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para-Bromophenyl[tris(pyrazolyl)]borate Complexes of Group 1 Metals, Thallium and Magnesium: Synthesis and Characterization of Transfer Agents for "Third-Generation" Tp Ligands

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In the course of finding ligands suitable for application in bioorganometallic systems, "third-generation" Tp-transfer agents *p*-BrC_6H_4TpM [M = Na (**1**), K (**2**), Rb (**3**), Cs (**4**), Tl (**5**); Tp = tris(pyrazolyl)borate], *p*-$BrC_6H_4Tp^*Tl$ (**6**) [Tp^* = tris(3,5-dimethylpyrazolyl)borate], $(p\text{-}BrC_6H_4Tp)_2Mg$ (**7**), *p*-BrC_6H_4TpMeK (**8**) [$TpMe$ = tris(3-methylpyrazolyl)borate] and *p*-$BrC_6H_4Tp^*K$ (**9**) bearing a functionalizable 4-bromophenyl group on the boron atom were synthesized and characterized. Monovalent **6** and magnesium-sandwich compound **7** were structurally characterized in the solid state by X-ray diffraction. Compound **6** forms a dimer by κ^2-coordination of Tl to one Tp ligand and to the bromine atom of a neighbouring 4-bromophenyl group.

Introduction

The tris(pyrazolyl)borate ligand system (Tp or $HBPz_3$, Pz = pyrazolyl) is one of the most well-studied ligands in inorganic chemistry.[1–4] Accordingly, an immense variety of Tp-containing complexes have been reported from all areas of the periodic table, and such complexes have been employed in vastly different areas of chemistry ranging from polymerization catalysis[2,5–9] to enzyme modelling.[10–13] Such widespread usage of this ligand family is derived, in large part, from the ease with which Tp ligands, including "second-generation" $Tp^{R,R'}$ ligands (Figure 1) that contain substituted pyrazole rings, may be synthesized.[1,2,4]

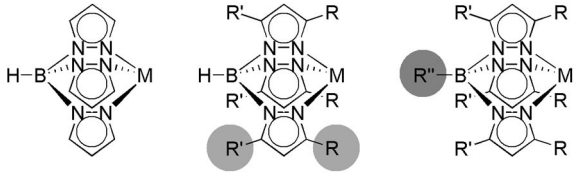

Figure 1. First (left), second (center) and third (right) generation Tp ligands. "Mutations" of the ligand from generation to generation are highlighted in shades of grey.

Facile derivatization of the parent Tp ligand allows fine-tuning of the desired ligand properties such as steric or electronic. Indeed, a vast number of Tp^{Rn} ligands, also denoted as "second-generation" scorpionates, have been reported, most of which focus on substitution at the 3- and 5-positions of the ring. In contrast, "third-generation" RTp derivatives in which the boron-bound hydride has been replaced by an alkyl or aryl group are very scarce. As an illustrative example, only ca. 2.5% of all types of Tp structures found on the CCD (Cambridge Crystal Database) are carbon-functionalized on the boron atom. Nonetheless, "third-generation" RTp ligands are an interesting member of the Tp family. The presence of the R group in RTp-containing complexes is known to extensively effect properties such a solubility, spin-state and solid-state structure.[14,15] In addition, RTp species have been employed in syntheses in which the [B–H] moiety is reactive. Furthermore, boron-substituted ligands, in which R is suitably functionalized, provide a means to covalently attach other groups or whole molecules. In this vein, we have been recently exploring the use of functionalized phenyl-Tp derivatives for use in bioorganometallic chemistry.[16–20] More specifically, we used benzoic acid functionalized Tp complexes for the synthesis of organometallic bioconjugates, compounds which contain a biomolecule (e.g., DNA/RNA, peptides) bound to an organometallic complex. The acid group within *p*-(CO_2H)-C_6H_4Tp complexes is useful for coupling to other organic functionalities, for example, alcohols or amines, to produce covalently linked bioconjugates by well-known synthetic methods. We recently reported the synthesis of bioconjugates of the pentapeptide Enkephalin with organometallic Tp–transition-metal complexes by coupling benzoic acid functionalized Tp complexes with peptides by standard solid-phase peptide synthesis (SPPS).[21–23] (Figure 2).

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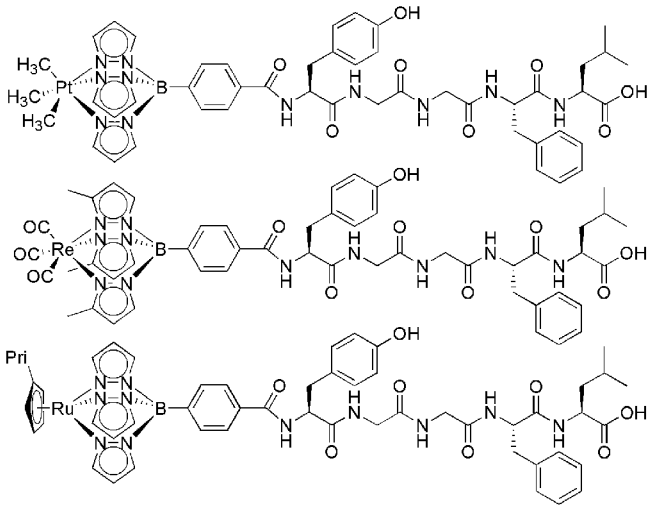


Figure 2. Peptide bioconjugates of organometallic *p*-(CO_2H)-C_6H_4Tp complexes.

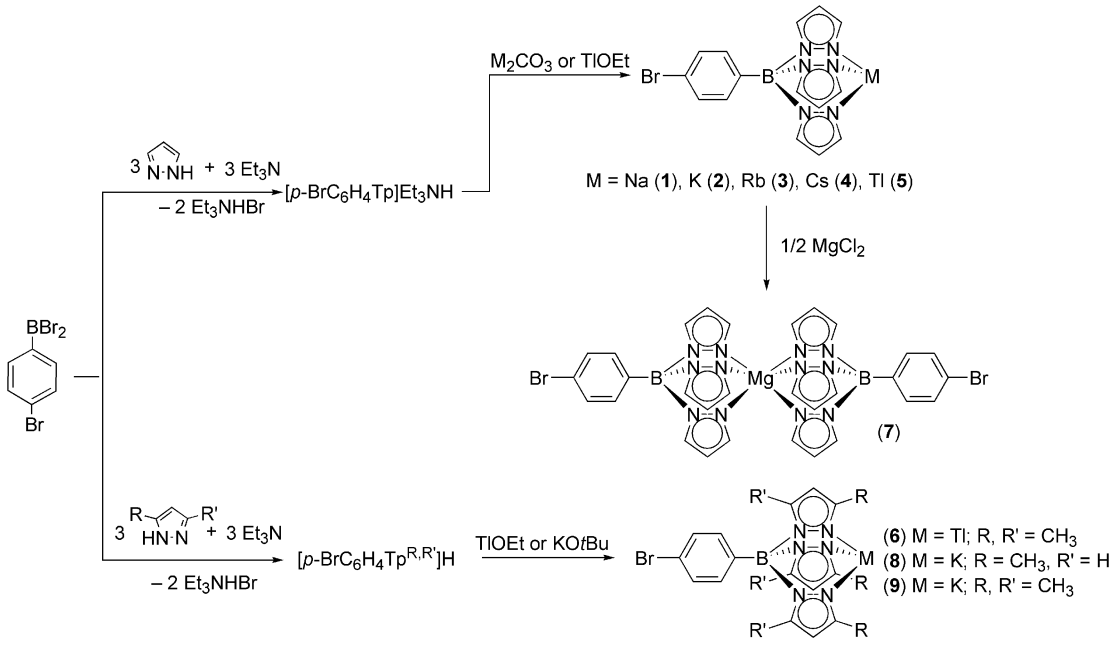
The acid-derivatized Tp complexes may be synthesized from the corresponding *p*-BrC_6H_4Tp species by a sequence of lithiation, carboxylation and protonation of the resulting lithium salt. Such a synthetic method is precedented by Faller et al. who synthesized the benzoic acid–Tp sandwich complex [*p*-$(CO_2H)C_6H_4Tp]_2Co$ by this method.[14]

In contrast, the ability to prepare and purify individual Tp–metal complexes usually depends upon the metal of the Tp transfer agent used. As such, it was judged desirable to have an array of different *p*-BrC_6H_4Tp transfer agents for our syntheses, and accordingly, we sought a general method for the preparation of potential *p*-BrC_6H_4Tp transfer agents.

Herein we demonstrate the syntheses of monovalent *p*-BrC_6H_4TpM complexes including the entire group 1 series and thallium, a novel synthesis of *p*-BrC_6H_4TpNa (**1**),[14] magnesium sandwich $(p\text{-}BrC_6H_4Tp)_2Mg$ **7** and substituted derivatives *p*-$BrC_6H_4Tp^{Me}K$ (**8**), *p*-BrC_6H_4Tp*Tl (**6**) and *p*-BrC_6H_4Tp*K (**9**). The solid-state structures of **6** and **7** were determined by single-crystal X-ray diffraction.

Results and Discussion

"Third-generation" RTp ligands substituted with alkyl and aryl groups at boron have been known since Trofimenkos initial publication on polypyrazolylborates, wherein he reported the alkali metal (M) derivatives *n*BuTpM and PhTpM synthesized by heating a solvent-free mixture of RBH_3M (R = *n*Bu, Ph, M = alkali metal) and pyrazole.[4] In 1967, he reported the synthesis of PhTp derivatives from the reaction of an aryl boron dihalide, $PhBCl_2$, with an excess amount of pyrazole.[24] Directly relevant to our work, complexes of the *p*-BrC_6H_4Tp ligand were reported in 1982 when *p*-BrC_6H_4TpNa was synthesized by the reaction of *p*-$BrC_6H_4B(OH)_2$ with pyrazole and sodium pyrazolide.[14] More recently, Reger et al. reported the syntheses of *p*-IC_6H_4TpNa and *p*-$IC_6H_4Tp^{Me}Na$ from the reaction of *p*-$IC_6H_4TpBBr_2$ with pyrazole and triethylamine, followed by treatment with sodium *tert*-butoxide.[15] Significantly, Reger et al. noted that this is the preferred preparative method for *p*-IC_6H_4TpNa rather than the methods reported for *p*-BrC_6H_4TpNa (vide supra) and the "standard method" of heating the functionalized lithium borohydride, that is, *p*-$BrC_6H_4BH_3Li$, in the presence of an excess amount of pyrazole. Regers preparative method is reminiscent of that previously reported by Wagner et al. to make the ferro-



Scheme 1. Syntheses of the *p*-BrC_6H_4TpM complexes.

cene-substituted thallium complex FcTpTl (Fc = $C_5H_5FeC_5H_5$).[25] Both syntheses generate a Brønsted acidic RTpH intermediate, which is subsequently deprotonated by a metal-containing Brønsted base that determines the specific identity of the resultant TpM species. As such, this method demonstrated the potential as a general method for making RTpM complexes by employing Brønsted bases of the appropriate metal M. We indeed found this to be the case and by using a slightly different modified version of Wagners and Regers preparations, we were able to synthesize group 1 and thallium complexes **1**–**6**, **8** and **9** as shown in Scheme 1. Magnesium Tp sandwich complex **7**, accidentally obtained by drying a *p*-BrC_6H_4TpK solution over anhydrous magnesium sulfate, was synthesized in reproducible preparations by ligand exchange between *p*-BrC_6H_4TpRb and magnesium chloride. We previously reported the syntheses of *p*-BrC_6H_4TpLi[23] and *p*-$BrC_6H_4Tp^{Me}Tl$.[21] One attractive feature of this synthetic method for group 1 *p*-BrC_6H_4TpM is the use of aqueous solutions of alkali metal bases, in particular their carbonates. This not only allows a simple synthesis of the entire series, but could also avoid the use of pyrophoric solutions of metal alkyls, for example, methyl or butyllithium. All of the alkali metal *p*-BrC_6H_4TpM complexes **1**–**4** and **7**–**9** are air stable as solids for at least one month, whereas thallium derivatives **5** and **6** were found to be mildly air sensitive and are best stored under an inert atmosphere. In the previous work of Wagner and Reger, the Tp intermediates are the "proton-salt" complexes *p*-IC_6H_4TpH and FcTpH, by virtue of the stoichiometry. As reported earlier,[23] we observed in our preparations that the presence of a third equivalent of triethylamine has different effects upon the resultant Tp intermediate depending upon whether the pyrazole is substituted or not. Aliquots taken from the reaction mixture after separation from the triethylammonium bromide byproduct were dried under vacuum and analyzed by ^{1}H NMR spectroscopy. The spectra of the crude products indicate the presence of *p*-$BrC_6H_4TpEt_3NH$, *p*-$BrC_6H_4Tp^{Me}H$ and *p*-$BrC_6H_4Tp^*H$ as the intermediates in each respective preparation. These intermediates were found to be slightly air and moisture sensitive, which is further supported by the generally lower yields obtained in the preparations involving aqueous solutions of M_2CO_3 compared to the preparations using potassium *tert*-butoxide or thallium ethoxide.

Molecular Structures of *p*-$BrC_6H_4Tp^*Tl$ (6) and (*p*-$BrC_6H_4Tp)_2Mg$ (7)

The solid-state structures of **6** and **7** were determined by X-ray diffraction. In **7**, the coordination geometry at magnesium is a distorted octahedron as shown in Figure 3. The metal-centred metrical parameters of **7** are similar to those observed in parent Tp_2Mg complexes.[26,27] For example, the range of Mg–N distances, 2.118–2.200 Å, compares well with those of $(Tp^{R,R'})_2Mg$ complexes found in the CCD database, 2.143–2.201 Å.[28] The same is true for the N–Mg–N angles ranging from 83.61–85.13° compared to 85.61–87.01° for the parent Tp_2Mg.[26,27]

The structure of **6** is remarkable in several ways. Most notably, the ligand binds to thallium in a dihapto fashion through only two of the three dimethylpyrazole rings. Whereas such coordination is unprecedented for the parent (i.e., $[H–B]Tp^{R,R'}Tl$) complexes, all of which have κ^3-C_3-symmetric ligands, κ^2-type structures are known for "boron-substituted" $RTp^{R,R'}Tl$ complexes such as MeTp*Tl.[29] In fact, 5 of the 10 structures found in the CCD exhibit κ^2-RTp ligand binding as shown in Figure 4. The origin of such non-C_3-symmetric ligation is a consequence of steric interactions between the boron-bound R group and the substituent at the pyrazole 5-position. Notably, in all these structures the third pyrazole is engaged in "secondary" bonding to thallium in which the Tl–N distances are significantly longer than the two "normal" Tl–N bonds. Moreover, with the exception of monomeric PhTp*t*BuTl, the third Tl–N interaction is intermolecular, producing aggregated solid-state structures. Thus, what makes **6** structurally unique is that one pyrazole not only shows interaction with the thallium atom of a neighbouring molecule, but additionally shows a van der Waals-type interaction with the bromine atom of a neighbouring molecule as depicted in Figure 4. The Tl–Br distance of 3.8150(6) Å is essentially

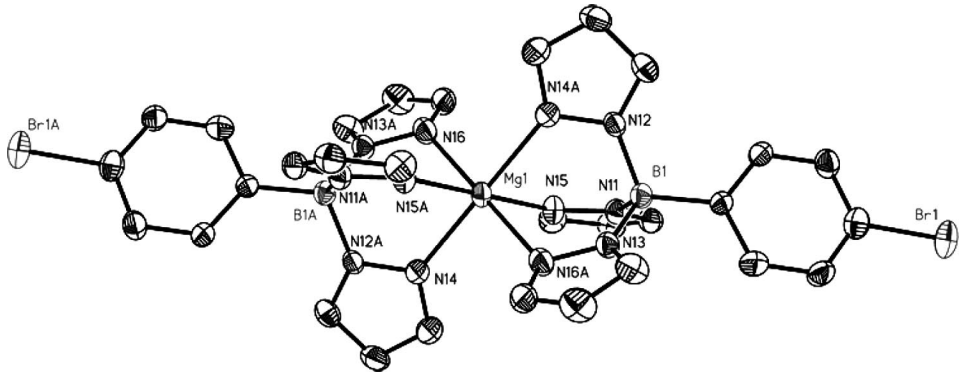


Figure 3. ORTEP plot of the structure of (*p*-$BrC_6H_4Tp)_2Mg$ (**7**; hydrogen atoms are omitted, ellipsoids at 50% probability). Selected bond lengths [Å]: Mg1–N15A 2.132(5), Mg1–N15 2.132(5), Mg1–N16 2.169(5), Mg1–N16A 2.169(5), Mg1–N14 2.187(5), Mg1–N14A 2.187(5). N–Mg–N angles are 83.61–85.13°.

identical to the sum of the Tl and Br van der Waals radii, 3.81 Å.[30] The Tl–N bond lengths for *p*-$BrC_6H_4Tp^*Tl$, 2.559(4) and 2.607(4) Å, are within the range found for the "normal" Tl–N bonds in $RTp^{R,R'}Tl$ complexes (2.528–2.780 Å) as well as for two-coordinate BpTl (ca. 2.57–2.80 Å) and parent TpTl (ca. 2.50–2.79 Å) complexes.[31] The same is found for the N–Tl–N angle of 69.63(12)° that matches the ones found for parent TpTl compounds (ca. 69.0–73.4°).[31] The distance of the thallium atom to the neighbouring pyrazole ring [3.135(4) Å] is found to be longer than for comparable MeTp*Tl [2.876(4) Å], probably due to the second interaction of the thallium atom to the bromine atom.[29]

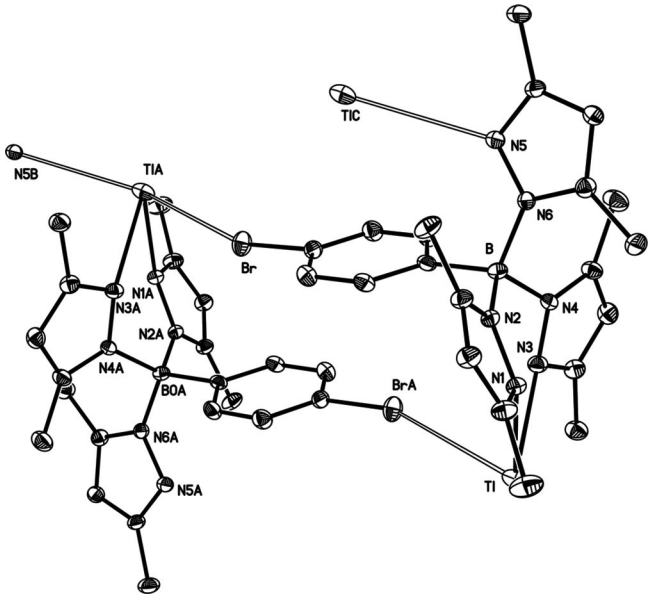


Figure 4. ORTEP plot of the dimer of *p*-BrC6H4Tp*Tl (**6**) showing intermolecular interactions (hydrogen atoms omitted, ellipsoids at 30% probability). Selected bond lengths [Å]: Tl–BrA 3.8150(6), Tl–N1 2.607(4), Tl–N3 2.559(4), TlA–N5B 3.135(4), N5–TlC 3.135(4). Selected angles [°]: N3–Tl–BrA 62.54(9), N3–Tl–N1 69.63(12), N1–Tl–BrA 102.27(9).

Conclusions

In summary, we have reported the synthesis and characterization of a series of transfer agents for functionalized *p*-BrC_6H_4Tp ligands. *p*-$BrC_6H_4Tp^*Tl$ (**6**) and $(p\text{-}BrC_6H_4Tp)_2Mg$ (**7**) were structurally characterized in the solid state by single-crystal X-ray diffraction, thereby demonstrating the structural resemblance to parent Tp ligands. As shown previously,[21–23] these ligands could serve as versatile synthetic handles in the labelling of biomolecules with organometallic moieties, thus extending the frequent use of Tp as a cyclopentadienyl surrogate to the field of bioorganometallic chemistry.

Experimental Section

General: Unless otherwise stated, all experimental techniques were carried out under an inert atmosphere of argon or N_2 by employing standard high-vacuum and Schlenk techniques and an M-Braun glove box. All reagents and anhydrous solvents were obtained from commercial sources and used as received. Dibromo(4-bromophenyl)borane (*p*-$BrC_6H_4BBr_2$) was synthesized following literature procedures.[23,32] The preparations and spectroscopic data of *p*-BrC_6H_4TpLi[23] and *p*-$BrC_6H_4Tp^{Me}Tl$[21] have been published previously. NMR spectra were recorded at ambient temperature with a Bruker DPX 250 spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) relative to the residual proton chemical shifts of the deuterated solvent set relative to external TMS. Coupling constants (*J*) are quoted in Hertz. $^{13}C\{^1H\}$ assignments of the carbon-type (i.e. C, CH, CH_2, CH_3) were made from a standard Attached Proton Test (APT) experiment protocol. Elemental analyses were carried out at the RUBiospek Biospectroscopy Department, Ruhr-University of Bochum.

Alternative Preparation of *p*-BrC_6H_4TpNa (1):[14] A solution of *p*-$BrC_6H_4BBr_2$ (0.85 g, 2.61 mmol) in dichloromethane (5 mL) was added dropwise over ca. 90 min to a cooled (0 °C) and rapidly stirred solution of pyrazole (0.55 g, 8.09 mmol) in dichloromethane (10 mL). At the end of the addition, triethylamine (0.82 g, 8.09 mmol) was added, and the mixture was stirred overnight at room temperature. The volatiles were removed from the mixture under reduced pressure, leaving a white solid that was extracted with THF (20 mL), filtered and cooled on an ice bath. An aqueous solution (5 mL) of sodium carbonate (0.15 g, 1.44 mmol) was added, and the mixture was vigorously stirred at room temperature for 2 h, after which the solvents were removed under reduced pressure. The residue was washed with Et_2O (3 × 5 mL) and hexane (1 × 5 mL) and dried under reduced pressure at 110 °C to give **1** as a white solid (0.26 g, 0.68 mmol, 24%). $C_{15}H_{13}BBrN_6Na$ (391.01): calcd. C 46.08, H 3.35, N 21.49; found C 45.57, H 3.82, N 21.28. ^1H NMR (250 MHz, [D$_6$]DMSO): δ = 7.41 (dd, *J* = 0.5, 1.8 Hz, 3 H, pz-5 H), 7.34 (d, *J* = 8.3 Hz, 2 H, part of C_6H_4), 7.22 (d, *J* = 8.3 Hz, 2 H, part of C_6H_4), 6.80 (dd, *J* = 0.5, 1.8 Hz, 3 H, pz-H3), 6.01 (t, *J* = 1.8 Hz, 3 H, pz-H4) ppm. ^{13}C NMR (62.5 MHz, [D$_6$]-DMSO): δ = 138.8 (CH), 136.3 (CH), 133.5 (CH), 128.4 (CH), 102.6 (CH) ppm.

***p*-BrC_6H_4TpK (2):** This compound was prepared analogously to **1** except that potassium carbonate was used instead of sodium carbonate. Yield: 20%. $C_{15}H_{13}BBrKN_6$ (407.12): calcd. C 44.25, H 3.22, N 20.64; found C 43.37, H 3.17, N 19.46. ^1H NMR (250 MHz, [D$_6$]DMSO): δ = 7.41 (dd, *J* = 2.2, 0.5 Hz, 3 H, pz-H5), 7.35 (d, *J* = 8.3 Hz, 2 H, part of C_6H_4), 7.22 (d, *J* = 8.3 Hz, 2 H, part of C_6H_4), 6.81 (dd, *J* = 0.5, 1.8 Hz, 3 H, pz-H3), 6.01 (t, *J* = 1.8 Hz, 3 H, pz-H4) ppm. ^{13}C NMR (62.5 MHz, [D$_6$]DMSO): δ = 138.6 (CH), 136.4 (CH), 133.3 (CH), 128.3 (CH), 102.4 (CH) ppm.

***p*-BrC_6H_4TpRb (3):** This compound was prepared analogously to **1** except that rubidium carbonate was used instead of sodium carbonate. The product was purified by extraction with warm (50 °C) acetone (2 × 50 mL). Filtration, removal of the solvent and drying at 110 °C overnight gave **3** as a white solid. Yield: 26%. $C_{15}H_{13}BBrN_6Rb$ (453.49): calcd. C 39.73, H 2.89, N 18.53; found C 39.74, H 2.43, N 18.09. ^1H NMR (250 MHz, [D$_6$]DMSO): δ = 7.41 (dd, *J* = 0.5, 1.8 Hz, 3 H, pz-H5), 7.37 (d, *J* = 8.3 Hz, 2 H, part of C_6H_4), 7.24 (d, *J* = 8.3 Hz, 2 H, part of C_6H_4), 6.80 (dd, *J* = 0.5, 1.8 Hz, 3 H, pz-H3), 6.01 (t, *J* = 1.8 Hz, 3 H, pz-H4) ppm. ^{13}C NMR (62.5 MHz, [D$_6$]DMSO): δ = 138.6 (CH), 136.5 (CH), 133.3 (CH), 128.2 (CH), 121.2 (CH), 102.5 (CH) ppm.

***p*-BrC_6H_4TpCs (4):** This compound was prepared analogously to **1** except that cesium carbonate was used instead of sodium carbonate. Yield: 26%. $C_{15}H_{13}BBrCsN_6$ (500.92): calcd. C 35.97, H 2.62, N 16.78; found C 35.54, H 2.86, N 15.81. ^1H NMR (250 MHz,

[D$_6$]DMSO): δ = 7.41 (dd, J = 0.5, 1.8 Hz, 3 H, pz-H5), 7.34 (d, J = 8.3 Hz, 2 H, part of C_6H_4), 7.22 (d, J = 8.3 Hz, 2 H, part of C_6H_4), 6.81 (dd, J = 0.5, 1.8 Hz, 3 H, pz-H3), 6.01 (t, J = 1.8 Hz, 3 H, pz-H4) ppm. ^{13}C NMR (62.5 MHz, [D$_6$]DMSO): δ = 138.5 (CH), 136.5 (CH), 133.3 (CH), 128.2 (CH), 102.6 (CH) ppm.

***p*-BrC$_6$H$_4$TpTl (5):** This compound was prepared analogously to **1** except that a solution of thallium ethoxide in THF was used instead of sodium carbonate. After stirring overnight, the product was isolated by filtration and purified by washing with methanol. A second crop of the product was obtained by removal of the solvent from the filtrate and purified as above. Combined yield: 36%. $C_{15}H_{13}BBrN_6Tl$ (572.40): calcd. C 31.47, H 2.29, N 14.68; found C 31.18, H 2.76, N 14.41. ^{1}H NMR (250 MHz, [D$_6$]DMSO): δ = 7.64 (dd, J = 2.3, 0.4 Hz, 3 H, pz-H5), 7.49 (d, J = 8.2 Hz, 2 H, part of C_6H_4), 7.44 (dd, J = 2.3, 0.4 Hz, 3 H, pz-H4), 7.05 (d, J = 8.2 Hz, 2 H, part of C_6H_4), 6.28 (t, J = 2.3 Hz, 3 H, pz-H4) ppm. ^{13}C NMR (62.5 MHz, [D$_6$]DMSO): δ = 139.3 (CH), 135.9 (CH), 134.1 (CH), 129.2 (CH), 103.1 (CH) ppm.

***p*-BrC$_6$H$_4$Tp*Tl (6):** This compound was prepared analogously to **5** except that 3,5-dimethylpyrazole was used instead of pyrazole. The product was purified by washing with hexane instead of methanol. Yield: 25%. $C_{21}H_{25}BBrN_6Tl$ (656.56): calcd. C 38.42, H 3.84, N 12.80; found C 39.14, H 4.18, N 13.29. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.35 (d, J = 8.2 Hz, 2 H, part of C_6H_4), 7.18 (d, J = 8.2 Hz, 3 H, part of C_6H_4), 5.84 (s, 3 H, pz-H4), 2.19 (s, 9 H, pz-CH_3), 1.67 (s, 9 H, pz-CH_3) ppm. ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 136.8 (CH), 130.3 (CH), 108.25 (CH), 14.1 (CH_3), 13.6 (CH_3) ppm.

(*p*-BrC$_6$H$_4$Tp)$_2$Mg (7): An aqueous solution (2 mL) of magnesium chloride (20 mg, 0.21 mmol) in water was added slowly to a solution of *p*-BrC$_6$H$_4$TpRb (200 mg, 0.44 mmol) in THF (4 mL), and the mixture was stirred for 1 h. After removal of the volatiles, the colourless residue was extracted with dichloromethane (2 × 4 mL), and the extract was filtered through a silica plug. Removal of the solvent yielded a colourless residue that was washed with water (2 × 2 mL) and diethyl ether (2 × 2 mL) and dried under lowered pressure at 110 °C overnight to give (*p*-BrC$_6$H$_4$Tp)$_2$Mg as a colourless powder (112 mg, 0.15 mmol, 71%). $C_{30}H_{26}B_2Br_2MgN_{12}$ (760.38): calcd. C 47.39, H 3.45, N 22.11; found C 47.34, H 3.66, N 22.12. ^{1}H NMR (250 MHz, [D$_6$]DMSO): δ = 7.58 (dd, J = 1.8, 0.5 Hz, 6 H, pz-H5), 7.54 (d, J = 8.3 Hz, 4 H, part of C_6H_4), 7.41 (d, J = 8.3 Hz, 4 H, part of C_6H_4), 7.18 (dd, J = 1.8, 0.5 Hz, 6 H, pz-H3), 6.19 (t, J = 1.8 Hz, 6 H, pz-H4) ppm. ^{13}C NMR (62.5 MHz, [D$_6$]DMSO): δ = 140.9 (CH), 135.1 (CH), 133.1 (CH), 128.3 (CH), 103.9 (CH) ppm.

***p*-BrC$_6$H$_4$Tp^{Me}K (8):** A solution of *p*-BrC$_6$H$_4$BBr$_2$ (3.47 g, 10.6 mmol) in dichloromethane (15 mL) was added dropwise to a cooled (0 °C) and well-stirred solution of 3-methylpyrazole (2.71 g, 33.0 mmol) in dichloromethane (8 mL) over 60 min. After complete addition, triethylamine (4.57 mL, 33.0 mmol) was added, and the solution was stirred at ambient temperature for 12 h. The volatiles were removed under reduced pressure, and the remaining colourless solid was extracted with THF (2 × 20 mL). Solid potassium *tert*-butoxide (1.20 g, 10.6 mmol) was added portionwise to the extract, and the resulting solution was stirred for 30 min. Removal of the volatile components gave a pale yellow solid, which was purified by washing with cold (–20 °C) diethyl ether (2 × 35 mL). Drying under reduced pressure gave *p*-BrC$_6$H$_4$Tp^{Me}K as a colourless powder (1.95 g, 4.34 mmol, 41%). $C_{18}H_{19}BBrKN_6$ (449.20): calcd. C 48.13, H 4.26, N 18.71; found C 47.33, H 4.31, N 18.10. ^{1}H NMR (250 MHz, [D$_6$]DMSO): δ = 7.37 (d, J = 8.2 Hz, 2 H, part of C_6H_4), 7.22 (d, J = 8.2 Hz, 2 H, part of C_6H_4), 6.70 (d, J = 1.8 Hz, 3 H, pz-H5), 5.75 (d, J = 1.8 Hz, 3 H, pz-H4), 2.12 (s, 9 H, pz-CH_3) ppm. ^{13}C NMR (62.5 MHz, [D$_6$]DMSO): δ = 146.2 (CH), 136.6 (CH), 134.3 (CH), 102.0 (CH), 13.9 (CH_3) ppm.

***p*-BrC$_6$H$_4$Tp*K (9):** This compound was prepared analogously to **8** except that 3,5-dimethylpyrazole was used instead of 3-methylpyrazole. Yield: 56%. $C_{21}H_{25}BBrKN_6$ (491.28): calcd. C 51.34, H 5.13, N 17.11; found C 50.83, H 4.97, N 17.53. ^{1}H NMR (250 MHz, [D$_6$]DMSO): δ = 7.15 (d, J = 8.2 Hz, 2 H, part of C_6H_4), 6.89 (d, J = 8.2 Hz, 2 H, part of C_6H_4), 5.55 (s, 3 H, pz-4 H), 1.98 (s, 9 H, pz-CH_3), 1.41 (s, 9 H, pz-CH_3) ppm. ^{13}C NMR (62.5 MHz, [D$_6$]DMSO): δ = 136.9 (CH), 128.0 (CH), 104.8 (CH), 14.0 (CH_3), 12.7 (CH_3) ppm.

X-ray Structure Determination of 6 and 7: A crystal of **6** (colourless needle), obtained by slow evaporation of a CH_2Cl_2 solution, was placed on a glass capillary in perfluorinated oil and measured in a cold gas flow. The intensity data were measured with a Bruker axs area detector (Mo-K_α radiation 0.71073 Å, ω scan) at –30 °C. $C_{21}H_{25}BBrN_6Tl$, M = 656.56, triclinic, a = 8.0989(6) Å, b = 8.3437(6) Å, c = 17.0443(12) Å, α = 85.7240(10)°, β = 78.4870(10)°, γ = 76.5310(10)°, V = 1097.07(14) Å^3, space group $P\bar{1}$, Z = 2, 7632 reflections collected, 4917 unique (R_{int} = 0.0157), $wR(F^2)$ = 0.0983 (all data). Structure solution with direct methods (SHELXS97) and refined against F^2 with all measured reflections (SHELXL97[33] and Platon/Squeeze[34]). A crystal of **7** (colourless needle), obtained by slow evaporation of a chloroform solution, was placed on a glass capillary in perfluorinated oil and measured in a cold gas flow. The intensity data were measured with a Bruker axs area detector (Mo-K_α radiation 0.71073 Å, ω scan) at –60 °C. $C_{30}H_{26}B_2Br_2MgN_{12}$, M = 760.38, triclinic, a = 10.957(3) Å, b = 12.144(4) Å, c = 12.517(4) Å, α = 97.219(7)°, β = 99.152(7)°, γ = 91.674(6)°, V = 1629.3(8) Å^3, space group $P\bar{1}$, Z = 2, 9090 reflections collected, 5706 unique (R_{int} = 0.0388), $wR(F^2)$ = 0.1905 (all data). Structure solution with direct methods (SHELXS97), and refined against F^2 with all measured reflections (SHELXL97[33] and Platon/Squeeze[34]). CCDC-741194 (for **6**) and -741193 (for **7**) contain 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.

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