Inhibition of [FeFe]-Hydrogenase by Formaldehyde: Proposed Mechanism and Reactivity of FeFe Alkyl Complexes

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Three isomers were detected and assigned as follows:

$\delta$ 22.59 (d, $J_{PP} = 7.3$ Hz), 9.45 (d, $J_{PP} = 7.4$ Hz), *trans*-dibasal; 34.46 (d, $J_{PP} = 7.7$ Hz), 24.10 (d, $J_{PP} = 7.6$ Hz), *cis*-dibasal; 18.41 (s), 9.21 (s), apical-basal.
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Exchange Process in [2]BAr\textsubscript{4} Determined by Spin Saturation Transfer

1D Spin-Saturation Transfer (SST) experiment (both \textsuperscript{31}P and \textsuperscript{1}H NMR) was used to monitor the slow exchange process in [2]BAr\textsubscript{4} in CD\textsubscript{2}Cl\textsubscript{2} at 298 K. One signal is selectively irradiated, and the signal intensity of the other peak connected with the irradiated signal via chemical exchange is monitored.

For exchange process of

\[
\begin{align*}
A & \xleftrightarrow{k_A} B \\
& \xrightarrow{k_B}
\end{align*}
\]

Selectively irradiation of peak A, the intensity of peak B changes following the equation below, and the exchange rate can be extracted:

\[
\frac{l(t)}{l(0)} = \frac{\tau'}{\tau} \exp\left(-\frac{t}{\tau'}\right) + \frac{\tau'}{T_1}
\]

\[
\tau' = \frac{1}{\frac{1}{T_1} + \frac{1}{\tau}}
\]

Where \(t\) is the irradiation time applied to peak A, \(T_1\) is the longitudinal (spin-lattice) relaxation time of peak B (measured by inversion-recovery method here), \(\tau\) is the life time of nuclei stays at site B, and the exchange rate \(k_B = 1/\tau\).
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Fitted with three parameter exponential equation: $l_t = A + B*\exp(-t/T_1)$.

Results:
$\delta$ 5.52, $T_1 = 1.29$ s; $\delta$ 4.79, $T_1 = 1.31$ s;
$\delta$ 4.17, $T_1 = 1.17$ s; $\delta$ 3.84, $T_1 = 1.17$ s.
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Figure S23. IR spectrum for reaction of [HFe₂((SCH₂)₂NH)(CO)₄(PMe₃)₂]BAr₄ ([H1]BAr₄) with 3 equiv paraformaldehyde in CH₂Cl₂ solution.

The result indicates the reaction of hydride tautomer [H1]⁺ with paraformaldehyde does not give [2]⁺, which highlight the role of the ammonium center in the conversion of 1 to [2]⁺.
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Assignments:
$\delta$ 80.11 (enriched with $^{13}$C) and 52.56 ($[\text{Fe}_2([\text{SCH}_2]_2\text{N}^{13}\text{CH}_2\text{OH})(\text{CO})_4($PMe$_3)_2]$);
$\delta$ 45.91 ($[\text{Fe}_2([\text{SCH}_2]_2\text{NH})(\text{CO})_4($PMe$_3)_2]$).

In order to examine whether there is exchange during the formation of N-CH$_2$OH, the reaction of $[\text{Fe}_2([\text{SCH}_2]_2\text{NH})(\text{CO})_4($PMe$_3)_2]$ with 0.25 equiv $^{13}$CH$_2$O in CD$_2$Cl$_2$ was checked at room temperature. According to the $^{13}$C NMR determined after 72 h, two new peaks appeared at $\delta$ 80.11 (enriched with $^{13}$C) and $\delta$ 52.56, which could be assigned to the 1 : 1 adduct of $[\text{Fe}_2([\text{SCH}_2]_2\text{N}^{13}\text{CH}_2\text{OH})(\text{CO})_4($PMe$_3)_2]$. However, the peak at $\delta$ 45.91 corresponding to the SCH$_2$ of $\text{Fe}_2([\text{SCH}_2]_2\text{NH})(\text{CO})_4($PMe$_3)_2$ has not been enriched, indicating no exchange during this process.
Figure S26. $^{13}$C NMR spectrum for the reaction of [Fe$_2$[(SCH$_2$)$_2$NH](CO)$_4$(PMe$_3$)$_2$] with 1 equiv CH$_2$O in CD$_2$Cl$_2$ at room temperature.

Assignments:
\[ \delta \text{ 80.15 and 52.60 ([Fe$_2$[(SCH$_2$)$_2$NCH$_2$OH](CO)$_4$(PMe$_3$)$_2$])}; \]
\[ \delta \text{ 90.23, 89.22, 87.34, 86.94, 86.50, 82.67 for -(CH$_2$)$_n$-OH and 52.30, 51.68 for SCH$_2$ ([Fe$_2$[(SCH$_2$)$_2$N(CH$_2$)$_n$OH](CO)$_4$(PMe$_3$)$_2$])}; \]
\[ \delta \text{ 45.91 ([Fe$_2$[(SCH$_2$)$_2$NH](CO)$_4$(PMe$_3$)$_2$])}. \]
Figure S27. IR spectra for reaction of $\text{Fe}_2(\text{pdt})(\text{CO})_4(\text{PMe}_3)_2 + \text{CH}_2\text{O} + \text{HBF}_4$ in $\text{CH}_2\text{Cl}_2$ solution.

According to the IR spectra, no reaction is evident when $\text{Fe}_2(\text{pdt})(\text{CO})_4(\text{PMe}_3)_2$ was treated with $\text{CH}_2\text{O}$. In the presence of 1 equiv $\text{HBF}_4$, bridging hydride $[\text{HFe}_2(\text{pdt})(\text{CO})_4(\text{PMe}_3)_2]\text{BF}_4$ was formed as the protonation product.
According to the IR spectra, no reaction is evident when 1 was treated with PhCHO. In the presence of HBF₄, ([Fe₂(SCH₂)₂NH₂]₂(CO)₂(PMe₃)₂)BF₄ ([1H]BF₄) was formed as the protonation product.
Figure S29. $^{13}$C NMR spectrum (CH$_2$ region) for the reaction of [Fe$_2$([SCH$_2$]$_2$NH](CO)$_4$(PMe$_3$)$_2$] (47 mM) + $^{13}$CH$_2$O + HBArF$_4$ (1 : 1 : 1) over time in CD$_2$Cl$_2$ at 296 K (top); Plot of peak intensity vs time, showing the decline in intensity of the signal at δ 76.66, 75.77, 75.49 (brown), and the increase in intensity of the signal at δ 59.03, 58.46, 58.16, 57.09 (blue) (bottom). The exchange process reaches equilibrium after ~90 minutes.
For the equilibrium

\[
A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B
\]

\(k_1\) is the rate coefficient for the reaction that consumes A; \(k_{-1}\) is the rate coefficient for the backwards reaction, then

\[
\frac{k_1}{k_{-1}} = \frac{[B]_e}{[A]_e}
\]

\([A]_e\) and \([B]_e\) are the concentrations of A and B at equilibrium, respectively. \([A]_0\) is the initial concentration of reactant A, \([A]_t\) is the concentration of A at time \(t\), then

\[
\ln \left( \frac{I_0 - I_e}{I_t - I_e} \right) = \ln \left( \frac{[A]_0 - [A]_e}{[A]_t - [A]_e} \right) = (k_1 + k_{-1})t
\]

**Figure S30.** Plot of \(\ln(\frac{(I_0 - I_e)(I_t - I_e)}{(l_0 - l_e)})\) vs reaction time (\([2]^+_0 = 47 \text{ mM}\)). *Fitting equation:* \(\ln(\frac{(I_0 - I_e)(I_t - I_e)}{(l_0 - l_e)}) = (k_1 + k_{-1})t\). *Results:* \(k_1 + k_{-1} = 8.31 \times 10^{-4} \pm 2.01 \times 10^{-5} \text{ s}^{-1}\). The linear plot indicates the kinetics of exchange are first order in the concentration of \([2]^+\), which points to an intramolecular process.
**Figure S31.** IR spectrum of crude $\text{Et}_4\text{N}[\text{Fe}_2(\text{SCH}_2)_2\text{NCH}_2\text{CN})(\text{CN})(\text{CO})_5]$ ($\text{Et}_4\text{N}[4]$) in CH$_3$CN solution.
Figure S32. ESI-MS spectrum of $\text{Et}_4\text{N}[\text{Fe}_2[(\text{SCH}_2)_2\text{NCH}_2\text{CN}](\text{CN})(\text{CO})_5]$ (Et$_4$N[4]) in CH$_3$CN solution.
Figure S33. ESI-MS spectrum of $^{13}$C labeled \( \text{Et}_4\text{N}[\text{Fe}_2((\text{SCH}_2)_2\text{NCH}_2\text{CN})(\text{CN})(\text{CO})_5] \) (\( \text{Et}_4\text{N}[4] \)) in \( \text{CH}_3\text{CN} \) solution.
Figure S34. $^1$H NMR spectrum of Et$_4$N[Fe$_2$((SCH$_2$)$_2$NCH$_2$CN)(CN)(CO)$_4$PPh$_3$] (Et$_4$N[5]) in CD$_2$Cl$_2$ at room temperature.
Figure S35. $^{31}$P NMR spectrum of $\text{Et}_4\text{N}[\text{Fe}_2[(\text{SCH}_2)_2\text{NCH}_2\text{CN}](\text{CN})(\text{CO})_4\text{PPh}_3]$ ($\text{Et}_4\text{N}[5]$) in CD$_2$Cl$_2$ at room temperature.
Figure S36. $^{13}$C NMR spectrum of $\text{Et}_4\text{N}[\text{Fe}_2((\text{SCH}_2)_2\text{NCH}_2\text{CN})(\text{CN})(\text{CO})_4(\text{PPh}_3)]$ ($\text{Et}_4\text{N}[5]$) in CD$_2$Cl$_2$ at room temperature.

Assignments:
$\delta$ 66.04, 15.48 (diethyl ether)
Figure S37. IR spectrum of Et₄N[Fe₂[(SCH₂)₂NCH₂CN](CN)(CO)₄PPh₃] (Et₄N[5]) in CH₂Cl₂ solution.
Figure S38. ESI-MS spectrum of Et$_4$N[Fe$_2$((SCH$_2$)$_2$NCH$_2$CN)(CN)(CO)$_4$PPh$_3$] (Et$_4$N[5]) in CH$_2$Cl$_2$ solution.
Figure S39. IR spectra of $(\text{Et}_4\text{N})_2\text{Fe}_2(\text{SCH}_2\text{NH})(\text{CN})_2(\text{CO})_4^{2-}$ ([3]$^{2-}$) + $[\text{HPPh}_3]\text{BF}_4$ in CH$_3$CN solution.
Figure S40. IR spectra of (Et$_4$N)[HFe$_2$((SCH$_2$)$_2$NH)(CN)$_2$(CO)$_4$] ((Et$_4$N)[H3]) + 2 equiv CH$_2$O in CH$_3$CN solution.
Figure S41. IR spectra for the reaction of (Et₄N)₂[Fe₂(pdt)(CN)₂(CO)₄] with CH₂O and [HPh₃]BF₄ in CH₃CN solution.
Figure S42. $^1$H NMR spectrum of $[\text{Fe}_2(\text{SCH}_2\text{NCH}_2\text{PPh}_3)(\text{CO})_4(\text{PMe}_3)_2]\text{BF}_4$ ([6]BF$_4$) in CD$_2$Cl$_2$ at room temperature.
Figure S43. $^{31}$P NMR spectrum of [Fe$_2$((SCH$_2$)$_2$NCH$_2$PPh$_3$)(CO)$_4$(PMe$_3$)$_2$]BF$_4$ ([6]BF$_4$) in CD$_2$Cl$_2$ at room temperature.
Figure S44. IR spectra of [Fe₂((SCH₂)₂NCH₂PPh₃)(CO)₄(PMe₃)₂]BF₄ ([6]BF₄) and [6]BArF₄ in CH₂Cl₂ solution.
Figure S45. ESI-MS spectrum of $[\text{Fe}_2((\text{SCH}_2)_{2}\text{NCH}_2\text{PPh}_3)(\text{CO})_4(\text{PMe}_3)_2]\text{BF}_4)$ ([6]BF$_4$) in CH$_2$Cl$_2$ solution.
Figure S46. $^1$H NMR spectrum of $^{13}$C labeled $[\text{Fe}_2((\text{SCH}_2)_2\text{NCH}_2\text{PPh}_3)(\text{CO})_4(\text{PMe}_3)_2]\text{BAr}^F_4$ ([6]BAr$^F_4$) in CD$_2$Cl$_2$ at room temperature.
Figure S47. $^{31}$P NMR spectrum of $^{13}$C labeled $[\text{Fe}_2((\text{SCH}_2)_2\text{NCH}_2\text{PPh}_3)(\text{CO})_4(\text{PMe}_3)_2]\text{BAr}^\text{F}_4$ ($^6\text{BAr}^\text{F}_4$) in CD$_2$Cl$_2$ at room temperature.
Figure S48. $^1$H NMR spectrum of Fe$_2$[(SCH$_2$)$_2$NMe](CO)$_4$(PMe$_3$)$_2$ in CD$_2$Cl$_2$ at room temperature.
**Figure S49.** $^{31}$P NMR spectrum of Fe$_2$[(SCH$_2$)$_2$NMe](CO)$_4$(PMe$_3$)$_2$ in CD$_2$Cl$_2$ at room temperature.
Figure S50. IR spectrum of Fe$_2$[(SCH$_2$)$_2$NMe](CO)$_4$(PMe$_3$)$_2$ in CH$_2$Cl$_2$ solution.
Figure S51. ESI-MS spectrum of Fe₂[(SCH₂)₂NMe](CO)₄(PMe₃)₂ in CH₂Cl₂ solution.
Table S1. Crystal Data and Structure Refinements.

| Identification code | ed79ks ([2]BARF₄) | ed04Ls ([1H]BF₄) |
|---------------------|-------------------|-------------------|
| Empirical formula   | C₄₅ H₃₆ B F₂₄ Fe₂ N O₄ P₂ S₂ | C₁₂.₆₇ H₂₅.₃₃ B Cl₁.₃₃ F₄ Fe₂ N O₄ P₂ S₂ |
| Formula weight      | 1359.32           | 627.51            |
| Temperature         | 100(2) K          | 100(2) K          |
| Wavelength          | 0.71073 Å         | 0.71073 Å         |
| Crystal system      | Triclinic         | Triclinic         |
| Space group         | P-1               | P-1               |
| Unit cell dimensions|                  |                   |
|                     | a = 13.5275(3) Å  | a = 14.0486(2) Å  |
|                     | b = 14.3475(4) Å  | b = 16.9932(3) Å  |
|                     | c = 16.5656(4) Å  | c = 17.3960(3) Å  |
| Volume              | 2661.82(11) Å³    | 3759.01(11) Å³    |
| Z                   | 2                 | 6                 |
| Density (calculated)| 1.696 Mg/m³       | 1.663 Mg/m³       |
| Absorption coefficient | 0.811 mm⁻¹      | 1.643 mm⁻¹       |
| F(000)              | 1360              | 1908              |
| Crystal size        | 0.228 x 0.184 x 0.064 mm³ | 0.191 x 0.153 x 0.107 mm³ |
| Theta range for data collection | 2.290 to 28.301°. | 2.149 to 28.307°. |
| Index ranges        |                  |                   |
|                     | -18<=h<=18, -19<=k<=19 | -18<=h<=18, -22<=k<=22 |
|                     | -22<=l<=22        | -23<=l<=23        |
| Reflections collected | 190539            | 222825            |
| Independent reflections | 13211 \[R(int) = 0.0312\] | 18706 \[R(int) = 0.0328\] |
| Completeness to theta = 25.242° | 99.9 %            | 99.9 %            |
| Absorption correction | Semi-empirical from equivalents | Semi-empirical from equivalents |
| Max. and min. transmission | 0.7457 and 0.7147 | 0.7457 and 0.7016 |
| Refinement method   | Full-matrix least-squares on F² | Full-matrix least-squares on F² |
| Data / restraints / parameters | 13211 / 52 / 743 | 18706 / 548 / 995 |
| Goodness-of-fit on F² | 1.023              | 1.050             |
| Final R indices [I>2sigma(I)] | R₁ = 0.0348, wR₂ = 0.0840 | R₁ = 0.0213, wR₂ = 0.0512 |
| R indices (all data) | R₁ = 0.0369, wR₂ = 0.0856 | R₁ = 0.0241, wR₂ = 0.0527 |
| Extinction coefficient | n/a               | n/a               |
| Largest diff. peak and hole | 1.246 and -0.990 e.Å⁻³ | 0.970 and -0.765 e.Å⁻³ |
**Table S2. Crystal Data and Structure Refinements.**

| Identification code | ed82Ls (Et₄N[5]) | ed15Ls ([6]BF₄) |
|---------------------|------------------|------------------|
| Empirical formula   | C₃₅ H₄₁ Fe₂ N₄ O₄ P S₂ | C₃₄.79 H₴₈.₄₄ B Cl₀.₁₄ F₄ Fe₂ N O₄.₉₃ P₃ S₂ |
| Formula weight      | 788.51           | 920.04           |
| Temperature         | 120(2) K         | 100(2) K         |
| Wavelength          | 0.71073 Å        | 0.71073 Å        |
| Crystal system      | Monoclinic       | Monoclinic       |
| Space group         | P₂₁/c            | P₂₁/c            |
| Unit cell dimensions|                  |                  |
| a = 16.8201(7) Å   | a = 13.5415(3) Å |
| b = 17.3607(7) Å   | b = 17.0231(4) Å |
| c = 13.5621(6) Å   | c = 18.4766(4) Å |
| Volume              | 3719.3(3) Å³     | 4173.68(16) Å³   |
| Z                   | 4                | 4                |
| Density (calculated)| 1.408 Mg/m³      | 1.464 Mg/m³      |
| Absorption coefficient | 0.978 mm⁻¹   | 0.977 mm⁻¹      |
| F(000)              | 1640             | 1904             |
| Crystal size        | 0.468 x 0.305 x 0.054 mm³ | 0.223 x 0.214 x 0.079 mm³ |
| Theta range for data collection | 1.983 to 26.477° | 2.089 to 27.500° |
| Index ranges        |                  |                  |
| -21<=h<=21, -21<=k<=21 | -17<=h<=17, -22<=k<=22 |
| -16<=l<=16          | -23<=l<=23       |
| Reflections collected | 73436          | 60739            |
| Independent reflections | 7636 [R(int) = 0.0605] | 9573 [R(int) = 0.0352] |
| Completeness to theta = 25.242° | 99.9 %       | 99.9 %           |
| Absorption correction | Semi-empirical from equivalents | Semi-empirical from equivalents |
| Max. and min. transmission | 0.7454 and 0.5933 | 0.7456 and 0.7005 |
| Refinement method   | Full-matrix least-squares on F² | Full-matrix least-squares on F² |
| Data / restraints / parameters | 7636 / 332 / 542 | 9573 / 90 / 511 |
| Goodness-of-fit on F² | 1.186          | 1.103            |
| Final R indices [l-2sigma(l)] | R1 = 0.0600, wR2 = 0.1300 | R1 = 0.0317, wR2 = 0.0718 |
| R indices (all data) | R1 = 0.0690, wR2 = 0.1341 | R1 = 0.0386, wR2 = 0.0750 |
| Extinction coefficient | n/a            | n/a              |
| Largest diff. peak and hole | 0.859 and -0.663 e.Å⁻³ | 0.504 and -0.344 e.Å⁻³ |
Intensity data were collected on a Bruker D8 Venture kappa diffractometer equipped with a Photon-II CPAD detector. An Iµs microfocus Mo source ($\lambda = 0.71073 \text{ Å}$) coupled with a multi-layer mirror monochromator provided the incident beam. The sample was mounted on a 0.3 mm nylon loop with the minimal amount of Paratone-N oil. Data was collected as a series of $\phi$ and/or $\omega$ scans. Data was collected at 100 K using a cold stream of $\text{N}_2(\text{g})$. The collection, cell refinement, and integration of intensity data was carried out with the APEX3 software.\(^1\) A multi-scan absorption correction was performed with SADABS\(^2\). The structure was phased with intrinsic phasing methods using SHELXT\(^3\) and refined with the full-matrix least-squares program SHELXL.\(^4\)

A structural model consisting of three target molecules, three BF\(_4\) anions, and two dichloromethane solvent molecules in the asymmetric unit was developed.

Two of the three BF\(_4\) anions were modeled as disordered over two orientations. Within each anion, all 1,2 and 1,3 distances were restrained to be similar (esd 0.01, 0.02 Å). Rigid-bond restraints (esd 0.004) were imposed on displacement parameters for all disordered sites and similar displacement amplitudes (esd 0.005) were imposed on disordered sites overlapping by less than the sum of van der Waals radii. The site occupancy ratios were allowed to freely refine.

Both dichloromethane solvent molecules were modeled as disordered over two orientations. Within each solvent molecule, all 1,2 and 1,3 distances were restrained to be similar (esd 0.01, 0.02 Å). Similar displacement amplitudes (esd 0.005) were imposed on disordered sites overlapping by less than the sum of van der Waals radii. The site occupancy ratios were allowed to freely refine.

H atom treatment - Methyl H atom positions, R-CH\(_3\), were optimized by rotation about R-C bonds with idealized C-H, R--H and H--H distances. All of the amine H atom positions were located in the difference map; their positions were allowed to freely refine. At convergence, all amine H atoms were in good H-bonding geometries. Remaining H atoms were included as riding idealized contributors. Methyl and amine H atom U's were assigned as 1.5 times $U_{eq}$ of the carrier atom; remaining H atom U's were assigned as 1.2 times carrier $U_{eq}$.

The -3 5 0 reflection was omitted from the final refinement due to being partially obscured by the beam stop support in some orientations.
Intensity data were collected on a Bruker D8 Venture kappa diffractometer equipped with a Photon-II CPAD detector. An Iµs microfocus Mo source (λ = 0.71073 Å) coupled with a multi-layer mirror monochromator provided the incident beam. The sample was mounted on a 0.3 mm nylon loop with the minimal amount of Paratone-N oil. Data was collected as a series of φ and/or ω scans. Data was collected at 100 K using a cold stream of N₂(g). The collection, cell refinement, and integration of intensity data was carried out with the APEX3 software.¹ A multi-scan absorption correction was performed with SADABS². The structure was phased with intrinsic phasing methods using SHELXT³ and refined with the full-matrix least-squares program SHELXL⁴.

A structural model consisting of the target molecule, a BF₄ counter ion, and a disordered solvent molecule position in the asymmetric unit was developed.

The solvent molecule position was refined as occupational disorder of diethyl ether and dichloromethane. The dichloromethane occupancy was only approximately seven percent; to maintain a reasonable geometry with such a low occupancy it was refined as an idealized, rigid fragment.⁵ Similar displacement amplitudes (esd 0.01) were imposed on disordered sites overlapping by less than the sum of van der Waals radii. The site occupancy ratio was allowed to freely refine.

H atom treatment - Methyl H atom positions, R-CH₃, were optimized by rotation about R-C bonds with idealized C-H, R--H and H--H distances. Remaining H atoms were included as riding idealized contributors. Methyl H atom U's were assigned as 1.5 times Ueq of the carrier atom; remaining H atom U's were assigned as 1.2 times carrier Ueq.

The 1 1 0, 1 0 0, and 0 1 1 reflections were omitted from the final refinement due to being partially obscured by the beam stop in some orientations. The 6 6 12 reflection was omitted from the final refinement due to being partially obscured by the Cu beam stop in some orientations. The -8 1 3 and -9 1 2 reflections both showed large F₀² vs. Fc² deviations with F₀² being larger than Fc². Inspection of individual frame images revealed that in several instances there was a hot pixel on the detector in close enough proximity to the reflection that it may have been included in the integration box. These reflections were omitted from the final refinement.
Intensity data were collected on a Bruker D8 Venture kappa diffractometer equipped with a Photon-II CPAD detector. An Iµs microfocus Mo source (λ = 0.71073 Å) coupled with a multi-layer mirror monochromator provided the incident beam. The sample was mounted on a 0.3 mm nylon loop with the minimal amount of Paratone-N oil. Data was collected as a series of φ and/or ω scans. Data was collected at 100 K using a cold stream of N\textsubscript{2}(g). The collection, cell refinement, and integration of intensity data was carried out with the APEX3 software.\textsuperscript{1} A multi-scan absorption correction was performed with SADABS\textsuperscript{2}. The structure was phased with intrinsic phasing methods using SHELXT\textsuperscript{3} and refined with the full-matrix least-squares program SHELXL.\textsuperscript{4}

A structural model consisting of the target molecule plus one BArF\textsubscript{24} anion in the asymmetric unit was developed.

Two of the CF\textsubscript{3} groups on the BArF\textsubscript{24} anion were modeled as disordered; the C20 group over two orientations and the C29 group over three orientations. Similarity restraints (esd 0.01 Å) were imposed on all disordered C---F bond distances. Within each disordered group, the fluorine displacement parameters were constrained to be the same. The C20 site occupancy ratio was allowed to freely refine. The site occupancies for the three C29 orientations were allowed to freely refine with in the restraint that the total occupancy was 1.000(1).

H atom treatment - Methyl H atom positions, R-CH\textsubscript{3}, were optimized by rotation about R-C bonds with idealized C-H, R--H and H--H distances. Remaining H atoms were included as riding idealized contributors. Methyl H atom U's were assigned as 1.5 times U\textsubscript{eq} of the carrier atom; remaining H atom U's were assigned as 1.2 times carrier U\textsubscript{eq}.

The -1 1 1 reflection was omitted from the final refinement due to being partially obscured by the beam stop in some orientations.
Intensity data were collected on a Bruker D8 Venture kappa diffractometer equipped with a Photon-II CPAD detector. An Iµs microfocus Mo source ($\lambda = 0.71073$ Å) coupled with a multi-layer mirror monochromator provided the incident beam. The sample was mounted on a 0.3 mm nylon loop with the minimal amount of Paratone-N oil. Data was collected as a series of $\varphi$ and/or $\omega$ scans. Data was collected at 120 K using a cold stream of $\text{N}_2(g)$. The collection, cell refinement, and integration of intensity data was carried out with the APEX3 software. A multi-scan absorption correction was performed with SADABS$^2$. The structure was phased with intrinsic phasing methods using SHELXT$^3$ and refined with the full-matrix least-squares program SHELXL.$^4$

A structural model consisting of the target molecule plus one tetraethylammonium cation in the asymmetric unit was developed.

The nitrile substituent on the adt bridge was modeled as disordered over two orientations. Similarity restraints (esd 0.01 Å) were imposed on all chemically equivalent bond distances. To maintain a more linear geometry about the nitrile group for the minor orientation, similarity restraints (esd 0.02 Å) were imposed on the distances between the nitrile nitrogen atoms and the CH$_2$H atoms. Similar displacement amplitudes were imposed on disordered sites overlapping by less than the sum of van der Waals radii. The site occupancy ratio was allowed to freely refine.

The tetraethylammonium cation was modeled as disordered over two orientations. All 1,2 and 1,3 distances of the cation were restrained to be similar (esd 0.01, 0.04 Å). Similar displacement amplitudes were imposed on disordered sites overlapping by less than the sum of van der Waals radii. The site occupancy ratio was allowed to freely refine.

H atom treatment - Methyl H atom positions, R-CH$_3$, were optimized by rotation about R-C bonds with idealized C-H, R--H and H--H distances. Remaining H atoms were included as riding idealized contributors. Methyl H atom U's were assigned as 1.5 times U$_{eq}$ of the carrier atom; remaining H atom U's were assigned as 1.2 times carrier U$_{eq}$.

The -1 1 1 and 0 2 0 reflections were omitted from the final refinement due to being partially obscured by the beam stop in some orientations.

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