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Preliminary communication

Bisdinitrogen complexes of molybdenum[1]

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Because the exact role of molybdenum and iron in nitrogenase is not known, there is great interest in the preparation of dinitrogen complexes of molybdenum. A few dinitrogen complexes of molybdenum have been reported. Reduction of Mo^{III}-acetylacetonate with triisobutylaluminum in the presence of phosphines under a nitrogen atmosphere yielded *trans*-$Mo(N_2)_2(diphos)_2$ where diphos is bis(diphenylphosphino)ethane[2] and $Mo(N_2)(PPh_3)_2(C_6H_{10})$[3]. No dinitrogen compounds were obtained with the phosphines tri-n-butylphosphine or diphenylethylphosphine[3]. The unusual $Mo(N_2)Cl(diphos)_2$ and the known $Mo(N_2)_2(diphos)_2$ have been synthesised by the reduction of phosphine substituted oxychloromolybdenum complexes[4]. The preparation of $Mo(N_2)_2(diphos)_2$ and *trans*-$Mo(N_2)_2(Ph_2PCH{=}CHPPh_2)_2$ by reduction of $MoCl_3(THF)_3$ has been reported[5]. The same reaction with PMe_2Ph gave evidence of a dinitrogen complex in the reaction solution but no pure dinitrogen complex was isolated. There is evidence that species containing molybdenum and bridged dinitrogen are formed between $ReCl(N_2)(PMe_2Ph)_4$ and $MoCl_4L_2$ where $L = Et_2O$, THF, PR_3 as well as between $MoCl(N_2)(diphos)_2$ and $MoCl_4(THF)_2$ [4,6].

We have prepared two new dinitrogen complexes of molybdenum of the type $Mo(N_2)_2L_4$ where L is a monodentate phosphine ligand. The bisdinitrogen compounds have been obtained by the reduction of $MoCl_4(PR_3)_2$ with sodium amalgam, in tetrahydrofuran, in the presence of two equivalents of PR_3, and under a stream of nitrogen. Crystalline products $Mo(N_2)_2L_4$ have been obtained where L is PPh_2Me and PMe_2Ph and L_2 is diphos. The diphos complex $Mo(N_2)_2(diphos)_2$ appears to be the previously reported *trans* compound. No dinitrogen compounds were obtained using triphenylphosphine or triphenylarsine, but with tri-n-butylphosphine an oil, which has strong IR bands in the $\nu(N_2)$ region, was obtained. A critical aspect of these preparations is the starting material. The reduction of $MoCl_4(RCN)_2$ with four equivalents of phosphine ligand did not give satisfactory results. Presence of excess monodentate ligand gave decreased yields and led to mixtures that were difficult to purify.

In a typical preparation $MoCl_4(PMe_2Ph)_2$ (1.9 mmol) was added to 30 ml of tetrahydrofuran containing 50 g of 1% sodium amalgam and PMe_2Ph (3.8 mmol). The mixture was stirred for 8 hours with nitrogen bubbling through the solution. The brown solution was poured from the amalgam and filtered. Tetrahydrofuran was removed under vacuum at room temperature. The oily solid was dissolved in benzene, and a yellow-brown powder was obtained upon addition of heptane and cooling to 0°. Crystallization from diethyl ether yielded the yellow crystalline $Mo(N_2)_2(PMe_2Ph)_4$ (0.2 g; 15% yield). The compounds $Mo(N_2)_2(diphos)_2$ (45% yield) and $Mo(N_2)_2(PPh_2Me)_4$ (41% yield) were prepared in a similar manner, but were isolated by removal of tetrahydrofuran followed by a single crystallization from benzene/methanol. All solvents were deaereated and manipulations carried out under nitrogen.

TABLE 1

DINITROGEN COMPLEXES AND THEIR IR SPECTRA IN THE N_2 REGION

A satisfactory analysis was obtained on solid complexes.

	phase	$\nu(N_2)$ cm^{-1}	m.p. [a] (°C)
trans-$Mo(N_2)_2(diphos)_2$	C_6H_6	1979s	165 (dec.)
trans-$Mo(N_2)_2(PPh_2Me)_4$	C_6H_6,CsBr	1926s	105–110 (dec.)
cis-$Mo(N_2)_2(PMe_2Ph)_4$	C_6H_6,CsBr	2010s, 1937s	110–120 (dec.)
$Mo(N_2)_2(P\text{-}n\text{-}Bu_3)_4$ [b]	film	2065m, 1980s, 1940m	

[a] Sealed tube, uncorrected. [b] Not obtained pure.

The two new compounds $Mo(N_2)_2(PMe_2Ph)_4$ and $Mo(N_2)_2(PPh_2Me)_4$ are stable as solids for several days in air, but decompose readily in solution. IR data for $\nu(N_2)$ are given in Table 1. The orange $Mo(N_2)_2(PPh_2Me)_4$ (Anal: C, 64.22; H, 5.35; Mo, 9.92. Calc: C, 64.19; H, 5.10; Mo, 9.83%) has one strong band at 1926 cm^{-1} attributable to N_2, and we conclude that it has a *trans* configuration similar to the diphos complex. The yellow $Mo(N_2)_2(PMe_2Ph)_4$ (Anal: C, 53.01; H, 6.38; Mo, 13.32. Calc: C, 53.04; H, 6.13; Mo, 13.24%) has two very strong bands, which suggest that it is the first isolated *cis* dinitrogen complex of molybdenum and appears to be analogous to the tungsten compound, *cis*-$W(N_2)_2(PPhMe_2)_4$ [7]. The $\nu(N_2)$ frequencies of the molybdenum complexes are at slightly higher frequency than those reported for the tungsten compounds, which may indicate a weaker metal dinitrogen bond for the molybdenum complexes. The PMR of the *cis*-molybdenum complex in benzene gave a complicated spectra in the methyl proton region. A doublet is centered at τ8.77 with J(PH) 13 Hz and a quartet at τ8.58 with J(PH) 5.7 Hz.

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