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Electronic Modification of a Sterically Demanding Anionic Pyridine Ligand

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Dedicated to Professor Cameron Jones on the occasion of his 60th birthday

The sterically demanding anionic pyridine ligand [4-(Ph₃B)-2,6-Mes₂py][−] ([1][−]) was used in salt metathesis reactions in order to obtain main group and transition metal complexes. Instead, reduction reactions were observed and identified as single electron transfer processes from [1][−] to the respective Lewis acidic cations. The electron transfer was confirmed by reduction of the trityl cation. In order to reduce the reductive power of [1][−] the borate function of the ligand was substituted with strongly electron withdrawing 3,5-bis(trifluoromethyl)phenyl groups to give [1^F][−]. The redox potential was shifted from +0.56 V to +1.32 V and hence, [1^F][−] cannot reduce the trityl

cation in contrast to [1][−]. Consequently, the measured pK_a value of 1^F-H (16.44) was lowered by two pK_a units compared with 1-H. Unfortunately, [1^F][−] still undergoes single electron transfer processes when used in salt metathesis reactions. We synthesized the anionic borane adduct [Li(THF)₄][1^F-BH₃] which demonstrates that [1^F][−] can be used as a ligand in main group chemistry. The determination of the crystal structures of [Li(THF)₄][1^F] and [Li(THF)₄][1^F-BH₃] revealed separated ion pairs while their analogs with the more electron rich [1][−] are contact ion pairs.

Introduction

Over the past few decades, great achievements have been made in the synthesis and isolation of main group compounds in low oxidation states and low coordination numbers. The isolation of the vast majority of these compounds was only made possible by the utilization of an appropriate ligand system, which can provide thermodynamic and kinetic stabilization. In the advent of the so-called ‘modern main group chemistry’^[1] bulky alkyl-, silyl-, amide- and aryl-groups were frequently used (e.g. CH(SiMe₃)₂, Si(SiMe₃)₃, N(SiMe₃)₂, Mes).^[2] However, during the 1980s concave ‘bowl-shaped’ ligands, became increasingly popular. The most prominent example are the *m*-terphenyls, established by the group of Power as ligands for both, transition metal and main group elements.^[3] These

ligands, which sterically shield a volume, the so-called ‘buried volume’, allowed for the isolation of a still increasing number of main group compounds in low oxidation states and unusual bonding situations.^[4] Among them is the alkyne analogue of germanium TerGeGeTer (Ter = *m*-terphenyl) featuring a Ge–Ge multiple bond.^[5] In 2005, Power *et al.* reported the dihydrogen activation at ambient conditions using TerGeGeTer to yield mixtures of Ter(H)GeGe(H)Ter, Ter(H)₂GeGe(H)₂Ter and TerGeH₃, demonstrating a reactivity typical for transition metals.^[6] In 2011, the group of Jones synthesized the digermene LGeGeL (L = N(SiMe₃)(Ar*); Ar* = 4-Me-2,6-(CHPh₂)-C₆H₂) substituted with a very bulky amide ligand.^[7] In contrast with the terphenyl substituted analog, the electron lone pair at the nitrogen atom of the amide ligand allows for N(p)→Ge(p) donation and thus prevents the formation of a Ge–Ge multiple bond. Nevertheless, the Ge–Ge single bond in (L)GeGe(L) was found to surpass the reactivity of its terphenyl substituted analog in terms of hydrogen activation. This selected example demonstrates how significant the influence of a ligand can be and motivates to synthesize new ligand systems with different electronic and steric properties.

Recently, our group reported the synthesis of the sterically demanding monoanionic pyridine ligand [4-(Ph₃B)-2,6-Mes₂py][−] ([1][−]).^[8] All three ligands, the terphenyl, the bulky amide and [1][−] can sterically shield a large volume, however, the bonding motifs of these ligands are quite different (Figure 1). The terphenyl can form a covalent single bond, while the amide can form a covalent single bond with participation of the electron lone pair of the nitrogen atom (π-bonding). The anionic pyridine [1][−] can form a dative bond via the electron lone pair of the pyridine nitrogen atom with a separated negatively charged borate group at the 4-position. So far, we only reported

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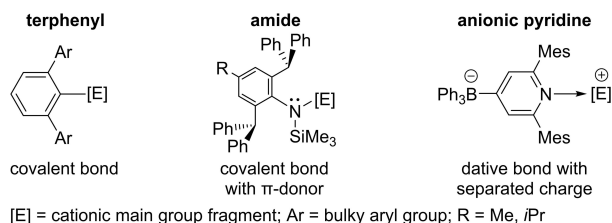


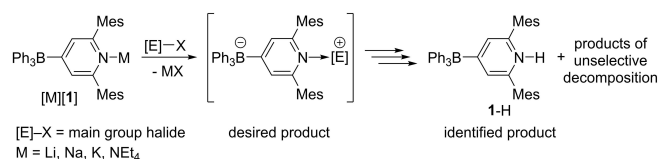
Figure 1. Illustration of the bonding motifs for terphenyl, amide and anionic pyridine ligands.

the insertion reaction of BH_3 into the N–Li bond of $1\text{-Li}(\text{THF})_2$ to give $1\text{-BH}_3\text{Li}(\text{THF})_3$. Here, we report on our attempts to introduce $[1]^-$ as a ligand for both, main group compounds and transition metal complexes.

Results and Discussion

The aim of our group's research was to use $[1]^-$ as a ligand to a wider range of main group halides by salt metathesis reactions and to study the bonding of $[1]^-$ in comparison to that of established monodentate monoanionic ligands (Figure 1). Unfortunately, addition of $[M][1]$ ($M = \text{Li, Na, K, NEt}_4$) to main group halides, including SiCl_4 , $\text{GeCl}_2 \cdot \text{dioxane}$, SnBr_2 , BCl_3 , AlBr_3 and GaCl_3 did not yield the sought-after adducts.

Instead, only the protonated anionic pyridine ligand 1-H was detected by NMR spectroscopy, alongside unidentified products suggesting unselective decomposition reactions (Scheme 1). This was unexpected, because the aforementioned main group halides were successfully substituted with the very bulky amide ligand $\text{N}(\text{SiMe}_3)\text{Ar}^*$ and also with the terphenyl 2,6-Mes₂-C₆H₃, which is virtually isosteric with $[1]^-$.^[9] The reactions were typically performed on a 0.2–0.4 mmol scale by addition of a solution (or suspension) of $[M][1]$ in either THF, diethyl ether, toluene or dichloromethane (2–5 ml) to a solution of an equimolar amount of the main group halide in the same solvent (2–5 ml) at -78°C . The reaction mixture was then allowed to reach room temperature over a period of 12 hours before being monitored by multinuclear NMR spectroscopy. Contamination with traces of moisture was ruled out by carefully drying the solvents and starting materials using standard techniques.^[10] When $[\text{NEt}_4][1]$ was added to a solution of $[(\text{Ph}_3\text{P})\text{Au}][\text{SbF}_6]$ in CH_2Cl_2 the reaction yielded a purple suspension indicating the formation of colloidal gold.^[11] The addition of $[\text{NEt}_4][1]$ to a solution of $[\text{Cu}(\text{NTf}_2)_2]$ resulted in the



Scheme 1. Attempted salt metathesis reactions of $[M][1]$ with main group halides.

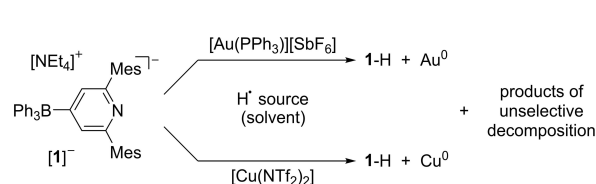
formation of a copper mirror. In both reaction mixtures, the protonated ligand 1-H was detected by NMR spectroscopy alongside decomposition products derived from the pyridine ligand (Scheme 2). Instead of the expected complex formation of $[1]^-$ with Au(I) and Cu(II), a reduction of the cations was observed. This can be rationalized by a single electron transfer (SET) from $[1]^-$ to the respective cation.

Related SET processes between sterically hindered Lewis acids and bases have been reported by Stephan and co-workers in 2017, including the archetypical *frustrated Lewis pair* $\text{Mes}_3\text{P}/\text{E}(\text{C}_6\text{F}_5)_3$ to be in an equilibrium with its so-called *frustrated radical pair* $[\text{Mes}_3\text{P}]^{\bullet+}/[\text{E}(\text{C}_6\text{F}_5)_3]^{\bullet-}$ and the topic has already been reviewed.^[12] These SET processes have also been reported between neutral Lewis bases (e.g. NHCs, CAACs) and cationic Lewis acids (e.g. $[\text{Ph}_3\text{C}]^+$).^[13] Furthermore, the group of Müller reported SET processes from neutral phosphanes to silylium cations for both, ‘frustrated’ and classical Lewis pairs showing that the steric ‘frustration’ is not a prerequisite.^[14]

An analogous SET process may proceed in the aforementioned attempted salt metathesis reactions starting from $[M][1]$ and main group halides $[\text{E}]-\text{X}$. The elimination of MX generates ion pairs of the type $[1]^-/[\text{E}]^+$. The same applies to the direct addition of $[1]^-$ to cationic complexes of Au(I) and Cu(II). The N-position of $[1]^-$ is sterically shielded by the two flanking mesityl substituents which apparently hinder the adduct formation and hence favor the SET process instead. The electron is transferred from the anion to the cation and should therefore even be energetically favored over the ones observed in neutral/neutral or neutral/cationic Lewis pairs. As a consequence, the neutral pyridine radical 1^\bullet must be formed during this process as well and reacts via H-atom transfer (HAT) from solvent molecules to yield the observed molecule 1-H. Analogous HAT reactions between reactive radicals and solvent molecules have been reported before.^[13,15]

In an attempt to exclude solvents as the H-atom source in order to isolate the proposed radical 1^\bullet the reaction of $\text{GeCl}_2 \cdot \text{dioxane}$ with both, $[\text{Li}(\text{Et}_2\text{O})_2][1]$ and $[\text{NEt}_4][1]$, was conducted in liquid SO_2 using NMR tubes with J. Young valves. The NMR analysis of the reaction mixtures revealed severe decomposition reactions and only 1-H could be identified as one of several products. However, no decomposition products were detected that derived from the solvates dioxane and diethyl ether or the counter ion $[\text{NEt}_4]^+$. This result shows that 1^\bullet is not stable and undergoes yet unidentified decomposition reactions with itself.

We were intrigued by the report of Severin *et al.*, who recently reported the reaction of an NHC with the trityl cation to proceed via a SET to give $[\text{NHC}]^{\bullet+}$ and $\text{Ph}_3\text{C}^\bullet$ as

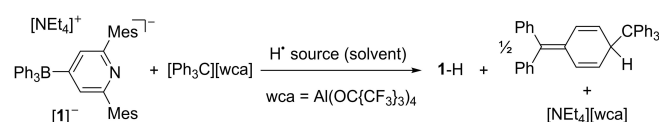


Scheme 2. Reduction of Au(I) and Cu(II) using $[1]^-$.

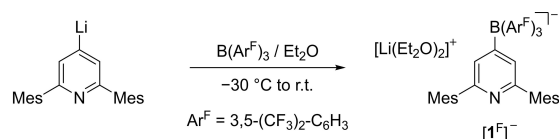
intermediates.^[13c] The proposed NHC radical cation could not be isolated or detected spectroscopically. However, the reaction eventually yielded a stable cross-coupling product of the NHC and the trityl cation. This prompted us to react $[\text{NEt}_4][1]$ with $[\text{Ph}_3\text{C}][\text{wca}]$ ($\text{wca} = \text{Al}(\text{OC}(\text{CF}_3)_3)_4$) in dichloromethane. And indeed, the Gomberg-dimer was detected in the reaction mixture alongside 1-H, confirming the role of $[1]^-$ as the reductant (Scheme 3).

Our intention was then to decrease the reductive power of $[1]^-$ to allow for its application as a ligand in coordination chemistry rather than a reductant. Therefore, the triphenyl borate group of $[1]^-$ was replaced by the strongly electron withdrawing tris(3,5-bis(trifluoromethyl)phenyl)borate group. The same borate group has already been successfully introduced to the backbone of NHCs to give the respective anionic NHCs.^[16] The addition of $\text{B}(3,5-(\text{CF}_3)_2-\text{C}_6\text{H}_3)_3$ to freshly prepared 4-Li-2,6-Mes₂py^[17] afforded $[1^F]^-$ as its lithium salt in 74% isolated yield (Scheme 4).

DFT calculations revealed a drastic change in the spatial and energetic location of the frontier orbitals of $[1]^-$ and $[1^F]^-$. While the HOMO of $[1]^-$ is located at the phenyl groups of the borate function, the HOMO of $[1^F]^-$ is located at the pyridine, including the electron lone pair of the nitrogen atom with an energy of -3.53 eV (Figure 3). The electron lone pair of the nitrogen atom of $[1]^-$ was identified in the HOMO-3 with a calculated energy



Scheme 3. Reduction of the trityl cation using $[1]^-$.



Scheme 4. Synthesis of $[1^F]^-$.

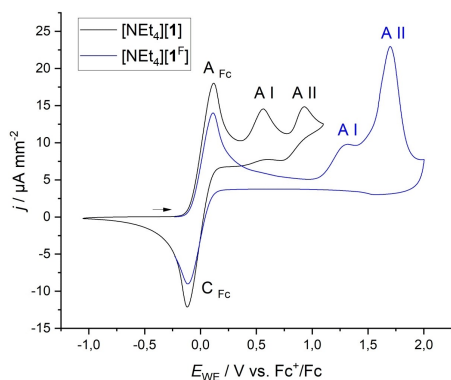


Figure 2. CV measurements for $[\text{NEt}_4][1]$ (black curve) and $[\text{NEt}_4][1^F]$ (blue curve) in presence of ferrocene.

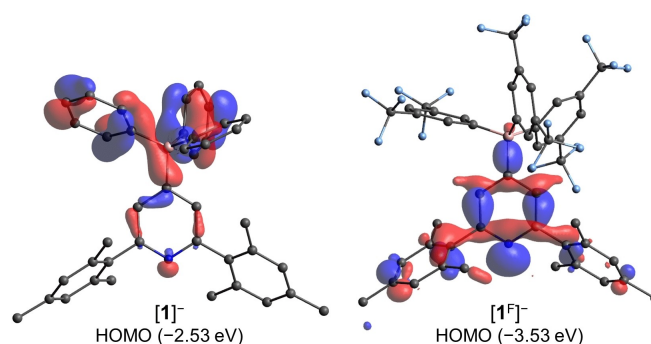


Figure 3. Frontier orbitals (± 0.04 a.u. contour surfaces) and energy levels of $[1]^-$ and $[1^F]^-$ (BP86-D3(BJ)/def-TZVP level of theory).

of -2.99 eV, making $[1^F]^-$ a significantly weaker electron donor. This decrease in energy of the electron lone pair of the N_{py}^- atom is directly reflected in the lower pK_a value of 16.44 measured for 1^F-H in acetonitrile compared with that for 1-H ($\text{pK}_a = 18.46$).^[8] However, the pK_a value of 1^F-H is still four pK_a units higher than that for unsubstituted pyridine ($\text{pK}_a = 12.53$).^[18] To quantify the redox potential of the two pyridines in solution CV measurements in CH_2Cl_2 (0.1 M $[\text{nBu}_4\text{N}][\text{PF}_6]$) using a glassy carbon disc electrode were performed (Figure 2). The oxidation potentials E_{p}^{ox} were detected at $+0.56$ V for $[1]^-$ (A I, black) and at $+1.32$ V for $[1^F]^-$ (A I, blue). The CVs of both compounds show two anodic peaks and no cathodic peak and the variation of reverse potential did not result in observable cathodic peaks. We deduce from this that fast homogeneous reactions after the heterogeneous electron transfer steps occur, indicating the instability of $[1]^*$ and $[1^F]^*$, respectively.

As a consequence of the E_{p}^{ox} -values, $[1^F]^-$ should not be able to reduce the trityl cation with a reported redox potential of 0.66 V.^[19] In accordance with the electrochemical measurements, no reaction was detected in a mixture of $[\text{NEt}_4][1^F]$ and $[\text{Ph}_3\text{C}][\text{wca}]$ in dichloromethane within 24 hours.

Unfortunately, when $[\text{M}][1^F]$ ($\text{M} = \text{NEt}_4, \text{Li}$) was used in salt metathesis reactions to obtain main group and transition metal complexes as already attempted for $[1]^-$ (Scheme 1), the same reactivity was observed and only the formation 1^F-H was detected (see experimental section for the synthesis and full characterization of 1^F-H). Therefore, we have to conclude that the reductive power of $[1^F]^-$ was indeed reduced compared to that of $[1]^-$. However, in presence of the *in situ* generated main group and transition metal cations the undesired SET process still takes place and does not allow for adduct formation.

We already reported the crystal structure of $1\text{-Li}(\text{THF})_2$ as a contact ion pair with a $\text{N}_{\text{py}}\text{-Li}$ distance of 199.4(3) pm. Reaction of this compound with $\text{BH}_3\text{-SMe}_2$ gave $1\text{-BH}_3\text{Li}(\text{THF})_3$ by insertion of the borane into the $\text{N}_{\text{py}}\text{-Li}$ bond (Figure 4, top).^[8] In the solid state, all three hydrogen atoms of the anion $[1\text{-BH}_3]^-$ showed short contacts to the lithium atom in the cation $[\text{Li}(\text{THF})_3]^+$. In contrast, the determination of the solid state structure by scXRD from crystals obtained from a tetrahydrofuran solution revealed $[\text{Li}(\text{THF})_4][1^F]$ as a separated ion pair. The compound crystallizes in the triclinic space group $P\bar{1}$ and its

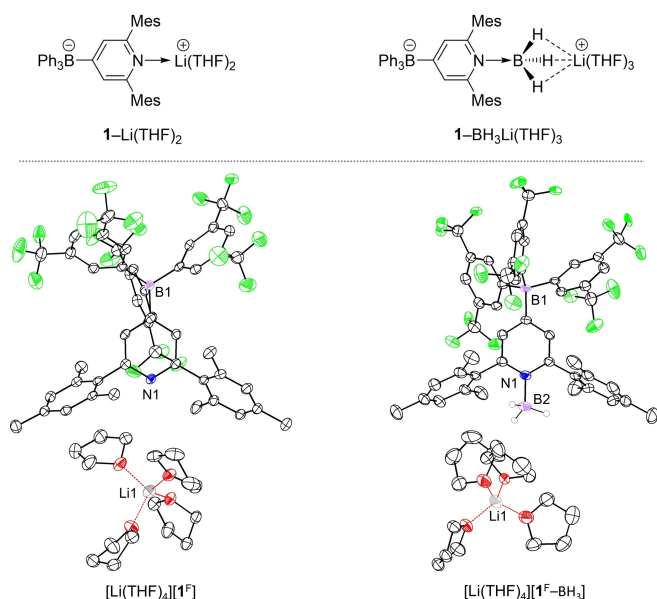


Figure 4. Top: Lewis structures of the previously reported contact ion pairs 1-Li(THF)₂ and 1-BH₃Li(THF)₃. Bottom: Crystal structures of [Li(THF)₄][1⁻] and [Li(THF)₄][1⁻-BH₃] (50% probability ellipsoids, hydrogen atoms (except B–H) omitted for clarity).

structure is depicted in Figure 4. The coordination sphere of the lithium cation is saturated with four THF ligands and the N...Li distance is 554.9(5) pm. When the lithium salt of [1⁻] was reacted with BH₃·SMe₂ the salt [Li(Et₂O)₂][1⁻-BH₃] was obtained in 89% isolated yield. Single crystals suitable for XRD were obtained from tetrahydrofuran and the structure determination revealed [Li(THF)₄][1⁻-BH₃] as a well separated ion pair with a B2...Li distance of 657.9(8) pm. The compound crystallizes in the monoclinic space group *P*2₁/*c* and its structure is depicted in Figure 4. The isolation of [1⁻-BH₃]⁻ demonstrates that [1⁻] can be used as a ligand for sterically very little demanding Lewis acids like BH₃ after all. The formation of the observed separated ion pairs is a consequence of the weaker donor strength of [1⁻]⁻ compared with [1⁻].

Conclusions

In this work, we attempted to introduce the sterically demanding anionic pyridine ligand [4-(Ph₃B)-2,6-Mes₂py]⁻ ([1⁻]) to main group compounds and transition metal complexes by salt metathesis reactions. Instead of the desired complexes, reduction reactions were observed. It was rationalized that [1⁻] is a reductant in presence of cationic Lewis acids. Analogous single electron transfer processes have been reported between neutral frustrated Lewis pairs and also from neutral Lewis bases to cationic Lewis acids to give the respective radical pairs. Here, the electron is transferred from [1⁻], a negatively charged Lewis base, to a positively charged Lewis acid. When [1⁻] was reacted with [Ph₃C]⁺ the Gomberg-dimer was formed, confirming the single electron transfer. The proposed radical 1[•] is highly

unstable and reacts via H-atom transfer from solvent molecules to give 1-H. When SO₂ was used as a solvent, decomposition of 1[•] was observed. In order to reduce the reductive power of [1⁻] the phenyl groups of the triphenyl borate group at the 4-position of [1⁻] were substituted with strongly electron withdrawing 3,5-bis(trifluoromethyl)phenyl groups to give [1⁻]^F. The electron withdrawing effect is directly reflected in a lower measured pK_a value of 1^F-H (16.44) compared with 1-H (18.46). Electrochemical measurements confirmed a shift in the redox potential from +0.56 V ([1⁻]) to +1.32 V ([1⁻]^F). Unfortunately, SET processes were also observed when [M][1^F] was used in salt metathesis reactions. However, when [Li(Et₂O)₂][1^F] was reacted with BH₃·SMe₂, the salt [Li(THF)₄][1^F-BH₃] was obtained. It was found by scXRD that both compounds are well separated ion pairs, while the already reported derivatives with [1⁻] are contact ion pairs. Nevertheless, the formation of the anionic adduct [1^F-BH₃]⁻ demonstrates that [1^F]⁻ can be used as a ligand after all.

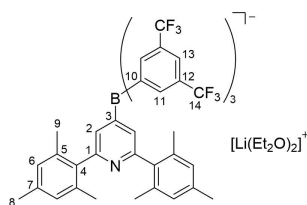
Experimental Section

General remarks. All reactions were carried out under argon atmosphere using standard Schlenk techniques in flame dried glassware or in a glove box under argon or nitrogen (water and oxygen content below 1 ppm). Solvents were dried and distilled under an argon atmosphere and kept over activated 3 Å molecular sieves: toluene, tetrahydrofuran and diethyl ether over sodium; dichloromethane, 1,4-dioxane and pentane over CaH₂. Deuterated benzene (C₆D₆) and deuterated dichloromethane (CD₂Cl₂) were dried over CaH₂. NMR data were recorded at r.t. either on a Bruker Avance II⁺ Widebore 400 MHz spectrometer or a Bruker Avance III HD 300 MHz spectrometer or a Bruker Avance DPX 200 MHz spectrometer using 5 mm tubes or special J. Young NMR tubes for excluding air and moisture. Topspin 3.2 was used for manipulation of the spectra. Chemical shifts are reported in ppm relative to Si(CH₃)₄ for ¹H and ¹³C, the BF₃·Et₂O complex for ¹¹B and CFCl₃ for ¹⁹F and 9.7 m LiCl in D₂O for ⁷Li. Coupling constant magnitudes, |J|, are given in Hz. Operating frequencies: Bruker Avance II⁺ Widebore 400 MHz: ¹H 400.17 MHz, ¹³C 100.62 MHz, ¹¹B 128.39 MHz, ¹⁹F 376.54 MHz, ⁷Li 155.52 MHz. Bruker Avance III HD 300 MHz: ¹H 300.18 MHz, ¹³C 75.48 MHz, ¹¹B 96.31 MHz, ¹⁹F 282.45 MHz, ⁷Li 116.66 MHz. Bruker Avance DPX 200 MHz: ¹H 200.13 MHz, ¹³C 50.32 MHz, ¹⁹F 188.31 MHz. ATR FTIR spectroscopy was performed at r.t. on a FTIR Bruker ALPHA with a QuickSnap Platinum ATR sampling module inside the glovebox. A KBr beam splitter was used for the spectra range from 4000 to 400 cm⁻¹. The spectra were recorded with 64 scans and a resolution of 2 cm⁻¹. Data processing was carried out with the OPUS 7.5 software package. The relative band intensities were described as follows: >0.66=strong (s), >0.33=medium (m) and >0.1=weak (w). FT-Raman spectra were recorded on a Bruker Vertex 70 spectrometer equipped with a RAM II module using a Ge detector cooled with liquid nitrogen. Raman spectra were recorded (back-scattering mode) at r.t. in flame-sealed glass capillaries (1064 nm, 25–40 mW power, range 4000 to 200 cm⁻¹, resolution 4 cm⁻¹). Data processing was carried out with the OPUS 7.5 software package. The relative band intensities were described as follows: >0.66=strong (s), >0.33=medium (m) and >0.1=weak (w). High resolution mass spectra (HRMS) were recorded on a Thermo Scientific Exactive Orbitrap instrument with ESI/APCI-source using electron spray ionization (ESI) (needle voltage: 2.5–5.0 kV; ion transfer tube 250', sheath/aux gas N₂). Melting points were determined on a Mel-Temp melting point

device. Compounds 1-H ,^[8] $\text{B}(3,5\text{-}(\text{CF}_3)_2\text{-C}_6\text{H}_2)_3$,^[16c,20] $(\text{Ph}_3\text{P})\text{AuCl}$,^[21] $\text{Cu}(\text{NTf}_2)_2$ ^[22] and $[\text{Ph}_3\text{C}][\text{Al}(\text{OC}(\text{CF}_3)_3)]$ ^[23] were prepared according to procedures in the literature. All other compounds used were purchased from commercial sources and used as received unless noted otherwise. $\text{GeCl}_2\cdot\text{dioxane}$ was recrystallized from 1,4-dioxane prior to use. All other compounds were purchased from commercial sources and used as received unless noted otherwise.

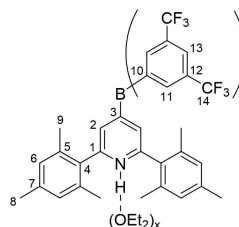
CCDC 2033814 ($1^{\text{F}}\text{-H}(\text{CH}_2\text{Cl}_2)$), 2033815 ($1^{\text{F}}\text{-H}(\text{Et}_2\text{O})$), 2033813 ($[\text{Li}(\text{THF})_4][1^{\text{F}}]$), 2033812 ($[\text{NEt}_4][1^{\text{F}}]$), 2163415 ($[\text{Li}(\text{THF})_4][1^{\text{F}}\text{-BH}_3]$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Synthesis of $[\text{Li}(\text{Et}_2\text{O})_2][1^{\text{F}}]$



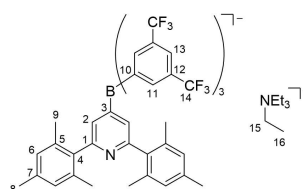
To a suspension of 4-*I*-2,6-Mes₂py (1.00 g, 2.27 mmol) in diethyl ether (50 ml) was added *n*-BuLi (1.56 ml, 1.6 M in hexane, 1.1 eq.) at -75°C . The reaction mixture was allowed to warm to r.t. over a period of 1.5 h. The supernatant yellow solution was filtered off the yellow precipitate. After addition of fresh diethyl ether (50 ml) and cooling to -30°C , a solution of $\text{B}(3,5\text{-}(\text{CF}_3)_2\text{-C}_6\text{H}_2)_3$ (1.47 g, 2.27 mmol, 1.0 eq.) in diethyl ether (20 ml) was added. The reaction mixture was allowed to warm to r.t. over a period of 12 h and was then concentrated to a volume of 10 ml. The supernatant solution was filtered off and the solid was washed with diethyl ether (2 \times 5 ml). Drying *in vacuo* gave pure $[\text{Li}(\text{Et}_2\text{O})_2][1^{\text{F}}]$ as an off-white powder. Yield: 1.87 g (74 %). Single crystals for XRD were obtained from a concentrated THF solution at -40°C . Mp: 129°C . $^1\text{H}\{^1\text{B}\}$ NMR (300 MHz, THF-*d*₈, 298 K): δ = 7.85 (s, 6 H, 11-*H*), 7.52 (s, 3 H, 13-*H*), 6.90 (s, 2 H, 2-*H*), 6.75 (s, 4 H, 6-*H*), 3.38 (Et₂O), 2.20 (s, 6 H, 8-*H*), 1.96 (s, 12 H, 9-*H*), 1.11 (Et₂O) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, THF-*d*₈, 298 K): δ = 169.3 (3-C)*, 163.3 (q, $^1J_{\text{CB}}$ = 48.4 Hz, 10-C), 158.0 (1-C), 141.0 (4-C), 136.1 (5-C), 136.0 (7-C), 135.6 (11-C), 129.8 (2-C), 129.6 (q, $^2J_{\text{CF}}$ = 32.1 Hz, 12-C), 128.1 (6-C), 125.4 (q, $^1J_{\text{CF}}$ = 272.6 Hz, 14-C), 117.6 (13-C), 66.1 (Et₂O), 21.0 (8-C), 20.3 (9-C), 15.5 (Et₂O) ppm. *detected via $^{13}\text{C},^1\text{H}$ HSQC/HMBC correlation NMR spectroscopy. $^{11}\text{B}\{^1\text{H}\}$ NMR (96 MHz, THF-*d*₈, 298 K): δ = -6.62 ppm. ^{19}F NMR (282 MHz, THF-*d*₈, 298 K): δ = -63.26 (s, 18F, CF₃) ppm. ^7Li NMR (117 MHz, THF-*d*₈, 298 K): δ = -0.38 ppm. ATR-IR (diamond): $\tilde{\nu}$ = 2983 (w), 2926 (w), 2898 (w), 1613 (w), 1584 (w), 1525 (w), 1485 (w), 1450 (w), 1381 (w), 1354 (m), 1274 (s), 1153 (w), 1120 (s), 1093 (w), 1060 (w), 1023 (w), 1005 (w), 931 (w), 922 (w), 912 (w), 898 (w), 888 (w), 855 (w), 839 (w), 797 (w), 786 (w), 742 (w), 723 (w), 717 (w), 711 (w), 678 (m), 668 (w), 564 (w), 519 (w), 445 (w), 414 (w) cm^{-1} . FT-Raman: $\tilde{\nu}$ = 3074 (w), 3058 (w), 3022 (w), 2976 (w), 2966 (w), 2928 (s), 2883 (w), 2768 (w), 2757 (w), 2744 (w), 1614 (s), 1593 (w), 1527 (w), 1486 (w), 1451 (w), 1383 (w), 1364 (w), 1325 (m), 1297 (w), 1246 (w), 1170 (w), 1137 (w), 1105 (w), 1049 (w), 1002 (s), 914 (w), 835 (w), 802 (w), 744 (w), 712 (w), 678 (w), 647 (w), 579 (w), 565 (m), 526 (w), 510 (w), 470 (w), 453 (w), 423 (w) cm^{-1} . HRMS: calculated for $\text{C}_{47}\text{H}_{33}\text{NBF}_{18}$ ($[1^{\text{F}}]^-$): 964.2424; found 964.2429.

Synthesis of $[\text{NEt}_4][1^{\text{F}}]$



Compounds $[\text{Li}(\text{Et}_2\text{O})_2][1^{\text{F}}]$ (500.0 mg, 0.45 mmol) and $[\text{NEt}_4]\text{Cl}$ (79.5 mg, 0.45 mmol, 1.0 eq.) were dissolved in dichloromethane (20 ml) and stirred at r.t. for 12 h. The reaction mixture was filtered and all volatile components were removed *in vacuo* to obtain $[\text{NEt}_4][1^{\text{F}}]$ as a colorless powder. Yield: 409.5 mg (82 %). Single crystals for XRD were obtained from a concentrated dichloromethane solution at -40°C . Mp: 76°C . $^1\text{H}\{^1\text{B}\}$ NMR (300 MHz, CD_2Cl_2 , 298 K): δ = 7.81–7.75 (m, 6 H, 11-*H*), 7.75 (s, 3 H, 13-*H*), 6.93 (s, 2 H, 2-*H*), 6.83 (s, 4 H, 6-*H*), 2.77 (t, $^3J_{\text{HH}}$ = 7.33 Hz, 8 H, 15-*H*), 2.24 (s, 6 H, 8-*H*), 1.94 (s, 12 H, 9-*H*), 0.93 (tt, $^3J_{\text{HH}}$ = 7.33 Hz, $^3J_{\text{HN}}$ = 1.85 Hz, 12 H, 16-*H*) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CD_2Cl_2 , 298 K): δ = 171.0 (3-C)*, 162.4 (q, $^1J_{\text{CB}}$ = 49.5 Hz, 10-C), 157.2 (1-C), 140.5 (4-C), 137.0 (7-C), 136.2 (5-C), 135.3 (11-C), 129.9 (2-C), 129.1 (q, $^2J_{\text{CF}}$ = 31.2 Hz, 12-C), 128.2 (6-C), 125.1 (q, $^1J_{\text{CF}}$ = 272.9 Hz, 14-C), 117.7 (13-C), 52.4 (t, $^2J_{\text{CN}}$ = 2.9 Hz, 15-C), 21.1 (8-C), 20.1 (9-C), 7.2 (tt, $^3J_{\text{CN}}$ = 7.33 Hz, $^3J_{\text{CN}}$ = 1.85 Hz, 16-C) ppm. *detected via $^{13}\text{C},^1\text{H}$ HSQC/HMBC correlation NMR spectroscopy. $^{11}\text{B}\{^1\text{H}\}$ NMR (96 MHz, CD_2Cl_2 , 298 K): δ = -6.71 ppm. ^{19}F NMR (282 MHz, CD_2Cl_2 , 298 K): δ = -62.76 (s, 18F, CF₃) ppm. ATR-IR (diamond): $\tilde{\nu}$ = 3011 (w), 2962 (w), 2921 (w), 2864 (w), 2860 (w), 1611 (w), 1578 (w), 1525 (w), 1483 (w), 1459 (w), 1440 (w), 1394 (w), 1378 (w), 1353 (m), 1272 (s), 1113 (s), 1094 (w), 1030 (w), 1000 (w), 931 (w), 885 (w), 854 (w), 839 (w), 801 (w), 784 (w), 742 (w), 715 (m), 675 (m), 577 (w), 561 (w), 555 (w), 449 (w), 402 (w) cm^{-1} . FT-Raman: $\tilde{\nu}$ = 3072 (w), 3018 (w), 2992 (w), 2925 (m), 2860 (w), 2756 (w), 1613 (m), 1593 (w), 1526 (w), 1487 (w), 1462 (w), 1383 (w), 1362 (w), 1321 (w), 1297 (w), 1244 (w), 1171 (w), 1116 (w), 1105 (w), 1048 (w), 1001 (s), 992 (w), 935 (w), 888 (w), 798 (w), 745 (w), 711 (w), 677 (w), 577 (w), 562 (w), 525 (w), 513 (w), 407 (w) cm^{-1} .

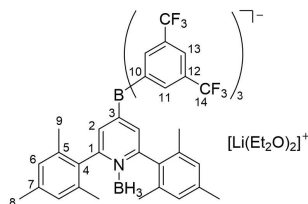
Synthesis of 1^{F}-H



To a solution of $[\text{Li}(\text{Et}_2\text{O})_2][1^{\text{F}}]$ (300 mg, 0.27 mmol) in 6 ml dichloromethane at 0°C was added 6 ml 0.5 M HCl. The mixture was stirred for 15 minutes. The two phases were separated. The aqueous phase was washed one time with dichloromethane and the separated organic phases were washed three times with brine. The organic phase was dried over MgSO_4 . The solvent was removed *in vacuo* and the remaining solid was recrystallized from a concentrated diethyl ether solution at -40°C to give colorless crystals of $1^{\text{F}}\text{-H}(\text{Et}_2\text{O})$. (N.B. single crystals were also obtained from a concentrated dichloromethane solution and determined as $1^{\text{F}}\text{-H}(\text{CH}_2\text{Cl}_2)$. See crystallographic section in the SI). Yield: 180 mg (63 %). Mp: 203°C (dec.). ^1H NMR (300 MHz, CD_2Cl_2 , 298 K): δ = 10.84 (s, 1H, N-*H*), 7.80–7.71 (m, 8H, 11-*H* and 2-*H*), 7.63 (s, 3H, 13-*H*), 7.00 (s, 4H, 6-*H*),

3.35 (Et₂O), 2.31 (s, 6H, 8-H), 1.99 (s, 12H, 9-H), 1.08 (Et₂O) ppm. ¹³C {¹H} NMR (75 MHz, CD₂Cl₂, 298 K): δ = 192.8 (3-C)*, 158.8 (q, ¹J_{CB} = 50 Hz, 10-C), 149.6 (1-C), 142.0 (7-C), 136.5 (5-C), 134.8 (11-C), 133.7 (2-C), 130.2 (q, ²J_{CF} = 32 Hz, 12-C), 129.4 (6-C), 129.0 (4-C), 124.7 (q, ¹J_{CF} = 275 Hz, 14-C), 119.0 (13-C), 65.9 (Et₂O), 21.3 (8-C), 20.0 (9-C), 15.4 (Et₂O) ppm. *detected via ¹³C, ¹H HSQC/HMBC correlation NMR spectroscopy. ¹¹B{¹H} NMR (128 MHz, CD₂Cl₂, 298 K): δ = −5.91 ppm. ¹⁹F NMR (188 MHz, CD₂Cl₂, 298 K): δ = −62.98 (s, 18F, CF₃) ppm. ATR-IR (diamond): ν̄ = 2984 (w), 2782 (w), 1615 (w), 1594 (w), 1483 (w), 1446 (w), 1383 (w), 1355 (m), 1276 (s), 1182 (w), 1136 (s), 1118 (s), 1068 (w), 1017 (w), 903 (w), 885 (w), 850 (w), 838 (w), 790 (w), 716 (w), 676 (s), 665 (w), 566 (w), 594 (w), 504 (w), 448 (w), 404 (w). FT-Raman: ν̄ = 2929 (w), 1614 (w), 1488 (w), 1384 (w), 1326 (w), 1095 (s), 1003 (w), 799 (w), 576 (s), 560 (s), 255 (w), 223 (w).

Synthesis of [Li(Et₂O)₂][¹F-BH₃]



To a suspension of [Li(Et₂O)₂][¹F] (1.61 g, 1.44 mmol) in diethyl ether (15 ml) was added BH₃·SMe₂ (0.15 ml, 1.59 mmol, 1.1 eq) at −85 °C. The reaction mixture was allowed to warm to room temperature over a period of 16 h. The reaction mixture was concentrated to minimum and the red supernatant solution filtered off and the remaining solid was dried *in vacuo* to give pure [Li(Et₂O)₂][¹F-BH₃] as an off-white powder. Yield: 1.45 g (89%). Single crystals of [Li(THF)₄][¹F-BH₃] for XRD were obtained from a saturated tetrahydrofuran solution at −40 °C. Mp: 167 °C. ¹H{¹B} NMR (300 MHz, THF-*d*₈, 298 K): δ = 7.86 (s, 6 H, 11-H), 7.54 (a, 3 H, 13-H), 7.17 (s, 2 H, 2-H), 6.77 (s, 4 H, 6-H), 3.39 (q, 7H, Et₂O), 2.23 (s, 6 H, 8-H), 1.90 (s, 12 H, 9-H), 1.62 (br. s, 3 H, B-H) ppm, 1.12 (t, 11H, Et₂O). ¹³C{¹H} NMR (75 MHz, THF-*d*₈, 298 K): δ = 176.7 (3-C)*, 162.1 (q, ¹J_{CB} = 50.2 Hz, 10-C), 157.1 (q, ³J_{CB} = 2.61 Hz, 1-C), 138.6 (4-C), 137.3 (7-C), 135.8 (5-C), 135.4 (11-C), 133.3 (2-C), 130.2 (qq, ²J_{CF} = 31.9 Hz, ³J_{CB} = 2.9 Hz, 12-C), 128.2 (6-C), 125.5 (q, ¹J_{CF} = 271.9 Hz, 14-C), 118.2 (13-C), 66.3 (Et₂O), 21.1 (8-C), 20.1 (9-C) ppm, 15.7 (Et₂O). *detected via ¹³C, ¹H HSQC/HMBC correlation NMR spectroscopy. ¹¹B{¹H} NMR (96 MHz, THF-*d*₈, 298 K): δ = −6.54 (pyridine-B), −17.20 (BH₃) ppm. ¹⁹F NMR (282 MHz, THF-*d*₈, 298 K): δ = −63.38 (CF₃) ppm. ⁷Li NMR (117 MHz, THF-*d*₈, 298 K): δ = −0.54 ppm. ATR-IR (diamond): ν̄ = 2967 (w), 2917 (w), 2884 (w), 2422 (w), 2338 (w), 1612 (w), 1592 (w), 1533 (w), 1482 (w), 1462 (w), 1353 (m), 1273 (s), 1182 (w), 1165 (m), 1119 (s), 1096 (m), 1042 (m), 931 (w), 918 (w), 890 (m), 862 (w), 856 (w), 840 (w), 742 (w), 728 (w), 716 (w), 710 (w), 681 (m), 674 (m), 411 (w) cm^{−1}. FT-Raman: ν̄ = 3078 (w), 3037 (w), 2987 (m), 2939 (m), 2918 (s), 2888 (s), 2757 (w), 2731 (w), 2422 (w), 2357 (w), 1613 (s), 1593 (m), 1534 (w), 1489 (w), 1450 (w), 1381 (w), 1365 (w), 1326 (m), 1298 (w), 1247 (w), 1172 (w), 1147 (w), 1104 (w), 1056 (m), 1003 (s), 960 (w), 924 (w), 906 (w), 803 (w), 743 (w), 730 (w), 691 (w), 676 (w), 577 (m), 567 (m), 524 (w), 479 (w), 404 (w) cm^{−1}. HRMS: calculated for C₄₇H₃₅NB₂F₁₈ (M⁺): 987.2752; found 978.2753.

Reduction of [Ph₃C]⁺ with [1][−]. To a solution of [Ph₃C][Al(OC(CF₃)₃)₄] (105.0 mg, 0.09 mmol) in dichloromethane (5 ml) was added a solution of [NET₄][1] (56.0 mg, 0.09 mmol, 1 eq.) in dichloromethane (4 ml) at −80 °C. The reaction mixture was allowed to warm up to r.t. over a period of 12 h. All volatile components were removed *in vacuo* to obtain an orange powder. Analysis of a sample dissolved CD₂Cl₂ by NMR spectroscopy identified 1-H as the only pyridine

species and the Gomberg-dimer by its characteristic olefinic signals in the ¹H NMR spectrum in the range between 5.93 ppm and 6.28 ppm (¹³C NMR: 128.5 ppm and 130.0 ppm) and the multiplet signal of the C(sp³) bound H-atom at 5.18 ppm (¹³C: 43.5 ppm).^[24]

Supporting Information: CV measurements, computational details, pK_s measurements and crystallographic section.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: pyridine · ligand design · redox-active · sterically demanding · main group chemistry

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