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REACTIONS OF LIGATING DINITROGEN WITH ALCOHOLS OR METAL HYDRIDES[1)]

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Treatment of cis-[$W(N_2)_2(PMe_2Ph)_4$] with 2-propanol/KOH yields hydrazine, whereas use of n-alcohols instead of 2-propanol gives ammonia as a main nitrogen hydride. Metal hydrides such as [$(\eta^5\text{-}C_5H_5)_2ZrHCl$], [$H_2Fe(CO)_4$] and [$NaAlH_2(OCH_2CH_2OCH_3)_2$] also react with the above dinitrogen complex to give ammonia in moderate yield.

Previous studies on the chemical behavior of transition metal dinitrogen complexes have revealed that the ligating dinitrogen in some complexes is susceptible to electrophilic attack by proton derived from acids to give ammonia and hydrazine.[2)] Detailed investigations of these protonation reactions have resulted in several suggested mechanisms for reduction.[1),2)] These reactions are, however, stoichiometric and the metals are finally oxidized to higher valent states. We wish here to describe the reactions of ligating dinitrogen with alcohols or metal hydrides to yield ammonia and hydrazine, which might give a break-through for the catalytic conversion of dinitrogen into nitrogen hydrides under mild conditions.

Chatt and his coworkers[3)] have previously reported that cis-[$W(N_2)_2(PMe_2Ph)_4$] gives ammonia in moderate yield on treatment with methanol or ethanol alone, either at reflux or under irradiation. Hydrogen transfer from alcohols, especially secondary alcohols, to unsaturated compounds is well known to be catalyzed by transition metal complexes.[4)] We have now investigated the reaction of dinitrogen complexes such as cis-[$M(N_2)_2(PMe_2Ph)_4$] (M = Mo or W), trans-[$M(N_2)_2(dpe)_2$] (M = Mo or W) (dpe = $Ph_2PCH_2CH_2PPh_2$), [$CoH(N_2)(PPh_3)_3$], and [$RuH_2(N_2)(PPh_3)_3$] with various kinds

Table 1. Yields[a)] of NH_3 and N_2H_4

Complex[b)]	Alcohol[c)]	NH_3		N_2H_4	
cis-[$W(N_2)_2(PMe_2Ph)_4$]	Methanol	1.36	(1.26)[d)]	0.11	(0.06)[d)]
	Ethanol	1.08	(0.53)[d)]	0.06	(tr)[d)]
	1-Propanol	1.08	(0.08)[d)]	0.02	(0.00)[d)]
	2-Propanol	0.03	(0.09)[d)]	0.45	(tr)[d)]
	1-Butanol	0.97		0.00	
	2-Butanol	0.33		0.02	
	tert-Butanol	0.11		tr	
	1-Pentanol	0.86		tr	
	2-Pentanol	0.26		tr	
	3-Pentanol	0.22		0.00	
cis-[$Mo(N_2)_2(PMe_2Ph)_4$]	2-Propanol	0.00		0.00	
trans-[$Mo(N_2)_2(dpe)_2$]	2-Propanol	tr		0.00	

a) Mol/M atom. b) Ca. 0.18 mmol. c) 5 ml with 4 mol KOH/M atom. d) Without KOH of alcohols. The cobalt, ruthenium, and molybdenum dinitrogen complexes did not give nitrogen hydrides. However, cis-$[W(N_2)_2(PMe_2Ph)_4]$ yields ammonia and hydrazine on treatment with alcohols in the presence of KOH at 52°C as shown in Table 1. It is of great interest to note that treatment of the complex with 2-propanol gives hydrazine as a main nitrogen hydride, whereas the use of n-alcohols leads to the predominant fomation of ammonia. The effect of KOH is remarkable. The reaction of the complex with 2-propanol gives a significant amount of hydrazine in the presence of KOH, though a small amount of ammonia is given in the absence of KOH. The reaction of the complex with n-alcohols gives ammonia even in the absence of KOH. The yield was improved by the addition of KOH in our investigation. The effect of the KOH seems to become larger, as the alkyl chains of n-alcohols get longer. We must await further investigations to understand the role of KOH and the reaction mechanism.

Several metal hydrides have also been tested as another hydrogen source for formation of nitrogen hydrides. Metal carbonyl hydrides have first been chosen since the hydride ligands show protonic character and are, therefore, expected to react with ligating dinitrogen. The iron carbonyl hydride $[H_2Fe(CO)_4]$ reacts with cis-$[W(N_2)_2(PMe_2Ph)_4]$ in methanol to form ammonia after base distillation of the residue obtained by removing the solvent. Surprisingly, the complexes $[(\eta^5\text{-}C_5H_5)_2\text{-}ZrHCl]$ and $[NaAlH_2(OCH_2CH_2OCH_3)_2]$, of which the hydrogen ligands are hydridic, also react with cis-$[M(N_2)_2(PMe_2Ph)_4]$ (M = Mo or W) to give ammonia in moderate yield as shown in Table 2. On the other hand, the ruthenium hydride $[(PPh_3)_3RuHCl]$ did not afford ammonia under similar reaction conditions. The reaction of ligating dinitrogen with metal hydrides described above might give a clue for elucidating the mechanism of nitrogen fixation in biological systems. Work is being continued in this area.

Table 2. Reaction of dinitrogen complexes with metal hydrides

Complex$^{a)}$	Hydride$^{b)}$	$NH_3$$^{c)}$	$N_2H_4$$^{c)}$	T/°C
cis-$[W(N_2)_2(PMe_2Ph)_4]$	$[(\eta^5\text{-}C_5H_5)_2ZrHCl]$	0.44	tr	52
	$[NaAlH_2(OCH_2CH_2OCH_3)_2]$	0.59	tr	r.t.
	$[H_2Fe(CO)_4]$	0.06	tr	-20—0
	$[NEt_3H][HFe_3(CO)_{11}]$	tr	tr	r.t.
	$[(PPh_3)_3RuHCl]$	tr	0.00	52
cis-$[Mo(N_2)_2(PMe_2Ph)_4]$	$[(\eta^5\text{-}C_5H_5)_2ZrHCl]$	0.19	0.00	52

a) Ca. 0.18 mmol. b) Ca. 8 mol/Mo or W atom. c) Mol/M atom. d) Reaction Temp.

References

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