Dialkylchromium complexes bearing a hydrotris(3,5-dimethylpyrazolyl)borate ligand: synthesis and crystal structures of Tp*CrMe$_2$(DMAP) and Tp*Cr(Cr(CH$_2$Ph)$_2$(DMAP) (DMAP = 4-dimethylaminopyridine)[1]

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Abstract

The synthesis and the crystallographic characterization of two dialkylchromium complexes possessing a Tp* ligand, i.e. Tp*CrMe$_2$(DMAP) (**4**) and Tp*Cr(CH$_2$Ph)$_2$(DMAP) (**5**) (Tp* = hydrotris(3,5-dimethylpyrazolyl)borate; DMAP = 4-dimethylaminopyridine), are described. Treatment of Tp*CrCl$_2$(DMAP) (**3**) with two equivalents of MeLi gave **4**, while the complex **5** was prepared by the reaction of **3** with two equivalents of PhCH$_2$MgCl. These complexes were found to be thermally robust and quite stable to air and moisture. Distorted octahedral geometry around each chromium center of **4** and **5** has been determined by X-ray analysis, the chromium center being surrounded with three nitrogen atoms of the Tp* ligand at facial positions, one nitrogen atom of the DMAP ligand, and two carbon atoms. The two benzyl ligands of **5** were found to coordinate to the chromium center in η^1-fashion. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Chromium; Hydrotris(3,5-dimethylpyrazolyl)borate; Crystal structure; Methyl complex; Benzyl complex

1. Introduction

Chromium based heterogeneous catalysts, such as Phillips catalyst [1] and UCC catalyst [2,3] are commercially applied to olefin polymerization. In spite of practical progress in these process, the oxidation state of the active chromium site and the mechanism of their catalytic systems have not been elucidated. The fundamental research of organochromium complexes has been carried out for this purpose [4–6]. Their paramagnetic nature and high sensitivity to air and moisture, however, have prevented the development of their chemistry [4]; except for some alkylchromium complexes bearing the cyclopentadienyl group or its derivative as an auxiliary ligand [6,7] including chroma-cyclopentane and -cycloheptane [8].

A tAdentate anionic Tp* (= hydrotris(3,5-dimethylpyrazolyl)borate), which is isoelectronic with the cyclopentadienyl ligand, has proven to be an effective ligand for stabilizing various transition metal complexes [9,10]. We anticipated that the sterically hindered coordination environment by the Tp* ligand would be able to serve for stabilizing alkylchromium complexes. Thus, we herein report on the synthesis and the crystal structures of dialkylchromium complexes of the formula Tp*CrR$_2$(DMAP) (**4**: R = Me; **5**: R = CH$_2$Ph; DMAP = 4-dimethylaminopyridine).

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[1] Dedicated to Professor Akira Nakamura for his contribution to organometallic and inorganic chemistry on the occasion of his retirement from Osaka University.

2. Results and discussion

2.1. Synthesis of dialkylchromium complexes bearing a Tp* ligand

Treatment of Tp*CrCl$_2$(THF) (**1**) with two equivalents of methyl lithium in THF resulted in the formation of a red solution, from which any identified product could not be isolated after removal of the volatile materials. It has been reported that dialkylchromium complexes such as Cp*CrMe$_2$(THF) [11] and Cp*Cr(CH$_2$SiMe$_3$)$_2$(THF) [12] were stable in THF, but decomposed during removing THF. It is likely to assume that the above reaction produced Tp*CrMe$_2$(THF) (**2**), but **2** had decomposed during removal of THF. In order to isolate the dimethylchromium complex, a more strongly coordinating ligand might be required. After several attempts, DMAP was consequently found to be a suitable stabilizing ligand . When we chose DMAP as a ligand, the first attempted reaction, addition of one equivalent of DMAP to a reaction mixture of **1** and two equivalents of MeLi in THF, did not afford any dimethyl complex. In contrast, reaction of a dichloro DMAP complex Tp*CrCl$_2$(DMAP) (**3**), derived from **1** and DMAP, with two equivalents of methyl lithium in THF yielded the corresponding dimethylchromium complex Tp*CrMe$_2$(DMAP) (**4**) in 41% yield. These findings suggest that DMAP adduct **3** can be formed readily because of the sufficient Lewis acidity of **1**; however, the coordination of DMAP to a nascent dimethyl species like **2** is assumed to be very slow.

3

4: R = CH$_3$

5: R = CH$_2$Ph
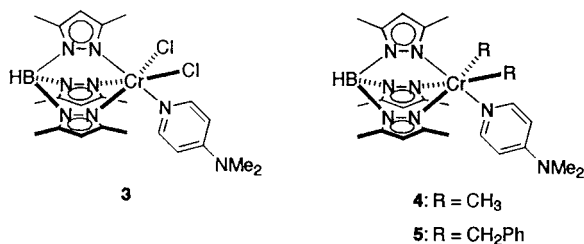
Complex **4** is a paramagnetic species and hence has been characterized by IR spectrum and elemental analysis, and its structure has entirely been determined by X-ray study (vide infra). The IR spectrum of **4** exhibited a B–H stretching absorption at 2510 cm^{-1}, indicating that **4** has a Tp* ligand bound to the chromium atom in a tridentate fashion [13]. It is recently reported that tridentate Tp* transition metal complexes show a B–H band at a higher frequency than 2500 cm^{-1}, while bidentate Tp* complexes show the same band at a lower frequency than 2500 cm^{-1} [13].

It is a notable feature that **4** is air- and moisture-stable and is thermally robust, though several air- and moisture-stable aqua alkylchromium complexes such as [MeCr(H$_2$O)s]$^{2+}$ and [PhCH$_2$Cr(H$_2$O)$_5$]$^{2+}$ have been

reported [14,15]. This is in sharp contrast to air- and moisture-sensitivity of organochromium complexes such as Cp*CrMe$_2$(THF) [11], Cp*Cr(CH$_2$SiMe$_3$)$_2$ (THF) [12], and [CpCrMe(μ-Cl)]$_2$ [16]. This unique stability of electronically much deficient organochromium complex **4** (15-electrons species) may be attributed to the property of the Tp* ligand which is more sterically bulkier and is a better electron donor than the Cp ligand on the organochromium moiety.

A dibenzylchromium complex **5** can also be prepared in a similar manner. When **3** was treated with two equivalents of benzylmagnesium chloride in a mixture of THF and 1,4-dioxane, **5** was obtained in 41% yield. The IR spectrum of **5** showed a single, sharp B–H absorption at 2540 cm^{-1} indicating that the Tp* ligand coordinates to the chromium center in a tridentate fashion, which was confirmed by the X-ray crystallographic study (vide infra). In this reaction, it is necessary to add 1,4-dioxane, which precipitates concomitant magnesium halide. In the absence of 1,4-dioxane, incomplete alkylation was observed due to the equilibrium, like Schlenk one, between the complex **5** and MgCl$_2$(THF)$_2$. It has been known that dialkyl complexes of early transition metals occasionally participate in Schlenk-type equilibrium with magnesium dihalides to form L_nM(R)X complexes [17,18], whereas complete dialkylation of early transition metal complexes sometimes proceeded using dialkyl or diaryl magnesium reagents, which can be obtained by the addition of 1,4-dioxane to RMgX [19].

2.2. Molecular structures of **4** and **5**

The structures of **4** and **5** have been established by X-ray crystallography, although spectroscopic data and
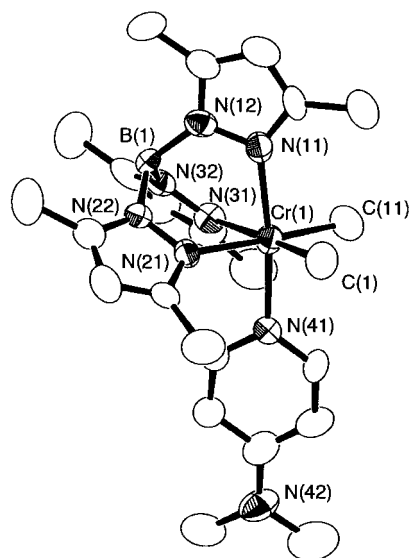

Fig. 1. ORTEP drawing of **4** with the numbering scheme. Hydrogen atoms are omitted for clarity.
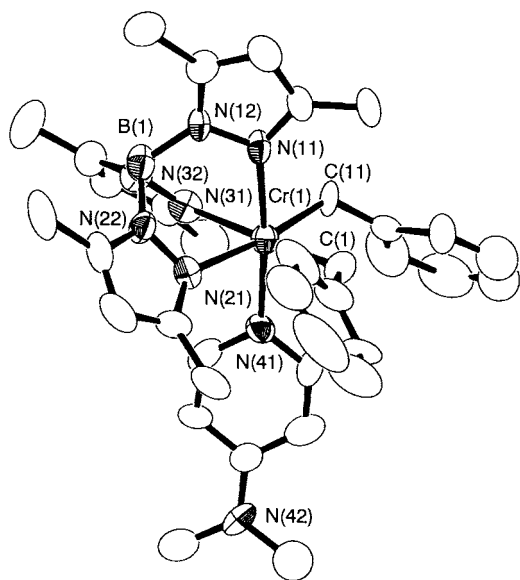
Fig. 2. ORTEP drawing of complex **5** with the numbering scheme. Hydrogen atoms are omitted for clarity.

elemental analysis had already provided a preliminary indication. Figs. 1 and 2 show the molecular structures of **4** and **5** respectively and selected bond distances and angles are summarized in Table 1. Each chromium center of **4** and **5** has a distorted octahedral environment where the chromium center was surrounded with four nitrogen atoms, three from the Tp* ligand and one from the DMAP, and two carbon atoms. The Tp*

ligand occupies three coordination sites in a facial fashion and thereby three N–Cr–N angles in the Tp*Cr fragment are acute; lying in the range of 85.6(3)–86.0(3)° for **4** and 82.9(4)–87.5(4)° for **5**. The average Cr–C bond distance of **4** (2.08 Å) is comparable to that observed for methylchromium(III) complexes, $[Cp*CrMe(THF)2]^+ BPh_4^-$ (2.056(8) Å) [20] and $[CpCrMe(\mu\text{-}Cl)]_2$ (2.073(3) Å) [21].

The two benzyl ligands of the complex **5** coordinate to the chromium center in an η^1 fashion with the angles of Cr(1)–C(1)–C(2) (125(1)°) and Cr(1)–C(11)–C(12) (128.4(10)°). The distances between Cr–C bonds (Cr(1)–C(1) = 2.12(1) Å and Cr(1)–C(11) = 2.13(1) Å) are comparable with those found for the Cr–C(η^1-benzyl) bonds of $Cp*Cr(CH_2Ph)_2(py)$ (py = pyridine) (2.125(9) and 2.139(9) Å) [12], $Cp*Cr(CH_2Ph)(bpy)$ (bpy = 2,2′-bipyridine) (2.111(6) Å) [12], and $Cp*Cr(\eta^1\text{-}CH_2Ph)(\mu\text{-}\eta^3{:}\eta^6\text{-}CH_2Ph)CrCp*$ (2.132(7) Å) [22].

The DMAP ligand coordinates to the chromium center; the Cr(1)–N(41) distances of **4** (2.116(9) Å) and **5** (2.11(1) Å) are comparable to the Cr–N(pyridine) distance (2.085(7) Å) of $Cp*Cr(CH_2Ph)_2(py)$ [12].

3. Conclusions

We have demonstrated that two air-stable dimethyl- and dibenzylchromium complexes bearing a Tp* ligand can be prepared by reaction of **3** with methyl lithium or benzyl Grignard reagent. The stability of the Cr–C bonds of these complexes may be attributed to the congestion by the bulky Tp* ligand together with the coordination of DMAP, being in contrast to the reported fact that organochromium compounds bearing monocyclopentadienenyl ligand are thermally robust but are very much sensitive to air and moisture. Catalytic activities of these alkyl chromium complexes are currently under investigation.

4. Experimental section

All manipulations involving air- and moisture-sensitive organometallic compounds were carried out using Schlenk techniques under argon. THF, toluene and hexane were dried over sodium benzophenone ketyl and then distilled before use. Compound $Tp*CrCl_2(DMAP)$ (**3**) was prepared according to the literature procedure [23]. MeLi was purchased from Kanto Chemical Company.

IR spectra were measured on a Jasco FT/IR-120 spectrometer. Elemental analyses were performed on a Perkin-Elmer 2400 microanalyzer. All melting points were measured in sealed tubes and were not corrected.

Table 1
Selected bond distances (Å) and angles (°) for complexes **4** and **5**

	4	**5**
Bond distances (Å)		
Cr(1)–N(11)	2.117(10)	2.19(1)
Cr(1)–N(21)	2.179(9)	2.22(1)
Cr(1)–N(31)	2.202(9)	2.19(1)
Cr(1)–N(41)	2.116(9)	2.11(1)
Cr(1)–C(1)	2.09(1)	2.12(1)
Cr(1)–C(11)	2.07(1)	2.13(1)
Bond angles (°)		
N(11)–Cr(1)–N(21)	85.6(3)	87.5(4)
N(11)–Cr(1)–N(31)	85.7(4)	87.2(4)
N(11)–Cr(1)–N(41)	172.3(4)	174.0(5)
N(11)–Cr(1)–C(1)	94.1(4)	90.3(5)
N(11)–Cr(1)–C(11)	92.7(4)	89.3(5)
N(21)–Cr(1)–N(31)	86.0(3)	82.9(4)
N(21)–Cr(1)–N(41)	89.8(3)	87.0(4)
N(21)–Cr(1)–C(1)	90.7(4)	95.9(5)
N(21)–Cr(1)–C(11)	177.5(4)	172.1(5)
N(31)–Cr(1)–N(41)	87.9(4)	89.7(4)
N(31)–Cr(1)–C(1)	176.8(4)	177.3(5)
N(31–Cr(1)–C(11)	92.1(4)	89.7(5)
N(41)–Cr(1)–C(1)	92.1(4)	92.7(5)
N(41)–Cr(1)–C(11)	91.7(4)	95.9(5)
C(1)–Cr(1)–C(11)	91.2(5)	91.4(5)

4.1. Preparation of Tp*CrMe$_2$(DMAP) (4)

An ethereal solution of MeLi (0.47 ml, 1.07 M diethyl ether solution) was added to a suspension of **3** (135.5 mg, 0.25 mmol) in THF (20 ml) at −78°C. The reaction mixture was gradually warmed and then stirred at room temperature overnight. After all volatiles were removed, the resulting residue was extracted with a portion of toluene (30 ml). The extract was concentrated in vacuo to give an orange solid of the crude product. Recrystallization of the product from a mixture of diethyl ether and THF at −20°C afforded **4** (55.6 mg, 41% yield) as orange crystals, m.p. 235–236°C. IR (Nujol/KBr): 2510 (ν(B–H)), 1610, 1540, 1445, 1415, 1225, 1200, 1115, 1065, 1040, 1020, 980, 950, 850, 810, 775, 695, 655, 620, 535, 470 cm^{-1}. Anal. Calc. for C$_{28}$H$_{48}$ON$_8$BCr: C, 58.43; H, 8.41; N, 19.47. Found: C, 58.21; H, 8.44; N, 19.01.

4.2. Preparation of Tp*Cr(CH$_2$Ph)$_2$(DMAP) (5)

An ethereal solution of benzylmagnesium chloride (2.32 ml, 0.5 M diethyl ether solution) was added to a suspension of **3** (314.5 mg, 0.58 mmol) in THF (20 ml) at −78°C, and then the temperature of the reaction mixture was allowed to rise to room temperature. 1,4-Dioxane (2.0 ml) was added to precipitate the magnesium salt, and the mixture was further stirred at room temperature overnight. Removal of all volatiles gave a residue, which was extracted with a sequential portion of a toluene and hexane mixture. The combined extract was concentrated in vacuo and then cooled at −20°C to afford **5** (154.4 mg, 41% yield) as red crystals, m.p. 282–285°C. IR (Nujol/KBr): 2540 (ν(B–H)), 1620, 1545, 1490, 1420, 1220, 1205, 1070, 1050, 1020, 860, 820, 790, 750, 700, 655, 540, 475, 435 cm^{-1}. Anal. Calc. for C$_{36}$H$_{46}$N$_8$BCr: C, 66.16; H, 7.09; N, 17.14. Found: C, 66.40; H, 7.00; N, 17.00.

4.3. Crystallographic data collections and structure determination of 4 and 5

Each suitable crystal was mounted in glass capillaries under argon. Data for complexes **4** and **5** were collected by a Rigaku AFC-7R diffractometer with a graphite monochromated Mo–K$_\alpha$ radiation and a 12 kW rotating anode generator. The incident beam collimator was 1.0 mm and the crystal to detector distance was 285 mm. Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections corresponded to the cells with dimensions listed in Table 2, where details of the data collection were summarized. The weak reflections ($I < 10\sigma(I)$) were rescanned (maximum of two rescans) and the counts were accumulated to assure good counting statistics.

Table 2
Crystal and refinement data for complexes **4** and **5**

Complex	4	5
Formula	C$_{24}$H$_{38}$N$_8$BCr·(C$_4$H$_{10}$O)	C$_{36}$H$_{46}$N$_8$BCr
Formula weight	551.52	653.62
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$ (# 14)	$P2_1/n$ (# 14)
a (Å)	12.535(4)	14.33(3)
b (Å)	17.088(4)	17.50(4)
c (Å)	14.491(3)	14.741(5)
β (°)	106.30(2)	104.79(5)
Z	4	4
V (Å^3)	2979(1)	3575(8)
$D_{calc.}$ (g cm^{-3})	1.230	1.214
Radiation	Mo–K$_\alpha$ ($\lambda =$ 0.71069 Å)	Mo–K$_\alpha$ ($\lambda =$ 0.71069 Å)
Crystal size (mm)	$0.5 \times 0.3 \times 0.2$	$0.3 \times 0.3 \times 0.1$
Absorption coefficient (cm^{-1})	4.17	3.57
Scan mode	ω–2θ	ω–2θ
Temperature (°C)	20	20
2θ max (°)	55.0	55.0
Data collected	6301	7246
Unique data	5989 ($R_{int} =$ 0.093)	6912 ($R_{int} =$ 0.108)
No. of observations ($I > 3\sigma(I)$)	1648	1762
No. of variables	320	405
R^a	0.067	0.078
R_w^b	0.085	0.092
Goodness-of-fit	1.48	1.59
Largest difference peak and hole (Δ) (e Å^{-3})	0.90 (max), −0.28 (min)	0.45 (max), −0.45 (min)

^{a} $R = \Sigma ||F_o| - |F_c||/|F_o|$.
^{b} $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$; $w = 1/\sigma^2(F_o)$; function minimized: $\Sigma w(|F_o| - |F_c|)^2$.

Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1. Three standard reflections were chosen and monitored every 150 reflections.

An empirical absorption correction based on azimuthal scans of several reflections was applied. The data were corrected for Lorentz and polarization effects. Each variation of intensities of three representative reflections was + 0.25% for **4** and + 0.67% for **5**, and thus linear correction factors were applied.

Calculations were performed for **4** and **5** using a TEXSAN crystallographic software package, and illustrations were drawn with ORTEP. Crystallographic calculations were performed on IRIS Indigo workstation. Measured non-equivalent reflections with $I > 3.0\sigma(I)$ were used for the structure determination. In the subsequent refinement the function $\Sigma w(|F_o| - |F_c|)^2$ was minimized, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factors amplitudes, respectively. The agreement indices are defined as $R = \Sigma ||F_o| - |F_c||/$

$\Sigma|F_o|$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(|F_o|)^2]^{1/2}$ where $w^{-1} = \sigma^2(F_o) = \sigma^2(F_o^2)/(4F_o^2)$.

The systematic absence $(h\ 0\ l)$ with $h + l = $ odd and $(0\ k\ 0)$ with $k = $ odd for both of the complexes **4** and **5** indicated the space group to be $P2_1/n$ (#14). The location of the Cr atom in each complex was determined by a direct method (SHELXS86) [24]. A series of standard full matrix least-squares refinement and Fourier synthesis revealed the remaining atoms. One diethyl ether was found as a solvent molecule. All hydrogen atoms were placed at the calculated positions $(C-H = 0.95\ \text{Å})$. All non-hydrogen atoms of **4** as anisotropic, and hydrogen atoms as isotropic temperature factor were refined to $R = 0.067$ and $R_w = 0.085$. Similarly, refinement for all non-hydrogen atoms of **5** as anisotropic, and hydrogen atoms as isotropic temperature factor reached to values $R = 0.078$ and $R_w = 0.092$. A weighting scheme, $1/w = \sigma_c^2 + (0.05|F_o|)^2$, was employed for both refinements.

Acknowledgements

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