Supporting information

A Mononuclear Tantalum Catalyst with a Peroxycarbonato Ligand for Olefin Epoxidation in Compressed CO_2

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Contents

1. Materials

Chemicals including tantalum pentoxide, acetic acid, potassium hydroxide, ammonium hydroxide were purchased from CRC (Sinopharm Chemical Reagent Co., Ltd, Shanghai). Tetrabutylphosphonium bromide ($[P_{4,4,4,4}]Br$) was obtained from Shanghai Macklin Biochemical Co., Ltd, Tributyl-n-octyl-phosphonium Bromide ($[P_{4,4,4,8}]Br$) and Tributyltetradecyl-phosphonium chloride ($[P_{4,4,4,14}]Cl$) were obtained from Tokyo Chemical Industry Co., Ltd. (TCI) or Aladdin.

2. Catalyst Characterization

Electrospray ionization high resolution mass spectra (ESI-HRMS) were recorded on a micrOTOF II spectrometer using CH_3OH as solvents. The reaction products were analyzed by using GC [a Shimadzu GC-2014 gas chromatograph equipped with the

KB-50 capillary column (30 m × 0.32 mm × 0.50 mm)] and GC-MS [Agilent 6890/5973 GC–MS equipped with the HP-5MS column (30 m × 0.25 mm × 0.25 mm)]. The elemental analysis of C and H was performed using an Elementar vario EI III C H N O S elemental analyzer and the ICP-AES analysis of Ta and P was performed on a Varian 710 instrument, respectively. The number of peroxide bonds was obtained by potential difference titration of Ce^{3+}/Ce^{4+}. High pressure FT-IR spectra were recorded on a Nicolet NEXUS 670 spectrometer. The catalyst was placed in the specially designed high-pressure IR cell, in which the cylindrical CaF_2 was used as sealing sheets. The cell was purged with CO_2 for 3 times and charged with CO_2 to the desired pressure. High pressured NMR spectra were recorded on a Bruker Avance 300 HD instrument (300 MHz ^1H NMR, 75 MHz ^{13}C NMR) equipped with a BBFO-Smartprobe. Measurements were carried out using a 5 mm sapphire NMR tube with a titanium pressure head equipped with a needle valve. The tube was always kept behind a protective shield and/or inside a cylinder made from polymethacrylate during handling, filling, transport and insertion into the magnet of the spectrometer. $[P_{4,4,4,4}]_3[Ta(O)_3(\eta^2\text{-}O_2)]$ (ca. 90 mg), CD_3OD (0.5 mL) and 30% H_2O_2 (1 drop, ca. 0.05 mL) was added into sapphire NMR tube which was connected with CO_2 setup. NMR tube was flushed and released for three times to remove the air inside and then a certain pressure of CO_2 was flushed inside the sapphire NMR tube in a controlled manner.

3. Catalyst Preparation

Preparation of Tantalum Acid

Tantalum acid ($Ta_2O_5 \cdot nH_2O$) was prepared by using the previously reported method.[1] In brief, a mixture of solid KOH (3.92 g, 70 mmol) and Ta_2O_5 (1.86 g, 7 mmol) was ground in a nickel crucible for 5 min and then was fused at 550 °C for 5 h. After cooling to room temperature, a plenty of water was added following the vacuum suction filtration. Acetic acid was added to the clear filtrate until the pH value dropped to 5. The white precipitate could be obtained, which was then washed with distilled water until neutral pH was attained, followed by drying at 50 °C for 1 h. The water content in the wet $Ta_2O_5 \cdot nH_2O$ was about 75 %.

Preparation of $(NH_4)_3[Ta(O_2)_4]$

Ammonium tetraperoxotantalate was prepared by following a previously reported method.[2] Tantalum acid (2.0 g) was dispersed in distilled water (2.0 ml) with a 30 wt.% solution of H_2O_2 (10 mL), and then pH value was adjusted to 10 using ammonia (25 wt.% solution). The cloudy solution was stirred for 0.5 h at 0 °C. When the solution became clear, addition of ethanol (50 mL) yields the white precipitate, which was filtered off, washed with ethanol and air-dried. $(NH_4)_3[Ta(O_2)_4]$: yield 0.65 g, 79%. Anal. Calcd for $(NH_4)_3[Ta(O_2)_4]$ (363.01): Ta 49.85. Found: Ta 48.86.

Preparation of Peroxotantalate Anion-based ILs

The $[P_{4,4,4,4}]OH$ ($P_{4,4,4,4}$=tetrabutylphosphonium) were prepared by using the previously reported method.[3] In brief, KOH (0.16 g, 2.4 mmol) and $[P_{4,4,4,4}]Br$ (0.59 g, 2.0 mmol) was added to the dry ethanol (5 mL) then the mixture was stirred vigorously at 0 °C for 12 h. The precipitated KCl and the excess of KOH were filtered off. The filtrate was mixed with an aqueous solution of $((NH_4)_3[Ta(O_2)_4]$ (0.32 g, 0.88 mmol) and then stirred at 40 °C for 3 h. The solution was concentrated and extracted by CH_2Cl_2 (20 ml) for three times. The extract was dried with anhydrous $MgSO_4$ and then evaporated at 40 °C for 2 h to obtain a bright yellow liquid. $[P_{4,4,4,4}]_3[Ta(O)_3(\eta^2\text{-}O_2)]$: Yield 0.6 g, 86%. Anal. Calcd for $(C_{16}H_{36}P)_3TaO_5$ $[P_{4,4,4,4}]_3[Ta(O)_3(\eta^2\text{-}O_2)]$ (1038): C 55.49; H 10.40; P 8.95; Ta 17.44. Found: C 52.32; H 9.87; P 8.35; Ta 16.04. Number of peroxide bonds=1.17.

$[P_{4,4,4,8}]_3[Ta(O)_3(\eta^2\text{-}O_2)]$ was prepared by using $[P_{4,4,4,8}]Br$ as a starting material in a similar method. The resulting material was a yellow viscous liquid. $[P_{4,4,4,8}]_3[Ta(O)_3(\eta^2\text{-}O_2)]$: yield 0.70 g, 87.1%. Anal. Calcd for $(C_{20}H_{44}P)_3TaO_5$ $[P_{4,4,4,8}]_3[Ta(O)_3(\eta^2\text{-}O_2)]$ (1206): C 59.71; H 10.95; P 7.71; Ta 15.09. Found: C 58.45; H 11.54; P 7.65; Ta 14.07. Number of peroxide bonds: 1.03.

$[P_{4,4,4,14}]_3[Ta(O)_3(\eta^2\text{-}O_2)]$ was prepared by using $[P_{4,4,4,14}]Cl$ as a starting material in a similar method. The resulting material was a yellow viscous liquid.

$[P_{4,4,4,14}]_3[Ta(O)_3(\eta^2\text{-}O_2)]$: yield 0.88 g, 90.5%. Anal. Calcd for $(C_{26}H_{56}P)_3TaO_5$ $[P_{4,4,4,14}]_3[Ta(O)_3(\eta^2\text{-}O_2)]$ (1458): C 64.16; H 11.5; P 6.38; Ta 12.39. Found: C 60.58; H 11.61; P 6.03; Ta 11.75. Number of peroxide bonds: 0.97.

4. Typical Reaction Procedure for the Catalytic Epoxidation of Olefins

A typical method for the epoxidation of olefins was as follows. A mixture of olefin (2 mmol), 30% aqueous H_2O_2 (2.0 mmol), CH_3OH (2.5 mL), dodecane (0.2 mmol) and the ILs catalysts (0.05 mmol) were placed in an autoclave equipped with a magnetic stirrer. The reactor was purged with CO_2 for 3 times and charged with CO_2 until the desired pressure was reached, then it was stirred at 40 °C for some time. When the reaction was finished, the reactor was cooled in an ice-water bath immediately, and the CO_2 was slowly vented while cyclohexane was used as absorption liquid to absorb the products entrained by CO_2. After that, the reaction mixture was extracted for three times with cyclohexane. The resulting extract was dried with Na_2SO_4 and then analyzed by using GC. The recovered catalyst was dried at 40 °C for 3 h under vacuum and was reused then by following the similar procedure. In some cases, the reaction was carried out sequentially under the pressure of N_2 or CO_2 (2.0 MPa).

5. Reaction Kinetics

The procedure for investigating the kinetic parameters for the epoxidation of cyclooctene was as follows: Batch size: 2.0 mmol cyclooctene, 2.0 mmol H_2O_2, 0.05 mmol Cat., 2.5 mL CH_3OH, 2.0 MPa CO_2. The reaction mixture was stirred vigorously using a magnetic stirrer and heated to the desired temperature (293-323 K). The reaction was monitored using gas chromatography. The rate constant was determined from the experimental data assuming pseudo-first order reaction kinetics and the activation energy for the process was determined using the Arrhenius equation based on the calculated rate constants at different temperatures.

6. CO_2 Adsorption

The IL catalyst ($[P_{4,4,4,4}]_3[Ta(O)_3(\eta^2\text{-}O_2)]$) (0.5 mmol) was added to methanol

(2.0 ml) containing hydrogen peroxide (5.0 mmol). After stirring for 10 min at 0 °C, diethyl ether was poured into the solution rapidly to precipitate the oxidizing species, which was washed carefully with a small amount of diethyl ether sequentially. The generated $[P_{4,4,4,4}]_3[Ta(\eta^2\text{-}O_2)_4]$ was purged with 3 MPa CO_2 at 0 °C. The weight-gain was analyzed by analytical balance. After finishing absorption, the resulting Ta-peroxocarbonate IL was dealt under reduced pressure condition at 50 °C for 2 h, and then was reactivated with H_2O_2.

7. Density Functional Theory Calculations

All stationary points were optimized by using PBE functional[4] as implemented in ADF 2013 program.[5] The triple-zeta Slater basis sets were used with a frozen core treatment composed of the 1s to 4spdf shells for tantalum and the 1s for O and C atoms. Scalar relativistic effect was taken into accounted in the ZORA formulation.[6] The nature of all stationary points was identified to be a minimum or a transition state by vibrational frequency analysis, and the reaction channels were confirmed by intrinsic reaction coordinate (IRC) calculations.[7] The solvent effect of water was included by using the Conductor-like Screening Model (COSMO)[8] as implemented in ADF2013.[9] The bond energy decomposition analysis was done according to the Morokuma-Ziegler scheme.[10]

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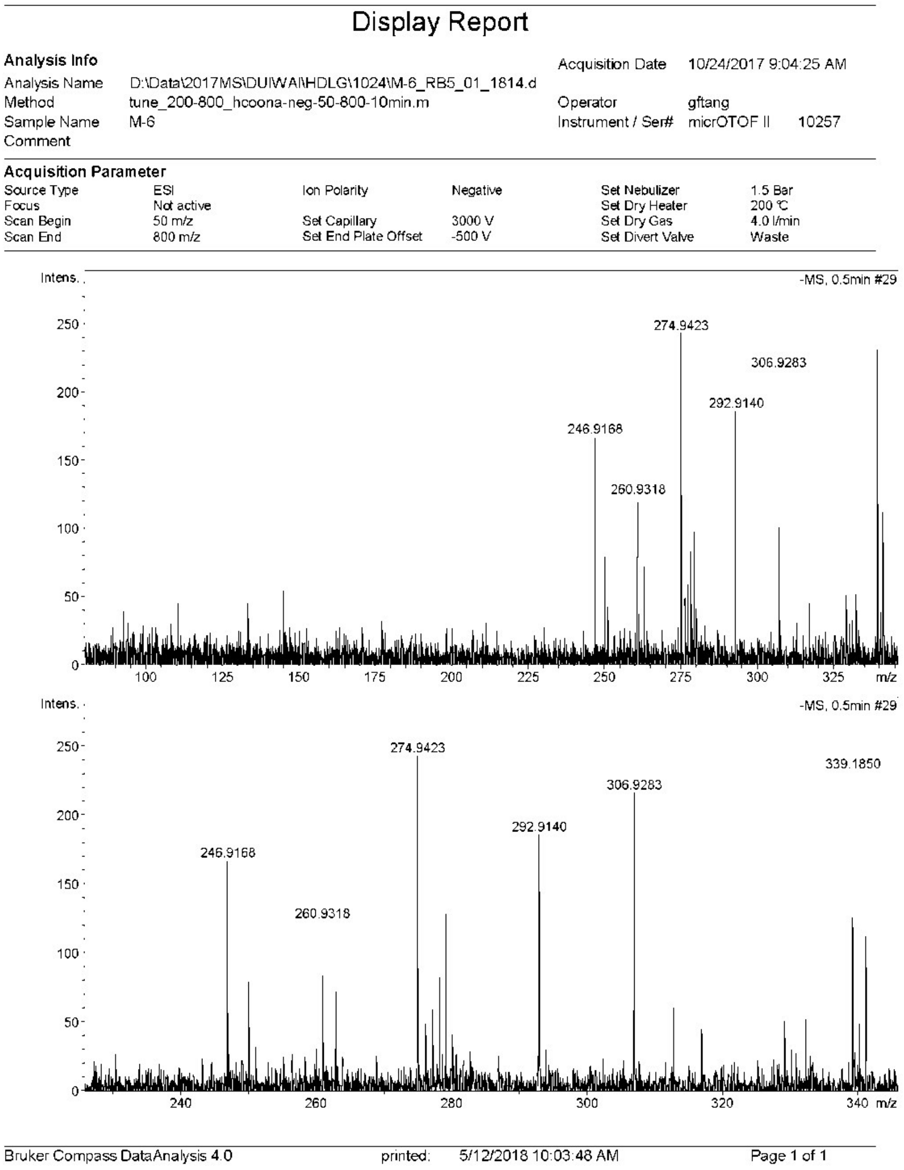
<Supplementary figures and tables>



Display Report

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Bruker Compass DataAnalysis 4.0 printed: 5/12/2018 10:03:48 AM Page 1 of 1

Fig. S1. HRMS of $[P_{4,4,4,4}]_3[Ta(\eta^2\text{-}O_2)_4]$ in CH_3OH dealt with 2.0 MPa CO_2.

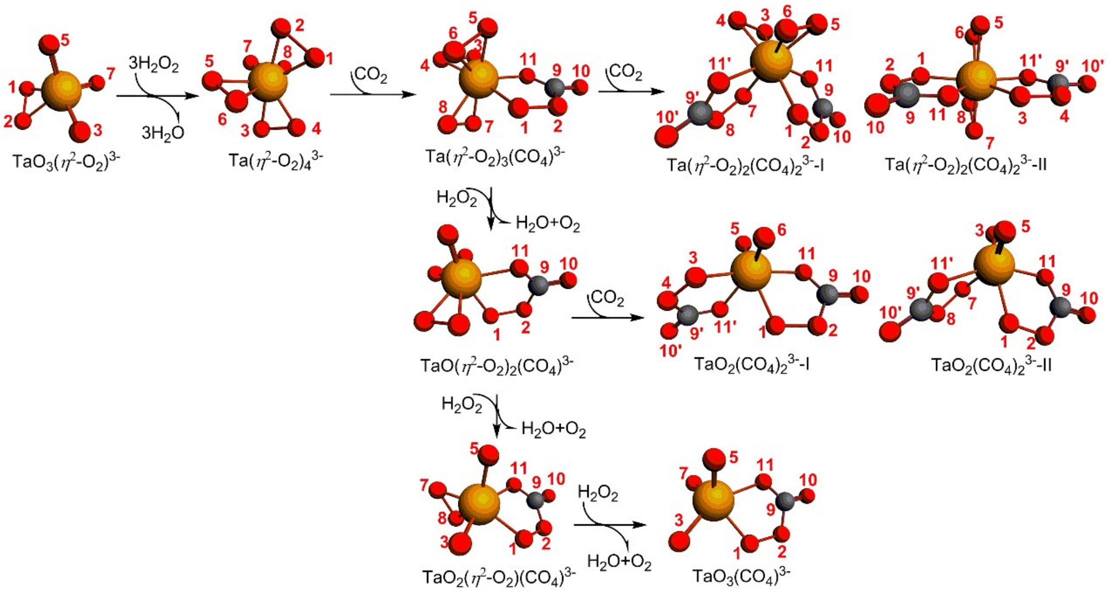

Fig. S2. The potential reaction route between the anion $[TaO_3(\eta^2\text{-}O_2)_4)]^{3-}$ and CO_2.

Table S1. Effect of Different Solvents on the Epoxidation of Cyclooctene.[a]

entries	temperature /°C	CO_2/MPa	solvent	Con./%	Sel./%
1	40	2	CH_2Cl_2	3.5	≥ 99
2	40	2	EtOAc	5.7	≥ 99
3	40	2	CH_3CN	3.4	≥ 99
4	40	2	ethanol	42.3	≥ 99
5	40	2	methanol	87.2	≥ 99

[a] Reaction condition: 2.0 mmol cyclooctene, 2.0 mmol H_2O_2, 0.05 mmol $[P_{4,4,4,4}]_3[Ta(O)_3(\eta^2\text{-}O_2)]$, 2.0 MPa CO_2, 2.5 mL solvent, 40 °C.

Table S2. Substitution of H_2O_2 in the Epoxidation of Cyclooctene.[a]

entries	oxidant	solvents	Con./%	Sel./%
1	H_2O_2	CH_3OH	87.6	≥ 99
2	TBHP	CH_3OH	2.6	≥ 99
3[b]	TBHP	CH_3OH	1.3	≥ 99

[a]Reaction condition: 2 mmol cyclooctene, 2 mmol oxidant, 0.05 mmol $[P_{4,4,4,4}]_3[Ta(O)_3(\eta^2\text{-}O_2)]$, 2 MPa CO_2, 2.5 mL CH_3OH, 40 °C. [b]Recation temperature: 60 °C.

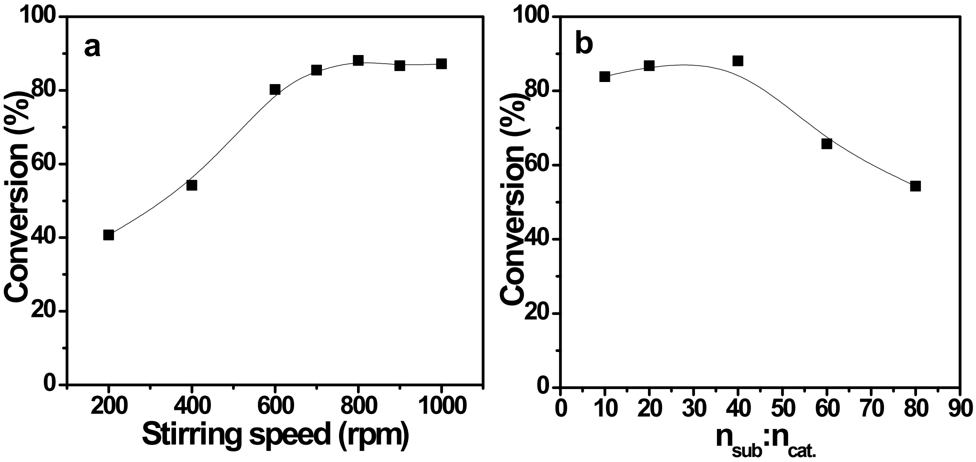

Fig. S3. (a) Effect of stirring speed on reaction rate. Reaction conditions: 2.0 mmol cyclooctene, 2.0 mmol H_2O_2, 0.05 mmol $[P_{4,4,4,4}]_3[Ta(O)_3(\eta^2\text{-}O_2)]$, 2.0 MPa CO_2, 2.5 mL CH_3OH, 40 °C. (b) Effect of the $n_{sub.}/n_{cat.}$ on epoxidation of cyclooctene. Reaction condition: 2.0 mmol cyclooctene, 2.0 mmol H_2O_2, Cat.= $[P_{4,4,4,4}]_3[Ta(O)_3(\eta^2\text{-}O_2)]$, 2.0 MPa CO_2, 2.5 mL CH_3OH, 40 °C, stirring speed=800 rpm.

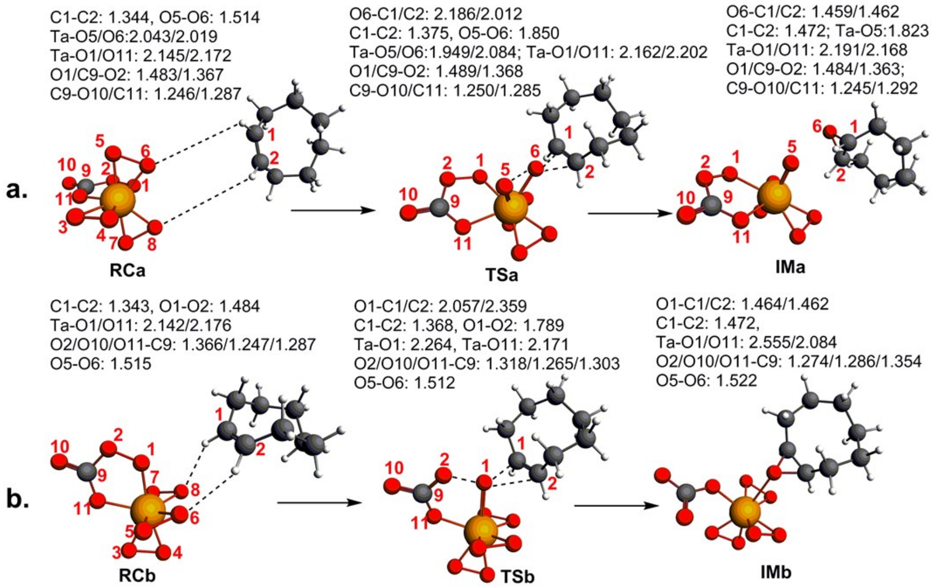

Fig. S4. The optimized stationary points along the epoxidation at sites *a* (top) and *b* (bottom) with key geometric parameters (bond length in Å, angle in degree). Color scheme: Ta: gold; O: red; C: dark grey; H: white.

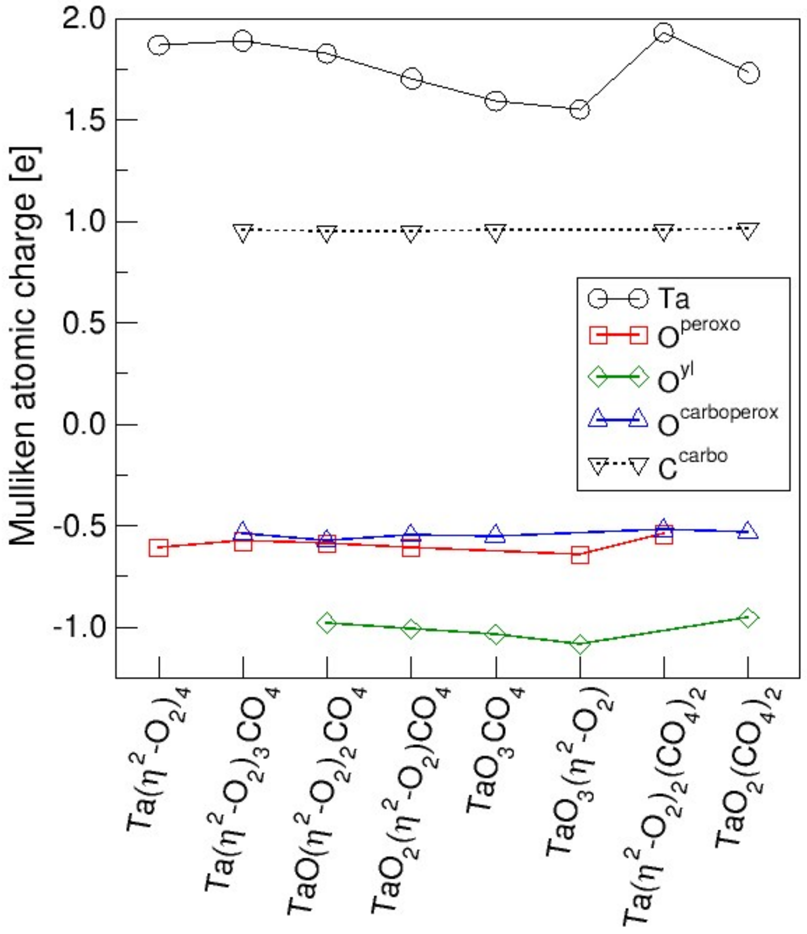

Fig. S5. Mulliken atomic charges of key atoms in the tantalum complexes. O^{peroxo} represents the O atoms of the η^2-peroxide ligand, O^{yl} the O atom that interacts with Ta via a Ta=O bond, $O^{carboperox}$ the O atom of the carbonate peroxide that coordinates with Ta, and C^{carbo} the C atom of the carbonate group.

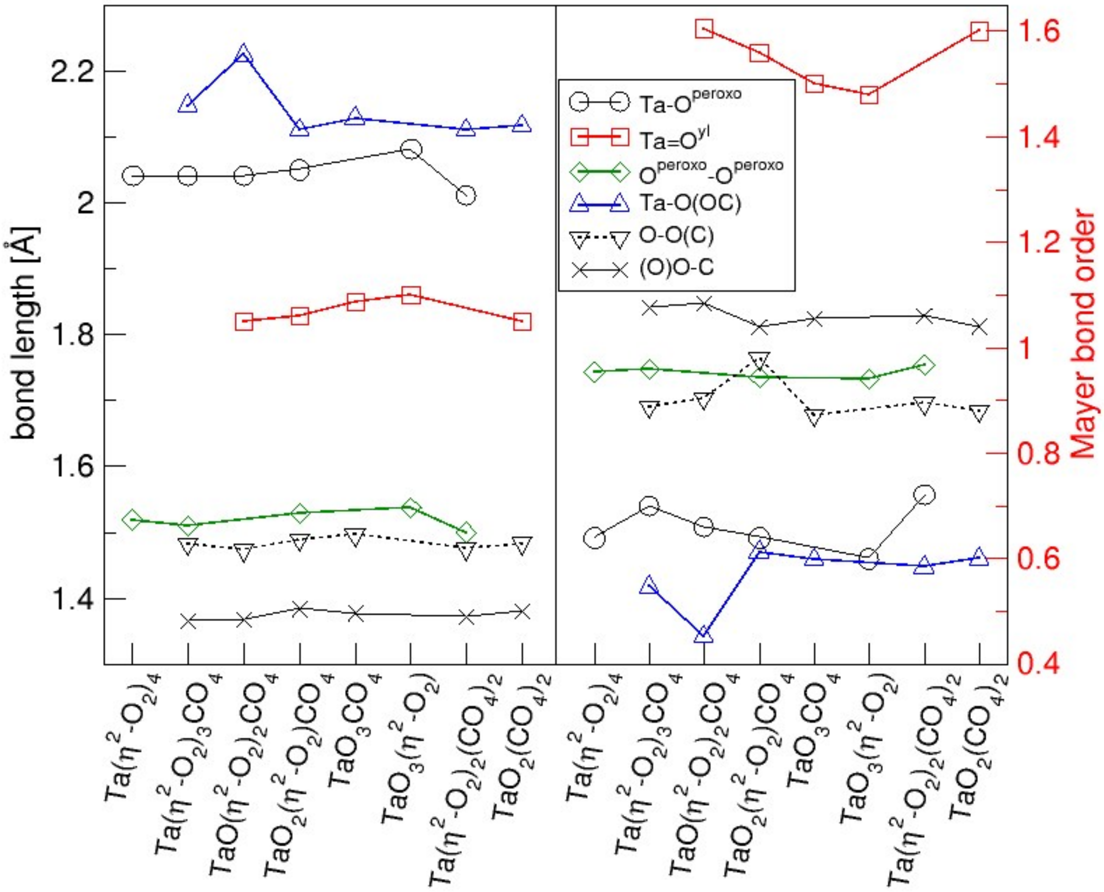

Fig. S6. Bond length (left) and Mayer bond order (right) of key bonds in the tantalum complexes.