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REACTION DERIVATIVES OF NITRIDOMOLYBDENUM(V) PORPHYRIN COMPLEXES

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Abstract—The nitrido atom in the nitridomolybdenum porphyrin complexes donates strongly to the metal centre with the formation of a strong triple bond, but it still retains enough electron density to be attacked by electrophiles such as iodo alkyls, forming organoimidomolybdenum porphyrin complexes. It reacts with Lewis acids like boron trifluoride to afford 1 : 1 adducts and with elemental sulphur, giving thionitrosyl molybdenum porphyrin complexes. Under severe conditions, the nitrido ligand in N≡Mo(TPP) behaves like an electrophile with tributylphosphine to give a phosphineiminato molybdenum porphyrin complex. The nitrido ligand in N≡Mo(TPP) can also replace one CO ligand of $M(CO)_6$(M = Mo, W) to form (TPP)Mo≡N—$M(CO)_5$.

The occurrence of nitrido metal complexes is widely spread over the transition metals, including 3*d*, 4*d* and 5*d* elements with simple ligands.[1] However, until recently, nitridometalloporphyrin complexes were limited to Cr,[2] Mo,[3] W,[4] Mn,[5] Fe,[6] and Os[7] metals. Contrary to the nitrido complexes with simple ligands, nitridoporphyrins have been reported to show limited reactivities at the nitrido group. Nitrogen atom transfer reactions and metal nitride activation by highly electron-deficient molecules may be the exceptions. Takahashi[8] observed the first example of complete intermetal nitrogen atom transfer from N≡Mn(4-MeTPP) and ClCr(4-MeTPP) (4-MeTPP = 4-methyl tetraphenylporphyrin). Groves and Takahashi[9] also reported metal nitride activation in N≡Mn(TMP) (TMP = tetramesitylporphyrin) by trifluoroacetic anhydride to give aziridines in the presence of double bonds. Since then, nitrogen transfer reactions between nitridoporphyrins of the type N≡M(por) (M = Cr, Mn) and chromium(III), manganese(III) and manganese(II) porphyrins have been widely developed by Woo[10] and Neely and Bottomley,[11] independently. However, the reactivities of the heavier analogues, nitridomolybdenum porphyrins, which may be considered as model substances for the study of dinitrogen assimilation are undeveloped. The nitrido and imido moieties in metal complexes are considered as plausible intermediates in the enzymatic dinitrogen fixation process.[12] In an extension of nitridomolybdenum porphyrin chemistry,[3] we have investigated the reactivity of the nitrido group in nitridomolybdenum porphyrins. Reported herein is adduct formation between N≡Mo(por) and various electrophiles, nucleophiles and binary carbonyls to afford corresponding 1 : 1 complexes, where 'por' is the dianion of tetra-

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phenylporphyrin (TPP) or tetramesitylporphyrin (TMP).

EXPERIMENTAL

IR spectra (as Nujol mulls) were measured on a P-E Model 983 spectrophotometer. Electronic spectra were obtained using a Cary 14 or JASCO UVIDEC-610 recording spectrophotometer. EPR spectra were recorded on a Varian E-12 spectrometer equipped with E-101 (for X-band spectra) and E-110 (for Q-band spectra) microwave bridges. Carbon, hydrogen and nitrogen analyses were carried out by the Korea Research Institute of Chemical Technology, Daejeon. All the samples were finely ground and thoroughly dried *in vacuo* at 100°C before microanalyses.

Reagents

Literature methods have been employed in the preparation of H_2TPP[13] and H_2TMP,[14] as well as N$\equiv$Mo(TPP) (**1**) and N$\equiv$Mo(TMP) (**2**).[3] Solvents were reagent grade and were further purified by known methods.[15] Toluene and THF were distilled from sodium benzophenone ketyl under nitrogen. Boron trifluoride etherate, sulphur, tributylphosphine, iodoethane, iodomethane, $Mo(CO)_6$ and $W(CO)_6$ were purchased from Aldrich Chemical Co. and used without further purification.

Preparation of complexes

[EtN = Mo(TPP)][I] (**3**). To a toluene solution of N$\equiv$Mo(TPP)(20 mg) in a test tube was added, via syringe, an excess amount of iodoethane, followed by stirring for 24 h at refluxing temperature under nitrogen. A colour change from dark purple to brownish green was observed. Brownish purple crystals were obtained on the side of the test tube, becoming a dark brown powder on slow cooling. The crystals were filtered and hand picked from the dark brown powder impurities, washed and finally dried *in vacuo*. IR (Nujol), cm^{-1}: 1595, 1439, 1336, 1226, 1203, 1174, 1068, 1016, 798, 750, 717, 702, 659, 601, 520, 441. Found: C, 63.1; H, 3.9; N, 7.9. Calc. for $C_{46}H_{33}N_5MoI$: C, 62.9; H, 3.8; N, 8.0%.

[MeN = Mo(TPP)][I] (**4**). This complex was prepared and isolated in an identical manner as described above, but with iodomethane in place of ethyl iodide. IR (Nujol), cm^{-1}: 1336, 1232, 1203, 1070, 1016, 798, 752, 717, 702, 661, 613, 522, 443, 418. Found: C, 62.3; H, 3.5; N, 8.1. Calc. for $C_{45}H_{31}N_5MoI$: C, 62,5; H, 3.6; N, 8.1%.

(TPP)Mo$\equiv$N—BF_3 (**5**). N$\equiv$Mo(TPP) (20 mg) was dissolved in 10 cm^3 of toluene. The cherry solution was collected and undissolved solid was filtered off. The beaker containing this solution was placed in a desiccator with another vessel containing $BF_3 \cdot Et_2O$ and the lid was closed. After 1 day, the colour of the solution changed from cherry to green with precipitation of the product on the bottom of the beaker. The product was hand picked from the black impurity powder under a microscope and dried *in vacuo*. IR (Nujol), cm^{-1}: 1591, 1226, 1201, 1178, 1072, 1062, 1015, 926, 857, 799, 755, 718, 704, 665. Found: C, 67.1; H, 3.7; N, 8.8. Calc. for $C_{44}H_{28}N_5MoBF_3$: C, 66.8; H, 3.6; N, 8.9%.

(TMP)Mo$\equiv$N—BF_3 (**6**). This complex was prepared and isolated in an identical manner. IR (Nujol), cm^{-1}: 1606, 1202, 1072, 1062, 1016, 932, 869, 853, 831, 804, 792, 766, 726, 674.

(TPP)Mo$\equiv$N—S (**7**). Sulphur (20 mg) and N$\equiv$Mo(TPP) (20 mg) were slurried in 4 cm^3 of fresh THF in a test tube. While continuing to bubble the mixture with nitrogen, the test tube was sealed with a rubber septum and the reaction mixture was subjected to reflux for 15 h. After cooling the solution, a brown powder was formed. The product was filtered, washed with acetonitrile and dried *in vacuo*. IR (Nujol), cm^{-1}: 1589, 1226, 1200, 1175, 1094, 1071, 1014, 967, 895, 793, 753, 716, 704, 660. Found: C, 70.1; H, 3.7; N, 9.3. Calc. for $C_{44}H_{28}N_5MoS$: C, 70.0; H, 3.7; N, 9.2%.

(TPP)Mo$\equiv$N—PBu_3 (**8**). N$\equiv$Mo(TPP) (20 mg) was dissolved in 3 cm^3 of tributylphosphine in a test tube and the mixture was bubbled with nitrogen for 10 min. The tube was sealed with a rubber septum and the reaction mixture was allowed to reflux for 15 h. Dark brown crystals formed upon cooling the reaction mixture. Crystals were collected by filtration, washed with pentane and dried *in vacuo*. IR (Nujol), cm^{-1}: 1589, 1170, 1152, 1091, 1063, 1003, 908, 778, 747, 713, 699. Found: C, 72.3; H, 5.6; N, 7.6. Calc. for $C_{56}H_{55}N_5MoP$: C, 72.7; H, 6.0; N, 7.6%.

(TPP)Mo$\equiv$N—$Mo(CO)_5$ (**9**). N$\equiv$Mo(TPP) (20 mg) and an excess molar amount of $Mo(CO)_6$ were put into 3 cm^3 of toluene in a test tube. The mixture was bubbled for 10 min with a nitrogen stream and sealed with a septum; the solution was heated at refluxing temperature for 12 h. Light purple crystalline (TPP)Mo$\equiv$N—$Mo(CO)_5$ was formed from the solution on slow cooling and was collected, washed with pentane and finally drive *in vacuo*. IR (Nujol), cm^{-1}: 2060, 1970, 1920, 1881, 1705, 1592, 1294, 1225, 1203, 1174, 1153, 1073, 1013, 964, 918, 844, 807, 801, 755, 722, 701. Found: C, 60.9; H, 2.9; N, 7.4. Calc. for $C_{49}H_{25}N_5Mo_2O_5$: C, 61.4; H, 2.9; N, 7.3%.

(TPP)Mo$\equiv$N—$W(CO)_5$ (**10**). This complex was prepared and isolated in a similar manner as described for $(TPP)Mo{\equiv}N{-}Mo(CO)_5$ but with $W(CO)_6$ in place of $Mo(CO)_6$. IR (Nujol), cm^{-1}: 2060, 1969, 1898, 1880, 1074, 1014, 802, 754, 721, 700, 659, 590, 576. Found: C, 56.4; H, 2.6; N, 7.4. Calc. for $C_{49}H_{25}N_5MoWO_5$: C, 57.4; H, 2.4; N, 6.8%.

RESULTS AND DISCUSSION

Nitridomolybdenum porphyrins, **1** or **2**, with HCl (g) have been reported to form readily the imidomolybdenum porphyrins, $[HN{=}Mo(TPP)][Cl]$ or $[HN{=}Mo(TMP)][Cl]$, respectively.[3] Similarly, **1** or **2** react with other electrophiles, Lewis acids, nucleophiles and binary carbonyls to produce the corresponding 1 : 1 complexes (Fig. 1). These include iodomethane, iodoethane, BF_3, elemental sulphur, tributylphosphine, $Mo(CO)_6$ and $W(CO)_6$. The stoichiometric composition of the compounds was established by chemical microanalysis, and the visible spectra for the adducts differed from the reactant **1** or **2**. More diagnostic, however, are the loss of the $Mo{\equiv}N$(1040 cm^{-1} in **1** and 1038 cm^{-1} in **2**) stretching frequencies and the appearance of new $Mo{\equiv}N$ frequencies due to adduct formation (Table 1). IR data of **3**, **4** and **8**–**10** showed the $Mo{\equiv}N$ frequencies to shift on complexation to lower frequencies, whereas they increased in **5** and **6**. More specifically, the nitrido group of **3** is sufficiently nucleophilic to attack iodoalkyls to give the corresponding organoimido complexes, **3** and **4**, respectively. The most significant IR spectral changes accompanying the formation or organoimido complexes from **3** are the disappearance of the band at 1040 cm^{-1} with the appearance of the new medium band at *ca* 750 cm^{-1} [$\nu(Mo{\equiv}N)$]. The electronic spectra of **3** and **4** show well known 'normal' metalloporphyrin spectra. The principal bands in **3** are the α (λ_{max} 613 nm), β (λ_{max} 575 nm) and Soret bands (λ_{max} 450 nm). These are all π (a_{1u}, a_{2u}) $\rightarrow \pi^*(e_g)$ in origin.[16] In comparison with the Soret band of the parent nitridomolybdenum porphyrin (λ_{max} 433 nm in **1**), **3** has a higher Soret absorption wavelength, indicating a smaller amount of π–π^* energy separation in this complex. Generally, the extent of π electron delocalization is related to the planarity of the porphyrin macrocyclic ring. This may be explained by the well-known *trans* effect of axial ligands.[17] The order of *trans* influence is given as nitrido > oxo > imido ≫ NO and CO, and the expectation of little tendency towards square pyramidal geometry for imido complexes.[18] Consistent with this, occupation of the *trans* site by water in the complex $[MeN = Mo(TPP)(H_2O)][I_3]$ has been confirmed by X-ray crystal structure determination.[19] However, it loses the coordinated water upon heating at 100°C for a few minutes. The qualitative appearance of solution EPR (six satellites and a strong central line which is further split into 11 lines) for **3** and **4** was still d^1 configurations around the molybdenum atom and was not substantially different from that of imidomolybdenum porphyrin complexes with a superhyperfine structure due to coupling of five nitrogen atoms ($I = 1$) to a single d electron.[3]

The Lewis acid BF_3 forms 1 : 1 complexes with **1** and **2**. The band at 1072 cm^{-1} was tentatively assigned to the $Mo{\equiv}N$ stretching frequency in **5** based on the related examples and Griffith's conclusion.[20,21] EPR spectra of **5** taken in toluene represent a typical d^1 molybdenum spectrum, resembling those of **1** or **2**.[3] Interestingly, the A_{Mo}

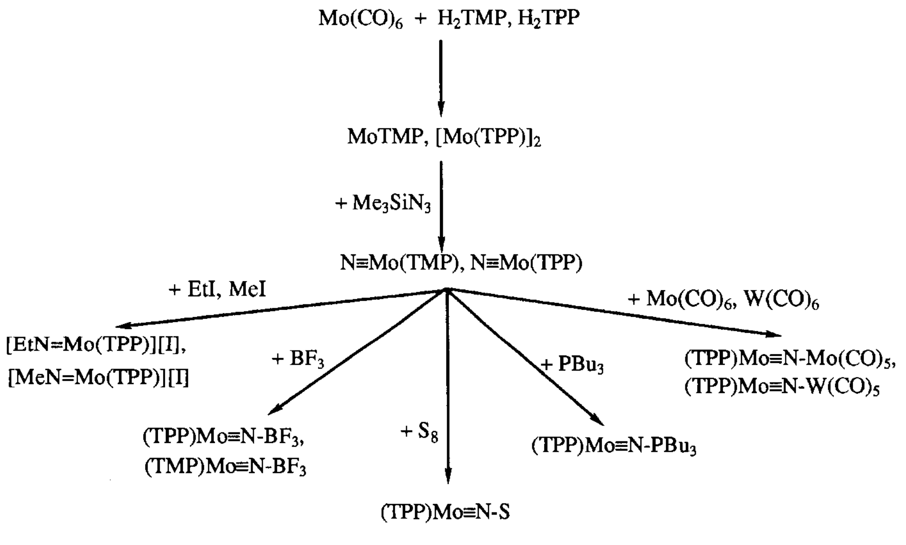

Fig. 1. Reaction scheme of nitridomolybdenum porphyrins.

Table 1. IR Spectral data (cm^{-1}) for nitridomolybdenum porphyrins and their derivatives

Material	Complex		$\nu(Mo{\equiv}N)$	Ref.
	$N{\equiv}Mo(TMP)$		1038	3
	$N{\equiv}Mo(TPP)$		1040	3
HCl	$[HN{=}Mo(TMP)][Cl]$	3284 [ν(NH)]	913	3
HCl	$[HN{=}Mo(TPP)][Cl]$	3341 [ν(NH)]	908	3
CH_3I	$[MeN{=}Mo(TPP)][I]$		752	[a]
CH_3CH_2I	$[EtN{=}Mo(TPP)][I]$		750	[a]
BF_3	$(TMP)Mo{\equiv}N{-}BF_3$	1062 [ν(BF)]	1072[b]	[a]
BF_3	$(TPP)Mo{\equiv}N{-}BF_3$	1062 [ν(BF)]	1072[b]	[a]
S_8	$(TPP)Mo{\equiv}N{-}S$	1094 [ν(NS)]	895	[a]
PBu_3	$(TPP)Mo{\equiv}N{-}PBu_3$	1063 [ν(PN)]	908	[a]
$Mo(CO)_6$	$(TPP)Mo{\equiv}N{-}Mo(CO)_5$	2060, 1970 1920, 1881 [ν(CO)]	918	[a]
$W(CO)_6$	$(TPP)Mo{\equiv}N{-}W(CO)_5$	2060, 1969 1898, 1880 [ν(CO)]	[c]	[a]

[a] This work.

[b] Tentative assignments due to broad ν(BF) in this region.

[c] Not observed.

value of 60.67 G was little changed upon coordination and increased in value compared to that of nitridomolybdenum porphyrin ($A_{Mo} = 60.4$ G in **1**). A nitrogen superhyperfine structure was not observed in **5**. The opposite was observed in imido or organoimido complexes and strongly indicates the strengthening of the molybdenum–nitrido bond on complexation with BF_3. In support of this conjecture is the report of the structural analysis of the acetonitrile–BF_3 complex, where the $C{\equiv}N$ bond distance (1.13 Å) in the BF_3 complex is slightly shorter than that (1.16 Å) in acetonitrile.[22] Therefore, it appears that there are significant differences between the two complexes, **5** and imido or organoimido complexes.

Compound **1** can be transformed to the thionitrosyl complex **7** with elemental sulphur in boiling THF. Complex **7** contains a typical thionitrosyl band at 1094 cm^{-1} and a decreased $Mo{\equiv}N$ stretching band at 895 cm^{-1} in the IR spectrum. This assignment was obvious since no other bands occur in the region 1150–1071 cm^{-1} except typical porphyrin bands. The thionitrosyl band at 1094 cm^{-1} in **7** lies at the lower end of the range.[23]

Compound **1** reacts with high boiling tributylphosphine to afford the corresponding phosphineiminato complex **8** [ν(P—N) 1063 cm^{-1} and $\nu(Mo{\equiv}N)$ 908 cm^{-1}]. Phosphineiminato complexes are common in Ru, Os and Re systems, and Pawson and Griffith[24] reported a series of complexes in which the phosphorus–nitrogen stretching modes have been assigned in the region 1050–1200 cm^{-1}. However, such behaviour has not been reported previously for nitridomolybdenum complexes. It appears that the strong phosphorus–nitrogen bonding drives the reaction to the formation of the phosphineiminato complex, and/or that the nitrido group in nitridomolybdenum porphyrin is unusually reactive and undergoes electrophilic attack on tertiary phosphine to produce such a complex. Compound **8** exhibited sharp ^1H NMR signals except for the β-pyrrolyl and phenyl protons. Since the location of the butyl groups in **8** is far from the molybdenum metal centre, they are not affected by the metal centre and show sharp resonances in the range 3–6 ppm. These signals are well separated from the unreacted tributyl resonance signals, which appeared at ~1 ppm.

Of much interest is the clean reaction of **1** with $Mo(CO)_6$ or $W(CO)_6$ to give **9** or **10**. In boiling toluene, the nitrido ligand replaces one CO ligand of $Mo(CO)_6$ or $W(CO)_6$, resulting in μ-nitrido species which are indefinitely stable in the solid state. The most pertinent features of the formation of μ-nitrido complexes are from the IR spectral results. The IR spectrum of **9** shows four bands at *ca* 2060, 1970, 1920 and 1881 cm^{-1}, and suggests the presence of different types of CO stretching modes in this complex. This can be achieved by the transformation of highly symmetric (O_h) $M(CO)_6$ (M = Mo, W) to the symmetry lowered $LM(CO)_5$. It is known that the monosubstituted $LM(CO)_5$ (L = pyridine, NHR_2 and PRR_2) shows four active bands when L is a relatively unsymmetrical ligand.[25] Compound **1** as substituting ligand should be in this category. Similarly to other adducts, **1** lost its typical band at 1040 cm^{-1} with a new band appearing at *ca* 918 cm^{-1} due to the formation of the μ-nitrido complex **9**.

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