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Thermally Stable Uranium Dinitrogen Complex with Siloxide Supporting Ligands

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Supporting Information

ABSTRACT: A new dinitrogen adduct of a homoleptic uranium tris(siloxide) complex, $[U{OSi(Mes)_3}_3]_2(\mu-\eta^2:\eta^2-N_2)$, is reported. Synthesis of the ¹⁵N-labeled isotopomer and Raman spectroscopy confirm the reductive activation of N₂ to a $(N_2)^{2-}$ dianion. The ¹⁵N NMR shift of the ¹⁵N₂-labeled isotopomer is also reported. Crystallographic characterization shows a side-on $(N_2)^{2-}$ coordinated in either an eclipsed or staggered conformation in different crystals. The U-N₂-U complex is stable to



vacuum and shows high thermal stability, retaining the formally reduced dinitrogen at 100 °C. The parent three-coordinate uranium(III) $[U{OSi(Mes)_3}_3]$ could not be isolated in our hands, with N₂-free syntheses affording only uranium(IV) compounds. The rational synthesis and full characterization of two such U(IV) byproducts, $[U{OSi(Mes)_3}{N(SiMe_3)_2}_3]$ and $[U{OSi(Mes)_3}_4]$, is also reported.

INTRODUCTION

Uranium(III) complexes are increasingly revealing unique small-molecule reactivity based upon the strong reducing potential of the $U^{\rm III}$ ion.^{1–3} Arene activation and C–H bond borylation exclusively using uranium,⁴ reductive carbon monoxide coupling,^{5,6} and carbon dioxide activation⁷ are but a few examples. The study of transition metal dinitrogen binding is now well advanced^{8,9} since the initial report of a transition metal dinitrogen complex.^{10,11} Particularly remarkable is the catalytic generation of ammonia from N_2 achieved by several molybdenum complexes¹²⁻¹⁶ with the ultimate goal of mimicking the huge scales of nitrogen fixation achieved by the Haber-Bosch process or nature's use of nitrogenase enzymes. Today, heterogeneous iron and ruthenium catalysts are used in the Haber–Bosch process,¹⁷ and iron centers are also present in nitrogenase enzymes;^{18,19} consequently much research has focused on molecular iron and ruthenium dinitrogen complexes and their reaction with dihydrogen.²⁰ However, it was also observed that heterogeneous uranium catalysts were also competent for the Haber–Bosch process,^{17,21} an interesting observation, as dinitrogen binding is still very rare in f-block coordination chemistry.^{22,23} Dinitrogen binding to an f-block cation was first demonstrated at a highly reducing Sm(II) center, through side-on binding in $\{(Cp^*)_2Sm\}_2(\mu-\eta^2:\eta^2-N_2)$ $(Cp^* = C_5Me_5)$, although binding was easily reversed, as the N₂ complex is in equilibrium with the N_2 -free complex.²⁴ Since then, f-block dinitrogen binding has advanced with the formation of N_2 compounds with more reducing Ln^{2+} centers, such as Tm, Dy, and Nd,^{25–27} due to the availability of suitable Ln^{2+} halides as starting materials.^{28–31} A new avenue for exploring lanthanide reduction chemistry was also pioneered by the combination of Ln^{3+} compounds with potassium under dinitrogen to generate the corresponding Ln_2^{3+} - $(N_2)^{2-}$ complexes, which were then used as reducing agents and

synthons for Ln²⁺ compounds that were too reducing to be isolate otherwise, at the time.^{32,33} This methodology has even been extended to Sc with the isolation of $\{(Cp^*)_2Sc\}_2(\mu-\eta^2:\eta^2-N_2)$.³⁴ Further reduction to an $(N_2)^{3-}$ species has also been demonstrated,^{35,36} and a recent report showed that photochemical activation of heteroleptic cyclopentadienyl derivatives of the lanthanides also leads to binding and reduction of dinitrogen.³⁷

The first reported actinide dinitrogen complex was formed by exposure of the "naked" U^{III} [tren'] fragment to N₂, affording ${\rm U(tren')}_2(\mu-\eta^2:\eta^2-N_2)$, A (tren' = N(CH₂CH₂NSi^fBuMe₂)₃), Chart 1, from which the N₂ readily dissociates under vacuum.^{38,39} Weaker N₂ binding was observed in the binuclear uranium-pentalene complex $\{U(Cp^*)(C_8H_4\{Si^iPr_3-1,4\}_2)\}_2(\mu$ - $\eta^{2}:\eta^{2}-N_{2})$, B,⁴⁰ and in mononuclear (Cp*)₃U($\eta^{1}-N_{2}$), C, in which the end-on-bound N2 can be maintained only at dinitrogen pressures above 5.4 atm.⁴¹ The heterometallic complex D was isolated using the combination of U^{III} and Mo^{III} amides and showed end-on bridging between the two metals.⁴² Most recently, we showed that the U(III) tris-(aryloxide) U(OTtbp)₃ (OTtbp = $O-2,4,6^{-t}Bu_3C_6H_2$) binds N₂ in a side-on geometry in $\{U(OTtbp)_3\}_2(\mu-\eta^2:\eta^2-N_2)$, E. This last complex releases N_2 only upon heating a solution to 80 °C, even in the presence of small O-containing reagents such as CO₂ and CO, whereas the di-tert-butyl aryloxide analogue, $\{U(ODtbp)_3\}_2(\mu-\eta^2:\eta^2-N_2)$ (Dtbp = 2,6^{-t}Bu₂C₆H₃), F, loses dinitrogen readily, and the majority of the product isolated in its synthesis is N₂-free.⁴³ The use of bulky siloxide ligands in low-coordinate transition metal^{44–49} and rare earth^{50–55} chemistry is well known, and a recent paper has detailed the use of $[OSi(O^tBu)_3]^-$ in U(III) chemistry.⁵⁶ We now describe

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Chart 1. Uranium Dinitrogen Compounds



major product

new dinitrogen compounds of uranium, stabilized using bulky trimesitylsiloxide ligands, which can be boiled in hydrocarbon solvent without loss of N_2 .

RESULTS

Scheme 1

Dinitrogen Binding. The bulky trimesitylsilanol HOSi- $(Mes)_3$ (Mes = mesityl, 2,4,6-Me₃C₆H₂) has previously been used to make model complexes for Al₂Me₆-grafted silica surfaces.⁵⁷ Protonolysis reactions between UN''_3 (N'' = $N(SiMe_3)_2)^{58}$ and 3 equivalents of HOSi(Mes)_3 were carried out in arene or *n*-hexane solvent, Scheme 1. In both cases, the title compound $[U{OSi(Mes)_3}_3]_2(\mu - \eta^2 : \eta^2 - N_2)$ (1) was formed, alongside other new byproducts, as observed by in situ ¹H NMR spectroscopy. The rate of formation of 1 was increased in n-hexane or by heating at 80 °C for 16 h. Careful crystallization was required to isolate 1 from the byproducts formed in any of the syntheses. The most effective techniques in our hands involve direct crystallization from either hot benzene reaction mixtures or directly from the synthesis carried out by layering *n*-hexane solutions of the two starting materials UN"₃ and HOSi(Mes)₃. Both result in modest isolated yields (up to 36%). The major byproducts are U^{IV} complexes: $U{OSi(Mes)_3}N''_3$ 2 predominates in ambient temperature syntheses, and $U{OSi(Mes)_3}_4$ 3 in elevated temperature syntheses. The identities of both have been confirmed by independent syntheses from the reaction of $(N'')_2 U(\kappa^2$ - $CH_2SiMe_2NSiMe_3$)⁵⁹ with 1 and 4 equivalents of HOSi(Mes)₃, respectively (see below). The parent three-coordinate uranium(III) U{OSi(Mes)₃}₃ could not be isolated in our hands. Reactions carried out by vacuum transfer of degassed solvents onto the reagents UN"₃ and HOSi(Mes)₃ gave almost identical ¹H NMR spectra to reactions performed under argon, dihydrogen, or carbon monoxide; in each case, the major product was identified as U{OSi(Mes)₃}N"₃ **2**, alongside a minor byproduct identified as U{OSi(Mes)₃}₄ **3** and small quantities of other unidentified products.

major by-product

The room-temperature ¹H NMR spectrum of **1** in d_8 -toluene (Figure SI.3) shows 15 different resonances from +10 to -17ppm, consistent with three distinct mesityl ligand environments. This could arise either from all Mes groups being magnetically inequivalent to each other in $[OSi(Mes)_3]^-$ and every [OSi(Mes)₃]⁻ ligand being equivalent or from three different [OSi(Mes)₃]⁻ ligand environments, in which each Mes group is magnetically equivalent to the other two in the same ligand. The chemical shifts for 1 are temperaturedependent and vary linearly with reciprocal temperature, consistent with the paramagnetism of the complex, but no fluxional process was observed between +100 and -80 °C (Figure SI.1). Resonances consistent with a single ligand environment were observed by ²⁹Si{¹H} (+63.6 ppm) NMR spectroscopy. ¹⁵N{¹H} NMR spectroscopy has been used to observe resonances for ¹⁵N₂-labeled lanthanide-dinitrogen complexes,³² and the ¹⁵N₂ resonance for the 98% ¹⁵N₂-labeled complex $1^{-15}N_2$ can be observed at +4213.5 ppm (Figure SI.2). This is at higher frequency than those seen previously for paramagnetic lanthanide complexes (+1001 ppm for Ln = Ce, 4f¹, and +2383 ppm for Ln = Pr, 4f², in { $(C_5Me_4H)_2Ln-(thf)$ } $_2(\mu-\eta^2:\eta^2-N_2)$,⁶⁰ but more importantly confirms that $(N_2)^{2-}$ in 1 is retained when samples are subjected to dynamic vacuum or stored in solution; the labeled ¹⁵N₂ was not observed to exchange with ¹⁴N₂.

Raman Spectroscopy. Raman spectroscopy was performed on samples of $1^{-14}N_2$ and $1^{-15}N_2$ sealed in glass capillaries (Figure 1). The spectrum of $1^{-14}N_2$ displays four



Figure 1. Raman spectra of powdered $1\text{-}^{15}N_2\text{-labeled}$ (upper) and $1\text{-}^{14}N_2$ (lower).

resonances between 1200 and 1700 cm⁻¹; the resonance at 1437 cm⁻¹ was absent in 1-¹⁵N₂ and was tentatively assigned as the $v_{\rm N-N}$. From reduced mass calculations, the $v_{\rm N-N}$ in $1^{-15}N_2$ is then predicted at 1388 cm⁻¹; however there was another resonance from the complex present in both isotopomers that was observed at a very similar frequency, which precluded the definitive assignment of the $v_{\rm N-N}$ in $1^{-15}N_{22}$ although this resonance is seen to increase in intensity in 1^{-15} N₂. The value observed for 1 correlates well to the $v_{\rm N-N}$ seen in the only other Raman spectroscopic study of a uranium-dinitrogen compound E $(1451 \text{ cm}^{-1})^{43}$ and to the yttrium N₂ compound $[\{(Me_3Si)_2N\}_2(thf)Y]_2(\mu-\eta^2:\eta^2-N_2)$ (1425 cm⁻¹),³⁵ where both compounds have been assigned a N=N bond order of 2, and is consistent with the reduction of N₂ to $(N_2)^{2-}$ in **1**. For the Nd compound $[\{C_5H_2({}^tBu)_3\}_2Nd]_2(\mu-\eta^2:\eta^2-N_2)$, a resonance at 1622 cm^{-1} was observed,³³ and these values are, as expected, significantly lower than free N_2 (2331 cm⁻¹).³³

Structural Chemistry. X-ray diffraction experiments were carried out on three different sets of crystals of 1, the first grown from a room-temperature slow diffusion reaction of the two reagents in *n*-hexane, the second from cooling of a heated benzene solution of the reagents, and the third from crystals of the benzene solvate placed under vacuum (see below). All three show dinitrogen bound side-on between two UX_3 (X = $OSi(Mes)_3$) fragments but with the X ligands oriented in a staggered conformation (1S) in the first (hexane) and eclipsed conformation (1E) in the latter two (both as a benzene solvate and after storage under vacuum), Figure 2. The N=N bond lengths are 1.124(12) Å for both N2 positions in 1E and 1.080(11) Å in 1S, shorter than the N=N bond lengths of 1.236(5) Å found in E^{43} and 1.232(10) Å in B^{40} and in end-on, bridging bimetallic D (1.232(11) Å).⁴² The N=N distances in both conformers are identical, within standard uncertainy, to that in A (1.109(7) Å),³⁸ in terminal-bound C (1.120(14) Å),⁴¹ and to the distance in free N₂ (1.0975 Å). There are a range of N=N distances observed in lanthanide N2 complexes; for



Figure 2. Thermal ellipsoid plots of the staggered **1S** (left) and eclipsed **1E** (right) isomers of **1**, together with Newman projections. Thermal ellipsoids are at 50% probability. Hydrogen atoms and all carbon atoms except the *ipso* carbons of the mesityl groups are omitted for clarity. Both positions of the disordered dinitrogen ligand in **1E** are shown in the end-on view (bottom right drawing). Green = U; blue = N; red = O; turquoise = Si; gray = C.

example [{(Me₃Si)₂N}₂(thf)Y]₂(μ - η ²: η ²-N₂) (for which a Raman-active N=N stretch was reported: 1.268(3) Å) and {(DtbpO)₂(thf)₂Dy}₂(μ - η ²: η ²-N₂) (1.257(7) Å)³⁵ are significantly longer than free N₂, but the distances in **1E** and **1S** are indistinguishable from that in weakly bound {(Cp*)₂Sm}₂(μ - η ²: η ²-N₂) (1.088(12) Å).²⁴

No agostic interactions are seen in the structures of 1 unlike in E. The U–O bond lengths are equivalent, 2.119(3)-2.128(3) Å for 1E and 2.131(4)-2.134(4) Å for 1S. This is identical to the U–O distance found in $[UCp_3(OSiPh_3)]$, 2.135(8) Å.⁶¹ The U–O distances for the terminal siloxide ligands in the U^{III} dimer $[U{OSi(O'Bu)_3}_2{\mu-OSi(O'Bu)_3}]_2$ were found to be slightly longer (mean 2.193(4) Å), while U– O siloxide distances in a U^{IV} bridging $(OCO_2)^{2-}$ compound are slightly shorter (mean 2.09(1) Å for the terminal siloxide ligands).⁵⁶ The Si–O bonds are also equivalent at 1.658(4)-1.663(4) Å in 1E and 1.659(3)-1.667(3) Å in 1S and unchanged from the free ligand (1.669(5) Å)

In order to confirm that N_2 is retained when the bulk sample is placed under vacuum, we carried out powder diffraction on a sample grown from benzene and subsequently placed under vacuum (Figure 3). The diffractogram, however, did not identify the structure grown from either n-hexane (1S) or benzene (1E), but instead a new phase was observed. The crystal structure of this phase was identified by single-crystal Xray diffraction from a single crystal in the same sample that had been placed under vacuum, and although the data are of poor quality and demonstrated connectivity only, it revealed the same eclipsed conformation of 1 (Figure SI.14) but in a different space group (C2/c in 1E rather than $P2_1/n$ in 1Evac). The structure shows the benzene lattice solvate molecules have been lost, as the unit cell volume had decreased by 2444 Å³, similar to the decrease expected from the loss of 24 benzene molecules (approximately 2592 Å³ using the 18 Å³ per atom as the approximate volume). This demonstrates the stability of the

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Figure 3. Identification of the phase of single crystals of 1E placed under vacuum, then ground to a powder, by comparison with the calculated powder pattern from the structure of 1Evac (calculated using the program Mercury).⁶²

uranium-dinitrogen complex to vacuum in the solid state, as the dinitrogen ligand has been retained despite the loss of solvent and gross structural change.

Thermal Stability Studies. ¹H NMR spectroscopy was used to monitor the stability of toluene solutions of 1 at 100 °C but did not reveal simple dissociation of N₂ as previously observed for U(OTtbp)₃.⁴³ Integration of the ¹H NMR spectra against an internal standard showed 92% of the complex intact after 30 min, but substantial loss of complex after another 30 min (60% remaining). However, heating the sample overnight (16 h) did not lead to complete loss of 1 (48% remained), indicating a more complicated decomposition process than the simple elimination of N₂. The products of decomposition appear to be predominantly U^{IV} byproducts with resonances for U{OSi(Mes)₃}₄ 3 having been tentatively assigned. This relatively slow decomposition at 100 °C represents remarkable stability for a uranium dinitrogen complex.

Uranium(IV) Complexes of the Siloxide Ligand. In order to facilitate identification of U^{IV} byproducts in the dinitrogen chemistry and to understand the ligand effect, hetero- and homoleptic complexes of U^{IV} with the trimes-itylsiloxide ligand were synthesized, Scheme 2. Reactions of the

Scheme 2



 U^{IV} metallacycle $[(N'')_2U(\kappa^2\text{-}CH_2\text{SiMe}_2\text{NSiMe}_3)]^{59}$ with 1 equivalent of HOSi(Mes)_3 at room temperature or 4 equivalents of HOSi(Mes)_3 at elevated temperature allowed the synthesis of colorless U{OSi(Mes)_3}{N(\text{SiMe}_3)_2}_3 2 and very pale pink U{OSi(Mes)_3}_4 3 in 40% and 22% isolated yields, respectively. ¹H NMR spectroscopy of benzene solutions of 2 shows multiple exchange processes occurring between -80

and +100 °C (Figure SI.5), although heating 2 at 100 °C also leads to further reaction presumably from ligand redistribution, as evidenced by growing resonances for the metallacycle $[(N'')_2 U(\kappa^2 - CH_2 SiMe_2 NSiMe_3)]$ occurring from the thermal decomposition of transiently formed UN"₄. The spectrum for 2 at 100 °C appears to be approaching the high-temperature regime of fast bond rotations, displaying averaged resonances for hydrogens of the $[OSi(Mes)_3]^-$ mesityl and $(N'')^$ trimethylsilyl groups; however, decreasing the temperature caused decoalescence of a number of signals in multiple stages, precluding a thorough assignment. The ¹H NMR spectrum of isolated 3 is much more straightforward with a single mesityl environment, indicating that the siloxide ligands are equivalent. However, ¹H NMR spectra of the crude reaction mixture and the spectrum of a previously heated sample of 3 (80 °C in benzene) are complicated by additional resonances for 8 CH and 12 CH₃ mesityl hydrogens. The ¹H VT NMR spectra show a broadening of all ligand resonances above 70 °C. Additionally, ¹H DOSY NMR spectroscopy of these samples showed that all these ligand resonances have the same diffusion coefficient, suggestive of a single complex with a size of approximately 2 Å smaller than that of 1, for which a diffusion coefficient was also measured (see Supporting Information (SI)). This suggested that dimerization or aggregation was not occurring at these temperatures. For these reasons, we suggest that the other species in the reaction mixtures that complicates the spectra is a lower symmetry isomer of 3. In complexes of the lanthanides with (OSiPh₃)⁻, such ligand rearrangements have been observed to be low-energy processes.⁶³ This would make the total yield of the reaction, calculated from the molar ratio of bound siloxide versus HN" produced, 61%. Complex 3 is acutely air and moisture sensitive and decomposes in the solid state and in solution under inert conditions (<3 ppm O_2), which precluded meaningful microanalysis. There is literature precedent for the thermal decomposition of uranium siloxide complexes, with the formation of hexamethyldisiloxane cited as a driving force.⁶⁴ The U^{III} dimer $[U{OSi(O^tBu)_3}_2{\mu-OSi (O^{t}Bu)_{3}$ had limited stability in organic solvents, which is not surprising, given the reducing nature of U^{III}. However, the U^{IV} carbonate complex of the same ligand, [U{OSi- $(O^{t}Bu)_{3}_{3}_{2}(\mu-\eta^{1}:\eta^{2}-CO_{3})$, was also observed to decompose to $U{OSi(O^tBu)_3}_4$ and an unknown carbonate complex over the course of several days.⁵⁶ In our case the instability of 3 was unexpected, given the stability of 1.

¹H NMR spectroscopy of the three compounds of the $[OSi(Mes)_3]^-$ ligand attest to the sterically congested nature of the multiple mesityl groups within the siloxide ligand and also the difficulty in interpretation of ¹H NMR spectra of these paramagnetic compounds, as assignment is necessarily based on relative integration rather than chemical shift.

X-ray diffraction experiments were carried out on single crystals of 2 and 3 grown from *n*-hexane and a toluene/*n*-hexane solution, respectively (Figure 4), and showed approximately tetrahedral uranium centers bound to four ligands. The U-O bond lengths (2.161(4) Å for 2, 2.128(3)-2.150(2) Å for 3) are significantly shorter than U-N bond distances (2.282(5)-2.308(5) Å), as seen generally for uranium alkoxides versus uranium amides, but equivalent within standard uncertainties to 1, as are the Si-O distances. The only structural parameter that does change between the complexes is the U-O-Si angle, which increases from 174° in 3 to 175.5° in 1 to the almost linear 178.8° in 2. The magnitude of this angle is greater than that observed for uranium aryloxide

Article



Figure 4. Displacement ellipsoid drawing of 2 (left) and 3 (right) with ellipsoids set at 50% probability. Hydrogen atoms are omitted, and carbon atoms in 3 are represented without thermal ellipsoids for clarity. Green = U; blue = N; red = O; turquoise = Si; gray = C. Selected bond lengths (Å) for 2: U1-O1 2.161(4), U1-N3 2.282(5), U1-N1 2.295(5), U1-N2 2.308(5), O1-Si1 1.659(4); selected bond lengths (Å) for 3: O1-U1 2.144(2), O2-U1 2.150(2), O3-U1 2.140(2), O4-U1 2.128(3), O1-Si1 1.657(3), O2-Si2 1.657(3), O3-Si3 1.658(3), O4-Si4 1.668(3).

	Mes Si O U	, ,∕ Si, N.Si, H H U	tBu tBu O U	tBu O tBu	\ Si∖N`Si` U
J-E (X-ray), Å J-E (calc. input), Å	2.12 - 2.16 2.1	2.280 2.3	2.105 2.1	2.108 2.1	2.28 - 2.31 2.3
% V _{bur}	22.3 %	23.7 %	25.2 %	25.4%	25.5 %

Figure 5. $%V_{bur}$ for large, monoanionic ligands ordered in increasing size. Calculated using the SambVca program (see text) and the parameters M-E = 2.1 Å with E = O, similar to 1; M-E = 2.3 for E = N (U-N_{av} = 2.295 Å in 2); sphere radius of 3.5 Å.

complexes, 65,66 and the combination of a short U–O bond and a large U–O–C angle has been used as an argument for π back-bonding in uranium alkoxides⁶⁷ and aryloxides. 65,66 However, the correlation between bond length and π -bond order ought not to be assumed as simple without knowing the extent of the ionic contribution to bonding, 68 and the linearity of the M–O–C bond in alkoxides has been demonstrated to be predominantly controlled by electrostatic effects in complexes of the lanthanides. 69 In complexes 1–3 the U–O–Si angle does appear to track with the relative steric bulk of the complexes (see below).

Estimation of the Steric Bulk of the Siloxide Ligand. Calculations of the "percentage buried volume" (% $V_{\rm bur}$) are useful to compare the steric demands of N-heterocyclic carbene and phosphine ligands and readily performed using a simple Web application.⁷⁰ We have explored whether this approach can be useful to determine the relative steric demands of bulky amide, aryloxide, and siloxide ligands.⁷¹ Coordinates for the ligands of interest were all taken from the U^{IV} compounds $U\{N(SiHMe_2)_2\}_4$ for $[N(SiMe_2H)_2]^{-,72}$ $[U\{OSi(Mes)_3\}\{N-(SiMe_3)_2\}_3]$ **2** for $[N(SiMe_3)_2]^-$ and $[OSi(Mes)_3]^-$, $\{(DtbpO)_3UOC\}_2$ for $[ODtbp]^{-,43}$ and $\{(TtbpO)_3UOC\}_2$ for [OTtbp]-.43 The process removes the uranium atom and places a dummy atom at a set distance away from the connecting element E (here, O or N) using an axis defined by two atoms for the planar aryloxides and amides or three atoms for the cone-shaped siloxide ligand. The intrinsic steric bulk of a ligand can be taken into account by using the same U-E distance, but we used two values to take into account the

shorter U–O distances; the standard parameters were U–E = 2.1 Å with E = O, similar to that seen in 1 (2.119–2.134 Å), and $U-E = 2.3 \text{ Å for } E = N (M-N_{av} = 2.295 \text{ Å in } 2)$, with a sphere radius of 3.5 Å for calculating the buried volume. The ligands can be ordered in increasing size, $[OSi(Mes)_3]^- <$ $[N(SiHMe_2)_2]^- < [OTtbp]^- \approx [ODtbp]^- \approx [N(SiMe_3)_2]^-$ (Figure 5), which indicates that the $[N(SiMe_3)_2]^-$ ligand has similar steric bulk to the aryloxides, but all three are significantly larger than the [OSi(Mes)₃]⁻ siloxide ligand used in this study. These were calculated assuming the U-O distance is 0.2 Å shorter than the U–N distance, although U–E distances can vary slightly depending on the nature of the other ligands (for the $[OSi(Mes)_3]^-$ ligand, average U-O in 3 is 2.141 Å and in 2 it is 2.161(4) Å; for [ODtbp]⁻, average U-O in [(DtbpO)₃U]₂(O₂C₂) is 2.108 Å, 2.135(4) Å in U(ODtbp)₄, and 2.145(8) Å in U(ODtbp)N"₃;⁶⁶ for $[N(SiMe_3)_2]^-$ in the same complex, average U–N is 2.285 Å compared to 2.295 Å in 2). U-E distances for U^{III} homoleptic UL₃ compounds are in general longer due to the larger ionic radius of U^{III} (1.165 Å for U^{III} and 1.03 Å for U^{IV} in six-coordinate octahedral environments).⁷³ For comparison, the $%V_{\rm bur}$ calculated values for the amides at a standard U-E distance (2.1 Å) have also been calculated (see SI) and produce a much larger value for N" (28.7%), as would be expected.

DISCUSSION

The binding of dinitrogen between two U^{III} cations is associated with reduction of the N_2 to the $(N_2)^{2-}$ diazenide dianion and concomitant formation of two U^{IV} centers, i.e., U

5f \rightarrow N₂ π -back-bonding.^{39,42,43,74,75} Traditionally, a shorter N–N distance close to, or indistinguishable from, free N_2 (1 and A) has been attributed to very weak N₂ binding and no reduction in the bond order from free N₂, while a longer N-N distance (B and E) has been attributed to stronger binding of the N₂ and formal reduction to the $(N_2)^{2-}$ dianion. Investigations of the first uranium-dinitrogen compound A, acknowledged the discrepancy between the experimental short N-N bond length and the calculations, which corroborated the direduced nature of the dinitrogen ligand. The authors attributed the short N-N distance found to the steric compression between ligands, which does not allow the uranium atoms to approach the dinitrogen ligand at an optimal distance.³⁹ They observed an average U–N distance of 2.419 Å to the dinitrogen ligand in A, but we observed average U-N distances of 2.459 Å in 1S, 2.411 Å in 1E, and 2.410 Å in E (the ligands in this complex are staggered), so the uranium centers appear to be the same distance from the N2 ligand in these complexes and also in **B** (av U–N = 2.412 Å) but have significantly different N–N distances.⁴⁰ Also, the U–O distances, which should shorten on a formal $U^{III} \rightarrow U^{IV}$ electron transfer associated with N2 reduction, change insignificantly for both 1 and E. We have previously noted that experimental N-N distances, whose data are based on electron density, rather than atomic position, can be unreliable, underestimating what is considered the standard (X-ray) definition for the interatomic N-N distance,43,76,77 and the vibrational data are a better indication of the degree of N2 reductive activation. Raman spectroscopy of 1S showed a band at 1437 cm⁻¹, similar to that seen in E (1451 cm⁻¹) and in agreement with a two-electron reduction and a N-N bond order of two.⁴³ In this work, there is a discrepancy between the short N-N distance observed in the molecular structure and the experimental evidence of N_2 reduction to $(N_2)^{2-}$ from Raman spectroscopy and the high thermal stability of 1.

Interestingly, we have been unable to isolate the N2-free, three-coordinate complex $U{OSi(Mes)_3}_3$ by N_2 elimination, by synthesis under argon, or as a solvato complex using benzene or thf/benzene or with 2,6-dimethylphenyl-isonitrile as a co-ligand, in contrast to $(THF)U(ODtbp)_3$ and $(THF)U-(OTtbp)_3$.^{43,78} The buried volume calculations have allowed us to consider the kinetic stabilization of uranium compounds for several ligands and are in agreement with our previous experimental finding that the much smaller ligand [N- $(SiHMe_2)_2$ could not stabilize U^{III},⁷² whereas the homoleptic UN''_3 is a well-known U^{III} precursor, although we have previously observed UN''_3 reactivity with arenes in a disproportionation pathway. The lack of solvent binding to UN''_{3} (such as thf) was presumed to be a consequence of steric shielding, but thf is readily and irreversibly bound to $U(ODtbp)_3$ and $U(OTtbp)_3$ to form four-coordinate complexes. Yet our calculations revealed the three-coordinate U^{III} aryloxide complexes to be similarly sterically hindered. In fact, coordination of an N-heterocyclic carbene to UN''_3 has been observed,⁷⁹ as well as reactivity with CO.⁸⁰ The trimesitylsiloxide ligand was calculated to be much less sterically bulky than the aryloxide ligands and $[\mathrm{N}'']^-$ and is also significantly smaller than $[N(SiHMe_2)_2]^-$, for which no homoleptic U^{III} compound could be isolated. The trimesitylsiloxide ligand could therefore also be insufficiently kinetically stabilizing to form the UX₃ complex without dinitrogen bound or insufficiently reducing. The absence of close ligand C-H groups that could provide agostic-like stabilizing interactions, which must benefit the

isolation of compound E, presumably also contributes to this. A distinct ligand effect in uranium dinitrogen binding is evident from the literature, where changes to the ligand environment have produced drastically different complex stabilities, and is well illustrated by the two closely related aryloxide complexes, where $U(OTtbp)_3$ forms a dinitrogen complex, E, stable to 80 °C, whereas the material isolated from the exposure of $U(ODtbp)_3$ to N_2 is predominantly dinitrogen-free. It is worth noting that the few f-block siloxide complexes known have mainly used ligands or reagents that contain secondary oxygen atoms, polyhedral organosilsesquioxanes,⁸¹ tris(*tert*-butoxy)siloxides,^{51,56} tetraphenyldisiloxanediols,^{82,83} or hexa-methylcyclotrisiloxanes,⁸⁴ which are both electronically and sterically different from the trimesitylsiloxide used in this study, but more importantly perhaps, the additional oxygen atoms present can act as donors for the metal centers, leading to a chelate effect, by bridging or otherwise, which stabilizes the resultant complexes.

CONCLUSION

The trimesitylsiloxide $[OSi(Mes)_3]^-$ ligand has been used for the first time in uranium chemistry and has allowed the encapsulation and reduction of N₂ to $(N_2)^{2-}$ in the most robust uranium dinitrogen complex yet observed, complex 1. The ligand is also capable of stabilizing heteroleptic and homoleptic U^{IV} species, but while the ability of the ligands to interdigitate and provide a protective environment around the reductively activated N₂ may be beneficial here, it makes spectroscopic study of the complexes difficult. Reasons for our inability to isolate a simple homoleptic or solvato-U^{III} adduct remain unclear.

EXPERIMENTAL SECTION

General Details. All manipulations were carried out under a dry, oxygen-free, dinitrogen atmosphere using standard Schlenk techniques or in MBraun Unilab or Vacuum Atmospheres OMNI-lab gloveboxes unless otherwise stated. THF, toluene, and n-hexane were degassed and dried using a commercial solvent system. Benzene, deuterated benzene, and toluene were boiled over potassium, vacuum transferred, and freeze-pump-thaw degassed three times prior to use. ¹H spectra were recorded on Bruker AVA 400 or 600 MHz NMR spectrometers at 298 K. ¹³C NMR spectra were recorded on a 500 MHz spectrometer equipped with a cryoprobe and referenced to internal solvent resonances. ¹⁵N spectra were recorded on a Bruker 400 MHz spectrometer referenced to an external sample of neat CH₃NO₂/ CD₃NO₂. The experiments were run inverse-gated with decoupling during acquisition (1 s) but not during the relaxation delay (2 s). Many experiments of 1024 scans covering 500 ppm each were run until the signal was located; then a longer collection (4096 scans) using different O 1p and sweep width settings was used to confirm the signal, and a line broadening of 10 Hz was applied. Chemical shifts are reported in parts per million and referenced to residual proton resonances calibrated against external TMS for ¹H, ¹³C, and ²⁹Si. Infrared spectra were recorded on Jasco 410 spectrophotometers. Solutions for UV-vis-NIR spectrophotometry were made in a nitrogen-filled glovebox, and spectra were recorded in a Teflon-tapped 10 mm quartz cell on a Jasco V-670 spectrophotometer. Raman spectroscopy was performed using a LabRam instrument equipped with a 50 mW He-Ne laser of wavelength 632.8 nm. [U{N-(SiMe₃)₂}₃] was synthesized as previously described in the literature⁸⁵ and sublimed prior to use. ClSiMes₃ (Mes = 2,4,6-Me₃C₆H₂) was synthesized as previously described in the literature,⁸⁶ and the subsequent hydrolysis was a larger scale adaption of a literature reaction⁵⁷ using ClSiMes₃ (3.03 g), KOH (10.3 g), ethanol (150 cm³), and water (70 cm³), which were heated to reflux overnight. The reaction mixture was reduced in volume and extracted with n-hexane,

Table 1. Crystallographic Data for All Compounds

	15	1E	1Evac	2	3	3	$HOSi(Mes)_3$
chemical formula	$C_{162}H_{198}N_2O_6Si_6U_2$	$\begin{array}{c} C_{162}H_{198}N_2O_6Si_6U_2{\cdot}6\\ (C_6H_6) \end{array}$	$C_{162}H_{198}N_2O_6Si_6U_2$	$C_{45}H_{87}N_3OSi_7U$	$\begin{array}{c} C_{108}H_{132}O_4Si_4U{\cdot}0.31\\ (C_{14}H_{10}),\ 3\ (C_6H_{14}) \end{array}$	$C_{108}H_{132}O_{4}Si_{4}U$	C ₂₇ H ₃₄ OSi
formula mass	2913.82	3382.47	2913.82	1120.84	2157.46	1844.60	402.63
cryst syst	triclinic	monoclinic	monoclinic	monoclinic	triclinic	cubic	monoclinic
a/Å	16.9787(4)	38.9299(14)	29.2851(19)	27.4437(7)	16.1405(4)	26.9997(1)	11.0984(5)
b/Å	17.1215(4)	18.1633(3)	17.6856(10)	22.2208(6)	17.1050(4)	26.9997(1)	12.1998(4)
c/Å	17.9145(4)	29.0426(9)	29.4728(17)	20.8071(6)	25.3526(6)	26.9997(1)	17.7889(8)
$lpha/{ m deg}$	109.763(2)	90.00	90.00	90.00	98.417(2)	90	90.00
β/\deg	92.606(2)	120.871(5)	95.943(6)	95.759(2)	95.6393(19)	90	104.370(4)
γ/deg	118.253(2)	90.00	90.00	90.00	117.137(2)	90	90.00
unit cell volume/Å ³	4182.4(2)	17626.5(13)	15182.6(16)	12624.6(6)	6052.6(3)	19682.3(2)	2333.23(17)
temp/K	170(2)	170(2)	170(2)	170(2)	170(2)	120(2)	170(2)
space group	$P\overline{1}$	C2/c	$P2_1/n$	C2/c	$P\overline{1}$	Pa3	C2/c
no. of formula units per unit cell, Z	1	4	4	8	2	8	4
absorption coeff, μ/mm^{-1}	2.025	1.932	2.231	2.733	1.430	1.749	0.116
no. of reflns measd	68 021	76 838	79 581	64 114	113 175	308 866	8406
no. of indep reflns	19 185	17 993	15 834	11 134	27 717	8200	1991
R _{int}	0.0748	0.0810	0.2808	0.1058	0.0633	0.1014	0.0463
final R_1 values $(I > 2\sigma(I))$	0.0632	0.0424	0.2573	0.0543	0.0478	0.0445	0.0778
final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1387	0.1051	0.5214	0.1071	0.1044	0.0962	0.1666
final R ₁ values (all data)	0.0821	0.0789	0.3565	0.0946	0.0699	0.0884	0.1094
final wR(F ²) values (all data)	0.1485	0.1125	0.5687	0.1185	0.1141	0.1209	0.1815

which was dried over MgSO₄, and the solvent was removed under reduced pressure. Recrystallization from *n*-hexane at -30 °C for 16 h gave colorless crystals (1.683 g, 58%). [(N")₂U(κ^2 -CH₂SiMe₂NSiMe₃)] was synthesized from the reaction between [UI₄(OEt₂)₂] and 4 KN(SiMe₃)₂ in toluene at 90 °C for 24 h; the product was obtained by sublimation of the crude solid obtained after removal of volatiles at 120 °C and 2 × 10⁻⁶ Torr.

Syntheses. [U{OSi(Mes)₃}₃]₂(μ - η ²: η ²- N_2), **1.** Method A: In *n*-Hexane. A dark purple *n*-hexane solution of U{N(SiMe₃)₂}₃ (305 mg, 0.424 mmol, 1 equiv, 30 cm³) was layered on top of a colorless *n*-hexane solution of HOSiMes₃ (512 mg, 1.27 mmol, 3 equiv, 30 cm³), and the mixture stored under an atmosphere of dinitrogen for 16 h, during which time a dark orange solution formed. Storage of this at $-30 \,^{\circ}$ C for 3 days yielded dark red crystals of [U{OSi(Mes)₃}₃]₂(μ - η ²: η ²-N₂), **1**, and a pale orange solution, which were separated by filtration and dried under vacuum (115 mg, 0.039 mmol, 18%). These crystals were suitable for an X-ray diffraction study (**1S**). Anal. Calcd for C₁₆₂H₁₉₈N₂O₆Si₆U₂·2(C₆H₁₄): C, 67.72; H, 7.38; N, 0.91. Found: C, 67.76; H, 7.27; N, 0.85.

Method B: In n-Hexane Solvent at 70 °C. An ampule was charged with U{N(SiMe₃)₂}₃ (52 mg, 0.073 mmol, 1 equiv), HOSi(Mes)₃ (88 mg, 0.22 mmol, 3 equiv), and *n*-hexane (2 cm³), and the resulting solution heated to 70 °C under an atmosphere of dinitrogen for 16 h. Red microcrystalline product was observed, and the solution was left to cool to room temperature. The pale yellow supernatant was removed, and the product [U{OSi(Mes)₃}₃]₂(μ - η^2 : η^2 -N₂) (1) dried under vacuum (44 mg, 0.015 mmol, 42%). ¹H NMR spectroscopy revealed a small amount of an impurity, indicating the need for careful crystallization to separate the desired complex from byproducts.

Method C: In Benzene Solvent at 80 °C. An ampule was charged with $U\{N(SiMe_3)_2\}_3$ (90 mg, 0.125 mmol, 1 equiv), HOSi(Mes)_3 (152 mg, 0.376 mmol, 3 equiv), and benzene (2 cm³), and the

resulting solution heated to 80 °C under an atmosphere of dinitrogen for 16 h. Red crystals of product were observed, and the solution was left to cool to room temperature. The supernatant was removed, and the product $[U{OSi(Mes)_3}_3]_2(\mu-\eta^2:\eta^2-N_2)$ (1) washed with *n*-hexane (2 cm³) and dried under vacuum (63 mg, 0.022 mmol, 35%). Single crystals for X-ray diffraction studies were grown from the hot benzene reaction as it cooled to room temperature (**1E**). For a solvated sample: Anal. Calcd for $C_{162}H_{198}N_2O_6Si_6U_2\cdot6(C_6H_6)$: C, 70.31; H, 6.97; N, 0.83. Found: C, 70.13; H, 6.89; N, 0.93.

Data for $[U{OSi(Mes)_3}_3]_2(\mu-\eta^2:\eta^2-N_2)$, **1**. ¹H NMR (400 MHz, 298) K, C₇D₈): δ (ppm) 9.59 (1 H, s, meta-H), 9.21 (1 H, s, meta-H), 9.03 (1 H, s, meta-H), 7.68 (1 H, s, meta-H), 6.78 (3 H, br s, Me), 5.03 (1 H, s, meta-H), 4.35 (3 H, s, Me), 4.13 (3 H, s, Me), 3.83 (3 H, s, Me), 2.57 (3 H, s, Me), 1.83 (3 H, s, Me), -0.42 (3 H, s, Me), -0.71 (1 H, s, meta-H), -3.44 (3 H, br s, Me), -17.16 (3 H, br s, Me). ¹³C NMR (125.76 MHz, 298 K, C₇D₈): δ (ppm) 151.21, 150.89, 149.13, 148.83, 147.54, 146.52, 142.51, 140.89, 139.61, 138.73, 136.93, 135.06, 134.38, 133.65, 132.00, 131.38, 129.64, 120.49, 28.61, 25.08, 24.87, 24.22, 22.74, 22.61, 17.74, 1.53, -51.13. ²⁹Si NMR (79.45 MHz, 298 K, C_7D_8): δ (ppm) 63.6. Raman (crystalline sample) cm⁻¹: 1282, 1372, 1437 (N₂), 1596. IR (nujol mull) cm⁻¹ (intensity): 1604 (s), 1547 (m), 1406 (m), 1260 (w), 1233 (w), 1064 (m), 1029 (m), 957 (w), 876 (m), 846 (m), 808 (s), 638 (s) . UV-vis-NIR (0.00083 M toluene solution) λ , nm (ϵ , M⁻¹ cm⁻¹): 673 (210), 809 (62), 897 (53), 1087 (50), 1153 (51), 1174 (50), 1292 (38), 1367 (32), 1820 (54), 2041 (110).

Freeze-pump-thaw degassing had no effect on the ¹H NMR spectroscopic resonances for the dinitrogen compound **1**. Reactions of UN''_{3} with 3 equivalents of HOSi(Mes)₃ performed under argon revealed no ¹H NMR spectroscopic resonances for the N₂ compound **1**, but resonances for U{OSi(Mes)₃}N''_{3} **2** and for U{OSi(Mes)₃}**4** 3 were observed, which increased when heated to 90 °C overnight.

¹⁵N₂-Labeled [U{OSi(Mes)₃}₃]₂(μ-η²:η²⁻¹⁵N₂): **1**-¹⁵N₂. An ampule was charged with U{N(SiMe₃)₂}₃ (83 mg, 0.115 mmol, 1 equiv) and HOSi(Mes)₃ (139 mg, 0.345 mmol, 3 equiv) and placed under vacuum. Benzene (2 cm³) was degassed by the freeze–pump–thaw method three times and vacuum transferred onto the solids. ¹⁵N₂ (98.3%, Cambridge isotopes) was then added to the still-frozen solution, the ampule was sealed, and the resulting solution was heated to 80 °C for 16 h, during which time red crystals of product were observed to form. The solution was allowed to cool to room temperature, the supernatant was removed, and the red crystalline product [U{OSi(Mes)₃}₃]₂(μ-η²:η²⁻¹⁵N₂) (1-¹⁵N₂) was washed with *n*-hexane (2 cm³) and dried under vacuum (62 mg, 0.021 mmol, 36%). ¹⁵N NMR (40.52 MHz, 298 K, C₇D₈): δ (ppm) 4213.5. Raman (crystalline sample) cm⁻¹: 1282, 1372 (overlapped ¹⁵N₂ and ligand), 1601.

 $U{OSi(Mes)_3}N''_3$ **2**. [(N'')₂U(κ^2 -CH₂SiMe₂NSiMe₃)] (168 mg, 0.233 mmol, 1 equiv) and HOSi(Mes)₃ (94 mg, 0.233, 1 equiv) were dissolved in toluene (5 cm³), and the solution was stored at room temperature for 16 h. All of the volatiles were removed under reduced pressure from the pale yellow solution, and the residues were extracted with *n*-hexane (10 cm³). The solution was filtered, reduced in volume to ca. 5 cm³, and stored at -30 °C for 16 h to afford colorless crystals of U{OSi(Mes)₃}N''₃ **2**, which were isolated by removal of the supernatant, washing once at -30 °C with *n*-hexane, and drying under vacuum (105 mg, 0.094 mmol, 40%). ¹H NMR (400 MHz, 333 K, C₇D₈): δ (ppm) 12.32 (s, 3 H, Mes-Me), 11.42 (s, 1 H, *meta*-H), 7.28 (s, 3 H, Mes-Me), 6.68 (s, 1 H, *meta*-H), 5.51 (vbr s, N(SiMe₃)) (SiMe₃)), 2.71 (s, 3 H, Mes-Me), -16.34 (vbr s, N(SiMe₃) (SiMe₃)). Anal. Calcd for C₄₅H₈₇N₃OSi₇U: C, 48.22; H, 7.82; N, 3.75. Found: C, 48.45; H, 7.92; N, 3.67.

U{*OSi*(*Mes*)₃/₄ **3**. [(N["])₂U(κ^2 -CH₂SiMe₂NSiMe₃)] (61 mg, 0.086 mmol, 1 equiv) and HOSi(Mes)₃ (138 mg, 0.340 mmol, 4 equiv) were dissolved in toluene (5 cm³), and the solution was heated at 100 °C for 16 h. All of the volatiles were removed under reduced pressure from the pale orange solution, *n*-pentane (5 cm³) was added, and the resultant suspension was sonicated for 10 min. The yellow solution was filtered, and the solids were washed with a further two times with *n*-pentane (5 cm³) and dried under vacuum to yield **3** as a very pale pink solid (31 mg, 0.017 mmol, 22%). ¹H NMR (400 MHz, 298 K, C₆D₆): δ (ppm) 6.66 (1 H, s, *meta*-H), 5.98 (1 H, s, *meta*-H), 2.42 (3 H, s, Me), 2.09 (3 H, s, Me), -0.97 (3 H, br s, Me). EI-MS *m*/*z* = 1844 (100%, M). Anal. Calcd for C₁₀₈H₁₃₂O₄Si₄U: C, 70.32; H, 7.21. Found: C, 57.81; H, 6.03.

Crystallographic Details. Diffraction experiments on these samples were carried out on single crystals covered in inert oil cooled to 170 K on an Oxford diffraction Excalibur four-circle diffractometer employing Mo K α radiation ($\lambda = 0.71073$ Å) or at 120 K; for 3 in $Pa\overline{3}$, on an Oxford diffraction SuperNova employing Mo K α radiation. The structures were solved by direct methods (XS) and refined by leastsquares on weighted F^2 values for all reflections (XL).⁸⁷ All hydrogen atoms were constrained to ideal geometries and refined with fixed isotropic displacement parameters except the O-H in the structure of HOSiMes₃, whose position was freely refined with a fixed isotropic displacement parameter. The crystals of 1E that were placed under vacuum did not diffract at high angle, and generally the data collected were poor, so only data out to $44^{\circ} 2\theta$ were included in the final refinement, which allowed the anisotropic refinement of only the U and Si atoms. Extensive use of restraints and constraints was required to model the OSi(Mes)₃ ligands, and only basic connectivity could be established. Refinement proceeded to give the residuals shown in Table 1. Complex neutral-atom scattering factors were used. Disordered hexane solvent in 1S, 2, and 3 in $Pa\overline{3}$ was modeled using the SQUEEZE subroutine in the PLATON software suite. 1E is a benzene solvate, and the N2 ligand was disordered over two positions 90° apart. The structure of HOSi(Mes)₃ (see SI) showed the entire molecule to be disordered over two positions. The structure of compound 3 was also determined as its n-hexane solvate, which also contained 0.31 equivalent of anthracene cocrystallized from an impurity in the starting material. The metallacycle used in this reaction was formed as a byproduct in the synthesis of the bridgingarene compound $N''_2 U(\mu\text{-}C_6H_6) UN''_2$ in which anthracene had been added.⁴

Powder diffraction experiments were carried out on samples flamesealed in capillaries using a Bruker D8 Advance diffractometer in transmittance mode employing Cu radiation from 5° to 40° 2θ in 0.02° increments at room temperature.

ASSOCIATED CONTENT

S Supporting Information

Additional spectroscopic data and full crystallographic data (cif format). This material is available free of charge via the Internet at http://pubs.acs.org. Codes for access to the full crystallographic data through the CCDC are in Table 1.

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Author Contributions

The project was conceived and carried out and the manuscript written by P.L.A., A.I.G., S.M.M., and J.H.F. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Arnold, P. L. Chem. Commun. 2011, 47, 9005.
- (2) Evans, W. J.; Kozimor, S. A. Coord. Chem. Rev. 2006, 250, 911.
- (3) Gardner, B. M.; Liddle, S. T. Eur. J. Inorg. Chem. 2013.

(4) Arnold, P. L.; Mansell, S. M.; Maron, L.; McKay, D. Nat. Chem. 2012, 4, 668.

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

(6) Arnold, P. L.; Turner, Z. R.; Bellabarba, R. M.; Tooze, R. P. Chem. Sci. 2011, 2, 77.

- (7) Lam, O. P.; Meyer, K. Polyhedron 2012, 32, 1.
- (8) Fryzuk, M. D. Chem. Commun. 2013, 49, 4866.
- (9) MacKay, B. A.; Fryzuk, M. D. Chem. Rev. 2004, 104, 385.
- (10) Allen, A. D.; Senoff, C. V. Chem. Commun. 1965, 621.
- (11) Senoff, C. V. J. Chem. Educ. 1990, 67, 368.
- (12) Yandulov, D. V.; Schrock, R. R. Science 2003, 301, 76.
- (13) Schrock, R. R. Proc. Natl. Acad. Sci. U.S.A. 2006, 103, 17087.
- (14) Schrock, R. R. Nat. Chem. 2011, 3, 95.

(15) Arashiba, K.; Miyake, Y.; Nishibayashi, Y. Nat. Chem. 2011, 3,

- 120.
- (16) Nishibayashi, Y. Dalton Trans. 2012, 41, 7447.

(17) Hellman, A.; Baerends, E. J.; Biczysko, M.; Bligaard, T.; Christensen, C. H.; Clary, D. C.; Dahl, S.; van Harrevelt, R.; Honkala, K.; Jonsson, H.; Kroes, G. J.; Luppi, M.; Manthe, U.; Norskov, J. K.; Olsen, R. A.; Rossmeisl, J.; Skulason, E.; Tautermann, C. S.; Varandas,

A. J. C.; Vincent, J. K. J. Phys. Chem. B 2006, 110, 17719.

(18) Howard, J. B.; Rees, D. C. Chem. Rev. 1996, 96, 2965.

(19) Hoffman, B. M.; Dean, D. R.; Seefeldt, L. C. Acc. Chem. Res. 2009, 42, 609.

(20) Rodriguez, M. M.; Bill, E.; Brennessel, W. W.; Holland, P. L. Science 2011, 334, 780.

(21) Fox, A. R.; Bart, S. C.; Meyer, K.; Cummins, C. C. Nature 2008, 455, 341.

(22) Gardiner, M. G. Materials 2010, 3, 841.

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- (23) Evans, W. J.; Lee, D. S. Can. J. Chem. 2005, 83, 375.
- (24) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. J. Am. Chem. Soc. 1988, 110, 6877.
- (25) Evans, W. J.; Allen, N. T.; Ziller, J. W. J. Am. Chem. Soc. 2001, 123, 7927.
- (26) Evans, W. J.; Allen, N. T.; Ziller, J. W. Angew. Chem, Int. Ed. 2002, 41, 359.
- (27) Evans, W. J.; Zucchi, G.; Ziller, J. W. J. Am. Chem. Soc. 2003, 125, 10.
- (28) 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.
- (29) Bochkarev, M. N.; Fagin, A. A. Chem.-Eur. J. 1999, 5, 2990.
- (30) Evans, W. J.; Allen, N. T.; Ziller, J. W. J. Am. Chem. Soc. 2000, 122, 11749.
- (31) Bochkarev, M. N.; Fedushkin, I. L.; Dechert, S.; Fagin, A. A.; Schumann, H. Angew. Chem., Int. Ed. 2001, 40, 3176.
- (32) 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.
- (33) Jaroschik, F.; Momin, A.; Nief, F.; Le Goff, X. F.; Deacon, G. B.; Junk, P. C. Angew. Chem., Int. Ed. **2009**, 48, 1117.
- (34) Demir, S.; Lorenz, S. E.; Fang, M.; Furche, F.; Meyer, G.; Ziller, J. W.; Evans, W. J. *J. Am. Chem. Soc.* **2010**, *132*, 11151.
- (35) Evans, W. J.; Fang, M.; Zucchi, G.; Furche, F.; Ziller, J. W.; Hoekstra, R. M.; Zink, J. I. J. Am. Chem. Soc. 2009, 131, 11195.
- (36) Fang, M.; Bates, J. E.; Lorenz, S. E.; Lee, D. S.; Rego, D. B.; Ziller, J. W.; Furche, F.; Evans, W. J. *Inorg. Chem.* **2011**, *50*, 1459.
- (37) Fieser, M. E.; Bates, J. E.; Ziller, J. W.; Furche, F.; Evans, W. J. J. Am. Chem. Soc. **2013**, 135, 3804.
- (38) Roussel, P.; Scott, P. J. Am. Chem. Soc. 1998, 120, 1070.
- (39) Roussel, P.; Errington, W.; Kaltsoyannis, N.; Scott, P. J. Organomet. Chem. 2001, 635, 69.
- (40) Cloke, F. G. N.; Hitchcock, P. B. J. Am. Chem. Soc. 2002, 124, 9352.
- (41) Evans, W. J.; Kozimor, S. A.; Ziller, J. W. J. Am. Chem. Soc. 2003, 125, 14264.
- (42) Odom, A. L.; Arnold, P. L.; Cummins, C. C. J. Am. Chem. Soc. 1998, 120, 5836.
- (43) Mansell, S. M.; Kaltsoyannis, N.; Arnold, P. L. J. Am. Chem. Soc. 2011, 133, 9036.
- (44) Krempner, C. Eur. J. Inorg. Chem. 2011, 1689.
- (45) Marshak, M. P.; Nocera, D. G. Inorg. Chem. 2013, 52, 1173.
- (46) Hulley, E. B.; Bonanno, J. B.; Wolczanski, P. T.; Cundari, T. R.;
- Lobkovsky, E. B. Inorg. Chem. 2010, 49, 8524.
- (47) Wolczanski, P. T. Polyhedron 1995, 14, 3335.
- (48) Kuiper, D. S.; Wolczanski, P. T.; Lobkovsky, E. B.; Cundari, T. R. J. Am. Chem. Soc. 2008, 130, 12931.
- (49) Wolczanski, P. T. Chem. Commun. 2009, 740.
- (50) Elvidge, B. R.; Arndt, S.; Spaniol, T. P.; Okuda, J. Dalton Trans. 2006, 0, 890.
- (51) Nishiura, M.; Hou, Z. M.; Wakatsuki, Y. Organometallics 2004, 23, 1359.
- (52) Fischbach, A.; Eickerling, G.; Scherer, W.; Herdtweck, E.; Anwander, R. Z. Naturforsch., B: Chem. Sci. 2004, 59, 1353.
- (53) Evans, W. J.; Golden, R. E.; Ziller, J. W. Inorg. Chem. 1991, 30, 4963.
- (54) Duncalf, D. J.; Hitchcock, P. B.; Lawless, G. A. J. Organomet. Chem. 1996, 506, 347.
- (55) Shao, P. C.; Berg, D. J.; Bushnell, G. W. Inorg. Chem. 1994, 33, 3452.
- (56) Mougel, V.; Camp, C.; Pécaut, J.; Copéret, C.; Maron, L.; Kefalidis, C. E.; Mazzanti, M. Angew. Chem., Int. Ed. **2012**, *51*, 12280– 12284.
- (57) Wrobel, O.; Schaper, F.; Brintzinger, H. H. Organometallics 2004, 23, 900.
- (58) Andersen, R. A. Inorg. Chem. 1979, 18, 1507.
- (59) Simpson, S. J.; Turner, H. W.; Andersen, R. A. Inorg. Chem. 1981, 20, 2991.

- (60) Evans, W. J.; Rego, D. B.; Ziller, J. W. Inorg. Chem. 2006, 45, 10790.
- (61) Porchia, M.; Brianese, N.; Casellato, U.; Ossola, F.; Rossetto, G.; Zanella, P.; Graziani, R. J. Chem. Soc., Dalton Trans. **1989**, 0, 677.
- (62) Macrae, C. F.; Bruno, I. J.; Chisholm, J. A.; Edgington, P. R.; McCabe, P.; Pidcock, E.; Rodriguez-Monge, L.; Taylor, R.; van de
- Streek, J.; Wood, P. A. J. Appl. Crystallogr. 2008, 41, 466.
 (63) McGeary, M. J.; Coan, P. S.; Folting, K.; Streib, W. E.; Caulton, K. G. Inorg. Chem. 1991, 30, 1723.
- (64) Brown, J. L.; Mokhtarzadeh, C. C.; Lever, J. M.; Wu, G.; Havton, T. W. Inorg. Chem. 2011, 50, 5105.
- (65) Van der Sluys, W. G.; Burns, C. J.; Huffman, J. C.; Sattelberger, A. P. J. Am. Chem. Soc. **1988**, 110, 5924.
- (66) Berg, J. M.; Clark, D. L.; Huffman, J. C.; Morris, D. E.; Sattelberger, A. P.; Streib, W. E.; Vandersluys, W. G.; Watkin, J. G. J. Am. Chem. Soc. **1992**, 114, 10811.
- (67) Bursten, B. E.; Casarin, M.; Ellis, D. E.; Fragala, I.; Marks, T. J. Inorg. Chem. **1986**, 25, 1257.
- (68) Cayton, R. H.; Chisholm, M. H.; Davidson, E. R.; DiStasi, V. F.; Du, P.; Huffman, J. C. *Inorg. Chem.* **1991**, *30*, 1020.
- (69) Russo, M. R.; Kaltsoyannis, N.; Sella, A. *Chem. Commun.* 2002, 2458.
- (70) Clavier, H.; Nolan, S. P. Chem. Commun. 2010, 46, 841.
- (71) Poater, A.; Cosenza, B.; Correa, A.; Giudice, S.; Ragone, F.; Scarano, V.; Cavallo, L. *Eur. J. Inorg. Chem.* **2009**, 2009, 1759.
- (72) Mansell, S. M.; Perandones, B. F.; Arnold, P. L. J. Organomet. Chem. 2010, 695, 2814.
- (73) Source: WebElements [http://www.webelements.com/].
- (74) Kaltsoyannis, N.; Scott, P. Chem. Commun. 1998, 1665.
- (75) Cloke, F. G. N.; Green, J. C.; Kaltsoyannis, N. Organometallics 2004, 23, 832.
- (76) Hirshfeld, F. L. Acta Crystallogr., Sect. A 1976, 32, 239.
- (77) Braga, D.; Koetzle, T. F. Acta Crystallogr., Sect. B 1988, 44, 151.
- (78) Van der Sluys, W. G.; Burns, C. J.; Huffman, J. C.; Sattelberger,
- A. P. J. Am. Chem. Soc. 1988, 110, 5924.
- (79) Nakai, H.; Hu, X. L.; Zakharov, L. N.; Rheingold, A. L.; Meyer, K. Inorg. Chem. **2004**, 43, 855.
- (80) Turner, Z. R.; Bellabarba, R.; Tooze, R. P.; Arnold, P. L. J. Am. Chem. Soc. 2010, 132, 4050.
- (81) Arnold, P. L.; Blake, A. J.; Hall, S. N.; Ward, B. D.; Wilson, C. Dalton Trans. 2001, 488.
- (82) Lorenz, V.; Fischer, A.; Jacob, K.; Bruser, W.; Gelbrich, T.; Jones, P. G.; Edelmann, F. T. *Chem. Commun.* **1998**, 2217.
- (83) Lorenz, V.; Fischer, A.; Jacob, K.; Bruser, W.; Edelmann, F. T. Chem.—Eur. J. 2001, 7, 848.
- (84) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. Organometallics 1991, 10, 134.
- (85) Clark, D. L.; Sattelberger, A. P.; Andersen, R. A. Inorg. Synth. 1997, 31, 307.
- (86) Zigler, S. S.; Johnson, L. M.; West, R. J. Organomet. Chem. 1988, 341, 187.
- (87) Sheldrick, G. M. Acta Crystallogr., Sect. A 2008, 64, 112.