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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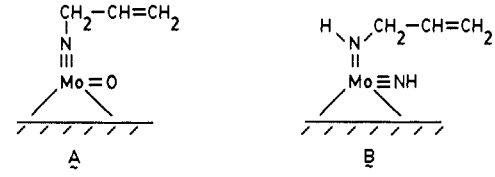
Received July 18, 1988

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

$$CH_2{=}CH{-}CH_3 + NH_3 + \tfrac{3}{2}O_2 \rightarrow CH_2{=}CH{-}C{\equiv}N + 3H_2O \quad (1)$$

°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.

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



A B

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.

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

$$WCl_6 + CH_2{=}CH{-}CH_2NHSiMe_3 \xrightarrow{L} CH_2{=}CH{-}CH_2{-}N{\equiv}W(Cl)_3(L) \quad (2)$$

1 (L = THF)

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**.

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,

$$\mathbf{1} + {}^t\mathrm{BuLi} \xrightarrow{L} CH_2{=}CH{-}CH{=}N{=}W(Cl)_2(L)_2 \quad (3)$$

2 (L = THF)

(1) Grasselli, R. K. In *Heterogeneous Catalysis*; Shapiro, B. L., Ed.; Texas A&M University Press: College Station, TX, 1984; p 182.
(2) Callahan, J. L.; Grasselli, R. K.; Milberger, E. C.; Strecker, H. A. *Ind. Eng. Chem. Prod. Res. Develop.* **1970**, *9*, 134.
(3) (a) Adams, C. R.; Jennings, T. *J. Catal.* **1963**, *2*, 63. (b) Adams, C. R.; Jennings, T. *Ibid.* **1964**, *3*, 549.
(4) Burrington, J. D.; Kartisek, C. T.; Grasselli, R. K. *J. Org. Chem.* **1981**, *46*, 1877.
(5) Martin, W.; Lunsford, J. H. *J. Am. Chem. Soc.* **1981**, *103*, 3728.
(6) (a) Haber, J.; Grzybowska, B. *J. Catal.* **1973**, *28*, 489. (b) Grzybowska, B.; Haber, J.; Janas, J. *Ibid.* **1977**, *49*, 150.
(7) (a) Burlington, J. D.; Grasselli, R. K. *J. Catal.* **1979**, *59*, 79. (b) Burrington, J. D.; Kartisek, C. T.; Grasselli, R. K. *Ibid.* **1983**, *81*, 489.
(8) Chan and Nugent have recently provided evidence for the addition of benzyl radicals to a *tert*-butylimido ligand in a Cr(VI) complex: Chan, D. M.-T.; Nugent, W. A. *Inorg. Chem.* **1985**, *24*, 1422.
(9) Schuit, G. C. A.; Gates, B. C. *CHEMTECH* **1983**, *13*, 693.
(10) Grasselli, R. K.; Burrington, J. D. *Ind. Eng. Chem. Prod. Res. Dev.* **1984**, *23*, 394.
(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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$Ph_3P{=}CH_2$, DBU, and pyridine) also react with **1**, but tractable products have thus far not been isolated from these reactions. A strong band at 1670 cm^{-1} is observed in the IR spectrum of **2** and is assignable as ν(C=N) of the allylideneamido ligand. The salient feature of the ^1H NMR spectrum of **2** is the appearance of a doublet at 4.91 δ for the azomethine proton. The only literature precedent for the formation of an alkylideneamido ligand from an organoimido ligand in a mononuclear complex concerns a group of alkylimido rhenium(V) species of the general formula $RCH_2N{\equiv}ReCl_3(PR'_3)_2$ (R = H, Me, Et);[15] interestingly, the ^1H NMR resonances for the α-methylene protons in these complexes are found to be shifted to high field (between ca. 0.5 and −0.5 δ). The formation of alkylideneamido ligands in this manner cannot be considered a general reaction type: modifying the coordination sphere of the above rhenium complexes by the introduction of dialkyldithiocarbamate ligands renders the alkylimido ligands inert to the abstraction reaction.[16] The dehydrohalogenation reaction of **1** can be reversed by treating benzene solutions of **2** with ethereal anhydrous HCl at room temperature.

In summary, the synthesis of **1** and its conversion to **2** via allylic hydrogen abstraction provide two complexes which feature ligands of presumed relevance to the ammoxidation of propylene and provide support for a crucial step in the proposed mechanism of acrylonitrile synthesis. Work is underway to extend these studies to the further modelling of ammoxidation chemistry.

Acknowledgment. We are grateful to the National Science Foundation (Grant No. CHE-8604359) for support of this research.

(14) ^1H NMR (400 MHz, $CDCl_3$, 298 K) δ 5.81 (m, 1 H, —C*H*=), 4.91 (d, J = 4.9 Hz, 1 H, N=C*H*), 5.49 (d, J = 16.9 Hz, 1 H, =C*H*$_2$ trans), 5.30 (d, J = 9.9 Hz, 1 H, =C*H*$_2$ cis), 3.87 (br, 8 H, —OC*H*$_2$CH$_2$—), 1.92 (br, 8 H, —OCH$_2$C*H*$_2$—); ^{13}C NMR (100.1 MHz, C_6D_6, 298 K) 134.6 (d, N=*C*H), 129.7 (d, —*C*H=), 118.2 (t, =*C*H$_2$), 68.5 (t, —O*C*H$_2$CH$_2$—), 25.1 (t, —OCH$_2$*C*H$_2$—); IR (Nujol, cm^{-1}) 1670, ν(C=N), 1632, ν(C=C).

(15) (a) Chatt, J.; Dosser, R. J.; King, F.; Leigh, G. J. *J. Chem. Soc., Dalton Trans.* **1976**, 2435. (b) Bakir, M.; Fanwick, P. E.; Walton, R. A. *Inorg. Chem.* **1988**, *27*, 2016.

(16) Goeden, G. V.; Haymore, B. L. *Inorg. Chem.* **1983**, *22*, 157.

Synthetic Studies of the Cyclopropyl Iminium Ion Rearrangement. 3. Application of the Cyclopropyl Acyliminium Ion Rearrangement to a Concise and Highly Convergent Synthesis of (±)-Lycorine

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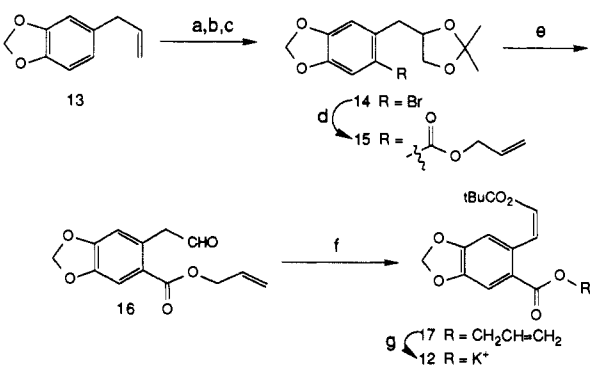
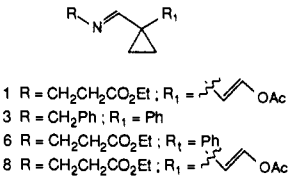
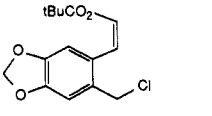
Previous studies of the cyclopropyl iminium ion rearrangement in our laboratores have demonstrated its utility for the synthesis of Δ^2-pyrrolines, particularly acid-sensitive dienamine systems which are unavailable by other methods.[1,2] Such a process would appear to provide an exceptionally concise approach to *Amaryllidaceae* alkaloids of the lycorine class.[2] Employing this approach obviates the lengthy sequences required to manipulate the stereochemistry and oxidation state of the ring C substituents by developing the correct stereochemical relationships and oxidation state directly early in the sequence.[3,4] However, a significant limitation was encountered in the application to cyclopropyl imines such as **1** which bear electronegative α substituents. The markedly reduced nucleophilicity of **1** rendered it unreactive to even highly activated alkyl halides such as **2**, mesylates, and even triflates.[5,6]

Scheme I[a]



[a] Reagents: (a) OsO_4 (catalytic), NMO (1.1 equiv), acetone/H_2O, 23 °C, 15 h; (b) acetone, TsOH (catalytic), 23 °C, 15 h; (c) NBS (1 equiv), DMF, 23 °C, 20 h; (d) *n*BuLi (1.1 equiv), THF, −78 °C, 30 min, then $ClCO_2CH_2CH{=}CH_2$ (1.1 equiv), THF, −78 °C (1 h) → 23 °C (1 h); (e) H_5IO_6 (1.2 equiv), 1 N HCl/THF (1:1), 23 °C, 3.5 h; (f) $((CH_3)_3CCO)_2O$ (1.1 equiv), Et_3N (1.3 equiv), DMF, 23 °C, 15 h; (g) $Pd(C_6H_5)_3P)_4$ (catalytic), $C_5H_{11}C(C_2H_5)CO_2K$, EtOAc/CH_2Cl_2 (1:1), 23 °C, 15 h.





In order to successfully implement our iminium ion approach to lycorine, the low nucleophilicity of imines such as **1** had to be overcome. We anticipated that the required enhanced reactivity could be achieved by generation and rearrangement of the related cyclopropyl acyliminium ions which should result from the reaction of cyclopropyl imines with acid halides. The chemistry of the *N*-acylcyclopropyliminium ions was expected to parallel the chemistry of the *N*-dialkylcyclopropyliminium ions as is observed for their acyclic counterparts.[7] Additionally, advantage could be taken of the greater stability and ease of purification of the resulting *N*-acyl enamides and dienamides relative to enammonium salts however at the expense of requiring an additional operation to effect deblocking and ring closure to the Δ^2-pyrroline.

The feasibility of the desired rearrangement was established by treatment of imine **3** (available via the Staudinger reaction of benzyl azide and 1-phenylcyclopropane carboxaldehyde (**4**)) with acetyl chloride in CH_2Cl_2 or CH_3CN at room temperature

(1) Boeckman, R. K., Jr.; Jackson, P. F.; Sabatucci, J. P. *J. Am. Chem. Soc.* **1985**, *107*, 2191.

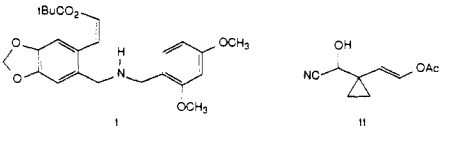
(2) Boeckman, R. K., Jr.; Sabatucci, J. P.; Goldstein, S. W.; Springer, D. M.; Jackson, P. F. *J. Org. Chem.* **1986**, *51*, 3740.

(3) (a) Tsuda, Y.; Sano, T.; Taga, J.; Isobe, K.; Toda, J.; Takagi, S.; Yamaki, M.; Murata, M.; Irie, H.; Tanaka, H. *J. Chem. Soc., Perkin Trans. 1* **1979**, 1358. (b) Sano, T.; Kashiwaba, N.; Toda, J.; Tsuda, Y.; Irie, H. *Heterocycles* **1980**, *14*, 1097. (c) Moller, O.; Steinberg, E.-M.; Torssell, K. *Acta Chem. Scand., Ser. B.* **1978**, *32*, 98. See also ref 2.

(4) (a) For an excellent recent review on the *Amaryllidaceae* alkaloids, see: Martin, S. F. In *The Alkaloids*; Academic Press, In.: 1987; Vol. 30, pp 251-376. (b) For a comprehensive survey of previous synthetic work directed toward the galanthan ring system, lycorine, and lycorine derivatives, see: Martin, S. F.; Tu, C.; Kimura, M.; Simonsen, S. H. *J. Org. Chem.* **1982**, *47*, 3634. (c) Stork, G.; Morgans, D. J. *J. Am. Chem. Soc.* **1979**, *101*, 7110.

(5) A number of α substituents including vinyl and phenyl render the resulting imines (including *N*-alkyl and *N*-benzyl derivatives) unreactive to alkylation. For example, treatment of **1** with benzyl triflate followed by nBu_4NCl resulted in recovery of **1** unchanged.

(6) Efforts to prepare the iminium ion by condensation of i and ii were thwarted by competing intramolecular reactions involving the enol ester.



(7) Speckamp, W. N. *Recueil* **1981**, *100*, 345.

0002-7863/88/1510-8250$01.50/0