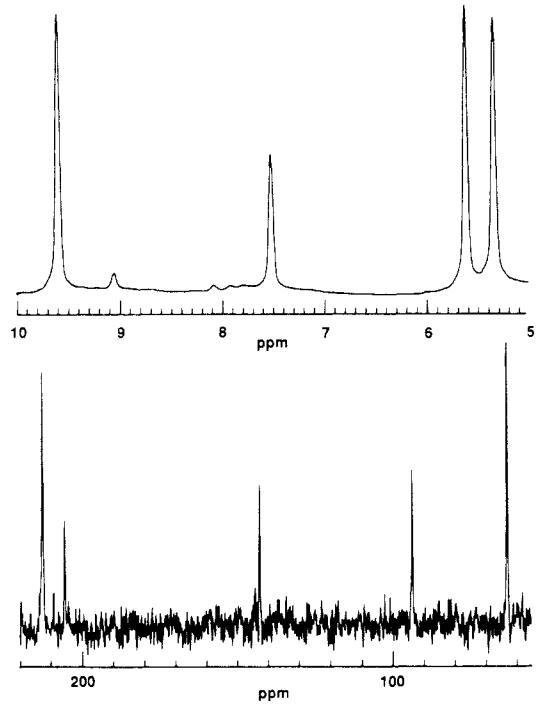

Figure 1. ^1H (upper) and ^{13}C NMR (lower) spectra of the 6-methylenebicyclo[3.1.0]hex-3-en-2-yl cation **3** at −110 °C.

Table I. NMR Spectral Assignments to the 6-Methylenebicyclo[3.1.0]hex-3-en-2-yl Cation (**3**)

	^1H NMR		^{13}C NMR	
position	rel intensity[d]	chem shift, δ[a,b]	mult[e,f]	chem shift, δ[a,c]
A	1.9	9.60	d	212.5
B	1.0	7.52	d	142.5
C	2.1	5.61	d	62.9
D	2.0	5.34	tr	93.4
E			s	205.4

[a] In ppm relative to Me_4Si. [b] Calibrated by setting the central peak of the methyl triplet of anhydrous ethanol to 1.11 ppm at 250 MHz at −110 °C. [c] Calibrated by setting the methyl peak of anhydrous ethanol to 17.2 ppm at 62.9 MHz at −110 °C. [d] Relative to signal from proton B set to unity. Estimated error ±10%. [e] $J_{C\text{-}H}$ could not be determined because of insufficient signal-to-noise ratio in the spectrum. [f] Proton and carbon with a given letter designation shown to be associated by off-resonance decoupling experiments.

Hz, the peak width of B increases from 10.4 to 40.2 Hz, and the peak width of C increases from 8.4 to 31.4 Hz. An Arrhenius plot of the data[7] shows an activation energy of 10.6 ± 0.2 kcal/mol and a value for log A of 14.3 ±0.2 (A in s^{-1}) for the circumambulation.[8] Based on these results, the KUBO program predicts that a rate of $\sim 10^4$ would be necessary to observe the onset of coalescence. Extrapolation from the line-width data yields a temperature of about −45 °C, which is above the temperature where decomposition occurs.

The chemical shifts for the A, B, and C protons of cation **3** match rather closely those of H_2 (δ 9.97), H_3 (δ 7.49), and H_1 (δ 5.27) of cation **1**. The circumambulatory sigmatropic rearrangement of the methylene-substituted cation **3**, however, is much faster than that of **1**: $k_3/k_1 = 2.2 \times 10^7$ at −110 °C. This difference must in some fashion be attributed to the terminal olefin, and it is tempting to speculate that it directly participates in the ring-walk process. For example, the rate enhancement might be associated with the dicyclopropylcarbinyl cationic character of species **7**, which could be an intermediate or transition state in the rearrangement of **3** but has no counterpart in the rearrangement of **1**.

From the fact that decomposition of **3** has a half-life of at least an hour at −70 °C, $\Delta G^{\ddagger}$ for ring-opening **3** → **4** may be estimated as at least 11.5 kcal/mol. It seems likely that this substantial barrier to realization of a highly exothermic reaction is associated with its orbital-symmetry-forbidden character.

Acknowledgment. R.M.J. acknowledges support by a fellowship administered by the American Chemical Society Division of Organic Chemistry and sponsored by the Proctor and Gamble Co. Partial support was also provided by National Science Foundation Grants CHE 8310857 and CHE 8506590.

(7) Peak A was chosen since it is least obscured by other signals in the spectrum and is located in a region free from rolls in the base line.

(8) The KUBO matrix used to represent the ring walk is available from the authors.

Intramolecular 2-Azaallyl Anion Cycloadditions. Application to the Synthesis of Fused Bicyclic Pyrrolidines

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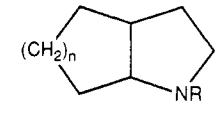
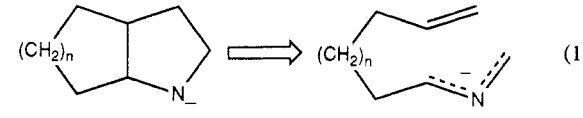
The widespread occurrence of the pyrrolidine ring in nitrogen-containing natural products makes synthetic methods for their assembly a high priority. Commonly, pyrrolidines are found fused to one or more additional rings, as in **1**.[2] In this paper, we report our initial successful investigations into the construction of such systems using the first examples of the intramolecular cycloaddition of 2-azaallyl anions (eq 1).[3]



1



(1)

Although 2-azaallyl anions were first studied by Ingold in 1929,[4] Kauffmann pioneered their cycloadditions in the early 1970's, leading to a review of his work in 1974.[5] Successful cycloaddition was possible with a variety of anionophiles, such as activated olefins, allenes, and acetylenes. Despite the obvious potential,

(1) Recipient of a Dreyfus Foundation Grant for Newly Appointed Faculty in Chemistry, 1984–1989.

(2) For example, mesembrine,[a] lycorine,[b] erysotrine,[c] dendrobine,[d] scandine,[e] and sirodesmin A.[f] (a) For a recent synthesis and leading references, see: Meyers, A. I.; Hanreich, R.; Wanner, K. T. *J. Am. Chem. Soc.* **1985**, *107*, 7776. (b) Fuganti, C. In *The Alkaloids*; Manske, R. F. H., Holmes, H. L., Eds.; Academic Press: New York, 1975; Vol. XV, Chapter 3. (c) Hill, R. K. *Ibid.* **1967**; Vol. IX, Chapter 12. (d) For a recent synthesis, see: Roush, W. R. *J. Am. Chem. Soc.* **1980**, *102*, 1390. (e) Cordell, G. A. *Introduction to the Alkaloids. A Biogenetic Approach*; Wiley: New York, 1981; pp 758–760. (f) Curtis, P. J.; Greatbanks, D.; Hesp, B.; Cameron, A. F.; Freer, A. A. *J. Chem. Soc., Perkin Trans 1* **1977**, 180. For an approach to bicyclic pyrrolidines with the nitrogen at the bridgehead position, see: Pearson, W. H. *Tetrahedron Lett.* **1985**, *26*, 3547.

(3) Intramolecular azomethine ylide cycloadditions have recently been reported, leading to ring systems such as **1**. Our approach should be complementary. See: (a) Wang, C.-L. J.; Ripka, W. C.; Confalone, P. N. *Tetrahedron Lett.* **1984**, *25*, 4613. (c) Confalone, P. N.; Huie, E. M. *J. Am. Chem. Soc.* **1984**, *106*, 7175. (c) DeShong, P.; Kell, D. A.; Sidler, D. R. *J. Org. Chem.* **1985**, *50*, 2309. (d) Smith, R.; Livinghouse, T. *Tetrahdron* **1985**, *41*, 3559. (e) Armstrong, P.; Grigg, R.; Jordan, M. W.; Malone, J. F. *Ibid.* **1985**, *41*, 3547. (f) Wenkert, D.; Ferguson, S. B.; Porter, B.; Qvarnstrom, A.; McPhail, A. T. J. *Org. Chem.* **1985**, *50*, 4114.

(4) Ingold, C. K.; Shoppee, C. W. *J. Chem. Soc.* **1929**, 1199.

(5) Kauffmann, T. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 627.

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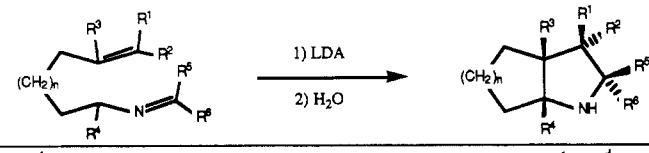
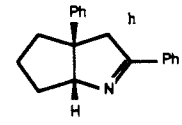
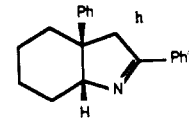
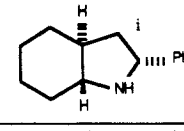
Table I. Synthesis of Bicyclic Pyrrolidines via 2-Azaallyl Anion Cycloadditions[a]

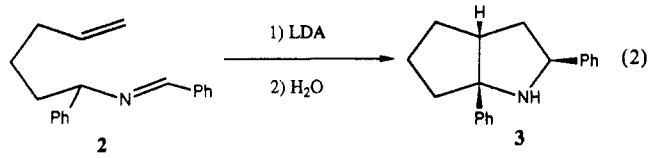


		imines[b]							products[d]						
entry	*n*	R^1	R^2	R^3	R^4	R^5	R^6	conditions[c]	R^1	R^2	R^3	R^4	R^5	R^6	yield, % (ratio)[e]
1	1	H	H	H	H	Ph	Ph	60 °C, 15 h	H	H	H	H	Ph	Ph	48/64[f]
2	1	H	H	H	H	H	Ph	RT, 18 h	H	H	H	H	H	Ph (**8**)	63 (5.1:1)
									H	H	H	H	Ph	H (**9**)	
3	1	H	H	H	H	H	4-OMePh	RT, 16 h	H	H	H	H	H	Ar	48 (9:1)
									H	H	H	H	Ar	H	
4	1	Me	H	H	H	H	Ph[g]	RT, 24 h	H	Me	H	H	H	Ph	40 (1.0:0.9:0.2:0.08)
		H	Me	H	H	H	Ph		H	Me	H	H	Ph	H	
									Me	H	H	H	Ph	H	
									Me	H	H	H	H	Ph	
5	1	H	H	Ph	H	H	Ph	RT, 20 h	H	H	Ph	H	H	Ph	58 (6:1:0.6)
									H	H	Ph	H	Ph	H	
															
6	2	H	H	Ph	H	H	Ph	RT, 16 h	H	H	Ph	H	Ph	H	64 (1.4:1:0.23)
									H	H	Ph	H	H	Ph	
															
7	2	H	H	H	H	H	Ph	RT, 19 h	H	H	H	H	H	Ph	40 (1.0:0.9:0.73)
									H	H	H	H	Ph	H	
															

[a] All new compounds have ^{1}H NMR, IR, and mass spectra and/or combustion analysis consistent with the indicated structure. [b] Preparation of imines: Amine[14] plus appropriate carbonyl compound (PhH, reflux, $-H_2O$). [c] LDA (1.5 equiv in cyclohexane) added to 0.05 M solution of imine in THF at ca. −70 °C, then warmed to indicated temperature. RT = room temperature. [d] Stereochemistry assigned by ^{1}H NMR couplings and difference NOE spectroscopy. [e] Isolated, purified products (silica gel or alumina chromatography). No attempts were made to optimize yields. NMR of crude products indicates actual yields are considerably higher. [f] Based on recovered starting material (75% conversion). [g] Cis:trans = 4:1. [h] Probably formed by LiH elimination.[15] Treatment of the imine produced in entry 5 with $NaBH_4$ gave a ca. 1:1 mixture of the two possible benzylic amines. [i] Appears to be only one isomer, tentatively assigned on the basis of the "W"-form of the anion.

application of this method to the synthesis of natural products has not been reported, primarily due to the limited types of anions that are available by imine deprotonation.[6]

Initially, we wished to examine a simple system wherein a known variety of 2-azaallyl anion (i.e., diaryl substituted) was generated in the presence of an intramolecularly tethered olefin. To this end, a 0.09 M solution of imine **2** in THF was treated with LDA (1.5 equiv) at −70 °C, and the resultant red solution was warmed to 60 °C for 2 h (eq 2). Aqueous workup and SiO_2



(2)

2 **3**

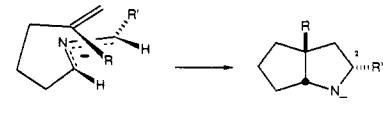
chromatography gave the perhydrocyclopenta[*b*]pyrrole **3** as a single isomer in 77% yield. The success of the intramolecular cyclization is enhanced by the very high stereoselectivity of the process. This example also demonstrates that *unactivated olefins* may be used in 2-azaallyl anion cycloadditions, a process known to be unsuccessful in the intermolecular mode.[5,7] Extension of this methodology to other examples is illustrated in Table I. The reactions generate cis-fused bicyclic pyrrolidines with high stereoselectivity,[8] and appear to be useful for the assembly of sterically congested systems. Despite reports the monoaryl imines have not been previously deprotonated,[5,9] entries 2–7 are successful. In fact, it was observed that lower temperatures were required, in contrast to anions bearing two phenyl groups.

The less stringent conditions required for cyclization of monoaryl-substituted anions (entries 2–7) seem to indicate that these systems cycloadd at a higher rate than diphenylazaallyl anions.

(6) Only anions bearing two or more aryl groups have been successful in cycloadditions, e.g., $PhCH{=}NCH(Li)Ph$. Imines $RCH_2N{=}CHCH_2R'$ will form 1-azaallyl anions rather than the desired 2-azaallyl anions: Hickmott, P. W. *Tetrahedron* **1982**, *38*, 3363. Exceptions: (a) Ahlbrecht, H.; Farnung, W. *Chem. Ber.* **1977**, *110*, 596. (b) Davis, S. E.; Schaffer, L. M.; Shealy, N. L.; Beam, C. F. *Synth. Commun.* **1977**, *7*, 261.

(7) An exception is the single report of the reaction of (1,3-diaryl-2-azaallyl)lithium compounds with ethylene (generated from THF and *n*-butyllithium): Kamata, K.; Terashima, H. *Heterocycles* **1980**, 14, 205.

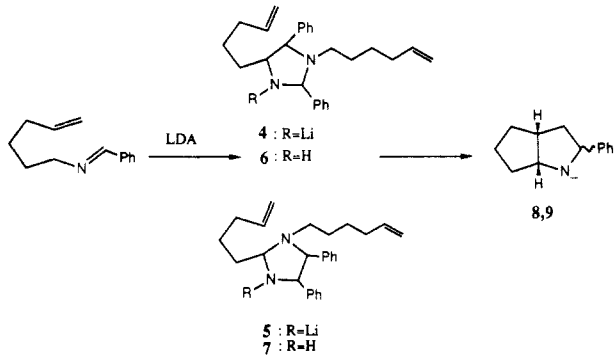
(8) The ring juncture stereochemistry and the often high stereoselectivity at C-2 may be rationalized if one considers the preferred "W"-form of 2-azaallyl anions:



For an excellent study of the geometry of 2-azaallyl anions, see: Young, R. N.; Ahmad, M. A. *J. Chem. Soc., Perkin Trans 2* **1982**, 35. See also ref 5. The example in eq 2 may be explained if the two phenyl rings occupy the "W" positions of the anion and the alkyl group occupies the sickle position.

(9) However, see: Popowski, E. *Z. Chem.* **1975**, *14*, 275. Smith, J. K.; Bergbreiter, D. E.; Newcomb, M. *J. Org. Chem.* **1985**, *50*, 4549.

In order to quantify this trend, kinetics were performed on the cyclization in entry 2. The expected first-order kinetics were not observed; in fact, evidence for an intermediate was obtained. Performing the deprotonation in THF-d_8 allowed observation of the rapid buildup of two new compounds by ^{1}H NMR, which were identified as the lithioimidazolidines **4** and **5**. These were slowly converted to the bicyclic pyrrolidines **8** and **9** after several hours at room temperature. Apparently, initial deprotonation is slow enough to allow intermolecular cycloaddition with the imine portion of a molecule of starting material.[10] In a separate experiment, workup at partial conversion allowed the isolation of the protio derivatives **6** and **7** of undefined stereochemistry. Resubjection of these imidazolidines to the reaction conditions (LDA, THF, room temperature) also gave **8** and **9**. Hence, for



the first time, it has been demonstrated that lithioimidazolidines are subject to anionic cycloreversion to 2-azaallyl anions.[11] Interestingly, this may allow a *new route to 2-azaallyl anions which does not rely on imine deprotonation*,[12] thereby obviating our reliance on one or more aryl groups in the anion.[13]

In summary, the first examples of intramolecular 2-azaallyl anion cycloadditions are reported. High stereoselectivity and a tolerance for olefin substitution makes the method very promising for synthetic endeavors. Our results in the imidazolidine area will be reported shortly, as well as our efforts directed toward natural products synthesis.

Acknowledgment. We are grateful to the Camille and Henry Dreyfus Foundation and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research. We would also like to thank the University of Michigan for a Baer Fellowship awarded to M.A.W.

(10) Cycloaddition of 2-azaallyl anions with imines to give imidazolidines has been previously observed.[5] For more recent examples, see: (a) Vo-Quang, L.; Vo-Quang, Y. *J. Heterocycl. Chem.* **1982**, *19*, 145. (b) Gracheva, R. A.; Potapov, V. M. Sivov, B. A.; Sivova, L. I. *J. Org. Chem. USSR (Engl. Transl.)* **1982**, *17*, 1963.

(11) Although the cycloreversion of lithioimidazolidines to 2-azaallyl anions has not been previously reported, similar anionic cycloreversions are known; see ref 5 and: (a) Bianchi, G.; De Micheli, C.; Gandolfi, R. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 721. (b) Kauffmann, T.; Busch, A.; Habersaat, K.; Scheerer, B. *Tetrahedron Lett.* **1973**, 4047. Imidazolidines have been reported to undergo cycloreversion to azomethine ylides: Amornraksa, K.; Grigg, R. *Tetrahedron Lett.* **1980**, *21*, 2197.

(12) For example, imidazolidines may be synthesized from carbonyl compounds and vicinal diamines. Anionic cycloreversion would then provide 2-azaallyl anions.

(13) Alternatively, oxidative cleavage of benzylic amines to amino acids[a] followed by decarboxylation[b] provides a route to the unsubstituted bicyclic pyrrolidines: (a) Hill, R. K.; Prakash, S. R.; Zydowsky, T. M. *J. Org. Chem.* **1984**, *49*, 1666. Ayres, D. C. *J. Chem. Soc., Perkin Trans. 1* **1978**, 585. (b) Dean, R. T.; Padgett, H. C.; Rapport, H. *J. Am. Chem. Soc.* **1976**, *98*, 7448.

(14) (a) Entries 1-3 use 5-hexenylamine: Cogdell, T. J. *J. Org. Chem.* **1972**, *37*, 2541. (b) Entry 4: from 5-hepten-1-ol (Ohloff, G.; Vial, C.; Naf, F.; Pawlak, M. *Helv. Chim. Acta* **1977**, *60*, 1161) by the sequence TsCl, pyr; NaN_3, Me_2SO; LAH, ether. (c) Entry 5: from 4-benzoylbutyric acid (Aldrich) by the sequence MeOH, HCl; Ph_3PCH_3Br, KO-*t*-Bu, THF; LAH, ether; TsCl, pyr; NaN_3, Me_2SO; LAH, ether. (d) Entry 6: same sequence as (c), except NaCN instead of NaN_3. (e) Entry 7: 6-bromo-1-hexene, NaCN, Me_2SO; LAH, ether.

(15) Lithium hydride elimination has been proposed to explain nonstereospecificity in some 2-azaallyl anion cycloadditions. See ref 10 and: (a) Vo-Quang, L.; Gaessler, H.; Vo-Quang, Y. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 880. (b) Vo-Quang, L.; Vo-Quang, Y.; Pouet, M. J.; Simonnin, M. P. *Tetrahedron* **1981**, *37*, 4343.

A Well-Characterized, Highly Active, Lewis Acid Free Olefin Metathesis Catalyst[1]

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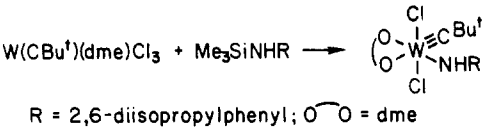
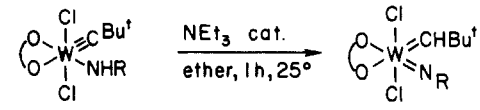
For almost 5 years it has been known that W(VI) alkylidene complexes will metathesize olefins.[2] Osborn has shown that what are likely to be highly electrophilic, cationic alkylidene complexes are formed in the presence of Lewis acids and that several of these systems will metathesize *cis*-2-pentene extremely efficiently.[2c,d] But olefins that contain basic functionalities probably will not be metathesized by catalysts that depend on a Lewis acid cocatalyst for activity. We report here the synthesis and reactivity of the first well-characterized, highly active, neutral olefin metathesis catalyst.

The design of efficient acetylene metathesis catalysts of the type $W(C\text{-}t\text{-}Bu)(OR'')_3$,[3] and the isolation of distorted TBP tungstenacyclobutadiene complexes of the type $W(C_3R'_3)(OR'')_3$,[3] led us to propose that alkylidene complexes of the type $W(CH\text{-}t\text{-}Bu)(NR)(OR'')_2$ would metathesize olefins via TBP tungstenacyclobutane intermediates if R and R'' are chosen carefully. By analogy with $W(C\text{-}t\text{-}Bu)(O\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)_3$[3a] and $W(C\text{-}t\text{-}Bu)[OCMe(CF_3)_2]_3$,[3b] we decided that $W(CH\text{-}t\text{-}Bu)(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)[OCMe(CF_3)_2]_2$ would be a good candidate. It was finally prepared via the sequence of reactions shown in eq 1-3.



(1)

R = 2,6-diisopropylphenyl; O⌒O = dme



(2)

All reactions proceed in high yield and the crystalline products

$$W(CH\text{-}t\text{-}Bu)(NR)(dme)Cl_2 + 2LiOR_F \xrightarrow{\text{ether}} W(CH\text{-}t\text{-}Bu)(NR)(OR_F)_2 \quad (3)$$

$$OR_F = OCMe(CF_3)_2$$

have all been characterized fully.[4a] The crucial reaction shown in eq 2 is based upon earlier work.[5] We assume $W(CH\text{-}t\text{-}Bu)(NR)(OR_F)_2$ to a pseudotetrahedral monomer in which H_α and C_β of the neopentylidene ligand lie in the C_α-W-N plane as a result of the strong donation of the imido ligand's π-electron pair. The alkylidene ligand does seem to be somewhat distorted toward a large $W\text{-}C_\alpha\text{-}C_\beta$ angle, as judged by $\delta(H_\alpha) = 8.87$ and $J_{CH_\alpha} = 110$ Hz,[4b] presumably as a result of the somewhat electrophilic and electronically unsaturated nature of the metal center.[6]

$W(CH\text{-}t\text{-}Bu)(NR)(OR_F)_2$ in pentane reacts rapidly with ethylene (2.4 equiv, 0 °C, 20 min) or with vinyltrimethylsilane

(1) Multiple Metal-Carbon Bonds. 43. For part 42, see: Freudenberger, J. H.; Schrock, R. R. *Organometallics*, in press.

(2) (a) Schrock, R. R.; Rocklage, S. M.; Wengrovius, J.; Rupprecht, G.; Fellmann, J. *J. Mol. Catal.* **1980**, *8*, 73. (b) Wengrovius, J.; Schrock, R. R.; Churchill, M. R.; Missert, J. R.; Youngs, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 4515. (c) Kress, J.; Wesolek, M.; LeNy, J.-P.; Osborn, J. A. *J. Chem. Soc., Chem. Commun.* **1981**, 1039. (d) Kress, J.; Wesolek, M.; Osborn, J. A. *J. Chem. Soc., Chem. Commun.* **1982**, 514.

(3) (a) Churchill, M. R.; Ziller, J. W.; Freudenberger, J. H.; Schrock, R. R. *Organometallics* **1984**, *3*, 1554. (b) Freudenberger, J. H.; Schrock, R. R.; Churchill, M. R.; Rheingold, A. L.; Ziller, J. W. *Organometallics* **1984**, *3*, 1563.

(4) (a) Full preparative, analytical, and spectroscopic details are provided as supplementary material. (b) In $W(CH\text{-}t\text{-}Bu)(NR)(OR_F)_2$ $\delta(C_\alpha) = 253.9$, $J_{CW} = 198$ Hz, $J_{HW} = 13$ Hz.

(5) Rocklage, S. M.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. *Organometallics* **1982**, *1*, 1332.

(6) Schrock, R. R. *Acc. Chem. Res.* **1976**, *12*, 98.

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