Supporting Information for

Towards Understanding of Lanthanide-Transition Metal Bonding: Investigations of the First Ce-Fe Bonded Complex

Corey P. Burns, Xin Yang, Siyoung Sung, Joshua D. Wofford, Nattamai S. Bhuvanesh, Michael B. Hall, and Michael Nippe*

Department of Chemistry, Texas A&M University

3255 TAMU, College Station, TX 77843 (USA)

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Materials and methods: Synthesis of 2,6-bis(methylenecyclopentadienyl)pyridine disodium salt (Na₂PyCp₂) and KFp was prepared as previously described^{S1,S2} and carried out under strict anaerobic and anhydrous conditions using an Ar filled glovebox (Vigor) and solvents dried and flushed with Ar using a solvent purification system (JC Meyer Solvent System). All glassware used in the glovebox was oven dried and cycled into the glovebox overnight. Sodium cyclopentadienide (0.1 mol in THF), and anhydrous Ce(OTf)₃ were purchased from STREM. The Ce(OTf)₃ was dried for two days at 180 °C under vacuum prior to use. Samples used for magnetic characterization were either single crystalline material or microcrystalline powders. Magnetic samples of 1, 2, and 3 were prepared with an eicosane matrix in a high purity NMR tube which was flame sealed under vacuum. The eicosane (Acros Organics) was melted in a hot water bath (42 °C) and was dispersed homogeneously throughout the sample. Magnetic characterization of 1, 2, and 3 were obtained using a Quantum Design MPMS 3 SQUID magnetometer. DC measurements were acquired under an applied 1000 Oe field at a temperature range of 2-300 K. AC measurements for 1, 2, and 3 under applied DC fields ranging from 500 Oe to 4000 Oe at temperature ranges of 4 to1.8 K. Elemental analysis was carried out by Midwest Microlab. Cyclic voltammograms (CVs) were recorded in a Ar-filled glovebox using a GAMRY Ref600 potentiostat with a three-electrode setup: glassy carbon disk (BasInc) working electrode, silver pseudo reference electrode, and platinum wire counter electrode (Alfa Aesar). All CVs were recorded in a 1.0 mM [(pyCp₂)Ce(thf)(OTf)] THF solution with 0.1 M tetrabutylammonium hexfluorophosphate as the supporting electrolyte. All potentials are referenced to the ferrocene/ferrocenium redox couple measured for internally added ferrocene. IR spectra were obtained in the solid state in an argon filled glove box (Vigor) equipped with an Agilent CARY 630 FT-IR spectrometer (32 background scans, 32 scans @ 650-4000 cm⁻¹, Apodization: Happ-Genzel). ⁵⁷Fe Mössbauer spectra were collected on a model MS4 WRC low-field, variable temperature spectrometer (See Co., Edina, MN). Temperatures were varied using a temperature controller on the heating coil on the sample holder. The instrument was calibrated using an α -Fe foil at room temperature. Obtained spectra were fitted using WMOSS software (See Co.)

Single Crystal X-Ray Crystallography:

Compound 1. A Leica MZ 75 microscope was used to identify a suitable yellow block with very well defined faces with dimensions (max, intermediate, and min) $0.272 \times 0.195 \times 0.143 \text{ mm}^3$ from a representative sample of crystals of the same habit. The crystal mounted on a nylon loop was then placed in a cold nitrogen stream (Oxford) maintained at 110 K.

A BRUKER APEX 2 Duo X-ray (three-circle) diffractometer was employed for crystal screening, unit cell determination, and data collection. The goniometer was controlled using the APEX2 software suite, v2008-6.0.^{S3,S4} The sample was optically centered with the aid of a video camera such that no translations were observed as the crystal was rotated through all positions. The detector was set at 6.0 cm from the crystal sample (APEX2, 512x512 pixel). The X-ray radiation employed was generated from a Mo X-ray tube (K α = 0.71073 Å with a potential of 40 kV and a current of 40 mA). 45 data frames were taken at widths of 1.0°. These reflections were used in the auto-indexing procedure to determine the unit cell. A suitable cell was found and refined by nonlinear least squares and Bravais lattice procedures. The unit cell was verified by examination of the h k l overlays on several frames of data. No super-cell or erroneous reflections were observed. After careful examination of the unit cell, an extended data collection procedure (5 sets) was initiated using omega scans.

Integrated intensity information for each reflection was obtained by reduction of the data frames with the program APEX2.^{S4} The integration method employed a three-dimensional profiling algorithm and all data were corrected for Lorentz and polarization factors, as well as for crystal decay effects. Finally, the

data was merged and scaled to produce a suitable data set. The absorption correction program SADABS^{S5} was employed to correct the data for absorption effects.

Systematic reflection conditions and statistical tests of the data suggested the space group Pnma. A solution was obtained readily (Z=4; Z'=0.5) using XT/XS in APEX2.^{S4,S6} Hydrogen atoms were placed in idealized positions and were set riding on the respective parent atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters. Absence of additional symmetry and voids were confirmed using PLATON (ADDSYM).^{S7,S8} The structure was refined (weighted least squares refinement on F2) to convergence.^{S4,S6,S9}

Compound 2. A Leica MZ 75 microscope was used to identify a suitable colorless plate with very well defined faces with dimensions (max, intermediate, and min) $0.221 \times 0.218 \times 0.083 \text{ mm}^3$ from a representative sample of crystals of the same habit. The crystal mounted on a nylon loop was then placed in a cold nitrogen stream (Oxford) maintained at 110 K.

A BRUKER APEX 2 Duo X-ray (three-circle) diffractometer was employed for crystal screening, unit cell determination, and data collection. The goniometer was controlled using the APEX2 software suite, v2008-6.0.^{S3,S4} The sample was optically centered with the aid of a video camera such that no translations were observed as the crystal was rotated through all positions. The detector was set at 6.0 cm from the crystal sample (APEX2, 512x512 pixel). The X-ray radiation employed was generated from a Mo X-ray tube (K α = 0.71073 Å with a potential of 40 kV and a current of 40 mA).

45 data frames were taken at widths of 1.0°. These reflections were used in the auto-indexing procedure to determine the unit cell. A suitable cell was found and refined by nonlinear least squares and Bravais lattice procedures. The unit cell was verified by examination of the h k l overlays on several frames of data. No super-cell or erroneous reflections were observed.

After careful examination of the unit cell, an extended data collection procedure (10 sets) was initiated using omega and phi scans.

Integrated intensity information for each reflection was obtained by reduction of the data frames with the program APEX2.^{S4} The integration method employed a three-dimensional profiling algorithm and all data were corrected for Lorentz and polarization factors, as well as for crystal decay effects. Finally, the data was merged and scaled to produce a suitable data set. The absorption correction program SADABS^{S5} was employed to correct the data for absorption effects.

Systematic reflection conditions and statistical tests of the data suggested the space group P21/n. A solution was obtained readily (Z=2; Z'=0.5) using XT/XS in APEX2.^{S4,S6} Hydrogen atoms were placed in idealized positions and were set riding on the respective parent atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters. Absence of additional symmetry and voids were confirmed using PLATON (ADDSYM).^{S7,S8} The structure was refined (weighted least squares refinement on F²) to convergence.^{S4,S6,S9}

Compound 3. A Leica MZ 75 microscope was used to identify a suitable yellow block with very welldefined faces with dimensions (max, intermediate, and min) $0.228 \times 0.213 \times 0.162 \text{ mm}^3$ from a representative sample of crystals of the same habit. The crystal mounted on a nylon loop was then placed in a cold nitrogen stream (Oxford) maintained at 110 K.

A BRUKER APEX 2 Duo X-ray (three-circle) diffractometer was employed for crystal screening, unit cell determination, and data collection. The goniometer was controlled using the APEX2 software suite, v2008-6.0.^{S3,S4} The sample was optically centered with the aid of a video camera such that no

translations were observed as the crystal was rotated through all positions. The detector was set at 6.0 cm from the crystal sample (APEX2, 512x512 pixel). The X-ray radiation employed was generated from a Mo sealed X-ray tube (K α = 0.70173Å with a potential of 40 kV and a current of 40 mA).

45 data frames were taken at widths of 1.0°. These reflections were used in the auto-indexing procedure to determine the unit cell. A suitable cell was found and refined by nonlinear least squares and Bravais lattice procedures. The unit cell was verified by examination of the h k l overlays on several frames of data. No super-cell or erroneous reflections were observed.

After careful examination of the unit cell, an extended data collection procedure (6 sets) was initiated using omega scans.

Integrated intensity information for each reflection was obtained by reduction of the data frames with the program APEX2.^{S4} The integration method employed a three-dimensional profiling algorithm and all data were corrected for Lorentz and polarization factors, as well as for crystal decay effects. Finally, the data was merged and scaled to produce a suitable data set. The absorption correction program SADABS^{S5} was employed to correct the data for absorption effects.

Systematic reflection conditions and statistical tests of the data suggested the space group Pna21. A solution was obtained readily using XT/XS in APEX2.^{S4,S6} Hydrogen atoms were placed in idealized positions and were set riding on the respective parent atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters. Thermal ellipsoid on O18 suggested a disorder and was modeled successfully between two positions with an occupancy ratio of 0.52:0.48. Appropriate restraints / constraints were added to keep the bond distances, angles, and thermal ellipsoids meaningful. Absence of additional symmetry and voids were confirmed using PLATON (ADDSYM).^{S7,S8} The structure was refined (weighted least squares refinement on F²) to convergence.^{S4,S6,S9}

Compound	1	2	3	
Formula	C ₂₈ H ₂₈ CeFeNO ₃	$C_{36}H_{30}Ce_2F_6N_2O_6S_2$	C22H23CeF3NO4S	
Crystal system	Orthorhombic	Monoclinic	Orthorhombic	
Space group	Pnma	$P2_1/n$	$Pna2_1$	
a, Å	17.612(2)	9.9043(3)	14.8353(4)	
b, Å	13.421(2)	9.2078(2)	9.9906(3)	
c, Å	10.146(1)	30.3459(6)	15.3663(4)	
a,°	90	90	90	
β,°	90	102.970(1)	90	
γ, °	90	90	90	
Volume, Å ³	2398(1)	1808.2(1)	2277.5(1)	
Ζ	4	2	4	
Т, К	110	110	110	
ρ_{calcd} (mg/m ³)	1.724	1.919	1.734	
F(000)	1244	1020	1180	
$\Theta_{\min}, \Theta_{\max}, \circ$	4.637, 27.498	2.054, 27.499	2.432, 32.990	
R_1^{a} , wR_2^{b} (I > 2 σ (I))	0.0195, 0.0444	0.0165, 0.0380	0.0242, 0.0453	
R_1^a , w R_2^b (all data)	0.0226, 0.0464	0.0174, 0.0384	0.0425. 0.0520	
$\ \overline{F_{o}} - F_{c}\ /3 F_{o} . \ ^{b}wR_{2} = [3[w(F_{o}^{2}-F_{c}^{2})^{2}]/3[w(F_{o}^{2})^{2}]]^{\frac{1}{2}}, w = 1/\sigma^{2}(F_{o}^{2}) + (aP)^{2} + bP, \text{ where } P = [\max(P_{o}^{2})^{2}]/3[w(F_{o}^{2})^{2}]^{\frac{1}{2}}, w = 1/\sigma^{2}(F_{o}^{2}) + (aP)^{2} + bP, \text{ where } P = [\max(P_{o}^{2})^{2}]/3[w(F_{o}^{2})^{2}]^{\frac{1}{2}}, w = 1/\sigma^{2}(F_{o}^{2}) + (aP)^{2} + bP, \text{ where } P = [\max(P_{o}^{2})^{2}]/3[w(F_{o}^{2})^{2}]/3[w(F_{o}^{2})^{2}]^{\frac{1}{2}}, w = 1/\sigma^{2}(F_{o}^{2}) + (aP)^{2} + bP, \text{ where } P = [\max(P_{o}^{2})^{2}]/3[w(F_{o}^{2})^{2}]/3[w(F_{o}^{2})^{2}]^{\frac{1}{2}}, w = 1/\sigma^{2}(F_{o}^{2})^{\frac{1}{2}}, w = 1/\sigma^{2}(F_{$				

 Table S1. Crystallographic Data for 1, 2, and 3.

 ${}^{a}R_{1} = 3||F_{o}| - |F_{c}||/3|F_{o}|. {}^{b}wR_{2} = [3[w(F_{o}^{2} - F_{c}^{2})^{2}]/3[w(F_{o}^{2})^{2}]]^{\frac{1}{2}}, w = 1/\sigma^{2}(F_{o}^{2}) + (aP)^{2} + bP, whom F_{o}^{2}) + 2(F_{c}^{2})]/3.$ P = [r

Table S2. Selected bond lengths and angles in molecular structures of 1, 2, and 3.				
	1	2	3	
Ce-C, Å (min-max range)	2.759(2) - 2.827(2)	2.730(2) - 2.794(2)	2.712(4) - 2.825(4)	
Ce-N, Å	2.779(2)	2.621(2)	2.618(3)	
Ce-Fe, Å	3.1546(5)	-	-	
Ce-O, Å (triflate)	-	2.561(1)	2.749(3)	
	-	2.546(1)	2.697(3)	
Ce-O, Å (thf)	2.533(2)	-	2.556(3)	
O-Ce-O, °	-	77.22(4)	76.5(1)	
	-		75.4(1)	
Fe-Ce-O, °	86.67(5)	-	-	

Computational details

The X-ray crystal structure of **1** was imported into Gaussian 09, Revision D.01^{S10} without further optimization (i.e. single point calculations). The BP86^{S11} functional was used, in combination with the 6-311G*^{S12} basis set for the C, H, O, N atoms, and the all-electron correlation consistent basis sets for Ce (cc-pVTZ-DK3)^{S13}, and Fe (cc-pVTZ-DK)^{S14}. The integration grid was set to ultrafine. The Douglas-Kroll-Hess (DKH)^{S15} 2nd order scalar relativistic scheme was applied. Furthermore, both single point calculations and geometry optimizations were performed for **1** with Orca 4.0.0^{S16} utilizing the BP86 functional, with the ZORA^{S17} Hamiltonian, in combination with the ZORA recontracted basis set ^{S18} for Ce (SARC-ZORA-TZVP), Fe, C, N, O, and H (ZORA-def2-TZVP). Topological analysis (Quantum Theory of Atoms in Molecules, QTAIM)^{S19} was performed on the Kohn-Sham orbitals generated from both Gaussian and Orca by employing AIMAll^{S20}. In addition, both single point calculations and geometry optimizations were performed for **1** with the ZORA method for scalar relativistic effects. QTAIM analyses were performed with the adf2aim utility, which is part of the ADF package.

Syntheses.

Synthesis of (thf)PyCp₂Ce-FeCp(CO)₂ (1): The material was prepared as previously described for (PyCp₂Dy-FeCp(CO)₂.^{S23} A solution of KFp (18.1 mg, 84 µmol) in THF (2 ml) and a solution of [(PyCp₂)Ce(μ -OTf)]₂ (50 mg, 84 µmol) in THF (2 ml) were placed in a freezer for 1 hour at -30 °C. The solution of KFp was added dropwise to the solution of [(PyCp₂)Dy(μ -OTf)]₂ and placed in the freezer. Yellow orange block crystals suitable for X-Ray diffraction formed over one week and the solution was decanted off and crystals were dried in a 74.0 % (52.3 mg) yield. IR (solid, cm⁻¹) 1890 (v_{CO}), 1814 (v_{CO}), 1599, 1570, 1418, 1427, 1231, 1170, 1021, 885, 812, 759, 670 Anal. Calcd. For C₂₈H₂₈CeFeNO₃ C, 54.03; H, 4.53; N, 2.25. Found: C, 53.82; H, 4.54; N, 2.22.

Synthesis of $[(PyCp_2)Ce(\mu-OTf)]_2$ (2) : The material was prepared as previously described for $[(PyCp_2)Dy(\mu-OTf)]_2$.^{S1} A 25 ml THF solution of Na₂PyCp₂ (0.5614, 2.01 mmol) was added dropwise to a 25 THF suspension of Ce(OTf)₃ (2.00 mmol, 1.175 g). The reaction was occasionally stirred manually for 2 h in a cold well at -30 °C and warmed to room temperature. After 2 d of stirring, the THF was removed and replaced with DCM (30 ml) and left to stir overnight. The solution was filtered and hexanes (50 ml) was slowly added to the filtrate and left overnight. The product was collected as golden yellow plate crystals in a 40.3 % (0.421 g) yield as golden yellow plate crystals. Anal. Calcd. For C₃₆H₃₀Ce₂F₆N₂O₆S₂ C, 41.38; H, 2.89; N 2.68. Found: C, 41.11; H, 2.94; N, 2.58.

Synthesis of $[(PyCp_2)Ce(thf)(OTf)]$ (3): The material was prepared as previously described for $[(PyCp_2)Dy(thf)(OTf)]$.^{S1} Approximately 50 mg of **2** was dissolved in 2 ml of THF and layered with 5 ml of hexanes and placed in a freezer (-30 °C) overnight. The resulting bright yellow block crystals were collected for further characterization. Close to quantitative yields were obtained. Anal. Calcd. For $C_{22}H_{23}CeF_3NO_4S$ C, 44.44; H, 3.90; N, 2.36. Found: C, 44.32; H, 3.94; N, 2.29.



Fig. S1 Cyclic voltammogram of **3** at scan rates 100-2000 mVs⁻¹ in a THF solution. Potentials were referenced to Fc/Fc^+ couple with 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte with an analyte concentration of 1 mM.



Fig. S2 ⁵⁷Fe Mössbauer spectra of **1** at 4.6 K. Black dots are experimental points. Red line corresponds to fit using parameter discussed in the text.



Fig. S3 Infrared spectrum of 1.



Fig. S4 Temperature dependence of $\chi_M T$ at 1000 Oe field for 1.



Fig. S5 Temperature dependence of $\chi_M T$ at 1000 Oe field for 2.



Fig. S6 Temperature dependence of $\chi_M T$ at 1000 Oe field for **3**.



Fig. S7 Plot of Magnetization Vs. Field at 8-1.8 K for 1.



Fig. S8 Plot of Magnetization Vs. Field at 8-1.8 K for 2.



Fig. S9 Plot of Magnetization Vs. Field at 8-1.8 K for 3.



Fig. S10 Plot of Magnetization Vs. H/T at 8-1.8 K for 1.



Fig. S11 Plot of Magnetization Vs. H/T at 8-1.8 K for 2.



Fig. S12 Plot of Magnetization Vs. H/T at 8-1.8 K for 3.



Fig. S13 In phase (χ_m) component of the ac susceptibility of 1 under varying dc fields at 3 K.



Fig. S14 Out of phase (χ_m) component of the ac susceptibility of 1 under varying dc fields at 3 K.



Fig. S15 In phase (χ_m) component of the ac susceptibility of 2 under varying dc fields at 3 K.



Fig. S16 Out of phase (χ_m) component of the ac susceptibility of 2 under varying dc fields at 3 K.



Fig. S17 In phase (χ_m) component of the ac susceptibility of 3 under varying dc fields at 3 K.



Fig. S18 Out of phase (χ_m) component of the ac susceptibility of 3 under varying dc fields at 3 K.



Fig. S19 Variable field Cole-Cole plot at 3 K for 1; open circles are experimental data and lines are fits to the generalized Debeye equation.



Fig. S20 Variable field Cole-Cole plot at 3 K for **2**; open circles are experimental data and lines are fits to the generalized Debeye equation.



Fig. S21 Variable field Cole-Cole plot at 3 K for **3** open circles are experimental data and lines are fits to the generalized Debeye equation.



Fig. S22 Field dependence of τ for 1 at 3 K. Red line corresponds to best fit result according to $\tau^{-1} = AH^4T + \frac{B_1}{1 + B_2H^2} + D.$ equation,







Fig. S24 Field dependence of τ for 3 at 3 K. Red line corresponds to best fit result according to B_1

$$\tau^{-1} = AH^4T + \frac{D_1}{1 + B_2H^2} + D.$$

equation,



Fig. S25 In phase (χ_m) component of the ac susceptibility of 1 under varying temperatures at 500 Oe.



Fig. S26 In phase (χ_m') component of the ac susceptibility of 2 under varying temperatures at 1500 Oe.



Fig. S27 In phase (χ_m) component of the ac susceptibility of 3 under varying temperatures at 4000 Oe.



Fig. S28 Out of phase (χ_m'') component of the ac susceptibility of 2 under varying temperatures at 1500 Oe.



Fig. S29 Out of phase (χ_m) component of the ac susceptibility of 3 under varying temperatures at 4000 Oe



Fig. S30 Variable temperature Cole-Cole plot for 1 under 500 Oe field; open circles are experimental data and lines are fits to the generalized Debeye equation.



Fig. S31 Variable temperature Cole-Cole plot for 2 under 1500 Oe field; open circles are experimental data and lines are fits to the generalized Debeye equation.



Fig. S32 Variable temperature Cole-Cole plot for 3 under 4000 Oe field; open circles are experimental data and lines are fits using CC fit software.



Fig. S33 Arrhenius plot for **1** (red), **2** (blue), and **3** (green), fitting solely to the linear region to an Orbach process. Open circles represent experimental data and the lines correspond to fit.

Calculation	Gaussian Single	Orca Single	Orca Full	ADF Single Point	ADF Full
	Point	Point	Optimization		Optimization
D(Ce-lcp), Å	1.60	1.60	1.60	1.60	1.60
D(Fe-lcp), Å	1.55	1.55	1.55	1.55	1.54
DI	0.3541	0.3424	0.3424	0.3549	0.3626
ρ(lcp) ^a	0.028	0.028	0.028	0.028	0.029
$\nabla^2 \rho (lcp)^b$	0.030	0.026	0.027	0.029	0.031
G (lcp) ^c	0.012	0.011	0.012	0.012	0.013
V (lcp) ^d	-0.016	-0.016	-0.016	-0.017	-0.018
H(lcp) ^e	-0.004	-0.005	-0.004	-0.005	-0.005

 Table S3. Computational analysis of 1.

^aρ (lcp): Electron density at line critical point / (e/bohr^3)

 ${}^{b}\nabla^{2}\rho$ (lcp): Laplacian of electron density (e/bohr^5)

^cG (lcp) Lagrangian form of kinetic energy density (hartree/bohr^3)

^dV (lcp) Virial Field=Potential energy density (hartree/bohr^3)

^eH (lcp) Electronic energy density (hartree/bohr^3)

Table S4. Parameters obtained from fitting the field dependence of τ for compounds 1, 2, and 3.

Compound	1	2	3
A, s ⁻¹ K ⁻¹ T ⁻⁴	14553	6076	621
$B_1 s^{-1}$	1224	3791	1296
B ₂ , T ⁻²	39975	3624	114
D, s ⁻¹	700	2628	1696

Table S5. Parameters obtained from fitting of the Arrhenius plots for compounds 1, 2, and 3. A, B_1 , B_2 , and n_2 were held at fixed values.

Compound	1	2	3
A, s ⁻¹ K ⁻¹ T ⁻⁴	14553	6076	621
C, s ⁻¹ K ⁻⁵	1.86	8.41	6.41
τ _{OTM} , s	0.083	0.022	0.015
τ^{-1}_{OTM} , s ⁻¹	12.1	46	68
n ₂ ,	5	5	5
U _{eff} , cm ⁻¹	29	28	38
τ_0 , s	3.50·10 ⁻⁹	3.02.10-9	1.66.10-10

References

S1 (a) G. Paolucci, J. Zanon, V. Lucchini, W. E. Damrau, E. Siebel, D. R. Fischer, J.
Organomet. Chem., 1994, 471, 97-104; (b) C. P. Burns, B. O. Wilkins, C. M. Dickie, T. P.

Latendresse, L. Vernier, K. R. Vignesh, N. S. Bhuvanesh, M. Nippe, *Chem. Commun.* 2017, **53**, 8419-8422.

- S2 J. S. Plotkin, S. G. Shore, *Inorg. Chem.*, 1981, **20**, 284-285.
- S3 XT, XS, BRUKER AXS Inc., 5465 East Cheryl Parkway, Madison, WI, USA, pp. 53711–
 5373.
- S4 APEX2 Program for Data Collection on Area Detectors, BRUKER AXS Inc., 5465 East Cheryl Parkway, Madison, WI, USA, pp. 53711–5373.
- G. M. Sheldrick, *SADABS*, "Program for Absorption Correction of Area Detector Frames",
 BRUKER AXS Inc., 5465 East Cheryl Parkway, Madison, WI 53711-5373 USA.
- S6 (a) G. M. Sheldrick, Acta. Cryst., 2008, A64, 112-122.; (2008); (b) G. M. Sheldrick, Acta.

Cryst. 2015, A71, 3-8; (c) G. M. Sheldrick, Acta Cryst., 2015, C71, 3-8.

- S7 A. L. Spek, J. Appl. Cryst. 2003, 36, 7-13.
- S8 A. L. Spek, "PLATON A Multipurpose Crystallographic Tool" Utrecht University, The Netherlands, 2008
- S9 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. J. Puschmann, *J. Appl. Cryst.* 2009, **42**, 339-341.
- S10 Gaussian 09, Revision D.01, M. J. Frisch et al., Gaussian, Inc., Wallingford CT, 2009.
- S11 (a) J. P. Perdew, Phys. Rev. B 1986, 33, 8822-8824; (b) A. D. Becke, *Phys. Rev. A*, 1988, 38, 3098-3100.
- S12 K. Raghavachari, J. S. Binkley, R. Seeger, and J. A. Pople, J. Chem. Phys., 1980, 72, 650-654.
- S13 Q. Lu and K. A. Peterson, J. Chem. Phys., 2016, 145, 054111-1-054111-13.
- S14 N. Balabanov, K. A. Peterson, J. Chem. Phys., 2005, 123, 064107-1-064107-15.

- S15 (a) M. Douglas, N. M. Kroll, Ann. Phys., 1974, 82, 89-155. (b) B. A. Hess, Phys. Rev. A, 1986, 33, 3742-3748.
- S16 ORCA 4.0.0, WIREs Comput Mol Sci 2018, 8:e1327.
- S17 E. van Lenthe, E. J. Baerends, J. G. Snijders, J. Chem. Phys., 1993, 99, 4597-4610.
- S18 D. A. Pantazis, X. Y. Chen, C. R. Landis, F. Neese, *J. Chem. Theory Comput.*, 2008, 4, 908-919.
- S19 R. F. W. Bader, Chem. Rev., 1991, 91, 893–928.
- S20 AIMAII, Version 17.01.25; Keith, T. A. TK Gristmill Software: Overland Park KS, 2017.
- S21 (a) G.te Velde, F.M. Bickelhaupt, E.J. Baerends, C. Fonseca Guerra, S.J.A. van Gisbergen, J.G. Snijders, T. Ziegler, *J. Comput. Chem.*, 2001, 22, 931-967; (b) C. Fonseca Guerra, J.G. Snijders, G. te Velde and E.J. Baerends, *Theor. Chem. Acc.*, 1998, 99, 391-403; (c) ADF2017, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, http://www.scm.com.
- S22 E. van Lenthe, E. J. Baerends, J. Comput. Chem., 2003, 24, 1142–1156.
- S23 C. P. Burns, X. Yang, J. D. Wofford, N. S. Bhuvanesh, M. B. Hall, M. Nippe, *Angew*, *Chem. Int. Ed.*, 2018, **57**, 1-6.