,6^{-t}Bu_3C_6H_2$ ) [14] have been structurally characterised. Such compounds should be useful precursors for dianionic bifunctional ligands in transition metal chemistry. In addition, the presence of a Pcontaining group is advantageous for reactivity studies by <sup>31</sup>P NMR spectroscopy.

We previously reported the synthesis of the PHfunctionalised ferrocene derivatives rac-[Fe{( $\eta^{5}$ -C<sub>5</sub>H<sub>4</sub>)CMe<sub>2</sub>PHR}<sub>2</sub>] [R = Ph, 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub> (Mes)] [15] the monosubstituted phosphanylalkylcyclopentadienyl

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complexes of group 4 metals,  $[{(\eta^5-C_5H_4)SiMe_2PHR}]$ - $ZrCl_3$ ] (R = Ph, Cy) and [{( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>)CMe<sub>2</sub>PH<sup>t</sup>Bu}- $MCl_3$  (M = Ti, Zr) [16] and of the metallocene derivatives [{( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>)CMe<sub>2</sub>PHR}<sub>2</sub>ZrCl<sub>2</sub>] and [{( $\eta^5$ - $C_5H_4$ )CMe<sub>2</sub>PHR $_2$ TiCl] (R = Ph, <sup>t</sup>Bu). The last-named slowly decompose on recrystallisation from THF, Et<sub>2</sub>O or toluene with formation of  $[{(\eta^5-C_5H_4)_2CMe_2}MCl_2]$ (M = Zr, Ti) and  $(PR)_n$   $(R = Ph, n = 4-6, R = {}^tBu$ , n = 4) and PH<sub>2</sub>R [17]. Recently, Erker and coworkers [18] reported the synthesis and catalytic properties in the polymerisation of olefins of the constrained-geometry  $[\{(C_5H_4)CMe_2PCy\}M(NR_2)_2]$ catalysts (M = Ti,R = Me, M = Zr, R = Et). Hou and coworkers [14] reported the synthesis of  $[{(\eta^5-C_5Me_4)SiMe_2PMes^*}]$ - $Ln(L)_n$ ] (Ln = Sm: L = THF, n = 1 or 3; L = MeOCH<sub>2</sub>-CH<sub>2</sub>OMe, n = 2; L = PO(NMe<sub>2</sub>)<sub>3</sub>, n = 2; Ln = Yb, L = THF, n = 3) and the polymerisation of ethene,  $\varepsilon$ caprolactone and 1,3-butadiene with the Sm<sup>II</sup> mono-THF complex.

We now report the synthesis and catalytic properties of the first PH-functionalised phosphanylalkylcyclopentadienyl complexes of chromium(III), [{( $\eta^{5}-C_{5}H_{4}$ )CMe<sub>2</sub>PHR}CrCl<sub>2</sub>(PMe<sub>2</sub>Ph)] (R = Ph (**2**), 'Bu (**3**)), and the first constrained-geometry chromium complex with a phosphanidoalkylcyclopentadienyl ligand, [{( $\eta^{5}-C_{5}H_{4}$ )CMe<sub>2</sub>PPh}CrCl]<sub>2</sub> (**1**).

Only a limited number of chromium complexes with chelating tertiary phosphanylalkylcyclopentadienyl ligands is known [19]. [{ $(\eta^5-C_5H_4)CH_2CH_2PR_2$ }CrCl<sub>2</sub>] (R = Me, Et, Pr, <sup>*i*</sup>Pr, <sup>*i*</sup>Bu, <sup>*t*</sup>Bu, neopentyl, hexyl, Cy, Ph, *o*-tolyl, 1-naphthyl) are accessible from the corresponding lithium cyclopentadienide and [CrCl<sub>3</sub>(THF)<sub>3</sub>] [19]; reaction with MeLi and R'MgCl gave the corresponding dimethyl and dialkyl derivatives (R' = Me, Pr, Cy, <sup>*t*</sup>Bu). The dichloride complex can be used with methyl alumoxane (Al:Cr = 100:1) as a catalyst for the polymerisation of ethene [20].

#### 2. Results and discussion

The lithium reagents Li[(C<sub>5</sub>H<sub>4</sub>)CMe<sub>2</sub>PHR] (R = Ph [10], 'Bu [17]) are readily accessible by reaction of LiPHR with 6,6-dimethylfulvene. The reaction of Li[(C<sub>5</sub>H<sub>4</sub>)CMe<sub>2</sub>PHPh] with [CrCl<sub>3</sub>(THF)<sub>3</sub>] yielded a pale blue powder, from which a small amount of blue crystals of [{( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>)CMe<sub>2</sub>PPh}CrCl]<sub>2</sub> (1) was obtained on recrystallisation from toluene/hexane (Eq. (1)). Attempts to synthesise 1 in better yield (a) by heating to reflux after addition of Li[(C<sub>5</sub>H<sub>4</sub>)CMe<sub>2</sub>PHPh] to [CrCl<sub>3</sub>(THF)<sub>3</sub>]; (b) by reaction of [{( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>)CMe<sub>2</sub>-PHPh}CrCl<sub>2</sub>(PMe<sub>2</sub>Ph)] with DBU (DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene); or (c) by reaction of Li[(C<sub>5</sub>H<sub>4</sub>)CMe<sub>2</sub>PHPh] with [CrCl<sub>3</sub>(THF)<sub>3</sub>] in the presence of DBU failed. The molecular structure (vide infra) shows a phosphanido-bridged dimer. However, the presence of a PH band at 2289 cm<sup>-1</sup> in the IR spectrum of the pale blue powder indicates that a mixture of products was obtained. The other product(s) could, however, not be obtained in pure form by fractional crystallisation, extraction or thin-layer chromatography. The formation of 6,6-dimethylfulvene in the reaction mixture, shown by <sup>1</sup>H NMR spectroscopy, indicated decomposition of the phosphanylalkylcyclopentadienyl ligand. Similarly, decomposition of Li[(C5H4)C-Me<sub>2</sub>PHPh] was observed on protonation with HCl gas in diethyl ether (formation of PH<sub>2</sub>Ph, LiCl and 6,6dimethylfulvene) and in reactions with AlCl<sub>3</sub>, for which elimination of HCl is proposed as the first reaction step [21]. A similar reaction is proposed here, with attack of CrCl<sub>3</sub> on the cyclopentadienyl ring (with elimination of LiCl) and/or at the phosphanyl group (with elimination of HCl).

Activation of the PH proton and elimination of HCl can be avoided if [CrCl<sub>3</sub>(PMe<sub>2</sub>Ph)<sub>3</sub>] is employed as starting material, as this prevents attack at the phosphanyl group, as well as subsequent reactions after formation of the cyclopentadienyl complexes, because coordination of the phosphanyl group to chromium is prevented. Dark green [CrCl<sub>3</sub>(PMe<sub>2</sub>Ph)<sub>3</sub>] is readily obtained from the reaction of CrCl3 with three equivalents of PMe<sub>2</sub>Ph in refluxing THF/toluene (if less PMe<sub>2</sub>Ph is employed, unconsumed insoluble CrCl<sub>3</sub> remains) [22]. After filtration, the solution of the phosphine complex was treated in situ with a solution of  $Li[(C_5H_4)C_5]$ Me<sub>2</sub>PHR] in THF at -50 °C, and the blue chromium(III)  $[{(\eta^5-C_5H_4)CMe_2PHR}CrCl_2(PMe_2Ph)]$ complexes  $(R = Ph (2), ^{t}Bu (3))$  were obtained in high yield (Eq. (1)).

Crystals of 2 and 3 are only slowly oxidised in air, while a blue solution of 3 in THF, toluene or  $CH_2Cl_2$ slowly turns green on prolonged exposure to air. In the IR spectra, complexes 2 and 3 exhibit a sharp PH absorption at 2278 (2) and 2276 cm<sup>-1</sup> (3). The <sup>31</sup>P{<sup>1</sup>H} NMR spectra (CH<sub>2</sub>Cl<sub>2</sub>/C<sub>6</sub>D<sub>6</sub>) show very broad signals  $(v_{1/2}$  ca. 900 Hz) at 92 (2) and 111 ppm (3) (cf.  $Li[(C_5H_4)CMe_2PHR]: -1.2 \text{ ppm } (R = Ph) [10]), 26.0$ ppm ( $\mathbf{R} = {}^{t}\mathbf{B}\mathbf{u}$ ) [17]. Typical of half-sandwich Cr<sup>III</sup> complexes, the <sup>1</sup>H NMR spectra of 2 and 3 ( $C_6D_6$ ) show several broad and isotropically shifted resonances ranging in chemical shift approximately from +11 to -30 ppm. Consistent with the structural similarity of **2** and 3, both spectra feature a series of very similar peaks, namely, those at 10.5, 5.0, ca 0.0 and ca. -28 ppm. These are likely associated with the PMe<sub>2</sub>Ph ligand and the geminal methyl groups of the cyclopentadienyl substituent, although the greater signal intensity at 0.0 ppm in 3 suggests accidental coincidence with the resonance of the *tert*-butyl group. The spectrum of **2** exhibits a few minor additional peaks, which are attributed to the Pbound phenyl ring. In summary, the <sup>1</sup>H NMR spectra of paramagnetic organometallics can rarely be unambi-



 $R = Ph (2), {}^{t}Bu (3)$ 

gously assigned. However, the spectra of 2 and 3 clearly show them to be closely related and are entirely consistent with the crystal structures. The cyclopentadienyl protons are probably too far shifted and broadened to be readily detectable.

In the UV–Vis spectra the blue complexes **2** and **3** show absorptions at  $\lambda = 661 (\log(\epsilon/\text{cm}^2 \text{ mol}^{-1}) = 4.69)$  and 667 nm  $(\log(\epsilon/\text{cm}^2 \text{ mol}^{-1}) = 4.72)$ , respectively.

No meaningful mass spectrum was obtained for 2, while for 3, a molecular ion peak as well as fragmentation products thereof were observed in the FAB mass spectrum.

#### 2.1. Molecular structures of 1 and 2

Crystals of 2 suitable for X-ray crystallography were obtained from a concentrated solution in diethyl ether at -30 °C. Compound 3 crystallises in very thin plates regardless of the solvent used for crystallisation. Therefore, only a poor data set was obtained, but it was sufficient to elucidate the structural motif, which is similar to that of 2.

Compounds 1 and 3 crystallise in the monoclinic space group  $P2_1/c$  with 2 and 8 formula units in the unit cell, respectively; 2 crystallises in the triclinic space group  $P\overline{1}$  with 4 formula units in the unit cell.

In 1, the centre of the  $Cr_2P_2$  ring coincides with a crystallographic centre of inversion. The  $Cr_2P_2$  ring forms a parallelogram with a  $Cr \cdots Cr$  distance of 2.9383(1) Å and a P-Cr-P bond angle of 102.75(2)° (Table 1). The cyclopentadienyl ring and the  $Cr_2P_2$  ring form an angle of 32.4(1)°; the cyclopentadienyl and

phenyl rings form an angle of  $35.8^{\circ}$ . The chromium atom, C1 of the cyclopentadienyl ring, C12 of the methylene bridge and P1 form a planar four-membered ring; this plane forms an angle of  $54.8(1)^{\circ}$  with the  $Cr_2P_2$  ring (see Fig. 1).

There are two independent molecules in the asymmetric unit of 2, which differ mainly in the configuration of the chiral P atoms, P1 and P3. One has R, and the other S configuration (see Fig. 2).

In 1, the Cr–P bond is 0.09 Å shorter than the coordinative Cr–P(PMe<sub>2</sub>Ph) bond in 2 (2.439(1) and 2.447(1) Å). Similar Cr–P bond lengths are observed in the phosphanido-bridged complexes  $[{(\eta^5-C_5Me_5)Cr}_2(\mu$ -



Fig. 1. Molecular structure of  $[\{(\eta-C_5H_4)CMe_2PPh\}CrCl]_2$  (1) showing the atom-numbering scheme employed (ORTEP plot, 50% probability, SHELXTL PLUS; XP [26]). Hydrogen atoms are omitted for clarity.



Fig. 2. Molecular structure of  $[{(\eta^5-C_5H_4)CMe_2PHPh}CrCl_2-(PMe_2Ph)]$  (2) showing the atom-numbering scheme employed (ORTEP plot, 50% probability, SHELXTL PLUS; XP [26]). Hydrogen atoms (other than PH) are omitted for clarity. There are two independent molecules in the unit cell.

PPh<sub>2</sub>)<sub>n</sub>( $\mu$ -Cl)<sub>3-n</sub>]<sup>+</sup> (n = 1, 2; Cr–P 2.385(2)–2.404(4) Å) [23] and the phosphine complexes [{( $\eta^{5}$ -C<sub>5</sub>H<sub>4</sub>)CH<sub>2</sub>-CH<sub>2</sub>PR<sub>2</sub>}CrCl<sub>2</sub>] (2.459(1) (R = Cy), 2.447(1) Å

Table 1

Selected distances [Å] and bond angles [°] for 1 and 2

(R = Ph)) [19]. The different environment of Cr in 1 and 2 has only minor influence on the Cr–C (cyclopentadienyl ring) and Cr–Cl distances (see Table 1).

#### 2.2. Ethylene polymerisation catalysis

Cyclopentadienyl chromium(III) complexes are known to catalyse the polymerization of ethylene, and in view of the structural novelty of the complexes described above their catalytic activity was evaluated. 10 mg of chromium compound and 100 equivalents of methylalumoxane (MAO) were dissolved in 50 ml toluene ([Cr]  $\approx 10^{-6}$  M) and exposed to 1.4 MPa of ethylene for 1 h at room temperature. Under these conditions both 2 and 3 produced moderate amounts of polyethylene (2, 0.54 g; 3, 1.38 g). Characterisation of the resulting polymers by <sup>13</sup>C NMR spectroscopy showed them to be highly linear polyethylene with negligible branching (2, 0.9 branches per 1000 backbone C atoms; 3, 1.9 branches per 1000 backbone C atoms). However, molecular weight determination by gel permeation chromatography (GPC) revealed a surprising difference between the two samples. Polyethylene obtained with 3 had a very narrow molecular weight distribution ( $M_n = 2220, M_w = 4710$ ,  $M_{\rm w}/M_{\rm n}=2.12$ ), consistent with a homogeneous singlesite catalyst. In contrast, the polymer produced by 2 was at least trimodal and accordingly had a much higher

Selected distances [7] and bolid angles [ ] for 1 and 2					
$[\{(\eta-C_5H_4)CMe_2PPh\}CrCl]_2 (1)$					
Cr(1)–C	2.203(2)-2.255(2)	C(6)-P(1)-C(12)	107.9(1)		
Cr(1)-P(1)	2.347(1)	C(1)-Cr(1)-P(1)	126.23(5)		
Cr(1)-P(1a)	2.360(1)	Cl(1)-Cr(1)-P(1)	103.47(2)		
$Cr(1) \cdot \cdot \cdot Cr(1a)$	2.9383(1)	P(1)-Cr(1)-P(1a)	102.75(2)		
P(1)– $Cr(1a)$	2.360(1)	C(6)-P(1)-Cr(1)	121.43(6)		
P(1)–C(6)	1.817(2)	C(12)-P(1)-Cr(1)	126.05(6)		
P(1)–C(12)	1.894(2)	C(1a)1-C(12)-P(1)	93.2(1)		
Cr(1)– $Cl(1)$	2.278(1)	$P(1) \cdots P(1a)$	3.678(1)		
$[\{(\eta^5-C_5H_4)CMe_2PHPh\}CrCl_2(PMe_2Ph)] (2)$					
Molecule 1		Molecule 2			
Cr(1)–C	2.191(3)-2.282(3)	Cr(2)–C	2.209(3)-2.290(3)		
Cr(1)–Cl	2.278(1)-2.292(1)	Cr(2)–Cl	2.288(1)-2.290(1)		
Cr(1)–P(2)	2.439(1)	Cr(2)–P(4)	2.447(1)		
P(1)–C(6)	1.910(4)	P(3)–C(28)	1.895(3)		
P(1)-H(p1)	1.36(4)	P(3)–H(p2)	1.34(4)		
C(9)-P(1)-C(6)	104.1(2)	C(31)-P(3)-C(28)	104.6(1)		
C(9)–P(1)–H(p1)	101.1(2)	C(31)–P(3)–H(p2)	101.2(1)		
C(6)–P(1)–H(p1)	98.2(2)	C(28)–P(3)–H(p2)	98.8(2)		
C(16)–P(2)–C(17)	103.2(2)	C(38)–P(4)–C(37)	104.2(2)		
C(15)-P(2)-C(16)	103.9(2)	C(38)–P(4)–C(39)	106.0(2)		
C(15)–P(2)–C(17)	105.9(2)	C(37)–P(4)–C(39)	104.6(2)		
C(15)-P(2)-Cr(1)	113.7(1)	C(39)–P(4)–Cr(2)	115.59(1)		
C(16)-P(2)-Cr(1)	112.1(1)	C(38)–P(4)–Cr(2)	113.6(2)		
C(17) - P(2) - Cr(1)	116.7(1)	C(37)–P(4)–Cr(2)	111.9(1)		
Cl(1)-Cr(1)-Cl(2)	97.97(4)	Cl(4)–Cr(2)–Cl(3)	97.5(1)		
Cl(1)–Cr(1)–P(2)	92.94(4)	Cl(4)–Cr(2)–P(4)	92.7(1)		
Cl(2)–Cr(1)–P(2)	89.61(4)	Cl(3)–Cr(2)–P(4)	91.4(1)		

polydispersity ( $M_n = 4830$ ,  $M_w = 617000$ ,  $M_w/M_n = 127.8$ ). The reasons for this disparity are not clear, given the subtle structural differences between the two catalyst precursors.

#### 3. Experimental

#### 3.1. General

All experiments were carried out under purified dry nitrogen. Solvents were dried and freshly distilled under argon. The NMR spectra were recorded with an AVANCE DRX 400 spectrometer (Bruker): <sup>1</sup>H NMR (400.13 MHz): internal standard solvent, external standard TMS; <sup>31</sup>P NMR (161.9 MHz): external standard 85% H<sub>3</sub>PO<sub>4</sub>. The IR spectra were recorded on an FT-IR spectrometer Perkin-Elmer System 2000 (KBr) in the range 350-4000 cm<sup>-1</sup>. UV-Vis spectra were recorded with a LAMBDA 900 (Perkin–Elmer). The magnetic moments were determined with a magnetic susceptibility balance of Johnson Mathey Alfa Products. EI MS: MAT 212 (Varian); FAB: ZAB-HSQ-VG Analytical Manchester. The melting points were determined in sealed capillaries under nitrogen and are uncorrected (Boetius).  $Li[(C_5H_4)CMe_2PHPh]$  [10]  $Li[(C_5H_4)CMe_2-$ PH<sup>t</sup>Bu] [17] and [CrCl<sub>3</sub>(PMe<sub>2</sub>Ph)<sub>3</sub>] [24] were prepared according to the literature procedures. CrCl<sub>3</sub> is commercially available (Merck).

#### 3.2. Synthesis of $[\{(\eta - C_5H_4)CMe_2PPh\}CrCl]_2(1)$

At ca. -50 °C a solution of Li[(C<sub>5</sub>H<sub>4</sub>)CMe<sub>2</sub>PHPh] (1.7 g, 7.7 mmol) in THF (10 ml) was slowly added to a suspension of [CrCl<sub>3</sub>(THF)<sub>3</sub>] (2.9 g, 7.7 mmol) in THF (25 ml). During the addition, [CrCl<sub>3</sub>(THF)<sub>3</sub>] slowly dissolved, and the initially colorless solution turned dark green after addition of several drops of the solution of the Li salt. The solution was stirred for 24 h at r.t., after which it had turned blue. Then the solvent was evaporated in vacuum and the slimy blue residue was washed with *n*-hexane to give 2.0 g of a blue powder after drying in vacuo. The blue powder was dissolved in toluene (15 ml) and layered with *n*-hexane. A blue powder was obtained and a small amount of blue crystals of **1** suitable for X-ray structure determination formed at the interface between the two solvents.

# 3.3. Synthesis of $[\{(\eta^5-C_5H_4)CMe_2PHPh\}CrCl_2-(PMe_2Ph)](\mathbf{2})$

 $CrCl_3$  (1.2 g, 7.6 mmol) was suspended in toluene (25 ml), and THF (25 ml) and PMe<sub>2</sub>Ph (3.3 ml, 22.8 mmol) were added quickly. The mixture slowly turned green and was refluxed for ca. 2 h, after which the reaction was

complete. The solution was filtered and the filtrate cooled to -50 °C. A solution of Li[(C<sub>5</sub>H<sub>4</sub>)CMe<sub>2</sub>PHPh] (1.7 g, 7.6 mmol) in THF (25 ml) was slowly added to this solution. During the addition, the initially green solution turned blue. The solution was stirred for 12 h at r.t. Then the solvent was evaporated in vacuo and the blue residue dissolved in CH<sub>2</sub>Cl<sub>2</sub> (25 ml). LiCl was separated from the blue solution by filtration and extracted twice with CH<sub>2</sub>Cl<sub>2</sub> (10 ml). The CH<sub>2</sub>Cl<sub>2</sub> fractions were combined and the solvent was evaporated in vacuum. The blue residue was washed with hexane (2 × 20 ml) and extracted repeatedly with Et<sub>2</sub>O (70 ml) to give 1.8 g (50%) of **2**; m.p. 114–117 °C. Blue crystals were obtained from a concentrated Et<sub>2</sub>O solution at -30 °C.

<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta = -28.3$  (br s), 0.3 (s), 4.5 (sh), 5.0 (s), 5.8 (s), 10.5 (s). <sup>31</sup>P NMR (CH<sub>2</sub>Cl<sub>2</sub>/C<sub>6</sub>D<sub>6</sub>):  $\delta = 92$  ppm. IR: 3076 (w, CH, C<sub>5</sub>H<sub>4</sub>), 3054 (w, CH, Ph), 2964, 2910 (m, CH, CH<sub>3</sub> (CMe)), 2866 (w, CH, CH<sub>3</sub> (PMe)), 2278 (m, PH), 1476, 1365 (m-st, CH<sub>3</sub> (CMe)), 1435 (st, CH<sub>3</sub> (PMe)), 1282, 1106 (w-m, PC (PMe<sub>2</sub>Ph), 955, 924, 829, 913 (st, CH, CH<sub>3</sub> (PMe)) 745, 694 (st, CH, Ph) 485 (m, PC (PMe<sub>2</sub>Ph)) cm<sup>-1</sup>. UV–Vis: log( $\varepsilon$ /cm<sup>2</sup> mol<sup>-1</sup>) = 4.69 ( $\lambda = 661$  nm).  $\mu_{eff} = 4.0$  B.M. ( $\mu_{calc} =$ 3.8). *Anal*. Calc. for C<sub>22</sub>H<sub>27</sub>Cl<sub>2</sub>CrP<sub>2</sub> (476.3): C, 55.5; H, 5.7. Found: C 53.9, H 5.3%.

## 3.4. Synthesis of $[\{(\eta^5-C_5H_4)CMe_2PH'Bu\}CrCl_2-(PMe_2Ph)](\mathbf{3})$

CrCl<sub>3</sub> (1.3 g, 8.2 mmol) was suspended in toluene (25 ml), and THF (25 ml) and PMe<sub>2</sub>Ph (3.5 ml, 24.2 mmol) were added quickly. The mixture slowly turned green and was refluxed for ca. 2 h, after which the reaction was complete. The solution was filtered and the filtrate cooled to -50 °C. A solution of Li[(C<sub>5</sub>H<sub>4</sub>)CMe<sub>2</sub>PH<sup>t</sup>Bu] (1.65 g, 8.2 mmol) in THF (10 ml) was slowly added to this solution. During the addition, the initially green solution turned blue. The solution was stirred at r.t. for 2 h and then refluxed for 1 h. Then the solvent was evaporated in vacuum and the blue residue dissolved in CH<sub>2</sub>Cl<sub>2</sub> (25 ml). LiCl was separated from the blue solution by filtration and extracted twice with CH<sub>2</sub>Cl<sub>2</sub> (10 ml). The CH<sub>2</sub>Cl<sub>2</sub> fractions were combined and the solvent was evaporated in vacuum. The blue residue was washed with hexane  $(2 \times 25 \text{ ml})$  and extracted repeatedly with Et<sub>2</sub>O (50 ml) to give 1.9 g (51%) of **3** as blue crystals; m.p. 143 °C.

<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta = -28.3$  (br s), 0.0 (s), 5.0 (s), 8.9 (br s), 10.5 (s). <sup>31</sup>P NMR (CH<sub>2</sub>Cl<sub>2</sub>/C<sub>6</sub>D<sub>6</sub>):  $\delta = 111$  ppm. IR: 3080 (w, CH, C<sub>5</sub>H<sub>4</sub>), 3054 (w, CH, Ph), 2953, 2892 (m-st, CH, CH<sub>3</sub> (CMe)), 2859 (m-st, CH, CH<sub>3</sub> (PMe)), 2295, 2276 (m, PH), 1474, 1365 (m-st, CH<sub>3</sub> (CMe)), 1436 (m-st, CH<sub>3</sub> (PMe)), 1411 (m-st, CH<sub>3</sub> (<sup>t</sup>Bu)) 1280, 1107 (m, PC (PMe<sub>2</sub>Ph)), 955, 924, 829, 913 (st, CH, CH<sub>3</sub> (PMe)) 744, 694 (st, CH, Ph) 485 (m, PC (PMe<sub>2</sub>Ph)), 408

Table 2Crystal data and structure refinement for 1 and 2

	1	2
Empirical formula	$C_{28}H_{30}Cl_2Cr_2P_2$	$C_{22}H_{27}Cl_2CrP_2$
M <sub>r</sub>	603.36	476.30
Temperature (K)	220(2)	220(2)
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$ (no. 14)	<i>P</i> 1 (no. 2)
a (Å)	8.7224(4)	13.738(2)
b (Å)	8.9261(4)	13.764(2)
<i>c</i> (Å)	17.0822(8)	13.885(2)
α (°)	90	88.986(3)
β (°)	96.4(1)	72.509(3)
γ (°)	90	72.607(3)
V (Å <sup>3</sup> )	1321.7(1)	2382.0(6)
Ζ	2	4
$\rho_{\rm calc}~({\rm Mg}~{\rm m}^{-3})$	1.516	1.328
F(000)	620	988
Crystal size (mm)	$0.70 \times 0.20 \times 0.05$	$0.3\times0.2\times0.2$
Absorption coefficient	1.162	0.844
$(\text{mm}^{-1})$	2 25 20 74	1 56 20 45
Deflections collected	2.33-20.74	1.50-29.45
Reflections collected	13070	15394
Independent reflections	3239	112/2
R <sub>int</sub>	0.0391	0.0271
Parameters	211	495
$R[I > 2\sigma I)]$	0.0300	0.0514
wR2 (all data)	0.0756	0.0999
$\Delta/\rho_{\rm min}$ (e A <sup>-5</sup> )	0.306	0.312
$\Delta/\rho_{\rm max}$ (e A <sup>-3</sup> )	-0.313	-0.369

(st, CrCl?) cm<sup>-1</sup>. FAB MS: m/z (%) = 455 (12) [M<sup>+</sup>], 420 (49) [M<sup>+</sup> - Cl], 317 (25) [M<sup>+</sup> - PMe<sub>2</sub>Ph], 282 (62) [M<sup>+</sup> - Cl - PMe<sub>2</sub>Ph], 139 (100) [PMe<sub>2</sub>Ph + H<sup>+</sup>], and fragmentation products thereof. EI MS: m/z = 362[M<sup>+</sup> - C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>], 317 [M<sup>+</sup> - PMe<sub>2</sub>Ph], 281 [M<sup>+</sup> - HCl - PMe<sub>2</sub>Ph], 225 [M<sup>+</sup> - HCl - PMe<sub>2</sub>Ph - 'Bu], 193 [M<sup>+</sup> - PMe<sub>2</sub>Ph - PH'Bu - Cl], 138 [PMe<sub>2</sub>Ph]<sup>+</sup>, 123 [PMePh], and fragmentation products thereof. UV-Vis: log( $\varepsilon$ /cm<sup>2</sup> mol<sup>-1</sup>) = 4.72 ( $\lambda$  = 667 nm).  $\mu_{eff}$  = 3.8 B.M. ( $\mu_{calc}$  = 3.8). Anal. Calc. for C<sub>20</sub>H<sub>31</sub>Cl<sub>2</sub>CrP<sub>2</sub> (456.3): C, 52.6; H, 6.8. Found: C, 52.0; H, 7.1%

#### 3.5. Data collection and structural refinement of 1 and 2

Data ( $\lambda$ (Mo K $\alpha$ ) = 0.71073 Å) were collected with a Siemens CCD (SMART) diffractometer. All observed reflections were used for refinement (SAINT) of the unitcell parameters. Empirical absorption correction with SADABS [25]. The structures were solved by direct methods (SHELXTL PLUS) [26]. For 1 and 2, Cr, P, Cl, and C atoms were refined anisotropically; H atoms were located by difference maps and refined isotropically (see Table 2).

#### 4. Supplementary material

CCDC-221773 (1) and -221774 (2) contain the supplementary crystallographic data for this paper. These

data can be obtained free of charge via www.ccdc.cam. ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44)-1223-336-033; or deposit@ccdc.cam.uk).

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