Synthesis, Characterization and Catalytic application of Water Stable η³-Allyl Dicarbonyl Complexes of Molybdenum(II)

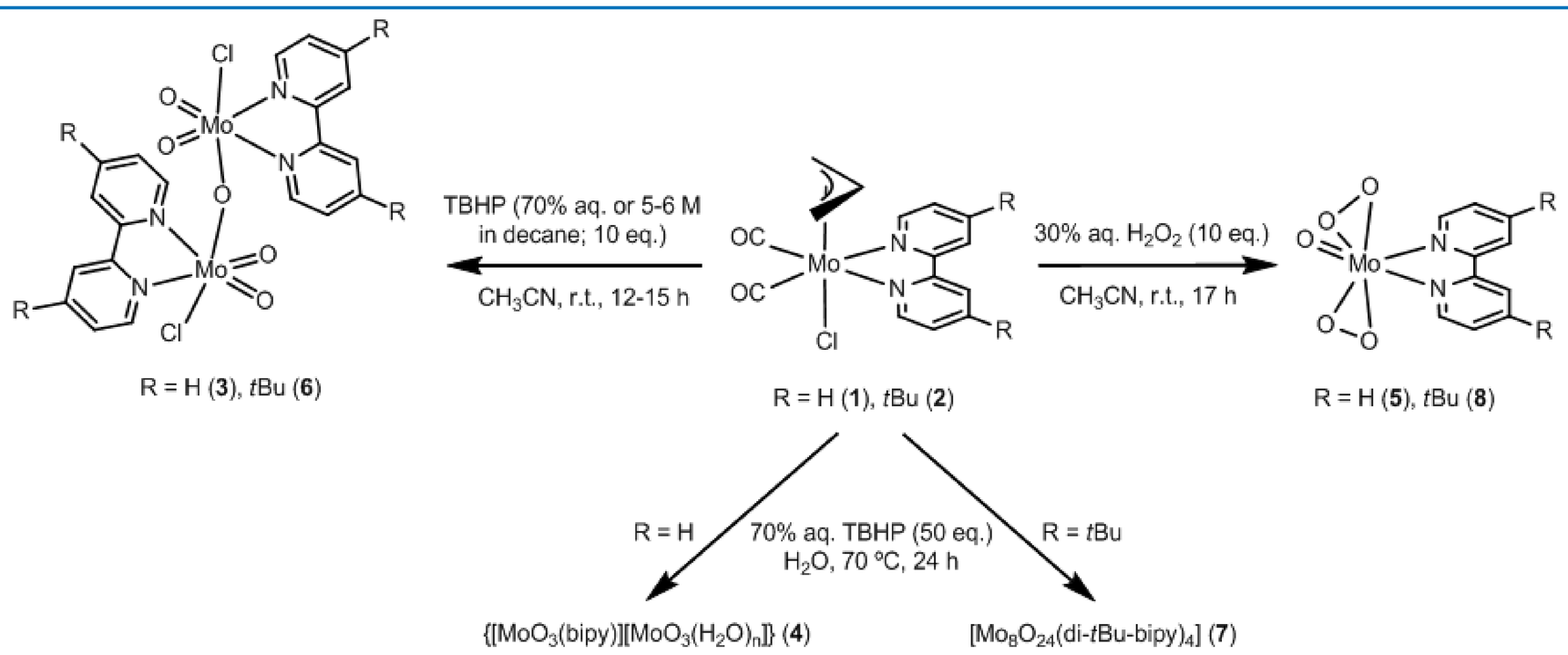
Carla A. Gamelas,[1] Ana C. Gomes,[2] Sofia M. Bruno,[2] Anabela A. Valente,[2] Martyn Pillinger,[2] Carlos C. Romão,[3] Isabel S. Gonçalves[2]

[1]Escola Superior de Tecnologia de Setúbal, Instituto Politécnico de Setúbal, 2910-761 Setúbal, Portugal;
[2]Department of Chemistry, CICECO, University of Aveiro, 3810-193 Aveiro, Portugal
[3]Instituto de Tecnologia Química e Biológica, UNL, 2781-901 Oeiras, Portugal;

Introduction

Allyl dicarbonyl complexes [Mo(η^3-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}(di-*t*Bu-bipy)$_4$] is obtained instead.[2]
Here we report on the use of the complexes [Mo(η^3-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.

Synthesis



Characterization

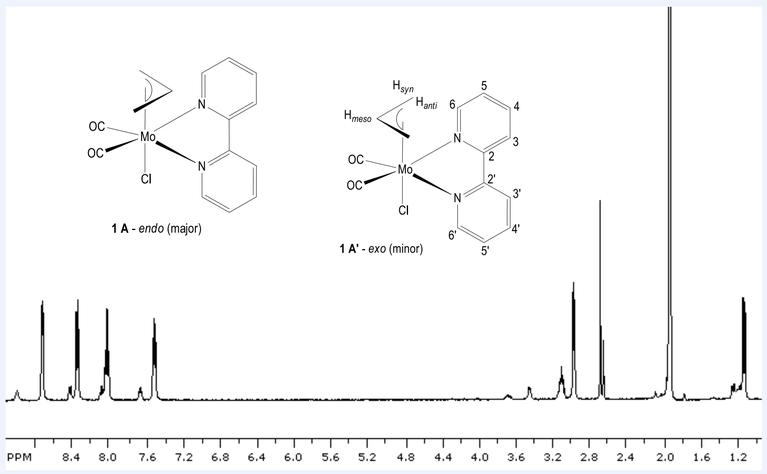


Figure 1. ^{1}H NMR spectrum of **1** in acetone-d_6 at r.t.

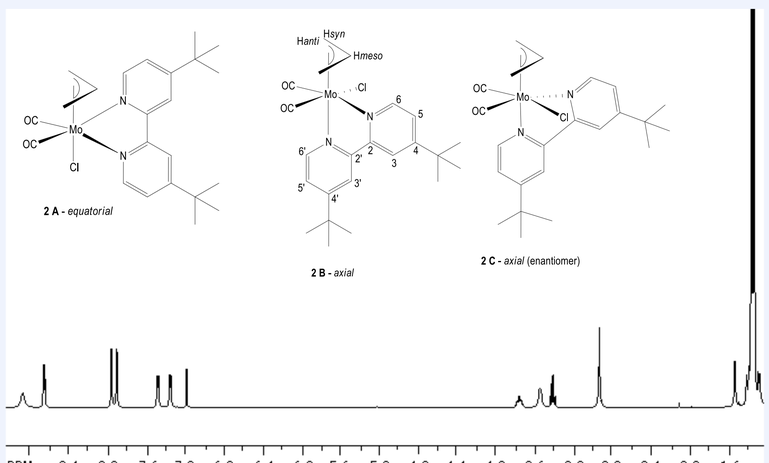


Figure 2. ^{1}H NMR spectrum of **2** in $CDCl_3$ at r.t. (as reported in the literature[4])

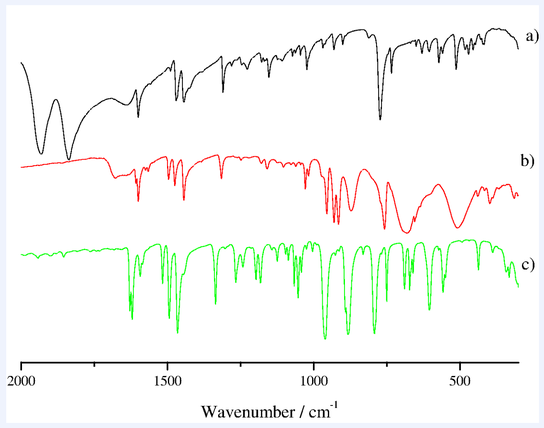


Figure 3. FT-IR spectra of compounds **1** (a), **4** (b), **5** (c)

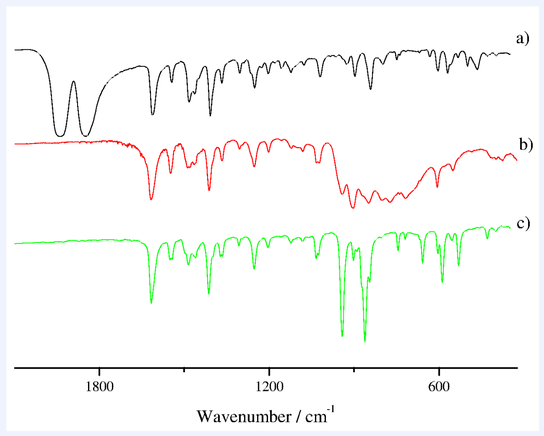


Figure 4. FT-IR spectra of compounds **2** (a), **7** (b), **8** (c)

Compound	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**,[3a] **5**,[3b] **6**,[3c] **7**,[2] and **8**.[3d]

Catalysis

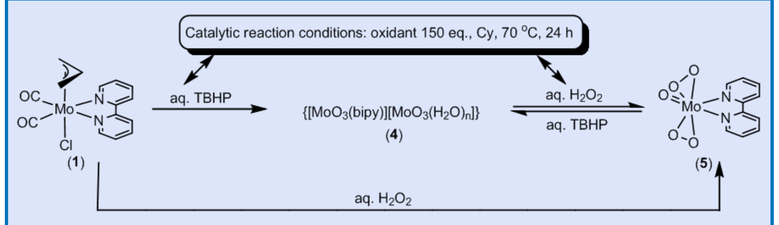


Table 1. Catalytic epoxidation of Cy with TBHP[a]

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(η^3-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}(di-*t*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

[1] Alonso, J. C.; Neves, P.; da Silva, M. J. P.; Quintal, S.; Vaz, P. D.; Silva, C.; Valente, A. A.; Ferreira, P.; Calhorda, M. J.; Felix, V.; Drew, M. G. B. *Organometallics* **2007**, *26*, 5548.
[2] Amarante, T. R.; Neves, P.; Coelho, A. C.; Gago, S.; Valente, A. A.; Paz, F. A. A.; Pillinger, M.; Gonçalves, I. S. *Organometallics* **2010**, *29*, 883.
[3] (a) Abrantes, M.; Amarante, T. R.; Antunes, M. M.; Gago, S.; Paz, F. A. A.; Margiolaki, I.; Rodrigues, A. E.; Pillinger, M.; Valente, A. A.; Gonçalves, I. S. *Inorg. Chem.* **2010**, *49*, 6865. (b) Schlemper, E. O.; Schrauzer, G. N.; Hughes, L. A. *Polyhedron* **1984**, *3*, 377. (c) Arzoumanian H.; Bakhtchadjian R. *Trans. Met. Chem.* **2006**, *31*, 681. (d) Amarante, T. R.; Paz, F. A. A.; Gago, S.; Gonçalves, I. S.; Pillinger, M.; Rodrigues, A. E.; Abrantes, M. *Molecules* **2009**, *14*, 3610.
[4] Rodrigues, C. W.; Limberg, C.; Pritzkow, H. *Chem. Commun.* **2004**, 2734.

Acknowledgments

We are grateful to FCT, POCI 2010, OE and FEDER for general funding, REDE/1517/RMN/2005 and REDE71504/REM/2005. EST-IPS is acknowledged for a short duration grant to C.A.G. The FCT is acknowledged for a post-doctoral grant to S.M.B. CICECO is acknowledged for financial support (including a post-doctoral grant to A.C.G.).