ORGANOMETALLICS

Reactivity Studies of (^tBu₃SiNH)(^tBu₃SiN=)₂WH Including Anionic Derivatives Featuring the Tris-tri-*tert*-butylsilylimide Tungsten Core

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Supporting Information



ABSTRACT: Treatment of $({}^{t}Bu_{3}SiNH)({}^{t}Bu_{3}SiN=)_{2}WH$ (1-H) with CX_{4} (X = Cl, Br, I) afforded $({}^{t}Bu_{3}SiNH)$ - $(^{t}Bu_{3}SiN=)_{2}WX$ (1-X, X = Cl, Br, I), but metatheses of 1-X with R⁻ equivalents gave mixed results. With MeLi, $(^{t}Bu_{3}SiNH)(^{t}Bu_{3}SiN=)_{2}WR$ (1-R, R = CH₃) was produced, but ArLi gave 1-Ar along with $[(^{t}Bu_{3}SiN=)_{3}WAr]Li$ (2-Li-Ar) and $[(^{Bu}_{3}SiN=)_{3}WH]M$ (2-M-H, M = Li). Alkylation attempts with BnK and 1-X cause deprotonation (X = Cl) to provide [('Bu₃SiN=)₃WX]M (2-M-X, M = K, X = Cl) and apparent electron transfer when X = I to give 1-Bn, 2-K-H, and bibenzyl. Two equivalents of ^tBuLi and 1-Cl afforded 2-Li-H via deprotonation of 1-H and byproducts likely derived from electron transfer. Exposure of 1-H to C_2H_4 , C_3H_6 , methylenecyclopentane, butadiene, propyne, HCC^tBu, p-tolunitrile, and tertbutylisocyanide gave insertion products 1-R (R = Et, "Pr, CH2°Pe, E-CH2CH=CHMe, CH=CHMe, CH=CHMe), 1-N= CHtol, and 1-CH=N^tBu, respectively. Thermolysis of 1-CH=N^tBu gave the cyanide complex 1-CN. 1-H and 1-Me resisted dihydrogen and methane elimination in nondonor solvents at 200 °C, but in pyridine, 1-H lost H₂ in a second-order process to give (^tBu₃SiN=)₃Wpy (ΔG°_{414K} = 4.5 kcal/mol). Thermolysis of 2-py under D₂ in C₆D₆ provided α -deuterated py. 2-M-H (M = Li, Na, K) and 2-K-R (R = Me, Et, "Pr) were generated by deprotonation of 1-H and 1-R, respectively, and various 1-M-X were synthesized similarly and via exposure of 1-Li-H to alkyl halides. Treatment of 2-Li-H with CH₃I provided 2-Li-I, but byproducts 1-CH₃ and 1-I suggested the potential intermediacy of a methane complex. X-ray crystal structures of 2-py, 2-H-K(OEt₂)₃, 2-H-K(crypt-2.2.2), the dimer $[2-H]_2(\mu$ -K)₂ (i.e., 2-K-H), and the trimer $[2-I]_3(\mu$ -K)₃ (i.e., 2-K-I) revealed similar tris-imido cores. Discussion of the general reactivity of 1-H, structural features, and plausible mechanisms of 2-py formation are included.

INTRODUCTION

A multiyear investigation of the activation of carbon–hydrogen bonds by d⁰ imido complexes¹⁻¹² culminated in the study of 1,2-RH elimination reactions of $(silox)_2$ (^tBu₃SiNH)TiR and corresponding 1,2-RH addition reactions to the purported d⁰ transient $(silox)_2$ Ti=NSi^tBu₃.⁸ Kinetics and thermodynamics studies established a linear free energy relationship (LFER) between the ease of CH bond activation and the strength of the titanium–carbon bond formed. A geometric factor involving compression of the reaction coordinate explained the greater propensity for sp² versus sp³ C–H bond activation in conjunction with the LFER.

While the foundation for understanding concerted bond activations by d⁰ imido functionalities was provided by the titanium cases and related 1,2-RH eliminations from (${}^{t}Bu_{3}SiNH$) $_{3}ZrR$,²⁻⁴ the role of alkane—or, more generally, hydrocarbon—complexes in the context of CH activation remained opaque to experimental observations, and pertinent periodic trends were not well established. As Scheme 1 shows, calculations by Cundari et al.¹³⁻¹⁸ were used to augment the experimental findings,^{1-12,19,20} and while the simple models

employed limited the accuracy of the calculations, reasonable agreement was found. The ease of 1,2-MeH elimination diminishes from first- to second- to third-row transition element as the corresponding enthalpy of reaction (ΔH°_{add}) corresponding to the addition of methane to the putative three-coordinate imide becomes more favorable.

The transition states for the second-row transition metal transient imido species are somewhat higher than either their first- or third-row congeners for groups 5 and 6, but otherwise the trends are as expected. A more favorable $\Delta H^\circ_{\rm add}$ is calculated when descending a column, as the exchange of a M=N π -bond for NH and MR σ -bonds becomes more favorable due to an increase in bond strengths, and the energy of the transient three-coordinate imido species rises. While the $\Delta\Delta H^\circ_{\rm add}$ are about the same from the first to third rows for groups 4–6 (~20 kcal/mol), the enthalpies of addition become progressively larger until $\Delta H^\circ_{\rm add}$ is calculated to be enormous (–60.3 kcal/mol) for the tris-imido (HN=)₃W.^{15,16} It may

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Article

seem that $(HN=)_3W$ is an 18 e⁻ complex, assuming each imide contributes 4 e⁻ (3 × 4 e⁻ + d⁶ = 18), and is therefore less prone to react with RH, but the calculations suggest the opposite. First, one pair of electrons pertaining to the tris-imido group is intrinsically nonbonding due to symmetry considerations,²¹ and second, competition for the d-orbitals among several π -donor ligands weakens the π -bonds from groups 4 to 5 to 6, and the three-coordinate transient species become progressively higher in energy.^{21–25} Experimentally, 1,2-MeH elimination data obtained directly or indirectly as MeH loss from ('Bu₃NH)₃HfMe,⁸ ('Bu₃SiNH)₂('Bu₃SiN=)VMe,¹⁹ and ('Bu₃SiNH)₂('Bu₃SiN=)TaMe^{5,26} complexes in addition to the Ti^{6–10,27} and Zr systems^{2–4,28} are in line with the calculations, leaving verification of group 6.²⁹

Although the calculations suggested that 1,2-RH elimination from (^tBu₃SiNH)(^tBu₃SiN=)₂WR could not be achieved $(\Delta H^{\ddagger}_{elim}$ for (H₂H)(HN=)₂WMe = 61.6 kcal/mol), the system was still intriguing because the enthalpy of binding for MeH to (HN=)₃W was substantial (-15.6 kcal/mol);^{15,16} hence even the free energy for binding was favorable ($\Delta G^{\circ}_{bind} =$ -8.4 kcal/mol). Three-coordinate imido species were also pyramidalized in the second and third rows in groups 5 and 6 due to $nd_{z2}/(n+1)p/(n+1)s$ mixing, a geometric distortion favorable toward binding.

The detection of a methane complex of rhodium, [{2,6-(^tBu₂PO)C₅H₃N}Rh(CH₄)]BAr^F₄],³⁰ cyclopentane,³¹ and cyclohexane³² adducts of rhenium, $CpRe(CO)_2(^{c}AlkH)$, the timeresolved implication of $\{\eta^2$ -HB(3,5-dimethylpyrazolyl)₃}Rh-(CO)(CyH)³³ and related species by IR spectroscopy, and X-ray crystal structures of n-heptane bound within the pocket of an iron porphyrin³⁶ and various cyclic alkanes bound to $[\kappa - O_{3y}N_3 - (2,4 - ({}^{t}Bu)C_6H_2O(6 - CH_2)tacn]U(RH)^{37}$ provide direct evidence of alkane binding to d^8 , d^6 , and f^3 metal centers. Previously, dynamic evidence, such as the interconversion of hydride and methyl resonances in tungsten,³⁸ rhenium,³⁹ and osmium⁴⁰ methyl-hydride species by ¹H NMR spectroscopy and chain walking in Cp*Rh(PMe₃)R(H) species⁴¹ highlighted alkane intermediates in oxidative addition/reductive elimination sequences. In a preliminary study, alkane complexes of the type ('Bu₃SiN=)₃W(RH) were indirectly implicated as a component of the free energy surface for alkane activation in group 6 through the addition of RX to $[({}^{t}Bu_{3}SiN=)_{3}WH]K.^{11,12}$

Prior to investigating the chemistry of transient alkane complexes of the $({}^{t}Bu_{3}SiN=)_{3}W$ core, a viable synthetic path to these complexes was developed, including the preparation of

(^tBu₃SiNH)(^tBu₃SiN=)₂WR. Herein is described the generation of tungsten complexes pertinent to Scheme 1 and anionic derivatives that permitted the indirect evaluation of alkane complexes as intermediates toward CH-bond activation. The preparation of (^tBu₃SiNH)(^tBu₃SiN=)₂WH (1-H) was previously reported⁴² as occurring via the addition of 6 equiv of LiNHSi^tBu₃ to Na(THF)₃[W₂Cl₇(THF)],⁴³ as illustrated in Scheme 2. An intermediate [(^tBu₃SiNH)₂ClW]₂ complex^{42,44} containing a tungsten-tungsten triple bond^{45,46} was isolated and shown to be a precursor to 1-H via the addition of 2 equiv of ^tBu₃SiNHLi. Precedent for anionic derivatives of tris-imido tungsten²² and molybdenum²³ was established by Wigley et al., via the utilization of 2,6-diisopropyl arylimido ligands.

RESULTS

Metathetical Routes to $({}^{t}Bu_{3}SiNH)({}^{t}Bu_{3}SiN=)_{2}$ WX/R. 1. $({}^{t}Bu_{3}SiNH)({}^{t}Bu_{3}SiN=)_{2}WX$ (1-X, X = Cl, Br, I). The most straightforward route to neutral tungsten alkyl derivatives required starting materials that could be subjected to metathesis by RM. With $({}^{t}Bu_{3}SiNH)({}^{t}Bu_{3}SiN=)_{2}WH$ (1-H)⁴² in hand as the primary starting material, its conversion to halides $({}^{t}Bu_{3}SiNH)({}^{t}Bu_{3}SiN=)_{2}WX$ (1-X, X = Cl, Br, I) was accomplished via treatment with CX₄ in hexanes (X = Cl) or benzene (X = Br, I) at 23 °C, as shown in eq 1. The chloride, bromide, and iodide complexes were isolated in 74%, 67%, and 75% yields, respectively, as yellow microcrystals upon precipitation from hexane or hexanes. Pertinent spectral parameters for the halides and all other complexes are listed in Table 1.

2. $({}^{t}Bu_{3}SiNH)({}^{t}Bu_{3}SiN=)_{2}WR$ (1-*R*, *CH*₃ (*CD*₃), *Ph*, 3-tolyl, 4-tolyl, *CH*₂*Ph*). Treatment of a cold diethyl ether solution of (${}^{t}Bu_{3}SiNH$)(${}^{t}Bu_{3}SiN=)_{2}WCl$ (1-Cl) with a slight excess (~1.1 equiv) of MeLi (or CD₃Li) afforded the colorless methyl derivative (${}^{t}Bu_{3}SiNH$)(${}^{t}Bu_{3}SiN=)_{2}WCH_{3}$ (1-CH₃ (or 1-NH-CD₃)) in modest yield (eq 2, 51%). The methyl group resonated at δ 1.43 in the ${}^{1}H$ NMR spectrum and displayed a ${}^{2}J_{WH}$ of 11 Hz, and its δ 21.62 signal in the ${}^{13}C{}^{1}H$ } NMR spectrum exhibited a ${}^{1}J_{WH}$ of 138 Hz.

Competing pathways limited the scope and purity of other tungsten alkyls generated by metathetical procedures. For example, treatment of $({}^{t}Bu_{3}SiNH)({}^{t}Bu_{3}SiN=)_{2}WCl$ (1-Cl) with a slight excess of PhLi (~1.3 equiv) in diethyl ether resulted in the formation of $({}^{t}Bu_{3}SiNH)({}^{t}Bu_{3}SiN=)_{2}WPh$ (1-Ph) contaminated with $[({}^{t}Bu_{3}SiN=)_{3}WPh]Li$ (2-Li-Ph) in a 7:3 ratio (eq 3). A slight excess of alkyllithium reagent was typically needed for conversion of the halide precursor, but if





the halide was completely consumed, 2-Li-Ph invariably appeared. The metathesis was not optimized to sufficient purity for elemental analysis of 1-Ph.

Related results were obtained from tolyllithiums designed to highlight any potential rearrangements. Treatment of (${}^{t}Bu_{3}$ SiN=)₂WCl (1-Cl) with 4-Me-C₆H₄Li in Et₂O afforded a mixture of (${}^{t}Bu_{3}$ SiNH)(${}^{t}Bu_{3}$ SiN=)₂W(C₆H₄-4-Me) (1-C₆H₄-4-Me), Li(${}^{t}Bu_{3}$ SiN=)₃W(C₆H₄-4-Me) (2-Li-C₆H₄-4-Me), and Li(${}^{t}Bu_{3}$ SiN=)₃WH (2-Li-H) in a ~5:2:3 ratio (eq 4). A similar reaction of (${}^{t}Bu_{3}$ SiNH)(${}^{t}Bu_{3}$ SiN=)₂WI (1-I) with 3-Me-C₆H₄Li in Et₂O provided a mixture of (${}^{t}Bu_{3}$ SiN=)₃W(C₆H₄-3-Me) (1-C₆H₄-3-Me), Li(${}^{t}Bu_{3}$ SiN=)₃W(C₆H₄-3-Me) (2-Li-C₆H₄-3-Me), and Li(${}^{t}Bu_{3}$ SiN=)₃WH (2-Li-H) in essentially the same ratio. During the course of the reaction, no isomerization of the tolyl fragment occurred. As subsequent studies showed, the results suggested that an alkane complex of the type $({}^tBu_3SiN{=})_3W(toluene)$ (2-tolH) is unlikely to be an intermediate in the alkylation. 11,12

Exposure of (^tBu₃SiNH)(^tBu₃SiN=)₂WCl (1-Cl) to potassium benzyl⁴⁷ in THF- d_8 in an NMR tube experiment produced the tris-imido tungsten chloride adduct $K(^{t}Bu_{3}SiN=)_{3}WCl$ (2-K-Cl), in near quantitative yield (eq 5). Since the objective was to generate some ('Bu₃SiNH)-(^tBu₃SiN=)₂WCH₂Ph (1-Bn) for spectral comparison, conditions were varied. A THF solution of excess PhCH₂K was slowly added to a diethyl ether solution of (^tBu₃SiNH)- $(^{t}Bu_{3}SiN=)_{2}WI$ (1-I) over the course of 5 min, producing 1-Bn as 40% of an inseparable mixture with $K(^{t}Bu_{3}SiN=)_{3}WH$ (2-K-H, 28%) and other unidentified products (eq 6). The distinguishing ¹H NMR spectral feature of 1-Bn was the CH₂ group at δ 3.57, which possessed tungsten satellites $({}^{2}J_{WH} = 15 \text{ Hz})$. When the addition of 2.5 equiv of PhCH₂K to 1-I occurred in THF, the reaction was optimized for the formation of 2-K-H, which was isolated as a white powder in 64% yield (eq 7). An NMR tube scale experiment in C_6D_6 of 1-I and PhCH2K confirmed the presence of 2-K-H as the sole organometallic product and bibenzyl as the organic byproduct.

The attempted arylations, and the benzylations with PhCH₂K gave products, i.e., K(^tBu₃SiN=)₃WH (2-K-H) and bibenzyl, that were consistent with electron transfer and possible hydrogen atom transfer processes. To further examine this possibility, reactions of (^tBu₃SiNH)(^tBu₃SiN=)₂WCl (1-Cl) and ^tBuLi were employed. In C_6D_{62} thermolysis of 1-Cl and 1 equiv of 'BuLi at 100 °C for ~6 h produced half an equivalent of Li(^tBu₃SiN=)₃WH (2-Li-H), isobutane, and isobutylene; half an equivalent of 1-Cl remained. As eq 8 illustrates, the use of 2 equiv of ^tBuLi caused a near quantitative conversion to 2-Li-H, which was accompanied by isobutene and isobutylene in a 1:1 ratio. (^tBu₃SiNH)- $(^{t}Bu_{3}SiN=)_{2}WH$ (1-H, ~5%) is present at the end of the reaction, suggesting that the ^tBuLi functioned as a 1e⁻ reductant, and the incipient W(V) species $({}^{t}Bu_{3}SiNH)({}^{t}Bu_{3}SiN=)_{2}W$ abstracted a hydrogen atom from the resulting ^tBu radical to

Table 1. ¹H and ¹³C{¹H} NMR Spectral Assignments^{*a*} for (^tBu₃SiNH)(^tBu₃SiN=)₂WX/R (1-X/R)

	¹ H NMR (δ (J (Hz)), assign.)		¹³ C{ ¹ H} NMR (δ , (assign.), J (Hz))		
compound	^t Bu ^b	NH and R	SiCMe ₃ ^b	SiC(CH ₃) ₃ ^b	R
(^t Bu ₃ SiNH)(^t Bu ₃ SiN) ₂ WH (1-H)	1.18	7.41 (NH)	22.72	30.53	
	1.34	13.34 $(J_{WH} = 356)$	23.95	31.11	
$(^{t}Bu_{3}SiNH)(^{t}Bu_{3}SiN)_{2}WCl$ (1-Cl)	1.22	7.18 (NH)	23.72	30.82	
	1.35		24.88	31.29	
$(^{t}Bu_{3}SiNH)(^{t}Bu_{3}SiN)_{2}WBr$ (1-Br)	1.22	7.34 (NH)	23.71	30.83	
	1.35		24.85	31.29	
$(^{t}Bu_{3}SiNH)(^{t}Bu_{3}SiN)_{2}WI$ (1-I)	1.22	7.50 (NH)	23.64	30.83	
	1.36		24.77	31.33	$a_1 \left(a \left(\left t \right \right) \right)$
$(Bu_3SINH)(Bu_3SIN)_2WCH_3$ (I-CH ₃)	1.19	0.59 (NH)	23.38	30.72	$21.62 (J_{WC} = 138)$
$({}^{t}Bu, SiNH)({}^{t}Bu, SiN)$. WEt (1-Et)	1.55	$1.43 (0_{WH} - 11, C11_3)$	24.55	30.72	1967 (CH.)
	1.34	$2.06 (t. 7. CH_2)$	23.31	31.22	$39.01 ({}^{1}L_{WG} = 137.$
	101	2100 (0,7) 0113)	21112	01.22	WCH ₂)
		2.36 (q, 7, CH ₂) ^c			
$(^{t}Bu_{3}SiNH)(^{t}Bu_{3}SiN)_{2}W^{n}Pr$ (1- ^{n}Pr)	1.21	6.54 (NH)	23.34	30.72	21.38 (CH ₃)
	1.34	1.05 (t, 7, CH ₃)	24.44	31.23	28.99 (CH ₂)
		$2.24-2.44 \text{ (m, (CH_2)_2)}^c$			39.01 (${}^{1}J_{WC} = 136$,
$({}^{t}Bu_{2}SiNH)({}^{t}Bu_{2}SiN)_{2}W(E-CH_{2}CH=CHMe)$ (1-E-CH_2CH=	1.21	6.58 (NH)	23.36	30.71	17.72 (CH ₂)
CHMe) ^c	1.34	$1.85 (d. 6. CH_2)$	23.30	31.18	48.49 (WCH ₂)
		3.05 (d, 7, CH ₂)			123.44 (CH)
		5.25 (dq, 15, 6, CH)			135.39 (CH)
		6.17 (dt, 15, 7, CH)			
$(^{t}Bu_{3}SiNH)(^{t}Bu_{3}SiN)_{2}WPh (1-Ph)^{d}$	1.19	6.90 (NH)	23.56	30.88	129.16 (CH)
	1.36	7.02 (t, 7, CH ⁴)	24.57	31.30	143.44 (CH)
		7.22 (m, CH ^{3,5})			$174.50 ({}^{1}J_{WC} = 181,$
		9 45 (J 7 CH ^{2,6})			WC)
$({}^{t}Bu, SiNH)({}^{t}Bu, SiN), WC, H_{-3}-Me^{c,d}$ (1-C, H_{-3}-Me)	1 2 1	$6.45 (u, 7, CH^{-})$	23 58	30 79	21.12 (CH.)
	1.21	$2.17 (CH_2)$	23.58	31.29	128.78 (CH)
	107	6.87 (d, 8, CH ⁴)	21.00	0112)	129.95 (CH)
		7.18 (t, 8, CH ⁵)			$136.87 (C^3)$
		8.26 (d, 8, CH ⁶)			140.13 (CH)
		8.35 (CH ²)			144.42 (CH)
					171.90 (WC ¹)
$({}^{t}Bu_{3}SiNH)({}^{t}Bu_{3}SiN)_{2}WC_{6}H_{4}-4-Me^{c_{3}f}(1-C_{6}H_{4}-4-Me)$	1.22	6.83 (NH)	23.58	30.81	21.49 (CH ₃)
	1.38 (CH ₃)	1.93	24.58	31.32	139.03 (CH)
		7.02 (d, 8, $CH^{3,3}$)			143.62 (CH)
(tp (2)) $(tp (2))$ $(tp (4))$ de	1.01	8.39 (d, 8, $CH^{2,0}$)			174.43 (C [*])
$(Bu_3SiNH)(Bu_3SiN)_2WCH_2Ph (I-Bn)^{3/2}$	1.21	6.74 (NH)			
	1.29	$5.37 (J_{WH} = 13, C11_2)$ 6.88 (t. 7 CH ⁴)			
		7.31 (d. 7. CH ²)			
(^t Bu ₃ SiNH)(^t Bu ₃ SiN) ₂ W(E-CH=CHMe) (1-E-CH=CHMe) ^{c,e}	1.23	6.63 (NH)	23.54	30.78	24.42 (CH ₃)
	1.37	1.70 (dd, 6, 1.5, CH ₃)	24.53	31.26	153.46 (CH)
		8.01 (dq, 15, 1.5, WCH)			167.63 (CH)
$(^{t}Bu_{3}SiNH)(^{t}Bu_{3}SiN)_{2}W(Z-CH=CHMe) (1-Z-CH=CHMe)^{e}$	1.23	6.75 (NH)			
	1.37	2.06 (dd, 6, 1.5, CH ₃)			
		7.11 (m, CH)			
		8.10 (dq, 11, 1.5, WCH)			<i>.</i>
$(Bu_3SiNH)(Bu_3SiN)_2W(E-CH=CHBu)$ (1-E-CH=CHBu) ^e	1.23	6.61 (NH)	23.65	30.81	29.02 (CMe ₃)
	1.37	1.05 ('Bu)	24.59	31.26	$30.86 ((CH_3)_3)$
		$(u, 18, J_{WH} = 10, WCH)$			WCH) $(J_{WC} = 182, WCH)$
		7.95 (d, 18, CH)			167.74 (CH)
$(^{t}Bu_{3}SiNH)(^{t}Bu_{3}SiN)_{2}W(N=C(H)-C_{6}H_{4}-4-Me)$ (1-N=CHtol)	1.38	4.03 (NH)	23.83	31.22	21.49 (CH ₃)
	1.36	1.93 (CH ₃)	24.55	31.35	129.67 (CH)
		6.92 (d, 8, CH)			129.73 (CH)
		7.51 (d, 8, CH)			135.16 (C)
		10.29 (NCH)			143.83 (C)
					176.05 (WNC)

Table 1. continued

	¹ H NMR (δ (J (Hz)), assign.)		¹³ C{ ¹ H} NMR (δ , (assign.), J (Hz))		
compound	^t Bu ^b	NH and R	SiCMe ₃ ^b	$SiC(CH_3)_3^{b}$	R
(^t Bu ₃ SiNH)(^t Bu ₃ SiN) ₂ WCH=N ^t Bu (1-CH=N ^t Bu)	1.35	4.60 (NH)	23.79	31.33	29.29 (Me ₃)
	1.33	1.13 (^t Bu)	24.50	31.24	61.89 (NCMe ₃)
		11.34 $(J_{\rm WH} = 21, \rm CH)$			214.18 $({}^{1}J_{WC} = 159, WC)$
('Bu ₃ SiNH)('Bu ₃ N) ₂ WCN (1-CN)	1.31	8.24 (NH)	23.20	30.52	$({}^{1}J_{WC} = 243, WC)^{c}$
	1.16		24.49	31.03	
(^t Bu ₃ SiNH)(^t Bu ₃ N) ₂ WCH=NMe (1-CH=NMe)	1.31	3.36 (NH)			
	1.31	3.07 (CH ₃)			
		10.72 $(J_{WH} = 19, CH)$			
(^t Bu ₃ SiN=) ₃ Wpy (2-py)	1.41	6.61 (m, C ^{3,5})	24.61	31.56	125.33
		6.44 (t, 7, C ⁴)			140.92
		9.04 (d, 7, C ^{2,6})			155.25
Li(^t Bu ₃ SiN=) ₃ WH (2-Li-H)	1.26	12.14 $(J_{WH} = 338)$	23.43	31.02	
Na(^t Bu ₃ SiN=) ₃ WH (2-Na-H)	1.42	7.20 $(J_{WH} = 314)$	23.87	31.52	
$K(^{t}Bu_{3}SiN=)_{3}WH (2-K-H)$	1.45	7.11 $(J_{WH} = 313)$	23.95	31.63	
[K-crypt 2.2.2][${}^{t}Bu_{3}SiN=$) ₃ WH] (2-H-Kc) ^g	1.16	2.58 (t, 5, CH ₂ N)	24.59	32.31	54.97 (CH ₂)
		2.58 (s, CH ₂ O)			68.69 (CH ₂)
		3.57 (t, 5, CH ₂ O)			71.52 (CH ₂)
		10.06 $(J_{WH} = 329)$			
$Li(^{t}Bu_{3}SiN=)_{3}WCl$ (2-Li-Cl)	1.28		24.52	31.70	
Na(^t Bu ₃ SiN=) ₃ WCl (2-Na-Cl)	1.47		24.88	31.71	
$K(^{t}Bu_{3}SiN=)_{3}WCl$ (2-K-Cl)	1.52		24.99	31.87	
Na(^t Bu ₃ SiN=) ₃ WBr (2-Na-Br)	1.51		24.90	31.79	
$K(^{t}Bu_{3}SiN=)_{3}WBr$ (2-K-Br)	1.52		24.94	31.88	
$Li(^{t}Bu_{3}SiN=)_{3}WI$ (2-Li-I)	1.28		24.33	31.22	
$K(^{t}Bu_{3}SiN=)_{3}WI$ (2-K-I)	1.53		24.81	31.95	
$K(^{t}Bu_{3}SiN=)_{3}WCH_{3} (2-K-CH_{3})^{g}$	1.15	0.65 (${}^{2}J_{\rm WH} = 12$)	25.31	32.37	10.85 (WC) ^{c,h}
$K(^{t}Bu_{3}SiN=)_{3}WCH_{2}CH_{3}$ (2-K-Et) ^g	1.42	0.62 (q, 8, CH ₂)	24.75	31.87	20.23 ^c
		1.87 (t, 8, CH ₃)			27.98
$K(^{t}Bu_{3}SiN=)_{3}WCH_{2}CH_{2}CH_{3} (2-K-^{n}Pr)^{g,t}$	1.38	$1.81 (m, CH_2)$	24.77	31.83	$20.50 (CH_2)$
		$2.10 (m, CH_2)$			29.05 (CH ₂)
		. 4			$40.25 (WC)^{c}$
$Li(^{t}Bu_{3}SiN=)_{3}WPh (2-Li-Ph)^{a_{j}}$	1.27	7.03 (t, 7, CH^4)	24.21	31.23	144.41 (CH)
		7.21 (t, 7, CH ^{3,5})			172.91 (C ¹ H)
		8.41 (d, 7, CH ^{2,6})			
$Li(^{t}Bu_{3}SiN=)_{3}W(C_{6}H_{4}-3-Me)$ (2-Li-C ₆ H ₄ -3-Me)	1.28	2.20 (s, CH_3)	24.24	31.23	21.20 (CH ₃)
		6.87 (d, 7, CH ⁴)			127.41 (CH)
		7.17 (t, 7, CH ³)			$136.30 (C^3)$
		8.19 (d, 7, CH°)			141.46 (CH)
		8.31 (s, CH ²)			159.45 (CH)
				_	172.78 (C'H)
$Li(Bu_3SiN=)_3W(C_6H_4-4-Me)$ (2-Li- $C_6H_4-4-Me)'$	1.29	2.01 (s, CH_3)	24.23	31.25	21.48 (CH_3)
		7.02 (d, 7, $CH^{3,3}$)			133.56 (CH)
		8.34 (d, 7, CH ^{2,0})			144.57 (CH)

^{*a*}Benzene- d_6 unless otherwise noted; all J_{WH} reported were obtained from W satellites that integrated to ~14% intensity, indicative of one tungsten center. ^{*b*}Amide listed first, imide second. ^{*c*}Tungsten satellites could not be confidently assigned. ^{*d*}CH^{*n*}, n = 1-6 phenyl positions. ^{*e*}Aryl position(s) obscured by C₆D₅H. ^{*f*}Aryl carbon not observed. ^{*g*}THF- d_8 . ^{*h*}Tentative assignment. ^{*i*}Me resonance obscured by 'Bu. ^{*j*}Aryl resonance(s) obscured by residual solvent.

form isobutylene. The second equiv of ^tBuLi deprotonates 1-H, as the experiment in eq 9 proved plausible.

Insertion Routes to (${}^{t}Bu_{3}SiNH$)(${}^{t}Bu_{3}SiN=$)₂WX/R. Metathesis procedures toward the preparation of (${}^{t}Bu_{3}SiNH$)-(${}^{t}Bu_{3}SiN=$)₂WR (1-R) that featured the displacement of halide by alkyl anion equivalents proved limited due to competing reduction and deprotonation events. Despite the saturated nature of (${}^{t}Bu_{3}SiNH$)(${}^{t}Bu_{3}SiN=$)₂WH (1-H), which can be construed as an 18e⁻ complex, an evaluation of insertion reactions appeared warranted. Exposure to olefins—typically in excess—and related unsaturated substrates met with reasonable success, as illustrated in Scheme 3. Treatment of 1-H with ethylene (16 equiv), propylene (16 equiv), and methylenecy-clopentane (10 equiv) led to the isolation of (${}^{t}Bu_{3}SiNH$)(${}^{t}Bu_{3}SiN=$)₂WEt (1-Et) and the propyl derivative (${}^{t}Bu_{3}SiNH$)-(${}^{t}Bu_{3}SiN=$)₂WⁿPr (1-ⁿPr) and disappearance of the hydride



more difficult the insertion process, as evidenced by the 150 °C, 3 d conditions that pertain to 1-CH_2 °Pe versus the roomtemperature conditions that led to ethylene capture. During the formation of 1-CH_2 °Pe, ~35% of the excess methylenecyclopentane underwent isomerization to 1-methylcyclopentene. Given the rather harsh conditions, it is uncertain whether the isomerization is derived from a 2,1-insertion event followed by β -H elimination or whether the reaction is catalyzed by a spurious impurity.

The most curious consequence of examining various insertion substrates was the case of butadiene, which afforded only one regioisomer in both the crude (\sim 90%) and isolated





(17%) samples: (^tBu₃SiNH)(^tBu₃SiN=)₂W(*E*-CH₂CH= CHMe) (1-*E*-CH₂CH=CHMe, ³J_{HH} = 15 Hz). This σ -allyl complex is likely derived from 2,1-insertion of butadiene,^{48,49} followed by rearrangement via the η ³-allyl, lending credence to the postulation that 2,1-insertion may be operational in the preceding isomerization discussion.

Propyne and 3,3-dimethylbutyne undergo insertion to afford the vinyl complexes (${}^{t}Bu_{3}SiNH$)(${}^{t}Bu_{3}SiN=$)₂W(CH= CHMe) (1-CH=CHMe) and (${}^{t}Bu_{3}SiNH$)(${}^{t}Bu_{3}SiN=$)₂W-(CH=CH^tBu) (1-CH=CH^tBu), which are both observed as mixtures of their *E*- and *Z*-isomers, with the *E*-isomer favored. It was later found that these compounds were light sensitive; hence the unexpected appearance of the *Z*-isomers, which should not arise from a standard 1,2-insertion event,⁵⁰ was rationalized on that basis. In the NMR tube experiment with excess propyne, a dark purple precipitate was also noted and was believed to be composed of substrate oligomers. In support of this hypothesis, the reaction of 1-H with acetylene immediately generated a solid consistent with the formation of acetylene oligomers.

A few nonolefinic substrates were assayed, and treatment of (^tBu₃SiNH)(^tBu₃SiN=)₂WH (1-H) with *p*-tolunitrile provided the *p*-tolylimino species (^tBu₃SiNH)(^tBu₃SiN=)₂WN= C(H)C₆H₄-4-Me (1-N=CHtol), produced from hydride reduction of the cyano group. The IR spectrum of 1-N= CHtol revealed a $\nu_{\rm NH}$ at 3280 cm⁻¹ and two absorptions at 1604 and 1662 cm⁻¹ in the region expected for $\nu_{\rm N=C}$ (1600– 1700 cm⁻¹),^{51,52} one of which is assigned to the imine and

the other to an aryl-based mode. The imino proton resonated at δ 10.29 in the ¹H NMR spectrum, and its corresponding carbon was assigned to a resonance at δ 176.05 in the ¹³C{¹H} NMR spectrum.

tert-Butylisocyanide underwent an immediate 1,1-insertion with 1-H to provide the light yellow formimidoyl (^tBu₃SiNH)-(^tBu₃SiN=)₂WCH=N^tBu (1-CH=N^tBu) in 62% isolated yield. The characteristic formimidoyl 53 proton resonated at δ 11.34 in the ¹H NMR spectrum with a ${}^{2}J_{WH} = 21$ Hz, and its corresponding carbon was located at δ 214.18 (¹ J_{CH} = 159 Hz) in the ${}^{\tilde{1}3}C\{{}^1H\}$ NMR with accompanying tungsten satellites (${}^{1}J_{WC} = 159 \text{ Hz}$). The IR spectrum of 1-CH=N^tBu exhibited two $\nu_{\rm CN}$ of 1559 and 1595 cm⁻¹, which may be indicative of two rotomers of the molecule; one with the imine group between the imides and another where the imine resides between the imide and amide. Thermolysis of 1-CH= N^tBu in hexanes at 100 °C for 3 d cleanly produced the cyanide complex (^tBu₃SiNH)(^tBu₃SiN=)₂WCN (1-CN), which was formulated on the basis of a resonance at δ 149.44 in the ${}^{13}C{}^{1}H$ NMR possessing a tungsten-carbon coupling (¹*J*) of 243 Hz and a weak $\nu_{\rm CN}$ = 2146 cm⁻¹ in the IR spectrum. An NMR tube reaction confirmed the quantitative nature of the conversion and revealed isobutene as an organic byproduct.

Use of methyl isocyanide afforded a purple-colored solution in C₆D₆ at 23 °C and resonances consistent with the generation of $({}^{t}Bu_{3}SiNH)({}^{t}Bu_{3}SiN=)_{2}WCH=NMe$ (1-CH=NMe). The compound subsequently decomposed over the course of 12 h to a number of unknown products with concomitant bleaching of the solution. Most early transition metal formimidoyl species adopt an η^2 -coordination mode,⁵³ but none of the spectral parameters can consistently distinguish between it and an η^1 -CH=NR species. Closely related structurally characterized complexes that differ in coordination of the formimidoyl show only a slightly increased $\nu_{\rm CN}$ and downfield ¹³C NMR spectroscopic chemical shift for the η^2 mode.⁵⁴ The colored solution of 1-CH=NMe may be indicative of a different coordination, but an η^2 -CH=NR must compete with the π -donation from the imides and amide. Since $({}^{t}Bu_{3}SiNH)({}^{t}Bu_{3}SiN=)_{2}WR$ (1-R) behave more like 18e⁻ compounds, the bulkier, lightly colored 1-CH=N^tBu is formulated as an η^1 -species. For comparison, 1-H was stable to an excess of CO (3 atm) until heated to 130 °C, when decomposition was evident.

Thermolyses of $({}^{t}Bu_{3}SiNH)({}^{t}Bu_{3}SiN=)_{2}WR$ (1-R, R = H, CH₃). Calculations by Cundari et al.¹⁶ suggested that 1,2-RH elimination from $({}^{t}Bu_{3}SiNH)({}^{t}Bu_{3}SiN=)_{2}WR$ (1-R, R = H, CH₃) would have very high activation energies (Scheme 1). With 1-H and 1-CH₂ and labeled derivatives available, extended thermolyses were conducted, and the results supported the calculations. As Scheme 4 reveals, thermolysis of 1-H for 1 week at 200 °C in C₆D₆ with D₂ incurred no label incorporation in the starting material, thereby ruling out several label scrambling paths under these conditions; no evidence of σ -bond metathesis,⁵⁵ 1,2-D₂ addition, or 1,2-H₂ elimination was obtained, nor was any solvent incorporation,⁵⁶ e.g., formation of $({}^{t}Bu_{3}SiND)({}^{t}Bu_{3}SiN=)_{2}W(C_{6}D_{5})$ (1-ND-C₆D₅), implicated. Similarly, thermolysis of 1-CD₃ for 1 week at 200 °C revealed no label scrambling between amide and methyl sites, $^{38-40}$ nor was any solvent (arene) activation and incorporation detected. Since the 1,2-elimination of dihydrogen and methane has typical, modest barriers in related systems (Scheme 1), the thermolyses clearly showed



that such events were not plausible for (${}^{t}Bu_{3}SiNH$)-(${}^{t}Bu_{3}SiN=$)₂WR, supporting studies with related arylimido species.²² Extended thermolyses of 1-H and 1-CH₃ in C₆D₆ at 200 °C for 30 d revealed no exchange with solvent and no decomposition.

Pyridine-Induced 1,2-H₂-Elimination from (^tBu₃SiNH)-(^tBu₃SiN=)₂WH (1-H). 1. Synthesis of (^tBu₃SiN=)₃Wpy (2-py). While inert toward 1,2-H₂-elimination in nondonating solvents, (^tBu₃SiNH)(^tBu₃SiN=)₂WH (1-H) was heated in pyridine at 140 °C for 36 h with occasional degassing of H₂ to afford orange (^tBu₃SiN=)₃Wpy (2-py) in 56% yield. Pyridine adduct 2-py is extremely stable and does not decompose upon extended thermolysis at 200 °C in C₆D₆. In contrast, dissolution of 2-py in py-d₅ resulted in displacement of py within seconds at 23 °C, as assessed by ¹H NMR spectroscopy. The apparent associative exchange of py in 2-py prompted consideration of a related mechanism for 1,2-H₂ elimination from 1-H.

The conditions of neat pyridine and dihydrogen degassing in the conversion of (^tBu₃SiNH)(^tBu₃SiN=)₂WH (1-H) to (^tBu₃SiN=)₃Wpy (2-py) prompted measurement of the equilibrium constant. A sealed NMR tube containing roughly 2 equiv of dihydrogen and 2-py in C₆D₆ was heated at 141 °C for 4 d until no changes in concentration were noted.⁵⁷ The equilibrium constant, as defined by 1-H + py \rightleftharpoons 2-py + H₂, was 4.4 × 10⁻³, which corresponds to ΔG° = 4.5 kcal/mol; that is, 2-py + H₂ is disfavored relative to 1-H and py. Under pseudofirst-order conditions, the loss of 1-H was monitored with various concentrations of py present, and plots of ln[1-H] versus time were found to be linear; the data are given in Scheme 5. Due to the approach to equilibrium, observations of the disappearance of 1-H were limited to 2–3 half-lives. From a plot of k_{obs} versus [py], a second-order rate constant of 5.9(2) × 10^{-6} M⁻¹ s⁻¹, corresponding to $\Delta G^{\dagger}_{for} = 34.4$ kcal/mol, was obtained. The expected observation of a second-order process was consistent with an associative path, where a five-coordinate intermediate of the type (^tBu₃SiNH)(^tBu₃SiN=)₂WH(py) (1-H-py) is likely. An alternative interchange pathway, where 1-H-py constitutes an activated complex where py enters as the H–H bond is being formed, cannot be distinguished on the basis of the kinetics data.

Another path involving deprotonation of the amide by pyridine, followed by loss of H₂ via dihydrogen loss from the complex ion $[({}^{t}Bu_{3}SiN=)_{3}WH][pyH]$ (2-H-pyH), is also a possibility, but deprotonation of the amide typically requires a much stronger base. Nonetheless the pK_{a} difference between $[pyH]^{+}$ (~3.4) and that of the amide (est. 20–30) is not too different than the activation energy for dihydrogen loss; the difficulty with this path is envisoning the microscopic reverse. It would seemingly require a displacement of py by H₂ that would enable complex ion formation by subsequent deprotonation of a dihydrogen complex.⁵⁸ Since 1,2-H₂ addition to an imide



from a dihydrogen complex is expected to be rapid, the proton transfer path is deemed less plausible. The contrast between the equilibrium in the tungsten case versus previous observations in the related titanium imide system is remarkable. Equilibrium studies have shown that $(silox)_2(^tBu_3SiN=)Tipy + H_2$ is 8.6 kcal/mol more stable than (silox)₂(^tBu₃SiNH)TiH + py.⁸ The origin of this $\Delta\Delta G^{\circ}$ of 13.1 kcal/mol is not clear, but several factors may be contributing. The metal-hydride bond strength is expected to be stronger for the group 6 element,⁵⁹ and the corresponding imide π -bond that is lost upon 1,2-H₂ addition is likely to be weaker for tungsten versus titanium; similar, more detailed arguments were presented in the Introduction. It is also conceivable that the smaller size of tungsten (cov. rad. W =1.30 Å;⁶⁰ cov. rad. Ti = 1.32 Å), in combination with the shorter multiple imide ligands compared to the siloxide, sterically favors the amide-hydride over the pyridine adduct. In addition, the reduced electrophilicity of tungsten may lower the interaction energy of the pyridine.

Thermolysis of (${}^{t}Bu_{3}SiN=)_{3}Wpy$ (2-py) with D₂ (~10 equiv) at 180 °C for 20 h in C₆D₆ revealed deuterium incorporation (~80%) in the α -positions of the released pyridine⁶¹ and some hydrogen in the amide (~80% D) and hydride (~83% D) positions. No incorporation into the remaining position of pyridine was noted, and HD and H₂ were observed in a ~3:1 ratio. A reversible CH bond activation at the α -position of a bound pyridine requires an additional step for deuterium incorporation. While σ -bond metathesis is an obvious candidate,⁵⁵ note that the process was not observed for (${}^{t}Bu_{3}SiN=)_{2}WH$ (1-H) and D₂, nor was any reversible activation of C₆D₆ revealed during the 200 °C

thermolysis illustrated in Scheme 4. An alternative possibility embraces the involvement of $({}^{t}Bu_{3}SiND)({}^{t}Bu_{3}SiN=)_{2}$ -W(N-pyridyl- α -D) (1-ND- α -pdyl), as illustrated by eq 10.



The pyridyl transient would be created via a 1,2-insertion of the pyridine into a W–D bond,^{61–69} and it generates hydrogen for the hydride and amide positions via β -H elimination. Equation 10 provides a rationale for the generation of HD, deuteration of the pyridine α -positions, and the presence of H in the amide-hydride.



 Structure of (^tBu₃SiN=)₃Wpy (2-py). An X-ray crystal structure determination of (^tBu₃SiN=)₃Wpy (2-py) was conducted, and a molecular view is presented in Figure 1. Selected details of the data collection and refinement are given in Table 2, and pertinent metric parameters are listed in Table 3. The asymmetric unit is comprised of two independent and almost identical distorted tetrahedral molecules, with $\angle N_{im}$ -W-N_{im} angles averaging 115.4(9)° and a $\angle N_{im}$ -W-N_{py} average angle of 102.6(13)°. The tungsten-imide distances average 1.820(19) Å, the pyridine is bound at a W–N distance of 2.148(2) Å, and the imides are nearly linear, with an average $\angle W-N_{im}-Si$) angle of 174.1(26)°. The metric parameters are not particularly striking, except that the imide distances are somewhat long for W(VI). For example, a rough average of d(W=N) in d⁰ bis-imido tungsten complexes is 1.74(3) Å.^{24,70} Recall that the $C_{3\nu}$ symmetry of the WN₃ core renders one pair of the 12 N(p π) electrons nonbonding by virtue of their a₂ symmetry, which has no match on the metal.²¹ In addition, competition among all three imides for metal receptor orbitals

renders the π -bonding modestly attenuated in this system, as discussed in the Introduction.^{21–25}

Syntheses and Characterizations of M[(^tBu₃SiN=)WH/ **X/R].** 1. $M[({}^{t}Bu_{3}SiN=)_{3}WH$. Deprotonation of $({}^{t}Bu_{3}SiNH)_{2}$ (^tBu₃SiN=)₂WH (1-H) was effected by ^tBuLi to produce $Li(^{t}Bu_{3}SiN=)_{3}WH$ (2-Li-H) according to eq 9, but a scale-up of the deprotonation reaction utilized neoPeLi, as indicated in eq 11. Sodium and potassium analogues were produced via the use of MH (M = Na, K) to afford M(${}^{t}Bu_{3}SiN=$)₃WH (2-M-H, M = Na, K in modest (unoptimized) yields as given in eq 12.⁷¹ The neutral hydride, 1-H, possesses a hydride resonance at δ 13.34 in its ¹H NMR spectrum, with a ${}^{1}J_{WH}$ of 356 Hz, and this is accompanied by a $\nu(WH)$ of 1910 cm⁻¹ in its IR spectrum.^{11,42} The LiH species, 2-Li-H, also has a downfield resonance at δ 12.14 with a similar ${}^{1}J_{WH}$ of 338 Hz in its ${}^{1}H$ NMR spectrum, and its IR spectrum manifested a ν (WH) of 1907 cm^{-1} , which is remarkably similar to the neutral complex. In modest contrast, the hydride shifts of $Na({}^{t}Bu_{3}SiN=)_{3}$ -WH (2-Na-H) and $K(^{t}Bu_{3}SiN=)_{3}WH$ (2-K-H) appear more



Figure 1. Molecular view of (^tBu₃SiN=)₃Wpy (2-py).

upfield at δ 7.20 (${}^{1}J_{WH} = 314$ Hz) and δ 7.11 (313 Hz), respectively, with ${}^{1}J_{WH}$ values that are somewhat attenuated. In addition, the ν (WH) values for 2-Na-H and 2-K-H are lower at 1855 and 1858 cm⁻¹, respectively. In general, the solubilities of M(${}^{1}Bu_{3}SiN=)_{3}WH$ (2-M-H) were consistent with neutral complexes; that is, they possessed solubilities that were not very different from (${}^{1}Bu_{3}SiNH$)(${}^{1}Bu_{3}SiN=)_{2}WR$ (1-R), and there was little difficulty in obtaining NMR spectra in benzene- d_{6} , perhaps due to alkalai metal-benzene interactions.^{72,73}

2. Structure of $({}^{t}Bu_{3}SiN=)_{3}WHK(OEt_{2})_{3}$ (2-H-K(OEt_{2})_{3}). When crystallized with diethyl ether present, K(${}^{t}Bu_{3}SiN=)_{3}WH$ (2-K-H) coordinated three ether molecules to afford (${}^{t}Bu_{3}SiN=)_{3}WHK(OEt_{2})_{3}$ (2-H-K(OEt₂)₃), whose structure was determined by X-ray crystallography. Selected details

regarding the data collection and refinement may be found in Table 2, while Table 3 contains pertinent metric information. As Figure 2a illustrates, 2-H-K(OEt_2)₃ is a pseudotetrahedral molecule with the potassium bound to the hydride at 2.71(7) Å and to three ether molecules with $d(K-O)_{av} = 2.744(14)$ Å that are staggered with respect to the tungsten core.⁷⁴ The W-H-K bridge angle is $153(2)^\circ$, and the tungsten-hydride distance is 1.72(6) Å,⁷⁵ slightly longer than the sum of covalent radii $(1.62 \text{ Å})^{59}$ and about the mean of a rather wide spectrum of d(WH) determined from X-ray studies.^{42,60,76–78} The tungsten-imido bonds average 1.806(4) Å, and the N-W-N angles are somewhat splayed from a tetrahedral value at 116.1(2)°, presumably reflecting the demonstrably greater steric influences among the imides versus the hydride. The N-W-H angles are correspondingly smaller, averaging 101.6(11)°, and the W–N–Si linkages are 166.9(23)°.

Few structures with a comparable W–H–M' (M' = alkali metal) connection have been reported;⁷⁷ hence the structure of Cp₂Mo(μ -H)K(18-crown-6)⁷⁴ is the most apt comparison, with a d(Mo–H) of 1.66 Å and a d(K–H) of 2.80 Å. Tungstenbridging hydride distances have been measured by neutron diffraction studies on [(Me₃P)₃H₂W](μ -H)₃[M'(crown)] (M'(crown) = K(18-c-6), Na(15-c-5)), and their values of 1.77(2) Å do not differ from the terminal distances of 1.77(2) Å.⁷⁸

3. Structure of [('Bu₃SiN=)₃WH][K(crypt-2.2.2)] (2-H-Kc). The molecular structure of [('Bu₃SiN=)₃WH][K(crypt-2.2.2)] (2-H-Kc) was also determined by X-ray crystallography, and two discrete ions—the [('Bu₃SiN=)₃WH]⁻ anion and the [K-(crypt-2.2.2)]⁺ cation—are clearly separated in the structure. Unfortunately, while the hydride pertaining to the anion was determined by a difference Fourier map and successfully refined, its d(WH) of 1.93(9) Å and H–W–N angles (118(2)°, 92(2)°, 90(2)°) likely reflect an inaccuracy in the model.^{42,60,76-78} Refinement and data collection parameters are given in Table 2 and the metrics of the molecule are listed

Table 2. Selected Crystallographic and Refinement Data for $({}^{t}Bu_{3}SiN=)_{3}Wpy$ (2-py), $({}^{t}Bu_{3}SiN=)_{3}WHK(OEt_{2})_{3}$ (2-H-K(OEt_{2})_{3}), $[({}^{t}Bu_{3}SiN=)_{3}WHI][K(crypt-2.2.2)]$ (2-H-Kc), $({}^{t}Bu_{3}SiN=)_{3}WHK$ (2-K-H), and $({}^{t}Bu_{3}SiN=)_{3}WIK$ (2-I-K)

	2-py ^a	$2-H-K(OEt_2)_3$	2 -H-Kc	2 -K-H ^b	2 -I-K ^c
formula	C ₄₁ H ₉₆ N ₄ Si ₂ W	C48H111N2O2Si2KW	C ₅₆ H ₁₂₀ N ₅ O ₆₅ Si ₂ KW	C ₂₆ H ₂₂ N ₂ Si ₂ KW	C111H245N2K2I2W
fw	903.26	1085.62	1282.85	864.27	3011.07
space group	Pbca	$P2_1/n$	$P\overline{1}$	$P\overline{1}$	$P\overline{1}$
Z	16	4	2	2	2
a, Å	17.948(4)	13.2546(2)	12.168(2)	12.941(1)	19.065(4)
b, Å	26.404(5)	22.01670(10)	17.080(3)	13.103(1)	20.937(4)
c, Å	42.901(9)	20.8776(3)	18.459(4)	16.293(1)	23.744(5)
α , deg	90	90	88.37(3)	70.85(4)	67.569(5)
β , deg	90	95.6070(10)	88.41(3)	71.47(4)	66.668(7)
γ, deg	90	90	69.99(3)	62.55(4)	63/299(6)
<i>V</i> , Å ³	20330.7(71)	6063.40(13)	3602.4(12)	2269.3(3)	7531.3(26)
$\rho_{\rm calc}$ g·cm ⁻³	1.180	1.189	1.183	1.265	1.328
μ , mm ⁻¹	2.371	2.069	1.755	2.741	3.079
temp, K	293(2)	165(1)	173(2)	295(2)	293(2)
λ, Å	0.91000	0.71073	0.71073	0.71073	0.71073
R indices $[I > 2\sigma(I)]^{d,e}$	$R_1 = 0.0651$	$R_1 = 0.0427$	$R_1 = 0.0519$	$R_1 = 0.0581$	$R_1 = 0.1055$
	$wR_2 = 0.1861$	$wR_2 = 0.1331$	$wR_2 = 0.1285$	$wR_2 = 0.1500$	$wR_2 = 0.2398$
R indices (all data) ^{d,e}	$R_1 = 0.0674$	$R_1 = 0.0788$	$R_1 = 0.0909$	$R_1 = 0.0671$	$R_1 = 0.1771$
	$wR_2 = 0.1919$	$wR_2 = 0.01685$	$wR_2 = 0.1820$	$wR_2 = 0.1661$	$wR_2 = 0.2705$
GOF ^f	1.006	1.045	1.079	1.041	1.088

^aTwo molecules per asymmetric unit. ^bHalf of the dimer is the asymmetric unit. ^cThe trimer is the asymmetric unit. ^d $R_1 = \sum ||F_0| - |F_c||/\sum |F_o|$. ^e $wR_2 = \sum w(|F_0| - |F_c|)^2 / \sum wF_0^2 |_{1^2}$. ^fGOF (all data) = $[\sum w(|F_0| - |F_c|)^2 / (n-p)]^{1/2}$, n = number of independent reflections, p = number of parameters.

Table 3. Selected Interatomic Bond Distances (Å) and Angles	(deg) for $({}^{t}Bu_{3}SiN=)_{3}Wpy$ (2-py), $({}^{t}Bu_{3}SiN=)_{3}WHK(OEt_{2})_{3}$
(2-H-K(OEt ₂) ₃), [(^t Bu ₃ SiN=) ₃ WH][K(crypt-2.2.2)] (2-H-Kc),	$(^{t}Bu_{3}SiN=)_{3}WHK (2-K-H), and (^{t}Bu_{3}SiN=)_{3}WIK (2-I-K)$

	2 -py ^{<i>a</i>}	2-H-K(OEt2)3	2 -H-Kc ^b	2 -K-H	2-I-K ^{c}
W1=N1	1.821(6), 1.842(8)	1.803(5)	1.809(4)	1.783(4)	1.68(3), 1.62(2), 1.56(2)
W1=N2	1.816(6), 1.795(7)	1.810(5)	1.802(4)	1.793(5)	1.75(3), 1.79(2), 1.79(2)
W1=N3	1.842(7), 1.804(6)	1.805(5)	1.802(4)	1.799(4)	1.82(2), 1.84(2), 1.84(2)
W1-X	2.148(7), 2.147(8)	1.72(6)	Ь	1.75(4)	2.724(2), 2.727(3), 2.726(3)
N-Si _{av}	1.736(12)	1.716(7)	1.704(6)	1.737(3)	1.78(10)
K1–H1, I		2.71(7)		2.64(4)	3.52(5)av
K1–H1′				2.43(4)	
K1…K1′				4.249(4)	
H1…H1′				2.77(5)	
K1-O1		2.756(4)	2.828(5)		
K1-O2		2.747(4)	2.825(5)		
K1-O3		2.728(6)	2.787(5)		
K1-O4			2.784(5)		
K1-O5			2.859(4)		
K1-O6			2.802(4)		
N1-W1-N2	114.6(3), 114.6(3)	116.1(2)	117.0(2)	114.3(2)	110.1(12), 110.5(8), 110.3(9)
N1-W1-N3	115.9(3), 116.8(3)	116.2(2)	117.3(2)	118.8(2)	113.4(11), 115.4(8), 113.8(11)
N2-W1-N3	115.5(3), 114.8(3)	115.9(2)	116.2(2)	117.8(2)	116.8(12), 115.5(10), 116.7(10)
N1-W1-X	100.8(3), 101.5(3)	101.8(17)	Ь	106.2(11)	102.8(6), 103.4(7), 101.8(8)
N2-W1-X	103.8(3), 102.1(3)	100.4(16)	Ь	88.9(14)	105.2(6), 105.1(7), 105.4(7)
N3-W1-X	103.4(3), 103.9(3)	102.5(18)	Ь	104.7(13)	107.2(8), 105.5(7), 107.7(8)
W1-N1-Si1	171.2(5), 172.9(4)	168.2(3)	175.4(3)	174.2((3)	170.3(20), 173.4(12), 173.0(12)
W1-N2-Si2	175.1(4), 177.9(5)	168.3(3)	175.7(3)	165.6(3)	174.6(12), 176.6(14), 176.3(16)
W1-N3-Si3	171.7(5), 175.9(4)	164.2(3)	175.0(3)	167.4(3)	178.8(14), 177.6(11), 177.1(13)
K1-H-K1'				113.9(15)	
H–K1–H′				66.1(15)	
O1-K1-O2		99.52(14)	$60.1(4)^d$		
O1-K1-O3		119.1(2)	$97.4(16)^d$		
O2-K1-O3		89.8(2)	$123.7(23)^d$		
O-K-O			$133.6(21)^d$		
O1-K1-H/N		136.3(11)			
O2-K1-H/N		101.1(10)			
O3-K1-H/N		99.1(11)			

^{*a*}Two molecules per asymmetric unit; chemically equivalent parameters listed together. ^{*b*}Hydride refined, but d(WC) = 1.93(9) Å and H–W–N angles of $118(2)^\circ$, $92(2)^\circ$, and $90(2)^\circ$ appear unreasonable. ^{*c*}Trimer is the asymmetric unit. Chemically equivalent parameters listed together; $\angle I-K-I = 83(2)^\circ$, $105(2)^\circ$, and $105(2)^\circ$; $\angle K-I-K = 118(2)^\circ$, $121(2)^\circ$, and $121(2)^\circ$; $\angle W-I-K = 97.4(6)_{av}^\circ$. ^{*d*}Fifteen O–K–O angles in the crypt 2.2.2 are in four groups averaged as indicated.



Figure 2. Molecular views of $({}^{t}Bu_{3}SiN=)_{3}WHK(OEt_{2})_{3}$ (2-H-K $(OEt_{2})_{3}$ (a)) and the $[({}^{t}Bu_{3}SiN=)_{3}WH]$ anion of $[({}^{t}Bu_{3}SiN=)_{3}WH][K(crypt-2.2.2)]$ (2-H-Kc (b); its hydride has been tentatively located).





in Table 3. The core of the $[({}^{t}Bu_{3}SiN=)_{3}WH]^{-}$ anion that is illustrated in Figure 2b is very similar to the previous cases, with $d(W=N)_{av} = 1.804(4)$ Å, N–W–N angles that average 116.8(6)°, and W–N–Si linkages that are nearly linear (175.4(4)°_{av}).

4. Structure of $K(^{t}Bu_{3}SiN=)_{3}WH$ (2-K-H). The most interesting of the hydride anion structures is the unsolvated version of K(^tBu₃SiN=)₃WH (2-K-H), whose structure was determined by X-ray crystallography to be dimeric (i.e., [2-H]₂- $(\mu$ -K)₂) in the solid state. Data collection and refinement information is listed in Table 2, while selected interatomic distances and angles are given in Table 3. The dimer shown in Figure 3 possesses a center of inversion about a planar K₂H₂ diamond core (\angle H1-K1-H1' = 66(2)°, \angle K1-H1-HK' = $113(2)^{\circ}$; $d(K1\cdots K1') = 4.249(4)$, $d(H1\cdots H1') = 2.77(5)$, with two symmetry-equivalent, flanking pseudotetrahedral tris-imido tungsten moieties. In addition to the two hydrides bound to each potassium, six ligand carbon atoms are within 3.23-3.93 Å, providing corresponding calculated CH…K contacts of 2.66-3.00 Å. This secondary coordination sphere is similar to that reported for {(Me₃Si)₂N]₂V[N(SiMe₃)SiMe₂CH₂]}₂{K- $(THF)_{2}^{3}$ which is composed of two almost identical vanadium monomers bridged by two separate K(THF)₂ units, and manifests H...K contacts of 3.01-3.52 Å that derive from the SiMe₃ groups. The d(WN) are the shortest in



Figure 3. Molecular (a) and core (b) views of $({}^{t}Bu_{3}SiN=)_{3}WHK$ (2-H-K, as $[2-H]_{2}(\mu$ -K)₂).

the series of hydrides, averaging 1.792(8) Å, and the N–W–N angles have slightly greater variance than the previous examples, averaging $117.0(27)^{\circ}$. The H–W–N1, –N2, and –N3 angles are $106.2(11)^{\circ}$, $88.9(14)^{\circ}$, and $104.7(13)^{\circ}$, respectively. The hydride is bound to the tungsten at 1.75(4) Å, and it is slightly asymmetric, with W–H1–K1 and W–H1–K1' angles of $117(2)^{\circ}$ and $124(2)^{\circ}$.

5. $K({}^{t}Bu_{3}SiN=)_{3}WR$ (2-K-R). The appearance of [(${}^{t}Bu_{3}SiN=)_{3}WPh$]Li (2-Li-Ph), Li(${}^{t}Bu_{3}SiN=)_{3}W(C_{6}H_{4}-3-Me)$ (2-Li-C₆H₄-3-Me), and Li(${}^{t}Bu_{3}SiN=)_{3}W(C_{6}H_{4}-4-Me)$ (2-Li-C₆H₄-4-Me) in the arylation attempts illustrated by eqs 3 and 4 prompted a brief survey of anion generation⁷¹ via KH and (${}^{t}Bu_{3}SiNH$)(${}^{t}Bu_{3}SiN=)_{2}WR$ (1-R, R = Me, Et, ${}^{n}Pr$). As eq 13 reveals, deprotonation of 1-Me, 1-Et, and 1- ${}^{n}Pr$ with KH was conducted in THF (or THF- d_{8}) with heating to produce the desired potassium tungsten alkyl compounds K(${}^{t}Bu_{3}SiN=)_{3}WR$ (2-K-R, R = Me, Et, ${}^{n}Pr$). Only the methyl derivative was isolated (50%), while the others were prepared quantitatively according to ${}^{1}H$ NMR assays.

6. $M({}^{t}Bu_{3}SiN=)_{3}WX$ (2-*M*-X). The production of K-(${}^{t}Bu_{3}SiN=)_{3}WCl$ (2-K-Cl) upon treatment of (${}^{t}Bu_{3}SiNH$)(${}^{t}Bu_{3}SiN=)_{2}WCl$ (1-Cl) with potassium benzyl in THF- d_{8} (eq 5) was likely a product of a simple acid—base reaction, prompting efforts at generalizing the process.²² As a consequence, (${}^{t}Bu_{3}SiNH$)-(${}^{t}Bu_{3}SiN=)_{2}WX$ (1-X, X = Cl, Br, I) were treated with KH in





THF and heated to afford the corresponding potassium tungsten halide complexes $K(^{t}Bu_{3}SiN=)_{3}WX$ (2-K-X, X = Cl, Br, I) in reasonable yields, as indicated by eq 14.



Alternative routes to the alkali halide derivatives were explored, and alkyl halides were used as a source of X. Treatment of Li(^tBu₃SiN=)₃WH (2-Li-H) with 1 equiv of CCl₄ quantitatively converts the hydride into the chloride, Li(^tBu₃SiN=)₃WCl (2-Li-Cl), and byproduct chloroform, as indicated by eq 15. Although the reaction looks like a simple displacement, electron transfer events are more common with CCl₄. Another substrate that is unlikely to undergo an S_N2-like displacement is ^{neo}PeCl, where abackside attack is known to be prohibitively inhibited by sterics. With 7 equiv of ^{neo}PeCl, Na(^tBu₃SiN=)₃WH (2-Na-H) was slowly converted to Na(^tBu₃SiN=)₃WCl (2-Na-Cl) with concomitant neopentane at 150 °C over 36 h, as shown in eq 16. Radical paths can be



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used to describe the results in eqs 15 and 16, but what would happen if CH_3I were the substrate?

Exposure of Li(^tBu₃SiN=)₃WH (2-Li-H) to 1 equiv of CH₃I in C₆D₆ yielded the LiI complex Li(^tBu₃SiN=)₃WI (2-Li-I) in 80% yield, but two unexpected products were also identified. The neutral methyl derivative, (^tBu₃SiNH)(^tBu₃SiN=)₂WCH₃ (1-CH₃), was detected in 12% yield, and the related iodide species, (^tBu₃SiNH)(^tBu₃SiN=)₂WI (1-I), was also present (8%). While radical paths can describe how these products formed, aspects of those reactions prompted additional investigations. This study, which invokes the intermediacy of alkane complexes in several reactions of M(^tBu₃SiN=)₃WH (2-M-H) and RX,^{11,12} will be fully described in a subsequent article.

7. Structure of $K({}^{t}Bu_{3}SiN=)_{3}WI$ (2-K-I). An X-ray crystallographic study of $K({}^{t}Bu_{3}SiN=)_{3}WI$ (1-K-I) that was crystallized from hexane revealed its solid-state structure to be a trimer, in contrast to cryoscopic molecular weight measurements that revealed 1-K-I as a monomer in benzene. Data collection and refinement information is given in Table 2, and various metrics are listed in Table 3, but the latter parameters show large variation due to poor data. Nonetheless, the structure shown in Figure 4 features a six-membered K₃I₃ ring, with the usual pseudotetrahedral tris-imido tungsten cores attached to the iodine atoms. The K₃I₃ ring has potassium—iodine distances



Figure 4. Molecular view of the trimer of $K(^{t}Bu_3SiN=)_3WI$ (2-K-I, as $[2-I]_3(\mu$ -K)_3); ball and stick presentation due to data quality.

that average 3.52(5) Å, I–K–I angles of 83(2)°, 105(2)°, and 105(2)°, fairly regular K–I–K angles of 118°(2), 121°(2), and 121(2)°, and W–I–K angles that average 97.4(6)°. The tungsten core parameters are comparable to the previous examples, yet reflect the limited resolution of the model, with d(WN) = 1.74(10) Å, N–W–N angles that average 113.6(27)°, and N–W–I angles averaging 104.9(19)°.

DISCUSSION

Metathetical Routes to $({}^{t}Bu_{3}SiNH)({}^{t}Bu_{3}SiN=)_{2}WR$ (1-R). Metathetical procedures employing $({}^{t}Bu_{3}SiNH)({}^{t}Bu_{3}SiN=)_{2}WX$ (1-X) proved complicated due to side reactions that were not unexpected, but counterproductive nonetheless. Scheme 6 summarizes the problems encountered during this approach. Displacement typically occurs more favorably for X = Cl > Br > I, since the softer halides tend to encourage reduction, but the evidence in this study is limited, and at times counterintuitive. (^tBu₃SiNH)(^tBu₃SiN=)₂WCH₃ (1-CH₃) is readily formed from 1-Cl (eq 2), yet KCH₂Ph deprotonates 1-Cl, but does transfer benzyl anion to 1-I to a modest extent. Metathetical reactions of this type are subject to the vagaries of the particular conditions employed, and no systematic study was made to segregate the various influences.

Substantial amounts of metathesis products 1-Me, 1-Bn, 1-Ph, 1-C₆H₄3-Me, and 1-C₆H₄-4-Me were generated, and electron transfer processes were suggested by the nature of the byproducts in several of these cases. In particular, the production of $M(^{t}Bu_{3}SiN=)_{3}WH$ (2-M-H, M = Li, K) in eqs 4, 6, and 7 implicated electron transfer events that often occur with ArLi and BnK reagents. One possible subsequent reaction is H-atom transfer,^{80,81} but only in the case of ^tBuLi and 1-Cl is this substantiated (eqs 8, 9); (^tBu₃SiNH)(^tBu₃- $SiN=_2WH$ (1-H) appears to be the initial product that is then deprotonated to generate M(^tBu₃SiN=)₃WH (2-M-H). No 1-H was detected in other instances in which electron transfer is likely to play a role, and the final 2-M-H product was likely formed from a subsequent second electron transfer from excess reducing agent. In the case of potassium benzyl (eq 7), dibenzyl was observed consistent with the generation of benzyl radical upon electron transfer. In this case, C_6D_6 was the solvent when the reaction was carried out on the NMR tube scale, and it is likely that excess KBn reduced the intermediate W(V) product formed upon reduction/halide loss to directly afford 2-M-H.

Insertion Routes to (^tBu₃SiNH)(^tBu₃SiN=)₂WR (1-R). Steric factors appear to govern the conditions necessary to effect olefin insertion routes to various alkyl complexes in Scheme 3. The only reaction that is particularly strange is the formation of (^tBu₃SiNH)(^tBu₃SiN=)₂W(E-CH₂CH=CHMe) (1-E-CH₂CH=CHMe) (>95%, ¹H NMR) upon reaction of butadiene with (^tBu₃SiNH)(^tBu₃SiN=)₂WH (1-H). It is difficult to reconcile this product without invoking a 2,1-insertion of $C_4H_{6^{1}}^{48,49}$ followed by rearrangement via an η^3 allyl, at a metal center that is significantly encumbered by its imide ligands. Two other reactions support this observation: (1) methylenecyclopentane is isomerized to 1-Me-cyclopentene in the course of insertion efforts, and (2) in the likely absence of σ -bond metathesis paths, deuteration of the α positions of the pyridine in eq 10 requires an insertion of pyridine into the tungsten-deuteride(hydride) bond. Alternatively, a bis-amide imide W(IV) species could conceivably mediate both formation of the 1-E-CH₂CH=CHMe product from butadiene and the scrambling in the pyridine deuteration studies via related NH abstraction⁸²⁻⁸⁴ and metalla-ene rearrangements that are illustrated in Scheme 7. The threecoordinate W(IV) intermediate⁸⁵ cannot be ruled out by the experiments presented, but the exchange of the W-H bond and W=N π -bonds for an NH bond is likely to be substantially endothermic.

Thermal Stability of (${}^{t}Bu_{3}NH$)(${}^{t}Bu_{3}SiN=$)₂WH/R (1-H/R). As calculated, and as predicted on the basis of known trends, 1,2-H₂ and 1,2-MeH elimination from (${}^{t}Bu_{3}SiNH$)(${}^{t}Bu_{3}SiN=$)₂WH (1-H) and (${}^{t}Bu_{3}SiNH$)(${}^{t}Bu_{3}SiN=$)₂WCH₃ (1-CH₃), respectively, are not observable according to Scheme 4.^{11,12,22} In the case of 1-H, the addition of pyridine permits exchange of the amide hydrogen and hydride positions with deuterium from D₂ (Scheme 5, eq 10). Unfortunately, since

Scheme 6



this process is associative in character, according to the kinetics study, several mechanisms, three of which are illustrated in Scheme 5 and a less likely one implicated in Scheme 7, cannot be easily ruled out.

Solution versus Solid -State Structures of $M({}^{t}Bu_{3}SiN=)_{3}$ -WH (2-M-H). Solid-state structures of $K({}^{t}Bu_{3}SiN=)_{3}WH$ (2-K-H) were determined under three separate sets of crystallization conditions, and three different species were identified, two with W–H–K connectivity and one without. While a discussion of hydride metric parameters is intrinsically problematic due to a lack of confidence in correctly locating the position of the hydride, other metrics show the tris-imido tungsten hydride core to be relatively constant.²⁴ The tungsten–imido bond lengths and core angles among

(^tBu₃SiN=)₃WHK(OEt₂)₃ (2-H-K(OEt₂)₃), [(^tBu₃SiN=)₃WH]-[K(crypt-2.2.2)] (2-H-Kc), and (^tBu₃SiN=)₃WHK (2-H-K) are very similar, despite the separated anion [(^tBu₃SiN=)₃WH] and cation [K(crypt-2.2.2)] pair in 2-H-K. For comparison, the pyridine in (^tBu₃SiN=)₃Wpy (2-py) appears to render the metal center more electron rich, as its W=N distances are slightly longer, but even this judgment must be tempered by the ~0.02 Å difference with respect to the hydrides, a small factor that might simply reflect added steric influences.

It is more interesting to speculate on what structure the hydrides possess in solution. A scale of solvent donicity has been developed,⁸⁶ and a brief NMR spectroscopic study of $K(^{t}Bu_{3}SiN=)_{3}WH$ (2-K-H) in various media revealed some correlations, as shown in Table 4. Nondonor and poor donor

Table 4. Hydride Chemical Shifts (¹H NMR) for $K(^{t}Bu_{3}SiN=)_{3}WH$ (2-K-H) and $[(^{t}Bu_{3}SiN=)_{3}WH]$ [K(crypt-2.2.2)] (2-H-Kc) in Various Solvents at 23 °C

compound	solvent	solvent donicity ^a	$\delta(WH)$	${}^{1}J_{\rm WH}$ (Hz)
2 -K-H	C_6D_6	0.003	7.20	313
2 -K-H	toluene- d_8	0.003	7.23	314
2 -K-H	CD_2Cl_2	0.026	7.27	313
2 -K-H	Et_2O-d_{10}	0.495	7.58	304
2 -K-H	acetone- d_6	0.483	9.97	327
2 -H-Kc	THF- d_8	0.515	10.06	329
2 -K-H	THF- d_8	0.515	10.09	329
2 -K-H	pyridine-d ₅	0.853	10.61	324
^{<i>a</i>} See ref 86.				

solvents afford hydride chemical shifts in the 7.2–7.6 ppm region, whereas good donors cause a change to 10.0–10.6 ppm. Likewise, the ${}^{1}J_{WH}$ values change from ~304–314 Hz to 324–329 Hz in concert with the shift changes. When crypt-2.2.2 is incorporated in the synthesis described by eq 11, the hydride shift in THF- d_8 appears to be that of the corresponding anion, $[({}^{t}Bu_3SiN=)_3WH]^-$, because it is the same as 2-K-H taken in the same solvent. The shift is at δ 10.06, with a ${}^{1}J_{WH}$ of 329 Hz and a corresponding $\nu(WH) = 1925$ cm⁻¹.

Since the structural study of 2-H-Kc shows separation of [K(crypt-2.2.2] from the tungsten anion, the chemical shift and IR stretching values may signify structural differences depending on solvation and alkali metal ion. Specifically, in strong donors the spectral parameters are likely to be those of the free anion, $[({}^{t}Bu_{3}SiN=)_{3}WH]^{-}$. While shifts and WH coupling pertaining to the Na and K hydrides are quite similar, those of Li(${}^{t}Bu_{3}SiN=)_{3}WH$ (2-Li-H) show greater similarity to the neutral hydride, (${}^{t}Bu_{3}SiN+)$ (${}^{t}Bu_{3}SiN=)_{2}WH$ (1-H), prompting speculation that the lithium is coordinated by the nitrogens

in 2-Li-H.⁸⁷ The larger Na and K substituents may be coordinated to the hydride and solvent or imide ligands within 2-M-H (M = Na, K). Note that the ^tBu chemical shifts are at δ 1.42 and 1.46 for the Na and K derivatives, respectively, compared to a δ 1.26 pertaining to 2-Li-H, when taken in $C_{\delta}D_{\delta}$. The ^tBu chemical shift differences between Li and Na or K exist for the halide derivatives $M(^{t}Bu_{3}SiN=)_{3}WX$ (2-M-X) as well as the hydrides. These are very large shift differences for the silimide groups and may reflect differing solution geometries; alternatively, the data may simply be a consequence of the greater covalency of lithium in its coordination.

CONCLUSIONS

Approaches to the synthesis of $({}^{t}Bu_{3}SiNH)({}^{t}Bu_{3}SiN=)_{2}WX/R$ (1-X/R) and $M(^{t}Bu_{3}SiN=)_{3}WH/X/R$ (2-M-H/X/R) have been explored herein, including metatheses, insertions, various halogenations, and deprotonations. None are general, yet each one is efficient for certain transformations. As expected from calculations and previous results, the thermal stability of $(^{t}Bu_{3}SiNH)(^{t}Bu_{3}SiN=)_{2}WH/R$ (1-H/R) with respect to dihydrogen and hydrocarbon loss is remarkable. The structures of $(^{t}Bu_{3}SiN=)_{3}Wpy$ (2-py), $(^{t}Bu_{3}SiN=)_{3}WHK(OEt_{2})_{3}$ (2-H- $K(OEt_2)_3)$, [(^tBu₃SiN=)₃WH][K(crypt-2.2.2)] (2-H-Kc), (^tBu₃-SiN=)₃WHK (2-H-K, as $[2-H]_2(\mu-K)_2$), and K(^tBu₃SiN=)₃WI (2-K-I, as $[2-I]_3(\mu$ -K)_3) have been elucidated by X-ray crystallography, and their tris-imido cores have been found to be very similar. The reaction of 2-Li-H and MeI provided products that hint at the formation of an intermediate methane complex;^{11,12} this subject will be featured subsequently.

EXPERIMENTAL SECTION

General Considerations. All manipulations were performed using either glovebox or high vacuum line techniques. All glassware was oven-dried. THF and ether were distilled under nitrogen from purple sodium benzophenone ketyl and vacuum transferred from the same prior to use. Hydrocarbon solvents were treated in the same manner with the addition of 1-2 mL/L tetraglyme. Benzene- d_6 and toluene- d_8 were dried over sodium, vacuum transferred, and stored over activated 4 Å molecular sieves. THF-d₈ was dried over sodium and vacuum transferred from sodium benzophenone ketyl prior to use. All glassware was base-washed and oven-dried. NMR tubes for sealed tube experiments were flame-dried under dynamic vacuum prior to use. Organic reagents and solutions of alkyllithiums were obtained from Aldrich Chemical. Ethylene, propene, and dihydrogen (Matheson) were passed through a -78 °C trap prior to use. Methyl-substituted aryl lithium reagents were prepared by the transmetalation of aryl iodides with "BuLi. ('Bu₃SiNH)-(^tBu₃SiN=)₂WH (1-H)⁴² and potassium benzyl⁴⁷ were prepared according to literature procedures. All other chemicals were commercially available and used as received.



Figure 5. Plausible solution structures for $M({}^{t}Bu_{3}SiN=)_{3}WH$ (2-M-H) rationalizing apparent NMR spectroscopic differences between M = Li and M = Na, K.

¹H, ¹³C{¹H}, and ²H{¹H} NMR spectra were obtained using Varian XL-200, XL-400, and Unity-500 spectrometers. Chemical shifts are reported relative to benzene- d_6 (¹H, δ 7.15; ¹³C, δ 128.00) or THF- d_8 (¹H, δ 3.58; ¹³C, δ 67.57). Infrared spectra were recorded on a Nicolet Impact 410 spectrophotometer interfaced to a Gateway PC. Combustion analyses were conducted by Oneida Research Services (Whitesboro, NY, USA) or Robertson Microlit Laboratories (Madison, NJ, USA). The Center for High Energy Synchrotron Studies (CHESS) at Cornell University was used for the X-ray crystallographic study of (^tBu₃SiN=)₃Wpy (2-py).

Procedures. 1. (${}^{t}Bu_{3}SiNH$)(${}^{t}Bu_{3}SiN=$)₂WCI (1-Cl). To a stirred solution of 1-H (3.36 g, 4.07 mmol) in 50 mL of hexane was vacuum transferred 2.5 mL of CCl₄ (0.026 mol, 6 equiv). The reaction continued to stir for 10 h at 23 °C, and the original colorless solution became yellow. After removal of all volatiles and filtration in hexane, the solution volume was reduced to 20 mL and cooled to -78 °C, producing 2.60 g of 1-Cl as yellow microcrystals that were collected by filtration (74%). IR (Nujol, cm⁻¹): 3261(m), 3245(m), 1468(s), 1387(s), 1131(s), 1041(s), 1008(s), 935(s), 841(s), 819(s), 622(s), 580. Anal. Calcd for C₃₆H₈₂N₃ClSi₃W: C, 50.24; H, 9.60; N, 4.88. Found: C, 50.54; H, 10.11; N, 4.66.

2. ('Bu₃SiNH)('Bu₃SiN=)₂WBr (1-Br). 1-H (300 mg, 3.63×10^{-4} mol) and CBr₄ (126 mg, 3.80×10^{-4} mol, 1.05 equiv) were combined in a flask, 15 mL of benzene was added, and the solution was stirred for 12 h at 23 °C. During this period, the original colorless solution slowly became pale yellow. After removal of all the volatiles, the remaining material was sublimed at 100 °C ($10^{-3}-10^{-4}$ Torr, 6 h). The solids were dissolved in hexanes, the volume was reduced to 3 mL, and the solution was cooled to -78 °C, producing 220 mg of yellow microcrystalline 1-Br (67%), collected by filtration. IR (Nujol, cm⁻¹): 3255(w), 3244(w), 1464(s), 1386(s), 1367(m), 1131(s), 1040(s), 1008(s), 935(m), 841(s), 820(s), 622(s), 580(s). Anal. Calcd for C₃₆H₈₂N₃BrSi₃W: C, 47.47; H, 9.13; N, 4.64. Found: C, 47.27; H, 9.21; N, 4.70.

3. $({}^{t}Bu_{3}SiNH)({}^{t}Bu_{3}SiN=)_{2}Wl$ (1-l). 1-H (3.56 g, 4.31 × 10⁻³ mol) and CI₄ (2.46 g, 4.73 × 10⁻³ mol, 1.1 equiv) were combined in a flask, and 40 mL of benzene was added. The reaction mixture was stirred for 20 h at 23 °C, and the orange solution did not perceptively change color. A small amount of brown, insoluble solid was filtered, and the reaction mixture was sublimed at 100 °C for 1 h to remove unreacted CI₄ and byproduct HCI₃. The remaining material was dissolved in hexanes, the volume reduced to 25 mL, and the solution cooled to -78 °C, yielding 2.65 g of a yellow precipitate. A second crop of 1-I of 420 mg gave a total yield of 75%. IR (Nujol, cm⁻¹): 3241(m, NH), 1468(s), 1386(s), 1365(m), 1131(s), 1040(s), 1008(s), 934(m), 890(w), 841(s), 819(s), 622(s), 579(s). Anal. Calcd for C₃₆H₈₂N₃ISi₃W: C, 45.42; H, 8.68; N, 4.41. Found: C, 44.70; H, 9.40; N, 4.41.

4. $({}^{t}Bu_{3}SiNH)({}^{t}Bu_{3}SiN=)_{2}WCH_{3}$ (1-CH₃). a. 1-CH₃. To a stirred solution of 1-Cl (380 mg, 4.42×10^{-4} mol) in diethyl ether was transferred 0.33 mL of CH3Li (1.5 M in OEt2, 1.1 equiv) via syringe under argon counterflow at 0 °C. The yellow solution was stirred for 2 h at 0 °C, then for 4 h at 23 °C, and the color faded. After removal of all volatiles and filtration in pentane, the solution volume was reduced to 3 mL and cooled to -78 °C, yielding 0.188 g (51%) of 1-Me, which was collected as a white powder by filtration. IR (Nujol, cm^{-1}): 3249(m, NH), 3241(w), 1465(s), 1385(s), 1364(m), 1184(w), 1147(s), 1129(s), 1050(s), 1009(s), 935(s), 850(s), 820(s), 621(s), 583(s). Anal. Calcd for C37H85N3Si3W: C, 52.89; H, 10.20; N, 5.00. Found: C, 52.55; H, 10.30; N, 4.80. b. 1-NH-CD₃ and thermolysis. 1-NH-CD₃ was similarly obtained by treatment of 1-Cl with LiCD₃. ²H NMR analysis revealed no D-incorporation at the amide position, and thermolysis of a C₆H₆ solution of 1-NH-CD₃ for 1 week at 200 °C in a sealed NMR tube revealed no change (²H NMR spectroscopy). IR (Nujol, cm⁻¹): 3250(m), 3242(w), 2215(w), 2210(w), 1476(s), 1385(s), 1364(s), 1148(s), 1130(s), 1050(s), 1010(s), 936(s), 849(s), 820(s), 620(s), 583(s).

5. $({}^{t}Bu_{3}SiNH)({}^{t}Bu_{3}SiN=)_{2}WCI$ (1-Cl) + PhLi. To a stirred solution of 1-Cl (490 mg, 5.69 × 10⁻⁴ mol) in ether was transferred 0.41 mL of PhLi (1.8 M in cyclohexane/diethyl ether, 1.3 equiv) via syringe under

argon counterflow at 0 °C. The yellow solution was allowed to stir 2 h at 0 °C and 12 h at 23 °C. After removal of volatile materials and filtration in pentane, the solution volume was reduced to 3 mL and cooled to -78 °C, precipitating a light yellow powder, collected by filtration. ¹H and ¹³C{¹H} NMR spectroscopy indicated a mixture of (¹Bu₃SiNH)(¹Bu₃SiN=)₂WPh (1-Ph, 70%) and Li(¹Bu₃SiN)₃WPh (2-Li-Ph, 30%).

6. $({}^{6}Bu_{3}SiNH)({}^{6}Bu_{3}SiN=)_{2}WCI$ (1-Cl) + $LiC_{6}H_{4}$ -4-Me. A solution consisting of 1-Cl (227 mg, 2.64 × 10⁻⁴ mol) and $LiC_{6}H_{4}$ -4-Me (41 mg, 3.96 × 10⁻⁴ mol, 1.5 equiv) in Et₂O was stirred at 0 °C for 1 h followed by 12 h at 23 °C. After removal of volatile materials and filtration in hexanes, ¹H and ¹³C{¹H} NMR spectroscopy indicated a mixture of (${}^{18}u_{3}SiNH$)(${}^{18}u_{3}SiN=$)₂W(C₆H₄-4-Me) (1-C₆H₄-4-Me, 50%), Li(${}^{18}u_{3}SiN=$)₃W(C₆H₄-4-Me) (2-Li-C₆H₄-4-Me, 18%), and Li(${}^{18}u_{3}SiN=$)₃WH (2-Li-H, 32%).

7. $({}^{t}Bu_{3}SiNH)({}^{t}Bu_{3}SiN=)_{2}WI$ (1-1) + $LiC_{6}H_{4}$ -3-Me. A solution consisting of 1-I (403 mg, 4.23 × 10⁻⁴ mol) and $LiC_{6}H_{4}$ -3-Me (65 mg, 6.62 × 10⁻⁴ mol, 1.6 equiv) in Et₂O was stirred at 0 °C for 1 h followed by 3 h at 23 °C. After removal of volatile materials and filtration in hexanes, the solution volume was reduced to 3 mL and cooled to -78 °C, precipitating 130 mg of a light yellow powder, which was collected by filtration. ¹H and ¹³C{¹H} NMR spectroscopy indicated a mixture of (${}^{18}u_{3}SiNH$)(${}^{18}u_{3}SiN=$)₂W($C_{6}H_{4}$ -3-Me) (1- $C_{6}H_{4}$ -3-Me, 51%), Li(${}^{18}u_{3}SiN=$)₃WH (2-Li-H, 31%).

8. $({}^{t}Bu_{3}SiNH)({}^{t}Bu_{3}SiN)_{2}WI$ (1-1) + $KCH_{2}Ph$. A solution of KBn (138 mg, 1.060 × 10⁻³ mol, 2.07 equiv) in 8 mL of THF was slowly added to a stirring solution of 1-I (506 mg, 5.31 × 10⁻⁴ mol) in 20 mL of Et₂O and allowed to react for 10 min, over which time a precipitate (KI) was observed to form. After removal of all volatile materials, 1 H and ${}^{13}C{}^{1}$ H} NMR analysis indicated a mixture consisting of 2-H-K (28%), 1-Bn (40%), and unidentified tungsten-containing products.

9. $({}^{t}Bu_{3}SiNH)({}^{t}Bu_{3}SiN)_{2}WEt$ (1-Et). Ethylene (610 Torr in a calibrated 283.1 mL gas bulb, 9.39 mmol, 16 equiv) was passed through a trap at -78 °C and condensed into a glass reaction vessel containing 1-H (480 mg, 5.80 × 10⁻⁴ mol) and 25 mL of hexanes. The reaction was stirred at 60 °C for 18 h followed by removal of all volatiles. The remaining material was slurried in 4 mL of THF and cooled to -78 °C, and the resulting white powder of 1-Et was collected by filtration (400, 81%). IR (Nujol, cm⁻¹): 3243(w), 3234(w), 1464(s), 1385(s), 1365(s), 1143(s), 1130(s), 1048(s), 1010(s), 934(m), 848(s), 820(s), 620(s), 583(s). Anal. Calcd for C₃₈H₈₇N₃Si₃W: C, 53.43; H, 10.27; N, 4.92. Found: C, 53.17; H, 10.10; N, 5.35.

10. $({}^{B}u_{3}SiNH)({}^{B}u_{3}SiN_{2}W^{n}Pr (1-{}^{n}Pr)$. Propene (560 Torr in a calibrated 283.1 mL gas bulb, 16 equiv) was passed through a trap at -78 °C and condensed into a glass reaction vessel containing 1-H (490 mg, 5.93 × 10⁻⁴ mol) and 30 mL of hexanes. The reaction was stirred at 60 °C for 48 h followed by removal of all volatiles. The remaining material was slurried in 4 mL of THF and cooled to -45 °C, and the resulting white powder was collected by filtration to yield 350 mg of 1- n Pr (68%). IR (Nujol, cm⁻¹): 3239(m), 1469(s), 1386(s), 1364(m), 1185(w), 1158(m), 1133(s), 1050(s), 1009(s), 934(m), 848(s), 820(s), 779(w), 665(w), 621(s), 581(s). Anal. Calcd for C₃₉H₈₉N₃Si₃W: C, 53.95; H, 10.33; N, 4.84. Found: C, 54.09; H, 10.32; N, 4.84.

11. $({}^{t}Bu_{3}SiNH)({}^{t}Bu_{3}SiN)_{2}W$ -E-CH₂CH=CHMe (1-E-CH₂CH= CHMe). To a glass reaction vessel containing 1-H (700 mg, 8.47 × 10⁻⁴ mol) in 15 mL of hexanes was vacuum transferred 2.3 mL of 1,3butadiene (2.77 × 10⁻² mol, 33 equiv). The reaction was stirred at 90 °C for 21 h followed by removal of all volatiles. Analysis of the reaction mixture by ¹H NMR spectroscopy revealed complete conversion to 1-E-CH₂CH=CHMe. The residue was dissolved in toluene, its volume reduced to 4 mL, and the solution cooled to -78 °C to yield 125 mg of white powder (17%). IR (Nujol, cm⁻¹): 3231(m), 1479(s), 1469(s), 1386(s), 1364(m), 1138(s), 1080(w), 1044(s), 1009(s), 965(m), 935(m), 845(s), 820(s), 665(w), 622(s), 580(s). Anal. Calcd for C₄₀H₈₉N₃Si₃W: C, 54.58; H, 10.19; N, 4.77. Found: C, 56.15; H, 10.25; N, 4.62. 12. $({}^{t}Bu_{3}SiNH)({}^{t}Bu_{3}SiN)_{2}WCH=CH^{t}Bu$ (1-CH=CH^tBu). 1-H (0.698 g, 8.45 × 10⁻⁴ mol) and ${}^{t}BuCCH$ (1.1 mL, 8.9 × 10⁻³ mol, 10 equiv) were stirred for 6 d at 105 °C in 20 mL of benzene, over which time the originally colorless solution changed to yellow. A flocculent, white solid was also produced, presumably acetylene oligomers. Following filtration the solvent was replaced with 4 mL of pentane. Cooling to -78 °C and filtering yielded 0.225 g (30%) of yellow 1-CH=CH^tBu. IR (Nujol, cm⁻¹): 3247(m, NH), 1568(w, C=C), 1479(s), 1468(s), 1387(s), 1363(m), 1128(s), 1042(s), 1009(s), 979(w) 934(m), 844(s), 821(s), 620(s), 580(s). Anal. Calcd for C₃₆H₉₃N₃Si₃W: C, 55.54; H, 10.32; N, 4.63. Found: C, 55.64; H, 10.55; N, 4.45.

13. $({}^{6}Bu_{3}SiNH)({}^{6}Bu_{3}SiN)_{2}WN = C(H)C_{6}H_{4}CH_{3}$ (1-N=C(H)tol). 1-H (0.498 g, 6.03 × 10⁻⁴ mol) and *p*-tolunitrile (0.180 g, 1.54 × 10⁻³ mol, 2.5 equiv) were stirred for 24 h at 100 °C in 20 mL of benzene, over which time the originally colorless solution changed to bright orange. Following filtration the solvent was replaced with 4 mL of hexane. Cooling to -78 °C and filtering yielded 0.245 g of orange 1-N=C(H)C_{6}H_{4}CH_{3}. A second crop yielded a further 77 mg for an overall yield of 57%. IR (Nujol, cm⁻¹): 3280(w), 1662(s), 1604(m), 1468(s), 1386(s), 1361(m), 1304(w), 1292(w), 1173(m), 1136(s), 1114(m), 1047(s), 1008(s), 960(w), 935(m), 922(m), 821(s), 753(w), 689(m), 665(s), 619(s), 579(s). Anal. Calcd for C₄₄H₈₉N₄Si₃W: C, 56.08; H, 9.52; N, 5.95. Found: C, 56.39; H, 9.22; N, 5.87.

14. (${}^{6}Bu_{3}SiNH$)(${}^{6}Bu_{3}SiN$)₂WCH=N ${}^{6}Bu$ (1-CH=N ${}^{6}Bu$). To a stirred benzene solution of *tert*-butylisocyanide (0.150 mL, 1.33 × 10⁻⁴ mol, 2.2 equiv) was added a benzene solution of 1-H (0.495 g, 5.99 × 10⁻⁴ mol). The resulting solution was allowed to stir for 1.5 h at 23 °C, and the original colorless solution turned light yellow. After removal of all volatiles and filtration in hexane, the solvent was replaced with 4 mL of THF, cooled to -78 °C, and filtered to yield 0.350 g of yellow 1-CH=N ${}^{t}Bu$ (62%). IR (Nujol, cm⁻¹): 3248(m, NH), 1595(m), 1559(m), 1469(s), 1388(s), 1363(s), 1276(w), 1226(w), 1195(m), 1134(s), 1041(s), 1009(s), 936(s), 895(w), 855(s), 843(s), 821(s), 733(m), 620(s), 581(s). Anal. Calcd for C₄₁H₉₂N₄Si₃W: C, 54.16; H, 10.20; N, 6.16. Found: C, 54.30; H, 10.47; N, 6.08.

15. (${}^{6}Bu_{3}SiNH$)(${}^{6}Bu_{3}SiN$)₂WCN (1-CN). A hexane solution of 1-CH=N^tBu (215 mg, 2.36 × 10⁻⁴ mol) was heated to 100 °C for 3 d. After removal of the volatiles, the remaining material was taken up in 2 mL of hexanes and cooled to -78 °C, which precipitated 97 mg (48%) of yellow, microcrystalline 1-CN, which was collected by filtration. An NMR tube scale reaction verified isobutane as an organic coproduct. IR (Nujol, cm⁻¹): 3241(w), 3228(w), 2146(w), 1475(s), 1387(s), 1366(m), 1125(s), 1038(s), 1008(s), 934(m), 840(s), 819(s), 622(s), 578(s). Anal. Calcd for C₃₇H₈₂N₄Si₃W: C, 52.21; H, 9.71; N, 6.58. Found: C, 51.91; H, 9.53; N, 6.30.

16. $({}^{t}Bu_{3}SiN)_{3}Wpy$ (2-py). A glass reaction vessel was charged with 1-H (2.00 g, 2.42 × 10⁻³ mol) followed by 40 mL of pyridine, the solution was stirred at 145 °C for a total of 36 h, and it was periodically degassed to remove H₂ as it changed from colorless to orange. All volatiles were removed, and the material was triturated with hexanes (10 × 5 mL) to remove excess pyridine. Dissolving the material in 13 mL of hexanes and cooling to -78 °C produced 1.23 g of orange 2py (56%) after collection by filtration. IR (Nujol, cm⁻¹): 1612(s), 1468(s), 1384(s), 1362(m), 1239(w), 1217(w), 1185(w), 1160(m), 1041(s), 1009(s), 934(s), 819(s), 756(s), 690(m), 656(w), 619(s), 580(s). Anal. Calcd for C₄₁H₈₆N₄Si₃W: C, 54.52; H, 9.60; N, 6.20. Found: C, 54.81; H, 9.91; N, 6.14. 2-py-d₅ was analogously obtained.

17. $Li({}^{*}Bu_{3}SiN)_{3}WH$ (2-Li-H). To a vessel loaded with 1-H (1.00 g, 1.21 × 10⁻³ mol) and ^{neo}PeLi (104 mg, 1.33 × 10⁻³ mol, 1.1 equiv) was transferred 25 mL of benzene. The solution was heated at 70 °C for 6 h, followed by removal of the volatiles. The solids were taken up in 20 mL of hexanes and filtered, and the solution volume was reduced to 3 mL. After addition of a small amount of THF, the solution was cooled to -78 °C for 1 h, and 2-Li-H was collected by filtration as a colorless precipitate (0.190 g, 17%). A ¹H NMR spectrum in C₆D₆ indicated 1 equiv of THF per 2-Li-H. An analogous reaction that was worked up in (Me₃Si)₂O yielded THF-free 2-Li-H in 21% yield. IR (Nujol, cm⁻¹): 1907(m), 1467(s), 1388(m), 1151(w), 1035(s), 1007(s), $935(m),\ 820(s),\ 621(s).$ Anal. Calcd for $C_{36}H_{82}N_3LiSi_3W$: C, 51.96; H, 9.93; N, 5.05. Found: C, 51.74; H, 10.04; N, 4.81.

18. Na(^tBu₃SiN)₃WH (2-Na-H). 1-H (510 mg, 6.17×10^{-4} mol) and NaH (165 mg, 6.88×10^{-3} mol, 11 equiv) were loaded into a bomb and stirred in 20 mL of THF for 24 h at 100 °C. After removal of the volatile materials, the residue was triturated with hexanes (3 × 5 mL), taken up in diethyl ether, and filtered. Reducing the solution volume to 3 mL and cooling to -78 °C precipitated 2-NaH, which was collected by filtration to yield 170 mg (28%). ¹H NMR analysis indicates 1 equiv of THF isolated per equiv of 2-Na-H. IR (Nujol, cm⁻¹): 1855(m, br, WH), 1460(s), 1377(s), 1365(s), 1305(w), 1160(m), 1055(s), 1023(s), 1006(s), 935(m), 890(w), 819(s), 722(w), 665(m), 613(s), 583(s). Anal. Calcd for C₃₆H₈₂N₃NaSi₃W: C, 50.98; H, 9.74; N, 4.95. Found: C, 50.62; H, 10.04; N, 4.68.

19. K(^tBu₃SiN)₃WH (2-K-H). a. To a stirred solution of 1-I (700 mg, 7.35×10^{-4} mol) in 20 mL of THF was transferred a KBz solution (240 mg in 4 mL of THF, 1.84×10^{-3} mol, 2.5 equiv) via syringe over the course of 10 min under argon counterflow at 0 °C. The reaction was stirred for 15 min, and a precipitate was observed (KI). After removal of all volatiles, the remaining material was sublimed at 90 °C under active vacuum. Subsequent dissolution in benzene, filtration, and collection in hexanes yielded 405 mg of white 2-K-H (64%). b. NMR tube scale. The preceding experiment was repeated on the NMR tube scale. The quantitative formation of 2-KH as the only tungsten-containing compound was confirmed along with the formation of 1 molar equiv of bibenzyl as organic side product. c. 1-H $(2.00 \text{ g}, 2.42 \times 10^{-3} \text{ mol})$ and KH $(388 \text{ mg}, 9.67 \times 10^{-3} \text{ mol}, 4 \text{ equiv})$ were combined in a flask and stirred in 50 mL of THF for 48 h at 23 °C, over which time the originally colorless solution became light red. After removal of the volatiles in vacuo, the remaining material was triturated with hexanes $(3 \times 5 \text{ mL})$, taken up in diethyl ether, and filtered to remove excess KH. The solvent volume was reduced to 8 mL, and the solution cooled to -78 °C, producing 1.64 g (79%) of colorless, microcrystalline 2-KH, which was collected by filtration as a THF-free white powder after being subjected to vacuum for 24 h. IR (Nujol, cm⁻¹): 1858(m, WH), 1465(s), 1384(s), 1365(m), 1150(w), 1036(s), 1006(s), 935(m), 820(s), 621(s), 579(s). Anal. Calcd for C₃₆H₈₂N₃Si₃KW: C, 50.03; H, 9.56; N, 4.86. Found: C, 50.19; H, 10.03; N. 4.69.

19. $[({}^{6}Bu_{3}SiN)_{3}WH][K(crypt-2.2.2)]$ (2-H-Kc). 2-KH (700 mg, 8.10 × 10⁻⁴ mol) in 15 mL of Et₂O was exposed to crypt-2.2.2 (310 mg, 8.23 × 10⁻⁴ mol, 1.02 equiv) for 1 h at 23 °C. The solution was filtered, reduced to 4 mL, and cooled to -78 °C, producing 0.575 mg of white 2-H-Kc, which was collected by filtration as a white powder. Another crop gave 87 mg for a total yield of 66%. IR (Nujol, cm⁻¹): 1925(m, br, WH), 1466(s), 1382(s), 1360(s), 1354(s), 1298(m), 1261(s), 1238(w), 1174(w), 1134(s), 1106(s), 1060(s), 1011(s), 952(s), 933(s), 818(s), 754(w), 613(s). Anal. Calcd for C₅₄H₁₁₈O₆N₅Si₃KW: C, 52.27; H, 9.59; N, 5.46. Found: C, 52.05; H, 9.25; N, 5.56.

20. $K(^{*}Bu_{3}SiN)_{3}WCH_{3}$ (2-K-Me). a. 1-Me (460 mg, 5.47 × 10⁻⁴ mol) and potassium hydride (45 mg, 1.12 × 10⁻³ mol, 2 equiv) were combined in a flask with 18 mL of THF and heated to 60 °C for 36 h. After removal of the volatiles *in vacuo*, the remaining material was triturated with hexanes (3 × 5 mL), taken up in diethyl ether, and filtered to remove excess KH. The solvent volume was reduced to 3 mL, and the solution cooled to -78 °C, depositing 240 mg (50%) of 2-K-Me, which was collected by filtration as a white powder. IR (Nujol, cm⁻¹): 1479(s), 1384(s), 1183(w), 1162(w), 1039(s), 1007(s), 932(m), 817(s), 617(s), 585(s). Anal. Calcd for C₃₇H₈₄N₃Si₃KW: C, 50.60; H, 9.64; N,4.78. Found: C, 49.88; H, 9.57; N, 4.33. b. K(⁴Bu₃SiN)₃WCD₃ (2-K-CD₃). Utilizing 1-CD₃ (111 mg, 1.32 × 10⁻⁴ mol) and KH (10 mg, 2.49 × 10⁻³ mol, 1.9 equiv), the above procedure produced 41 mg (35%) of 2-KCD₃. IR (Nujol, cm⁻¹): 2213(w), 2203(w), 1456(s), 1365(m), 1157(w), 1047(s), 1034(s), 1015(m), 1006(s), 931(w), 818(s), 614(s).

21. $K(^{t}Bu_{3}SiN)_{3}WCI$ (2-K-CI). 1-Cl (438 mg, 5.09 × 10⁻⁴ mol) and potassium hydride (82 mg, 2.04 × 10⁻³ mol, 4 equiv) were combined in a flask with 15 mL of THF and heated at 60 °C for 24 h as the colorless solution became light yellow. After removal of the volatiles *in vacuo*, the remaining material was triturated with hexanes (3 × 5 mL),

taken up in diethyl ether, and filtered to remove excess KH. The solvent volume was reduced to 5 mL, and the solution cooled to -40 °C, depositing large cubes of yellow 2-KCl. The material was collected by filtration, yielding 245 mg (54%) of 2-K-Cl as a Et₂O-free yellow powder after exposure to vacuum for 12 h. IR (Nujol, cm⁻¹): 1469(s), 1384(s), 1362(m), 1165(w), 1089(m), 1048(s), 1010(s), 936(m), 820(s), 621(s), 584(s). Anal. Calcd for C₃₆H₈₁N₃ClKSi₃W: C, 48.11; H, 9.08; N, 4.68. Found: C, 47.93; H, 9.21; N, 4.39.

22. $K(^*Bu_3SiN)_3WI$ (2-K-I). 1-I (230 mg, 2.42 × 10⁻⁴ mol) and KH (62 mg, 1.55 × 10⁻³ mol, 6 equiv) were loaded into a bomb and stirred in 15 mL of THF for 15 h at 60 °C. The initially yellow solution did not perceptively change color. After removal of the volatile materials, the remaining material was triturated with hexanes three times, taken up in diethyl ether, and filtered, removing the excess KH. Reduction of the solution volume to 2 mL of Et₂O, followed by addition of 2 mL of hexanes, precipitated 2-KI. Cooling to -78 °C and filtering isolated 147 mg (61%) of 2-KI as a yellow powder after 24 h under dynamic vacuum. IR (Nujol, cm⁻¹): 1470(s), 1384(s), 1362(m), 1162(w), 1042(s), 1010(s), 935(m), 820(s), 620(s), 582(s). Anal. Calcd for C₃₆H₈₁N₃Si₃KIW: C, 43.67; H, 8.25; N, 4.24. Found: C, 42.87; H, 8.56; N, 3.91. M_w (benzene cryoscopy): calcd, 990; found, 997(50).

NMR Tube Reactions. General. Flame-dried NMR tubes, sealed to 14/20 ground glass joints, were charged with metal reagent (typically 10 mg, $\sim 1 \times 10^{-5}$ mol) in the drybox and removed to the vacuum line on needle valve adapters. The NMR tube was degassed, and after transfer of deuterated solvent, the volatile reagents were introduced by vacuum transfer via a calibrated gas bulb at -196 °C. The tubes were then sealed with a torch. Solid substrates were loaded with the metal complex followed by solvent transfer on the vacuum line and flame sealing.

23. (${}^{B}U_{3}SiNH$)(${}^{B}U_{3}SiN=$)₂WCl (1-Cl) + PhCH₂K. 1-Cl and 1 equiv of PhCH₂K were loaded into an NMR tube, and THF- d_{8} was condensed in at 77 K. Once warmed, the solution turned from orange (due to dissolved KBz) to light yellow over the course of 1 min. Initial 1 H and ${}^{13}C{}^{1}$ H} NMR spectra indicated the formation of 2-K-Cl and toluene.

24. (${}^{B}Bu_{3}SiNH$)(${}^{C}Bu_{3}SiN=$)₂WCl (1-Cl) + 1 equiv of ${}^{t}BuLi$. 1-Cl and 1.3 equiv of solid ${}^{t}BuLi$ were loaded into an NMR tube and heated to 100 °C for 6 h in C₆D₆. The initial 1 H NMR spectrum (10 min) indicated the presence of only the two reagents. At 40 min the reaction mixture contained unreacted 1-Cl, 2-Li-H (20% total W), 1-H (10%), and a 1:1 mixture of isobutylene and isobutane. At 3 h, the 2-Li-H concentration increased to 40%, and after 6 h the reaction is complete with 60% 2-Li-H, 10% 1-H, and 30% unreacted 1-Cl.

25. $({}^{t}Bu_{3}SiNH)({}^{t}Bu_{3}SiN=)_{2}WCl$ (1-Cl) + 2 equiv of ${}^{t}BuLi$. 1-Cl and 2 equiv of ${}^{t}BuLi$ were heated at 100 °C for 6 h in C₆D₆. After 3 h the 1 H NMR spectrum indicated a solution composition of 80% 2-Li-H, 10% 1-Cl, 10% 1-H, and a 1:1 mixture of isobutylene and isobutane. The final spectrum shows 95% 2-Li-H with 5% 1-H.

26. $({}^{t}Bu_{3}SiNH)({}^{t}Bu_{3}SiN=)_{2}WH$ (1-H) + 1 equiv of ${}^{t}BuLi$. 1-H and 1 equiv of ${}^{t}BuLi$ were heated at 100 °C in C₆D₆ for 6 h, producing 2-LiH and isobutane.

27. (^tBu₃SiNH)(^tBu₃SiN=)₂WCH₂^cPe (1-CH₂^cPe). 1-H and 10 equiv of methylenecyclopentane were heated at 150 °C for 3 days. The ¹H and ¹³C{¹H} spectra revealed loss of 1-H and essentially one new product (~95%), consistent with the formation of 1-CH₂^cPe, but its alkyl resonances were obscured by the excess reagent. Over the course of the reaction, resonances consistent with the formation of 1-methylcyclopentene³⁶ were observed.

28. (${}^{6}Bu_{3}SiNH$)(${}^{6}Bu_{3}SiN=$)₂W-E-CH=CHMe (1-E-CH=CHMe). 1-H and 10 equiv of MeCCH were combined with C₆D₆ and sealed in an NMR tube. Upon warming to 23 °C, a flocculent dark purple solid was immediately produced and assumed to be propyne oligomers. The initial spectrum indicated the presence of both reagents, so the mixture was heated at 70 °C for 6 d. The ¹H and ¹³C{¹H} NMR spectra indicated quantitative formation of 1-CH=CHMe in an E:Z ratio of 8:1. No effort was made to shield this reaction from light.

29. $({}^{t}Bu_{3}SiNH)({}^{t}Bu_{3}SiN=)_{2}WCH=NMe$ (1-CH=NMe). 1-H and 1 equiv of MeNC in C₆D₆ immediately produced a purple solution

upon warming from 77 K. The ¹H NMR spectra indicated quantitative formation of 1-CH==NMe. Over the course of 24 h, the solution bleaches as 1-CH==NMe degrades, and unidentified compounds appear.

30. (^{*k*}Bu₃SiNH)(^{*k*}Bu₃SiN)₂WH (1-H) + py \rightleftharpoons (^{*k*}Bu₃SiN)₃Wpy (2-py) + H₂. 2-py (15 mg, 1.7 × 10⁻⁵ mol) and H₂ (300 Torr at 77 K, ~1.5 × 10⁻⁴ mol, 8.8 equiv) were heated to 141 °C for 7 days in ~0.6 mL of C₆D₆. The headspace of the NMR tube was estimated to be ~2.4 mL. Equilibrium was established after 4 d, and the K_{eq} value was measured by integrating the resonances attributable to 2-py, 1-H, H₂, and py in the ¹H NMR spectrum. A preacquisition delay of 60 s was used due to the prolonged relaxation time of H₂ (*T*₁ = 5.8(6) s). The equilibrium constant was adjusted for differences in H₂ solubility between spectral observation at 296 and 414 K. This required the temperature dependence of the Henry's law constant.⁵⁷

31. (^{*Bu*₃SiN)₃Wpy (2-py) + D_2 (excess). 2-Py (15 mg, 1.7 × 10⁻⁵ mol) and D_2 (435 Torr at 77 K, ~3 atm at 403 K) in C_6D_6 were heated to 180 °C for 2 days. ¹H NMR spectroscopy indicated ~80% deuterium incorporation at the hydride and amide sites of product 1-N(D/H)-D/H, ~80% deuteration of the α -H positions of free pyridine, H₂, and HD. The percent label incorporation was detected at the other pyridine sites.}

32. $({}^{*}Bu_{3}SiNH)({}^{*}Bu_{3}SiN=)_{2}WEt$ (1-Et) + KH (excess). 1-Et and ~5 equiv of KH in THF- d_{8} were heated at 70 °C for 15 h to give a colorless solution. 1 H and ${}^{13}C{}^{1}$ H} NMR spectra indicated quantitative production of K(${}^{*}Bu_{3}SiN$)₃WEt (2-K-Et) and H₂.

33. $({}^{r}Bu_{3}SiNH)({}^{r}Bu_{3}SiN=)_{2}W^{n}Pr$ (1- ${}^{n}Pr$) + *KH* (excess). 1- ${}^{n}Pr$ and ~5 equiv of KH in THF- d_{8} were heated at 70 °C for 15 h, resulting in a colorless solution. ${}^{1}H$ and ${}^{13}C{}^{1}H{}$ NMR spectra indicated quantitative production of K(${}^{t}Bu_{3}SiN)_{3}W^{n}Pr$ (2-K- ${}^{n}Pr$) and H₂.

34. (${}^{6}Bu_{3}SiNH$)(${}^{6}Bu_{3}SiN=$)₂WBr (1-Br) + KH (excess). 1-Br and ~5 equiv of KH in THF- d_{8} were heated at 70 °C for 15 h. ¹H and ${}^{13}C{}^{1}H$ NMR spectra indicated quantitative production of K-(${}^{16}Bu_{3}SiN$)₃WBr (2-K-Br) and H₂.

35. $Li(^{*}Bu_{3}SiN)_{3}WH$ (2–Li-H) + CCl_{4} (excess). 2-Li-H and 1 equiv of CCl₄ in C₆D₆ immediately produced Li(^{*}Bu₃SiN)₃WCl (2-Li-Cl) and HCCl₃ according to an assay by ¹H NMR (C₆D₆: δ 6.13).

36. $Na({}^{t}Bu_{3}SiN)_{3}WH$ (2-Na-H) + ${}^{neo}PeCI$ (excess). 2-Na-H and 7 equiv of ${}^{neo}PeCI$ in $C_{6}D_{6}$ were heated to 150 °C for 36 h. ${}^{1}H$ and ${}^{13}C{}^{1}H$ } NMR spectra indicated quantitative production of Na-(${}^{t}Bu_{3}SiN$)_3WCl (2-Na-Cl) and ${}^{neo}PeH$.

37. $Li(^{t}Bu_{3}SiN)_{3}WH$ (2-Li-H) + CH₃I. 2-Li-H and 1 equiv of CH₃I in C₆D₆ were heated to 60 °C for 24 h. ¹H and ¹³C{¹H} NMR spectra indicated formation of a mixture consisting of 2-Li-I (80%), (^tBu_{3}SiNH)(^tBu_{3}SiN=)_{2}WCH_{3} (1-CH₃, 12%), and (^tBu_{3}SiNH)-(^tBu_{3}SiN)_{2}WI (1-I, 8%).

Kinetics Procedures: 1-H + Excess Pyridine. Solutions of 1-H and an appropriate amount of pyridine were prepared in C₆D₆ in 2 mL volumetric flasks. Bis(trimethylsilyl) ether (~0.5 μ L) was added as an internal integration standard. Three samples of 0.6 mL each were transferred to flame-dried 5 mm NMR tubes joined to 14/20 joints and attached to needle valves. The tubes were subjected to three freeze-pump-thaw degas cycles prior to flame sealing under vacuum. The three NMR tubes were simultaneously submerged in a 141.0 °C polyethylene glycol bath with a Tamson immersion circulator. The temperature was stable to ± 0.3 °C. The rates of disappearance were monitored measuring the integrated intensity of the hydride resonance at selected time intervals. All runs were monitored for 3-4 half-lives to determine the approach-to-equilibrium process; 2-3 half-lives were assessed as being representative of the forward rate process. Rates and uncertainties were obtained from nonlinear, nonweighted least-squares fitting to the exponential form of the rate expression, averaged for the three simultaneous runs.

Single-Crystal X-ray Diffraction Studies. 38. (${}^{t}Bu_{3}$ -SiN=)₃Wpy (2-py). An orange needle of 2-py, obtained by slow evaporation of a saturated hexane solution, was cut to 0.2 × 0.15 × 0.1 mm, mounted, and sealed in a glass capillary for data collection. The data were collected at the Cornell High Energy Synchrotron Source (CHESS). The X-ray wavelength was 0.91000 Å, the crystal to detector distance was set to 42 mm, and a 2048 × 2048 pixel charge-coupled device was used to record the diffraction data. Data were collected as 5 s, 10° rotations, with a total of 360° covered. The first frame was indexed using the program DENZO, ⁸⁸ yielding an orthorhombic crystal system. The data were indexed using DENZO and scaled together with SCALEPACK. ⁸⁸ The structure was solved (SHELXS)⁸⁹ by direct methods and refined by full-matrix least-squares on F^2 using anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were introduced geometrically. A total of 9504 symmetry-independent reflections were collected, and 9123 were greater than $2\sigma(I)$. A semiempirical absorption correction from equivalents was applied, and the refinement utilized $w^{-1} = \sigma^2(F_o^2) + (0.1502p)^2 + 23.7640p$, where $p = (F_o^2 + 2F_c^2)/3$. *39.* (*'Bu*₃*SiN=*)₃*WHK*(*O*Et₂)₃ (*2*-*H*-*K*(*O*Et₂)₃. A colorless crystal

 $(0.4 \times 0.25 \times 0.1 \text{ mm})$ of 2-K-H, obtained by slow evaporation of a saturated diethyl ether solution at -23 °C, was immersed in polyisobutylene, extracted out with a glass fiber, placed on the goniometer head under a 165 K nitrogen stream, and centered on a Siemens SMART CCD area detector system (see Table 2). Preliminary diffraction data revealed a monoclinic crystal system, and a hemisphere routine was used for data collection. The data were processed with the Bruker SAINT program to yield 35 914 reflections, of which 13 553 were symmetry independent ($R_{int} = 0.0486$) and 8560 were greater than $2\sigma(I)$. The data were corrected for absorption with SADABS, and the refinement utilized $w^{-1} = \sigma^2 (F_0^2) + (0.1000p)^2 +$ 0.0000*p*, where $p = (F_p^2 + 2F_c^2)/3$. The structure was solved by direct methods (SHELXS),⁸⁹ completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures (SHELXL).⁸⁹ After an initial refinement with all non-hydrogen atoms treated anisotropically, the difference Fourier map exhibited a maximum with reasonable geometric parameters for a bridging hydride. This atom subsequently underwent successful isotropic refinement.

40. [(^tBu₃SiN=)₃WH][K(crypt-2.2.2)] (2-H-Kc). A colorless crystal $(0.5 \times 0.23 \times 0.25 \text{ mm})$ of 2-H-Kc, obtained by slow evaporation of a saturated diethyl ether solution, was loaded into a glass capillary tube, sealed, and placed on a Siemens SMART CCD area detector system (see Table 2). A hemisphere routine³⁵ was used for data collection. The model includes one-half molecule of diethyl ether per asymmetric unit, located on the center of symmetry. The data were processed with the Bruker SAINT program to yield 21 561 reflections, of which 14 926 were symmetry independent ($R_{\rm int} = 0.0324$) and 8807 were greater than $2\sigma(I)$. The data were corrected for absorption by SADABS, and the refinement utilized $w^{-1} = \sigma^2 (F_0^2) + (0.0668p)^2 +$ 6.0095*p*, where $p = (F_0^2 + 2F_c^2)/3$. The structure was solved by direct methods (SHELXS),⁸⁹ completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures (SHELXL).⁸⁹ After an initial refinement with all non-hydrogen atoms treated anisotropically, the difference Fourier map exhibited a maximum with reasonable geometric parameters for a bridging hydride. This atom subsequently underwent successful isotropic refinement.

41. $K(^{t}Bu_{3}SiN)_{3}WH$ (2-K-H). A colorless crystal (0.6 \times 0.5 \times 0.4 mm) of 2-KH, obtained by slow evaporation of a saturated benzene solution, was loaded in a glass capillary and placed on a Siemens SMART CCD area detector system (see Table 2). The data were subsequently processed with the Bruker SAINT program to yield 13 041 reflections, of which 9148 were symmetry independent (R_{int} = 0.0356) and 7838 were greater than $2\sigma(I)$. The data were corrected for absorption with SADABS, and the refinement utilized $w^{-1} = \sigma^2(F_o^2) + \sigma^2(F_o^2)$ $(0.1034p)^2$ + 5.9010p, where $p = (F_o^2 + 2F_c^2)/3$. The structure was solved by direct methods (SHELXS),⁸⁹ completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures (SHELXL).⁸⁹ After an initial refinement with all nonhydrogen atoms treated anisotropically, the difference Fourier map exhibited a maximum with reasonable geometric parameters for a bridging hydride. This atom subsequently underwent successful isotropic refinement.

42. $K(^{*}Bu_{3}SiN)_{3}WI$ (2-K-I). A light yellow crystal (0.4 × 0.3 × 0.2 mm) of 2-K-I, obtained by slow evaporation of a saturated hexane

solution, was loaded into a glass capillary and placed on a Siemens SMART CCD area detector system (see Table 2). The data were subsequently processed with the Bruker SAINT program to yield 22 565 reflections, of which 17 259 were symmetry independent (R_{int} = 0.0797) and 8486 were greater than $2\sigma(I)$. The structure was solved by direct methods (SHELXS),⁸⁹ completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures (SHELXL).⁸⁹ The refinement utilized $w^{-1} = \sigma^2 (F_0^2) + (0.1000p)^2 +$ 0.0000p, where $p = (F_o^2 + 2F_c^2)/3$. All non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms were included at calculated positions. Constraints were applied to the geometries of the 'Bu₃Si fragments such that chemically equivalent inter- and intra-atomic distances were constrained to equal the same least-squares variables (e.g., all $d(SiC_q)$ are equivalent; all $d(C_qC)$ are equivalent, etc.). In addition to the trimer, a diffusely formed and positionally disordered small molecule was located near the center of symmetry. This was treated and refined as three carbon atoms per asymmetric unit.

ASSOCIATED CONTENT

S Supporting Information

CIF files for 2-py, 2-H-K(OEt_2)₃, 2-H-Kc, 2-K-H, and 2-K-I. This material is available free of charge via the Internet at http://pubs.acs.org.

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Biography



Photo provided by Peter T. Wolczanski.

Peter T. Wolczanski obtained his B.S. in Chemistry at the Massachusetts Institute of Technology in 1976. There he helped Prof. Mark S. Wrighton initiate studies on the photoelectrolysis of H_2O with TiO₂ and SrTiO₃ photoelectrodes. Despite a mediocre GPA, his undergraduate research and some temperance led to matriculation at the California Institute of Technology, where he was a Fluor Fellow in Prof. John E. Bercaw's group. Investigation of zirconium hydrides and the reduction of CO and related molecules ensued, leading to his Ph.D. in 1981, and honors as a McKoy Award winner. After a 2 month postdoctoral stint with Dr. William P. Schaefer at Caltech, designed to permit participation in one last backpacking trip, he became an Assistant Professor at Cornell University.

Professor Wolczanski's research interests have included the synthesis and reactivity of early-transition-metal complexes with small molecules, such as dioxygen, carbon monoxide, carbon dioxide, methane, and hydrocarbons, and the generation of solid state and polymeric inorganic materials from molecular precursors. Studies

continue to emphasize the reactivity of low-coordinate molecules in bond activations, but new interests in metal-metal bonding, the consequences of aggregation, and the influences of electronic states on chemical reactivity have cropped up. He has recently begun to focus on generating strong field environments for first-row transition metals in an effort to induce C-C bond forming processes and broaden their scope as catalysts in a number of transformations.

Professor Wolczanski is an Alfred P. Sloan Fellow, an American Academy of Arts & Sciences Fellow, winner of the 2011 ACS Award in Organometallic Chemistry, and the George W. & Grace L. Todd Professor of Chemistry & Chemical Biology at Cornell. He was the chair of the Organometallics Gordon Research Conference in 2002 and has served on the Organometallics and Inorganic Chemistry advisory boards.

He married Elizabeth A. Wood in June of 1993, and lives with her, their 14.6 year old son Alex, and 12.5 year old daughter Grace in a wooded area, where they fight a never-ending battle against the evil forces of nature (i.e., deer & weeds). Occasionally he escapes to the golf course, thereby inducing further stress in this ulterior quest for perfection. There he also attempts to teach his children while fighting the urge to strangle them as they step in his line while 4-putting most greens. Usually this is followed by an attack on his wine cellar in order to lower his score. In the winter he can often be found in some frigid building rooting on his hockey-playing children or helping coach Grace while attempting to avoid pneumonia.

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