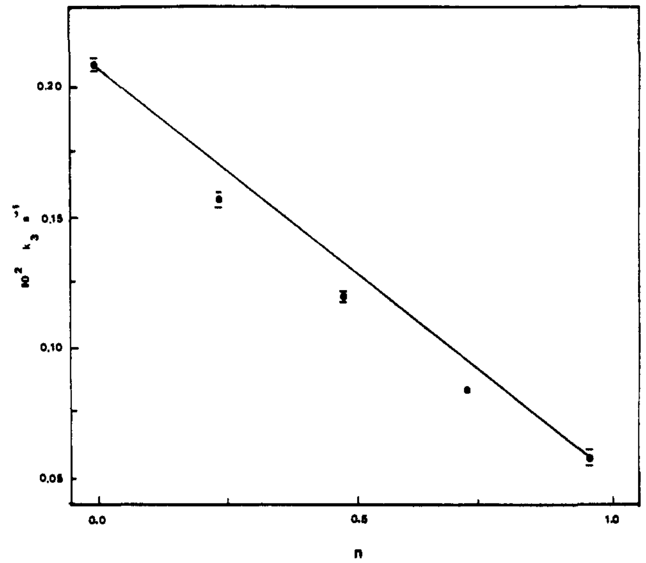

Figure 1. Proton inventory for methyl chymotrypsin catalyzed hydrolysis of *N*-acetyl-L-Tyr-ethyl ester was determined by using the proflavin displacement technique. Kinetic data are deacylation (k_3) rate constants. Rate constants were determined by using the proflavin displacement technique (Bernhard, S. A.; Lee, B. F.; Tashijan, Z. H. *J. Mol. Biol.* **1966**, *18*, 405) in a procedure similar to that of Henderson.[6] Methyl chymotrypsin was purified according to a modified procedure of Matta (personal communication to J. D. S.). Phenylmethylsulfonyl fluoride was added to the methyl enzyme stock solution to destroy any residual activity due to native enzyme. The proflavin displacement technique gave reproducible results with different batches of methyl enzyme. Native α-chymotrypsin was added to the cuvettes, after initial acylation of the methyl enzyme, to rapidly hydrolyze any remaining substrate. This procedure obviates any potential problems with contamination by native enzyme.

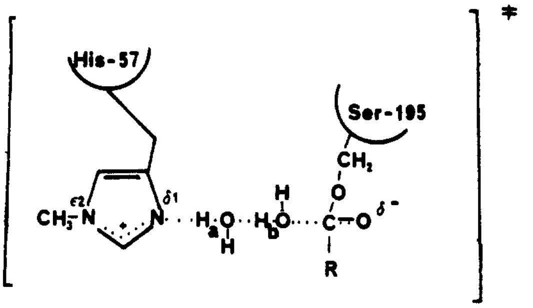

Figure 2. Two-proton mechanism for the methyl chymotrypsin deacylation reaction.

Table I. Methyl Chymotrypsin Catalyzed Hydrolysis of *N*-Acetyl-L-Tyr-ethyl Ester[a]

atom fraction deuterium[b] n	experimental[c] $10^2\ k_3$, s^{-1}	two-proton fit[d] $10^2\ k_3$, s^{-1}	three-proton fit[e] $10^2\ k_3$, s^{-1}
0.000	0.207 ± 0.002	0.207	0.207
0.239	0.155 ± 0.003	0.162	0.162
0.479	0.118 ± 0.002	0.123	0.123
0.718	0.082 ± 0.001	0.089	0.089
0.957	0.056 ± 0.003	0.061	0.061

[a] At pH 7.64 or the equivalent pD, 0.05 M phosphate buffer, 20 μM proflavin, methyl chymotrypsin = 9.24 μM, native chymotrypsin = 0.76 μM, [S] = 4.9 mM, 1.6% v/v CH_3CN. [b] Atom fraction deuterium was determined by the falling drop method by Josef Nemeth. [c] Experimental rate constants are the average of three runs for the deacylation rate. [d] Calculated by using $^nk_3 = 0.00207(1 - n + 0.520n)^2$ based on the Gross–Butler equation.[4] [e] Calculated by using $^nk_3 = 0.00207(1 - n + 0.418n)(1 - n + 0.804n)^2$ based on the Gross-Butler equation.

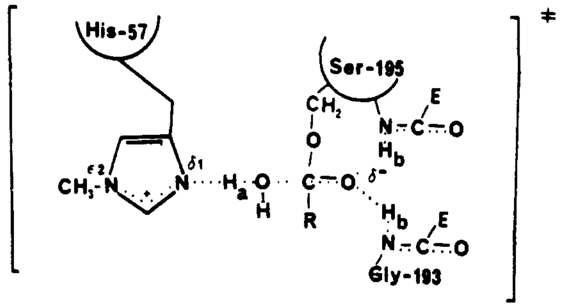

Figure 3. Three-proton mechanism for the methyl chymotrypsin deacylation reaction.

reported the detection of the acyl enzyme intermediate for methyl chymotrypsin with *N*-acetyl-L-Phe-[1-^{13}C]ethyl ester at room temperature.[8] This is additional support for acylation on Ser-195 of the modified enzyme. The results clearly indicate that one need not invoke charge-relay catalysis to explain multiple proton catalysis in the mechanism of action of serine proteases. The most important result of this study may be the observation that one can obtain bowl-shaped proton inventories with a modified charge-relay system. This weakens the arguments that the observation of such proton inventories with native enzyme is strong support for classic charge-relay catalysis. Further proton inventory studies with various substrates and with modified and mutant enzymes will be important, as has been suggested by Schowen.[3]

Acknowledgment. We thank Dr. Michael S. Matta for suggesting the use of trypsin inhibitor agarose to purify methyl chymotrypsin. We thank Dr. Ganesa Gopalakrishnan for helpful discussions concerning this research. This work was supported by NIH grant GM 31960 and, in part, by the Robert A. Welch Foundation through a predoctoral fellowship to J.D.S.

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Spectroscopic and Structural Investigation of the Unbridged Dirhodium Cation $[Rh_2(CH_3CN)_{10}]^{4+}$

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Twenty years ago Maspero and Taube reported the synthesis of the dirhodium aquo species $[Rh_2(H_2O)_{10}]^{4+}$ from a reduction of $[Rh(H_2O)_5Cl]^{2+}$ by $[Cr(H_2O)_6]^{2+}$.[1] Subsequent claims[2] that the $Rh_2(aq)^{4+}$ species could also be prepared by the action of strong acids on solutions of dirhodium tetraacetate remain unsubstantiated,[3] although the reverse reaction of $Rh_2^{4+}(aq)$ with sodium acetate to produce $Rh_2(O_2CCH_3)_4(H_2O)_2$ proceeds in fairly high yield.[1] The dimeric formulation of the aquo cation is based upon solution spectroscopic and magnetic properties as well as by its ion exchange behavior, but attempts to precipitate or crystallize the material have failed to produce a solid form of $[Rh_2(H_2O)_{10}]^{4+}$.[1,4]

Since this early work, numerous binuclear rhodium(II) compounds have been prepared and studied in solution as well as by X-ray crystallography.[5] Among these are the partially solvated cations of general formula $[Rh_2(O_2CR)_2L_6](X)_2$ (L = CH_3CN, py; X = BF_4, PF_6, CF_3SO_3) prepared by treating acetonitrile solutions of $Rh_2(O_2CCH_3)_4$ with strong acids[6] or alkylating

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(1) Maspero, F.; Taube, H. *J. Am. Chem. Soc.* **1968**, *90*, 7361.
(2) (a) Legzdins, P.; Rempel, G. L.; Wilkinson, G. *Chem. Commun.* **1969**, 825. (b) Legzdins, P.; Mitchell, R. W.; Rempel, G. L.; Ruddick, J. D.; Wilkinson, G. *J. Chem. Soc. A.* **1970**, 3322.
(3) Wilson, C. R.; Taube, H. *Inorg. Chem.* **1975**, *14*, 2276.
(4) (a) Wilson, C. R.; Taube, H. *Inorg. Chem.* **1975**, *14*, 405. (b) Ziolkowski, J. J.; Taube, H. *Bull. Acad. Pol. Sci. Ser. Chim.* **1973**, *21*, 113.
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reagents.[7] Several laboratories have reported parallel chemistry for $Mo_2(O_2CCH_3)_4$.[6a-10] Structural determinations of $[M_2(O_2CCH_3)_2(L)_4(L')_2](BF_4)_2$ (M = Rh, Mo, L = L′ = CH_3CN; M = Rh, L = CH_3CN, L′ = py) revealed that the dinuclear cations possess a cisoid arrangement of bridging acetate groups and six molecules of coordinated solvent; two are axially ligated, and four occupy the remaining equatorial positions.[8] The solvent ligands are easily displaced as demonstrated by NMR studies[7] and substitution reactions.[11]

One of our current interests is the preparation of heteronuclear coordination and carbonyl cluster compounds by ion-molecule reactions and by condensation of pairs of activated binuclear metal complexes, especially charged species that may undergo clusterification by cation–anion annihilation. In addition, this chemistry possesses excellent potential for the preparation of new ionic or charge-transfer materials, avenues that we are also investigating. A host of anionic dimers and clusters are known for a variety of metals and ligand sets, but cationic complexes are much less prevalent.[12] During our search for reactive cationic precursors we noted the existence of the aforementioned complexes, in particular the hydrated Rh_2^{4+} species with an unsupported Rh–Rh bond. Since our cluster chemistry is carried out in nonaqueous solvents, we set out to prepare an organic soluble analogue of Rh_2^{4+}(aq). We now report the facile one-step synthesis and crystallization of $[Rh_2(MeCN)_{10}](BF_4)_4$.[13]

Addition of an excess of Et_3OBF_4 to a room temperature acetonitrile solution of $Rh_2(O_2CCH_3)_4$ produces the purple complex $[Rh_2(O_2CCH_3)_2(MeCN)_6](BF_4)_2$ as previously reported.[7] Upon heating the reaction for several days, however, the purple color is gradually replaced by an orange solution, and dark orange-red crystals of $[Rh_2(CH_3CN)_{10}](BF_4)_4$ are deposited on the bottom of the flask. Addition of diethyl ether to the reaction solution produces a pale orange precipitate which may be recrystallized from acetonitrile–diethyl ether: combined yield 85%.[14]

The infrared spectrum of $[Rh_2(CH_3CN)_{10}](BF_4)_4$ revealed the presence of coordinated acetonitrile and the tetrafluoroborate counterion, but no acetate bands were evident, in accord with the assigned formula.[15] A ^1H NMR spectrum of the product in CD_3CN exhibits two singlets at δ +1.96 and +2.64 that we attribute to the resonances of axial and equatorial CH_3CN groups, respectively. The electronic spectral properties of the title compound in acetonitrile solvent are quite different from those exhibited by Rh(II,II) compounds with oxygen donor ligands.[16] The lowest energy transition of $[Rh_2(CH_3CN)_{10}]^{4+}$ occurs at λ_{max} (nm) = 468 ($\epsilon = 5.70 \times 10^2\ M^{-1}\ cm^{-1}$); two additional bands are located at 365 (1.2×10^3) and 277 (2.2×10^4). Electrochemical measurements performed in 0.2 M tetra-*n*-butylammonium hexafluorophosphate–CH_3CN reveal that the redox properties of the new compound are limited to a single irreversible reduction located at $E_{p,c} = -0.05$ V vs Ag/AgCl. The lack of an accessible oxidation in the cyclic voltammogram of $[Rh_2(CH_3CN)_{10}]^{4+}$ is not surprising in view of the high positive charge on the metal centers.

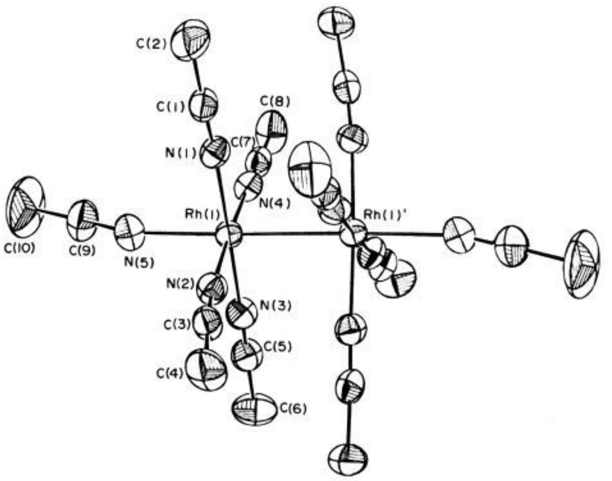

Figure 1. ORTEP drawing of the $[Rh_2(CH_3CN)_{10}]^{4+}$ cation. Some important distances (Å) and angles (deg) are as follows: Rh(1)–Rh(1)′, 2.624 (1); Rh(1)–N(1), 1.986 (4); Rh(1)–N(2), 1.980 (4); Rh(1)–N(3), 1.995 (4); Rh(1)–N(4), 1.985 (4); Rh(1)–N(5), 2.191 (5); N(1)–C(1), 1.131 (5); N(2)–C(3), 1.159 (6); C(1)–C(2), 1.460 (7); C(9)–C(10), 1.437 (10); Rh(1)′–Rh(1)–N(1), 90.2 (1); Rh(1)′–Rh(1)–N(5), 178.1 (1); Rh(1)–N(1)–C(1), 176.2 (4); N(1)–C(1)–C(2), 177.1 (5); Rh(1)–N(5)–C(9), 166.1 (5); N(5)–C(9)–C(10), 178.4 (7).

The identity of $[Rh_2(CH_3CN)_{10}](BF_4)_4$ was confirmed by a crystallographic study following general procedures described elsewhere.[17-19] The molecular cation, depicted in Figure 1, consists of two Rh atoms ligated only by acetonitrile ligands. As the drawing shows, the coordination geometry about each Rh(II) center is pseudooctahedral with a central square plane occupied by four equatorial CH_3CN ligands and two additional vertices defined by an axial CH_3CN group and the other Rh atom. In the absence of constraints engendered by sets of bridging ligands one would expect a singly-bonded binuclear complex to exhibit a structure that minimizes steric repulsions, and, indeed, the cation adopts a twisted conformation in which the two planar Rh(MeCN)$_4$ units are rotated by $\chi_{av} = 44.8[2]°$ from an eclipsed geometry. The idealized molecular symmetry is thus D_{4d}, but the crystallographically imposed symmetry (C_2) is much lower, owing to the considerable deviation from linearity of the axial CH_3CN ligands (Rh(1)–N(5)–C(9) = 166.1 (5)°) and to a lesser degree the equatorial groups (Rh(1)–N(2)–C(3) = 174.4 (4)°). Bonding interactions between Rh and the N-donor atoms fall within expected ranges, with the Rh–N(axial) distance ~0.2 Å longer than the Rh–N(equatorial) distances. Additional important interatomic dimensions are listed in the caption for Figure 1.

A point of considerable interest in the structure of the new compound is the value of 2.624 (1) Å for the Rh–Rh separation. This distance is much shorter than the unsupported Rh–Rh bonds found in $Rh_2(dmg)_4(PPh_3)_2$ (2.936 (2) Å)[20] and $[Rh_2(p\text{-}CH_3C_6H_4NC)_8I_2]^{2+}$ (2.785 (2) Å)[21] but somewhat longer than

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[6] (a) Telser, J.; Drago, R. S. *Inorg. Chem.* **1984**, *23*, 1798. (b) Baranovskii, I. B.; Golubnichaya, M. A.; Dikareva, L. M.; Shchelokov, R. N. *Russ. J. Inorg. Chem.* **1984**, *29*, 872. (c) Baranovskii, I. B.; Golubnichaya, M. A.; Zhilyaev, A. N.; Shchelokov, R. N. *Soviet J. Coord. Chem.* **1988**, 369.

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[13] During the course of our work, a paper appeared in the Soviet literature (ref 6c) which described the preparation of several related complexes from $Rh_2(O_2CCH_3)_4$ and CF_3SO_3H, but no structural data was included.

[14] Anal. Calcd for $C_{20}H_{33}F_{16}N_{10}B_4Rh_2$: C, 24.93; H, 3.13; F, 31.55. Found: C, 25.44; H, 3.58; F, 31.37.

[15] Infrared data (Nujol mull, CsI, cm^{-1}): ν(C≡N), 2342 m, 2317 m, 2300 w; ν(B–F), 1024 vs, 1062 vs; 522 w, 455 w.

[16] (a) Dubicki, L.; Martin, R. L. *Inorg. Chem.* **1970**, *9*, 673. (b) Norman, J. G.; Kolari, H. J. *J. Am. Chem. Soc.* **1978**, *100*, 791. (c) Norman, J. G.; Renzoni, G. E.; Case, D. A. *J. Am. Chem. Soc.* **1979**, *101*, 5256. (d) Martin, D. S.; Webb, T. R.; Robbins, G. A.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 475. (e) Miskowski, V. M.; Schaefer, W. P.; Sadeghi, B.; Santarsiero, B. D.; Gray, H. B. *Inorg. Chem.* **1984**, *23*, 1154. (f) Agaskar, P. A.; Cotton, F. A.; Falvello, L. R.; Han, S. *J. Am. Chem. Soc.* **1986**, *108*, 1214.

[17] (a) Bino, A.; Cotton, F. A.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 3558. (b) Cotton, F. A.; Frenz, B. A.; Deganello, G.; Shaver, A. *J. Organomet. Chem.* **1973**, *50*, 227.

[18] Calculations were done on a VAXSTATION 2000 Computer or a VAX 11/780 computer at the Department of Chemistry, Michigan State University, East Lansing, MI with the VAX-SDP software package.

[19] The complex crystallizes in the monoclinic space group $C2/c$ with $a = 18.123$ (2) Å, $b = 11.920$ (1) Å, $c = 18.243$ (3) Å, $\beta = 99.58$ (1)°, $V = 3886$ (2) Å^3, $Z = 4$, $d_{calcd} = 1.647$ g/cm^3, and $\mu(\text{Mo } K_\alpha) = 9.383$ cm^{-1}. A Nicolet P3/F diffractometer was used to collect 2802 unique data in the range, $4 \le 2\theta \le 47°$ at 23 ± 1 °C; 2395 data with $F_o^2 > 3\sigma(F_o^2)$ were used in refinement. Refinement of 235 parameters gave residuals of $R = 0.052$ and $R_w = 0.080$. The quality-of-fit index is 2.33, and the largest shift/esd = 0.13.

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[21] Olmstead, M. M.; Balch, A. L. *J. Organomet. Chem.* **1978**, *148*, C15.

the values reported for a variety of $Rh_2(bridge)_4L_2$ molecules whose distances fall in the narrow range 2.3–2.5 Å.[5] We believe that $[Rh_2(CH_3CN)_{10}]^{4+}$ with a fully staggered set of small equatorial ligands provides a more reliable measure of a Rh(II) single bond in the absence of constraints or repulsions. The surprisingly short Rh–Rh interactions found in the tetracarboxylato and related molecules are very likely a consequence of the small-bite nature of the ligands.[16b]

Instances of a binuclear solvated cation are rare,[9] yet this example is easily prepared and quite stable in solution and in the solid state. Potential uses of $[Rh_2(CH_3CN)_{10}]^{4+}$ are numerous, for example, as a synthon for new ionic materials or clusters. Moreover, bioinorganic chemists may find it a convenient precursor for dirhodium(II,II) porphyrin and macrocyclic systems. Some of these studies are already underway in our laboratory.

Acknowledgment. I am grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to Michigan State University for an All-University Research Initiation Grant. X-ray equipment was supported by a grant from the National Science Foundation (CHE-8403823).

Supplementary Material Available: Tables of crystallographic parameters, atomic positional parameters and equivalent isotropic displacement parameters, bond distances and angles, and anisotropic thermal parameters (8 pages); a table of observed and calculated structure factors (35 pages). Ordering information is given on any current masthead page.

Modelling the Ammoxidation of Propylene to Acrylonitrile: The Conversion of an Allylimido(2–) Ligand to an Allylideneamido(1–) Ligand

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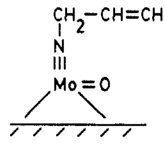
Received July 18, 1988

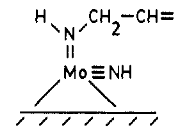
The heterogeneous oxidation of propylene by O_2 in the presence of ammonia to yield acrylonitrile (i.e., the "ammoxidation" of propylene) constitutes the largest volume example of an allylic oxidation process in industrial practice.[1] This process, developed by SOHIO,[2] now accounts for virtually all of the approximately 4 000 000 tons of acrylonitrile produced annually worldwide. The reaction (eq 1) is typically carried out at temperatures of 400–500 °C with a catalyst of the minimal composition $(Bi_2O_3{\cdot}nMoO_3)$; under these conditions, the yield of acrylonitrile is ca. 65%. Similar reactions employing isobutylene, β-methylstyrene, or methylbenzenes in place of propylene are used in the manufacture of methacrylonitrile, cinnamonitrile, benzonitriles, and terephthalonitriles.

$$CH_2{=}CH{-}CH_3 + NH_3 + {}^3\!/_2O_2 \rightarrow CH_2{=}CH{-}C{\equiv}N + 3H_2O \quad (1)$$

As is often the case with heterogeneous processes, many of the intimate details of the mechanism of acrylonitrile formation are not entirely understood; certain aspects of the ammoxidation reaction of propylene have, however, been delineated and are generally well-accepted. The rate-limiting step in the reaction is hydrogen abstraction from propylene to form a symmetric allyl radical.[3-5] Several studies strongly suggest that the sites responsible for this initial allylic hydrogen abstraction are associated with the [Bi–O] components of the catalyst, whereas subsequent C–N bond formation involves the interaction of the allyl fragment with a molybdenum imido (Mo≡NH) site.[6-8] The resulting molybdenum site has been described as featuring either an (allylimido)molybdenum(VI) unit,[9] **A**, or an (allylamido)molybdenum(V) unit,[10,11] **B**. The next step along the path to acrylonitrile has been proposed to involve abstraction of one of the allylic hydrogen atoms, forming a coordinated allylideneamido fragment, with a concomitant two-electron reduction of the molybdenum site. We wish to report the successful modelling of this crucial step in the Grasselli mechanism via the synthesis of an (allylimido)tungsten(VI) complex and its conversion into an (allylideneamido)tungsten(IV) species via allylic hydrogen abstraction.

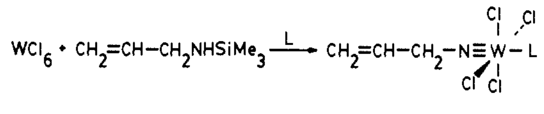


A



B

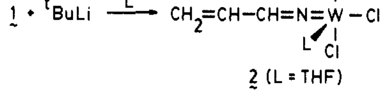
The reaction of allyltrimethylsilylamine with tungsten hexachloride in toluene solution, followed by addition of tetrahydrofuran, yields dark red microcrystals of the (allylimido)tungsten(VI) complex $CH_2{=}CH{-}CH_2{-}N{\equiv}WCl_4(THF)$, **1**, as shown in eq 2.[12] **1** apparently represents the first example of an allylimido complex to be reported. Its depiction in the trans geometry is in accord with the structure established by X-ray crystallography for a related *p*-tolylimido complex, *p*-tolN≡WCl_4(THF).[13] The ^1H NMR spectrum of **1** displays the expected characteristic patterns for both the vinylic portion of the allylimido ligand and for the bound THF ligand. Significantly, the resonance for the α-methylene protons appears as a doublet at 7.57 δ; the corresponding resonance in allylamine occurs at 3.24 δ. The dramatic downfield shift observed for these protons suggests a considerable drift of electron density towards the W(VI) center in **1**.



$$WCl_6 + CH_2{=}CH{-}CH_2NHSiMe_3 \xrightarrow{L} CH_2{=}CH{-}CH_2{-}N{\equiv}WCl_4L \quad (2)$$

1 (L = THF)

When 1 equiv of a *t*-BuLi solution in hexane/THF is slowly added to an ice-cooled benzene solution of **1**, an overall dehydrohalogenation reaction takes place, forming the (allylideneamido)tungsten(IV) complex, $[CH_2{=}CH{-}CH{=}N{=}WCl_3(THF)_2]$ **2**, as shown in eq 3.[14] Other bases (including Et_3N,



$$\mathbf{1} + {}^tBuLi \xrightarrow{L} CH_2{=}CH{-}CH{=}N{=}WCl_3L_2 \quad (3)$$

2 (L = THF)

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(2) Callahan, J. L.; Grasselli, R. K.; Milberger, E. C.; Strecker, H. A. *Ind. Eng. Chem. Prod. Res. Develop.* **1970**, *9*, 134.

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(11) Formation of an (allylimido)molybdenum(V) species by transfer of the amido hydrogen atom to the coordinated NH ligand in **B** is also a possibility, though not explicitly delineated in the Grasselli mechanism.

(12) Anal. Calcd for $C_7H_{13}NOCl_4W$: C, 18.57; H, 2.89; N, 3.09. Found: C, 18.85; H, 2.98; N, 3.16. ^1H NMR (400 MHz, $CDCl_3$, 298 K) δ 7.57 (d, *J* = 5.5 Hz, 2 H, NCH_2), 6.07 (m, 1 H, —CH=), 5.72 (d, *J* = 17.1 Hz, 1 H, =CH_2 trans), 5.60 (d, *J* = 10.3 Hz, 1 H, =CH_2 cis), 4.70 (br, 4 H, —OCH_2CH_2—), 2.15 (br, 4 H, —OCH_2CH_2—); ^{13}C NMR (100.1 MHz, $CDCl_3$, 298 K) δ 129.5 (d, —CH=), 121.7 (t, =CH_2), 73.2 (t, —OCH_2CH_2—), 68.0 (t, NCH_2), 25.7 (t, —OCH_2CH_2—); IR (Nujol, cm^{-1}) 1632, ν(C=C).

(13) Bradley, D. C.; Errington, R. J.; Hursthouse, M. B.; Short, R. L.; Ashcroft, B. R.; Clark, G. R.; Nielson, A. J.; Rickard, C. E. F. *J. Chem. Soc., Dalton Trans.* **1987**, 2067.

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