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PREPARATION AND PROPERTIES OF MOLYBDENUM AND TUNGSTEN DINITROGEN COMPLEXES 9. CONVERSION OF THE LIGATING DINITROGEN INTO HYDRAZINE

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The complex cis-$W(N_2)_2(PMe_2Ph)_4$ or $WBr_2(NNH_2)(PMe_2Ph)_3$ gave 0.60-0.65 mol N_2H_4/mol W upon treatment with excess of HCl gas in 1,2-dimethoxyethane. Molybdenum diazoalkane complexes $MoCl_2(NN{=}CRR')(PMe_2Ph)_3$ also afforded hydrazine as the major product in the reaction with HCl gas.

Recently Chatt et al.$^{1)}$ have extensively studied the protonation of the ligating dinitrogen in molybdenum and tungsten complexes in relevance to nitrogen fixation and found that treatment of cis-$M(N_2)_2(PMe_2Ph)_4$ and trans-$M(N_2)_2(PMePh_2)_4$ (M = Mo or W) with a variety of acids, typically H_2SO_4 in methanol, gives mainly ammonia, together with a little hydrazine for W, and not for Mo. We have now found the new reduction systems which gave hydrazine in preference to ammonia upon the protonation of the dinitrogen ligating to molybdenum and tungsten.

When excess of dry HCl gas was bubbled through the suspension of cis-$W(N_2)_2(PMe_2Ph)_4$ (I) or $WBr_2(NNH_2)(PMe_2Ph)_3$ (II) in 1,2-dimethoxyethane (DME) for about 5 min., hydrazine was formed in relatively higher yields as shown in Table 1, compared with the recent results of Chatt et al. using $WCl_3(NHNH_2)(PMePh_2)_2$.$^{1b)}$ When methanol was used as solvent instead of DME, the yield of hydrazine remarkably decreased while the yield of ammonia greatly increased. It is interesting to note that treatment of the complex (I) with excess of aqueous HCl in methanol yields the hydrazido(2-) complex $WCl_2(N_2H_2)(PMe_2Ph)_3$ without further reduction of the ligating dinitrogen.$^{2)}$

We previously developed a new method for preparing diazoalkane complexes containing the group $M\underset{\leftarrow}{=}N{-}N{=}CRR'$ by condensation of hydrazido(2-) complexes $[MF(NNH_2)(Ph_2PCH_2CH_2PPh_2)_2]BF_4$ (M = Mo or W) with aldehydes or ketones.$^{3)}$ Follwing this discovery, formation of hydrazine in a high yield has recently been found on treatment of a diazoalkane complex $\mathrm{WBr_2(NN{=}CMe_2)(PMe_2Ph)_3}$ with HBr gas in dichloromethane, which is also obtained by the similar condensation method.[4] As an extention of our studies on diazoalkane complexes, we have now prepared a new series of diazoalkane complexes of molybdenum $\mathrm{MoCl_2(NN{=}CRR')(PMe_2Ph)_3}$ (III) as shown in eq. (1). These complexes give rise to strong ν(C=N) bands in the 1525-1570 $\mathrm{cm^{-1}}$ region of the infrared spectra. The ^{1}H nmr spectra show two triplets and one doublet in an 1 : 1 : 1

$$\text{cis-Mo(N}_2)_2(\text{PMe}_2\text{Ph})_4 \xrightarrow[\text{MeOH}]{\text{aq. HCl}} \text{MoCl}_2(\text{NNH}_2)(\text{PMe}_2\text{Ph})_3 \xrightarrow[\text{CH}_2\text{Cl}_2]{\text{RR'C=O}}$$

$$\text{mer-MoCl}_2(\text{NN=CRR'})(\text{PMe}_2\text{Ph})_3 \xrightarrow[\text{CH}_2\text{Cl}_2]{\text{HCl gas}} \text{N}_2\text{H}_4 + \text{NH}_3 \qquad (1)$$

area ratio characteristic of methyl groups attached to phosphorus, indicating a meridional configuration of phosphines. As observed in the diazoalkane complexes reported previously,[3,4] the substituents R and R' are in inequivalent positions. Treatment of these complexes with HCl gas in dichloromethane yields hydrazine together with ammonia (Table 1), though the analogous diazoalkane complex of tungsten $\mathrm{WCl_2(NN{=}CMe_2)(PMe_2Ph)_3}$ is not changed by the similar treatment.[4]

Further studies are now in progress to get more information on subtle factors which determine the reduction cource of ligating dinitrogen to hydrazine or ammonia.

Table 1. Yields of $\mathrm{N_2H_4}$ and $\mathrm{NH_3}$ upon treatment with HCl gas

complex	solvent	yield (mol/mol M)	
		$\mathrm{N_2H_4}$	$\mathrm{NH_3}$
I	DME	0.63	0.22
I	MeOH	0.33	0.64
II	DME	0.64	0.05
III (R=Me,R'=Ph; ν(C=N) 1525 $\mathrm{cm^{-1}}$)	$\mathrm{CH_2Cl_2}$	0.12	0.21
III (R=Me,R'=Me; ν(C=N) 1570 $\mathrm{cm^{-1}}$)	$\mathrm{CH_2Cl_2}$	0.32	0.22

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