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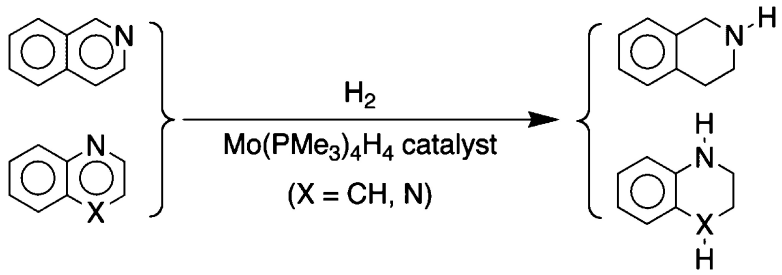

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New Modes for Coordination of Aromatic Heterocyclic Nitrogen Compounds to Molybdenum: Catalytic Hydrogenation of Quinoline, Isoquinoline, and Quinoxaline by $Mo(PMe_3)_4H_4$

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Hydrodenitrogenation (HDN), the process by which nitrogen is removed from fossil fuels, is typically performed by using a molybdenum sulfide catalyst supported on Al_2O_3 and promoted by either cobalt or nickel sulfide.[1−3] Despite the important role played by molybdenum, however, few studies of simple molecular compounds have established the coordination mode preferences of molybdenum for heterocyclic nitrogen compounds, and none have shown catalytic reactivity of relevance to HDN. In this paper, we report that $Mo(PMe_3)_4H_4$ provides a catalyst for hydrogenation of quinoline, isoquinoline, and quinoxaline.

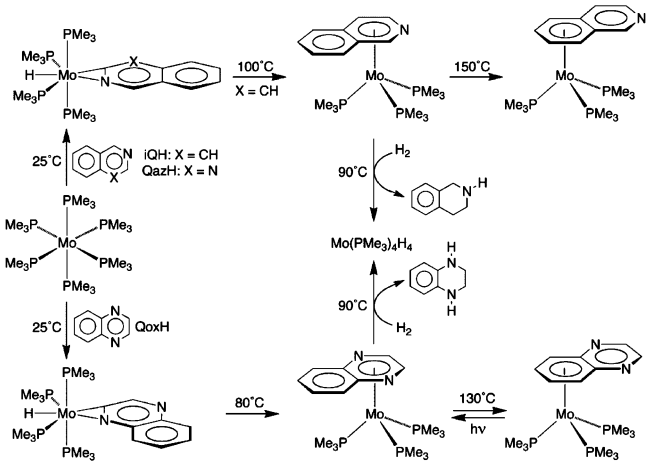
We have recently reported that $Mo(PMe_3)_6$ reacts with quinoline (QH) at 80 °C to give (η^6-C_5N-QH)$Mo(PMe_3)_3$,[4] the first example of a complex in which quinoline coordinates via its heterocyclic ring.[5] At higher temperatures, however, (η^6-C_5N-QH)$Mo(PMe_3)_3$ undergoes a haptotropic shift of the quinoline ligand to give the isomer (η^6-C_6-QH)$Mo(PMe_3)_3$ in which the ligand coordinates via its carbocyclic ring. In an effort to define further the coordination chemistry of molybdenum relevant to hydrodenitrogenation, we have investigated the reactivity of $Mo(PMe_3)_6$ towards other heterocyclic nitrogen compounds with two fused six-membered rings that are related to quinoline, namely isoquinoline (iQH), quinoxaline (QoxH), and quinazoline (QazH). Significantly, the reactivity observed for these molecules is quite distinct from that of quinoline.

For example, in marked contrast to the reaction between $Mo(PMe_3)_6$ and quinoline, which requires heating at 80 °C to give (η^6-C_5N-QH)$Mo(PMe_3)_3$, the corresponding reaction of isoquinoline proceeds rapidly at room temperature to yield (η^2-N,C-iQ)$Mo(PMe_3)_4H$, as a result of cleavage of a C−H bond adjacent to nitrogen (Scheme 1). The formation of (η^2-N,C-iQ)$Mo(PMe_3)_4H$ is reversible and treatment with excess PMe_3 regenerates $Mo(PMe_3)_6$ and isoquinoline. The reversible formation of (η^2-N,C-iQ)$Mo(PMe_3)_4H$ is analogous to the corresponding reaction of pyridine, which forms the η^2−pyridyl derivative (η^2-N,C-C_5H_4N)$Mo(PMe_3)_4H$.[4] In this regard, the reaction between $Mo(PMe_3)_6$ and isoquinoline more resembles that of pyridine than that of quinoline.

X-ray diffraction studies on (η^2-N,C-iQ)$Mo(PMe_3)_4H$ demonstrate that the C−H bond of isoquinoline which is cleaved is at the 3-position,[6] and *not* the peri position (Scheme 1).[7] C−H bond cleavage at the 3-position is presumably favored because it generates an isomer in which the isoquinolinyl ligand is directed away from the bulk of the phosphine ligands, whereas C−H cleavage at the peri position would give an isomer that would exhibit more pronounced steric interactions with the PMe_3 ligands.[8]

While (η^2-N,C-iQ)$Mo(PMe_3)_4H$ is the kinetic product of the reaction between $Mo(PMe_3)_6$ and isoquinoline, (η^2-N,C-iQ)$Mo(PMe_3)_4H$ dissociates PMe_3 and converts sequentially to (η^6-C_5N-iQ)$Mo(PMe_3)_3$ and (η^6-C_6-iQ)$Mo(PMe_3)_3$ upon heating.[9] The adoption of these three coordination modes is significant because isoquinoline otherwise displays the κ^1-N-coordination mode.[10]

Scheme 1.



Quinoxaline and quinazoline, derivatives of quinoline that feature two nitrogen atoms, also react with $Mo(PMe_3)_6$ at room temperature to undergo oxidative addition of an adjacent C−H bond to give (η^2-N,C-Qox)$Mo(PMe_3)_4H$ and (η^2-N,C-Qaz)-$Mo(PMe_3)_4H$,[7] respectively (Scheme 1).[11] At elevated temperatures, (η^2-N,C-Qox)-$Mo(PMe_3)_4H$ converts sequentially to (η^6-C_4N_2-QoxH)$Mo(PMe_3)_3$ and (η^6-C_6-QoxH)-$Mo(PMe_3)_3$.[12] The observed reactivity of quinoxaline and quinazoline towards $Mo(PMe_3)_6$ is unprecedented for these heterocycles which otherwise coordinate via only their nitrogen atoms.[13]

Hydrogenation of the heterocyclic ring is generally considered to be a prerequisite for HDN of N−heteroaromatic compounds because the N−C bonds of saturated cyclic amines are typically weaker than those of their unsaturated counterparts.[14,15] For this reason, we have examined the reactivity of the various (η^6-NHetH)-$Mo(PMe_3)_3$ compounds towards H_2. Significantly, both (η^6-C_5N-iQH)$Mo(PMe_3)_3$ and (η^6-C_4N_2-QoxH)$Mo(PMe_3)_3$ react with H_2 at 90 °C to give $Mo(PMe_3)_4H_4$ and release 1,2,3,4-tetrahydroisoquinoline and 1,2,3,4-tetrahydroquinoxaline, respectively (Scheme 1). Together with the fact that (η^6-C_5N-QH)$Mo(PMe_3)_3$ reacts with H_2 to liberate 1,2,3,4-tetrahydroquinoline,[4] it is evident that the molybdenum center is capable of selectively hydrogenating the heterocyclic ring of a variety of fused derivatives, a consequence of the fact that η^6-coordination of the heterocyclic ring is kinetically favored in this system. The selective hydrogenation of the heterocyclic ring is important because a considerable saving of hydrogen and energy during HDN would be achieved if *only* the heterocyclic ring of polyaromatic nitrogen compounds were to be selectively hydrogenated.

The stoichiometric hydrogenation of the heterocyclic rings of quinoline, isoquinoline, and quinoxaline is of considerable interest since such reactions have not been reported for other molybdenum

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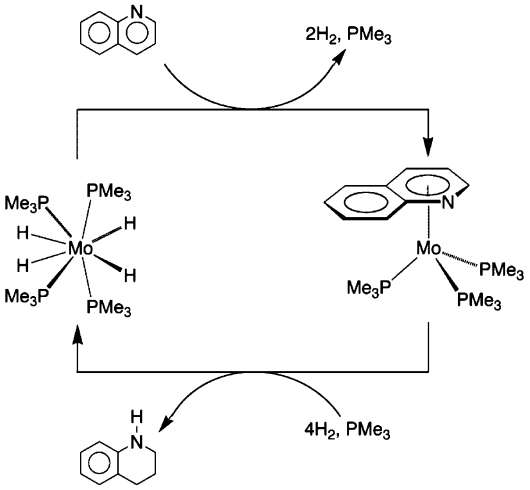
Scheme 2.



systems. To develop further this finding, we sought to obtain a catalytic system for hydrogenation using molybdenum. Specifically, we focused attention on $Mo(PMe_3)_4H_4$ because (i) it is the principal molybdenum-containing product of the aforementioned hydrogenation reactions and (ii) it also reacts with quinoline, isoquinoline, and quinoxaline to give (η^6-C_5N-QH)$Mo(PMe_3)_3$, (η^6-C_5N-iQH)-$Mo(PMe_3)_3$, and (η^6-C_4N_2-QoxH)$Mo(PMe_3)_3$, respectively (Scheme 2, illustrated for quinoline). On the basis of these two observations, it is evident that $Mo(PMe_3)_4H_4$ could, in principle, provide a catalyst for hydrogenation of these heterocyclic nitrogen compounds. Indeed, $Mo(PMe_3)_4H_4$ catalyzes the hydrogenation of quinoline, isoquinoline, and quinoxaline to 1,2,3,4-tetrahydroquinoline, 1,2,3,4-tetrahydroisoquinoline, and 1,2,3,4-tetrahydroquinoxaline, respectively (Scheme 2, illustrated for quinoline).[16−18] The efficiency of the catalytic cycle is, however, low, and this may be attributed to a variety of factors, one of which is the fact that the various (η^6-NHetH)$Mo(PMe_3)_3$ complexes convert to isomers in which the carbocyclic rings coordinate to the molybdenum, and these isomers are relatively unreactive towards hydrogenation,[19] an observation which indicates that the coordination mode plays an important role in determining the ability to hydrogenate the heterocycle.

In summary, isoquinoline, quinoxaline, and quinazoline react with $Mo(PMe_3)_6$ to give (η^2-NHet)$Mo(PMe_3)_4H$ as a result of cleavage of the C−H bond adjacent to the nitrogen atom. The C−H bond cleavage is reversible and, in the case of isoquinoline and quinoxaline, (η^2-NHet)$Mo(PMe_3)_4H$ converts sequentially to isomers of (η^6-NHetH)$Mo(PMe_3)_3$ in which the heterocycle coordinates via the heterocyclic and carbocyclic rings. The coordination modes observed in these complexes are quite distinct from the κ^1-mode that has been previously adopted by these heterocycles. As such, the structures of these molybdenum complexes provide insight into the nature of reactive intermediates involved in hydrodenitrogenation, a suggestion which is bolstered by the observations that (i) isomers of (η^6-NHetH)$Mo(PMe_3)_3$ in which the heterocyclic ring coordinates to molybdenum may be hydrogenated and (ii) $Mo(PMe_3)_4H_4$ is the first simple molybdenum complex to effect catalytic hydrogenation of these heterocyclic nitrogen compounds, a necessary step in hydrodenitrogenation.

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Supporting Information Available: Experimental details, computational data, and crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(6) The numbering system is one in which the peri position is no. 1 and N is no. 2.
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(8) DFT calculations indicate that the observed isomer is 5.8 kcal mol^{-1} lower in energy than the isomer which is metallated adjacent to the ring junction (see Supporting Information).
(9) The molecular structures of (η^6-C_5N-iQH)$Mo(PMe_3)_3$, (η^6-C_6-iQH)Mo-$(PMe_3)_3$, (η^6-C_4N_2-QoxH)$Mo(PMe_3)_3$, and (η^6-C_6-QoxH)$Mo(PMe_3)_3$ have been determined by X-ray crystallography. In each case the heterocycle is displaced from symmetric η^6-coordination towards a "flat" η^4-coordination mode such that the Mo−C distances for the ring junction carbon atoms are longer than those for the nonjunction carbon atoms of the coordinated ring. This type of displacement is also observed for the naphthalene derivative (η^6-NpH)$Mo(PMe_3)_3$. See: Zhu, G.; Janak, K. E.; Figueroa, J. S.; Parkin, G. *J. Am. Chem. Soc.* **2006**, *45*, 5452−5461.
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(11) The formation of (η^2-*N*,*C*-Qox)$Mo(PMe_3)_4H$ is reversible, with excess PMe_3 regenerating $Mo(PMe_3)_6$.
(12) The haptotropic shift may be reversed by photolysis although the transformation is not quantitative (ca. 60% yield).
(13) Due to the presence of two nitrogen atoms, quinoxaline and quinazoline also adopt the μ-η^1:η^1 mode as a bridging ligand linking two metal centers.
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(15) It should be noted, however, that there are examples of pyridine C−N bond cleavage, without prior hydrogenation, by metals other than molybdenum. See: (a) Kleckley, T. S.; Bennett, J. L.; Wolczanski, P. T.; Lobkovsky, E. *J. Am. Chem. Soc.* **1997**, *119*, 247−248. (b) Gray, S. D.; Weller, K. J.; Bruck, M. A.; Briggs, P. M.; Wigley, D. E. *J. Am. Chem. Soc.* **1995**, *117*, 10678−10693. (c) Weller, K. J.; Filippov, I.; Briggs, P. M.; Wigley, D. E. *Organometallics* **1998**, *17*, 322−329. (d) Bailey, B. C.; Fan, H.; Huffman, J. C.; Baik, M.-H.; Mindiola, D. J. *J. Am. Chem. Soc.* **2006**, *128*, 6798−6799.
(16) The catalytic activity of the system is not quenched by mercury, thereby indicating that the active species is not molybdenum particles formed by a degradation reaction. See Supporting Information.
(17) Catalytic hydrogenation reactions were performed in cyclohexane at 110 °C under H_2 (ca. 80 atm) for one week. Turnover numbers: 1,2,3,4-tetrahydroquinoline (21), 1,2,3,4-tetrahydroisoquinoline (24), and 1,2,3,4-tetrahydroquinoxaline (8).
(18) For catalytic hydrogenation of *N*-heteroaromatic compounds by complexes of metals other than molybdenum, e.g., Ru, Os, and Rh, see reference 3d.
(19) Upon prolonged heating (4 weeks) at 90 °C under H_2 (ca. 1 atm), (η^6-C_6-QoxH)$Mo(PMe_3)_3$ can be converted primarily to 5,6,7,8-tetrahydroquinoxaline as a result of the hydrogenation of the carbocyclic ring. However, hydrogenation of (η^6-C_6-QoxH)$Mo(PMe_3)_3$ is much slower than that of (η^6-C_4N_2-QoxH)$Mo(PMe_3)_3$, which typically requires ca. 4 days under comparable conditions. Therefore, hydrogenation of (η^6-C_6-QoxH)-$Mo(PMe_3)_3$ is negligible in the time scale and reaction conditions of hydrogenation of (η^6-C_4N_2-QoxH)$Mo(PMe_3)_3$.

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