Electronic Supplementary Material (ESI) for Dalton Transactions.

A Homoleptic η^2 Hydroxylaminato Ce^{IV} Complex with S_4 Symmetry

Walter L. Dorfner, Patrick J. Carroll, Eric J. Schelter*

P. Roy and Diana T. Vagelos Laboratories, Department of Chemistry, University of Pennsylvania, 231 South 34th Street, Philadelphia, Pennsylvania 19104

E-mail: schelter@sas.upenn.edu

Electronic Supplementary Information

Experimental Procedures

General Methods. All reactions and manipulations were performed under an inert atmosphere (N_2) using standard Schlenk techniques or in a Vacuum Atmospheres, Inc. Nexus II drybox equipped with a molecular sieves 13X / Q5 Cu-0226S catalyst purifier system. Glassware was oven-dried overnight at 150 °C prior to use. ^1H NMR were obtained on a Bruker DMX-300 Fourier transform NMR spectrometer at 300 MHz. Chemical shifts were recorded in units of parts per million downfield from residual proteo solvent peaks (^1H). Elemental analyses were performed at the University of California, Berkeley Microanalytical Facility using a Perkin-Elmer Series II 2400 CHNS analyzer. UV-Vis data were collected on a Cary 5000 spectrometer in toluene in 1 mm path length air-free quartz cuvettes. The infrared spectra were obtained from 400–4000 cm^{-1} using a Perkin Elmer 1600 series infrared spectrometer.

Materials. Et_2O, CH_2Cl_2, hexanes, pentane, and toluene were purchased from Fisher Scientific. These solvents were sparged for 30 min with dry argon and dried using a commercial two-column solvent purification system comprising columns packed with Q5 reactant and neutral alumina respectively (for hexanes and pentane), or two columns of neutral alumina (for Et_2O and CH_2Cl_2). All solvents were stored over 3 Å molecular sieves. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc. and stored over 3 Å molecular sieves overnight prior to use. 2-Bromo-4-*tert*-butylanisole was prepared according to a literature procedure.[1] $Ce[N(SiMe_3)_2]_3$ was also prepared according to a published procedure.[2] PbO_2 and a 1.6 M ^{n}BuLi solution in hexanes were used as received from Acros Organics. 2-Methyl-2-nitrosopropane was prepared by a modified procedure.[3]

X-Ray Crystallography. X-ray intensity data were collected on a Bruker APEXII CCD area detector employing graphite-monochromated Mo-Kα radiation (λ=0.71073 Å) at a temperature of 143(1) K. In all cases, rotation frames were integrated using SAINT,[5] producing a listing of unaveraged F^2 and $\sigma(F^2)$ values which were then passed to the SHELXTL[6] program package for further processing and structure solution on a Dell Pentium 4 computer. The intensity data were corrected for Lorentz and polarization effects and for absorption using TWINABS[7] or SADABS.[8] The structures were solved by direct methods (SHELXS-97).[9] Refinement was by full-matrix least squares based on F^2 using SHELXL-97.[9] All reflections were used during refinements. The weighting scheme used was $w=1/[\sigma^2(F_o^2)+ (0.0907P)^2 + 0.3133P]$ where $P = (F_o^2 + 2F_c^2)/3$. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a riding model.

Electrochemistry. Voltammetry experiments (CV) were performed using a CH Instruments 620D Electrochemical Analyzer/Workstation and the data were processed using CHI software v9.24. All experiments were performed in an N_2 atmosphere drybox using electrochemical cells that consisted of a 4 mL vial, glassy carbon working electrode, a platinum wire counter electrode, and a silver wire plated with AgCl as a quasi-reference electrode. The working electrode surfaces were polished prior to each set of experiments. Potentials were reported versus ferrocene, which was added as an internal standard for calibration at the end of each run. Solutions employed during these studies were ~3 mM in analyte and 100 mM in $[^{n}Bu_4N][PF_6]$ for **LH** or $[^{n}Pr_4N][BAr^F]$ for **1** in 2 mL of acetonitrile. All data were collected in a positive-feedback IR compensation mode.

Synthetic Details and Characterization.

Synthesis of 2-(*tert*-butylhydroxylamino)-4-*tert*-butylanisole (LH). The synthesis of **LH** was accomplished by modifying a related procedure.[4] A 250 mL Schlenk flask was charged in an inert atmosphere glovebox with 2-bromo-4-*tert*-butylanisole (1.29 g, 5.30 mmol, 1.00 equiv) and 80 mL of Et_2O. The flask was cooled to –78 °C under inert atmosphere on a Schlenk line. A 1.6 M solution of ^{n}BuLi in hexanes (4.0 mL, 6.4 mmol, 1.2 equiv) was added dropwise to the solution using a syringe and the resulting pale yellow solution was stirred for 2 h. A flask was charged in a glovebox with 2-methyl-2-nitrosopropane (0.920 g, 10.6 mmol, 2.00 equiv) and 20 mL of Et_2O. The blue solution of 2-methyl-2-nitrosopropane was cooled to –78 °C on a Schlenk line and was added *via* cannula transfer into the solution of lithiated starting material. The resulting green solution was stirred for 2 h at –78 °C. The solution was warmed slowly to RT and a degassed, saturated solution of NH_4Cl was added (30 mL) to quench the reaction. The aqueous layer was removed, and the organic layer was washed with distilled water. The aqueous layer was again removed, and the organic volatiles were removed under reduced pressure. The resulting yellow solid was brought into a dry box. The solid was then suspended in 10 mL of hexanes and was collected by filtration over a medium porosity fritted filter, and washed with 20 more mL of hexanes. The solid was washed with hexanes to remove any unreacted starting material, resulting in an off-white solid. Air stable, X-ray diffraction quality crystals were grown from toluene layered with hexanes in the freezer. Yield 0.77 g, 3.1 mmol, 58 %; ^{1}H NMR (300 MHz, pyridine-d_5) δ 10.02 (s, 1H, OH), 8.09 (d, J = 2.7 Hz, 1H), 7.22 (dd, J = 8.4, 2.7 Hz, 1H), 6.95 (d, J = 8.4 Hz, 1H), 3.76 (s, 3H), 1.43 (s, 9H), 1.33 (s, 9H); ^{13}C NMR (75 MHz, pyridine-

d_5) δ 153.3, 143.4, 140.9, 125.4, 123.2, 112.6, 61.5, 56.2, 34.7, 32.1, 26.4 ppm. ESI-MS *m/z*: calcd. for $[C_{15}H_{26}NO_2]^+$: 252.1964; found, 252.1972.

Synthesis of Ce[η²-ON(ᵗBu)(2-OMe-5-ᵗBu-C₆H₃)]₄ (1). **LH** (50. mg, 0.20 mmol, 1.0 equiv) was dissolved in toluene. Solid PbO_2 (285 mg, 1.19 mmol, 6.0 equiv) was added, and the solution turned dark red and was stirred for 12 h. The solution was filtered through a Celite packed coarse porosity fritted filter to give a clear red solution, to which **LH** (150. mg, 0.597 mmol, 3.0 equiv) was added. To this mixture, a yellow solution of $Ce[N(SiMe_3)_2]_3 \cdot C_7H_8$ (142 mg, 0.20 mmol, 1.0 equiv) in toluene was added dropwise. The resulting dark red solution was stirred for 10 minutes and volatiles were removed under reduced pressure to yield a dark red solid. This solid was dissolved in hexanes, filtered, and volatiles were again removed to yield a red powder. X-ray diffraction quality crystals were grown from slow evaporation of pentane at –25 °C. Yield 206 mg, 0.181 mmol, 90.5%; ^{1}H NMR (300 MHz, benzene-*d_6*) δ 7.50 (s, 4H, Ar), 7.11 (d, *J* = 2.4 Hz, 4H, Ar), 6.73 (d, *J* = 8.7 Hz, 4H, Ar), 3.68 (s, 12H, OMe), 1.38 (s, 36H, ᵗBu), 1.19 (s, 36H, ᵗBu); ^{13}C NMR (75 MHz, benzene-*d_6*) δ 153.0, 141.7, 140.8, 125.4, 123.0, 110.3, 64.9, 55.5, 34.6, 32.3, 26.9. Elemental analysis found (calculated) for $C_{60}H_{96}N_4O_8Ce$: C, 63.27 (63.13); H, 8.31 (8.48); N, 4.84 (4.91)

Figure S1: ^{1}H NMR Spectra of **LH** in d^5-pyridine

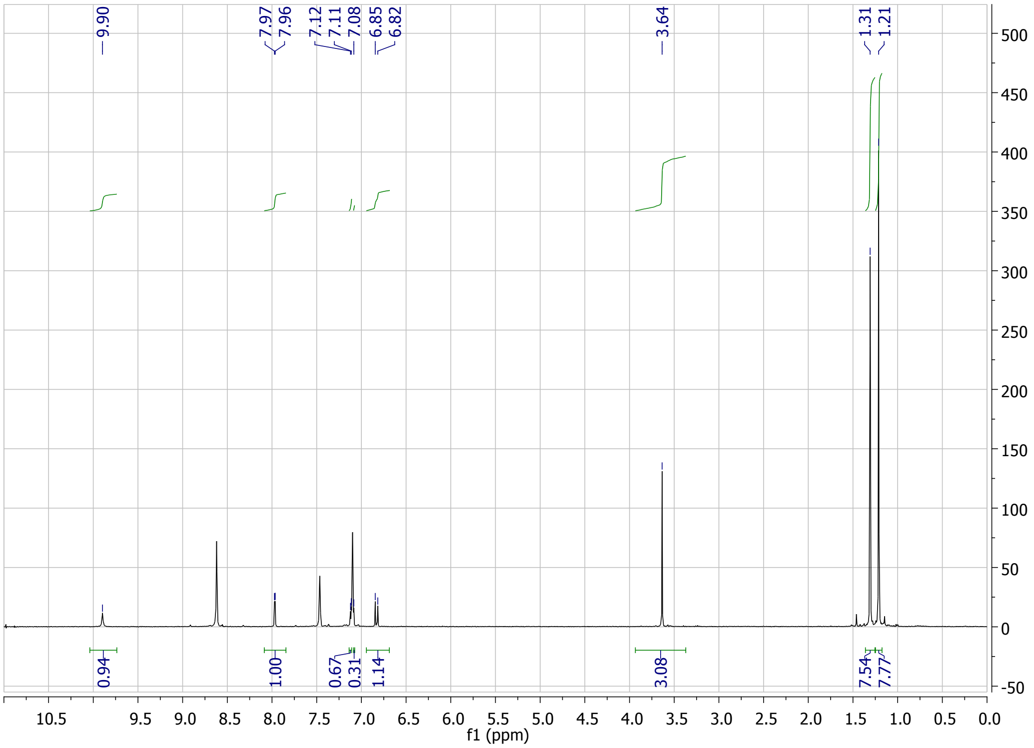


Figure S2: ^{1}H NMR Spectra of **L•** in d^6-benzene

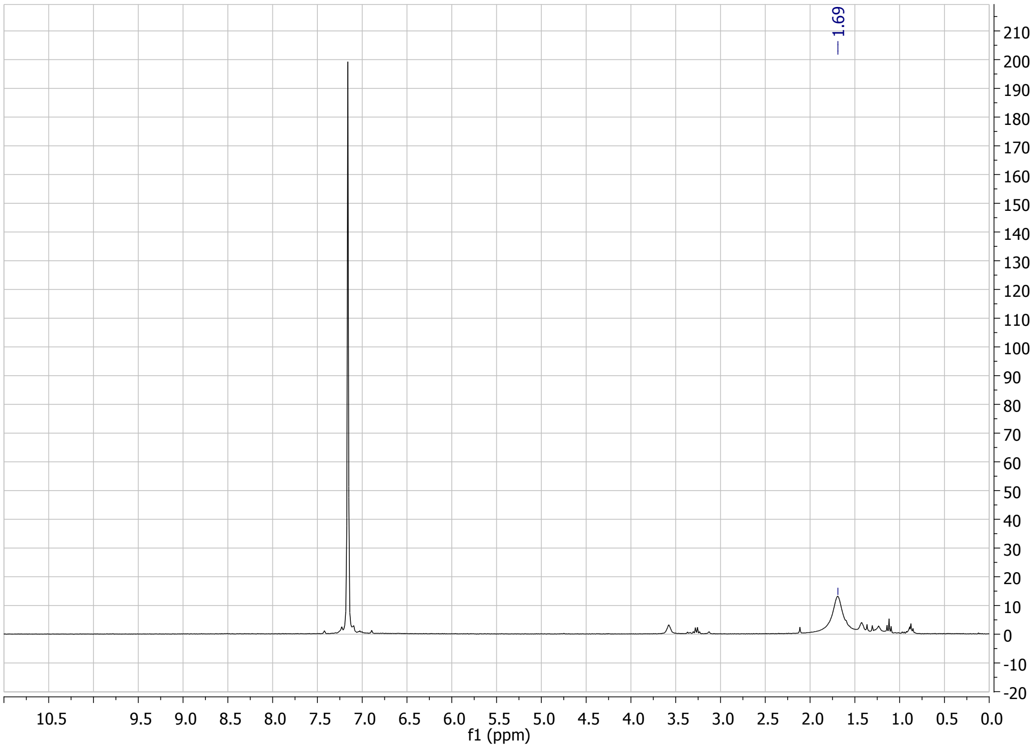


Figure S3: ^{1}H NMR Spectra of **1** in *d*^{6}-benzene

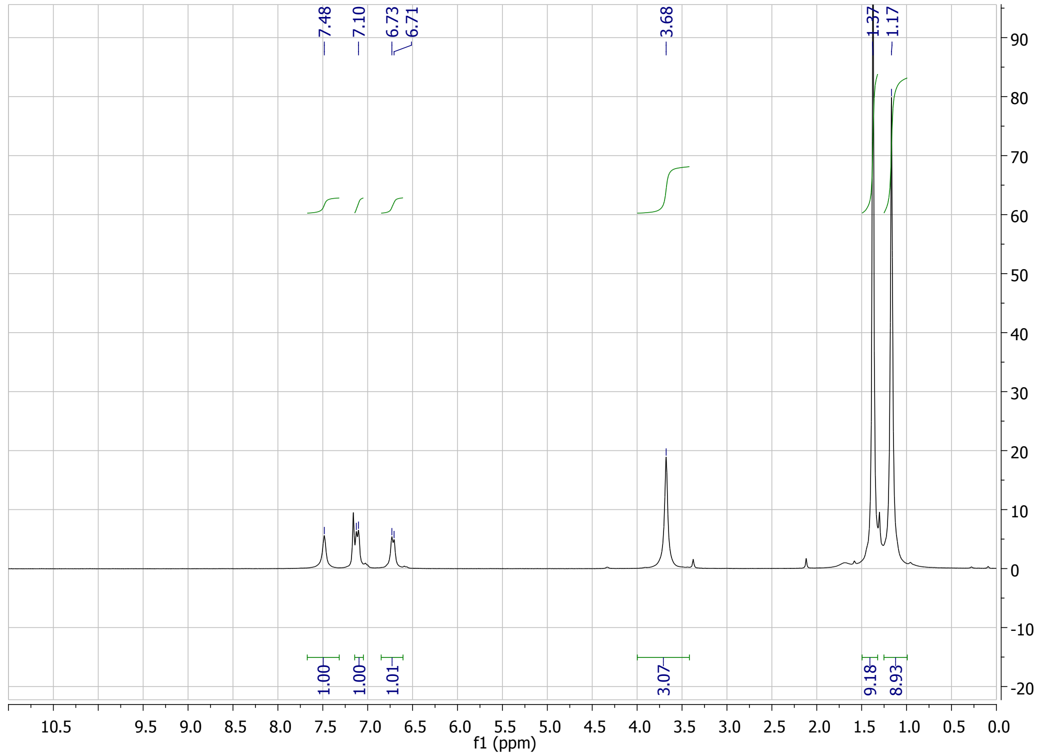


Figure S4: CV of **1** in ACN (50 mV/s)

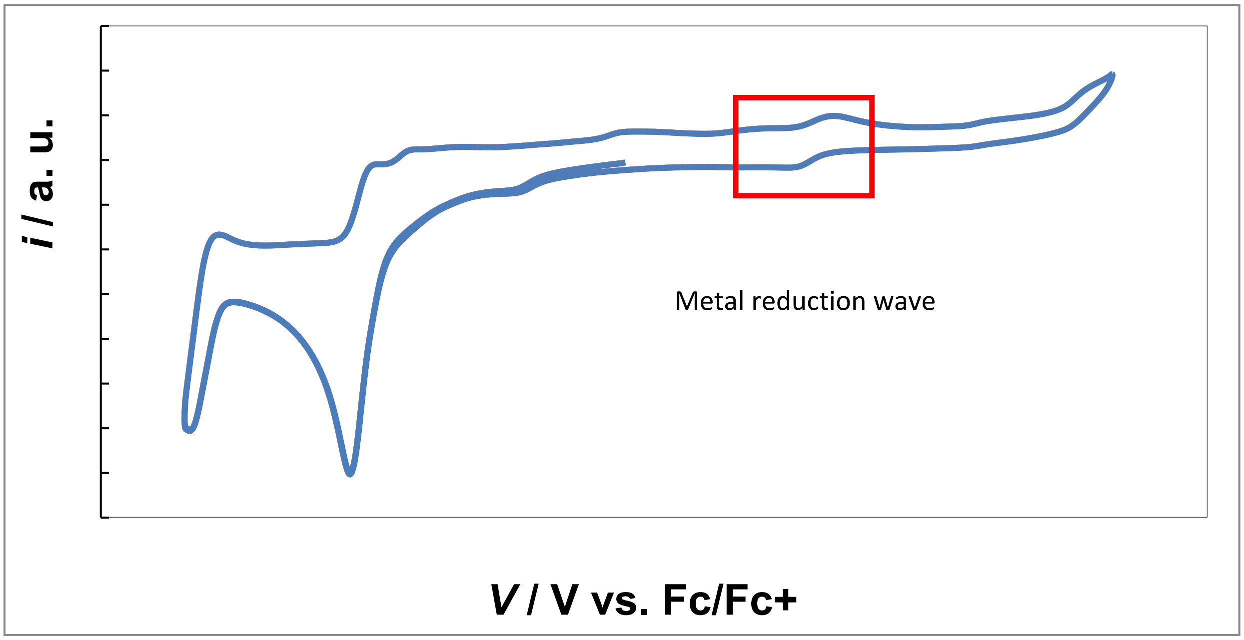
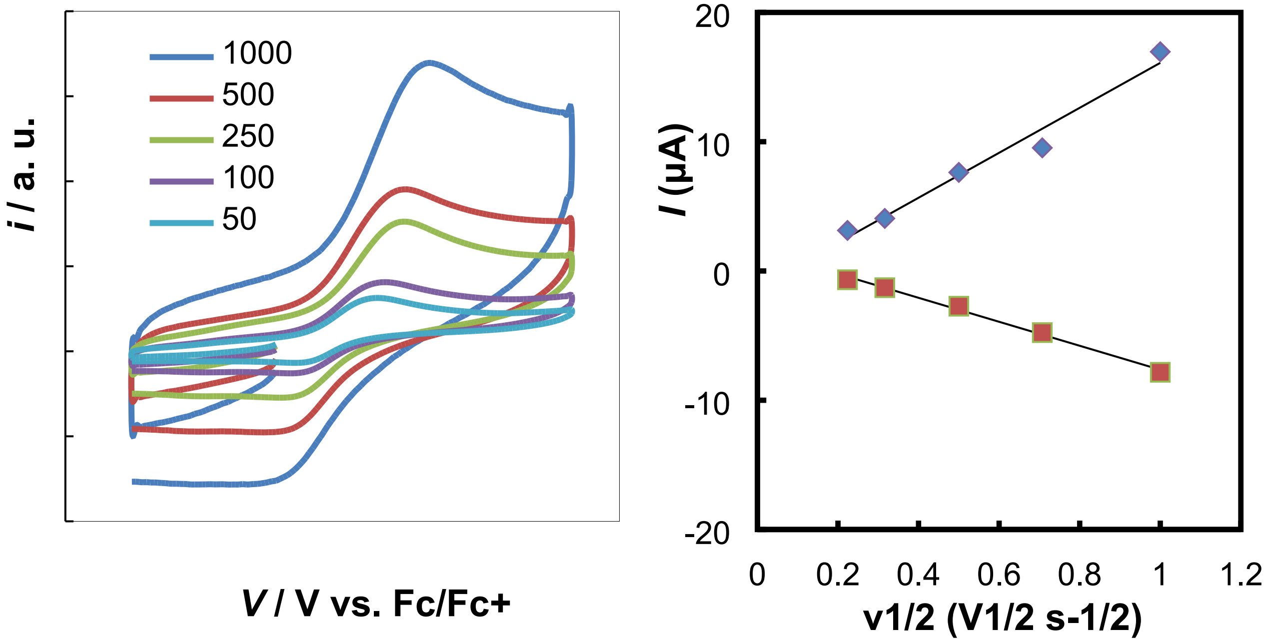


Figure S5: Scan rate dependence of **1** in ACN with Randles-Sevcik plot.



Computational Details. Geometry optimizations were completed using Gaussian 09 Revision C.01.[5] The B3LYP hybrid DFT method was employed, with a 28-electron small core pseudopotential on cerium with published segmented natural orbital basis set incorporating quasi-relativistic effects[6,7], and the 6-31G* basis set on all other atoms. Initial coordinates for the geometry optimization of **1** were taken from the crystal structure. A frequency calculation at the same level of theory confirmed that the geometry was a minimum and returned no negative frequencies. MO's were rendered with the program Chemcraft v1.6.[8] The program AOMix[9,10] was used to characterize atomic orbital contributions and mayer bond orders using fragment molecular orbital analysis. Fragments used were 1 – Ce and 2 – [η^2-ON(^{t}Bu)(2-OMe-C_6H_4)]$_4$.

Figure S6. Optimized geometry of 2-(*tert*-butylhydroxylamino)-4-*tert*-butylanisole (**LH**)

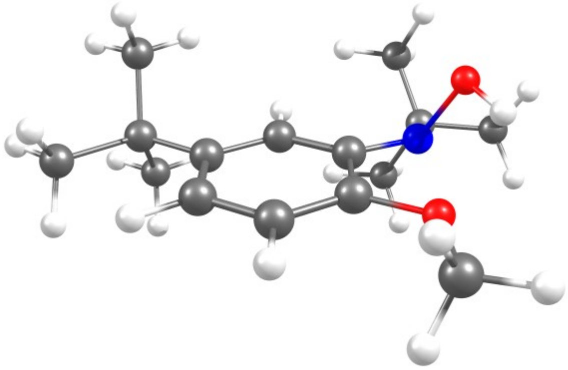


Table S1. Optimized coordinates of 2-(*tert*-butylhydroxylamino)-4-*tert*-butylanisole (**LH**)

6	-1.101642000	0.789485000	-0.363644000
6	-0.425864000	-0.392223000	-0.028907000
6	-1.117393000	-1.568924000	0.257319000
6	-2.525469000	-1.519040000	0.204342000
6	-3.232837000	-0.369012000	-0.148865000
6	-2.490227000	0.810817000	-0.434938000
7	-4.644814000	-0.248623000	-0.284175000
8	-3.227142000	1.915018000	-0.774896000
6	-2.533162000	3.120219000	-1.089711000
8	-5.120164000	0.666987000	0.739180000

6	-0.416310000	-2.886245000	0.639095000
6	1.117854000	-2.745809000	0.647545000
6	-0.791131000	-3.989048000	-0.379649000
6	-0.865120000	-3.325612000	2.053429000
6	-5.598326000	-1.382016000	-0.393318000
6	-6.947991000	-0.764939000	-0.820216000
6	-5.134049000	-2.312080000	-1.530064000
6	-5.806927000	-2.154018000	0.928330000
1	-0.525486000	1.681771000	-0.579675000
1	0.657348000	-0.364527000	0.002505000
1	-3.083312000	-2.411768000	0.449228000
1	-3.303997000	3.849752000	-1.341709000
1	-1.953226000	3.482781000	-0.232695000
1	-1.865869000	2.981881000	-1.948524000
1	-5.077949000	1.519230000	0.269941000
1	1.454124000	-1.995541000	1.372231000
1	1.573134000	-3.702698000	0.926446000
1	1.507389000	-2.467946000	-0.338481000
1	-1.869747000	-4.179594000	-0.398911000
1	-0.292866000	-4.931558000	-0.121449000
1	-0.481139000	-3.707250000	-1.392728000
1	-0.379241000	-4.269062000	2.330968000
1	-0.594675000	-2.571348000	2.801637000
1	-1.947948000	-3.480928000	2.109307000
1	-7.327663000	-0.083222000	-0.056050000
1	-6.833371000	-0.207647000	-1.756452000
1	-7.687349000	-1.557642000	-0.977059000
1	-4.222807000	-2.865190000	-1.294316000
1	-4.957650000	-1.736853000	-2.445530000
1	-5.922649000	-3.043628000	-1.734895000
1	-6.606656000	-2.893206000	0.806299000
1	-6.101163000	-1.464191000	1.724891000
1	-4.911280000	-2.689427000	1.255082000

Figure S7. Optimized geometry of Ce[η^2-ON(^{t}Bu)(2-OMe-C_6H_4)]$_4$ (**1′**)

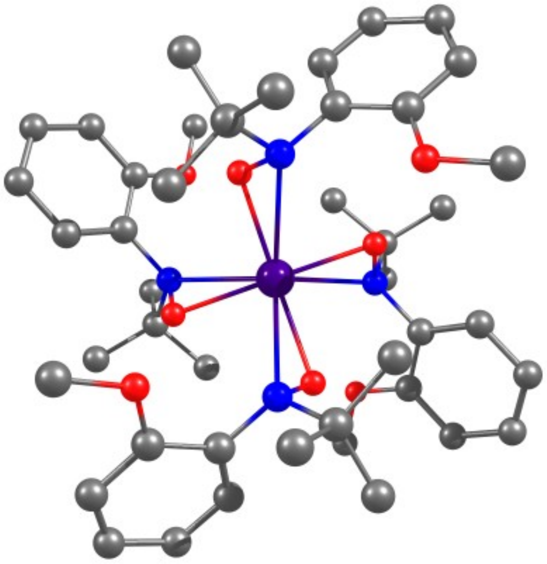


Table S2. Optimized coordinates of Ce[η^2-ON(^{t}Bu)(2-OMe-C_6H_4)]$_4$ (**1′**)

58	0.000000000	0.000000000	0.000000000
8	1.357698000	-1.713847000	0.394603000
8	2.989794000	1.057771000	2.824749000
7	1.900353000	-1.172474000	1.589297000
6	3.279528000	-0.782697000	1.356910000
6	4.083648000	-1.488847000	0.457972000
6	5.404171000	-1.111473000	0.203525000
6	5.934734000	0.000000000	0.855171000
6	5.144719000	0.734664000	1.743506000
6	3.816196000	0.361712000	1.993178000
6	3.502523000	2.211138000	3.483012000
6	1.713792000	-2.188820000	2.716035000
6	2.307739000	-1.641264000	4.022656000
6	0.209273000	-2.411761000	2.913237000
6	2.387039000	-3.529761000	2.364936000
8	1.713847000	1.357698000	-0.394603000
8	-1.057771000	2.989794000	-2.824749000
7	1.172474000	1.900353000	-1.589297000
6	0.782697000	3.279528000	-1.356910000
6	1.488847000	4.083648000	-0.457972000
6	1.111473000	5.404171000	-0.203525000
6	0.000000000	5.934734000	-0.855171000

6	-0.734664000	5.144719000	-1.743506000
6	-0.361712000	3.816196000	-1.993178000
6	-2.211138000	3.502523000	-3.483012000
6	2.188820000	1.713792000	-2.716035000
6	1.641264000	2.307739000	-4.022656000
6	2.411761000	0.209273000	-2.913237000
6	3.529761000	2.387039000	-2.364936000
8	-1.357698000	1.713847000	0.394603000
8	-2.989794000	-1.057771000	2.824749000
7	-1.900353000	1.172474000	1.589297000
6	-3.279528000	0.782697000	1.356910000
6	-4.083648000	1.488847000	0.457972000
6	-5.404171000	1.111473000	0.203525000
6	-5.934734000	0.000000000	0.855171000
6	-5.144719000	-0.734664000	1.743506000
6	-3.816196000	-0.361712000	1.993178000
6	-3.502523000	-2.211138000	3.483012000
6	-1.713792000	2.188820000	2.716035000
6	-2.307739000	1.641264000	4.022656000
6	-0.209273000	2.411761000	2.913237000
6	-2.387039000	3.529761000	2.364936000
8	-1.713847000	-1.357698000	-0.394603000
8	1.057771000	-2.989794000	-2.824749000
7	-1.172474000	-1.900353000	-1.589297000
6	-0.782697000	-3.279528000	-1.356910000
6	-1.488847000	-4.083648000	-0.457972000
6	-1.111473000	-5.404171000	-0.203525000
6	0.000000000	-5.934734000	-0.855171000
6	0.734664000	-5.144719000	-1.743506000
6	0.361712000	-3.816196000	-1.993178000
6	2.211138000	-3.502523000	-3.483012000
6	-2.188820000	-1.713792000	-2.716035000
6	-1.641264000	-2.307739000	-4.022656000
6	-2.411761000	-0.209273000	-2.913237000
6	-3.529761000	-2.387039000	-2.364936000
1	3.645411000	-2.334858000	-0.057335000
1	6.006839000	-1.683109000	-0.496578000
1	6.960313000	0.310132000	0.674171000

1	5.565597000	1.606068000	2.230702000
1	3.822329000	2.975598000	2.764301000
1	2.678176000	2.600563000	4.081461000
1	4.343194000	1.957543000	4.140390000
1	1.853681000	-0.687030000	4.299387000
1	2.113639000	-2.364065000	4.822854000
1	3.390953000	-1.503398000	3.955786000
1	-0.254961000	-2.817034000	2.011248000
1	0.050941000	-3.124431000	3.730647000
1	-0.298541000	-1.478666000	3.177687000
1	3.474169000	-3.428290000	2.287934000
1	2.174400000	-4.262983000	3.151015000
1	2.004564000	-3.918819000	1.417641000
1	2.334858000	3.645411000	0.057335000
1	1.683109000	6.006839000	0.496578000
1	-0.310132000	6.960313000	-0.674171000
1	-1.606068000	5.565597000	-2.230702000
1	-1.957543000	4.343194000	-4.140390000
1	-2.600563000	2.678176000	-4.081461000
1	-2.975598000	3.822329000	-2.764301000
1	1.503398000	3.390953000	-3.955786000
1	2.364065000	2.113639000	-4.822854000
1	0.687030000	1.853681000	-4.299387000
1	1.478666000	-0.298541000	-3.177687000
1	3.124431000	0.050941000	-3.730647000
1	2.817034000	-0.254961000	-2.011248000
1	3.918819000	2.004564000	-1.417641000
1	4.262983000	2.174400000	-3.151015000
1	3.428290000	3.474169000	-2.287934000
1	-3.645411000	2.334858000	-0.057335000
1	-6.006839000	1.683109000	-0.496578000
1	-6.960313000	-0.310132000	0.674171000
1	-5.565597000	-1.606068000	2.230702000
1	-3.822329000	-2.975598000	2.764301000
1	-2.678176000	-2.600563000	4.081461000
1	-4.343194000	-1.957543000	4.140390000
1	-1.853681000	0.687030000	4.299387000
1	-2.113639000	2.364065000	4.822854000

1	-3.390953000	1.503398000	3.955786000
1	0.254961000	2.817034000	2.011248000
1	-0.050941000	3.124431000	3.730647000
1	0.298541000	1.478666000	3.177687000
1	-3.474169000	3.428290000	2.287934000
1	-2.174400000	4.262983000	3.151015000
1	-2.004564000	3.918819000	1.417641000
1	-2.334858000	-3.645411000	0.057335000
1	-1.683109000	-6.006839000	0.496578000
1	0.310132000	-6.960313000	-0.674171000
1	1.606068000	-5.565597000	-2.230702000
1	1.957543000	-4.343194000	-4.140390000
1	2.600563000	-2.678176000	-4.081461000
1	2.975598000	-3.822329000	-2.764301000
1	-1.503398000	-3.390953000	-3.955786000
1	-2.364065000	-2.113639000	-4.822854000
1	-0.687030000	-1.853681000	-4.299387000
1	-1.478666000	0.298541000	-3.177687000
1	-3.124431000	-0.050941000	-3.730647000
1	-2.817034000	0.254961000	-2.011248000
1	-3.918819000	-2.004564000	-1.417641000
1	-4.262983000	-2.174400000	-3.151015000
1	-3.428290000	-3.474169000	-2.287934000

References

(1) Del Rosso, P. G.; Almassio, M. F.; Garay, R. O. *Tetrahedron Lett.* **2011**, *52*, 4911–4915.

(2) Bradley, D. C.; Ghotra, J. S.; Hart, F. A. *J. Chem. Soc. Dalton Trans.* **1973**, 1021–1023.

(3) Stowell, J. C. *J. Org. Chem.* **1971**, *36*, 3055–3056.

(4) Osanai, K.; Okazawa, A.; Nogami, T.; Ishida, T. *J. Am. Chem. Soc.* **2006**, *128*, 14008–14009.

(5) Gaussian 09, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A.

J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.

(6) Cao, X.; Dolg, M. *J. Mol. Struct. THEOCHEM* **2002**, *581*, 139–147.

(7) Dolg, M.; Stoll, H.; Preuss, H. *J. Chem. Phys.* **1989**, *90*, 1730–1734.

(8) Grigoriy, D. A. Z.; Zhurko, A. http://chemcraftprog.com/.

(9) Gorelsky, S. I. *AOMix: Program for Molecular Orbital Analysis*; 2013.

(10) Gorelsky, S. I.; Lever, A. B. P. *J. Organomet. Chem.* **2001**, *635*, 187–196.