SUPPORTING INFORMATION

Synthesis, Characterization and Reactivity of Ti(IV)-monosubstituted Keggin Polyoxometalates

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Figure S1. ^1H NMR spectrum of **4** (0.01 M in *d*-MeCN at 20°C).

Figure S2. UV-vis spectrum of **4** (0.125 mM in MeCN, path length = 1 cm, 20°C).

Figure S3. **A:** ^{31}P NMR spectrum of $[\text{Bu}_4\text{N}]_4[\text{PTi}(\text{OMe})\text{W}_{11}\text{O}_{39}]$ (**3**), $[\text{Bu}_4\text{N}]_8[(\text{PTiW}_{11}\text{O}_{39})_2\text{O}]$ (**1**) and $[\text{Bu}_4\text{N}]_4[\text{PTi}(\text{OH})\text{W}_{11}\text{O}_{39}]$ (**2**) in equilibrium ($[\mathbf{3}]_0 = 0.02$ M, $[\text{H}_2\text{O}] = 1.1$ M, MeCN, 7 days) and **B:** the corresponding ^1H NMR spectrum in *d*-MeCN.

Figure S4. ^{31}P NMR spectra of $[\text{Bu}_4\text{N}]_4[\text{PTi}(\text{OH})\text{W}_{11}\text{O}_{39}]$ (**2**) and $[\text{Bu}_4\text{N}]_4[\text{PTi}(\text{OAr})\text{W}_{11}\text{O}_{39}]$ (**4**) in equilibrium ($[\text{ArOH}]_0 = [\text{TMP}]_0 = 0.5$ M, MeCN, 7 days): (a) $[\mathbf{2}]_0 = 0.01$ M; (b) $[\mathbf{2}]_0 = 0.02$ M.

Figure S1. ^1H NMR spectrum of **4** (0.01 M in d -MeCN, 20 °C). Admixtures in d -MeCN are marked by asterisks.

Figure S2. UV-vis spectrum of **4** (0.1 mM in MeCN, path length = 1 cm, 20 °C).

Figure S3. **A:** ^{31}P NMR spectrum of $[\text{Bu}_4\text{N}]_4[\text{PTi}(\text{OMe})\text{W}_{11}\text{O}_{39}]$ (**3**), $[\text{Bu}_4\text{N}]_8[(\text{PTiW}_{11}\text{O}_{39})_2\text{O}]$ (**1**) and $[\text{Bu}_4\text{N}]_4[\text{PTi}(\text{OH})\text{W}_{11}\text{O}_{39}]$ (**2**) in equilibrium ($[\mathbf{3}]_0 = 0.02\text{ M}$, $[\text{H}_2\text{O}] = 1.1\text{ M}$, MeCN, 7 days) and **B:** the corresponding ^1H NMR spectrum in *d*-MeCN.

Figure S4. ^{31}P NMR spectra of $[\text{Bu}_4\text{N}]_4[\text{PTi}(\text{OH})\text{W}_{11}\text{O}_{39}]$ (**2**) and $[\text{Bu}_4\text{N}]_4[\text{PTi}(\text{OAr})\text{W}_{11}\text{O}_{39}]$ (**4**) in equilibrium ($[\text{ArOH}]_0 = [\text{TMP}]_0 = 0.5\text{ M}$, MeCN, 7 days): (a) $[\mathbf{2}]_0 = 0.01\text{ M}$; (b) $[\mathbf{2}]_0 = 0.02\text{ M}$.