The Use of $(Me_3Si)_2NN(SiMe_3)_2$ as a Reagent for the Synthesis of μ-Dinitrogen Complexes or as a Homogeneous One-electron Reducing Agent

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The reaction of $NbCl_5$ with $(Me_3Si)_2NN(SiMe_3)_2$, in the presence of tetrahydrofuran (thf) gives high yields (*ca.* 80%) of $[\{NbCl_3(thf)_2\}_2N_2]$ (A); (A), or its tantalum analogue, reacts with $Me_3SiS_2CNEt_2$ to give a high yield of the dinitrogen complexes with exclusively sulphur co-ligands $[\{M(S_2CNEt_2)_3\}_2N_2]$ (M = Nb or Ta), and reaction of $[MoCl_4L_2]$ (L = MeCN or thf) with $(Me_3Si)_2NN(SiMe_3)_2$ gives $[MoCl_3L_3]$ in high yield, together with N_2.

The recently reported indirect synthesis[1] of the unique 'diimido-like' bridged dinitrogen complexes of niobium and tantalum $[\{MCl_3(thf)_2\}_2N_2]$ (thf = tetrahydrofuran) (M = Nb or Ta) (A) involves several steps, and the intermediacy of alkylidene complexes, which in the case of niobium are thermally unstable. We here report the high yield (*ca.* 80%) one-step synthesis of $[\{NbCl_3(thf)_2\}_2N_2]$ by the stoicheiometric reaction of $NbCl_5$ with $(Me_3Si)_2NN(SiMe_3)_2$[2] and thf in dichloromethane. The analogous reaction with $TaCl_5$ gives an, as yet, uncharacterised product containing N–$SiMe_3$ groups. Compounds (A) (M = Nb or Ta) are key intermediates for the preparation of a wide range of bridged dinitrogen complexes of niobium and tantalum derived by ligand metathesis.[1]

Treatment of (A) (M = Nb or Ta) with an excess of trimethylsilyl diethyldithiocarbamate, $Me_3SiS_2CNEt_2$, in dichloromethane yields the first examples of dinitrogen complexes in which the co-ligands are exclusively sulphur donors $[\{M(S_2CNEt_2)_3\}_2N_2]$ (B) as brown (M = Nb) or orange (M = Ta) microcrystalline materials. Appropriate elemental analyses were obtained and the complexes react with an excess of hydrohalic acids in thf to give quantitative yields of hydrazine. A medium intensity i.r. band at *ca.* 850 cm^{-1} is assigned to ν(NN), as is found in complexes (A).[1] The ^1H n.m.r. spectra indicate that the complexes are fluxional at ambient temperature, consisting of a simple triplet and quartet for all the S_2CNEt_2 ligands. This behaviour is identical to that observed with the analogous $[M(NR)(S_2CNEt_2)_3]$ (R = alkyl) and $[M(NNMe_2)(S_2CNEt_2)_3]$ reported recently.[3]

The reaction of other silylated hydrazines and amines with MCl_5 has been exploited to yield hydrazido(2−)- and imido-complexes respectively, as shown in equations (1) and (2) (L = thf or tertiary phosphine; R = Ph or Me_3Si). Tris(trimethylsilyl)amine eliminates only two Me_3Si groups to give a trimethylsilylimido-complex [equation (3)].

$$[\{MCl_3(thf)_2\}_2N_2]$$

(A)

$$MCl_5 + (Me_3Si)_2NNMe_2 \xrightarrow{L} [MCl_3(NNMe_2)L_2] + 2Me_3SiCl \quad (1)$$

$$MCl_5 + (Me_3Si)_2NR \xrightarrow{L} [MCl_3(NR)L_2] + 2Me_3SiCl \quad (2)$$

$$MCl_5 + (MeSi)_3N \xrightarrow{L} [MCl_3(NSiMe_3)L_2] + 2Me_3SiCl \quad (3)$$

By contrast the complexes $[MoCl_4L_2]$ (L = MeCN or thf) react with $(Me_3Si)_2NN(SiMe_3)_2$ to give $[MoCl_3L_3]$ in high yield together with dinitrogen and Me_3SiCl in the stoicheiometry represented by equation (4). The reaction may proceed *via* an unstable bridged $Me_3SiNNSiMe_3$ complex or *via* an unstable μ^4-N_2 complex $[(L_2Cl_3Mo)_2NN(MoCl_3L_2)_2]$. Analogously WCl_6 in CH_2Cl_2 is reduced to WCl_5 and $WOCl_4$ in MeCN to $[WOCl_3(MeCN)_2]$ in excellent yields. Since the only other products are Me_3SiCl and N_2 this is a particularly clean way to effect such reductions.

$$4[MoCl_4L_2] + (Me_3Si)_2NN(SiMe_3)_2 \xrightarrow{L} 4[MoCl_3L_3] + 4Me_3SiCl + N_2 \quad (4)$$

Despite the dependence of the reaction products on the metal ion involved these represent extremely convenient synthetic routes to these complexes. We are currently investigating the potential of $(Me_3Sn)_2NN(SnMe_3)_2$, where the comparative weakness of the Sn–N bond should facilitate the reactions described above.

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