

$[(\text{Tp}^{\text{tBu, Me}})\text{CrR}]$: A New Class of Mononuclear, Coordinatively Unsaturated Chromium(II) Alkyls with *cis*-Divacant Octahedral Structure

Jörg L. Kersten, Robin R. Kucharczyk, Glenn P. A. Yap, Arnold L. Rheingold, and Klaus H. Theopold*

Abstract: Reaction of CrCl_2 with $\text{Tp}^{\text{tBu, Me}}\text{K}$ yielded $[\text{Tp}^{\text{tBu, Me}}\text{Cr}(3\text{-}t\text{Bu}, 5\text{-MepzH})\text{Cl}]$ (**1**) and $[\text{Tp}^{\text{tBu, Me}}\text{CrCl}]$ (**2**), while the same reaction in the presence of pyridine gave **1** and $[\text{Tp}^{\text{tBu, Me}}\text{Cr}(\text{py})\text{Cl}]$ (**3**). Alkylation of **3** with Grignard reagents produced the chromium(II) alkyls $[\text{Tp}^{\text{tBu, Me}}\text{CrR}]$ (**4**, $\text{R} = \text{Et}$; **5**, $\text{R} = \text{Ph}$; **6**, $\text{R} = \text{CH}_2\text{SiMe}_3$), which reversibly added to pyridine to form the five-coordinate adducts $[\text{Tp}^{\text{tBu, Me}}\text{Cr}(\text{py})\text{R}]$ (**7**, $\text{R} = \text{Et}$; **8**, $\text{R} = \text{Ph}$; **9**, $\text{R} =$

CH_2SiMe_3). **1**, **2**, **4**, and **5** were structurally characterized by X-ray diffraction. The four-coordinate molecules **2**, **4**, and **5** adopt a highly unusual *cis*-divacant octahedral coordination geometry, while **1** is

the first five-coordinate $\text{Tp}^{\text{tBu, Me}}$ -complex of a first-row transition metal. Despite their coordinative unsaturation, chromium alkyls **4–6** do not polymerize ethylene, or even react with it. This observation is inconsistent with the catalytic activity commonly ascribed to divalent chromium in heterogeneous polymerization catalysts. Attempts to oxidize **4–6** (e.g., with $[\text{Cp}_2\text{Fe}]\text{BPh}_4$) to cationic chromium(III) alkyls failed, yielding $[\text{Tp}^{\text{tBu, Me}}\text{Cr}(\text{thf})][\text{BPh}_4]$ (**10**) instead.

Keywords

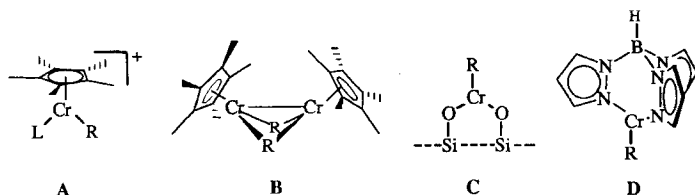
alkenes · chromium · *cis*-divacant octahedral geometry · polymerizations · tris(pyrazolyl)borate complexes

Introduction

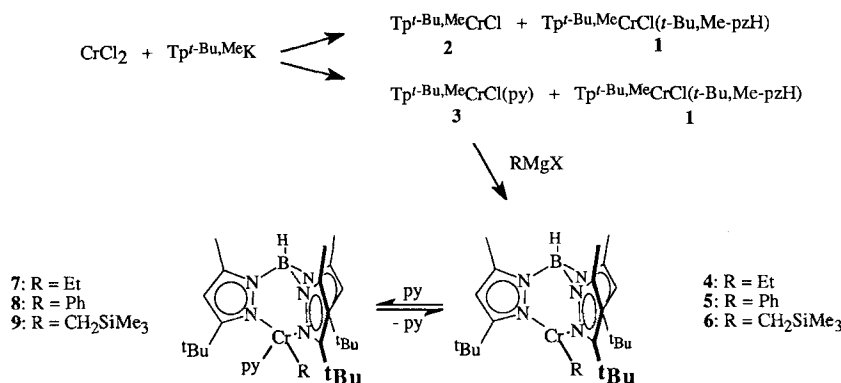
Coordinatively unsaturated chromium alkyls on oxide supports have been implicated as key intermediates in the chromium-catalyzed polymerization of olefins.^[1] One of the unresolved questions regarding such catalysts is the formal oxidation state of the chromium in the active site, most often proposed to be +II or +III. For catalysts carrying a cyclopentadienyl group on the chromium (e.g. the “Union Carbide catalyst”, Cp_2Cr on SiO_2),^[2] we have built a case based on the reactivity of model compounds that chromium(III) alkyls (**A**, $\text{R} = \text{alkyl}$) are responsible for the polymerization activity.^[3] One of the arguments against catalytic activity in the lower oxidation state was

the isolation of a class of chromium(II) alkyls of the type $[\{\text{Cp}^*\text{Cr}(\mu\text{-R})\}_2]$ (**B**), which did not react with ethylene.^[4] However, the extreme coordinative unsaturation of the hypothetical “ Cp^*CrR ” fragment, combined with the limited steric protection offered by the pentamethylcyclopentadienyl ligand, resulted in the formation of metal–metal bonded dinuclear complexes. It might be argued that the role of the heterogeneous support of commercial catalysts includes site isolation of the catalytic centers and prevention of metal–metal bonding, which might adversely affect the reaction with olefins. Thus, we were looking for ways to stabilize mononuclear, coordinatively unsaturated chromium(II) alkyls.

Another impetus for this work was the desire to investigate the reactivity of chromium alkyls in a coordination environment lacking cyclopentadienyl ligands. We note that the widely used “Phillips catalyst” (inorganic chromium on SiO_2)^[5] presumably features oxide ligation of chromium (for example, **C**). In a step toward a significantly “harder” coordination environment of the metal, we have chosen to employ a nitrogen-based ligand, namely a tris(pyrazolyl)borate (**TP**).^[6] The use of sterically hindered **TP** ligands has facilitated the isolation of a wide variety of metal complexes with low coordination numbers.^[7] Specifically, we have employed so-called “tetrahedral enforcers”,^[8] like the $\text{Tp}^{\text{tBu, Me}}$ anion ($\text{Tp}^{\text{tBu, Me}} = \text{hydrotris}(3\text{-}t\text{ert-butyl-5-methylpyrazolyl})\text{borate}$), to good effect in cobalt chemistry.^[9] The apparent dearth of **TP**Cr complexes like **D** in the extant literature added further appeal to an exploration of their chemistry.^[10]



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Scheme 1. Synthesis of hydrotris(3-*tert*-butyl-5-methylpyrazolyl)borate (Tp^{tBu,Me}) complexes of chromium.

Results and Discussion

Synthesis and Structure: Addition of CrCl₂ to a stirred suspension of Tp^{tBu,Me}K in THF yielded a turquoise solution; subsequent extraction of the solid reaction products with pentane gave a blue powder, ultimately identified as [Tp^{tBu,Me}Cr(3-*t*Bu,5-MepzH)Cl] (**1**, 20% yield; 5-MepzH = 5-methylpyrazole), and extraction of the pentane-insoluble residue with Et₂O afforded green [Tp^{tBu,Me}CrCl] (**2**, 51% yield; Scheme 1). The coordinated pyrazole of **1** most probably originates from some residual pyrazole in the Tp^{tBu,Me}K (coordinated to potassium). In the absence of any known chromium complexes of such sterically hindered tris(pyrazolyl)borate ligands, and as a baseline for structural considerations, the crystal structures of both **1** and **2** were determined by X-ray diffraction; the results are shown in Figures 1 and 2 and selected interatomic distances and angles are listed in Tables 1 and 2.

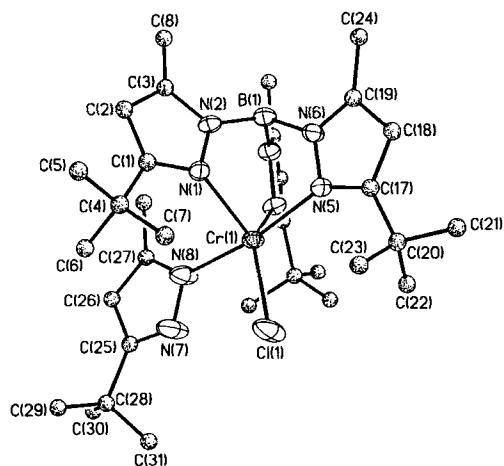


Figure 1. ORTEP diagram of [Tp^{tBu,Me}Cr(3-*tert*-butyl-5-methylpyrazolyl)Cl] (**1**) showing the atom labeling scheme (thermal ellipsoids at 30% probability). The unnumbered pyrazolyl ring follows the same numbering pattern as the numbered ones. Hydrogen atoms are omitted for clarity.

The Tp^{tBu,Me} ligand owes its pseudonym of “tetrahedral enforcer” to the pronounced tendency to produce four-coordinate molecules of more or less distorted tetrahedral geometry.^[8] In contrast, **1** provides a rare example of a true five-coordinate complex of a first-row transition metal with an η³-Tp^{tBu,Me} ligand (other than those containing small bidentate ligands such as

O₂⁻ or NO₃⁻).^[7] The coordination environment around chromium is close to trigonal bipyramidal, with N(5) of the Tp ligand and N(8) of the coordinated pyrazole serving as the axial ligands (N(8)–Cr(1)–N(5), 169.8(2)°); the remaining ligands (N(1), N(3), Cl(1)) define the equatorial plane (sum of angles, 359.6°), although the N(1)–Cr(1)–N(3) angle is constrained to 101.4(2)° by the nature of the Tp ligand. In a notable deviation from established structural principles for trigonal bipyramidal metal complexes,^[11] the most electronegative substituent of **1** (i.e., Cl(1)) occupies an equatorial position, and the axial Cr–N bonds are somewhat shorter—and presumably stronger—than the equatorial ones. We surmise that the relatively large radius of the Cr^{II} ion enables the formation of a five-coordinate complex, while the severe steric interactions between the ligands are responsible for the unusual structural details.

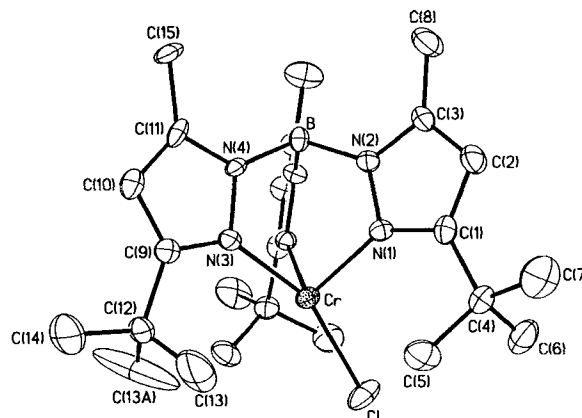


Figure 2. ORTEP diagram of [Tp^{tBu,Me}CrCl] (**2**) showing the atom labeling scheme (thermal ellipsoids at 30% probability). The unnumbered pyrazolyl ring follows the same numbering pattern as the numbered ones. Hydrogen atoms are omitted for clarity.

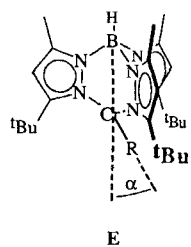
Table 1. Selected interatomic distances (Å) and angles (°) for [Tp^{tBu,Me}Cr(3-*t*Bu,5-MepzH)Cl] (**1**).

Cr(1)–N(1)	2.209(6)	Cr(1)–N(3)	2.181(6)
Cr(1)–N(5)	2.148(6)	Cr(1)–N(8)	2.144(7)
Cr(1)–Cl(1)	2.357(3)		
N(8)–Cr(1)–N(5)	169.8(2)	N(8)–Cr(1)–N(3)	89.3(3)
N(5)–Cr(1)–N(3)	84.4(2)	N(8)–Cr(1)–N(1)	89.5(3)
N(5)–Cr(1)–N(1)	83.8(2)	N(3)–Cr(1)–N(1)	101.4(2)
N(8)–Cr(1)–Cl(1)	85.3(2)	N(5)–Cr(1)–Cl(1)	104.9(2)
N(3)–Cr(1)–Cl(1)	130.8(2)	N(1)–Cr(1)–Cl(1)	127.4(2)

Table 2. Selected interatomic distances (Å) and angles (°) for [Tp^{tBu,Me}CrCl] (**2**). Primed atom labels refer to the second independent molecule in the asymmetric unit.

Cr–N(1)	2.145(6)	Cr–N(1a)	2.145(6)
Cr–N(3)	2.026(8)	Cr–Cl	2.297(3)
Cr–N(1')	2.144(6)	Cr–N(1a')	2.144(6)
Cr–N(3')	2.046(8)	Cr–Cl'	2.290(3)
N(3)–Cr–N(1)	86.2(2)	N(3)–Cr–N(1a)	86.2(2)
N(1)–Cr–N(1a)	102.9(3)	N(3)–Cr–Cl	156.3(2)
N(1)–Cr–Cl	108.1(2)	N(1a)–Cr–Cl	108.1(2)
N(3')–Cr'–N(1')	87.3(2)	N(3')–Cr'–N(1a')	87.3(2)
N(1')–Cr'–N(1a')	101.0(3)	N(3')–Cr'–Cl'	153.8(3)
N(1')–Cr'–Cl'	108.8(2)	N(1a')–Cr'–Cl'	108.8(2)

Compound **2** is indeed a four-coordinate molecule; it sits on a crystallographic mirror plane defined, inter alia, by the boron atom, the pyrazole containing N(3) and N(4), as well as the chromium atom and its chloride ligand. However, the structure also reveals a remarkable distortion from the expected C_{3v} symmetry.



The chloride ligand is positioned far off the threefold axis established by the Tp ligand (i.e., the B–Cr vector, **E**) with $\alpha(\mathbf{2}) = 31.8^\circ$, and approximately *trans* to one of the pyrazole nitrogens (N(3)–Cr–Cl, $156.3(2)^\circ$). We have previously noted similar distortions in cobalt chemistry and traced their electronic origin with the help of EHMO and DFT calculations.^[12] The apparent lack of any steric reasons for the

distortion leaves us to assume an electronic driving force in this instance too; its recurrence in the corresponding organometallic derivatives (see below) establishes a consistent structural phenomenon. A detailed comparison of the structural parameters of **1** and **2** shows slightly shorter bonds overall in **2** ($\Delta(\text{Cr}–\text{Cl})$ 0.02 Å, $\Delta(\text{Cr}–\text{N}_{av})$ 0.06 Å), as expected for a complex of lower coordination number.

Attempts to use **2** and **1** as starting materials for the preparation of chromium alkyls were not successful. Reactions with lithium alkyls or Grignard reagents resulted in extensive decomposition and failed to produce isolable organometallic derivatives. Reasoning that a donor ligand might stabilize coordinatively unsaturated alkyls, but that the active proton of the coordinated pyrazole would interfere with the formation of chromium–carbon bonds, we sought to prepare the analogous pyridine adduct. Addition of 2 equivalents of pyridine followed by 1 equivalent of CrCl_2 to a suspension of $\text{Tp}^{t\text{Bu},\text{Me}}\text{Cr}$ in THF yielded a mixture of **1** and green $[\text{Tp}^{t\text{Bu},\text{Me}}\text{Cr}(\text{py})\text{Cl}]$ (**3**) in 15% and 65% isolated yields, respectively. The two complexes were easily separated by means of their different solubilities. Interestingly, the presence of an excess of pyridine did not prevent the formation of pyrazole complex **1**, and its persistence suggested that pyrazole is a better ligand for chromium than pyridine. Indeed, pure **3** reacted quantitatively with free 3-*tert*-butyl-5-methylpyrazole to form **1** and free pyridine. One reason for the greater stability of **1** may be the formation of a $\text{N}–\text{H}\cdots\text{Cl}$ hydrogen bond, as indicated by a broad $\nu_{\text{N}–\text{H}}$ at $\approx 3200\text{ cm}^{-1}$. Based on the similarity of their spectroscopic properties, we presume that the molecular structures of **3** and **1** are also closely related.

Reactions of **3** with various Grignard reagents afforded a series of chromium alkyls of the general type $[\text{Tp}^{t\text{Bu},\text{Me}}\text{CrR}]$ in reasonable yields (54–67%, see Scheme 1). These light blue compounds were very air-sensitive, but thermally stable for prolonged periods at ambient temperature. Two of the compounds, namely **4** and **5**, were structurally characterized by X-ray diffraction; their molecular structures are depicted in Figures 3 and 4, and selected interatomic distances and angles are listed in Tables 3 and 4. Both **4** and **5** are four-coordinate molecules; their structures are similar and related to that of **2**. Specifically, they feature the same distortion from C_{3v} symmetry toward a geometry that is best described as a “*cis*-divacant octahedron”, that is, a structure derived from an octahedron by removal of two ligands *cis* to each other. However, for the organometallic

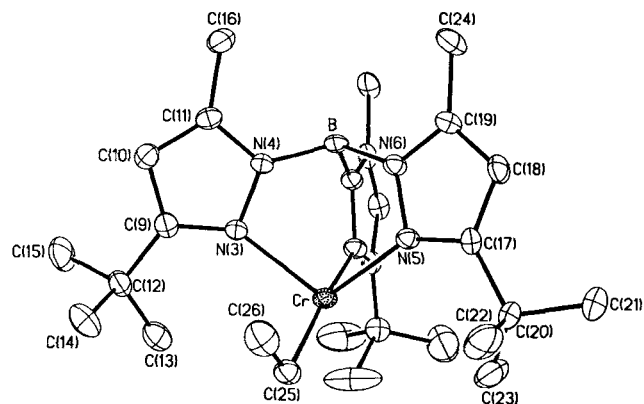


Figure 3. ORTEP diagram of $[\text{Tp}^{t\text{Bu},\text{Me}}\text{CrEt}]$ (**4**) showing the atom labeling scheme (thermal ellipsoids at 30% probability). The unnumbered pyrazolyl ring follows the same numbering pattern as the numbered ones. Hydrogen atoms are omitted for clarity.

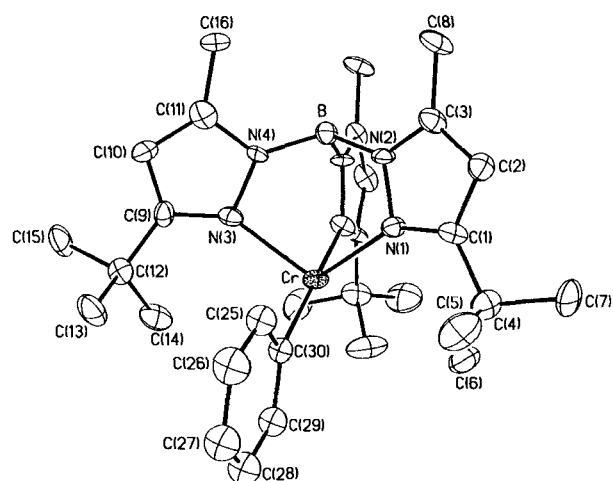


Figure 4. ORTEP diagram of $[\text{Tp}^{t\text{Bu},\text{Me}}\text{CrPh}]$ (**5**) showing the atom labeling scheme (thermal ellipsoids at 30% probability). The unnumbered pyrazolyl ring follows the same numbering pattern as the numbered ones. Hydrogen atoms are omitted for clarity.

Table 3. Selected interatomic distances (Å) and angles ($^\circ$) for $[\text{Tp}^{t\text{Bu},\text{Me}}\text{CrEt}]$ (**4**).

Cr–N(1)	2.122(4)	Cr–N(3)	2.157(4)
Cr–N(5)	2.153(4)	Cr–C(25)	2.111(5)
C(25)–C(26)	1.531(6)		
N(1)–Cr–N(3)	83.7(2)	N(1)–Cr–N(5)	84.83(14)
N(5)–Cr–N(3)	107.4(2)	C(25)–Cr–N(1)	168.8(2)
C(25)–Cr–N(3)	99.7(2)	C(25)–Cr–N(5)	104.1(2)
C(26)–C(25)–Cr	116.3(3)		

Table 4. Selected interatomic distances (Å) and angles ($^\circ$) for $[\text{Tp}^{t\text{Bu},\text{Me}}\text{CrPh}]$ (**5**).

Cr–N(1)	2.128(8)	Cr–N(3)	2.124(8)
Cr–N(5)	2.098(7)	Cr–C(30)	2.129(5)
N(3)–Cr–N(1)	107.5(3)	N(5)–Cr–N(1)	86.1(3)
N(5)–Cr–N(3)	85.1(3)	C(30)–Cr–N(1)	100.2(3)
N(3)–Cr–C(30)	96.4(3)	N(5)–Cr–C(30)	172.8(3)
C(29)–C(30)–Cr	124.8(4)	C(25)–C(30)–Cr	115.2(4)

derivatives the distortion is even more pronounced, as indicated by the deviation of the chromium-bound carbon atom from the B–Cr axis ($\alpha(\mathbf{4}) = 44.2^\circ$ and $\alpha(\mathbf{5}) = 49.2^\circ$) and its near-perfect *trans* relationship to one of the pyrazolyl nitrogens (**4**: N(1)–Cr–C(25) $168.8(2)^\circ$; **5**: N(5)–Cr–C(30) $172.8(3)^\circ$). Another notable

feature is the absence of any indication of an agostic Cr-H-C interaction in these electronically unsaturated 12-electron complexes.^[13] Thus, the ethyl ligand of **4** is actually turned away from the empty coordination sites of the metal, and the bond angle at the α -carbon (Cr-C(25)-C(26) 116.3(3)°) is larger than the tetrahedral value. All of these features leave the four-coordinate complexes poised, both electronically and sterically, to add another ligand.

The two canonical structures of four-coordinate molecules are tetrahedral and square planar configurations. The *cis*-divacant octahedral geometry adopted by **4** and **5**, and to a lesser degree by **2**, is essentially unknown in transition-metal chemistry,^[14] and an explanation for its occurrence in this particular instance is needed. While the majority of four-coordinate complexes of divalent chromium have square planar structures, that choice is obviously not available to tris(pyrazolyl)borate complexes, because of the tripod nature of the Tp ligand. However, a hypothetical tetrahedral complex with a high-spin d^4 electronic configuration would be subject to a Jahn–Teller distortion. Even taking into account the trigonal distortion of an ideal tetrahedron into the C_{3v} structure of a typical TpMX complex (the N–M–N angles are diminished from the tetrahedral value), which partially removes the degeneracy of the t_2 levels, would not suffice to remove the electronic degeneracy. Still searching for stabilization, the molecule must further lower its symmetry, and its only remaining choice is the movement of the fourth ligand off the threefold axis.

An alternative rationalization can be given in terms of crystal field stabilization energies (CFSE). For a high-spin d^4 complex both square planar and *cis*-divacant octahedral geometries provide more CFSE than the tetrahedral structure.^[15] However, as noted above, square planar coordination is not possible with the Tp ligand, thus leaving the observed structure as the most stable alternative. The energetic stabilization attendant upon moving the fourth ligand away from the threefold axis can also be traced in a Walsh diagram. We have carried out such an analysis (at the EHMO level) for the closely related TpCoI.^[12] Population of the levels of this diagram with the appropriate number of electrons clearly shows the driving force for the distortion observed for TpCrX. We conclude that a variety of theoretical models of inorganic stereochemistry can be used to rationalize the unusual structural preference of this set of compounds. Whatever the cause, these complexes are uniquely suited for our purpose, in that they are mononuclear, coordinatively unsaturated Cr^{II} alkyls with an obvious site for coordination of another ligand (e.g. ethylene monomer).

Physical Properties and Reactivity: Complexes **1–6** are light blue or green solids featuring one broad absorption in the visible region of the spectrum (λ_{\max} : 693–804 nm). They are paramagnetic, and their effective magnetic moments (μ_{eff} (RT): 4.7–5.2 μ_B) are consistent with the four unpaired electrons expected of high-spin Cr^{II}. Likewise, ¹H NMR spectra of these complexes exhibit broad and isotropically shifted resonances. However, for isostructural complexes the chemical shifts of the Tp^{tBu,Me} ligand remain roughly constant. For example, the *tert*-butyl groups of all the four-coordinate molecules resonate in the range $\delta = 4.6–9.0$, the 5-methyl substituents appear in the range $\delta = 48.0–55.3$, and the pyrazole hydrogens are found in

the interval $\delta = 12.0–18.4$. The resonances of the alkyl ligands were only partially observable. Thus **6** exhibited a large peak at $\delta = -1.5$, which was assigned to the trimethylsilyl group. The relatively small intensities of the phenyl resonances of **5** made their unambiguous assignment in the ¹H NMR spectrum difficult. However, a ²H NMR spectrum of [D₅]5, with all positions on the phenyl ligand deuterated, revealed three resonances at $\delta = -184$ (*ortho*), 21 (*meta*), and -103 (*para*). It has been noted that ²H NMR spectra of deuterium-labeled paramagnetic complexes exhibit significantly smaller linewidths than ¹H NMR spectra of unlabeled analogues.^[16] This phenomenon, combined with the absence of interfering Tp ligand resonances from the ²H NMR spectrum, permitted the identification of all the phenyl resonances of **5**. The assignments of the *ortho* and *meta* protons are based on the greater linewidth and isotropic shift of the resonance at $\delta = -184$, both of which are presumably due to the closer proximity of the *ortho* protons to the metal-based unpaired spins. Furthermore, this particular assignment is consistent with the characteristic alternation of upfield and downfield shifts exhibited by protons attached to an aromatic ring transmitting the Fermi contact shift by π spin density delocalization.^[17]

True to their nature as both Cr^{II} compounds and metal alkyls, **4–6** are very sensitive to air and moisture, decomposing rapidly on exposure to either. However, when protected from these agents, the complexes are stable for prolonged periods at ambient temperature, both in the solid state and in solution. The coordinatively unsaturated nature of the four-coordinate metal alkyls leads to the ready addition of certain Lewis bases. For example, addition of one equivalent of pyridine to solutions of **4–6** resulted in an immediate color change to red-brown, and standard workup yielded the corresponding pyridine adducts [Tp^{tBu,Me}Cr(py)R] (**7**, R = Et; **8**, R = CH₂SiMe₃; **9**, R = Ph) as brown solids in reasonable yields. Given the stability of these complexes, it might seem surprising that they are not formed during the alkylation of **3**; however, we presume that the nascent magnesium halide (MgCl₂) formed in this reaction abstracts the pyridine from the chromium and effectively removes it from solution. The ¹H NMR spectra of **7–9** feature Tp-ligand resonances, which are similar to those of five-coordinate **1** and **3** and significantly different from those of their precursors. From this observation and their chemical composition, we assume that the molecular structures of these base adducts are closely related to that of **1** (see Figure 1).

A prime motivation for the preparation of the complexes described herein was the question as to *whether coordinatively unsaturated chromium(II) alkyls lacking any metal–metal interactions would polymerize olefins*. Therefore, the catalytic activity of **4–6** with respect to ethylene polymerization was tested. When a [D₆]benzene solution of **4** at ambient temperature was exposed to an excess of ethylene (1 atm), no reaction was observed (no apparent precipitate of polyethylene). The ¹H NMR spectrum of the solution recorded after 30 min showed the unperturbed resonances of **4** and free ethylene. Heating of the solution did not produce any polymer; however, spectroscopic monitoring revealed the onset of decomposition of **4**. In an attempt to ascertain the effect of elevated ethylene pressure, pentane solutions of **4–6** (≈ 0.02 M) were placed in an autoclave and pressurized with ethylene to 35 atm. After 1 hour at room

temperature, the autoclave was opened, but no polyethylene formation was observed. On the basis of these experiments, we can rule out any ethylene polymerization activity of **4–6** alone in homogeneous solution.

We have previously shown that coordinatively unsaturated chromium(III) alkyls containing the Cp*Cr moiety catalyze the polymerization of ethylene.^[3] A direct comparison of the reactivity of isostructural TpCr alkyls in the +II and +III oxidation states would be informative vis-à-vis the rampant speculation regarding the valence state of catalyst active sites. For this reason, we attempted to oxidize complexes **4–6** to isostructural complexes of the type $[\text{Tp}^{\text{tBu,Me}}\text{Cr}^{\text{III}}\text{R}]^+\text{X}^-$. For example, addition of one equivalent of $[\text{Cp}_2\text{Fe}][\text{BPh}_4]$ to a THF solution of **4** resulted in a color change from blue to yellow. Extraction of the solid residue with toluene effected the removal of Cp₂Fe and left a blue solid. Recrystallization of the latter from THF/pentane gave blue crystals of $[\text{Tp}^{\text{tBu,Me}}\text{Cr}(\text{thf})][\text{BPh}_4]$ (**10**) in good yield. Similar oxidation of **5** and **6** produced the same compound. Apparently the product of oxidation, $[\text{Tp}^{\text{tBu,Me}}\text{Cr}]^+$, is not stable and decomposes by loss of the alkyl ligand. This result is somewhat surprising in light of the ready accessibility and stability of a wide variety of Cp*Cr^{III} alkyls; however, for the time being we must forgo an appraisal of the polymerization activity of trivalent chromium alkyls coordinated by Tp ligands. We are pursuing various avenues to stabilize $\text{Tp}^{\text{tBu,Me}}\text{Cr}$ alkyls in higher oxidation states, and the results of these experiments will be described in due course.

Conclusions

The use of a sterically hindered tris(pyrazolyl)borate ligand of the “tetrahedral enforcer” variety has enabled the synthesis of coordinatively unsaturated chromium(II) alkyls in a relatively hard coordination environment. Despite their electron deficiency (12-electron configurations!) these molecules are unable to engage in metal–metal bonding. They adopt highly unusual “*cis*-divacant octahedral” structures, which leave open two coordination sites for binding of further ligands. The apparent stability of $[\text{Tp}^{\text{tBu,Me}}\text{CrEt}]$ suggests that β -hydrogen elimination is not a facile process in this system. Despite these auspicious features, the alkyls fail to catalyze the polymerization of ethylene. Thus they provide the strongest empirical evidence yet for our assertion that divalent chromium is not responsible for the activity of commercial olefin polymerization catalysts containing chromium.

Experimental Section

General Techniques: All manipulations of compounds were carried out by standard Schlenk, vacuum, and glove-box techniques. Pentane, diethyl ether, tetrahydrofuran and toluene were distilled from purple Na–benzophenone/ketyl solutions. C₆H₆, C₆D₆, and [D₈]THF were all predried with Na and stored under vacuum over Na/K alloy. Pyridine was dried with CaH₂ and vacuum distilled over 4 Å molecular sieves. CrCl₂ was purchased from Strem; Grignard reagents were purchased from Aldrich and were titrated with diphenylacetic acid prior to use. $\text{Tp}^{\text{tBu,Me}}\text{K}$ was prepared according to literature procedures.^[9] CP grade ethylene was purified with a column of MnO and 4 Å molecular sieves. ¹H NMR spectra were taken on Bruker AM250 or WM250 spectrometers. ²H NMR spectra were recorded on the

Bruker WM250 spectrometer, with a 10 mm broad band probe tuned to the ²H resonance frequency. FTIR spectra were recorded on a Mattson Alpha Centauri spectrometer with a resolution of 4 cm⁻¹. Mass spectra were obtained by the University of Delaware Mass Spectrometry Facility. Elemental analyses were performed by Oncida Research Services, Whitesboro, N. Y. 13492. Note that the elemental analyses of these complexes frequently resulted in low and irreproducible nitrogen values, despite extensive purification and repeated analyses. This may be a result of formation of chromium nitride during the combustion; in any case, NMR spectroscopy served as a better indicator of sample purity. Room-temperature magnetic susceptibilities were determined with a Johnson Matthey Magnetic Susceptibility Balance, which utilizes a modification of the Gouy method. Molar magnetic susceptibilities were corrected for diamagnetism with Pascal's constants.

[$\text{Tp}^{\text{tBu,Me}}\text{Cr}(\text{3-tert-butyl-5-methylpyrazole})\text{Cl}$] (1**) and [$\text{Tp}^{\text{tBu,Me}}\text{CrCl}$] (**2**):** $\text{Tp}^{\text{tBu,Me}}\text{K}$ (330 mg, 0.714 mmol) was suspended in THF (25 mL). CrCl₂ (87 mg, 0.711 mmol) was added to the resulting solution with vigorous stirring. After 3 h the turquoise reaction mixture was filtered. The solvent was removed in vacuo, and the residue was dissolved in toluene. Insoluble solids were removed by filtration, and solvent evaporation yielded a blue residue which was extracted with 60 mL pentane. Filtration of the extracts yielded a blue solution and an insoluble pale green solid. Evaporation of the blue solution gave 91 mg (0.140 mmol, 20%) of sky-blue **1** after drying in vacuo. Recrystallization of **1** from pentane gave crystals suitable for X-ray analysis. ¹H NMR ([D₆]benzene): $\delta = -23.0$ (br, 1H), -3.1 (br, 1H), 2.0 (br, 9H), 11.0 (br, 27H), 19.2 (br, 3H), 35.9 (br, 9H), 47.8 (br, 3H); IR (KBr): $\tilde{\nu} = 3206$ (m), 2960 (s), 2929 (s), 2866 (m), 2541 (m), 1557 (m), 1543 (s), 1272 (s), 1224 (s), 1356 (s), 1194 (s), 1130 (w), 1100 (w), 1069 (s), 785 (s), 701 (m), 644 (m), 519 (w), 501 (w), 445 (w), 419 (w) cm⁻¹; MS: m/z (%) = 510 (100.0), 123 (79.0), 511 (43.6), 512 (37.1), 509 (16.1); UV/Vis (THF): $\lambda = 781$ nm ($\epsilon = 59 \text{ M}^{-1} \text{ cm}^{-1}$); m.p. = 187.5–189.0 °C; $\mu_{\text{eff}} = 4.9 \mu_{\text{B}}$ (293 K); C₃₂H₅₄BClCrN₈ (649.1): calcd C 59.21, H 8.39, N 17.26; found C 59.82, H 7.52, N 12.42. Extraction of the pale green solid (see above) with diethyl ether, followed by filtration and solvent removal, gave a powder which was dried in vacuo to yield 184 mg (0.360 mmol, 51%) of pale green **2**. Slow evaporation of diethyl ether from solution gave crystals suitable for X-ray crystallographic analysis. ¹H NMR ([D₆]benzene): $\delta = 56.21$ (br, 9H), 12.02 (br, 3H), 14.4–3.5 (vbr, 27H); IR (KBr): $\tilde{\nu} = 2960$ (s), 2930 (s), 2907 (s), 2867 (m), 2543 (m), 1541 (s), 1505 (m), 1471 (s), 1425 (s), 1382 (m), 1362 (s), 1338 (m), 1280 (w), 1240 (m), 1184 (s), 1123 (w), 1103 (w), 1063 (s), 1028 (m), 984 (m), 868 (w), 855 (w), 841 (w), 808 (m), 785 (s), 763 (m), 728 (w), 680 (w), 666 (w), 643 (m), 520 (w), 445 (w) cm⁻¹; MS: m/z (%) = 123 (77.4), 138 (14.1), 161 (10.7), 509 (15.4), 510 (100.0), 511 (38.7), 512 (42.5); UV/Vis (Et₂O): $\lambda = 817$ nm ($\epsilon = 162 \text{ M}^{-1} \text{ cm}^{-1}$); m.p. = 290 °C; $\mu_{\text{eff}} = 5.0(1) \mu_{\text{B}}$ (293 K); C₂₄H₄₀BClCrN₆ (510.9): calcd C 56.42, H 7.89, N 16.45; found C 57.27, H 7.94, N 14.14.

[$\text{Tp}^{\text{tBu,Me}}\text{Cr}(\text{py})\text{Cl}$] (3**) and [$\text{Tp}^{\text{tBu,Me}}\text{Cr}(3\text{-tBu-5-Me-pzH})\text{Cl}$] (**1**):** $\text{Tp}^{\text{tBu,Me}}\text{K}$ (3.24 g, 7 mmol) was suspended in THF (100 mL). Pyridine (1.13 mL, 14 mmol) followed by CrCl₂ (0.72 g, 5.85 mmol) was added to the stirred suspension. The grey suspension turned green after ca. 30 min. The mixture was stirred for 3 h at room temperature; the solvent was evaporated in vacuo and the solid residue was extracted twice with pentane (30 mL). Evaporation of the blue solution yielded a blue solid, which was recrystallized from pentane at -30 °C. The crystallization yielded blue crystals of **1**; yield: 0.649 g (15%). After extraction with pentane the solid residue was extracted several times with ether (60 mL). Evaporation of the green solution and recrystallization from ether yielded green solid [$\text{Tp}^{\text{tBu,Me}}\text{Cr}(\text{py})\text{Cl}$] (**3**). Yield: 2.24 g (65%). ¹H NMR ([D₈]THF): $\delta = -39.8$ (br, 1H), 11.3 (br, 27H), 16.3 (br, 3H), 34.7 (br, 9H), 47.0 (br, 2H); IR (KBr): $\tilde{\nu} = 2960$ (s), 2929 (s), 2866 (s), 2541 (m), 1604 (m), 1543 (s), 1472 (s), 1356 (s), 1331 (s), 1224 (m), 1194 (s), 1069 (s), 1016 (m), 855 (w), 785 (w), 701 (m), 644 (m) cm⁻¹; MS: m/z (%) = 510 (100.0), 511 (45.8), 512 (41.4), 79 (27.0), 509 (25.1), 52 (14.3); UV/Vis (THF): 804 nm ($\epsilon = 70 \text{ M}^{-1} \text{ cm}^{-1}$); m.p. = 283 °C; $\mu_{\text{eff}} = 5.2 \mu_{\text{B}}$ (293 K); C₂₉H₄₅BClCrN₇ (590.0): calcd C 59.04, H 7.69, N 16.62; found C 58.61, H 7.47, N 16.30.

Hydrotris(3-tert-butyl-5-methylpyrazolyl)boratoethylchromium(II)

($[\text{Tp}^{\text{tBu,Me}}\text{CrEt}]$, **4**): $[\text{Tp}^{\text{tBu,Me}}\text{CrCl}(\text{py})]$ (0.500 g, 0.85 mmol) was dissolved in ether (50 mL) and the solution was cooled to -30 °C. 0.425 mL of a solution of C₂H₅MgCl in Et₂O (2.0 M, 0.85 mmol) was added dropwise to the cooled solution. The solution changed color to blue immediately and a white solid

precipitated. The solvent was removed in vacuo and the solid residue was extracted three times with pentane (20 mL). The blue solution was evaporated and the blue solid recrystallized from pentane at -30°C to yield blue crystals of $[\text{Tp}^{\text{Bu},\text{Me}}\text{CrC}_2\text{H}_5]_2$; yield: 0.287 g (67%). $^1\text{H NMR}$ ($[\text{D}_6]$ benzene): $\delta = 4.7$ (br, 27H), 18.3 (br, 3H), 50.1 (br, 9H); IR (KBr): $\tilde{\nu} = 2951$ (s), 2865 (s), 2541 (m), 1541 (s), 1472 (m), 1430 (s), 1359 (s), 1241 (m), 1181 (s), 1060 (s), 1022 (m), 985 (m), 785 (s), 645 (s), 446 (cm^{-1}); MS: m/z (%) = 123 (100.0), 287 (76.3), 95 (30.4), 475 (19.6), 424 (15.5); UV/Vis (THF): $\lambda = 707$ nm ($\epsilon = 140 \text{ M}^{-1} \text{ cm}^{-1}$); m.p. = 126°C (decomp); $\mu_{\text{eff}} = 5.0 \mu_{\text{B}}$ (293 K); $\text{C}_{26}\text{H}_{45}\text{BCrN}_6$ (504.5): calcd C 61.90, H 8.99, N 16.66; found C 61.93, H 8.64, N 16.53.

Hydrotris(3-*tert*-butyl-5-methylpyrazolyl)boratophenylchromium(II)

($[\text{Tp}^{\text{Bu},\text{Me}}\text{CrPh}]$, **5**): $[\text{Tp}^{\text{Bu},\text{Me}}\text{CrCl}(\text{py})]$ (0.500 g, 0.85 mmol) was dissolved in ether (50 mL). The solution was cooled to -30°C . 0.28 mL of a solution of $\text{C}_6\text{H}_5\text{MgBr}$ in Et_2O (3.0 M, 0.85 mmol) was added dropwise to the cooled solution. The solution immediately changed color to blue and a white solid precipitated. The solvent was removed in vacuo and the solid residue was extracted three times with pentane (20 mL). The blue solution was evaporated and the blue solid recrystallized from pentane at -30°C to yield blue crystals of $[\text{Tp}^{\text{Bu},\text{Me}}\text{CrPh}]$; yield: 0.310 g (66%). $^1\text{H NMR}$ ($[\text{D}_6]$ benzene): $\delta = -102.2$ (br, 1H), 7.4 (br, 27H), 18.7 (br, 5H), 52.9 (br, 9H); IR (KBr): $\tilde{\nu} = 3040$ (m), 2960 (s), 2864 (s), 2538 (s), 1540 (s), 1470 (s), 1430 (s), 1360 (s), 1241 (m), 1184 (s), 1119 (m), 1060 (s), 985 (m), 785 (s), 702 (s), 651 (cm^{-1}); MS: m/z (%) = 474 (100.0), 475 (79.2), 473 (37.9), 337 (31.1), 552 (26.7); UV/Vis (THF): $\lambda = 692$ nm ($\epsilon = 130 \text{ M}^{-1} \text{ cm}^{-1}$); m.p. = 192°C ; $\mu_{\text{eff}} = 4.9 \mu_{\text{B}}$ (293 K); $\text{C}_{30}\text{H}_{42}\text{BCrN}_6$ (552.5): C 65.21, H 8.21, N 15.21; found C 64.89, H 8.26, N 14.45.

Hydrotris(3-*tert*-butyl-5-methylpyrazolyl)borato- $[\text{D}_3]$ phenylchromium(II)

($[\text{Tp}^{\text{Bu},\text{Me}}\text{CrC}_6\text{D}_5]$, $[\text{D}_3]$): $[\text{Tp}^{\text{Bu},\text{Me}}\text{CrCl}(\text{py})]$ (0.500 g, 0.85 mmol) was dissolved in ether (50 mL) and the solution was cooled to -30°C . A solution of $\text{C}_6\text{D}_5\text{MgBr}$ in Et_2O (1.70 mL, 0.5 M, 0.85 mmol) was added dropwise to the cooled solution. The solution changed color to blue immediately and a white solid precipitated. The solvent was removed in vacuo and the solid residue was extracted three times with pentane (20 mL). The blue solution was evaporated and the blue solid recrystallized from pentane at -30°C to yield blue crystals of $[\text{Tp}^{\text{Bu},\text{Me}}\text{CrC}_6\text{D}_5]$; yield: 0.320 g (67%). $^1\text{H NMR}$ ($[\text{D}_6]$ benzene): $\delta = 4.0$ (br, 27H), 18.4 (br, 3H), 52.4 (br, 9H); $^2\text{H NMR}$ (C_6H_6): $\delta = -183.8$ (br, 2H), -102.9 (br, 1H), 21.0 (br, 2H); IR (KBr): $\tilde{\nu} = 2960$ (s), 2864 (s), 2538 (m), 2254 (m), 1540 (s), 1469 (s), 1431 (s), 1360 (s), 1241 (m), 1192 (s), 1119 (m), 1060 (s), 1029 (m), 985 (m), 792 (s), 639 (m), 535 (cm^{-1}); MS: m/z (%) = 474 (100.0), 475 (72.3), 169 (56.9), 83 (56.6), 123 (32.2).

Hydrotris(3-*tert*-butyl-5-methylpyrazolyl)boratotrimethylsilylmethyl-

chromium(II) ($[\text{Tp}^{\text{Bu},\text{Me}}\text{CrCH}_2\text{SiMe}_3]$, **6**): $[\text{Tp}^{\text{Bu},\text{Me}}\text{CrCl}(\text{py})]$ (0.500 g, 0.85 mmol) was dissolved in ether (50 mL) and the solution was cooled to -30°C . A solution of $(\text{CH}_3)_3\text{SiCH}_2\text{MgCl}$ in Et_2O (0.85 mL, 1.0 M, 0.85 mmol) was added dropwise to the cooled solution. The solution changed color to blue-green after 5 min and a white solid precipitated. The solvent was removed in vacuo, and the solid residue was extracted three times with pentane (20 mL). The blue solution was evaporated and the blue-green solid recrystallized from pentane at -30°C to yield blue-green crystals of $[\text{Tp}^{\text{Bu},\text{Me}}\text{CrCH}_2\text{SiMe}_3]$; yield: 0.258 g (54%). $^1\text{H NMR}$ ($[\text{D}_6]$ benzene): $\delta = -1.5$ (br, 9H), 4.6 (br, 27H), 15.4 (br, 3H), 48.0 (br, 9H); IR (KBr): $\tilde{\nu} = 2959$ (s), 2864 (s), 2545 (m), 1540 (s), 1459 (m), 1457 (s), 1361 (m), 1247 (m), 1241 (w), 1194 (s), 1061 (m), 1029 (w), 985 (w), 858 (m), 784 (m), 734 (cm^{-1}); MS: m/z (%) = 73 (100.0), 475 (88.2), 123 (50.0), 476 (40.6), 474 (40.0); UV/Vis (THF): $\lambda = 752$ nm ($\epsilon = 164 \text{ M}^{-1} \text{ cm}^{-1}$); m.p. = 131°C (decomp); $\mu_{\text{eff}} = 4.6 \mu_{\text{B}}$ (293 K); $\text{C}_{28}\text{H}_{51}\text{BCrN}_6\text{Si}$ (562.7): calcd C 59.77, H 9.14, N 14.94; found C 58.56, H 8.82, N 14.46.

Hydrotris(3-*tert*-butyl-5-methylpyrazolyl)boratoethylpyridinechromium(II)

($[\text{Tp}^{\text{Bu},\text{Me}}\text{Cr}(\text{py})\text{Et}]$, **7**): Pyridine (6.1 μL , 0.076 mmol) was added to a solution of $[\text{Tp}^{\text{Bu},\text{Me}}\text{CrEt}]$ (0.038 g, 0.076 mmol) in pentane (10 mL). The solution immediately turned brown. Evaporation of solvent and recrystallization of the solid residue from pentane gave orange-brown crystals of $[\text{Tp}^{\text{Bu},\text{Me}}\text{Cr}(\text{py})\text{Et}]$ in 61% yield (0.027 mg). $^1\text{H NMR}$ ($[\text{D}_6]$ benzene): $\delta = -44.0$ (br, 1H), 1.0 (br, 2H), 6.8 (br, 27H), 12.4 (br, 3H), 34.5 (br, 9H); IR (KBr): $\tilde{\nu} = 3111$ (w), 2957 (s), 2982 (s), 2459 (m), 2279 (w), 1604 (m), 1543 (s), 1475 (s), 1431 (s), 1359 (s), 1194 (s), 1072 (s), 975 (m), 924 (w),

845 (w), 782 (s), 700 (s), 633 (m), 547 (w), 517 (m), 447 (cm^{-1}); MS: m/z (%) = 476 (22.3), 475 (36.4), 123 (100.0), 79 (46.6), 52 (38.5).

Hydrotris(3-*tert*-butyl-5-methylpyrazolyl)boratophenylpyridinechromium(II)

($[\text{Tp}^{\text{Bu},\text{Me}}\text{Cr}(\text{py})\text{Ph}]$, **8**): To a solution of $[\text{Tp}^{\text{Bu},\text{Me}}\text{CrPh}]$ (0.050 g, 0.091 mmol) in 10 mL pentane was added pyridine (7.3 μL , 0.091 mmol). The solution immediately turned brown. Evaporation of solvent and recrystallization of the solid residue from pentane gave orange-brown crystals of $[\text{Tp}^{\text{Bu},\text{Me}}\text{Cr}(\text{py})\text{Ph}]$ in 49% yield (0.028 g). $^1\text{H NMR}$ ($[\text{D}_6]$ benzene): $\delta = -86.5$ (br, 1H), -2.0 (br, 2H), 9.7 (br, 27H), 13.1 (br, 3H), 37.9 (br, 9H); IR (KBr): $\tilde{\nu} = 3375$ (w), 3033 (m), 2958 (s), 2905 (s), 2864 (m), 2541 (m), 2511 (m), 1602 (m), 1542 (s), 1506 (m), 1467 (m), 1443 (s), 1422 (s), 1354 (s), 1239 (m), 1194 (s), 1069 (s), 1025 (w), 979 (m), 840 (w), 784 (s), 702 (m), 644 (m), 518 (w), 457 (cm^{-1}); MS: m/z (%) = 475 (100.0), 281 (51.8), 169 (81.9), 79 (61.3).

Hydrotris(3-*tert*-butyl-5-methylpyrazolyl)boratotrimethylsilylmethylpyridine-

chromium(II) ($[\text{Tp}^{\text{Bu},\text{Me}}\text{Cr}(\text{py})\text{CH}_2\text{SiMe}_3]$, **9**): Pyridine (5.4 μL , 0.067 mmol) was added to a solution of $[\text{Tp}^{\text{Bu},\text{Me}}\text{CrCH}_2\text{SiMe}_3]$ (0.038 g, 0.068 mmol) in pentane (10 mL). The solution immediately turned brown. Evaporation of solvent and recrystallization of the solid residue from pentane gave red-brown crystals of $[\text{Tp}^{\text{Bu},\text{Me}}\text{Cr}(\text{py})\text{CH}_2\text{SiMe}_3]$ in 35% yield (0.015 mg). $^1\text{H NMR}$ ($[\text{D}_6]$ benzene): $\delta = -1.0$ (br, 9H), 9.0 (br, 27H), 10.5 (br, 1H), 34.2 (br, 3H), 44.5 (br, 9H), 48.0 (br, 2H); IR (KBr): $\tilde{\nu} = 3110$ (w), 2958 (s), 2906 (s), 2865 (m), 2548 (w), 2462 (m), 1604 (m), 1544 (s), 1480 (s), 1444 (s), 1424 (s), 1358 (s), 1238 (m), 1196 (s), 1071 (s), 1027 (m), 987 (m), 906 (w), 854 (s), 795 (s), 728 (m), 701 (s), 674 (m), 633 (m), 519 (w), 434 (cm^{-1}); MS: m/z (%) = 475 (15.2), 138 (10.7), 123 (42.3), 79 (70.5), 73 (100.0).

Hydrotris(3-*tert*-butyl-5-methylpyrazolyl)boratotetrahydrofuranchromium(II)

tetraphenylborate ($[\text{Tp}^{\text{Bu},\text{Me}}\text{Cr}(\text{thf})\{\text{BPh}_4\}]$, **10**): $[\text{Tp}^{\text{Bu},\text{Me}}\text{CrEt}]$ (200 mg, 0.397 mmol) and $[\text{Cp}_2\text{Fe}\{\text{BPh}_4\}]$ (176 mg, 0.349 mmol) were placed in a flask, to which THF (10 mL), which had been cooled to -30°C , was added. The suspension was stirred for 20 min, while its color changed from green-blue to dark yellow. The THF was removed in vacuo and the solid residue washed several times with toluene until the washings remained colorless. The blue solid was recrystallized from THF/pentane at -30°C . It yielded 202 mg (72%) of $[\text{Tp}^{\text{Bu},\text{Me}}\text{Cr}(\text{thf})\{\text{BPh}_4\}]$. $^1\text{H NMR}$ ($[\text{D}_8]$ THF): $\delta = 7.7$, 7.1 (20H), 13.3 (br, 27H), 38.4 (br, 9H); IR (KBr): $\tilde{\nu} = 3121$ (w), 3052 (s), 3037 (s), 2964 (s), 2865 (s), 2804 (s), 2543 (m), 1579 (s), 1540 (s), 1475 (s), 1426 (s), 1363 (s), 1240 (m), 1178 (s), 1061 (s), 1031 (s), 920 (m), 791 (s), 704 (s), 640 (s), 612 (s), 522 (m), 477 (cm^{-1}); UV/Vis (THF): $\lambda = 698$ nm ($\epsilon = 25.4 \text{ M}^{-1} \text{ cm}^{-1}$); m.p. = 183°C ; $\mu_{\text{eff}} = 5.2 \mu_{\text{B}}$ (293 K); $\text{C}_{52}\text{H}_{66}\text{B}_2\text{CrN}_6\text{O}$ (866.8): calcd C 72.06, H 7.91, N 9.70; found C 71.62, H 7.98, N 9.69.

Crystallographic Structure Determinations: Crystal, data collection, and refinement parameters are given in Table 5. Suitable crystals for single-crystal X-ray diffraction were selected and mounted in nitrogen-flushed, thin-walled capillaries, which were flame-sealed. All specimens of these compounds diffracted weakly and broadly. The unit-cell parameters were obtained by the least-squares refinement of the angular settings of 24 reflections ($20^{\circ} \leq 2\theta \leq 25^{\circ}$). No evidence of symmetry higher than triclinic was observed in either the photographic or the diffraction data for **1**, **4**, and **5**; photographic data indicated a monoclinic crystal system for **2**, and the systematic absences in the diffraction data indicated the space groups $P2_1$ or $P2_1/m$. The presence of a molecular mirror plane and the value of Z in **2**, along with the E -statistics, suggested the centrosymmetric space-group options for all four structures. The refinement produced chemically reasonable and computationally stable results of refinement. The structures were solved by direct methods, completed by subsequent difference Fourier syntheses and refined by full-matrix least-squares procedures. No absorption corrections were required because there was $<10\%$ variation in the integrated intensities of the ψ -scans. The four *tert*-butyl groups on the pyrazolyl ligands of **1** were fixed as rigid tetrahedra with a common carbon-carbon bond distance. Complex **2** contains two independent but chemically equivalent molecules, each located on a mirror plane. Complex **5** contains one half of an inversionally disordered molecule of pentane in the asymmetric unit at approximately 80% occupancy. The phenyl ring in **4** was fixed as a rigid planar group to conserve data. The carbon atoms of the phenyl ring and the solvent molecule in **5** were refined isotropically. All other non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were treated as idealized contributions, except for those on the disordered solvent molecule in **5**, which

Table 5. Crystallographic data for [Tp^{tBu},MeCr(3-*t*Bu-5-MepzH)Cl] (1), [Tp^{tBu},MeCrCl] (2), [Tp^{tBu},MeCrEt] (4), and [Tp^{tBu},MeCrPh]·0.4C₅H₁₂ (5).

	1	2	4	5
crystal parameters				
formula	C ₃₂ H ₅₄ BClCrN ₈	C ₂₄ H ₄₀ BClCrN ₆	C ₂₆ H ₄₅ BCrN ₆	C ₃₀ H ₄₅ BCrN ₆ ·0.4C ₅ H ₁₂
<i>M_r</i>	685.12	1021.76	504.49	581.39
crystal system	triclinic	monoclinic	triclinic	triclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>m</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> (Å)	11.895(3)	9.614(3)	11.327(4)	11.458(5)
<i>b</i> (Å)	13.815(4)	17.410(4)	11.632(4)	11.949(5)
<i>c</i> (Å)	13.803(4)	17.400(4)	12.799(5)	13.372(5)
α (°)	76.05(2)	—	65.70(3)	98.62(3)
β (°)	88.16(2)	101.91(2)	73.35(3)	107.33(3)
γ (°)	66.22(2)	—	87.06(3)	94.75(3)
<i>V</i> (Å ³)	2009(1)	2850(1)	1468.2(9)	1712(1)
<i>Z</i>	2	4	2	2
crystal dimensions (mm)	0.42 × 0.33 × 0.26	0.51 × 0.27 × 0.22	0.25 × 0.22 × 0.12	0.40 × 0.22 × 0.09
crystal color, habit	blue plate	pale blue block	blue block	blue plate
ρ_{calcd} (g cm ⁻³)	1.133	1.191	1.141	1.128
μ (MoK α), (cm ⁻¹)	3.84	5.17	4.13	3.63
<i>T</i> (K)	255(2)	298(2)	232(2)	225(2)
data collection				
radiation	MoK α (= 0.71073 Å)			
2 θ scan range (°)	4.0–45.0	4.0–48.0	4.0–45.0	4.0–42.0
refl. collected	5505	4200	3805	3916
indep. refl.	5245	4055	3620	3715
indep. obs. refl.	3742	2067	2556	1642
$F_o \geq 4\sigma(F_o)$				
refinement [a]				
<i>R</i> (<i>F</i>) (%)	10.68	7.72	6.09	8.15
<i>R</i> (<i>wF</i> ²) (%)	28.41	11.98	12.08	16.54
<i>N_o</i> / <i>N_c</i>	9.62	6.17	8.32	5.27

[a] $R = \sum \Delta / \sum (F_o)$, $\Delta = |F_o - F_c|$; quantity minimized = $R(wF^2) = \sum [w(F_o^2 - F_c^2)^2] / \sum [(wF_o^2)^2]^{1/2}$.

were ignored. All software and sources of the scattering factors are contained in the SHELXTL (5.3) program library (G. Sheldrick, Siemens XRD, Madison, WI).

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100143. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge, CB21EZ, UK (Fax: Int. code + (1223) 336-033; e-mail: deposit@chemcrs.cam.ac.uk).

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