

Magnesium alkylperoxides incorporating fluorinated β -diketiminato ligands: synthesis, structure and reactivity in the epoxidation of enones

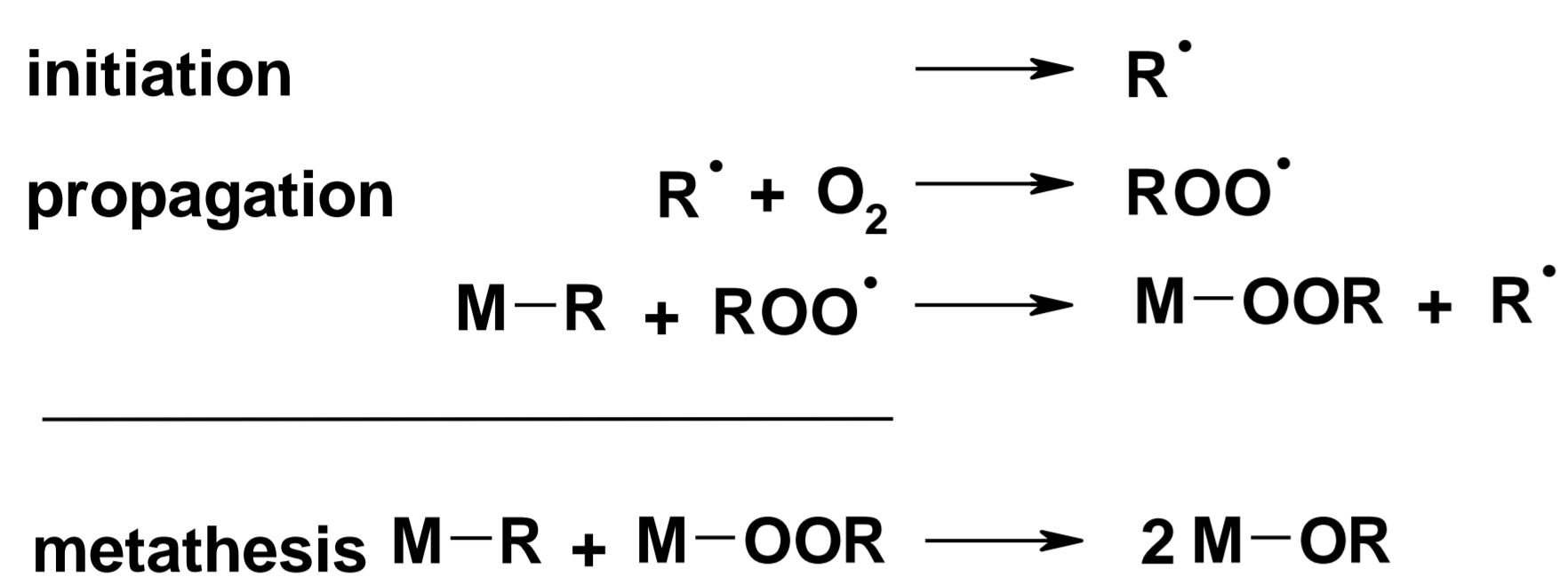
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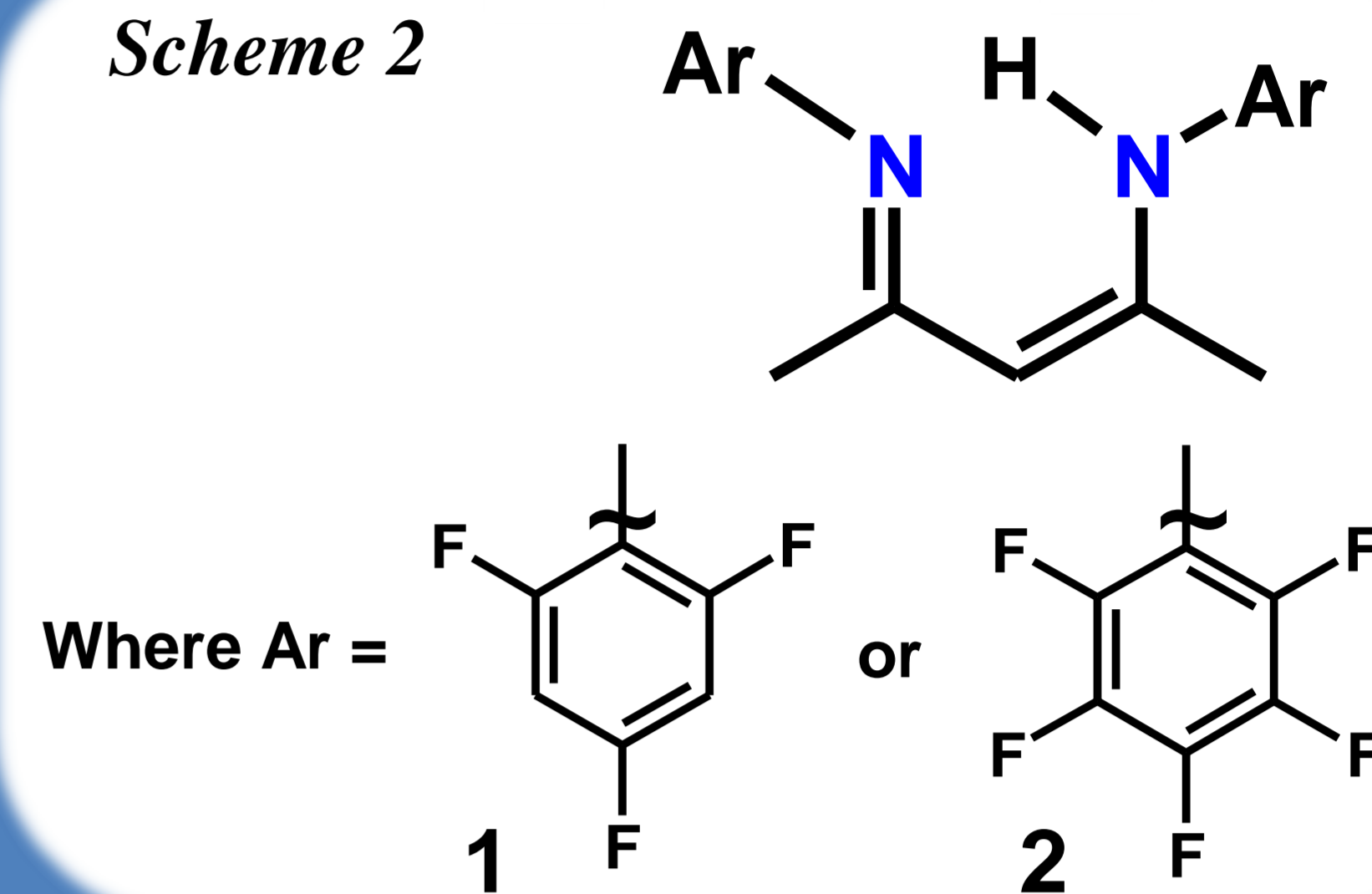
Introduction

Scheme 1



Reactivity of magnesium alkyls towards O_2 has remained the subject of fierce debate in organometallic chemistry.¹ Common wisdom states that the oxygenation of $RMgX$ is uncontrollably fast and a radical-chain mechanism is generally accepted for these reactions (Scheme 1).² The first magnesium alkylperoxide was isolated and structurally characterized by Bailey and co-workers in 2003.³ However, this compound was not obtained in its pure form, but co-crystallized with the corresponding magnesium alkoxide. Herein, we demonstrate that the controlled oxygenation of magnesium alkyls stabilized by fluorinated β -diketiminato ligands (Scheme 2) at low temperature leads selectively to the corresponding magnesium alkylperoxides. Moreover, our studies indicate that the resulting $(N,N)MgOOR$ complexes possess high catalytic activity in the epoxidation of enones.

Scheme 2

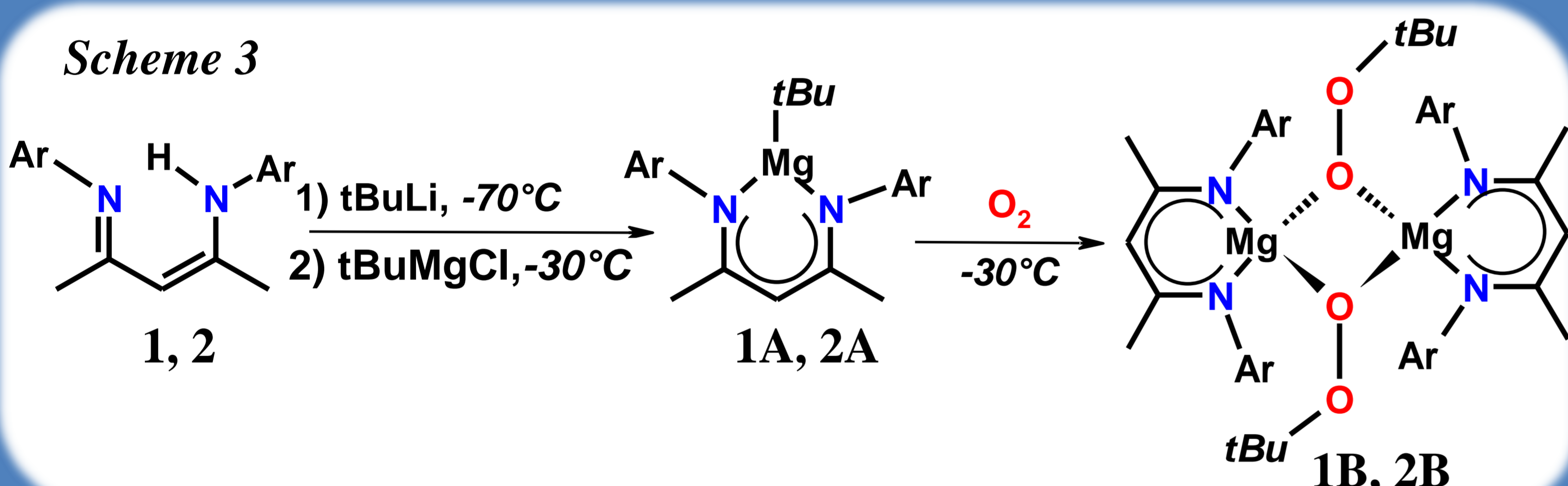


Results and discussion

Synthesis of magnesium alkylperoxides and alkoxides

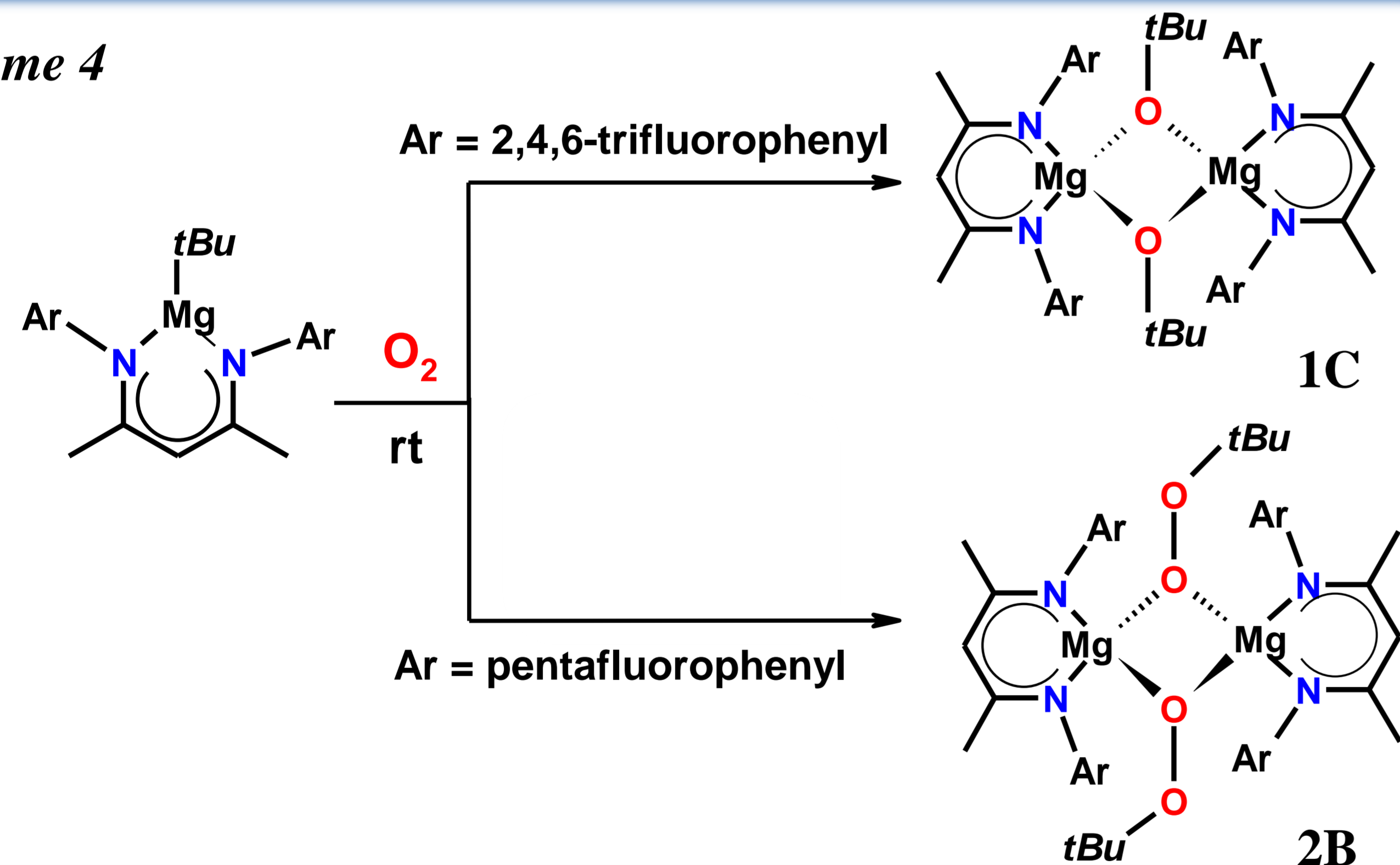
The parent alkylmagnesium species 1A and 1B were readily prepared by salt metathesis with the in situ generated lithium salt of the corresponding proligand and tert-butylmagnesium chloride. Next, the controlled oxygenation of the resulting alkylmagnesium complexes with dry O_2 at $-30^\circ C$ allowed to isolate magnesium peroxides (1B and 2B, Scheme 3).

Scheme 3

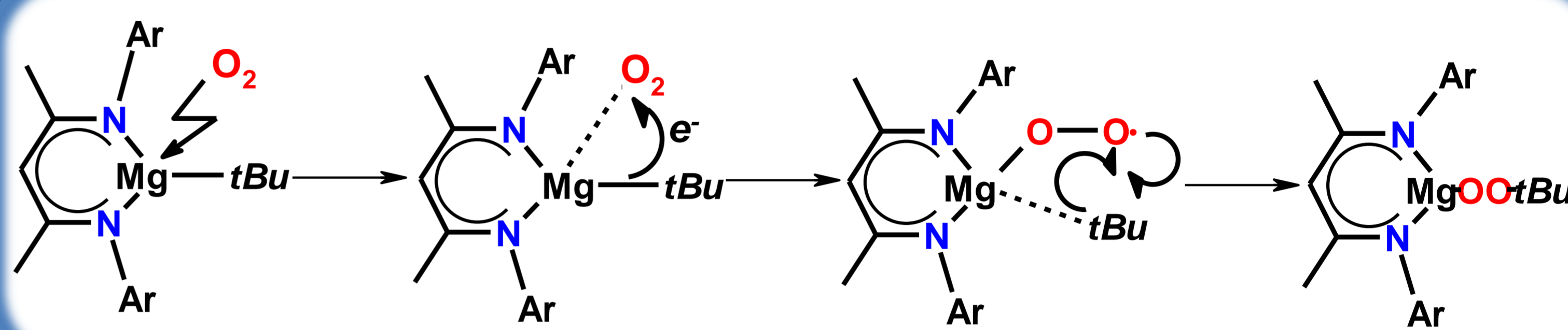


Interestingly, the oxygenation of 1A and 1B with dry O_2 at room temperature led to magnesium alkoxide 1C or magnesium alkylperoxide 2B, respectively. (Scheme 4).

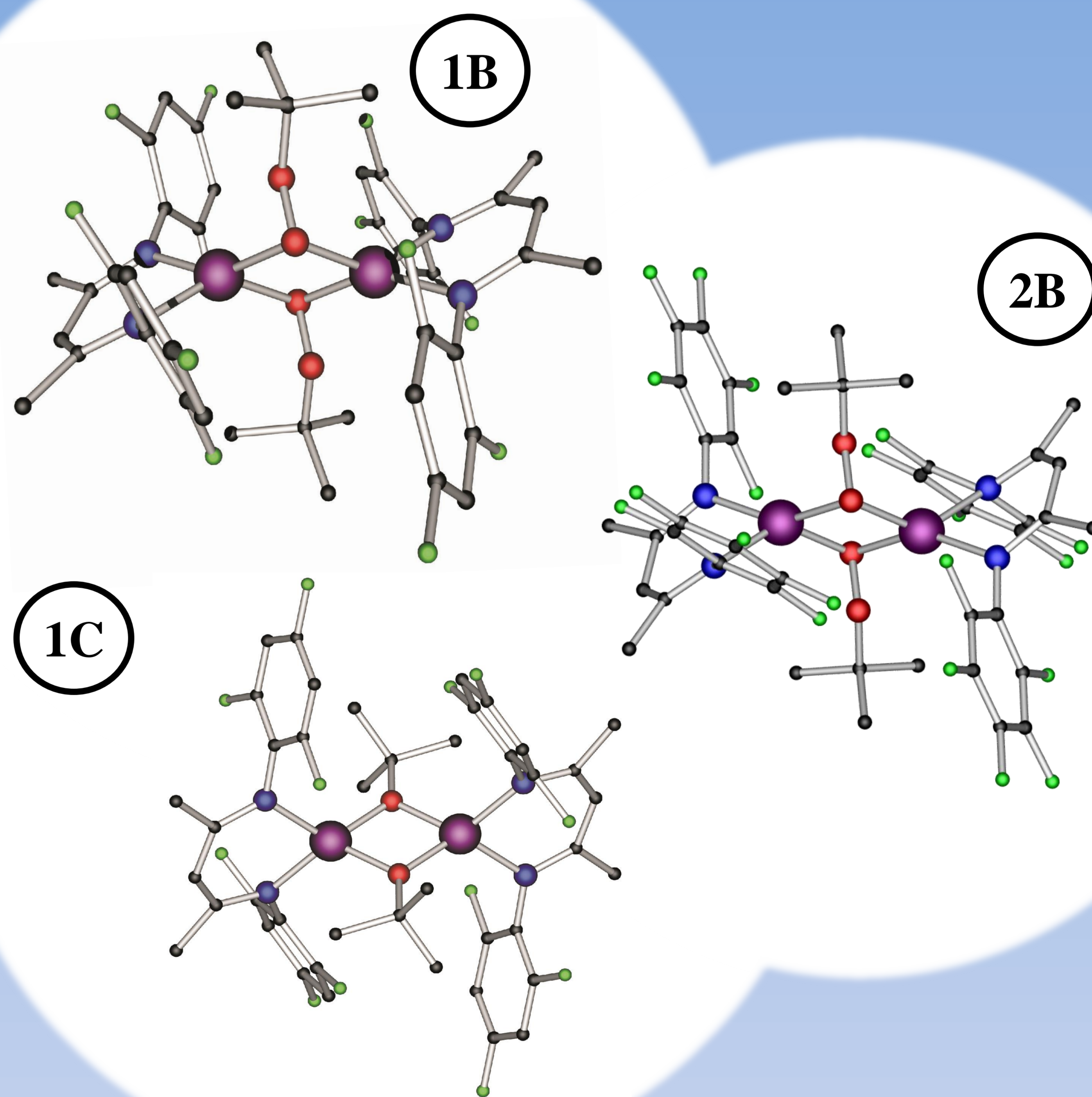
Scheme 4



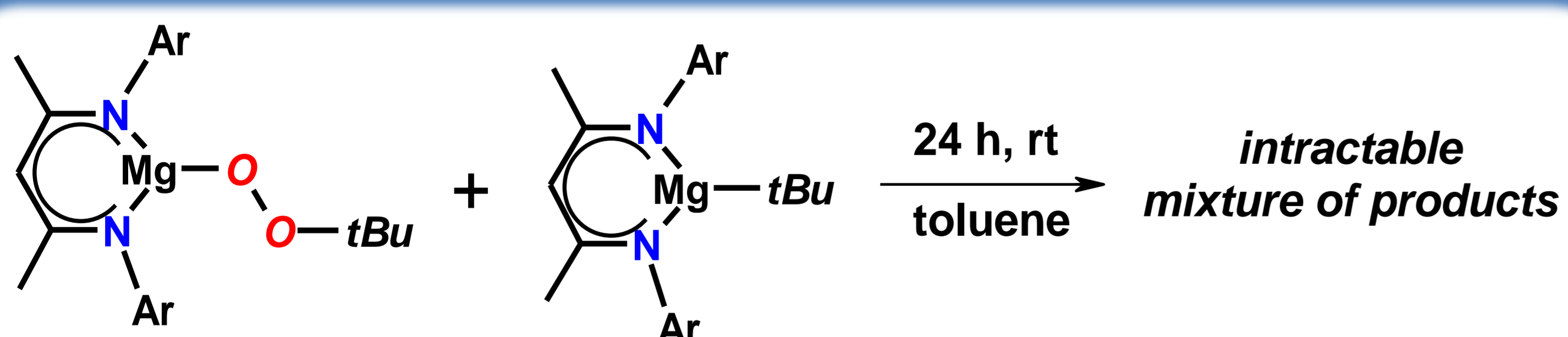
Proposed mechanism for the oxygenation of magnesium alkyls



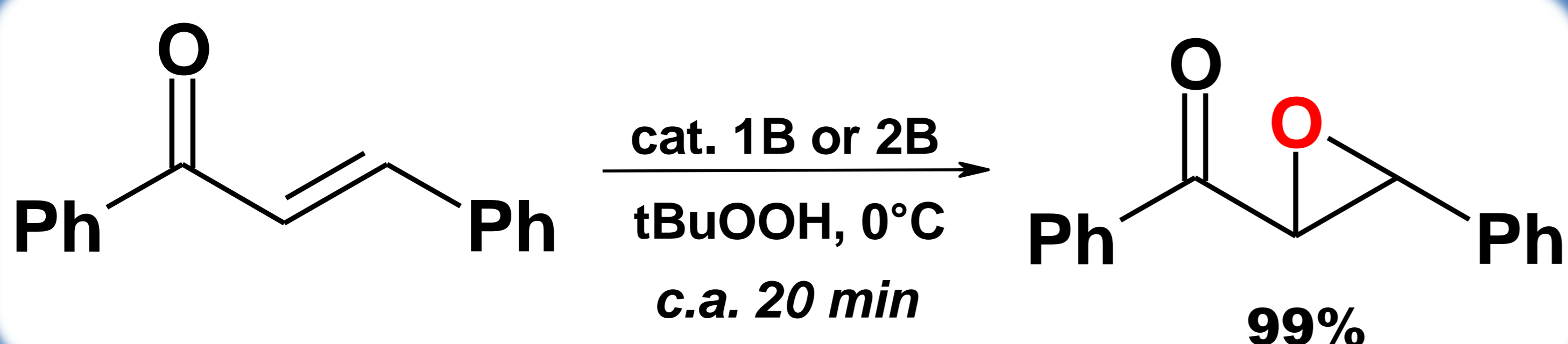
Structures of the magnesium alkylperoxides and alkoxide



Control methathesis between 2A and 2B



Catalytic epoxidation of *trans*-chalcone



Summary

- The oxygenation of $(N,N)MgOtBu$ complexes at low and room temperature was investigated
- Two, novel magnesium alkylperoxides stabilized by fluorinated β -diketiminato ligands were synthesized and structurally characterized
- Catalytic activity of both $(N,N)MgOOR$ complexes in the epoxidation of enones was examined

References

1. A. G. Davies and B. P. Roberts, *J. Chem. Soc. B* 1968, 1074.
2. G. Sosnovsky and J. H. Brown, *Chem. Rev.* 1966, 66, 529.
3. P. J. Bailey, R. A. Coxall, C. M. Dick, S. Fabre, L. C. Henderson, C. Herber, S. T. Liddle, D. Loroño-González, A. Parkin and S. Parsons, *Chem. Eur. J.* 2003, 9, 4823.
4. T. Pietrzak, M. Kubisiak, I. Justyniak, K. Zelga, E. Bojarski, E. Tratkiewicz, Z. Ochal and J. Lewiński, *Chem. Eur. J.* 2016, 22, 17776.