

The Preparation of Mono- and Di-nuclear Dinitrogen Complexes of Molybdenum(I), and New Routes to *trans*-[Mo(N₂)₂(Ph₂PCH₂CH₂PPh₂)₂]

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Summary Mononuclear dinitrogen complexes of uni- and zero-valent molybdenum and a dinuclear species with very low $\nu(\text{N}\equiv\text{N})$ have been prepared from novel precursors.

MONONUCLEAR dinitrogen complexes of molybdenum have been reported,^{1,2} but few experimental details are available.

During a study of phosphine-substituted chloromolybdenum complexes^{3,4} we found new routes to the complex Mo(N₂)₂(diphos)₂ and prepared a new mononuclear dinitrogen complex which we formulate as MoCl(N₂)(diphos)₂ (diphos = Ph₂PCH₂CH₂PPh₂).

Reduction of MoOCl₂(diphos) (I)⁴ with LiAlH₄ in tetrahydrofuran (THF) yields the green complex MoOCl₂(diphos)(THF) (II) which deteriorates on attempted purification and is best prepared and used *in situ*. Further reduction of (II) with zinc dust under N₂ in the presence of an excess of phosphine yields a mixture of products (III) and (IV) (in variable proportions). Both are air-stable and exhibit very strong bands in the $\nu(\text{N}\equiv\text{N})$ region: yellow (III) [(Nujol) 2030vw, 1970vs, 1950sh, (CH₂Cl₂) 1975 cm⁻¹] and orange (IV) [(Nujol) 2035vw, 1985vs, (CHCl₃) 1973 cm⁻¹].

We have prepared (IV) alone by reduction of MoCl₃(diphos)₂ or MoCl₂(diphos)₂³ with 2% Na/Hg in tetrahydrofuran, and the product is apparently identical to *trans*-[Mo(N₂)₂(diphos)₂] reported earlier,² although the i.r. frequencies assigned to $\nu(\text{N}\equiv\text{N})$ differ slightly from the quoted values. We found it difficult to repeat the literature preparation from Mo(acac)₃ (acac = acetylacetonate).

We formulate the yellow product (III) as MoCl(N₂)(diphos)₂. Best yields of (III) are obtained by reduction of MoOCl₂(diphos)(THF) with zinc dust (Mo : Zn ratio = 1 : 2) in tetrahydrofuran for 20 h in the presence of nitrogen. However, nitrogen analyses tend to be low. Thus, a sample shown to be pure by i.r. methods has a lower nitrogen content than that expected for MoCl(N₂)(diphos)₂. Samples which give the required nitrogen content for (III) always show a shoulder at 1985 cm⁻¹ in the i.r. spectrum attributable to small amounts of (IV). A longer reduction period or use of an excess of zinc results in further reduction to (IV). Analogous compounds have also been obtained using *cis*-Ph₂PCH=CHPPh₂ as ligand.

We have also studied the reaction of the co-ordinated dinitrogen of (III) and (IV) with high-valent transition-metal species. MoCl(N₂)(diphos)₂ reacts with MoCl₄(THF)₂ (1 : 1 ratio) in tetrahydrofuran to give a blue solid with greatly reduced $\nu(\text{N}\equiv\text{N})$ [(Nujol) 1770, 1720 cm⁻¹]. Mo(N₂)₂(diphos)₂ loses its co-ordinated dinitrogen on similar treatment. The blue product appears to be analogous to the species obtained by Chatt *et al.*^{5,6} with a rhenium dinitrogen complex and formulated as dinitrogen-bridged dinuclear complexes.

The dual role of molybdenum, which when present in different oxidation states can thus markedly affect the N-N bond strength, again poses the question as to the precise roles of molybdenum and iron in the nitrogen-fixing enzyme.

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