Teaching old compounds new tricks: efficient N$_2$ fixation by simple Fe(N$_2$)(diphosphine)$_2$ complexes

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Electronic Supplementary Information

Contents:

1. Experimental details............................................................................................ 1
2. NMR spectra........................................................................................................ 9
3. IR spectra............................................................................................................. 13
4. Raman spectra.................................................................................................... 13
5. UV-vis spectra................................................................................................... 14
6. Cyclic voltammograms....................................................................................... 15
7. X-ray diffraction data for 3............................................................................... 17
8. References.......................................................................................................... 18

1. Experimental details

General considerations

All chemical manipulations were performed under a N$_2$ or Ar atmosphere either using standard Schlenk-line techniques or a MBraun Labmaster DP glovebox, unless stated otherwise. Solvents were purchased from VWR: pentane and hexane were dried using an Innovative Technology Pure Solv™ SPS-400; THF and Et$_2$O were distilled from dark green Na/fluorenone indicator. Solvents were degassed by thorough sparging with N$_2$ or Ar gas and stored in gas-tight ampoules; pentane, hexane and Et$_2$O were stored over a K mirror. Deuterated solvents were freeze-pump-thaw degassed, dried, and stored in gas-tight ampoules over 4 Å molecular sieves: THF-d$_8$ (Sigma-Aldrich, 99.5 atom % D); DMSO-d$_6$ (VWR, 99.5 atom % D). $^{15}$N$_2$ (Cambridge Isotope Laboratories, 98% $^{15}$N) was transferred from a breakseal flask using a Toepler pump. FeCp$_2$ was purchased from Sigma-Aldrich and purified by sublimation and recrystallisation from cold pentane. Para-dimethylaminobenzaldehyde (pdmab) was purchased from Sigma-Aldrich and purified by recrystallisation from cold EtOH. NH$_4$Cl and N$_2$H$_4$·2HCl were purchased from Sigma-Aldrich. K$_2$C$_8$,$^1$ [“Bu$_4$N][BARF$_{24}$]$^2$ trans-Fe(Cl)$_2$(dmpe)$_2$,$^3$ [trans-Fe(H)(N$_2$)(dmpe)$_2$][BPh$_4$]$_3$ trans-Fe(Cl)$_2$(depe)$_2$,$^3$ [trans-Fe(H)(N$_2$)(depe)$_2$][BPh$_4$]$_3$ 2,6,-
dimethylpyridinium (lutidinium) triflate [(LutH)OTf] and H(OEt)2(BArF24) [BArF24 = B(3,5-(CF3)2C6H3)4] were prepared according to literature procedures.

NMR spectra were recorded using Bruker AV-400 (400.4 MHz) spectrometers. Chemical shifts, δ, are reported in parts per million (ppm). 1H chemical shifts are given relative to Me₄Si and referenced internally to the residual proton shift of the deuterated solvent employed. 31P and 15N chemical shifts were referenced (δ = 0) externally to 85% H₃PO₄ (aq) and neat CH₃NO₂, respectively. 1H and 31P NMR spectra of solutions prepared in non-deuterated solvents incorporate an internal reference capillary containing a solution of ca. 0.1 M PPh₃ in C₆D₆ and are referenced to residual C₆D₅H and PPh₃ (δ = −5.3) resonances, respectively. Air or moisture sensitive samples were prepared inside the glovebox using NMR tubes fitted with J. Young valves.

Infrared (IR) spectra were recorded using a Perkin Elmer FT-IR Spectrum GX spectrometer. Samples were measured as KBr pellets, which were prepared by grinding the sample with KBr (Sigma, FT-IR grade), and pressing in an air-tight Specac® die using a Specac® manual hydraulic press. Raman spectra were recorded on a LabRAM Infinity instrument (Horiba Jobin-Yvon Ltd., Middlesex, UK) using a He-Ne (red) 633 nm laser, calibrated by reference to the 520.7 nm band of a silicon wafer. Samples were prepared inside an Ar glovebox and deposited as a fine powder on the wall of a sealable quartz cuvette. 14N2 stretches were confirmed through comparison with the shifted 15N2 stretch of the corresponding 15N isotopically labelled sample.

Electronic spectra were recorded using a Perkin Elmer Lambda 20 UV-visible spectrophotometer. Samples were prepared inside the glovebox using a quartz cuvette with an optical path length of 1 cm and fitted with a J. Young valve.

Electrochemical experiments were carried out using an AutoLab potentiostat controlled by Nova. Measurements were performed inside an Ar or N₂ glovebox on room temperature Et₂O solutions containing the sample (2 mM) and [5Bu₄N][BArF24] electrolyte (50 mM). A three-electrode configuration was employed: a Pt working electrode (PWE) (BASi, Indiana, USA); a Pt wire counter electrode (99.99 %; GoodFellow, Cambridge, UK); and an Ag wire pseudo-reference electrode (99.99 %; GoodFellow, Cambridge, UK). The PWE and Ag wire were polished using alumina/H₂O, and all electrodes rinsed with Et₂O and dried in a 100 °C oven prior to each measurement. Measurements were calibrated to the ferrocene/ferrocenium couple in Et₂O at the end of each run, and iR-compensated to within 80 ± 5 % of the solution uncompensated resistance.

Single crystal X-ray diffraction data for 3 was collected with an Oxford Diffraction Xcalibur unit; the crystal was mounted on a glass fibre using perfluoropolyether oil and measured in a stream of N₂ at 173 K. The structure was solved by direct methods using SHELX.⁶

Elemental analyses were performed by Mr. S. Boyer of the London Metropolitan University.
Synthesis and characterisation.

FeN₂(dmpe)₂ (1). Solutions of 1 can be obtained by dissolving [(Fe(dmpe)₂₂(μ-N₂)] (3) under N₂. Attempts to grow a single crystal of 1 suitable for X-ray crystallography have yielded only crystals of 3.

³¹P{¹H} NMR (162 MHz, hexane) δ: 63.3 (s).

FeN₂(depe)₂ (2). (N.B. this reaction requires a N₂ atmosphere.) To a stirred suspension of Mg powder (564 mg, 23.2 mmol) in 15 mL of THF was added 1,2-dibromoethane (0.2 mL, 2.31 mmol). The mixture was heated to 40 °C for 30 min to activate the Mg, evolving C₂H₄ gas. After allowing the mixture to cool to RT, a solution of FeCl₂(depe)₂ (2.5 g, 4.64 mmol) in 30 mL of THF was slowly added and the mixture subsequently sonicated for 20 min. The reaction is typically complete after 2 days of stirring under N₂ with periodic sonication. The resulting orange solution was filtered before addition of 1,4-dioxane (3.95 mL, 46.3 mmol), precipitating a fine white solid. After stirring for 12 h, the mixture was filtered through a pad of Celite® on a sintered glass frit and rinsed through with additional THF (3 x 40 mL). THF was subsequently removed in vacuo and the remaining solid extracted with pentane (3 x 40 mL). Concentration of the pentane solution and slow cooling to −78 °C yielded orange crystals which were collected by filtration, washed with cold pentane, and then dried in vacuo (2.1 g, 91%).

³¹P{¹H} NMR (162 MHz, hexane) δ: 84.4 (s).

IR (KBr, cm⁻¹): 1956 (14N₂), 1889 (15N₂).

CV (vs Cp₂Fe⁺/0, Et₂O): −2.03 V (Fe⁺/Fe⁰).

Fe¹⁵N₂(depe)₂ (2-¹⁵N₂). In a Rotaflo® ampoule under an Ar atmosphere, Mg powder (113 mg, 4.65 mmol) was activated with 1,2-dibromoethane in THF as above. THF was then removed by decanting and the mixture submerged in a liquid N₂/pentane bath (−131 °C). A solution of FeCl₂(depe)₂ (500 mg, 0.927 mmol) in 10 mL of THF was added under Ar and the mixture degassed and left under static vacuum. With the mixture still frozen, ¹⁵N₂ (2 eq.) was delivered into the ampoule via a Toepler pump. After thawing, the mixture was sonicated for 20 min and subsequently stirred for 2 days with periodic sonication. The reaction was worked up as above, under an Ar atmosphere (350 mg, 76%).

1 and 2 generated in-situ by the method of Leigh et al. Following the method of Leigh et al., [trans-Fe(H)(N₂)(PP)₂][BPh₄] (PP = dmpe, depe) and KO'Bu (2 eq.) were combined in THF under a N₂ atmosphere, stirred for 3 h (PP = dmpe) or 24 h (PP = depe), and then filtered through Celite®.

[(Fe(dmpe)₂₂(μ-N₂)] (3). FeCl₂dmpe₂ (4 g, 9.37 mmol) and KC₈ (5.065 g, 37.5 mmol) were transferred into a Rotaflo® ampoule and sealed. With the ampoule submerged in a liquid N₂ bath, 40 mL of hexane was slowly added under a 1 bar N₂ pressure and the ampoule resealed. After removal of the liquid N₂ bath and allowing the ampoule to thaw behind a blast shield, a N₂ pressure of ca. 4 bar was obtained. The mixture was subsequently sonicated for 20 min and left to stir for 3 days with periodic sonication. After carefully releasing the pressure, the mixture was filtered through a pad of Celite® on a sintered glass frit and the remaining solids extracted with additional hexane (4 x 40 mL).
The filtrate and extracts were combined and the hexane removed in vacuo to yield a red solid consisting of mainly 1 with some 3. Suspending this solid in 1-2 mL of hexane under an Ar atmosphere with minimal stirring for 5 days results in almost complete conversion to 3. Minor impurities consisting of 1, [[Fe(dmpe)₂]₂(μ-dmpe)], and cis-Fe(H)(dmpe)₂ can be removed by recrystallisation from hexane under Ar to yield red crystals of 3 in >98% purity by $^{31}$P NMR (3.21 g, 93%).

Anal. Calcd. for C₂₄H₆₄N₂Fe₂P₈: C, 38.94; H, 8.71; N, 3.78. Found: C, 38.93; H, 8.85; N, 3.89.

$^{31}$P{¹H} NMR (162 MHz, hexane) δ: 66.0 (s).

$^{15}$N{¹H} NMR (40.55 MHz, hexane) δ: −55.05 (s).

¹H NMR (40.55 MHz, THF-d₈, 253 K) δ: 1.44–1.30 (overlapped, 40H, 'CH₂CH₂' and Me); 1.20–1.14 (br s, 24H, Me'). [N.B. the proton resonances of the dmpe ligands could not be resolved in other common solvents; assignment of these resonances was confirmed by $¹H–^{31}$P HSQC NMR.]

Raman (solid, cm⁻¹): 1933 (¹⁴N₂), 1870 (¹⁵N₂).

UV-vis (pentane, nm {M cm⁻¹}: 275 (29,974); 365 (42,312).

CV (vs Cp₂Fe⁰⁰⁰⁰⁰, Et₂O): −2.23 V (Fe⁺/Fe⁰).

[[Fe(dmpe)₂]₂(μ-¹⁵N₂)] (3·¹⁵N₂). FeCl₂dmpe₂ (400 mg, 0.937 mmol) and KC₈ (633 mg, 4.68 mmol) were transferred into a Rotaflo® ampoule and sealed. With the ampoule submerged in a liquid N₂/pentane (−131 °C) bath, 10 mL of hexane was added under an Ar atmosphere and the mixture degassed and left under static vacuum. With the mixture still frozen, $^{15}$N₂ (1.5 eq.) was delivered into the ampoule via a Toepler pump. After thawing, the mixture was sonicated for 20 min and subsequently stirred for 5 days with periodic sonication. The reaction was worked up as above, under an Ar atmosphere (240 mg, 69%).

Acidification experiments

**General procedure.** Inside a glovebox under either an Ar (for compound 3) or N₂ (for all other compounds) atmosphere, the chosen compound was carefully weighed (0.016 mmol Fe), dissolved in a minimum of solvent, and then filtered through a Celite® frit into bulb A of the distillation apparatus (Figure S1). Additional solvent was used to rinse through any remaining residue on the Celite® frit, up to a total volume of 0.5 mL. The apparatus was then sealed under an Ar or N₂ atmosphere before being transferred to a dual vacuum/gas (Ar or N₂) manifold. With the solution stirring at the desired temperature, precooled acid was added either via a syringe (HCl, 1 M in Et₂O; TIOH, neat; 10 eq. per Fe) or cannula (TIOH, 0.32 M in pentane or Et₂O; 10 eq. per Fe). The mixture was stirred at the desired temperature for 30 min, then allowed to warm to room temperature for a further 30 min. During this time, additional HCl (1 M in Et₂O; 20 eq. per Fe) was added to the second empty flask.
(bulb B). The volatiles in bulb A were subsequently removed in vacuo, and both bulbs were submerged in liquid N\textsubscript{2} baths. To the frozen acidified mixture in bulb A, aqueous KOH (40\%, 1.5 mL) was added via a syringe (caution: this should be performed under a N\textsubscript{2} flow rather than Ar, which freezes at the temperature of liquid N\textsubscript{2}). With the contents of both bulbs frozen, the entire apparatus was evacuated to ca. 10\textsuperscript{-2} mbar and sealed under a static vacuum by closing all three J. Young valves. Bulb B was then sealed, thawed to room temperature, and stirred for a further 5 min. All volatiles in bulb B were subsequently removed in vacuo and the remaining residue was dissolved in aqueous HCl (1 M, 0.5 mL) from which a 50 μL aliquot was removed for hydrazine analysis (vide infra). The remaining 0.9 fraction was once more dried in vacuo and subsequently redissolved in DMSO-d\textsubscript{6} (0.45 mL) for ammonia analysis (vide infra).

In control experiments it was found that N\textsubscript{2}H\textsubscript{4} (b.p. 114 °C; N\textsubscript{2}H\textsubscript{4}·H\textsubscript{2}O, b.p. 120 °C) does not entirely transfer across during the base distillation, which must be carried out at room temperature due to the known decomposition of N\textsubscript{2}H\textsubscript{4} to NH\textsubscript{3}, N\textsubscript{2}, and H\textsubscript{2}.\textsuperscript{11} In order to quantify any N\textsubscript{2}H\textsubscript{4} in the remaining residue, aq. HCl (12 M, 1.26 mL; 1 M, 1 mL) was added at 0 °C (caution: exothermic), and the mixture subsequently filtered through a Celite\textsuperscript{®} frit, and rinsed with additional aq. HCl (1 M) up to a total volume of 5 mL. In a 5 mL volumetric flask, this solution was rinsed with BuOH (3 X 1 mL) to extract residual Fe-species/contaminants, yielding a clear solution, which was remade up to 5 mL with further aq. HCl (1 M). A fraction of this 5 mL solution was subsequently analysed for hydrazine (vide infra).

Quantification of NH\textsubscript{3}

After treatment with base (vide supra), NH\textsubscript{3} was distilled from the reaction mixture onto HCl, thus chemically trapping it as NH\textsubscript{4}Cl, which could then be quantified by \textsuperscript{1}H NMR spectroscopy, as reported by others.\textsuperscript{12} NH\textsubscript{4}\textsuperscript{+} (δ = 7.3, 1:1:1 triplet, \textsuperscript{1}J\textsubscript{NH} = 51 Hz, DMSO-d\textsubscript{6}; Figure S2) was integrated relative to the vinylic protons of 2,5-dimethylfuran,\textsuperscript{13} contained within a DMSO-d\textsubscript{6} capillary insert (δ = 5.83, s, 2H, T\textsubscript{1} = 20.5 s), which was calibrated using a standard 0.032 M solution of NH\textsubscript{4}Cl in DMSO-d\textsubscript{6}. To establish whether the N in NH\textsubscript{4}\textsuperscript{+} produced in the acidification experiments is sourced from the N\textsubscript{2} ligand in the Fe complex, a THF solution of \textsuperscript{15}N\textsubscript{2} isotopically labelled 2 (2\textsuperscript{15}N\textsubscript{2}) was acidified with TfOH inside an Ar glovebox (in the absence of N\textsubscript{2}); subsequent analysis by \textsuperscript{1}H NMR spectroscopy (as above), resolved a characteristic 1:1 double corresponding to \textsuperscript{15}NH\textsubscript{4}\textsuperscript{+} (δ = 7.4, d, \textsuperscript{1}J\textsubscript{NH} = 71 Hz, DMSO-d\textsubscript{6}; Figure S2).
Quantification of $\text{N}_2\text{H}_4$

Both the volatile (distilled) and the BuOH washed, non-volatile fractions were analysed separately for $\text{N}_2\text{H}_4$ by a standard spectrophotometric method, which employs an acidic pdmab indicator solution to generate a yellow azine dye with a characteristic electronic absorption feature at 458 nm. Accordingly, aliquots taken from these two fractions were diluted to a suitable concentration and the $\text{N}_2\text{H}_4$ was quantified by comparison to the calibration curve in Figure S1. Importantly, it was determined through control experiments (Table S1, entries 20-30) that the presence of NH$_3$ and/or dmpe and depe does not interfere with this method. Likewise, the BuOH washed, non-volatile fraction does not absorb within the range of the UV-vis spectrum measured and thus interference from any residual Fe-species/contaminants may also be ruled out (Figure S3).

Figure S1. Left: distillation apparatus for the acidification reactions; compounds were acidified in the smaller bulb (A), and base-distilled onto additional acid within the larger bulb (B). Right: UV-vis calibration curve ($\lambda_{\text{max}} = 458$ nm) for the pdmab hydrazine test.
Figure S2. $^1$H NMR spectra (DMSO-d$_6$) of $^{14}$NH$_4^+$ and $^{15}$NH$_4^+$ generated from the addition of TfOH, inside an Ar glovebox, to THF solutions of 2 and 2-$^{15}$N$_2$, respectively, and subsequent base distillation onto HCl.

Figure S3. Exemplar UV-vis spectra used for the spectrophotometric determination of N$_2$H$_4$ produced in an acidification reaction (2, TfOH, Et$_2$O, rt). Aliquots taken from the distillate and the BuOH washed, non-volatile remainder were analysed both with and without pdmab indicator.
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</table>

⁴ Yield per Fe; ⁵ averaged over all runs; ³ yield assuming each Fe supplies a max. of two electrons, averaged over all runs.
Figure S4. $^{31}$P NMR spectra of Fe($^{15}$N$_2$)(dmpe)$_2$ (1-$^{15}$N$_2$) and [[Fe(dmpe)$_2$]$_2$($\mu$-$^{15}$N$_2$)] (3-$^{15}$N$_2$) generated from the reduction of trans-Fe(Cl)$_2$(dmpe)$_2$ under $^{15}$N$_2$ with KC$_8$ (4 eq.) in hexane: (i) reaction mixture after 3 days; (ii) redissolved in hexane after removal of volatiles and drying in vacuo; (iii) recrystalised from hexane under argon; P = PMe$_2$. 

2. NMR spectra
Figure S5. $^{15}\text{N}(^1\text{H})$ NMR spectrum of [[Fe(dmpe)$_2$(μ-$^{15}$N$_2$)] (3-$^{15}$N$_2$) in hexane under an Ar atmosphere.

Figure S6. $^{15}\text{N}(^1\text{H})$ NMR spectrum of Fe($^{15}$N$_2$)(dmpe)$_2$ (1-$^{15}$N$_2$) and [[Fe(dmpe)$_2$(μ-$^{15}$N$_2$)] (3-$^{15}$N$_2$) generated in situ from the reduction of trans-Fe(Cl)$_2$(dmpe)$_2$ under $^{15}$N$_2$ with KC$_6$ (4 eq.) in hexane.
Figure S7. $^{15}$N($^1$H) NMR spectrum of Fe($^{15}$N$_2$)(dmpe)$_2$ ($^{1,15}$N$_2$) generated *in situ* from the deprotonation of *trans*-Fe(H)($^{15}$N$_2$)(dmpe)$_2$[BPh$_4$] in THF under a $^{15}$N$_2$ atmosphere.

Figure S8. $^1$H NMR spectrum of [{Fe(dmpe)$_2$$_2$}(μ-$^1$N$_2$)] (3) recorded in THF-d$_8$ at 253 K.
Figure S9. $^1$H–$^{31}$P HSQC NMR spectrum of [[Fe(dmpe)$_2$]$_2$(μ-N$_2$)] (3) recorded in THF-d$_8$ at 253 K; [[Fe(dmpe)$_2$]$_2$(μ-dmpe)] (4) denoted by *.

Figure S10. $^{31}$P NMR determined concentrations of 3 (♦) and 1 (■) from the in-situ decomposition of 3 in pentane (10 mM) under an Ar atmosphere; t½ (3) = 13 days.
3. IR spectra

![IR spectra of Fe($^{14}$N$_2$)(depe)$_2$ (2) and Fe($^{15}$N$_2$)(depe)$_2$ (2-$^{15}$N$_2$) recorded as KBr pellets; P = PEt$_2$.](image1.png)

**Figure S11.** IR spectra of Fe($^{14}$N$_2$)(depe)$_2$ (2) and Fe($^{15}$N$_2$)(depe)$_2$ (2-$^{15}$N$_2$) recorded as KBr pellets; P = PEt$_2$.

4. Raman spectra

![Raman spectra of [{Fe(dmpe)$_2$}(μ-$^{14}$N$_2$)] (3, blue) and [{Fe(dmpe)$_2$}(μ-$^{15}$N$_2$)] (3-$^{15}$N$_2$, green) recorded on powdered samples using a He-Ne (red) 633nm laser; P = PMe$_2$.](image2.png)

**Figure S12.** Raman spectra of [{Fe(dmpe)$_2$}(μ-$^{14}$N$_2$)] (3, blue) and [{Fe(dmpe)$_2$}(μ-$^{15}$N$_2$)] (3-$^{15}$N$_2$, green) recorded on powdered samples using a He-Ne (red) 633nm laser; P = PMe$_2$. 
5. UV-vis spectra

**Figure S13.** UV-vis spectra of [Fe(dmpe)$_2$($\mu$-N$_2$)] (3) recorded in pentane under an Ar atmosphere.

**Figure S14.** UV-vis spectra of [Fe(dmpe)$_2$($\mu$-N$_2$)] (3) recorded in Et$_2$O under either an Ar or N$_2$ atmosphere.
6. Cyclic voltammograms

**Figure S15.** Cyclic voltammetry measurements of Fe(N$_2$)(depe)$_2$ (2); recorded in Et$_2$O under a N$_2$ atmosphere; [nBu$_4$N][BArF$_{24}$] electrolyte; potential plotted relative to the Cp$_2$Fe$^{+}$/0 couple; arrow indicates direction of scan.

**Figure S16.** Cyclic voltammetry measurements of [[Fe(dmpe)$_2$]$_2$(μ-N$_2$)] (3); recorded in Et$_2$O under an Ar atmosphere; [nBu$_4$N][BArF$_{24}$] electrolyte; potential plotted relative to the Cp$_2$Fe$^{+}$/0 couple; arrow indicates direction of scan.
Figure S17. Cyclic voltammetry measurements of Fe(N₂)(dmpe)₂ (1); recorded in Et₂O under a N₂ atmosphere; 250 mV s⁻¹ scan rate; ["Bu₄N][BARF₂₄] electrolyte; potential plotted relative to the Cp₂Fe⁺/₀ couple; arrow indicates direction of scan.
7. X-ray diffraction data for 3

The P(1), P(4) dmpe ligand coordinated to Fe(1) was found to be disordered; two orientations of ca. 61 and 39% occupancy were identified. Similarly, the P(21), P(24) and P(31), P(34) dmpe ligands coordinated to Fe(2) were found to be disordered; two orientations of ca. 64 and 36% occupancy were identified. Only the non-hydrogen atoms of the major occupancy orientations were refined anisotropically.

Formula: \( \text{C}_{24}\text{H}_{64}\text{Fe}_{2}\text{N}_{2}\text{P}_{8} \)

Formula weight: 740.23

Temperature: 173 K

Diffractometer, wavelength: OD Xcalibur 3, 0.71073 Å

Crystal system, space group: Triclinic, P-1

Unit cell dimensions:
- \( a = 9.3450(4) \) Å, \( \alpha = 90.674(3)^\circ \)
- \( b = 9.6733(3) \) Å, \( \beta = 90.671(4)^\circ \)
- \( c = 23.4652(10) \) Å, \( \gamma = 115.639(3)^\circ \)

Volume, Z: 1911.86(14) Å\(^3\), 2

Density (calculated): 1.286 mg/m\(^3\)

Absorption coefficient: 1.110 mm\(^{-1}\)

\( F(000) \): 788

Crystal colour / morphology: Red tabular needles

Crystal size: 0.41 x 0.35 x 0.06 mm\(^3\)

\( \theta \) range for data collection: 2.94 to 29.32°

Index ranges: \(-11 \leq h \leq 12, -13 \leq k \leq 13, -15 \leq l \leq 31\)

Reflections collected / unique: 15856 / 8760 \{R(int) = 0.0202\]

Reflections observed \([F>4\sigma(F)]\): 7245

Absorption correction: Analytical

Max. and min. transmission: 0.937 and 0.728

Refinement method: Full-matrix least-squares on \( F^2 \)

Data / restraints / parameters: 8760 / 452 / 407

Goodness-of-fit on \( F^2 \): 1.024

Final R indices \([F>4\sigma(F)]\): R1 = 0.0431, wR2 = 0.0900

R indices (all data): R1 = 0.0556, wR2 = 0.0984

Largest diff. peak, hole: 0.774, -0.637 eÅ\(^{-3}\)

Mean and maximum shift/error: 0.000 and 0.001
8. References