Electronic Supplementary Information

A regioselective Huisgen reaction inside a Keplerate polyoxomolybdate nanoreactor

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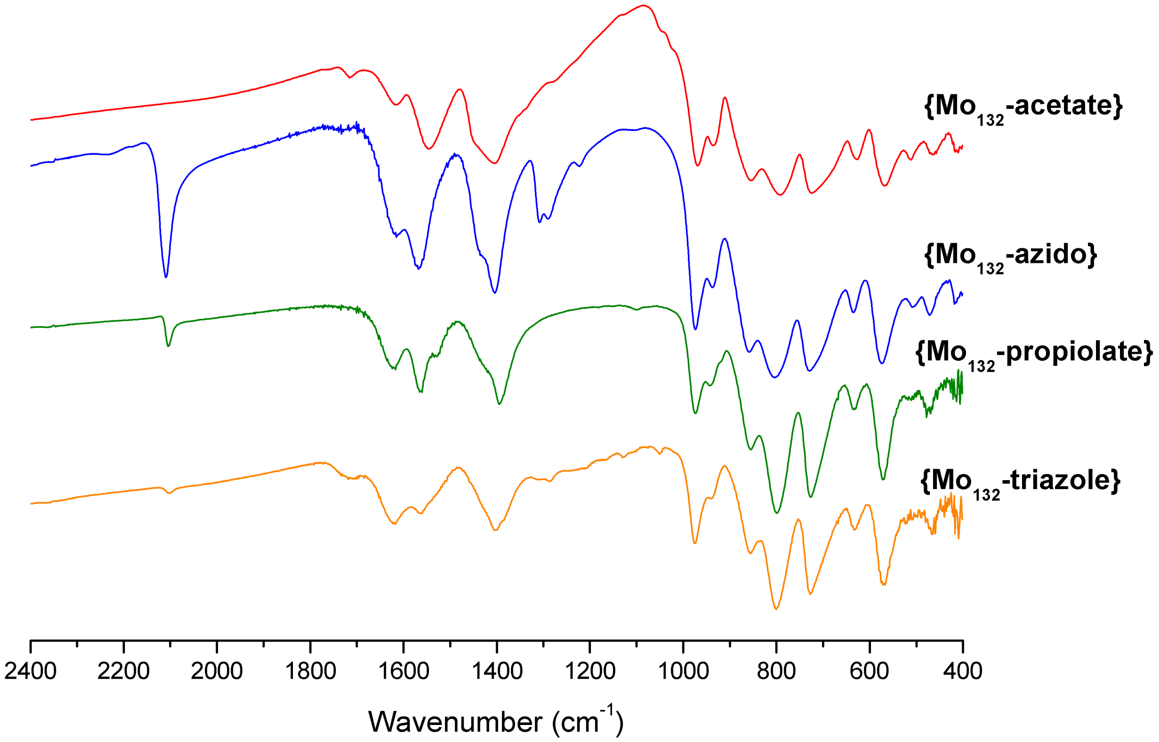

Figure S1. IR spectra (transmission, KBr pellets) of **{Mo$_{132}$-acetate}**, **{Mo$_{132}$-azido}**, **{Mo$_{132}$-propiolate}**, **{Mo$_{132}$-triazole}**.

A shift toward higher wavenumbers of the bands characteristic of the **{Mo$_{132}$}** framework is observed for **{Mo$_{132}$-azido}**, **{Mo$_{132}$-propiolate}** and **{Mo$_{132}$-triazole}** when compared to **{Mo$_{132}$-acetate}**. This is in accordance to the reduced negative charge due to the partial replacement of carboxylate ligands by water molecules.

{Mo$_{132}$-acetate}
ν = 1615, 1544, 1404, 969, 936, 855, 791, 627, 568, 512, 466, 411 cm^{-1}
{Mo$_{132}$-azido}
ν = 2108, 1615, 1568, 1403, 1289, 974, 938, 859, 803, 729, 634, 574, 472, 414 cm^{-1}
{Mo$_{132}$-propiolate}
ν = 2104, 1617, 1560, 1395, 974, 855, 799, 727, 635, 575, 478 cm^{-1}
{Mo$_{132}$-triazole}
ν = 2104, 1617, 1564, 1404, 1290, 975, 936, 855, 801, 727, 633, 572, 468 cm^{-1}

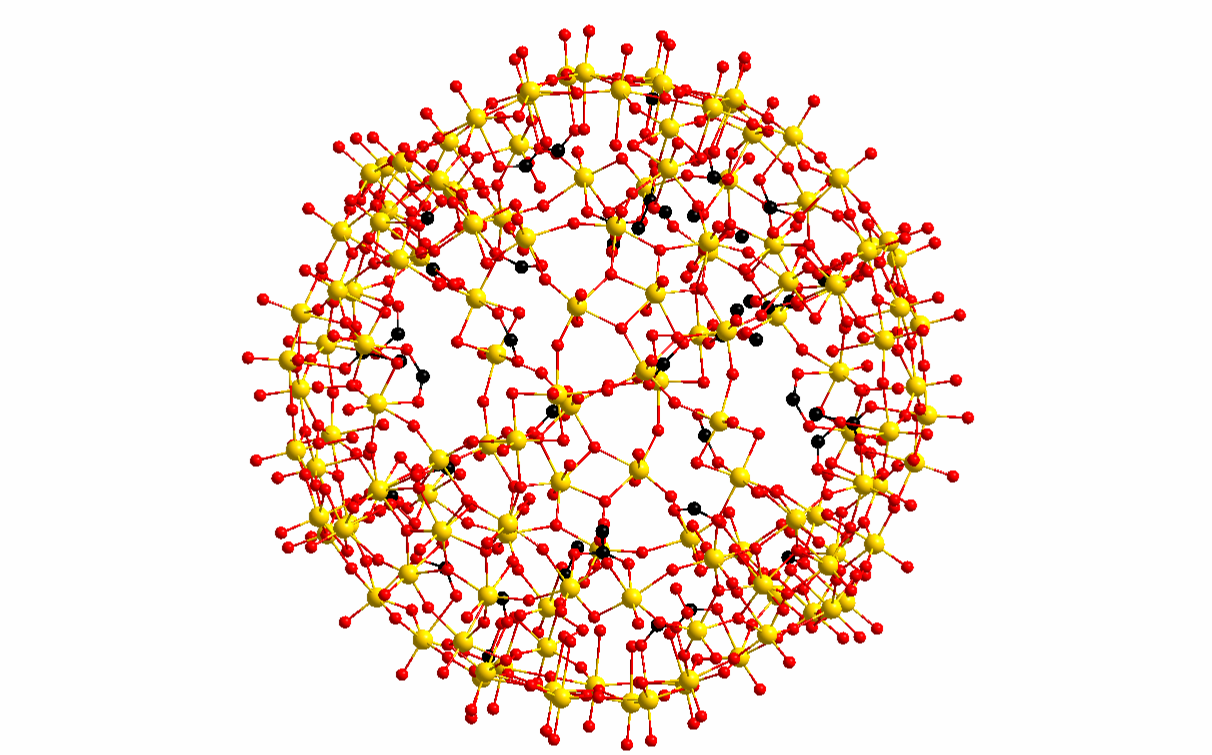

Figure S2. Partial structure of **{Mo$_{132}$-azido}** as determined by study of a low-quality single crystal. The resolution of the data is around 1 Å, too low to resolve the interior of the Keplerate. Crystal data: trigonal, space group *R*-3, $a = 32.4830$, $c = 73.2200$, $V = 66907$ Å^3, $Z = 3$. Molybdenum atoms are yellow, oxygen red, carbon black.

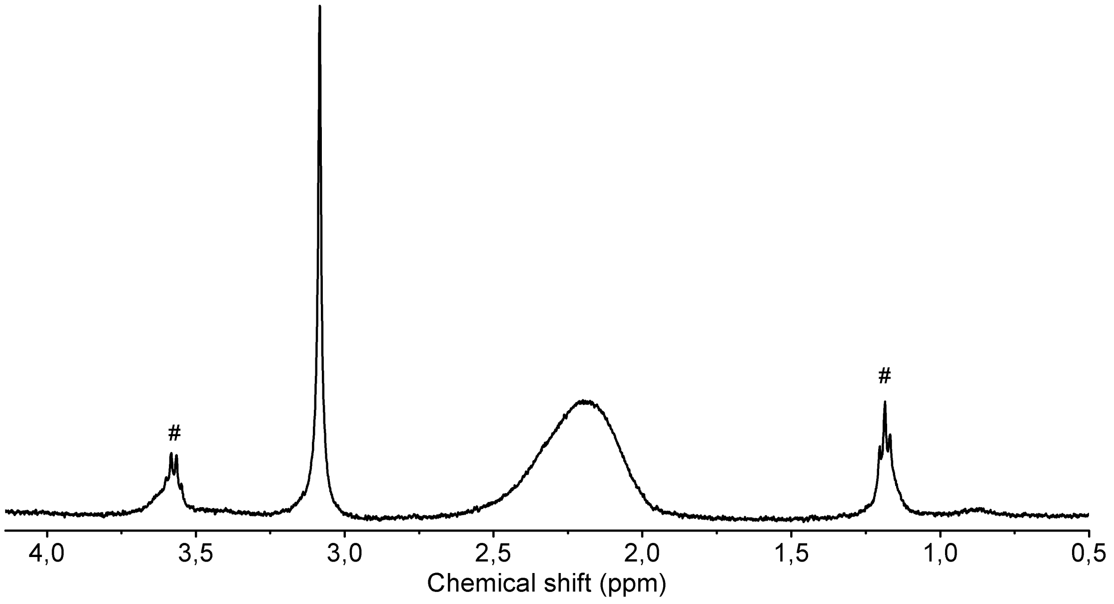

Figure S3. ^{1}H NMR spectra of **{Mo$_{132}$-propiolate}** in D_2O, showing the sharp signal of free propiolic acid and the broad signal of its coordinated counterpart. Signals marked # are due to a contamination by ethanol.

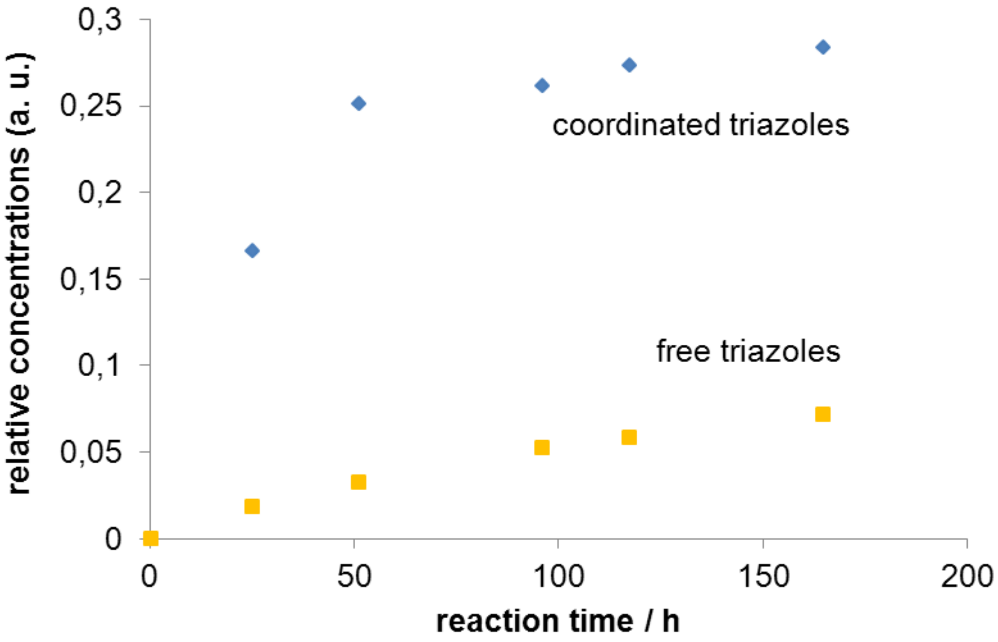

Figure S4. Time evolution of the relative concentrations of free and coordinated triazoles in a solution of **{Mo$_{132}$-azido}** and propiolic acid in D_2O. Conditions: **{Mo$_{132}$-azido}** (85.4 mg, 3 µmol) was dissolved in degassed D_2O (3.42 mL), then propiolic acid (10.7 µL, 170 µmol) was added. An aliquot of the solution was introduced in an NMR tube under argon. Traces of ethanol present in the tube were used as an internal standard. Coordinated triazole concentration was determined by difference between well-resolved CH_2 protons (free triazole, free and coordinated azidoacetic acid) and total amount of CH_2 protons as determined by inspection of the first spectrum measured within a few minutes of the reaction start.

Note: The speed of the reaction outside the Keplerate and the resulting triazole isomer ratio are highly dependent on the exact conditions of the reaction. Even in the absence of Keplerate, even very small changes to e.g. reaction vessel, stirrer bar, or solvent (D_2O *vs*. H_2O, with the difference in purity it entails) induce drastic changes to the reaction between azidoacetic and propiolic acid, most probably caused by fluctuating trace metal amounts. pH and temperature can also influence the outcome of the reaction.

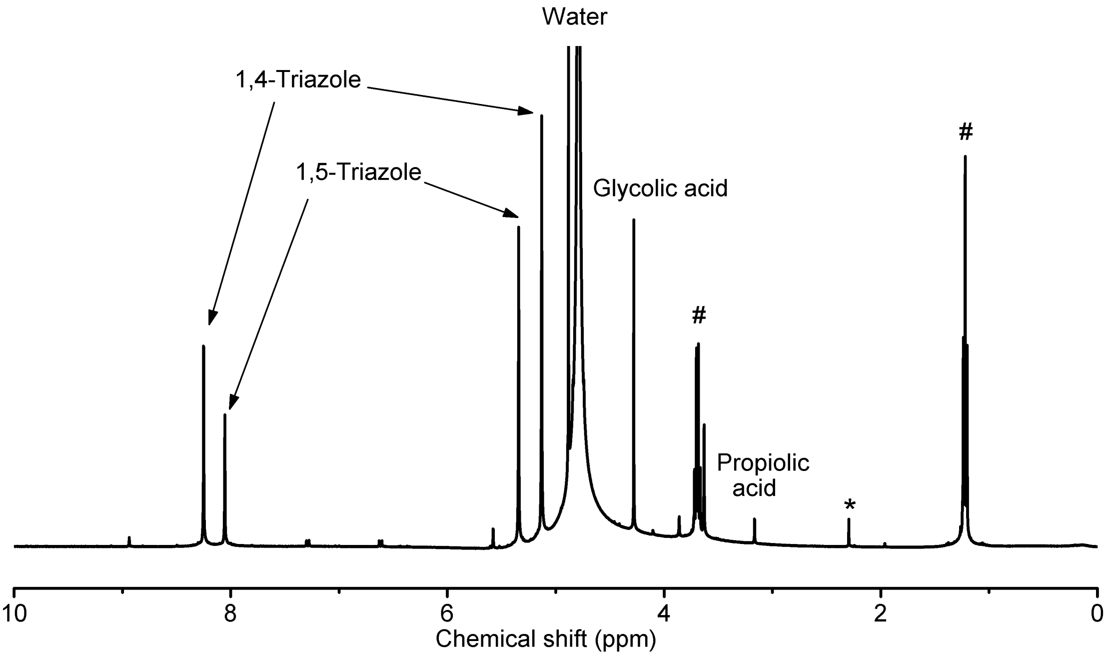

Figure S5. ^{1}H NMR spectrum of **{Mo$_{132}$-triazole}** after breaking of the Keplerate shell, evaporation and redissolution in D_2O. Glycolic acid, placed in a coaxial tube, is used as internal reference for quantification. The signals marked by # and * result from a contamination by ethanol and acetone, respectively. No azidoacetic acid ($\delta = 3.9$ ppm) can be detected.