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Mono(arene) Complexes of Thallium(I) Supported by a Weakly Coordinating Anion

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Discrete cationic mono(arene) complexes of thallium(I), [Tl(Cp$_2$Fe)]$^+$ and [Tl(C$_6$Me$_6$)]$^+$, were synthesized as [H$_2$N{B(C$_6$F$_5$)$_3$}$_2$]$^-$ salts. The Tl···centroid distance of 2.723 Å to the arene in [Tl(C$_6$Me$_6$)]$^+$ is the shortest described to date. This remarkably strong arene π-bonding is confirmed by DFT calculations, which give a Tl−C$_6$Me$_6$ interaction energy of 163 kJ mol^{-1}.

Introduction

Thallium(I) salts of weakly coordinating anions represent convenient halide-abstracting agents. They are commonly used for ligand metathesis purposes and for the generation of coordinatively unsaturated metal complexes; in contrast to their silver congeners, they do not decompose upon exposure to light and are less likely to be involved in redox side reactions.[1−6] Some time ago, we reported the facile preparation and structure of the amidodiborate [H$_2$N{B(C$_6$F$_5$)$_3$}$_2$]$^-$,[7] a "super-weakly" coordinating anion which we have employed successfully to support various polymerization catalysts[7,8] and a number of highly electrophilic complexes of main-group heavy metals such as cadmium,[9] tin,[10] and mercury.[11] This anion is comparable in stability to the well-known [B(C$_6$F$_5$)$_4$]$^-$ but frequently offers improved crystallization properties and hence facilitates structural characterization.

Unlike transition metals, p-block metals do not readily form π-arene complexes.[12] Monovalent thallium is no exception, and even though Tl(I)−arene complexes have been known for almost 40 years,[13] only a few examples of structurally characterized salts are available from the literature.[14] Very recently, we have prepared several thallium(I) sandwich and multidecker complexes stabilized by weakly coordinating anions and structurally characterized three Tl(I) arene salts, [Tl(toluene)$_3$]$^+$[X]$^-$ (**1**), [Tl(C$_6$Me$_6$)$_2$]$^+$[X]$^-$·2.5CH$_2$Cl$_2$ (**2**), and the ferrocene adduct [Tl$_2$(Cp$_2$Fe)$_3$]$^{2+}$[X]$^-_2$·5CH$_2$Cl$_2$ (Cp = cyclopentadienyl; [X]$^-$ = [H$_2$N{B(C$_6$F$_5$)$_3$}$_2$]$^-$).[15] The intimate structural details of these Tl(I) arene complexes showed that the amidodiborate counterion exerted a minimal influence on the structure of the cations. For instance, the Tl···centroid distances (2.789 and 2.855 Å) to the electron-rich arenes in **2** were the shortest reported to date by some amount and reflected the complete absence of interaction between the thallium atom and the anion. We have now been able to isolate some half-sandwich complexes of Tl(I) and report here the syntheses and characterization of the mono(arene) adducts [Tl(Cp$_2$Fe)][H$_2$N{B(C$_6$F$_5$)$_3$}$_2$] (**3**) and [Tl(C$_6$Me$_6$)][H$_2$N{B(C$_6$F$_5$)$_3$}$_2$] (**4**), which exhibit remarkably strong π-arene interactions between the metal atom and the electron-rich arenes.

Results and Discussion

The addition at room temperature of 2.2 equiv of crystalline Cp$_2$Fe to a colorless solution of **1** (prepared as previously described[15]) in dichloromethane gives a fine orange powder in nearly quantitative yield (Scheme 1). The initial orange color of the Fe(II) moiety was retained during the course of the reaction, an immediate indication that no unwanted redox process had taken place.[16] NMR characterization and elemental analyses were performed at this stage and were consistent with the formulation [Tl(Cp$_2$Fe)][H$_2$N{B(C$_6$F$_5$)$_3$}$_2$] (**3**).

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[16] We have, for instance, shown that the analogous reaction with the more electron-rich decamethylferrocene instantly proceeds following a redox pathway to yield elemental thallium and the dark green Fe(III) species [Cp*$_2$Fe][H$_2$N{B(C$_6$F$_5$)$_3$}$_2$].[15]

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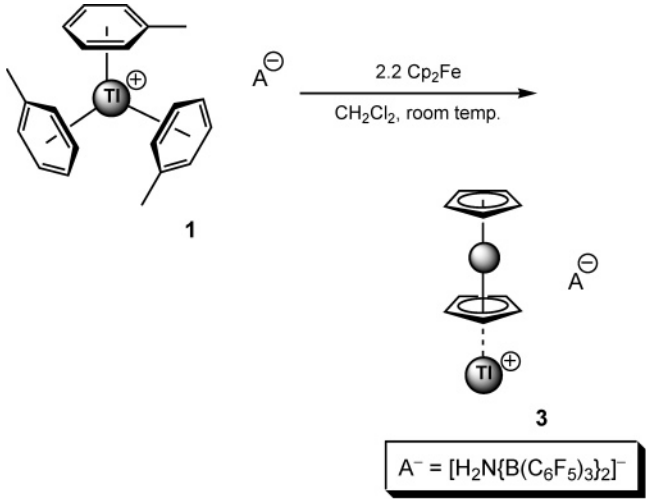
Scheme 1



Surprisingly, only one ferrocene unit was found per thallium atom. The similar reaction of the *bis(toluene)* adduct [Tl(toluene)$_2$][$H_2N\{B(C_6F_5)_3\}_2$] with an equimolar amount of Cp_2Fe in CH_2Cl_2 yielded a product of more complicated structure, [$Tl_2(Cp_2Fe)_3$][$H_2N\{B(C_6F_5)_3\}_2$]$_2$•5CH_2Cl_2 (**I**), where the two independent cations [$Tl(Cp_2Fe)$]$^+$ and [$Tl(Cp_2Fe)_2$]$^+$ were found in a 1:1 ratio.[15] Compound **3** is extremely soluble in dichloromethane, only slightly less so in chloroform, and sparingly soluble in aromatic hydrocarbons. X-ray-quality crystals of [$Tl(Cp_2Fe)$][$H_2N\{B(C_6F_5)_3\}_2$]•CH_2Cl_2 (**3**•CH_2Cl_2) were isolated as orange plates by slow recrystallization from a dichloromethane/light petroleum mixture stored at −26 °C.

Each asymmetric unit consists of one ion pair and one molecule of dichloromethane coordinated to the thallium atom (Figure 1). In the cation, the cyclopentadienyl ring is η^5-coordinated to the thallium atom, with a Tl(1)−Ct(1) distance to the centroid of 2.794 Å. The Fe(1)−Ct(1) length of 1.637 Å is unexceptional. The overall geometry is close to linear, with Fe(1)−Ct(1)−Tl(1) and Ct(1)−Fe(1)−Ct(2) angles of 174.79 and 179.56°, respectively. The thallium atom exhibits a number of contacts to five nonbonded fluorine atoms from three distinct anions in the range 3.1859(3)−3.3306(3) Å (the van der Waals radii for thallium and fluorine atoms are respectively 2.00 and 1.35 Å).[17] There is no clear geometric pattern to these contacts, and they are probably best regarded as deriving from packing requirements. Finally, there is also a single short contact to one chlorine atom of the solvent molecule; the Tl(1)•••Cl(2) distance of 3.5915(4) Å is much shorter than the sum of the van der Waals radii for thallium (2.00 Å) and chlorine (1.80 Å).[17] Interestingly, the Tl−centroid distance in **3**•CH_2Cl_2 is much shorter than those observed in the two cations [$Tl(Cp_2Fe)$]$^+$ and [$Tl(Cp_2Fe)_2$]$^+$ found in **I** (2.923 and 2.9309 Å, respectively).[15] While it is obvious that the distance in [$Tl(Cp_2Fe)_2$]$^+$ should be longer due to electronic effects, the discrepancy between the two [$Tl(Cp_2Fe)$]$^+$ moieties in **3**•CH_2Cl_2 and **I** is most probably the result of packing effects. The geometry in the dichloromethane molecule is not perturbed by the contact to thallium, as indicated by the two comparable C(11)−Cl(1) and C(11)−Cl(2) bond lengths of 1.767(8) and 1.724(7) Å and by the Cl(1)−C(11)−Cl(2) angle of 113.5(4)°, which lies in the normal range.

The anion displays the expected bent structure around the nitrogen atom (B(1)−N(1)−B(2) = 133.3(3)°) and pattern of five intramolecular N−H•••F hydrogen bonds in the range 1.97(3)−2.42(4) Å.[7−9,11]

Although no solid residue could be seen, a murky solution was obtained upon stirring **2** in diethyl ether at room temperature, regardless of the amount of solvent used. Upon removal of the solvent and workup with light petroleum, a fine white powder was obtained which was suspended in toluene at 75 ± 3 °C, and argon was bubbled through the mixture for over 1 h. The colorless material obtained after workup and drying under vacuum was identified as [$Tl(C_6Me_6)$][$H_2N\{B(C_6F_5)_3\}_2$] (**4**) (Scheme 2). It seems reasonable to assume that **4** was formed by (i) replacement of *one* of the C_6Me_6 molecules in the starting material **2** by one or more Et_2O molecules after treatment in this solvent, followed by (ii) exchange of Et_2O molecules for toluene after purging with argon in hot toluene and (iii) removal of the toluene ligand(s) under dynamic vacuum ($<10^{-3}$ mmHg).

Attempts to form thallium π−arene complexes with hexamethylbenzene have previously been reported to have failed,[14a] until our isolation of the [$Tl(C_6Me_6)_2$]$^+$ sandwich, and DFT calculations suggested that tris(arene) complexes are more stable than bis(arene) compounds.[15] Thus, the formation of **4** was unexpected, and the compound represents the first example of a cationic mono-C_6Me_6 adduct of monovalent thallium.

Upon recrystallization from a 2:1 dichloromethane−light petroleum mixture at −26 °C, single crystals of [$Tl(C_6Me_6)$][$H_2N\{B(C_6F_5)_3\}_2$]•2CH_2Cl_2 (**4**•2CH_2Cl_2) were isolated as colorless blocks which were suitable for X-ray diffraction. The asymmetric unit consists of one ion pair and two molecules of dichloromethane, only one of which exhibits a close interaction with the thallium atom (Figure 2). In the cation, the thallium atom is bound in an η^6 fashion to a single aromatic ring. The distance from the thallium to the centroid of the ring is 2.723 Å, the shortest reported to date, with corresponding Tl−C distances in the range 2.993(8)−3.130(11) Å. For comparison, prior to this the strongest known Tl−arene interactions were those found in the sandwich complex **2**, with Tl•••centroid distances of 2.789 and 2.855 Å, substantially longer than that in **4**•2CH_2Cl_2.[15]

As was the case for **3**, there is a close contact to one chlorine atom of a solvent molecule, Tl(1)•••Cl(2) = 3.448(4) Å, while the geometry of this dichloromethane molecule is not significantly perturbed by coordination. Finally, the environment about the thallium atom is completed by five close contacts to fluorine atoms between 3.154(5) and 3.325(5) Å, which do not have any apparent directional nature.

Thallium−mono(arene) complexation was found previously in Schmidbaur's [(mes)Tl($GaBr_4$)]$_4$ (mes = 1,3,5-$C_6H_3Me_3$), where the mesitylene is bound to a seven-coordinate thallium atom that is also linked to six bridging bromides.[14a] By contrast, compounds **3** and **4** represent examples of discrete thallium half-sandwich structures, with minimal interactions with the anion. The η^6-arene coordination mode of thallium differs notably from that of comparable silver(I) complexes, which, in spite of an early proposal of η^6 coordination,[18] tend to show metal−arene interactions that are best described as somewhere between η^1 and η^2.[19]

DFT calculations were carried out on **3**•CH_2Cl_2 and **4**•2CH_2Cl_2 using the Amsterdam density functional (ADF) program

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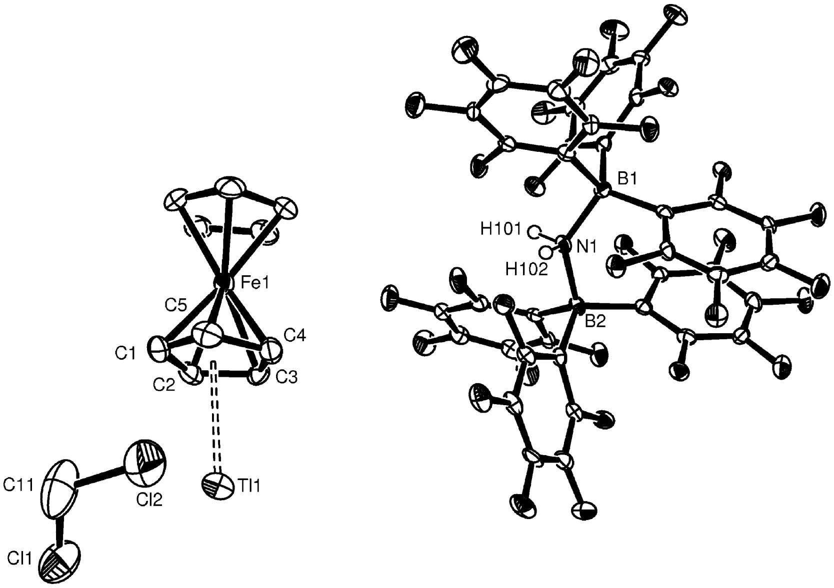
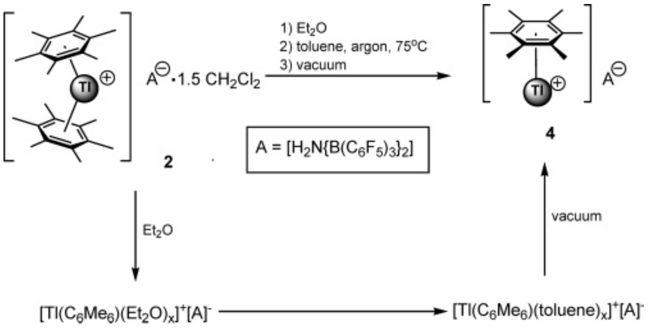


Figure 1. ORTEP representation of the structure of **3**·CH_2Cl_2 showing 50% probability ellipsoids. Hydrogen atoms (except those on the nitrogen atom) have been omitted for clarity. Selected bond lengths (Å) and angles (deg) with estimated standard deviations: Fe(1)−Ct(1) = 1.637, Tl(1)−Ct(1) = 2.794, Tl(1)−C(1) = 3.1336(2), Tl(1)−C(2) = 3.0757(3), Tl(1)−C(3) = 2.9710(3), Tl(1)−C(4) = 2.9670(2), Tl(1)−C(5) = 3.0735(2), C(11)−Cl(1) = 1.767(8), C(11)−Cl(2) = 1.724(7); Fe(1)−Ct(1)−Tl(1) = 174.79, Ct(1)−Fe(1)−Ct(2) = 179.56, B(1)−N(1)−B(2) = 133.3(3), Cl(1)−C(11)−Cl(2) = 113.5(4).

Scheme 2



suite (see Experimental Section). In both cases, the calculated Mulliken charge on the thallium atom of +0.88 was extremely close to the formal oxidation state, indicating that the bulk of the charge in these adducts is located on the metal. The interaction energy between the thallium atom and the aromatic ring was determined for each compound. For $[Tl(Cp_2Fe)]^+$ (in **3**·CH_2Cl_2), it was found to be 129 kJ mol^{-1}, with a calculated ideal Tl···C distance of 2.978 Å close to the experimental values. In comparison, the interaction energy provided by the C_6Me_6 molecule for $[Tl(C_6Me_6)]^+$ (in **4**·$2CH_2Cl_2$) of 163 kJ mol^{-1} is substantially higher. As one could anticipate, it is also greater than the calculated Tl−C_6Me_6 interaction energy in the sandwich cation $[Tl(C_6Me_6)_2]^+$ (in the starting material **2**), where the overall interaction is found to be 243.4 kJ mol^{-1}, corresponding to an average Tl−C_6Me_6 bond energy of 121.7 kJ mol^{-1}.[15] These findings clearly confirm that the strongest Tl−arene interactions are found in **4**·$2CH_2Cl_2$, where the metal center is stabilized by a single molecule of the very electron donating C_6Me_6.

Investigations on the molecular orbital structures of both complexes were conducted and showed that virtually all the valence MOs are localized on the arene rings: there is little, if any, covalency in these complexes. In both cases, the MOs with Tl character involve only the Tl s orbital, and the highest occupied Tl-containing MO is antibonding between the Tl and π-system of the rings. The next MO down is largely nonbonding, and then there is some Tl−ring bonding.

In conclusion, discrete mono(arene) thallium(I) half-sandwich complexes have proved accessible in good yield. As indicated by X-ray diffraction crystallography and DFT calculations, the Tl−arene interaction with the electron-rich C_6Me_6 in **4**·$2CH_2Cl_2$ is the strongest reported so far. The use of the $[Tl(arene)]^+$ synthon is currently being explored.

Experimental Section

General Procedures. All manipulations were performed under argon using standard Schlenk techniques with flame-dried glassware. Solvents were predried and distilled under an inert atmosphere over sodium (low-sulfur toluene), sodium−benzophenone (diethyl ether, THF), sodium−potassium alloy (light petroleum, boiling point 40−60 °C), or calcium hydride (dichloromethane). NMR solvents were dried over activated 4 Å molecular sieves and degassed by several freeze−thaw cycles. ^1H, $^{13}C\{^1H\}$, ^{11}B, and ^{19}F NMR spectra were recorded using a Bruker DPX300 spectrometer. ^1H NMR spectra (300.13 MHz) are referenced to the residual protons of the deuterated solvent used. ^{13}C NMR spectra (75.47 MHz) were referenced internally to the D-coupled ^{13}C resonances of the NMR solvent. ^{11}B (96.29 MHz) and ^{19}F (282.38 MHz) NMR spectra were referenced externally to $BF_3·Et_2O$ and $CFCl_3$, respectively. Chemical shifts are reported in ppm, and all coupling constants are reported in hertz. Thallium ethoxide and ferrocene were used without further purification. Hexamethylbenzene was sublimed under dynamic vacuum (10^{-3} mmHg). $[Tl(toluene)_3][H_2N\{B(C_6F_5)_3\}_2]$ (**1**) and $[Tl(C_6Me_6)_2][H_2N\{B(C_6F_5)_3\}_2]·2.5CH_2Cl_2$ (**2**) were prepared according to literature methods.[15] *Caution!* Thallium compounds are highly toxic; great care must be taken when manipulating TlOEt.

Synthesis of $[Tl(Cp_2Fe)][H_2N\{B(C_6F_5)_3\}_2]$ (3). Crystals of Cp_2Fe (0.09 g, 0.48 mmol) were rapidly added at room temperature via a sidearm to a solution of **1** (0.33 g, 0.22 mmol) in dichloromethane (20 mL). The resulting deep orange solution was stirred at room temperature for 75 min. The volatiles were removed in vacuo to give an orange solid, and thorough washing with light petroleum (3 × 40 mL) followed by drying under vacuum yielded

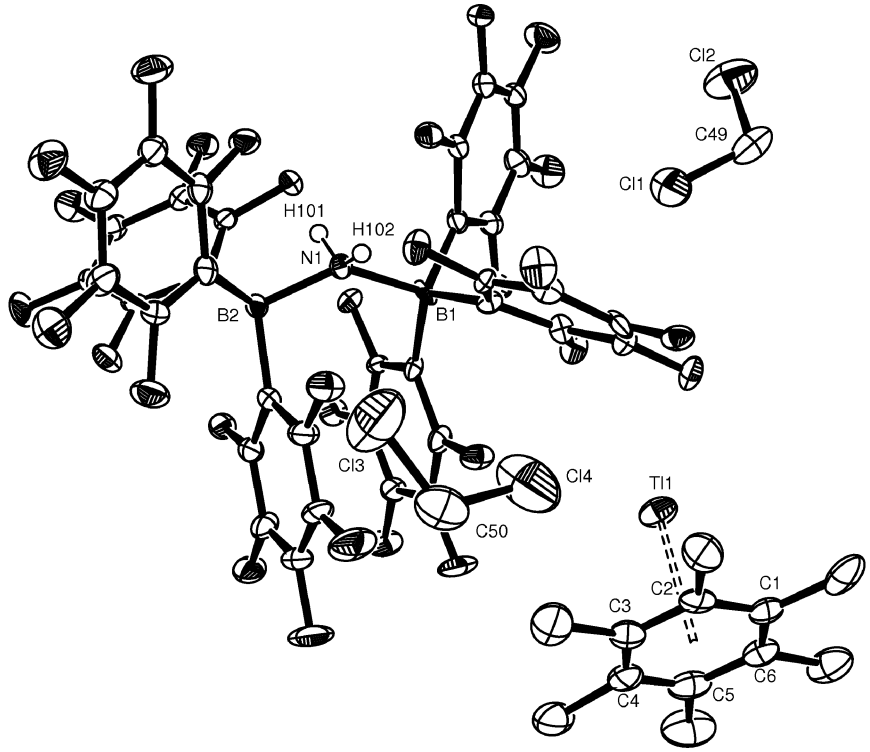


Figure 2. ORTEP representation of the structure of **4**·2CH$_2$Cl$_2$ showing 50% probability ellipsoids; hydrogen atoms (except those on the nitrogen atom) have been omitted for clarity. Selected bond lengths (Å) and angles (deg) with estimated standard deviations: Tl(1)−Ct(1) = 2.723, Tl(1)−C(1) = 3.060(9), Tl(1)−C(2) = 2.993(8), Tl(1)−C(3) = 3.012(8), Tl(1)−C(4) = 3.104(11), Tl(1)−C(5) = 3.130(11), Tl(1)−C(6) = 3.105(11), C(49)−Cl(1) = 1.743(13), C(49)−Cl(2) = 1.755(11), C(50)−Cl(3) = 1.744(14), C(50)−Cl(4) = 1.698(13); B(1)−N(1)−B(2) = 133.3(6), Cl(1)−C(49)−Cl(2) = 112.5(6), Cl(3)−C(50)−Cl(4) = 114.2(7).

Table 1. Selected Crystal Data and Structure Refinement Data for Compounds 3·CH$_2$Cl$_2$ and 4·2CH$_2$Cl$_2$

	3·CH$_2$Cl$_2$	**4**·2CH$_2$Cl$_2$
formula	$C_{47}H_{14}B_2Cl_2F_{30}FeNTl$	$C_{50}H_{24}B_2Cl_4F_{30}NTl$
formula wt	1515.33	1576.49
cryst descripn	orange plate	colorless block
cryst dimens/mm	0.45 × 0.22 × 0.01	0.38 × 0.12 × 0.08
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$
a/Å	11.2982(7)	11.4167(8)
b/Å	13.0684(10)	13.8539(7)
c/Å	16.363(2)	33.436(2)
α/deg	94.492(9)	90
β/deg	102.001(8)	90.153(5)
γ/deg	97.920(6)	90
V/Å^3	2326.3(4)	5288.4(6)
Z	2	4
T/K	140(2)	140(2)
μ/mm^{-1}	4.047	3.402
no. of data collected	30 487	68 805
no. of unique data	10 536	12 123
R_{int}	0.0532	0.0691
R1 ($I > 2\sigma(I)$)	0.0426	0.0702
wR2 (all data)	0.0953	0.1774

a fine orange powder. Elemental analysis and NMR spectroscopy characterization were consistent with the formulation [Tl(Cp$_2$Fe)][H$_2$N{B(C$_6$F$_5$)$_3$}$_2$]. Yield 0.30 g, 95%. ^{1}H NMR (CD$_2$Cl$_2$, 25 °C, 300.13 MHz): δ 5.70 (br, 2H, NH_2), 4.44 (br s, 10H, C$_5$$H_5$). ^{13}C{^{1}H} NMR (CD$_2Cl_2$, 25 °C, 75.47 MHz): δ 150.2, 146.5, 140.0, 138.1, 136.9, 135.1 (all aryl C_6F$_5$), 70.9 (C_5H$_5$). ^{11}B NMR (CD$_2$Cl$_2$, 25 °C, 96.29 MHz): δ −5.3. ^{19}F NMR (CD$_2$Cl$_2$, 25 °C, 282.38 MHz): δ −133.4 (d, $^3J_{FF}$ = 19.8 Hz, 12F, *o*-F), −160.5 (t, $^3J_{FF}$ = 19.8 Hz, 6F, *p*-F), −166.0 (t, $^3J_{FF}$ = 19.8 Hz, 12F, *m*-F). Anal. Calcd for **3** ($C_{46}H_{12}B_2F_{30}FeNTl$; 1430.39): C, 38.63; H, 0.85; N, 0.98. Found: C, 38.76; H, 0.89; N, 1.06. Single crystals of [Tl(Cp$_2$Fe)][H$_2$N{B(C$_6$F$_5$)$_3$}$_2$]·CH$_2$Cl$_2$ (**3**·CH$_2$Cl$_2$) were obtained as orange plates by recrystallization from a CH$_2$Cl$_2$/light petroleum mixture (2:1) stored at −26 °C, and their structure was determined by X-ray diffraction crystallography.

Synthesis of [Tl(C$_6$Me$_6$)][H$_2$N{B(C$_6$F$_5$)$_3$}$_2$] (4). Colorless crystalline **2** (0.36 g, 0.20 mmol) was stirred at room temperature in diethyl ether (30 mL) for 90 min. The solution never became totally clear, though no precipitate could be seen. The volatiles were pumped off to give an off-white solid, which was thoroughly washed with light petroleum until a fine white powder was obtained. This material was then suspended in toluene (80 mL) at 75 ± 3 °C, and dry argon was bubbled through the mixture for 75 min. Removal of volatiles under vacuum yielded a white solid, which was washed repeatedly with light petroleum and then extracted with dichloromethane (7 mL). Removal of the solvent and drying in vacuo left a colorless powder (0.13 g, 65%). Elemental analysis and NMR characterization indicated the composition [Tl(C$_6$Me$_6$)][H$_2$N{B(C$_6$F$_5$)$_3$}$_2$]. ^{1}H NMR (CD$_2$Cl$_2$, 25 °C, 300.13 MHz): δ 5.70 (br s, 2H, NH_2), 2.36 (s, 18H, CH_3). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 25 °C, 75.47 MHz): δ 149.5, 146.5, 141.2, 138.8, 137.6, 135.6 (all aryl C_6F$_5$), 136.0 (C_6Me$_6$), 16.5 (CH$_3$). ^{11}B NMR (CD$_2$Cl$_2$, 25 °C, 96.29 MHz): δ −5.3. ^{19}F NMR (CD$_2$Cl$_2$, 25 °C, 282.38 MHz): δ −133.4 (d, $^3J_{FF}$ = 19.8 Hz, 12F, *o*-F), −160.6 (t, $^3J_{FF}$ = 19.8 Hz, 6F, *p*-F), −166.1 (t, $^3J_{FF}$ = 19.8 Hz, 12F, *m*-F). Anal. Calcd for **4** ($C_{48}H_{20}B_2F_{30}NTl$, 1406.62): C, 40.99; H, 1.43; N, 1.00. Found: C, 40.83; H, 1.54; N, 0.92. X-ray-quality crystals of [Tl(C$_6$Me$_6$)][H$_2$N{B(C$_6$F$_5$)$_3$}$_2$]·2CH$_2$Cl$_2$ (**4**·2CH$_2$Cl$_2$) were readily grown as colorless blocks by recrystallization from a dichloromethane−light petroleum mixture (2:1) kept at −26 °C.

Computational Details. Calculations were performed with the Amsterdam density functional (ADF) program suite, version 2006.01b.[20−24] Scalar relativistic corrections[25] were included via

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(20) ADF2000; Department of Theoretical Chemistry, Vrije Universiteit, Amsterdam, 2000.

the ZORA to the Dirac equation.[27−28] The Tl valence basis set was taken from the ADF ZORA/TZP directory and employs uncontracted, Slater-type functions, of primarily triple-ζ quality, to represent the 4f, 5s, 5p, 5d, 6s, and 6p orbitals. A similar basis set was employed for Fe, in which the valence orbitals considered were 3s, 3p, 3d, 4s, and 4p. For C and H a ZORA/DZP (double-ζ plus polarization) basis was used. The frozen core approximation was used; Tl (4d), Fe(2p), and C(1s). The local density parametrization of Vosko, Wilk, and Nusair[28] was employed in conjunction with the PBE[29] gradient corrections. The ADF numerical integration parameter was set to 4.0 in all geometry optimizations, and the energy gradient convergence criterion was set to 1×10^{-3} au/Å. Mulliken population analyses were performed.[30]

X-ray Diffraction. Crystals of **3**·CH_2Cl_2 and **4**·$2CH_2Cl_2$ were mounted on glass fibers and fixed in the cold nitrogen stream on an Oxford Diffraction Xcalibur 3 CCD diffractometer equipped with Mo Kα radiation and graphite monochromator. Intensity data were measured by thin-slice ω and φ scans. Data were processed using the CrysAlis CCD and RED[31] programs. The structures were determined by the direct methods in SIR92[32] and refined by full-matrix least-squares methods on F^2 in SHELXL.[33] The non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms, except those bonded to nitrogen, were included in idealized positions, and their U_{iso} values were set to ride on the U_{eq} values of the parent carbon atoms. Hydrogen atoms bonded to nitrogen were located in the difference Fourier map, and the N−H distance was restrained to 0.88(2) Å. Crystal and refinement data are collected in Table 1.

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Supporting Information Available: CIF files and tables giving crystallographic data for compounds **3**·CH_2Cl_2 and **4**·$2CH_2Cl_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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