Journal of Molecular Catalysis, *43* (1987) 141 - 152

HYDROLYSIS AND REDUCTIVE HYDROLYSIS OF NITRIDOMOLYBDENUM(VI) COMPLEXES: A MODEL REACTION IN THE PURPORTED CATALYTIC CYCLES OF DINITROGEN FIXATION

NORIKAZU UEYAMA, HIROKO FUKASE, HIROAKIZAIMA, SEIICHI KISHIDA and AKIRA NAKAMURA*

Department of Macromolecular Science, Faculty of Science, Osaka University, Toyonaka, Osaka 560 (Japan)

(Received March 10, 1987; accepted July 14, 1987)

Summary

The hydrolysis of the Mo≡N group in nitridomolybdenum(VI) complexes was studied using Raman spectroscopy by tracing the ν(Mo≡N) band at 1027 cm^{-1} for [$MoNCl_3(bpy)$], 1045 cm^{-1} for [$MoNCl_2(PPh_3)_2$], 1042 cm^{-1} for [$MoNCl_3(OPPh_3)_2$] and at 1056 cm^{-1} for [Et_4N][$MoNCl_4$] in the solid state. The coordination of phosphine and phosphine oxide ligands to Mo≡N species facilitates reductive hydrolysis to give ammonia in 11 - 13% yield under mild conditions. The Mo≡N group of [Et_4N][$MoNCl_4$] is also reactive, but only a trace of ammonia was formed under the mild conditions. [$MoNCl_3(bpy)$] is photolabile and inert to the hydrolysis. The Raman study of the Mo≡N vibration and the determination of ammonia indicate an increased formation of ammonia by basic hydrolysis, but suggest the formation of an undefined nitride species with acidic or reductive hydrolysis.

Introduction

The nitridomolybdenum species has been considered to be one of the key intermediates in biological nitrogen fixation [1]. Reductive hydrolysis of the nitridomolybdenum intermediate to ammonia and a low-valent molybdenum species is assumed to be a crucial step for a catalytic nitrogen fixing cycle. Chatt *et al.* have found that protolytic decomposition of dinitrogen phosphine complexes of Mo and W proceeds through the nitridometal species [2]. Simple nitridomolybdenum complexes *e.g.* [$MoNCl_4$]$^{1-}$ have been synthesized and some of their coordination chemistry has been investigated [3 - 5]. As to the reactions, Chatt and Dilworth reported almost

---

*Author to whom correspondence should be addressed.

0304-5102/87/$3.50

quantitative yields of ammonia by the protolysis of $[MoNCl_2(PPh_3)_2]$ or $[MoNCl_3(OPPh_3)_2]$ [6]. Dehnicke and Strahle also reported on ammonia formation from other nitridomolybdenum complexes [7]. It is important to further investigate the reactivity of the Mo≡N groups under various conditions, especially under mild reductive conditions because the Mo=N species has been considered to be one of the key intermediates in the nitrogen fixation cycle.

Our current effort in the chemistry of nitrogen fixation is focused on the reactivity of nitridomolybdenum complexes ligated with various thiolato ligands, since the sulfur-coordinating atom is important in the active site of nitrogenase. Our preliminary results indicated formation of only a small amount of ammonia by hydrolysis of a simple nitrido complex, $[Et_4N][MoNCl_4]$, compared to the reactivity of polymer-bound nitridomolybdenum(VI) complexes [8]. The fate of the nitrido ligand in reductive or hydrolytic reactions has been investigated by analysis for ammonia, hydrazine or dinitrogen, and also for the solid product containing molybdenum. The presence of Mo≡N or Mo=NH species in the product is thus important. These species are stable in hydrolytic conditions, but their detection remains difficult. For example, there has been no suitable method to detect nitridomolybdenum species in the reaction mixture, because of the confused assignments of the ν(Mo≡N) frequency in the IR bands [3, 4]. For this purpose, Raman spectroscopy is uniquely satisfactory for the detection of Mo≡N groups. Raman Mo≡N stretching bands have been reported in the cases of $[MoNCl_3]$ (at 1023 and 1020 cm^{-1}) and $[MoNCl_5]^{2-}$ (at 1027 cm^{-1}) by Kolitsch and Dehnicke [9]. The assignment could be confirmed by investigation on a variety of nitridomolybdenum complexes now known.

In this paper, we present the Raman spectra of a series of Mo≡N species upon hydrolysis of nitridomolybdenum(VI) complexes by a reductive, acidic or basic reagent. A possible correlation of the ν(Mo≡N) frequencies with their reactivities toward hydrolysis is sought. The yields of ammonia from the nitrido complexes were found to vary depending on the hydrolysis conditions and on the ligand environment, which requires a systematic study.

Experimental section

All solvents were dried over sodium or calcium hydride and were purified by distillation under argon. All operations for syntheses of molybdenum complexes were carried out under argon.

Materials

Bipyridyl (bpy) and sodium azide used were of commercial grade. $[MoCl_4(MeCN)_2]$ was prepared by the literature method [10]. $[(n\text{-}Bu)_4N][BH_4]$ was also prepared by the procedure described in the literature [11].

Tetrachlorobis(tetrahydrofuran)molybdenum(IV), [$MoCl_4(thf)_2$]

The method reported by Allen *et al.* was used [11]. THF (10 ml) was added to [$MoCl_4(MeCN)_2$] (2.6 g, 8.1 mmol) and the mixture was stirred for 2 h to give a yellow suspension of [$MoCl_4(thf)_2$]. The complex was collected with filtration, washed with THF, and dried *in vacuo*. The product was a microcrystalline orange-yellow powder (2.3 g, 75% yield). Anal. Calcd for $C_8H_{16}O_2Cl_4Mo$: C, 25.16; H, 4.22%. Found: C, 25.42; H, 4.18%. IR (nujol): 820 cm^{-1} due to the characteristic band of coordinated THF.

Trichloro(nitrido)(bipyridyl)molybdenum(VI), [$MoNCl_3(bpy)$]

The method reported by Seyferth and Taube [4] was applied. NaN_3 (0.56 g, 8.58 mmol) was added to a stirred suspension of [$MoCl_4(MeCN)_2$] (2.63 g, 8.23 mmol) in MeCN (60 ml). Dinitrogen was evolved rapidly to give a clear orange-red solution. The resulting NaCl was removed by filtration. The addition of bpy (1.35 g, 8.64 mmol) in MeCN (15 ml), to the filtrate resulted in the precipitation of the product as a brown powder. The complex was filtered off, washed with CH_2Cl_2 and n-hexane, and dried *in vacuo* (1.96 g, 90% yield). Anal. Calcd for $C_{10}H_8N_3Cl_3Mo$: C, 32.25; H, 2.16; N, 11.28; Mo, 25.76%. Found: C, 27.38; H, 1.90; N, 10.14; Mo, 24.0%. IR (nujol): $\nu(Mo{\equiv}N)$, 1023 cm^{-1}. Raman (632.8 nm excitation): $\nu(Mo{\equiv}N)$, 1027 cm^{-1}. ^1H NMR (CD_3CN): 7.90, 8.20, 9.48 ppm (m, bpy). λ_{max} (THF): 350 nm (ϵ: 2000).

Tetraethylammonium tetrachloro(nitrido)molybdenum(VI), [Et_4N][$MoNCl_4$]

Me_3SiN_3 (0.53 g, 4.60 mmol) was added to a stirred suspension of [$MoCl_4(thf)_2$] (1.70 g, 4.45 mmol) in CH_2Cl_2 (40 ml). Addition of Et_4NCl (0.74 g, 4.47 mmol) to the resulting clear red solution caused the product to crystallize as orange-red needles. The complex was filtered off, washed with THF and n-hexane, and recrystallized from CH_2Cl_2/THF/n-hexane (1.27 g, 75.1% yield). Anal. Calcd for $C_8H_{20}N_2Cl_4Mo$: C, 25.15; H, 5.28; N, 7.33%. Found: C, 25.85; H, 5.65; N, 7.33%. IR (nujol): $\nu(Mo{\equiv}N)$, 1056 cm^{-1}. Raman (632.8 nm excitation): $\nu(Mo{\equiv}N)$, 1055 cm^{-1}. λ_{max} (THF): 310 nm (ϵ: 1400), 370 nm (ϵ: 2600), 445 nm (ϵ: 250).

Trichloro(nitrido)bis(triphenylphosphine oxido)molybdenum(VI), [$MoNCl_3(OPPh_3)_2$]

The method reported by Chatt and Dilworth [3] was used for the preparation of this complex. Addition of $OPPh_3$ (1.84 g, 6.61 mmol) to a benzene solution (30 ml) of [$MoNCl_3(thf)_x$] (3.26 mmol) caused the product to crystallize as pale-yellow plates. The complex was collected by filtration, washed with n-hexane, and dried *in vacuo* (1.96 g, 78.0% yield). Anal. Calcd for $C_{36}H_{30}NCl_3O_2P_2Mo$: C, 55.95; H, 3.91; N, 1.81%. Found: C, 56.19; H, 4.35; N, 1.68. IR (nujol): $\nu(Mo{\equiv}N)$, 1042 cm^{-1}. Raman (632.8 nm excitation): $\nu(Mo{\equiv}N)$, 1042 cm^{-1}.

Dichloro(nitrido)bis(triphenylphosphine)molybdenum(V), [MoNCl$_2$(PPh$_3$)$_2$]

This complex was prepared by the method reported by Chatt and Dilworth [3]. Me_3SiN_3 (0.36 g, 3.12 mmol) was added to a stirred suspension of $[MoCl_4(thf)_2]$ (1.25 g, 3.27 mmol) in CH_2Cl_2 (40 ml). Three equivs of PPh_3 (2.60 g, 0.91 mmol) were added to the resulting orange-red solution. The product slowly crystallized from the solution as a bright yellow-green solid. The complex was filtered off, washed with n-hexane, and dried *in vacuo* (1.17 g, 51% yield). Anal. Calcd for $C_{36}H_{30}NCl_2P_2Mo$: C, 61.30; H, 4.29; N, 1.99%. Found: C, 59.76; H, 4.26; N, 1.97%. IR (nujol): $\nu(Mo{\equiv}N)$, 1049 cm^{-1}. Raman (632.8 nm excitation); $\nu(Mo{\equiv}N)$, 1045 cm^{-1}.

Formation of ammonia from the nitridomolybdenum complexes

To a stirred solution (4 ml) of nitridomolybdenum complexes (5×10^{-2} mmol), 5 - 20 equivs of reagents ($NaBH_4$, $[(n\text{-}Bu)_4N][BH_4]$, HCl, H_2SO_4, etc.) was added at 30 °C and stirred for 2 h. The solvents and ammonia were distilled under reduced pressure into a reservoir cooled by liquid nitrogen. The residue was dried *in vacuo* and was sealed for the measurement of Raman spectra. The amount of ammonia was determined by the colorimetric method [12].

The detection of ammonia and dinitrogen by mass spectroscopy was carried out by gas insertion into the ion source of a Jeol OlSG double focusing mass spectrometer coupled to a JMA-2000 computer. The nitridomolybdenum(VI) complexes were hydrolyzed by a HCl–THF solution at 0 °C. Dinitrogen generated from NH_4Cl and NaBrO in aqueous solution was used as reference.

Physical measurements

IR spectra were recorded on a Jasco model DS-405G by a Nujol method under argon atmosphere. Raman spectra were taken on a Jasco R-800 spectrometer in conjunction with a NEC Ar^+ laser with photon-counting systems. Laser power at the sample was maintained below 50 mW to minimize sample deterioration. The weak signals were enhanced by a signal-to-noise time averaging method.

Results and discussion

Detection of Mo≡N group by Raman spectroscopy

Before any discussion on nitridomolybdenum(VI) complexes, the purity of $[MoNCl_3(bpy)]$ prepared from $[MoCl_4(thf)_2]$ and sodium azide must be discussed because of the possible contamination by azide-containing complexes, $[MoN(N_3)_xCl_{3-x}(bpy)]$. Figure 1-c shows a typical Raman spectrum of pure $[MoNCl_3(bpy)]$ as a solid. A strong band due to $\nu(Mo{\equiv}N)$ was observed at 1027 cm^{-1}. The Raman spectra of a contaminated product are shown in Fig. 1-d. Two broad Raman Mo≡N bands for $[MoN(N_3)_xCl_{3-x}(bpy)]$ were observed in the range 980 - 1030 cm^{-1}, and an IR band was

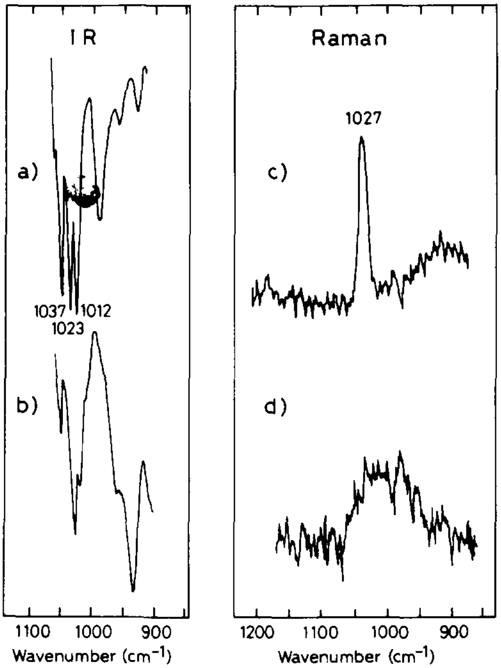


Fig. 1. IR and Raman spectra of (a and c) $MoNCl_3(bpy)$ (brown-ochre) and (b and d) $MoNCl_{3-x}(N_3)_x(bpy)$ (dull purple).

observed at 972 cm^{-1} (Fig. 1-b). The broad Mo≡N bands indicate the contamination by many kinds of azidonitridomolybdenum(VI) complexes. Actually, Schweda and Strahle reported an IR band at 972 cm^{-1} for $[MoN(N_3)_3(bpy)]$, but no Raman data are available [13].

Although two Raman bands assignable for bipyridyl (bpy) ligand were observed at 990 and 1050 cm^{-1} in many bpy complexes, the bpy ligand of $[MoNCl_3(bpy)]$ did not exhibit any strong resonance Raman band of the ligand around 1000 - 1050 cm^{-1} with a weak excitation line of 5145 Å. The IR spectrum of $[MoNCl_3(bpy)]$ has been discussed previously for its Mo≡N stretching vibration [3, 4], but without any definite assignment. Seyferth *et al.* could not assign the band, but suggested one of the bands at 1010, 1020 and 1035 cm^{-1} to be Mo≡N stretching. Chatt *et al.* assigned the IR ν(Mo≡N) at 1009 cm^{-1} by ^{15}N-isotopic substitution. Therefore, the Raman band at 1027 cm^{-1} of $[MoNCl_3(bpy)]$ corresponds to its IR band at 1009 cm^{-1}.

Since the Raman band due to the Mo≡N group of $[MoNCl_3(bpy)]$ was found to be photosensitive, the spectrum was refined by the signal-to-noise time averaging method using weak power (20 mW) at the 488.0 nm or 514.5 nm excitation line. When irradiated with strong power (150 mW) at these excitation lines, a new band was observed at 1030 cm^{-1} with a continuous decrease in the band intensity at 1027 cm^{-1}. Although the structure of the species generated by the photoreaction is unknown at present, it can

TABLE 1

The Raman and IR bands assignable to ν(Mo≡N) in nitridomolybdenum(VI) complexes in the solid state

Complex	Raman (cm^{-1})	IR (cm^{-1})	
		This work	L[illegible]
$MoNCl_3(bpy)$	1027	1023	1009 [1]
$MoNCl_3(OPPh_3)_2$	1042	1038	1038 [1]
$MoNCl_2(PPh_3)_2$	1045	1049	1049 [1]
$[Me_4N][MoNCl_4]$	1050	1058	1054 [5]
$[Et_4N][MoNCl_4]$	1056	1055	
$[(n\text{-}Bu)_4N][MoNCl_4]$	1065	1063	1065 [4]

be speculated by the Raman results that the complex possesses a Mo≡N group with one or two Mo—Cl groups.

Table 1 lists the Raman bands and the IR band for some other typical nitridomolybdenum(VI) complexes; $[MoNCl_2(PPh_3)_2]$, $[MoNCl_3(OPPh_3)_2]$ and $[Et_4N][MoNCl_4]$ exhibited the Raman bands due to ν(Mo≡N) at 1045, 1042 and 1056 cm^{-1}, respectively. These Raman bands correspond to the IR bands of ν(Mo≡N) reported in the literature [1, 4, 7]. The ν(Mo≡N) bands of these nitridomolybdenum(VI) complexes did not change in intensity even with strong power (200 mW) at the 488.0 nm excitation line. The inertness to laser light is remarkable, and different from that of $[MoNCl_3(bpy)]$. The presence of the bpy ligand thus causes photochemical changes through photon absorption at the heterocyclic rings. The higher frequency (1042 - 1065 cm^{-1}) suggests a stronger bond character of the Mo≡N group in these non-bpy complexes. Actually, Campochiaro *et al.* reported the higher ν(Mn≡N) frequency in nitridomanganese(V) porphyrinato complexes compared to that of Cr≡N in the related nitridochromium(V) complex [14]. Donovan-Mtunzi *et al.* have shown the ^{15}N chemical shifts of $[Mo(^{15}N)(S_2NEt_2)_3]$ and $[MoX(^{15}N)(dppe)_2]$ (X = Cl, Br; dppe = 1,2-bis(diphenylphosphino)ethane) [15]. Such data for the ^{15}N chemical shifts may be also helpful for interpretation of the various Mo≡N bond characters.

Formation of ammonia by reductive hydrolysis and protolytic decomposition

Nitridomolybdenum(VI) complexes had been considered to be very susceptible to hydrolysis and air oxidation. Chatt *et al.* reported quantitative formation of ammonia from $[MoNCl_2(OPPh_3)_2]$ by acid hydrolysis. However, our attempts at the hydrolysis of $[MoNCl_4]^{1-}$ gave only a small yield of ammonia. The conflict led us to investigate the hydrolysis with other nitrido complexes. The study on the reductive hydrolysis of these complexes seems to be important for the completion of a smooth catalytic cycle of nitrogen fixation.

The reductive hydrolysis by $[(n\text{-}Bu)_4N][BH_4]$ of an ethanol solution of $[MoNCl_3(bpy)]$ gave only 1.2% of ammonia, and some forms of nitrido-

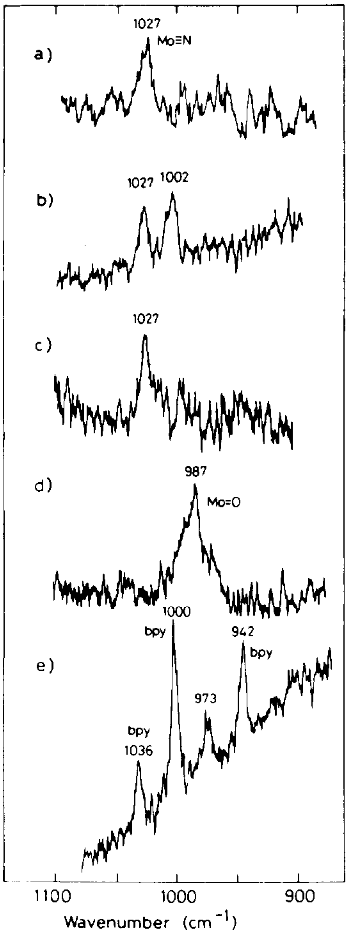


Fig. 2. Raman spectra of (a) $MoNCl_3$(bpy), (b) $MoNCl_3$(bpy) reduced by $[BH_4]^-$, (c) $MoNCl_3$(bpy) reduced by $[BH_4]^-$ in EtOH, (d) solid materials obtained from soluble part of $MoNCl_3$(bpy) solution treated with HCl, and (e) insoluble part of the solution after treatment with HCl.

molybdenum species still remained as unhydrolyzed residues. The Raman spectrum of the residue after removal of the solvents still exhibited the $Mo{\equiv}N$ band at 1027 cm^{-1}, as shown in Fig. 2. A new band at 1002 cm^{-1} due to $\nu(Mo{\equiv}N)$ was observed on the reduction of the [$MoNCl_3$(bpy)] by $[(n\text{-}Bu)_4N][BH_4]$ in THF. The new band, which is probably due to a reduced $Mo{\equiv}N$ species or a ligand-exchanged $Mo{\equiv}N$ species by $[BH_4]^-$ (Fig. 2-b and c), disappeared with addition of ethanol.

Figure 2-d shows the Raman spectrum of the species obtained by evaporation of a THF solution extracted from the strongly acidic hydrolysis product of [$MoNCl_3$(bpy)] (with conc. HCl). In this case, a Raman band at 982 cm^{-1} is assignable to $\nu(Mo{=}O)$, since the corresponding IR band was observed at 972 cm^{-1}. The THF-insoluble part gave the Raman spectrum

TABLE 2

Amount of ammonia from nitridomolybdenum(VI) complexes by reductive hydrolyses with $[BH_4]^-$ or $[BH_4]^-$/EtOH and by protolytic decomposition with hydrochloric acid or NaOH/EtOH system

Complex	Yields of ammonia (%)[a]			
	$[BH_4]^-$[b]	$[BH_4]^-$/EtOH[c]	HCl[d]	NaOH/EtOH[e]
$MoNCl_3(bpy)$	0.0	1.2	9.8	31.4
$MoNCl_3(OPPh_3)_2$	0.3	6.8	13.7	26.3
$MoNCl_2(PPh_3)_2$	0.0	0.002	11.2	37.3
$[Et_4][MoNCl_4]$	0.0	10.2	0.8	51.2

Conditions: reaction time (2 h) at 30 °C; [Mo(VI)] = 5×10^{-2} mmol.

[a] The yields were estimated on the basis of Mo(VI) content.

[b] $[(n\text{-}Bu)_4N][BH_4]/[Mo(VI)]$ = 5 (mol/mol) in 4 ml THF.

[c] $[(n\text{-}Bu)_4N][BH_4]/[Mo(VI)]$ = 5 (mol/mol) in THF/ethanol (3 ml/1 ml).

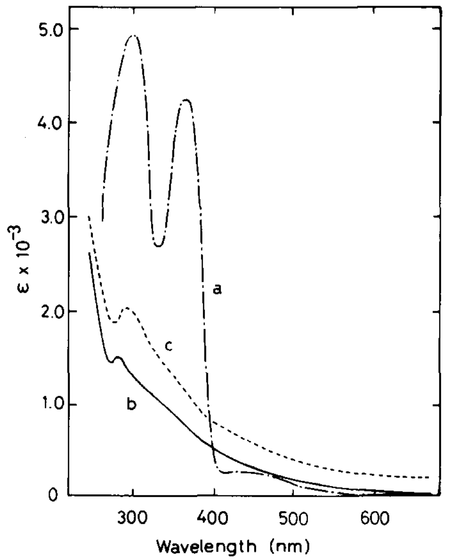
[d] HCl/[Mo(VI)] = 10 (mol/mol) in 4 ml THF.

[e] NaOH/[Mo(VI)] = 10 (mol/mol) in THF/ethanol (3 ml/1 ml).

shown in Fig. 2-e. Three sharp peaks at 1036, 1000 and 942 cm^{-1} are due to the characteristic bands of bipyridyl hydrochloride salt. The Raman bands of ν(Mo=O) were reported to be observed at 950 cm^{-1} for $Na_2[Mo_2O_2(\mu\text{-}O)_2(cys)_2]\cdot 5H_2O$ or $Na_2[Mo_2O_2(\mu\text{-}O)_2(his)_2]$ [16]. The observation of a ν(Mo=O) IR band at 1008 cm^{-1} has been reported for $[MoOCl_4]^-$ [17]. Presence of electronegative chloro ligands causes an increase in the Mo=O stretching vibration.

Our results indicated that the Mo≡N group of $[MoNCl_3(bpy)]$ was much less susceptible to reductive hydrolysis than those of the other nitridomolybdenum complexes mentioned later. Table 2 lists the yields of ammonia from various nitridomolybdenum complexes by reductive hydrolysis with $[(n\text{-}Bu)_4N][BH_4]$ or $[(n\text{-}Bu)_4N][BH_4]$/EtOH and protolytic decomposition with hydrochloric acid or sodium hydroxide/EtOH. In the case of the reductive and protolytic hydrolyses of $[MoNCl_3(bpy)]$, 1.2 and 9.8% of ammonia were detected, respectively, whereas the corresponding basic hydrolysis results in the formation of 31.4% of ammonia. These results indicate that under neutral or acidic conditions the release of ammonia from Mo≡N groups is not prevalent, and probably is prevented by the formation of somewhat stable hydrolytic intermediates containing μ-NH_2 or μ-NH ligands. The intermediate seems to be easily decomposed by sequential addition of NaOH/EtOH.

The reduction of $[(n\text{-}Bu)_4N][MoNCl_4]$ was accomplished with five equivs of $[(n\text{-}Bu)_4N][BH_4]$ in THF. The reduction to the Mo(V) stage was monitored by visible spectra, as shown in Fig. 3. Three absorption maxima of $[MoNCl_4]^-$ at 300, 360 and 460 nm disappeared upon reduction by $[BH_4]^-$ in THF, and only a weak peak was observed at 290 nm, but no detectable ammonia was observed (Table 2). The addition of ethanol to a



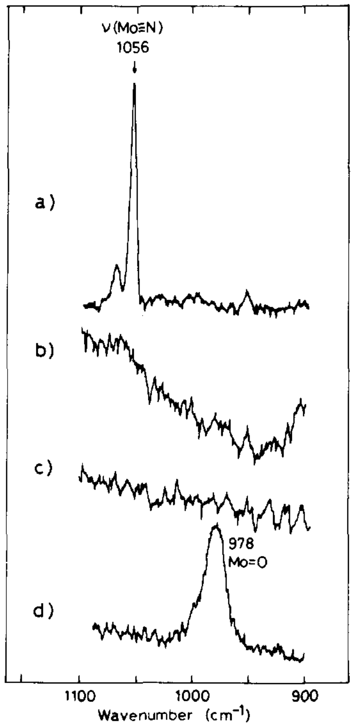
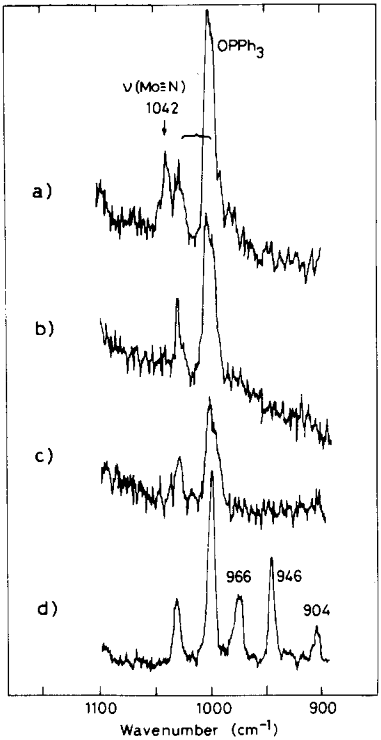


Fig. 3. Absorption spectra of (a) $[(n\text{-Bu})_4N][MoNCl_4]$ in THF, (b) species (a) reduced with $[(n\text{-Bu})_4N][BH_4]$ in THF, and (c) species (a) reduced with $[(n\text{-Bu})_4N][BH_4]$ in the presence of ethanol in THF.

Fig. 4. Raman spectra of (a) $[Et_4N][MoNCl_4]$, (b) $[Et_4N][MoNCl_4]$ reduced by $[BH_4]^-$ in THF, (c) $[Et_4N][MoNCl_4]$ reduced by $[BH_4]^-$ in EtOH, and (d) $[Et_4N][MoNCl_4]$ decomposed by HCl.

THF solution of the reduced nitridomolybdenum complex was accompanied by vigorous generation of dihydrogen. The amount of ammonia formed reached 10.2%.

Figure 4-a shows the Raman spectra of $[Et_4N][MoNCl_4]$ in the solid state, which exhibit a sharp $\nu(Mo{\equiv}N)$ band at 1056 cm^{-1} (IR band at 1055 cm^{-1}). This band disappeared upon reduction with $[(n\text{-Bu})_4N][BH_4]$ in ethanol (Fig. 4-c). In this case, a trace of ammonia (10.2%) was detected. Hydrolysis of the complex by conc. HCl results in the appearance of a new band at 978 cm^{-1} which is assignable to $\nu(Mo{=}O)$, corresponding to its IR band at 960 cm^{-1}. The basic hydrolysis in ethanol resulted in the formation of a large amount (51.2%) of ammonia from $[Et_4N][MoNCl_4]$. The reduction or the reductive hydrolysis of $[MoNCl_3(OPPh_3)_2]$ or $[MoNCl_2(PPh_3)_2]$ gave only a trace of ammonia. By acidic hydrolysis, a substantial amount of ammonia (11 - 14%) was generated, while 26 - 37% ammonia was found by the basic hydrolysis, as listed in Table 2. The discrepancy from the reported data may be due to the difference in reaction conditions. In both cases, the



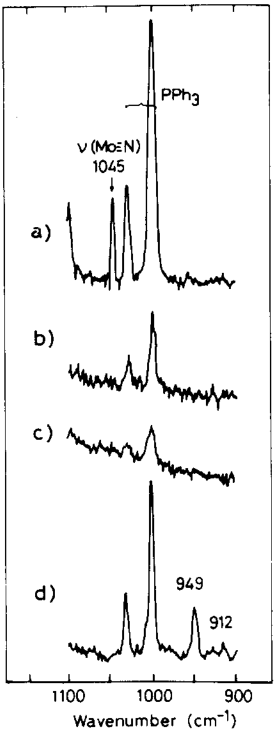


Fig. 5. Raman spectra of (a) $MoNCl_3(OPPh_3)_2$, (b) $MoNCl_3(OPPh_3)_2$ reduced by $[BH_4]^-$, (c) $MoNCl_3(OPPh_3)_2$ reduced by $[BH_4]^-$ in EtOH, and (d) $MoNCl_3(OPPh_3)_2$ decomposed by HCl.

Fig. 6. Raman spectra of (a) $MoNCl_2(PPh_3)_2$, (b) $MoNCl_2(PPh_3)_2$ reduced by $[BH_4]^-$, (c) $MoNCl_2(PPh_3)_2$ reduced by $[BH_4]^-$ in EtOH, and (d) $MoNCl_2(PPh_3)_2$ decomposed by HCl.

Mo≡N stretching bands disappeared upon reduction or reductive hydrolysis. The fate of the nitrido ligand must be sought among the molybdenum-containing solid residues obtainable after the reaction.

The Raman bands of ν(Mo≡N) for $[MoNCl_3(OPPh_3)_2]$ and $[MoNCl_2(PPh_3)_2]$ were observed at 1042 cm^{-1} (IR band at 1038 cm^{-1}) and 1045 cm^{-1} (IR band at 1049 cm^{-1}) as shown in Figs. 5-a and 6-a. The acid hydrolysis of $[MoNCl_3(OPPh_3)_2]$ resulted in formation of a yellow-green residue which had Raman bands at 904, 946 and 966 cm^{-1} (IR bands at 907, 945 and 975 cm^{-1}) due to the presence of various kinds of Mo=O groups (Fig. 5-d). The acid hydrolysis of $[MoNCl_2(PPh_3)_2]$ gave similarly a residue with Raman bands at 912 and 949 cm^{-1} (IR bands at 920, 935, 947 and 973 cm^{-1} assignable to ν(Mo=O)) as shown in Fig. 6-d.

Although the complete disappearance of Mo≡N groups with reduction by $[BH_4]^-$ was suggested from the results of Raman spectra, only slight ammonia formation was detected. The possibility of the formation of a stable reduced Mo species having a coordinated nitrogen group was examined

TABLE 3

The formation of ammonia from $[Et_4N][MoNCl_4]$

Reagents	Ammonia/[Mo(VI)] (%)
$[(n\text{-}Bu)_4N][BH_4]$[a]	0.0
$[(n\text{-}Bu)_4N][BH_4]/EtOH$[b]	10.2
$[(n\text{-}Bu)_4N][BH_4]/HCl$[b]	10.7
$[(n\text{-}Bu)_4N][BH_4]/NaOH/EtOH$[b]	13.7
EtOH[c]	0.0
HCl[a]	0.0
NaOH/EtOH[c]	51.2

Conditions: reaction time (2 h) at 30 °C; [Mo(VI)], 5×10^{-2} mmol; $[BH_4]^-/[Mo(VI)]$ = 5 (mol/mol); HCl/[Mo(VI)] = 10 (mol/mol).

[a] Four ml of THF was used.

[b] After $[(n\text{-}Bu)_4N][BH_4]$ was added to a solution of Mo(VI) complex in 3 ml THF, EtOH (1 ml), HCl in THF (1 ml), or NaOH in EtOH (1 ml) was added respectively.

[c] EtOH/THF = 1 ml/3 ml.

by addition of HCl instead of ethanol to the reduced species of $[Et_4N]$-$[MoNCl_4]$. The results are shown in Table 3. After the nitrido complex is pre-reduced by $[BH_4]^-$, the amount of ammonia obtained by acidic hydrolysis does not depend on the concentration of H^+. Thus, about 90% of the coordinated nitrogen atoms may remain in the residue as inert complexes, which are stable to the strong acid or base used, or may be released as dinitrogen. An attempt was made to detect dinitrogen in the reaction system of $[MoNCl_3(bpy)]$ and 1 M HCl–THF solution in diglyme. No detectable mass peak at *m/e* 28 for dinitrogen was found in the products.

Previously, we examined the reactivity of the Mo≡N group of polymer-bound nitridomolybdenum(VI) complexes [8]. No remarkable super-dilution effect of the polymer support was observed. Thus, the formation of species with Mo—Mo bonds is excluded. A possible explanation for the lack of dinitrogen formation is that most of the Mo≡N groups react with the borohydride anion and form extremely stable polymeric boronitride, $(BN)_n$, species after generating dihydrogen. Actually, such boron nitride has been reported to be stable even to mineral acids except hydrofluoric acid [18]. Figure 7 shows a proposed scheme for the reductive hydrolysis of Mo≡N complexes. The imido complexes should smoothly generate ammonia, as Bevan *et al.* have indicated the formation of ammonia for $[Mo(NH)X(dppe)_2]X$ (X = halide) by hydrolysis.

The difference in yields of ammonia between $[Et_4N][BH_4]$/ethanol (18.3%) and $NaBH_4$/ethanol (1.2%) systems is caused by the solubility of the former complex in THF. Absence of reduction of the Mo≡N species by the latter system before the addition of ethanol is due to its insolubility in THF. In the case of reduction by the former system, the nitridomolybdenum(VI) complex was first reduced by $[(n\text{-}Bu)_4N][BH_4]$ and then protonated by

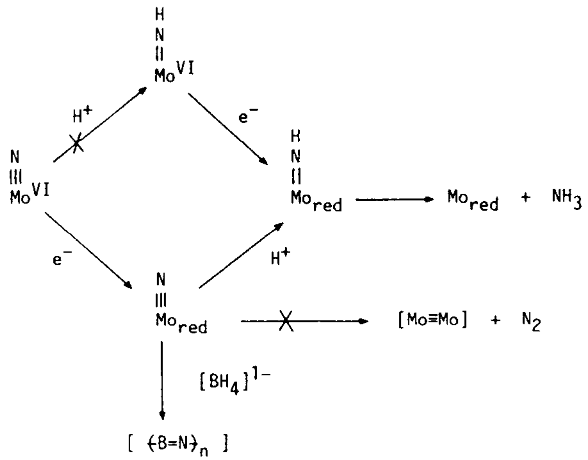


Fig. 7. Proposed scheme for the reductive hydrolysis of Mo≡N complexes.

ethanol. The usage of phenol instead of ethanol results in a fair increase (18.3%) in ammonia, supporting the protonation of the reduced species as the first step for hydrolysis.

The limited amounts of ammonia formed from nitridomolybdenum(VI) complexes suggest an important clue concerning the purported nitrogen-fixing cycles based on simple molybdenum complexes.

References

1 J. Chatt, J. R. Dilworth and R. L. Richards, *Chem. Rev., 78* (1978) 589.
2 J. Chatt, A. J. Pearman and R. L. Richards, *J. Chem. Soc., Dalton Trans.*, (1977) 1852.
3 J. Chatt and J. R. Dilworth, *J. Indian Chem. Soc.*, (1977) 13.
4 K. Seyferth and R. J. Taube, *J. Organometall. Chem., 229* (1982) C19.
5 K. Dehnicke, U. Weiher and J. Strahle, *Z. Naturforsch., 32b* (1977) 1361.
6 J. Chatt and J. R. Dilworth, *J. Chem. Soc., Chem. Commun.*, (1975) 983.
7 K. Dehnicke and J. J. Strahle, *Angew. Chem. Int. Ed. Engl., 20* (1981) 413.
8 N. Ueyama, H. Zaima, H. Okada and A. Nakamura, *Inorg. Chim. Acta, 89* (1984) 19.
9 W. Kolitsch and K. Dehnicke, *Z. Naturforsch., 25b* (1970) 1080.
10 E. A. Allen, B. J. Briston and G. W. A. Fowles, *J. Chem. Soc.*, (1964) 4531.
11 E. A. Allen, K. Feenan and G. W. A. Fowles, *J. Chem. Soc.*, (1965) 1636.
12 Y. Morita and K. Ogawara, *Nippon Kagaku Zasshi, 84* (1963) 56.
13 E. Schweda and J. Strahle, *Z. Naturforsch., 35b* (1980) 1146.
14 C. Campochiaro, J. A. Hofmann, Jr., and D. F. Bocian, *Inorg. Chem., 24* (1985) 449.
15 S. Donovan-Mtunzi, R. L. Richards and J. Mason, *J. Chem. Soc., Dalton Trans.*, (1984) 1329.
16 N. Ueyama, M. Nakata, T. Araki, A. Nakamura, S. Yamashita and T. Yamashita, *Inorg. Chem., 20* (1981) 1934.
17 R. J. Collin, W. P. Griffith and D. Pawson, *J. Mol. Struct., 19* (1973) 531.
18 P. C. Bevan, J. Chatt, J. R. Dilworth, R. A. Henderson and G. L. Leigh, *J. Chem. Soc., Dalton Trans.*, (1982) 821.