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Di- and tri-valent chlorochromium complexes bearing hydrotris(3,5-diisopropylpyrazolyl)borato ligand (Tp^{iPr2}), $Tp^{iPr2}CrCl_n(L)$ (n = 1, 2) and $[Tp^{iPr2}Cr(\mu\text{-}Cl)]_2$: flexible coordination behavior of the Tp^{iPr2} ligand and reduction features of Cr(II) species †

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Divalent chlorochromium complexes bearing the Tp^{iPr2} ligand [hydrotris(3,5-diisopropylpyrazolyl)borato], $Tp^{iPr2}Cr^{II}Cl(L)$ [L = 3,5-diisopropylpyrazole (**1a**), py (**1b**), bipy (**2**)] and $Tp^{iPr2}Cr^{II}(\mu\text{-}Cl)]_2$ (**3**), were prepared by treatment of $CrCl_2$ with a Tp^{iPr2} salt in the presence (**1**,**2**)/absence (**3**) of a donor (L). Reaction of **1** with benzyl chloride results in quantitative conversion to the corresponding trivalent dichlorochromium species, $Tp^{iPr2}Cr^{III}Cl_2(L)$ (**6**), while reaction with CH_2Cl_2 gives the methylene-inserted product, $Tp^{iPr2}Cr^{III}Cl(CH_2\text{-}L)$ **7**, *via* a carbene intermediate, which is supported by cyclopropanation of styrene with CH_2Cl_2 in the presence of **3**. The Cr(II) complex **1b** induces reductive coupling of benzaldehyde to give a 3,4-diphenyl-2,5-dioxachromacyclopent-3-ene, $Tp^{iPr2}Cr[\kappa^2\text{-}O\text{–}C(Ph)\text{=}C(Ph)\text{–}O]$ **8**. Steric tuning effects of the Tp^{iPr2} ligand leads to a variety of coordination geometries including five-coordinate square-pyramidal and trigonal-bipyramidal structures and a six-coordinate octahedral structure as revealed by crystallographic characterization.

Introduction

Hydrotris(pyrazolyl)borato ligands (Tp^R) are versatile ancillary ligands in inorganic studies of transition metal complexes as well as main group metal compounds.[1,2] Tp^R ligands, 6e-donating tripodal N_3-ligands, are formally isoelectronic with cyclopentadienyl ligands (η^5-C_5R_5), which have been utilized as auxiliary ligands for organometallic compounds and, in addition to this feature, Tp^R ligand can create a coordination environment very similar to those frequently found in the active sites of some types of metalloproteins, *i.e.* a coordination environment created by three facially arranged imidazolyl rings of histidine residues.[3] We have revealed various features of Tp^R ligands in investigations ranging from bioinorganic studies of dioxygen complexes to organometallic studies of hydrocarbyl and dinuclear complexes. In particular, the flexible coordination and physical properties of the 3,5-diisopropyl derivative, Tp^{iPr2} [hydrotris(3,5-diisopropylpyrazolyl)borato],[2] lead to successful isolation and characterization of intriguing but unstable complexes which are otherwise difficult to isolate.[3] The Tp^{iPr2} ligand, which is sterically demanding, causes kinetic stabilization of labile species but the steric effect can be tuned by the conformation of the isopropyl groups, which are unsymmetrical with respect to rotation around the C–$CHMe_2$ axis. The situation is in contrast to the *tert*-butyl substituent, which is C_3-symmetrical with respect to the C–CMe_3 axis. For instance, $Tp^{tBu,R}$ ligand[2] bearing *tert*-butyl substituents at the 3-positions (proximal to the metal center) cannot form a $[Tp^{tBu,R}M(\mu\text{-}X)]_2$-type dinuclear species, whereas the Tp^{iPr2} ligand affords a variety of dinuclear complexes $[Tp^{iPr2}M(\mu\text{-}X)]_2$, where the CH moieties of the isopropyl substituents point toward the metal side to reduce steric congestion around the metal centers.[4] In addition, Tp^R ligands with alkyl chains such as Tp^{iPr2} and $Tp^{tBu,R}$ make complexes soluble in less polar organic solvents including hydrocarbons, which would provide a hydrophobic environment around the metal center.

We have been carrying out a systematic synthetic study of dioxygen complexes bearing Tp^R ligands and the central metal is now extended to early transition metals such as vanadium[5] and chromium; the latter is the subject of the present study. In contrast to Tp^R complexes of other transition metals the study of chromium species has been limited. The major concern of Tp^RCr complexes resides in the Philips ethylene polymerization catalyst involving a chromium species as the key component and comparative studies on the isoelectronic η^5-C_5R_5 and $Tp^{tBu,Me}$ complexes were reported by Theopold and coworkers.[6,7] Chromocene analogues such as $Tp^R{}_2Cr$ and $Tp^RCr(\eta^5\text{-}C_5R_5)$ have also been studied.[8] Other than these aspects, however, little attention has been paid to Tp^RCr complexes.[9] Chromium reagents have been widely used in organic synthesis, *i.e.* low valent chromium(II) species as reducing agents and higher valent Cr(VI) species as oxidizing agents.[10,11] In particular, reduction and reductive coupling of organic compounds are mediated by Cr(II) species. Because, however, Cr(II) species are sensitive toward air and moisture, they are usually generated *in situ* and therefore little is known about their structure and reactivity. Thus the chemistry of extremely unstable four- or five-coordinate Cr(II) species with vacant coordination site(s) remains to be studied.[12]

Herein we wish to describe the results of the synthesis and characterization of a series of di- and tri-valent chlorochromium complexes bearing the Tp^{iPr2} ligand. A variety of coordination modes result from the flexible coordination behavior of the Tp^{iPr2} ligand and unique behavior of the Cr(II) species as a reductant has been observed.[13]

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† Electronic supplementary information (ESI) available: figures showing the atomic numbering schemes for **1a**,**b**, **2**, **3**, **6a**,**b**, **7a**, **8** and **9**. See http://www.rsc.org/suppdata/dt/b2/b207326a/

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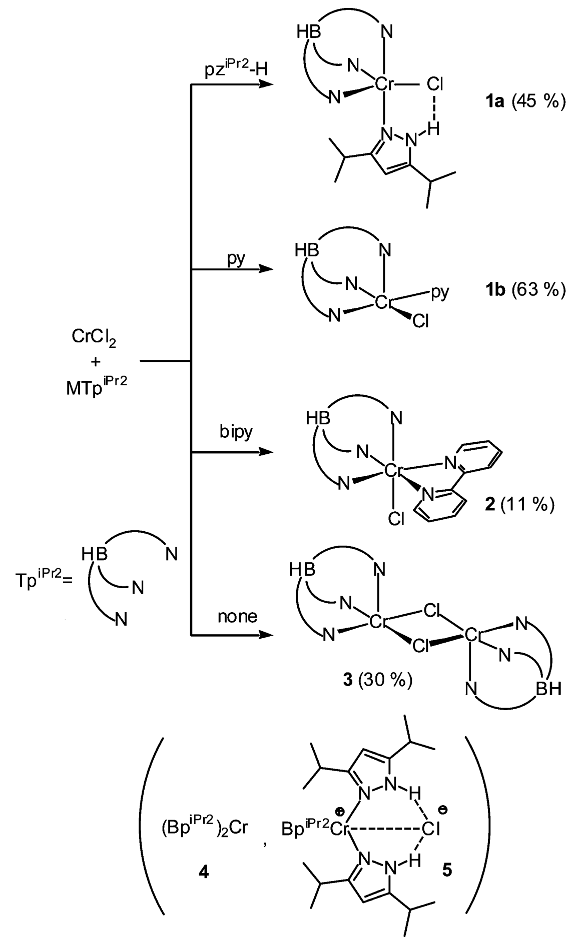
Results and discussion

Synthesis and characterization of chlorochromium(II) complexes, Tp^{iPr2}CrCl(L)

Treatment of CrCl$_2$ with a Tp^{iPr2} salt in the presence of a donor (L) gave a series of paramagnetic green or blue chlorochromium(II) complexes, Tp^{iPr2}CrCl(L) [L = pz^{iPr2}-H (**1a**),[2] py (**1b**), κ^2-bipy (**2**)], in moderate yields after removal of the volatiles followed by extraction with MeCN and crystallization (Scheme 1). Reaction of CrCl$_2$ with KTp^{iPr2} in the absence of a donor afforded the blue–green dinuclear di-μ-chloro complex **3** in 30% yield. Washing with hydrocarbons (*e.g.* pentane and hexane) before crystallization facilitated isolation of the adducts **1**–**3**, because byproducts **4** and **5** (see below) could be washed out of the mixture. The Cr(II) species were so sensitive to air and moisture that all manipulations were carried out in a glove box filled with argon.



Scheme 1

Because spectroscopic properties of the obtained products are rather featureless, they have been characterized by X-ray crystallography. ORTEP[35] views of the Cr(II) complexes **1a**,**b**, **2** and **3** are shown in Figs. 1 and 2, and structural parameters for their core parts are compared in Table 1. All products contain a κ^3-Tp^{iPr2} ligand as is consistent with the ν_{BH} values larger than 2500 cm^{-1}.[14] Except for the octahedral complex **2** with the κ^2-bipy ligand, the other complexes with monodentate ligands adopt five-coordinate structures. The square pyramidal structure observed for the py adduct **1b** is in contrast to the trigonal-bipyramidal structures of the pz^R-H adducts **1a** (with the N11–Cr1–N41 axis) and Tp^{tBu,Me}CrCl(pz^{tBu,Me}-H) **A**.[6b] The difference can be conveniently characterized by the τ values [0.13 (**1b**) *vs.* 0.76 (**1a**) and 0.65 (**A**)].[15] The compact py ligand in **1b**, which does not suffer steric repulsion with the remaining part of the molecule, should lead to the square-pyramidal structure, a typical coordination structure of five-coordinate Cr(II) complexes. The Cr–N$_{axial}$ distance is substantially longer than the Cr–N$_{basal}$ distances as usually observed for square-pyramidal structures. Contrastingly, the bulky pz^R-H ligands in **1a** and **A** cause deformation to a trigonal-bipyramidal coordination structure due to steric repulsion between the Tp^R and pz^R-H ligands. The pz^R-H ligand is accommodated in the pocket formed by the two basal pz^R rings of the Tp^R ligand. Such an orientation of the pz^{iPr2}-H ligand is, in part, supported by a hydrogen bonding interaction between Cl1 and H0, as is evident from the Cl1 ··· H0 (2.31 Å) and Cl1 ··· N42 distances [3.034(4) Å]. Although such an interaction was not discussed for **A**,[6b] the Cl ··· N distance (2.89 Å)[16] suggests an analogous hydrogen bonding interaction. The hydrogen bonding interaction causes a shift of the N–H vibration (3257 cm^{-1}) of the coordinated pz^{iPr2}-H molecule to lower energies when comparing **6a** with the free N–H group (3451 cm^{-1}; see below).

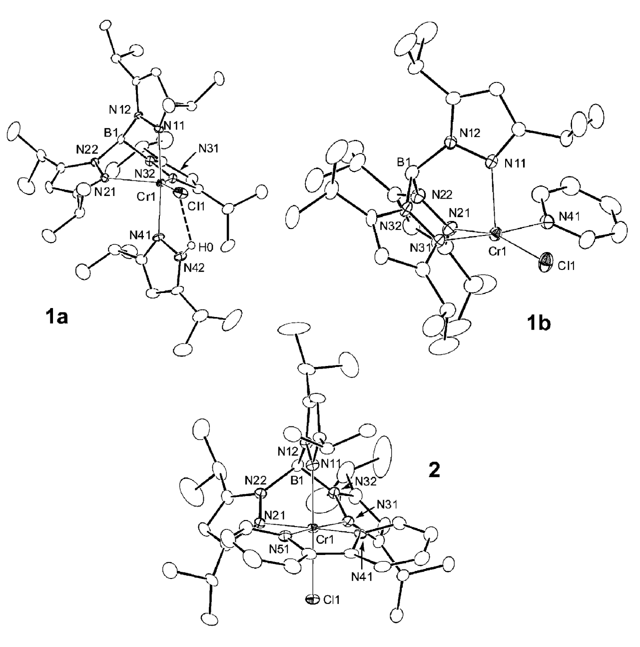


Fig. 1 Molecular structures of **1a**,**b**, and **2** showing the 30% thermal ellipsoids.

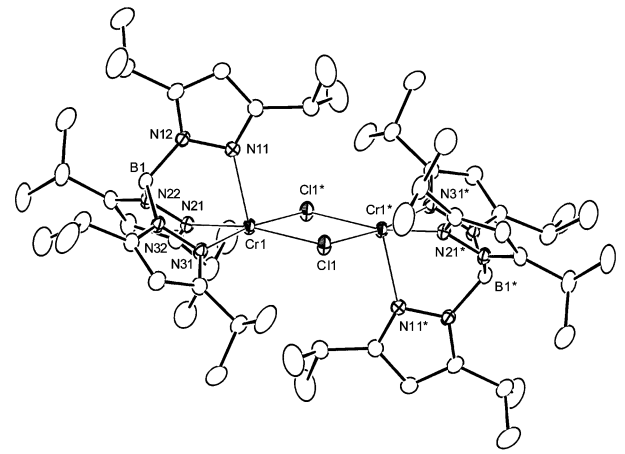


Fig. 2 Molecular structure of **3** showing the 30% thermal ellipsoids.

The dinuclear di-μ-chloro complex **3** obtained by the metathesis in the absence of a donor also adopts a square-pyramidal coordination geometry close to an ideal one as judged by the *trans*-N$_{basal}$–Cr–Cl angles (>175°) and the τ value (0.06).[15] The overall centrosymmetric structure is very similar to that of [Tp^{iPr2}Pd(μ-Cl)]$_2$ previously reported by us.[4a] The Cr–N$_{axial}$ distance is longer than the Cr–N$_{basal}$ distances, and the two Cr–Cl

Table 1 Selected bond lengths (Å) and angles (°) for $Tp^{iPr2}Cr(X)(Y)(Z)$

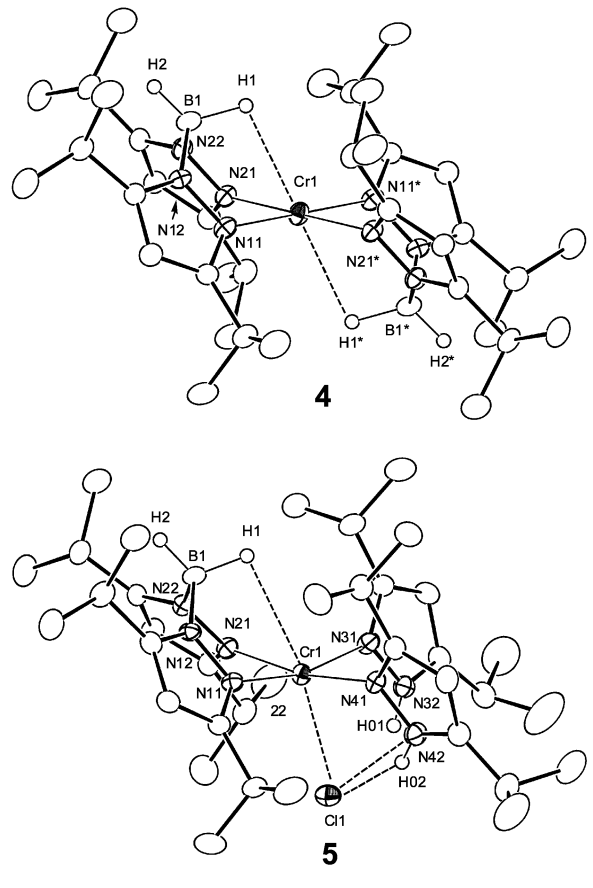
	1a	**1b**	**2**	**3**	**6a**	**6b**	**7a**
X	Cl1	Cl1	Cl1	Cl1	Cl1	Cl1	Cl1
Y	N41	N41	N41	Cl1′	C12	C12	C12
Z	—	—	N51	—	N41	N41	C1
M–N11	2.123(3)	2.243(4)	2.065(5)	2.310(2)	2.078(4)	2.062(3)	2.145(4)
M–N21	2.219(4)	2.099(4)	2.107(4)	2.107(3)	2.101(4)	2.128(2)	2.102(4)
M–N31	2.104(3)	2.118(5)	2.128(4)	2.104(2)	2.079(4)	2.119(3)	2.102(4)
M–X	2.391(1)	2.354(1)	2.341(2)	2.424(1)	2.322(2)	2.3025(9)	2.339(2)
M–Y	2.146(3)	2.158(4)	1.973(4)	2.4261(9)	2.306(1)	2.311(1)	2.333(2)
M–Z	—	—	1.978(4)	—	2.084(4)	2.126(3)	2.181(6)
N11–M–N21	82.3(1)	92.4(1)	87.2(2)	91.81(9)	87.8(2)	88.19(9)	86.5(2)
N11–M–N31	82.9(1)	86.6(2)	87.4(2)	84.76(9)	89.2(2)	88.0(1)	87.1(1)
N11–M–X	102.59(9)	104.7(1)	175.9(1)	100.13(7)	89.0(1)	91.74(7)	91.3(1)
N11–M–Y	169.5(1)	90.4(2)	93.2(2)	82.46(3)	90.6(1)	90.94(8)	91.1(1)
N11–M–Z	—	—	93.9(2)	—	178.3(2)	179.5(1)	173.7(2)
N21–M–N31	95.4(1)	82.9(2)	88.7(1)	85.8(1)	86.1(2)	85.8(1)	88.0(1)
N21–M–X	116.3(1)	162.9(1)	90.1(1)	168.02(7)	174.4(1)	175.73(8)	177.3(1)
N21–M–Y	91.9(1)	88.7(2)	176.2(1)	103.88(7)	89.8(1)	89.81(7)	90.9(1)
N21–M–Z	—	—	96.9(1)	—	90.8(2)	91.3(1)	88.0(2)
N31–M–X	148.2(1)	97.3(1)	89.5(1)	96.21(8)	89.2(1)	89.95(7)	90.3(1)
N31–M–Y	89.0(1)	170.9(1)	95.1(1)	171.35(7)	175.9(1)	175.49(7)	178.0(1)
N31–M–Z	—	—	174.2(2)	—	89.7(2)	91.9(1)	89.5(2)
X–M–Y	87.8(1)	91.8(1)	89.7(1)	97.54(3)	94.88(5)	94.47(4)	90.70(5)
X–M–Z	—	—	89.5(1)	—	92.2(1)	88.73(7)	94.1(1)
Y–M–Z	—	—	79.2(2)	—	90.4(1)	89.13(8)	92.1(1)
τ^{a}	0.76	0.13	—	0.06	—	—	—

[a] Ref. 15.

separations are virtually the same but are slightly longer than those of mononuclear complexes **1** and **2**. Characteristic dissimilarities are noted for the dimeric, square-pyramidal structure of $[Tp^{iPr2}CrCl]_2$ **3** when compared with (a) the monomeric, tetrahedral structures of other first row metal complexes, $Tp^{iPr2}MCl$ (M = Mn, Fe, Co, Ni, Cu)[17] and (b) the monomeric *cis*-divacant octahedral structure of $Tp^{tBu,Me}CrCl$ **B**[6b] bearing the more bulky $Tp^{tBu,Me}$ ligand. Tp^R ligands have been recognized as "tetrahedral enforcers"[1] and such a property is evident for the (a)-series complexes but not for **3**. Lack of such a capability for chromium complexes is further supported by complex **B**. Although dimerization through the chloro-bridging can be prevented by introduction of the bulky $Tp^{tBu,Me}$ ligand, the resultant monomeric four-coordinate species **B** does not adopt a tetrahedral structure but the *cis*-divacant octahedral structure. Thus the square-pyramidal structure of **3** should not result from deformation from a tetrahedral structure caused by the chloro-bridging but from the intrinsic property of Tp^RCr complexes; Tp^RCrL_x species prefer a structure resulting from removal of ligand(s) from an octahedral structure, *i.e.* a five-coordinate square-pyramidal structure or four-coordinate *cis*-divacant octahedral structure or four-coordinate square-planar structure [see for example $(Bp^R)_2M$-type complexes below]. Early transition metal-Tp^R complexes tend to adopt an octahedral geometry with coordination of additional ligands or ligand-bridging,[7] presumably because (i) Lewis acidity of the central metal is larger than that of late transition metals as those in (a)-type complexes and (ii) early transition metals are shorter in valence electrons when compared with late transition metals. The difference between the monomeric (**B**) and dimeric structures (**3**) of $[Tp^RCrCl]_n$-type complexes of the same composition [point(b)] comes from the steric tuning effect of the Tp^{iPr2} ligand as mentioned in the Introduction.

The octahedral structure of the bipy complex **2** is evident from the inter-ligand angles (except for N41–Cr1–N51) being close to 90° (87.2–96.9°) and all Cr–N distances in the narrow range (1.973–2.128 Å).

The Bp^{iPr2} complexes **4** and **5**[2] obtained as byproducts of the metathesis (see above) were characterized by X-ray crystallography and IR. Despite several attempts, sufficient quantities of pure samples for full characterization could not be obtained, because air-sensitive **4** and **5** needed to be separated from a mixture by hand. Molecular structures of **4** and **5** are shown in Fig. 3 and structural parameters are compared with related compounds in Table 2. At first glance, the two complexes can be regarded as square-planar complexes with two κ^2-Bp^R type ligands. But when the conformations of six-membered rings of



4

5

Fig. 3 Molecular structures of **4** and **5** showing the 30% thermal ellipsoids.

Table 2 Selected structural parameters for Bp^RM complexes[a]

	4	5		
X	N11*	N31		
Y	N21*	N41	$(Bp^{H2})_2Cr$ **C**[b,c]	$Bp^{H2}ZrCpCl_2$ **D**[d]
M–N11	2.049(3)	2.100(3)	2.06	2.280(3)
M–N21	2.074(3)	2.083(3)	2.07	2.280(3)
M–X	2.049(3)	2.142(4)	2.06	
M–Y	2.074(3)	2.139(3)	2.07	
M · · · B1	2.986(4)	3.095(5)	3.22	2.957(5)
N11–M–N21	85.9(1)	87.5(1)	90.3	79.7(1)
N11–M–X	180	166.8(1)	180	
N11–M–Y	94.1(1)	89.6(1)	89.7	
N21–M–X	94.1(1)	88.6(1)	89.7	
N21–M–Y	180	168.4(1)	180	
X–M–Y	85.9(1)	91.7(1)	90.3	
M–N11–N12	115.2(2)	117.0(3)	120.5	115.4(3)
M–N21–N22	115.3(2)	116.6(2)	120.5	115.4(3)
N11–N12–B1	116.5(3)	117.5(3)	120.1	111.6(2)
N21–N22–B1	116.0(3)	118.5(3)	119.5	111.6(2)

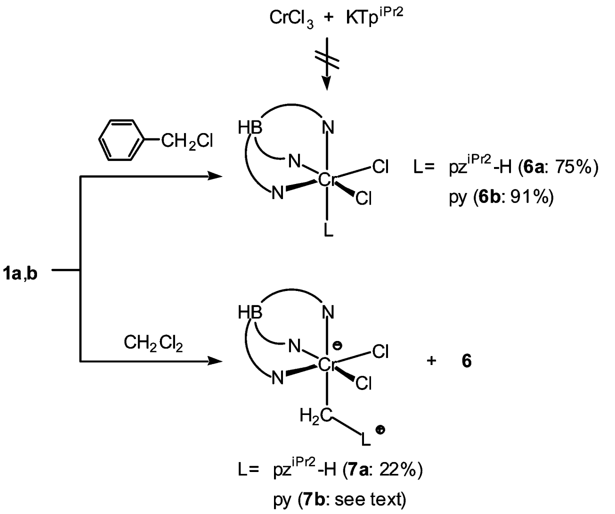
[a] Interatomic distances in Å, bond angles in degrees. [b] Ref. 9*a*. [c] Calculated from the reported atomic coordinates. [d] Ref. 18.

the $Bp^{iPr2}M$ moieties are inspected in detail, the boat form conformation suggests an attractive interaction between the B and Cr atoms. Because the B · · · Cr distances of *ca.* 3 Å are comparable to that in the zirconium complex $Bp^{H2}ZrCpCl_2$ **D** [2.957(5) Å],[18] for which a three center-two electron B–H · · · M interaction has been demonstrated, a similar interaction should operate for **4** and **5**. Although such an interaction was not discussed for the parent $(Bp^{H2})_2Cr$ complex **C**,[9a] the similar structural parameters (Table 2) suggest an analogous interaction.

Reger pointed out that the B · · · M distance in the absence of a B–H · · · M interaction is *ca.* 3.8 Å.[18,19] The B · · · M distances of **4**, **5**, and **D** are substantially shorter than this criterion and the B–H · · · M interaction is supported by lower energy shifts of ν_{BH} vibrations below 2300 cm^{-1}. When the B · · · M distances of the $(Bp^R)_2Cr$ complexes **4** and **C** are compared, that of **4** with the bulky Bp^{iPr2} ligand is shorter than that of **C** by *ca.* 0.2 Å. Steric repulsion among bulky isopropyl substituents in **4** should cause folding of the boat conformation with the shorter B · · · M separation. The 3c–2e B–H · · · M interactions found in these molecules should contribute to stabilization of such electron-deficient species as **4** and **5** through donation of electrons of the B–H moiety to the electron deficient metal center. Complex **5** contains, in addition to the Bp^{iPr2} ligand, the analogous N_2-ligand system, which consists of two pyrazole molecules and one chloride anion. Interatomic distances [Cl1 · · · N31 3.373(4); Cl2 · · · N41 3.339(3) Å] suggest N–H · · · Cl hydrogen bonding interactions and furthermore weak coordination of the Cl atom is evident from the Cr · · · Cl distance [2.661(1) Å], which is longer than those in **1**–**3** (~2.3 Å). Because a pure sample of the Tp^{iPr2} ligand was used in these syntheses, the Bp^{iPr2} ligand did not come from Bp^{iPr2} included as an impurity. Formation of Bp^{iPr2} should involve hydride-pz^{iPr2} anion exchange or disproportionation on Tp^{iPr2} but the mechanism for the unprecedented scrambling process remains to be studied.

Reduction features of Cr(II) complexes

(i) Oxidative addition of organic halides leading to Cr(III) complexes. The activity of the Cr(II) species as reductants was first examined by reaction with organic halides. Treatment of the mononuclear Cr(II) complexes **1** with benzyl chloride resulted in one electron oxidation at the chromium center associated with Cl atom transfer to give green dichlorochromium(III) complexes **6**,[7] which were found to be stable in the air (Scheme 2). GLC analysis of the solution phase revealed formation of 1,2-diphenylethane, which should result from dimerization of benzyl radical, the other product formed *via* electron transfer to benzyl chloride. Similar clean oxidative chlorination of **1** was observed with 1,2-dichloroethane and carbon tetrachloride but reactions with simple alkyl halides such as isopropyl chloride and methyl iodide resulted in the formation of a mixture of products.[20] It should be noted that Cr(III) complexes including **6** could not be obtained by reaction of Cr(III) salts [*e.g.* $CrCl_3$ and $Cr(NO_3)_3$] with a Tp^{iPr2} salt. Lewis acidic Cr(III) salts may induce decomposition of the Tp^{iPr2} ligand to give an intractable mixture of products.[21]



Scheme 2

Dissolution of the Cr(II) complexes **1** in CH_2Cl_2 resulted in oxidative addition of not only the chlorine atom but also the organic fragment to give a mixture of **6** and the zwitterionic methylene-inserted product **7**. The ion peaks at *m*/*z* = 719 (**7a** − Cl) and 166 (CH_2pz^{iPr2}-H) supported the formation of **7a**; these peaks were shifted to *m*/*z* 721 and 168, respectively, when CD_2Cl_2 was used in place of CH_2Cl_2.[22] Thus the methylene unit in **7a** came from CH_2Cl_2. The oxidation state of the central metal(III) was determined on the basis of the magnetic susceptibility (μ_{eff} = 3.67 μ_B). The μ_{eff} value, which is consistent with a high spin d^3 electronic configuration [S = 3/2; μ(spin only) = 3.87 μ_B],[23] is comparable to that of a Cr(III) species **6a** (μ_{eff} = 3.96 μ_B) but substantially smaller than that of a Cr(II) d^4 species (*cf.* **1a**: 4.68 μ_B). Although the pyridine adduct **7b** could not be isolated, FD-MS analyses together with a labeling experiment using CD_2Cl_2 suggested formation of an analogous

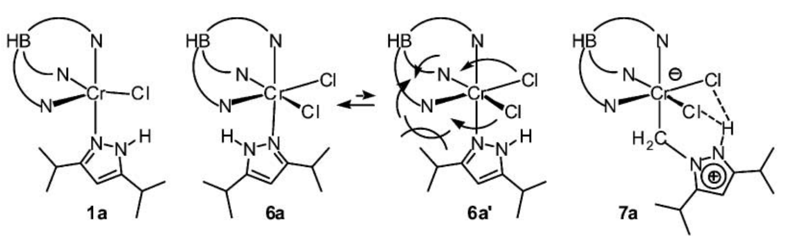


Chart 1

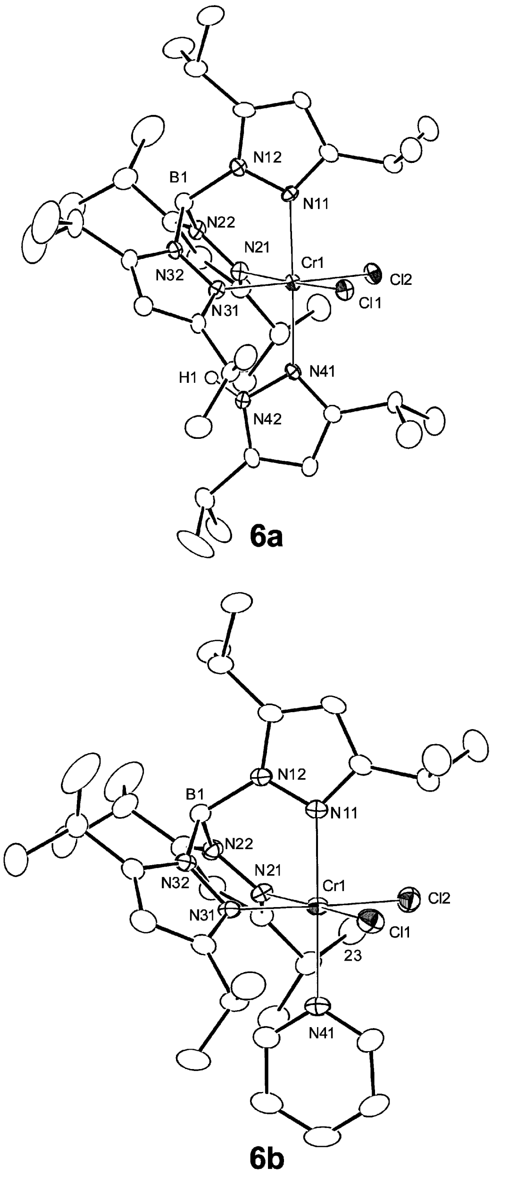


Fig. 4 Molecular structures of **6a**,**b** showing the 30% thermal ellipsoids.

species [with CH_2Cl_2: *m*/*z* = 682 (**7b**), 94 (CH_2py); with CD_2Cl_2: *m*/*z* = 684 (**7b**-d_2), 96 (CD_2py)].

The dichlorochromium(III) complexes **6a**,**b** and **7a** were also characterized by X-ray crystallography. Molecular structures of **6** and **7** are shown in Figs. 4 and 5, and the structural parameters are compared with the Cr(II) complexes (Table 1). Complexes **6** are octahedral as is clearly indicated by the inter-ligand angles (86.1–94.8°) close to 90°. No significant difference is observed for the Cr–N and Cr–Cl distances in the Cr(II) and Cr(III) complexes. The octahedral core geometry of the product **7a** obtained from CH_2Cl_2 (Fig. 5) is essentially the same as those of **6** and, taking into account the hydrogen bonding interaction with the protonated pyrazolyl group [*cf.* Cl2 ··· N42 3.086(6); Cl1 ··· N42 3.171(6) Å], **7a** has been assigned as the zwitterionic methylene-inserted complex. Because the hydrogen bonding interaction based on the six-membered ring structure is much stronger than that in the five-membered ring structure as in **7a**, its N–H vibration (3165 cm^{-1}) becomes broader and is shifted to much lower energies when compared with those of **1a** and **6a** (see above).

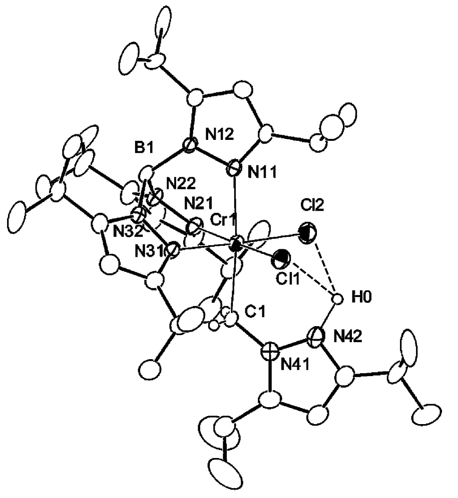
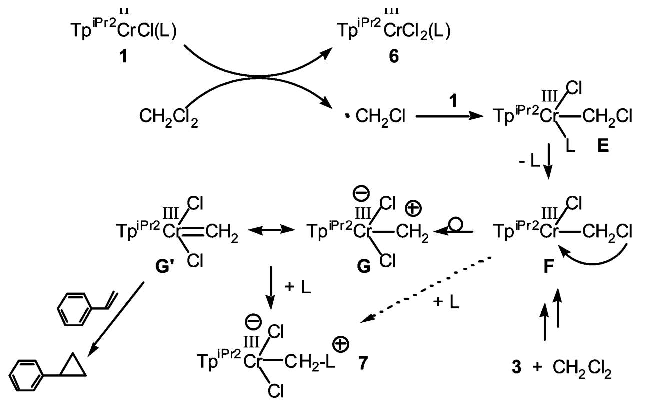


Fig. 5 Molecular structure of **7a** showing the 30% thermal ellipsoids.

It is notable that different arrangements of the pz^{iPr2}-H ligand are observed for **1a**, **6a** and **7a** (Chart 1). In **1a** and **7a** the N–H moiety of the pyrazole molecule points toward the side of the chloro ligand(s), whereas that in **6a** points toward the opposite side. The differences could be interpreted in terms of a combination of (i) the oxidation state of the central chromium atom, (ii) the presence/absence of hydrogen bonding interaction and (iii) the steric repulsion among the isopropyl substituents of the Tp^{iPr2} ligand and the coordinated pyrazole molecule. The trigonal-bipyramidal geometry of **1a** with a larger N_{basal}–Cr–N_{basal} bite angle [N21–Cr1–N31 95.4° (**1a**) *vs.* 86.1° (**6a**), 85.8° (**6b**)] forms a void, which is wide enough to accommodate the pz^{iPr2}-H molecule, and such an arrangement is supported by the H ··· Cl hydrogen bonding interaction as discussed above. In contrast to this situation, the Cr(III) complex **6a** lacks a hydrogen bonding interaction due to the decreased electron density at the chloro ligand caused by the increase of the oxidation state of the central metal (II ⟶ III). In addition, due to the acute N_{basal}–Cr–N_{basal} angle of an octahedral species the pz^{iPr2}-H ligand is excluded to minimize the steric repulsion among the isopropyl groups (*cf.* **6a′**), because the N–H moiety in **6a** suffers much less steric repulsion with the Tp^{iPr2} ligand. In the zwitterionic Cr(III) species **7a**, the anionic metal center increases the electron density at the chloro ligand enough to form a hydrogen bonding interaction and insertion of the methylene group brings the bulky pz^{iPr2} moiety away from the congested metal center.

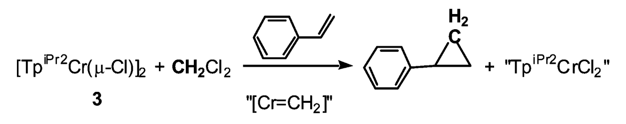
A plausible mechanism for formation of the methylene-inserted products **7** is summarized in Scheme 3. Interaction of **1** with CH_2Cl_2 forms the chlorochromium(III) complex **6** and chloromethyl radical *via* chlorine atom transfer as discussed for the oxidative addition of benzyl chloride. Oxidative addition of the resultant chloromethyl radical to the Cr(II) species **1** leads to



Scheme 3

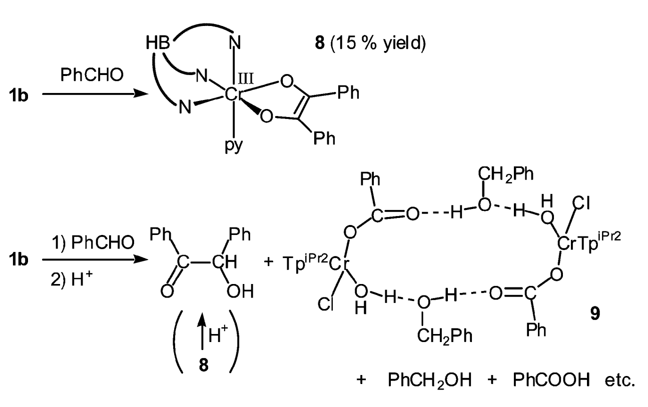
the formation of the chloromethylchromium(III) intermediate **E**. Several mechanisms are feasible for the subsequent formal exchange between Cl and L in **E**. The reaction route shown in Scheme 3 involves a sequence of elimination of L (**F**), α-elimination of the Cl atom (**G**) and addition of L at the methylene moiety in **G**.

Alternatively, the zwitterionic complex **7** could be formed by nucleophilic displacement reaction of **G** by L but the mechanism involving the methylene intermediate **G** (**G′**) is based on the result of olefin cyclopropanation mediated by **3**.[24] Agitation of a CH_2Cl_2 solution of **3** in the presence of styrene produced cyclopropylbenzene (Scheme 4). Although the yield was low (2% yield), no cyclopropanation occurred at all in the absence of **3**. It is suggested that in the present cyclopropanation the Cr(II) species **3** served as a reducing agent as well as a Cl-abstracting agent, although no characterizable inorganic product could be isolated from the reaction mixture.



Scheme 4

(ii) Reductive coupling of benzaldehyde. Reductive C–C coupling of carbonyl compounds is one of the characteristic reactivities of Cr(II) species as mentioned in the Introduction.[10,11] A Tp^{iPr2}Cr^{II} species was found to mediate such a type of reaction. Treatment of the pyridine adduct **1b** with benzaldehyde in ether for 10 h at room temperature gave the dark red product **8** in 15% yield (Scheme 5). Hydrolytic workup of the resultant mixture gave a mixture of products, from which benzoin (the hydrolysis product of **8**)[25] and a very small amount of the aquo-benzoato-chloro complex **9** were isolated by chromatographic separation. Benzyl alcohol and benzoic acid were also detected by GLC analysis of the mixture. Formation of **8** and benzoin clearly indicates the capability of the Cr(II) species for reductive C–C bond formation.



Scheme 5

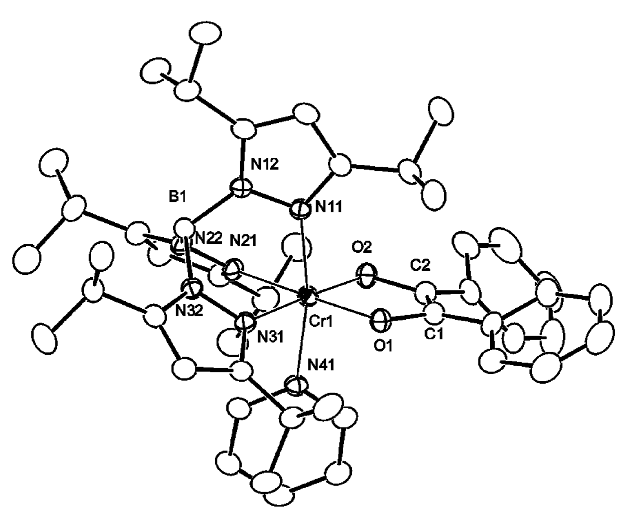


Fig. 6 Molecular structure of **8** showing the 30% thermal ellipsoids (one of two independent molecules).

Table 3 Selected structural parameters for **8**[a]

	Molecule 1 (a-series)	Molecule 2 (b-series)
Cr–O1	1.923(2)	1.917(2)
Cr–O2	1.912(2)	1.914(3)
Cr–N11	2.104(3)	2.110(3)
Cr–N21	2.111(3)	2.099(3)
Cr–N31	2.092(3)	2.110(3)
Cr–N41	2.150(3)	2.134(3)
O1–C1	1.376(4)	1.367(4)
C1–C2	1.366(5)	1.353(5)
C2–O2	1.363(4)	1.373(4)
C1–C51	1.469(5)	1.478(5)
C2–C61	1.465(5)	1.470(5)
O1–Cr–O2	83.7(1)	83.3(1)
Cr1–O1–C1	111.8(2)	112.7(2)
O1–C1–C2	115.7(3)	115.5(3)
C1–C2–O2	115.7(3)	116.0(3)
C2–O2–Cr	112.5(2)	112.2(2)
cis-N–Cr–N	84.6–90.3(1)	84.7–92.2(1)
Σ(C1)[b]	359.7	359.8
Σ(C2)[c]	359.8	359.9
Σ[d]	539.4	539.7
O1–C1–C2–O2	7.2(4)	3.4(4)

[a] Interatomic distances in Å, bond angles in degrees. [b] Sum of bond angles around C1. [c] Sum of bond angles around C2. [d] Sum of interior angles of the five-membered metallacycle.[26]

The coupling product **8** and the aquo-benzoato-chloro complex **9** were characterized by X-ray crystallography. The molecular structure of **8** is shown in Fig. 6 and selected structural parameters are listed in Table 3. A unit cell of **8** contains two independent molecules with essentially the same geometries. The chromium centers adopt normal octahedral coordination geometries without any notable differences to the compounds listed in Table 1. The five-membered 2,5-dioxachromacyclopent-3-ene structure results from reductive coupling of two molecules of benzaldehyde. Although formation of a saturated 2,5-dioxachromacyclopentane structure is expected for simple reductive coupling, the planarity of the five-membered ring (see the Σ values in Table 3)[26] as well as the C1,2 atoms [Σ(C1,2)] clearly leads to the assignment of **8** as a 2,5-dioxachromacyclopent-3-ene. In accord with this assignment, the C1–C2 distances [1.366(5) Å (a-series); 1.353(5) Å (b-series)] are substantially shorter than those of C–C single bonds (1.53

Å) and closer to C=C lengths (1.32 Å)[27] and the C1–O1 and C2–O2 distances [1.363(4)–1.376(4) Å] are comparable to C–O lengths (1.34 Å).[27] The minor product **9** is characterized as a Cr(III) complex coordinated by aquo, benzoato and chloro ligands as is consistent with the IR data containing ν_{OH}, ν_{BH}[14] and $\nu_{C=O}$ vibrations. Ion peaks derived from the monomeric unit {*m*/*z* = 673 [$Tp^{iPr2}Cr(Cl)(OCOPh)$], 637 [$Tp^{iPr2}Cr(OCOPh)$]} were also observed by FD-MS. In addition to the normal octahedral core structure, a unique hydrogen bonding interaction has been found. The oxygen atoms of the aquo and benzoato ligands are bridged by benzyl alcohol molecules through hydrogen bonds leading to the dimeric cyclic structure. Complex **9** should be formed *via* a complicated reaction sequence. It is notable, however, that benzyl alcohol resulting from reduction of benzaldehyde is included in **9**, while the benzoato moiety should come from benzoic acid included as an impurity of benzaldehyde.

Reductive coupling of carbonyl compounds leading to 1,2-diol after hydrolytic workup (pinacol coupling)[11] has been frequently observed upon treatment of carbonyl compounds with metals (*e.g.* alkali and alkali earth metals)[27] but, to our knowledge, a dehydrogenative version leading to 2,5-dioxachromacyclopent-3-ene derivatives has no precedent. (Reductive coupling of acyl halide to give 2,5-dioxametallacyclopent-3-ene is known.) The formation of **8** should be explained in terms of a combination of reductive coupling and dehydrogenation. Because the bipy-Cr(II) complex **2** also afforded benzoin under similar conditions, the reductive coupling may proceed *via* outer sphere electron transfer from the Cr(II) center to benzaldehyde. Coupling of the resultant anion radical forms the ethane-1,2-dioxyl radical, and subsequent coordination and dehydrogenation would finally lead to **8**.

Conclusions

Treatment of $CrCl_2$ with a Tp^{iPr2} salt in the presence/absence of a donor (L) gives the extremely air-sensitive Tp^{iPr2}Cr(II) species: five-coordinate species with a κ^1-donor (**1**), six-coordinate species with a κ^2-donor (**2**) and five-coordinate dinuclear species with two bridging chloro ligands (**3**). Such structural diversity results from the steric tuning effect of the Tp^{iPr2} ligand. It is also revealed that a Tp^RCrL_x complex prefers a coordination geometry resulting from removal of ligand(s) from an octahedral geometry such as five-coordinate square-pyramidal structure, four-coordinate *cis*-divacant octahedral structure and four-coordinate square-planar structure. In other words, Tp^R ligands do not serve as “tetrahedral enforcers” for chromium as typically observed for first row late transition metal complexes.[1,3]

The Cr(II) species **1** are cleanly converted to the corresponding Cr(III) species **6** upon treatment with benzyl chloride. On the other hand, interaction of **1** with CH_2Cl_2 provides the methylene-inserted product **7**. The formation of **7** is interpreted in terms of the methylene intermediate **G**(**G′**), which is supported by the result of a cyclopropanation reaction. Reductive coupling of benzaldehyde to give **8** is found to be mediated by a Cr(II) species. Derivative chemistry of the $Tp^{iPr2}CrCl_x(L)$ complexes is now under further study and will be reported in due course.

Experimental

All manipulations were carried out in a glove box filled with argon. CH_2Cl_2 (P_4O_{10}), MeOH [$Mg(OMe)_2$], MeCN (CaH_2), THF, pentane and hexane (Na–K/benzophenone) were treated with appropriate drying agents, distilled, and stored under argon. IR (measured as KBr pellets; reported in cm^{-1}) and FD-MS spectra were obtained on a JASCO FT/IR 5300 and JEOL JMS-700 spectrometer, respectively. Magnetic susceptibility was measured on a Sherwood Scientific MSB-AUTO. KTp^{iPr2} and $NaTp^{iPr2}$ were prepared according to the literature procedure.[28] Other chemicals including anhydrous $CrCl_2$ purchased from Aldrich were used as received without further purification.

Preparation of $Tp^{iPr2}CrCl(pz^{iPr2}\text{-}H)$ 1a

To a MeOH solution (20 mL) of $CrCl_2$ (600 mg, 4.88 mmol) was added a THF solution (20 mL) containing KTp^{iPr2} (2.342 g, 4.64 mmol) and 3,5-diisopropylpyrazole (909 mg, 5.97 mmol). The volatiles were removed under reduced pressure and the residue was extracted with MeCN. Filtration followed by extraction and cooling at −36 °C gave **1a** as blue crystals (1.457 g, 2.07 mmol, 45% yield). **1a**: IR 3257 (ν_{NH}), 2532 (ν_{BH}), 1560 cm^{-1} ($\nu_{C=N}$). $\mu_{eff} = 4.68\ \mu_B$. Anal. calc. for $C_{36}H_{62}N_8BClCr$: C, 61.31; H, 8.86; N, 15.89. Found: C, 58.42; H, 8.61; N, 15.41%.

Preparation of $Tp^{iPr2}CrCl(py)$ 1b

To a MeOH solution of $CrCl_2$ (1.10 g, 8.94 mmol) was added $NaTp^{iPr2}$ (3.65 g, 7.48 mmol) dissolved in THF (15 mL) and pyridine (10 mL). The volatiles were removed under reduced pressure and the residue was washed with hexane and then extracted with MeCN. Filtration followed by concentration and cooling at −36 °C gave **1b** as green crystals (1.84 g, 2.91 mmol, 63% yield). **1b**: IR 2554 (ν_{BH}), 1604 cm^{-1} ($\nu_{C=N}$). Anal. calc. for $C_{32}H_{51}N_7BClCr$: C, 60.80; H, 8.13; N, 15.52. Found: C, 59.32; H, 8.60; N, 15.82%.

Preparation of $Tp^{iPr2}CrCl(bipy)$ 2

(i) One-pot synthesis. To a MeOH solution (20 mL) of $CrCl_2$ (455 mg, 3.62 mmol) was added a THF solution (20 mL) containing KTp^{iPr2} (1.497 g, 2.97 mmol) and bipy (430 mg, 2.75 mmol). The volatiles were removed under reduced pressure and the residue was washed with pentane and hexane and then extracted with MeCN. Filtration followed by extraction and cooling at −36 °C gave **2** as dark purple crystals (221 mg, 0.312 mmol, 11% yield).

(ii) From 1b. To **1b** (512 mg, 0.810 mmol) dissolved in a mixture of ether (20 mL) and MeCN (5 mL) was added bipy (127 g, 0.83 mmol). Work up as described above gave **2** as blue crystals (137 mg, 0.193 mmol, 24% yield). **2**: IR 2545 (ν_{BH}), 1579, 1571 cm^{-1} ($\nu_{C=N}$). Anal. calc. for $C_{38}H_{55.5}N_{8.5}BClCr$ (**2**·0.5MeCN): C, 62.66; H, 7.68; N, 15.81. Found: C, 62.54; H, 7.68; N, 16.32%.

Preparation of $[Tp^{iPr2}Cr(\mu\text{-}Cl)]_2$ 3

To $CrCl_2$ (455 mg) dissolved in a mixture of MeOH (3 mL) and MeCN (12 mL) was added a toluene solution (18 mL) of KTp^{iPr2} (1.57 g, 3.11 mmol) and the resultant mixture was stirred for 50 min. After removal of the volatiles the residue was extracted with THF and the volatiles were again removed under reduced pressure. The obtained residue was washed with toluene and then crystallized from THF–pentane to give **3** as blue–green crystals (511 mg, 0.462 mmol, 30% yield). **3**: IR 2545 cm^{-1} (ν_{BH}). Despite several attempts an analytically pure sample of **3** could not be obtained due to its extreme air-sensitivity.

Isolation of byproducts 4 and 5

The residue obtained by evaporation of the hydrocarbon washings (see above) under reduced pressure was crystallized from MeCN to give a mixture of red (**4**) and blue crystals (**5**), which were separated by hand. **4**: IR 2475, 2352, 2306, 2264, 2216 cm^{-1} (ν_{BH}). **5**: 3176 (ν_{NH}), 2471, 2359, 2326, 2283 cm^{-1} (ν_{BH}). Sufficient quantities of pure samples for full characterization could not be obtained despite several attempts.

Preparation of $Tp^{iPr2}CrCl_2(pz^{iPr2}\text{-}H)$ 6a

To a toluene solution (30 mL) of **1b** (508 mg, 0.720 mmol) was added benzyl chloride (87 µL, 0.76 mmol) and the resultant mixture was stirred for 14 h at ambient temperature. After removal of the volatiles under reduced pressure the residue was washed with pentane and then crystallized from THF–pentane at −36 °C to give **6a** as green crystals (398.2 mg, 0.528 mmol, 75% yield). **6a**: IR 3451 (ν_{NH}), 2548 (ν_{BH}), 1564 cm^{-1} ($\nu_{C=N}$). $\mu_{eff} = 3.96\ \mu_B$. MD-MS: m/z = 740 (M^+). Anal. calc. for $C_{36}H_{62}N_8BCl_2Cr$: C, 58.38; H, 8.44; N, 15.13. Found: C, 57.46; H, 8.05; N, 15.38%.

Preparation of $Tp^{iPr2}CrCl_2(py)$ 6b

To a toluene solution (40 mL) of **1b** (1.51 g, 2.40 mmol) was added benzyl chloride (285 µL, 2.04 mmol) and the resultant mixture was warmed in a warm water bath until the solution color changed from green to brown and finally to green. Work up similar to that of **6a** gave **6b** as green crystals (1.46 g, 2.19 mmol, 91% yield). **6b**: IR 2551 (ν_{BH}), 1607 cm^{-1} ($\nu_{C=N}$). FD-MS: m/z = 666 (M^+). Anal. calc. for $C_{32}H_{51}N_7BCl_2Cr$: C, 57.58; H, 7.70; N, 14.69. Found: C, 57.98; H, 7.85; N, 14.12%. **6b** was also obtained in 45% yield by stirring a CH_2Cl_2 solution of **1b** for 3.5 h at ambient temperature.

Reaction of 1a with CH_2Cl_2 to give $Tp^{iPr2}CrCl_2(pz^{iPr2}\text{-}H)$ 6a and $Tp^{iPr2}CrCl_2(CH_2\text{-}pz^{iPr2}\text{-}H)$ 7a

A CH_2Cl_2 solution (1 mL) of **1a** (176 mg, 0.250 mmol) was stirred for 1 h at ambient temperature. After removal of the volatiles under reduced pressure the residue was crystallized from MeCN. The air-stable green **6a** (78 mg, 0.105 mmol, 42% yield) and brown crystals **7a** (41 mg, 0.54 mmol, 22% yield) were separated by hand. **7a** : IR 3165 (ν_{NH}), 2549 (ν_{BH}), 1576 cm^{-1} ($\nu_{C=N}$). $\mu_{eff} = 3.67\ \mu_B$. Anal. calc. for $C_{37}H_{64}N_8BCl_2Cr$: C, 58.88; H, 8.56; N, 14.85. Found: C, 58.77; H, 8.29; N, 15.47%.

Reaction of 1b with CH_2Cl_2 to give $Tp^{iPr2}CrCl_2(py)$ 6b and $Tp^{iPr2}CrCl_2(CH_2\text{-}py)$ 7b

Upon dissolution of **1b** (203 mg, 0.321 mmol) in CH_2Cl_2 (2 mL) the green color of the solution changed to brown. After stirring for 3 h the volatiles were removed under reduced pressure and crystallization of the residue gave **6b** as green crystals (96 mg, 0.144 mmol, 45% yield). Although **7b** could not be isolated from the mixture, **7b** was detected by an FD-MA analysis of the reaction mixture (see text).

Reaction of 1c with benzaldehyde

(i) Synthesis of 8. To an ethereal solution (10 mL) of **1c** (112 mg, 0.177 mmol) was added benzaldehyde (90 µL, 0.88 mmol) and the resultant mixture was stirred for 10 h at room temperature. The color of the solution changed from green to brown–red. After removal of the volatiles under reduced pressure the residue was crystallized from acetonitrile. Filtration gave dark red crystals **8** (21 mg, 0.03 mmol, 15% yield), which were dried *in vacuo*. IR 2544 (ν_{BH}), 1700 ($\nu_{C=O}$), 1647 ($\nu_{C=C}$), 1604 cm^{-1} ($\nu_{C=N}$). FD-MS 848 (M^+ + MeCN), 728 (M^+ − py).

(ii) Isolation of benzoin after hydrolytic workup. To an ethereal solution (60 mL) of **1c** (2.32 g, 3.66 mmol) was added benzaldehyde (3.7 mL, 33 mmol) and the resultant mixture was stirred for 24 h at room temperature. Then 3% aq. HCl solution was added to the reaction mixture and the products were extracted with ether. Column chromatographic separation on alumina gave benzoic acid and benzyl alcohol (eluted with hexane) and benzoin (125 mg, 0.59 mmol, 16% yield). Elution with CH_2Cl_2 gave a dark red band, from which **9** was isolated as dark red crystals in 1.4% yield. **9**: IR 3368 (ν_{OH}), 2554 (ν_{BH}), 1669 cm^{-1} ($\nu_{C=O}$). FD-MS: m/z = 673 [$Tp^{iPr2}Cr(Cl)(OCOPh)$], 637 [$Tp^{iPr2}Cr(OCOPh)$]. An analytically pure sample of **9** could not be obtained. The yield of benzoin obtained by GLC analysis of a reaction mixture using anthraquinone as an internal standard was 17%.

Cyclopropanation of styrene with 3 in CH_2Cl_2

3 (52 mg, 0.047 mmol) was dissolved in a mixture of styrene (2 mL, 17.3 mmol) and CH_2Cl_2 (2.5 mL) containing dodecane (internal standard). The yield of cyclopropylbenzene, which was identified by GC-MS analysis as well as comparison of the retention time with that of an authentic sample, was determined by GLC analysis. Dependence of the yield on the reaction time was not observed.

X-Ray crystallography

Crystallographic data are summarized in Table 4. Single crystals of **1a** (MeCN), **1b** (MeCN), **2** (MeCN), **3** (THF–pentane), **4** (MeCN), **5** (MeCN), **6a** (THF–pentane), **6b** (THF–pentane), **7a** (MeCN), **8** (MeCN) and **9** (hexane) were obtained by recrystallization from the solvent systems shown in parentheses and mounted on glass fibers.

Diffraction measurements were made on a Rigaku RAXIS IV imaging plate area detector with Mo Kα radiation (λ = 0.71069 Å) at −60 °C. Indexing was performed from two oscillation images, which were exposed for 5 min. The crystal-to-detector distance was 110 mm ($2\theta_{max}$ = 55°). Data collection parameters were as follows: the oscillation range/the number of oscillation images/the exposed time: 5.0°/36/450 sec/deg (**1a**); 3.0°/60/600 sec/deg (**1b**); 5.0°/36/450 sec/deg (**2**); 4.5°/40/850 sec/deg (**3**); 5.0°/36/600 sec/deg (**4**); 5.0°/36/500 sec/deg (**5**); 3.0°/60/750 sec/deg (**6a**); 3.0°/60/850 sec/deg (**6b**); 2.0°/90/450 sec/deg (**7a**); 5.0°/36/650 sec/deg (**8**); 5.0°/36/450 sec/deg (**9**). Readout was performed with a pixel size of 100 × 100 µm. Neutral scattering factors were obtained from the standard source. In the reduction of data, Lorentz and polarization corrections and empirical absorption corrections were made.[29] Crystallographic data and results of structure refinements are listed in Table 3.

The structural analysis was performed on an IRIS O2 computer using teXsan structure solving program system obtained from the Rigaku Corp., Tokyo, Japan.[30] Neutral scattering factors were obtained from the standard source.[31]

The structures were solved by a combination of direct methods (SHELXS-86[32] or SIR92)[33] and Fourier synthesis (DIRDIF94).[34] Least-squares refinements were carried out using SHELXL-97[32] (refined on F^2) linked to teXsan. All the non-hydrogen atoms were refined anisotropically. Unless otherwise stated methyl hydrogen atoms were refined using riding models and other hydrogen atoms were fixed at the calculated positions. Details of the refinements were as follows:

1b: The disordered MeCN solvate was refined taking into account two components (N51–C511 : N52–C512 = 0.5 : 0.5) and hydrogen atoms attached to them were not included in the refinement.

1a: The hydrogen-bonded H0 atom was refined isotropically.

2: Hydrogen atoms attached to the MeCN solvate were fixed at the final stage of the refinement.

3: One of the two types of the THF solvate molecules were disordered and refined isotropically taking into account two components (O51–C511–521–531–541 : O52–C512–522–532–542 = 0.33 : 0.67) and hydrogen atoms attached to them were not included in the refinement.

4, **5**: The BH_2 hydrogen atoms and the NH hydrogen atoms (**5**) were refined isotropically.

6b: One of the two pentane solvates was sitting on a crystallographically imposed site and disordered. Two components (C621 : C622 = 0.5 : 0.5) were taken into account with isotropic refinements. Hydrogen atoms attached to them were not included in the refinement.

Table 4 Crystallographic data

	1a	**1b**·MeCN	**2**·MeCN	**3**·4THF	**4**	**5**	**6a**·2MeCN	**6b**·1.5pentane	**7a**·3MeCN	**8**·1.5MeCN	**9**
Formula	$C_{36}H_{62}N_8BClCr$	$C_{34}H_{54}N_8BClCr$	$C_{39}H_{57}N_9BClCr$	$C_{70}H_{124}N_{12}O_4$-$B_2Cl_2Cr_2$	$C_{36}H_{64}N_8B_2Cr$	$C_{36}H_{64}N_8BClCr$	$C_{40}H_{68}N_{10}$-BCl_2Cr	$C_{39.5}H_{69}N_7$-BCl_2Cr	$C_{43}H_{73}N_{11}BCl_2Cr$	$C_{49}H_{65.5}N_{8.5}O_2$-BCr	$C_{41}H_{61}N_6O_4$-$BClCr$
Formula weight	705.20	673.11	750.20	1394.35	682.57	707.21	822.76	775.74	877.84	868.42	800.23
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic	Triclinic	Triclinic	Monoclinic	Monoclinic	Orthorhombic	Triclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$C2/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$Pbac$	$P\bar{1}$	$C2_1/c$
T/K	213	213	213	213	213	213	213	213	213	213	213
a/Å	13.4411(5)	9.838(1)	12.769(1)	23.705(1)	10.565(2)	11.9100(8)	9.8029(4)	12.5153(4)	19.115(1)	18.305(4)	27.5884(9)
b/Å	17.0438(5)	24.305(3)	17.813(2)	17.4924(8)	10.893(3)	17.384(2)	25.021(1)	17.1143(5)	40.473(3)	19.783(5)	17.6345(6)
c/Å	17.3368(5)	16.502(2)	9.922(2)	19.2719(9)	8.853(2)	10.5505(9)	19.785(1)	20.4006(4)	13.0623(9)	14.399(4)	19.9811(4)
α/°			95.27(4)		89.143(5)	92.709(4)				99.06(2)	
β/°	92.584(3)	104.60(1)	111.20(3)	102.149(1)	96.89(2)	101.804(7)	96.416(3)	91.463(2)		100.95(1)	92.699(2)
γ/°			86.79(8)		96.60(1)	103.243(1)				101.12(1)	
V/Å^3	3967.6(2)	3818.7(9)	2094.6(7)	7812.2(7)	1004.9(4)	2071.2(3)	4822.6(4)	4368.2(2)	10105(1)	4920(2)	9710.2(5)
Z	4	4	2	4	1	2	4	4	8	4	8
μ/mm^{-1}	0.391	0.403	0.375	0.398	0.319	0.374	0.385	0.419	0.372	0.278	0.331
No. of diffractions collected	31611	19949	14526	30880	6647	14936	30303	35302	21577	22127	36691
No. of variables	444	436	473	422	230	456	506	458	608	1132	499
$R1$ for data with $I > 2\sigma(I)$	0.0615 (for 4000 data)	0.0788 (for 3830 data)	0.0835 (for 4935 data)	0.0581 (for 5014 data)	0.0744 (for 2407 data)	0.0713 (for 4570 data)	0.0879 (for 4992 data)	0.0593 (for 5477data)	0.0881 (for 5001 data)	0.0841 (for 12034 data)	0.0859 (for 7189 data)
$wR2$	0.1794 (for all 8952 data)	0.2203 (for all 7437 data)	0.2104 (for all 8148 data)	0.1713 (for all 8743 data)	0.1888 (for all 3963 data)	0.1820 (for all 8175 data)	0.2300 (for all 10091 data)	0.1742 (for all 9276 data)	0.2370 (for all 9009 data)	0.2245 (for all 16054 data)	0.2928 (for all 10184 data)

7a: The isopropyl groups distal from the metal center were found to be disordered and refined taken into account two components with 0.5 : 0.5 occupancies and C48A was refined isotropically. Hydrogen atoms H0 and H1a,b were refined isotropically and the other hydrogen atoms were fixed at the final stage of the refinement.

8: Hydrogen atoms attached to MeCN solvates were fixed at the calculated positions.

9: In addition to the benzyl alcohol molecule included in the hydrogen bonded system another molecule of benzyl alcohol was included as a solvate. Because, however, it was highly disordered, it was not included in the refinement. No notable interactions (*e.g.* coordination and hydrogen bond) between the hydrogen bonded system and the solvate benzyl alcohol molecule were found.

CCDC reference numbers 190631–190641.

See http://www.rsc.org/suppdata/dt/b2/b207326a/ for crystallographic data in CIF or other electronic format.

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2 Abbreviations used in this paper: Tp^{R}: hydrotris(pyrazolyl)borato ligands; Bp^{R}: dihydrobis(pyrazolyl)borato ligands; Tp^{iPr2}, Bp^{iPr2}: 3,5-diisopropylpyrazolyl derivatives; Tp^{tBu,Me}: 3-*t*-butyl-5-methylpyrazolyl derivative; Tp^{tBu,R}: 3-*tert*-butyl-5-alkyl(R)pyrazolyl derivative; Bp^{H2}: the parent Bp ligand with H-substituents; pz^{R}: pyrazolyl group.

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