CHEMISTRY LETTERS, pp. 453-454, 1982. © The Chemical Society of Japan 1982

REACTIONS OF COORDINATED DINITROGEN WITH ALCOHOL/KETONE SYSTEMS[1)]

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Treatment of cis-$[W(N_2)_2(PMe_2Ph)_4]$ (I) with alcohol/ketone systems such as methanol/acetone at 50 °C followed by base distillation yields hydrazine as a main nitrogen hydride. Addition of KOH to the systems results in an increase of free hydrazine formation.

Extensive studies on transition metal dinitrogen complexes have disclosed that coordinated dinitrogen reacts with various reagents to give ammonia and hydrazine. Treatment of cis-$[W(N_2)_2(PMe_2Ph)_4]$ (I) with H_2SO_4 in methanol gives ammonia in high yield,[2)] whereas the reaction of (I) with HCl gas in 1,2-dimethoxyethane produces hydrazine in moderate yield.[3)] Transition and non-transition metal hydrides such as $[HCo(CO)_4]$ and $[NaAlH_2(OCH_2CH_2OCH_3)_2]$ also react with (I) to give ammonia after base distillation (decomposition of the products with 40 % aqueous solution of KOH).[4-6)]

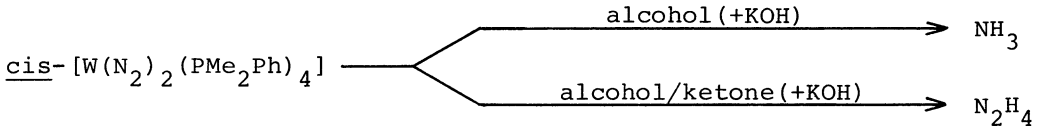
Chatt and his coworkers have previously found that (I) gives ammonia in moderate yield on treatment with methanol or ethanol alone, either at reflux or under irradiation.[2)] In a previous paper,[4)] we reported that the yield of ammonia was much increased by the addition of KOH, and hydrazine was the main product with 2-propanol. But it has recently been found that some ammonia, but no hydrazine, is produced with fractionally distilled 2-propanol, and acetone was contained in the 2-propanol used in the previous experiments. We wish here to describe the reactions of (I) with alcohol/ketone systems at 50 °C, which give hydrazine as a main nitrogen hydride.

Table 1. Yields of NH_3 and N_2H_4 in the reactions of cis-$[W(N_2)_2(PMe_2Ph)_4]$ with alcohol/ketone systems[a)]

Alcohol	Ketone	Yield of NH_3[b)]			Yield of N_2H_4[b)]		
		free[d)]	b.d.[e)]	total	free[d)]	b.d.[e)]	total
Methanol[c)]	———	1.01	0.25	1.26	0	0.06	0.06
Methanol	Acetone	0	0.08	0.08	0.08	0.59	0.67
Methanol	Butanone	0.01	0.11	0.12	0.07	0.56	0.63
Ethanol[c)]	———	0.24	0.29	0.53	0	0	0
Ethanol	Acetone	0.02	0.10	0.12	0.04	0.12	0.16
Ethanol	Butanone	0.02	0.03	0.05	0.01	0.12	0.13
2-Propanol[c)]	———	0	0.08	0.08	0	0	0
2-Propanol	Acetone	0	0.02	0.02	0.02	0.06	0.08

a) cis-$[W(N_2)_2(PMe_2Ph)_4]$ ca. 0.19 mmol, alcohol 4 ml/ketone 1 ml, 50 °C, 18 hr.
b) Mol/W atom. c) Alcohol 5 ml. d) Before base distillation of the reaction mixture.
e) After base distillation.

The results are shown in Table 1. More than 1 mol/W atom of ammonia is formed in the reaction with methanol alone. In contrast, the reaction in the presence of acetone or butanone followed by base distillation converts the coordinated dinitrogen mainly into hydrazine. Similarly, with other alcohols, ammonia is the main product in the absence of ketones while hydrazine is formed in moderate yield in the presence of ketones.



Effect of adding KOH to the above systems is shown in Table 2. The total amount of hydrazine increases in each alcohol/ketone system, a large part of which is formed before base distillation. The study of varying the ratio of acetone to methanol indicated that the yield of total hydrazine reaches the maximum value (ca. 0.8 mol/W atom) in the range of 10 ~ 30 vol % acetone in methanol. In conclusion, the presence of ketones in the reactions of the complex (I) with alcohols seems to change the reduction course of coordinated dinitrogen. Although it has been confirmed that ammonia once formed is not transformed into hydrazine, further investigations must be awaited to elucidate the detailed reaction mechanism.

Table 2. Yields of NH_3 and N_2H_4 in the presence of KOH[a)]

Alcohol	Ketone	Yield of NH_3[b)]			Yield of N_2H_4[b)]		
		free	b.d.	total	free	b.d.	total
Methanol	Acetone	0	0.05	0.05	0.72	0.12	0.84
Methanol	Butanone	0.02	0	0.02	0.29	0.49	0.78
Ethanol	Acetone	0.02	0.42	0.44	0.49	0.05	0.54
Ethanol	Buthanol	0.03	0.20	0.23	0.20	0.45	0.65
2-Propanol[c)]	———	0.38	0	0.38	0.02	0	0.02
2-Propanol	Acetone	0	0	0	0.31	0.09	0.40

a) KOH ca. 0.76 mmol (4 mol/W atom). Other reaction conditions are the same as in Table 1. b) Mol/W atom. c) Alcohol 5 ml.

References

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(Received February 5, 1982)