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Synthesis and diverse general oxidative cyclization catalysis of high-valent $Mo^{VI}O_2(HL)$ to ubiquitous heterocycles and their chiral analogues with high selectivity

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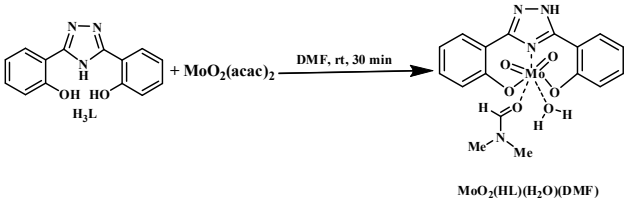
First synthesis and diverse oxidative cyclization catalysis property of a high-valent Mo^{VI}-triazole are demonstrated towards highly selective construction of benzimidazoles, benzthiazoles, isoxazolines, isoxazoles and their chiral analogues.

The discovery of a new metal complex and its diverse catalytic activity is a significant challenge in the chemical science. The transition metals of lower to medium oxidation states are now dominating in the catalysis.[1] The metal complex of higher oxidation state has only a limited application in the catalytic organic transformation. For example, metabolic oxidation, CO_2-activated insertion, C-O hydrogenolysis and our recently reported oxidative cyclization are the few interesting organic transformations executed utilizing Fe^{V}-cytochrome P450, U^{V}-carbamate, Zr^{IV}-triflate and Mn^{VI}–nanoparticles, respectively.[2] The inexpensive and readily available high-valent metals have tremendous potential accommodating a number of ligand sites, functionalities and substrates, and bringing them in the close proximity leading to simultaneous construction of multiple homo- and heteroatomic bonds, and cyclic frameworks. The electronic and steric parameters of the high-valent metal simultaneously enable producing high selectivity, which is one of the key factors of an efficient catalyst. Additionally, the higher oxidation state of the catalyst provides a unique power for executing simultaneous oxidation process in presence of molecular oxygen or other stoichiometric oxidants. The higher oxidation state of the biologically essential molybdenum compounds has attracted considerable attention especially due to its outstanding enzymatic activities[3] and olefin metathesis.[4] Herein we communicate the discovery of high-valent Mo^{VI}-ONO complexes (Scheme 1), its properties, diverse general oxidative cyclization catalysis and selectivity for most frequently synthesized ubiquitous heterocycles such as functionalized benzimidazoles, benzthiazoles, isoxazolines, isoxazoles and their chiral analogues.

Scheme 1. Synthesis of Mo^{VI}-ONO complex



The benzimidazoles are versatile compounds used in a wide range of scientific and industrial applications such as important building blocks for many organic syntheses, catalysis, fluorescence, chemosensing, crystal engineering, corrosion science, materials, organic electronics, medicinal research, pharmaceuticals, agrochemicals, textiles and cosmetics.[5] The widely used oxidative cyclocondensation among the o-phenylenediamines and aldehydes to benzimidazoles has a serious problem of forming two products[6d] namely 2-substituted- and 1,2-disubstituted benzimidazoles (Table 1). In addition to the huge number of reports on synthesis of valuable benzimidazoles,[6] the development of an efficient, benign and highly selective strategy is still in demand especially affording 2-substituted benzimidazoles and their chiral analogues[7] bearing free-NH for wide range of applications in the nanoscience and pharmaceutical industry. The scope of the benign oxidative cyclization catalysis can be extended towards synthesis[8] of the therapeutically[9] useful benzothiazoles utilising labile 2-aminothiophenols and aldehydes.[8,9] The isoxazolines[10] and isoxazoles[11] are essential building blocks of numerous natural products, useful synthons, chiral macrocycles and bioactive compounds for the wide range of medicinal applications.[12] In fact these are the most frequently synthesised five member heterocycles through 1,3-dipolar nitrile oxide cycloadditions.[13,14]

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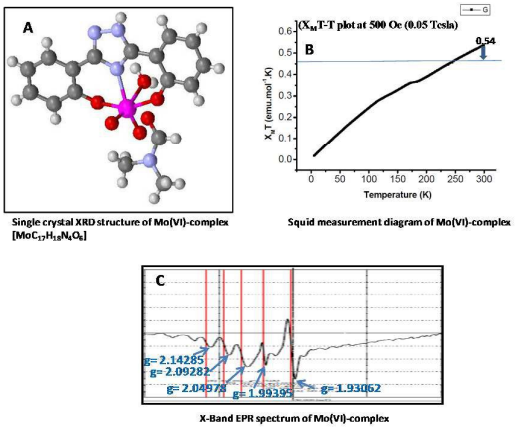
Organometallic chemistry of 3,5-bis(2-hydroxyphenyl)-1*H*-1,2,4-triazoles (H_3L, Scheme 1) was first studied by Ryabukhin in 1983.[15] To the best of our knowledge Mo^{VI}-complex with the "ONO" ligand is unknown in the literature. We have devised a simple procedure to access Mo^{VI}-1,2,4-triazoles complex from $MoO_2(acac)_2$ under the benign reaction conditions (Scheme 1). The structure of the new high-valent compound was established by the single crystal X-Ray crystallography (panel A, Figure 1),[16] NMR, FTIR, SQUID (panel B) and EPR (panel C) analyses. Interestingly the XRD structure of triclinic symmetry with P-1 space group reveals higher binding site of Mo^{VI}, which is associated with water and DMF [$MoO_2(HL)(H_2O)DMF$]. The loosely bound Mo^{VI}–N (HL), Mo^{VI}–O (H_2O) and Mo^{VI}–O (DMF) may be useful for binding substrates during oxidative catalysis processes. The Mo^{VI}-complex is expected to be diamagnetic with a d^0 electronic configuration[17] and the higher oxidation state species revealed unexpectedly high magnetic moment measured in squid (0.54 BM, panel B) with hyperfine X-band EPR spectrum (panel C). The free-N-H of the complex may play the vital role during catalytic process through transforming coordinated N-Mo^{VI} σ-bond as per requirement in push-pull mechanism of the catalytic cycles.



Single crystal XRD structure of Mo(VI)-complex $[MoC_{17}H_{18}N_4O_8]$

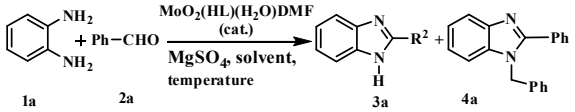
Squid measurement diagram of Mo(VI)-complex

X-Band EPR spectrum of Mo(VI)-complex

Figure 1. Experimental data and images of the new Mo^{VI}-ONO complex

To explore the oxidative catalytic activity of the new high-valent metal complex we initially executed cyclocondensation cum oxidation reaction using 10 mol% of $MoO_2(HL)(H_2O)(DMF)$, o-phenelenediamine (**1a**, 1 mmol), benzaldehyde (**2a**, 1.1 mmol), desiccant $MgSO_4$ and solvent dichloromethane under the aerobic conditions at ambient temperature (entry 1, Table 1). Gratifyingly the desired product 2-(phenyl)-1*H*-benzimidazole (**3a**, Figure 1) was obtained with excellent selectivity. The possible byproduct **4a** (Scheme 2) was not found from the post reaction mixture, which is the major concern of most of the reported methods. The moderate yield (68%) of the desired product **3a** (entry 1, Table 1) has led us to optimise the reaction using nonpolar, polar and protic solvents (entries 2-5), and the yield of the benzimidazole **3a** was significantly improved (86%, entry 5) in THF medium, probably due to better stabilization of the intermediates in the transition state through coordination of THF as ligand. However we found small amount of corresponding aldodimine, which was not converted into **3a**. The catalyst loading was optimised to 8 mol% (entries 6-8). There was a little improvement in yield using co-catalyst $CeCl_3$ (10 mol%)[9d,18] and Urea-H_2O_2, but not with the $PhI(OAc)_2$[19] (entries 8,9). The role of molecular oxygen as a stoichimetric oxidant in the oxidative cyclocondensation process (entries 10,11) was essential and it was verified by conducting two separate experiments, such as in the absence

Table 1. Development and optimization of the reaction



1a 2a 3a 4a

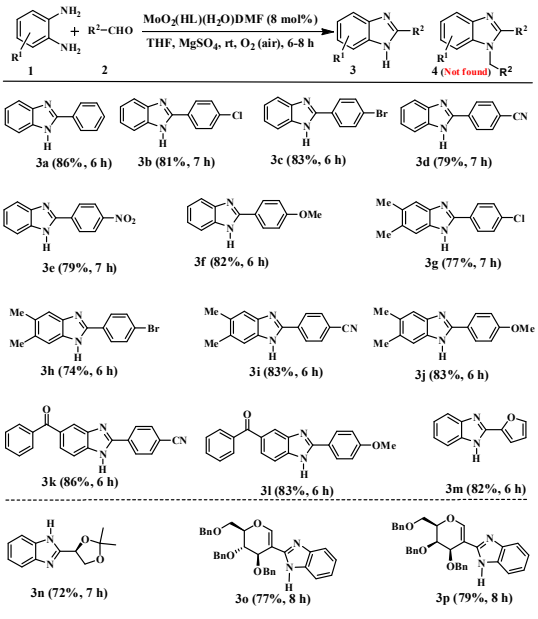
Entry	Catalyst[a]	Reaction conditions[b,c]	Conversion(%)	Yield(%)[d]
1	$MoO_2(HL)$	DCM, $MgSO_4$, 7 h	98	68
2	$MoO_2(HL)$	PhMe, $MgSO_4$, 24 h	60	45
3	$MoO_2(HL)$	MeOH, $MgSO_4$, 12 h	40	25
4	$MoO_2(HL)$	MeCN, $MgSO_4$, 16 h	80	56
5	$MoO_2(HL)$	THF, $MgSO_4$, 6 h	100	86
6	**$MoO_2(HL)$[e]**	**THF, $MgSO_4$, 7 h**	**100**	**86**
7	$MoO_2(HL)$[f]	THF, $MgSO_4$, 20 h	90	79
8	$MoO_2(HL)$, $CeCl_3$[g]	THF, Urea-H_2O_2, $MgSO_4$, 6 h	100	89
9	$MoO_2(HL)$	$PhI(OAc)_2$, THF, $MgSO_4$, 12 h	100	55
10	$MoO_2(HL)$	THF, $MgSO_4$, Ar,9 h	10	5[h]
11	$MoO_2(HL)$	THF, $MgSO_4$, O_2, 6 h	100	88
12	$MoO_2(acac)_2$	THF, $MgSO_4$, 24 h	50	35

[a]Catalyst loading: 10mol%; [b]Arial oxygen; [c]rt; [d]Isolated product after purification; [e]8 mol%; [f]7 mol%; [g]10 mol%, [h]Not isolated.

(entry 10) and presence of. oxygen (entry 11). Our attempt to use simple $MoO_2(acac)_2$ as a catalyst (entry 12) was unsuccessful, which indicates the presence of HL around the Mo^{VI} essential for empowering it as a work-horse in the catalysis.

After this promising result in hand (entry 6, Table 1), the versatility of the benign synthetic approach involving the catalyst $MoO_2(HL)(H_2O)DMF$ was successfully examined (Scheme 2) the cyclocondensation cum oxidation of various functionalised aromatic

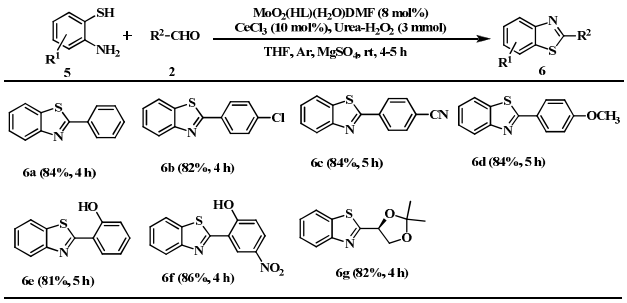
Scheme 2. Synthesis of functionalized and chiral benzimidazoles



aldehydes (**2b**-**f**) with different o-phenylenediamines (**1a**-**c**) at ambient temperature under the similar reaction conditions to afford corresponding benzimidazoles (**3b**-**m**) with fast reaction rate (6-7 h) and high yield (74-86%). Both the electron-deficient, electron-rich and heteroaromatic substituents were tolerated in this catalytic process. Our aim was to develop a benign strategy for synthesising sensitive and labile molecules. The benign strategy was utilized successfully towards direct synthesis of valuable glyceral- and glycal-based chiral benzimidazoles (**3n**-**p**).

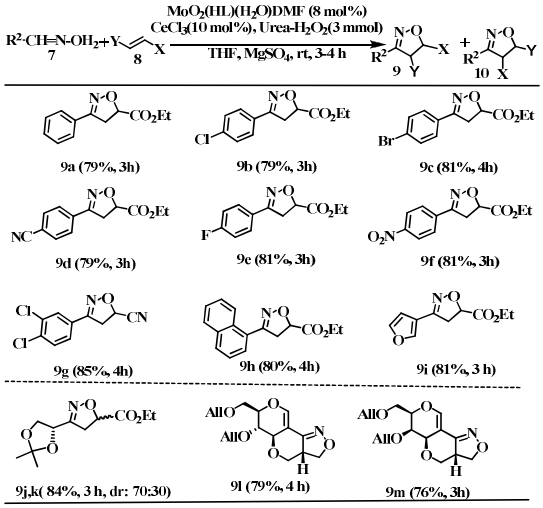
Next, we explored the possibility of synthesising another ubiquitous framework, benzothiazole using the powerful high-valent catalyst (Scheme 3). Gratifyingly the optimised reaction conditions (entry 6, Table 1) afforded the desired product 2-phenylbenzothiazole (**6a**, Scheme 3) from 2-aminothiophenol (**5a**) and benzaldehyde (**2a**). However, the yield (45%) and reaction time (24 h) were not encouraging due to oxidative dimerization of precursor 2-aminothiophenol (**5a**) through formation of S-S bond in the presence of molecular oxygen. After several attempts using various potential oxidants [$PhI(OAc)_2$, PhIO, NMPO etc.], $CeCl_3$ (10 mol%) was found as an efficient co-catalyst for oxidative cyclization process using non-aqueous urea-hydrogen peroxide as a stoichiometric oxidant. Herein the role of $CeCl_3$[20] is to supply oxygen from urea-hydrogen peroxide for the oxidative cyclization process. The heterocycle was obtained in high yield (83%) after 4 h at room temperature under the argon atmosphere. We have executed the reaction in the absence of $MoO_2(HL)(H_2O)DMF$ catalyst and the reaction was unsuccessful. Further, the dehydrative cyclisation cum oxidation process was carried out between **4a** bearing oxidation prone –SH group and functionalised aromatic aldehydes (**2b**-**i**), which rapidly (4-5 h) furnished respective benzothiazoles (**6b**-**g**) in excellent yield (82-89%). The sugar-based chiral benzothiazole **6h** was successfully synthesised with high yield (82%). The most of the reported catalytic methods are incapable of direct access to sugar-based chiral benzothiazole. The in situ generated urea was recovered and recycled through formation of urea-hydrogen peroxide using hydrogen peroxide.

Scheme 3. Synthesis of benzothiazoles with Mo^{VI}-Ce^{III} combo catalyst



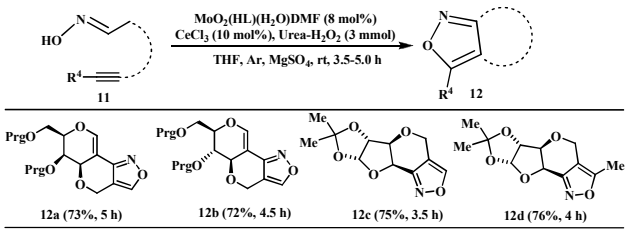
After getting the applicability of the new high-valent $MoO_2(HL)(H_2O)DMF$ catalyst, it was further examined for the synthesis of another most frequently synthesised five member *N*-heterocycle isoxazoline generated *via* intermolecular 1,3-dipolar cycloaddition of nitrile oxides and functionalised olefins. The benzaldehyde aldoxime (**7a**) and ethyl acrylate (**8a**) were treated with the combo catalyst $MoO_2(HL)(H_2O)DMF$ (8 mol%)-$CeCl_3$ (10 mol%) at ambient temperature. To our delight the desired isoxazoline **9a** (Scheme 4) was generated selectively without formation of the corresponding other regioisomer **10a**. However the cycloaddition reaction was arrested in the absence of $MoO_2(HL)(H_2O)DMF$ catalyst. The versatility of the benign synthetic approach is verified with several precursors bearing electron-rich and electron-deficient aromatic substituents, which were tolerated in this benign approach to achieve isoxazolines **9b-l** with excellent regioselectivity. The respective regioisomer (**10**) was not found from the powerful catalysis process, which is the major concern of the existing methods. The heterocycle based isoxazoline (**9i**) and sugar-based chiral isoxazolines (**9l-0**) were also achieved in good yield.

Scheme 4. Synthesis of isoxazolines through nitrile oxide cycloaddition



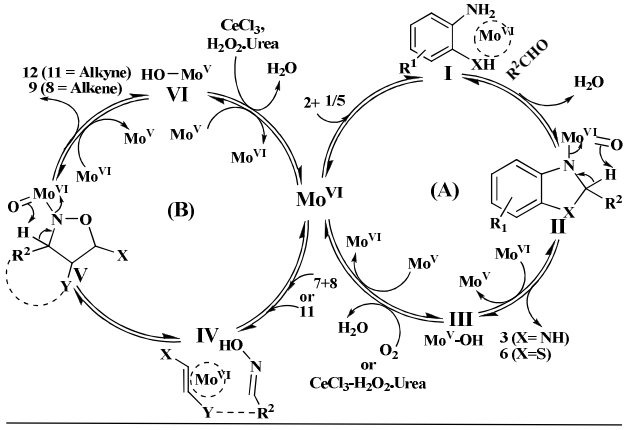
The versatility of this benign catalysis of high-valent $Mo^{VI}O_2(HL)(H_2O)DMF$ was also verified in the asymmetric intramolecular cycloaddition reaction of nitrile oxide with alkynes for synthesis of chiral fused-isoxazoles of allyl-substituted glycalaldoximes and pentose sugar analogues (**11**, Scheme 5). The synthetic tool with sugar-based nitrile oxides provides an excellent opportunity for constructing nature-like and unnatural organic molecules. Under the catalytic conditions the chiral oximes (**11a-d**) underwent smoothly through highly stereoselective fashion to produce sugar-based chiral isoxazoles (**12a-d**) in good yield (72-76%). The $CeCl_3$ co-catalyst has the crucial role as an oxygen carrier from Urea-H_2O_2 to the Mo^{VI}-catalyst for executing the oxidative intramolecular dipolar cycloaddition reactions.

Scheme 5. Synthesis of sugar-based chiral isoxazoles



Possible mechanism of the diverse cyclocondensation cum oxidation and oxidative cycloaddition reactions is shown in Scheme 6. First step for the oxidative cyclocondensation cum oxidation is expected to proceed through coordination of the high-valent catalyst with the substrates (**I**, cycle **A**, Scheme 6) and subsequent selective cyclisation to form intermediate **II**. It smoothly releases the desired products benzimidazoles (**3**) and benzothiazoles (**5**) through reductive elimination of Mo^{V}-complex (**III**), which is eventually regenerated to the Mo^{VI}-complex for the next catalytic cycle through oxidation with oxygen or $CeCl_3$-Urea.H_2O_2. The eliminating C-*H* of intermediate **II** for benzimidazole is relatively more acidic with that of benzothiazole due to presence of more electron withdrawing two C-N bonds. Thus molecular oxygen-Mo^{VI}-complex transforms easily **II** in to benzimidazole (**3**). The highly regioselective synthesis of isoxazolines (**9**) and isoxazoles (**12**) were also followed similar catalytic cycle (cycle **B**, Scheme 6). Herein the role of $CeCl_3$ is as an oxygen carrier to Mo^{V}-OH for regenerating the active Mo^{VI}-catalyst using H_2O_2-urea as a stoichiometric oxidant.[20] However involvement of co-catalyst $CeCl_3$ (**IV**→**V**) in the cyclisation step can't be avoided. The high regioselectivity in the all oxidative cyclisation processes can be explained in terms of strong binding of the substrates and successive hetero- and homonuclear coupling through large binding site of the powerful high-valent metal-complex during formation of **I**→**II** (**A**) and **IV**→**V**(**B**).

Scheme 6. Possible catalytic cycles by the high-valent metal complex



In conclusion, we have discovered a high-valent $MoO_2(HL)(H_2O)(DMF)$-complex with rarely used H_3L ligand and found it as a powerful catalyst for oxidative cyclocondensation using oxygen as a stoichiometric oxidant to furnish 2-substituted benzimidazoles selectively. In contrast to the commonly used epoxidation catalysis by Mo^{VI}-complexes, herein the $MoO_2(HL)(H_2O)(DMF)$-complex had shown diverse highly selective synthesis of ubiquitous 2-substituted benzimidazoles, 2-substituted benzothiazoles, isoxazolines, isoxazoles and their chiral analogues. Herein we demonstrated the Mo^{VI}(HL) as an attractive catalyst for developing benign, simple and general oxidative cyclization processes with excellent selectivity. We anticipate that the discovery of a new high-valent catalyst, its novel properties and robust oxidative cyclization catalysis will find considerable application in chemical science towards devising new strategies to functional molecules and discovery of prospective new high-valent catalysts.

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Synthesis and diverse general oxidative cyclization catalysis of high-valent $Mo^{VI}O_2(HL)$ to ubiquitous heterocycles and their chiral analogues with high selectivity

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First synthesis and diverse oxidative cyclization catalysis property of a high-valent Mo^{VI}-triazole are demonstrated towards highly selective construction of benzimidazoles, benzthiazoles, isoxazolines, isoxazoles and their chiral analogues.