

The Use of $(\text{Me}_3\text{Si})_2\text{NN}(\text{SiMe}_3)_2$ as a Reagent for the Synthesis of μ -Dinitrogen Complexes or as a Homogeneous One-electron Reducing Agent

Jonathan R. Dilworth,^a Stephen J. Harrison,^a Richard A. Henderson,^a and David R. M. Walton^b

^a A.R.C. Unit of Nitrogen Fixation, University of Sussex, Brighton BN1 9RQ, U.K.

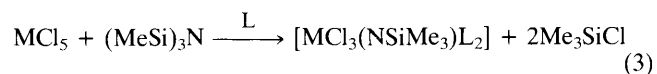
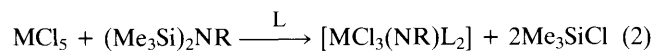
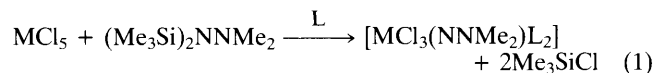
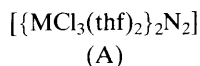
^b School of Chemical and Molecular Sciences, University of Sussex, Brighton BN1 9QJ, U.K.

The reaction of NbCl_5 with $(\text{Me}_3\text{Si})_2\text{NN}(\text{SiMe}_3)_2$, in the presence of tetrahydrofuran (thf) gives high yields (ca. 80%) of $[\{\text{NbCl}_3(\text{thf})_2\}_2\text{N}_2]$ (A); (A), or its tantalum analogue, reacts with $\text{Me}_3\text{SiS}_2\text{CNEt}_2$ to give a high yield of the dinitrogen complexes with exclusively sulphur co-ligands $[\{\text{M}(\text{S}_2\text{CNEt}_2)_3\}_2\text{N}_2]$ (M = Nb or Ta), and reaction of $[\text{MoCl}_4\text{L}_2]$ (L = MeCN or thf) with $(\text{Me}_3\text{Si})_2\text{NN}(\text{SiMe}_3)_2$ gives $[\text{MoCl}_3\text{L}_3]$ in high yield, together with N_2 .

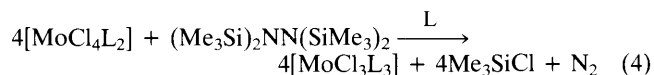
The recently reported indirect synthesis¹ of the unique 'diimido-like' bridged dinitrogen complexes of niobium and tantalum $[\{\text{MCl}_3(\text{thf})_2\}_2\text{N}_2]$ (thf = tetrahydrofuran) (M = Nb or Ta) (A) involves several steps, and the intermediacy of alkylidene complexes, which in the case of niobium are thermally unstable. We here report the high yield (ca. 80%) one-step synthesis of $[\{\text{NbCl}_3(\text{thf})_2\}_2\text{N}_2]$ by the stoichiometric reaction of NbCl_5 with $(\text{Me}_3\text{Si})_2\text{NN}(\text{SiMe}_3)_2$ and thf in dichloromethane. The analogous reaction with TaCl_5 gives an, as yet, uncharacterised product containing N-SiMe₃ 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, $\text{Me}_3\text{SiS}_2\text{CNEt}_2$, in dichloromethane yields the first examples of dinitrogen complexes in which the co-ligands are exclusively sulphur donors [$\{\text{M}(\text{S}_2\text{CNEt}_2)_3\}_2\text{N}_2$] (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 $\nu(\text{NN})$, 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 $[\text{M}(\text{NR})(\text{S}_2\text{CNEt}_2)_3]$ (R = alkyl) and $[\text{M}(\text{NNMe}_2)(\text{S}_2\text{CNEt}_2)_3]$ 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)].



By contrast the complexes $[\text{MoCl}_4\text{L}_2]$ (L = MeCN or thf) react with $(\text{Me}_3\text{Si})_2\text{NN}(\text{SiMe}_3)_2$ to give $[\text{MoCl}_3\text{L}_3]$ in high yield together with dinitrogen and Me_3SiCl in the stoichiometry represented by equation (4). The reaction may proceed *via* an unstable bridged $\text{Me}_3\text{SiNNSiMe}_3$ complex or *via* an unstable $\mu^4\text{-N}_2$ complex $[(\text{L}_2\text{Cl}_3\text{Mo})_2\text{NN}(\text{MoCl}_3\text{L}_2)_2]$. Analogously WCl_6 in CH_2Cl_2 is reduced to WCl_5 and WOCl_4 in MeCN to $[\text{WOCl}_3(\text{MeCN})_2]$ in excellent yields. Since the only other products are Me_3SiCl and N_2 this is a particularly clean way to effect such reductions.



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 $(\text{Me}_3\text{Sn})_2\text{NN}(\text{SnMe}_3)_2$, where the comparative weakness of the Sn-N bond should facilitate the reactions described above.

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References

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