BF₃·OEt₂ and TMSOTf: A Synergistic Combination of Lewis Acids

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Supplementary Information

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(a) Analysis of mixtures of TMSOTf and BF₃·OEt₂ in CDCl₃ by NMR spectroscopy

To a dry quartz NMR tube with a Young® valve was added dry CDCl₃ (0.8 ml) under a stream of nitrogen. To this was added BF₃·OEt₂ (18 μl, 0.10 mmol) and TMSOTf (15 μl, 0.10 mmol). The NMR tube was sealed and NMR data was acquired on a multinuclear Eclipse ECP-300 instrument. Five species were observed, namely BF₃·OEt₂, TMSOTf, BF₂OTf·OEt₂, TMSF and Me₂SiF₂ in an apparent ratio of 1.18: 0.95: 0.84: 1.00: 0.02 respectively. Data for BF₃·OEt₂: ¹H NMR (300 MHz, CDCl₃) δ = 1.44 (6H, t, J = 7.1 Hz, OCH₂CH₃), 4.22 (4H, q, J = 7.1 Hz, OCH₂CH₃); ¹³C NMR (75 MHz, CDCl₃) δ = 13.2, 69.8; ¹¹B NMR (96 MHz, CDCl₃) δ = -0.62 (bs); ¹⁹F NMR (282 MHz, CDCl₃) δ = -152.8 (bs). Data for TMSOTf: ¹H NMR (300 MHz, CDCl₃) δ = 0.50 (9H, s, CH₃); ¹⁹F NMR (282 MHz, CDCl₃) δ = -76.9 (bs, OTf). Data for BF₂OTf·OEt₂: ¹H NMR (300 MHz, CDCl₃) δ = 1.52 (6H, t, J = 7.1 Hz, OCH₂CH₃), 4.44 (4H, q, J = 7.1 Hz, OCH₂CH₃); ¹³C NMR (75 MHz, CDCl₃) δ = 13.2, 72.5 (t, 3J_C-F = 2.5 Hz); ¹¹B NMR (96 MHz, CDCl₃) δ = -1.30 (bs); ¹⁹F NMR (282 MHz, CDCl₃) δ = [-146.4 (1.6F, bs, ¹¹BF₂) and -146.3 (0.4F, bs, ¹⁰BF₂)], -76.7 (3F, t, 5J_F-F = 2.8 Hz, OTf). Data for TMSF: ¹H NMR (300 MHz, CDCl₃) δ = 0.23 (9H, d, 3J_H-F = 7.5 Hz, CH₃); ¹⁹F NMR (282 MHz, CDCl₃) δ = -157.7
(1F, decet, $^3J_{F-H} = 7.5$ Hz, SiF). Data for Me$_2$SiF$_2$: $^1$H NMR (300 MHz, CDCl$_3$) $\delta = 0.35$ (6H, t, $^3J_{H-F} = 6.2$ Hz, CH$_3$); $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta = -131.3$ (2F, septet, $^3J_{F-H} = 6.2$ Hz, SiF).

$^1$H NMR spectrum of 1:1 mixture of TMSOTf:BF$_3$·OEt$_2$ in CDCl$_3$

$^{11}$B NMR spectrum of 1:1 mixture of TMSOTf:BF$_3$·OEt$_2$ in CDCl$_3$
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$^{19}$F NMR spectrum of 1:1 mixture of TMSOTf:BF$_3$·OEt$_2$ in CDCl$_3$

$^{13}$C NMR spectrum of 1:1 mixture of TMSOTf:BF$_3$·OEt$_2$ in CDCl$_3$
To a dry NMR tube was added dry CDCl$_3$ (0.8 ml) followed by Lewis acid (0.10 mmol) and triethylphosphine oxide (varying amounts). The sample was sealed and analysed by $^1$H NMR, $^{31}$P NMR and/or $^{19}$F spectroscopy. The following data was acquired

(i) OPEt$_3$ without Lewis acid: $^{31}$P NMR (121 MHz, hexane) $\delta = 47.2$; $^{31}$P NMR (121 MHz, CDCl$_3$) $\delta = 56.0$; $^1$H NMR (300 MHz, CDCl$_3$) $\delta = 1.17$ (9H, dt, $^3J_{H-P} = 15.8$ Hz and $^1J_{H-H} = 7.6$ Hz, CH$_3$), 1.71 (6H, dq, $^2J_{H-P} = 11.8$ Hz and $^1J_{H-H} = 7.6$ Hz, CH$_2$).

(ii) OPEt$_3$ (0.25 eq.) with BF$_3$-OEt$_2$: $^{31}$P NMR (121 MHz, CDCl$_3$) $\delta = 79.0$ (q, $^3J_{P-F} = 5.6$ Hz, BF$_3$-OPEt$_3$); $^1$H NMR (300 MHz, CDCl$_3$) free diethyl ether and BF$_3$-OPEt$_3$ adduct with the following chemical shifts $\delta = 1.28$ (9H, dt, $^3J_{H-P} = 18.0$ Hz and $^1J_{H-H} = 7.7$ Hz, CH$_3$), 2.09 (6H, dq, $^2J_{H-P} = 12.3$ Hz and $^1J_{H-H} = 7.6$ Hz, CH$_2$).

(iii) OPEt$_3$ (0.25 eq.) with TMSOTf (1.0 eq.): $^{31}$P NMR (121 MHz, CDCl$_3$) $\delta = 88.1$ (s, tentatively assigned as HOTf.OPEt$_3$), 92.8 (s, TMSOTf.OPEt$_3$); $^1$H NMR (300 MHz, CDCl$_3$) $\delta = 0.41$ (9H, s, TMSOTf.OPEt$_3$), 0.50 (33H, s, TMSOTf), 1.30 (10.8H, m, methyl of HOTf.OPEt$_3$ and TMSOTf.OPEt$_3$), 2.21 (1.2H, m, tentatively assigned to methylene of HOTf.OPEt$_3$), 2.40 (6H, m, methylene of TMSOTf.OPEt$_3$).

(iv) OPEt$_3$ (1.65 eq.) with TMSOTf (1.0 eq.) and BF$_3$-OEt$_2$ (2.0 eq.): $^{31}$P NMR (121 MHz, CDCl$_3$) $\delta = 79.0$ (q, $^3J_{P-F} = 5.6$ Hz, BF$_3$-OPEt$_3$), 84.6 (br. s, BF$_2$OTf.OPEt$_3$), 84.8 (t, $^3J_{P-F} = 2.2$ Hz, BF$_2$(OPEt$_3$)$_2$); $^1$H NMR (300 MHz, CDCl$_3$) $\delta = 0.22$ (9H, d, $^3J_{H-F} = 7.5$ Hz, TMSF), 1.19-1.35 (22.9H, m, methyl moieties of Et$_2$O, BF$_3$-OPEt$_3$, BF$_2$OTf.OPEt$_3$ and BF$_2$(OPEt$_3$)$_2$), 2.10-2.21 (9.9H, m, methylene moieties of BF$_3$-OPEt$_3$, BF$_2$OTf.OPEt$_3$ and BF$_2$(OPEt$_3$)$_2$), 3.70 (12H, br. s, OCH$_2$).
(v) OPEt$_3$ (1.5 eq.) with TMSOTf (1.0 eq.) and BF$_3$·OEt$_2$ (1.1 eq.): $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta = -157.6$ (decent, $^2J_{F-H} = 7.5$ Hz, TMSF), $[\delta = -145.9$ (br. s, $^{11}$BF$_3$·OPEt$_3$) and -145.8 (br. s, $^{10}$BF$_3$·OPEt$_3$)], $[\delta = -139.5$ (br. s, $^{11}$BF$_2$OTf·OPEt$_3$) and -139.4 (br. s, $^{10}$BF$_2$OTf·OPEt$_3$)], -137.9 (1:1:1:1 q, $^1J_{F-B} = 13.0$ Hz, $^{11}$BF$_2$(OPEt$_3$)$_2$), -78.5-77.0 (m, OTf).
(vi) OPEt$_3$ (4.7 eq.) with TMSOTf (1.0 eq.) and BF$_2$·OEt$_2$ (2.0 eq.): $^{31}$P NMR (121 MHz, CDCl$_3$) $\delta = 79.0$ (q, $^3J_{P-F} = 5.6$ Hz, BF$_3$·OPEt$_3$), 84.8 (t, $^3J_{P-F} = 2.2$ Hz, BF$_2$·(OPEt$_3$)$_2$); $^1$H NMR (300 MHz, CDCl$_3$) $\delta = 0.22$ (9H, d, $^3J_{H-F} = 7.5$ Hz, TMSF), 1.07-1.30 (76H, m, methyl moieties of Et$_2$O, BF$_3$·OPEt$_3$ and BF$_2$·(OPEt$_3$)$_2$), 1.72 (11H, methylene of free OPEt$_3$), 2.10-2.21 (26H, m, methylene moieties of BF$_3$·OPEt$_3$ and BF$_2$·(OPEt$_3$)$_2$), 3.70 (9H, q, OCH$_2$).
31P spectrum of (vi)

J_P-F = 2.2 Hz

J_P-F = 5.6 Hz

"free ligand" see discussion below

1H spectrum of (vi)

Methylene signals of phosphine oxide
In the $^{31}\text{P}$ spectrum of (vi) the signal for “free ligand” is extremely broad. Since the resonances of the complexed species are still relatively sharp, there remains at least two possibilities for such a phenomenon: (i) trace amounts of protic acid are present and the broad signal represents an average of two species (free and protonated ligand). (ii) in the existing BF$_3$ and BF$_2$ complexes there exists a rapidly exchanging second coordination sphere of ligand (see figure below).

\[
\begin{align*}
\text{Possible second coordination sphere of ligand}
\end{align*}
\]

In the 1970s Gutmann introduced a quantitative parameter for describing the electrophilic character of solvents.$^{1}$ They found that the $^{31}\text{P}$ chemical shift of triethylphosphine oxide was very sensitive to solvent; donation of electron density from oxygen to the electrophilic solvent, decreased the electron density on phosphorous causing a downfield shift. The $\delta$ values were normalised relative to that of the Et$_3$PO-SbCl$_5$ adduct dissolved in 1,2-dichloroethane, which was given the arbitrary number of 100; the chemical shift for Et$_3$PO in hexane was given the value 0. These values are termed “acceptor numbers” or $AN$s. This method has been extended by Beckett and co-workers to include Lewis acids.$^{2}$ The phosphine oxide complexes described herein, in addition to providing further evidence for BF$_2$OTf·OEt$_2$ also provides us with a relative order of Lewis acidity. The downfield shift of the $^{31}\text{P}$ resonance upon complexation suggests the following order of decreasing Lewis acidity: TMS$^+$ (92.8 ppm) > H$^+$ (88.1 ppm) > BF$_2$OTf (84.6 ppm)> BF$_3$ (79.0 ppm). As a caveat, although Beckett and co-workers have shown that there is a linear correlation between the Gutmann and Childs methods, others have shown that this trend doesn’t strictly apply to all Lewis acids.$^{3, 4}$ Britozsek and co-workers suggest that the non-linear behavior can be rationalised in terms of the hard soft acid base classification; for example taking a hard Lewis acid such as BF$_3$, its interaction with a carbonyl group (having a $\pi$ orbital covalent which is largely
covalent in character) will be weaker than its interaction with phosphine oxide, whose double bond has more ionic character. As we have shown in this communication, the concentration of the Lewis acid-Lewis base complex can be just as important as the reactivity of the Lewis acid-Lewis base complex.

(C) Quantification of Lewis acidity: Method of Childs

To a dry NMR tube was added dry CDCl₃ (0.8 ml) followed by Lewis acid (0.10 mmol) and crotonaldehyde (0.03 mmol). The sample was sealed and analysed by ¹H NMR spectroscopy. In most cases data was acquired at low temperatures (as low as -55 °C) in order to reduce the rate of ligand exchange. The following data was acquired:

(a) trans-crotonaldehyde without Lewis acid: ¹H NMR (CDCl₃, r.t.) δ = 2.03 (3H, dd, J = 6.8, 1.7 Hz, H4), 6.15 (1H, ddq, J = 15.5, 8.0, 1.7 Hz, H2), 6.88 (1H, dq, J = 15.5, 6.8 Hz, H3), 9.50 (1H, d, J = 8.0 Hz, H1).

(b) trans-crotonaldehyde with BF₃·OEt₂: ¹H NMR (CDCl₃, -55 °C.) the spectrum showed free crotonaldehyde which was ~0.05 ppm downfield of those chemical shifts given in (a), free diethyl ether, BF₃·OEt₂ and a new species which is assigned as the BF₃ crotonaldehyde complex with the following chemical shifts δ = 2.45 (3H, br. d, J = 7.0 Hz, H4), 6.77 (1H, br. dd, J = 15.2, 9.5 Hz, H2), 8.05 (1H, br. dq, J = 15.2, 7.0 Hz, H3), 9.15 (1H, br. d, J = 9.3 Hz, H1).

(c) trans-crotonaldehyde with TMSOTf: ¹H NMR (CD₂Cl₂, r.t.) the spectrum showed one set of signals for the TMS moiety (δ = 0.50, s) and one for crotonaldehyde with the following chemical shifts δ = 2.13 (3H, dd, J = 6.9, 1.5 Hz, H4), 6.31 (1H, ddq, J = 15.6,
8.3, 1.5 Hz, H2), 7.17 (1H, dq, J = 15.6, 6.9 Hz, H3), 9.42 (1H, br. d, J = 8.3 Hz, H1). The NMR sample was then cooled from room temperature to -90 °C in increments of 20 °C (See figure below). As the temperature was lowered, the H3 resonance broadened slightly and was observed to shift further downfield; at -90 °C [Δδ(H3)] was measured to be 0.70 ppm. Although chemical shift of free crotonaldehyde is inherently dependent upon temperature [Δδ(H3) is ~0.1 ppm between room temperature and -55 °C], the large downfield shift observed here indicates an increase in the concentration of complexed species 1 and/or 2 due to the decreasing TΔS term. The large temperature effect on Keq suggests that ΔS is of significant magnitude which suggests that the entropically more demanding hypervalent species 1 rather than 2 predominates. Unfortunately, even at -90 °C the H3 resonance remained averaged and thus we are unable to compare the reactivity of complex 1 or 2 to that of the BF3 or BF2OTf complex.

VT-NMR of a solution of TMSOTf and crotonaldehyde
(d) *trans*-crotonaldehyde with TMSOTf and BF$_3$OEt$_2$: $^1$H NMR (CDCl$_3$, -55 °C) the spectrum showed a set of crotonaldehyde signals which are assigned as the BF$_3$-crotonaldehyde complex as given in (b); signals for TMSF, BF$_3$OEt$_2$, BF$_2$OTfOEt$_2$, the TMS moiety (TMSOTf and other species) and broad signals for free etherate and crotonaldehyde were also apparent; a further set of relatively sharp crotonaldehyde signals are assigned as the BF$_2$OTf-crotonaldehyde complex with the following chemical shifts $\delta = 2.13$ (3H, br. d, $J = 7.0$ Hz, H4), 6.89 (1H, br. dd, $J = 14.9$, 9.3 Hz, H2), 8.34 (1H, br. dq, $J = 14.9$, 7.0 Hz, H3), 9.14 (1H, br. d, $J = 9.3$ Hz, H1).

(D) Analysis of mixtures of TMSOTf and BF$_3$OEt$_2$ in CH$_3$CN by NMR spectroscopy

To a dry quartz NMR tube with a Young® valve was added dry CH$_3$CN (0.8 ml) under a stream of nitrogen. To this was added BF$_3$OEt$_2$ (18 μl, 0.10 mmol) and TMSOTf (15 μl, 0.10 mmol). The NMR tube was sealed and NMR data was acquired on a multinuclear ECP-300 instrument. For $^1$H the spectrum, the solvent signal was pre-saturated; the signals are broad due to the lack of a deuterium lock. $^1$H NMR (300 MHz, CDCl$_3$) $\delta = 0.23$ (21.0H, br. d, $^3J_{H-F} = 7.4$ Hz, TMSF), 0.50 (14.1H, br. s, averaged signal of TMSOTf, TMS.CH$_3$CN and TMS.OEt$_2$), 1.31 (16.2H, br. t, $J = 7.1$ Hz, methyl of Et$_2$O, BF$_3$OEt$_2$ and perhaps TMS.OEt$_2$). 1.45 (6H, br. q, $J = 7.1$ Hz, methyl of BF$_2$OTfOEt$_2$), 3.93 (10.8H, br. q, $J = 7.1$ Hz, methylene of Et$_2$O, BF$_3$OEt$_2$ and perhaps TMS.OEt$_2$), 4.48 (4H, br. q, $J = 7.1$ Hz, methylene of BF$_2$OTfOEt$_2$); $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta = -156.7$ (~3F, decet, $^3J_{F-H} = 7.4$ Hz, TMSF), -149.3 (~6.0F, br. s, BF$_3$OEt$_2$ and BF$_3$-CH$_3$CN), [\$\delta = -146.1$ (~2.4F, bs, $^{11}$BF$_2$OTfOEt$_2$) and -146.0 (~0.6F, bs, $^{10}$BF$_2$OTfOEt$_2$)], [-140.2 (~0.8F, bs, $^{11}$BF$_n$L$_{n-4}$) and -140.1 (~0.2, bs, $^{10}$BF$_n$L$_{n-4}$)], [-139.7 (~0.8F, bs, $^{11}$BF$_n$L$_{n-4}$) and -139.6 (~0.2F, bs, $^{10}$BF$_n$L$_{n-4}$)], -77.8—77.6 (~9.0F, m, OTf), -77.5 (~4.5F, t, $^5J_{F-F} = 2.9$ Hz, BF$_2$OTfOEt$_2$), -77.4 (~1.0F, br. s, OTf); $^{11}$B NMR
(96 MHz, CDCl$_3$) $\delta$ = -3.59 (1B, br. s), -1.56 (1B, bs), [-0.86 (br. s) and -0.70 (br. s), ~10B].

$^1$H NMR spectrum of 1:1 mixture of TMSOTf:BF$_3$OEt$_2$ in CH$_3$CN
$^{19}$F NMR spectrum of 1:1 mixture of TMSOTf:BF$_3$OEt$_2$ in CH$_3$CN

$^{11}$B NMR spectrum of 1:1 mixture of TMSOTf:BF$_3$OEt$_2$ in CH$_3$CN
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