Insights into the Mechanistic and Synthetic Aspects of the Mo/P-Catalyzed Oxidation of N-Heterocycles

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X-ray Data Collection and Structure Solution Refinement. Crystals suitable for X-ray diffraction were mounted in Paratone oil onto a glass fiber and frozen under a nitrogen cold stream maintained by an X-Stream low-temperature apparatus. The data were collected at 98(2) K using a Rigaku AFC12/Saturn 724 CCD fitted with Mo Kα radiation (λ = 0.71073 Å). Data collection and unit cell refinement were performed using Crystal Clear software. The total number of data were measured in the range (see table 3) using ω scans. Data processing and absorption correction, giving minimum and maximum transmission factors, see table 3, were accomplished with Crystal Clear and ABSCOR, respectively. The structure, using SHELXL-97, was solved by direct methods and refined (on F²) using full-matrix, least-squares techniques. All non-hydrogen atoms were refined with anisotropic displacement parameters. All carbon bound hydrogen atom positions were determined by geometry and refined by a riding model. An electron density peak was used to identify the hydrogen atoms bound to the solvent molecule and the displacement parameters were set to 1.5 times the displacement parameters of the bonded atom. Compounds 26-29 have been assigned the following CCDC numbers: 26 (CCDC 981527), 27 (CCDC 981529), 28 (CCDC 981530), 29 (CCDC 981531).

Table 1. Selected bond distances for the molybdenum complexes 26-29 (Å).

<table>
<thead>
<tr>
<th>Complex</th>
<th>O→Mo</th>
<th>O→N→Mo</th>
<th>P→O→Mo</th>
<th>N→Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>26</td>
<td>1.925(3),1.949(3) [1.479(4)] 1.928(3),1.945(3) [1.482(4)]</td>
<td>1.688(2)</td>
<td>2.257(3) [1.341(4)] 2.114(2) [1.371(4)]</td>
<td></td>
</tr>
<tr>
<td>29</td>
<td>1.920(4),1.919(4) [1.458(6)] 1.924(3),1.996(3) [1.470(5)]</td>
<td>1.669(4)</td>
<td>[1.345(10)]</td>
<td>2.023(4) [1.528(4)]</td>
</tr>
<tr>
<td>27</td>
<td>1.933(2),1.960(2) [1.475(3)] 1.937(2),1.959(2) [1.481(3)]</td>
<td>1.687(2)</td>
<td>2.122(2) [1.354(3)] 2.195(2) [1.344(3)]</td>
<td></td>
</tr>
</tbody>
</table>
The O–O bond distance is specified in brackets. The N–O bond distance is specified in brackets. The P–O bond distance is specified in brackets.

Table 2. Selected hydrogen bond distances and angles for the molybdenum complexes.

<table>
<thead>
<tr>
<th>Complex</th>
<th>D-H(Å)</th>
<th>H---O(Å)</th>
<th>D---O(Å)</th>
<th>D-H---O(°)</th>
<th>Symmetry Operators</th>
</tr>
</thead>
<tbody>
<tr>
<td>26 (O8-H8c---O6)</td>
<td>0.97(2)</td>
<td>2.06(7)</td>
<td>2.815(6)</td>
<td>133(7)</td>
<td>x, 1+y, z</td>
</tr>
<tr>
<td>26 (O8-H8b---O7)</td>
<td>0.98(2)</td>
<td>1.77(4)</td>
<td>2.695(6)</td>
<td>156(8)</td>
<td>163</td>
</tr>
<tr>
<td>26 (C11-H11a--O8)</td>
<td>0.93</td>
<td>2.36</td>
<td>3.263(6)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>28 (C10-H10a----O5)</td>
<td>0.93</td>
<td>2.34</td>
<td>3.19(1)</td>
<td>152</td>
<td>-x,-y,-z</td>
</tr>
<tr>
<td>28 (C10-H1a---O4)</td>
<td>0.93</td>
<td>2.44</td>
<td>3.29(1)</td>
<td>153</td>
<td>1-x,1-y,1-z</td>
</tr>
</tbody>
</table>

Table 3. Crystallographic parameters for Mo complexes 26-29.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>26</th>
<th>29</th>
<th>27</th>
<th>28</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C₁₈H₁₆MoN₂O₈</td>
<td>C₄₀H₃₀Mo₄N₄O₃₂P</td>
<td>C₂₀H₁₈MoN₂O₇</td>
<td>C₁₀H₃MoN₂O₆</td>
</tr>
<tr>
<td>Formula weight</td>
<td>484.27</td>
<td>1502.48</td>
<td>494.30</td>
<td>348.12</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Triclinic</td>
<td>orthorhombic</td>
<td>Triclinic</td>
<td>Triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P-1</td>
<td>Fddd</td>
<td>P-1</td>
<td>P-1</td>
</tr>
<tr>
<td>a(Å)</td>
<td>7.3259(13)</td>
<td>12.468(3)</td>
<td>8.1944(14)</td>
<td>7.136(14)</td>
</tr>
<tr>
<td>b(Å)</td>
<td>7.9556(14)</td>
<td>24.565(5)</td>
<td>8.3391(14)</td>
<td>7.593(14)</td>
</tr>
<tr>
<td>c(Å)</td>
<td>15.181(3)</td>
<td>36.887(7)</td>
<td>15.475(3)</td>
<td>12.48(2)</td>
</tr>
<tr>
<td>α(°)</td>
<td>91.695(4)</td>
<td>90</td>
<td>95.507(3)</td>
<td>94.746(18)</td>
</tr>
<tr>
<td>β(°)</td>
<td>91.210(4)</td>
<td>90</td>
<td>96.472(3)</td>
<td>105.60(3)</td>
</tr>
<tr>
<td>γ(°)</td>
<td>97.655(4)</td>
<td>90</td>
<td>106.989(3)</td>
<td>112.22(3)</td>
</tr>
<tr>
<td>Volume(Å³)</td>
<td>876.2(3)</td>
<td>11298(4)</td>
<td>995.6(3)</td>
<td>589.9(18)</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
<td>8</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>ρ(calc.)</td>
<td>1.835</td>
<td>1.767</td>
<td>1.649</td>
<td>1.960</td>
</tr>
<tr>
<td>λ</td>
<td>0.71073</td>
<td>0.71073</td>
<td>0.71073</td>
<td>0.71073</td>
</tr>
<tr>
<td>Temp.(K)</td>
<td>98(2)</td>
<td>98(2)</td>
<td>98(2)</td>
<td>98(2)</td>
</tr>
<tr>
<td>F(000)</td>
<td>488</td>
<td>5968</td>
<td>500</td>
<td>344</td>
</tr>
<tr>
<td>μ(mm⁻¹)</td>
<td>0.803</td>
<td>0.992</td>
<td>0.705</td>
<td>1.137</td>
</tr>
<tr>
<td>T_{min}, T_{max}</td>
<td>0.729, 1.000</td>
<td>0.800, 1.000</td>
<td>0.702, 1.000</td>
<td>0.326, 1.000</td>
</tr>
<tr>
<td>2θ_{range}(°)</td>
<td>5.16 to 55.00</td>
<td>4.94 to 52.00</td>
<td>4.74 to 55.00°</td>
<td>5.18 to 51.00°</td>
</tr>
<tr>
<td>Reflections Collected</td>
<td>6281</td>
<td>17628</td>
<td>7267</td>
<td>2879</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>3401 [R(int) = 0.0613]</td>
<td>2771 [R(int)=0.0815]</td>
<td>4507 [R(int)=0.0466]</td>
<td>2161 [R(int) = 0.0705]</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>3401 / 0 / 268</td>
<td>2771 / 0 / 184</td>
<td>4507 / 0 / 271</td>
<td>2161 / 0 / 172</td>
</tr>
<tr>
<td>wR(F² all data)</td>
<td>0.01053</td>
<td>0.1353</td>
<td>0.0860</td>
<td>0.1363</td>
</tr>
<tr>
<td>R(F obsd data)</td>
<td>0.0389</td>
<td>0.0545</td>
<td>0.0342</td>
<td>0.0601</td>
</tr>
</tbody>
</table>

S2
<table>
<thead>
<tr>
<th>GOOF on $F^2$</th>
<th>1.013</th>
<th>1.124</th>
<th>1.012</th>
<th>1.052</th>
</tr>
</thead>
<tbody>
<tr>
<td>Observed data</td>
<td>[I $&gt; 2\sigma(I)$]</td>
<td>3185</td>
<td>2623</td>
<td>4261</td>
</tr>
<tr>
<td>Largest and mean shift / s.u.</td>
<td>0.0015/ 0.000</td>
<td>0.002/ 0.000</td>
<td>0.001/ 0.000</td>
<td>0.000/ 0.000</td>
</tr>
</tbody>
</table>

\[ wR_2 = \left\{ \Sigma \left[ w(F_o^2 - F_c^2)^2 \right] / \Sigma \left[ w(F_o^2) \right] \right\}^{1/2} \]
\[ R_1 = \Sigma ||F_o|| - ||F_c|| / \Sigma |F_o| \]

References
2-Bromopyridine 1-oxide (5)
6-Bromo-2-pentylquinoline 1-oxide (6)
Quinoxaline 1-oxide (8)
3,4-Dimethylpyridine 1-oxide (10)
4,7-Dichloroquinoline 1-oxide (14)
Isoquinoline 2-oxide (15)
1,10-Phenanthroline 1-oxide (16)
6-Bromoquinoline 1-oxide (18)
2-Phenylpyridine 1-oxide (19)
7-Chloro-4-methoxyquinoline 1-oxide (20)
3-Phenylpyridine 1-oxide (21)
4-Methylquinoline 1-oxide (23)
5,7-Dichloro-2-methylquinolin-8-ol 1-oxide (32)
4-Cyanopyridine 1-oxide (33)