Complexes of Trimethylsilyl Trifluoromethanesulfonate with N, O and P Donors

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Complexes of Trimethylsilyl Trifluoromethanesulfonate with N, O and P Donors

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Abstract

The Lewis acceptor chemistry of Me₃SiOTf with p-block Lewis bases has been explored and a library of complexes has been characterized by spectroscopic and, where possible, crystallographic methods. Compounds with the generic formula [Me₃Si(L)][OTf] (L = 4-dmap, pyr, imz, OPMε₃, OPCy₃, OPPh₃, OpyrMe, dmso, PMe₃) were isolated from 1:1 mixtures of Me₃SiOTf and the respective ligand in CH₂Cl₂. Characterization by NMR spectroscopy confirmed the solution stability of all but [Me₃Si(PMe₃)][OTf], with indications that the latter dissociates into PMe₃ and Me₃SiOTf. Solid-state structures of [Me₃Si(4-dmap)][OTf], [Me₃Si(pyr)][OTf], [Me₃Si(OPCy₃)][OTf], [Me₃Si(OPPh₃)][OTf], [Me₃Si(OpyrMe)][OTf] and [Me₃Si(PMe₃)][OTf] were elucidated by single crystal X-ray diffraction, confirming the envisaged ionic formulations resulting from the displacement of the OTf anion from the silicon center of Me₃SiOTf by the incoming ligand. Mixtures of Me₃SiOTf with other related donors, including ChPPh₃ (Ch = S or Se), NEt₃, SMe₂, PPh₃, 2,2′-bipy or Me₂CO show no evidence of reaction under ambient conditions, reflecting the lower basicity and/or greater steric encumbrance of these ligands. Reactions of Me₃SiOTf with bis-donor ligands yielded complexes of the generic formulae [Me₃Si(L-L)SiMe₃][OTf]₂ (L-L = 4,4′-bipy, tmeda, dmpe) and [Me₃Si(L-L)][OTf] (L-L = 4,4′-bipy, tmeda, dmpe). The tmeda and dmpe complexes, however, were found to dissociate in solution, with complexes only prevailing in the solid phase. X-ray diffraction studies of [Me₃Si(4,4′-bipy)SiMe₃][OTf]₂ and [Me₃Si(dmpe)SiMe₃][OTf]₂ confirmed the expected connectivities and ionic formulations, with Si-ligand bond lengths comparable to those observed in [Me₃Si(pyr)][OTf] and [Me₃Si(PMe₃)][OTf], respectively.

Keywords
Lewis Acids, Lewis Bases, Main Group, Silicon, Coordination Chemistry
Introduction

The ubiquitous $p$-block Lewis acid trimethylsilyl trifluoromethanesulfonate, $\text{Me}_3\text{SiOTf}$, was first reported in 1970 by Roesky and Giere, and has applications in a broad array of processes including Lewis acid catalysis, functional group silylations, frustrated Lewis pair (FLP) chemistry, and halide abstraction/metathesis. In the latter context, $\text{Me}_3\text{SiOTf}$ has been extensively employed to heterolytically dissociate $\text{E}_2\text{X}$ bonds with concomitant release of the weakly coordinating OTf anion (as exemplified in Scheme 1a), a process facilitated by the particularly high halide affinity of silicon, and volatility of $\text{Me}_3\text{SiX}$ ($\text{X} = \text{Cl, F}$). When, however, the $\text{E}_2\text{X}$ bond is particularly strong and the ligand is appropriately sterically encumbered, the formation of complexes of $\text{Me}_3\text{SiOTf}$ can instead be observed. Complexes are also implicated in the action of related trialkylhalosilanes as silylating agents, a process normally carried out in the presence of a Lewis base as an activating agent or as a proton acceptor (Scheme 1b/c). Such silylations have been postulated to occur via a pre-equilibrium quaternization of the Lewis base by the silane, with the resulting complex the active silylating reagent.

![Scheme 1](https://mc06.manuscriptcentral.com/cjc-pubs)

Scheme 1. Application of $\text{Me}_3\text{SiOTf}$ as (a) a halide abstractor, and (b/c) a silylating reagent in the presence of a Lewis base.

Despite the intuitive formation of complexes between $\text{Me}_3\text{SiOTf}$ and Lewis bases, few examples of such compounds have been reported, and of those only a minority have been fully characterized by modern standards, with no reports of their crystallographic study. With a view to extending the reported coordination chemistry of this silicon acceptor, and identifying a library of ‘side-products’ for the above described applications of $\text{Me}_3\text{SiOTf}$, we have investigated its reactions with a series of $p$-block Lewis bases, the products of which
have been characterized by spectroscopic, analytic and where possible, crystallographic means.

Results

Treatment of CH$_2$Cl$_2$ solutions of Me$_3$SiOTf with one equivalent of the monodentate donors 4-(dimethylamino)pyridine (4-dmap), pyridine (pyr), imidazole (imz), OPMe$_3$, OPCy$_3$, OPPh$_3$, 4-methylpyridine-N-oxide (OpyrMe) or dimethylsulfoxide (dmso) over 1 h at ambient temperature led to the isolation of colourless solids in good yield. In all cases, the products were spectroscopically characterized as derivatives of [Me$_3$Si(L)][OTf] (L = 4-dmap, pyr, imz, OPMe$_3$, OPCy$_3$, OPPh$_3$, OpyrMe, dmso), and were purified by recrystallization from CH$_2$Cl$_2$/Et$_2$O at -30 °C. For all eight complexes, $^1$H and $^{13}$C NMR spectra illustrate resonances which are distinct from those of Me$_3$SiOTf (see Tables 1 and 2) and the free ligand, respectively. The $^1$H NMR resonances of the respective SiMe$_3$ moieties appear over a significant range, 0.20 - 0.76 ppm, with the only apparent trend that the nitrogen donors led to downfield NMR shifts relative to that of Me$_3$SiOTf, and oxygen donors, with the exception of dmso, a downfield shift. The $^{29}$Si NMR resonances for the complexes all appear as sharp, well-resolved singlets in the range 26.6 - 48.5 ppm (Table 2), consistent with tetra-coordinate silicon centers, and in line with previous $^{29}$Si NMR data for such complexes. For the phosphine oxide adducts [Me$_3$Si(OPMe$_3$)][OTf], [Me$_3$Si(OPCy$_3$)][OTf] and [Me$_3$Si(OPPh$_3$)][OTf], the $^{31}$P{$^1$H} NMR spectra show the expected singlet resonances (δ$_P$ = 82.1, 84.6, 52.2 ppm, respectively), in all cases shifted significantly downfield (>20 ppm) from the values for the respective free ligands, consistent with coordination to the Lewis acidic silicon center of Me$_3$SiOTf.

Table 1. Selected properties of Me$_3$SiOTf.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$^1$H δ (ppm)</th>
<th>$^{29}$Si δ (ppm)</th>
<th>Solvent Dielectric Constant (ε$^{24}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CDCl$_3$</td>
<td>0.51</td>
<td>43.3</td>
<td>4.81</td>
</tr>
<tr>
<td>CD$_2$Cl$_2$</td>
<td>0.50</td>
<td>44.1</td>
<td>8.93</td>
</tr>
<tr>
<td>CD$_3$CN</td>
<td>0.47</td>
<td>46.1</td>
<td>36.64</td>
</tr>
</tbody>
</table>
Table 2. Selected NMR spectroscopic data for derivatives of [Me$_3$Si(L)][OTf] in CDCl$_3$.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$^1$H δ (ppm) of SiMe$_3$</th>
<th>$^{29}$Si δ (ppm)</th>
<th>$^{31}$P δ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Me$_3$Si(4-dmap)][OTf]</td>
<td>0.53</td>
<td>31.6</td>
<td>-</td>
</tr>
<tr>
<td>[Me$_3$Si(pyr)][OTf] *</td>
<td>0.69</td>
<td>42.1</td>
<td>-</td>
</tr>
<tr>
<td>[Me$_3$Si(imz)][OTf]</td>
<td>0.62</td>
<td>26.6</td>
<td>-</td>
</tr>
<tr>
<td>[Me$_3$Si(OPMe$_3$)][OTf]</td>
<td>0.37</td>
<td>32.6</td>
<td>82.1</td>
</tr>
<tr>
<td>[Me$_3$Si(OPCy$_3$)][OTf]</td>
<td>0.20</td>
<td>31.1</td>
<td>84.6</td>
</tr>
<tr>
<td>[Me$_3$Si(OPPh$_3$)][OTf]</td>
<td>0.25</td>
<td>37.4</td>
<td>52.3</td>
</tr>
<tr>
<td>[Me$_3$Si(OpyrMe)][OTf]</td>
<td>0.41</td>
<td>48.5</td>
<td>-</td>
</tr>
<tr>
<td>[Me$_3$Si(dms)][OTf]</td>
<td>0.76</td>
<td>42.6</td>
<td>-</td>
</tr>
<tr>
<td>[Me$_3$Si(PMe$_3$)][OTf] *</td>
<td>0.50</td>
<td>53.7</td>
<td>-53.7</td>
</tr>
</tbody>
</table>

* Recorded in CD$_3$CN due to low solubility in CDCl$_3$.  
* Recorded in CD$_2$Cl$_2$ (Insoluble in CDCl$_3$, decomposes in CD$_3$CN).  
* Sparing solubility precludes the recording of meaningful $^{29}$Si spectrum.

The solid-state structures of [Me$_3$Si(4-dmap)][OTf], [Me$_3$Si(pyr)][OTf], [Me$_3$Si(OPCy$_3$)][OTf], [Me$_3$Si(OPPh$_3$)][OTf] and [Me$_3$Si(OpyrMe)][OTf] were elucidated by X-ray diffraction and confirmed the expected connectivities in all cases. [Me$_3$Si(4-dmap)][OTf] crystallized in the P$_2_1/c$ space group with a single formula unit in the asymmetric unit (Figure 1a). The silicon center is coplanar with the carbon-nitrogen framework of the dmap ligand, and the Si-N bond [1.836(2) Å] is slightly shorter than the sum of the covalent radii ($\Sigma_{CR}$) of the two elements [1.87 Å]. The shortest Si---OTf contact measures 3.794(2) Å, which is beyond the sum of the van der Waal’s radii ($\Sigma_{vdW}$) of the two elements [3.62 Å], consistent with an ionic formulation. The related pyridine complex, [Me$_3$Si(pyr)][OTf] is structurally similar (Figure SI-1) to that of [Me$_3$Si(4-dmap)][OTf], but exhibits a slightly longer Si-N bond [1.859(1) Å], consistent with the lesser basicity of pyridine, with the magnitude comparable to those previously reported in [Me$_3$Si(pyr)][Br] [1.856(7) Å] and [Me$_3$Si(pyr)][I] [1.859(9) Å]. The shortest Si---OTf interaction [3.82(5) Å] in [Me$_3$Si(pyr)][OTf] is again greater than $\Sigma_{vdW}$, implying an ionic formulation. The phosphine oxide complex [Me$_3$Si(OPCy$_3$)][OTf] crystallized with two closely related formula units in the asymmetric unit (Figure SI-2), with an average Si-OPCy$_3$ bond length of 1.690(3) Å ($\Sigma_{CR} = 1.79$ Å). The average O-P bond length [1.552(3) Å] is longer than that reported in OPCy$_3$ [1.490(2) Å], in line with coordination to the Lewis acidic Me$_3$Si$^+$ moiety. The average Si-O-P angle [158.3°] is relatively wide given the presence of a lone pair at the oxygen center, which may reflect the steric constraints imposed by the cyclohexyl groups at phosphorus and the SiMe$_3$ moiety. As for [Me$_3$Si(4-dmap)][OTf] and [Me$_3$Si(pyr)][OTf], the magnitude of the shortest Si-OTf inter-ion contact [3.855(5) Å; $\Sigma_{vdW} = 3.62$ Å] is consistent with an ionic formulation. The related [Me$_3$Si(OPPh$_3$)][OTf] (Figure 1b), is structurally
similar to [Me₃Si(OPCy₃)][OTf], but adopts a significantly narrower Si-O-P angle [142.56(6)°] and shorter Si-OPR₃ bond [1.7141(9) Å], as expected given the lower steric encumbrance and reduced basicity of PPh₃ relative to PCy₃. The trend in Si-O-Pn bond angles is continued in the structure of [Me₃Si(OpyrMe)][OTf], in which the Si-O-N angle measures 118.4(1)° (Figure SIg3). The Si-OpyrMe bond is, however, slightly longer [1.723(1) Å] despite the reduced steric encumbrance about the oxygen center, possibly a consequence of the slightly closer approach of the OTf anion in this case [shortest Si-OTf contact: 3.543(1) Å; cf. [Me₃Si(OPCy₃)][OTf] 3.855(5) Å and [Me₃Si(OPPh₃)][OTf] 3.766(1) Å] which unlike those in [Me₃Si(OPCy₃)][OTf] and [Me₃Si(OPPh₃)][OTf] is a Si---F contact.

![Figure 1. Solid-state structures of the cation in (a) [Me₃Si(4-dmap)][OTf], (b) [Me₃Si(OPPh₃)][OTf] and (c) [Me₃Si(PMe₃)][OTf]. All hydrogen atoms are omitted for clarity.](image)

**Table 3.** Selected solid-state parameters for derivatives of [Me₃Si(L)][OTf].

<table>
<thead>
<tr>
<th>Compound</th>
<th>Si-Ligand Bond Length (Å)</th>
<th>Pn-O-Si Angle (°)</th>
<th>Shortest Inter-Ion Contact (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Me₃Si(4-dmap)][OTf]</td>
<td>1.836(2) [Si-N]</td>
<td>-</td>
<td>3.794(2) [Si-O]</td>
</tr>
<tr>
<td>[Me₃Si(pyr)][OTf]</td>
<td>1.859(1) [Si-N]</td>
<td>-</td>
<td>3.82(5) [Si-O]</td>
</tr>
<tr>
<td>[Me₃Si(OPCy₃)][OTf]</td>
<td>av. 1.690(3) [Si-O]</td>
<td>158.3(2)</td>
<td>3.855(5) [Si-O]</td>
</tr>
<tr>
<td>[Me₃Si(OPPh₃)][OTf]</td>
<td>1.7141(9) [Si-O]</td>
<td>142.56(6)</td>
<td>3.766(1) [Si-O]</td>
</tr>
<tr>
<td>[Me₃Si(OpyrMe)][OTf]</td>
<td>1.723(1) [Si-O]</td>
<td>118.4(1)</td>
<td>3.543(1) [Si-F]</td>
</tr>
</tbody>
</table>

Reaction of Me₃SiOTf with PMe₃ in CH₂Cl₂ at ambient temperature was found to lead to the immediate precipitation of a fine colourless solid, characterized as [Me₃Si(PMe₃)][OTf]. The solid was isolated via filtration, but subsequent drying under high vacuum led to significant mass loss, attributed to the removal of volatile PMe₃ (b.p. 38 °C) and Me₃SiOTf (b.p. 140 °C) from the complex. The isolated solids proved, however, to be
sparingly soluble in CD$_2$Cl$_2$, and produced a $^1$H NMR spectrum that shows two broad signals of equal intensity assigned to the six methyl groups at silicon and phosphorus, respectively. The $^1$H chemical shifts of these signals are very similar to those of free PMe$_3$ and Me$_3$SiOTf, suggesting that the P-Si interaction is weak in solution. Consistently, the $^{31}$P NMR spectrum of the dissolved solid shows only a slight downfield shift (-53.7 ppm) relative to free PMe$_3$ (-60 ppm). The instability of the compound under vacuum precluded further gravimetric analysis of the solids, but single crystals were furnished from a saturated solution in CH$_2$Cl$_2$ at -30 °C and although illustrating significant disorder in the OTf anion, confirm the expected connectivity (Figure 1c). The cation, an inorganic analogue of 2,2,3,3-tetramethylbutane, exhibits a counterintuitive eclipsed conformation, and a typical Si-P bond length [2.294(1) Å; $\Sigma_{CR}$ 2.27 Å].$^{25}$ No reaction was evident between Me$_3$SiOTf and the sterically encumbered solid phosphines PR$_3$ (R = Cy or tBu), with exclusively unreacted phosphine recovered upon removal of all volatiles under vacuum. The feasibility of the formation of complexes between Me$_3$SiOTf and sterically bulky phosphines is, nonetheless, underlined by reports of the isolation of [Me$_3$Si(PrBu$_3$)][Me$_3$SiCCB(C$_6$F$_5$)$_3$]$^{29}$ [iPr$_3$Si(PrBu$_3$)][B(C$_6$F$_5$)$_4$]$^{30}$ (Si-P = 2.4843(5) Å) and [Me$_2$(Ph)Si(PrBu$_3$)][HB(C$_6$F$_5$)$_3$]$^{31}$ (Si-P = 2.3764(8) Å), with the latter two complexes notably based upon more heavily sterically encumbered silicon acceptors. We postulate that the presence of more weakly coordinating anions in these cases leads to an increased Lewis acidity at the silicon center relative to that found in Me$_3$SiOTf. Mixtures of Me$_3$SiOTf with 2-$dmap$, NEt$_3$, PPh$_3$, SPPh$_3$, SePPh$_3$, SME$_2$ or Me$_2$CO produced no evidence of reaction at ambient temperature (see experimental section), even in the absence of solvent (explored for the representative examples of PPh$_3$ and SPPh$_3$ using excess Me$_3$SiOTf). We postulate that the formation of stable complexes of Me$_3$SiOTf with these ligands is precluded by their increased steric bulk and/or less basic donor centers, although note that NEt$_3$ has previously been suggested to form a solution-stable complex with Me$_3$SiOTf at -83 °C.$^{19}$

Mixtures of Me$_3$SiOTf with the bidentate donors 4,4'-bipyridine (4,4'-bipy), N,N,N’N'-tetramethylethlenediamine (tmeda) and 1,2-bis(dimethylphosphino)ethane (dmpe) in 2:1 stoichiometries furnished colourless solids in each case upon removal of all volatiles, with crude yields consistent with the quantitative formation of [Me$_3$Si(L-L)SiMe$_3$][OTf]$_2$ [L-L = 4,4'-bipy, tmeda, dmpe]. Following purification by recrystallization, $^1$H and $^{13}$C NMR spectra of all three indicate the presence of –SiMe$_3$ moieties and the respective ligand in the expected 2:1 ratio. Only in the case of [Me$_3$Si(4,4'-bipy)SiMe$_3$][OTf]$_2$, however, is the shift in the $^1$H NMR resonance for –SiMe$_3$ versus that of Me$_3$SiOTf significant (Tables 1 and 3). The $^{29}$Si
NMR spectra of all three compounds, show minimal shifts from that of Me₃SiOTf (Tables 1 and 3), and all appear as singlet resonances. Given the minimal changes observed in the chemical shifts of [Me₃Si(tmeda)SiMe₃][OTf]₂ and [Me₃Si(dmpe)SiMe₃][OTf]₂, and singlet ²⁹Si NMR resonance for the latter case, these complexes are postulated to be stable only in the solid-state, dissociating to restore Me₃SiOTf and the free ligand in solution. A similar observation has been reported for the reaction of Me₃SiOTf with the related monodentate donor NMe₃.¹⁹ Consistently, 1:1 mixtures of Me₃SiOTf with 4,4'-bipy, tmeda or dmpe yield solids upon removal of volatiles under vacuum which are spectroscopically consistent with the formulations [Me₃Si(L-L)][OTf]₂ (L-L = 4,4'-bipy, tmeda, dmpe), but recrystallization of the tmeda and dmpe complexes ultimately furnished crystalline solids consistent with the previously characterized 2:1 formulations [Me₃Si(tmeda)SiMe₃][OTf]₂ and [Me₃Si(dmpe)SiMe₃][OTf]₂. Presumably, in solution the Si-L bonds in the tmeda and dmpe complexes are sufficiently labile to restore the free acid and base upon dissolution in CH₂Cl₂, with the crystallization of the 2:1 complexes i.e. the preferred presence of these species in the solid-state, favoured due to the increased lattice enthalpy of their dicationic formulations. No reaction was observed between Me₃SiOTf and the related donors 2,2'-bipyridine (2,2'-bipy) or 1,2-bis(diphenylphosphino)ethane (dppe) under ambient conditions (see experimental section), likely due to the significant steric constraints at the donor centers in these ligands.

Table 3. Selected spectroscopic parameters for derivatives of [Me₃Si(L-L)SiMe₃][OTf]₂.

<table>
<thead>
<tr>
<th>Compound</th>
<th>¹H δ (ppm) of -SiMe₃</th>
<th>²⁹Si δ (ppm)</th>
<th>³¹P δ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Me₃Si(4,4'-bipy)SiMe₃][OTf]₂</td>
<td>0.76</td>
<td>44.0⁹</td>
<td>-</td>
</tr>
<tr>
<td>[Me₃Si(tmeda)SiMe₃][OTf]₂</td>
<td>0.50</td>
<td>43.7⁷</td>
<td>-</td>
</tr>
<tr>
<td>[Me₃Si(dmpe)SiMe₃][OTf]₂</td>
<td>0.50</td>
<td>42.5</td>
<td>-46.7</td>
</tr>
<tr>
<td>[Me₃Si(4,4'-bipy)][OTf]</td>
<td>0.73</td>
<td>42.6</td>
<td>-</td>
</tr>
</tbody>
</table>

⁹ Recorded in CDCl₃. ⁷ Recorded in CD₃CN due to reduced solubility.

The solid-state structures of [Me₃Si(4,4'-bipy)SiMe₃][OTf]₂ and [Me₃Si(dmpe)SiMe₃][OTf]₂ (Figure 2) were elucidated by X-ray diffraction following recrystallization from MeCN/Et₂O at -30 °C, confirming the expected connectivities. The 4,4'-bipy complex [Me₃Si(4,4'-bipy)SiMe₃][OTf]₂ exhibits two closely related Si-N bonds (av. 1.869(1) Å; ΣCR 1.87 Å), comparable in magnitude to that observed in [Me₃Si(pyr)][OTf] [1.859(1) Å], with the two pyridine rings illustrating a torsion angle of 36.0(2)⁶, presumably due to packing effects (Figure 2). Both OTf anions are well separated from the dication, with the shortest Si-OTf interaction [3.713(2) Å; Σvdw 3.62 Å] consistent.
with an ionic formulation. A molecule of MeCN also interacts with one of the silicon centers, with a Si-NCMe bond length of 3.625(2) Å and the coordinating nitrogen essentially coplanar with both Si and N atoms of the dication. The structure of \([\text{Me}_3\text{Si}(\text{dmpe})\text{SiMe}_3][\text{OTf}]_2\), illustrates Si-P bonds of similar magnitude \([2.3061(1) \text{ Å}; \Sigma_{\text{CR}} = 2.27 \text{ Å}]^{25}\) to that observed in \([\text{Me}_3\text{Si}(\text{PMe}_3)][\text{OTf}]\) (cf. 2.294(1) Å), and as for the PMe₃ complex the two Si-P sub-units of the centrosymmetric cation exhibit fully eclipsed conformations. The shortest Si-OTf interaction \((3.658(2) \text{ Å}; \Sigma_{\text{vdW}} 3.62 \text{ Å})\) is beyond \(\Sigma_{\text{vdW}}\), consistent with an ionic formulation.

![Figure 2. Solid-state structure of the dications in (a) \([\text{Me}_3\text{Si}(4,4'\text{-bipy})\text{SiMe}_3][\text{OTf}]_2\) and (b) \([\text{Me}_3\text{Si}(\text{dmpe})\text{SiMe}_3][\text{OTf}]_2\). All hydrogen atoms and solvent molecules are omitted for clarity.](image)

Table 3. Selected solid-state metrical parameters for derivatives of \([\text{Me}_3\text{Si}(\text{L-L})\text{SiMe}_3][\text{OTf}]_2\).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Si-Donor Bond Length (Å)</th>
<th>Shortest Inter-Ion Contact (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Me}_3\text{Si}(4,4'\text{-bipy})\text{SiMe}_3][\text{OTf}]_2)</td>
<td>1.865(1) [Si-N] 1.872(1) [Si-N]</td>
<td>3.713(2) [Si-O]</td>
</tr>
<tr>
<td>([\text{Me}_3\text{Si}(\text{dmpe})\text{SiMe}_3][\text{OTf}]_2)</td>
<td>2.3061(1) [Si-P]</td>
<td>3.658(2) [Si-O]</td>
</tr>
</tbody>
</table>

Summary

The reactions of Me₃SiOTf with an extensive library of \(p\)-block Lewis bases have been systematically explored, and the resulting complexes characterized by spectroscopic and, where possible, crystallographic methods. Reactions of Me₃SiOTf with a variety of classical mono- and \(\text{bis}\)-donor ligands give complexes of the generic formulae \([\text{Me}_3\text{Si}(\text{L})][\text{OTf}]\) \([\text{L} = 4\text{-dmap}, \text{pyr}, \text{imz}, \text{OPMe}_3, \text{OPCy}_3, \text{OPPh}_3, \text{OpyrMe}, \text{dmso}, \text{PMe}_3], \quad \text{[Me}_3\text{Si(4,4’-bipy)], \quad [Me}_3\text{Si(4,4’-bipy)] OTf}]\) which have been comprehensively characterized as ionic compounds. Generally the
complexes remain robust in solution, but complexes with PMe₃, dmpe and tmeda were found to be labile towards dissociation in solution to give the free ligand and Me₃SiOTf. Attempts to prepare 1:1 complexes of Me₃SiOTf with the bis-donor ligands were only successful in the case of [Me₃Si(4,4'-bipy)][OTf] which proved to be a robust complex. Reactions of Me₃SiOTf with one equivalent of dmpe or tmeda instead preferentially formed the previously described 2:1 complexes in the solid state, likely due to the increased lattice enthalpies of these dicationic formulations. Mixtures of Me₃SiOTf with 2-dmap, NEt₃, PPh₃, SPPh₃, SePPh₃, SMe₂ or Me₂CO, dppe or 2,2'-bipy did not show evidence of complex formation, likely due to the lesser basicity and/or increased steric encumbrance of these ligands.

The library of compounds characterized in this study develops the coordination chemistry of a surprisingly under-explored area of the main group, and provides characterization data for potential side-products and reaction intermediates in the use of Me₃SiOTf as a halide abstraction/silylation agent in the presence of Lewis bases, facilitating further employment of this reagent in these contexts.

Acknowledgements

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Experimental Section

Unless otherwise stated all experiments were carried out under nitrogen gas, either using standard Schlenk techniques or within an MBraun glovebox. All non-deuterated solvents were collected from a Grubbs-type solvent purification system, and subsequently distilled from CaH₂ and stored over molecular sieves. Deuterated solvents were purchased from Sigma Aldrich Ltd. and purified by distillation from CaH₂ in the case of CDCl₃, and were stored over 4 Å (CDCl₃, CD₂Cl₂) or 3 Å (CD₃CN) molecular sieves. Me₃SiOTf was purchased from Sigma Aldrich Ltd. and purified by vacuum transfer. 4-(dimethylamino)pyridine (4-dmap) and 2,2'-bipyridine (2,2'-bipy) were purchased from Sigma Aldrich Ltd., and purified by sublimation and recrystallization from CH₂Cl₂, respectively. OPPh₃, OPMe₃, SPPh₃, SePPh₃ and PPh₃ were purchased from Sigma Aldrich Ltd, and imidazole from Biobasic Canada Inc., with all reagents dried under high vacuum overnight. SbPh₃, PtBu₃, PCy₃, anhydrous dimethylsulfoxide (dmso) and 2-(dimethylamino)pyridine (2-dmap) were purchased from Sigma Aldrich Ltd. and used as
received. 4,4’-bipyridine (4,4’-bipy) was purchased from Alfa Aesar and purified by recrystallization from CH$_2$Cl$_2$. N, N, N’, N’-tetramethylethylene diamine (tmeya) and NEt$_3$ were purchased from Sigma Aldrich Ltd. and purified by distillation from CaH$_2$. Me$_3$P and 1,2-bis(dimethylphosphino)ethane (dmpe) were purchased from Strem Chemicals and the former purified by vacuum transfer.

NMR spectra were recorded using Bruker Avance 500, 360 or 300 MHz spectrometers, at 298 K unless otherwise stated. Chemical shifts are reported relative to residual proteo-solvent peaks (¹H, ¹³C), or to external H$_3$PO$_4$ (³¹P); CFCl$_3$ (¹⁹F); Me$_4$Si (²⁹Si). IR spectra were recorded on a Perkin Elmer Frontier FT-IR spectroscope operating in ATR mode.

X-ray crystallographic data were collected at either the University of British Columbia, Vancouver, the University of Alberta, Edmonton, or the MAX Diffraction Facility at McMaster University, Hamilton (for full details of the respective procedures see supporting information). Molecular structures presented in the manuscript were plotted using ORTEP-3 V2.02, with thermal ellipsoids at the 50% probability level. CCDC depositions 1422165-1422172 contain the supplementary crystallographic data for this paper.

Elemental analyses were performed by Canadian Microanalytical Service Ltd., Delta British Columbia, Canada.

Preparative Procedures

**Synthesis of [Me$_3$Si(L)][OTf]:** The syntheses of all compounds of this class were carried out via analogous methodologies. The synthesis of [Me$_3$Si(4-dmap)][OTf] is therefore presented in full as a representative example.

**[Me$_3$Si(4-dmap)][OTf]:** To a solution of Me$_3$SiOTf (364 mg, 1.64 mmol) in CH$_2$Cl$_2$ (8 mL) was added solid 4-dmap (200 mg, 1.64 mmol) at ambient temperature and the resulting mixture then stirred for 1 h before the removal of all volatiles under high vacuum to yield a colourless solid. Yield (crystalline): 0.52 g, 92%; $^1$H NMR (300 MHz, CDCl$_3$): $\delta_{H}$ 8.06-8.01 (2H, m, Ar-H), 6.99-6.94 (2H, m, Ar-H), 3.18 (6H, s, NMe$_2$), 0.53 (9H, s, SiMe$_3$); $^{19}$F NMR (283 MHz, CDCl$_3$): $\delta_{F}$ -78.16 (s, CF$_3$); $^{13}$C{$^1$H} NMR (76 MHz, CDCl$_3$): $\delta_{C}$ 156.8 (s, Ar), 142.6 (s, Ar), 120.7 (q, $J_{CF} = 321$ Hz, CF$_3$), 108.5 (s, Ar), 39.8 (s, NMe$_2$), -1.3 (s, SiMe$_3$); $^{29}$Si NMR (72 MHz, CDCl$_3$): $\delta_{Si}$ 31.6 (s, SiMe$_3$); FT-IR (ATR, Ranked Intensities): 1644(11), 1271(6), 1248(5), 1217(3), 1148(7), 1028(2), 835(10), 802(8), 754(9), 634(1), 518(4) cm$^{-1}$; Mpt: 82-84 °C; Elemental Analysis: Calculated C 38.36, H 5.56, N 8.13, Found C 37.85, H 5.75, N 8.32.
[Me₃Si(pyr)][OTf]: Colourless solid. Yield (crystalline): 0.18 g, 86%; ¹H NMR (300 MHz, CD₂CN): δH 8.81-8.76 (2H, m, Ar-H), 8.52 (1H, tt, JH:H = 8 and 1 Hz, Ar-H), 8.05-7.99 (2H, m, Ar-H), 0.69 (9H, s, -SiMe₃); ¹⁹F NMR (283 MHz, CD₂CN): δF -79.19 (s, CF₃); ¹³C{¹H} NMR (76 MHz, CD₂CN): δC 147.9, (s, Ar), 147.5 (s, Ar), 129.2 (s, Ar), 118.2 (q, JCF = 321 Hz, CF₃), -0.6 (s, -SiMe₃); ²⁹Si NMR (71.6 MHz, CD₂CN): δSi 42.1 (s, SiMe₃); FT-IR (ATR, Ranked Intensities): 1251(4), 1223(3), 1155(5), 1027(2), 862(10), 848(9), 756(6), 682(7), 633(1), 517(8) cm⁻¹; Mpt: 116-118 °C.

[Me₃Si(imz)][OTf]: Colourless solid. Yield (crystalline): 0.13 g, 65%; ¹H NMR (300 MHz, CDCl₃): δH 13.20 (1H, br. s, NgH), 8.68 (1H, br. s, ArgH), 7.41 (2H, br. s, ArgH), 0.62 (9H, s, -SiMe₃); ¹⁹F NMR (283 MHz, CDCl₃): δF 78.56 (s, CF₃); ¹³C{¹H} NMR (91 MHz, CDCl₃): δC 121.7 (v. br. s), 120.3 (q, JCF = 321 Hz, gCF₃), 1.1 (s, gSiMe₃); ²⁹Si NMR (72 MHz, CDCl₃): δSi 26.6 (s, SiMe₃); FT-IR (ATR, Ranked Intensities): 1258(2), 1222(8), 1162(6), 1099(9), 1027(2), 983(11), 830(5), 768(4), 627(1), 516(7), 468(10); Mpt: >70 °C (decomposed); Elemental Analysis: Calculated C 27.42, H 4.18, N 9.64, Found C 28.96, H 4.51, N 10.20.

[Me₃Si(OPMe₃)][OTf]: Colourless solid. Yield (crystalline): 0.14 g, 68%; ¹H NMR (300 MHz, CDCl₃): δH 2.09 (9H, d, JPH = 15 Hz, gPMe₃), 0.37 (9H, s, -SiMe₃); ¹⁹F NMR (283 MHz, CDCl₃): δF 78.34 (s, CF₃); ³¹P{¹H} NMR (122 MHz, CDCl₃): δP 82.1 (br. s, gOPMe₃); ¹³C{¹H} NMR (76 MHz, CDCl₃): δC 120.7 (q, JCF = 321 Hz, gCF₃), 14.7 (d, JPC = 69 Hz, -OPMe₃), 0.9 (s, -SiMe₃); ²⁹Si NMR (72 MHz, CDCl₃): δSi 32.6 (s, -SiMe₃); FT-IR (ATR, Ranked Intensities): 1254(4), 1225(7), 1154(5), 1093(8), 1030(3), 961(6), 842(2), 635(1), 516(9), 355(10); Mpt: 193-195 °C; Elemental Analysis: Calculated C 27.42, H 4.18, N 9.64, Found C 28.96, H 4.51, N 10.20.

[Me₃Si(OPCy₃)][OTf]: Colourless solid. Yield (crystalline): 0.14 g, 68%; ¹H NMR (300 MHz, CDCl₃): δH 2.44-2.28 (3H, m, Cy), 2.00-1.81 (12H, m, Cy), 1.81-1.69 (3H, m, Cy), 1.51-1.15 (15H, m, Cy), 0.38 (9H, s, -SiMe₃); ³¹P{¹H} NMR (CDCl₃, 122 MHz): 84.5 (s, gOPCy₃); ¹⁹F NMR (283 MHz, CDCl₃): δF 78.15 (s, gCF₃); ³¹P{¹H} NMR (CDCl₃, 122 MHz): δP 84.4 (s, gOPCy₃); ¹³C{¹H} NMR (76 MHz, CDCl₃): δC 120.7 (q, JCF = 321 Hz, -CF₃), 14.7 (d, JPC = 69 Hz, -OPCy₃), 0.9 (s, -SiMe₃); ²⁹Si NMR (72 MHz, CDCl₃): δSi 32.6 (s, -SiMe₃); FT-IR (ATR, Ranked Intensities): 1259(2), 1229(7), 1154(5), 1093(8), 1030(3), 961(6), 842(2), 635(1), 516(9), 355(10); Mpt: 193-195 °C.

[Me₃Si(OPPh₃)][OTf]: Colourless solid. Yield (crystalline): 0.20 g, 60%; ¹H NMR (300 MHz, CDCl₃): δH 7.84-7.76 (3H, m, Ph), 7.73-7.57 (12H, m, Ph), 0.25 (9H, s, -SiMe₃); ¹⁹F
NMR (283 MHz, CDCl₃): δF -78.01 (s, CF₃); ³¹P {¹H} NMR (122 MHz, CDCl₃): δP 52.2 (s, -OPPh₃); ¹³C {¹H} NMR (76 MHz, CDCl₃): δC 135.9 (d, J_CF = 3 Hz, Ph), 132.3 (d, J_CF = 13 Hz, Ph), 130.2 (d, J_CF = 14 Hz, Ph), 121.3 (d, J_CF = 111 Hz, Ph), 120.7 (q, J_CF = 321 Hz, -CF₃), 0.8 (s, -SiMe₃); ²⁹Si NMR (72 MHz, CDCl₃): δSi 37.4 (s, -SiMe₃); FT-IR (ATR, Ranked Intensities): 1262(9), 1118(4), 1028(8), 837 (7), 728(3), 688(6), 633(2), 529(1), 514(5), 488(10); Mpt: 121-123 °C.

[Me₃Si(OpyrMe)][OTf]: Colourless solid. Yield (crystalline): 0.16 g, 70%; ¹H NMR (300 MHz, CDCl₃): δH 8.77 – 8.72 (2H, m, ArgH), 7.98-7.92 (2H, m, ArgH), 2.63 (3H, s, ArgCH₃), 0.41 (9H, s, -SiMe₃); ¹³F NMR (283 MHz, CDCl₃): δF -78.31 (s, CF₃); ¹³C {¹H} NMR (76 MHz, CDCl₃): δC 157.1 (s, Ar), 140.4 (s, Ar), 130.2 (s, Ar), 116.5 (q, J_CF = 320 Hz, -CF₃), 21.7 (s, Ar-CH₃), -1.4 (s, SiMe₃); ²⁹Si NMR (72 MHz, CDCl₃): δSi 48.5 (s, SiMe₃); FT-IR (ATR, Ranked Intensities): 1262(1), 1221(8), 1208(9), 1145(3), 1031(6), 844(2), 753(10), 635(4), 513(7), 458(5); Mpt: 123-125 °C; Elemental Analysis: Calculated C 36.25, H 4.87, N 4.23, Found C 35.81, H 4.95, N 4.32.

[Me₃Si(dmso)][OTf]: Colourless solid. Yield (crystalline): 0.19 g, 92%; ¹H NMR (300 MHz, CDCl₃): δH 3.29 (6H, s, S(CH₃)₂), 0.42 (9H, s, -SiMe₃); ¹³F NMR (283 MHz, CDCl₃): δF -77.96 (s, CF₃); ¹³C {¹H} NMR (76 MHz, CDCl₃): δC 120.4 (q, J_CF = 321 Hz, -CF₃), 37.4 (s, S(CH₃)₂), 0.1 (s, -SiMe₃); ²⁹Si NMR (72 MHz, CDCl₃): δSi 45.5 (s, -SiMe₃); FT-IR (ATR, Ranked Intensities): 1244(3), 1223(6), 1156(4), 1024(5), 940(10), 854(7), 830(2), 765(11), 633(1), 570(9), 515(8); Mpt: 56-58 °C.

[Me₃Si(PMe₃)][OTf]: Colourless solid. Yield (crystalline): 0.16 g, 71%; ¹H NMR (300 MHz, CD₃CN): δH 9.00 (4H, d, J_HH = 6 Hz, Ar-H), 8.40 (4H, d, J_HH = 6 Hz, Ar-H), 0.76 (18H, s, -SiMe₃); ¹⁹F NMR (283 MHz, CD₃CN): δF -79.10 (s, CF₃); ³¹P {¹H} NMR (203 MHz, CD₂Cl₂): δP -53.7 (br.s, -PMe₃); ¹³C {¹H} NMR (126 MHz, CD₂Cl₂): δC 14.5 (s, -PMe₃), -0.4 (s, -SiMe₃); *Elemental analyses and ²⁹Si NMR and FT-IR spectroscopies were precluded by the limited solubility of this compound in CD₂Cl₂ and instability under vacuum, respectively.

[Me₃Si(4,4'-bipy)SiMe₃][OTf]: Off-white solid. Yield (crystalline): 0.24 g, 71%; ¹H NMR (300 MHz, CD₃CN): δH 9.00 (4H, d, J_HH = 6 Hz, Ar-H), 8.40 (4H, d, J_HH = 6 Hz, Ar-H), 0.76 (18H, s, -SiMe₃); ¹⁹F NMR (283 MHz, CD₃CN): δF -79.10 (s, CF₃); ¹³C {¹H} NMR (76 MHz, CD₃CN): δC 151.4 (s, Ar), 148.9 (s, Ar), 126.9 (s, Ar), 122.0 (q, J_CF = 321 Hz, -CF₃), -0.7 (s, SiMe₃); ²⁹Si NMR (72 MHz, CD₃CN): δSi 44.0 (s, -SiMe₃); FT-IR (ATR, Ranked Intensities): 1262(3), 1223(5), 1157(9), 1027(2), 866(8), 845(4), 828(7), 635(1), 516(8), 352(10); Mpt: 156-158 °C.

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\([\text{Me}_3\text{Si(tmeda)SiMe}_3][\text{OTf}]_2\): Colourless solid. Yield (crystalline): 0.41 g, 73%; \(^1\text{H}\) NMR (300 MHz, CDCl\(_3\)) \(\delta \)H 2.46 (4H, s, CH\(_2\)), 2.29 (12H, s, -NMe\(_2\)), 0.50 (18H, s, -SiMe\(_3\)); \(^19\text{F}\) NMR (283 MHz, CDCl\(_3\)) \(\delta \)F -77.23 (s, CF\(_3\)); \(^{13}\text{C}\{^1\text{H}\} \text{NMR} (76 \text{ MHz, CDCl}_3) \delta \)C 118.4 (q, \(J_{CF} = 318 \text{ Hz, CF}_3\) 57.2 (s, CH\(_2\)), 45.7 (s, -N(CH\(_3\))\(_2\)), 0.1 (s, -Si(CH\(_3\))\(_3\)); \(^{29}\text{Si} \text{NMR} (72 \text{ MHz, CDCl}_3) \delta \)Si 43.7 (s, -SiMe\(_3\)); FT-IR (ATR, Ranked Intensities): 1277(6), 1221(1), 1149(2), 1025(3), 995(9), 975(8), 754(10), 633(4), 573(7), 515(5); Mpt: 104-106 °C; Elemental Analysis: Calculated C 29.99, H 6.11, N 5.00, Found C 29.32, H 5.89, N 5.07.

\([\text{Me}_3\text{Si(dmpe)SiMe}_3][\text{OTf}]_2\): Colourless solid. Yield (crystalline): 0.51 g, 86%; \(^1\text{H}\) NMR (300 MHz, CDCl\(_3\)) \(\delta \)H 1.50-1.39 (4H, m, -CH\(_2\)P-), 1.04 (12H, br. s, -PMe\(_2\)), 0.50 (18H, s, -SiMe\(_3\)); \(^{19}\text{F}\) NMR (283 MHz, CDCl\(_3\)) \(\delta \)F 77.14 (s, CF\(_3\)); \(^{31}\text{P}\{^1\text{H}\} \text{NMR} (146 \text{ MHz, CDCl}_3) \delta \)P 46.7 (s, dmpe); \(^{13}\text{C}\{^1\text{H}\} \text{NMR} (76 \text{ MHz, CDCl}_3) \delta \)C 118.4 (q, \(J_{CP} = 318 \text{ Hz, CF}_3\)), 27.1 (s, -PMe\(_2\)), 13.5 (s, -PCH\(_2\)CH\(_2\)P-), 0.2 (s, -SiMe\(_3\)); \(^{29}\text{Si} \text{NMR} (72 \text{ MHz, CDCl}_3) \delta \)Si 42.5 (s, -SiMe\(_3\)); FT-IR (ATR, Ranked Intensities): 1252(1), 1223(6), 1145(4), 1029(3), 835(7), 751(8), 634(2), 620(5), 571(10), 516(9); Mpt: 103-105 °C.

\([\text{Me}_3\text{Si(4,4′-bipy)}][\text{OTf}]\): Off-white solid. Yield (crystalline): 0.24 g, 92%; \(^1\text{H}\) NMR (300 MHz, CD\(_2\)CN): \(\delta \)H 8.82 (4H, br. s, Ar-H), 8.05 (4H, br. s, Ar-H), 0.73 (18H, s, -SiMe\(_3\)); \(^{19}\text{F}\) NMR (283 MHz, CD\(_2\)CN): \(\delta \)F -79.14 (s, CF\(_3\)); \(^{13}\text{C}\{^1\text{H}\} \text{NMR} (76 \text{ MHz, CD}_2\text{CN}) \delta \)C 150.1 (s, Ar), 149.2 (s, Ar), 124.8 (s, Ar), -0.8 (s, SiMe\(_3\)); \(^{29}\text{Si} \text{NMR} (72 \text{ MHz, CD}_2\text{CN}) \delta \)Si 42.6 (s, -SiMe\(_3\)); FT-IR (ATR, Ranked Intensities): 1257(2), 1221(6), 1148(6), 1086(10), 1027(3), 851(5), 809(4), 779(9), 634(1), 515(7); Mpt: 108-100 °C.

**Attempted syntheses of [Me\(_3\)Si(tmeda)]\text{SiMe}_3][\text{OTf}] and [Me\(_3\)Si(dmpe)]\text{SiMe}_3]][\text{OTf}]:** To a solution of Me\(_3\)SiOTf in CD\(_2\)Cl\(_2\) at ambient temperature was added neat dmpe or tmeda, and the resulting clear colourless mixtures stirred at ambient temperature for 2 h before removing all volatiles under high vacuum. The resulting colourless solids were then analyzed by \(^1\text{H}\) NMR spectroscopy, with chemical shifts and relative integrals consistent with the desired 1:1 complexes, although notably the former were unshifted from those of the 2:1 complexes. Upon recrystallization from CH\(_2\)Cl\(_2\)/Et\(_2\)O at -30 °C, in both cases crystalline material spectroscopically consistent with the 2:1 complexes [Me\(_3\)Si(tmeda)SiMe\(_3\)]\text{SiMe}_3][\text{OTf}] and [Me\(_3\)Si(dmpe)SiMe\(_3\)][\text{OTf}], respectively, were exclusively obtained.

**Mixtures of Me\(_3\)SiOTf and PnPh\(_3\) (Pn = P or Sb) or ChPPh\(_3\) (Ch = S or Se):** To solutions of Me\(_3\)SiOTf (50 mg, 0.22 mmol) in CH\(_2\)Cl\(_2\) (3 mL) at ambient temperature was added solid PnPh\(_3\) or ChPPh\(_3\) (0.22 mmol), and the resulting clear, colourless mixture stirred for 2 h. All
volatiles were then removed under high vacuum, furnishing colourless solids which were analyzed by $^1$H, and where relevant $^{31}$P NMR spectroscopy. In all cases NMR spectra indicated the presence of only unreacted PnPh$_3$ or ChPPh$_3$, respectively, with no evidence for complex formation, and unreacted Me$_3$SiOTf presumably removed under high vacuum.

**Mixtures of Me$_3$SiOTf and PCy$_3$, PrBu$_3$ or dppe:** To solutions of Me$_3$SiOTf (50 mg, 0.22 mmol) in CH$_2$Cl$_2$ (3 mL) at ambient temperature was added solid PR$_3$ or dppe (0.22 mmol), and the resulting clear, colourless mixtures stirred for 2 h. All volatiles were then removed under high vacuum, furnishing colourless solids which were analyzed by $^1$H and $^{31}$P NMR spectroscopies, which indicated in all cases the presence of exclusively unreacted phosphine.

**Mixtures of Me$_3$SiOTf and NEt$_3$, 2-dmap, Me$_2$CO or SMe$_2$:** To solutions of Me$_3$SiOTf (50 mg, 0.22 mmol) in CH$_2$Cl$_2$ (3 mL) at ambient temperature was added neat NEt$_3$, 2-dmap, Me$_2$CO or SMe$_2$ (0.22 mmol), and the resulting clear, colourless mixtures stirred for 2 h. All volatiles were then removed under high vacuum to yield a very small quantity of colourless oil in all cases. $^1$H NMR spectroscopic analysis indicated the presence of only residual, unconsumed reagents, and were inconsistent with the formation of the desired complexes.

**References**

(24) These values correspond to the relevant proteo-solvents; CRC Handbook of Chemistry and Physics; 85 edition.; CRC Press, 2005.
Graphical Abstract

\[
\begin{align*}
[\text{Me}_3\text{Si(L))][\text{OTf}] & \quad [\text{Me}_3\text{Si(L-L)SiMe}_3][\text{OTf}]_2 \\
\text{Me}_3\text{SiOTf} & \\
\text{L} = \begin{array}{c} N, O \text{ or } P \\
\text{mono-donor ligand}
\end{array} & \text{L-L} = \begin{array}{c} N \text{ or } P \\
\text{bis-donor ligand}
\end{array}
\end{align*}
\]