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ABSTRACT: Tetrrel bonding is the noncovalent interaction of group IV elements with electron donors. It is a weak, directional interaction that resembles hydrogen and halogen bonding yet remains barely explored. Herein, we present an experimental investigation of the carbon-centered, three-center, four-electron tetrrel bond, \([N-C-N]^-\), formed by capturing a carbenium ion with a bidentate Lewis base. NMR-spectroscopic, titration calorimetric, and reaction-kinetic evidence for the existence and structure of this species is reported. The studied interaction is by far the strongest tetrrel bond reported so far and is discussed in comparison with the analogous halogen bond. The necessity of the involvement of a bidentate Lewis base in its formation is demonstrated by providing spectroscopic and crystallographic evidence that a monodentate Lewis base induces a reaction rather than stabilizing the tetrrel bond complex. A vastly decreased Lewis basicity of the bidentate ligand or reduced Lewis acidity of the carbenium ion weakens—or even prohibits—the formation of the tetrrel bond complex, whereas synthetic modifications facilitating attractive orbital overlaps promote it. As the geometry of the complex resembles the \(S_n2\) transition state, it provides a model system for the investigation of fundamental reaction mechanisms and chemical bonding theories.

INTRODUCTION

Noncovalent interactions are receiving vastly increasing interest. Over the past decade, the hydrogen bond has been redefined,¹ and the analogous halogen,² pnicogen,³ chalcogen,⁴,⁵ aerogen,⁶ and coinege-metal⁷ bonds have been categorized⁸ as either σ-hole⁹ or E-bond interactions.⁷ These interactions, \(Z-X\cdots Y\), are typically observed between a Lewis base, \(Y\), and a region of positive electrostatic potential on atom \(Z\), being an electrophile connected to atom \(X\), along the extension of the \(Z-X\) bond. The stronger the interaction, the shorter and more directional the \(X-Y\) bond is and the longer the \(Z-X\) bond is. When the Lewis basicity of the atoms \(Z\) and \(Y\) are closely matched \((Z \approx Y)\), the central electrophilic atom \(X\) is equally shared between them, and accordingly the \(Z-X\) and \(X-Y\) bonds are equally strong and equally long. These interactions were described as three-center, four-electron bonds.¹¹ With a proton being the electrophilic atom (\(X = H\)), this special bond \((Y-X-Y)\) is commonly termed a “low-barrier”, a “short”, or a “strong” hydrogen bond.¹² The low-barrier \(N-H-N\) and \(O-H-O\) hydrogen bonds received great interest, as they were proposed to be extra strong—up to \(\sim 125\) \(\text{kJ/mol}\)—and accordingly to stabilize transition states and intermediates, for example, in enzyme-catalyzed reactions.¹³,¹⁴ Their true nature and geometry, however, remains the subject of intense debates.¹⁵⁻¹⁷ The analogous \(Y-X-Y\) halogen bond is static and symmetric, both in solutions and in the solid state, and possesses a partial covalent character.¹⁶⁻²³ Whereas conventional halogen bonds, \(R-X\cdots Y\), are up to \(\sim 40\) \(\text{kJ/mol}\) energy, the three-center, four-electron halogen bonds are significantly stronger, 120⁻150 \(\text{kJ/mol}\).¹⁹,²¹ Due to its exceptional strength, the three-center \(N-I-N\) halogen bond is applicable for stabilization of intricate complex supramolecular complexes, for instance.²⁴,²⁶ The noncovalent interactions in which tetrrel elements, i.e., those belonging to group IV of the periodic system, act as electrophiles are typically very weak,

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<10 kJ/mol. Both computational and experimental evidence is available for the lightest tetrel element, carbon, forming tetrel bonds. Complexes possessing a three-center, four-electron tetrel bond with carbon acting as the electrophilic center correspond to a pentacoordinate configuration that is commonly referred to as an "activated complex" or "transition state". This labile geometry involves a trigonal bipyramidal carbon with three of its substituents situated in one plane, while the incoming nucleophile and leaving group are positioned apically in a linear three-center, four-electron tetrel bond. Among other reactions, the classical bimolecular tetrel bond, geometrically forced into the apical positions of the electrophile, as well as its investigation in solution, has raised vast interest. All model systems so far explored experimentally are intramolecular and possess two intramolecular electron-donor functionalities geometrically forced into the apical positions of the electrophilic carbon, trapping it in a (pseudo)pentacoordinate configuration.

By contrast, the investigation of intermolecular complexes that require formation of a thermodynamically stable three-center, four-electron tetrel bond, allowing dissociation or smooth adjustment of bond distances and angles for a stable geometry, has so far lagged behind. Herein, we present the first intermolecular three-center, four-electron tetrel bond complex possessing a carbon as the central electrophile, as well as its investigation in solution.

Lately, the analogy of the three-center, four-electron tetrel bond of carbons to those of the isoelectronic halogen bond, such as that of the central halogen of the triiodide ion, \([\text{I}^-\cdots\text{I}^-\cdots\text{I}^-]\), and of \([\text{N}^-\cdots\text{X}^-\cdots\text{N}^-]\) complexes, has been recognized. The three-center halogen bond of \([\text{N}^-\cdots\text{X}^-\cdots\text{N}^-]\) complexes is formed by the donation of two unshared electrons of the nitrogen into the "p-holes", that is, the two lobes of the vacant p-orbital of the halogen(I) (Figure 1). These p-holes are analogous to the electron depleted σ-hole that gives rise to the formation of classical halogen, chalcogen, pnictogen, and tetrel bonds. Whereas the three-center, four-electron halogen bond complexes have been assessed experimentally, the corresponding compounds encompassing three-center, four-electron tetrel bond complexes have so far been studied in silico, but rarely under standard laboratory conditions. The molecular system studied here resembles the one we previously applied for the assessment of the isoelectronic halogen bond. Similar to the cationic halogen, \(X^+\), held in position by two N−X halogen bonds, the carbenium carbon, \(C^+\), of \(1a\)−f (Figures 1 and 2) has an empty p-orbital capable of simultaneously forming two N−C bonds upon overlapping with the nonbonding orbital of the two nitrogen donors that are positioned at optimal distance and in an ideal orientation provided by \(2a\)−c. This orbital overlap is expected to yield two bonds possessing a partial covalent character. The resulting complex (3a−f, Figure 2) ought to have a three-center, four-electron \([\text{N}^-\cdots\text{C}^-\cdots\text{N}^-]\) tetrel bond and a trigonal bipyramidal geometry, analogous to that of the transition state of \(S_2\). Here, we present the synthesis, solution NMR-spectroscopic, calorimetric, and kinetic investigations of the intermolecular tetrel bond complexes 3.

### RESULTS AND DISCUSSION

**Synthesis.** 1,2-Bis(pyridin-2-ylethynyl)benzenes \(2a\)−c were synthesized following a published procedure. Pyridine, 4-picoline, \(1a\), and \(1f\) were commercially available, whereas \(1d\) and \(1e\) were synthesized from their triaryl alcohol and triaryl halide precursors, respectively (Supporting Information). To generate complexes 3a−f (Figure 2 and Table 1), \(1a\)−f and ligands \(2a\)−c (1:1) were mixed at room temperature under dry conditions in an NMR tube, using dry CDCl\(_3\) as solvent. For the generation of 5b−c (Figure 2 and Table 1), 2 equiv of pyridine or picoline were added to the CDCl\(_3\) solution of triphenylcarbenium tetrafluoroborate, \(1a\).

**Structure Elucidation.** As \(^{15}\text{N}\) NMR has an inherently wide chemical shift range of ~800 ppm, it is expected to provide large, easy-to-detect chemical shifts changes upon formation of weak molecular complexes in which a nitrogen acts as a Lewis base. Accordingly, ~100 ppm \(^{15}\text{N}\) NMR coordination shifts, \(Δ^{15}\text{N}\text{coord}\), have been reported for formation of \([\text{N}^-\cdots\text{I}^-\cdots\text{N}^-]\) halogen-bonded complexes. Following literature conventions, the chemical shift difference of the complex and the free ligand, that is, \(Δ^{15}\text{N}\text{coord} = Δ^{15}\text{N}\text{complex} − Δ^{15}\text{N}\text{free}\), is defined as the chemical shift change observed on the bidentate ligand is accompanied by a large \(^{13}\text{C}\) NMR chemical shift change of the carbenium carbon (Table 1). The observation of a single set of \(^{15}\text{N}\) NMR signals for \(3a\)−f suggests the formation of complexes in which the carbenium carbon is equally bound to both Lewis basic nitrogens (Table 1 and Figure 3). Accordingly, the \(^{15}\text{N}\) NMR chemical shift change observed on the bidentate ligand is accompanied by a large \(^{13}\text{C}\) NMR chemical shift change of the carbenium carbon (Table 1) of the interaction partner, thus supporting the formation of a \([\text{N}^-\cdots\text{C}^-\cdots\text{N}^-]\) three-center, four-electron tetrel bond in \(3a\)−d, while revealing the formation of no, or very weak, complexes for \(3e\)−f. The observed \(^{15}\text{N}\) complexation shifts, \(Δ^{15}\text{N}\text{coord}\), are comparable in magnitude yet are somewhat smaller than those observed for the isoelectronic halogen-bonded compounds.

Upon mixing \(1a\) with 1,2-bis(phenylethynyl)benzene, an analogue of \(2c\) lacking any Lewis basic nitrogen, no \(^{13}\text{C}\) NMR
chemical shift alteration on 1a could be observed (Figure S1, Supporting Information), corroborating that the interaction seen for 3a−f involves the nitrogens. As an additional control to confirm the involvement of the trityl carbon in the interaction responsible for the formation of 3a−f, the 15N NMR shift of 2c was measured in the presence of tri-p-tolylmethanol. This resulted in no nitrogen chemical shift alteration of 2c (Figure S2, Supporting Information). The two control experiments confirm that the large Δδ15Ncoord and Δδ13Ccoord observed for 3c cannot be due to moisture-induced...
decomposition of 1a and subsequent hydrogen bonding of triphenylmethanol to 2c.

Whereas bidentate ligands 2a–c promote formation of a symmetric \([N\cdots C\cdots N]^+\) complex, or possibly a rapidly equilibrating pair of asymmetric \([N\cdots C\cdots N]^+ \rightleftharpoons [N\cdots C\cdots N]^+\) complexes, \(5c\), the monodentate Lewis bases pyridine and picoline form asymmetric ion pairs with 1a as indicated by the observation of two sets of 15N NMR chemical shifts for asymmetric structure with a strongly and a weakly coordinating nitrogen revealed by two sets of signals. Note that the structure drawn for 3c is not necessarily its most stable conformation.

Figure 4. Molecular structure of 1-tritylpyridin-1-ium tetrafluoroborate. The thermal displacement parameters are shown at the 50% probability level.

carbonium ion 1a, whereas its monodentate analogue, pyridine, undergoes N-alkylation with the electrophile. The \(\delta^{15}N \pm 144.0\) ppm of 3c indicates a strong N–C bond, which is close in chemical shift to that of the covalently functionalized pyridine of 5c (\(\delta^{15}N \pm 153.3\) ppm). Strong complexation for 3c was supported by the comparable translational diffusion coefficients of 1a (11.5 \(\times 10^{-10}\) m\(^2\) s\(^{-1}\)) and 2c (13.8 \(\times 10^{-10}\) m\(^2\) s\(^{-1}\)) of the complex. The diffusion coefficients of 1a and one of the pyridines (\(\Delta \delta^{15}N_{\text{coord}} \pm 86.3\) ppm) of complex 5c are similar (9.8 \(\times 10^{-10}\) and 9.4 \(\times 10^{-10}\) m\(^2\) s\(^{-1}\)), indicating that these are connected, whereas the second weakly complexing pyridine (\(\Delta \delta^{15}N_{\text{coord}} \pm 8.8\) ppm) has a diffusion coefficient (25.6 \(\times 10^{-10}\) m\(^2\) s\(^{-1}\)) that indicates that this pyridine moves independently of 1a in solution.

Dynamics. Compounds 3a–c might be involved in a bell–clapper-type rearrangement, \(38\) that is, instead of being present as a static and symmetric \([N\cdots C\cdots N]^+\) tetrabond complexes, they might exist in solution as dynamic mixtures of rapidly exchanging complexes possessing a covalent C–N bond and a pyridine weakly connected through a conventional C–N tetrabond, \([N\cdots C\cdots N]^+ \rightleftharpoons [N\cdots C\cdots N]^+\). To differentiate between the possibilities of a static and symmetric complex versus a mixture of rapidly interconverting, weakly coordinating ones, we followed the standard procedures of the field, \(39\) acquiring \(^1H\) and \(^1C\) NMR and \(^1H,^{15}N\) HMBC spectra for 3d at various temperatures. Both the static and dynamic geometries are expected to show a single sharp set of NMR signals at higher temperatures. A single set of signals is expected to remain detectable also at low temperature for a static \([N\cdots C\cdots N]^+\) tetrabond complex, whereas for a dynamic mixture of asymmetric structures, two sets of signals, or at least significant signal broadening, is expected. \(38\) We observed a single sharp set of \(^1H\), \(^13C\), and \(^15N\) NMR signals at all temperatures, including at \(\pm 40\) °C (Figures S3–S5, Supporting Information). This observation is best compatible with a static and symmetric geometry, even if it cannot fully exclude a very low barrier \([N\cdots C\cdots N]^+ \rightleftharpoons [N\cdots C\cdots N]^+\) interconversion, with an energy barrier \(\Delta G^\ddagger \approx 38\) kJ/mol and half-life of the possible interconverting states \(t_{1/2} \approx 6.4\) ms, when estimated from the chemical shift difference of pyridine (4c, \(\delta^{15}N \approx 67\) ppm) and 1-tritylpyridinium ion (5c, \(\delta^{15}N \approx 153\) ppm) as model compounds for the equally populated, not exchanging free versus N-alkylated end states, the \(^15N\) NMR observation frequency \(50.67\) MHz, and a coalescence temperature \(\approx -40\) °C. \(53\) To detect a possible low Barrier interconversion, we further performed isotopic perturbation of equilibrium (IPE) NMR measurements. \(33,55\) Similar to earlier studies of related systems, we compared the temperature dependence of the secondary deuteration isotope effects of 3d to those of a static reference, 2c, and of its hydrogen-bonded \([N\cdots H\cdots N]^+ \rightleftharpoons [N\cdots H\cdots N]^+\) complex used as a dynamic reference, as described in detail elsewhere. \(51,58,21,56\) Selective deuterium labeling of 2c was performed at the pyridine carbon closest to the nitrogen, \(59\) and isotope effects were collected in the temperature range \(25 \pm 40\) °C, for all pyridine carbons. Signal overlaps prohibited us from determining the temperature dependence of three- and four-bond isotope effects and, hence, from drawing a reliable conclusion from the IPE NMR study (for details, see pages S46–S48 in the Supporting Information). Overall, the variable-temperature study suggests that 3 is expectedly present in solution as a static and symmetric \([N\cdots C\cdots N]^+\) tetrabond complex; however, we cannot fully exclude the possibility of interconversion of...
analogous asymmetric $[\text{N} \cdots \text{C}]^+$ geometries encompassing conventional N–C covalent and N···C tetrel bonds.

Despite repeated attempts, the crystallization of 3c and 3d remained unsuccessful. It should, however, be noted that X-ray crystallography would not necessarily be able to describe the geometry of three-center tetrel bond complexes in solution. The analogous $[\text{N} \cdots \text{H} \cdots \text{N}]^+$ hydrogen bond complexes were shown to be a rapidly interconverting mixture of asymmetric geometries in solution, whereas they are static, symmetric complexes in the solid state.15 Preliminary density functional theory (DFT) calculations of 5c and 3c were unable to reproduce the experimental observations (see Supporting Information pages S51–S66 for details). This may indicate the need for higher-level computational approaches or that our structural interpretation of the NMR data is not sufficiently accurate. DFT has previously correctly predicted the geometry of an analogous asymmetric, intramolecular three-center tetrel bond complex.37 Continued experimental and computational investigations of the above and closely related molecular systems are expected to be capable of verifying or refuting the proposed structures of 3a–f.

**Binding Affinity.** Isothermal titration calorimetry was conducted to determine the binding strength of complex 3c. Titration of the CH$_2$Cl$_2$ solution of 2c with triphenylcarbenium tetrafluoroborate, 1a, dissolved in CH$_2$Cl$_2$, indicates the formation of a strong 1:1 complex characterized by $K_1 = 1.9$ nM, $\Delta G^{\circ}_1 = -49.8$ kJ/mol, $\Delta H^{\circ}_1 = -93.4$ kJ/mol, and $-T\Delta S^{\circ}_1 = 43.7$ kJ/mol. Upon addition of an excess of 1a, a 2:1 (2c/1a) complex 6c is generated in a second, weaker binding step with $K_2 = 237$ nM, $\Delta G^{\circ}_2 = -37.8$ kJ/mol, $\Delta H^{\circ}_2 = -53.1$ kJ/mol, and $-T\Delta S^{\circ}_2 = 15.3$ kJ/mol (Figure 5). Formation of the latter dialkylated 6c is in line with the smooth reaction of pyridine with triphenylcarbenium tetrafluoroborate, 1a, to form 1-tritylpyridin-1-ium tetrafluoroborate (5c). In the doubly positively charged complex 6c, the charge of the carbenium is presumably distributed over the entire conjugated aromatic system, akin to the analogous halogen-bonded complexes.35,21 The formation of 6c upon addition of an excess of 1a to 2c was also confirmed by NMR ($\delta^{15}$N $-143.7$ ppm; Supporting Information, Figure S56). The free energy $\Delta G^{\circ}_{1,2}$ of the initial complex formation results from a remarkable enthalpic contribution, which is partly offset by a substantial loss of entropy; for 6c, both contributions are

Figure 5. Titration of the bidentate ligand 2c with 1a yields the strong 1:1 complex, 3c (top). Upon addition of an excess of 1a, the 1:2 complex of 1a/2c, 6c, is formed, as revealed by the bimodal shape of the isotherm (bottom). Isothermal titration calorimetry was performed at 25 °C. Triphenylcarbenium tetrafluoroborate 1a at a concentration of 6.6 mM was titrated to the bidentate ligand 2c at a concentration of 0.5 mM. The main panel shows the isotherm depicting normalized heats of reaction, Q, as a function of the 1a/2c molar ratio in the calorimeter cell (blue circles) along with uncertainties (blue horizontal lines) resulting from baseline assignment and peak integration.57 Nonlinear least-squares fits (red solid line) were based on the presumption of two interaction sites,58 as reflected in the bimodal shape of the isotherm. Inset: The corresponding raw thermogram displaying differential heating power, $\Delta p$, versus time, t. Best-fit parameter values and associated confidence intervals are summarized in the text, with the detailed analysis contained in the Supporting Information. Note that the structure drawn for 3c is not necessarily its most stable conformation.

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largely reduced in magnitude, but the reaction remains purely enthalpy-driven. A reverse titration, that is, addition of a CH2Cl2 solution of 2c into the solution of 1a, supported the above binding model (Supporting Information).

**Electron Density.** Upon complexation, a considerable deshielding of the nitrogen of 2a–c and shielding of the carbenium carbon of 1a–f were observed. The magnitude of the observed chemical shift changes (Table 1) are expected to reflect the electron density alteration of the studied complexes, even if they do not necessarily correlate with bond strength.21 Upon decreasing the electron deficiency of the carbenium carbon, 3c → f, smaller Δδ15Ncoord and Δδ13Ccoord are detected (Table 1). This may be due to a gradual weakening of the [N···C···N]⁺ tetrel bond interaction upon decreasing the electrophilicity of the carbenium carbon.

Increasing electron density of the Lewis basic nitrogen of the bidentate ligand, 2a < 2c < 2b, is associated with an increase of Δδ15Ncoord in the order 3a < 3c < 3b. In contrast, Δδ13Ccoord remains virtually unaltered. The weak electron-donating effect of a 4-Me substituent does not have a vast influence on the coordination shifts as reflected by the comparable Δδ15Ncoord and Δδ13Ccoord of 3b and 3c as well as 5b and 5c.

**Masking Lewis Acidity by Tetrel Bond Formation.** Triphenyl carbenium ions are powerful Lewis acid catalysts that were used, for example, to facilitate Diels–Alder reactions.28–30 Such reactions do not proceed in the absence of a catalyst, while upon activation with 0.5 mol % triphenylcarbenium ion, they give high conversion within 30 min. To provide additional evidence for the participation of the carbenium p-orbital in a tetrel bond, involving an orbital interaction, we ran the Diels–Alder condensation of acrolein and cyclohexadiene (Figure 6) in the presence of 1a, 3c, and 7. Here, 7 denotes 2-((2-(phenylethynyl)phenyl)ethynyl)-1-tritylpyridin-1-ium, formed upon mixing 1a and 2-((2-(phenylethynyl)phenyl)ethynyl)pyridine (Supporting Information, page S8), a mononitrogen analogue of 3c. We monitored the progress of each reaction by acquiring the 1H NMR integral of the starting material and the product using their order rate in the presence of 7.

**Figure 6.** Progress of the Diels–Alder condensation, run under literature conditions,59 of 1,3-cyclohexadiene (1.2 equiv) and acrolein (1 mmol) in CD2Cl2 in the presence of 0.5 mol % 1a or 3a was monitored by 1H NMR in an NMR tube at 25 °C for 1 h. The integral of the signals of the aldehyde proton of the starting material and of the product was used to follow the progress of the reaction. Whereas the reaction catalyzed by 1a (red) progresses with a second-order rate, the addition of 2c inhibits it (green) through masking the Lewis acidic 1a by formation of the tetrel bond complex 3c.

geometry and energy. Thus, formation of the [N–C–N]⁺ complex is associated with ~50 kJ/mol change in free energy, as detected by isothermal titration calorimetry. This complex possesses by far the strongest tetrel bond so far reported.60,61 Its high stability is corroborated by the inability of the complex to act as a Lewis acid catalyst in a Diels–Alder reaction at room temperature. The observation of a single set of NMR signals even at low temperatures suggests that the complex has a symmetric three-center, four electron bond, whose electron density can be modulated by substitution. However, our observations cannot fully exclude a very low barrier interconversion of asymmetric species in solution. It should be noted that we were unable to confirm the symmetric [N–C–N]⁺ geometry by computation on the DFT level. Further computational studies of the complexes studied herein may thus provide critical insights for theoretical chemistry and, possibly, a more accurate structural interpretation of the NMR and ITC data of 3a–f.

The formation of a stable three-center, four-electron tetrel bond complex requires the involvement of a bidentate Lewis base whose donors are positioned at an optimal distance and geometry to promote simultaneous overlaps with the unfilled p-orbital of a carbenium ion. Upon use of 2 equiv of an analogous monodentate Lewis base, the carbenium does not form a stable bidentate complex but rather N-alkylates the electron donor. It should be noted that the isoelectronic [bis(pyridine)iodine]⁺ and [bis(pyridine)bromine]⁺-type halogen-bonded model systems are stable in solution.19,20,23 Thus, in contrast with the [N–C–N]⁺ complexes, the [N–X–N]⁺ ones do not require the use of a bidentate ligand for thermodynamic stability, highlighting an intriguing difference between halogen and tetrel bonding. The difference in tetrel,
halogen, and hydrogen bonding is further demonstrated by the fact that [N\(=\text{C}−\text{N}\)]\(^{1+}\) and [N\(=\text{I}−\text{N}\)]\(^{1+}\) complexes are strong, static, and symmetric, whereas the analogous [N\(=\text{H}−\text{N}\)]\(^{1+}\) complexes are present in solution as mixtures of rapidly interconverting asymmetric tautomers, [N\(=\text{H}−\text{H}−\text{N}\)]\(^{1+}\) \(\rightleftharpoons\) [N\(−\text{H}···\text{H}−\text{N}\)]\(^{1+}\), and lack extra stabilization.\(^{5,17}\) Despite its fundamental importance, the three-center, four-electron bond responsible for the stability of 3a–f remains an unsolved challenge for bonding theories.\(^{92}\) Its further investigation is expected to provide critical insights in numerous fields, not least in synthetic and theoretical chemistry.

The structure of 3a–f resembles the transition state geometry of the S\(_{\text{N}}\text{2}\) reaction,\(^{93}\) with the position of the Lewis bases and the carbonium carbon corresponding to that of the linearly arranged nucleophile, the central carbon, and the leaving group in the latter. Similar to the S\(_{\text{N}}\text{2}\) transition state, the central carbon of these complexes forms a three-center, four-electron bond within a trigonal bipyramidal geometry. Therefore, these compounds may be superior model systems for the S\(_{\text{N}}\text{2}\) transition state as compared with the previously proposed, isoelectronic three-center, four-electron halogen bonds.\(^{3,14}\) Compounds 3a–f are thermodynamically stable at room temperature in solution and are easily modifiable through simple synthetic transformations. By an independent variation of the electron density of the apically positioned Lewis bases, the geometry of the [N\(=\text{C}−\text{N}\)]\(^{1+}\) complex ought to be adjustable to reflect various stages of the S\(_{\text{N}}\text{2}\) reaction. Hence, the presented tetrel bond complexes and their close analogues are expected to be applicable to gain further insights into fundamental reaction mechanisms and chemical bonding theories.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.8b09367.

Details on the synthesis and spectroscopic data for compound identification, and details on the NMR, computational, X-ray diffractometric, and kinetic investigations (PDF)

CIF file for 1-tritylpyridin-1-ium-BF\(_{4}\) (CIF)

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### Notes

The authors declare no competing financial interest.

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