

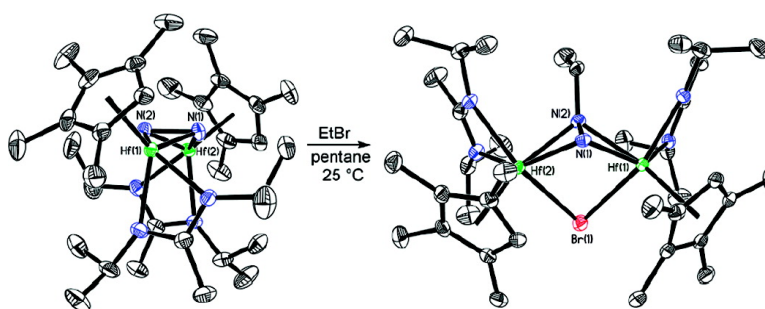
Communication

Extreme N#N Bond Elongation and Facile N-Atom Functionalization Reactions within Two Structurally Versatile New Families of Group 4 Bimetallic “Side-on-Bridged” Dinitrogen Complexes for Zirconium and Hafnium

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Extreme N≡N Bond Elongation and Facile N-Atom Functionalization Reactions within Two Structurally Versatile New Families of Group 4 Bimetallic “Side-on-Bridged” Dinitrogen Complexes for Zirconium and Hafnium

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The development of transition-metal-based catalysts that can mediate N-atom functionalization reactions of dinitrogen at, or near, ambient conditions remains an academic challenge with enormous potential synthetic and societal benefits.¹ In this regard, seminal experimental contributions reported by the groups of Fryzuk^{1d,2} and Chirik,^{1e,3} along with subsequent theoretical investigations,⁴ have now served to validate a “side-on-bridging N₂” structural motif as a means by which to achieve a high degree of N≡N bond elongation within at least two different families of group 4 bimetallic dinitrogen complexes of general formula, [L_nM]₂(μ-η²:η²-N₂) (M = Zr and Hf). As quantified by crystallographically derived solid-state nitrogen–nitrogen bond distances, *d*(N–N), these investigators have further demonstrated that a significant increase in the magnitude of this parameter correlates well with a lowering of barriers, relative to those of free N₂, for an increasing range of desired N-atom functionalization processes, including hydrogenation and hydrosilylation.^{1–3} However, as the increasing database for these two families of compounds attests, side-on-bridging N₂ complexation by itself is not a sufficient guarantee for a strongly activated N≡N bond. Indeed, as experimental and theoretical studies with the Fryzuk and Chirik systems have matured, it is becoming increasingly apparent that only a small window of synthetic derivatives might potentially exist that can deliver the requisite steric and electronic features of the supporting ancillary ligand environment for achieving successful side-on-bridging N₂ complexation that occurs in concert with low barriers for N-atom functionalization. Herein, we now introduce two new synthetically versatile and readily accessible families of [L_nM]₂(μ-η²:η²-N₂) (M = Zr and Hf) complexes that can support an extreme degree of N≡N bond elongation as manifested in *d*(N–N) values of up to 1.64 Å, as well as low barriers for N-atom functionalization involving hydrogenation, hydrosilylation, and, for the first time, alkylation with alkyl bromides at ambient temperature within a range of structural variants.

Scheme 1 summarizes results obtained for chemical reduction of Zr(IV) and Hf(IV) monocyclopentadienyl, guanidinate (X = NMe₂), and amidinate (X = Me) dichloride precursors of general formula, (η⁵-C₅Me_nR)M[N(R')C(X)N(R')]Cl₂ (R = H or Me).⁵ More specifically, by employing 3 equiv of potassium graphite (KC₈) in tetrahydrofuran (THF) at low temperature under an atmosphere of N₂ (1 atm), the corresponding series of group 4 bimetallic N₂ complexes, **1–6**, were reproducibly obtained in modest isolated yields as highly air-sensitive, dark blue or dark purple, diamagnetic crystalline solids for which analytical, spectroscopic, and single-crystal X-ray analyses are fully consistent with the side-on-bridged N₂ structures depicted.⁵ As derived from the last of these techniques, Figure 1 presents the molecular structures of **2** and **5** that serve as representative examples, and Table 1 provides a listing of selected geometric parameters for the entire

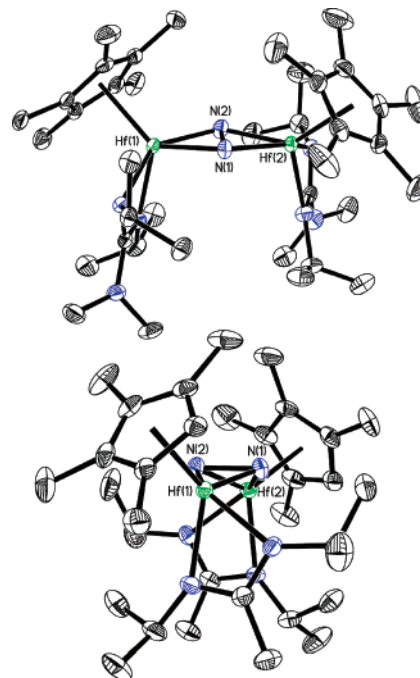
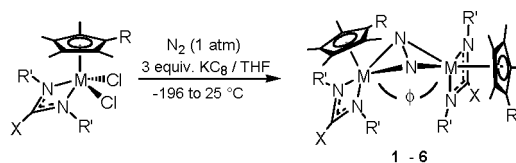


Figure 1. Molecular structures (30% thermal ellipsoids) of (top) **2** and (bottom) **5**. Hydrogen atoms have been removed for the sake of clarity.

Scheme 1



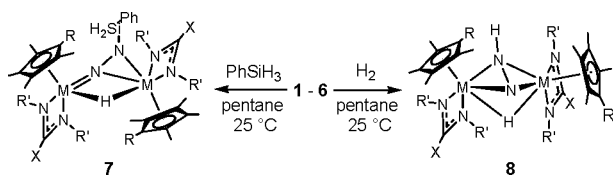
1: M = Zr, X = NMe₂, R = Me, R' = *i*-Pr (19%); **2**: M = Hf, X = NMe₂, R = Me, R' = *i*-Pr (39%); **3**: M = Hf, X = NMe₂, R = H, R' = *i*-Pr (45%); **4**: M = Hf, X = Me, R = Me, R' = *i*-Pr (36%); **5**: M = Hf, X = Me, R = H, R' = *i*-Pr (34%); **6**: M = Hf, X = Me, R = Me, R' = Et (27%)

series, **1–6**, from which several striking structural features and trends can be deduced regarding the extent of N≡N bond elongation that has been achieved in these complexes. Thus, to begin, for both M = Zr and Hf, *d*(N–N) values all exceed 1.51 Å [cf. *d*(N–N) of 1.0975 and 1.47 Å in free N₂ and N₂H₄, respectively],⁶ with a significant increase being observed in going from the second to third row metal while keeping all other structural features of the supporting ligands constant.⁷ Further, the entire range of *d*(N–N) values exhibited by the hafnium complexes, **2–6**, which reach the upper limit of 1.635(5) Å, are without precedent for N₂ activation through bimetallic coordination,^{1,8} and these values greatly exceed the previously recorded longest *d*(N–N) value of 1.548(7) Å observed in [(PNP)ZrX]₂(μ-η²:η²-N₂) [(PNP) = N(SiMe₂CH₂P(*i*-

Table 1. Selected Solid-State Molecular Parameters for **1–6**^a

	M, X R, R'	$d(M_1N_{1,2})$ (Å)	$d(M_2N_{1,2})$ (Å)	$d(N_1N_2)$ (Å)	$180-\phi^a$ (°)	θ^b (°)
1	Zr, NMe ₂	2.044(2)	2.048(2)	1.518(2)	12.5	72.1
	Me, <i>i</i> -Pr	2.044(2)	2.034(2)			
2	Hf, NMe ₂	2.027(3)	2.032(3)	1.581(4)	10.9	72.0
	Me, <i>i</i> -Pr	2.030(3)	2.021(3)			
3	Hf, NMe ₂	2.018(5)	2.041(5)	1.600(6)	20.0	70.5
	H, <i>i</i> -Pr	2.033(5)	2.020(5)			
4	Hf, Me	2.018(2)	2.023(2)	1.611(4)	22.4	72.8
	Me, <i>i</i> -Pr	2.023(2)	2.018(2)			
5	Hf, Me,	2.020(3)	2.020(3)	1.630(4)	33.3	68.8
	H, <i>i</i> -Pr	2.032(3)	2.020(3)			
6	Hf, Me	2.027(4)	2.013(4)	1.635(5)	31.4	67.8
	Me, Et	2.010(4)	2.028(4)			

^a The ϕ is defined as the angle between the two M–N–N planes; see Scheme 1. ^b Dihedral angle defined by Cnt(1)–Hf(1)–Hf(2)–Cnt(2), where Cnt(*n*) is the calculated centroid for the cyclopentadienyl ring on each metal center.

Scheme 2

Pr)₂)₂, X = Cl]⁹ and that of 1.423(11) Å obtained for the only previously known and structurally characterized [L_{*n*}Hf]₂(μ - η^2 : η^2 -N₂) complex where L_{*n*} = (η^5 -C₅Me₄H).^{1d,7} In this respect, a ¹⁵N NMR (40.5 MHz, benzene-*d*₆) spectrum of ¹⁵N₂ (99%) labeled **3** provided a chemical shift of δ 483 ppm (relative to liquid NH₃ as an external reference), and this can be compared to 590.5 ppm reported for [(η^5 -C₅Me₄H)₂Hf]₂(μ - η^2 : η^2 -N₂).⁷

As Table 1 reveals, all the M₂N₂ cores in **1–6** adopt a distinctly nonplanar geometry with an apparent strong correlation existing between an increase in $d(N-N)$ with an increase in the M₂N₂ fold angle parameter ($180^\circ - \phi$) that simultaneously has only a minor attenuating effect on metal–nitrogen bond lengths involving the μ - η^2 : η^2 -N₂ moiety. Although similar ligand-dependent relationships of $d(N-N)$ and $d(M-N)$ with M₂N₂ fold angle have previously been predicted,^{4c,f} until now, no experimental confirmation has existed, and in fact, observations of nonplanar M₂N₂ geometries in side-on-bridged N₂ bimetallic complexes employing early transition metals are quite rare.^{3b,9b,10} In the present two families of compounds, an empirically driven programmed reduction in nonbonded steric interactions between ligand substituents on adjacent metal centers, as mapped by the series **2–6**, led to a steady increased folding of the M₂N₂ core, and this result appears to further confirm a computationally predicted increased ground-state stabilization for a nonplanar Zr₂N₂ configuration relative to a planar geometry in Fryzuk's [(PNP)ZrX]₂(μ - η^2 : η^2 -N₂) system in the absence of overriding steric effects of the ancillary ligands.^{4c,f} Here, however, it is also important to mention that the authors of these latter studies further conclude that a nonplanar geometry, with an associated larger $d(N-N)$ value, is obtainable only through mixing of wavefunctions of the Zr₂N₂ core with those of properly oriented ligand-based amide lone pairs. Since compounds **1–6** lack this ligand-specific feature, further insights regarding the electronic structural preference in the present series for side-on bridging N₂ complexation that also gives rise to significantly nonplanar geometries and highly elongated N≡N bonds must await the results of future detailed computational investigations. However, with respect to this, it is interesting to note that chemical reduction under identical conditions of the group 5 Ta(V) trichloride, (η^5 -C₅Me₅-

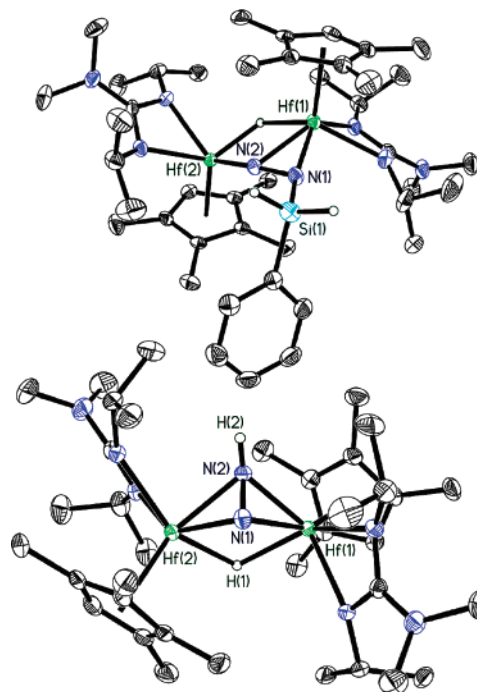
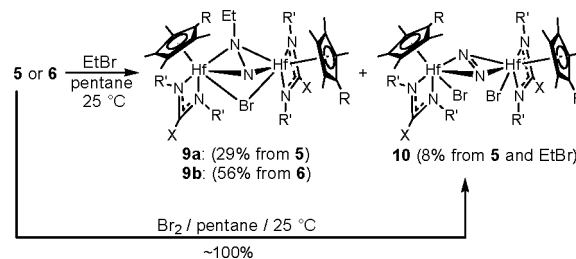


Figure 2. Molecular structures (30% thermal ellipsoids) for (top) **7a** and (bottom) **8a**. Hydrogen atoms have been removed for the sake of clarity except selected ones represented by small spheres of arbitrary size.

Scheme 3

Ta[(*i*-Pr)C(Me)N(*i*-Pr)]Cl₃, provided the open-shell, d^1, d^1 bimetallic “end-on-bridged” N₂ complex, {(η^5 -C₅Me₅)Ta(IV)[N(*i*-Pr)C(Me)N(*i*-Pr)]₂(μ - η^1 : η^1 -N₂)}, in spite of what would qualitatively appear to be nearly identical steric requirements of the ligand environment about the metal center, vis-à-vis compound **4**.¹¹

As Scheme 2 demonstrates, **1–6** all proved to be highly reactive at ambient temperature toward both hydrosilylation and hydrogenation in which single H₃SiPh and H₂ addition, respectively, provides a N-atom functionalized product that further incorporates a bridging hydride (μ -H) on the basis of both solution NMR spectroscopy and single-crystal X-ray crystallography.⁵ Thus, as a representative example, Figure 2 presents the molecular structures for **7a** and **8a** that were obtained in 51 and 49% isolated yields, respectively, from **3** (M = Hf, X = NMe₂, R = H, R' = *i*-Pr) according to Scheme 2,⁵ and here it can be seen that, whereas hydrosilylation yields a novel end-on, side-on (μ - η^1 : η^2)-NN(SiH₂Ph) configuration,¹² hydrogenation provides the previously observed μ - η^2 : η^2 -N₂H geometry.^{1,2} In both structures, however, relatively long N–N bond lengths are present with $d(N-N)$ values of 1.422(5) and 1.526(3) Å for **7a** and **8a**, respectively. Accordingly, it is possible that formation of the μ -H interaction after initial H₂ addition is responsible for establishing a higher barrier toward subsequent N-atom functionalizations at ambient temperature.^{1,4} The presence of N–N bonding in **8** was further supported by NMR spectroscopy with ¹⁵N₂ (99%) labeled **8a**: ¹H NMR (400 MHz, C₆D₆) δ (ppm) 4.61 [H_a N_aN_b, ddd, $^1J(^{15}N_a-^1H_a) = 69.5$ Hz, $^2J(^{15}N_b-^1H_a) = 3.4$

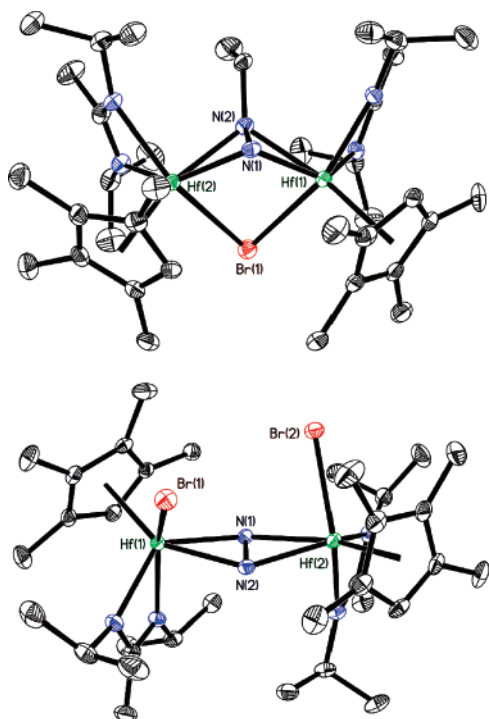


Figure 3. Molecular structures (30% thermal ellipsoids) for (top) **9a** and (bottom) **10**. Hydrogen atoms have been removed for the sake of clarity.

Hz, $^3J(\text{H}_a-\text{H}_b) = 2.1$ Hz]; ^{15}N NMR (40.5 MHz, C_6D_6) δ (ppm) 143.7 [$\text{H}_a\text{N}_a\text{N}_b$, dd, $^1J(^{15}\text{N}_a-\text{H}_a) = 69.5$ Hz, $^1J(^{15}\text{N}_a-^{15}\text{N}_b) = 8.5$ Hz], 391.7 [$\text{H}_a\text{N}_a\text{N}_b$, dd, $^1J(^{15}\text{N}_a-^{15}\text{N}_b) = 8.5$ Hz, $^2J(^{15}\text{N}_a-\text{H}_a) = 3.4$ Hz].

Given the extreme degree of $\text{N}\equiv\text{N}$ bond activation that is indicated by the magnitude of the $d(\text{N}-\text{N})$ values in Table 1, we were intrigued by the possibility of being able to extend the range of N-atom functionalization reactions that might now be accessible with these new families of group 4 bimetallic $[\text{L}_n\text{M}]_2(\mu-\eta^2:\eta^2-\text{N}_2)$ complexes.^{1,13} Thus, as Scheme 3 reveals, it was quite gratifying to discover that the hafnium-based compounds, **5** and **6**, undergo rapid reaction with bromoethane (EtBr) to provide the N-alkylated products **9a** and **9b** in 29 and 56% isolated yields, respectively, that was accompanied, in the case of **5**, by a small amount ($\sim 8\%$) of a co-product that was ultimately determined to be the dibromide product **10**.¹⁴ Figure 3 presents the molecular structures of **9a** and **10** that were obtained by single-crystal X-ray analysis, and that of **9b** is provided in the Supporting Information.⁵ Regarding differences in reactivity, it is interesting to note that, while **5** reacted with 1 equiv of EtBr over the course of 30 min at 25 °C, **6** reacted instantaneously (~ 1 min) and compounds **1–4** failed to react at all even after extended periods of times. Whether these differences for **1–6** correlate with $d(\text{N}-\text{N})$ values or are governed by steric effects of the ligand environment remains to be determined, as well as whether co-production of **10** is indicative of a radical (or caged radical complex) mechanism.¹⁵ As with hydrogenation, the N-alkylated products **9a** and **9b** possess relatively long N–N bond lengths with $d(\text{N}-\text{N})$ values of 1.531(4) and 1.515(13) Å, respectively; however, these compounds do not undergo further N-alkylation in the presence of excess EtBr or at elevated temperatures.

Finally, the much shorter N–N bond length observed for **10** [$d(\text{N}-\text{N}) = 1.253(3)$ Å] suggested that formal oxidation to a side-on-bridging diazenido, $\mu-\eta^2:\eta^2-[\text{N}_2]^{2-}$, had occurred, and indeed, reaction of **5** at room temperature with 1 equiv of Br_2 provided a near quantitative yield of **10** according to Scheme 3, which, to the best of our knowledge, is a unique transformation.⁵ Additional experimental and computational investigations are currently in progress to further explore the scope and mechanisms of N-alkylation and other N-atom functionalization reactions involving the two new families of $[\text{L}_n\text{M}]_2(\mu-\eta^2:\eta^2-\text{N}_2)$ complexes reported herein.

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Supporting Information Available: Experimental details, including CIF reports for **1–6**, **7a**, **8a**, **9a**, **9b**, and **10**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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