1598 *Inorg. Chem.* **1997**, *36*, 1598−1601

Fluoro[η^3-hydrotris(3-R-5-methylpyrazol-1-yl)borato]zinc(II): The First TpZnF Complexes, Convenient Precursors to Zinc Hydride Complexes[†,‡]

Wolfgang Kläui,[*,§] **Uwe Schilde,**[∥] **and Michael Schmidt**[§]

Institut für Anorganische Chemie und Strukturchemie, Heinrich-Heine-Universität Düsseldorf,
Universitätsstrasse 1, D-40225 Düsseldorf, Germany, and Institut für Anorganische Chemie und
Didaktik der Chemie, Universität Potsdam, Am Neuen Palais 10, D-14415 Potsdam, Germany

Received October 15, 1996[⊗]

Fluoro[η^3-tris(3-R-5-methylpyrazol-1-yl)hydroborato]zinc(II) complexes, $\mathrm{Tp^{R,Me}ZnF}$ (with R = *p*-Tol, *t*-Bu), have been prepared by metathesis of $\mathrm{Tp}^{p-\mathrm{Tol,Me}}\mathrm{ZnOAc}$ with KF in MeOH/THF and by reaction of $\mathrm{KTp}^{t-\mathrm{Bu,Me}}$ with $Zn(ClO_4)_2$ and KF in MeOH. The molecular structure of $\mathrm{Tp}^{p-\mathrm{Tol,Me}}\mathrm{ZnF}$ has been determined by X-ray crystallography. Crystal data: $a = 11.8719(12)$, $c = 37.051(3)$ Å; trigonal, space group $R3c$ (No. 161); $Z = 6$. The complex contains tetrahedrally coordinated Zn(II). The tolyl rings deviate by 21° from coplanarity with the pyrazolyl plane. The reaction of $\mathrm{Tp}^{p-\mathrm{Tol,Me}}\mathrm{ZnF}$ with $\mathrm{py{\cdot}BF_3}$ leads to the tetrafluoroborate salt $[\mathrm{Tp}^{p-\mathrm{Tol,Me}}\mathrm{Zn(py)}]^+\mathrm{BF_4}^-$. The analogous reaction with $\mathrm{Et_2O{\cdot}BF_3}$ probably gives a solvent complex $[\mathrm{Tp}^{p-\mathrm{Tol,Me}}\mathrm{Zn(Et_2O)}]^+\mathrm{BF_4}^-$ that however could not be isolated. Triethylsilane reacts with $\mathrm{Tp}^{p-\mathrm{Tol,Me}}\mathrm{ZnF}$ to yield the zinc hydride $\mathrm{Tp}^{p-\mathrm{Tol,Me}}\mathrm{ZnH}$. Trimethylsilyl derivatives $\mathrm{Me_3Si{-}X}$ (X = Cl, Br, I, NCO, OAc) similarly give $\mathrm{Tp}^{p-\mathrm{Tol,Me}}\mathrm{ZnX}$, whereas bis(trimethylsilyl) malonate yields the bridged complex $\mathrm{Tp}^{p-\mathrm{Tol,Me}}\mathrm{Zn{-}O{-}C(O){-}CH_2{-}C(O){-}O{-}ZnTp}^{p-\mathrm{Tol,Me}}$.

Introduction

Ternary halide complexes of the type $\mathrm{TpM^{II}X}$ (X = Cl, Br, I), where $[\mathrm{Tp}]^-$ is a tris(pyrazolyl)hydroborato ligand, are accessible via different routes. Their properties are well-known, and X-ray structures of various complexes of this type have already been published.[1] It is, however, striking that ternary metal fluoro complexes of $[\mathrm{Tp}]^-$ are rare. We are aware of only two compounds, of the type $\mathrm{Tp}^{t-\mathrm{Bu}}\mathrm{FeF}$ and $\mathrm{Tp}^{t-\mathrm{Bu}}\mathrm{CoF}$, which have been prepared by Parkin et al. through fluoride abstraction from $[\mathrm{BF_4}]^-$. The X-ray structure of $\mathrm{Tp}^{t-\mathrm{Bu}}\mathrm{CoF}$ has been determined.[2]

We are interested in fluoro complexes because of their synthetic potential. For example, trimethylsilyl compounds $\mathrm{Me_3SiX}$ can react with metal fluorides M−F to give M−X and $\mathrm{Me_3SiF}$. The high thermodynamic stability of the Si−F bond[3] and the volatility of $\mathrm{Me_3SiF}$ easily drives such reactions to completion. In this paper, we report the preparation and spectroscopic characterization of the hitherto unknown complexes $\mathrm{Tp}^{p-\mathrm{Tol,Me}}\mathrm{ZnF}$ (**1**) and $\mathrm{Tp}^{t-\mathrm{Bu,Me}}\mathrm{ZnF}$ (**2**).[4] The X-ray structure and some typical reactions of **1** are also described.

Experimental Section

Materials and Methods. The potassium salts $\mathrm{KHB(3\text{-}R\text{-}5\text{-}Me\text{-}pz)_3}$ were synthesized from 3-R-5-methylpyrazole (R = *t*-Bu and *p*-Tol) and potassium borohydride in dimethylacetamide as described for similarly substituted tris(pyrazolyl)borates.[5] The reagent $\mathrm{py{\cdot}BF_3}$ was prepared according to a published procedure.[6] All air-sensitive reactions were performed under an N_2 atmosphere or by using standard Schlenk and vacuum-line techniques. Solvents were dried by standard methods and stored under dinitrogen. All other chemicals were reagent grade and used as received. Membrane filters (regenerated cellulose, 1.0 μm, Schleicher & Schuell, RC 60) were used to remove small particles. Elemental analyses were performed in the Department of Pharmaceutical Chemistry, University of Düsseldorf, using a Perkin-Elmer 240 C elemental analyzer. NMR spectra were obtained on a Bruker AM 200 spectrometer. Infrared spectra were recorded as KBr pellets with a Bruker 66 spectrometer. Mass spectra were measured on a Varian MAT 311 A mass spectrometer (EI at 70 eV) or on a VG-Analytical FAB ZAB-HF (MNBA matrix).

Synthesis of $\mathrm{Tp}^{p-\mathrm{Tol,Me}}\mathrm{ZnOAc}$. (a) First 2.82 g (5.00 mmol) of KHB(3-*p*-tolyl-5-me-pz)$_3$ was dissolved in 100 mL of a mixture of CH_2Cl_2/THF (4:1). Then 1.10 g (5.01 mmol) of $\mathrm{Zn(OAc)_2{\cdot}2H_2O}$ was added, and the resulting slurry was stirred for 8 h at room temperature. The solvent was removed under reduced pressure, and the residue was dissolved in CH_2Cl_2. After filtration and addition of hexane, the solution was slowly evaporated in an open tube to yield colorless crystals (2.7 g, 83%; mp = 222−224 °C). MS: 648 M^+ (70%), 477 (100%). Anal. Calcd for $C_{35}H_{37}BN_6ZnO_2$: C, 64.7; H, 5.74; N, 12.9. Found: C, 64.4; H, 6.01; N, 12.6.

Synthesis of $\mathrm{Tp}^{p-\mathrm{Tol,Me}}\mathrm{ZnF}$. A suspension of 2.50 g (3.85 mmol) of $\mathrm{Tp}^{p-\mathrm{Tol,Me}}\mathrm{ZnOAc}$ in 30 mL of MeOH was heated to reflux. THF was added to the boiling suspension in small doses until a clear solution was obtained. A solution of 261 mg (4.50 mmol) of KF in 5 mL of MeOH was added dropwise with stirring. The resulting white suspension of $\mathrm{Tp}^{p-\mathrm{Tol,Me}}\mathrm{ZnF}$ was then refluxed for 1 h more. After the reaction had cooled to room temperature, the precipitate was filtered off and was thoroughly washed with hot water, methanol, and diethyl ether. After drying in vacuo, 2.1 g (90%) of analytical pure $\mathrm{Tp}^{p-\mathrm{Tol,Me}}\mathrm{ZnF}$ were obtained. The solid was insoluble in water and methanol and only slightly soluble in CH_2Cl_2, THF, and hot toluene. Mp = 192 °C. MS: 608 M^+ (64%), 438 (100%). Anal. Calcd for $C_{33}H_{34}BN_6ZnF$: C, 65.0; H, 5.62; N, 13.8. Found: C, 64.9; H, 5.45; N, 13.8.

[†] Dedicated to Prof. Dr. G. Huttner on the occasion of his 60th birthday.

[‡] Part of the planned Ph.D. thesis of Michael Schmidt.

[§] Heinrich-Heine-Universität Düsseldorf.

[∥] Universität Potsdam.

[⊗] Abstract published in *Advance ACS Abstracts,* March 1, 1997.

(1) (a) Le Cloux, D. D.; Keyes, M. C.; Osawa, M.; Reynolds, V.; Tolman, W. B. *Inorg. Chem.* **1994**, *33*, 6361. (b) Rheingold, A. L.; White, C. B.; Trofimenko, S. *Inorg. Chem.* **1993**, *32*, 3471. (c) Hartman, F.; Kläui, W.; Kremer-Aach, A.; Mootz, D.; Strerath, A.; Wunderlich, H. *Z. Anorg. Allg. Chem.* **1993**, *20*, 619. (d) Calabrese, J. C.; Trofimenko, S. *Inorg. Chem.* **1992**, *31*, 4810. (e) Alsfasser, R.; Powell, A. K.; Trofimenko, S.; Vahrenkamp, H. *Chem. Ber.* **1993**, *126*, 685.

(2) Gorrell, I. B.; Parkin, G. *Inorg. Chem.* **1990**, *29*, 2452.

(3) (a) Farber, M.; Srivastava, R. D. *J. Chem. Soc., Faraday Trans.* **1968**, 1089. (b) Ehlert, T. C. ; Margrave, J. L. *J. Chem. Phys.* **1964**, 1066.

(4) The nomenclature adopted here for tris(pyrazolyl)hydroborato ligands is based on that described by Trofimenko. See: Trofimenko, S. *Chem. Rev.* **1993**, *93*, 943.

(5) (a) Rasika Dias, H. V.; Hui-Ling Lu; Ratcliff, R. E.; Bott, S. G. *Inorg. Chem.* **1995**, *34*, 1975. (b) Trofimenko, S.; Calabrese, J. C.; Thompson, J. S. *Inorg. Chem.* **1987**, *26*, 1507.

(6) Iijima, K.; Noda, T.; Maki, M.; Sasase, T.; Shibata, S. *J. Mol. Struct.* **1986**, *144*, 169.

S0020-1669(96)01249-9 CCC: $14.00

Synthesis of Tp$^{t-\mathrm{Bu,Me}}$ZnF. A solution of 1.00 g (2.16 mmol) of KTp$^{t-\mathrm{Bu,Me}}$ in 10 mL of MeOH was added to 10 mL of a solution of 0.66 g (2.20 mmol) $Zn(ClO_4)_2\cdot2H_2O$ in MeOH. White $KClO_4$ precipitates immediately. After for 15 min of stirring, a solution of 0.29 g (5.0 mmol) of KF in 5 mL of MeOH was added. After 2 h, the precipitate was filtered off and dried in vacuo. The dried residue was stirred in 5 mL of CH_2Cl_2 for 1 h. After microfiltration, the clear solution was mixed with 5 mL of hexane and set aside in a crystallizing dish. Then 0.91 g (83%) of Tp$^{t-\mathrm{Bu,Me}}$ZnF was obtained as colorless crystals. Mp = 295−297 °C dec. MS: 506 M^+ (36%), 368 (100%). Anal. Calcd for $C_{24}H_{40}BN_6ZnF$: C, 56.9; H, 7.96; N, 16.6. Found: C, 56.9; H, 8.21; N, 16.4.

Synthesis of Tp$^{p-\mathrm{Tol,Me}}$ZnCl and Related Compounds. A suspension of (0.10 g, 0.16 mmol) **1** in 5 mL of CH_2Cl_2 was stirred with a slight excess of Me_3SiCl at room temperature for 10 min. CH_2Cl_2 and excess Me_3SiCl were removed in vacuo, and the residue was recrystallized from CH_2Cl_2/hexane. Colorless crystals (0.10 g, 88%; mp = 222 °C) were isolated. MS: 624 M^+ (41%), 453 (100%). Anal. Calcd for $C_{33}H_{34}BN_6ZnCl$: C, 63.3; H, 5.47; N, 13.4. Found: C, 63.1; H, 5.50; N, 13.5.

Other Tp$^{p-\mathrm{Tol,Me}}$ZnX complexes were prepared similarly from Me_3SiX, with X = Br, I, NCO, OAc.

Tp$^{p-\mathrm{Tol,Me}}$ZnBr: (0.08 g, 73%; mp = 245 °C). MS: 670 M^+ (60%), 499 (100%). Anal. Calcd for $C_{33}H_{34}BN_6ZnBr$: C, 59.1; H, 5.11; N, 12.5. Found: C, 59.3; H, 5.10; N, 12.5.

Tp$^{p-\mathrm{Tol,Me}}$ZnI: (0.06 g, 51%; mp = 242 °C). MS (FD ionization): 716 M^+ . Anal. Calcd for $C_{33}H_{34}BN_6ZnI$: C, 55.2; H, 4.77; N, 11.7. Found: C, 55.2; H, 4.90; N, 11.5.

Tp$^{p-\mathrm{Tol,Me}}$ZnNCO: (0.09 g, 83%; mp = 276 °C). MS: 631 M^+ (41%), 460 (100%). Anal. Calcd for $C_{34}H_{34}BN_7ZnO$: C, 64.5; H, 5.41; N, 15.5. Found: C, 64.5; H, 5.39; N, 15.5.

Tp$^{p\text{-}\mathrm{Tol,Me}}$ZnOAc: (0.10 g, 96%). Characterization data: see above.

Reaction of 1 with Bis(trimethylsilyl) Malonate. A suspension of 0.20 g (0.33 mmol) **1** in 5 mL of THF was mixed with 0.04 g (0.16 mmol) of bis(trimethylsilyl) malonate. The solution was stirred for 2 h at room temperature. The solvent was removed in vacuo, and the residue was recrystallized from CH_2Cl_2/hexane. Colorless crystals (200 mg, 81%; mp = 178 °C) were isolated. MS (FAB): 1283 M^+ (4.0%), 584 (100%). Anal. Calcd for $C_{69}H_{70}B_2N_{12}Zn_2O_4\cdot2.5CH_2Cl_2$: C, 58.1; H, 4.99; N, 11.1. Found: C, 57.6; H, 5.07; N, 11.3.

Reaction of 1 with py·BF$_3$. To a suspension of 0,30 g (0.49 mmol) of **1** in 5 mL of CH_2Cl_2 was added an equimolar quantity of py·BF_3. The solution was stirred for 1 h. After addition of toluene, the solution was filtered through a membrane. Slow evaporation of the solvent in an open tube yielded colorless needles (0.22 g, 59%; mp = 181 °C). ^{19}F NMR (CD_2Cl_2): 9.42 q (^{11}B), 9.47 s (^{10}B), Anal. Calcd for $C_{38}H_{39}B_2F_4N_7Zn$: C, 60.3; H, 5.19; N, 13.0. Found: C, 58.1; H, 5.06; N, 12.4.

Reaction of 1 with Trimethylsilyl (Trimethylsilyl)carbamate. A suspension of 1.00 g (1.64 mmol) of **1** in 20 mL of THF was stirred with 0.17 g (0.82 mmol) of trimethylsilyl (trimethylsilyl)carbamate. After 24 h of stirring, the suspension had nearly dissolved. The solvent was evaporated in vacuo, and the residue was washed carefully with ether. After the residue was dissolved in CH_2Cl_2, filtered through a membrane, and of hexane added, the solvent was slowly evaporated. Colorless crystals (0.45 g, 43%) of Tp$^{p-\mathrm{Tol,Me}}$ZnNCO were obtained. From the mother liquor 0.30 g of the unreacted starting material Tp$^{p-\mathrm{Tol,Me}}$ZnF could be isolated. Characterization data for Tp$^{p-\mathrm{Tol,Me}}$ZnNCO: see above.

Reaction of 1 with Triethylsilane. A suspension of 0.61 g (1.00 mmol) of **1** in 10 mL of toluene was stirred with an excess (0.58 g, 5.00 mmol) of triethylsilane under reflux for 24 h. All volatile components were removed in vacuo. The residue was washed with anhydrous diethyl ether and dried. After the residue was dissolved hot toluene and filtered while hot, the Schlenk tube was placed in a Dewar vessel filled with hot water. Colorless crystals (0.48 g, 81%) of Tp$^{p-\mathrm{Tol,Me}}$ZnH grew over a period of 2 days. MS (FD ionization): 592 [M^+ + 1]. IR data (KBr, cm^{-1}): 2556 (ν (B−H)), 1743 (ν (Zn−H)), ^{1}H NMR (ppm, toluene-d_8): (Zn−H) 5.23. Anal. Calcd for $C_{33}H_{35}BN_6Zn$: C, 66.97; H, 5.96; N, 14.20. Found: C, 66.85; H, 5.96; N, 14.03.

Table 1. Crystallographic Data for [(η^3-HB(3-p-Tol-5-Me-pz)$_3$ZnF]

empirical formula	$C_{33}H_{34}BFN_6Zn$
fw	609.84
cryst syst	rhombohedric
space group	$R3c$
a (Å)	11.8719(12)
b (Å)	11.8719(12)
c (Å)	37.051(3)
V (Å^3)	4522.4(7)
ρ_{calcd} (g cm^{-1})	1.344
radiation (λ (Å))	Mo Kα (0.710 73)
Z	6
μ (cm^{-1})	8.54
temp (°C)	25
cryst dimens (mm)	0.34 × 0.31 × 0.30
scan type	$\omega/2\theta$
scan width (deg)	1.00
$\theta_{\max}$ (deg)	30
no. of reflns recorded	2946
no. of obsd reflns	1491 ($I > 2\sigma(I)$)
no. of params refined	133
R^a (for reflns $F_o > 4\sigma(F_o)$)	0.0425
R$_w$^{b}	0.0962
GOF^c	1.022
max shift/esd in final l.s. cycle	0.001
final max, min $\Delta\rho$ (e/Å^3)	0.443; −1.203

^{a} $R = \sum(||F_o| - |F_c||)/\sum|F_o|$. ^{b} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(|F_o|^2]^{1/2}$. $w = 1/[\sigma^2(F_o{}^2) + (0.0625P)^2]$ where $P = (F_o{}^2 + 2F_c{}^2)/3$. ^{c} $\mathrm{GOF} = [\sum w(|F_o| - |F_c|)^2/(N_{\mathrm{observns}} - N_{\mathrm{params}})]^{1/2}$.

X-ray Data Collection and Structure Solution and Refinement for Complex Tp$^{p-\mathrm{Tol,Me}}$ZnF (1). Crystals suitable for X-ray investigation were grown by slowly cooling down a saturated solution of **1** in hot toluene under dinitrogen. The crystal was mounted on a glass fiber. X-ray intensity data were recorded at room temperature. The measurements were performed with a STOE STADI 4 diffractometer with graphite-monochromated molybdenum Kα radiation. Crystallographic data are summarized in Table 1. Cell parameters were obtained by least-squares methods from the setting of 23 high-order reflections. Three standard reflections were monitored every 2 h and showed no systematic decrease in intensity. Reflection data were corrected for Lorentz and polarization effects. An empirical absorption was carried out using XABS2.[7] The structure was solved by direct methods with SHELXS-86[8] and successive difference Fourier synthesis using SHELXL-93.[9] Hydrogen atoms on the phenyl rings and methyl groups were refined in calculated positions as riding atoms with U_{iso}=1.2U_{eq} of the corresponding C atom (with C−H = 0.93 and 0.96 Å, respectively). The hydrogen atom at boron was located from the difference Fourier map. Full-matrix least-squares anisotropic refinement on F^2 was carried out for all atoms except for the hydrogen atoms, which were refined isotropically. The refinement converged to conventional R = 0.0425 and R_w = 0.0962. Scattering factors were taken from ref 10. Crystallographic data are given in Table 1.

Results and Discussion

When planing the synthesis of a TpZnF complex, we chose [Tp$^{p-\mathrm{Tol,Me}}$]$^-$ as a sterically demanding ligand to avoid formation of Tp_2Zn. The p-tolyl groups in the 3-position form a very helpful ^{1}H NMR spectroscopic probe that is easier to analyze than the unsubstituted phenyl group. The methyl groups at the 5-position help to protect the B−N bonds. Former work in our laboratory with the ligand [Tp$^{\mathrm{Ph}}$]$^-$ had shown that protic solvents in combination with KF as fluorinating agent caused [Tp$^{\mathrm{Ph}}$]$^-$ to decompose.[11]

---

(7) Parkin, S.; Moezzi, B.; Hope, H.; XABS2. An empirical absorption correction program, *J. Appl. Crystallogr.* **1995**, *28*, 53.

(8) Sheldrick, G. M. SHELXS-86. Program for the Solution of Crystal Structures. Göttingen, Germany, 1986.

(9) Sheldrick, G. M. SHELXL-93. Program for the Refinement of Crystal Structures. Göttingen, Germany, 1993.

(10) *International Tables for Crystallography*; D. Riedel: Dordrecht, The Netherlands, 1992; Vol. C, Tables 4.2.6.8 and 6.1.1.4.

(11) Kläui, W.; Kremer-Aach, A. Unpublished results.

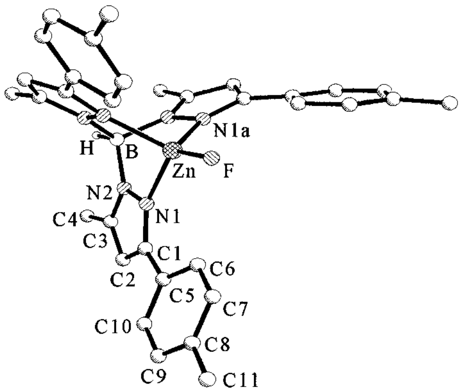


Figure 1. Ball and stick diagram of {η^3-HB(3-*p*-Tol-5-Me-pz)$_3$ZnF}.

Table 2. Bond Lengths (Å) for [η^3-HB(3-*p*-Tol-5-Me-pz)$_3$ZnF]

Zn−F	1.849(4)	N1−N2	1.386(5)	C3−N2	1.351(7)
Zn−N1	2.042(4)	C2−C3	1.379(7)	C3−C4	1.493(6)
C5−C6	1.394(4)	C2−C1	1.383(7)	C9−C8	1.372(8)
C5−C10	1.388(7)	C6−C7	1.404(7)	C8−C11	1.518(7)
C5−C1	1.474(6)	C7−C8	1.373(8)	B−N2	1.550(5)
N1−C1	1.347(6)	C10−C9	1.391(7)	B−H	1.17(9)

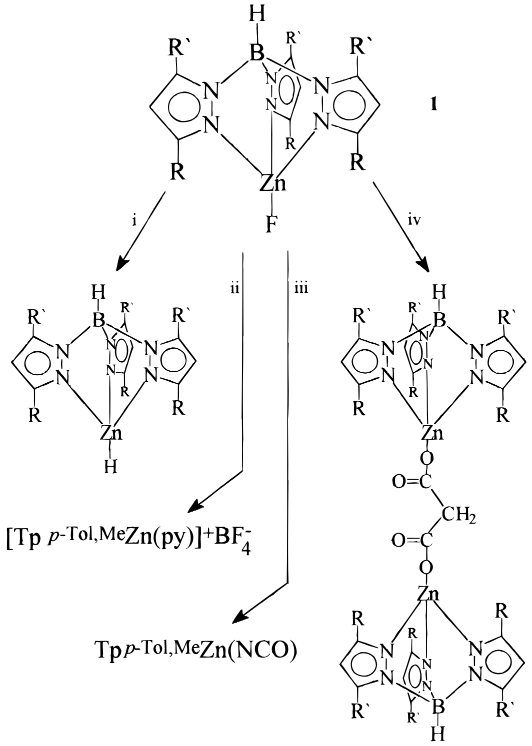
Table 3. Bond Angles (deg) for [η^3-HB(3-*p*-Tol-5-Me-pz)$_3$ZnF]

F−Zn−N1	121.54(11)	C8−C7−C6	121.5(5)
N1−Zn−N1a	95.14(14)	C9−C10−C5	121.2(5)
C6−C5−C10	117.6(4)	N2−C3−C2	107.9(4)
C6−C5−C1	122.5(4)	N2−C3−C4	123.0(5)
C10−C5−C1	119.8(4)	C2−C3−C4	129.1(2)
C1−N1−N2	106.3(4)	C8−C9−C10	121.4(6)
C1−N1−Zn	143.6(3)	C3−N2−N1	109.4(4)
N2−N1−Zn	110.0(3)	C3−N2−B	130.1(4)
C3−C2−C1	106.6(5)	N1−N2−B	120.3(4)
N1−C1−C2	109.8(5)	C9−C8−C7	118.1(5)
N1−C1−C5	122.0(4)	C9−C8−C11	122.1(5)
C2−C1−C5	128.0(5)	C7−C8−C11	119.7(5)
C5−C6−C7	120.3(5)	N2−B−H	109.0(3)

$\mathrm{Tp}^{p\text{-Tol,Me}}$ZnF is obtained by metathesis of $\mathrm{Tp}^{p\text{-Tol,Me}}$ZnOAc with potassium fluoride in a methanol/tetrahydrofuran mixture. As far as we know, this is the first example of a TpZnF complex. Its molecular structure, determined by X-ray diffraction, is shown in Figure 1. The fluoro complex is mononuclear with the tris(pyrazolyl)hydroborato ligand in a η^3 coordination mode. The zinc center is appropriately described as trigonally distorted tetrahedral, with F−Zn−N and N−Zn−N bond angles of 121 and 95°. The Zn−F bond length of 1.849(4) Å (Table 2) is shorter by 6% than the sum of the covalent radii. This shortening seems typical for $\mathrm{TpZn^{II}}$ halide complexes, since the Zn−X bonds in other TpZn−X complexes (with X = Cl, Br, I) are also shorter by about 6%.[12]

The ^{19}F NMR spectrum of **1** in $CDCl_3$ shows a singlet at −219 ppm vs $CFCl_3$. This is a typical but rather high-field value.[13] Extremely high-field chemical shifts have also been reported for the ^{1}H NMR signals of the ethyl ligands in $\mathrm{Tp^{Ph}}$ZnEt and $\mathrm{Tp^{Cum,Me}}$ZnEt.[14] They can be attributed to the ring current effect of the three aryl substituents that surround the ethyl protons. Since the fluorine in **1** is in a similar environment, we have speculated whether or not the anisotropy effect of the tolyl groups could also explain the fluorine chemical shift in **1**. Fluorine chemical shifts are usually not very susceptible to anisotropy effects. To clarify the situation, we have prepared $\mathrm{Tp}^{t\text{-Bu,Me}}$ZnF (**2**) as an analog of **1** which consequently lacks the influence of ring current effects. The ^{19}F NMR spectrum of **2** in $CDCl_3$ shows a singlet at −207 ppm vs $CFCl_3$. We therefore attribute the 12 ppm high-field shift in **1** to the influence of the anisotropy cone of the three tolyl groups.

Scheme 1[a]



[a] With R = *p*-Tol and R′ = Me. Reagents: (i) triethylsilane; (ii) py·BF_3; (iii) *N*,*O*-bis(trimethylsilyl)carbamate; (iv) bis(trimethylsilyl) malonate.

The reactivity of the zinc fluoride complex **1** toward a number of reagents has been examined. Some of the results are summarized in Scheme 1.

Trimethylsilyl derivatives of the type Me_3Si−X (X = Cl, Br, I, NCO, OAc) rapidly cleave the Zn−F bond. Elimination of Me_3Si−F furnishes complexes of the type $\mathrm{Tp}^{p\text{-Tol,Me}}$Zn−X. The use of bis(trimethylsilyl) malonate similarly yields the bimetallic complex $\mathrm{Tp}^{p\text{-Tol,Me}}$Zn−O−C(O)-$CH_2$-C(O)−O−$\mathrm{ZnTp}^{p\text{-Tol,Me}}$.

Reaction with trimethylsilyl (trimethylsilyl)carbamate, $Me_3SiNHC(O)OSiMe_3$, did not lead to an analogous bridged complex. An isocyanate complex $\mathrm{Tp}^{p\text{-Tol,Me}}$Zn−NCO is formed instead, presumably after elimination of both Me_3SiF and Me_3SiOH.[15] We have not been able to isolate any intermediate product by varying the zinc fluoride/carbamate ratio or the reaction temperature.

The reaction of $\mathrm{Tp}^{p\text{-Tol,Me}}$ZnF with triethylsilane is an elegant way to prepare monomeric zinc hydride complexes. Most zinc hydride compounds tend to polymerize, and the only other monomeric zinc hydride seems to be the structurally characterized complex $\mathrm{Tp}^{t\text{-Bu}}$ZnH. It has been prepared by Parkin et al. from $\mathrm{TlTp}^{t\text{-Bu}}$ and ZnH_2.[16] Decomposition of the alleged TlH to metallic thallium provides the driving force for its formation. The complex $\mathrm{Tp}^{p\text{-Tol,Me}}$ZnH is characterized by the ^{1}H NMR resonance attributable to the Zn−H group at 5.26

---

[12] Parkin, G. *Adv. Inorg. Chem.* **1995**, *42*, 291.

[13] ^{19}F NMR measurements for $\mathrm{Tp}^{m\text{-Py,Me}}$ZnF delivered $\delta = -181.4$ ppm vs $CFCl_3$. Vahrenkamp, H. Universität Freiburg, unpublished results.

[14] Vahrenkamp, H. Universität Freiburg, personal communication.

[15] This probably would condense to give Me_3Si−O−$SiMe_3$ and H_2O under the reaction conditions.

[16] (a) Han, R.; Gorrell, I. B.; Looney, A. G.; Parkin, G. *J. Chem. Soc., Chem. Commun.* **1991**, 717. (b) Looney, A. G.; Han, R.; Gorrell, I. B.; Cornebise, M.; Yoon, K.; Parkin, G.; Rheingold, A. L. *Organometallics* **1995**, *14*, 274.

ppm.[17] The hydride resonance for $Tp^{t-Bu}ZnH$ had been observed at 5.36 ppm.[18] Both values are low-field of the area where most of the known zinc hydride resonances are observed.[19]

A suspension of **1** in diethyl ether dissolves upon addition of $Et_2O{\cdot}BF_3$. We postulate that abstraction of the fluoride ligand by BF_3 gives the tetrafluoroborate salt of the cationic ether complex $[Tp^{p-Tol,Me}Zn(Et_2O)]^+$, but we have not been able to isolate this salt. Evaporation of the solvent leads back to **1** with formation of a small amount of decomposition products. The analogous reaction of **1** with $py{\cdot}BF_3$, however, yields a stable cationic complex, $[Tp^{p-Tol,Me}Zn(py)]^+BF_4^-$.

Concluding Remarks

With the abstraction of fluoride from $Tp^{p-Tol,Me}ZnF$ (**1**) with BF_3, we have found an interesting synthetic route to tris(pyrazolyl)borate−zinc complexes. An alternative convenient pathway to zinc complexes TpZnX is the reaction of **1** with trialkylsilyl derivatives R_3SiX. It allows, e.g., the preparation of TpZnH. Such zinc hydride complexes are by themselves an important precursor for the preparation of other zinc complexes. Hence we consider the easily accessible fluoro complexes **1** and **2** a promising step forward in exploring properties and structures of tris(pyrazolyl)borate−zinc complexes.

Supporting Information Available: Tables listing detailed ^1H and ^{13}C NMR data (4 pages). Tables in CIF format listing detailed crystallographic data for **1** is available on the Internet only. Ordering and access information is given on any current masthead page.

IC961249D

---

(17) In toluene-d_8.

(18) In benzene-d_6.

(19) (a) Neils, T. L.; Burlitch, J. M. *Inorg. Chem.* **1989**, *28*, 1607. (b) Goeden, G. V.; Caulton, K: G. *J. Am. Chem. Soc.* **1981**, *103*, 7354. (c) De Koning, A. J.; Boersma, J.; van der Kerk, G. J. M. *J. Organomet. Chem.* 1980, *195*, 1.