SHORT COMMUNICATION

A New, Efficient and Direct Preparation of TlTp and Related Complexes with TlBH$_4$

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Establishment of a highly reliable and safe procedure for the preparation of TlBH$_4$ has led to, for the first time, a simple approach to TlTp-related complexes, which are known as mild and efficient Tp-transfer reagents to a variety of metals. The practical use of this method has been demonstrated by the efficient synthesis of (*S*,*S*,*S*)-TlTp^{4Bo3MeCpenta} from a new and hard-to-obtain chiral pyrazole (HPz). In view of the importance of the scorpionates, this new method should attract the attention of researchers in a wide range of scientific and technological fields.

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Introduction

Hydrotris(1-pyrazolyl)borato anions [Tp^{R1,R2,R3}] are monoanionic, C_{3v}, *fac*-type ligands (scorpionates)[1,2] useful for the preparation of a wide range of metal complexes. This is because introduction of various substituents at the C(3), C(4), and C(5) positions of the pyrazole moiety finely tunes the steric and electronic properties of these ligands as well as the metal coordination sphere.[3] Over 200 scorpionates have been described since the first report by Trofimenko in 1966,[4] and their complexes have made important contributions in numerous different areas such as catalytic reactions,[5] metalloenzyme modelling,[6] and technomimetic molecules.[7] Thallium(I) derivatives of Tp^{R1,R2,R3} ligands have frequently been used as mild and efficient reagents for the transfer of ligands to a variety of transition metals because of their lower reducing ability than that of the corresponding alkali metal salts.[8] Furthermore, the stability and crystallinity of the Tl complexes facilitate the isolation and structural characterization of new Tp^{R1,R2,R3} ligands. The high value-added thallium complexes are generally prepared in two steps: (i) KTp^{R1,R2,R3} is synthesized from KBH$_4$ and the corresponding pyrazole derivatives (HPz^{R1,R2,R3}), and (ii) the potassium salt reacts with TlNO$_3$ to giving **2**.[9] The process is simple, but the requirement of excess HPz^{R1,R2,R3} sometimes causes a problem in the isolation of KTp^{R1,R2,R3}. Furthermore, the removal of the by-product KNO$_3$ in the second step decreases the efficiency of the process. These disadvantages should become much more significant in the case where HPz^{R1,R2,R3} is hard to obtain.[10] Naturally, the more TlTp^{R1,R2,R3} is used, the more an efficient and direct method of synthesis becomes necessary. Equation (1) should represent the most straightforward method of preparation, but the route is unproven because of the ambiguity in the preparation and the physical properties of TlBH$_4$.[11] This communication describes, for the first time, the synthesis of TlBH$_4$, its detailed physical properties, and a single-step process for the preparation of TlTp^{R1,R2,R3}.

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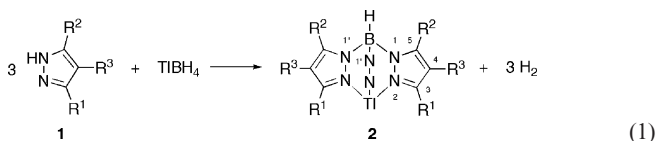
Results and Discussion

TlBH$_4$ is described by only three groups. In the first report by Wiberg in 1957,[11a] the instability of the compound prepared from TlOR/LiBH$_4$ is noted. Waddington succeeded in the synthesis by use of TlNO$_3$ and KBH$_4$, although the details are not described.[11b] Ortega recently reported the potential synthesis of TlBH$_4$ starting from TlOH/Tl$_2$CO$_3$/B$_2$H$_6$ on the basis of the result obtained for the synthesis of NaBH$_4$ (3.7–47% yield).[11c] First, the seemingly most promising TlNO$_3$/KBH$_4$ method was re-examined, and the results are listed in Table 1. By considering the instability of KBH$_4$ in water, 1 mol-equiv. KBH$_4$ was added as a solid at 23 °C into a 0.1-M aqueous solution of

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⌨ Supporting information for this article is available on the WWW under http://www.eurjic.org or from the author.

$TlNO_3$ in one portion (Entry 1). Separation of the resulting white solid followed by rinsing with CH_3OH and ether gave almost pure $TlBH_4$ in 5-% yield. The ICP analysis showed a Tl/B/K ratio of 1:1.00:<0.01.[12] An increase in the concentration to 0.2 M with 1–2 mol-equiv. KBH_4 was not significantly effective (Entries 2 and 3), while the low solubility of $TlNO_3$ led to an incomplete reaction for the 1-M solution of $TlNO_3$ (Entry 4).[13] The use of TlOAc, which is more soluble in water than $TlNO_3$ (ca. 12.5 M vs. 0.4 M), dramatically enhanced the yield of $TlBH_4$ (Entry 8). $TlBH_4$ was isolated in 75% yield ([TlOAc] = 1.0 M, 1 mol-equiv. KBH_4, 23 °C, 60 s). Both lowering and raising the concentration of TlOAc resulted in decreased yields (Entries 5–9). The use of 2 mol-equiv. KBH_4 improved the yield by ca. 10% (Entry 10). Furthermore, addition of 0.1 mol-equiv. KOH with respect to TlOAc lead to the isolation of $TlBH_4$ in 94% yield (Entry 11). TlOH also gave the same effect (Entry 12).[14] The basic conditions may stabilize KBH_4.[15] When TlOAc and KBH_4 were mixed in a 1:1 ratio without solvent followed by washing with water, $TlBH_4$ was obtained (Entry 13), but both the yield and purity were low. The highly water soluble TlF (ca. 3.5 M) can also be used (Entry 14),[16] but the use of the less expensive TlOAc is recommended. The TlOAc/KBH$_4$ method is reproducible over the range 0.5–50 mmol with yields of 85–94%.[12] The IR spectrum (1050 cm^{-1}) is consistent with that reported.[11b] The ratio of Tl/B/K was determined by ICP to be 1:1.00:<0.01.[12] In the solid-state ^{11}B NMR spectrum, the signal appears as a broad but symmetrical singlet (half value of 1050 Hz) at δ = –50 ppm, which is lower than that for KBH_4 (δ = –60 ppm). The shape implies the formation of a highly symmetrical BH_4 species. The ^{11}B signal in a [D$_7$]DMF solution appears at δ = –31.7 ppm as a quintet with $^1J_{^{11}BH}$ = 81.5 Hz. Under the same conditions, the chemical shift for KBH_4 (δ = –37.9 ppm) is ca. 6 ppm higher, which is consistent with that observed in the solid-state NMR spectrum.

The ^{1}H nucleus resonates at δ = 2.51 ppm as a quartet with $^1J_{^{11}BH}$ = 81.9 Hz and as a septet with $^1J_{^{10}BH}$ = 27.5 Hz in a 4:1 ratio, which is consistent with the natural abundance of ^{11}B and ^{10}B. These spectroscopic results clearly indicate that the gray–white solid obtained above can be expressed as $TlBH_4$.

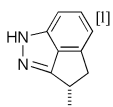With the pure $TlBH_4$ compound in hand, the synthesis of the simplest TlTp was attempted. $TlBH_4$ and 3 mol-equiv. HPz were heated at 140 °C for 1 h without the use of any solvent and then at 180 °C for 4 h in a Schlenk tube under an argon atmosphere to give a 97:0:3 mixture of TlTp, $TlBH_2(Pz)_2$, and $TlB(Pz)_4$ in 99% conversion after $CHCl_3$ extraction of the reaction mixture.[12] Solidification of the products from a mixture of CH_2Cl_2 and CH_3OH afforded TlTp with a high purity in 90% isolated yield. The NMR spectrum was identical to that reported.[12] As shown in Table 2, the present new method is applicable to a variety of pyrazole derivatives, HPz^{R1,R2,R3}, in which the groups are alkyl, aryl, halogen groups, etc. (Entries 2–8). With unsymmetrical HPz^{Me} and HPz^{Ph}, TlTp^{Me} and TlTp^{Ph} in which the substituents are located at the C(3) position are predominantly formed so as to avoid the steric repulsion between Me or Ph and B–H.[1] The use of 1H-indazole (benzo-1H-pyrazole) afforded exclusively TlTp^{4Bo}[2] but not TlTp^{3Bo}[2] because of the higher acidity of N(1)H of 1H-indazole and the higher aromaticity that is maintained with TlTp^{4Bo}.[17] Reaction of 4,5,6,7-tetrahydro-1H-indazole with $TlBH_4$ proceeded with low regioselectivity.[18] Particularly important is the synthesis of (S,S,S)-TlTp^{4Bo3MeCpenta} (Entry 9).[19] Treatment of synthetic (S)-HPz^{4Bo3MeCpenta}[19] with $TlBH_4$ at 160 °C for 1 h, then at 180 °C for 5 h, afforded the thallium)complex in a 90% yield. Its high purity facilitates its crystallization from CH_2Cl_2 and CH_3OH, which leads to its successful X-ray diffraction analysis (Figure 1).[20] The new chiral benzopyrazole that has a fused five-membered ring generated only a

Table 1. Re-examination of the synthesis of TlBH$_4$ from TlX and KBH$_4$ on the basis of Waddington's method.[a]

Entry	TlX X	Conc. [M]	KBH$_4$ [mol-equiv.]	Yield [%]	TlBH$_4$ TlBH$_4$/KBH$_4$ ratio[b]	Tl/K/B ratio[c]
1	NO$_3$	0.1	1	5	>99.5:0.5	1:1.00:<0.01
2	NO$_3$	0.2	1	27	>99.5:0.5	1:1.02:<0.01
3	NO$_3$	0.2	2	19	>99.5:0.5	1:0.99:<0.01
4	NO$_3$	1.0[d]	1	_[e]	–	–
5	OAc	0.2	1	40	>99.5:0.5	1: 0.99:<0.01
6	OAc	0.5	1	61	>99.5:0.5	1: 0.99:<0.01
7	OAc	1.0	1	75	98:2	1: 0.99:0.02
8	OAc	1.0[f]	1	75	>99.5:0.5	1:1.00:<0.01
9	OAc	1.5	1	_[g]	65:35	–
10	OAc	1.0[f]	2	85	>99.5:0.5	1:1.00:<0.01
11	OAc	1.0[f,h]	2	94	>99.5:0.5	1:1.00:<0.01
12	OAc	1.0[f,i]	2	93	>99.5:0.5	1: 0.99:<0.01
13	OAc	_[j]	1	_[k]	48:52	–
14	F	1.0	1	80	>99.5:0.5	1: 0.99:<0.01

[a] Reactions were carried out on a 1-mmol scale at 23 °C for 30 s in water unless otherwise specified. KBH_4 was added as a solid. [b] Analyzed by solid-state ^{11}B NMR spectroscopy (TlBH$_4$: δ = –50 ppm, KBH$_4$: δ = –60 ppm). The ^{11}B signals for a sample prepared from 500.00 mg TlBH$_4$ and 0.25 mg KBH$_4$ appear in a 99.6:0.4 ratio. A ratio >99.5:0.5 means that no signal for KBH_4 was observed.[12] [c] ICP analysis.[12] [d] Not soluble for concentrations >0.4 M at 25 °C. [e] 0.19 g of the crude mixture was isolated. The sample was explosive probably because of the presence of $TlNO_3$ or KNO_3. [f] Stirred for 60 s. [g] 0.13 g of the crude mixture was isolated. [h] KOH (0.1 mmol) was added. [i] TlOH (0.1 mmol) was added. [j] Solid TlOAc and KBH$_4$ were mixed at 23 °C for 10 min, and the mixture was then washed with water, CH_3OH, and ether. [k] 0.15 g of the crude mixture was isolated.

Table 2. Direct TlTp^{R1,R2,R3} (**2**) synthesis by the TlBH$_4$ method from HPz^{R1,R2,R3} (**1**).[a]

Entry	Pyrazole species **1**	Conversion [%][b]	Products[c] 2:3:4[d]	Yield of **2** [%][e]
1		99	97:0:3	97 (94)
2		96	97:0:3	93 (92)[f,g]
3		99	99:0:1	98 (95)[f,h]
4		87	98:1:1	85 (82)
5		100	94:6:0	93 (86)
6		98	99:0:1	97 (93)[f,i]
7		100	100:0:0[j]	99 (97)[f,k]
8		93	99:1:0[j]	92 (88)
9		95	97:2:1	92 (90)[f,m]

[a] Reactions were carried out by mixing TlBH$_4$ and **1** in a 1:3 ratio without solvent at 140–160 °C for 1 h under an Ar stream and then at 180 °C for 4–5 h in a sealed system.[12] The values for the percentage conversion, percentage yield, and the product ratio are rounded in the first decimal place. [b] Consumption of **1**. [c] Determined by ^{1}H- and ^{11}B NMR analyses (CDCl$_3$, 23 °C, 50 mM) of the products obtained after CHCl$_3$ extraction followed by evaporation. The chemical shifts of TlTp, TlBH$_2$(Pz)$_2$, TlB(Pz)$_4$ are δ = –2.67 ppm (d, J_{BH} = 111 Hz, BH), δ = –9.26 ppm (t, J_{BH} = 100 Hz, BH$_2$), δ = 0.13 ppm (s, B), respectively.[12] According to the order of the chemical shifts and the coupling patterns, other thallium borato complexes were tentatively assigned. [d] **3**: TlBH$_2$(Pz^{R1,R2,R3})$_2$. **4**: TlB(Pz^{R1,R2,R3})$_4$. [e] Values in parentheses are based on the calculated mass of **2** in the crude products obtained after workup. [f] Formation of TlTp^{R1,R2,R3} and its regioisomers TlTp^{R1,R2,R3}* is possible. [g] The regioisomer ratio was 94.4:5.1:0.5:0. [h] Virtually only TlTp^{Ph} was formed. [i] A very small amount of TlTp^{4Bo}* was observed. [j] Less than 0.4% of **3** or **4** is present. [k] The regioisomer ratio was 48.6:38.9:11.8:0.7. [l] TlBH$_4$/HPz^{4Bo3MeCpenta} = 1:2.5. [m] Other isomers were not observed.
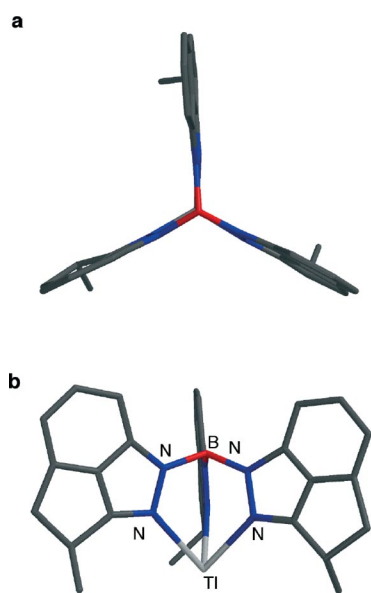

Figure 1. Molecular structure of (*S*,*S*,*S*)-TlTp^{4Bo3MeCpenta} in the crystalline state (a: top view, b: side view). The hydrogen atoms are omitted for clarity.

single regioisomer (*S*,*S*,*S*)-TlTp^{4Bo3MeCpenta} because of the similarities in the electronic and steric effects.[1,17]

Conclusions

In summary, we have established a simple and straightforward process for the synthesis of the complexes TlTp^{R1,R2,R3} from TlBH$_4$ and 3 mol-equiv. HPz^{R1,R2,R3}. The present method should satisfy the conditions required for the preparation of the complexes TlTp^{R1,R2,R3} from hard-to-obtain HPz^{R1,R2,R3} compounds. In view of the importance of the scorpionates, this new method should attract the attention of the researchers in a wide range of scientific and technological fields.[5–7] In addition, establishment of a highly reproducible, reliable, and safe procedure as well as the obtaining of a series of spectroscopic data for TlBH$_4$ should enhance its utility.

Experimental Section

Instrumentation: NMR spectra were recorded at 23 °C on a JEOL JNM-ECA-600 spectrometer. The chemical shifts are expressed in

ppm downfield from tetramethylsilane or in ppm relative to CHCl₃ and CDON(CD₃)CD₂H (¹H NMR: δ = 7.26 and 2.91 ppm, ¹³C NMR: δ = 77.0 ppm). For ¹¹B NMR spectra, $BF_3 \cdot O(C_2H_5)_2$ (δ = 0 ppm) was used as an external standard. Solid-state ¹¹B NMR spectra were obtained at 25 °C on a JEOL JNM-ECA 700 spectrometer with a magic-angle spinning of 15 kHz, and its chemical shifts are reported in ppm relative to $B(OH)_3$. Signal patterns for the ¹H NMR spectra are indicated as follows: s, singlet; d, doublet; t, triplet; quart, quartet; quint, quintet; m, multiplet; br., broad signal. IR spectra were measured on a PERKIN ELMER SPECTRUM 2000 by using the Nujol method. X-ray crystallographic analysis was conducted on a Rigaku Saturn 70 CCD system, and the structure was solved by direct methods by using the Crystal-Structure crystallographic software. ICP analysis was determined by a VISTA-PRO, CCD Simultaneous ICP-OES analyzer.

Materials: Argon gas was purified by passage first through a column of BASF R3–11 catalyst at 80 °C and then through a column of granular calcium sulfate. [D₇]DMF was purchased from Aldrich and Cambridge Isotope Laboratories (CIL), [D]chloroform from CIL, methanol from KISHIDA CHEMICAL, chloroform, dichloromethane, ether, and distilled water from Nacalai tesque. All solvents were used without further purification. 3-Phenyl-1H-pyrazole was purchased from ACROS, 4-bromo-3,5-dimethyl-1H-pyrazole, 4-methyl-1H-pyrazole, potassium borohydride, 4,5,6,7-tetrahydro-1H-indazole, and thallium fluoride from Aldrich, 3-methyl-1H-pyrazole from JANSSEN CHIMICA, thallium nitrate from KANTO CHEMICAL, thallium acetate from KISHIDA CHEMICAL, 3,5-dimethyl-1H-pyrazole and 1H-indazole from TCI, 1H-pyrazole from Merck, nitric acid, potassium chloride, and potassium hydroxide from Nacalai tesque, and boric acid from Wako Chemicals. (S)-HPz^4Bo3MeCpenta[19] and thallium hydroxide[21] were synthesized. HPz^4Bo3MeCpenta: ¹H NMR (600 MHz, CDCl₃), δ = 1.51 (d, J_{HH} = 7.57 Hz, 3 H, CH₃), 3.32 (dd, J_{HH} = 2.75, 16.53 Hz, 1 H, CHH), 3.92 (m, 1 H, CH₃CH), 4.05 (dd, J_{HH} = 6.89, 16.53 Hz, 1 H, CHH), 6.85 (d, J_{HH} = 7.57 Hz, 1 H, aromatic), 7.08 (d, J_{HH} = 7.57 Hz, 1 H, aromatic), 7.38 (t, J_{HH} = 7.57 Hz, 1 H, NCCHCH), 9.74 (br. s, 1 H, NH) ppm; ¹³C NMR (151 MHz, CDCl₃): δ = 19.9, 37.7, 47.9, 107.3, 114.8, 132.2, 136.3, 137.9, 139.2, 162.9 ppm; M.p.: 129 °C.

10 g-Scale Synthesis of TlBH₄: Thallium acetate (13.2 g, 50 mmol) and potassium hydroxide (0.28 g, 5.0 mmol) were placed in a 300-mL round bottle flask and dissolved in water (50 mL). Several small portions of potassium borohydride (5.4 g, 100 mmol) were added as a finely ground solid to the vigorously stirred solution at 23 °C. The temperature was increased to 25 °C. After 60 s, the whole mixture was quickly passed through filter paper on a glass filter funnel (ϕ = 8 cm), and the gray–white solid was washed with cooled methanol (20 mL × 5) and ether (50 mL × 5). After drying under vacuum (0.01 Torr) for 1 h, thallium borohydride was obtained as a gray–white solid (10.2 g, 93%). ¹H NMR (600 MHz, [D₇]DMF): δ = 2.51 (quart, $^1J_{^{11}BH}$ = 81.9 Hz, ¹¹BH₄), 2.51 (septet, $^1J_{^{10}BH}$ = 27.5 Hz, ¹⁰BH₄) ppm. ¹¹B NMR (193 MHz, [D₇]DMF): δ = –31.7 (quint, $^1J_{^{11}BH}$ = 81.5 Hz, BH₄) ppm. Solid-state ¹¹B NMR (700 MHz): δ = –50.2 (s, ¹¹BH) ppm. The ¹¹B signal for KBH₄ was not observed, while a sample prepared from 500.00 mg TlBH₄ and 0.25 mg KBH₄ presented ¹¹B signals at δ = –50.2 ppm and at δ = –59.7 ppm in a 99.6:0.4 ratio.[12] IR (Nujol): $\tilde{\nu}_{max}$ = 2180, 1050 cm⁻¹. ICP-OES: Tl/B/K = 1:1.00:<0.01.

Supporting Information (see footnote on the first page of this article): The IR, ¹H- and ¹¹B NMR spectra of TlBH₄ and the general procedure for the synthesis of TlTps is given.

Acknowledgments

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[2] The abbreviation rule for Tp^R1,R2,R3 {[BH(Pz^R1,R2,R3)₃]⁻} basically followed that defined by Trofimenko. Superscripted R¹, R², and R³ correspond to the substituents at the C(3), C(5), and C(4) on the pyrazolyl ring, respectively. The priority of C(3) is the highest, followed by C(5) and then C(4). When the structure cannot be defined uniquely, the carbon number is attached before the substituent: R¹ = R² = R³ = H: Tp; R¹ = CH₃, R² = R³ = H: Tp^Me; R¹ = C₆H₅, R² = R³ = H: Tp^Ph; R¹ = R² = H, R³ = CH₃: Tp^4Me; R¹ = R² = CH₃, R³ = H: Tp^Me2 (Tp*); R¹ = H, R²–R³ = (CH)₄: Tp^4Bo; R¹–R³ = (CH)₄, R² = H: Tp^3Bo; R¹ = H, R²–R³ = (CH₂)₄: Tp^4mt4; R¹–R³ = (CH₂)₄, R² = H: Tp^3mt4; R¹ = R² = CH₃, R³ = Br: Tp^Me2,Br (Tp*^Br). The regioisomers were described by the addition of "*" to the end of the superscripts (e.g.: Tp^R1,R2,R3 versus Tp^R1,R2,R3*). The discrimination of three possible regioisomers, [BH(Pz^R1,R2,R3)₂(Pz^R2,R1,R3)]⁻, [BH(Pz^R1,R2,R3)(Pz^R2,R1,R3)₂]⁻, and [BH(Pz^R2,R1,R3)₃]⁻ are not referred to.

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[9] Abbreviation "–N–N–" in the compound **2** structure is a pyrazolyl group matching the one at the right or left pyrazole structure of **2**.

[10] For the chiral Tp ligands see: a) D. D. LeCloux, W. B. Tolman, *J. Am. Chem. Soc.* **1993**, *115*, 1153–1154; b) M. C. Keyes, B. M. Chamberlain, S. A. Caltagirone, J. A. Halfen, W. B. Tolman, *Organometallics* **1998**, *17*, 1984–1992; c) G. R. Motson, O. Mamula, J. C. Jeffery, J. A. McCleverty, M. D. Ward, A.

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[12] For details see Supporting Information.

[13] *Caution*: The crude solid compounds obtained with TlNO$_3$ (>0.4 M) and 1–2 mol-equiv. KBH$_4$ sometimes exploded on impact. Further optimization was abandoned.

[14] Reaction of TlOH (0.2 M) with 1 mol-equiv. KBH$_4$ in water gave "TlBH$_4$ with a Tl/B/K ICP analysis of 1:1.00:<0.01" in less than 20% yield.

[15] J. B. Brown, M. Srensson, *J. Am. Chem. Soc.* **1957**, *79*, 4241–4242.

[16] With less water soluble thallium halides (TlCl, 0.016 M; TlBr, 0.001 M; TlI, 0.00018 M), small amounts of TlBH$_4$ were obtained. Other less soluble thallium salts (Tl$_2$SO$_4$, 0.096 M; Tl$_2$CO$_3$, 0.11 M) afforded TlBH$_4$ in <10% yield.

[17] A. L. Rheingold, G. Yap, S. Trofimenko, *Inorg. Chem.* **1995**, *34*, 759–760.

[18] R. M. Claramunt, M. D. S. María, J. Elguero, S. Trofimenko, *Polyhedron* **2004**, *23*, 2985–2991.

[19] (*S*)-HPz^{4Bo3MeCpenta} = (*S*)-3-methyl-3,4-dihydro-1*H*-cyclopenta[*cd*]indazole. The chiral pyrazole is characterized by the high planarity of cyclopentanoindazole moiety. Furthermore, coexistence of 1*H*-indazole and the C(3) substituent can realize a high N(1) selectivity in the formation of TlTp^{4Bo3RCpenta}. The synthetic method for HPz^{4Bo3RCpenta} (R = H, CH$_3$, *i*-C$_3$H$_7$, *t*-C$_4$H$_9$, and C$_6$H$_5$) and the chiral recognition ability of the Tp^{4Bo3RCpenta} ligands will be separately published in due course.

[20] CCDC-661627 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[21] M. Nakahara (Ed.) in *Dictionary of Inorganic Compounds and Complexes*, Kodansha-Scientific Publisher, Tokyo, **1997** (in Japanese).