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Reactions of Coordinated Dinitrogen. 10 [1]. N-alkylation of the Alkyldiazenido Complexes of Molybdenum

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The recent report [2] of the secondary alkylation of dinitrogen complexes of molybdenum and tungsten prompted us to report our findings in this area [3]. We were encouraged to look for a systematic alkylation of the alkyldiazenido ligand (equation 1; X = Br or I; R and R′ = alkyl, dppe = $Ph_2PCH_2CH_2PPh_2$)

$$MoX(NNR)(dppe)_2 + R'X \longrightarrow [MoX(NNRR')(dppe)_2]X \quad (1)$$

($Ph_2PCH_2CH_2PPh_2$) by three pieces of information. (1) The apparent anomalous formation of $[WBr(NNMe_2)(dppe)_2]Br$ from the reaction of methyl bromide and $W(N_2)_2(dppe)_2$ [4]. (2) The cyclization of 1,4-dibromobutane, for example, upon reaction with $Mo(N_2)_2(dppe)_2$ to form $[MoBr(N\overline{NCH_2CH_2CH_2CH_2})(dppe)_2]Br$ [5]. (3) The analogous cyclization of 1-bromo-4-chlorobutane to form $[MoBr(N\overline{NCH_2CH_2CH_2CH_2})(dppe)_2]Cl$ in which the bromide ion is coordinated to molybdenum while chloride ion is the outer sphere ion [6]. This latter clearly occurs in two steps. Firstly alkylation of coordinated dinitrogen by the alkyl bromide end of the molecule (equation 2) occurs. Secondly, an intramolecular alkylation of the

$$Mo(N_2)_2(dppe)_2 + Br(CH_2)_4Cl \longrightarrow MoBr(NNCH_2CH_2CH_2CH_2Cl)(dppe)_2 + N_2 \quad (2)$$

$$\underset{A}{MoBr(NNCH_2CH_2CH_2CH_2Cl)(dppe)_2} \longrightarrow \underset{B}{[MoBr(N\overline{NCH_2CH_2CH_2CH_2})(dppe)_2]Cl} \quad (3)$$

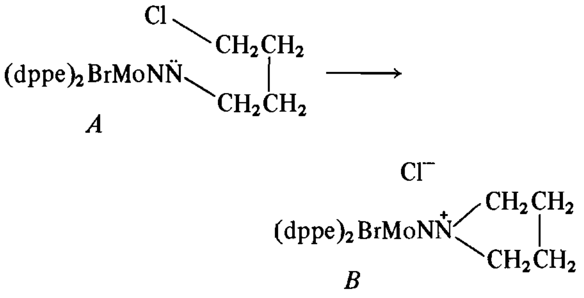
carbon-bound nitrogen atom occurs which involves cleavage of the carbon–chlorine bond. Whatever the mechanism of this second substitution reaction (free radical, S_N2, *etc.*), an alkyl bromide or alkyl iodide should react more readily in this step. It was at this point that we began to look at the reactions of alkyl bromides and alkyl iodides with $MoBr(NNBu)(dppe)_2$, *1*, as a general route to dialkylhydrazido complexes.

At *ca.* 0 °C, methyl fluorosulfonate reacts rapidly with *1* in benzene solution to form $[MoBr(NNMeBu^n)(dppe)_2]SO_3F$ in 97% yield. The reaction of methyl iodide with *1* in the absence of solvent at room temperature produced the same complex cation although in significantly lower yield. The ^1H NMR spectra confirmed the presence of the nitrogen-bound methyl group [δ (NCH_3) 1.47 ppm ($CDCl_3$ solution)] and the ^{31}P NMR spectra showed one singlet [42.6 ppm relative to 85% H_3PO_4] indicating that the two dppe ligands are occupying the four equitorial sites within the coordination sphere.

Primary alkyl bromides (*e.g.*, 6-bromo-1-hexene) did not react with *1* at room temperature. However, when heated together at 60 °C in the absence of solvent secondary alkylation occurred although significant decomposition was observed with the formation of phosphonium salts. Allyl bromide reacted under similar conditions to afford $[MoBr(NNBu(C_3H_5))(dppe)_2]Br$.

Heating mixtures of *1* and secondary alkyl bromides resulted in the formation of the butylhydrazido complex $[MoBr(NNHBu)(dppe)_2]Br$ [7]. This product arises from *1* behaving as a base causing elimination rather than substitution to occur.

n-Butyl and t-butyl chloride showed no evidence of reaction with *1*. It seems clear that the facile cyclization of *A* to form *B* is the result of anchiomeric assistance with the transition state being stabilized by the



chelating effect of the five membered ring. The presence of the eight phenyl groups of the two dppe ligands causes considerable steric hindrance towards secondary alkylation. This can be demonstrated by comparing the reactions of $Mo(N_2)_2(dppe)_2$ and $Mo(N_2)_2(Et_2PCH_2CH_2PEt_2)_2$ with methyl bromide. Under similar conditions, the former complex produces the methyldiazenido complex, $MoBr(NNMe)(dppe)_2$ whereas the latter directly forms the dimethylhydrazido complex, $[\mathrm{MoBr(NNMe_2)(Et_2PCH_2CH_2PEt_2)_2]Br}$ [1]. However, the dramatic effect of anchiomeric assistance is demonstrated by the rapid cyclization of 1,4-dibromopentane with *1* to form $[\mathrm{MoBr(N\overline{NCH(CH_3)CH_2CH_2CH_2})(ddpe)_2]Br}$* [6] in which both a primary and secondary carbon atom are attached to nitrogen even when two dppe ligands are present.

Systematic alkylation of the alkydiazenido ligand in the types of complexes discussed above is limited by the steric bulk of the dppe ligands. Further work in this area requires use of less bulky phosphine ligands.

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*This complex was treated with $\mathrm{NaBF_4}$ and analyzed as the $\mathrm{BF_4^-}$ salt. *Anal.* Calcd for $\mathrm{C_{57}H_{58}BBrF_4MoN_2P_4}$: C, 59.14; H, 5.05; N, 2.41; Br, 6.90. Found C, 58.59; H, 5.27; N, 2.39; Br, 6.32.