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Solvent-free one-pot synthesis of thallium complexes of Tp $[BH(Pz)_3]^-$ (Pz = pyrazolate) and its derivatives

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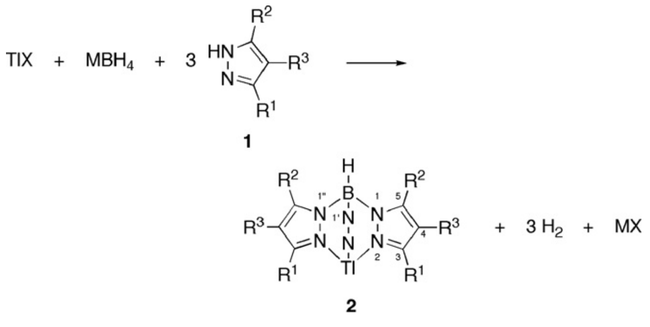
Abstract

Heating a 0.5:1:3 mixture of Tl_2SO_4, KBH_4, and HPz or 3-, 4-, and/or 5-substituted derivatives without the use of any solvent afforded the corresponding thallium complexes of hydrotris(1-pyrazolyl)borate (Tp), and its various substituted forms in high yields. This simple and efficient method should enhance the utility of TlTp-related complexes, which are widely used as mild Tp ligand transfer reagents in the preparation of a variety of transition metal Tp complexes.

Trofimenko's C_{3v} *fac*-type ligands, hydrotris(1-pyrazolyl)borate (Tp) and its various substituted forms are widely known as scorpionates.[1,2] Their metal complexes attract much attention in numerous different fields such as catalytic reactions,[3] metalloenzyme modelling,[4] and technomimetic molecules.[5] Thallium(I) complexes of scorpionates are frequently used as mild and efficient reagents for the transfer of ligands to a variety of transition metals.[6] This is because of their many advantages such as being less reducing than the corresponding alkali metal salts, their high stability, and the ease of isolation and structural characterization of new Tp^{R^1,R^2,R^3} ligands due to their high crystallinity. The thallium complexes are generally prepared in two steps: First, KTp^{R^1,R^2,R^3} is synthesized from KBH_4 and the corresponding pyrazole derivatives (HPz^{R^1,R^2,R^3}), and then the potassium salt is reacted with $TlNO_3$.[7] While the process is simple, the requirement to use an excess of HPz^{R^1,R^2,R^3} sometimes causes a problem in the isolation of the KTp^{R^1,R^2,R^3}. Furthermore, the removal of the byproduct, KNO_3, in the second step decreases the efficiency of the process. The use of explosive metal nitrate under reductive conditions is also undesirable. Due to the high utilization of $TlTp^{R^1,R^2,R^3}$, a more efficient and direct method of synthesis is desirable. This Letter describes a one-pot synthesis of TlTp-related compounds just by mixing Tl_2SO_4, KBH_4, and pyrazole derivatives in a 0.5:1:3 mol ratio without the use of any solvent.



a: $R^1 = R^2 = R^3 = H$
b: $R^1 = CH_3$, $R^2 = R^3 = H$
c: $R^1 = C_6H_5$, $R^2 = R^3 = H$
d: $R^1 = R^2 = H$, $R^3 = CH_3$
e: $R^1 = R^2 = CH_3$, $R^3 = H$
f: $R^1 = H$, $R^2—R^3 = (CH)_4$
g: $R^2 = H$, $R^1—R^3 = (CH_2)_4$
h: $R^1 = R^2 = CH_3$, $R^3 = Br$

Initially, the optimum choice of TlX[8] and MBH_4 was investigated on a 0.5 mmol scale by fixing **1** to HPz, **1a** only. A 1:1:3 mixture of TlX, MBH_4, and **1a** was mixed

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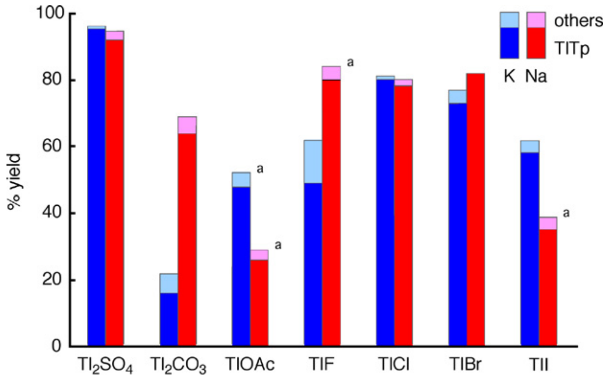


Fig. 1. Effect of varying TlX and MBH_4 in one-pot synthesis of TlTp under standard condition (0.5 mmol scale, Tl:M:HPz = 1:1:3, 140 °C 1 h then 180 °C 5 h). Others are mainly $TlBH_2(Pz)_2$ and $TlB(Pz)_4$. [a] Undetermined compounds with <10% intensity of TlTp ^{11}B signal were contained.

in a mortar and heated at 140 °C for 1 h followed by 180 °C for 5 h. Partition of the mixture between $CHCl_3$ and water followed by concentration of the $CHCl_3$ extract afforded a solid. The yield and purity were assessed by ^1H and ^{11}B NMR spectroscopy. The results are shown in Figure 1. Blue and red bars correspond to the yield of TlTp obtained with KBH_4 and $NaBH_4$, respectively. Pale colors indicate the formation of subproducts, mainly $TlBH_2(Pz)_2$ **3** and $TlB(Pz)_4$ **4**. The combination of Tl_2SO_4 and KBH_4 afforded, after 96% conversion of HPz, a 99:1:0 mixture of TlTp, $TlBH_2(Pz)_2$, and $TlB(Pz)_4$. KBH_4 is more efficient than $NaBH_4$ with TlX (X = 1/2(SO_4), OAc, Cl, I), while the opposite effect is observed with Tl_2CO_3, TlF, and TlBr. The combinations TlF/$NaBH_4$ and TlBr/$NaBH_4$ are also effective, but do not match the yield of TlTp with the Tl_2SO_4/KBH_4 system. The Tl_2SO_4/KBH_4/HPz method obtained by the preliminary screening was successfully confirmed by a 10 g-scale synthesis of TlTp.[9] The ^1H, ^{13}C, and ^{11}B NMR spectra after a single precipitation (86% isolated yield) are shown in Figure 2. The NH signal of HPz at δ 11 completely disappeared and the three unsymmetrical protons and carbons at C(3), C(4), and C(5) resonate at δ 7.6, 6.2, and 7.7 and at δ 139, 104, and 136, respectively. The BH signal coupled with the ^{11}B nucleus appears as a quartet with $J_{BH} = 111$ Hz, while the ^{11}B resonates at δ −2.7 as a doublet. The ICP analysis of the sample showed Tl:B:K = 1:1.00:< 0.01. All of the above data clearly indicate the formation of TlTp of high purity.

The Tl_2SO_4/KBH_4 method is applicable to a variety of pyrazoles (**1**) as shown in Table 1. Symmetrical pyrazoles **1a**, **1d**, **1e**, and **1h** (entries 1, 4, 5, and 8) and unsymmetrical pyrazoles **1b**, **1c**, and **1f** (entries 2, 3, and 6) gave the corresponding **2**,[10] TlTp, $TlTp^{4Me}$, $TlTp^{Me2}$, $TlTp^{Me2,Br}$, $TlTp^{Me}$, $TlTp^{Ph}$, and $TlTp^{4Bo}$,[2] respectively, with high purities. Use of tetrahydroindazole **1g** led to a 29:42:24:4 mixture of four regioisomers (entry 7).[11]

In the present solvent-free one-pot preparation of TlTp and related compounds, there are two possible reaction pathways. One is via $TlBH_4$,[12] which would be produced by KBH_4 reacting with 0.5 equiv of Tl_2SO_4. Reaction of $TlBH_4$ with 3 equiv of HPz would give TlTp with the liberation of H_2 gas. The other pathway is via KTp generated by the reaction of KBH_4 and 3 equiv of HPz followed by the reaction with 0.5 equiv of Tl_2SO_4. To examine these reaction pathways the following two component mixtures, KBH_4/Tl_2SO_4, $TlBH_4$/HPz, KBH_4/HPz, and KTp/Tl_2SO_4, were independently mixed at 180 °C for 5 h and then analyzed by solid-state ^{11}B NMR or IR using Nujol.[13] $TlBH_4$[12] and KTp[14] were synthesized according to literature methods. The KBH_4/Tl_2SO_4 system resulted in no reaction (solid-state ^{11}B NMR: δ −60 for KBH_4, δ −50 for $TlBH_4$[12]). Although the direct preparation of TlTp from $TlBH_4$ and HPz is possible, the lack of reaction for KBH_4/Tl_2SO_4 suggests that the $TlBH_4$ pathway is unlikely. On the other hand, the KBH_4/HPz system afforded a 9:1 mixture of KTp and $KBH_2(Pz)_2$, and KTp/Tl_2SO_4 gave a significant amount of TlTp (IR analysis: 2388 cm^{-1} for KTp[14] and 2443 cm^{-1} for TlTp[15]) in the reaction system. Although the formation of TlTp, via a small amount of $TlBH_4$ generated, cannot be completely ruled out, the most plausible route is by the way of KTp.

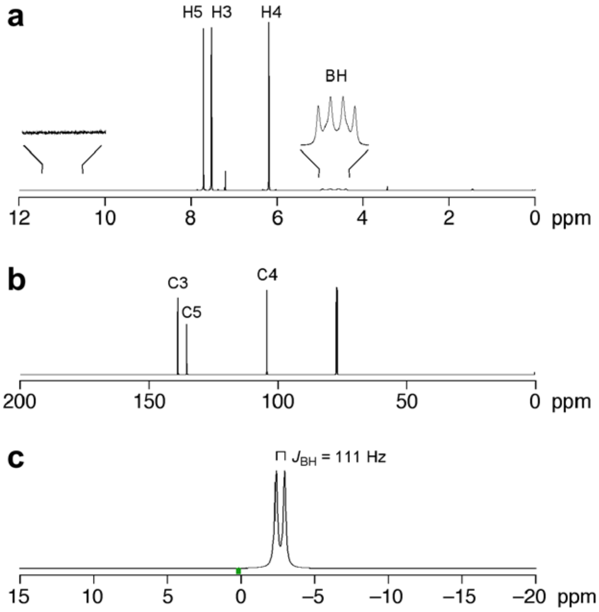
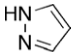
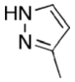
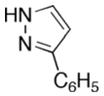
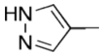
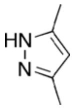
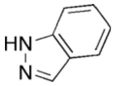
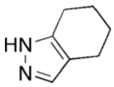
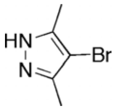


Fig. 2. ^1H (**a**), $^{13}C\{^1H\}$ (**b**), and ^{11}B NMR (**c**) spectra of TlTp ($CDCl_3$ 23 °C, 50 mM). Green-filled signal is assignable to $TlB(Pz)_4$.

In summary, we have established a simple and efficient process for the synthesis of $TlTp^{R^1,R^2,R^3}$ complexes just by mixing three components, Tl_2SO_4, KBH_4, and pyrazoles. While the yields and purities are not perfect, the method is superior to the conventional routes from many viewpoints including chemical yields, operability, and applicability. The present method should satisfy the conditions required for the preparation of the $TlTp^{R^1,R^2,R^3}$ complexes from difficult-to-obtain HPz^{R^1,R^2,R^3} compounds. In view of the importance of the scorpionates, the new method should attract much attention in a wide range of scientific and technological fields.

Table 1
Preparation of TlTp and related complexes[a]

Entry	HPz^{R^1,R^2,R^3} (**1**)		% Convn[b]	Product[c]	
				2:**3**[d]:**4**[d]	% Yield of **2**[e]
1	**a**		96	99:1:0[f]	96 (87)
2	**b**		100	100:0:0[f]	100 (74)[g,h]
3	**c**		97	98:1:1	95 (77)[g]
4	**d**		97	99:0:1	96 (65)
5	**e**		98	93:7:0	92 (75)
6	**f**		99	99:0[f]:0[f]	98 (78)[g]
7	**g**		61	99:0[f]:1	60 (51)[g,i]
8	**h**		98	100:0:0	98 (82)

[a] Reactions were carried out by mixing Tl_2SO_4 (0.25 mmol), KBH_4 (0.5 mmol), and HPz^{R^1,R^2,R^3} (1.5 mmol) at 120–160 °C for 1 h under an Ar stream then 180 °C for 4–7 h in a sealed system unless otherwise specified. The values of % convn, % yield, and the product ratio were rounded in the first decimal place.

[b] Consumption of **1**.

[c] Determined by ^1H and ^{11}B NMR analyses of the products obtained after $CHCl_3$ extraction followed by evaporation. The chemical shifts of TlTp, $TlBH_2(Pz)_2$, and $TlB(Pz)_4$ are δ −2.68 (d, $J_{BH} = 111$ Hz, *B*H), δ −9.30 (t, $J_{BH} = 100$ Hz, BH_2), and δ 0.13 (s, *B*), respectively. According to the order of the chemical shifts and the coupling patterns, other thallium borates were tentatively assigned.

[d] **3**: $TlBH_2(Pz^{R^1,R^2,R^3})_2$. **4**: $TlB(Pz^{R^1,R^2,R^3})_4$.

[e] Values in parentheses are based on the calculated mass of **2** in the crude products obtained after workup. For the detailed workup, see Ref. 9.

[f] Contains less than 0.4% of **3** or **4**.

[g] Formation of $TlTp^{R^1,R^2,R^3}$ and its regioisomers $TlTp^{R^1,R^2,R^{3*}}$ is possible.

[h] The regioisomer ratio was 90:9:1:0.

[i] The regioisomer ratio was 29:42:24:4.

Acknowledgments

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References and notes

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2. The abbreviation rule for Tp^{R^1,R^2,R^3} ($[BH(Pz^{R^1,R^2,R^3})_3]^-$) basically followed that defined by Trofimenko. The superscripted R^1, R^2, and R^3 correspond to the substituents at 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: $R^1 = R^2 = R^3 = H$: Tp, $R^1 = CH_3$; $R^2 = R^3 = H$: Tp^{Me}, $R^1 = C_6H_5$; $R^2 = R^3 = H$: Tp^{Ph}, $R^1 = R^2 = H$; $R^3 = CH_3$: Tp^{4Me}, $R^1 = R^2 = CH_3$; $R^3 = H$: Tp^{Me2} (Tp^*), $R^1 = H$; R^2–$R^3 = (CH)_4$: Tp^{4Bo}, R^1–$R^3 = (CH)_4$; $R^2 = H$: Tp^{3Bo}, $R^1 = H$; R^2–$R^3 = (CH_2)_4$: Tp^{4mt4}, R^1–$R^3 = (CH_2)_4$; $R^2 = H$: Tp^{3mt4}, $R^1 = R^2 = CH_3$; $R^3 = Br$: $Tp^{Me2,Br}$ (Tp^{*Br}). The regioisomers were described by the addition of '∗' at the end of the superscripts (e.g., Tp^{R^1,R^2,R^3} vs $Tp^{R^1,R^2,R^{3*}}$). The discrimination of three possible regioisomers, $[BH(Pz^{R^1,R^2,R^3})_2(Pz^{R^2,R^1,R^3})]^-$, $[BH(Pz^{R^1,R^2,R^3})(Pz^{R^2,R^1,R^3})_2]^-$, and $[BH(Pz^{R^2,R^1,R^3})_3]^-$ are not referred.
3. The catalytic reactions reported before 1999 are reviewed in Ref. 1d. The recent reports and the ones not listed in Ref. 1d, are as follows. C–C bond formation: (a) Domhöver, B.; Kläui, W.; Kremer-Aach, A.; Bell, R.; Mootz, D. *Angew. Chem., Int. Ed.* **1998**, *37*, 3050–3052; Oxidation: (b) Santos, A. M.; Kühn, F. E.; Bruus-Jensen, K.; Lucas, I.; Romão, C. C.; Herdtweck, E. *J. Chem. Soc., Dalton Trans.* **2001**, 1332–1337; Reduction: (c) Chan, W.-C.; Lau, C.-P.; Chen, Y.-Z.; Fang, Y.-Q.; Ng, S.-M.; Jia, G. *Organometallics* **1997**, *16*, 34–44; (d) Yin, C.; Xu, Z.; Yang, S.-Y.; Ng, S. M.; Wong, K. Y.; Lin, Z.; Lau, C. P. *Organometallics* **2001**, *20*, 1216–1222; (e) Alvarado, Y.; Busolo, M.; López-Linares, F. *J. Mol. Catal. A: Chem.* **1999**, *142*, 163–167. For the chiral Tp ligands, see: (f) LeCloux, D. D.; Tolman, W. B. *J. Am. Chem. Soc.* **1993**, *115*, 1153–1154; (g) Keyes, M. C.; Chamberlain, B. M.; Caltagirone, S. A.; Halfen, J. A.; Tolman, W. B. *Organometallics* **1998**, *17*, 1984–1992; (h) Motson, G. R.; Mamula, O.; Jeffery, J. C.; McCleverty, J. A.; Ward, M. D.; von Zelewsky, A. *J. Chem. Soc., Dalton Trans.* **2001**, 1389–1391; (i) Babbar, P.; Brunner, H.; Singh, U. P. *Indian J. Chem., Sect. A* **2001**, *40*, 225–227; (j) Singh, U. P.; Babbar, P.; Hassler, B.; Nishiyama, H.; Brunner, H. *J. Mol. Catal. A: Chem.* **2002**, *185*, 33–39.
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8. $TlNO_3$ must not be used. Mixing $TlNO_3$ with KBH_4 in a solid state sometimes causes an explosion.
9. Procedure: *Because of the toxicity of thallium compounds, all of the processes should be done in a well-benched fumed hood.* 1*H*-Pyrazole (5.11 g, 75.1 mmol), Tl_2SO_4 (6.31 g, 12.5 mmol), and KBH_4 (1.35 g, 25.0 mmol) were placed in a 80-mL Young-type Schlenk tube (wall thickness: 5 mm. The pressure is released through Teflon valve at ca.

3 atm. The use of pressure-tight glass is recommended) containing a magnetic stirring bar. The whole system was evacuated and filled with argon. The tube was immersed in an oil bath so that the level of the solids in the tube was slightly below the surface of the oil. The mixture was stirred at 140 °C for 1 h under an argon stream in an open system, and then the Schlenk tube was sealed by closing the Teflon Young's tap. At this stage, ca. 65:35 TlTp and $\mathrm{TlBH_2(Pz)_2}$ mixture is formed. After 2-h heating at 180 °C, the mixture was allowed to cool to room temperature. The Schlenk tube was connected to an argon line, and then the internal pressure, which had been raised by the evolution of hydrogen gas, was carefully released. Subsequent 3-h heating at 180 °C in the closed system followed by cooling to room temperature afforded a white solid. Chloroform (300 mL) was added, and the resulting suspension was washed three times with water (300 mL). Drying of the organic layer over $\mathrm{Na_2SO_4}$ (100 g), followed by filtration and evaporation in vacuo gave as a white solid (9.65 g) in 99% conversion of 1*H*-pyrazole. The crude products were determined by ^{1}H and ^{11}B NMR analyses to consist of TlTp, $\mathrm{TlBH_2(Pz)_2}$, and $\mathrm{TlB(Pz)_4}$ in a 98:1:1 ratio, indicating that TlTp forms in 97% yield. The mass of TlTp is calculated to be 9.35 g, which corresponds to 90% yield. Single precipitation from $\mathrm{CH_2Cl_2}$ (10 mL) and $\mathrm{CH_3OH}$ (20 mL) afforded TlTp with high purity in 86% isolated yield (see Fig. 2 for NMR spectra).

10. Abbreviation '–N–N–' in compound **2** structure is a pyrazolyl group matching the one at the right or left pyrazole structure of **2**.
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13. The use of KBr method causes K/Tl exchange. The ^{11}B signals of KTp and TlTp could not be discriminated either in the solid-state NMR (δ −24) or in the solution-state NMR (δ −2.4 in DMF-d_7).
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