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REDUCTION OF COORDINATED DINITROGEN IN cis-$W(N_2)_2(PMe_2Ph)_4$ BY MEANS OF ACIDIC HYDRIDOMETAL CARBONYLS, $H_2Fe(CO)_4$ AND $HFeCo_3(CO)_{12}$

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Formation of ammonia and hydrazine was quantitatively analyzed in the reaction of cis-$W(N_2)_2(PMe_2Ph)_4$ with acidic hydridometal carbonyls, $H_2Fe(CO)_4$ or $HFeCo_3(CO)_{12}$ after treatment of the products with aqueous KOH.

Hydrogenation of coordinated dinitrogen by means of acids to form ammonia and hydrazine1 - 4) has been one of the most remarkable achievements in the chemistry of nitrogen fixation.5) Studies on the reactions of transition metal hydrides with dinitrogen complexes are necessary to find a clue to catalytic systems to reduce dinitrogen under mild conditions. So far the reactions of tertiary phosphine hydrides with dinitrogen complexes resulted in only substitution reactions of the dinitrogen by hydride ligands.6, 7)

We have now found that treatment of cis-$W(N_2)_2(PMe_2Ph)_4$1) with acidic hydridometal carbonyls, $H_2Fe(CO)_4$8) and $HFeCo_3(CO)_{12}$9) gives reasonable yields of ammonia and hydrazine after decomposition of the products with 40% aqueous KOH. The reactions were carried out either in methanol or in tetrahydrofuran in dark at -20 ∿ 20 °C under hydrogen or nitrogen atmosphere. The reaction mixtures were evaporated under reduced pressure at 0 °C with a trap containing 0.1 N H_2SO_4. The contents of the trap and the residue were separately treated with 40% aqueous KOH and the products were distilled into 0.1 N H_2SO_4. Ammonia and hydrazine in each distillate were determined by colorimetric methods using indonaphtol10) and p-dimethylaminobenzaldehyde11), respectively. The table summarizes the experimental conditions and the yields of ammonia and hydrazine. The control experiments (Exp 1 and 2) in the absence of the hydride complexes indicated that the amounts of ammonia and hydrazine were very small. When sulfuric acid was used instead of the hydrides (Exp 3), the amounts of ammonia and hydrazine were comparable to those reported by Chatt et al.1)

The best yields of ammonia were 0.25 mol per W atom for $H_2Fe(CO)_4$ (Exp 9) and 0.32 mol for $HFeCo_3(CO)_{12}$ (Exp 17). The best yields of hydrazine were 0.17 mol per W atom for $H_2Fe(CO)_4$ (Exp 12) and 0.05 mol for $HFeCo_3(CO)_{12}$ (Exp 16). The hydrazine/ammonia ratio tended to be higher in shorter reaction times in the $H_2Fe(CO)_4$ experiments. The influence of hydrogen atmosphere upon the improvement of the yields was significant. However, increase of hydrogen pressure above 3 atm had adverse effects. The reaction with manganese hydridocarbonyl $HMn(CO)_5$, acidity of which is low,12) gave a little ammonia and no hydrazine (Exp 25).

The above results suggest that some acidic hydridometal carbonyls are likely to protonate ligating dinitrogen in the tungsten dinitrogen complex. The scope of the present reaction and the possibility of exploring the activation of molecular hydrogen to reduce coordinated dinitrogen are under further investigation.

Table. Yields of ammonia and hydrazine from cis-$W(N_2)_2(PMe_2Ph)_4$

Exp no.	Hydride	Fe/W mol ratio	Atmosphere[a]	Solvent	t/°C	Reaction time/h	NH_3[b]	N_2H_4[b]
1	none		$N_2(1)$	MeOH	20	20	0.01	0.01
2	none		H_2	MeOH	20	20	0	t
3	H_2SO_4		$N_2(1)$	MeOH	20	20	1.84	0.03
4	$H_2Fe(CO)_4$	30	N_2	MeOH	-10	20	0.05	0.01
5	$H_2Fe(CO)_4$	30	H_2	MeOH	-10	20	0.19	0.01
6	$H_2Fe(CO)_4$	30	N_2	THF	-10	20	0.01	0.01
7	$H_2Fe(CO)_4$	30	H_2	THF	-10	20	0.03	0.01
8	$H_2Fe(CO)_4$	2	H_2	MeOH	-10	20	t	0.01
9	$H_2Fe(CO)_4$	3	H_2	MeOH	-10	20	0.25	0.04
10	$H_2Fe(CO)_4$	6	H_2	MeOH	-10	20	0.17	0.02
11	$H_2Fe(CO)_4$	15	H_2	MeOH	-10	20	0.18	0.01
12	$H_2Fe(CO)_4$	30	H_2	MeOH	-10	1	0.10	0.17
13	$H_2Fe(CO)_4$	30	H_2	MeOH	-10	4	0.23	0.01
14	$H_2Fe(CO)_4$	30	H_2	MeOH	-10	138	0.28	0.03
15	$H_2Fe(CO)_4$	30	H_2	MeOH	-20	45	0.20	0.01
16	$HFeCo_3(CO)_{12}$	12.4	$N_2(1)$	MeOH	20	20	0.05	0.05
17	$HFeCo_3(CO)_{12}$	18.1	H_2	MeOH	20	20	0.32	0.01
18	$HFeCo_3(CO)_{12}$	1.8	H_2	MeOH	20	20	t	t
19	$HFeCo_3(CO)_{12}$	3.0	H_2	MeOH	20	20	0.06	0.01
20	$HFeCo_3(CO)_{12}$	6.4	H_2	MeOH	20	20	0.09	0.01
21	$HFeCo_3(CO)_{12}$	6.5	H_2	MeOH	20	1	0.03	t
22	$HFeCo_3(CO)_{12}$	5.5	$H_2(0.8)$	MeOH	20	20	0.09	0.01
23	$HFeCo_3(CO)_{12}$	6.0	$H_2(3)$	MeOH	20	20	0.19	0.03
24	$HFeCo_3(CO)_{12}$	5.9	$H_2(4)$	MeOH	20	20	0.04	0.02
25	$HMn(CO)_5$	9.2[c]	H_2	MeOH	-10	20	0.01	0

[a] 0.3 atm unless otherwise stated in parentheses [b] mol per W atom (sum of the amounts from the trap and residue, see text) [c] Mn/W mol ratio [t] trace (less than 0.005)

Referances

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