

Trivalent [(C₅Me₅)₂(THF)Ln]₂(μ-η²:η²-N₂) Complexes as Reducing Agents Including the Reductive Homologation of CO to a Ketene Carboxylate, (μ-η⁴-O₂C—C=C=O)²⁻

William J. Evans,* David S. Lee, Joseph W. Ziller, and Nikolas Kaltsoyannis

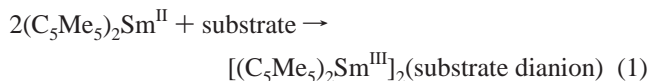
Contribution from the Departments of Chemistry, University of California, Irvine, California 92697-2025, and University College London, 20 Gordon Street, London WC1H 0AJ, U.K.

Received June 9, 2006; E-mail: wevans@uci.edu; n.kaltsoyannis@ucl.ac.uk

Abstract: The [Z₂Ln(THF)]₂(μ-η²:η²-N₂) complexes (Z = monoanionic ligand) generated by reduction of dinitrogen with trivalent lanthanide salts and alkali metals are strong reductants in their own right and provide another option in reductive lanthanide chemistry. Hence, lanthanide-based reduction chemistry can be effected in a diamagnetic trivalent system using the dinitrogen reduction product, [(C₅Me₅)₂(THF)Ln]₂(μ-η²:η²-N₂), **1**, readily obtained from [(C₅Me₅)₂La][BPh₄], KC₈, and N₂. Complex **1** reduces phenazine, cyclooctatetraene, anthracene, and azobenzene to form [(C₅Me₅)₂La]₂[μ-η³:η³-(C₁₂H₈N₂)], **2**, (C₅Me₅)La-(C₈H₈), **3**, [(C₅Me₅)₂La]₂[μ-η³:η³-(C₁₄H₁₀)], **4**, and [(C₅Me₅)La(μ-η²-(PhNNPh)(THF)]₂, **5**, respectively. Neither stilbene nor naphthalene are reduced by **1**, but **1** reduces CO to make the ketene carboxylate complex {[(C₅Me₅)₂La]₂[μ-η⁴-O₂C—C=C=O](THF)}₂, **6**, that contains CO-derived carbon atoms completely free of oxygen.

Introduction

For many years reductive organometallic lanthanide chemistry focused on the reactivity of the divalent metallocenes of Eu, Yb, and Sm.^{1–6} These one electron reductants typically react with substrates in a 2:1 ratio to make [(C₅R₅)₂Ln]₂(substrate dianion) complexes in which the substrate was reduced by two electrons, e.g., eq 1.



Although these reactions led to a wealth of new lanthanide chemistry, the reactivity was limited to these three divalent ions and gave paramagnetic trivalent products in each case. This made characterization of the products more difficult and routinely required X-ray crystallography to definitively identify the product. In many cases, when crystals suitable for X-ray diffraction were not obtainable with these metals, the products could not be unambiguously identified.⁷

One approach to obtaining suitable crystals in lanthanide chemistry is to vary the size of the trivalent ion among the 14

possibilities from La³⁺ to Lu³⁺, ions that gradually change in size from 1.160 Å to 0.977 Å, respectively (Shannon eight-coordinate radii).⁸ Unfortunately, this was not possible with the Eu²⁺, Yb²⁺, and Sm²⁺ reductions, since only three divalent ions were available and they differed significantly in reduction potential.⁹ Recently, molecular reductive divalent lanthanide chemistry has been expanded to include three, additional, fully characterized, highly reactive, divalent ions, Tm²⁺,¹⁰ Dy²⁺,^{11,12} and Nd²⁺.¹³ Although this expands the range of ion sizes possible, the trivalent products of each of these ions are still paramagnetic, and their divalent reactivity is not always analogous since they differ significantly in reduction potential.⁹

A further development in reductive lanthanide chemistry revealed that this divalent chemistry could be mimicked by combinations of a trivalent lanthanide salt and an alkali metal such as LnZ₃/K and LnZ₂Z'/K in which Z¹⁻ = [N(SiMe₃)₂]¹⁻, (C₅Me₄H)¹⁻, (C₅H₃Bu₂-1,3)¹⁻, [C₅H₃(SiMe₃)₂-1,3]¹⁻, (C₅H₂Bu₃)¹⁻, and (C₅Me₅)¹⁻ and [Z']¹⁻ = [BPh₄]¹⁻ and I¹⁻, e.g., eq 2.^{14–19}

(8) Shannon, R. D. *Acta Crystallogr.* **1976**, A32, 751–767.

(9) Morss, L. R. *Chem. Rev.* **1976**, 76, 827–841.

(10) Bochkarev, M. N.; Fedushkin, I. L.; Fagin, A. A.; Petrovskaya, T. V.; Ziller, J. W.; Broomhall-Dillard, R. N. R.; Evans, W. J. *Angew. Chem., Int. Ed. Engl.* **1997**, 36, 133–135.

(11) Evans, W. J.; Allen, N. T.; Ziller, J. W. *J. Am. Chem. Soc.* **2000**, 122, 11749–11750.

(12) Bochkarev, M. N.; Fagin, A. A. *Chem.—Eur. J.* **1999**, 5, 2990–2992.

(13) Bochkarev, M. N.; Fedushkin, I. L.; Fagin, A. A.; Dechert, S.; Schumann, H. *Angew. Chem., Int. Ed.* **2001**, 40, 3176–3178.

(14) Evans, W. J.; Lee, D. S.; Ziller, J. W. *J. Am. Chem. Soc.* **2004**, 126, 454–455.

(15) Evans, W. J.; Lee, D. S.; Rego, D. B.; Perotti, J. M.; Kozimor, S. A.; Moore, E. K.; Ziller, J. W. *J. Am. Chem. Soc.* **2004**, 126, 14574–14582.

(16) Evans, W. J.; Lee, D. S.; Lie, C.; Ziller, J. W. *Angew. Chem., Int. Ed.* **2004**, 43, 5517–5519.

(17) Evans, W. J.; Lee, D. S.; Johnston, M. A.; Ziller, J. W. *Organometallics* **2005**, 24, 6393–6397.

† University of California.

‡ University College London.

(1) Marks, T. J.; Ernst, R. D. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Chapter 21.

(2) Edelmann, F. T. In *Comprehensive Organometallic Chemistry II*; Lappert, M. F., Ed.; Pergamon: Oxford, 1995; Chapter 2.

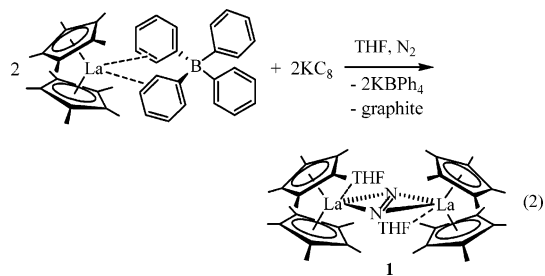
(3) Hart, F. A. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: Oxford, 1987; Chapter 39.

(4) Evans, W. J. *J. Organomet. Chem.* **2002**, 652, 61–68.

(5) Evans, W. J.; Davis, B. L. *Chem. Rev.* **2002**, 102, 2119–2136.

(6) Evans, W. J. *Polyhedron* **1987**, 6, 803–835.

(7) Evans, W. J. Unpublished results on substrates as diverse as cyclohexene and NO.



These reactions were applied to reduce dinitrogen and were effective in making (N₂)²⁻ complexes of general formula [Z₂(THF)Ln]₂(μ-η²:η²-N₂) with the proper combination of Ln and Z for all of the lanthanides, La–Lu, except radioactive Pm and readily reducible Eu, Yb, and Sm. The Eu, Yb, and Sm analogues were not accessible presumably because metal reduction to the divalent LnZ₂ occurred before N₂ reduction. This LnZ₃/K method provided the first opportunities to accomplish reductive lanthanide chemistry with the diamagnetic ions, La³⁺, Y³⁺, and Lu³⁺.

Since the [Z₂(THF)Ln]₂(μ-η²:η²-N₂) complexes contain a reduced dinitrogen ligand, (N₂)²⁻, they embody a considerable reductive capacity on their own. In the course of examining the reactivity of the Ln₂(μ-η²:η²-N₂) complexes, we have found that they can function as convenient reductive reagents that can complement the LnZ₃/K reduction system. As described here, they sometimes can provide products not readily obtainable from LnZ₃/K or any other currently available reductive lanthanide metal system.

In this report we examine the reductive reactivity of [(C₅Me₅)₂(THF)La]₂(μ-η²:η²-N₂), **1**,¹⁶ and its potential to generate [(C₅Me₅)₂La]₂(substrate dianion) products of the type previously obtainable only from divalent (C₅R₅)₂Ln(THF)_x metallocenes (R = alkyl, H), eq 1,^{1–6} and the LnZ₃/K and LnZ₂Z'/K reduction systems.^{14–19} The lanthanum complex was chosen since both **1** and its products are diamagnetic and can be completely characterized by NMR spectroscopy. To determine the range of reductive chemistry of **1**, a series of polycyclic aromatic hydrocarbons with well established reduction potentials was examined. These have previously been used to evaluate the reductive chemistry of (C₅Me₅)₂Sm²⁰ and other lanthanide systems.^{21–23} In addition, to calibrate the reductive chemistry of **1** versus the extensively explored (C₅Me₅)₂Sm,²⁴ several substrates previously reduced by the divalent metallocene were also examined including carbon monoxide.²⁵

Experimental Section

The manipulations described below were performed under nitrogen with the rigorous exclusion of air and water using Schlenk, vacuum line, and glovebox techniques. The [(C₅Me₅)₂La(THF)]₂(μ-η²:η²-N₂)

starting material, **1**, was prepared according to the literature.¹⁶ Solvents were sparged with argon and dried over columns containing Q-5 and molecular sieves. Ultrahigh purity carbon monoxide gas (Airgas) was purified using a Matheson Tri-Gas purification column (model 6410). ¹³C gas (99%) was purchased from Cambridge Isotopes Laboratories. High-pressure carbon monoxide reactions were conducted using a Fischer–Porter aerosol reaction vessel. NMR solvents were dried over sodium potassium alloy, degassed, and vacuum transferred before use. ¹H NMR and ¹³C NMR spectra were recorded with a Bruker DRX 500 MHz spectrometer. IR samples were prepared as KBr pellets and the spectra were obtained on a Perkin-Elmer 2000 FT-IR system. Elemental analyses were performed by Analytische Laboratorien (Lindlar, Germany). Complexometric analyses were carried out as previously described.²⁶

[(C₅Me₅)₂La]₂[μ-η³:η³-(C₁₂H₈N₂)], **2**. In a glovebox, **1** (50 mg, 0.05 mmol) and phenazine (9 mg, 0.05 mmol) were combined in 10 mL of THF and stirred. The mixture immediately became dark red and was allowed to stir overnight. Evaporation of the solvent yielded a dark red powder. ¹H NMR spectroscopy showed quantitative conversion of starting material to the previously characterized [(C₅Me₅)₂La]₂[μ-η³:η³-(C₁₂H₈N₂)].²⁷

(C₅Me₅)La(C₈H₈), **3**. Compound **1** (171 mg, 0.173 mmol) and 1,3,5,7-cyclooctatetraene (19.5 μL, 0.173 mmol) were combined in 10 mL of C₆H₆ and stirred. The mixture immediately became yellow and was allowed to stir overnight. Evaporation of the solvent yielded a yellow powder. ¹H NMR spectroscopy showed quantitative conversion of starting material to the previously characterized (C₅Me₅)La(C₈H₈)²⁸ and (C₅Me₅)₃La²⁹ in a 1:1 ratio.

[(C₅Me₅)₂La]₂[μ-η³:η³-(C₁₄H₁₀)], **4**. Compound **1** (50 mg, 0.05 mmol) and anthracene (9 mg, 0.05 mmol) were combined in 10 mL of THF and stirred. The mixture immediately became dark green and was allowed to stir overnight. Evaporation of the solvent yielded a dark green powder. ¹H NMR spectroscopy showed quantitative conversion of starting material to the previously characterized [(C₅Me₅)₂La]₂[μ-η³:η³-(C₁₄H₁₀)].³⁰ The identity of **4** was also confirmed by X-ray crystallography.

[(C₅Me₅)La(μ-η²:η²-PhNNPh)(THF)]₂, **5**. Compound **1** (76 mg, 0.08 mmol) and azobenzene (14 mg, 0.08 mmol) were combined in 10 mL of benzene and stirred. The dark green mixture was allowed to stir overnight. Evaporation of the solvent yielded a dark green powder. At room temperature over 2–3 days a concentrated sample of this compound in C₆D₆ produced colorless crystals of [(C₅Me₅)La(μ-η²:η²-PhNNPh)(THF)]₂ (20 mg, 25%). ¹H NMR (THF-*d*₈) δ 2.09 (s, 15H, C₅Me₅), 6.18 (m, 2H, phenyl), 6.47 (m, 2H, phenyl), 6.77 (m, 2H, phenyl), 6.95 (m, 2H, phenyl), 7.13 (m, 2H, phenyl). ¹³C NMR could not be obtained due to the limited solubility of the compound. Anal. Calcd for C₅₂H₆₆N₄La₂O₂: La, 26.29. Found: La, 26.7. Crystals suitable for X-ray crystallography were grown from C₆D₆ and contained C₆D₆ in the crystal lattice.

{[(C₅Me₅)₂La]₂[μ-η⁴-O₂C–C=C=O](THF)]₂, **6**. A Fischer–Porter aerosol reaction vessel was charged with **1** (200 mg, 0.20 mmol) and dissolved with C₆H₆ to a total volume of 13 mL. The reaction vessel was degassed by three freeze–pump–thaw cycles and then pressurized to 90 psi with CO. The orange reaction mixture darkened in color, and orange crystals formed over a period of 3–5 days at room temperature. The pressure was released, and the vessel was evacuated to the vapor pressure of the solvent and taken into a glovebox. The solution was decanted to leave crystalline {[(C₅Me₅)₂La]₂[μ-η⁴-O₂C–C=C=O]}-

- (18) Cassani, M. C.; Gun'ko, Y. K.; Hitchcock, P. B.; Hulkes, A. G.; Khvostov, A. V.; Lappert, M. F.; Protchenko, A. V. *J. Organomet. Chem.* **2002**, *647*, 71–83.
 (19) Jaroschik, F.; Nief, F.; Ricard, L. *Chem. Commun.* **2006**, 426–428.
 (20) Evans, W. J.; Gonzales, S. L.; Ziller, J. W. *J. Am. Chem. Soc.* **1994**, *116*, 2600–2608.
 (21) Fagan, A. A.; Bochkarev, M. N.; Kozimor, S. A.; Ziller, J. W.; Evans, W. J. *Z. Anorg. Allg. Chem.* **2005**, *631*, 2848–2853.
 (22) Bochkarev, M. N. *Chem. Rev.* **2002**, *102*, 2089–2117.
 (23) Fedushkin, I. L.; Bochkarev, M. N.; Dechert, S.; Schumann, H. *Chem.—Eur. J.* **2001**, *7*, 3558–3563.
 (24) Evans, W. J.; Hughes, L. A.; Hanusa, T. P. *J. Am. Chem. Soc.* **1984**, *106*, 4270–4272.
 (25) Evans, W. J.; Grate, J. W.; Hughes, L. A.; Zhang, H.; Atwood, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 3728–3730.

- (26) Evans, W. J.; Engerer, S. C.; Coleson, K. M. *J. Am. Chem. Soc.* **1981**, *103*, 6672–6677.
 (27) Scholz, J.; Scholz, A.; Weimann, R.; Janiak, C.; Schumann, H. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1171–1174.
 (28) Schumann, H.; Kohn, R. D.; Reier, F.-W.; Dietrich, A.; Pickardt, J. *Organometallics* **1989**, *8*, 1388–1392.
 (29) Evans, W. J.; Davis, B. L.; Ziller, J. W. *Inorg. Chem.* **2001**, *40*, 6341–6348.
 (30) Thiele, K.-H.; Bambirra, S.; Schumann, H.; Hemling, H. *J. Organomet. Chem.* **1996**, *517*, 161–163.

(THF)₂ (37 mg, 19%). $\{[(C_5Me_5)_2La]_2[\mu-\eta^4-O_2C-C=C=O](THF)_2\}$ shows no solubility in benzene, toluene, and hexanes, but the compound is slightly soluble in THF. ¹H NMR (THF-*d*₈) δ 1.98 (s, 30H, C₅Me₅), 2.07 (s, 30H, C₅Me₅). ¹³C NMR (THF-*d*₈) δ 11.33 (C₅Me₅), 11.65 (C₅Me₅), 118.59 (C₅Me₅), 121.00 (C₅Me₅) resonances associated with the ketene-carboxylate dianion were not located due to the limited solubility of the compound. IR (KBr)³¹ 2958s, 2904s, 2854s, 2142s, 2118s, 1365w, 1254s, 1019w, 874w, 766w cm⁻¹. Anal. Calcd for C₉₄H₁₃₆La₄O₈: C, 57.91; H, 7.03; La, 28.50. Found: C, 56.98; H, 6.85; La, 29.46.

$\{[(C_5Me_5)_2La]_2[\mu-\eta^4-O_2^{13}C-^{13}C=O](THF)_2\}$, **6**-¹³CO. Following the procedure above but using ¹³CO, **6**-¹³CO was made from **1** (200 mg, 0.20 mmol) dissolved in C₆H₆ to a total volume of 13 mL. ¹H NMR (THF-*d*₈) δ 1.98 (s, 30H, C₅Me₅), 2.07 (s, 30H, C₅Me₅). ¹³C NMR (THF-*d*₈) δ 11.33 (C₅Me₅), 11.65 (C₅Me₅), 23.40 (dd, *J*_{CC} = 103 Hz, 165 Hz, O₂¹³C-¹³C=O), 118.59 (C₅Me₅), 121.00 (C₅Me₅), 129.75 (dd, *J*_{CC} = 165 Hz, ²*J*_{CC} = 16 Hz, O₂¹³C-¹³C=O), 167.16 (dd, *J*_{CC} = 103 Hz, ²*J*_{CC} = 16 Hz, O₂¹³C-¹³C=O). IR (KBr)³¹ 2956s, 2898s, 2853s, 2071s, 2030s, 1438s, 1232s, 1019w, 863w, 740w cm⁻¹.

X-ray Data Collection, Structure Solution, and Refinement. The SMART³² program package was used to determine the unit-cell parameters and for data collection (25 s/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT³³ and SADABS³⁴ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL³⁵ program. The analytical scattering factors³⁶ for neutral atoms were used throughout the analysis.

$[(C_5Me_5)_2La(\mu-\eta^2:\eta^2-(PhNNPh)(THF))_2]$, **5**. The diffraction symmetry was *mmm*, and the systematic absences were consistent with the orthorhombic space group *Pbca* which was later determined to be correct. The structure was solved by direct methods and refined on *F*² by full-matrix least-squares techniques. Hydrogen atoms were located from a difference Fourier map and refined (*x*, *y*, *z* and *U*_{iso}). The molecule was located about an inversion center. There were two molecules of benzene solvent present per formula unit. Data are given in Table 1.

$\{[(C_5Me_5)_2La]_2[\mu-\eta^4-O_2C-C=C=O](THF)_2\}$, **6**. The structure was solved by direct methods and refined on *F*² by full-matrix least-squares techniques. Hydrogen atoms were included using a riding model. The molecule was located about an inversion center. There were four molecules of benzene solvent present per formula unit. A disordered benzene molecule was included using multiple components with partial site-occupancy factors. Data are given in Table 1.

Computational Details. A B3LYP geometry optimization of free (O₂C-C=C=O)²⁻ was performed using the Gaussian 03 code,³⁷ starting from the crystallographic coordinates of the (C₃O₃)²⁻ moiety in **6**. The 6-311+G* basis set was employed. The stationary point obtained was confirmed as a true minimum by harmonic vibrational frequency analysis. This analysis was repeated with the ¹²C atoms replaced by ¹³C atoms.

Results

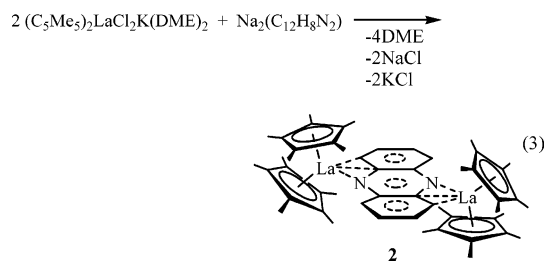
The reductive reactivity of $[(C_5Me_5)_2(THF)La]_2(\mu-\eta^2:\eta^2-N_2)$, **1**, was first examined with phenazine, since it is easily reduced

Table 1. X-ray Data Collection Parameters for Compounds **5** and **6**

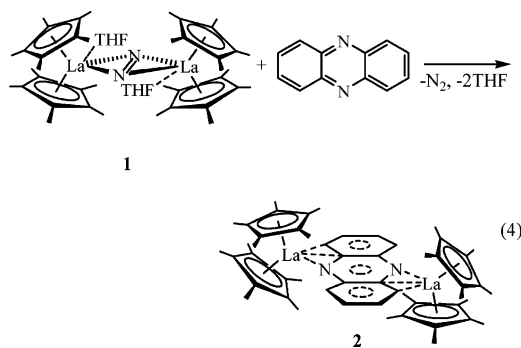
empirical formula	C ₅₂ H ₆₆ N ₄ O ₂ La ₂ 2(C ₆ H ₆) 5	C ₉₄ H ₁₃₆ O ₈ La ₄ 4(C ₆ H ₆) 6
formula weight	1213.12	2262.10
temperature (K)	163(2)	163(2)
crystal system	orthorhombic	triclinic
space group	<i>Pbca</i>	<i>P</i> $\bar{1}$
<i>A</i> (Å)	17.444(3)	14.234(6)
<i>B</i> (Å)	16.079(3)	14.365(6)
<i>C</i> (Å)	20.064(4)	15.917(7)
α (deg)	90	91.539(7)
β (deg)	90	114.067(7)
γ (deg)	90	109.738(7)
volume (Å ³)	5627.5(18)	2745(2)
<i>Z</i>	4	1
ρ_{calcd} (Mg/m ³)	1.432	1.368
μ (mm ⁻¹)	1.544	1.578
R1 ^a [<i>I</i> > 2.0 σ (<i>I</i>)]	0.0201	0.0550
wR2 ^a (all data)	0.0500	0.1591

^a Definitions: wR2 = $[\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$, R1 = $\sum|F_o| - |F_c|/\sum|F_o|$.

(reduction potential -0.364 V vs SCE³⁸), and the anticipated product, $[(C_5Me_5)_2La]_2[\mu-\eta^3:\eta^3-(C_{12}H_8N_2)]$, **2**, had previously been made from (C₅Me₅)₂LaCl₂K(DME)₂ and Na₂(C₁₂H₈N₂) in THF via eq 3.²⁷ Phenazine was immediately reduced by **1** in



THF to dark red $[(C_5Me_5)_2La]_2[\mu-\eta^3:\eta^3-(C_{12}H_8N_2)]$, **2**, eq 4.

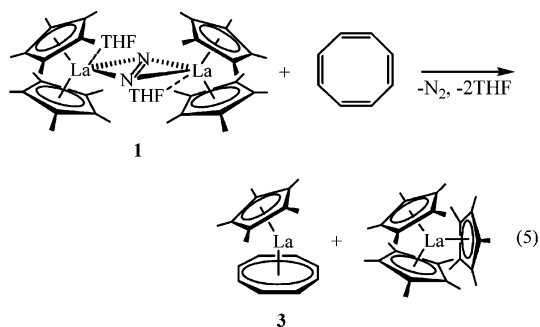


Complex **2** was identified by ¹H NMR spectroscopy in comparison with the crystallographically characterized sample reported earlier.³⁰ The samarium analogue of **2** had previously been made from 2 equiv of (C₅Me₅)₂Sm and 1 equiv of phenazine according to eq 1.²⁰

1,3,5,7-Cyclooctatetraene, which has reduction potentials of -1.83 and -1.99 V vs SCE,³⁸ is reduced by **1** to form (C₅Me₅)₂La(C₈H₈), **3**,²⁸ and (C₅Me₅)₃La²⁹ in quantitative yield, eq 5. The identity of **3** was confirmed by spectroscopic comparison with the complex originally synthesized from NaC₅Me₅ and (C₈H₈)LaCl(THF)_x.²⁸ The identity of (C₅Me₅)₃La was also

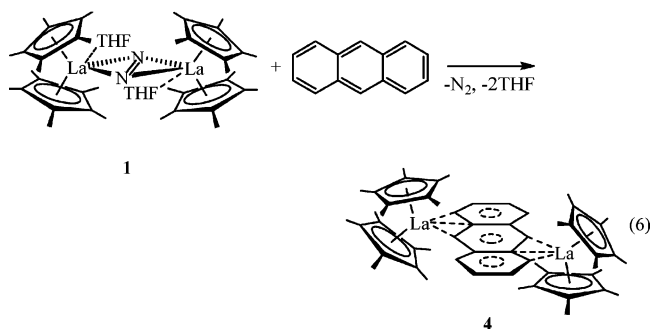
- (31) It should be noted that carboxylates can transfer from their original metals to potassium in the course of preparing KBr pellets. For example, see: Deacon, G. B.; Phillips, R. J. *Coord. Chem. Rev.* **1980**, *33*, 227–250. However, this would not be expected to change the composition of the ketene carboxylate unit being analyzed.
- (32) *SMART Software Users Guide*, version 5.1; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1999.
- (33) *SAINT Software Users Guide*, version 6.34A; Bruker Analytical X-ray Systems Inc.: Madison, WI, 2003.
- (34) Sheldrick, G. M. *SADABS*, version 2.05; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 2001.
- (35) Sheldrick, G. M. *SHELXTL*, version 6.12; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 2001.
- (36) *International Tables for X-ray Crystallography*; Kluwer Academic Publishers: Dordrecht, 1992; Vol. C.
- (37) Frisch, M. J. et al. *Gaussian 03*, revision D.01; Gaussian Inc.: Wallingford, CT, 2004.

(38) de Boer, E. *Adv. Organomet. Chem.* **1964**, *2*, 115–155.



established by 1H NMR spectroscopy. Equation 5 constitutes yet another reaction pathway to the sterically crowded $(C_5Me_5)_3-Ln$ complexes.⁵ $(C_5Me_5)_2Sm$ and $(C_5Me_5)_3Sm$ reduce C_8H_8 to form $(C_5Me_5)Sm(C_8H_8)$ and $(C_5Me_5)_3Sm$ in reactions analogous to eq 5.³⁹

Anthracene, which has reduction potentials of -1.98 V and -2.44 V vs SCE,³⁸ was also reduced by **1** to form dark green $[(C_5Me_5)_2La]_2[\mu-\eta^3:\eta^3-(C_{14}H_{10})]$, **4**, in quantitative yield, eq 6.

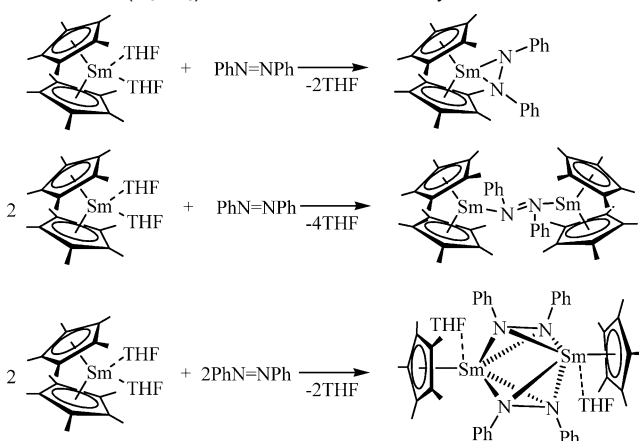


The identity of **4** was confirmed by NMR spectroscopy and X-ray crystallography in comparison with data in the literature on the compound prepared from $(C_5Me_5)_2LaCl_2K(DME)_2$ and $Na_2(C_{14}H_{10})$.³⁰ The samarium analogue $[(C_5Me_5)_2Sm]_2[\mu-\eta^3:\eta^3-(C_{14}H_{10})]$ is also prepared from the reaction of anthracene with either $(C_5Me_5)_2Sm^{20}$ or $(C_5Me_5)_3Sm$.³⁹ Complex **4** is inert to THF compared to the samarium analogue, $[(C_5Me_5)_2Sm]_2[\mu-\eta^3:\eta^3-(C_{14}H_{10})]$, which reverts back to a divalent complex, $(C_5Me_5)_2Sm(THF)_2$, and anthracene in THF.²⁰

Neither stilbene (-2.22 V vs SCE³⁸) nor naphthalene (-2.60 V vs SCE³⁸) were reduced by **1**. In comparison, $(C_5Me_5)_2Sm$ reduces stilbene^{40,41} but not naphthalene.²⁰ Overall, this survey of polycyclic aromatic substrates suggests that $[(C_5Me_5)_2(THF)-Ln]_2(\mu-\eta^2:\eta^2-N_2)$ has substantial reductive capacity comparable to that of $(C_5Me_5)_3Sm$,³⁹ but it is not quite as reducing as $(C_5Me_5)_2Sm$.

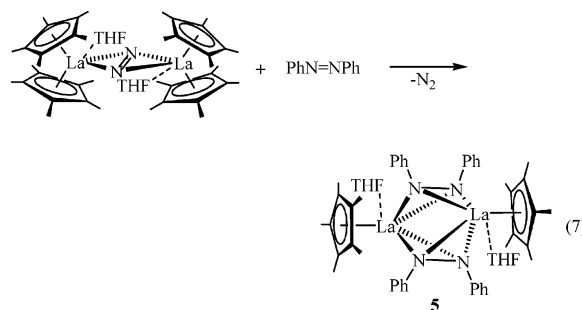
Azobenzene, which has reduction potentials of -1.35 to -1.41 V and -1.75 to -2.03 V vs SCE,⁴² was examined as a substrate since there is an extensive chemistry known with $(C_5Me_5)_2Sm(THF)_2$.⁴³⁻⁴⁵ As shown in Scheme 1, $(C_5Me_5)_2Sm(THF)_2$ can reduce azobenzene by one electron to make a radical anion complex, $(C_5Me_5)_2Sm(PhNNPh)$,⁴⁵ or by two electrons

Scheme 1. $(C_5Me_5)_2Sm$ Reduction Chemistry with $PhN=NPh$



to make either the unusual dark blue complex $[(C_5Me_5)_2Sm]_2-(PhNNPh)$ ⁴³ that still has a short $N=N$ bond or $[(C_5Me_5)Sm(\mu-\eta^2:\eta^2-PhNNPh)(THF)]_2$,⁴⁵ which forms via ligand redistribution. The last complex was isolated from the samarium reaction over a period of a few weeks.

Complex **1** reduces azobenzene to generate $[(C_5Me_5)La(\mu-\eta^2:\eta^2-PhNNPh)(THF)]_2$, **5**, in the course of a few days, eq 7.



Complex **5** is an analogue of the last samarium complex mentioned above. Similar complexes, namely $\{[(Me_3Si)_2N]_2Sm\}_2-[(\mu-\eta^2:\eta^2-PhNNPh)(THF)]_2$,⁴⁶ $[(C_5H_5)_2Yb(\mu-\eta^2:\eta^2-PhNNPh)(THF)]_2$,⁴⁵ and $[Tm(\mu-\eta^2:\eta^2-PhNNPh)(THF)]_2$,⁴⁷ were made from azobenzene and $[(Me_3Si)_2N]_2Sm(THF)_2$, $(C_5H_5)_2Yb(THF)$, and TmI_2 , respectively. Two additional examples, $[Ho(\mu-\eta^2:\eta^2-PhNNPh)(ePh)(pyridine)]_2$ and $[Er(\mu-\eta^2:\eta^2-PhNNPh)(SePh)(pyridine)]_2$,⁴⁸ were made from Ho and Er metal in the presence of PhEPh (E = Se, Te) and azobenzene in pyridine.

Complex **5** was characterized by X-ray crystallography, Figure 1, Table 1. The complex displays metrical parameters similar to those of the several $(PhNNPh)^{2-}$ lanthanide complexes cited above, Table 2. Each lanthanum in **5** has 2.821(2) Å to 2.852(2) Å $La-C(C_5Me_5)$ distances and a 2.604(1) Å $La-O(THF)$ bond distance that are in the range normal

- (39) Evans, W. J.; Perotti, J. M.; Kozimor, S. A.; Champagne, T. M.; Davis, B. L.; Nyce, G. W.; Fujimoto, C. H.; Clark, R. D.; Johnston, M. A.; Ziller, J. W. *Organometallics* **2005**, *24*, 3916–3931.
- (40) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1990**, *112*, 219–223.
- (41) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1990**, *112*, 2314–2324.
- (42) Thomas, F. G.; Boto, K. G. *The Chemistry of the Hydrazo, Azo, and Azoxy Groups*; Patai, S., Ed.; Wiley: New York, 1975; Chapter 12.

- (43) Evans, W. J.; Drummond, D. K.; Bott, S. G.; Atwood, J. L. *Organometallics* **1986**, *5*, 2389–2391.
- (44) Evans, W. J.; Drummond, D. K. *J. Am. Chem. Soc.* **1986**, *108*, 7440–7441.
- (45) Evans, W. J.; Drummond, D. K.; Chamberlain, L. R.; Doedens, R. J.; Bott, S. G.; Zhang, H.; Atwood, J. L. *J. Am. Chem. Soc.* **1988**, *110*, 4983–4994.
- (46) Brady, E. D.; Clark, D. L.; Keogh, D. W.; Scott, B. L.; Watkin, J. G. *J. Am. Chem. Soc.* **2002**, *124*, 7007–7015.
- (47) Katkova, M. A.; Fukin, G. K.; Fagin, A. A.; Bochkarev, M. N. *J. Organomet. Chem.* **2003**, *682*, 218–223.
- (48) Kornienko, A.; Freedman, D.; Emge, T. J.; Brennan, J. G. *Inorg. Chem.* **2001**, *40*, 140–145.

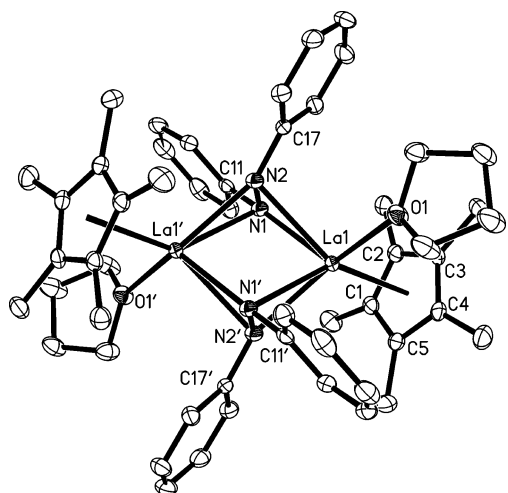


Figure 1. Thermal ellipsoid plot of $[(C_5Me_5)_2La(\mu-\eta^2:\eta^2-PhNNPh)(THF)]_2$, **5**, drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $[(C_5Me_5)_2La(\mu-\eta^2:\eta^2-PhNNPh)(THF)]_2$, **5**

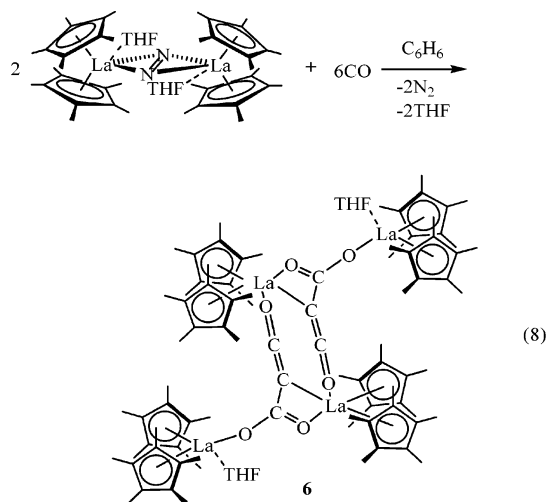
La1–Cnt1 ^a	2.562	La1–N1'	2.6383(16)
La1–O1	2.6041(14)	La1–N2'	2.4364(16)
La1–N1	2.4202(16)	N1–N2	1.471(2)
La1–N2	2.6346(16)		
N1–La1–N2	33.50(5)	La1–N1–La1'	91.96(5)
N1'–La1–N2'	33.40(5)	La1'–N2–La1	91.68(5)
N1–La1–N1'	88.04(5)	C17–N2–N1	114.61(14)
N2–La1–N2'	88.32(5)	C17–N2–La1'	157.98(13)
N2–La1–N1'	74.88(5)	C17–N2–La1	108.80(11)
N1–La1–N2'	82.61(5)	C11–N1–N2	114.61(15)
N2–N1–La1	81.27(9)	C11–N1–La1	163.84(13)
N1–N2–La1	65.23(8)	C11–N1–La1'	97.32(11)

^a Cnt1 is the centroid formed from C(1)–C(5).

for eight-coordinate La^{3+} .^{49–53} The 1.471(2) Å NN distance is in the NN single bond range,⁴⁵ and the angles around the each nitrogen atom are consistent with sp^3 hybridization. The La1–N1 and La1–N2' distances of 2.420(2) Å and 2.436(2) Å are appropriate for La^{3+} –N single bonds,^{54–56} and the La1–N2 and La1–N1' bond distances of 2.635(2) Å and 2.638(2) Å are similar to distances between La^{3+} and neutral N donor atom ligands.^{57–61}

The reductive chemistry of **1** with CO was also examined. Treatment of **1** in benzene with CO at 90 psi in a Fisher–Porter aerosol reaction vessel generates a dark orange solution from which single crystals of low solubility can be obtained. The crystals were identified as $\{[(C_5Me_5)_2La]_2[\mu-\eta^4-O_2C-C=C=O](THF)_2\}$, **6**, Figures 2 and 3, by X-ray crystallography. Equation 8 shows the overall reaction which involves a two electron reduction of three CO molecules to a $(CO)_3^{2-}$ dianion.

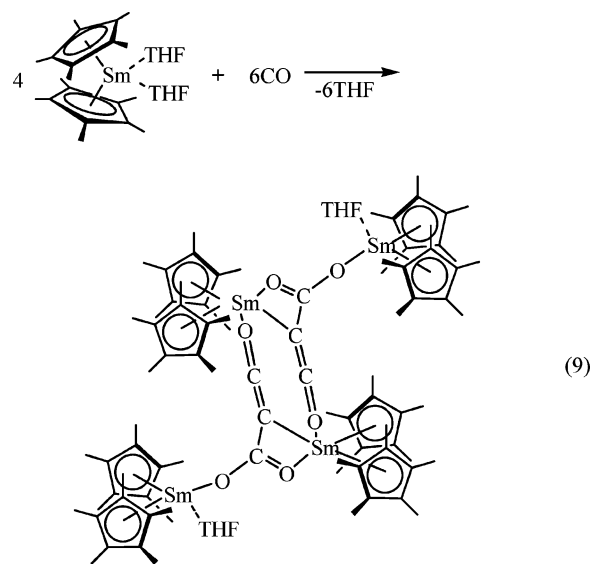
- (49) Evans, W. J.; Foster, S. E. *J. Organomet. Chem.* **1992**, 433, 79–94.
 (50) Rogers, R. D.; Atwood, J. L.; Emad, A.; Sikora, D. J.; Rausch, M. D. *J. Organomet. Chem.* **1981**, 216, 383–392.
 (51) Trifonov, A. A.; Van de Weghe, P.; Collin, J.; Domingos, A.; Santos, I. *J. Organomet. Chem.* **1997**, 527, 225–237.
 (52) McGeary, M. J.; Coan, P. S.; Folting, K.; Streib, W. E.; Caulton, K. G. *Inorg. Chem.* **1991**, 30, 1723–1735.
 (53) Deacon, G. B.; Gatehouse, B. M.; Shen, Q.; Ward, G. N. *Polyhedron* **1993**, 12, 1289–1294.
 (54) Bradley, D. C.; Ghotra, J. S.; Hart, F. A.; Hursthouse, M. B.; Raitby, P. *R. J. Chem. Soc., Dalton Trans.* **1977**, 1166–1172.
 (55) Guan, J.; Jin, S.; Lin, Y.; Shen, Q. *Organometallics* **1992**, 11, 2483–2487.
 (56) Evans, W. J.; Anwander, R.; Doedens, R. J.; Ziller, J. W. *Angew. Chem., Int. Ed. Engl.* **1994**, 33, 1641–1644.



Complex **6** is a dimer with a molecular center of inversion. Each monomeric unit contains one THF-solvated and one unsolvated trivalent $[(C_5Me_5)_2La]^+$ metalocene.

This net 2+ charge is balanced by an $(O_2CCCO)^{2-}$ fragment that has bond lengths and angles, Table 3, consistent with the formation of a ketene carboxylate dianion, $(\mu-\eta^4-O_2C-C=C=O)^{2-}$, Scheme 2a. The fact that the central carbon in the homologated product has no C–O bond indicated that complete cleavage of CO occurred in this reaction.⁶¹

A ketene carboxylate complex like **6** was reported previously from the reaction of $(C_5Me_5)_2Sm(THF)_2$ and CO, eq 9.²⁵ Due



to the paramagnetism of Sm^{3+} in that product, a detailed NMR analysis could not be made. Table 3 presents a comparison between the bond distances and angles for the two compounds.

- (57) van Staveren, D. R.; van Albada, G. A.; Haasnoot, J. G.; Kooijman, H.; Lanfredi, A. M. M.; Nieuwenhuizen, P. J.; Spek, A. L.; Ugozzoli, F.; Weyhermuller, T.; Reedijk, J. *Inorg. Chim. Acta* **2001**, 315, 163–171.
 (58) Evans, W. J.; Giarikos, D. G.; Ziller, J. W. *Organometallics* **2001**, 20, 5751–5758.
 (59) Fukuda, Y.; Nakao, A.; Hayashi, K. *J. Chem. Soc., Dalton Trans.* **2002**, 527–533.
 (60) Giesbrecht, G. R.; Collis, G. E.; Gordon, J. C.; Clark, D. L.; Scott, B. L.; Hardman, N. J. *J. Organomet. Chem.* **2004**, 689, 2177–2185.
 (61) Mehdoui, T.; Berthet, J.-C.; Thuery, P.; Ephritikhine, M. *J. Chem. Soc., Dalton Trans.* **2005**, 1263–1272.

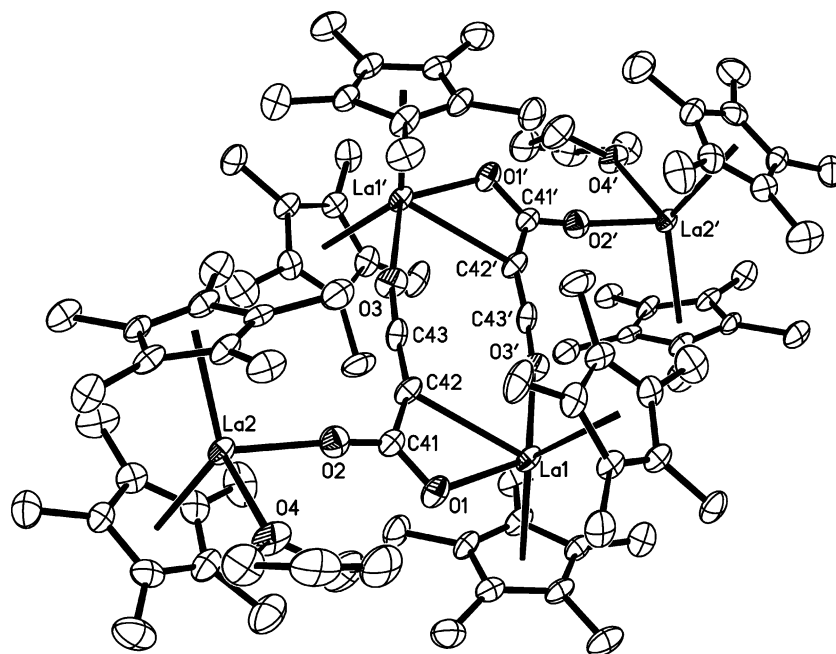


Figure 2. Thermal ellipsoid plot of $\{[(C_5Me_5)_2La]_2[\mu-\eta^4-O_2C-C=C=O](THF)_2\}$, **6**, drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

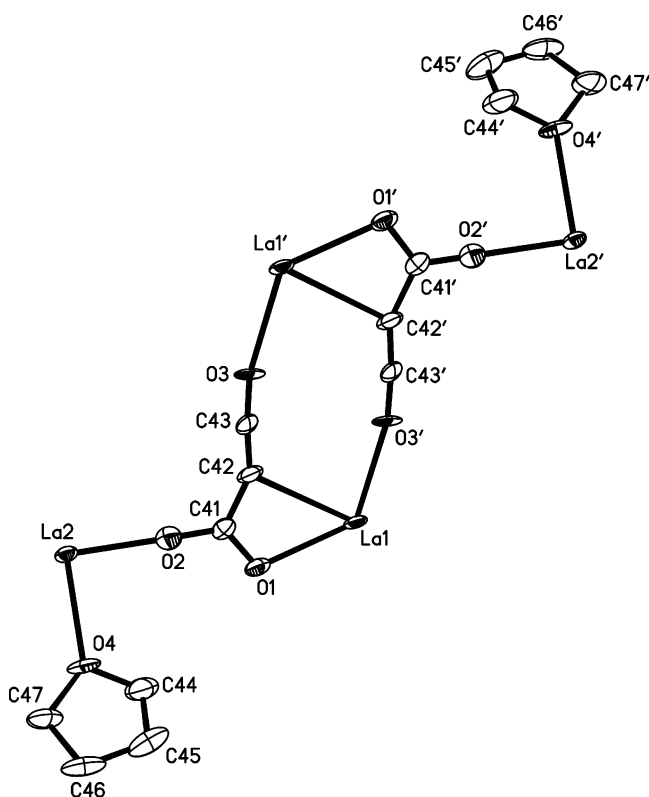


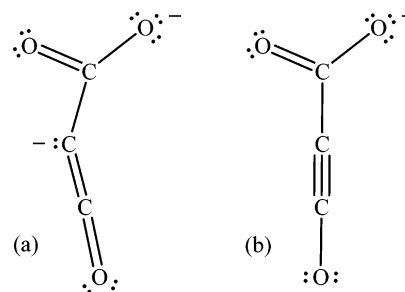
Figure 3. Thermal ellipsoid plot of the core structure of $\{[(C_5Me_5)_2La]_2[\mu-\eta^4-O_2C-C=C=O](THF)_2\}$, **6**, with $(C_5Me_5)^{1-}$ ligands omitted (drawn at the 50% probability level).

The C43–O3 distance of 1.207(9) Å in **6** is in the C=O double bond range and is comparable to C=O distances in other metal-substituted ketene compounds. For example, $(C_5H_5)(CO)(PMe_3)_2W\{C(CO)C_6H_4Me\}$ has a 1.21(3) Å C=O bond.⁶² The

Table 3. Comparisons of Selected Bond Distances (Å) and Angles (deg) for $\{[(C_5Me_5)_2Ln]_2[\mu-\eta^4-O_2C-C=C=O](THF)_2\}$ Complexes (Ln = Sm and La, **6**)

	Sm	La
Ln1–O1	2.39(1)	2.490(5)
Ln1–C42	2.77(2)	2.797(7)
Ln1–O3'	2.38(1)	2.490(5)
Ln2–O2	2.25(1)	2.342(6)
Ln2–O4	2.47(1)	2.557(5)
C41–O1	1.25(2)	1.280(8)
C41–O2	1.31(2)	1.277(9)
C43–O3	1.23(2)	1.207(9)
C41–C42	1.41(3)	1.419(10)
C42–C43	1.22(3)	1.254(11)
C42–C43–O3	172(2)	173.2(8)
O1–C41–C42	117(2)	116.7(7)
O2–C41–C42	122(2)	121.5(6)
Ln1–C42–C43	125(2)	122.2(6)
C41–C42–C43	150(2)	149.6(8)

Scheme 2. Two Possible Structures for a Ketene Carboxylate Ligand, $(O_2CCCO)^{2-}$



1.254(11) Å C42–C43 distance in **6** is comparable to the 1.24–(3) Å length in the tungsten ketene complex just mentioned,⁶² but the error limits are large on all of these measurements. Compared to the normal $C(sp^2)=C(sp^2)$ double bond range of 1.29–1.40 Å,⁶³ the C42–C43 length is short, a fact discussed

(62) Kreissl, F. R.; Frank, A.; Schubert, U.; Lindner, L. L.; Huttner, G. *Angew. Chem., Int. Ed.* **1976**, *15*, 632–633.

(63) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1–S19.

further below. The O3–C43–C42 angle of 173.2(8)° in **6** is not perfectly linear, but it is similar to the 172(2)° CCO angle in $\{[(C_5Me_5)_2Sm]_2[\mu-\eta^4-O_2C-C=C=O](THF)_2\}^{2+}$.²⁵ Metal ketene compounds show a wide range of CCO bond angles ranging from 126.3(2)° in $(C_5Me_5)_2Zr(pyridine)(\eta^2-H_2CCO)$ ⁶⁴ to the 177(1)° CCO angle in $[Mn_2\{\mu-C(CO)Ph\}(CO)_6(C_5H_5)]$.⁶⁵

The carboxylate group bridges La1 and La2 in a $\mu-\eta^1:\eta^1$ -mode. The 2.342(6) Å La2–O2 linkage of the solvated lanthanide metallocene unit is the only contact between La2 and the $(O_2CCO)^{2-}$ moiety. This La2–O2 distance is within the range for La–O single bonds,^{66–70} and is shorter than neutral oxygen donor bonds to eight-coordinate La^{3+} . For example, the La–O(THF) distances in $[(C_5Me_5)_2La(THF)(\mu-\eta^1:\eta^3-C_4H_6)La(C_5Me_5)_2]$ ⁷¹ and **5** are 2.637(3) and 2.604(1) Å, respectively. The La(2)–O(4) La–O(THF) bond in **6** is 2.557(4) Å.

The La1–O1 carboxylate linkage, 2.490(5) Å, is between these ranges. However, La1 is also oriented toward the ketene carboxylate via a 2.797(7) Å La1–C42 distance. This is long compared to the La–C single bonds in the literature, e.g., 2.627–(10) and 2.651(8) Å in $(C_5Me_5)La[CH(SiMe_3)_2]_2(THF)$ ⁷² and 2.535(8) and 2.588(10) Å in $(C_5Me_5)La[CH(SiMe_3)_2]_2$,⁷³ and is comparable to the 2.773(8) to 2.879(8) Å La–C(C_5Me_5) bond distances in **6**.

La1 is also bound to the other ketene carboxylate unit via a 2.490(5) Å La1–O3' length. This oxygen donor bond linkage and its symmetry equivalent link the two halves of the dimer together. This linkage, like La1–O1, is between a typical La–O single bond and La←O donor bond distances. This intermediate length, along with the shorter distance found for C42–C43, suggests that contributions from structure (b) shown in Scheme 2 are possible. Also consistent with this is the fact that C(41)–C(42) is 1.419(10) Å, a value closer to the 1.431 Å average C(sp²)–C(sp) distance than the 1.460 C(sp²)–C(sp²) average.⁶³

Overall these distances indicate considerable delocalization in the bonding of the ketene carboxylate dianions. A similar pattern was observed in the samarium analogue, as indicated in Table 3. This table illustrates how much the metrical parameters can change between two analogous lanthanide complexes with differing metal radii.

Complex **6** displays an IR absorption with a maximum at 2142 cm^{–1} and a lower energy shoulder. The maximum is suspiciously close to that of free CO, 2143 cm^{–1}. However, since the IR sample was run as a KBr³¹ pellet in the absence of CO gas, it was unlikely that the observed absorption was from CO. In fact, the ν_{CO} stretching frequencies of RR'C=C=O ketenes range from 2080 to 2250 cm^{–1} and hence 2142 cm^{–1} is a reasonable frequency for the ketene carboxylate moiety.⁷⁴

- (64) Moore, E. J.; Strauss, D. A.; Armantrout, J.; Santarsiero, B. D.; Grubbs, R. H.; Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 2068–2070.
 (65) Tang, Y.; Sun, J.; Chen, J. *J. Chem. Soc., Dalton Trans.* **1998**, 4003–4008.
 (66) Deacon, G. B.; Forsyth, C. M.; Harika, R.; Junk, P. C.; Ziller, J. W.; Evans, W. J. *J. Mater. Chem.* **2004**, *14*, 3144–3149.
 (67) Deacon, G. B.; Gatehouse, B. M.; Shen, Q.; Ward, G. N. *Polyhedron* **1993**, *12*, 1289–1294.
 (68) Blech, P.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Dalton Trans.* **1990**, 3557–3561.
 (69) Clark, D. L.; Gordon, J. C.; Huffman, J. C.; Vincent-Hollis, R. L.; Watkin, J. G.; Zwick, B. D. *Inorg. Chem.* **1994**, *33*, 5903–5911.
 (70) Evans, W. J.; Golden, R. E.; Ziller, J. W. *Inorg. Chem.* **1993**, *32*, 3041–3051.
 (71) Scholz, A.; Smola, A.; Scholz, J.; Loebel, J.; Schumann, H.; Thiele, K.-H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 435–436.
 (72) Van der Heijden, H.; Schaverien, C. J.; Orpen, A. G. *Organometallics* **1989**, *8*, 255–258.
 (73) Klooster, W. T.; Brammer, L.; Schaverien, C. J.; Budzelaar, P. H. M. *J. Am. Chem. Soc.* **1999**, *121*, 1381–1382.

To ensure that the ketene carboxylate ligand generated in this reaction arose from the CO reagent and to check the validity of the ν_{CO} assignment in the IR spectrum, the synthesis in eq 9 was conducted with ¹³CO. As expected, the analogue of **6** made from ¹³CO, namely, **6-¹³CO**, lacked the 2142 cm^{–1} band and had a new absorption at lower energy. The absorption displayed a maximum at 2071 cm^{–1} along with a lower energy shoulder.

To evaluate this isomer shift, B3LYP calculations on the $(O_2C-C=C=O)^{2-}$ moiety were carried out. Optimization of the structural input from the coordinates of the X-ray crystal structure generated a linear C–C–O substructure such that the overall unit had C_{2v} symmetry. The stretching frequency calculated for this structure is 2189 cm^{–1} for the highest energy normal mode. The next highest energy vibration is at 1490 cm^{–1}, attributable primarily to a C=C stretch. Calculations on the ¹³C isotope predict a vibrational frequency of 2106 cm^{–1}. Although the frequency predictions on the idealized C_{2v} $(O_2C-C=C=O)^{2-}$ ligand free of the three metallocenes that are attached to it do not match exactly the experimentally observed numbers, the ratio of these numbers, 0.962, compares well with the 0.967 ratio of the 2142 and 2071 cm^{–1} frequencies. Since the calculations assume a harmonic approximation for the potential wells that tends to overestimate frequencies, the higher calculated frequencies are not unexpected.

6-¹³CO was also valuable in defining the ¹³C NMR resonances of the ketene carboxylate moiety. These were not observed in the spectrum of **6** due to its low solubility. **6-¹³CO** displayed three doublets of doublets at δ 23.4, 129.7, and 167.2 ppm in THF-*d*₈. Since the ¹³C NMR resonance centered at 23.4 ppm showed strong coupling, $J_{CC} = 103$ and 166 Hz, to two different ¹³C nuclei, this was assigned as the middle ¹³C atom in the ketene carboxylate ligand. The shift is in the upfield region observed for many other beta carbons in ketenes: beta carbon resonances have been observed at –20 to 125 ppm, but most resonate between 0 and 50 ppm.⁷⁴ The doublet of doublets centered at 167.2 ppm is assigned as the carboxylate ¹³C, since it is in the range of carboxylate moieties.⁷⁵ The 103 Hz coupling to the central carbon is slightly larger than values for sp²–sp² ¹³C coupling constants that are typically in the range of 67 to 95 Hz.⁷⁶ The 16 Hz coupling is reasonable for ² J_{CC} coupling. For example, ² J_{CC} in H₂C=CH–CH=CH₂ and in HC≡C–C≡CH is <1 and 18.9 Hz, respectively.⁷⁶ This leaves the doublet of doublets centered at 129.7 ppm to be assigned as the ¹³C carbonyl atom. This shift is upfield from previously reported values, 161 to 206 ppm in ketenes.⁷⁴ The stronger 165 Hz coupling to the central carbon is reasonable considering that these two carbons are formally connected with a double bond, and the contributing structure (b) in Scheme 2 has an even higher bond order.

To further substantiate these assignments, 2-D NMR data were desirable. Since compounds containing three ¹³C nuclei each of which has no attached hydrogen are rarely available, it was uncertain what conditions were appropriate for obtaining these data. After some experimentation, an appropriate set of parameters was selected. A ¹³C/¹³C COSY experiment provided data consistent with the interpretation that the doublet of

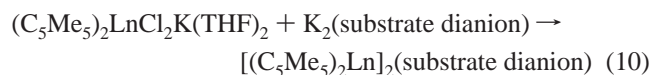
- (74) Tidwell, T. T. *Ketenes*; Wiley-Interscience: New York, 1995; Chapter 2.
 (75) Silverstein, R. M.; Webster, F. X. *Spectrometric Identification of Organic Compounds*; Wiley: New York, 1998; Chapter 5.
 (76) Kalinowski, H.-O.; Berger, S.; Braun, S. *Carbon-13 NMR Spectroscopy*; Wiley: New York, 1988; Chapter 4.

doublets centered at 129.7 and 167.2 ppm is correlated with the doublet of doublets centered at 23.4 ppm. The IR and NMR data on **6**-¹³C_O provide strong evidence that the ketene carboxylate arises from a two electron reductive homologation of CO.

Discussion

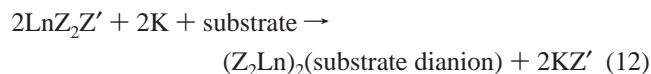
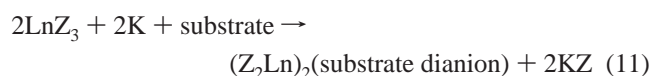
Equations 4–8 indicate that the trivalent lanthanum complex, [(C₅Me₅)₂(THF)Ln]₂(μ-η²:η²-N₂), **1**, can function as a reducing agent much like (C₅Me₅)₂Sm. Hence, in addition to the LnZ₃/M and LnZ₂Z'/M systems that bring reductive chemistry to lanthanides that do not have readily accessible divalent states, the “downstream” dinitrogen reduction products, [Z₂(THF)Ln]₂(μ-η²:η²-N₂), made via LnZ₃/M and LnZ₂Z'/M, can also have this capacity. Before discussing in detail the reactivity of **1**, it is beneficial to review the various lanthanide-based reaction pathways that can lead to reduction products of the type [(C₅Me₅)₂Ln]₂(substrate dianion) originally accessible only for Eu, Yb, and Sm via eq 1.

Potentially the most direct route to [(C₅Me₅)₂Ln]₂(substrate dianion) complexes, the substitution of the [(μ-Cl₂)K]¹⁻ component of the “ate” salt [(C₅Me₅)₂Ln]₂(μ-Cl₂)K by K₂(substrate dianion), is shown in eq 10.



This is how complex **2** was initially made, e.g., eq 3.^{27,30} This is the synthetically preferable route since the “ate” salt is a starting material for the complexes used in the other approaches. However, this substitution route requires that two conditions be met: the K₂(substrate dianion) must be accessible; i.e., the substrate dianion must be obtainable by alkali metal reduction and the substitution must be viable. Substitution reactions with [(C₅Me₅)₂Ln]₂(μ-Cl₂)K salts are successful in some cases, but they are notoriously unproductive in others. It is often not possible to displace the [Cl₂K]¹⁻ unit. Indeed, the frequent formation of ate salts in organolanthanide chemistry attests to the stability of this unit.⁷⁷ This is the reason divalent (C₅Me₅)₂-Sm chemistry, available through eq 1, is so valuable and why so many trivalent lanthanide metallocene complexes are made with samarium. Sm²⁺ could be used to form the [(C₅Me₅)₂-Ln]₂(substrate dianion) product without going through an ate salt route.

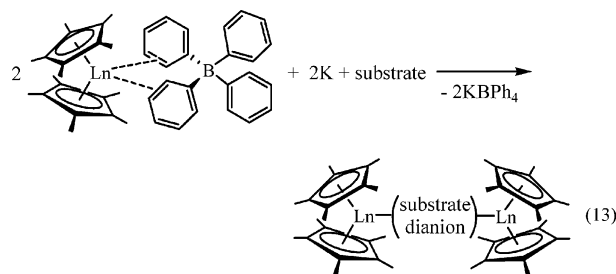
If the K₂(substrate dianion) is not accessible or if [(C₅Me₅)₂-Ln]₂(μ-Cl₂)K substitution fails, the LnZ₃/K and LnZ₂Z'/M routes, eqs 11 and 12, respectively,



offer alternative routes to [Z₂Ln]₂(substrate dianion) complexes for all of the lanthanides, e.g., eq 2. In the LnZ₃/K case for (Z)¹⁻ = (C₅Me₅)¹⁻, this is synthetically challenging since the (C₅Me₅)₃Ln precursors, Ln = La–Sm, are highly reactive.³⁹ In the (C₅Me₅)¹⁻ ligand case, the LnZ₂Z'/M route is preferable via the precursor to (C₅Me₅)₃Ln, namely (C₅Me₅)₂Ln(μ-Ph₂BPh₂),

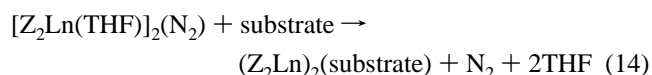
(77) Evans, W. J.; Boyle, T. J.; Ziller, J. W. *Inorg. Chem.* **1992**, *31*, 1120–1122.

eq 13. The tetraphenylborate salts are known for all the



lanthanides⁷⁸ and provide a method via eq 13 to do reductive chemistry with any of the metals. This is the reaction that leads to [(C₅Me₅)₂(THF)Ln]₂(μ-η²:η²-N₂), **1**, eq 2, using N₂ as a substrate. The dinitrogen reduction reaction is a system in which reduction of substrate by potassium alone fails; i.e., eq 10 has not been possible with N₂. In cases such as this, eqs 11 and 12 are the best route.

It would seem that using the downstream reduction product, [(C₅Me₅)₂(THF)Ln]₂(μ-η²:η²-N₂), as an alternative reductant, eq 14,



would not be valuable since this would require one more step from that already done in eqs 11 and 12. However, there are some substrates that are not reduced cleanly in good yield via eqs 11 and 12 that are reducible by [(C₅Me₅)₂(THF)Ln]₂(μ-η²:η²-N₂). The most compelling example of this to date is the CO reduction, eq 8. The ketene carboxylate product, **6**, has not been obtainable via eqs 11 or 12. Hence, eq 14 provides yet another option in lanthanide reduction chemistry for all the lanthanides and is likely to have its own special niche in the reduction arsenal depending on the substrate.

An estimate of the reductive reactivity of [(C₅Me₅)₂(THF)-Ln]₂(μ-η²:η²-N₂) can be obtained by comparison with other divalent reductants. This trivalent La₂N₂ complex is a stronger reductant than (C₅H₅)₂Eu,⁷⁹ (C₅H₅)₂Yb,⁸⁰ and (C₅H₅)₂Sm⁸¹ as well as some of the trivalent tris(pentamethylcyclopentadienyl) complexes, (C₅Me₅)₃Ln, which reduce substrates via sterically induced reduction.⁵ For the sterically crowded (C₅Me₅)₃Ln complexes, the reduction capacity depends on the size of the metal: the smaller metals give more crowded and more reactive complexes. Hence, (C₅Me₅)₃La is only capable of reducing phenazine (−0.364 V vs SCE)³⁸ and not 1,3,5,7-cyclooctatetraene (−1.83, −1.99 V vs SCE),³⁹ whereas **1** is capable of reducing both. The more crowded and more powerful reductant, (C₅Me₅)₃Sm, can also reduce 1,3,5,7-cyclooctatetraene but reduces azobenzene only by one electron (cf. Scheme 1).^{5,39} Hence, **1** appears to be a stronger reductant than (C₅Me₅)₃Sm. The reduction of anthracene, but not stilbene, indicates that **1** is not as reducing as (C₅Me₅)₂Sm which can reduce both substrates.^{20,40,41}

One of the unusual aspects of (C₅Me₅)₂Sm reduction chemistry is that several of the reductions can be reversed by addition

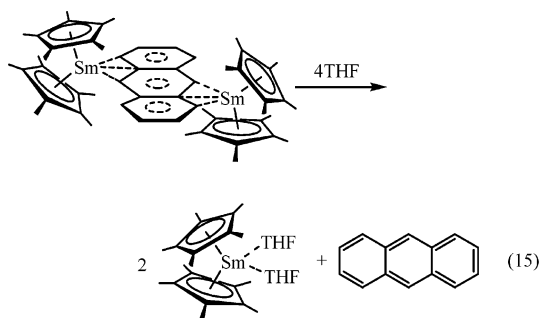
(78) Evans, W. J.; Seibel, C. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1998**, *120*, 6745–6752.

(79) Fischer, E. O.; Fischer, H. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 132–133.

(80) Fischer, E. O.; Fischer, H. *J. Organomet. Chem.* **1965**, *3*, 181–187.

(81) Watt, G. W.; Gillow, E. W. *J. Am. Chem. Soc.* **1969**, *91*, 775–776.

of THF. As shown in eq 15, the reduction product obtained from anthracene reverts back to the neutral substrate and Sm^{2+} in the presence of THF.²⁰ The same THF-induced Sm^{3+} to Sm^{2+}



reaction occurs with organosamarium stilbene,⁴⁰ styrene,⁴⁰ and dinitrogen⁸² reduction products. Hence, the balance between reducibility of Sm^{3+} and the substrate in these reactions can be tipped by the energy of THF solvation. Thermodynamic data suggest that this is not a large number.⁸³ In contrast, THF does not reverse the reductions that generate either the dinitrogen product, **1**, or the anthracene product, **4**. In fact, these complexes are generated in THF. Presumably, THF does not decompose **1** or **4** because it is much more difficult to reduce La^{3+} than Sm^{3+} . Hence, the use of $[(\text{C}_5\text{Me}_5)_2(\text{THF})\text{La}]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-N}_2)$ as a reductant provides an anthracene complex that is stabilized compared to the samarium analogue.

Overall this study indicates that **1** can reduce substrates with reduction potentials at least as negative as -2.03 V vs SCE, but not as negative as -2.22 V vs SCE. Since the phenazine and anthracene products can be accessed via ate salt substitution reactions, eq 10,^{27,30} complex **1** is not the optimum precursor for these particular products. Formation of **5** and **6** has not been reported by any other route, however.

The formation of the CO reduction product **6** is one reaction in which the reactivity obtained via the $\text{Ln}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-N}_2)$ reduction system cannot be mimicked by either ate salt substitution or LnZ_3/K or $\text{LnZ}_2\text{Z}'/\text{K}$ chemistry. The latter system with CO gives multiple products by NMR spectroscopy and, in our hands, we have not been able to isolate a pure product. In fact, no other lanthanide-based reduction system has been able to generate a ketene carboxylate analogue of the $(\text{C}_5\text{Me}_5)_2\text{Sm}/\text{CO}$ product, $\{[(\text{C}_5\text{Me}_5)_2\text{Sm}]_2[\mu\text{-}\eta^4\text{-O}_2\text{C}-\text{C}=\text{C}=\text{O}](\text{THF})\}_2$.²⁵ This has been unfortunate since the samarium product was obtained in low yield and had such low solubility that it was difficult to characterize. The combination of solubility and paramagnetism rendered NMR analysis of little value.

This was particularly troubling since high-pressure studies of the $(\text{C}_5\text{Me}_5)_2\text{Sm}/\text{CO}$ reaction system showed no evidence of the formation of $\{[(\text{C}_5\text{Me}_5)_2\text{Sm}]_2[\mu\text{-}\eta^4\text{-O}_2\text{C}-\text{C}=\text{C}=\text{O}](\text{THF})\}_2$ but only an IR absorption at 2153 cm^{-1} attributed to the free CO that was in the pressure cell.⁸⁴ In retrospect, considering the 2142 cm^{-1} absorption of **6**, the 2153 cm^{-1} absorption could arise from a ketene carboxylate.

The use of **1** as a reductant provides a unique new way to obtain this ketene carboxylate product. In this case, the use of

the $\text{Ln}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-N}_2)$ reduction system allows the ketene carboxylate to be obtained in a fully characterizable diamagnetic complex. Since **1** has better solubility properties than the Sm analogue, this is an example in which variation of the size of the metal is crucial to full characterization of the system.

Both the IR and ^{13}C NMR spectra of **6**- $^{13}\text{C}\text{O}$ indicate that all of the carbon atoms in the ketene carboxylate arise from the labeled $^{13}\text{C}\text{O}$. Hence, if the formation of the ketene carboxylate does arise from impurities in the CO as previously suggested,⁸⁴ these impurities also have been selectively labeled with $^{13}\text{C}\text{O}$.

Since the **1**/CO reaction gives several other products, we are hopeful that this system or variations of this system will provide some isolable intermediates on the pathway to **6** that may provide some insight into how the complex is made. Since this reaction apparently involves the rare complete cleavage of the CO triple bond, it is desirable to get more mechanistic data. This was challenging with the paramagnetic samarium system but is more viable with La^{3+} . For example, the oxygen substituted cyclopropene derivative, the $(\text{CO})_3^{2-}$ delatate dianion, recently obtained by reduction of CO with $[\text{C}_8\text{H}_8(\text{Si}^i\text{Pr}_3)_2]\text{U}(\text{C}_5\text{-Me}_5)$ could be one of the intermediates.⁸⁵

Conclusion

The results presented here show that $\text{Ln}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-N}_2)$ complexes provide another option for accomplishing reductive chemistry with the lanthanides. Moreover, reduction with these reagents does not require an alkali metal, steric crowding, or an isolable molecular divalent state. Like sterically induced reduction and the LnZ_3/K and $\text{LnZ}_2\text{Z}'/\text{K}$ methods, this extends the chemistry that was previously accessible only through paramagnetic divalent metals to a wider range of metals including diamagnetic systems that allow detailed NMR analysis. $\text{Ln}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-N}_2)$ reduction is complementary to the other methods and will be of value when the other methods fail for either synthetic or reactivity reasons. In addition, comparing the differences in the reactivity of LnZ_3/M vs Ln_2N_2 may shed considerable light on the mechanisms of these trivalent lanthanide reductions.

The power of the $\text{Ln}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-N}_2)$ reduction method is substantial. Complete cleavage of the CO bond can be achieved. This bond scission is likely to be the result of a combination of the special nature of the reductive chemistry as well as the high Lewis acidity of the lanthanides.

Acknowledgment. We thank the United States National Science Foundation for support of this research, the Engineering and Physical Sciences Research Council of the United Kingdom for computing resources under Grant GR/S06233 (to N.K.), Dr. Philip R. Dennison for help with the ^{13}C COSY experiment, Professor Max Wolfsberg for directing us to the modern methods of isotope shift calculations, and the Arnold and Mabel Beckman Foundation and the ARCS Foundation for a fellowship (to D.S.L.)

Supporting Information Available: X-ray diffraction data, atomic coordinates, thermal parameters, complete bond distances and angles, and complete ref 37. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA0640851

(82) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1988**, *110*, 6877–6879.
 (83) Nolan, S. P.; Stern, D.; Marks, T. J. *J. Am. Chem. Soc.* **1989**, *111*, 7844–7853.
 (84) Selg, P.; Brintzinger, H. H.; Schultz, M.; Andersen, R. A. *Organometallics* **2002**, *21*, 3100–3107.

(85) Summerscales, O. T.; Cloke, F. G. N.; Hitchcock, P. B.; Green, J. C.; Hazari, N. *Science* **2006**, *311*, 829–831.