Diazoalkane Complexes of Molybdenum†

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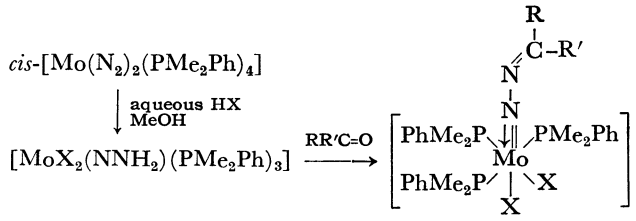
Synopsis. The hydrazido(2-) complexes $[MoX_2(NNH_2)(PMe_2Ph)_3]$ (X=Cl or Br) derived from bis(dinitrogen) complex and HX react with aldehydes or ketones to give a series of diazoalkane complexes $[MoX_2(\rightleftharpoons N-N=CRR')(PMe_2Ph)_3]$.

Extensive studies on the reactions of coordinated dinitrogen in well defined complexes to form C–N bonds have been undertaken in order to open a new chemistry of dinitrogen. Aroyl, acyl, and alkyl halides have been shown to react with the dinitrogen complexes of molybdenum and tungsten, *trans*-$[M(N_2)_2(dpe)_2]$ (M=Mo or W; dpe=$Ph_2PCH_2CH_2PPh_2$), to afford the complexes containing organo-nitrogen ligands.[1] The same reactions with the dinitrogen complexes of mono(tertiary) phosphines $[M(N_2)_2(L)_4]$ (M=Mo or W; L=PMe_2Ph or $PMePh_2$), however, released the coordinated dinitrogen as dinitrogen gas.[2] We have recently found a more versatile route to the formation of C–N bonds from coordinated dinitrogen, which involved the condensation of the hydrazido (2-) complexes $[MF(NNH_2)(dpe)_2][BF_4]$ derived from *trans*-$[M(N_2)_2(dpe)_2]$ (M=Mo or W) and HBF_4 with a variety of aldehydes or ketones (RR' C=O) to yield the diazoalkane complexes $[MF(\rightleftharpoons N-N=CRR')(dpe)_2][BF_4]$.[3] We report here preparation of diazoalkane complexes of molybdenum containing PMe_2Ph by the similar condensation reactions.

Results and Discussion

The hydrazido(2-) complexes $[MoX_2(NNH_2)(PMe_2Ph)_3]$ (X=Cl or Br) which are readily obtained from *cis*-$[Mo(N_2)_2(PMe_2Ph)_4]$ and aqueous HX in methanol[4] condense with aldehydes or ketones to give



diazoalkane complexes. The condensation reactions are markedly accelerated by catalytic amount of acids, though the reaction of aldehydes occurs smoothly even in the absence of acids. Spectroscopic data of the diazoalkane complexes are given in Table 1. These complexes give rise to strong ν(C=N) bands in the 1520—1570 cm^{-1} region of the infrared spectra. The ^{1}H-NMR spectra show two triplets and one doublet with intensity 6H each which are characteristic of virtually coupled *meridional* phosphine methyls in a complex lacking a plane of symmetry containing the phosphines. As observed in the diazoalkane complexes reported previously,[3,5] the substituents R and R' are in inequivalent positions. Thus, the complex $[MoCl_2(N_2CMe_2)(PMe_2Ph)_3]$ exhibits two singlets at 1.5 (intensity 3H) and 1.7 ppm (intensity 3H) assignable to the methyls on the nitrogen-bearing carbon.

Acetophenone readily condenses with the complexes $[MoX_2(NNH_2)(PMe_2Ph)_3]$, though it does not react with the hydrazido(2-) complexes $[MF(NNH_2)(dpe)][BF_4]$ (M=Mo or W) probably because of a steric effect.[3] In the case of acetylacetone, one of the two carbonyl groups condenses with the $MoNNH_2$ group and other remains free (ν(C=N), 1570; ν(C=O), 1720 cm^{-1}). The complex dissolved in CD_2Cl_2 shows a complicated NMR spectrum, which is interpreted in

Table 1. New diazoalkane complexes of molybdenum $[MoX_2(N_2CRR')(PMe_2Ph)_3]$

X	R	R'	Yield (%)	Analytical data[a] C	H	N	ν(C=N) (cm^{-1})	NMR (alkyl region) (ppm)
Cl	Ph	H	41	53.04 (53.23)	5.79 (5.63)	3.83 (4.01)	1530	
Cl	Me	Me	42	50.06 (49.78)	6.50 (6.05)	4.26 (4.30)	1570	1.5s(3H), 1.7s(3H)
Cl	$(CH_2)_5$		90	52.36 (52.10)	6.67 (6.28)	4.29 (4.05)	1560	1.4—2.4m(10H)
Br	$(CH_2)_5$		71	46.74 (46.17)	5.95 (5.56)	3.96 (3.59)	1555	1.3—2.3m(10H)
Cl	Me	Ph	71	53.41 (53.86)	6.15 (5.80)	3.39 (3.93)	1525	2.1s(3H)
Br	Me	Ph	86	47.86 (47.90)	5.38 (5.16)	3.49 (3.49)	1520	1.9s(3H)
Cl	Me	CH_2COMe	45	50.12 (51.41)	6.14 (6.11)	4.18 (4.14)	1570	

a) Calculated values are in parenthesis. b) Methyl protons of PMe_2Ph are omitted. s=singlet, m=multiplet.

† Preparation and Properties of Molybdenum and Tungsten Dinitrogen Complexes.12.

terms of an equilibrium between keto and enol forms ($C\underline{H}_3CO$–, $C\underline{H}_3C(OH)$=, $C\underline{H}_3CN$–, 1.9—2.2; –$C\underline{H}$=C(OH)–, 4.8; –$C\underline{H}_2COCH_3$, 3.3 ppm). Chatt and Hidai *et al.*[5] have recently shown that diazoalkane complexes of tungsten containing PMe_2Ph are prepared by the similar condensation reactions and treatment of the complex $[WBr_2(N_2CMe_2)(PMe_2Ph)_3]$ with HBr gas in CH_2Cl_2 yields hydrazine and acetone azine in moderate yields. On the other hand, when the diazoalkane complex of molybdenum $[MoCl_2(N_2CMe_2)(PMe_2Ph)_3]$ are treated with an excess of HCl gas in CH_2Cl_2, 0.22 mol of ammonia and 0.32 mol of hydrazine per metal atom are formed, together with a trace of acetone azine.[6]

Experimental

All reactions were carried out under dry dinitrogen using standard Schlenk-tube techniques. The complexes *cis*-$[Mo(N_2)_2(PMe_2Ph)_4]$ and $[MoX_2(NNH_2)(PMe_2Ph)_3]$ (X= Cl or Br) were prepared by published methods.[4] Analytical data of the diazoalkane complexes of molybdenum are shown in Table 1.

Preparation of $[MoCl_2(N_2CHPh)(PMe_2Ph)_3]$. To a suspension of $[MoCl_2(NNH_2)(PMe_2Ph)_3]$ (183 mg, 0.300 mmol) in CH_2Cl_2 (3 ml) was added benzaldehyde (121 μl, 1.20 mmol) at room temperature. After stirring for several minutes, a greenish-brown homogeneous solution was produced. After a further 6 h, hexane (3 ml) was added to the solution to give greenish-brown crystals, which were filtered off, washed with ether, and then dried *in vacuo* (86 mg, yield 41%).

Preparation of $[MoCl_2\{N_2C(CH_2)_5\}(PMe_2Ph)_3]$. To a suspension of $[MoCl_2(NNH_2)(PMe_2Ph)_3]$ (212 mg, 0.347 mmol) in CH_2Cl_2 (3 ml) was added cyclohexanone (0.29 ml, 2.8 mmol) and one drop of concentrated (*ca.* 35%) hydrochloric acid. A red homogeneous solution was immediately obtained. After stirring for 15 min, the volume was reduced *in vacuo* to *ca.* 1 ml and hexane (4 ml) was added. Red needles precipitated from the solution, which were filtered off, washed with ether, and dried *in vacuo* (215 mg, yield 90%).

In similar fashion were prepared $[MoBr_2\{N_2C(CH_2)_5\}(PMe_2Ph)_3]$, $[MoCl_2(N_2CMePh)(PMe_2Ph)_3]$, $[MoBr_2(N_2CMePh)(PMe_2Ph)_3]$, $[MoCl_2(N_2CMe_2)(PMe_2Ph)_3]$, and $[MoCl_2\{N_2CMe(CH_2COMe)\}(PMe_2Ph)_3]$.

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