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The Reactivity of $Mo(PMe_3)_6$ towards Heterocyclic Nitrogen Compounds: Transformations Relevant to Hydrodenitrogenation

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Hydrodenitrogenation (HDN), the process by which nitrogen is removed from fossil fuels, is essential for minimizing NO_x emissions, and thereby provides an important counterpart to hydrodesulfurization (HDS).[1] The nitrogen-containing components that are most resilient to HDN are heterocyclic compounds that contain five-membered pyrrole and six-membered pyridine rings. HDN is typically performed at high temperature (350−500 °C) and H_2 pressure (200 atm) using a molybdenum sulfide catalyst supported on Al_2O_3 and promoted by either cobalt or nickel sulfide. Discerning the coordination mode preferences for heterocyclic nitrogen compounds to molybdenum is, therefore, paramount to understanding the mechanisms of hydrodenitrogenation. However, despite the important role that molybdenum plays in HDN, the coordination chemistry of molybdenum with five- and six-membered nitrogen heterocycles is not well defined. In this communication, we address this issue by reporting the synthesis and structures of a variety of molybdenum complexes that are obtained by reactions with five- and six-membered heterocyclic nitrogen compounds, including pyrrole, indole, carbazole, pyridine, quinoline, and acridine.

We have previously exploited the high reactivity of $Mo(PMe_3)_6$[2] to observe reactions of relevance to hydrodesulfurization. For example, $Mo(PMe_3)_6$ reacts with thiophene to give (η^5-C_4H_4S)Mo-$(PMe_3)_3$ and (η^5-C_4H_5S)$Mo(PMe_3)_2$(η^2-CH_2PMe_2), the first examples of η^5-thiophene and η^5-butadiene-thiolate molybdenum complexes.[3] On the basis of the success of these studies, we have investigated the reactivity of $Mo(PMe_3)_6$ towards heterocyclic nitrogen compounds.

$Mo(PMe_3)_6$ reacts with pyrrole (pyrH) to give the η^5-pyrrolyl complex (η^5-pyr)$Mo(PMe_3)_3H$. While (η^5-pyr)$Mo(PMe_3)_3H$ is an analogue of the cyclopentadienyl derivative $CpMo(PMe_3)_3H$, it should be noted that simple molybdenum−pyrrolyl complexes are, to our knowledge, unknown. In contrast to the reaction with pyrrole which yields a single product, the corresponding reaction of indole with $Mo(PMe_3)_6$ yields sequentially (η^1-indolyl)$Mo(PMe_3)_4H$,[4] (η^5-indolyl)$Mo(PMe_3)_3H$, and (η^6-indolyl)$Mo(PMe_3)_3H$, which respectively exhibit η^1-, η^5-, and η^6-coordination of the indolyl ligand.

The molecular structure of (η^6-indolyl)$Mo(PMe_3)_3H$ has been determined by X-ray diffraction (Figure 1),[5] thereby confirming that the indolyl ligand binds through the six-membered arene ring. The observation of η^6-coordination in this system is particularly interesting because indolyl ligands typically bind in either an η^1-manner through the nitrogen atom[6] or an η^5-manner through the five-membered heterocyclic ring.[7] η^6-Indolyl coordination via the arene ring is very rare, and structurally characterized examples are limited to derivatives in which the heterocyclic ring is alkylated.[8,9]

Coordination through the six-membered ring is also unexpected since it requires the ligand to bind through the ring which is formally

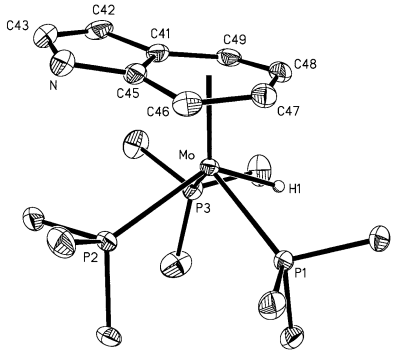
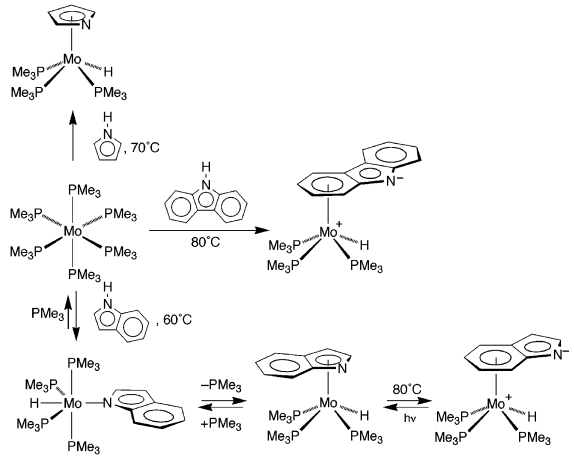


Figure 1. Molecular structure of (η^6-indolyl)$Mo(PMe_3)_3H$.

Scheme 1



associated with the lower negative charge. As such, the complex may be regarded to be zwitterionic, with a formal positive charge on the molybdenum, and a formal negative charge on the nitrogen of the indolyl ligand.[10] In this regard, it is also noteworthy that the hydrogen is retained on the molybdenum center, rather than being transferred to the basic nitrogen atom to give an indole complex (η^6-indole)$Mo(PMe_3)_3$.[11]

Addition of excess PMe_3 to the η^5-indolyl complex (η^5-indolyl)-$Mo(PMe_3)_3H$ at room-temperature regenerates (η^1-indolyl)Mo-$(PMe_3)_4H$ and ultimately releases indole, forming $Mo(PMe_3)_6$, thereby demonstrating that the oxidative addition of the N−H bond is reversible. By comparison to the facile room-temperature equilibration between the η^1- and η^5-indolyl complexes, (η^1-indolyl)$Mo(PMe_3)_4H$ and (η^5-indolyl)$Mo(PMe_3)_3H$,[12] the barrier for the η^5-to-η^6-ring shift is substantial, requiring temperatures of ca. 80 °C for efficient conversion.[13,14] The stability of the η^6-indolyl complex (η^6-indolyl)$Mo(PMe_3)_3H$ is such that it does not revert to (η^5-indolyl)$Mo(PMe_3)_3H$ under thermal conditions. The η^6-to-η^5-

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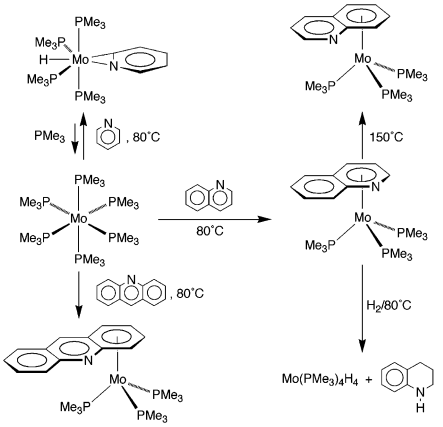
Scheme 2



isomerization may, nevertheless, be achieved by photolysis, although the conversion is not quantitative (Scheme 1).

Preferential coordination of the arene ring is not restricted to the indolyl ligand. Thus, the reaction of carbazole with $Mo(PMe_3)_6$ yields (η^6-carbazolyl)$Mo(PMe_3)_3H$,[15] in which the carbazolyl ligand coordinates via the arene ring rather than the heterocyclic ring. Carbazolyl ligands typically coordinate in an η^1-manner,[16] and there are no structurally characterized examples of either η^5- or η^6-carbazolyl transition metal complexes listed in the Cambridge Structural Database.[17]

The reactions of the six-membered heterocyclic nitrogen compounds, pyridine, quinoline, and acridine towards $Mo(PMe_3)_6$ are interesting because each follows a different course. Pyridine reacts with $Mo(PMe_3)_6$ to give an η^2-pyridyl derivative [η^2-(C_5H_4N)]$Mo(PMe_3)_4H$ as a result of α-C−H bond cleavage. The formation of an η^2-pyridyl derivative complex in this system is of note because the reaction of the related zerovalent complex $Mo(PMePh_2)_4(N_2)_2$ with pyridine yields sequentially the η^1- and η^6-coordinated derivatives, (η^1-C_5H_5N)$Mo(PMePh_2)_3(N_2)_2$ and (η^6-C_5H_5N)$Mo(PMePh_2)_3$,[18] with no evidence for C−H bond activation. The C−H cleavage of pyridine by $Mo(PMe_3)_6$ is, nonetheless, reversible, with addition of excess PMe_3 regenerating $Mo(PMe_3)_6$ and pyridine.

In contrast to the C−H bond activation reaction of pyridine, the corresponding reactions of quinoline and acridine give products of the type (η^6-ArH)$Mo(PMe_3)_3$ in which both ligands coordinate in an η^6-manner (Scheme 2), rather than the more commonly observed η^1-coordination mode via the nitrogen atom.[19,20] An interesting difference between the quinoline and acridine reactions, however, is that whereas only carbocyclic coordination is observed for acridine, both carbocyclic and heterocyclic coordination modes are observed for quinoline, i.e. [η^6-(C_6)-quinoline]$Mo(PMe_3)_3$ and [η^6-(C_5N)-quinoline]$Mo(PMe_3)_3$. The isolation of the less stable [η^6-(C_5N)-quinoline]$Mo(PMe_3)_3$ isomer is particularly significant because coordination through the heterocyclic ring of quinoline is unprecedented.[1c]

Hydrodenitrogenation of polycyclic organonitrogen compounds, such as quinoline, may involve hydrogenation of both the heterocyclic and carbocyclic rings. It has, however, been noted that a considerable saving of hydrogen and a more useful ultimate product (namely propylbenzene) would be obtained if the heterocyclic ring of quinoline were to be selectively hydrogenated.[1d] Therefore, it is of relevance that [η^6-(C_5N)-quinoline]$Mo(PMe_3)_3$ reacts with H_2 at 80 °C to give inter alia $Mo(PMe_3)_4H_4$ and release 1,2,3,4-tetrahydroquinoline, the product of selectively hydrogenating the heterocyclic ring.[21] In contrast, the isomer with quinoline coordinated by the carbocyclic ring, i.e. [η^6-(C_6)-quinoline]$Mo(PMe_3)_3$, is stable to H_2 under comparable conditions, thereby demonstrating that coordination by the heterocyclic ring facilitates reduction of quinoline.

In summary, the reactions of $Mo(PMe_3)_6$ towards a variety of five- and six-membered heterocyclic nitrogen compounds provide a series of complexes, including the first structurally characterized η^6-indolyl and η^6-(C_5N)-quinoline derivatives, that may serve as structural models for the coordination of such heterocycles to molybdenum in heterogeneous HDN catalysts.

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Supporting Information Available: Experimental details (PDF) and crystallographic CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) The equilibrium between (η^1-indolyl)$Mo(PMe_3)_4H$ and (η^5-indolyl)$Mo(PMe_3)_3H$ plus PMe_3 is characterized by the thermodynamic parameters: $\Delta H = 7.8(3)$ kcal mol^{-1}; $\Delta S = 24.6(11)$ eu.
(13) The η^5-to-η^6-ring shift is characterized by $\Delta H^{\ddagger} = 25(1)$ kcal mol^{-1} and $\Delta S^{\ddagger} = -8(3)$ eu.
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(15) Monitoring the reaction by ^{1}H NMR spectroscopy provides evidence for the reversible formation of (η^1-carbazolyl)$Mo(PMe_3)_4H$ as an intermediate.
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