Mo(VI) Catalysts Obtained from η^3-Allyl Dicarbonyl Precursors: Synthesis, Characterization and Catalytic Performance in Cyclooctene Epoxidation

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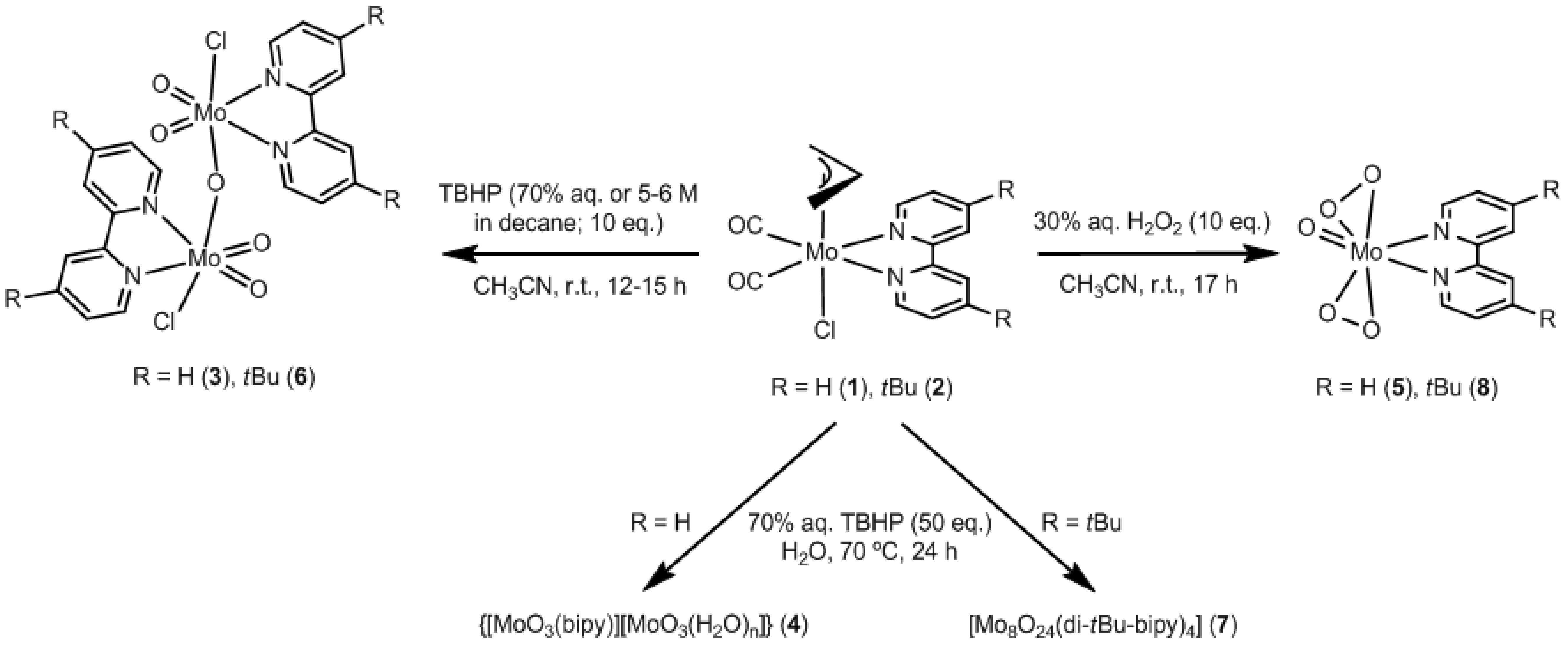
Introduction

Allyl dicarbonyl complexes $[Mo(\eta^3\text{-}C_3H_5)X(CO)_2(L)_n]$ (X = halide) have been found to act as catalyst precursors for several reactions, namely the polymerization of dienes and the epoxidation of olefins.[1] In our recent investigations of complexes *cis*-$[Mo(CO)_4(L)]$, we found that the nature of the bidentate ligand L influences the species formed by oxidative decarbonylation and their catalytic performance in olefin epoxidation: with L = bipy, the organic-inorganic hybrid $[MoO_3(bipy)]$ is obtained; with L = di-*t*Bu-bipy, the polynuclear complex $[Mo_8O_{24}(\text{di-}t\text{Bu-bipy})_4]$ is obtained instead.[2]

Here we report on the use of the complexes $[Mo(\eta^3\text{-}C_3H_5)Cl(CO)_2(L)]$ (L = bipy (**1**), di-*t*Bu-bipy (**2**)) as catalyst precursors in the epoxidation of cyclooctene (Cy) using aqueous TBHP or H_2O_2 as oxidant. Additionally, oxidative decarbonylation was performed for both catalysts, in aqueous media, and the obtained products were characterized and also used as catalysts.[3]

Synthesis


TBHP (70% aq. or 5-6 M in decane; 10 eq.)
CH_3CN, r.t., 12-15 h

30% aq. H_2O_2 (10 eq.)
CH_3CN, r.t., 17 h

R = H (**3**), *t*Bu (**6**)

R = H (**1**), *t*Bu (**2**)

R = H (**5**), *t*Bu (**8**)

R = H

70% aq. TBHP (50 eq.)
H_2O, 70 °C, 24 h

R = *t*Bu

$\{[MoO_3(bipy)][MoO_3(H_2O)_n]\}$ (**4**)

$[Mo_8O_{24}(\text{di-}t\text{Bu-bipy})_4]$ (**7**)

Characterization

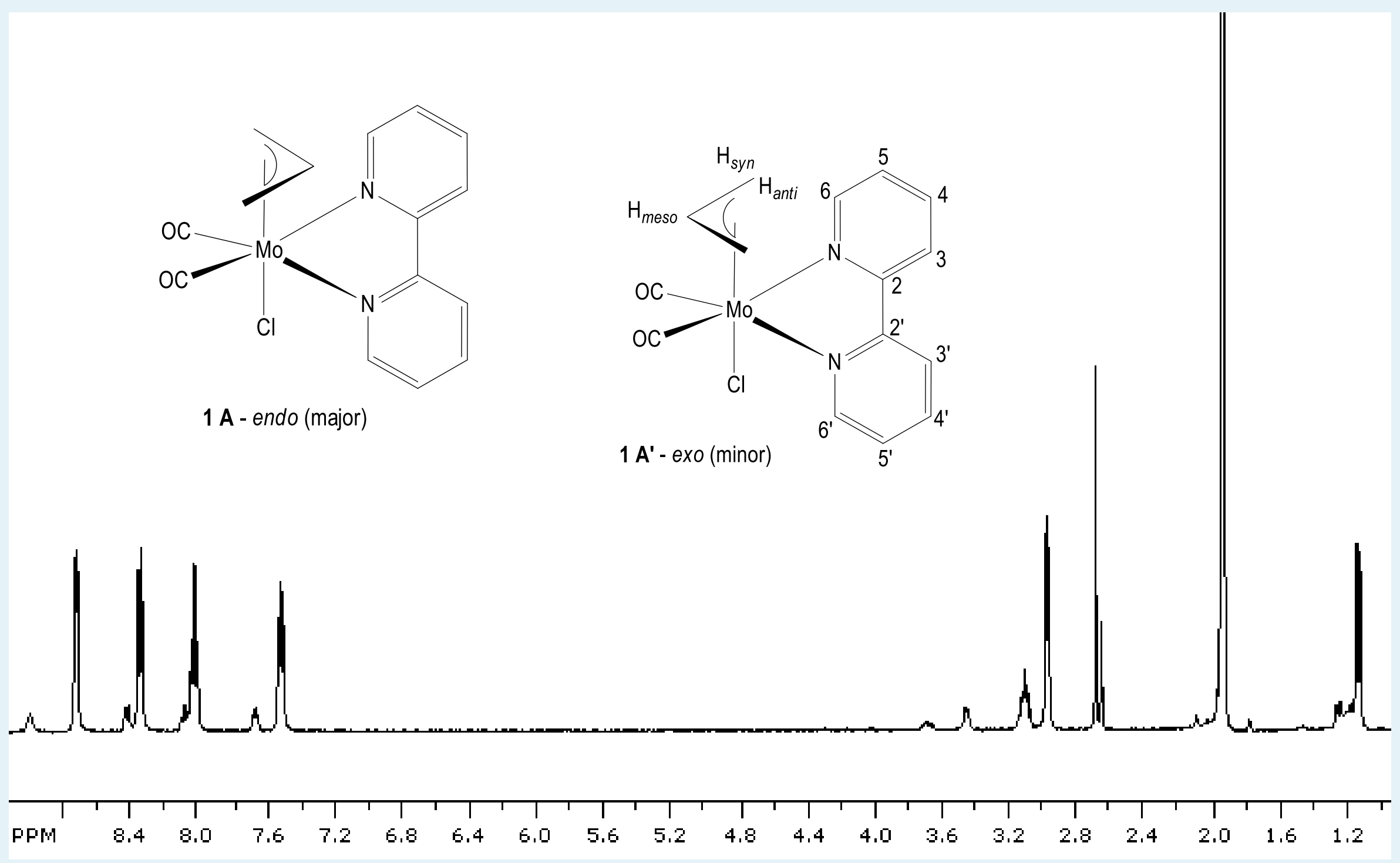


Figure 1. ^1H NMR spectrum of **1** in acetone-d_6 at r.t.

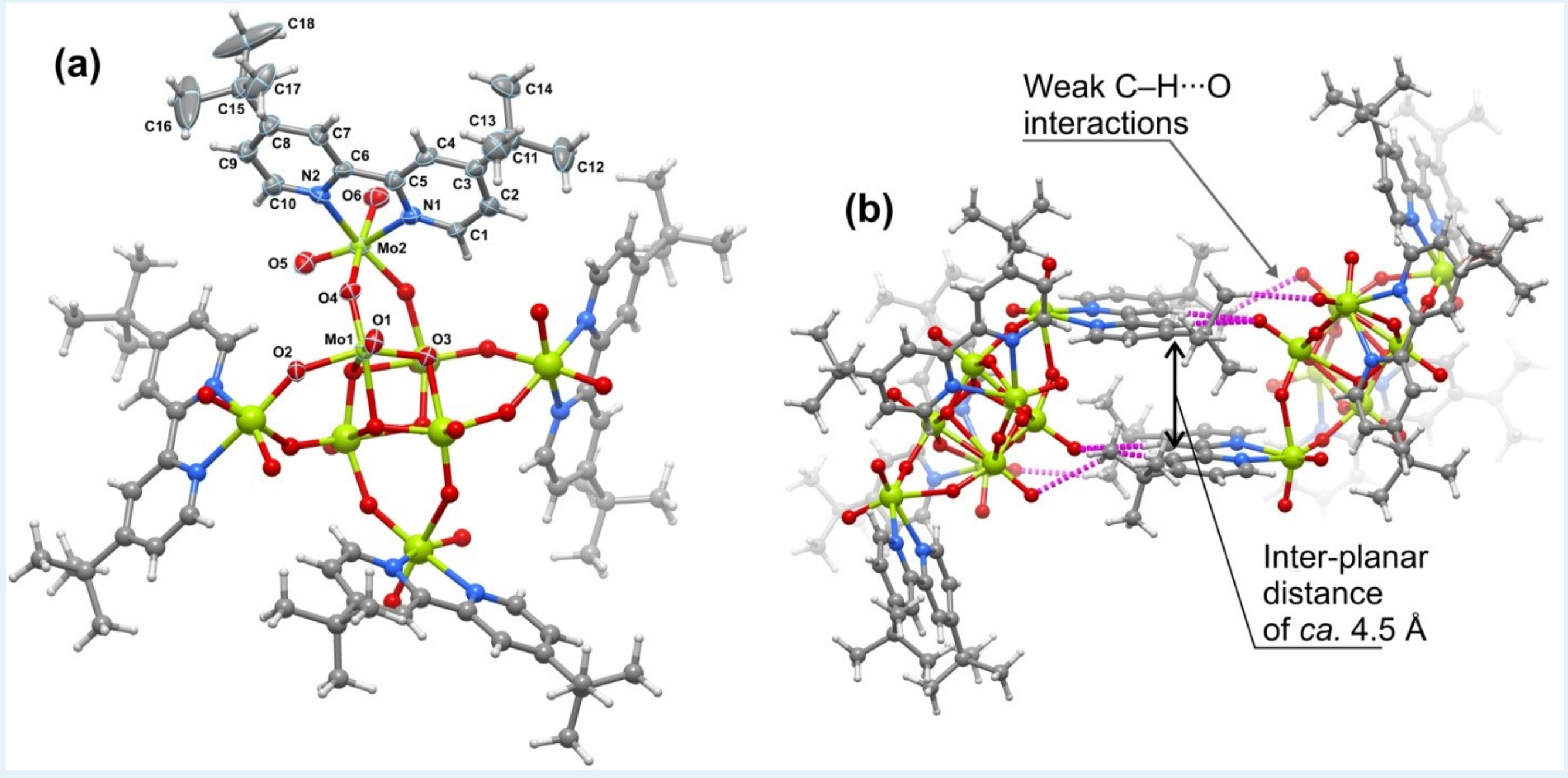


Figure 2 (a) Schematic representation of the windmill-type complex $[Mo_8O_{24}(\text{di-}t\text{Bu-bipy})_4]$ **(7).**Thermal ellipsoids drawn at the 50% probability level.
(b) Portion of the crystal structure of **7** depicting the most structurally robust C–H···O short contacts.

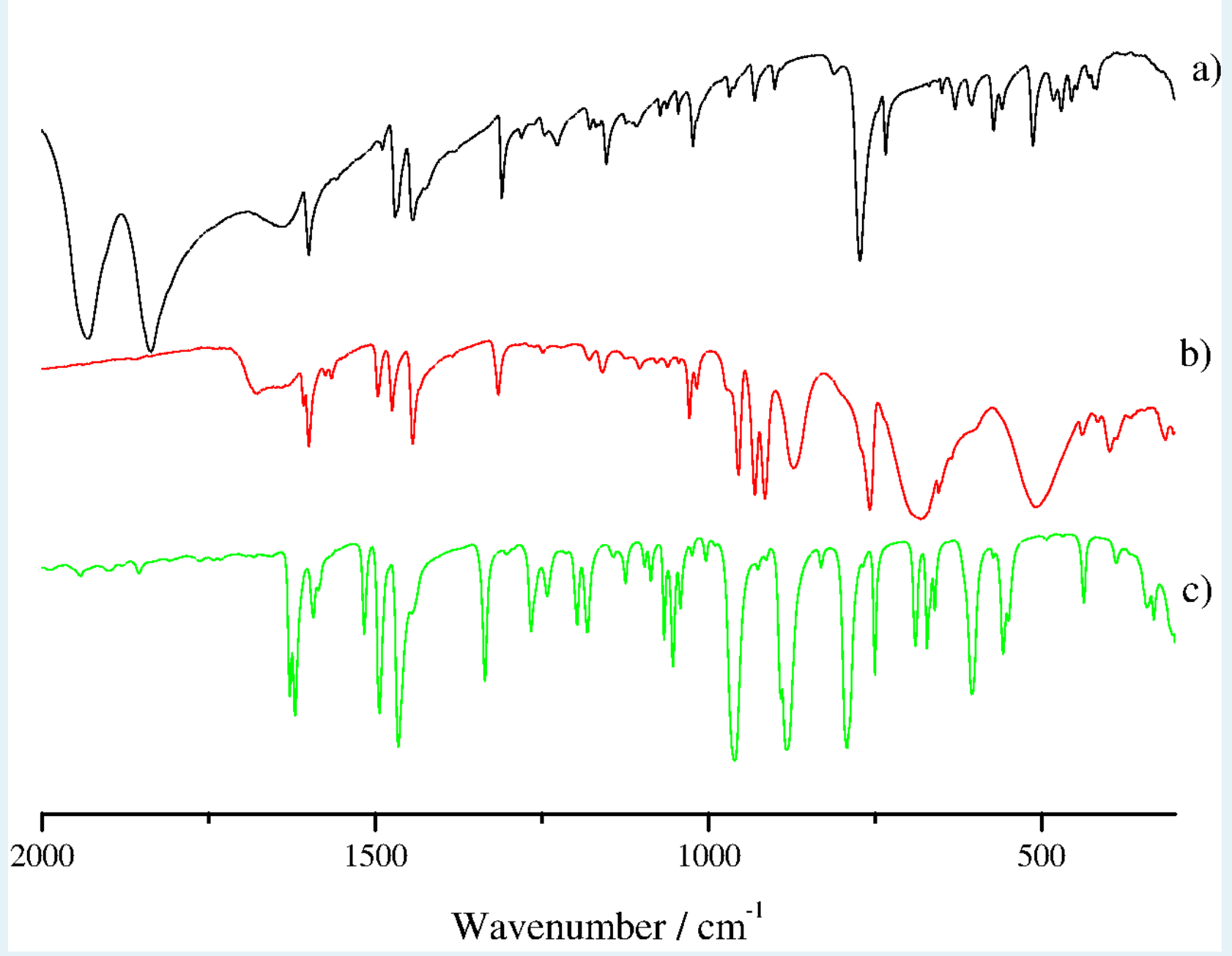


Figure 3. FT-IR spectra of compounds **1** (a), **4** (b), **5** (c)

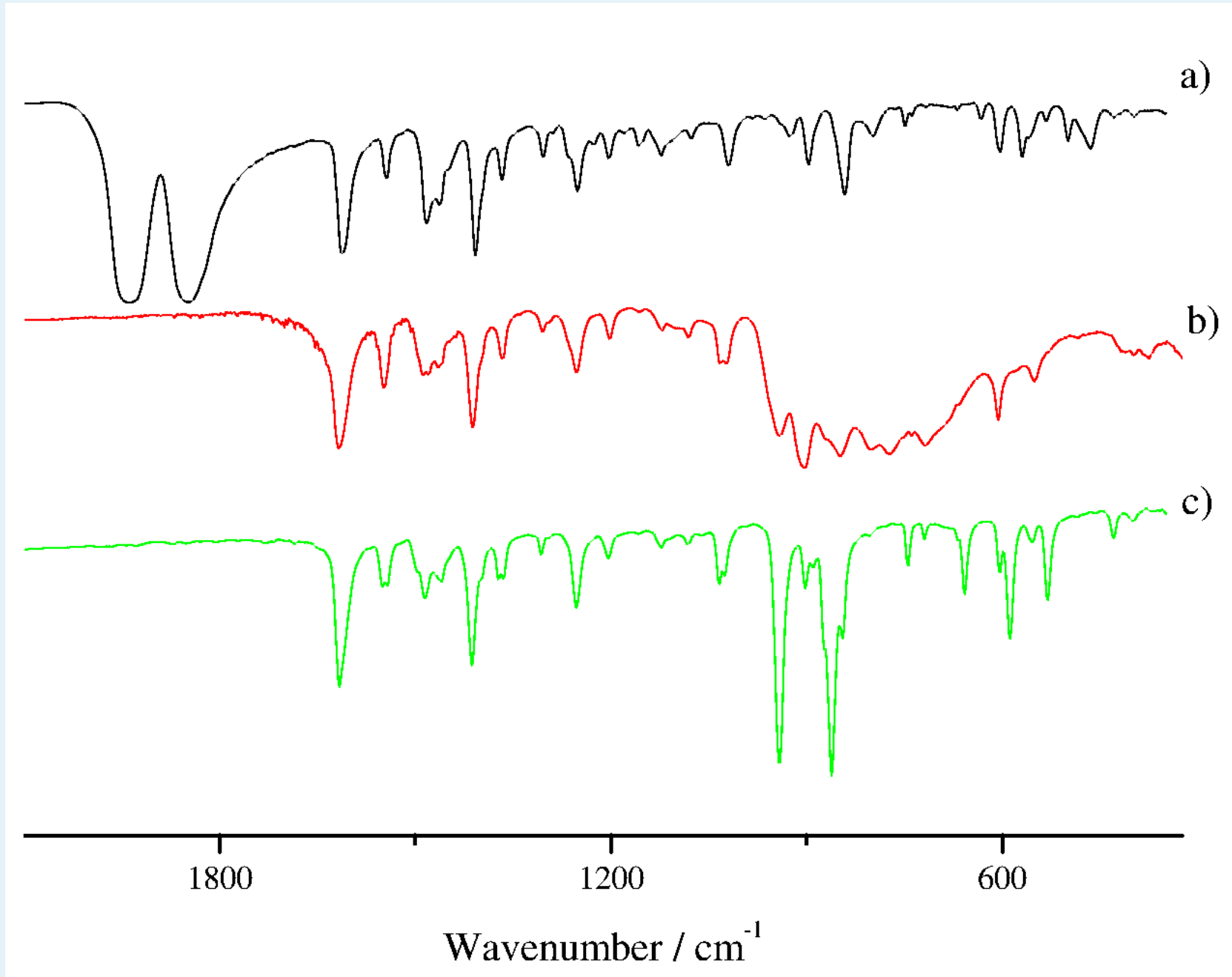


Figure 4. FT-IR spectra of compounds **2** (a), **7** (b), **8** (c)

Comp.	Selected FT-IR (cm^{-1})
1	1932vs, 1837vs (CO), 1600m (C=N bipy)
3	1600s (C=N bipy), 931vs, 903vs (Mo=O), 789vs (Mo–O–Mo)
4	955s, 930s, 915s, 868s (Mo=O), 682s (Mo–O–Mo), 514s (OMo_3)
5	939vs (Mo=O), 861s (O-O), 651m, 583m, 536m ($Mo(O_2)_2$)
7	942 vs, 903vs (Mo=O), 849s, 773s, 719s (Mo-O-Mo)

With the exception of **3**, the oxo Mo(VI) compounds have been previously prepared by different routes: **4**,[4a] **5**,[4b] **6**,[4c] **7**,[2] and **8**.[4d]

Catalysis

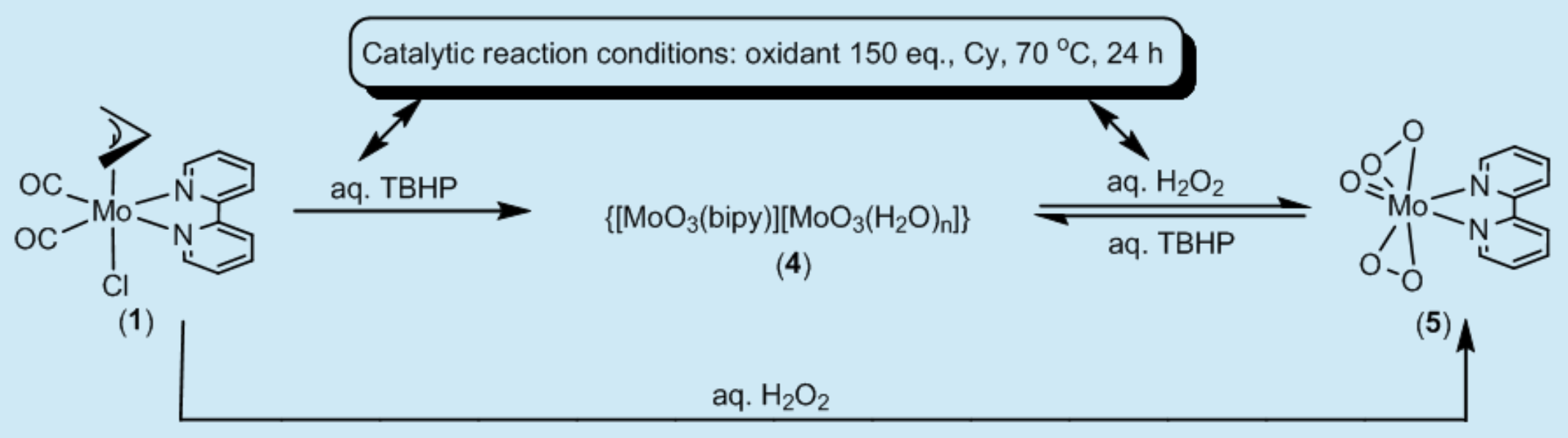

Catalytic reaction conditions: oxidant 150 eq., Cy, 70 °C, 24 h

Table 1. Catalytic epoxidation of Cy with TBHP[a]

Compound	Solvent	Yield (%)[b]	Identified solid after 24h[c]
1	H_2O	37	**4** (TY≈60%)
1	CH_3CN	19	**4**
3	H_2O	32	**4**
4	H_2O	38	**4**
5	H_2O	28	**4**
2	H_2O	87	—
2	CH_3CN	59	—
6	H_2O	96	—
7	H_2O	90	—
8	H_2O	98	—

Table 2. Catalytic epoxidation of Cy with H_2O_2[a]

Compound	Solvent	Yield (%)[b]	Identified solid after 24h[c]
1	CH_3CN	66	**5**
3	CH_3CN	71	**5**
4	CH_3CN	79	**5**
5	CH_3CN	54	**5**
2	CH_3CN	26	**8**
6	CH_3CN	54	**8**
7	CH_3CN	75	**8**
8	CH_3CN	81	**8**

[a] mmoles of Mo:Cy:oxidant = 0.018:1.8:2.75, 24 h reaction, 70 ºC, 800 rpm, total volume ≈ 1.25 mL; [b] CyO yield (100% selectivity); [c] solid formed identified by FT-IR spectroscopy; TY = theoretical wt.% yield of product formed.

Conclusions

The η^3-allyl dicarbonyl complexes $[Mo(\eta^3\text{-}C_3H_5)Cl(CO)_2(L)]$ (L = bipy, **1**; di-*t*Bu-bipy, **2**) are convenient precursors to oxo Mo(VI) compounds that selectively catalyze the epoxidation of Cy in aqueous media. Reaction of **1** or **2** with the oxidant results in oxidative decarbonylation. When the oxidant is H_2O_2 aq., the oxodiperoxo complexes $MoO(O_2)_2(L)$ (**5**, **8**) are formed. By contrast, when the oxidant is TBHP aq., different oxo Mo(VI) compounds are formed, depending on the ligand L and the reaction conditions: oxo-bridged dimers $[MoO_2Cl(L)]_2O$ (**3**, **6**), the hybrid $\{[MoO_3(bipy)][MoO_3(H_2O)_n]\}$ (**4**), the octanuclear complex $[Mo_8O_{24}(\text{di-}t\text{Bu-bipy})_4]$ (**7**).

We anticipate that the extension of these studies to other η^3-allyl dicarbonyl complexes, including chiral derivatives, will provide novel oxo Mo(VI) compounds, possibly active in aqueous catalysis.

References

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Acknowledgments

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