# Preparation of Stable Imido(Nitrene)-complexes of Molybdenum and their Conversion into Nitrido-complexes

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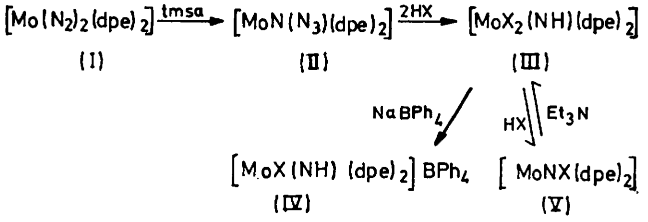
*Summary* The reaction of $[Mo(N_2)_2(dpe)_2]$ (dpe = $Ph_2PCH_2CH_2PPh_2$) with trimethylsilyl azide gives the azido-nitrido-complex, $[MoN(N_3)(dpe)_2]$, which is converted by hydrohalic acids HX (X = Cl or Br) to the imido(nitrene)-complexes, $[Mo(NH)X_2(dpe)_2]$; these, on treatment with base, give the nitrido-complexes, $[MoNX(dpe)_2]$ which revert to the imido-complexes on treatment with acid.

The imido or nitrene ligand NH† has been postulated in the formulation of some polynuclear complexes of uncertain structure, prepared in liquid ammonia;[1] in these it is thought to be a bridging ligand. As a terminal ligand it is known only as an unstable intermediate in certain inorganic reactions.[2] We now report the preparation of well-defined mononuclear NH complexes by the protonation of molybdenum(IV) nitrido-complexes, prepared by the reaction of trimethylsilyl azide (tmsa) with *trans*-$[Mo(N_2)_2(dpe)_2]$ according to the Scheme. Previously we have prepared molybdenum(V) and (VI) nitrido-complexes by the action of tmsa on molybdenum(IV) halido-complexes with



Scheme

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† Although the species NH is often known as 'nitrene,' IUPAC recommends the name 'imido' for the ligand NH, and 'aminylene' for the diradical NH. Here we use 'imido' which arbitrarily assigns to the metal, a formal oxidation state two units higher than would the 'nitrene' notation. The diamagnetism is consistent with either formal oxidation state, but the absolute charge on the metal will probably lie about half-way between that corresponding to the two formal oxidation states represented by compounds $[MoCl_2(dpe)_2]$ and $[MoCl_4(PMe_2Ph)_2]$.

elimination of trimethylsilyl chloride and dinitrogen.[3] Our new preparative reaction must clearly follow a different course, which we have not yet elucidated.

The reaction of tmsa with the dinitrogen complex [Mo(N$_2$)$_2$(dpe)$_2$] (I) in refluxing tetrahydrofuran or acetonitrile gives an azido-nitrido-complex, [MoN(N$_3$)(dpe)$_2$] (II) in 45—50% yield with evolution of 3·3 moles of dinitrogen. The complex (II) is an air-stable monomeric diamagnetic crystalline solid with $\nu$(Mo$\equiv$N) at 980 cm$^{-1}$ and $\nu$(N$_3$) at 2040 cm$^{-1}$. $^{31}$P n.m.r. spectra suggest the same *trans* configuration as the complex (I). The monomeric imido-complexes [MoX$_2$(NH)(dpe)$_2$] (III) were obtained in 80—90% yield as air-stable pinkish-purple solids by the addition at 20 °C of an excess of concentrated aqueous HX(X = Cl or Br) to a methanolic suspension of (II). One halide ion is abstracted from (III) by sodium tetraphenylborate in methanol to give the purple salt, [Mo(NH)X(dpe)$_2$]-BPh$_4$ (IV). The complexes (III) and (IV) are diamagnetic, but show no $^1$H n.m.r. resonance assignable to the imido-proton even in dry solvents. However, $\nu$(N–H) appears as a weak band in their i.r. spectra in the region 3300—3400 cm$^{-1}$; these bands are shifted appropriately on deuteriation of the NH by MeOD.

Deprotonation of the complexes (III) with triethylamine in acetonitrile at 20 °C gives the novel molybdenum (IV) nitrido-complexes [MoNX(dpe)$_2$] (V) in 80—90% yield. These are yellow crystalline substances with $\nu$(Mo$\equiv$N) at about 980 cm$^{-1}$. Treatment of the complexes (V) with an excess of dichlorine *in vacuo* liberates 90—95% of the nitride ligand as dinitrogen. Acids react with the complexes (V) to regenerate the imido-complexes.

There is a striking parallel between the reactions of the nitrido and bis dinitrogen complexes with acid in methanol at 20 °C. Those complexes which contain two molecules of dpe produce complexes of the protonated nitrogen ligands NH (as above) and N$_2$H$_2$[4] respectively, but no ammonia. However those, such as [MoCl$_3$N(OPPh$_3$)$_2$][5] [MoCl$_2$N(PMePh$_2$)$_2$][5] and [Mo(N$_2$)$_2$(PMe$_2$Ph)$_4$],[6] which contain only monodentate ligands produce ammonia rapidly.

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