Letter

Activation of Aromatic Amines. Reaction of Aromatic Amines with Oxoperoxo-(pyridine-2,6-dicarboxylato)(hexamethylphosphoramide)molybdenum(VI)

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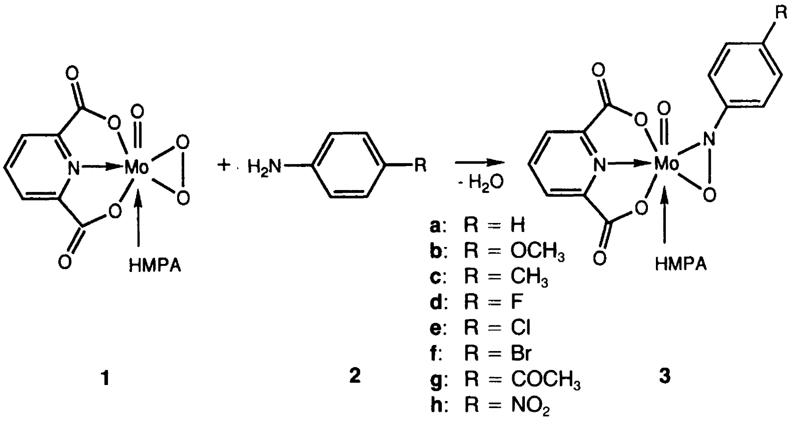
Activation of molecular nitrogen and nitrogen-containing species has received much less attention than the related activation of molecular oxygen and oxygen species.[1] In this paper we present a new reaction of a transition metal peroxo complex in relation to activation of nitrogen compounds: oxoperoxo-(pyridine-2,6-dicarboxylato)(hexamethylphosphoramide)molybdenum(VI) (**1**)[2] reacts with aromatic amines (**2**) with formation of oxo-(*N*-arylhydroxylamido-*O*,*N*)(pyridine-2,6-dicarboxylato)(hexamethylphosphoramide)molybdenum(VI) (**3**)[3] (Scheme 1). The complex **3** is found to decompose to azoxy- and azobenzenes and to transfer the nitrene group to triphenylphosphine.

Complex **1** (1.0 mmol) reacts with 1.0 mmol of an aromatic amine **2** in 25 ml of methylene chloride at room temperature giving **3** in good yield (>80 %). The reaction time depends on the substituent R in **2**; an aromatic amine with a *para*-methoxy group reacts within a few hours, whereas the *para*-nitro analogue requires days to complete the reaction. The complex **3** can also be prepared directly from dioxo-(pyridine-2,6-dicarboxylato)(hexamethylphosphoramide)molybdenum(VI) (**4**) by first mixing 1.0 ml of 35 % H_2O_2 with 1.0 mmol of **4** in 25 ml of methylene chloride for 1 h and then adding 1.0 mmol of the aromatic amine. The structure of **3** has been verified by ^1H and ^{13}C NMR[4] spectroscopy. The complex **3a** crystallizes in the orthorhombic space group. The dimensions of the unit cell were determined by X-ray methods as: $a = 13.079$, $b = 13.898$ and $c = 12.511$ Å, which are similar to those reported for a recently published structure.[3]

The reaction between **1** and **2** is of second order (first order in [**1**] and first order in [**2**]). The rate of disappearance of both **1** and **2**, as well as the formation of **3**, has been studied under second-order conditions. The variation in the value of log (k/k_0) for the disappearance of **1** in the reaction shown in Scheme 1 with different *para*-substituted aromatic amines was found to correlate with the Hammett σ values, as shown in Fig. 1.

The ϱ value for the Hammett plot in Fig. 1 has been calculated as −2.3 (correlation coefficient = 0.96), i.e. electron-donating substituents increase the reaction rate, while electron-withdrawing groups decrease the reaction rate. This leads us to tentatively suggest a mechanism for the formation of **3** from **1** and **2** as outlined in Scheme 2.

The first step is attack of the nitrogen of the aromatic



a: R = H
b: R = OCH_3
c: R = CH_3
d: R = F
e: R = Cl
f: R = Br
g: R = $COCH_3$
h: R = NO_2

Scheme 1. **1** **2** **3**

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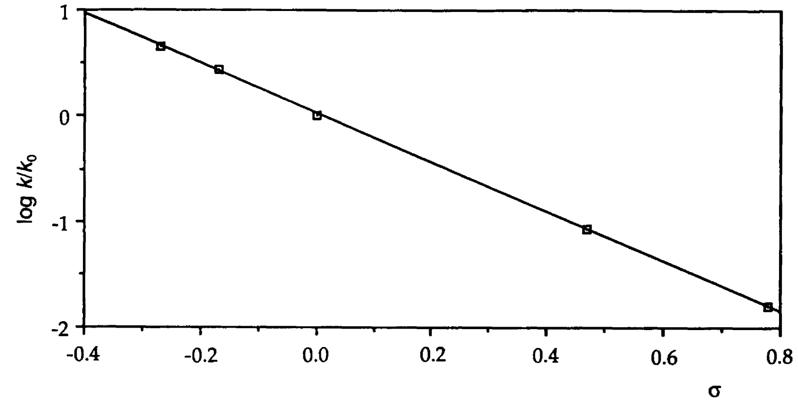

Fig. 1. Hammett plot for the reaction of **1** with **2a**, **2b**, **2c**, **2g** and **2h**.

amine at the peroxo-oxygen in **1**, which is known to be of electrophilic nature.[5] Proton transfer to the negatively charged oxygen followed by a nucleophilic attack of the amino nitrogen at molybdenum with elimination of water leads to **3**. One could also envisage another mechanism in which **1** transfers an oxygen to **2**, producing a hydroxylamine and the dioxomolybdenum(VI) complex **4**, followed by the addition of the hydroxylamine to the dioxomolybdenum(VI) species. The experimental results show that no dioxomolybdenum(VI) complex is formed during the reaction, which supports the mechanism outlined in Scheme 2.

The oxo-(*N*-arylhydroxylamido-*O*,*N*)(pyridine-2,6-dicarboxylato)(hexamethylphosphoramide)molybdenum(VI) complexes **3** contain an activated form of the aromatic amine, since these complexes readily decompose to give mainly azoxybenzene and azobenzene upon heating (Scheme 3).

For the complex **3a**, 10 % of azoxybenzene and < 2 % of azobenzene are isolated after heating under reflux in 1,2-dichloroethane for 48 h. It has also been observed that the complexes containing an aromatic amine with an electron-donating group in the *para* position most easily undergo the reaction depicted in Scheme 3. The molybdenum-*N*-arylhydroxylamido-*O*,*N* fragment in **3** is isoelectronic with the η^2-peroxo transition-metal complexes, but does not show a similar ability to transfer the R–N group to an alkene giving the corresponding aziridine, as we have found **3** to be unreactive with styrene as the substrate.[6] However, reaction of **3a** with Ph_3P leads to transfer of the N–Ph fragment giving $Ph_3P{=}NPh$. Further work is in progress to study the properties of **3**, and attempts are being made to develop nitrogen-transfer systems.

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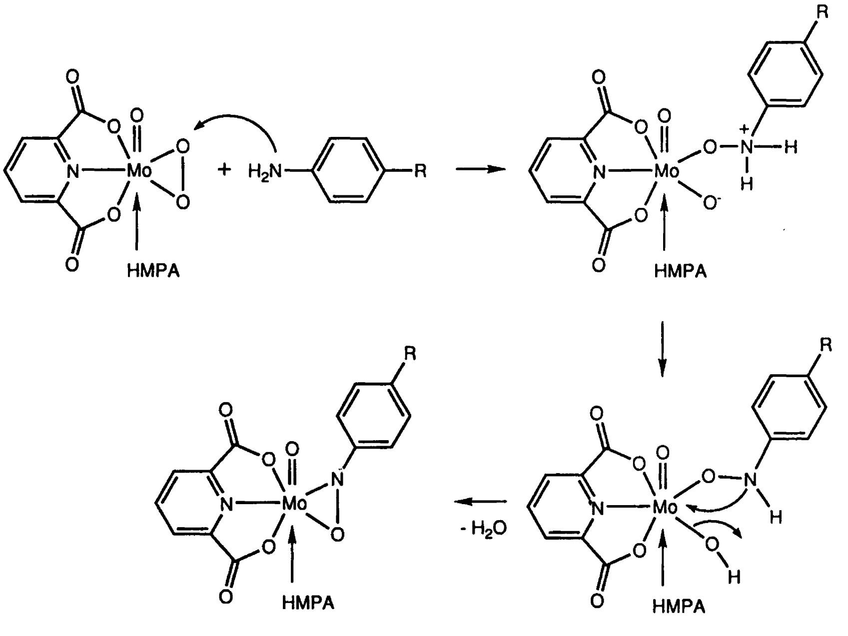
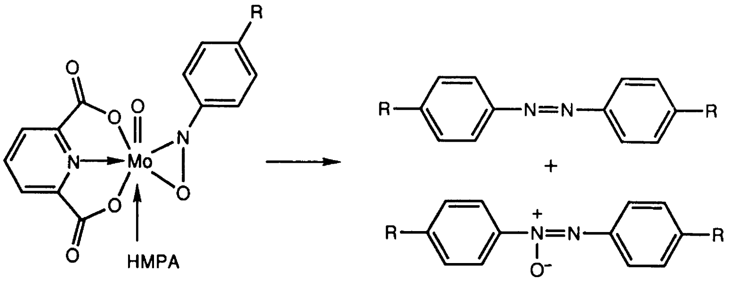


Scheme 2.



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Scheme 3.

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6. It should be noted that a molybdooxaziridine with a *para*-chlorophenyl group present has been found to react with 2-methyl-2-hexene to give the corresponding allylic amine; see Ref. 3a.

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