Formation of η^6-Pyridine Complexes of Molybdenum(0) by a σ to π Rearrangement in $Mo(N_2)_2(NC_5H_4\text{-}4\text{-}R)(PMePh_2)_3$, R=H, Me

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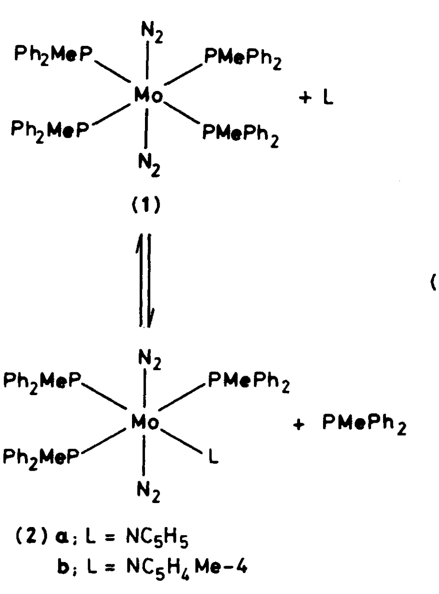
The new complexes *trans,mer*-$Mo(N_2)_2(NC_5H_4\text{-}4\text{-}R)(PMePh_2)_3$, R=H, Me lose dinitrogen *in vacuo* at 25 °C in arene solvents to give $Mo(\eta^6\text{-}NC_5H_4R)(PMePh_2)_3$, the first stable η^6-pyridine complexes of molybdenum.

Pyridine readily forms σ-bonded complexes of zerovalent group 6 metals such as $M(CO)_3(NC_5H_5)_3$, M=Cr, Mo, and W, but the only π-complex so far reported is $Cr(\eta^6\text{-}NC_5H_5)(PF_3)_3$.[1,2] We have found that the electron-rich fragment $Mo(PMePh_2)_3$ generated by magnesium reduction of solutions of $MoCl_5$ and $PMePh_2$ or by decomposition *in vacuo* of *trans*-$Mo(N_2)_2(PMePh_2)_4$ (**1**) has a high affinity for six-electron π ligands[3] and as reported here allows the stabilization of the η^6-pyridine ligand on molybdenum.

The precursors to the π-complexes are the new bis-dinitrogen compounds *trans,mer*-$Mo(N_2)_2(L)(PMePh_2)_3$ (**2a**) and (**2b**) which form rapidly as in equilibrium (1). The equilibrium constants from ^{31}P n.m.r. studies of tetrahydrofuran (THF) solutions at 30 °C are 4 for (**2a**) and 7 for (**2b**) but only (**1**) can be precipitated from these mixtures. However the complexes of general formula (**2**) were isolated as purple solids; (**2a**), 50%, (**2b**), 30% yield, contaminated with (**1**) (5—10%) by stirring a suspension of the dinitrogen complex (**1**) with a five-fold excess of ligand L in pentane under N_2 at 25 °C for 24 h. Complexes containing the nitrogen donors *N*-methylimidazole and 3-picoline can also be isolated. THF solutions of (**2**) which are stable under N_2 for one week at 25 °C gave one i.r. band due to *trans*-dinitrogen ligands at 1914 cm^{-1} for both complexes and ^{31}P n.m.r. resonances consistent with *mer*-phosphine ligands (Table 1). Similar complexes of tungsten have been prepared.[4] Reaction (1) is a rare example of a ligand substitution reaction in a molybdenum dinitrogen complex where the dinitrogen ligands are retained.[5]

Purple benzene or toluene solutions of the dinitrogen complexes (**2**) are unstable *in vacuo* at 25 °C (reaction 2) and during 78 h they turned brown and deposited red-brown precipitates. Recrystallization of the precipitates from THF–MeOH gave thermally stable, slightly oxygen sensitive red crystals of the π-complexes $Mo(\eta^6\text{-}NC_5H_4\text{-}4\text{-}R)(PMePh_2)_3$, (**3a**) (40%) and (**3b**) (40%). The complexes were analytically pure and displayed single peaks in their ^{31}P n.m.r. spectra (Table 1) with chemical shifts near to the value of 33.9 p.p.m. observed for the phosphorus atoms σ-bonded to the molybdenum in $Mo(\eta^6\text{-}C_6H_5PMePh)(PMePh_2)_3$.[3] The proton resonances of the π-pyridine ligands in compounds (**3**) were shifted upfield by 1.9—2.5 p.p.m. from corresponding resonances of the σ-bonded ligands in (**2**) (Table 1).



Resonances due to (**3**) were the only product peaks observable in the ^{31}P spectra of solutions from reaction (2) even though small amounts of a brown, unidentified material were formed as a side product that lowers the yield. There was no evidence for π-complexation of the arene solvents in reaction (2) to give known η^6-benzene or toluene complexes[6] and this suggests that the pyridine ligands remain co-ordinated throughout the reactions. Reaction (2) represents a lower temperature route to π-heterocycle complexes than similar reactions that involve the loss of two carbonyl ligands from complexes containing η^1-heterobenzenes bonded to $Mo(CO)_5$[7,8] or the η^1-pyrrolyl ligand in $Fe(\eta^5\text{-}C_5H_5)(\eta^1\text{-}NC_4H_4)(CO)_2$.[9] The facile σ to π rearrangement of complexes (**2**) is explained by the lability of the dinitrogen ligands and by the weakness of the σ-bond between the nitrogen donor and the electron rich molybdenum centre.[10] Chromium carbonyls form stable σ-bonds with pyridine so that π-complexes are only obtained when the pyridine ligands are substituted at the 2 and/or 6 positions to hinder σ-bonding with the metal.[11–13]

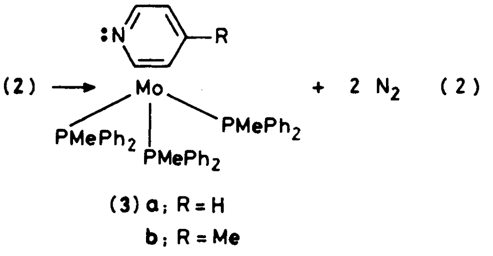


Table 1. $^{31}P^a$ and $^1H^b$ N.m.r. data for the pyridine complexes.

Complex	δ(^{31}P) /p.p.m.	J^2_{P-P} /Hz	δ(^{1}H) *ortho*	δ(^{1}H) *meta*	δ(^{1}H) *para*
(**2a**)	26.0 d 36.5 t	9.8	8.14 d *J* 6 Hz	5.74 t *J* 6 Hz	6.25 t *J* 6 Hz
(**3a**)	32.9 s		5.60 b	3.44 b	4.39 b
(**2b**)	26.0 d 37.0 t	9.8	8.03 d *J* 6 Hz	5.63 d *J* 6 Hz	(1.56)[c]
(**3b**)	33.3 s		5.46 b	3.73 b	(1.38)[c]

[a] Solvent for (**2**): THF; solvent for (**3**): C_6H_6; referenced to 85% H_3PO_4; s = singlet, d = doublet, t = triplet, b = broad. [b] In C_6D_6 *vs.* Me_4Si. Complexes (**2**) both gave P–Me doublets at δ 1.91, *J* 5 Hz, and virtual triplets at δ 1.68. Complexes (**3**) gave broad singlets at δ 1.68. [c] The picoline methyl resonance.

Phosphine substituted π-heterocycle complexes are known to be more thermally robust than carbonyl analogues.[2,13] Complexes (**3**) were inert to arene exchange reactions at 90 °C. Substitution of a labile phosphine ligand in (**3b**) by t-butyl isonitrile occurred rapidly at 25 °C without loss of the π-pyridine ligand. Further substitution reactions are being studied as well as reactions with hydrogen since π-pyridine complexes are being considered as models for intermediates in hydrodenitrogenation processes used for upgrading fuels.[13]

We have found that the dinitrogen complex (**1**) decomposes with loss of N_2 at 80 °C in toluene under Ar to give a mixture (^{31}P n.m.r. evidence) containing $Mo(\eta^6\text{-}C_6H_5PMePh)(PMePh_2)_3$ (50%) along with other π-bonded arylphosphine species. Here again π-complexation of the arene ring of a σ-bonded ligand is favoured over that of the solvent. A pathway to solvent co-ordination does exist since the reaction of (**1**) with benzene is driven to precipitate the insoluble product $Mo(\eta^6\text{-}C_6H_6)(PMePh_2)_3$.[3]

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