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

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A unique ruthenium-thiolate molecular rhomboid (◇)-[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 (○)-[Ru(SAr)$_2$(CO)$_2$]$_8$ at elevated temperature. The use of a (○)-[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 polygons[1] and wheels,[2] constitutes an ever-increasing area in supramolecular chemistry. As a class of molecular polygons, molecular rhomboids assembled by metal–ligand coordination have received considerable attention;[1,3] notable examples in the literature were assembled through a ''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] coordination (Fig. 1, upper left). In the course of our studies on the reactivity and catalytic application of ruthenium- and osmium-thiolate wheels (○)-[M(SAr)$_2$(CO)$_2$]$_n$ (n = 6, 8) reported recently,[4] we came upon a molecular rhomboid (◇)-[Ru(SAr)$_2$(CO)$_2$]$_8$ which was based on metal–thiolate coordination and was formed from the isomerization of a molecular wheel (○)-[Ru(SAr)$_2$(CO)$_2$]$_8$ (Fig. 1, lower). Such unprecedented wheel-to-rhomboid isomerization of (○)-[Ru(SAr)$_2$(CO)$_2$]$_n$, along with the catalytic properties of this type of molecular wheel toward nitrene transfer reactions, is reported herein. We examined a previous report of chelate-induced wheel-to-square transformation, *i.e.* from [Fe(pd)(O$_2$CEt)]$_{12}$ (pdH$_2$ = 1,3-propanediol) to [{Fe$_3$O(pd)$_2$(O$_2$CEt)(tpy)$_2$}$_4$](ClO$_4$)$_8$ (tpy = 2,2′:6′,2″-terpyridine), upon treatment with tpy and NaClO$_4$ resulting in major changes in the components of the metallacycle (Fig. 1, upper right).[5]

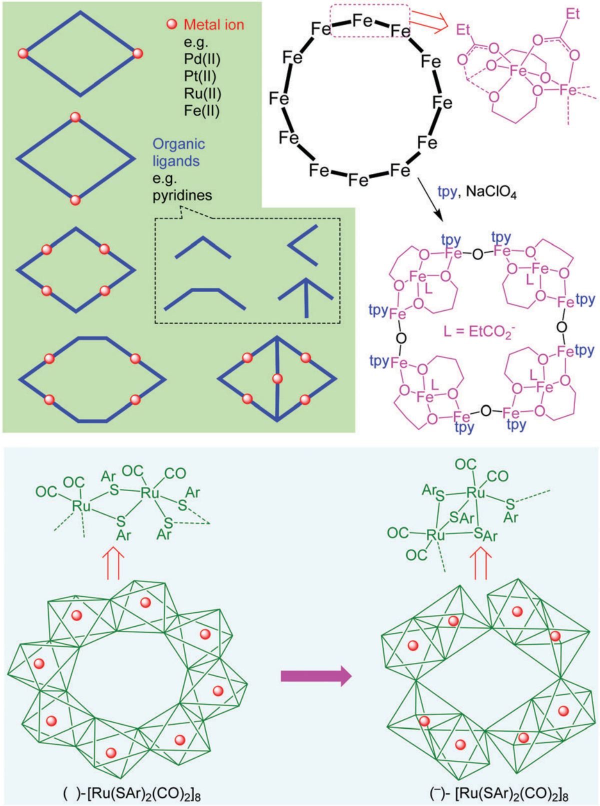

Fig. 1 Upper left: Literature examples of molecular rhomboids. Upper right: Wheel-to-square transformation reported in the literature.[5] Lower: Molecular rhomboid and wheel-to-rhomboid isomerization reported in this work; the molecular rhomboid consists of eight octahedra linked by alternate face- and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

The molecular rhomboid (◇)-[Ru(SAr)$_2$(CO)$_2$]$_8$ represents a unique example of an octanuclear metallacycle consisting of eight octahedra linked in an alternate face- and vertex-sharing manner (Fig. 1, lower),[6] unlike its wheel isomer (○)-[Ru(SAr)$_2$(CO)$_2$]$_8$ and

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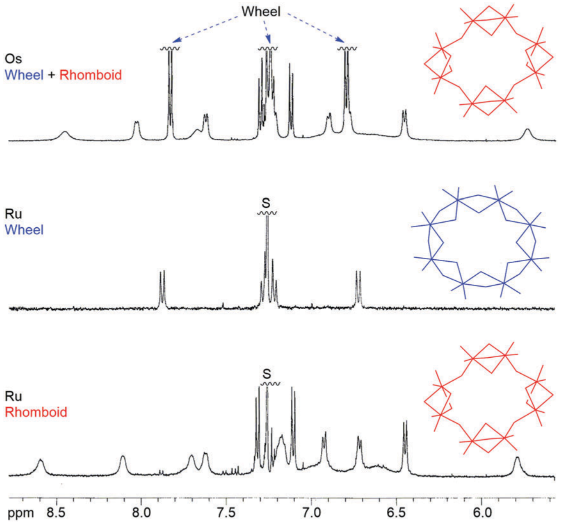


Fig. 2 ^{1}H NMR spectra (in the aromatic regions) of the (○)- and (◇)-[Os(S-p-^{t}BuC$_6$H$_4$)$_2$(CO)$_2$]$_8$ mixture (upper), (○)-[Ru(S-p-^{t}BuC$_6$H$_4$)$_2$(CO)$_2$]$_8$ (middle), and (◇)-[Ru(S-p-^{t}BuC$_6$H$_4$)$_2$(CO)$_2$]$_8$ (lower) in CDCl$_3$ at 298 K.

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.[9] Cyclic ensembles composed of edge-, vertex-, and/or face-sharing polyhedra are of high importance.[2,8,10] The formation of (◇)-[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 higher than 6,[6] which could show intriguing structures and properties.

Complex (◇)-[Ru(SAr)$_2$(CO)$_2$]$_8$ was identified during our further development of the chemistry of (○)-[M(SAr)$_2$(CO)$_2$]$_n$ (n = 6, 8);[4] the latter was synthesized by reaction of M$_3$(CO)$_{12}$ with ArSH at 120 °C (M = Ru) or 150 °C (M = Os). In the subsequent studies of these self-assembly reactions, we found that treatment of Os$_3$(CO)$_{12}$ with ArSH (Ar = p-^{t}BuC$_6$H$_4$) at 160 °C afforded a mixture of two products, as revealed by ^{1}H NMR measurements (Fig. 2, upper). One product gave only two sets of Ar (p-^{t}BuC$_6$H$_4$) signals, like previously reported highly symmetric (○)-[M(SAr)$_2$(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 (◇)-[Os(S-p-^{t}BuC$_6$H$_4$)$_2$(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 (◇)-[Os(S-p-^{t}BuC$_6$H$_4$)$_2$(CO)$_2$]$_8$ in its pure form have not been successful. We then turned our attention to the Ru system. Interestingly, treatment of Ru$_3$(CO)$_{12}$ with ArSH (Ar = p-^{t}BuC$_6$H$_4$) at 160 °C afforded (◇)-[Ru(S-p-^{t}BuC$_6$H$_4$)$_2$(CO)$_2$]$_8$ which was isolated with reasonable purity. This complex could also be obtained in a stepwise manner, *i.e.*, reaction of Ru$_3$(CO)$_{12}$ with p-^{t}BuC$_6$H$_4$SH at 120 °C to give a (○)-[Ru(S-p-^{t}BuC$_6$H$_4$)$_2$(CO)$_2$]$_8$ wheel,[4] followed by heating of the wheel in p-^{t}BuC$_6$H$_4$SH at 160 °C (Scheme 1).

The ^{1}H NMR spectrum of (◇)-[Ru(S-p-^{t}BuC$_6$H$_4$)$_2$(CO)$_2$]$_8$ at room temperature (Fig. 2, lower) resembles that of the structurally characterized (◇)-[Os(S-p-^{t}BuC$_6$H$_4$)$_2$(CO)$_2$]$_8$ (Fig. 2, upper) but is dramatically different from that of the structurally characterized (○)-[Ru(S-p-^{t}BuC$_6$H$_4$)$_2$(CO)$_2$]$_8$ wheel[4] (Fig. 2, middle). Variable-temperature (298–223 K) ^{1}H NMR spectra of (◇)-[Ru(S-p-^{t}BuC$_6$H$_4$)$_2$(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 ^{1}H–^{1}H COSY NMR spectrum (Fig. 5), the signals belong to 8 sets of the p-^{t}BuC$_6$H$_4$ groups, in agreement with a centrosymmetric structure of (◇)-[M(S-p-^{t}BuC$_6$H$_4$)$_2$(CO)$_2$]$_8$ revealed by the X-ray crystal structure of the Os counterpart (Fig. 3).

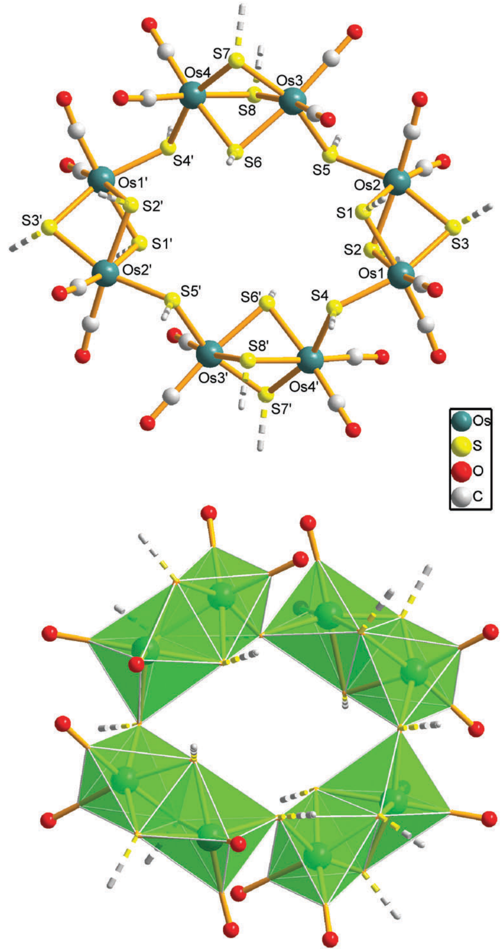
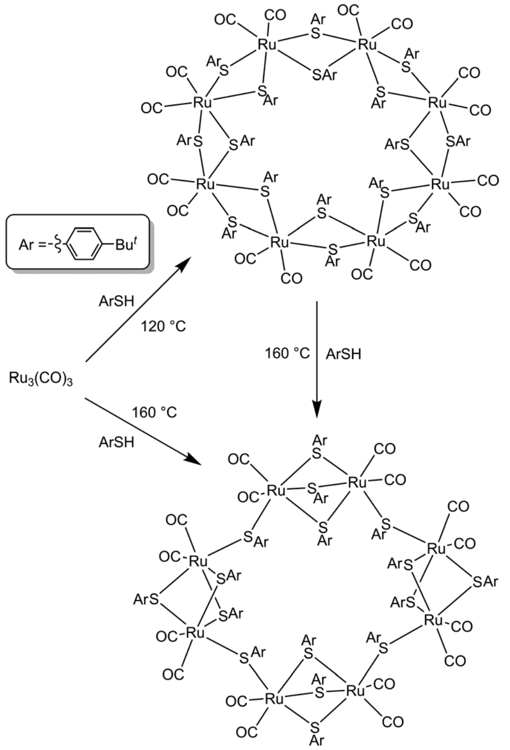


Fig. 3 X-ray crystal structure of (◇)-[Os(S-p-^{t}BuC$_6$H$_4$)$_2$(CO)$_2$]$_8$ with omission of all p-^{t}BuC$_6$H$_4$ groups. The bonds connecting p-^{t}BuC$_6$H$_4$ groups and S atoms are shown as dashed lines. Upper: Ball and stick representation. Lower: Polyhedral representation.

Upon treatment with a silver(I) salt such as AgOTf, (◇)-[Ru(S-p-^{t}BuC$_6$H$_4$)$_2$(CO)$_2$]$_8$ can rapidly bind Ag$^+$ ions in solution, as suggested by the marked shift of the ^{1}H NMR signals after addition of AgOTf to a solution of this complex in CDCl$_3$. X-ray crystallographic studies of a crystal obtained from the reaction mixture revealed a rhomboid structure with the formulation of (◇)-{Ag[Ru(S-p-^{t}BuC$_6$H$_4$)$_2$(CO)$_2$]$_8$}$^+$ (Fig. 6).

Apart from the abovementioned wheel-to-rhomboid isomerization, (○)-[Ru(SAr)$_2$(CO)$_2$]$_n$ wheels can also be used for nitrene transfer catalysis. To allow comparison of the catalytic activity



Scheme 1 Synthesis of (◇)-$[Ru(S\text{-}p\text{-}^tBuC_6H_4)_2(CO)_2]_8$.

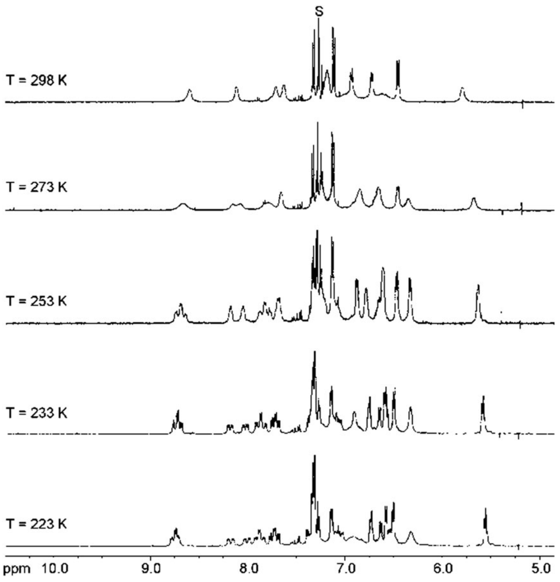


Fig. 4 Variable-temperature ^1H NMR spectra (in the aromatic regions) of (◇)-$[Ru(S\text{-}p\text{-}^tBuC_6H_4)_2(CO)_2]_8$ in $CDCl_3$.

between (○)-$[Ru(SAr)_2(CO)_2]_n$ and its Cu(I) complex (○)-$\{Cu[Ru(SAr)_2(CO)_2]_n\}^+$ (the latter is known for n = 6 but not for n = 8[4]), the structurally characterized (○)-$[Ru(S\text{-}p\text{-}^iPrC_6H_4)_2(CO)_2]_6$ and (○)-$\{Cu[Ru(S\text{-}p\text{-}^iPrC_6H_4)_2(CO)_2]_6\}^+$ reported previously[4] 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 (○)-$\{Cu[Ru(S\text{-}p\text{-}^iPrC_6H_4)_2(CO)_2]_6\}^+$ afforded the aziridination product in 82% yield, higher than the

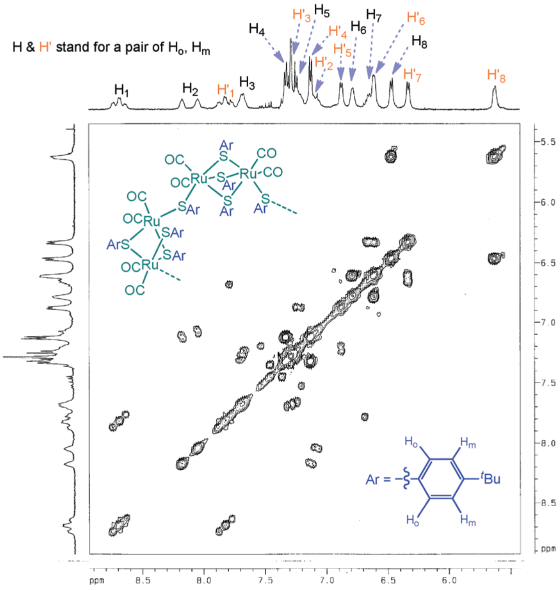


Fig. 5 ^1H–^1H COSY NMR spectrum (in the aromatic region) of (◇)-$[Ru(S\text{-}p\text{-}^tBuC_6H_4)_2(CO)_2]_8$ in $CDCl_3$ at 253 K.

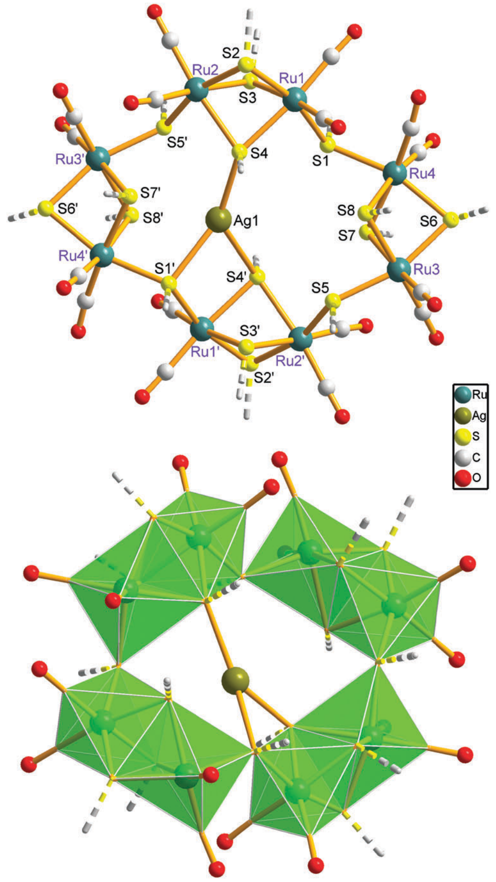
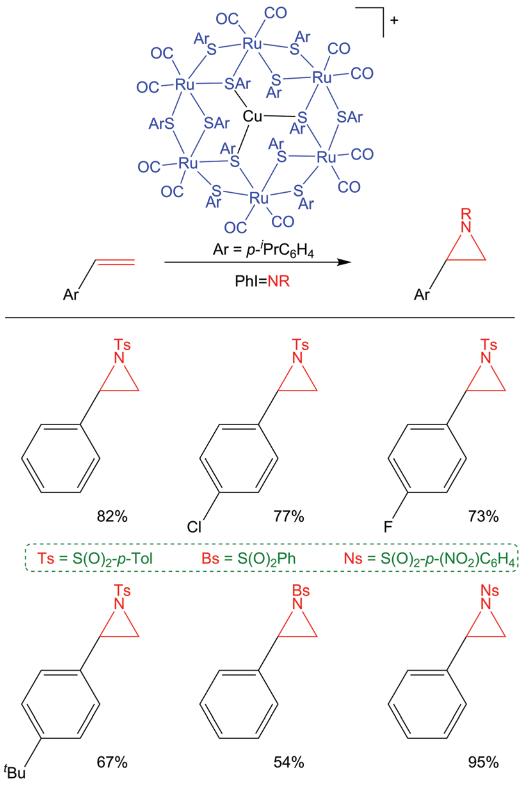


Fig. 6 X-ray crystal structure of (◇)-$\{Ag[Ru(S\text{-}p\text{-}^tBuC_6H_4)_2(CO)_2]_8\}^+$ with omission of all $p\text{-}^tBuC_6H_4$ groups. The bonds connecting $p\text{-}^tBuC_6H_4$ groups and S atoms are shown as dashed lines. Upper: Ball and stick representation. Lower: Polyhedral representation.



Scheme 2 Aziridination of alkenes catalysed by (◯)-$\{Cu[Ru(S\text{-}p\text{-}{}^iPrC_6H_4)_2(CO)_2]_6\}^+$.

product yield of 9% obtained for (◯)-$[Ru(S\text{-}p\text{-}{}^iPrC_6H_4)_2(CO)_2]_6$. For comparison, the same reaction catalysed by 2 mol% of $[Cu(MeCN)_4]PF_6$ gave the aziridine product in 40% yield. Possibly, the Cu(I) site of (◯)-$\{Cu[Ru(S\text{-}p\text{-}{}^iPrC_6H_4)_2(CO)_2]_6\}^+$ is mainly responsible for the aziridination activity and its molecular wheel environment enhances the catalytic activity compared with $[Cu(MeCN)_4]PF_6$. (◯)-$\{Cu[Ru(S\text{-}p\text{-}{}^iPrC_6H_4)_2(CO)_2]_6\}^+$ was then used as a catalyst for aziridination of styrenes with PhI═NR (R = Bs, Ts, and Ns), which afforded the aziridination products in up to 95% yield (Scheme 2).

We monitored the reaction of (◯)-$\{Cu[Ru(S\text{-}p\text{-}{}^iPrC_6H_4)_2(CO)_2]_6\}^+$ with PhI═NR (R = 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 PhI═NTs and PhI═NBs, respectively. This new cluster peak possibly resulted from binding of the nitrene (NR) group by the molecular wheel (see Fig. 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 an 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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