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Synthesis of Ketazines from Dinitrogen Coordinated to Tungsten†

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Synopsis. When treated with a methanol/acetone mixture at 50 °C, the complex *trans*-$[W(N_2)_2(PPh_2Me)_4]$ gives acetone azine in moderate yield, although the yield is slightly lower than that from *cis*-$[W(N_2)_2(PMe_2Ph)_4]$. Under UV irradiation, these dinitrogen complexes produce acetone azine even at room temperature.

Direct synthesis of organonitrogen compounds from molecular nitrogen and a relatively cheap organic feedstock is an attractive field in the chemistry of nitrogen fixation. We have already reported that one dinitrogen ligand in the complex *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ (**1**) is converted mainly to ammonia by reaction with alcohols at 50 °C, whereas ketazines are produced in good yields when complex **1** is treated with alcohol/ketone mixtures (ROH/$R^1R^2C{=}O$) at 50 °C.[1] The ligating dinitrogen is first protonated by alcohols to give intermediate complexes $[W(OR)_2(NNH_2)(PMe_2Ph)_3]$. In the presence of ketones, the intermediate complexes are more amenable to the condensation with ketones[2] than to the protonation at the terminal nitrogen atom. The resulting diazoalkane complexes $[W(OR)_2(NN{=}CR^1R^2)(PMe_2Ph)_3]$ react with alcohols to liberate hydrazones ($H_2NN{=}CR^1R^2$), which further condense with ketones to form ketazines as the final products. Thus, 0.88 mol of acetone azine per W atom is formed by treating complex **1** with a methanol/acetone mixture. The yield is further improved up to 0.94 mol/W atom by the addition of base to the system. Since acetone azine is easily converted to hydrazine by hydrolysis, this reaction is considered as a potential method for the synthesis of hydrazine from dinitrogen. In this paper, we wish to describe the application of this reaction system to a series of tungsten and molybdenum dinitrogen complexes $[M(N_2)_2(PR_3)_4]$ (M=W or Mo; PR_3=tertiary phosphines).

Results and Discussion

Investigations of the reactions of a series of tungsten and molybdenum dinitrogen complexes $[M(N_2)_2(PR_3)_4]$ with alcohol/ketone mixtures have disclosed that, in addition to complex **1**, *trans*-$[W(N_2)_2(PPh_2Me)_4]$ (**2**) also gives acetone azine in moderate yield by reaction with methanol/acetone mixtures at 50 °C. However, none of the other dinitrogen complexes *cis*-$[Mo(N_2)_2(PMe_2Ph)_4]$, *trans*-$[M(N_2)_2(dpe)_2]$, *trans*-$[M(N_2)(^nPrCN)(dpe)_2]$ and *trans*-$[W(N_2)_2(dpe)(PPh_2Me)_2]$(M=W or Mo; dpe=$Ph_2PCH_2CH_2PPh_2$) produces acetone azine under similar conditions.

In Table 1 is shown the yield of acetone azine obtained by treatment of complex **2** with methanol/acetone mixtures. It is to be noted that use of a methanol/acetone mixture with the volume ratio 4:1 gives only a trace amount of the azine from complex **2**, although the azine is formed in high yield from complex **1** under similar conditions. This is only because complex **2** is scarcely soluble in the mixed solvent. Therefore, if toluene or THF is added to this system to dissolve complex **2**, the yield of the azine is remarkably improved. A great difference of complex **2** from complex **1** is observed in the effect of base addition to the reaction system. For complex **1**, the yield of the azine is improved almost up to 1 mol/W atom in the presence of KOH or NaOMe.[1] However, for complex **2**, addition of base strongly supresses the formation of the azine.

The mechanism for formation of the azine from complex **2** may be essentially the same as that from complex **1** (*vide supra*). Actually, the hydrido-hydrazido(2-) complex $[WCl_3H(NNH_2)(PPh_2Me)_2]$, which is derived from complex **2** and HCl in CH_2Cl_2, reacts with methanol/acetone mixtures at 50 °C to produce acetone azine in moderate yield (0.31 mol/W atom). The azine is probably formed *via* a diazoalkane complex derived from the condensation of the hydrazido(2-) complex with acetone. Details of the condensation of hydrido-hydrazido(2-) complexes with carbonyl compounds will be reported separately.[3]

Formation of ketazines from ligating dinitrogen in complexes **1** and **2** by treatment with alcohol/ketone mixtures does not proceed at room temperature but only at an elevated temperature (50 °C). However, under irradiation by mercury lamp, the complexes give ketazines very smoothly at room temperature, although the yields of ketazines are lower than those in the reactions at 50 °C and ethanol or 2-propanol does not work as the proton source instead of methanol. Addition of NaOMe slightly increases the yield of acetone azine (Table 2). In the UV irradiated reaction, a suspension of the reaction mixture gradually turns to a dark solution within about 3 h. The yields of ketazines are no longer increased after 4 h.

Experimental

All manipurations were carried out under dinitrogen using standard Schlenk tube techniques. Complexes *cis*-$[W(N_2)_2(PMe_2Ph)_4]$,[4] *trans*-$[W(N_2)_2(PPh_2Me)_4]$,[5] and $[WCl_3H(NNH_2)(PPh_2Me)_2]$[5] were prepared according to the published methods.

Reactions of Complex 2 with Methanol/Acetone Mixtures.

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† Preparation and Properties of Molybdenum and Tungsten Dinitrogen Complexes. 22.

TABLE 1. FORMATION OF ACETONE AZINE FROM *trans*-[W(N_2)$_2$(PPh_2Me)$_4$](**2**)[a]

Run	System				Yield
	Methanol	Acetone	Solvent	NaOMe	mol/W atom
	ml	ml	ml	mol/W atom	
1	5	5	—	—	0.62
2	5	5	—	—	0.74[b,c]
3	8	2	—	—	Tr.
4	2	1	Toluene, 3	—	0.64[b]
5	5	5	—	4	0
6	2	1	THF, 3	—	0.24[b]
7	2	1	THF, 3	4	0.05[b]

a) Complex **2**, 100 mg; Reaction time, 18 h; Reaction temperature, 50 °C. b) The yield of N_2H_4 after base distillation of the reaction mixture. c) 0.20 mol NH_3/W atom was also formed.

TABLE 2. FORMATION OF KETAZINES FROM *cis*-[W(N_2)$_2$(PMe_2Ph)$_4$] (**1**) AND *trans*-[W(N_2)$_2$(PPh_2Me)$_4$] (**2**) UNDER UV IRRADIATION[a]

Complex[b]	System			Yield of Ketazines
	Alcohol	Ketone	NaOMe	mol/W atom
	ml	ml	mol/W atom	
1	MeOH, 4	Acetone, 1	—	0.46
1	MeOH, 4	Acetone, 1	4	0.66
1	MeOH, 4	Diethyl ketone, 1	—	0.40
1	EtOH, 4	Acetone, 1	—	Tr.
2	MeOH, 4	Acetone, 4	—	0.17

a) Reaction temperature, r.t.; Reaction time, 4 h. b) Complex **1**, 150 mg; Complex **2**, 100 mg.

In a typical run, complex **2** (*ca.* 100 mg) was suspended in a methanol (5 ml)/acetone (5 ml) mixture under dinitrogen and stirred for 18 h at 50 °C. The orange-red suspension was gradually converted into a dark blue solution. Acetone azine produced (0.62 mol/W atom) was quantitatively analyzed by an Ohkura Model 103 Gas Chromatograph equipped with a 5 mm×2 m stainless steel column packed with PEG 6000. When methanol/acetone/toluene and methanol/acetone/THF mixtures were used, the yield of the azine was determined by measuring the amount of hydrazine obtained by base distillation of the reaction mixture.

Reaction of Complex 2 with Methanol/Acetone/NaOMe Mixtures. Complex **2** was treated with a methanol (5 ml)/acetone (5 ml) mixture in the presence of NaOMe (4 mol/W atom) for 18 h at 50 °C. A considerable amount of unreacted complex **2** was recovered from the mixture and formation of acetone azine was not observed. When THF (3 ml) was added to a methanol (2 ml)/acetone (1 ml) mixture to dissolve complex **2**, acetone azine was formed in low yield (0.05 mol/W atom), which is much lower than that without NaOMe (0.24 mol/W atom).

Reactions of Complexes 1 and 2 with Alcohol/Ketone Mixtures under UV Irradiation. Complex **1** or **2** (100—130 mg) charged in a quartz Schlenk tube was suspended in an alcohol/ketone mixture and irradiated by Ushio 500 W mercury lamp. The reaction temperature was kept at room temperature by cooling with a fan. Acetone azine and diethyl ketone azine were analyzed by GLC as described above.

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