

Wheel-to-rhomboid isomerization as well as nitrene transfer catalysis of ruthenium-thiolate wheels

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A unique ruthenium-thiolate molecular rhomboid (\diamond)-[Ru(SAr)₂(CO)₂]₈ which consists of eight octahedra linked by alternate face- and vertex-sharing was produced by isomerization of the molecular wheel (O)-[Ru(SAr)₂(CO)₂]₈ at elevated temperature. The use of (O)-[Ru(SAr)₂(CO)₂]₆ wheel for catalytic aziridination of alkenes via nitrene transfer is also described.

The construction of metallacycles with fascinating shapes, such as molecular polygons¹ and wheels,² constitutes an ever-increasing area in supramolecular chemistry. As a type of molecular polygons, molecular rhomboids assembled by metal-ligand coordination have received a considerable attention,^{1,3} notable examples in the literature were assembled through “bottom-up” strategy and based on Pd(II)-pyridine,^{3a,b,e} Pt(II)-pyridine,^{3c-h,j,l} Pt(II)-carboxylate,³ⁱ or Ru(II)/Fe(II)-pyridine^{3k} coordinations (Fig. 1, upper left). In the course of our studies on the reactivity and catalytic application of ruthenium- and osmium-thiolate wheels (O)-[M(SAr)₂(CO)₂]_n (n = 6, 8) reported recently,⁴ we came upon a molecular rhomboid (\diamond)-[Ru(SAr)₂(CO)₂]₈ which was based on metal-thiolate coordination and was formed from the isomerization of a molecular wheel (O)-[Ru(SAr)₂(CO)₂]₈ (Fig. 1, lower). Such unprecedented wheel-to-rhomboid isomerization of (O)-[Ru(SAr)₂(CO)₂]_n, along with the catalytic properties of this type of molecular wheels toward nitrene transfer reactions, is reported herein. We noted a previous report of chelate-induced wheel-to-square transformation, i.e. from [Fe(pd)(O₂CET)]₁₂ (pdH₂ = 1,3-propanediol) to [[Fe₃O(pd)₂(O₂CET)(tpy)₂]₄](ClO₄)₈ (tpy = 2,2':6',2''-terpyridine), upon treatment with tpy and NaClO₄ resulting in major changes in the components of the metallacycle (Fig. 1, upper right).⁵

The molecular rhomboid (\diamond)-[Ru(SAr)₂(CO)₂]₈ represents a unique example of an octanuclear metallacycle consisting of eight octahedra linked in alternate face- and vertex-sharing manner (Fig. 1,

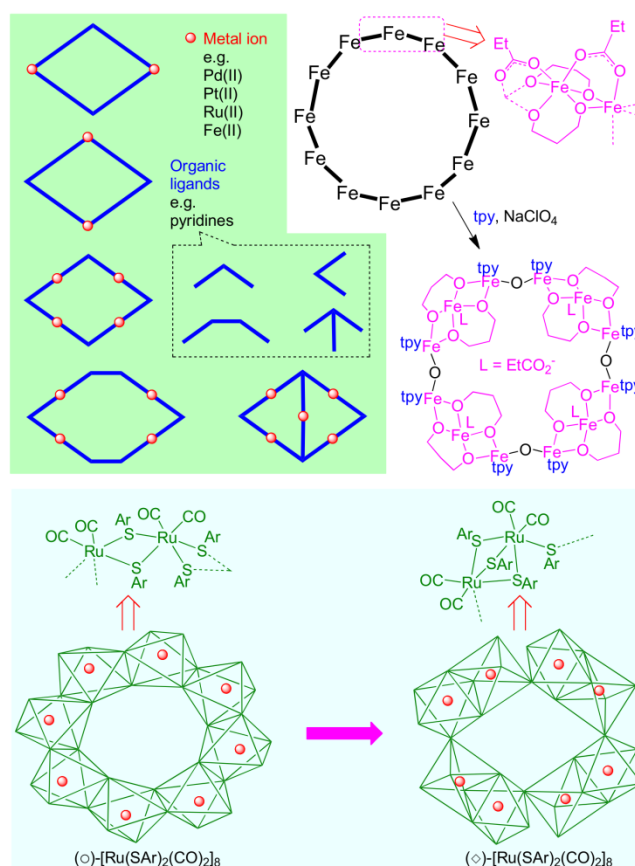


Fig. 1 Upper left: Literature examples of molecular rhomboids. Upper right: Wheel-to-square transformation reported in literature.⁵ Lower: Molecular rhomboid and wheel-to-rhomboid isomerization reported in this work; the molecular rhomboid consists of eight octahedra linked by alternate face- and vertex-sharing.

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lower),⁶ unlike its wheel isomer (O)-[Ru(SAr)₂(CO)₂]₈ and other related octanuclear or higher-nuclearity molecular wheels in which the octahedra are linked by edge-sharing,^{4,5,7} by alternate edge- and vertex-sharing,⁸ or by alternate face- and edge-sharing mode.⁹ Cyclic ensembles comprised of edge-, vertex-, and/or face-sharing polyhedra are of high importance.^{2,8,10} The formation of (\diamond)-[Ru(SAr)₂(CO)₂]₈ observed in this work demonstrates the

feasibility of utilizing alternate face- and vertex-sharing octahedra to construct metallacycles with nuclearity of higher than 6,⁶ which could show intriguing structures and properties.

Complex $(\diamond)\text{-}[\text{Ru}(\text{SAr})_2(\text{CO})_2]_8$ was identified during our further development of the chemistry of $(\circ)\text{-}[\text{M}(\text{SAr})_2(\text{CO})_2]_n$ ($n = 6, 8$);⁴ the latter was synthesized by reaction of $\text{M}_3(\text{CO})_{12}$ with ArSH at 120 °C ($\text{M} = \text{Ru}$) or 150 °C ($\text{M} = \text{Os}$). In subsequent studies of these self-assembly reactions, we found that treatment of $\text{Os}_3(\text{CO})_{12}$ with

ArSH ($\text{Ar} = p\text{-}^t\text{BuC}_6\text{H}_4$) at 160 °C afforded a mixture of two products, as revealed by ^1H NMR measurements (Fig. 2, upper). One product gave only two sets of Ar ($p\text{-}^t\text{BuC}_6\text{H}_4$) signals, like previously reported highly symmetric $(\circ)\text{-}[\text{M}(\text{SAr})_2(\text{CO})_2]_n$ wheels,⁴ whereas the other product showed multiple sets of the Ar signals corresponding to a structure with lower symmetry. Recrystallization of the mixture of products in chloroform/pentane gave a crystal suitable for X-ray crystallographic studies. The crystal structure determined corresponds to a centrosymmetric molecular rhomboid $(\diamond)\text{-}[\text{Os}(\text{S}\text{-}p\text{-}^t\text{BuC}_6\text{H}_4)_2(\text{CO})_2]_8$ (Fig. 3), a structure that can account for the multiple sets of Ar signals depicted in the top of Fig. 2. Attempts to prepare $(\diamond)\text{-}[\text{Os}(\text{S}\text{-}p\text{-}^t\text{BuC}_6\text{H}_4)_2(\text{CO})_2]_8$ in pure form have not been successful. We then turned attention to the Ru system. Interestingly, treatment of $\text{Ru}_3(\text{CO})_{12}$ with ArSH ($\text{Ar} = p\text{-}^t\text{BuC}_6\text{H}_4$) at 160 °C afforded $(\diamond)\text{-}[\text{Ru}(\text{S}\text{-}p\text{-}^t\text{BuC}_6\text{H}_4)_2(\text{CO})_2]_8$ which was isolated with a reasonable purity. This complex could also be obtained in a stepwise manner, i.e., reaction of $\text{Ru}_3(\text{CO})_{12}$ with $p\text{-}^t\text{BuC}_6\text{H}_4\text{SH}$ at 120 °C to give $(\circ)\text{-}[\text{Ru}(\text{S}\text{-}p\text{-}^t\text{BuC}_6\text{H}_4)_2(\text{CO})_2]_8$ wheel,⁴ followed by heating of the wheel in $p\text{-}^t\text{BuC}_6\text{H}_4\text{SH}$ at 160 °C (Scheme 1).

The ^1H NMR spectrum of $(\diamond)\text{-}[\text{Ru}(\text{S}\text{-}p\text{-}^t\text{BuC}_6\text{H}_4)_2(\text{CO})_2]_8$ at room temperature (Fig. 2, lower) resembles that of the structurally

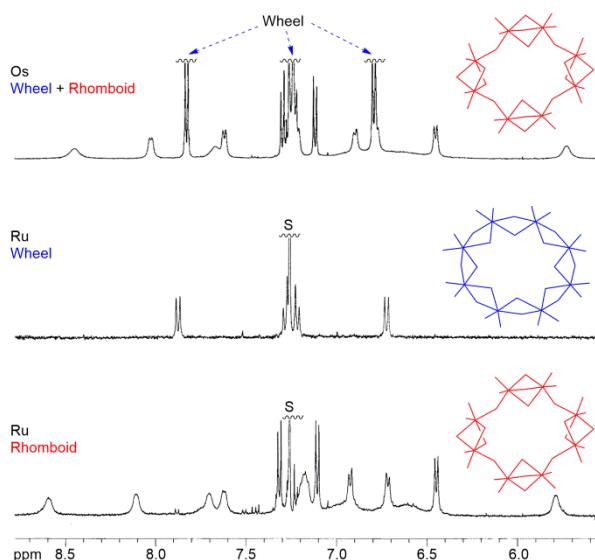
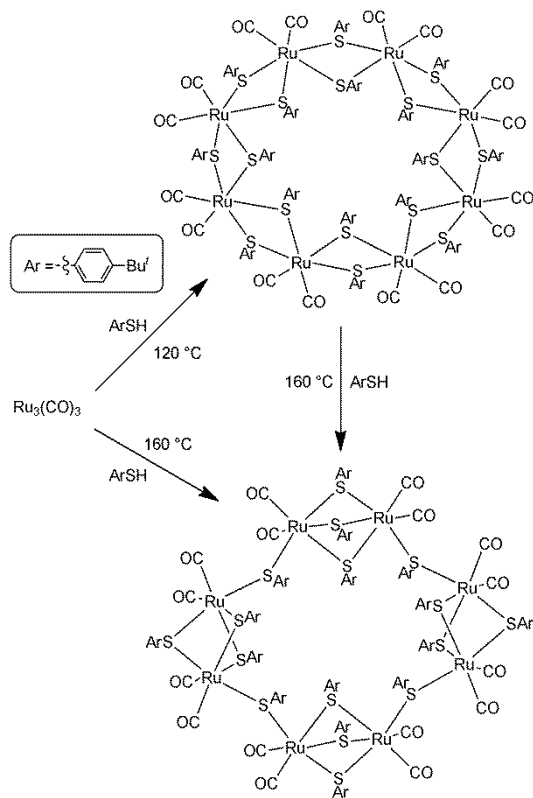


Fig. 2 ^1H NMR spectra (in aromatic region) of $(\circ)\text{-}$ and $(\diamond)\text{-}[\text{Os}(\text{S}\text{-}p\text{-}^t\text{BuC}_6\text{H}_4)_2(\text{CO})_2]_8$ mixture (upper), $(\circ)\text{-}[\text{Ru}(\text{S}\text{-}p\text{-}^t\text{BuC}_6\text{H}_4)_2(\text{CO})_2]_8$ (middle), and $(\diamond)\text{-}[\text{Ru}(\text{S}\text{-}p\text{-}^t\text{BuC}_6\text{H}_4)_2(\text{CO})_2]_8$ (lower) in CDCl_3 at 298 K.



Scheme 1 Synthesis of $(\diamond)\text{-}[\text{Ru}(\text{S}\text{-}p\text{-}^t\text{BuC}_6\text{H}_4)_2(\text{CO})_2]_8$.

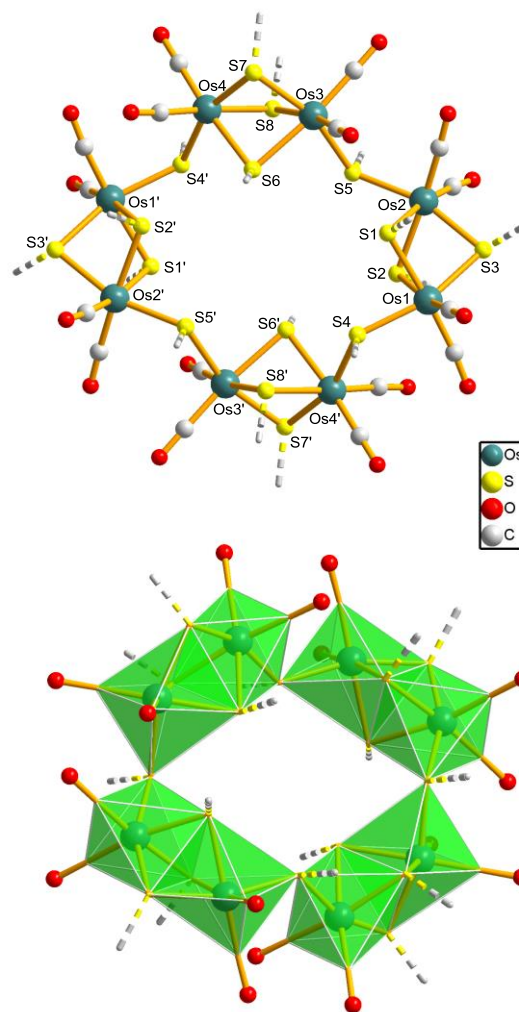


Fig. 3 X-ray crystal structure of $(\diamond)\text{-}[\text{Os}(\text{S}\text{-}p\text{-}^t\text{BuC}_6\text{H}_4)_2(\text{CO})_2]_8$ with omission of all $p\text{-}^t\text{BuC}_6\text{H}_4$ groups. The bonds connecting $p\text{-}^t\text{BuC}_6\text{H}_4$ groups and S atoms are shown as dashed lines. Upper: Ball and stick representation. Lower: Polyhedral representation.

characterized (\diamond)-[Os(*S-p*^tBuC₆H₄)₂(CO)₂]₈ (Fig. 2, upper) but is dramatically different from that of the structurally characterized (\circ)-[Ru(*S-p*^tBuC₆H₄)₂(CO)₂]₈ wheel⁴ (Fig. 2, middle). Variable-temperature (298–223 K) ¹H NMR spectra of (\diamond)-[Ru(*S-p*^tBuC₆H₄)₂(CO)₂]₈ (Fig. 4) revealed some extent of fluxional behaviour of the metallacycle in solution, and the signals became better resolved at low temperatures. Based on these spectral changes and the ¹H-¹H COSY NMR spectrum (Fig. 5), the signals belong to 8 sets of the *p*^tBuC₆H₄ groups, in agreement with a centrosymmetric structure of (\diamond)-[M(*S-p*^tBuC₆H₄)₂(CO)₂]₈ revealed by X-ray crystal structure of the Os counterpart (Fig. 3).

Upon treatment with a silver(I) salt such as AgOTf, (\diamond)-[Ru(*S-*

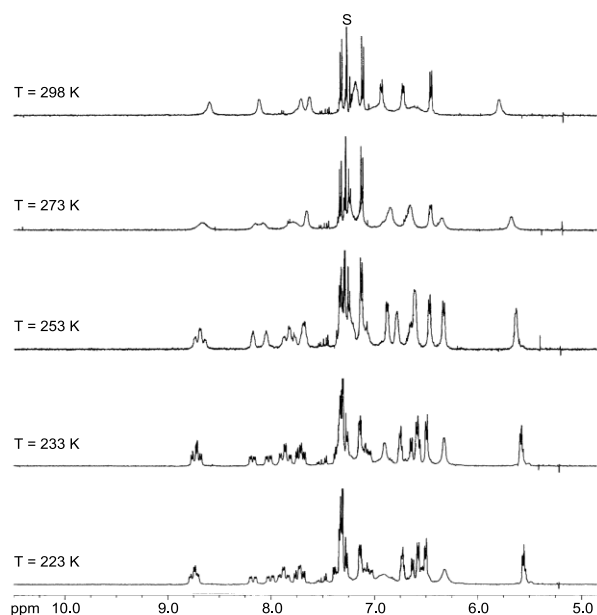


Fig. 4 Variable-temperature ¹H NMR spectra (in aromatic region) of (\diamond)-[Ru(*S-p*^tBuC₆H₄)₂(CO)₂]₈ in CDCl₃.

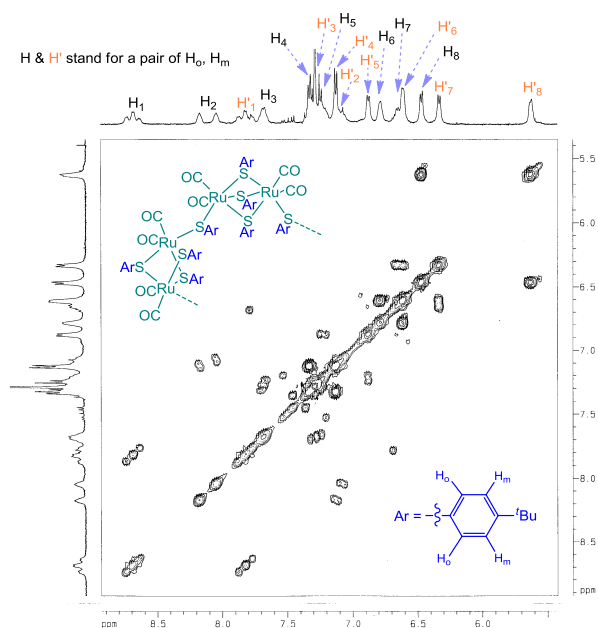


Fig. 5 ¹H-¹H COSY NMR spectrum (in aromatic region) of (\diamond)-[Ru(*S-p*^tBuC₆H₄)₂(CO)₂]₈ in CDCl₃ at 253 K.

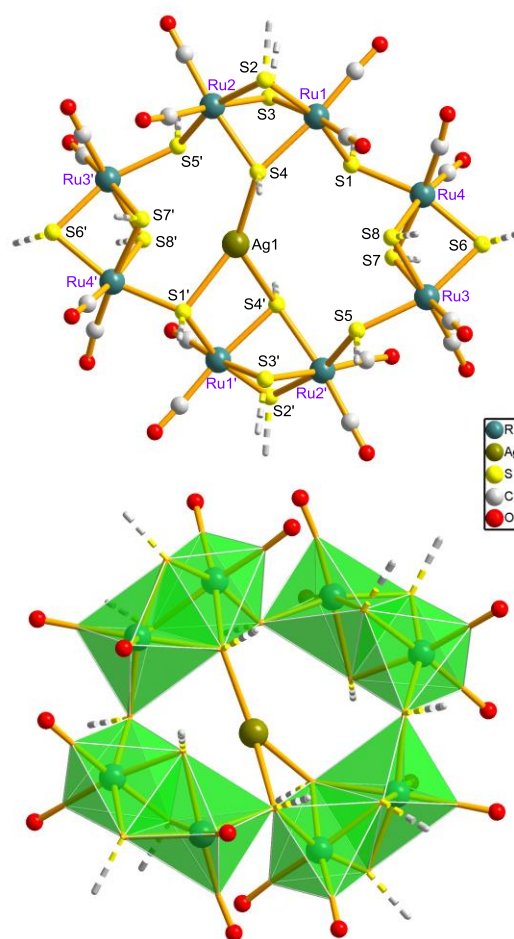
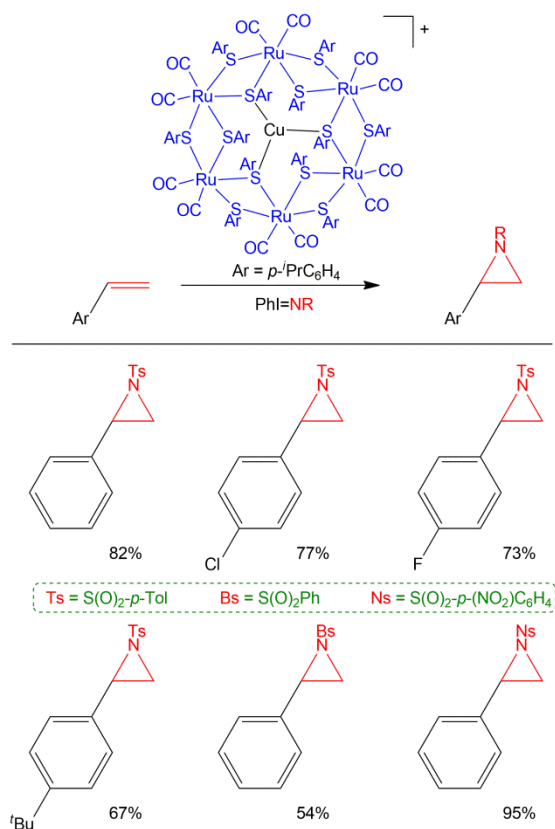


Fig. 6 X-ray crystal structure of (\diamond)-[Ag(Ru(*S-p*^tBuC₆H₄)₂(CO)₂)]₈⁺ with omission of all *p*^tBuC₆H₄ groups. The bonds connecting *p*^tBuC₆H₄ groups and S atoms are shown as dashed lines. Upper: Ball and stick representation. Lower: Polyhedral representation.

p^tBuC₆H₄)₂(CO)₂]₈ can rapidly bind Ag⁺ ion in solution, as suggested by the marked shift of the ¹H NMR signals after addition of AgOTf to a solution of this complex in CDCl₃. X-ray crystallographic studies of a crystal obtained from the reaction mixture revealed a rhomboid structure with the formulation of (\diamond)-[Ag(Ru(*S-p*^tBuC₆H₄)₂(CO)₂)]₈⁺ (Fig. 6).

Apart from the abovementioned wheel-to-rhomboid isomerization, (\circ)-[Ru(SAr)₂(CO)₂]_n wheels can also be used for nitrene transfer catalysis. To allow comparison of the catalytic activity between (\circ)-[Ru(SAr)₂(CO)₂]_n and its Cu(I) complex (\circ)-[Cu(Ru(SAr)₂(CO)₂]_n⁺ (the latter is known for n = 6 but not for n = 8⁴), the structurally characterized (\circ)-[Ru(*S-p*^tPrC₆H₄)₂(CO)₂]₆ and (\circ)-[Cu(Ru(*S-p*^tPrC₆H₄)₂(CO)₂)]₆⁺ reported previously⁴ were employed in this work as examples for such studies. At a catalyst loading of 1 mol%, the reaction of PhI=NTs with styrene (3 equiv) in MeCN at 80 °C catalysed by (\circ)-[Cu(Ru(*S-p*^tPrC₆H₄)₂(CO)₂)]₆⁺ afforded the aziridination product in 82% yield, higher than the product yield of 9% obtained for (\circ)-[Ru(*S-p*^tPrC₆H₄)₂(CO)₂]₆. For comparison, the same reaction catalysed by 2 mol% of [Cu(MeCN)₄]PF₆ gave the aziridine product in 40% yield. Possibly, the Cu(I) site of (\circ)-[Cu(Ru(*S-p*^tPrC₆H₄)₂(CO)₂)]₆⁺ is mainly responsible for the aziridination activity and its molecular wheel environment enhances the catalytic activity compared with [Cu(MeCN)₄]PF₆. (\circ)-



Scheme 2 Aziridination of alkenes catalysed by $(\text{O})\text{-}\{\text{Cu}[\text{Ru}(\text{S-}i\text{-}p\text{-PrC}_6\text{H}_4)_2(\text{CO})_2\}_6\}^+$.

$\{\text{Cu}[\text{Ru}(\text{S-}i\text{-}p\text{-PrC}_6\text{H}_4)_2(\text{CO})_2\}_6\}^+$ was then used as catalyst for aziridination of styrenes with $\text{PhI}=\text{NR}$ ($\text{R} = \text{Bs}$, Ts , and Ns), which afforded the aziridination products in up to 95% yield (Scheme 2).

We monitored the reaction of $(\text{O})\text{-}\{\text{Cu}[\text{Ru}(\text{S-}i\text{-}p\text{-PrC}_6\text{H}_4)_2(\text{CO})_2\}_6\}^+$ with $\text{PhI}=\text{NR}$ ($\text{R} = \text{Ts}$, Bs) in CH_2Cl_2 by ESI-MS measurements, which revealed the formation of a new cluster peak at m/z 2962 and 2948 for the reaction using $\text{PhI}=\text{NTs}$ and $\text{PhI}=\text{NBs}$, respectively. This new cluster peak possibly resulted from binding of the nitrene (NR) group by the molecular wheel (see Figs. S6–S9 in the ESI[†]). In the literature, catalytic applications of metal molecular wheels remain sparse.² Nitrene transfer reactions catalysed by metal complexes have received tremendous attention,¹¹ but such reactions catalysed by molecular wheels have not been reported previously.

In summary, a novel type of molecular rhomboid, constituted by eight octahedra linked by alternate face- and vertex-sharing mode, has been obtained, which is remarkably stable and could be formed by wheel-to-rhomboid isomerization of a ruthenium-thiolate wheel at high temperature. The present work also demonstrates the potential utility of a molecular wheel in catalytic nitrene transfer reactions.

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Notes and references

- (a) R. Chakrabarty, P. S. Mukherjee and P. J. Stang, *Chem. Rev.*, 2011, **111**, 6810; (b) T. R. Cook and P. J. Stang, *Chem. Rev.*, 2015, **115**, 7001.
- (a) S. J. Lippard, *Nature*, 2002, **416**, 587; (b) E. J. L. McInnes, S. Piligkos, G. A. Timco and R. E. P. Winpenny, *Coord. Chem. Rev.*, 2005, **249**, 2577; (c) G. Mezei, C. M. Zaleski and V. L. Pecoraro, *Chem. Rev.*, 2007, **107**, 4933; (d) R. W. Saalfrank, H. Maid and A. Scheurer, *Angew. Chem., Int. Ed.*, 2008, **47**, 8794; (e) P. Thanasekaran, C.-H. Lee and K.-L. Lu, *Coord. Chem. Rev.*, 2014, **280**, 96.
- For examples, see: (a) M. Fujita, S. Nagao, M. Iida, K. Ogata and K. Ogura, *J. Am. Chem. Soc.*, 1993, **115**, 1574; (b) M. Fujita, F. Ibukuro, H. Hagihara and K. Ogura, *Nature*, 1994, **367**, 720; (c) T. Yamamoto, A. M. Arif and P. J. Stang, *J. Am. Chem. Soc.*, 2003, **125**, 12309; (d) S.-S. Sun, C. L. Stern, S. T. Nguyen and J. T. Hupp, *J. Am. Chem. Soc.*, 2004, **126**, 6314; (e) B. Chatterjee, J. C. Noveron, M. J. E. Resendiz, J. Liu, T. Yamamoto, D. Parker, M. Cinke, C. V. Nguyen, A. M. Arif and P. J. Stang, *J. Am. Chem. Soc.*, 2004, **126**, 10645; (f) A. Kaloudi-Chantzea, N. Karakostas, C. P. Raptopoulou, V. Psycharis, E. Saridakis, J. Griebel, R. Hermann and G. Pistolis, *J. Am. Chem. Soc.*, 2010, **132**, 16327; (g) J. B. Pollock, G. L. Schneider, T. R. Cook, A. S. Davies and P. J. Stang, *J. Am. Chem. Soc.*, 2013, **135**, 13676; (h) I. V. Grishagin, J. B. Pollock, S. Kushal, T. R. Cook, P. J. Stang and B. Z. Olenyuk, *Proc. Natl. Acad. Sci. USA*, 2014, **111**, 18448; (i) Y. Ye, T. R. Cook, S.-P. Wang, J. Wu, S. Li and P. J. Stang, *J. Am. Chem. Soc.*, 2015, **137**, 11896; (j) M. Zhang, S. Li, X. Yan, Z. Zhou, M. L. Saha, Y.-C. Wang and P. J. Stang, *Proc. Natl. Acad. Sci. USA*, 2016, **113**, 11100; (k) Y. Li, Z. Jiang, M. Wang, J. Yuan, D. Liu, X. Yang, M. Chen, J. Yan, X. Li and P. Wang, *J. Am. Chem. Soc.*, 2016, **138**, 10041; (l) Z. Zhou, X. Yan, M. L. Saha, M. Zhang, M. Wang, X. Li and P. J. Stang, *J. Am. Chem. Soc.*, 2016, **138**, 13131.
- (a) S. L.-F. Chan, L. Shek, J.-S. Huang, S. S.-Y. Chui, R. W.-Y. Sun and C.-M. Che, *Angew. Chem., Int. Ed.*, 2012, **51**, 2614; (b) Y. Kan, K. C.-H. Tso, S. L.-F. Chan, X. Guan and C.-M. Che, *New J. Chem.*, 2013, **37**, 1811.
- T. C. Stamatatos, A. G. Christou, C. M. Jones, B. J. O'Callaghan, K. A. Abboud, T. A. O'Brien and G. Christou, *J. Am. Chem. Soc.*, 2007, **129**, 9840.
- For examples of tetra- and hexanuclear metallacycles consisting of alternate face- and vertex-sharing octahedra, see: (a) A. Herzog, F.-Q. Liu, H. W. Roesky, A. Demsar, K. Keller, M. Noltemeyer and F. Pauer, *Organometallics*, 1994, **13**, 1251; (b) E. F. Murphy, T. Lübben, A. Herzog, H. W. Roesky, A. Demsar, M. Noltemeyer and H.-G. Schmidt, *Inorg. Chem.*, 1996, **35**, 23; (c) E. F. Murphy, R. Murugavel, H. W. Roesky, M. Noltemeyer and H.-G. Schmidt, *Z. Anorg. Allg. Chem.*, 1996, **622**, 579; (d) C. E. Pohl-Ferry, J. W. Ziller and N. M. Doherty, *Chem. Commun.*, 1999, 1815; (e) J. T. Golden, D. N. Kazul'kin, B. L. Scott, A. Z. Voskoboynikov and C. J. Burns, *Organometallics*, 2003, **22**, 3971; (f) R. Ye, Y. Qin, A.-Q. Jia, Q. Chen and Q.-F. Zhang, *Inorg. Chim. Acta*, 2013, **405**, 218.
- (a) K. L. Taft and S. J. Lippard, *J. Am. Chem. Soc.*, 1990, **112**, 9629; (b) K. L. Taft, C. D. Delfs, G. C. Papaefthymiou, S. Foner, D. Gatteschi and S. J. Lippard, *J. Am. Chem. Soc.*, 1994, **116**, 823.
- U. Kortz, A. Müller, J. van Slageren, J. Schnack, N. S. Dalal and M. Dressel, *Coord. Chem. Rev.*, 2009, **253**, 2315.
- B. Salignac, S. Riedel, A. Dolbecq, F. Sécheresse and E. Cadot, *J. Am. Chem. Soc.*, 2000, **122**, 10381.
- (a) E. Cadot and F. Sécheresse, *Chem. Commun.*, 2002, 2189; (b) H. N. Miras, G. J. T. Cooper, D.-L. Long, H. Bögge, A. Müller, C. Streb and L. Cronin, *Science*, 2010, **327**, 72.
- Selected reviews: (a) L. Degennaro, P. Trincherà and R. Luisi, *Chem. Rev.*, 2014, **114**, 7881; (b) D. Karila and R. H. Dodd, *Curr. Org. Chem.*, 2011, **15**, 1507; (c) J. A. Halfen, *Curr. Org. Chem.*, 2005, **9**, 657; (d) P. Müller and C. Fruit, *Chem. Rev.*, 2003, **103**, 2905.